DETERMINATION OF THE ABSOLUTE
VISCOSITY OF SOME
REFRIGERANTS

DETERMINATION OF THE ABSOLUTE
VISCOSITY OF SOME
REFRIGERANTS

By

ABDUL JABBAR MAHMUD AL-SALOUM
B.ENG.

A Thesis

Submitted to the Faculty of Graduate
Studies in Partial Fulfilment of the
Requirements for the Degree

Master of Engineering

McMaster University,
Hamilton, Ontario.

MASTER OF ENGINEERING (1968)
(Mechanical Engineering)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: DETERMINATION OF THE ABSOLUTE VISCOSITY OF SOME REFRIGERANTS

AUTHOR: ABDUL JABBAR MAHMUD AL-SALOUM
B.Eng. (University of Liverpool).

SUPERVISOR: Dr. B. Latto.

NUMBER OF PAGES: xii, 173

SCOPE AND CONTENTS:

An experimental determination of the absolute dynamic viscosity of two refrigerants at atmospheric pressure is reported in this thesis. The work has been carried out for the vapour phase of two halogenated hydrocarbon compounds, Freons 12 and 22 in the general temperature range -39.7 to 91.8°C. The maximum error of the data obtained is believed to be ±3.1%. Comparison of the results of this work with previous secondary measurements, on the same compounds, reveals that the maximum deviation of previous measurements are +5% and -6% for Freons 12 and 22 respectively, over the common temperature range.

Both the data obtained in this work and those of previous workers have been correlated with polynomials of degrees 2 to 5 and an approximate form of the Sutherland Equation for the viscosity of gases.

An analysis of previous measurements for Freons 11, 12, 13, 14, 21, 22, 23, 114,115, 13B1, and C318 in the vapour phase, and Freons 11, 12, 21, 22, 113, 114, 115, 12B1, 12B2, 114B2, and C318 in the liquid phase has been carried out and reported in Appendix (X7).

ACKNOWLEDGEMENT

The author is sincerely indebted to Dr. B. Latto for the guidance, assistance and support that he provided. Many thanks are also due to those persons who offered technical assistance. Mr. K. F. Crowe of DuPont of Canada, provided many technical information bulletins, and his help is gratefully acknowledged. Mrs. A. Woodrow's concern and restless hours of thesis typing is very much appreciated. Dr. V. Johnson of the Cryogenics Data Centre, National Bureau of Standards, Mr. R. Everett, of the Library, I. Mech. Eng., and Mrs. G. Wilson of McMaster Science Library were very helpful during the course of the literature survey, for which they are thanked.

The author wishes to extend his thanks to Pennsalt Chemical Corporation, Olin Chemicals, Union Carbide, DuPont of Canada, Stauffer Chemical Co., Kaiser Chemicals and Carrier Corporation, who supplied invaluable technical information.

The experimental work reported here was supported by the National Research Council, Grant No. A2937.

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

APPENDICES

LIST OF TABLES

APPENDICES

NOMENCLATURE

SYMBOL	DESCRIPTION
UPPER CASE	
A, AO, A1, ... etc.	Constants
B	Constant
C	Constant
C	Centigrade Temperature Scale
D	Diameter of Rolling Ball
F	Fahrenheit Temperature Scale
K	Constant
K	Kelvin Temperature Scale
P	Pressure
Q	Mass Flow Rate
Re	Reynold Number
T	Absolute Temperature
V	Volume
W	Weight
LOWER CASE	
ao, a1,.....etc.	Constants
d	Diameter
dℓ	Length Difference
dp	Pressure Difference
e	Equivalent Length of Mercury Pellet
g	Constant of Gravity Acceleration

SYMBOL	DESCRIPTION
ℓ	Length
h	Height of Spherical Segment of Mercury Pellet
m	Kinetic Energy Correction Constant
n	Couette Correction Constant
p	Pressure
t	Temperature in Relative Units
t	Time
v	Velocity
x	Development Length

GREEK SYMBOLS

UPPER CASE

Δ	Difference
Σ	Sum

LOWER CASE

α	Angle of Inclination
α	Coefficient of Thermal Expansion of Glass of Capillary Tubes
δ	Small Increment
ε	Coefficient of Slip Correction
η	Dynamic Viscosity

SYMBOL	DESCRIPTION
θ	Time
λ	Length of Part of Mercury Pellet or Thread
ν	Kinematic Viscosity
π	Constant
ρ	Density

SUBSCRIPTS

a	Relating to Air
b	Relating to Rolling Ball
b	Relating to Boiling Temperature
c	Relating to Calibration Fluid
e	Relating to Conditions at Exit
f	Relating to Fluid
g	Relating to Gas
i	Relating to Conditions at Entrance
m	Relating to Mercury
n	Degree of Polynomial
v	Relating to Vapour
w	Relating to Water

I INTRODUCTION

The importance of the availability of thermophysical properties of commonly used fluids in the field of heat transfer and related studies can not be overemphasized. One of the least available properties in the literature is viscosity. The diversified industrial applications of the halogenated hydrocarbon compounds calls for an accurate evaluation of their properties in order to make efficient utilization possible.

It appears that, despite the numerous undertakings, no attempt has previously been made to determine the absolute viscosity data of the halogenated hydrocarbons. Secondary viscometers have previously been employed to determine the variation of viscosity with temperature in both the vapour and liquid phases. The accuracy of such measurements is necessarily dependent on that of the calibrating fluids, and the range of temperature investigation can not be extended to a region where the viscosity of the calibrating fluid is unknown.

A viscometer of the series-capillary type was designed and developed to determine the absolute viscosity of gases or liquids at atmospheric pressure. The two capillary tubes used in this viscometer are replaceable, and therefore different gases or liquids can be investigated at wide temperature ranges with the same viscometer. The series-capillary viscometer has the advantage of eliminating the kinetic energy correction as opposed to a single-capillary or a parallel-capillary type viscometer.

The experimental work reported here was confined to the vapour phase of the Freon compounds. The absolute viscosity of Freons* 12 and 22 was determined in the temperature range -39.7 to 91.8°C and at atmospheric pressure. A comparison of the absolute measurements of this work with those determined previously by secondary viscometers is also presented.

---

* FREON is Du Pont's registered trademark for the halogenated hydrocarbon compounds.

II LITERATURE SURVEY

II.1 Text:

The survey covers those compounds listed in Table 1, page 29 in both the liquid and vapour phases.

The first paper to appear on the viscosity of the halogenated hydrocarbons was by Hovorka and Geiger (1)* in 1933. The authors evaluated the viscosity of Freon 113** in the liquid region in the temperature range 30.0 to 9.0°C using a rolling ball viscometer. The viscosity of Freon 113 was also evaluated at its boiling temperature by extrapolating their experimental results. No error analysis was reported.

In 1936 Awbery and Griffiths (2) carried out viscosity measurements on Freon 12** in the liquid phase in the temperature range -15°C to 30°C using a falling plug viscometer. Benzene, pentane, ether and water were used as the calibrating liquids and oil as the temperature regulating liquid. A deviation of the calibrating curve was reported between those measurements before and after the test. A smoothed curve was then used to evaluate the viscosities of the tested liquids. Upon plotting the natural

---

* The numbers in parantheses refer to references.

** The authors also evaluated viscosity data of Difluorotetrachloroethane and other physical properties of the two compounds, however, the survey is limited to the viscosity of those refrigerants listed in Table 1.

logarithim of the viscosity values of Freon 12 against the reciprocal of the absolute temperature the results appeared to fit a straight line. No mention of the scatter or the experimental error incurred was reported.

Benning and Markwood (3), 1939 appear to be the first to report viscosity measurements of Freon 11, 12, 21, 22 and 113 in the vapour region. The measurements were carried out in the temperature range 0 to 50°C and a pressure range 1 to 9 atmospheres for the first four refrigerants. Viscosities of Freon 113 were reported in the temperature range 0 to 90°C and a pressure of 0.1 to 0.3 atmospheres. A rolling ball viscometer inclined by 80° to the horizontal was employed and air was utilized as the calibrating fluid. When calculating the vapour viscosities, Benning and Markwood neglected the variation of the calibration constant with temperature. They also assumed that the ratio of the differences of the densities of the sphere and the vapour and the sphere and the calibration air to be unity

i.e. $(\rho_s - \rho_{vapour})/(\rho_s - \rho_{air}) = 1$

where ρ_s is the density of the sphere. This introduced an error of ± 0.5% in the viscosity values of the heaviest vapour, which was thought to be justified since it was less than their experimental error. With this in mind, they calculated the viscosity as a direct ratio

i.e. $\eta_{vapour} = (\Theta_{vapour}/\Theta_{air}) x \eta_{air}$

where Θ is the time of fall of the sphere. Furthermore, the viscosities of the calibration air at the required temperatures were calculated as follows:

$$\eta_t = (\Theta_t / \Theta_{20}) x \eta_{air}$$

where t is the temperature, η_{20} is the standard viscosity value of air at 20 degrees C, and Θ_{20} is the time of fall of the sphere through air at 20 degrees C determined experimentally. It was shown that the viscosity results of the Freon vapours tested satisfied the equation

$$\eta = A\sqrt{T} - B$$

where A and B are constants and T is the absolute temperature. Viscosity values of Freons 11, 12 and 113 in the liquid phase and at saturation pressures were reported in the temperature range -30 to 60 degrees C. In this case the viscometer was calibrated with water and chloroform. Again the temperature coefficient of the instrument was neglected. The experimental data were found not to fit the usual equation

$$\eta = A\ e^{K/T},$$

but could be represented accurately by the empirical equation

$$\eta = C/(A + t)^{a}$$

where C, A and a are constants for a certain liquid and 't' is the temperature. This result is not surprising since the first equation is only valid for a constant pressure, while the viscosities of Benning and Markwood were evaluated at saturation pressures.

Throughout the above tests, whether on liquids or vapours, the temperature was measured with a mercury-in-glass thermometer placed in the return of the constant temperature bath which surrounded the pressurised viscometer.

In 1945, Graham (4), followed the method outlined by Benning and Markwood (3) in measuring the viscosity of Freon - C318. For the liquid region the rolling ball viscometer was calibrated with distilled water and the viscosity of liquid C318 was measured at five temperatures in the range 0 to 71.5 degrees C at saturation pressures The vapour viscosity measurements were carried out at atmospheric pressure and in the temperature range 3 to 97 degrees C. The viscometer was calibrated using air for the latter measurements. It was also observed by Graham (4) that at a temperature of 97 degrees C, a tenfold increase in pressure resulted in 20% increase of the vapour viscosity of Freon C318.

The viscosity measurements of halogenated hydrocarbon compounds carried out at Purdue University, which is henceforth reported, appears to have been initiated by Coughlin (5) in 1953, who measured the viscosity of Freons 22, 23 and 115 in the vapour phase. A rolling ball viscometer was then used for this work, with air as the calibrating fluid and Ethyl Alcohol as the temperature stabilizing liquid, in the temperature range -36.0 to 60.0°C and at a pressure of one atmosphere. The accuracy of these measurements was reported by Coughlin to be of the order of ± 0.4 to ± 0.8 percent. Those figures are thought to be optmistic as is evident from later experiments. For Freon 22 a deviation of the order of ± 0.7 percent from the experimental measurements by Benning and Markwood (3) on the vapour of the same compound was reported. However, in the temperature range -34.0 to 1.4°C, at which Benning and Markwood (3) evaluated their reported results by extrapolation of the experimental ones, there is a deviation of 2.31 percent. Coughlin believed that his results were more reliable in this temperature range since they were experimentally determined. Moreover, the inclination angle with the horizontal used by Coughlin was 15° as opposed to 80° used by Benning and Markwood.

Makita (6) in his search for the effect of the pressure on the viscosity of vapour, employed a rolling ball viscometer of his own design (7) which was basically the same as those used by earlier investigators. The time of fall of a steel ball, which was a close fit in a glass tube, through a fixed distance of the fluid under test was recorded for several tube inclinations to the horizontal. Dry air was used as the calibrating gas. The viscometer was designed to withstand 23.2 atmospheres of internal pressure. The theoretical justification of such a viscometer was based on a paper published by Hubbard and Brown (8). No effect of the variation of temperature upon the calibration constant could be detected, while the effect of pressure was found to give rise to an error of 1.0% in the measurement of the viscosity of a gas by that viscometer. The Freon vapours were tested in the following ranges of pressure and temperatures:

FREON	TEMP. RANGE DEG. C	PRESS. RANGE ATMOSPHERES
12	25 to 200	1.0 to 15.48
22	25 to 200	1.0 to 18.39
21	25 to 150	1.0 to 6.77

A rather interesting comparison is made by Makita between his experimental viscosity values at atmospheric pressure and those he calculated using Chapman and Cowling's approach based on the kinetic theory, to which reference is made in the former's paper. The theory is valid for nonpolar smooth spherical molecules. An equation of the form

$$\eta = AT^{1/2} e^{-D/T}$$

where A and D are constants, was fitted to Makita's results with an error of 2.0 percent, as shown below:

FREON	A	D	PERCENTAGE DEVIATION FROM KINETIC THEORY
12	9.423	-16.04	3.8 to 16.1% higher
22	11.16	-23.80	3.9 to 7.5% higher
21	8.892	-16.61	4.2 to 14.1% higher

The deviation of the theoretical curve from that of the experimental data can be expected, since the Freon molecule is complex when compared to the relatively simple theoretical model. A linear relationship between the viscosity of the Freons tested and the vapour pressures of their liquids was given by Makita in the form

$$\text{Log}\ \eta = K \log P + C$$

where K and C are fixed by the pressure at which the viscosity is desired, and P is the vapour pressure of their liquids. The deviation of experimental values from the above equation was found to be within 5.0 percent. It was also evident from Makita's viscosity isobars that the viscosity of the Freon vapours increases with increasing pressure, and that the slope of those constant pressure lines decreases with increasing pressure.

In 1955, Wellman (9) designed his own rolling ball viscometer which could withstand temperatures up to 400 degrees F and pressures up to 500 psia. The viscometer was calibrated using air at inclinations of 15, 40, and 80 degrees with the horizontal. The temperature range was from 20.0 to 90.0 degrees C at increments of 10 degrees C and at a pressure of one atmosphere. The calibration constant, which was supposed to be independent of the inclination angle for the range of Reynold Numbers that were employed was found to agree only within a range of ± 2 percent for the different inclinations. The air viscosity values used in this calibration were those supplied by the National Bureau of Standards and were only accurate to ± 1.0 percent. It was also found experimentally by Wellman, that the calibration constant increased at the rate of 3 percent for a temperature increase of 100 degrees C as opposed to a theoretical increase of 0.057 percent for the same temperature increase. Calibration with air was also carried out in the temperature range 30.0 to 90.0 degrees C and pressures up to 20 atmospheres, but no pressure dependence of the calibration constant could be detected. On the basis of the above calibrations Wellman carried out his tests on the vapours of Freon - 12 in the temperature range 2.9 to 90.0 degrees C and pressures of 1 to 20.0 atmospheres at increments of apporximately 4 atmospheres. Freon-13 was tested in the temperature range 30.2 to 88.3 degrees C and pressures of one to 14.5 atmospheres at increments of approximately 7 atmospheres. Freon-14 was tested in the temperature range 30.1 to 88.4 degrees C and at essentially atmospheric pressure. Only one single point was obtained for Freon-114 at a temperature of 30.2 degrees C and atmospheric pressure. For three of the Freon vapours at atmospheric pressure, Wellman fitted an equation of the form

$$\eta \times 10^4 = A\sqrt{T} - B$$

with constants A and B as follows:

FREON	A	B
12	14.34	122.6
21	15.27	152.2
13	17.95	171.0

No information about the scatter of the experimental data or the maximum deviation of the data from the fitted curves was reported by Wellman, however the author's calculations using the same results of Wellman reveal the following:

FREON	STANDARD ERROR OF ESTIMATE	MAX. DEVIATION, CP	MAX. % ERROR
12	7.78×10^{-5}	1.359×10^{-4}	1.116
21	3.13×10^{-5}	5.892×10^{-5}	-0.483
13	4.40×10^{-5}	4.148×10^{-5}	0.257

A comparison was made by Wellman between his results on the vapour of Freon 12 and those reported earlier by Benning and Markwood (3). It was found that there was a marked difference between the two sets. Using the same air viscosity values as those used by himself, Wellman recalculated the reported values of Benning and Markwood. Further comparison showed that the maximum difference between the two sets of values was ± 1.8 percent where Wellman's value is the higher one. The results of Freon 21 were also compared with recalculated values of Benning and Markwood, and the maximum difference was found to be ± 5.7 percent at the lowest temperatures.

Throughout the tests carried out by Wellman the temperature was measured by means of a single nickel resistance thermometer which could be screwed on the side of the viscometer tube and the resistance could be maintained within ± 0.05 degrees C. However, there was no way of detecting any thermal gradients along the tube which might have existed. One of the major sources of error in Wellman's work was in timing the falling sphere between two fixed marks. This gave rise to an overall error of ± 1.5 percent. The error analysis of Wellman shows that the maximum error in measuring the magnitude of the viscosity of the tested Freons was of the order of 2.73 percent.

Due to the lack of liquid viscosity data at that time, Kinser (10) in 1956 set out to measure the liquid phase viscosities of the Freons 11, 12, 21, 22, 113, 114, 115 and 12B1 at atmospheric pressure and in the temperature range -70 degrees C to the saturation temperatures at atmospheric pressure. It appears that Kinser used the viscometer designed by Wellman (9) with a smaller diameter sphere. Ethyl ether was used as the calibrating liquid since its viscosity values were well known. The calibration constant was found to be constant down to -40 degrees C, however, below this temperature it was found to decrease with decreasing temperature. A comparison was made by Kinser between his results and those of Benning and Markwood. The maximum percentage deviations were found to be as follows:

FREON	MAXIMUM PERCENTAGE DEVIATION
11	+ 3.58
12	- 0
21	+ 7.921
22	+16.70
114	- 4.60

No explanation could be found by Kinser as to the cause of the wide deviations. It is suspected that this error was cuased by the different pressures used by these workers, the fact which seems to have been overlooked. The viscosities of Freon 115 could not be calculated since density data were unattainable at the time.

The temperature during the above tests by Kinser was measured by means of a single Copper-Constantan thermocouple placed inside the entrance chamber of the viscometer. The time was measured with a stop-clock which introduced an estimated overall error of ± 1.5 percent into the results. The maximum experimental error was found to be ± 4.21 percent. Kinser felt that a primary measurement of viscosity was necessary to settle the dispute amongst workers, unfortunately, however, there appears to be no record of any attempt to carry out Kinser's suggestions.

Kamien (11) in 1959, published his paper on the effect of pressure and temperature on the vapours of Freons 12, 13, 14, 21, 22, 23, 114, 115 and C318. The apparatus used was that designed by Wellman (9). Measurement of the above mentioned nine Freons were reported at 1, 3 and 6 atmospheres in the temperature range 30 to 90 degrees C at intervals of approximately 20 degrees C. Fewer measurements were reported at 6 and 12 atmospheres of pressure in the same temperature range excluding Freons 21 and C318. Air was used as the calibrating gas at one atmosphere, whilst nitrogen was used for the higher pressure calibrations.

The variation of the viscosity of the nine refrigerants with temperature at atmospheric pressure was correlated by an equation of the form

$$\eta = A\sqrt{T} + B$$

and the constants A and B were calculated for each Freon. The measurements made on refrigerants 12, 21 and 22 were compared with those made by Benning and Markwood, Wellman, Coughlin and Makita. Incidentally, the Benning and Markwood results were those recalculated using the same viscosity values of air as those used by Kamien: apparently following the suggestion made by Wellman mentioned above. Kamien pointed out that the agreement between these measurements was thought to be good if Makita's measurements were neglected, however, no supporting data to this statement was given.

On the effect of pressure on the viscosity of those vapours, it was found that the viscosity increased with increasing pressures for all vapours investigated, the fact which supports Makita's findings, and that this increase was only appreciable over 6 atmospheres. Neither correlations of the effect of pressure on viscosity nor any analysis of the experimental errors was reported by Kamien.

Lilios (12) in 1957, employed two different types of secondary viscometers to measure the liquid phase viscosity of refrigerants at atmospheric pressure. The first viscometer employed was a rolling ball which was previously used by investigators at Purdue University by which he tested Freons 12, 12B1, 13B1, 113 and C318, whilst the second instrument utilized was a capillary type viscometer which he used to test Freons 12B2, 114B2, 12B1 and 12. Both viscometers were calibrated with ethyl ether and the temperature was measured by means of a single copper-constantan thermocouple which was stated to be calibrated to within ± 0.05 degrees C. Measurements were made in the temperature range -70 degrees C up to the saturation temperatures. Lilios also calculated the viscosity of Freon 115 at temperatures of -62.22, -51.11 and -40.00 degrees C using the experimental data obtained earlier by Kinser (10). As mentioned previously, Kinser was unable to calculate the viscosity values at that time due to the lack of the pertinent density data. Comparing the viscosity values obtained using the rolling ball viscometer with the results of Kinser, it was found by Lilios that for Freon 12 the maximum deviation was at -60 degrees C where the former's value was 18 percent higher. The measurements made on Freon 12 using the capillary viscometer were found to be as much as 10 percent lower than those obtained using the rolling ball viscometer at -60 degrees C. The viscosity of Freon C318 at 0 degrees C, reported by Graham (4), was found to be 15 percent higher than that found by Lilios. Except for one point estimated in Bulletin (B-4) of du Pont de Nemours Co. Ltd. at a temperature of -55 degrees C, no data could be found by Lilios for Freon 13B1 to compare with his own. This single point which was reported to have an estimation accuracy of ± 30 percent was found to be 28 percent lower than that found by Lilios at the same temperature. A curve was fitted by Lilios to Kinser's viscosity values for Freon 12B1 and gave a deviation of ± 4 percent from his own results obtained using the rolling ball viscometer. At -60 degrees C, where deviation is usually large, Lilios' viscosity value of Freon 12B1 obtained with a capillary viscometer, was found to agree more closely with Kinser's for the same temperature than the measurement made with the rolling ball viscometer. Estimated values of the viscosity of Freon 114B2 were found to be 2 percent lower than the values of Lilios. It should be pointed out that Lilios' viscosity values for Freon 114B2 have been recalculated by du Pont de Nemours Co. Ltd. using improved density data and have been published in their Bulletin Number (X-50A). The maximum deviation between estimated viscosity of Freon 12B2, which is given in the duPont Bulletin (B-4) and the measurements made by Lilios, was found to be -4 percent.

In calculating the results Lilios neglected the kinetic energy correction, often referred to as the end correction, for the measurements that he made with the capillary viscometer. The maximum error introduced in the results because of such an assumption would be of the order of 0.4 percent. It was pointed out by Lilios that his measurements made with the rolling ball viscometer were inferior to those made on the capillary viscometer. It was felt that temperature gradients existed along the tube of the rolling ball viscometer and that the temperature of the fluid being tested, which was contained in this tube, differed appreciably from that of the temperature control bath surrounding the tube where the temperature was measured. It was recommended by Lilios that the measurements made with the rolling ball viscometer should be repeated using a capillary type viscometer, because the latter instrument was believed to be more accurate. One of the major difficulties encountered by Lilios was that of achieving thermal stability at low temperatures. Since the effect of temperature variation on the viscosity of liquids is more pronounced at low temperatures ,it was thought that this explained the disagreement of workers in this range.

Despite the recommendations made by Lilios regarding the use of a rolling ball viscometer, McCullum (13) in 1958 carried out his measurements on the same viscometer used earlier by Wellman. McCullum's object was to extend previous vapour viscosity data of refrigerants at one atmosphere to the temperature range 100 to 200 degrees C. The viscosity of the vapours of Freons 11, 21, 23, 114 and 115 were thus measured in the temperature range 90 to 200 degrees C. Nitrogen was employed to calibrate the viscometer in the same temperature range; with the viscometer tube inclined at 40 degrees to the horizontal. The calibration constant was found to decrease by 3 percent for a temperature increase of 100 degrees C as opposed to an increase of the same magnitude for the same increase in temperature reported earlier by Wellman. The temperature was measured by the same nickel resistance thermometer used by Wellman. The resistance of this thermometer agreed with the values determined by Wellman for the temperature range 0 to 100 degrees C. However, above 100 degrees C, where Wellman extrapolated his experimental calibration values, there existed a deviation which was 1.4 degrees C at a temperature of 150 degrees C. McCullum combined the results of previous workers who had used the same apparatus at Purdue University, with his own and correlated the combined values at atmospheric pressure in the temperature range 30 to 200 degrees C. Those correlations were made for Freons 21, 23, 114 and 115. The commonly used equations for correlating the viscosity as a linear function of the square root of the absolute temperature, was found to fit the experimental data for Freons 21, 23, 114 and 115 with an error of ± 2 percent. McCullum shows that his experimental measurements were correct to within a maximum error of ± 2.2 percent, if an assumed error of ± 0.6 percent due to the thermometer calibration inaccuracy was neglected. It is surprising to find no mention of the possible temperature gradients along the rolling tube in McCullum's work, a fact which was pointed out very clearly by Lilios; an earlier investigator.

In an effort to evaluate the viscosities of flourinated hydrocarbon vapours at elevated pressures, Tsui (14) in 1959 used Wellman's rolling ball viscometer. Tsui thought that in order to avaoid the problem of the rolling ball sticking to the tube, which was experienced by earlier workers, it would be preferable to use a larger clearence between the tube and the ball. Since it was also desirable to keep the flow around the ball laminar, the angle of inclination of the tube with the horizontal was kept at 4 and 5 degrees during these tests. For some low viscosity Freons, however, it was found impossible to avoid turbulent flow even at those small inclinations. Consequently a relatively large error was immediately introduced in such measurements. Tsui carried out his measurements on Freons 11, 12, 13, 14, 21, 22, 23, 114, 115, 13B1, and C318 covering a temperature range of 90 to 150 degrees C and a pressure range of 1 to 20 atmospheres. Nitrogen was used to calibrate the viscometer.

The viscosity values of Nitrogen at high pressures were calculated by Tsui on the basis of a correlation given by Kestin and Wang to which reference is made in the former's work under the section "Viscosity Values of Nitrogen". The calibration constant was found to vary in magnitude with both pressure and temperature. At a certain temperature the effect of increasing the pressure from 1 to 5 atmospheres was such that the calibration constant decreased rapidly, whilst above 5 atmospheres the decrease became less in magnitude and steadied out at approximately 0.05 percent per atmosphere. The effect of increasing the temperature was to diminish the rapid decrease in the constant between 1 and 5 atmospheres. At a fixed pressure the calibration constant was found to increase at the rate of 1 percent for an increase of temperature of 100 degrees C. The measurements made by Tsui were found to be fairly consistent as the maximum deviation from the mean values was found to be within ± 0.5 percent throughout the tests. The error analysis of Tsui indicates that the maximum experimental error incurred for those measurements made when the flow was laminar was of the order of ± 1.59 percent, while for the turbulent flow tests it was about 6.6 percent. A comparison with the results of Wellman, Kamien and McCullum showed that at atmospheric pressure there was an agreement of ± 5 percent. At higher pressures Tsui's results were found to be as much as 15 percent higher than those obtained by Wellman and Kamien. It was also confirmed by Tsui that when the viscosity results of the vapours tested are plotted against the square root of the absolute temperature, they can be closely represneted by a straight line.

Willbers (15) in 1961 carried out his viscosity measurements in the temperature range - 40 to 15 degrees C and at pressures of 1 to 12 atmospheres. The purpose of Willber's investigation was to cover the above field where only few measurements had previously been made for Freons 12, 13, 14, 22, 23, 13B1, 115 and C318. In addition a 50 percent mole mixture of Freons 13B1 and 22 was tested. Following the footsteps of previous workers at Purdue University, Willbers made his measurements on the viscometer originally designed by Wellman. An improvement was made during those tests by developing a method of cleaning the rolling ball to avoid sticking without dismantling the viscometer. This was achieved by flushing the viscometer with Freon 11 under vacuum conditions. The calibration of the instrument was made with nitrogen. The calibration constant was found to increase by about 1 percent when the inclination angle of the tube with the horizontal was changed from 20 to 30 degrees at one atmosphere. It was also found that the calibration constant decreased with increasing temperature, and that the rate of this decrease was higher at low temperatures. The average rate of decrease was 0.4 percent per degree C, which is much larger than any found by previous investigators using the same apparatus. The effect of increasing the pressure from 1 to 6 atmospheres was to decrease the calibration constant at the rate of 1.7 percent per atmosphere. From 6 to 12 atmospheres, the calibration constant decreased at the rate of 0.3 percent per atmosphere. This trend is similar to that found earlier by Tsui. Willber's results made at one atmosphere were compared to extrapolated results of Wellman, Kamien, McCullum, Tsui and Coughlin and were found to agree within ± 1.5 percent. At higher pressures the agreement was only within ± 5 to ± 7 percent. The maximum experimental error was estimated at ± 1.5 percent when excluding the error in temperature measurement.

The work that was done by Riley (16) in 1963 signifies a demarkation from the relatively rough measurements carried out at Purdue University with the rolling ball viscometer. In his study of the temperature effect on the liquid viscosities of Freons 11 and 12, Riley used an Ostwald type capillary viscometer which had been designed at the same University by Wensely in 1958 and to which reference is made in Riley's thesis. According to Riley, the reason for the change to such a viscometer was that for low temperature work the density of the rolling ball became less than the fluid being investigated which rendered the rolling ball viscometer unworkable. For a pressure of one atmosphere, measurements were made over a temperature range of - 110 to 20 degrees C for Freon 11, and - 110 to -40 degrees C for Freon 22. The temperature was controlled by first circulating liquid nirogen around the viscometer container until the temperature reached a value below the desired one. The nitrogen, which had been prechilled by passing it through a bath of refrigerated alcohol, was throttled and passed through coils around the container. The amount of nitrogen gas was manually regulated until thermal equilibrium was achieved. The viscometer container was insulated from the atmosphere by placing it in a vacuum vessel provided with a radiation shield. The vacuum inside this vessel could be maintained at 5.0×10^{-4} milimeters of mercury. The temperature of the liquids tested was measured by means of three copper-constantan thermocouples which were attached to the efflux bulb, the capillary tube, and the collection bulb of the viscometer respectively. These thermocouples were calibrated to be accurate within ± 0.05 degrees C. Ethyl ether was used to calibrate the viscometer over the temperature range of interest. It appears that Riley took some care in cleaning the viscometer and eliminating the vapour content before taking his measurements. Due to the presence of foreign particles in the viscometer, the source of which could not be detected, the efflux time during the calibration could only be reproduced within 2 percent. For this reason Riley felt that his calibration data was questionable. Another major difficulty experienced by Riley was that of maintaining thermal equilibrium especially when the efflux time at low temperatures became as high as 20 minutes. A temperature variation of one degree C and a gradient of 0.6 degrees C was reported to be the worst case. The net error in the viscosity results due to the temperature variation alone was of the order of 2 to 3 percent at - 105 degrees C. Using the method of least squares, Riley fitted two polynomials of the form:

$$\text{Viscosity} = \sum_{1}^{n} a_{n-1} t^{n}$$

where the a's are constants and 't' is the temperature, to his measurements. A polynomial of the fifth degree gave a maximum deviation of 1.6 percent and a mean deviation of 0.025 percent for Freon 11 data ,on the other hand, a fourth degree polynomial with a maximum deviation of 1.2 percent and a mean deviation of 9.29 x 10^{-5} was found to fit the Freon 22 data best. The results of Riley were found to be lower than the measurements of Kinser or Benning and Markwood for Freon 11. The maximum deviation from the results of Benning and Markwood was 8 percent at - 35 degrees C. For Freon 22, an extrapolated value of Riley's results at - 30 degrees C was 2 percent higher than the Benning and Markwood experimental result at the same temperature. The results of Kinser were 14 percent higher at - 40 degrees C and 11 percent lower at - 65 degrees C. The maximum relative error in Riley's work was $\pm$ 5.0 percent at - 105 degrees C. This was mostly due to the temperature instability at such a low temperature. The relative error in the ,viscosity measurements by Riley at 0 degrees C was only $\pm$ 1.79 percent where the temperature instability error was only $\pm$ 0.1 percent. The work done by Riley is considered by this present author to be very good.

Eisele (17), in 1965, measured the viscosity of Freons 11, 12 and 22 in the liquid phase using a calibrated Cannon-Ubbelohde capillary type viscometer. Those measurements were carried out at the saturation pressures of the respective Freons. The temperature range investigated by Eisele was -95 to 70 degrees F for Freon 12; -30 to 50 degrees F for Freon 22; and -8 to 90 degrees F for Freon 11. In order to check the calibration constants for the instrument, which was a standard item purchased from the manufacturer, Eisele (17) carried out his own calibration using water and ethyl ether. The difference in the calibration constant was found to be of the order of 1.4%. Nevertheless, Eisele (17) used the calibration constant value supplied by the manufacturer on the belief that the purity of the calibration liquids used by the manufacturer had been higher. Eisele managed to hold the temperature of the viscometer constant to within ± 0.25 degree F by enclosing the viscometer chamber in an outer vessel filled with a suitable liquid Freon held at a constant saturation pressure. Hence the temperature could be controlled by varying the saturation pressure of the Freon in the outer vessel. Eisele employed Freons 11, 12, 13, and 14 in the outer jacket for the temperature control. By varying the saturation pressures between atmospheric and 100 psiag a working temperature range of -198.4 to 201.0 degrees F could be obtained. Superheating of the vapour in contact with its liquid inside the outer vessel introduced a temperature gradient along the viscometer. Eisele overcame this difficulty by initially cooling the viscometer to a temperature below that desired using liquid nitrogen. Then by allowing the viscometer chamber to absorb the necessary heat from the surroundings, the temperature gradient ceased to exist since the vapour superheating was eliminated. The design particulars of the viscometer chamber and the surrounding chamber are included in Eisele's thesis. Another modification introduced by Eisele on the methods employed by an earlier investigator Riley (16) was that of holding the test liquid inside a chamber mounted above the Cannon-Ubbelohde viscometer and enclosed by the viscometer chamber. This insured that the test liquid could be held at a constant temperature before allowing it to run through the capillary viscometer. The temperature of the liquid under test was measured by means of two copper-constantan thermocouples placed inside the viscometer chamber. Eisele found that by plotting the results for the kinematic viscosity that he obtained, against the inverse of the absolute temperature, straight line correlations could be obtained. These straight line correlations were based on an approximate form of the Eyring Equation, to which reference is made in Eisele'e thesis. Empirical equations of the form

$$\nu = \nu_b \ \text{exp.} \left(\frac{T_b}{T} - 1 \right)$$

were also fitted by Eisele to his own data for Freons 11, 12, and 22, within an experimental scatter of ± 1%, where ν is the kinematic viscosity and subscript "b" refers to boiling point property. A general equation of the above form, based on the average values of γ_b and T_b for Freons 11, 12, and 22 was also developed by Eisele. This latter equation can be used to predict the viscosity data of all three Freons within a maximum deviation of 15%. Eisele compared the data he obtained for liquid Freon 12 with the data obtained earlier by Awberry and Griffiths (2), and Benning and Markwood (3), and found that the latter's differed by as much as 20% from that of his own, while the maximum deviation of Awberry and Griffiths' data was 5%. For Freon 11, Eisele found that a correlation could be found for the temperature range -20 to 70 degrees F such that it would fit the data of Riley (16), Benning and Markwood (3), Kinser (10), and his own data within ± 4%. For Freon 22, Eisele's data was found to be lower than that of Benning and Markwood. In his error analysis, Eisele shows that his viscosity data above the normal boiling point were in error by ± 1.5%; mainly due to the kinetic energy effect which he neglected. At lower temperatures the viscosity data is claimed to be accurate to within ±0.7%, any errors being due mainly to temperature instabilities. It must be pointed out here that Eisele's data does not include the calibration error for the instrument he used.

Very recently, Gordon (18) used Eisele's instrument to measure the viscosity of Freons. Gordon obtained data for the liquid phase of Freons 11, 12, 13B, 22, 115, C318 and 502 within the temperature range -20 to 100 degrees F, and for Freon 13 in the general range -100 to 0 degrees F. According to Gordon the data verifies the results of

Eisele (17) and agrees well with those of Riley (16), Lilios (12). To the author's knowledge, the work done by Gordon (18) is still unattainable, therefore, not much more could be said about it.

II.2 Concluding Comments on the Literature Survey

1. If there is a need for absolute values of viscosity of liquid and vapour refrigerants, which the author feels is the case, the whole field of pressure and temperature data is open to a much more thorough investigation.

2. The viscosity measurements of Freon vapours and liquids under pressure are very few in number.

3. Table 2 is a summary of the available experimental work which has been done and can be consulted for the availability of data on the viscosity of the halogenated hydrocarbon refrigerants.

4. Appendix (X7) is an analysis of the results that appear in this literature survey in both the liquid and vapour phases at atmospheric pressure.

REFRIGERANT	NAME	FORMULA	MOLECULAR WEIGHT
11	Trichloromonofluoromethane	CCl_3F	137.381
12	Dichlorodifluoromethane	CCl_2F_2	120.924
12B1	Monobromomonochlorodifluoromethane	$CBrClF_2$	165.383
12B2	Monochlorotrifluoromethane	$CClF_3$	209.842
13	Monochlorotrifluoromethane	$CClF_3$	104.467
13B1	Monocromotrifluoromethane	CBrF3	148.926
14	Tetrafluoromethane	CF4	88.010
21	Dichlorofluoromethane	$CHCl_2F$	102.932
22	Monochlorodifluoromethane	$CHClF_2$	86.475
23	Trifluoromethane	CHF_3	70.018
113	Trichlorotrifluoroethane	$CCl_2F - CClF_2$	187.391
114	Dichlorotetrafluoroethane	$CClF_2 - CClF_2$	170.934
114B2	Dibromotetrafluoroethane	$CBrF_2 - CBrF_2$	129.926
115	Monochloropentafluoroethane	$CClF_2 - CF_3$	154.477
C318	Octafluorocyclobutane	C4F8	200.040

TABLE 1. CHEMICAL NAMES AND MOLECULAR WEIGHTS OF REFRIGERANTS

FREON	1933	1939	1939	1945	1953	1954	1955	1956	1956	1957	1958	1959	1961	1963	1965	1967
22		(3)· V			(5)· V	(6)· V P		(10)· L	(11)· V P			(14)· V P	(15)· V	(16)- L	(17)- L	(18)-
23					(5)· V				(11)· V P		(13)· V	(14)· V P	(15)· V			
113	(1)· L	(3)· V P	(3)· L P					(10)· L		(12)· L						
114							(9)· V	(10)· L	(11)· V P		(13)· V	(14)· V P				
114B2										(12)- L						
115					(5)· V			(10)· L	(11)· V P		(13)· V	(14)· V P	(15)· V.			(18)-
C318				(4)· L & V					(11)· V P	(12)· L		(14)· V P	(15)· V			(18)-
50% 13B1/22													(15)· V			

TABLE 2. CHRONOLOGICAL LISTING OF LITERATURE ON FREON VAPOURS AND LIQUIDS

KEY: L LIQUID PHASE, V VAPOUR PHASE, . ROLLING OR FALLING PLUG VISCOMETERS, - CAPILLARY VISCOMETER

∸ BOTH VISCOMETERS, P UNDER PRESSURE

NOTE: Number in brackets indicate references.

FREON	1936	1939	1939	1954	1955	1956	1956	1957	1958	1959	1961	1963	1965	1967	
11		(3)· V	(3)· L P			(10)· L			(13)· V	(14)· V P		(16)- L	(17)- L	(18)-	
12	(2)· L	(3)· V	(3)· L P	(6)· V P	(9)· V P	(10)· L	(11)· V P	(12)÷ L		(14)· V P	(15)· V		(17)- L	(18)-	
12B1						(10)· L	(11)· L	(12)÷ L							
12B2								(12)- L							
13					(9)· V P		(11)· V P			(14)· V P	(15)· V				
13B1								(12)· L		(14)· V P	(15)· V			(18)-	
14							(11)· V P			(14)· V P	(15)· V				
21		(3)· V		(6)· V P	(9)· V P	(10)· L	(11)· V P		(13)· V	(14)· V P					

TABLE 2 / CONTINUED

KEY: L LIQUID PHASE, V VAPOUR PHASE, . ROLLING OR FALLING PLUG VISCOMETERS, - CAPILLARY VISCOMETER
∔ BOTH VISCOMETERS, P UNDER PRESSURE

NOTE: Number in brackets indicate references.

III THEORY OF THE SERIES CAPILLARY VISCOMETER

The parameters governing the laminar flow of fluids through smooth circular pipes of uniform diameters can be related by the Poiseulle Equation:

$$\eta = \frac{\pi a^4 \rho}{8Q} \times \frac{dp}{d\ell} \qquad (1)$$

where "η" and "ρ" are the dynamic viscosity and the density of the fluid respectively, "a" is the radius of the tube, "Q" is the mass flow rate and $\frac{dp}{d\ell}$ is the pressure drop per unit length of the pipe. Equation (1) only applies to that portion of the pipe where the velocity profile of the flow is fully developed. Since the pressure drop is measured at either end of the pipe, a correction has to be applied to equation (1) to allow for the flow development at the entrance to the pipe. Equation (1) can be modified to include this correction in the form

$$\eta = \frac{\pi a^4 \rho}{8Q} \frac{[P_i - P_e]}{[\ell i - \ell e]} - \frac{mQ}{8\pi\ell} \qquad (2)$$

where subscripts "i" and "e" refer to conditions at the entrance and exit of the pipe, and "m" is a constant. The constant "m" has been found by Boussinesq to have a value of 1.12, see Barr (24) and experimental findings appear to confirm this value. The correction for flow development is often referred to as the "kinetic energy correction" or the "end correction".

Another correction that can be allowed for is the "Couette Correction". This allows for the small amount of energy used in overcoming the viscous forces between the converging and diverging streamlines at the entrance and exit of the pipes. It takes the form of a hypothetical increase "n x a" to the length of the pipe. The constant "n" is found experimentally to have values in the range 0 to 6.

Allowing for the "Couette Correction" and for thermal expansion or contraction of the pipe, equation (2) becomes:

$$\eta = \frac{\pi a^4 \rho \Delta P \ (1 + 3\alpha t)}{8Q \ (\ell + na)} - \frac{mQ}{8\pi (1 + \alpha t)(\ell + na)} \tag{3}$$

where $\ell = \ell i - \ell e$, "ΔP" = $P_i - P_e$, "α" is the coefficient of thermal expansion of the material of the capillary tube, and "t" is the temperature difference between the test temperature and that at which the pipe diameter is measured.

Let subscripts 1 and 2 refer to the first and second capillaries. Then we can write

$$\eta = \frac{\pi a_1^4 \ \rho_1 \ \Delta P_1}{8Q \ (\ell_1 + n_1 a_1)} - \frac{m_1 Q}{8\pi \ (1 + \alpha t)(\ell_1 + n_1 a_1)} \tag{4}$$

$$\eta = \frac{\pi a_2^4 \ \rho_2 \ \Delta P_2}{8Q(\ \ell_2 + n_2 a_2)} \quad \frac{m_2 Q}{8\pi \ (1 + \alpha t)(\ell_2 + n_2 a_2)} \tag{5}$$

From equation (4)

$$m_1 = \frac{8\pi(1 + \alpha t)(\ell_1 + n_1 a_1)}{Q} \times \left[\frac{\pi a_1^4 \rho_1 \Delta P_1 (1 + 3\alpha t)}{8Q(\ell_1 + n_1 a_1)} - \eta\right] \qquad (6)$$

Assuming that $m_1 = m_2$ and substituting (6) in (5) we get

$$\eta = \frac{\pi a_2^4 \Delta P_2 (1 + 3\alpha t)\rho_2}{8Q(\ell_2 + n_2 a_2)} - \left[\frac{\pi a_1^4 \rho_1 \Delta P_1 (1 + 3\alpha t)}{8Q(\ell_1 + n_1 a_1)} - \eta\right]$$

$$\times \frac{8\pi(1 + \alpha t)(\ell_1 + n_1 a_1)}{Q} \cdot \frac{Q}{8\pi(1 + \alpha t)(\ell_2 + n_2 a_2)}$$

$$\eta\left[1 - \frac{(\ell_1 + n_1 a_1)}{(\ell_2 + n_2 a_2)}\right] = \frac{\pi a_2^4 \, \Delta P_2 (1 + 3\alpha t)\, \rho_2}{8Q(\ell_2 + n_2 a_2)}$$

$$- \frac{\pi a_1^4 \Delta P_1 \rho_1 (1 + 3\alpha t)}{8Q(\ell_1 + n_1 a_1)} \times \frac{(\ell_1 + n_1 a_1)}{(\ell_2 + n_2 a_2)}$$

or

$$\eta\left[(\ell_2 + n_2 a_2) - (\ell_1 + n_1 a_1)\right] = \frac{\pi a_2^4 \Delta P_2 (1 + 3\alpha t)\rho_2}{8Q}$$

$$- \frac{\pi a_1^4 \Delta P_1 (1 + 3\alpha t)\rho_1}{8Q}$$

Assuming that $n_2 = n_1$, and since a_1 can be chosen to be very nearly equal to a_2, we can write

$$\eta = \frac{\pi a_2^4 (1 + 3\alpha t)}{8Q(\ell_2 - \ell_1)} \left[\Delta P_2 \rho_2 - \left(\frac{a_1}{a_2}\right)^4 \Delta P_1 \rho_1\right] \qquad (7)$$

In deriving the Poiseulle Equation (1) one of the assumptions made is that of no slip at the wall of the pipe. In practice, this condition might not be strictly true. Knudsen (49) has developed a semi-empirical equation to allow for the slip correction. This takes the form: -

$$\eta_t = \eta \times (1 + \frac{8\varepsilon}{d}) \qquad (8)$$

where "η_t" is the true value of the viscosity, "η" is the viscosity as calculated from equation (7), "d" is the diameter of the pipe and ε is the slip correction factor which is given by:

$$\varepsilon = \frac{k \times 2.128 \times \eta}{\sqrt{P\rho}} \qquad (9)$$

In the expression (9), "P" is the absolute pressure, "ρ" is the density of the test fluid, and "k" is an empirical constant depending on the fluid being investigated. Latto (34) has shown that neglecting the slip correction for superheated steam under atmospheric pressure would cause the viscosity values to be about 0.06% lower than the true values as calculated by expression (7). In this work the slip correction was neglected for two reasons; namely

1. The empirical constant "k" of expression (7) was unattainable for the Freon Compounds.
2. The magnitude of such a correction is expected to be very small.

The reader is referred to Barr (24), for a more thorough discussion on the theory and experimental techniques with regard to capillary viscometers.

IV DESIGN CONSIDERATIONS

When designing a capillary viscometer, it is necessary to estimate the order of magnitude of the parameters governing the flow of a fluid through the capillary tube. Of particular interest are the Reynold's Number, the mass or volume flow rate and the development length of the velocity profile at the entrance to the capillary. Since the Poiseuille Equation, upon which such a design is based, is strictly limited to conditions of laminar flow, the Reynold's Number has to be less than 2000. The volume flow rate must be estimated so as to decide upon an appropriate flowmeter device. The series-capillary viscometer has the prime advantage of eliminating the end correction, which is the error introduced by the developing flow at the entrance of the capillaries. However, it is essential to insure that the development length does not become predominant. That is to say, for a particular length of a capillary tube the development length should not exceed a small portion of the total length of the same tube. A ratio of development length "x" to the total capillary "ℓ" of 25% appears to be reasonable. The value of "x" has been found to be $x = 0.0288\,Re.d$, thus it can be calculated.

Consider the Poiseuille Equation

$$Q = \frac{\pi d^4 \rho}{128\,\eta} \cdot \frac{dp}{dl}$$

and the Reynold's Number

$$Re = \frac{\rho \cdot v \cdot d}{\eta} = \frac{\rho \cdot d^3}{32\,\eta^2} \times \frac{dp}{dl}$$

Both the mass flow rate "Q" and the Reynold's Number "Re" are functions of the capillary diameter "d", the pressure drop per unit length $\frac{dp}{d\ell}$, the dynamic viscosity η, and the dnesity ρ. In order to investigate the variation of "Re" and "Q" with temperature it is necessary to estimate the variation of both the density and the viscosity of the fluid under test with temperature. Since the variation of the diameter with temperature is small (the coefficient of linear expansion for glass is of the order of 3.3×10^{-6} per °C), it can be neglected for the purpose of estimation.

Linear equations of the form

$$1/\rho \text{ cu.ft.}/\text{lb}_m = A1 \times t + A0,$$ where

t is the temperature in degrees F and A1 and A0 are constants, were determined for the variation of specific volume of the Freon vapours with temperature at atmospheric pressure. This was done by the method of least squares. Where the constants A0 and A1 are given in Table 3 together with the temperature range and the pressure for which they are valid.

The linear equations of the form

$$\eta = A\sqrt{T} + B$$

where T is the absolute temperature, which were found by Witzell (19), were used to estimate the variation of the viscosity with temperature. It must be mentioned here that the viscosity equations are based on secondary measurements using mainly the rolling ball viscometer, but they were considered adequate for the purpose of estimation.

In order to assess the more pertinent design criteria for the capillary a family of curves were established based on a pressure drop of 1 cm. of mercury per 10 cm. of capillary tube length. The Reynold's Number, the mass flow rate and the development length were calculated for different capillary diameters over the temperature range of interest. These capillary selection curves are shown in the figures (1) to (7) for Freons 11, 12, 13, 14, 21, 22 and 114 in the vapour phase at atmospheric pressure.

Freon	Temp.Range in Deg. F	Pressure lbf in/sq.in	A0	A1	Standard Error of Est. x10^2	Greatest Error x10^3 cu.ft/lbm	Maximum % Error	Data Source Ref. No.
11	+79 → + 290	16.0	2.13704	0.00510	0.17752	2.35379	-0.093	26
12	-17.99 → +190.0	16.0	2.45383	0.00587	0.44824	10.00303	-0.426	27
13	-113 → +500	15.0	3.09120	0.00697	1.1833	37.76845	-1.644	33
14	-20 → +100	14.696	3.87226	0.00847	0.35709	8.96469	-0.412	28
21	+52 → +330	16.0	2.89452	0.00670	0.21457	3.78251	-0.117	29
22	-38.06 → +270	16.0	3.46915	0.00804	0.71638	17.65493	-0.558	30
113	+122.10 → +430	16.0	1.55252	0.00373	0.17690	3.50320	-0.175	32
114	+42.30 → +250	16.0	1.72044	0.00410	0.11451	2.06068	-0.075	29
115	-20 → +300	15.0	2.06466	0.00478	0.25837	5.15661	-0.262	31

TABLE 3 STRAIGHT LINE CORRELATION OF SPECIFIC VOLUME IN CU.FT./LBM.
VERSUS TEMP. IN DEG. F FOR FREON VAPOURS

FREON 11 (VAPOUR)

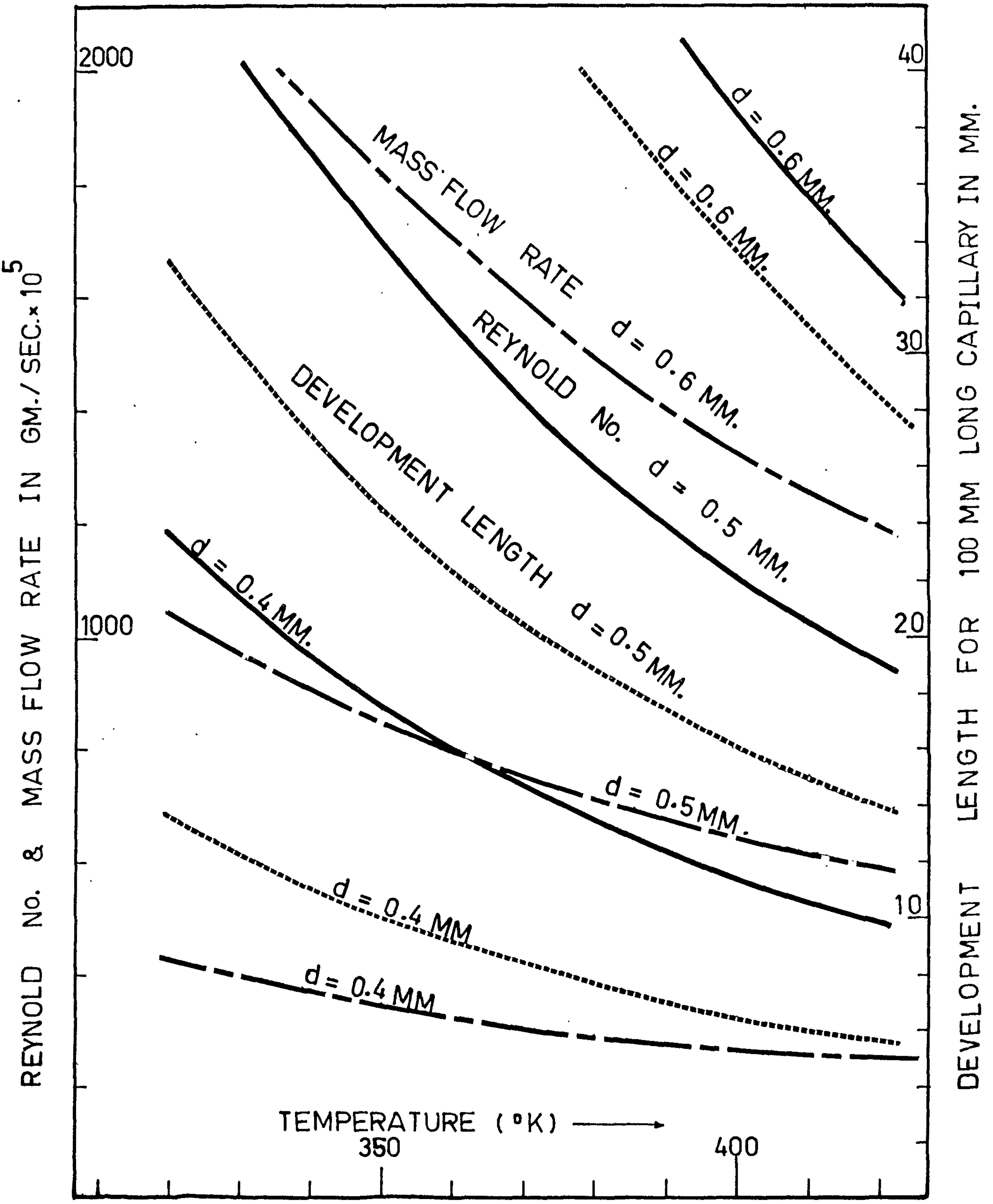


FIGURE 1 MASS FLOW RATE, DEVELOPMENT LENGTH AND REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 11 AT ATMOSPHERIC PRESSURE

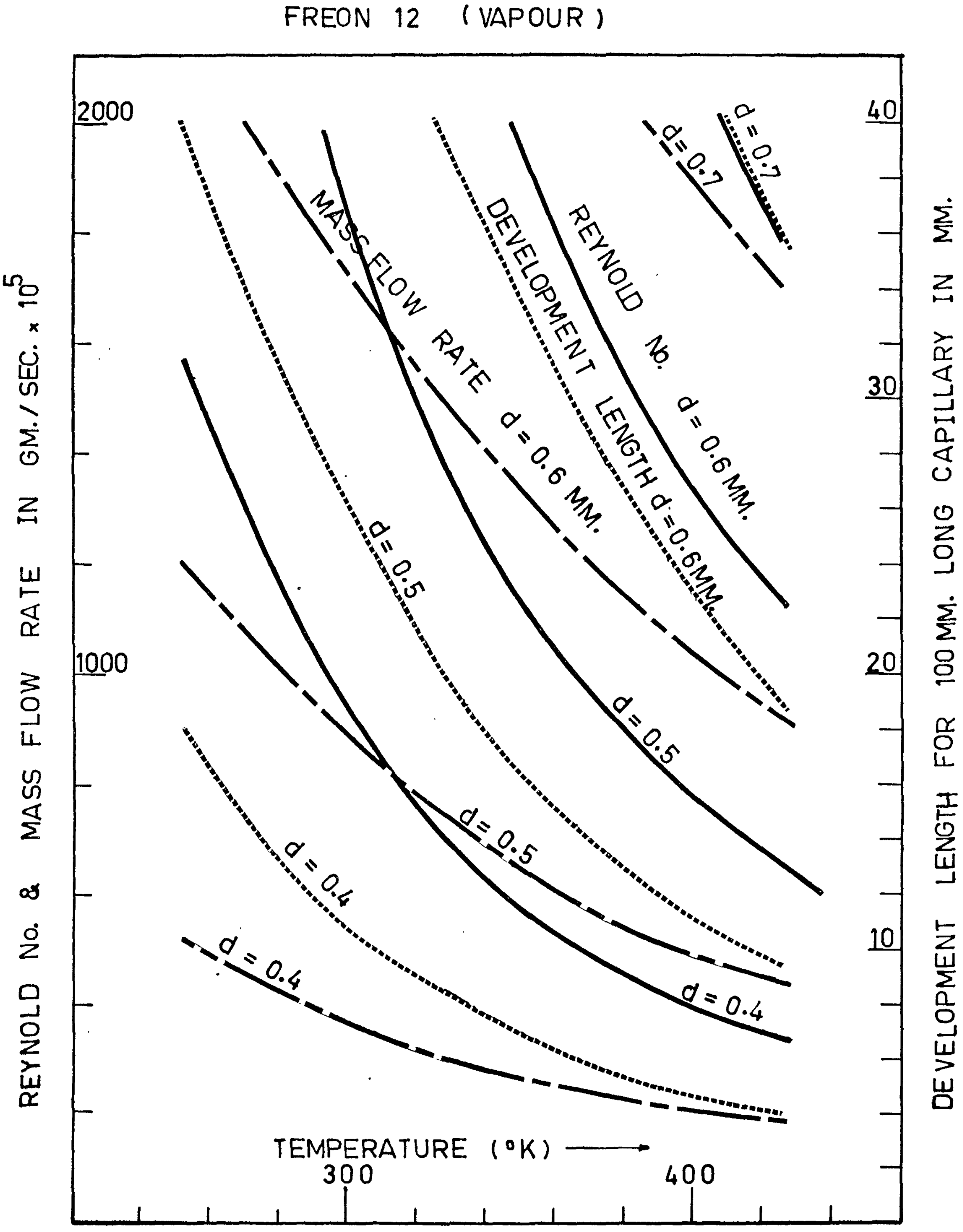


FIGURE 2 . MASS FLOW RATE, DEVELOPMENT LENGTH AND REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 12 AT ATMOSPHERIC PRESSURE

FREON 13 (VAPOUR)

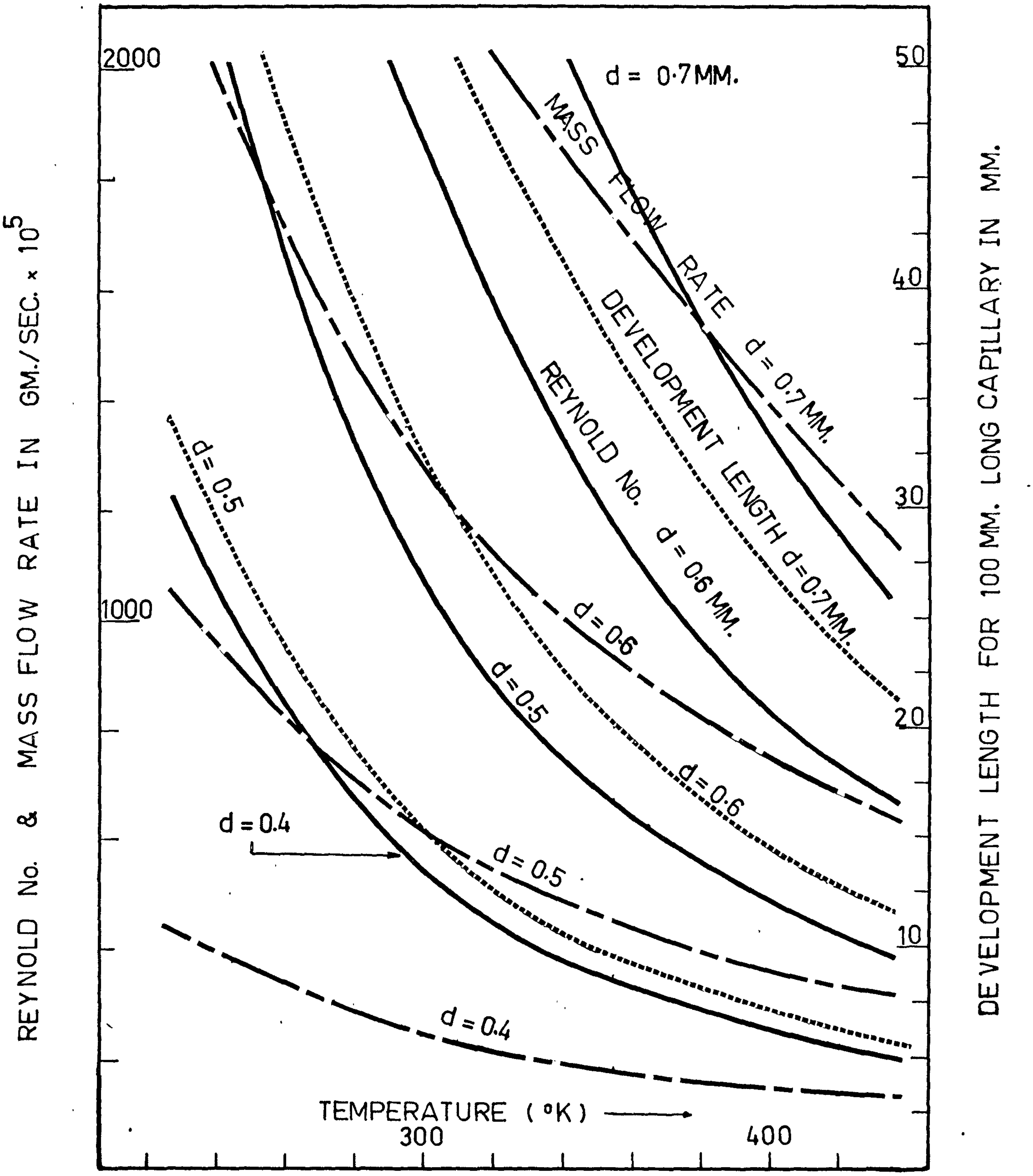


FIGURE 3 MASS FLOW RATE, DEVELOPMENT LENGTH AND REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 13 AT ATMOSPHERIC PRESSURE

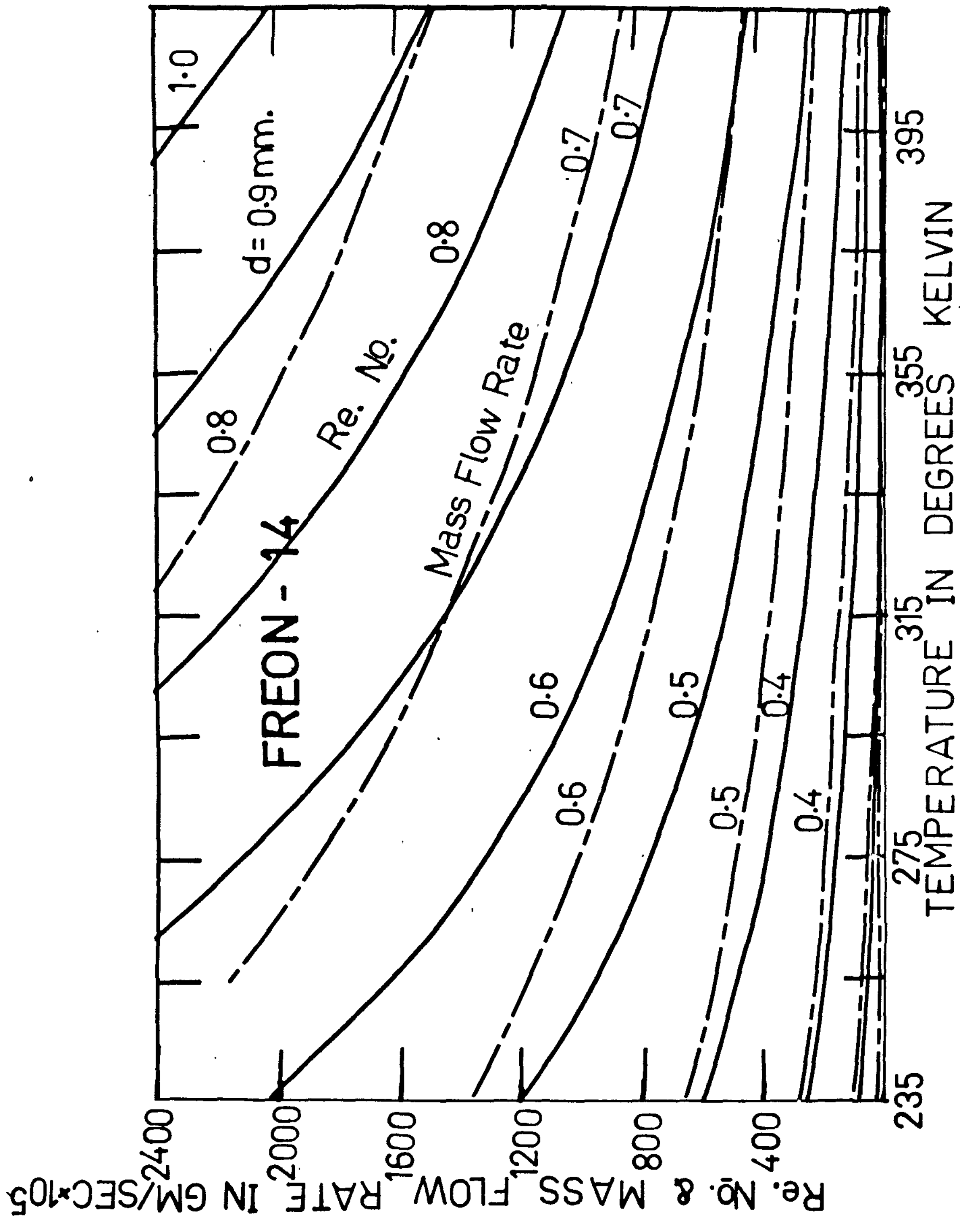


FIGURE 4 MASS FLOW RATE, REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 14 AT ATMOSPHERIC PRESSURE

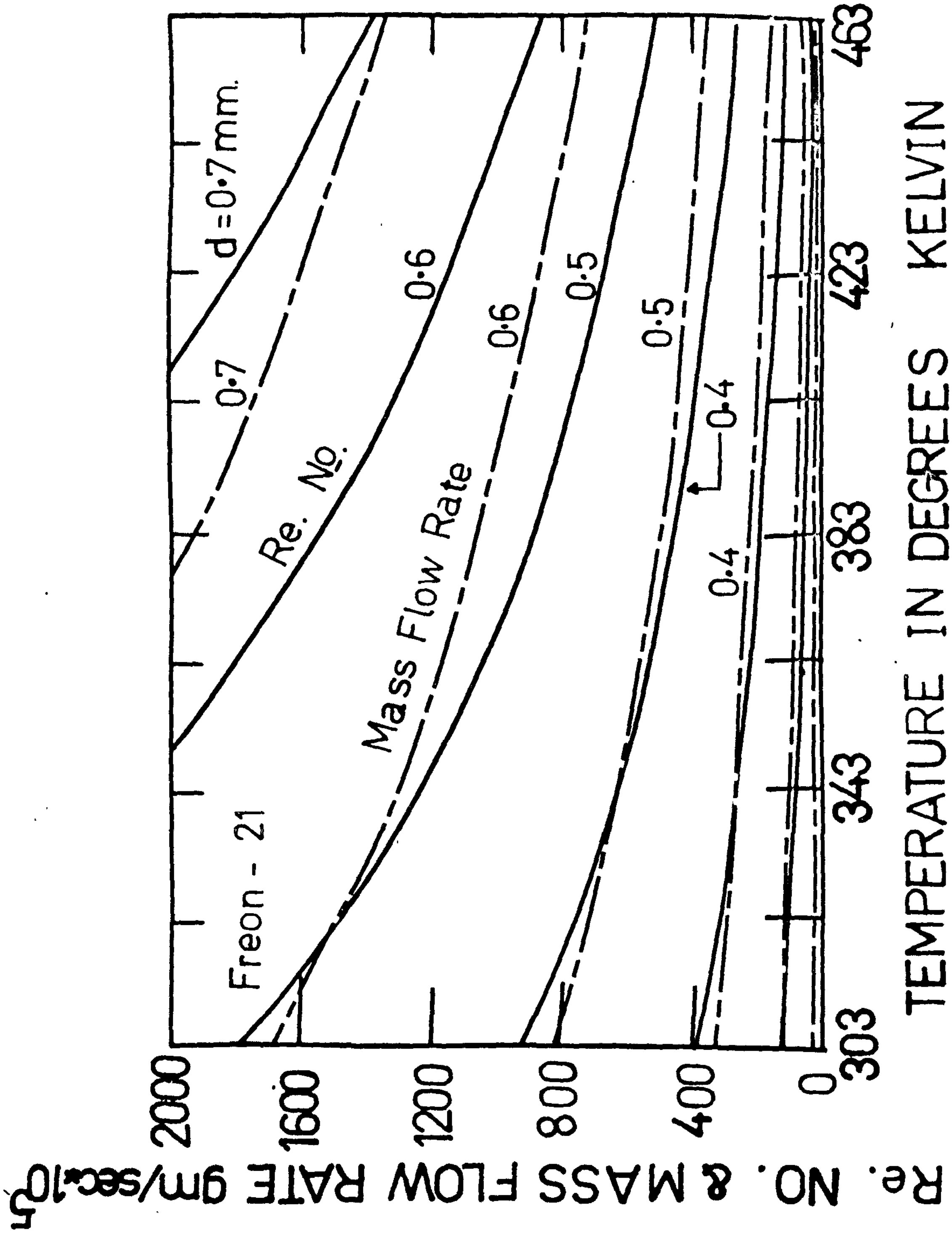


FIGURE 5 MASS FLOW RATE, REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 21 AT ATMOSPHERIC PRESSURE

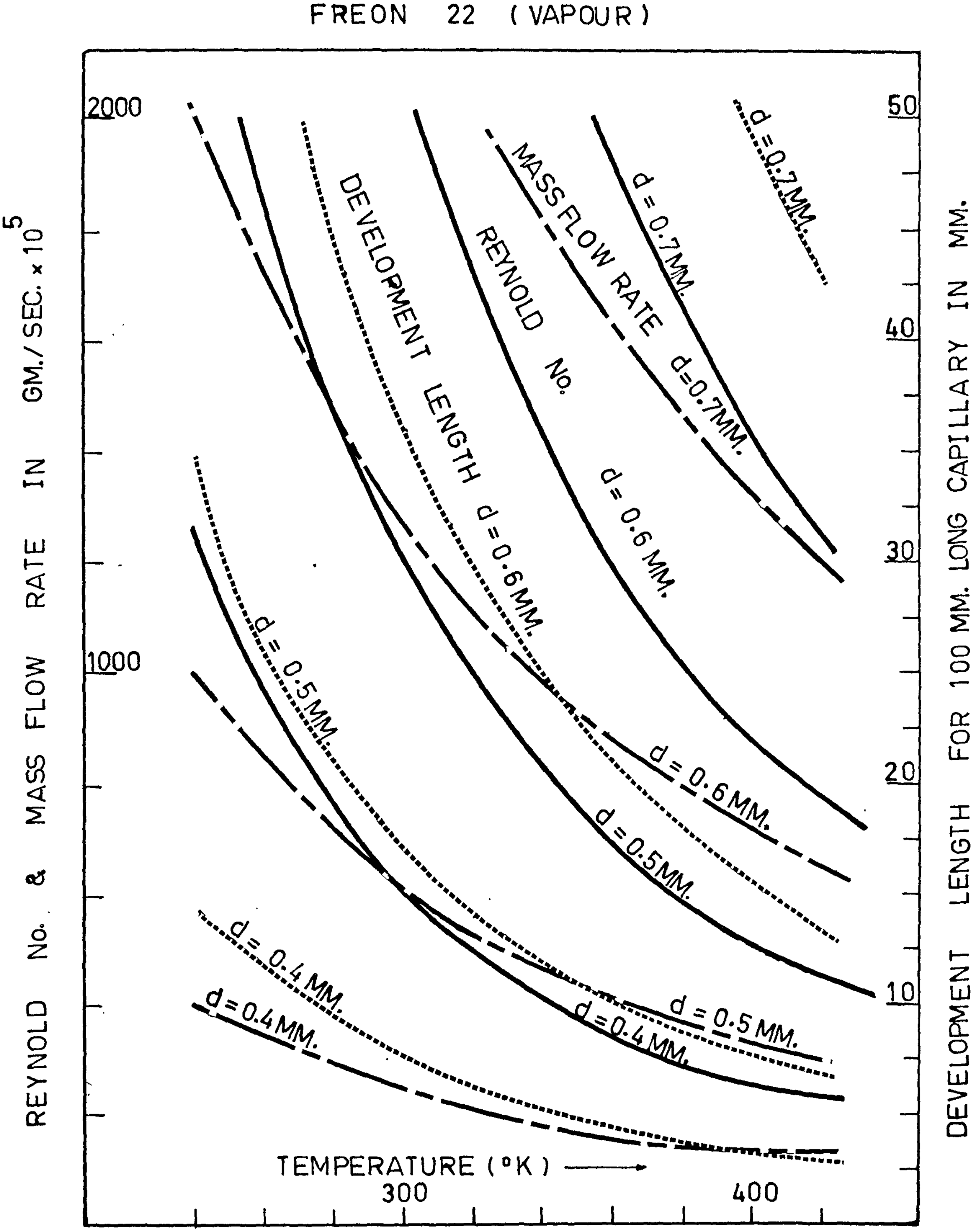


FIGURE 6 MASS FLOW RATE, DEVELOPMENT LENGTH AND REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 22 AT ATMOSPHERIC PRESSURE

FREON 114 (VAPOUR)

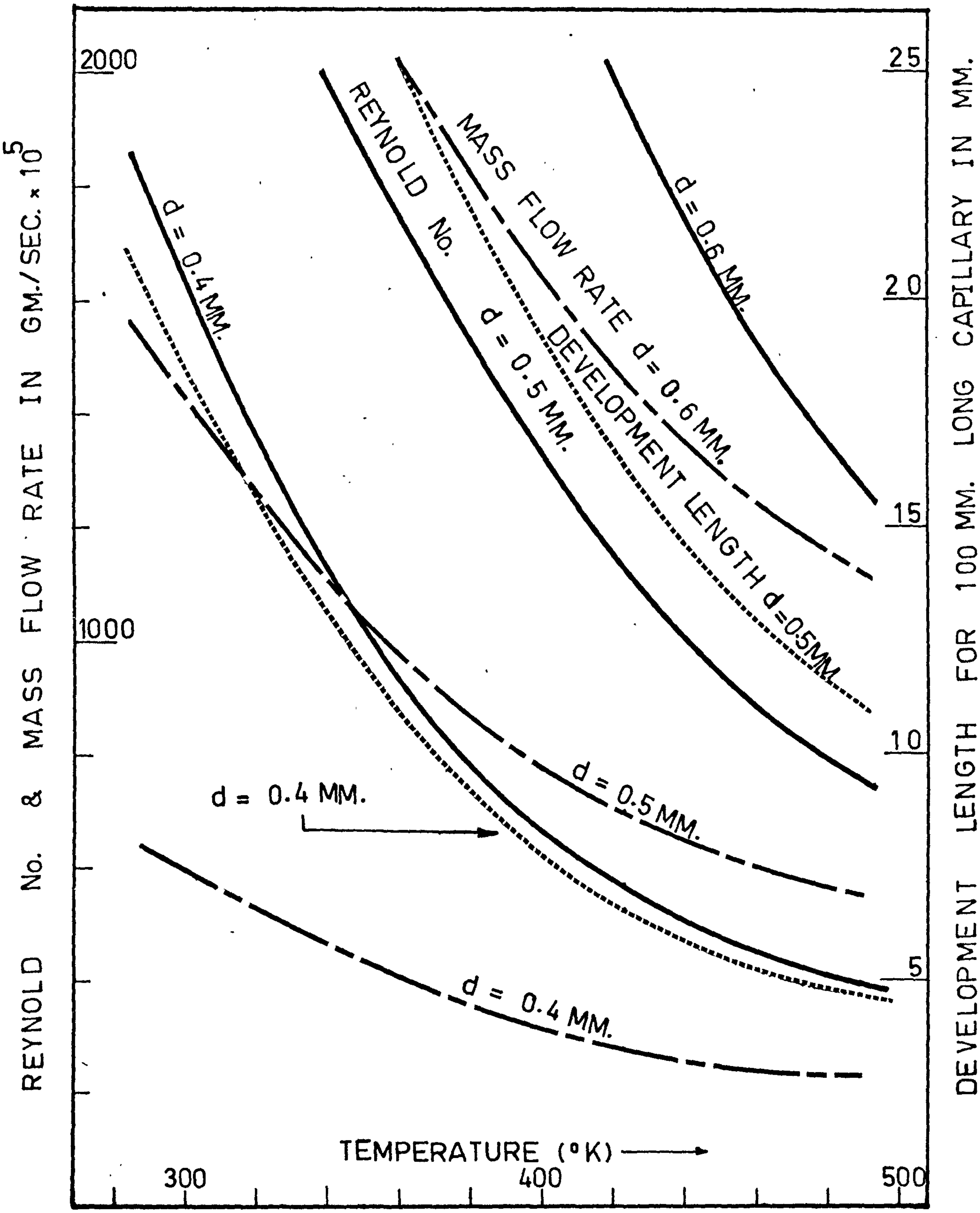


FIGURE 7 MASS FLOW RATE, DEVELOPMENT LENGTH AND REYNOLD'S NUMBER VERSUS TEMPERATURE IN °K FOR FREON 114 AT ATMOSPHERIC PRESSURE

V DESCRIPTION OF THE APPARATUS

V. 1 Introduction:

In his work on the measurement of absolute viscosity of steam at elevated temperatures and atmospheric pressure, Latto (34), has made a thorough survey of the methods of viscosity measurement. He concluded that the series - capillary viscometer would be the most suitable device for primary measurements. The reasons being:

1. The theory behind such a viscometer is well developed (see Theory Chapter IV).
2. The kinetic energy correction at the entrance to the capillaries, which is usually difficult to determine experimentally, is eliminated.
3. The capillary tubes can be treated separately to yield the kinetic energy correlation.

On this basis Latto (34) optimized the design of the series capillary viscometer and obtained extensive results on steam which have an accuracy range of ± 0.57 to ± 0.74%.

The present viscometer was designed at McMaster University by B. Latto and was developed by the author. The auxiliary equipment was also developed by the author. The final apparatus which was used is described below.

V. 2 The Viscometer:

The viscometer is of the series - capillary type as shown in figure (8). The gas under test is supplied to the entrance plenum chamber via a temperature stability tube. The stabilizing tube is a 1/4" O.D. copper tube bent in the form of a "U" loop which extends through the entire length of the viscometer cell. The two capillary tubes that are utilized are "Veridia" precision bore tubes supplied by "John Glass Ltd" (See Appendix X3 for Capillary Calibration), and have a length ratio of approximately 2:1. The longer capillary tube is positioned upstream so as to keep the difference between the pressure inside the intermediate chamber and atmospheric pressure as small as possible. The viscometer is primarily made of copper. The chambers were made from a 2-1/2" O.D. copper tube which has a wall thickness of 1/8". The 1/8" thick copper side plates were braized to the tube pieces. The lines of braizing and the faces of the chambers were coated with a film of "Epoxy" resin in order to make the unit leak proof see figure (9). In order to hold the viscometer chambers rigidly together, two 1/4" stainless steel rods were used to connect the three chambers. This was done with the aid of V-blocks and accurate dial indicators so as to insure that the chambers would be in line when connected by the rods. The alignment was necessary because any misalignment would result in bending stress on the glass capillary tubes and would consequently make the latter susceptible to breakage.

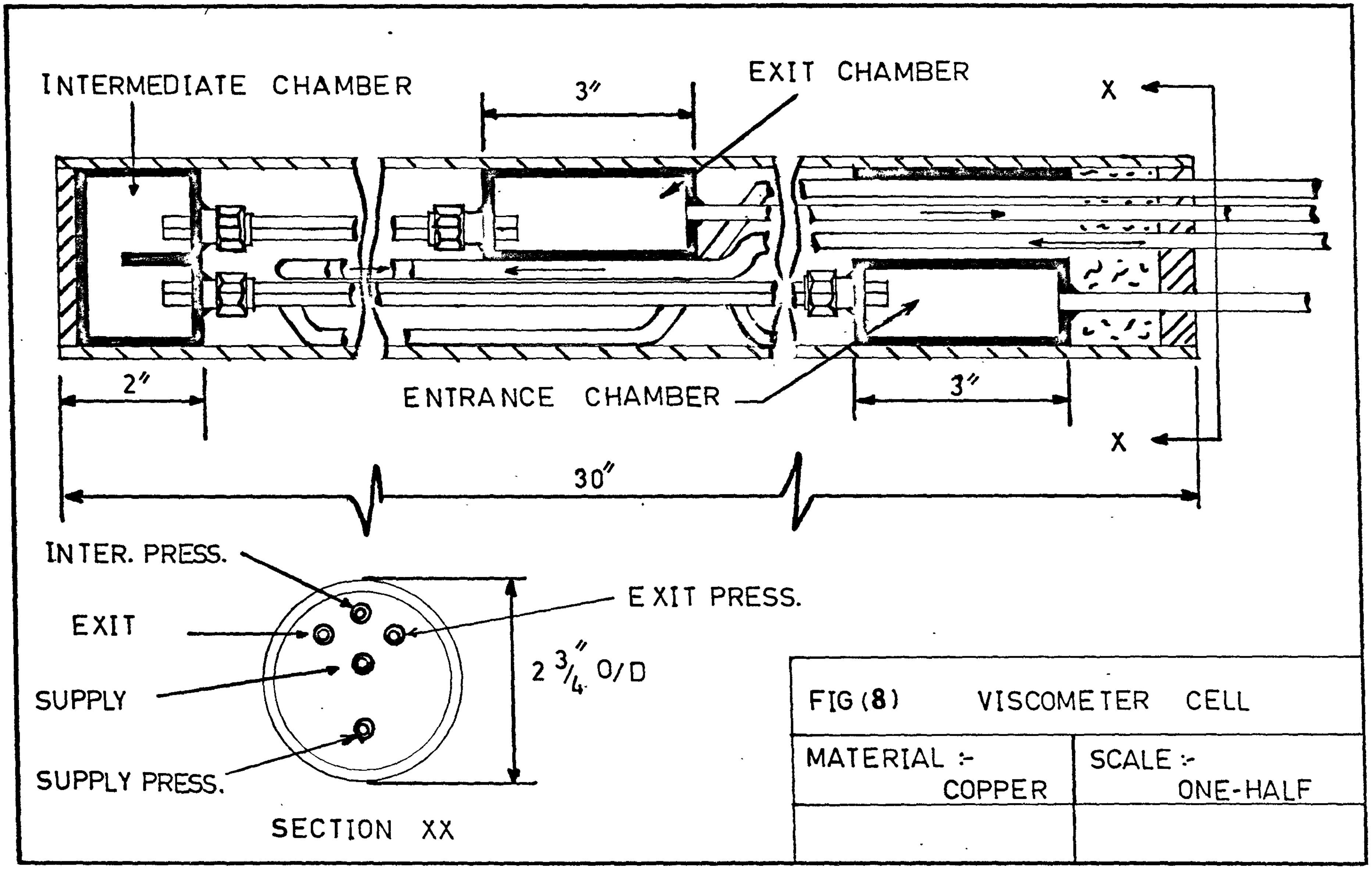


FIG (8) VISCOMETER CELL

MATERIAL :- COPPER	SCALE :- ONE-HALF

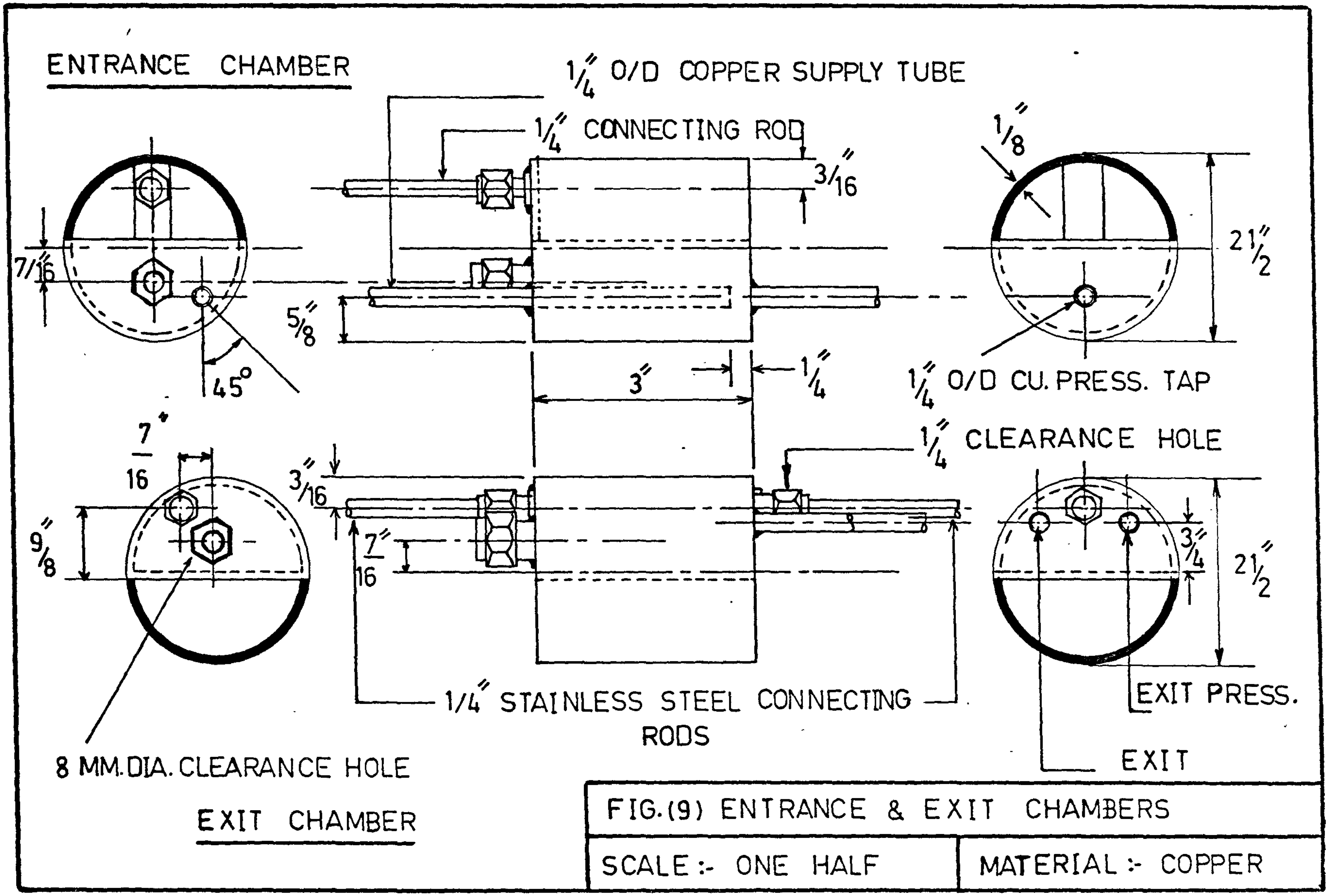


FIG. (9) ENTRANCE & EXIT CHAMBERS

SCALE :- ONE HALF	MATERIAL :- COPPER

The viscometer has the feature of accommodating capillary tubes of different outside diameters up to 8 mm., see figure (9). This feature has two advantages. Firstly, for different fluids or different temperature ranges (see Design Considerations - Chapter V) the selected capillary tube can be used in the same viscometer. Secondly, the capillary tubes that are used in a certain test can be taken out for recalibration in order to be able to detect any deformation or change in diameter of that glass capillary tube.

One of the serious problems experimentally was to insure that there is no fluid leakage where the capillaries entered the end chambers. This was especially important since the actual flow rates were small and thus any slight leakage could cause very large errors over the temperature range between room temperature and the extreme value used. At present, very few materials are available that can remain flexible over a wide range of temperatures. Silicone rubber that will remain flexible in the temperature range -56°C to 260°C is commercially available from "Armet Industries" as product No. (AR129A). This material has a "Silastic 55U" rubber base that is manufactured by "Dow Corning Corporation". It is understood from Eisele (17) that the Freon vapours attack the Silicone rubbers chemically, and that the latter have the problem of "linear-swell" when used as gaskets or packings, but for short duration of use it is considered to be adequate. Due to the limited choice, this material was used to form the packing between the capillary tubes and the end chambers. The packings were machined from a 3/4" Silicone rubber rod to fit different capillary tube diameter sizes. If more severe temperature conditions are to be met in future, "Armet Industries" product No. (AR155) which is capable of withstanding a temperature range of -90°C to 260°C may be considered.

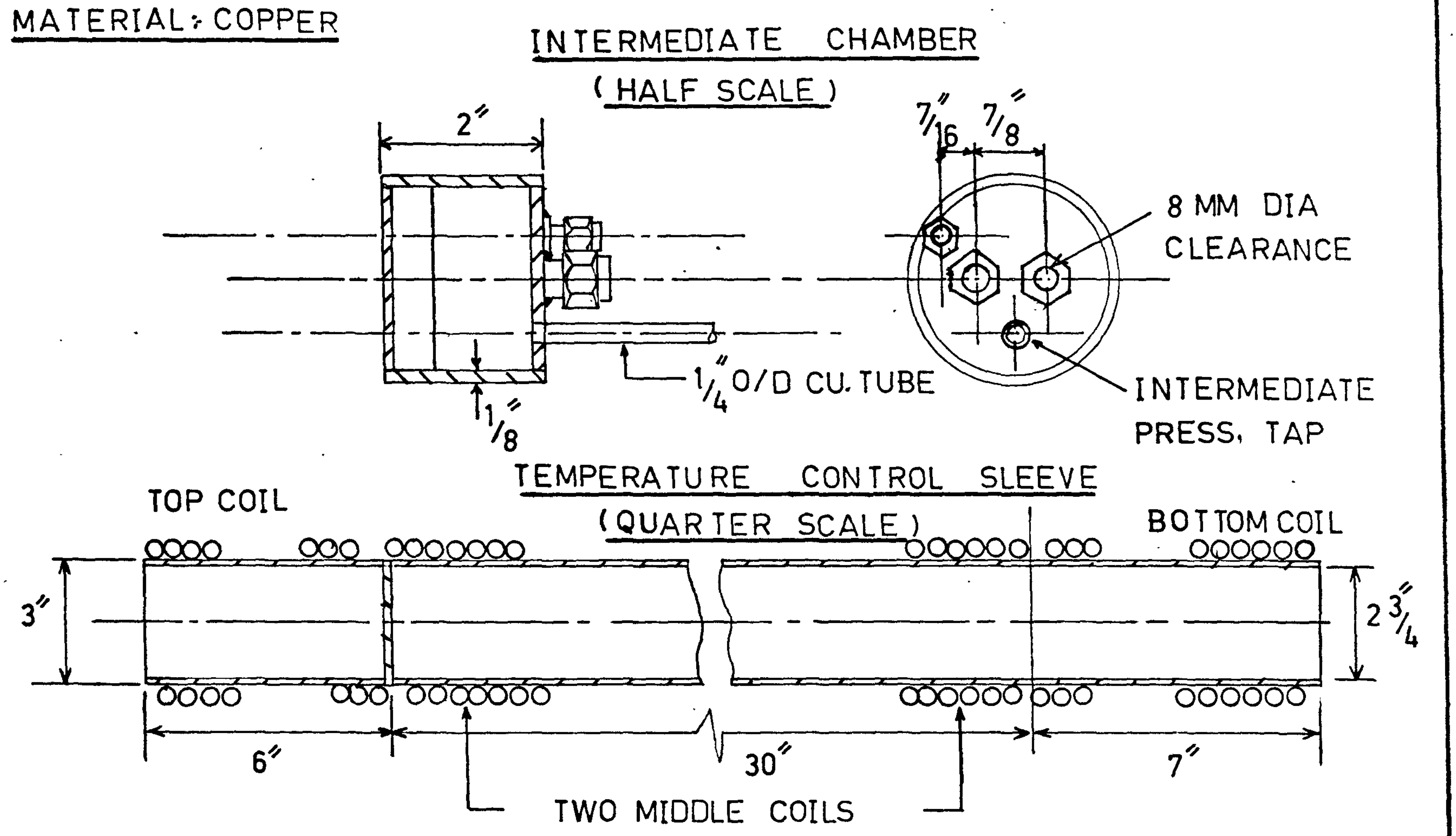
As can be seen from figure (9), the pressure taps are 1/4" O.D. copper tubes. Except for the entrance chamber pressure tap, all pressure taps were connected to 3/16" I.D. rubber tubes. Steel wires were wrapped around those connections to stop any possible fluid leakage. The rubber tubings were necessary for safe assembly purposes.

The assembled viscometer fitted tightly into a 30" long copper pipe that had a wall thickness of 1/8" see figure (8). The viscometer was held in this tube by two 1/2" thick copper discs that fitted tightly inside both ends of the tube, and are fastened to the tube by grub "Allen screws" . . The discs on the left hand side of figure (8) has a 1/2" diameter hole to allow the trapped air to escape when fitting the viscometer into the tube; whilst the disc on the right hand side of the same figure has the necessary holes to allow the three pressure taps, the supply and exit lines. The space between the right hand side disc and the entrance chamber was filled with cotton wool.

V. 3 Temperature Control:

The viscometer cell as shown in figure (8) fits tightly into the sleeve shown in figure (10). The temperature control sleeve is essentially a 2-3/4" I.D. copper tube which has a wall thickness of 1/8". Four 1/4" O.D. copper tube coils were soldered

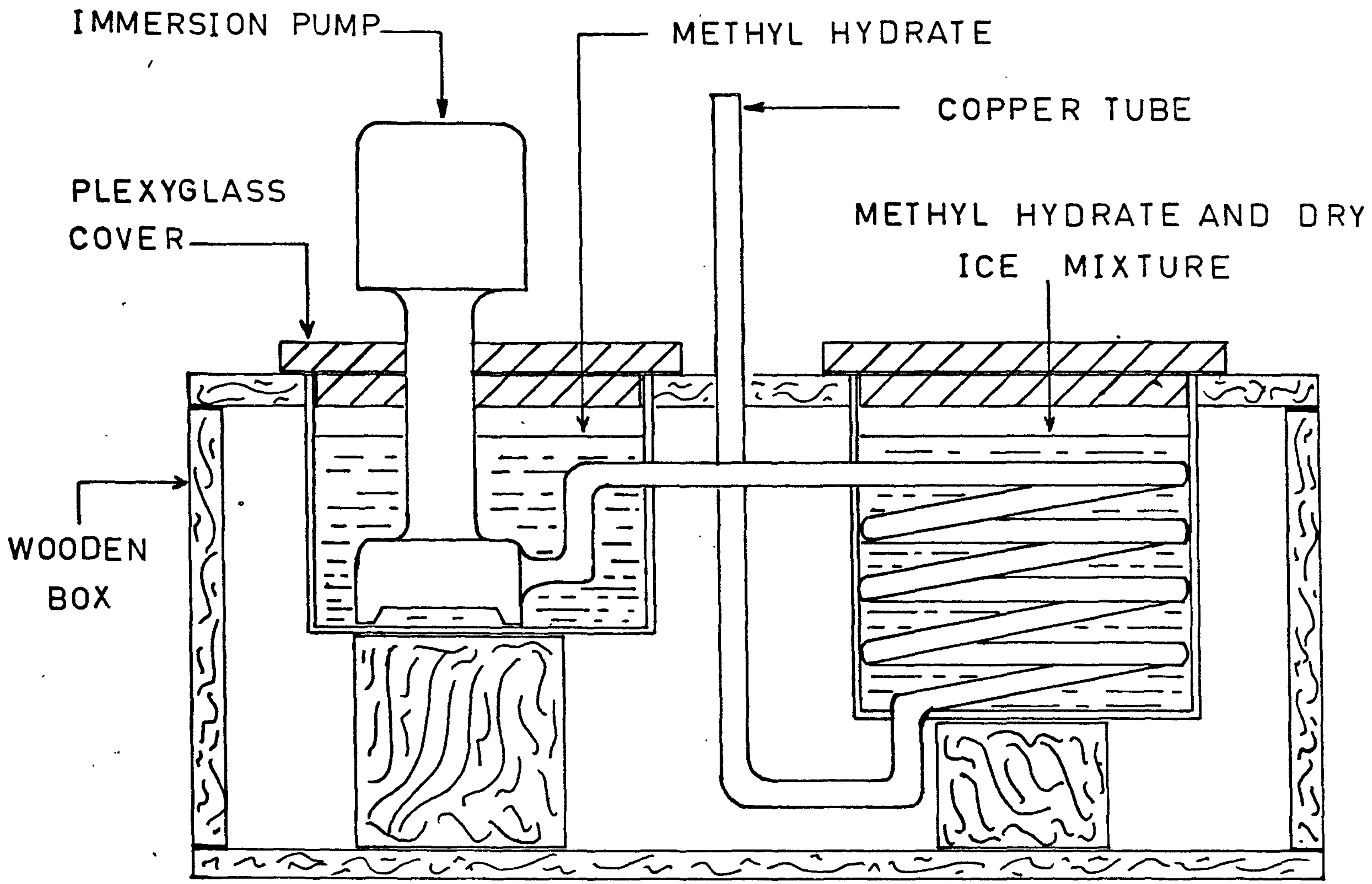
MATERIAL: COPPER



ALL COILS ARE SOLDERED TO BODY

FIG. 10 INTERMEDIATE CHAMBER AND TEMPERATURE CONTROL SLEEVE to the outside of the sleeve. By passing fluids at certain flow rates and temperature, the temperature of the viscometer cell can be controlled. The viscometer cell is positioned beneath the two middle coils by a plate braized at 6" from the top coil end. This plate is provided with a 2" diameter hole to allow the air to escape when fitting the viscometer cell inside the temperature control sleeve. The rate of flow through the coils surrounding the sleeve is governed by four "Whitey" (1VF4) "Vee-Stem" valves having an orifice of 0.172", which were connected to the four supply lines see figure (X6.2). The temperature of the sleeve was controlled by varying the flow rate of the fluid which was supplied from a constant temperature bath which was controlled to a given temperature. Different heat exchange fluids were used:

1. Medium pressure steam for the temperature range 100 to 120°C.
2. Hot or cold water for the temperature range 90 to 0°C. The temperature of the water bath was maintained with a uniformity of ± 0.25°C by a "Porta-Temp" model (66590) and Porta-Cool (66591).
3. A methyl alcohol and dry ice mixture was used for the temperature range 0 to -40°C. The mixture bath was designed and made as shown in figure (11).
4. Nitrogen vapour was forced by air pressure (not exceeding 5 lbf/in^2) from a liquid nitrogen dewer flask to reach temperatures between -40° and -200°C.



ALL SPACES FILLED WITH POLYSTYRENE INSULATION

FIGURE 11 SCHEMATIC DIAGRAM OF DRY ICE MIXTURE BATH

The viscometer cell and temperature control coils were placed in an 11-1/4" I.D. cylindrical body filled with polystyrene insulation; see figure (12).

V.4 Flow Measurement:

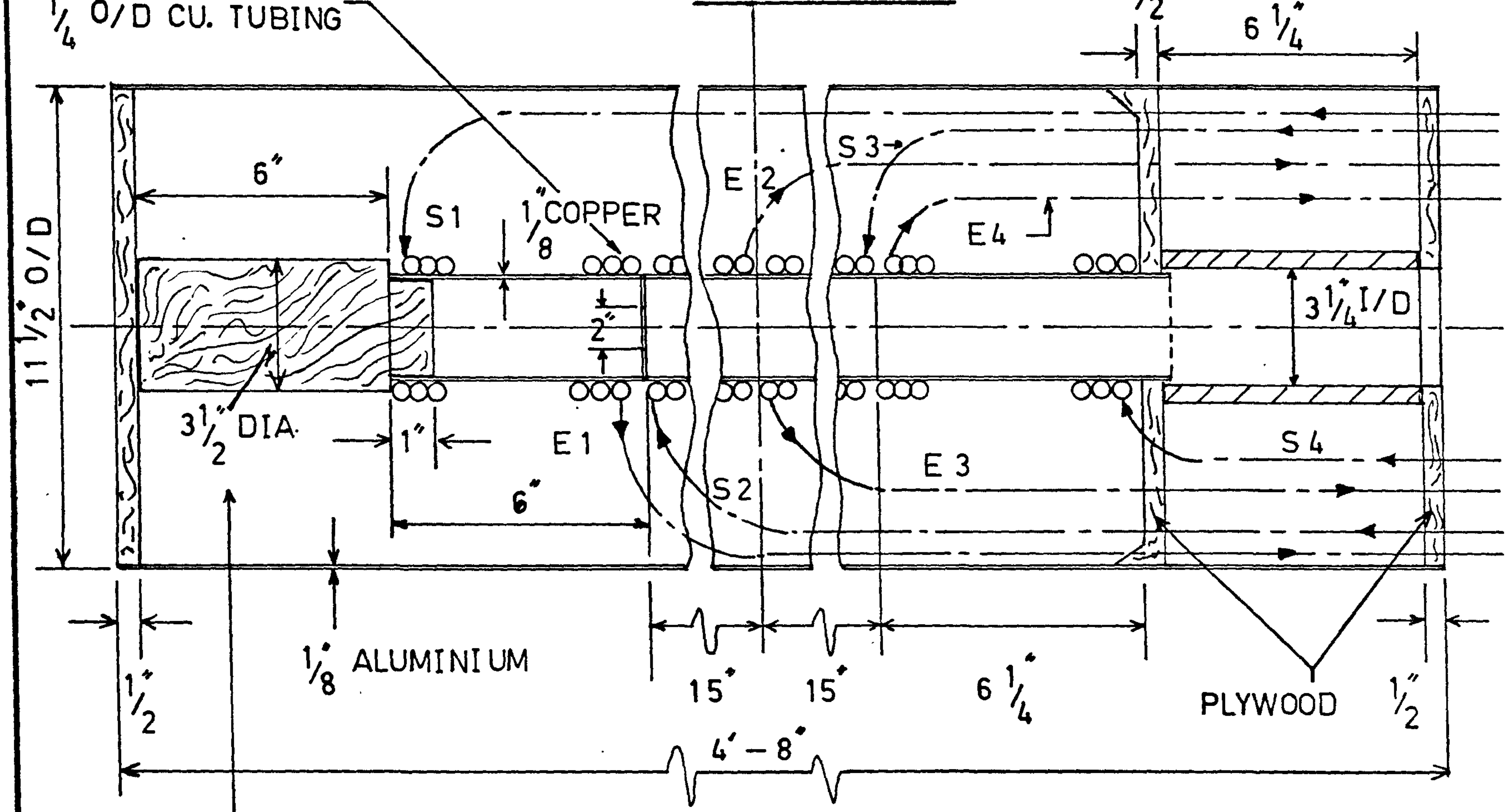
When using a capillary viscometer, it is desirable to keep the volume flow rate of the gas through the capillary tube as small as possible. This is so, since the development length of the flow inside the capillary is a direct function of the Reynold's Number. Also, it is more economical to use small flow rates since the system is an open one; see Design Considerations - Chapter V. In the Poiseulle equation the viscosity is governed directly by the accuracy of the flow rate measurement. The measurement of the flow rate can be achieved either by direct volume displacement measurement or, alternatively, by measuring the mass of the condensate of the gas that is passed through the capillaries. But since most of the Freon compounds are in the vapour phase at room temperature and atmospheric pressure, the second method would require elaborate condensing and weighing instrumentation. The volume flow rate to be measured in this work is of the order of 0.25 to 0.5 cu. cm./sec. Some flowmeters, that are capable of measuring such small flows, and which were considered for use in this work are listed below.

1. Continuous Operation Flowmeter

Chavet (35), in 1962, constructed a continuous flowmeter on the basis of the work done by Dushman to whom reference

FIG. 12 VISCOMETER THERMAL INSULATION JACKET

(SCALE:- 1/4 : 1)



ALL SPACES FILLED WITH POLYSTYRENE FOAM INSULATION is made in the former's paper. The flowmeter consists of a capillary tube connected at either end to a mercury reservoir. A short mercury pellet, about 2 cm. in length, is pushed through the capillary tube by the entering gas. As the mercury pellet falls into the reservoir at the end of the tube, it forces as pellet out of the mercury reservoir at the other end of the capillary tube and so the operation continues. By measuring the time it takes the pellet to traverse the distance between two fixed points on the capillary tube, the volume flow rate is evaluated. Chavet (35) used two such flowmeters with capillary tube diameters of 2.7 and 1 mm. The devices were capable of measureing flows of up to 0.6 cu. cm./sec. and 0.16 cu. cm./sec. respectively. Latto (47) has designed a flowmeter working on the same principal, which has a 3mm. diameter capillary tube.

2. Soap Film in Capillary Tube

A flowmeter was designed by Black et. al. (36) in 1964. The principal of operation of this instrument is basically the same as the flowmeter described above. In this case, however, a soap film is introduced into the capillary tube at one end. Black (36) measured flow rates of helium gas of the order of 0.016 cm./sec. to 2.5 cm./sec. The accuracy of this flowmeter was claimed by Black to be ± 2%.

3. Thermistor Flowmeter

Veprek (37) in 1963, constructed a thermistor flowmeter which incorporates a temperature stabilizing coil. The change in the resistance of a heating wire is taken as a measure of the flow rate of the gas passing the wire. Flow rates of the order of 0.05 cu. cm./sec. to 5 cu. cm./sec. were measured by Veprek (37) within an accuracy of ± 3% at a temperature of 29.4°C.

4. Soap Film (Burette) Flowmeter

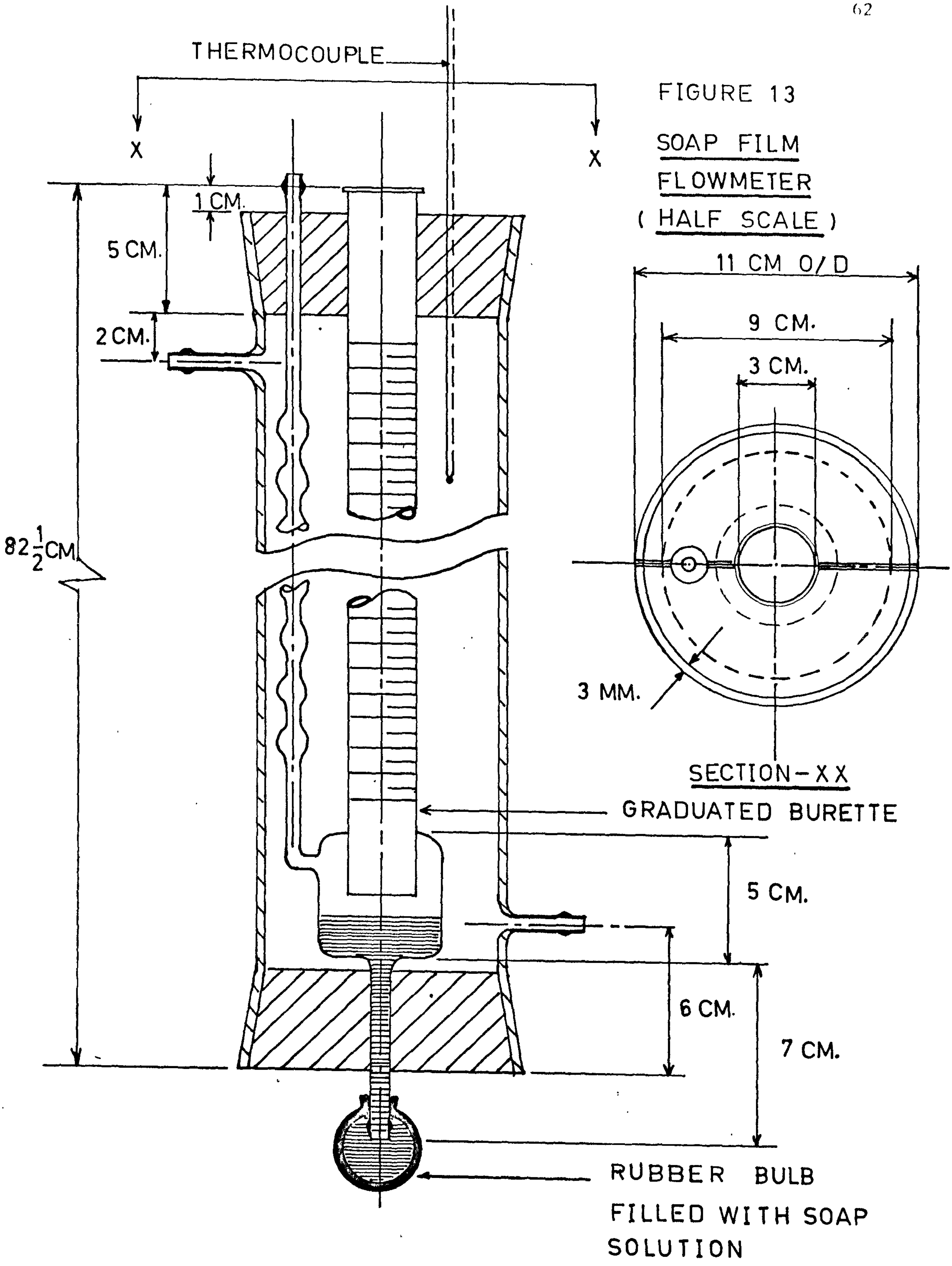
The soap film flowmeter has been in use for many years. It was first suggested by Barr (34) in 1934. This flowmeter consists simply of a calibrated burette. A soap film is formed at one end of the burette, and the soap film movement through a known volume is timed. Although this instrument is very simple in construction, it appears to be one of the most accurate means that are presently known for measuring gas flow rates.

Levy (38) in 1964, claimed that an accuracy of ±0.25% could be achieved with a soap film flowmeter for flow rates of the order of 0.1 to 100 cm^3/sec. Harrison et al (39) in 1967 made a thorough investigation of the potential accuracy of soap film flowmeters. Harrison (39) constructed and tested different size soap film flowmeters to measure flow rates in the range 0.8 cu. cm./sec. to 166 cu. cm./sec. The results of Harrison and co-workers clearly indicate that the repeatability of their measurements with different soap film flowmeters was not better than ± 1.0%.

After making a thorough investigation of the methods to measure gas flow rates, it was decided that a soap film flowmeter, as shown in figure (13), would be used. The burette was enclosed in a jacket filled with water at room temperature. The gas is admitted at the top where it is passed through a heat exchanger tube to stabilize the temperature of the gas to that of the bath. The 100 cu. cm. burette of this flowmeter was calibrated by filling it up to the 100 cu. cm. mark with water at room temperature. This water was drained and weighed on a "Mettler Multi-Purpose Balance" model (H4) which has a weighing accurancy of ± 0.001 grams. Five such measurements were made. The volume of the burette was found to be 2.8% lower than the indicated graduations, and the maximum deviation of all weighings from the mean was ±0.2%. A photocell timing circuit, which had been designed by the Electrical Engineering Department at McMaster, was made. It had been hoped to use this circuit for actuating a timer when the soap bubble traverses the photocells. Presently, the circuit is not operating in a consistent manner. It is thought this is due primarily to the inadequacy of the photocells' illumination. An "Excelsior Park" stop-watch was operated manually to time the soap bubble movement.

FIGURE 13

SOAP FILM FLOWMETER (HALF SCALE)



V. 5 Pressure Measurement:

The pressure drop across the capillary tubes was measured by means of a three-limb differential water manometer. Each limb of the manometer had a three-way (B19/26) stop cock. This made it possible to vent any of the three limbs to atmosphere when it proved necessary. The manometer was used at room temperature, and the temperature of the water inside it was measured by means of thermocouple that was immersed inside a fourth limb provided for this purpose; see figure (X6.6). The stop-cocks were lubricated with "Vacuum-Seal" lubricant and held tight to the manometer limbs by means of helical springs. The stop-cock joints were capable of maintaining a pressure of 30 cm. of water for a period of 12 hours without any loss of pressure. The water level was observed by means of a cathetometer which was provided with a spirit-level and an adjusting screw to keep it horizontal. The smallest division that could be read on the cathetometer scale was 0.001 cm. With the aid of illuminating lights the water level in any of the three limbs could be located by the cathetometer to within ±0.01 cm. on the cathetometer scale.

V. 6 Temperature Measurement:

One of the prime objects of this work was to investigate the variation of the viscosity of the Freon compounds with temperature, and thus it was essential to insure that the temperature of the viscometer was both constant at any setting and uniform along the entire length of the viscometer. For this reason, seven thermocouples were installed along the inside of the viscometer cell at approximately 2" spacings. One thermocouple was used to measure the pressure differential manometer temperature and another to measure the temperature of the flowmeter water jacket. The wire used for the thermocouple was from the same reel of copper - constantan gauge 20 wire as supplied by "Thermo-Electric Inc". The thermocouple junctions were all arc welded by means of a 30V, 20 amp. D.C. supply. The reader is referred to reference (40) for further information on the techniques of arc welding. The thermocouple junctions were mounted on the surface of a 3/8" O.D. copper tube pieces that were 1-1/2" in length. The mounted junctions were then covered with "Polyolefin Shrinkable Tubing", commercially available from, "Alpha Wire Limited" as product FIT(500-4). By heating it to a temperature of 327°C, the polyolefin tube, which was covering the thermocouple junctions, was shrunk onto the 3/8" O.D. copper tubes, thereby forming a protective shield for the thermocouple junction against water vapour condensation. The advantage in using the polyolefin tube, is that it will remain flexible over the temperature range -67°C to 250°C. The cold junctions of the thermocouples were also arc welded and enclosed individually in separate glass tubes of 1 cm. I.D. filled with molten wax. By allowing the wax to freeze, the cold junctions were held rigidly inside the glass tubes. The cold junction points were kept at the same level, at about the bottom of an insulated dewer flask filled with a freezing ice mixture. A 12 point switch box filled with kerosene was used to select individual thermocouples for e.m.f. measurement.

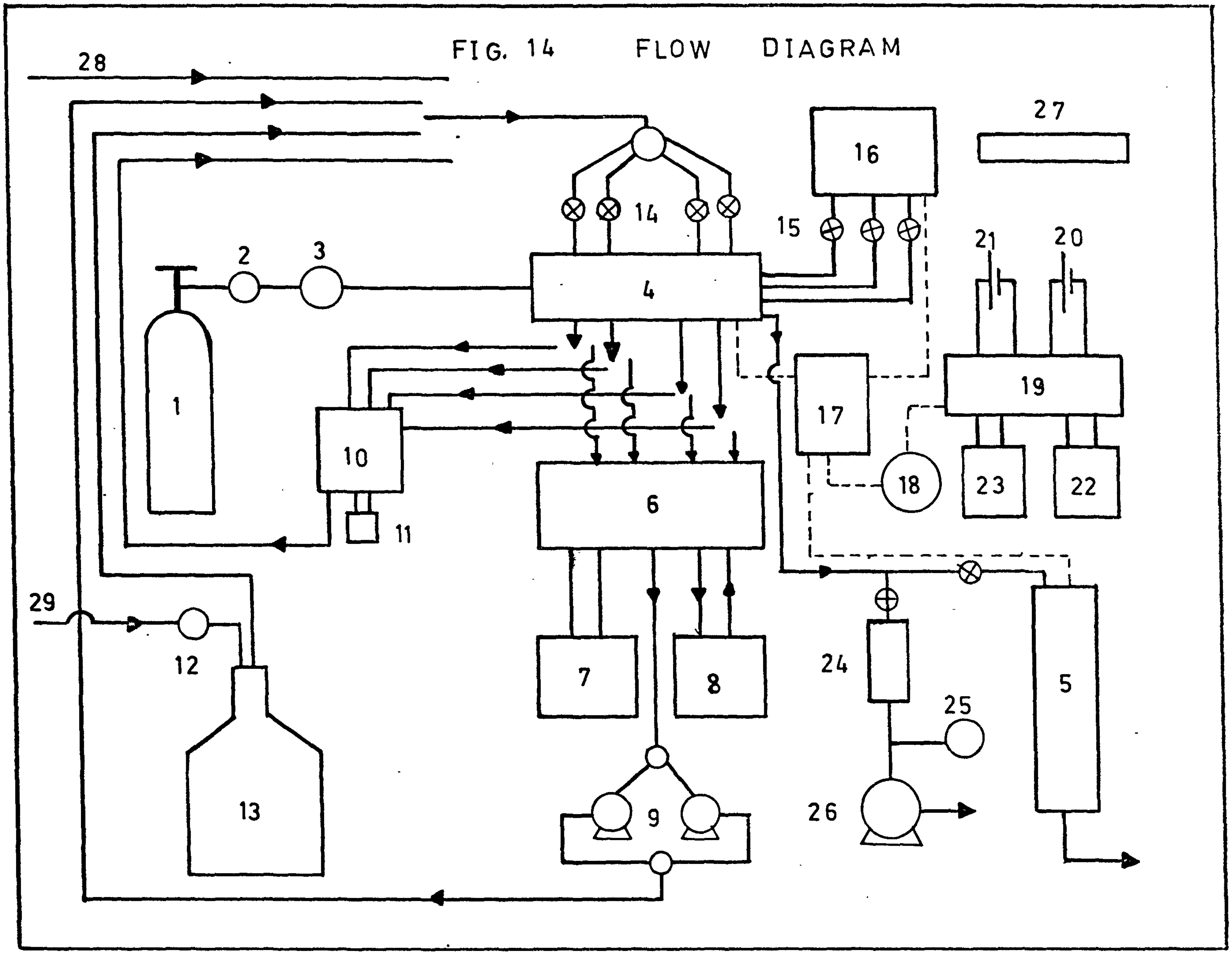
The e.m.f. measuring equipment consisted of a "Guidline" model (9461A) potentiometer which was used in conjunction with a "Guideline" model (9460) photocell amplifier and a "Guideline" model (9461A) galvanometer. This set-up was capable of measuring potentials of the order of 1×10^{-7} volts.

VI EXPERIMENTAL PROCEDURE

Two calibrated precision-bore capillary tubes (nos. 6 and 7) of 0.5 mm nominal diameter were cut to the required lengths of 47.375 and 26.958 cm. for use in the series - capillary viscometer. The capillary tubes and the viscometer chambers were thoroughly cleaned with chromic acid and rinsed with water and acetone so as to remove any particles that might disturb the flow inside the capillary tubes. The viscometer was then assembled as shown in figure (8). Dry air was passed through the assembled viscometer for a period of one hour to drive out of the viscometer any acetone or water vapours that might have remained inside. The viscometer was then tested for leaks, and when it proved leak-proof, it was fitted in the viscometer cell. The viscometer cell was in turn fitted into the temperature control jacket as shown in figure (12). The open end of the jacket was filled with cotton wool so as to insulate the viscometer cell completely.

The auxiliary equipment, for temperature, pressure and flow measurement and control was connected as shown in the flow diagram figure (14). The differential manometer three-way stop-cocks were all closed, and the viscometer, the pressure taps and the supply line were evacuated by connecting the outlet line to the vacuum pumps. Vacuum pressures of approximately 29" Hg. were employed. The viscometer supply line which had been closed when evacuating; was connected to a supply of helium gas. By opening

FIG. 14 FLOW DIAGRAM



SEE FOLLOWING PAGES FOR LEGEND

DETAILS OF FLOW DIAGRAM

1. Test Gas Bottle
2. "Matheson" High Pressure Regulator Model (11)
3. "Matheson" Low Pressure Regulator Model (70)
4. Viscometer and Jacket
5. Soap Film Flowmeter and Jacket
6. Water Constant Temperature Bath
7. "Porta-Cool" Model (66590), Stirrer, 1000 w Heater and Temperature Control
8. "Porta-Cool" Model (66591), Freon-12 Cooler
9. Two "Little-Giant" 1/3 H.P. Model (2-0M) Centrifugal Pumps
10. Ethyl Alcohol and Dry Ice Mixture Box
11. "Little Giant" Model (LGV-600 PU) Immersion Pump
12. "Watts" Model (M-0125) Air Regulator
13. Liquid Nitrogen Dewer Vessel
14. "Whitey" Model (IVF4) Vee Stem Valves
15. Two-Way B19/26 Stop Cocks
16. Three Limb Water Manometer
17. Cold Junction of Thermocouples
18. Thermocouple Switch Box
19. "Guideline" Model (9461A) Potentiometer
20. "Guideline" 1.01859V Standard Cell
21. Six Volt Battery
22. "Guideline" Model (9460) Photocell Galvanometer Amplifier (6V)
23. "Guideline" Model (9461A) Galvanometer
24. Silica Gell Dryer

25. Pirani Vacuum Gauge
26. "Edwards" Vacuum Pump
27. Cathetometer
28. Medium Pressure Steam Line
29. 20 lbf/in^2 Air Pressure Line

N. B. Dotted Lines Indicate Thermocouple the supply line the viscometer was purged with helium gas completely. This was repeated several times to insure that the viscometer was free of any water vapour. The same procedure was repeated with the test gas, and finally the outlet line was connected to the flowmeter.

The temperature of the viscometer was raised or lowered to the desired value by using one of the four fluids provided for this purpose, as was described in the Description of the Apparatus, Chapter VI. With the aid of the sensitive galvanometer, the temperature drift of the thermocouples inside the viscometer was detected. When the thermocouples' e.m.f. drift became negligible with time, the viscometer was assumed to have reached a steady state. In order to minimize the temperature gradients, the flow control valves of the temperature control coils were adjusted manually in the necessary pattern. In most cases, the temperature gradients could be minimized to less than 1°C along the entire length of the viscometer. However, at certain points it proved difficult to minimize the temperature gradients, and a maximum temperature gradient of 2°C was considered acceptable.

The manometer valves were opened to the pressure tap lines, and the volume flow rate of the test gas was adjusted by means of the low pressure regulator on the supply line, meanwhile observing the pressure drop that resulted on the manometer. The flow rate, at any temperature was adjusted such that the pressure drop did not exceed 12 cm. of water across the long capillary tube. The cathetometer was adjusted with the aid of the spirit-level to a horizontal position, and was focused on the middle limb of the manometer. It was insured that the water level inside the manometer was stable before taking any readings.

The volume flow rate was measured on the soap film flowmeter. The range of displaced volumes that were timed was 60 to 80 c.c. depending on the rate of flow.

When the apparatus was first ready for viscosity measurement, it was desirable to test it for reliability. Since the viscosity of nitrogen gas, which was readily available, is known to better than ± 2.0% in the temperature range of interest, -100°C to 150°C, it was used to test the apparatus. (This was not a calibration). The viscosity of nitrogen gas was measured in the temperature range -36°C to 71°C.

After having tested the viscometer for reliability, the viscosity of Freons 12 and 22 were measured in the temperature range -29.2°C to 74.7°C and -39.7°C to 91.758°C respectively. The results were calculated as shown in Appendix X4. The atmospheric pressure was taken as that which prevailed whilst making every measurement.

VII RESULTS AND DISCUSSION

The results that were obtained for Nitrogen, Freon 12 and Freon 22 are listed in Table 4.

The viscosity of nitrogen was determined in the temperature range 237 to 344°K to test the reliability of the apparatus used in this work. Those results were compared to the recommended values for the viscosity of nitrogen given in the "Thermophysical Porperties Research Center Data Book" (41), which are quoted to be accurate to ± 2%. The percentage deviations of the present experimental results from the "TPRC" recommended values are listed in Table 4. It is evident that the experimental results are generally lower than those recommended. It must be mentioned in this regard that the recommended values are correlated from about twenty sets of experimental data obtained by different workers. Therefore, the experimental results of this work can be taken to be in agreement with other workers on nitrogen. Only one point at a temperature of 278.97°K deviates by more than 2% from the recommended values. It is suspected that this was caused by temperature instability of the viscometer at that particular setting.

The viscosity of Freon - 12 was measured between its saturation temperature of approximately 244°K and 348°K. A polynomial of the third degree (see figure 15) was chosen to fit the viscosity values obtained as a function of temperature in degrees K. This polynomial

TABLE 4

RESULTS

1. NITROGEN GAS

Temp. °K	Viscosity Poise x 10^4		Percentage Deviation
	This Work	TPRC	
344.26	2.001	1.976	+1.265
343.87	1.958	1.973	-0.760
330.41	1.913	1.915	-0.104
319.93	1.850	1.871	-1.122
300.81	1.741	1.784	-2.470
300.46	1.773	1.783	-0.561
300.13	1.759	1.781	-1.235
299.77	1.748	1.780	-1.798
299.64	1.767	1.779	-0.675
296.94	1.760	1.767	-0.396
278.97	1.730	1.683	+2.793
276.41	1.666	1.671	-0.299
271.97	1.650	1.651	-0.061
252.64	1.525	1.545	-1.294
246.26	1.532	1.527	+0.320
237.29	1.459	1.483	-1.618

2. FREON - 12

Temp. °K	Viscosity in Poise x 10^4
347.871	1.497
332.689	1.416
326.764	1.399
323.634	1.365
313.487	1.370
311.399	1.355
299.043	1.216
297.746	1.232
292.975	1.266
284.556	1.194
279.025	1.114
278.036	1.090
275.714	1.125
275.411	1.170
271.325	1.144
270.981	1.150
259.831	1.125
247.082	1.042
243.857	1.050

TABLE 4/CONTINUED

3. FREON 22

Temp. °K	Viscosity in Poise x 10^4
364.908	1.581
348.912	1.474
334.841	1.396
317.492	1.318
300.265	1.255
299.438	1.270
299.233	1.246
285.411	1.188
273.422	1.097
264.870	1.113
259.338	1.112
247.983	1.025
243.060	1.090
233.476	0.942

TABLE 4/CONTINUED

is given by

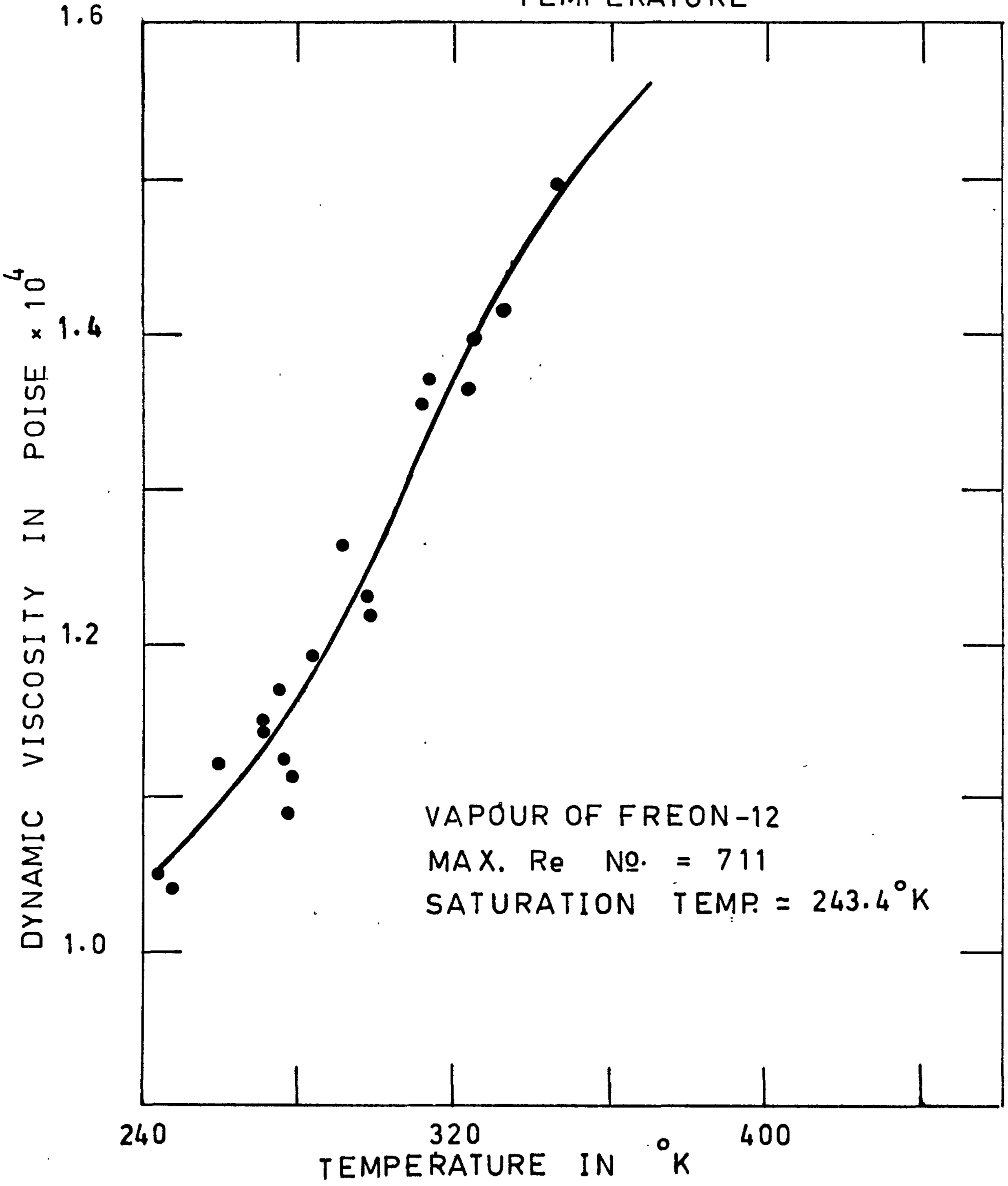
$$\eta \text{ CP} = 9.74765 \times 10^{-2} - 9.29302 \times 10^{-4} \times T + 3.19168 \times 10^{-6} \times T^2 - 3.45649 \times 10^{-9} \times T^3$$

The mean deviation of all points from this third degree polynominal was found to be 2.51967 x 10^{-4} Centipoise. As shown in figure (16), 95% of all the values lie within ± 4% from the fitted curve, whilst one point, or 5% of the 19 values determined, is 5.7% low. The scatter of the values is considered to be high, and is expected to have been caused by the instability of the viscometer temperature. This difficulty was experienced since the time for taking one reading was about 20 minutes, during which time it proved difficult to maintain a constant temperature. This was especially true at low temperatures.

In figure (17) the results of this work for Freon - 12 are plotted together with secondary measurements that have been taken by previous workers using the rolling ball viscometer. It can be seen from figure (17) that although previous workers might have obtained viscosity values with less scatter than this work, the inherent inaccuracies that were introduced by the calibration of their instruments resulted in viscosity gradients that are inconsistant for the same temperature range.

The combined results for Freon - 12 were fitted to a fourth degree polynomial of the form

FIG. 15. THREE DEGREE POLYNOMIAL FIT TO THE DYNAMIC VISCOSITY OF FREON-12 VS. TEMPERATURE



$$\text{VISCOSITY CP} = 9.74765 \times 10^{-2} - 9.29302 \times 10^{-4}\,T + 3.19168 \times 10^{-6}\,T^{2} - 3.45649 \times 10^{-9}\,T^{3}$$

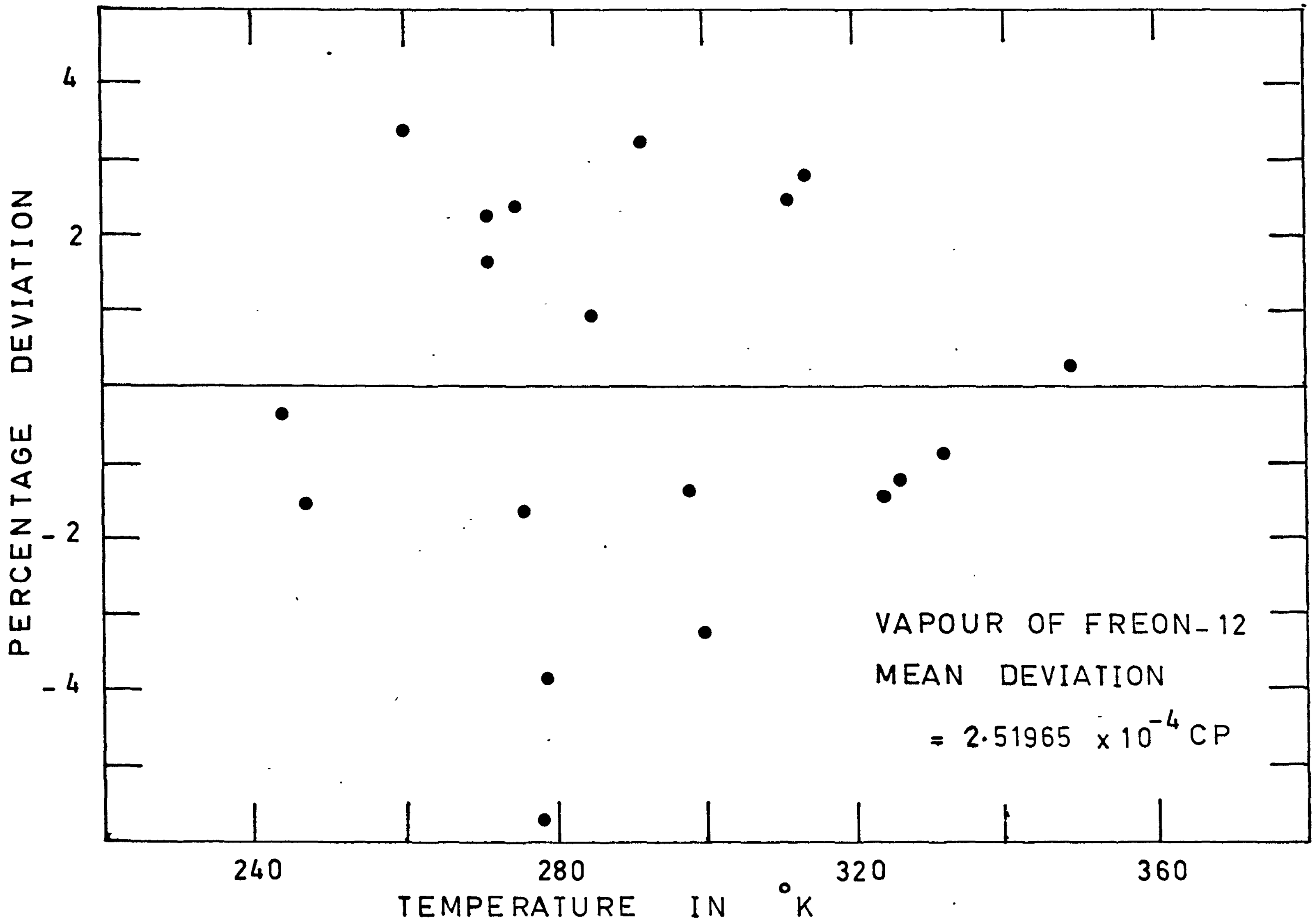
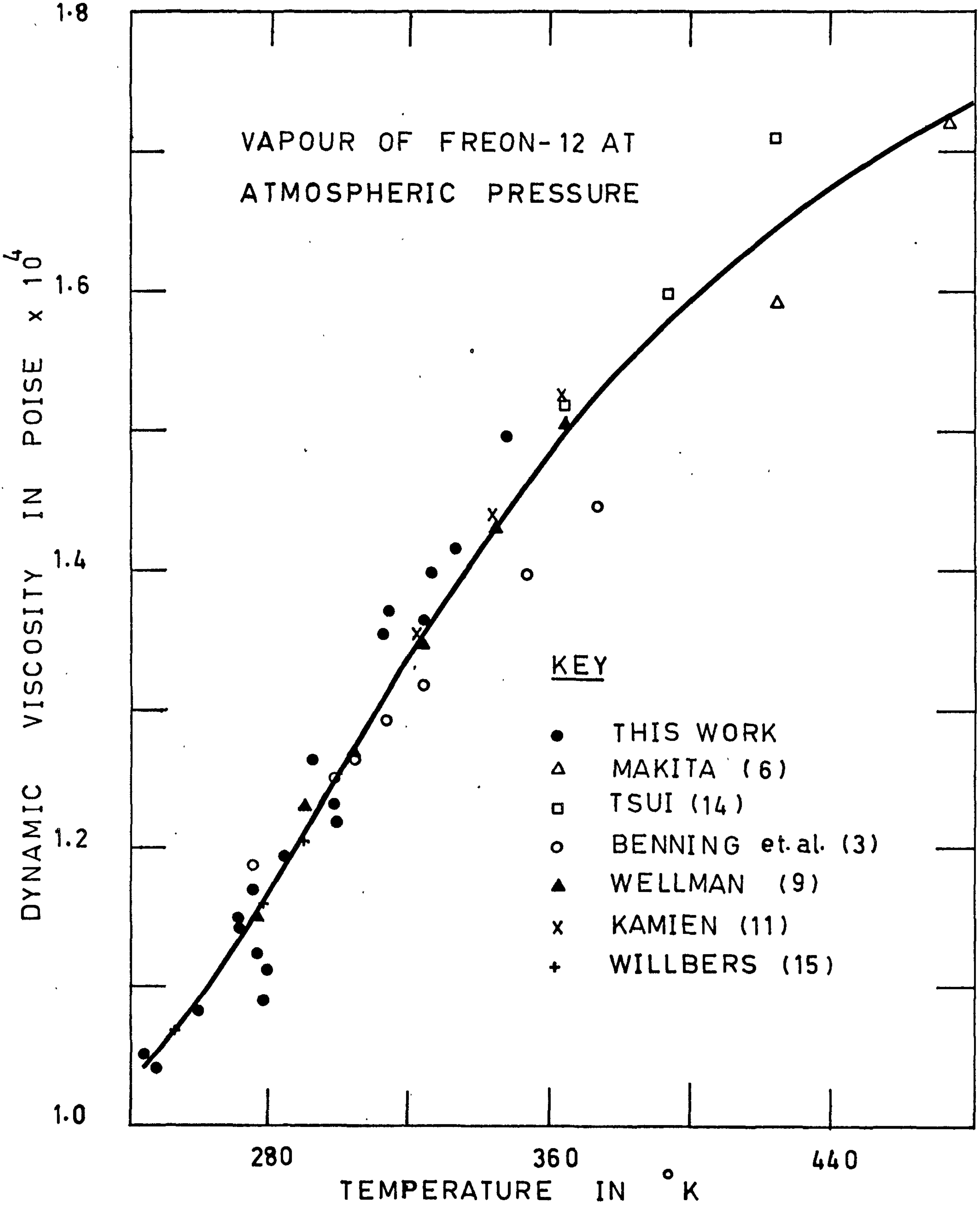


FIG. 16. DEVIATION PLOT OF EXPERIMENTAL RESULTS FOR FREON-12 FROM THE THIRD DEGREE FITTED POLYNOMIAL

FIG.17. THE DYNAMIC VISCOSITY OF FREON-12 VS. TEMPERATURE FITTED TO A FOURTH DEGREE POLYNOMIAL



$$\eta \text{ CP} = 9.30090 - 1.06183 \times 10^{-1} \times T$$
$$+ 4.81217 \times 10^{-4} \times T^{2} - 9.09019 \times 10^{-7} \times T^{3}$$
$$+ 6.22980 \times 10^{-10} \times T^{4}$$

The mean deviation of all points from this fitted curve was found to be 2.24446×10^{-2} Centipoise. The results for Freon - 12 were also fitted with an equation of the form

$$\eta \text{ CP} = A1\sqrt{T°K} + AO, \text{ where}$$

AO and A1 are constants. This equation can be thought of as an approximate form of the Sutherland's Equation for the variation of the viscosity of gases with temperature; namely

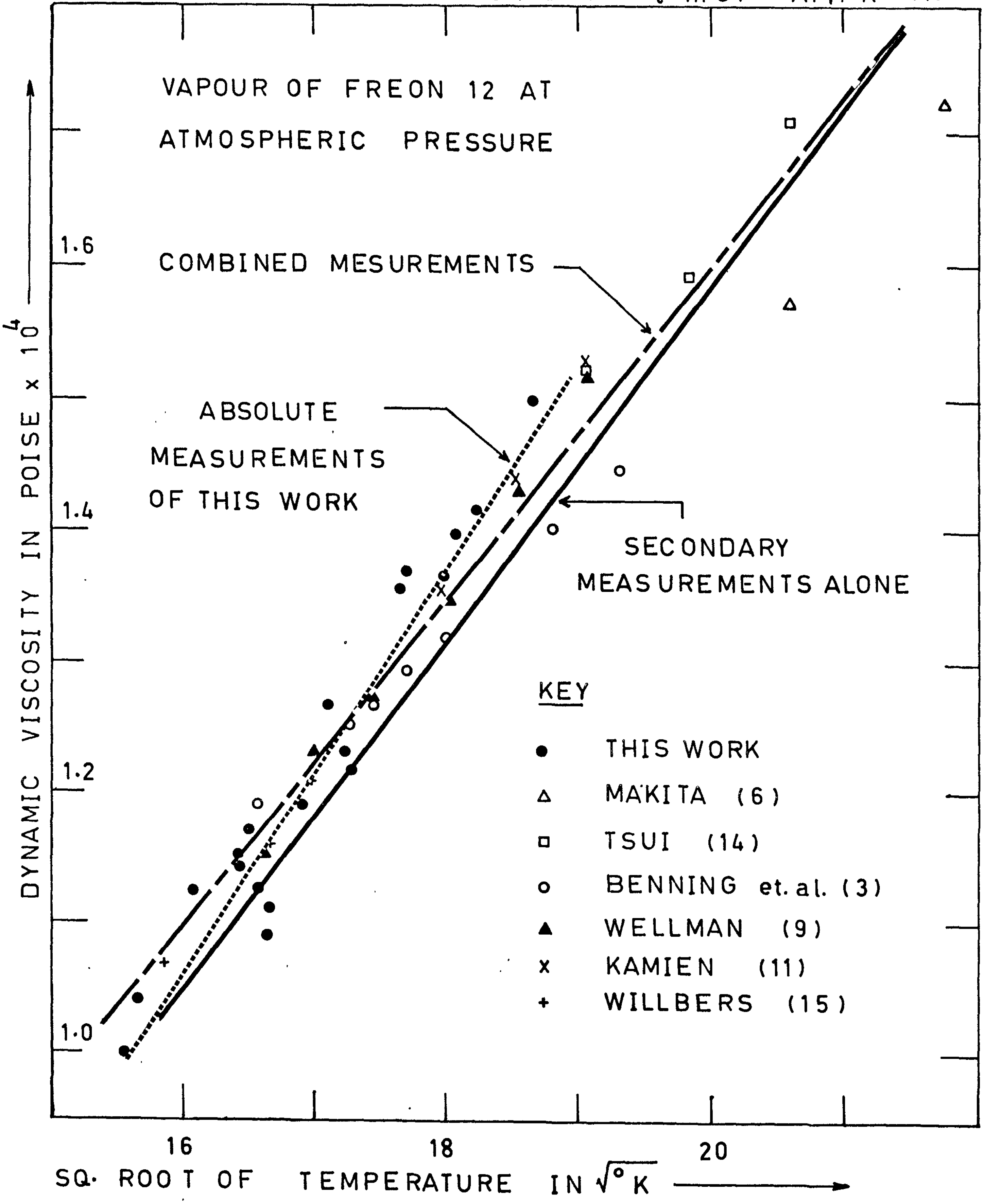
$$\eta = \frac{AT^{3/2}}{(B + CT)}$$, where A, B and C are all constants.

Figure (18) shows a comparison between the results of this work, the combined results and previous measurements when fitted with the above equation. The constants for those fits are as follows

RESULTS	$A1 \times 10^{3}$	$AO \times 10^{2}$	STANDARD ERROR OF ESTIMATE $\times 10^{4}$ CP
This Work	1.54554	-1.40664	3.504
Combined	1.25870	-0.92006	3.865
Previous	1.19593	-0.807067	1.756

It is evident from figure (18), that over the temperature range of the results of this work, previous measurements are generally lower.

FIG. 18. COMPARISON OF MEASUREMENTS OF THE DYNAMIC VISCOSITY OF FREON-12 VS. TEMPERATURE WHEN FITTED TO THE EQUATION η in CP = A1$\sqrt{T°K}$ + A0



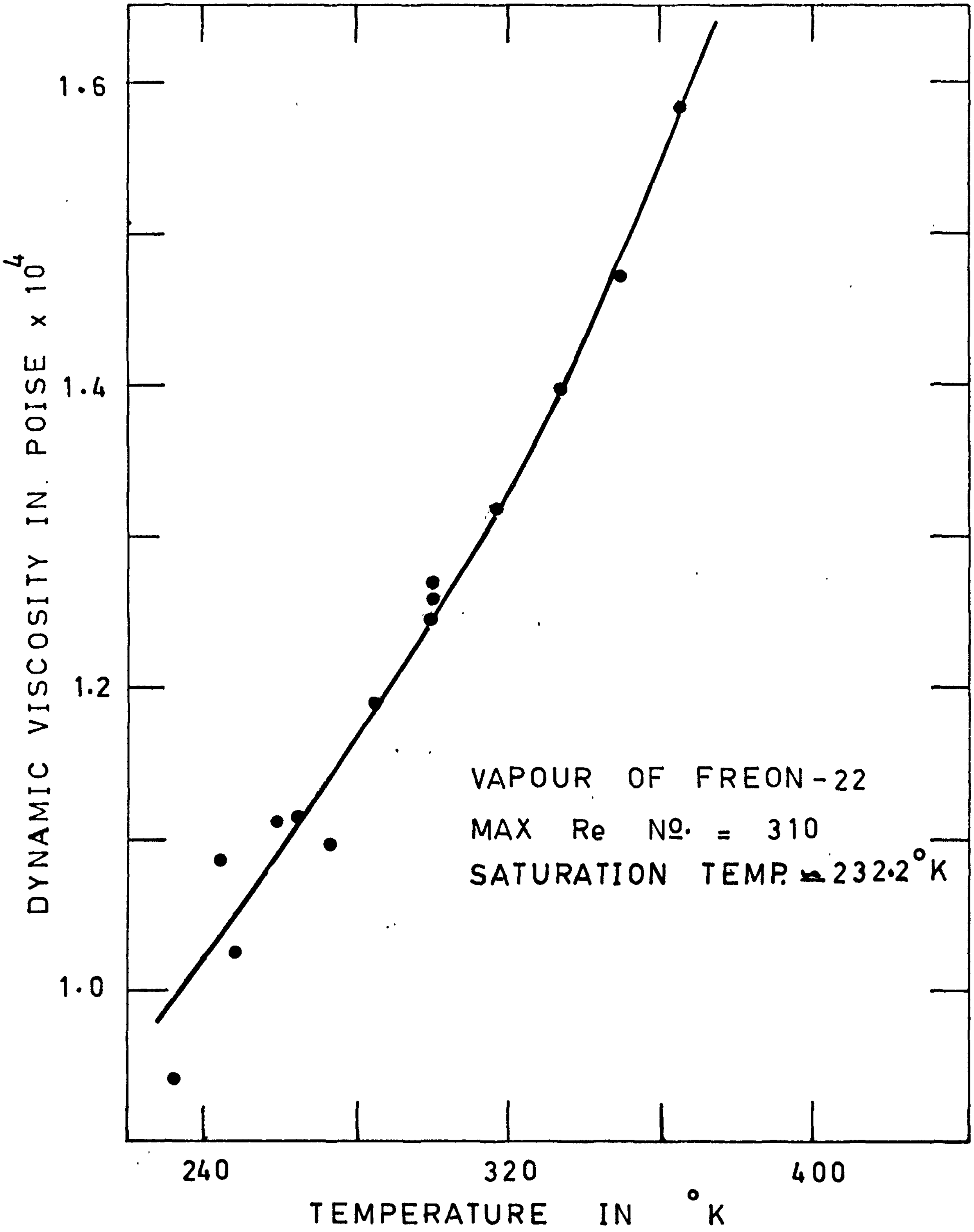
Moreover, at higher temperatures the magnitude of deviation increases reaching 5% at 350°K. The straight line fit for the combined results is provided so that average values of the viscosity can be estimated over the temperature range that has so far been investigated. Freon - 12, that has been investigated so far can be used.

The viscosity of Freon - 22, in this work, was evaluated in the temperature range between the saturation temperature of 233°K and 365°K. Greater care was taken in this case to maintain the temperature of the viscometer constant during the period of a test. This resulted in less scatter of the viscosity values when compared to the results obtained on Freon - 12. Figure (19) is a plot of the viscosity values that were obtained for Freon -22 versus temperature. A third degree polynomial was found to fit the data best. This is given by

$$\eta \; CP = -3.92585 \times 10^{-2} + 4.64713 \times 10^{-4} \times T$$
$$-1.50179 \times 10^{-6} \times T^2 + 1.75874 \times 10^{-9} \times T^3,$$

where T is the temperature in degrees K. The mean deviation of all viscosity values for Freon - 22 from this curve was found to be $= 1.69216 \times 10^{-4}$ Centipoises. As can be seen from figure (20), the maximum scatter of the points occurs in the vicinity of the saturation temperature. This is justified inasmuch as it is difficult to determine exactly the deviation of the viscometer from the saturation temperature; especially since the latter is pressure

FIG. 19. THE DYNAMIC VISCOSITY OF FREON-22 VS. TEMPERATURE FITTED TO A THIRD DEGREE POLYNOMIAL



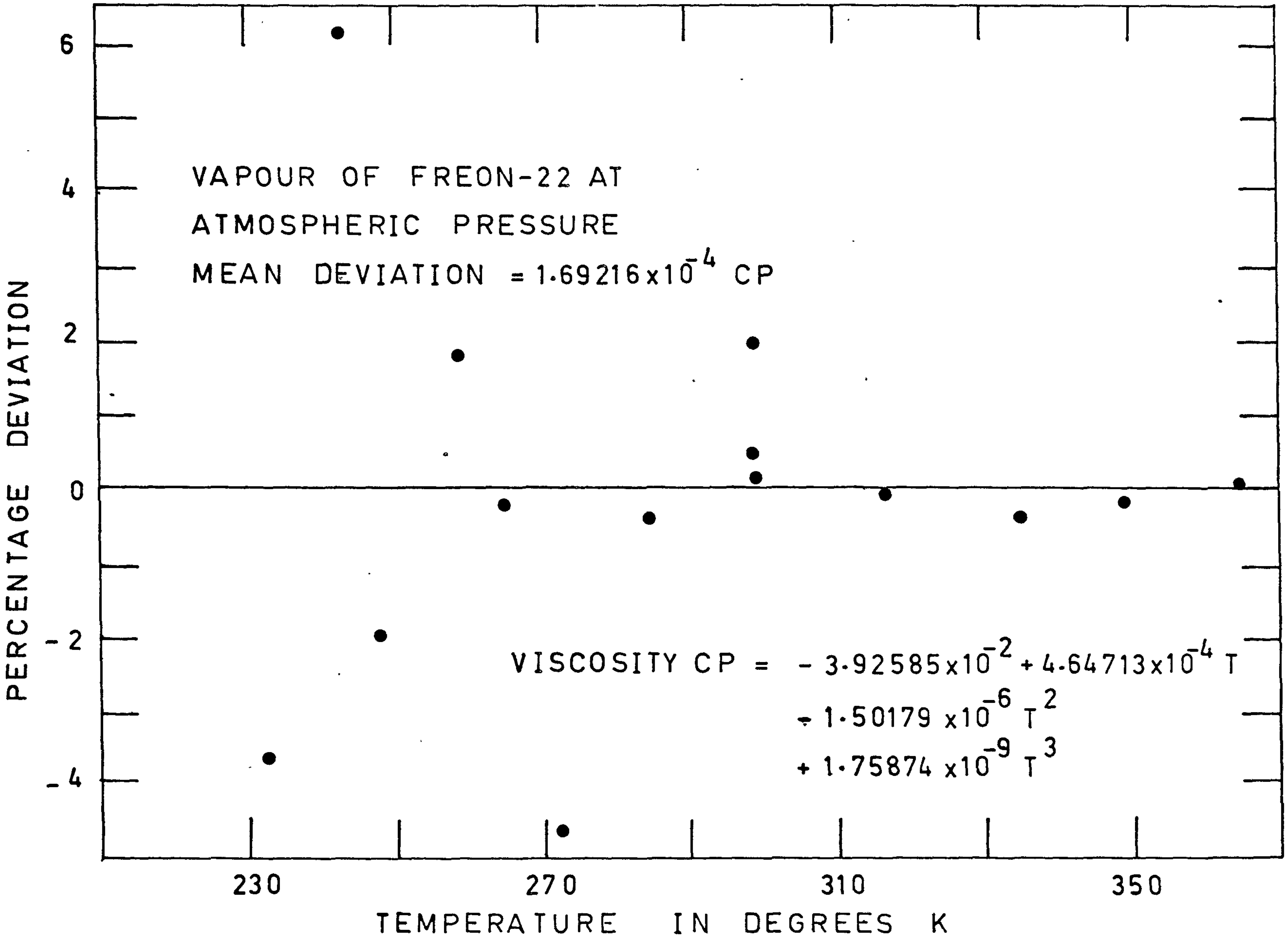


FIG. 20. DEVIATION PLOT OF EXPERIMENTAL RESULTS FOR FREON-22 FROM THE THIRD DEGREE FITTED POLYNOMIAL

dependent.

Figure (21) is a plot of the results of this work for Freon -22 and those of previous workers using secondary methods of viscosity measurements. It is evident from figure (21) that the results of Coughlin (5), Willbers (15), Benning et al (3), and Kamien (11) are generally higher than the values obtained in this work, whilst the results of Makita (6) appear to be low. A fourth degree polynomial was fitted to the combined results so as to be able to predict the viscosity of Freon - 22 over the widest possible temperature range. This polynomial is given by

$$\eta\ CP = 2.61912 \times 10^{-2} - 2.69363 \times 10^{-4} \times T + 1.32053 \times 10^{-6} \times T^2 - 2.33241 \times 10^{-9} \times T^3 + 1.42194 \times 10^{-12} \times T^4$$

The mean deviation of all points from this curve was found to be - 2.40601 x 10^{-4} Centipoise.

Figure (22) is a comparison of the absolute and secondary measurements of the viscosity of Freon 22, when correlated seperately by the equation

$$\eta\ CP = A1 \cdot \sqrt{T} + A0$$

The constants A1 and A0 were found to be as follows.

RESULTS	A1 x 10^3	A0 x 10^2	STANDARD ERROR OF ESTIMATE CP
This Work	1.48669	-1.30815	3.214 x 10^{-4}
Previous Measurements	1.36745	-1.06426	2.293 x 10^{-4}

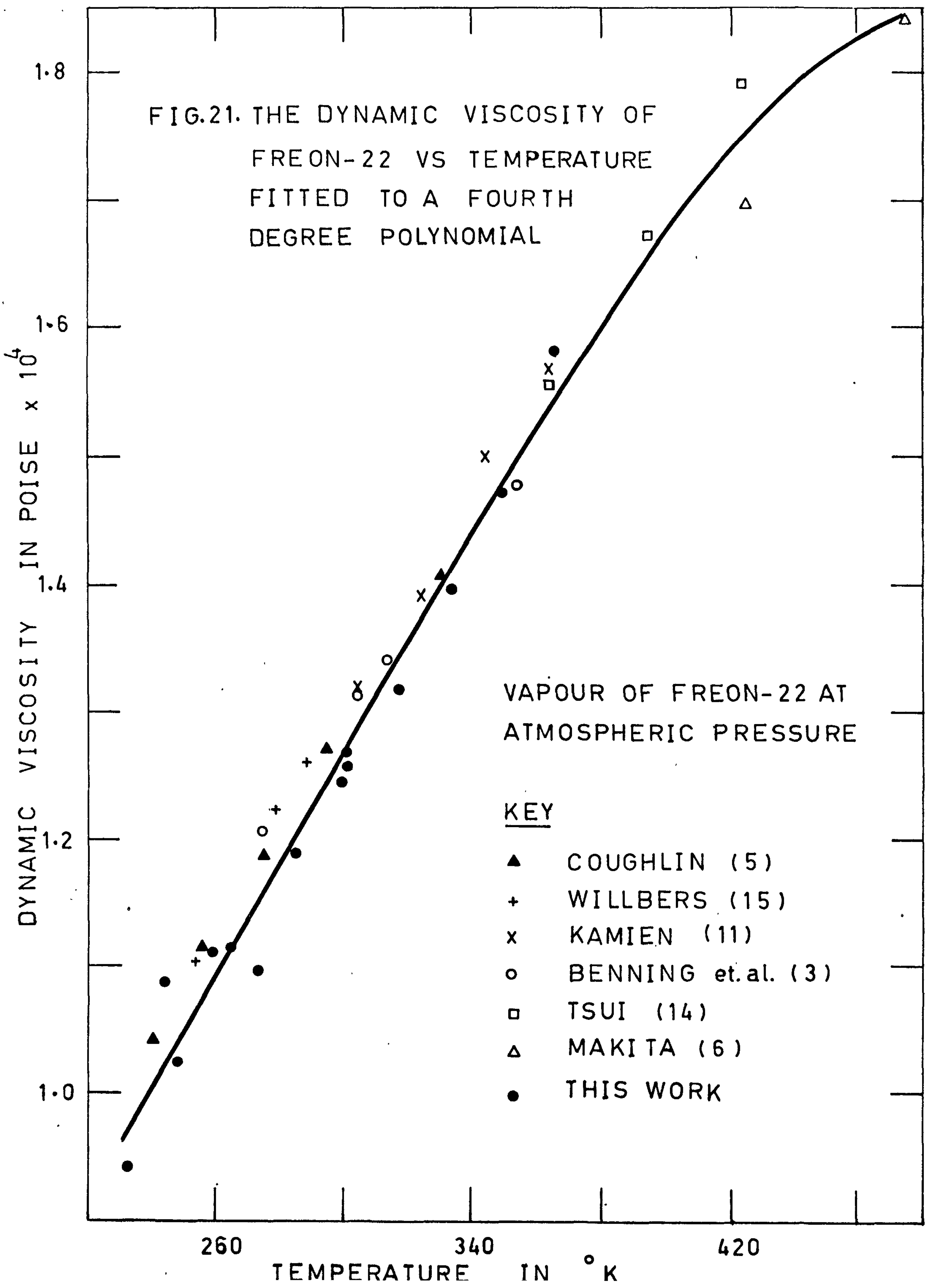


FIG.21. THE DYNAMIC VISCOSITY OF FREON-22 VS TEMPERATURE FITTED TO A FOURTH DEGREE POLYNOMIAL

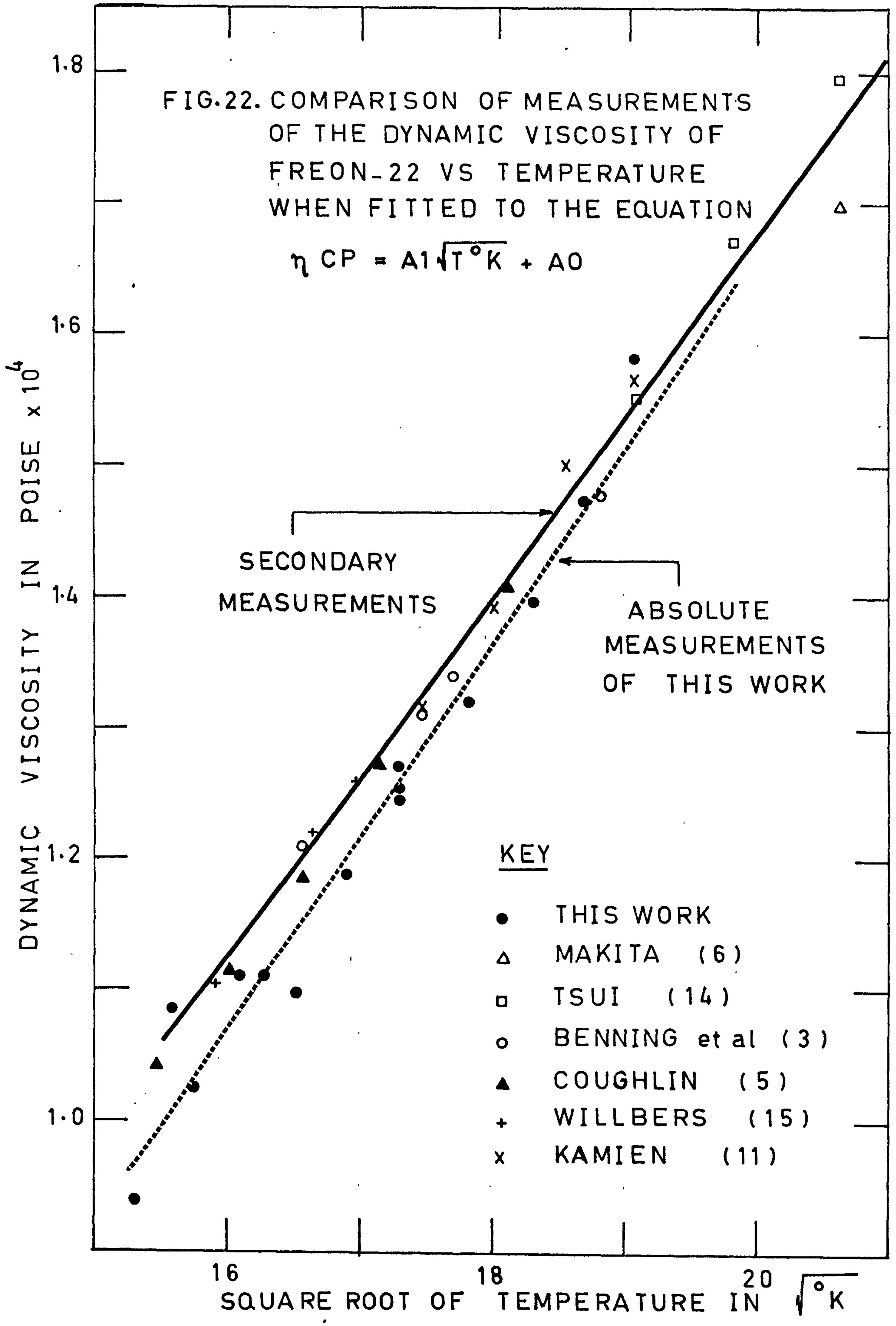


FIG.22. COMPARISON OF MEASUREMENTS OF THE DYNAMIC VISCOSITY OF FREON-22 VS TEMPERATURE WHEN FITTED TO THE EQUATION

$\eta\ CP = A1\sqrt{T^{\circ}K} + A0$

Thus, it is evident that the previous measurements are generally higher. The maximum deviation of previous measurements from this work occurs at about 235°K where it is about 6%.

The maximum Reynold's Number that prevailed during the viscosity measurement of both Freons in this work was of the order of 711, which is well within the lower limit for laminar flow of 2000. Therefore, the maximum development length in either of the capillary tubes used is given by

$$\begin{aligned} x &= (0.028)(Re)(d) \\ &= (0.028)(711)(0.05) \\ &= \underline{0.995\ \text{cm}}. \end{aligned}$$

This length is 4% of the entire length of the shorter capillary.

VIII CONCLUSIONS

The absolute viscosity of the vapours of two refrigerants, Dichlorodifluoromethane (Freon - 12) and Monochlorodifluoromethane (Freon - 22), has been determined at atmospheric pressure and in the general temperature range -39.7 to 91.8°C, by using a viscometer of the series-capillary type. The maximum experimental error of the data thus obtained is believed to be ± 3.1%.

The experimental results have been fitted to polynomials of the form

$$\eta = \sum_{i=0}^{i=n} a_i T^i,$$

and an approximate form of the Sutherland Equation

$$\eta = A \sqrt{T\,°K} + B,$$

by the method of least squares.

The maximum deviation of the experimental results for Freon - 12 from previous measurements over the common temperature range is +5%, whilst that for Freon - 22 is -6%.

The results of this work and those of previous workers were combined and correlated using polynomials and equations of the form given above to yield relationships that are useful in predicting the variation of the viscosity of Freons 12 and 22 over the entire temperature range that has so far been investigated by all workers

IX RECOMMENDATIONS

1. One of the major sources of error in the experimental determination of the absolute viscosity in this work appears to be the pressure measurement (see Appendix X.5). Thus, if it is desired to increase the accuracy of the measurement, methods of improving the pressure measurement should be investigated.

2. It is felt that the method of manually controlling the rate of flow through the heat exchanger coils is inadequate and time consuming. The possibility of controlling the flow automatically by temperature sensors governing solenoid valves should be investigated, in order to minimize temperature gradients along the viscometer.

3. Figures (15) and (19) show that the viscosity gradient with temperature, decrease as the temperature is decreased in the vicinity of the saturation temperature. This warrants further investigation.

APPENDIX I

TABLES OF PREVIOUS MEASUREMENTS

TABLE X.1.1

THE VISCOSITY OF FREON VAPOURS UNDER ATMOSPHERIC PRESSURE*

FREON 11

TEMP° K**	VISCOSITY CP	REF. NO.
313.15	0.01135	(3)
352.15	0.01250	(3)
363.15	0.01313	(14)
363.15	0.01324	(13)
392.15	0.01348	(13)
393.15	0.01421	(14)
421.15	0.01548	(14)
423.15	0.01523	(14)

FREON 12

TEMP° K**	VISCOSITY CP	REF. NO.
253.15	0.010716	(15)
275.15	0.01187	(3)
276.05	0.01154	(9)
278.15	0.011609	(15)
289.15	0.012098	(15)
289.35	0.01232	(9)

* All the data reported here are at atomspheric pressure, except for some points by Wellman (9) where the values were taken as under atmospheric pressure provided it did not exceed 19.6 lbf/in^2.

** The freezing point of water has been taken as 273.15° KELVIN.

FREON 12

298.15	0.01251	(3)
302.75	0.01273	(9)
303.34	0.01274	(11)
303.38	0.01274	(11)
304.15	0.01265	(3)
313.15	0.01293	(3)
322.63	0.01355	(11)
322.71	0.01362	(11)
323.15	0.01348	(9)
323.15	0.01318	(3)
343.15	0.01438	(11)
343.29	0.01436	(11)
343.45	0.01433	(9)
353.15	0.01399	(3)
363.10	0.01525	(11)
363.11	0.01523	(11)
363.15	0.01506	(9)
363.15	0.01518	(14)
373.15	0.01446	(3)
393.15	0.01598	(14)
423.15	0.01710	(14)
423.15	0.01572	(6)
473.15	0.01723	(6)

FREON 21 (Continued on Page 96)

322.76	0.01251	(11)
343.15	0.01331	(11)
343.17	0.01328	(11)
343.35	0.01307	(9)
353.15	0.01293	(3)
361.55	0.01381	(9)
363.13	0.01399	(11)
363.13	0.01399	(11)
363.15	0.01383	(13)
363.15	0.01370	(14)
393.15	0.01510	(13)
393.15	0.01481	(14)
421.15	0.01627	(13)
423.15	0.01595	(14)
423.15	0.01486	(6)
463.15	0.01709	(13)

FREON 22

239.15	0.01043	(5)
254.15	0.011041	(15)
256.15	0.01115	(5)
274.15	0.01188	(5)
275.15	0.01207	(3)
278.15	0.012217	(15)

FREON 22

288.15	0.012616	(15)
294.15	0.01273	(5)
302.99	0.01316	(11)
303.28	0.01317	(11)
304.15	0.01313	(3)
313.15	0.01340	(3)
322.75	0.01391	(11)
422.81	0.01391	(11)
329.15	0.01407	(5)
343.18	0.01500	(11)
343.23	0.01500	(11)
353.15	0.01477	(3)
363.12	0.01472	(11)
363.12	0.01572	(11)
363.15	0.01551	(14)
393.15	0.01673	(14)
423.15	0.01791	(14)
423.15	0.01697	(6)
473.15	0.01861	(6)

FREON 23

236.15	0.01043	(5)
239.15	0.01170	(5)
256.15	0.01256	(5)

FREON 13

235.15	0.011803	(15)
253.15	0.012496	(15)
279.15	0.013916	(15)
288.45	0.01341	(9)
289.15	0.014115	(15)
303.04	0.01480	(11)
303.34	0.01488	(11)
303.65	0.01415	(9)
322.65	0.01511	(9)
322.65	0.01605	(11)
322.65	0.01601	(11)
342.65	0.01617	(9)
343.08	0.01638	(11)
343.08	0.01635	(11)
361.45	0.01702	(9)
363.14	0.01769	(11)
363.14	0.01769	(11)
363.15	0.01722	(14)
393.15	0.01849	(14)
423.15	0.01968	(14)

FREON 14

235.15	0.014204	(15)
254.15	0.015126	(15)
278.15	0.016433	(15)
289.15	0.017072	(15)
303.08	0.01762	(11)
303.15	0.01762	(11)
322.89	0.01868	(11)
322.91	0.01868	(11)
343.10	0.01903	(11)
343.16	0.01903	(11)
363.12	0.01971	(11)
363.13	0.01971	(11)
363.15	0.02050	(14)
393.15	0.02192	(14)
423.15	0.02319	(14)

FREON 21

(Continued from Page 93)

303.13	0.01170	(11)
303.15	0.01172	(11)
303.15	0.01138	(9)
304.05	0.01158	(3)
313.15	0.01184	(3)
322.65	0.01213	(9)
322.75	0.01249	(11)

FREON 23

274.15	0.01343	(5)
278.15	0.014066	(15)
288.15	0.014733	(15)
295.15	0.01426	(5)
302.95	0.01545	(11)
303.10	0.01545	(11)
322.90	0.01609	(11)
322.91	0.01609	(11)
334.15	0.01588	(5)
343.22	0.01719	(11)
343.29	0.01719	(11)
363.12	0.01787	(11)
363.13	0.01787	(11)
363.15	0.01781	(14)
363.15	0.01780	(13)
392.15	0.01960	(13)
393.15	0.01918	(14)
421.15	0.02072	(13)
423.15	0.02052	(14)
453.15	0.02185	(13)
473.15	0.02273	(13)

FREON 114

303.14	0.01162	(11)
303.03	0.01161	(11)
304.15	0.01164	(3)
313.15	0.01193	(3)
323.15	0.01223	(3)
322.96	0.01249	(11)
322.96	0.01250	(11)
343.25	0.01300	(11)
343.37	0.01304	(11)
353.15	0.01298	(3)
363.13	0.01363	(11)
363.14	0.01362	(11)
363.15	0.01365	(14)
363.15	0.01365	(13)
392.15	0.01488	(13)
393.15	0.01471	(14)
421.15	0.01589	(13)
423.15	0.01564	(14)
453.15	0.01688	(13)
473.15	0.01749	(13)

FREON 115

234.15	0.011592	(15)
253.15	0.010948	(15)
246.15	0.01105	(5)
274.15	0.01171	(5)
278.15	0.011901	(15)
289.15	0.012266	(15)
294.15	0.01244	(5)
303.13	0.01291	(11)
303.34	0.01291	(11)
322.74	0.01376	(11)
322.76	0.01376	(11)
324.15	0.01371	(5)
343.30	0.01442	(11)
343.38	0.01442	(11)
363.10	0.01505	(11)
363.11	0.01505	(11)
363.15	0.01501	(13)
363.15	0.01510	(14)
392.15	0.01620	(13)
393.15	0.01616	(14)
422.15	0.01757	(13)
423.15	0.01721	(14)
454.15	0.01823	(13)
473.15	0.01928	(13)

FREON C318

276.15	0.01098	(4)
288.15	0.011601	(15)
301.15	0.01177	(4)
303.28	0.01202	(11)
303.34	0.01202	(11)
322.73	0.01266	(11)
322.81	0.01266	(11)
323.15	0.01231	(4)
343.30	0.01364	(11)
343.38	0.01364	(11)
363.13	0.01434	(11)
363.14	0.01434	(11)
363.15	0.01359	(14)
370.15	0.01365	(4)
393.15	0.01477	(14)
423.15	0.01589	(14)

FREON 13B1

235.15	0.012401	(15)
278.15	0.014882	(15)
288.15	0.015256	(15)
363.15	0.01664	(14)
393.15	0.01993	(14)
423.15	0.02124	(14)

TABLE X.1.2

THE VISCOSITY OF FREON LIQUIDS UNDER ATMOSPHERIC PRESSURE

FREON 11

TEMP°K*	VISCOSITY CP	REF. NO.
171.35	2.647	(16)
182.55	2.017	(16)
195.75	1.552	(16)
208.75	1.246	(16)
213.15	1.380	(10)
222.85	1.014	(16)
233.15	1.136	(10)
233.15	0.935	(10)
238.15	0.822	(16)
243.15	0.785	(10)
253.15	0.669	(10)
253.25	0.645	(16)
265.15	0.585	(10)
271.05	0.531	(16)
284.75	0.458	(16)
295.71	0.416	(17)
297.35	0.397	(16)

* The freezing point of water has been taken as 273.15° KELVIN

FREON 12

208.15	0.731	(10)
210.37	0.536	(17)
213.15	0.620	(10)
213.15	0.457	(12)
213.15	0.509	(12)
223.15	0.406	(12)
223.15	0.456	(12)
223.15	0.507	(10)
233.15	0.362	(12)
233.15	0.432	(10)
233.15	0.407	(12)
243.15	0.367	(12)
243.15	0.362	(10)
243.15	0.326	(12)
243.25	0.375	(3)
244.82	0.347	(17)
244.87	0.347	(17)
245.76	0.342	(17)
250.93	0.323	(17)
250.93	0.323	(17)
252.95	0.343	(3)
258.15	0.322	(2)
263.15	0.313	(2)

FREON 22

213.15	0.422	(10)
223.15	0.354	(10)
224.15	0.392	(16)
230.85	0.361	(16)
233.15	0.298	(10)
238.70	0.221	(17)

FREON C318

243.15	0.885	(12)
253.15	0.732	(12)
263.15	0.611	(12)
273.15	0.523	(12)

FREON 21

208.15	0.958	(10)
213.15	0.850	(10)
223.15	0.703	(10)
233.15	0.591	(10)
243.15	0.556	(3)
243.15	0.496	(10)
248.15	0.466	(10)

FREON 114

208.15	1.575	(10)
213.15	1.352	(10)
223.15	1.110	(10)
243.15	0.731	(3)
243.15	0.754	(10)
253.15	0.640	(10)
263.15	0.556	(10)

FREON 115

210.93	0.693	(12)
222.04	0.591	(12)
233.15	0.504	(12)

FREON 12B1

209.15	1.153	(10)
213.15	0.760	(12)
213.15	0.927	(12)
213.15	1.005	(10)
223.15	0.762	(10)
233.15	0.590	(12)
233.15	0.634	(10)
233.15	0.661	(12)
243.15	0.595	(10)
253.15	0.475	(12)
253.15	0.485	(12)

	FREON 12B1	
253.15	0.496	(10)
263.15	0.436	(10)
273.15	0.397	(12)
	FREON 12B2	
213.15	1.270	(12)
233.15	0.960	(12)
253.15	0.760	(12)
273.15	0.618	(12)
	FREON 13B1	
203.15	0.475	(12)
208.15	0.456	(12)
213.15	0.403	(12)
218.15	0.374	(12)
	FREON 114B2	
213.15	2.78	(19)
213.15	2.779	(12)
233.15	1.839	(12)
233.15	1.84	(19)
253.15	1.32	(19)
253.15	1.319	(12)
273.15	0.987	(12)
273.15	0.90	(19)
293.15	0.76	(19)

FREON 113

243.15	1.64	(12)
253.15	1.37	(12)
257.78	1.47	(10)
262.23	1.34	(10)
267.37	1.20	(10)
263.15	1.12	(12)
273.15	0.950	(12)
283.15	0.806	(12)
293.15	0.686	(12)

X2 THERMOCOUPLE CALIBRATION

X 2 THERMOCOUPLE CALIBRATION

X2.1 Introduction

The ten copper-constantan thermocouples used were calibrated against a calibrated thermo-electric thermocouple No. 705. The cold junctions were kept at 32°F, both during calibration and actual use, by placing them in an ice water mixture. The thermo-electric copper-constantan thermocouple had been calibrated by Thermo-Electric (Canada) Ltd. against a Standard, N.B.S. Thermocouple APHSSP-992/1 for -112, -100, and -50 degrees F, and against Standard, N.B.S. Thermocouple APH-1421 for 50, 100, and 150 degrees F. The uncertainty of the Standard Thermocouples APHSSP-992/1 and APH-1421 are ± 0.1 and ± 0.06 degrees C respectively. The deviation of e.m.f. of thermocouple 705 in Millivolts from the N.B.S. circular 561 copper-constantan thermocouple tables are given below for a reference junction temperature of 32 degrees F.

Temp. Deg. F	Deviation in M.V.
-112	+0.014
-100	+0.021
-50	+0.009
+50	+0.009
+100	+0.012
+150	+0.010

In order to limit the uncertainty in temperature as close as possible to that of the Standard Thermocouples, it was necessary to calibrate at fixed temperatures. Since the production of constant temperatures over the temperature range of the primary calibration requires an elaborate set-up, physical phase-change temperatures were used. It must be stressed here that the purpose was not to achieve those changing phase temperatures exactly, because the calibration was secondary in nature. Moreover, the production of such temperatures would require pure materials kept under certain conditions, and would therefore be equally difficult. The reader is referred to reference (43) for a thorough discussion on primary calibration. Thus, mixtures of ice and water, and solid mercury and liquid mercury were used as two calibrating temperatures, while the sublimation point of solid CO_2 and the boiling water temperature were used as two other temperatures. Before taking every reading the potentiometer circuit was standardized. No drift of e.m.f. reading was at all detectable during all the measurements except in the case of boiling water where there was an oscillation of not more than ± 0.0002 Millivolts. The measurements are given in Table (X2.1) below. Figure (X2.1) shows the calibration curve of all the thermocouples.

X2.2 Dry Ice Sublimation Temperature

The calibrated thermocouple 705 was placed centrally in an insulated thermal flask with the thermocouple to be calibrated radially placed around thermocouple 705. The flask was then filled with crushed dry ice and left to settle to a steady temperature for about three hours before noting the e.m.f. readings.

X2.3 Mercury Melting Temperature

In order to obtain the mercury melting temperature, the mercury was frozen in plastic trays by spraying the mercury surface with liquid nitrogen. The cubes were then left at room temperature to allow for any remaining liquid nitrogen to boil off. The mercury cubes were then placed inside an insulated thermal flask already containing liquid mercury so as to form the required mixture. In order to avoid contamination of the thermocouples, they were placed individually together with the calibrated thermocouple inside a glass tube having one end sealed such that the thermocouple points were below the mercury mixture level. The flask top was insulated from room temperature by a rubber stopper. A time of about two hours was allowed for the thermocouples to reach a steady temperature before the readings were taken. The same procedure was then repeated for the other nine thermocouples.

X2.4 Ice Melting Temperature

As in the case of the dry ice calibration the ten thermocouples were placed radially around the calibrated thermocouple and the bundle was placed in an insulated bath of ice-water mixture. This was left for approximately three hours before the readings were taken.

X2.5 Boiling Water Temperature

For the boiling water temperature, the thermocouples were wrapped around thermocouple 705 such that all the thermocouple points were approximately in the same radial plane. The bundle was then placed in a large beaker filled with tap water. The water was boiled for about ten minutes prior to taking the readings. The atmospheric pressure was also noted.

TABLE X2.1 THERMOCOUPLE CALIBRATION

Dry Ice Sublimation Temperature

Thermocouple No.	Thermocouple E.M.F. in M.V.	Thermocouple 705 E.M.F. in M.V.
1	-2.73295	-2.73224
2	-2.75240	-2.73224
3	-2.73575	-2.73265
4	-2.72714	-2.73265
5	-2.73361	-2.73265
6	-2.72440	-2.73280
7	-2.76482	-2.73340
8	-2.76012	-2.73340
9	-2.74433	-2.73340
10	-2.71791	-2.73340

Mercury Melting Point Temperature

1	-1.38180	-1.41810
2	-1.44156	-1.42767
3	-1.39600	-1.40898
4	-1.35040	-1.38640
5	-1.37620	-1.39750
6	-1.36481	-1.42415
7	-1.44903	-1.42906
8	-1.43970	-1.41140
9	-1.41410	-1.41001
10	-1.33712	-1.38500

TABLE X2.1/CONTINUED

Ice-Water Mixture Temperature

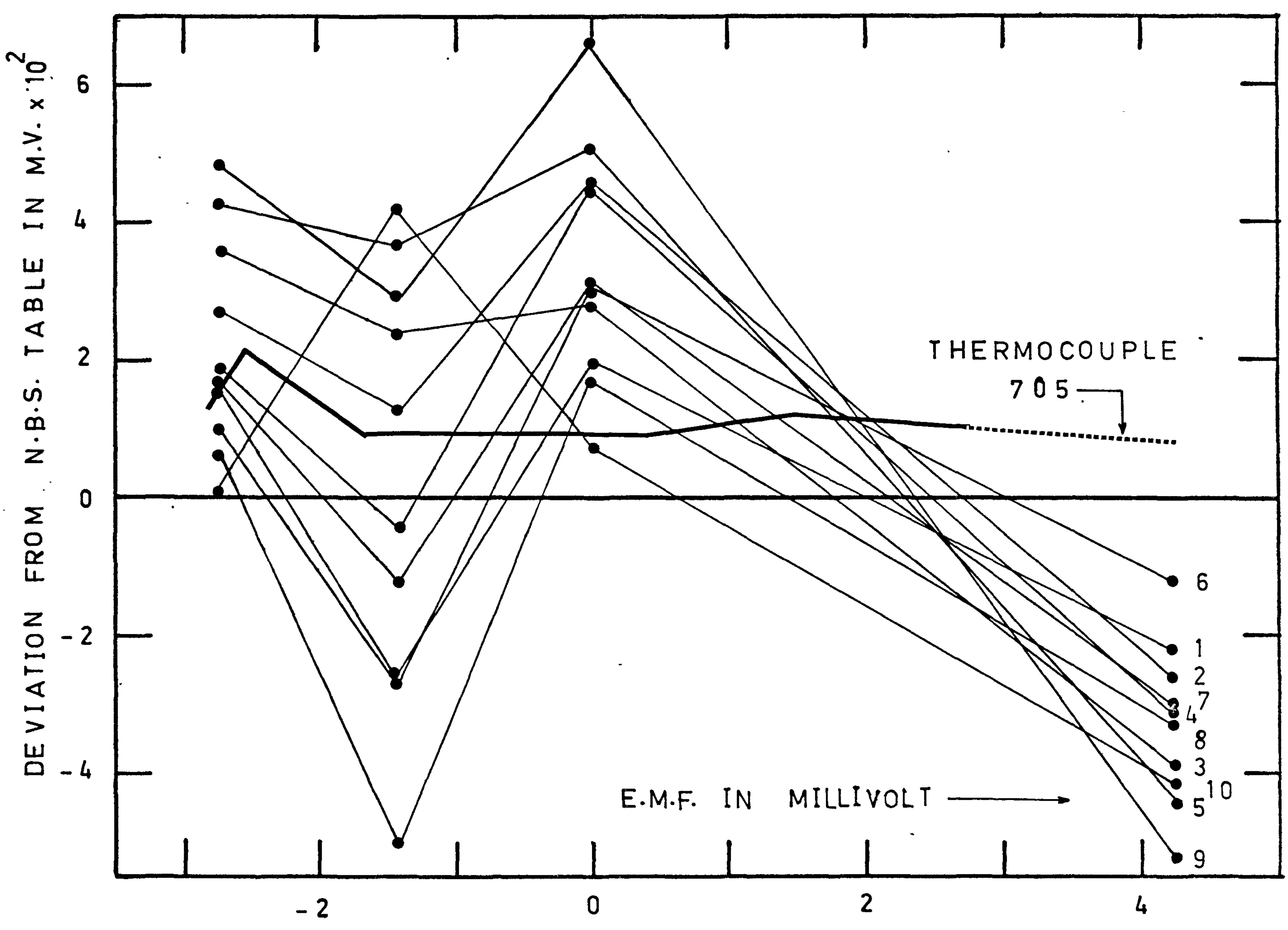
1	0.02000	0.01025
2	0.04840	0.01186
3	0.04694	0.01035
4	0.03294	0.01095
5	0.04569	0.01095
6	0.01990	0.01085
7	0.08406	0.01088
8	0.05156	0.01081
9	0.04744	0.01053
10	0.00824	0.01075

Boiling Water Temperature *

1	4.242	4.272
2	4.225	4.272
3	4.233	4.272
4	4.252	4.272
5	4.234	4.272
6	4.236	4.272
7	4.212	4.272
8	4.219	4.272
9	4.238	4.272
10	4.226	4.272

* All readings had an oscillation of not more than ± 0.0002 Millivolts. Atmospheric pressure was equal to 29.405 inches of mercury.

FIGURE (X2·1) THERMOCOUPLE CALIBRATION CURVES



X3 CALIBRATION OF CAPILLARY TUBES

X3 CALIBRATION OF THE CAPILLARY TUBES

In deriving the equation for flow through a capillary tube, it was assumed that the diameter of the tube was uniform along its entire length; see Chapter IV. It is, therefore, essential to insure that the diameter of the capillary tube is accurately determined, and that it is uniform along the entire length of the tube. This is important since the diameter is raised to the fourth power in the flow equation.

Several ways of determining the average diameter of the capillary tube have been tried by Latto (34); namely:

1. Measuring the electrical resistance of a mercury thread filling the capillary tube.
2. Using X-rays to examine the tubes.
3. Passing a short mercury pellet along the tube and observing the variation of its length with the aid of a cathotometer. Then by filling the tube with a long mercury thread and weighing it accurately, both the variation in diameter of the capillary tube along its length and the average diameter can be determined.

Latto (34) reported that he obtained more reliable data using the latter method. H. Schultze (44), in 1901, was the first to introduce a method whereby both the weight of the small mercury pellet and the mercury thread may be combined to give an average value of the diameter which he thought would be more accurate than using the long thread alone. The method of Schultze (44) was later modified by Fisher (45) and used by Carr (46) to determine the average diameter of glass capillary tubes. The method as modified by Fisher (45) is outlined below.

The short pellet inside the capillary tube is assumed to take a general shape of a frustum of a right circular cone, capped at each end with spherical portions as shown in figure (X3.1).

The equivalent length of such a pellet (see next page) is given by:

$$e = \lambda + 1/2\ (h_1 + h_2) \tag{1}$$

For conditions of laminar flow in a capillary tube the total pressure drop along the length of the capillary tube under consideration is given by:

$$\int_o^{\ell} dP = \frac{8Q\eta}{\pi\rho} \int_o^{\ell} \frac{d\ell}{a^4} \tag{2}$$

Thus if we can determine the integral $\int_o^{\ell} \frac{d\ell}{a^4}$ directly, it will be possible to determine the average value for the capillary tube radius "a".

Let the volume of the small pellet be "v", then

$$v = e.\pi.a^2 \tag{3}$$

Substituting (3) in (2) we get

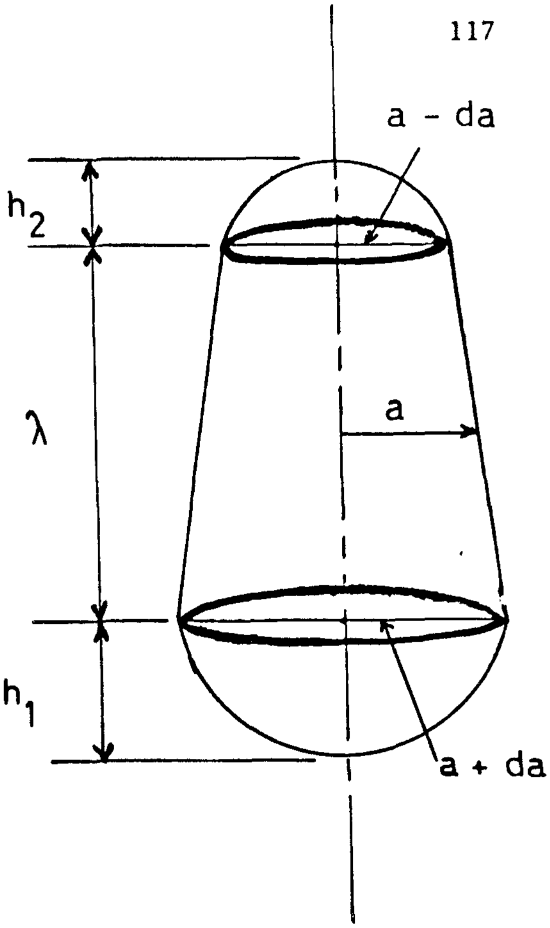
$$\int_0^{\ell} \frac{d\ell}{a^4} = \int_0^{\ell} \frac{e^2\pi^2 d\ell}{v^2} \tag{4}$$

The volume of the long mercury thread "V" is given by;

$$V = \int_{\ell_1}^{\ell_2} \pi a^2 d\ell \tag{5}$$

where "ℓ_2" and "ℓ_1" are the two lengths measured from one end of the

The pellet is assumed to have the shape of a frustum of a right circular cone capped at each end with a spherical segment.



FIG(X3·1) MERCURY PELLET

The volume of the pellet is given by :

$$\pi a^2 \left[\left(1 + \frac{da^2}{3a^2}\right) . \lambda + \left(\frac{h_1^3 + h_2^3}{6a^2}\right) + \left(\frac{h_1 + h_2}{2}\right)\left(\frac{d^2a}{a^2} + 1\right) + \frac{da}{a}(h_1 - h_2) \right]$$

Since $\frac{da}{a}$, h_1^3, h_2^3, & $(h_1 - h_2)$ are small compared to λ, we can neglect them. Thus, the equivalent length;

$$e = \lambda + \frac{1}{2}(h_1 + h_2) .$$

capillary tube, between which the thread extends

Substituting (3) in (5); we get

$$V = \int_{\ell_1}^{\ell_2} \frac{v}{e} \cdot d\ell$$

Now, since "v" is constant, we can write

$$v = \frac{V}{\int_{\ell_1}^{\ell_2} \frac{d\ell}{e}} \qquad (6)$$

Substituting (6) in (4) we get

$$\int_0^{\ell} \frac{d\ell}{a^4} = \frac{\pi^2}{V^2} \int_0^{\ell} e^2 d\ell \times \left[\int_{\ell_1}^{\ell_2} \frac{d\ell}{e}\right]^2 \qquad (7)$$

The volume "V" is used in equation (7) since its value can be determined more accurately than the volume "v" as in equation (4).

In this work, several capillary tubes of different diameters and having an initial length of about 60 cm. were calibrated using both the short pellet and the long mercury thread. The rig for those measurements is shown in figure (X.6.5).

The method suggested by Fisher (45) was attempted on one of the capillaries that were calibrated (No. 9). The readings for capillary No. 9 are listed in Table X3.1.

In order to evaluate the integrals

$\int_0^{\ell} e^2 d\ell$ and $\int_{\ell_1}^{\ell_2} \frac{d\ell}{e}$, two numerical integration methods were attampted. The first was Simpson's Parabolic Rule, using Lagrange's interpolation formula. This method, however, was not successful, since Lagrange's Interpolation Formula proved inaccurate in predicting the values of the curve to be integrated towards the two ends of the curve. It is suggested that this method be repeated breaking the curve to be integrated into smaller segments. The second method was to use the trapezoidal rule of integration. This method is known to be inaccurate.

The integrals were also evaluated graphically. Furthermore, by using the weight of the long thread, which was measured on a "Mettler" model (H4) balance that has an accuracy of ± 0.001 grams, the average value of the diameter of the capillary tube was evaluated.

The results for the methods used were as follows:

Capillary No. 9

Method	Average Diameter of Tube in Millimeters
Fisher's Method	
(a) Integrating by Simpson's parabolic rule	Failed
(b) Integrating Graphically	0.41756

(c) Integrating by the Trapezoidal rule	0.41926
Gravimetric Method	0.39565

It is evident from the above results that the difference between the gravimetric method and that due to Fisher is about 5%. The inaccuracy is expected to have been caused by the integration methods used. For this reason, the results obtained by weighing the long mercury thread were taken in preference to the other methods. It would also improve the results, if the method suggested by Fisher was repeated using shorter mercury pellets than those employed in this work as appears in Table (X3.1).

TABLE X3.1

CAPILLARY TUBE CALIBRATION

CAPILLARY NO. 9

Nominal Dia. = 0.4 mm.

POSITION ALONG TUBE CM	λ CM	h_1 CM	h_2 CM	1/c CM^{-1}	c^2 CM^2	Temp. °C
2.8525	2.839	0.013	0.011	0.3537	7.992	
5.6480	2.846	0.013	0.008	0.3527	8.040	22.0
8.4455	2.847	0.016	0.011	0.3529	8.029	
11.2950	2.856	0.017	0.013	0.3520	8.071	
13.8645	2.827	0.012	0.007	0.3549	7.938	
16.4575	2.871	0.014	0.008	0.3497	8.180	
19.2670	2.858	0.011	0.009	0.3511	8.111	22.0
22.0395	2.861	0.013	0.012	0.3511	8.114	
24.8440	2.858	0.013	0.013	0.3515	8.094	
27.6025	2.859	0.011	0.013	0.3512	8.105	
30.3760	2.848	0.012	0.008	0.3524	8.054	
33.1555	2.843	0.012	0.007	0.3523	8.057	22.0
35.8730	2.842	0.012	0.009	0.3532	8.017	23.0
38.6865	2.841	0.010	0.012	0.3534	8.009	
41.4415	2.815	0.011	0.009	0.3565	7.868	
44.149	2.858	0.013	0.014	0.3516	8.091	
46.8865	2.841	0.010	0.011	0.3533	8.012	23.0
49.631	2.842	0.012	0.010	0.3532	8.0146	
52.333	2.846	0.015	0.014	0.3532	8.0174	
55.077	2.846	0.016	0.013	0.3532	8.0174	
57.900	2.880	0.012	0.013	0.3487	8.2256	23.5

Gravimetric Method: At a temperature of 24.0°C:

Length of mercury thread = 59.681 cm.

Mass of mercury thread = 0.9936 gm

Average diameter by gravimetric method = 0.39565 mm.

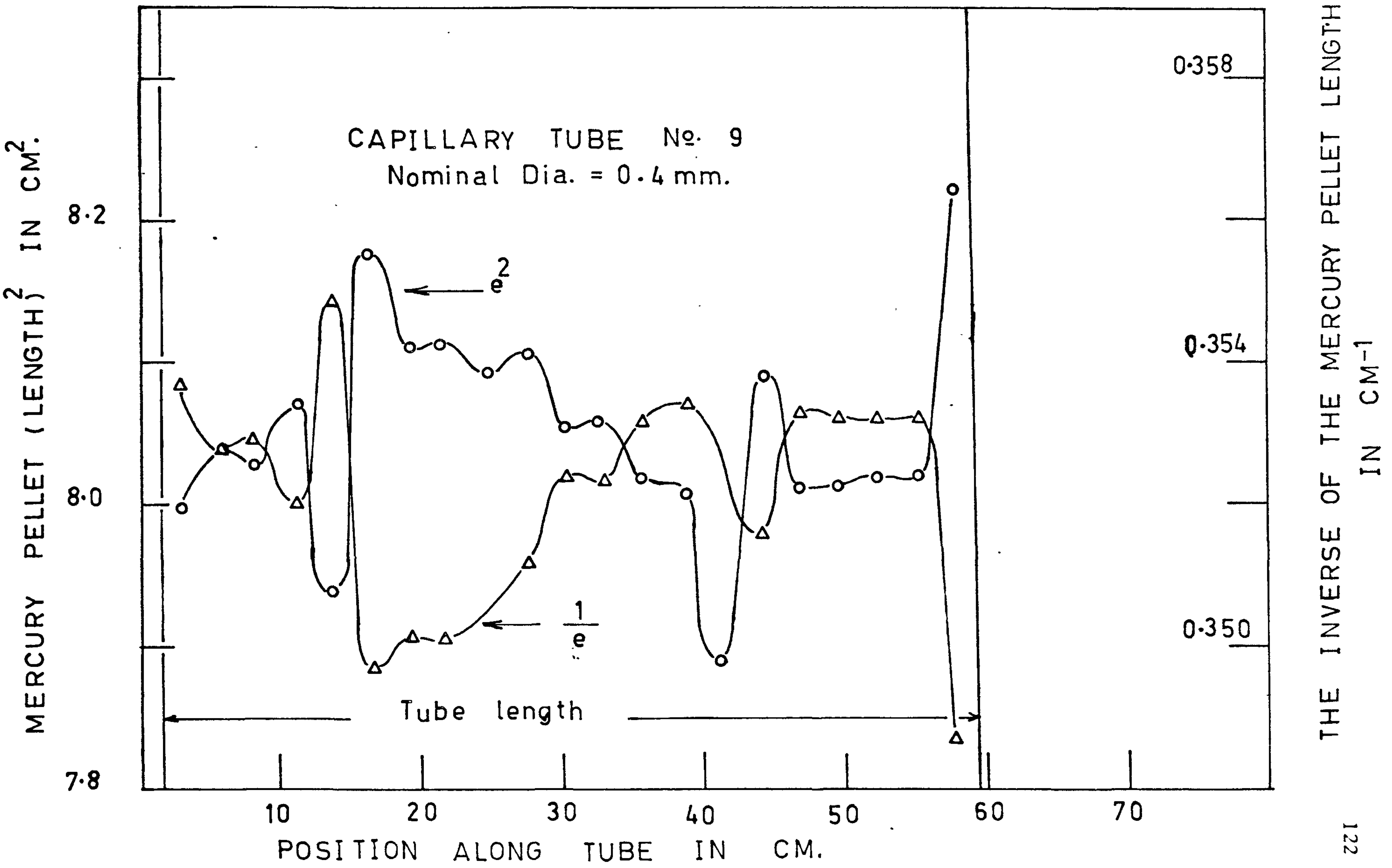


FIG X3·2 CAPILLARY TUBE CALIBRATION

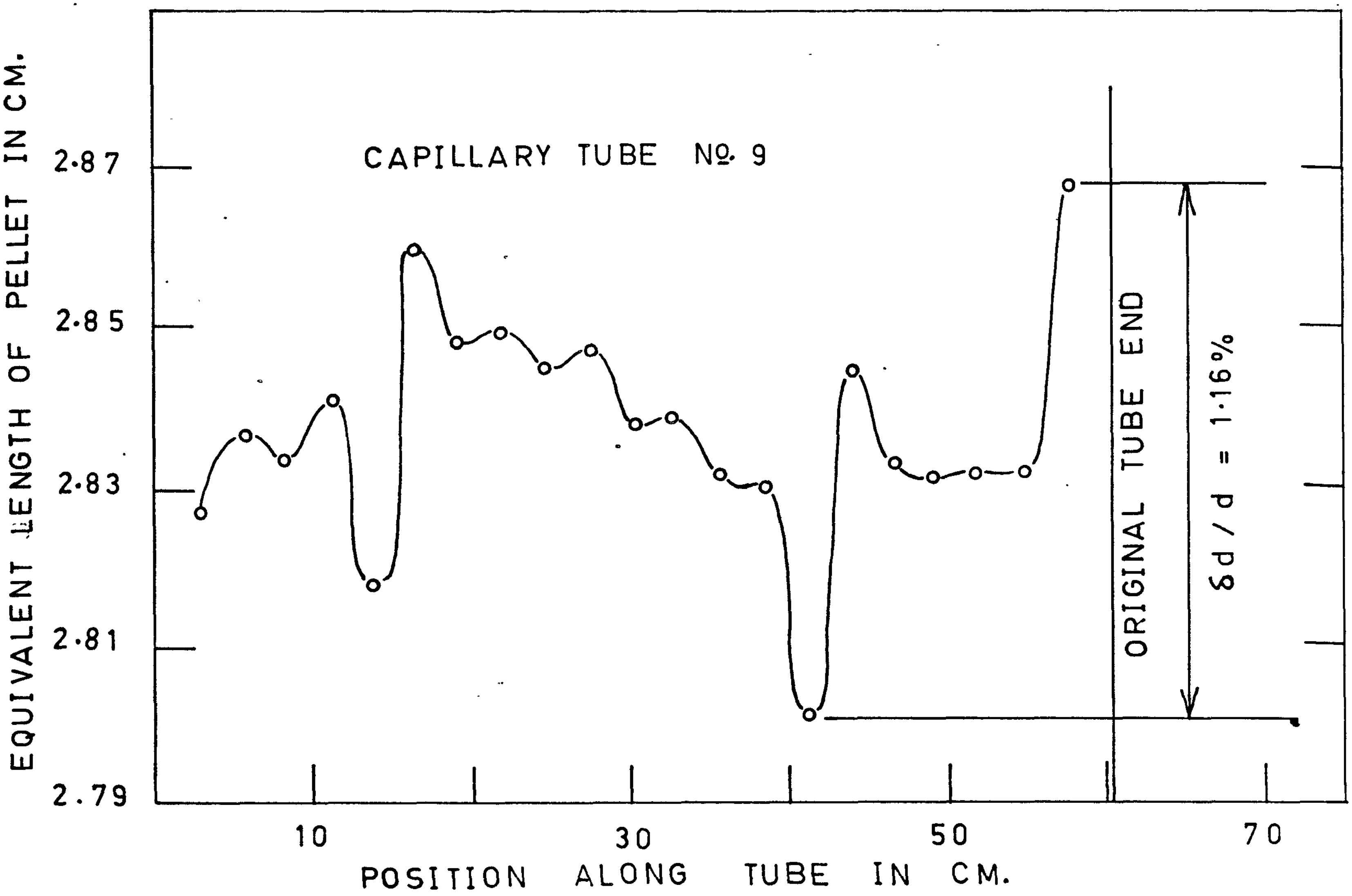


FIG X3·3 CAPILLARY TUBE CALIBRATION

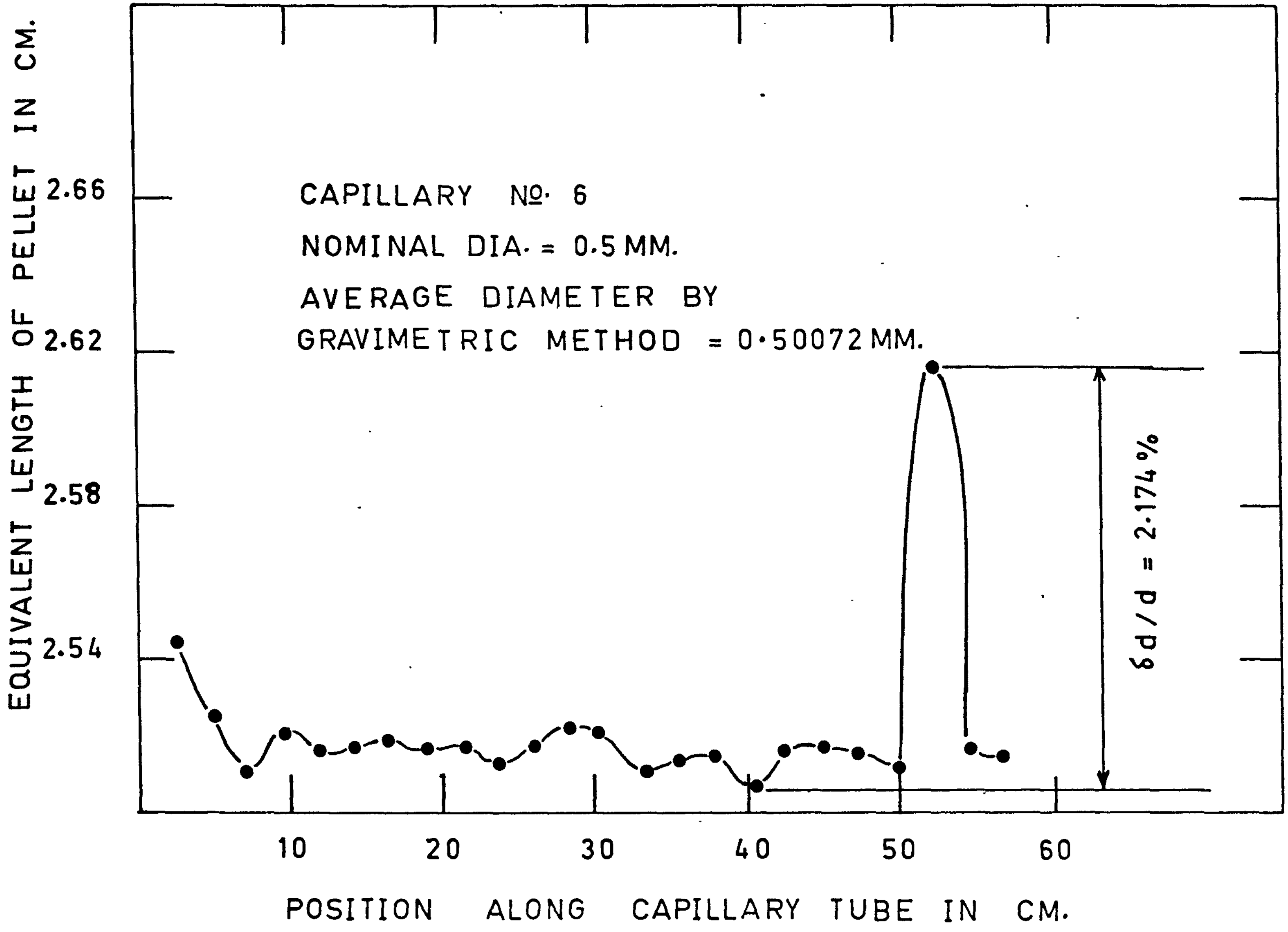


FIG. X3.4 CAPILLARY TUBE CALIBRATION

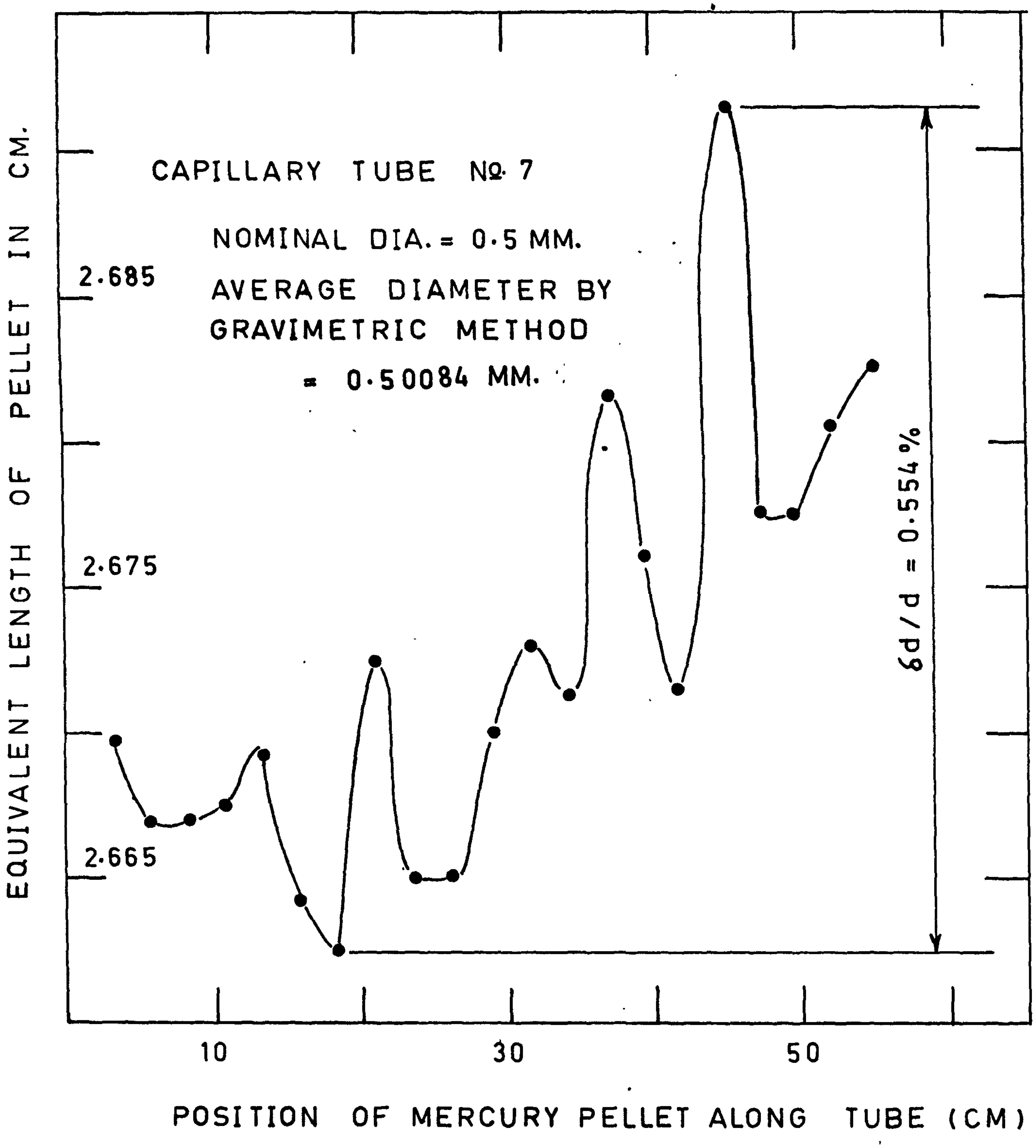


FIGURE X3·5 CAPILLARY TUBE CALIBRATION

X4 SAMPLE CALCULATION

X4 SAMPLE CALCULATION

One of the Freon 22 readings was chosen arbitrarily to illustrate a typical calculation.

The thermocouple readings were as follows:-

E.M.F. in M.V.

Thermocouples Inside Viscometer							Flowmeter	Manometer
-1.4451	-1.14923	-1.4806	-1.4372	-1.4703	-1.4422	-1.4700	+0.6981	+0.8276
Corrected E.M.F. using the Thermocouple Calibration Curves, figure (X2.1)								
-1.4391	-1.4873	-1.4626	-1.4212	-1.4603	-1.4422	-1.4520	+0.6521	+0.7956
Temperature in Degrees C (N.B.S. Circular 561)								
-39.294	-40.686	-40.00	-38.771	-39.912	-39.382	-39.676	+16.625	+20.225

The average temperature of the seven thermocouples inside the viscometer is = -39.674 degree C = 233.476 degree K. The barometer reading was 29.56 inches of Hg and the volume flow rate of Freon 22 through the capillary tubes was 0.2966 Cu. Cm./Sec. as measured on the "Soap Film Flowmeter". The pressure drop across the long and short capillary tubes was 7.288 and 4.258 cm. of water respectively measured on the differential water manometer.

The absolute value of the dynamic viscosity for the series capillary viscometer is given by

$$\eta = \frac{\pi d_1^4 (1 + 3\alpha t) g}{128 Q (\ell_1 - \ell_2)} \times \left[\Delta P_1 \rho_1 - \left(\frac{d_2}{d_1}\right)^4 \Delta P_2 \rho_2\right] \qquad (1)$$

The average diameters of the two capillary tubes used in this test was found by the "Mercury Thread Method" (see Calibration of Capillary Tubes, Appendix X3) to be as follows.

Tube	Length	Diameter
Long	47.375 Cm.	0.50072 mm.
Short	26.958 Cm.	0.50084 mm.

In equation (1) the densities ρ_1 and ρ_2 must be evaluated at the mean pressure inside the capillary tubes. The mean pressures inside the tubes were taken as follows:-

$$P_{1m} = P_{atm.} + \Delta P_2 + 1/2\Delta P_1$$

$$P_{sm} = P_{atm.} + 1/2\Delta P_2$$

where P_{1m} and P_{sm} are the mean pressures inside the long and short capillaries respectively, $P_{atm.}$ is the atmospheric pressure, ΔP_2 and ΔP_1 are the pressure drops across the short and long capillaries respectively.

Thus $P_{1m} = 29.56 \times 2.54 + \frac{\rho_w}{\rho_m}(4.258 + 3.644)$, where ρ_m and ρ_w are the densities of mercury and water at the manometer temperature of 20.225 degrees C in this reading.

From the Handbook of Chemistry and Physics (27) at a temperature of 20.255°C $\rho_m = 13.5457$ gm/c.c.

and $\rho_w = 0.998157$ gm/c.c.

$P_{1m} = 75.082 + 0.3138 + 0.2685 = \underline{75.6643}$ cm. of mercury

$P_{sm} = 75.082 + 0.1569 = \underline{75.2389}$ cm. of mercury

Using Du Pont's Bulletin No. R-22, (30) on the thermodynamic properties of Freon 22, the densities ρ_1 and ρ_2 were evaluated by interpolating for both temperature and pressure.

At -39.674 degree C and 75.6643 Cm. Hg., the specific volume of Freon 22 was found to be 3.4434 cu. ft./lb_m

While at -39.674 degree C and 75.2389 cm. of Hg., the specific volume of the same Freon was found to be 3.4638 cu. ft./lb_m

The volume flow rate was measured at atmospheric pressure and a temperature of 16.625 degree C. At these conditions the specific volume of Freon 22 was found to be 4.3871 cu. ft./lb_m

The calibration of the flowmeter indicated that the true volume was 2.8% higher than that indicated by the burette graduation. Therefore, the true volume flow rate is given by

$$Q' = \frac{0.2966 \times 1.028}{} = 0.3049 \text{ cu. cm./sec.}$$

The value of the acceleration due to gravity was estimated by the Department of Energy, Mines and Resources, for a point in the vicinity of the City Hall in Hamilton. The co-ordinates of this point have been estimated (48) as:

latitude	43	15.5N
longitude	79	52.2W
height above sea level		316 feet

At which $g = 980.3941$ cm./sec^2

The coefficient of thermal expansion for the material of the capillary tubes $\alpha = 3.3 \times 10^{-6}$ per degree C.

Therefore,

$$\eta = \frac{3.141593 \times (0.050072)^4 \times 980.3941 \times (1.0 - 9.9 \times 10^{-6} \times 59.674) \times 0.99816}{128 \times (47.375 - 26.958) \times 0.3049}$$

$$\times\ 4.3871 \left[\frac{7.288}{3.4434} - \left(\frac{0.50084}{0.50072} \right)^4 \times \frac{4.258}{3.4638} \right]$$

This gives $\eta = 0.9422 \times 10^{-4}$ Poise

Thus we conclude that the absolute value of the dynamic viscosity at 233.476 deg. K. and atmospheric pressure is $= 0.9422 \times 10^{-4}$ Poise.

X5 ERROR ANALYSIS

X5 ERROR ANALYSIS

Starting with the basic Poiseulle Equation

$\eta = \frac{\pi d^4 g \Delta P}{128\ Q\ell}$, and taking the natural logorithum

of both sides, we get:

$$\ell n\ \eta = \ell n\ (\frac{\pi}{128}) + 4\ \ell n\ d + \ell n\ g + \ell n\ (\Delta P) - \ell n\ Q - \ell n\ \ell$$

Differnetiating

$$\frac{\delta\eta}{\eta} = 4\ \frac{\delta d}{d} + \frac{\delta g}{g} + \frac{\delta\ (\Delta P)}{\Delta P} - \frac{\delta Q}{Q} - \frac{\delta\ell}{\ell}$$

But since we are interested in the maximum percentage error in the viscosity η, we assume that all the terms on the right hand side of the above equation are additive

i.e.

$$\frac{\delta\eta}{\eta} = 4\ \frac{\delta d}{d} + \frac{\delta g}{g} + \frac{\delta\ (\Delta P)}{\Delta P} + \frac{\delta Q}{Q} + \frac{\delta\ell}{\ell}$$

The Capillary Diameter Error [$\delta d/d$].

The diameter of the capillary tube was evaluated from the equation

$$d^2 = \frac{4W_m}{\pi[L + \frac{1}{2}\ (h_1 + h_2)]\rho m},$$

where W_m is the weight of the mercury thread (see Capillary

Calibration Appendix X3), L is the length of the thread, ρm is the density of mercury at the calibration temperature, whilst h_1 and h_2 are the heights of the spherical caps at either end of the thread.

$$\text{Let} \quad L_e = L + \frac{1}{2} (h_1 + h_2)$$

Then, we have $$d^2 = \frac{4W_m}{\pi \, L_e \, \rho m}$$

Taking the natural logarithum of both sides and differentiating, we get

$$2 \frac{\delta d}{d} = \frac{\delta W_m}{W_m} + \frac{\delta L_e}{L_e} + \frac{\delta \rho_m}{\rho_m}$$

The weight 'W_m' was measured on a "Mettler" scale which is capable of measuring weights up to 160 gms with an accuracy of ± 0.001 gms. The capillary tubes that were used in this work were approximately 60 cm. long at the time of calibration and having a nominal diameter of 0.5 mm. The weight of the mercury thread for those capillary tubes was of the order of 1.5 gms.

Therefore

$$\frac{\delta W_m}{W_m} = \pm 0.067 \, \%$$

The length of the mercury thread was measured on a "Griffin and George" Cathetometer of a "Beck" microscope having a range of 50 mm. The eyepiece of the microscope was provided with double hairline cross-heads. The smallest division that could be read on the cathetometer was 0.001 cm. Therefore, the accuracy of of a measuring a 60 cm. length is ± 0.004%.

The density of mercury 'ρm' at the capillary calibration temperature was read from table (F4) of the "Handbook of Chemistry and Physics" (50). Those values are accurate to better than 1 in 1000. No temperature variation of the glycerine bath, in which the capillary tubes were immersed prior to the long thread calibrations, could be detected.

Thus $$2\frac{\delta d}{d} = \pm 0.049\%$$

or $$\frac{\delta d}{d} = \pm 0.025\%$$

Acceleration due to Gravity $(\frac{\delta g}{g})$

The value of the acceleration due to gravity 'g' was estimated by the Department of Mines, Energy and Resources (48). The accuracy of the estimation was quoted as ± 0.0005%.

Pressure Drop $(\frac{\delta\ (\Delta P)}{\Delta P})$.

Now $\Delta P = \rho_w h$

$$\frac{\delta\ (\Delta P)}{\Delta P} = \frac{\delta\rho_w}{\rho_w} + \frac{\delta h}{h}\ .$$

were 'ρ_w' is the density of the water inside the manometer, and h is the height of the water column. The value of h was measured on a "Griffin & George" Cathetometer. The smallest division on the cathetometer scale that could be read was 0.001 cm. However, the water miniscus could only be located to ±0.01 cm. The smallest pressure drop that was employed was of the order of 2 cm. The measurement of the height 'h' would involve two such observations, and thus the accuracy of the measurement is ± 1.0% or better.

The water density 'ρw' was read from the "Handbook of Chemistry and Physics" (50). The accuracy of those tables is better than 1 in 100,000. The temperature variation of the water was less than 0.1°C in all cases. Such temperature variation would limit the accuracy of the density values to 1 in 10,000 in the worst case.

Thus $\frac{\delta\ (\Delta P)}{\Delta P} = \pm\ 1.01\%$

<u>Flow Rate</u> $(\frac{\delta Q}{Q})$.

The mass flow rate through the capillary tubes was calculated from the equation

$$Q = \frac{V}{t}\rho$$

where V is the value flow in time t measured on the flowmeter burette, and ρ is the density of the test gas.

As before $\frac{\delta Q}{Q} = \frac{\delta V}{V} + \frac{\delta t}{t} + \frac{\delta \rho}{\rho}$.

The accuracy of the flowmeter calibration

$$\frac{\delta V}{V} = \pm\ 0.25\%.$$

The "Excelsior Park" stop-watch was calibrated against the "University Clock" over a period of 8 hours. The stop-watch was found to be 0.037% slower than the clock.

The density values for Nitrogen gas was found by interpolation from reference (42). The accuracy of those values are quoted to be accurate to $\pm 0.1\%$. The Freon density values were based on those given reference (26) for Freon 12 and reference (30) for Freon 22.

The average deviation of the quoted values for Freon 22 from the experimental results is $\pm$ 0.07%. Taking the accuracy of the density values as $\pm 0.1\%$, we get

$$\frac{\delta Q}{Q} = \pm\ 0.387\%$$

Length $(\frac{\delta \ell}{\ell})$

The maximum error in measuring the capillary tube lengths would be incurred in measuring the shorter tube which was 25 cm. long. Since, this length was measured on cathetometer having a smallest division of 0.001 cm. on its scale, the accuracy of the measurement

$$\frac{\delta \ell}{\ell} = 0.08\%$$

Individual Errors	Magnitude %
$4\ \frac{\delta d}{d}$	$\pm$ 0.1
$\frac{\delta g}{g}$	$\pm$ 0.0005
$\frac{\delta(\Delta P)}{\Delta P}$	$\pm$ 1.01
$\frac{\delta Q}{Q}$	$\pm$ 0.387

$\frac{\delta \ell}{\ell}$ $\pm$ 0.08%

Therefore $\frac{\delta \eta}{\eta} = \pm 1.4975\%$

Temperature

One of the factors that can affect the accuracy of the results and which has not been accounted for in the assessment of errors above is the temperature gradient along the viscometer.

Assuming that the viscosity of the gases tested follows the equation

$$\eta = A \sqrt{T} + B$$

then $$\frac{\delta \eta}{\eta} = \frac{1}{2} \frac{\delta T}{T}$$

For a maximum temperature gradient of 2°C at the lowest test temperature of 230°K

$$\frac{\delta \eta}{\eta} = \pm 0.435\%$$

If this source of error is added to the above, the maximum percentage error to within which the viscosity is measured for one tube = $\pm$ 1.933%.

The above analysis is only for one capillary tube. The series capillary viscometer utilizes two such tubes. If we assume that the errors resulting from the diameter calibration, the pressure drop measurement and the length measurement for the second capillary are additive with the maximum percentage error that was calculated for one capillary tube.

Then $\frac{\delta\eta}{\eta} = \pm [1.933 + 0.1 + 1.01 + 0.08]$

$$\frac{\delta\eta}{\eta} = \pm 3.123\%$$

Thus we conclude that the maximum percentage error due to all factors for viscosity measurements in this work is

$$\pm 3.123\%$$

APPENDIX X6

ILLUSTRATIONS

FIGURE X6.1. TEST FACILITY

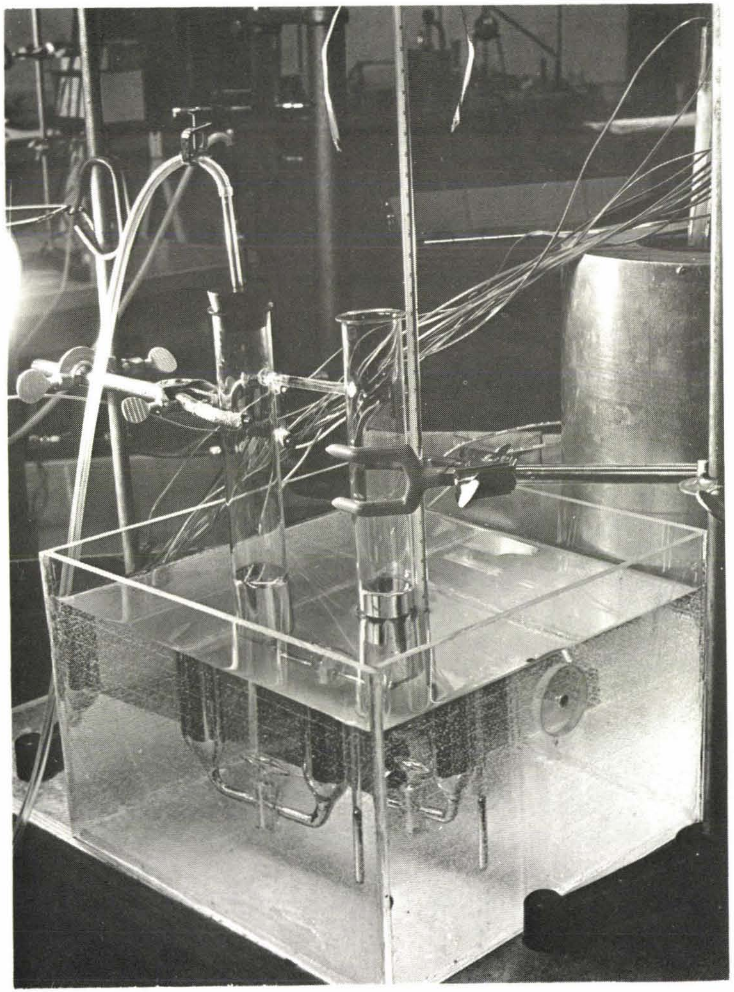


FIGURE X6.3. A LEAK DETECTION METHOD

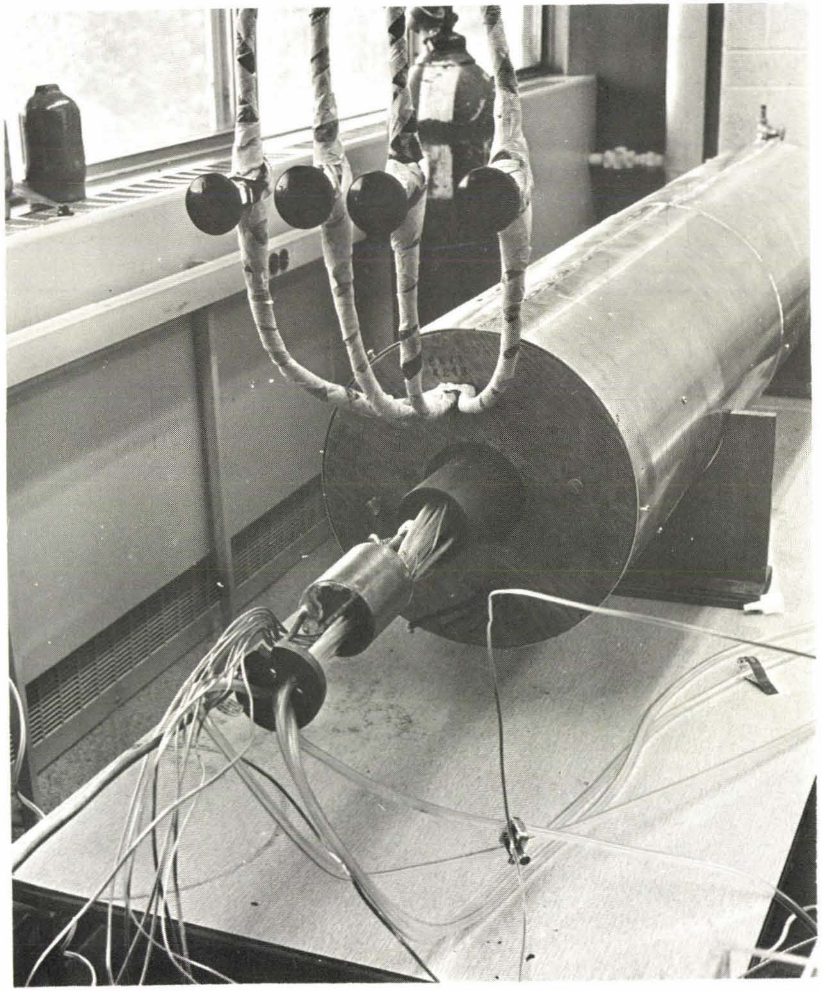


FIGURE X6.2. VIEW OF VISCOMETER AND TEMPERATURE CONTROL JACKET

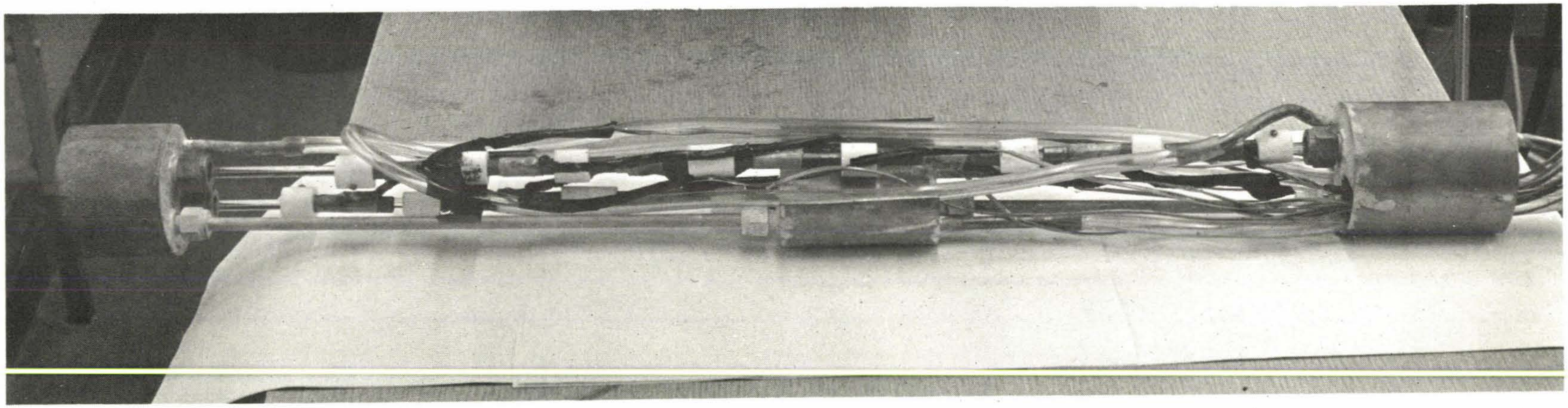


FIGURE X6.4 THE ASSEMBLED SERIES-CAPILLARY VISCOMETER

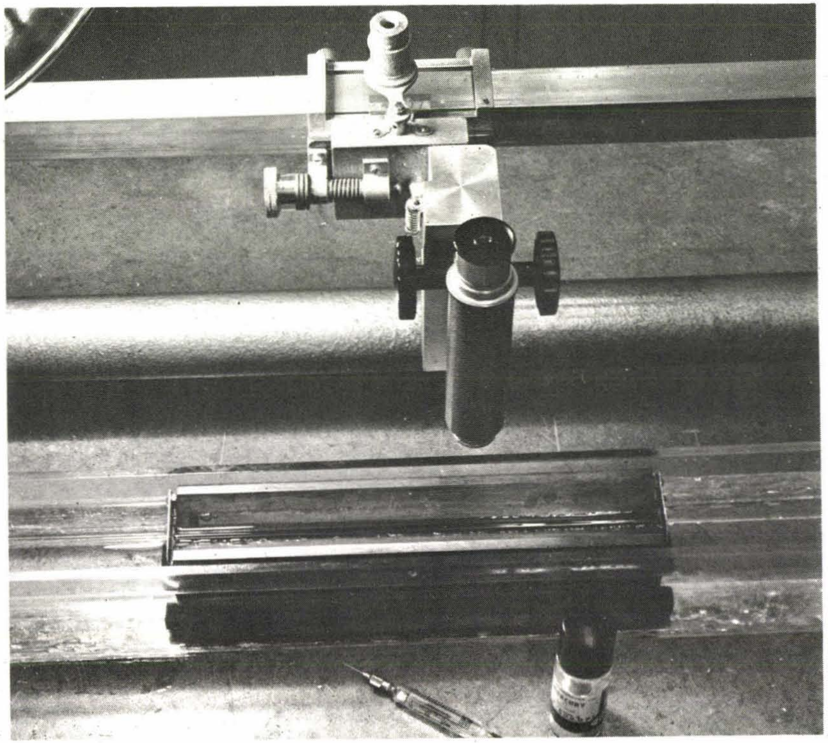


FIGURE X6.5. APPARATUS FOR CAPILLARY TUBE CALIBRATION

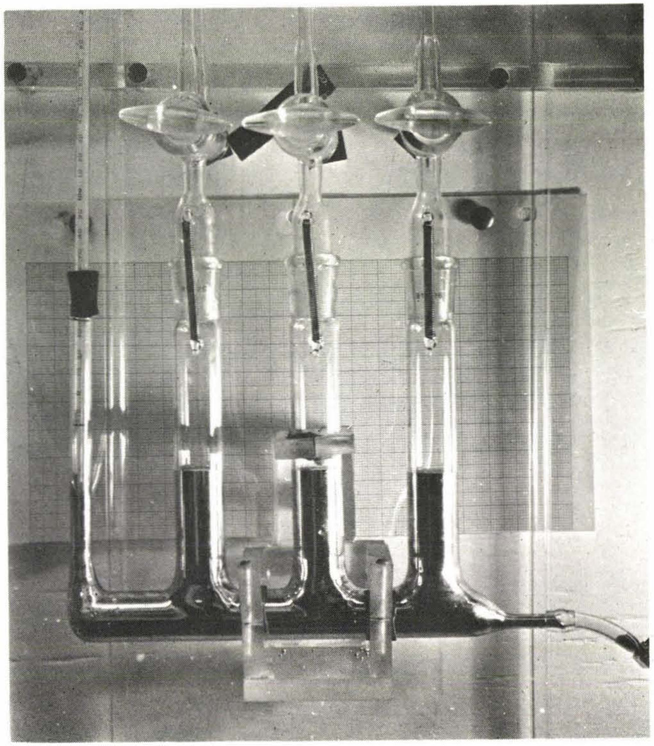


FIGURE X6.6. THE THREE LIMB DIFFERENTIAL MANOMETER

X7 ANALYSIS OF PREVIOUS MEASUREMENTS

X.7 ANALYSIS OF PREVIOUS MEASUREMENTS

X.7.1 Introduction

The viscosity measurements of the halogenated hydrocarbons that appear in the literature are few in number for an individual compound and are spread over a wide range of temperature. As explained in the literature survey, Chap. II , the measurements up to the present date have been secondary. Except for the work done by Awberry and Griffiths (2) who used a falling plug viscometer, and some recent attempts by Lilios (12), Eisele (17), Riley (16), and Gordon (18) who used a capillary type viscometer, all workers in this field made their measurement with a rolling ball type viscometer. The fact that all previous investigators, employing different kinds of viscometers, calibrated their apparatus with a secondary fluid, i.e. calibrating fluid, has limited the accuracy of their measurements at the outset. This, of course, is due to inherent inaccuracies in the property values of the secondary fluid. Moreover, the investigations have been limited to those temperature and pressure ranges where a calibrating fluid has already been investigated. Thus no attempts have previously been made below - 110 degrees C at atmospheric pressure simply because no suitable fluid properties are known to any degree of accuracy to justify secondary measurements. The viscosity values of fluids at high pressures are also scarce. Those working at high pressures and normal temperatures had to estimate the viscosity values of their secondary fluids.

Most major manufacturers and distributors of refrigerants in North America, apparently base their recommended viscosity values for their products on the data presented in a paper by Witzell (19) who in 1965 published correlations of the viscosity measurements of liquids and vapours of refrigerants. Those correlations were based on the work that had been carried out at Purdue University and Du Pont Co. Inc. A considerable amount of data for the liquid phase of Freons 11, 12, and 22 by Riley (16) and Eisele has come to light since the publication of those correlations. Also in the case of liquid refrigerants Witzell (19) seems to correlate viscosity data obtained at atmospheric pressure with those obtained at saturation pressures for the same liquids. For the vapour phase at atmospheric pressure, Witzell (19) did not include the data obtained by Makita and Graham (4). In the case of Freon (114-B2) whose density values were not well known at the time of the correlations, new, more accurate values have made it possible to recalculate the viscosity values which were given in Du Pont's Publication Number (X-50A); reference (20).

X.7.2 Theory of The Falling Plug Viscometer

The falling plug viscometer used by Awberry and Griffiths (2) is based on the concept that the drag force on a plug falling under the effect of its own weight in a closely fitting tube filled with a liquid is proportional to the viscosity of that liquid. Thus the terminal velocity with which the plug descends after its initial acceleration from the rest position is a certain function of the viscosity of the liquid. Since the flow around the plug would be very difficult to analyse theoretically, the falling plug viscometer has always been used as a secondary apparatus.

X.7.3 Theory of The Rolling Ball Viscometer

The rolling ball viscometer is essentially a smooth spherical ball of a well known diameter rolling down a closely fitting tube, filled with the fluid being investigated which is, inclined at a certain angle to the horizontal. If the tube is kept at a constant temperature along its entire length then the viscosity of the fluid inside it will be constant. When the ball starts rolling down the tube from an initial position of rest at the higher end of the tube, it will accelerate to a velocity where the weight component minus the buoyant force is just balanced by the drag force on the ball. One of the serious limitations that can be pointed out at this stage is that the density of the ball has to be higher than that of the liquid being investigated. This limitation forced Lilios (12) to resort to a capillary viscometer when he was investigating liquid refrigerants at low temperatures.

It was assumed by earlier workers that the drag on the sphere would be that given by Stoke's Equation of the drag on a sphere placed in an infinte flow; namely

Drag Force = $3\pi\eta V_bD_b$, where η is the viscosity, V_b and D_b are the terminal velocity and the diameter of the ball respectively. From this relation they put

Weight Force - Buoyant Force = Drag Force at terminal velocity, or $(4/3\pi D_b^3/8\ (\rho_b - \rho_f))g\ \sin\alpha = 3\pi\eta V_bD_b$, where ρ_s and ρ_f are the densities of the ball and the fluid respectively, α is the angle of inclination of the tube to the horizontal and g is the acceleration due to gravity.

Thus $\eta = CD_b^3\ (\rho_b - \rho_f)\ g\ \sin\alpha/V_bD_b$, where C is a constant. And since $V_b = \ell/t$, where ℓ is the distance between two fixed points on the tube and t is the time of ball traverse between those points, then

$\eta = C_1D_b^3(\rho_b - \rho_f)\ g\ \sin\alpha\ .\ t/\ell D_b$, where C_1 is a constant.

Now, for a certain ball of known diameter and for the same length of tube "ℓ" and inclination angle, one can write

$\eta = k\ (\rho_b - \rho_f)\ t$, where k is a constant. For the different calibrations, k was evaluated for a particular instrument and a particular fluid. Hovorka and Geiger (1), Benning and Markwood (3), and Coughlin (4) all assumed that "k" was constant for different conditions of pressure and temperature. Thus giving

$\eta c/\eta f = (\rho_b - \rho_c)\ t_c\ /\ (\rho_b - \rho_f)\ t_f$, where subscripts "c" and "f" refer to the calibrating fluid and the fluid under test respectively.

The drawbacks of using the rolling ball viscometer are quite obvious. Firstly, the theory behind the rolling ball viscometer is only very partially developed, since the complexity of the flow between the tube and the ball is expected to be far removed from the conditions of Stoke's flow around a sphere, which refers to an infinite fluid condition. It has been reported by many users that the problem of the ball sticking to the tube is a very real one. Secondly, the contradiction of the results of different workers as to the variation of "k" with pressure and temperature illustrate the point that the reproducibility of the flow for a set of conditions is very difficult if not impossible.

Hubbard and Brown (8), in 1943, carried out a dimensional analysis of the variables involved in the calibration of the rolling ball viscometer. By correlating the variables involved, using extensive experimental data on the rolling ball viscometer that they conducted, they arrived at an equation relating the viscosity to the resistance factor on the rolling ball. The variation of the calibration coefficient of the viscometer with temperature and the ratio of the diameter of the ball to that of the tube was also investigated. A critical Reynold Number beyond which the flow around the ball is expected to be turbulent, was also defined.

Lewis (21), in 1953, attempted to make an approximate theoretical analysis of the flow in the rolling ball viscometer. He obtained an expression for the calibration constant in terms of the diameters of the ball and the tube. However, Lewis concluded that his relation would only be useful in finding the order of magnitude of those sizes in designing a viscometer, and, for more accurate work the calibration should be evaluated experimentally.

X.7.4 Correlations

Since the existing data is the only source of information on the viscosity of those refrigerants, an attempt has been made here to make improved correlations of the available data. However the correlations should be used with caution, since their reliability is only within the limits of error of the available experimental data used . Until more accurate absolute measurements are available the correlations presented here should be useful for estimating viscosities of refrigerants. Two types of correlations have been attempted here for the variation of the dynamic viscosity with temperature for vapour and liquid refrigerants at atmospheric pressure.

1. For the viscosity of vapours it has been well established that the variation of the viscosity with temperature follows approximately the relation

$$\eta = A1 \sqrt{T} + A0 \qquad (1)$$

where η is the dynamic viscosity, T is the absolute temperature and

A1 and A0 are constants. The reader is refered to the discussion by Johnson (22) on the source of equation (1). Equations of the form of equation (1) were fitted to all the available data for the vapours of the refrigerants being considered. The constants A1 and A0 and the standard error of estimate of those fits are listed in Table X7.1, Figures (X7.1) to (X7.11) illustrate the deviation of individual points from those fits.

For the liquid phase of refrigerants under atmospheric pressure, it has been reported by many investigators including Reid and Sherwood (23) that an equation of the form

$\ell n\eta = A1/T + A0$ (2), using the same notation as before,

appears to fit the pertinent data quite well.

Since it is also well established that at a fixed temperature an increase in pressure results in an increase in the viscosity of liquids, it is suspected that the wide spread of data about the equations fitted by Witzell (19) was because he included viscosity data which were obtained by Benning and Markwood (3) at saturation pressures. A close inspection of Witzell's fits reveal that the deviation of the experimental points from the fitted equations increase in magnitude as the saturation pressure increases above the atmospheric value.

In this present work, only data obtained at atmospheric pressure were correlated using a form of equation (2). The constants A0 and A1 and the standard error of estimate of those fits are given in Table X7.3.

2. The data can be more accurately represented by a polynomial of the form

$$Y = \sum_{i=0}^{i=n} a_i x_i \qquad (3)$$

where n is the degree of the polynomial. The criteria for choosing the degree of a polynomial to fit a certain number of data is again an intuitive choice. Generally speaking, however, there is no practical benefit in fitting a high degree polynomial which would approximate all the points with a high degree of accuracy. Firstly, because the points used are only accurate to within the experimental error, and secondly, such a polynomial might become more tedious to use than the original data. Polynomials of degree 2 to 6 were fitted to the vapour and liquid viscosity data of every refrigerant as a function of the absolute temperature and at atmospheric pressure. For a certain refrigerant and a certain phase the mean deviation of all points from the fitted polynomial was taken as a measure of how well the data fits that particular polynomial. The constants of the polynomials that gave the least mean deviation for $n \leq 5$ are listed in Tables X7.2 and X7.3 for the vapour and liquid phases respectively.

Appendix X1 contains lists of the data used in the above correlations.

Freon	Temp. Range in Deg. K	AO x 10^2	Al x 10^3	Standard Error of Est. x 10^4	Greatest Error x 10^4 Centipoise	Maximum % Error	No. of Data Points
11	313.15 →423.15	-1.452717	1.45486	1.756	2.968	2.118	8
12	253.15 →473.15	-0.807067	1.19593	3.532	8.104	4.993	29
13	235.15 →423.15	-1.228651	1.55230	3.225	6.675	4.741	20
13B1	235.15 →423.15	-1.299107	1.66259	0.813	1.447	0.982	6
14	235.15 →423.15	-1.108797	1.64555	3.057	5.595	2.760	15
21	303.15 →463.15	-1.152636	1.32911	2.864	9.542	6.034	23
22	239.15 →473.15	-1.064260	1.36745	2.293	5.166	2.954	25
23	236.15 →473.15	-1.612327	1.78838	3.271	9.291	8.179	24
114	303.14 →473.15	-1.190147	1.34605	1.477	4.139	3.090	20
115	234.15 →473.15	-1.000814	1.32327	3.289	13.515	13.197	24
C-318	276.15 →423.15	-0.902151	1.20669	2.624	5.443	3.835	16

TABLE X7.1 CORRELATION CONSTANTS FOR THE VISCOSITY OF FREON VAPOURS AT ONE ATMOSPHERE

η IN CP = A1 $\sqrt{T^{o}K}$ + A0

TABLE X7.2

POLYNOMIALS FITTED TO PREVIOUS MEASUREMENTS OF THE VAPOURS OF SOME REFRIGERANTS AT ATMOSPHERIC PRESSURE

(VISCOSITY IN CENTIPOISE AS A FUNCTION OF
TEMPERATURE IN DEGREES KELVIN)

FREON 11

Temperature Range = 313.15 → 423.15°K.

Number of Experimental Values = 8

$$\eta \text{ CP} = -5.65401 \times 10^{-4} + 3.77983 \times 10^{-5} \times T + 4.08739 \times 10^{-11} \times T^2$$

Mean Deviation = 1.4608×10^{-4} Centipoise

Maximum Percentage Deviation = + 2.171%

FREON 12

Temperature Range = 253.15 → 473.15°K

Number of Experimental Values = 29

$$\eta \text{ CP} = -1.69793 \times 10^{-1} + 2.63335 \times 10^{-3} \times T - 1.56099 \times 10^{-5} \times T^2 + 4.63941 \times 10^{-8} \times T^3 - 6.79399 \times 10^{-11} \times T^4 + 3.90667 \times 10^{-14} \times T^5$$

Mean Deviation = 2.04751×10^{-4} Centipoise

Maximum Percentage Deviation = -5.483%

FREON 13

Temperature Range = 235.15 → 423.15°K

Number of Experimental Values = 20

$$\eta \text{ CP} = 4.09101 \times 10^{-4} + 5.04764 \times 10^{-5} \times T - 1.09960 \times 10^{-8} \times T^2$$

Mean Deviation = 2.48553×10^{-4} Centipoise

Maximum Percentage Deviation = -4.803%

FREON 14

Temperature Range = 235.15 → 423.15°K

Number of Experimental Values = 15

$$\eta \text{ CP} = -2.91699 \times 10^{-2} + 3.57349 \times 10^{-4} \times T - 9.68434 \times 10^{-7} \times T^2 + 9.85442 \times 10^{-10} \times T^3$$

Mean Deviation = 1.98632×10^{-4} Centipoise

Maximum Percentage Deviation = +2.045%

FREON 21

Temperature Range = 303.15 → 463.15°K

Number of Experimental Values = 23

$$\eta \text{ CP} = 1.62336 \times 10^{-1} - 1.75185 \times 10^{-3} \times T + 7.33253 \times 10^{-6} \times T^2 - 1.32055 \times 10^{-8} \times T^3 + 8.80554 \times 10^{-12} \times T^4$$

Mean Deviation = 1.99007×10^{-4} Centipoise

Maximum Percentage Deviation = -5.916%

TABLE X7.2 / CONTINUED

FREON 22

Temperature Range = 239.15 → 473.15°K

Number of Experimental Values = 25

$$\eta\ CP = 5.68499 \times 10^{-3} - 1.54801 \times 10^{-5} \times T + 2.07128 \times 10^{-7} \times T^{2} - 2.46867 \times 10^{-10} \times T^{3}$$

Mean Deviation = 1.32144×10^{-4} Centipoise

Maximum Percentage Deviation = - 3.227%

FREON 23

Temperature Range = 236.15 → 473.15°K

Number of Experimental Values = 24

$$\eta\ CP = -1.10324 \times 10^{-1} + 1.29328 \times 10^{-3} \times T - 5.18186 \times 10^{-6} \times T^{2} + 9.48000 \times 10^{-9} \times T^{3} - 6.44574 \times 10^{-12} \times T^{4}$$

Mean Deviation = 2.10616×10^{-4} Centipoise

Maximum Percentage Deviation = -4.580%

FREON 114

Temperature Range = 303.14 → 473.15°K

Number of Experimental Values = 20

$$\eta\ CP = 2.17058 \times 10^{-3} + 2.88717 \times 10^{-5} \times T + 7.72306 \times 10^{-9} \times T^{2}$$

Mean Deviation = 8.73692×10^{-5} Centipoise

Maximum Percentage Deviation = +1.596%

TABLE X7.2 / CONTINUED

FREON 115

Temperature Range = 234.15 → 473.15°K

Number of Experimental Values = 24

$$\eta\ CP = 1.32563 \times 10^{-1} - 1.46106 \times 10^{-3} \times T + 6.33405 \times 10^{-6} \times T^{2} - 1.17309 \times 10^{-8} \times T^{3} + 8.03323 \times 10^{-12} \times T^{4}$$

Mean Deviation = 1.26205×10^{-4}

Maximum Percentage Deviation = -3.158%

FREON 13B1

Temperature Range = 235.15 → 423.15°K

Number of Experimental Values = 6

$$\eta\ CP = -2.74922 \times 10^{-3} + 7.50882 \times 10^{-5} \times T - 4.38904 \times 10^{-8} \times T^{2}$$

Mean Deviation = 7.61361×10^{-5} Centipoise

Maximum Percentage Deviation = +0.948%

FREON C318

Temperature Range = 276.15 → 423.15°K

Number of Experimental Values = 16

$$\eta\ CP = -1.65543 \times 10^{-2} + 1.86784 \times 10^{-4} \times T - 4.18496 \times 10^{-7} \times T^{2} + 3.73191 \times 10^{-10} \times T^{3}$$

Mean Deviation = 1.98901×10^{-4} Centipoise

Maximum Percentage Deviation = -3.821%

TABLE X7.2 / CONTINUED

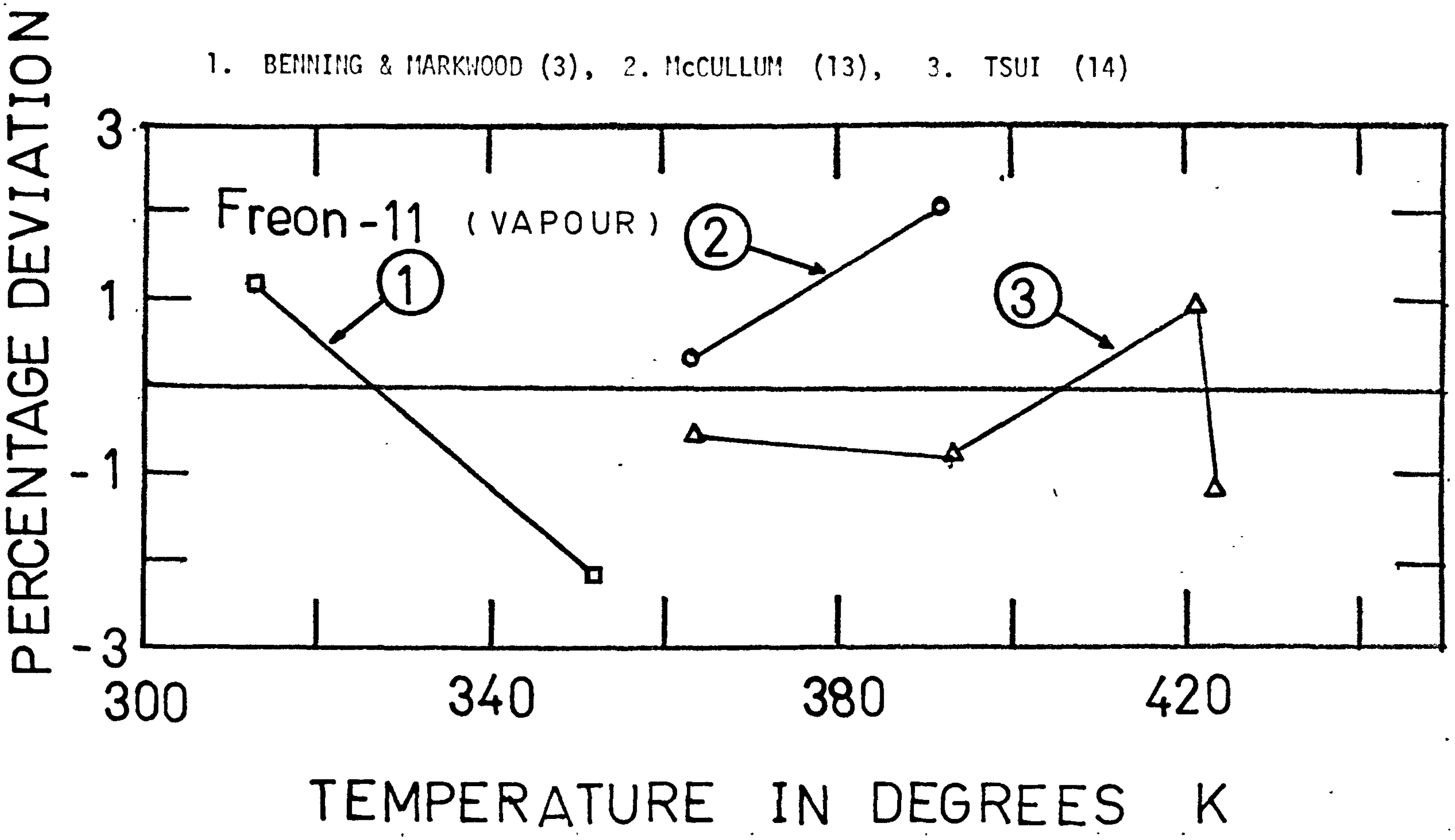


FIGURE X7.1 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 11 FROM THE FITTED EQUATION

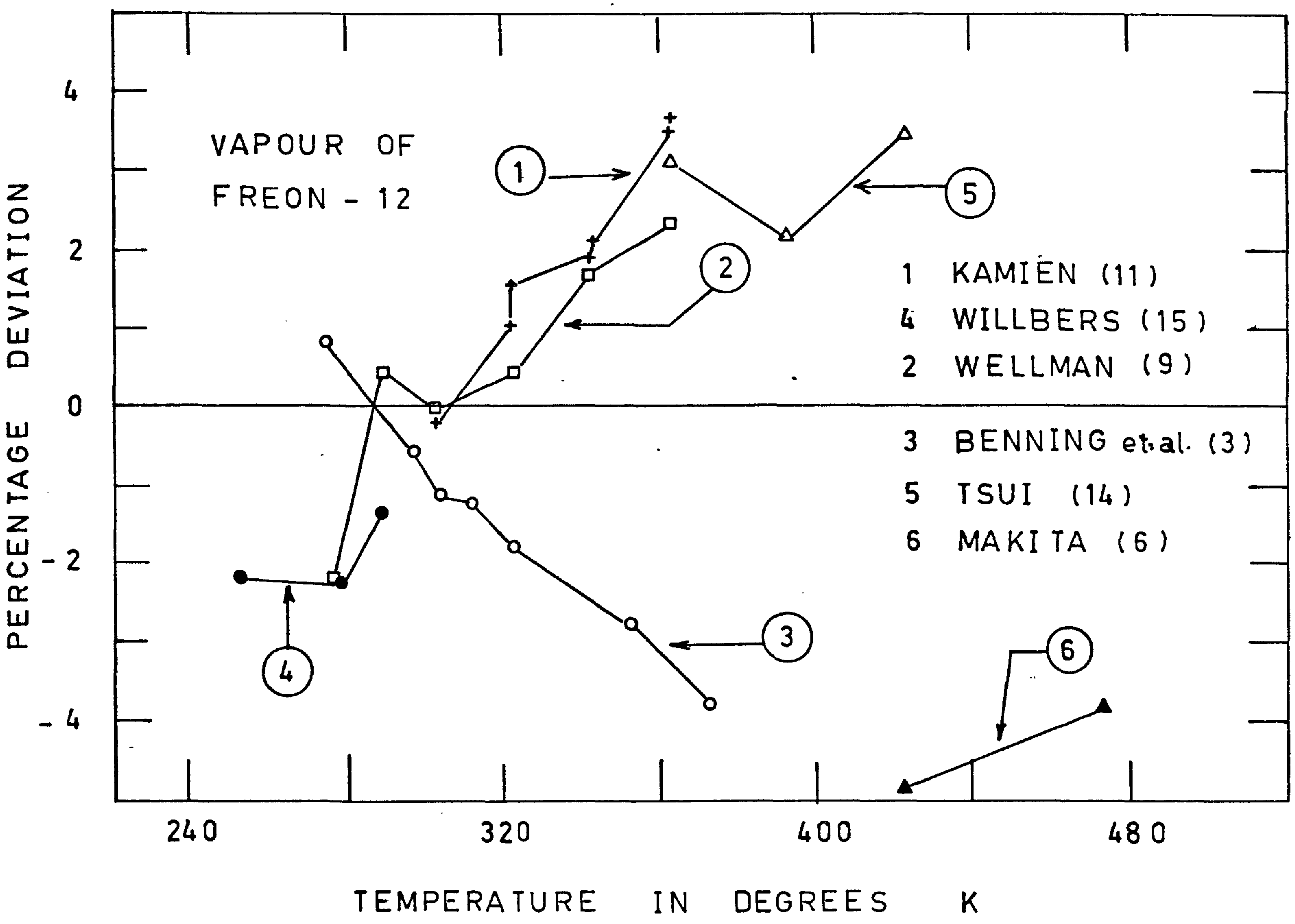


FIGURE X7.2 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 12 FROM THE FITTED EQUATION

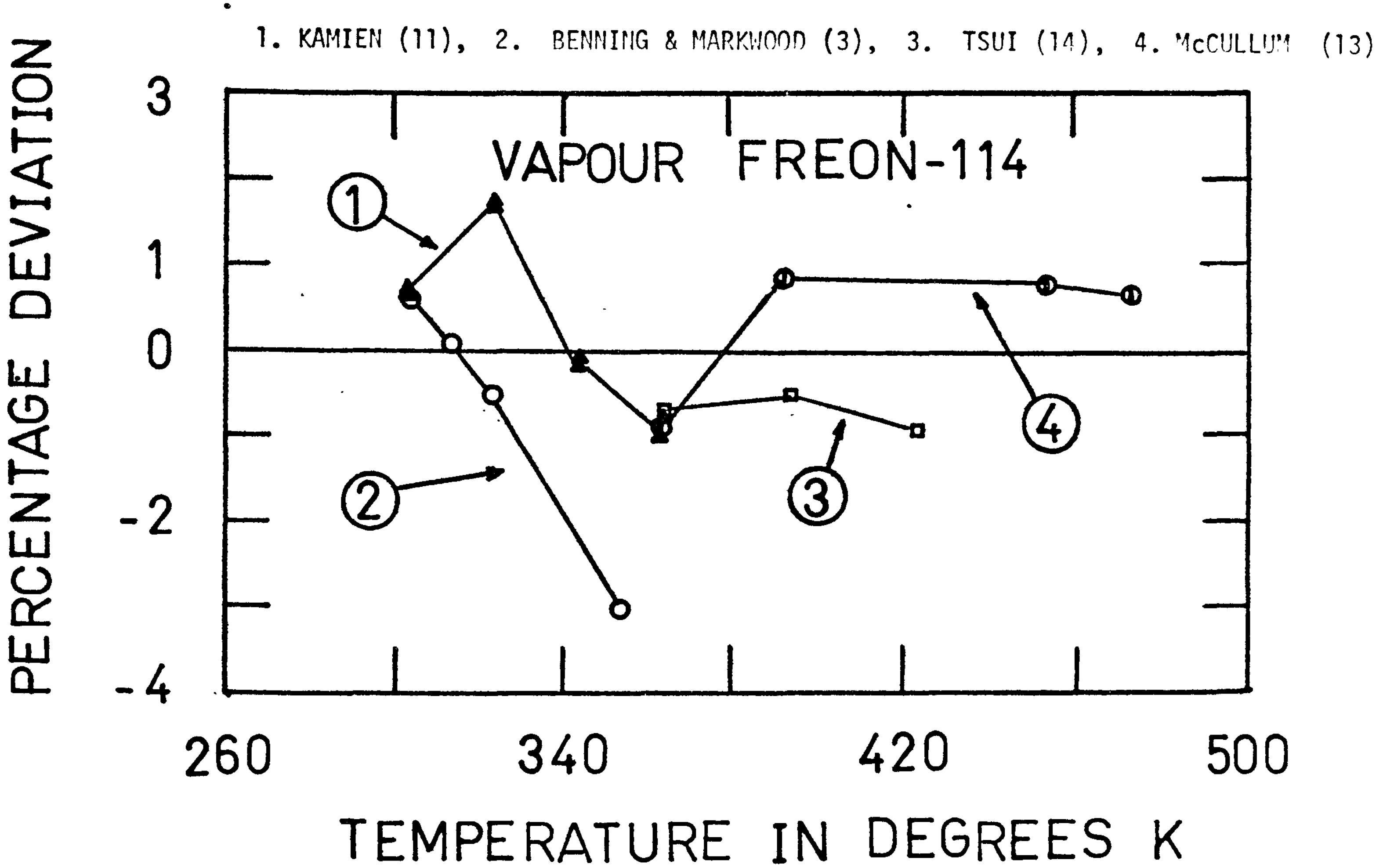


FIGURE X7.3 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 114
FITTED EQUATION

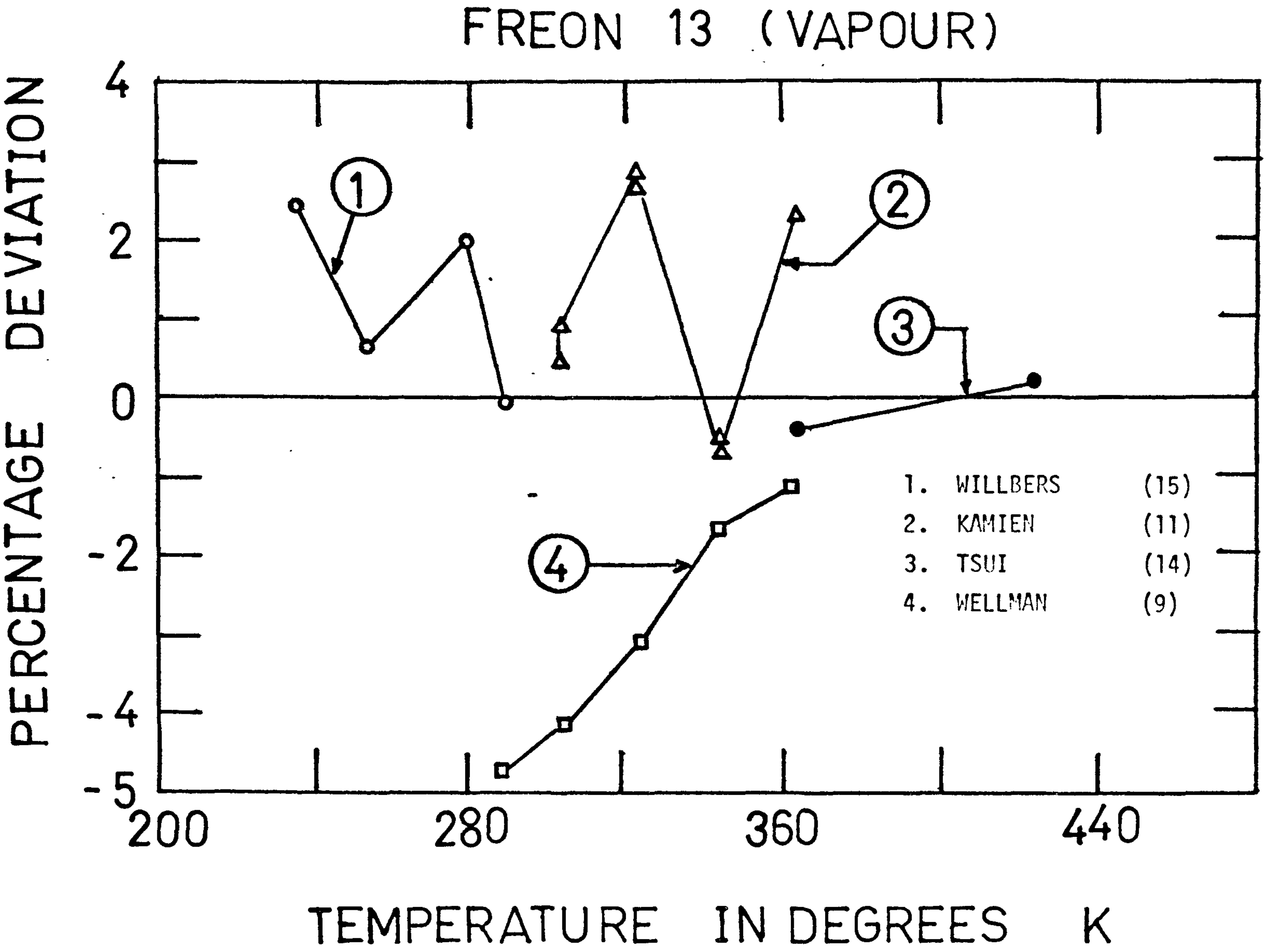


FIGURE X7.4 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 13 FROM THE FITTED EQUATION

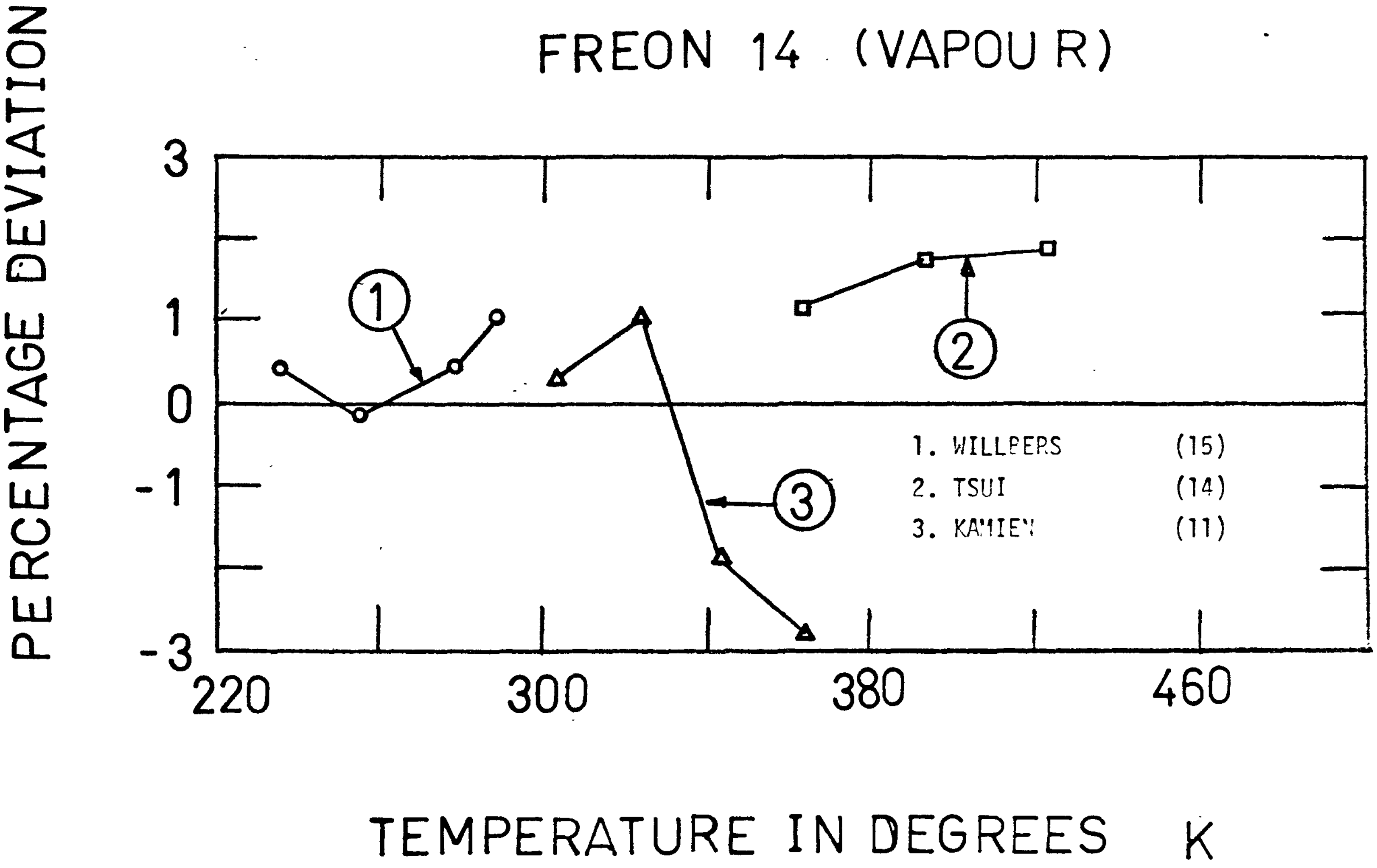


FIGURE X7.5 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 14 FROM THE FITTED EQUATION

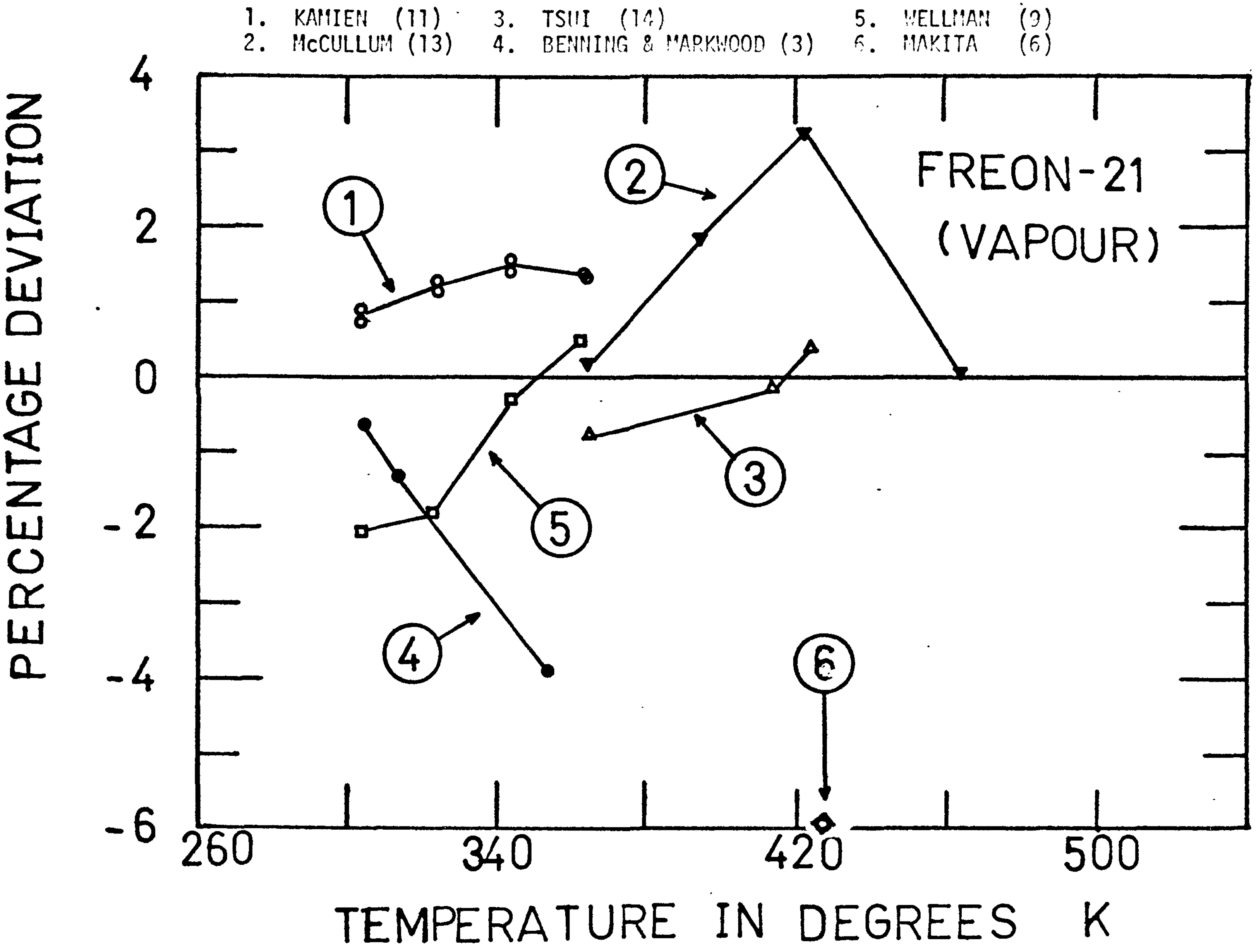


FIGURE X7.6 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 21 FROM THE FITTED EQUATION

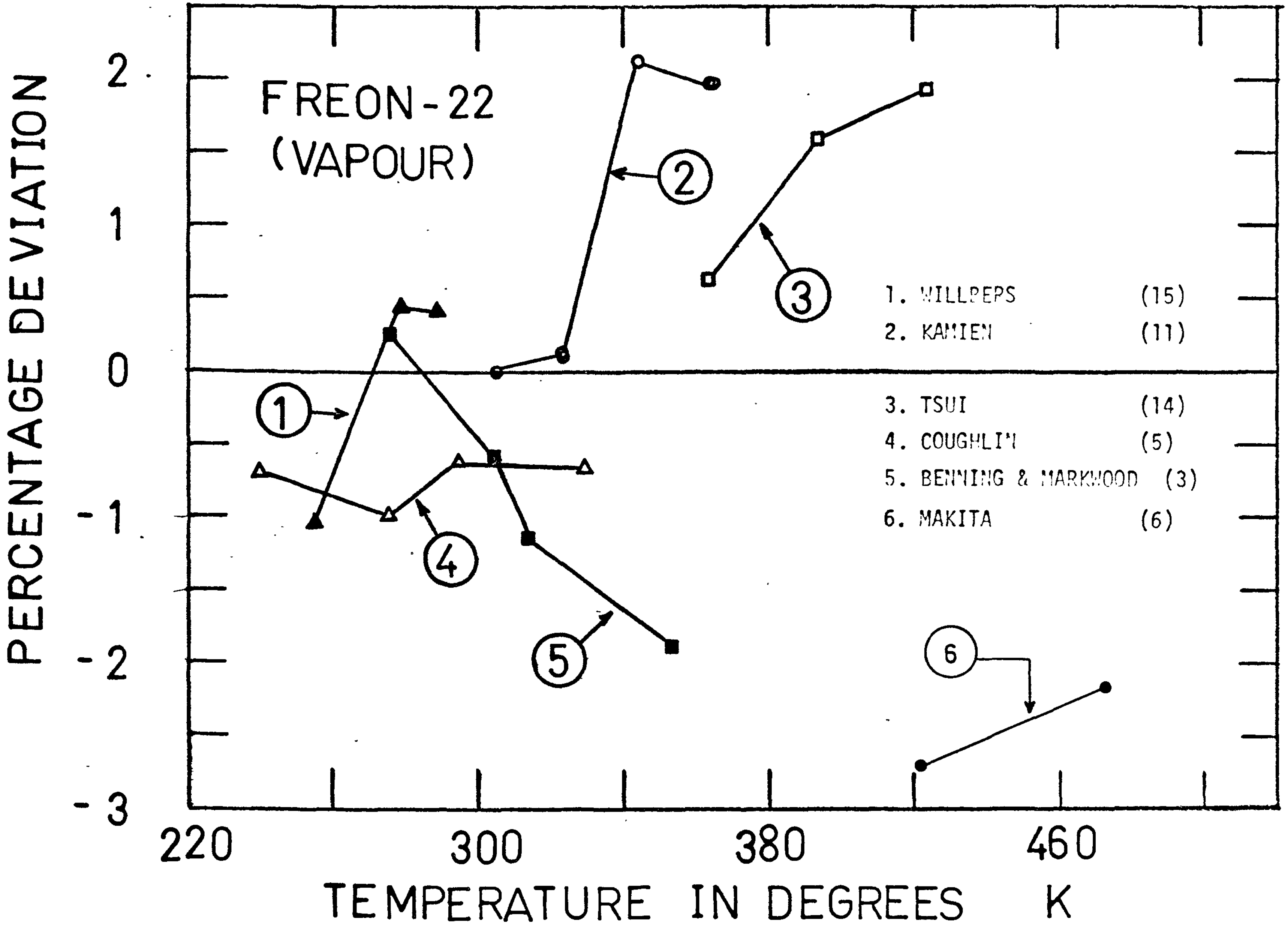


FIGURE X7.7 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 22 FROM THE FITTED EQUATION

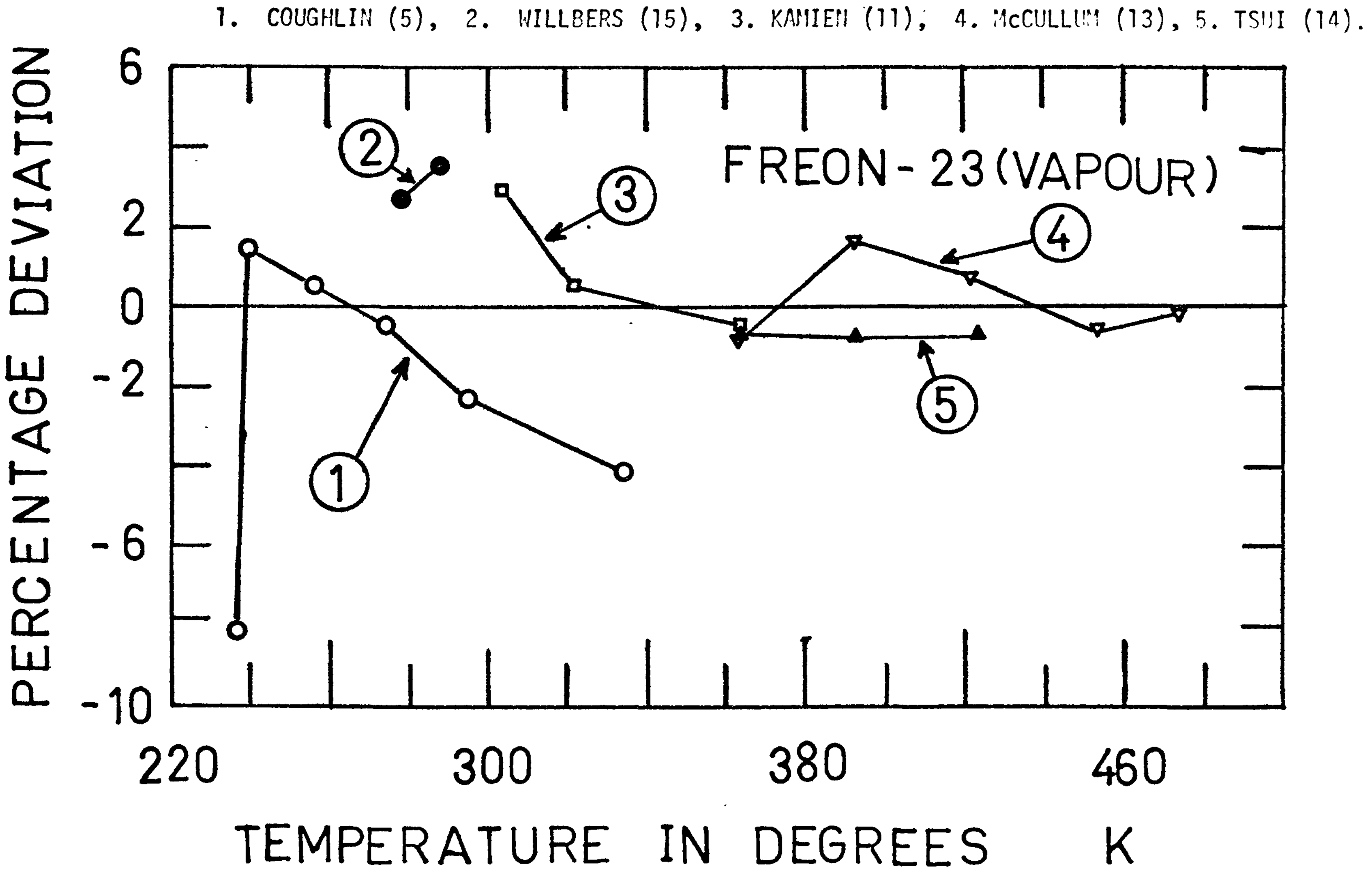


FIGURE X7.8 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 23 FROM THE FITTED EQUATION

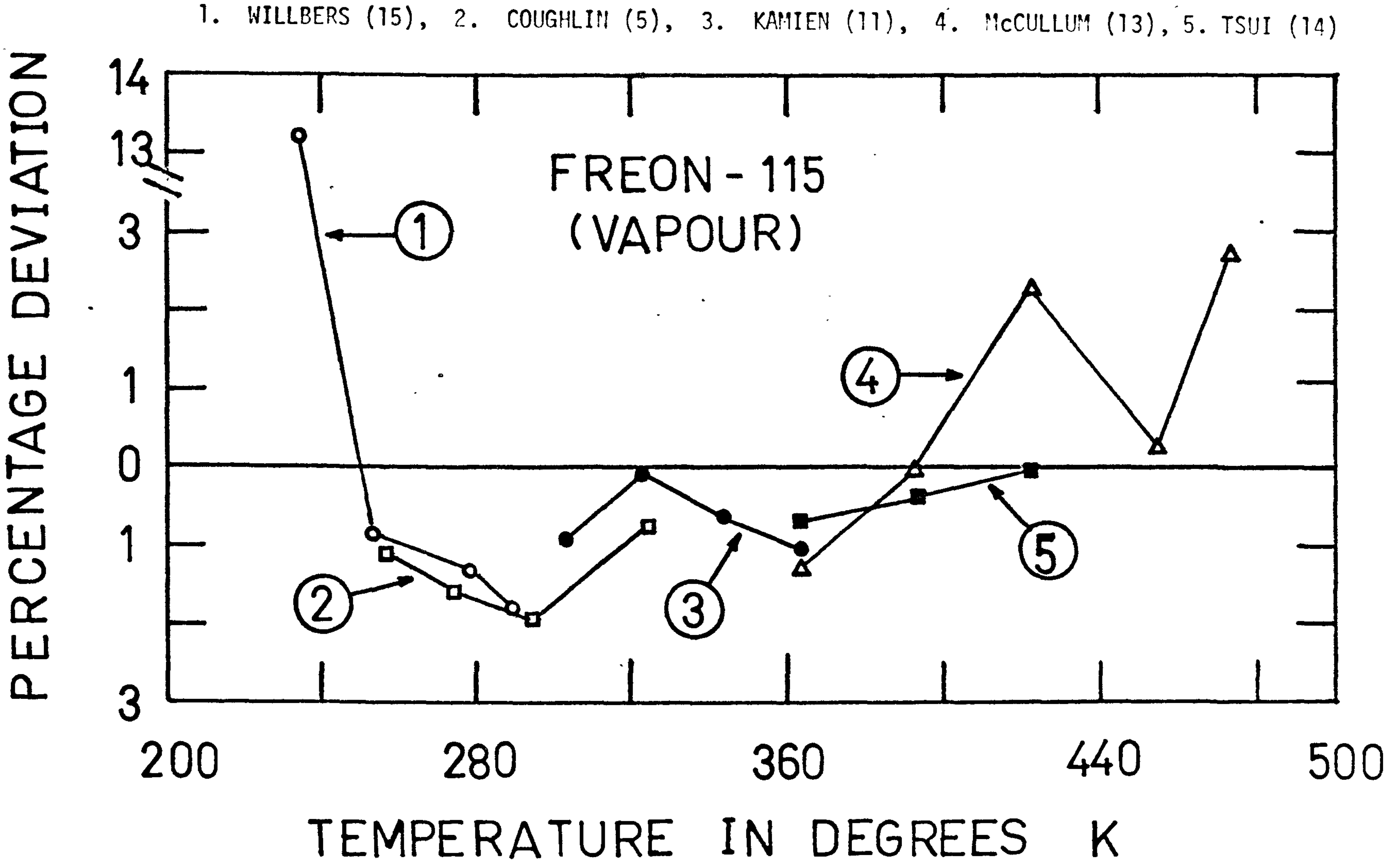


FIGURE X7.9 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 115 FROM THE FITTED EQUATION

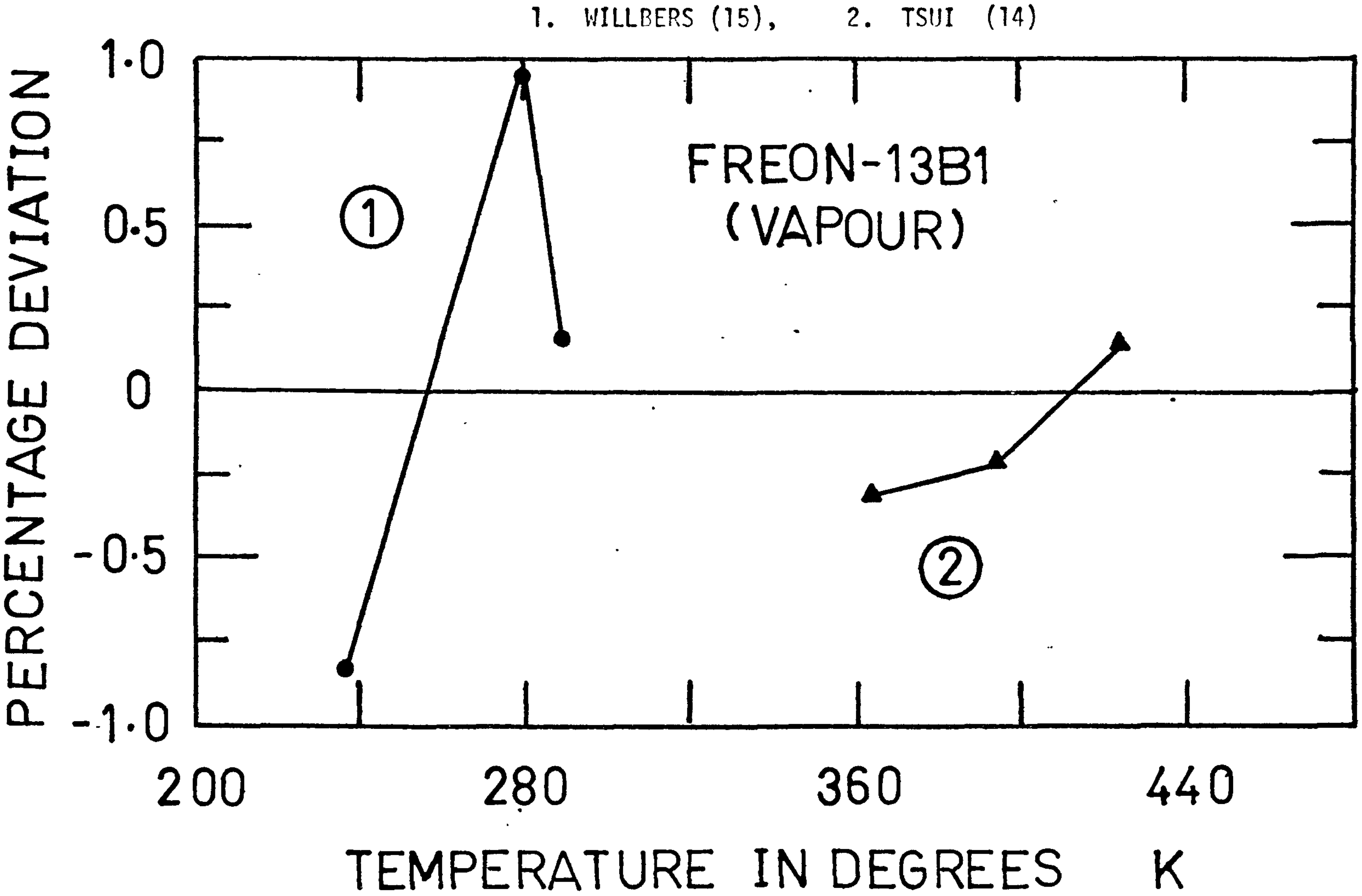


FIGURE X7.10 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON 13B1 FROM THE FITTED EQUATION

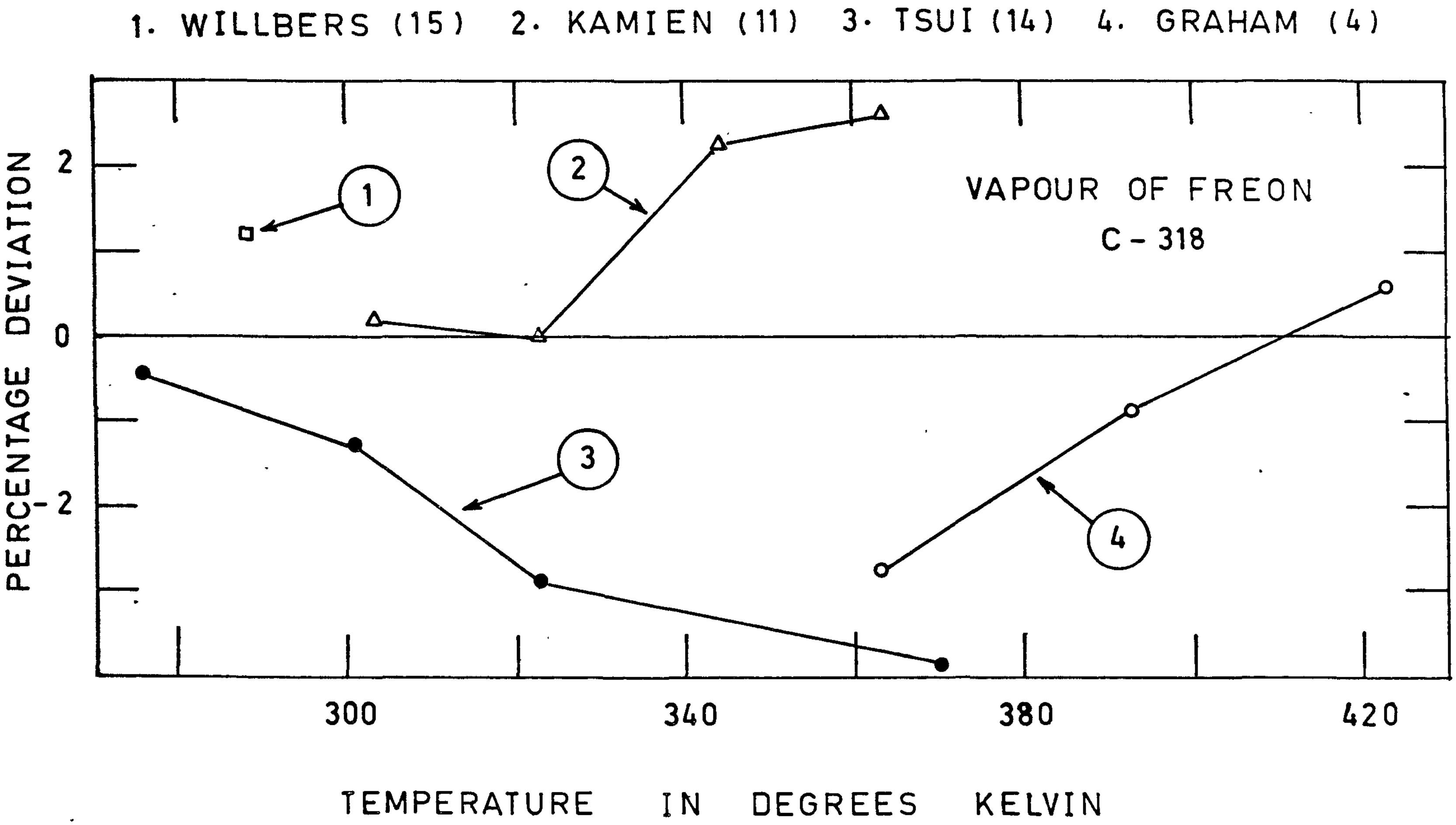


FIGURE X7.11 DEVIATION PLOT OF PREVIOUS MEASUREMENTS ON THE VAPOUR OF FREON C-318 FROM THE FITTED EQUATION

FREON	TEMP. RANGE IN DEG. K	AO	A1	STANDARD ERROR OF EST. x 10^2	GREATEST ERROR x 10^2 CENTIPOISE	MAXIMUM PERCENTAGE ERROR	NO. OF DATA POINTS
11	171.35 → 297.35	-3.41314	764.422	8.60853	26.18251	29.951	17
12	208.15 → 303.15	-3.78737	674.202	7.40081	1.53094	26.491	39
21	208.15 → 248.15	-4.29714	882.809	3.52093	4.24588	8.268	7
22	168.15 → 238.70	-3.61925	575.672	12.00646	7.79286	-26.069	11
113	243.15 → 293.75	-4.08520	1309.330	7.37445	15.47110	11.763	9
114	208.15 → 263.15	-4.54092	1035.553	1.70054	3.14112	-3.084	7
115	210.93 → 233.15	-3.70288	704.228	0.38084	0.31327	0.553	3
12B1	209.15 → 273.15	-4.08467	853.126	7.74740	16.10894	-17.489	14
12B2	213.15 → 273.15	-3.03350	697.721	0.18653	0.22023	0.291	4
114B2	213.15 → 293.15	-3.80338	1028.984	2.61989	6.43737	-6.675	9
C318	243.15 → 273.15	-4.92972	1168.763	0.27729	0.26780	-0.436	4

TABLE X7.3 CORRELATION CONSTANTS OF FREON LIQUIDS AT ONE ATMOSPHERE

$$\eta \text{ in CP} = e^{(A1/T + Ao)}$$

TABLE X7.3

POLYNOMIALS FITTED TO PREVIOUS MEASUREMENTS OF THE LIQUIDS OF SOME REFRIGERANTS AT ATMOSPHERIC PRESSURE

(VISCOSITY IN CENTIPOISE AS A FUNCTION
OF TEMPERATURE IN DEGREES KELVIN)

FREON - 11

Temperature Range = 171.35 → 297.35°K

Number of Experimental Values = 17

$$\eta\ CP = 5.41660 \times 10^{2} - 1.12576 \times 10^{1} \times T + 9.36996 \times 10^{-2} \times T^{2} - 3.88524 \times 10^{-4} \times T^{3} + 8.00968 \times 10^{-7} \times T^{4} - 6.56239 \times 10^{-10} \times T^{5}$$

Mean Deviation = 4.29854×10^{-2} Centipoise

Maximum Percentage Deviation = +15.768%

FREON -12

Temperature Range = 208.15 → 303.15°K

Number of Experimental Values = 39

$$\eta\ CP = 1.47483 \times 10^{2} - 2.25580 \times T + 1.29683 \times 10^{-2} \times T^{2} - 3.30988 \times 10^{-5} \times T^{3} + 3.16054 \times T^{4}$$

Mean Deviation = 2.24117×10^{-2} Centipoise

Maximum Percentage Deviation = -21.250%

FREON - 21

Temperature Range = 208.15 → 248.15°K

Number of Experimental Values = 7

η CP = 9.36165 x 10^{1} - 1.16384 x T

+ 4.88540 x 10^{-3} x T^{2} - 6.88286 x 10^{-6} x T^{3}

Mean Deviation = 1.8652 x 10^{-2} Centipoise

Maximum Percentage Deviation = +6.465%

FREON - 22

Temperature Range = 168.15 → 238.70°K

Number of Experimental Values = 11

η CP = -5.93141 x 10^{1} + 1.30662 x T

-1.04637 x 10^{-2}x T^{2} + 3.66753 x 10^{-5} x T^{3}

-4.77306 x 10^{-8} x T^{4}

Mean Deviation = 1.60733 x 10^{-2} Centipoise

Maximum Percentage Deviation = +8.954%

FREON - 113

Temperature Range = 243.15 → 293.15°K

Number of Experimental Values = 9

η CP = -1.59638 x 10^{2} + 1.86265 x T

-7.09470 x 10^{-3} x T^{2} + 8.89101 x 10^{-6} x T^{3}

Mean Deviation = 5.93925 x 10^{-2} Centipoise

Maximum Percentage Deviation = -10.786%

TABLE X7.3/CONTINUED

FREON - 114

Temperature Range = 208.15 → 263.15°K

Number of Experimental Values = 7

η CP = $6.63933 \times 10^{1} - 7.37758 \times 10^{-1} \times T$

$+ 2.78664 \times 10^{-3} \times T^{2} - 3.54869 \times 10^{-6} \times T^{3}$

Mean Deviation = 1.19946×10^{-2} Centipoise

Maximum Percentage Deviation = -2.048%

FREON - 115

Temperature Range = 210.93 → 233.15°K

Number of Experimental Values = 3

η CP = $5.47533 - 3.54891 \times 10^{-2} \times T$

$+6.07621 \times 10^{-5} \times T^{2}$

Mean Deviation = 2.98458×10^{-12}

Maximum Percentage Deviation = -7.575×10^{-10}%

FREON 114B2

Temperature Range = 213.15 → 293.15°K

Number of Experimental Values = 9

η CP = $4.01618 \times 10^{2} - 6.03483 \times T$

$+3.44391 \times 10^{-2} \times T^{2} - 8.79399 \times 10^{-5} \times T^{3}$

$+ 8.45054 \times 10^{-8} \times T^{4}$

Mean Deviation = 1.00000×10^{-2} Centipoise

Maximum Percentage Deviation = -4.833%

FREON - 12B1

Temperature Range = 209.15 → 273.15°K

Number of Experimental Values = 14

η CP = $9.79672 \times 10^{3} - 2.00097 \times 10^{2} \times T$

$$+ 1.63234 \times T^2 - 6.64712 \times 10^{-3} \times T^3$$

$$+ 1.35110 \times 10^{-5} \times T^4 - 1.09663 \times 10^{-8} \times T^5$$

Mean Deviation = 3.37326×10^{-2} Centipoise

Maximum Percentage Deviation = -20.127%

FREON - 12B2

Temperature Range = 213.15 → 273.15°K

Number of Experimental Values = 4

$$\eta \text{ CP} = 9.67846 - 6.18415 \times 10^{-2} \times T$$

$$+ 1.05000 \times 10^{-4} \times T^2$$

Mean Deviation = 5.20000×10^{-3}

Maximum Percentage Deviation = +1.026%

FREON - C318

Temperature Range = 243.15 → 273.15°K

Number of Experimental Values = 4

$$\eta \text{ CP} = 1.46125 \times 10^{1} - 9.59687 \times 10^{-2} \times T$$

$$+ 1.62500 \times 10^{-4} \times T^2$$

Mean Deviation = 9.9996×10^{-5} Centipoise

Maximum Percentage Deviation = +0.024%

XI REFERENCES

1. Hovorka, F. and F. E. Geiger,
"Thermodynamic Properties of Trifluorotrichlorethane and Difluorotetrachloroethane", J. Am. Chem. Soc., 55, 47-60, 1933.

2. Awberry, J.H. and E. Griffiths,
"The Viscosities of Some Liquid Refrigerants", Phys. Soc., Proc., 48, pt. 3, 372, 1936.

3. Benning, A. F. and W. H. Markwood, Jr.,
"The Viscosities of Freon Refrigerants", reprint from the April, 1939, issue of Refrigerating Engineering.

4. Graham, D.P.,
"Properties of PF-1 (Octafluorocyclobutane)", JLR-69-8, No. 1, Serial No. 18958, Du Pont de Nemours.

5. Coughlin, J.,
"The Vapour Viscosities of Refrigerants", Ph.D. thesis, School of Mechanical Engineering, Purdue University, Indiana, 1953.

6. Makita, T.,
"The Viscosity of Freons Under Pressure", Rev. Phy. Chem. of Japan, 24, No. 2, 1954.

7. Makita, T.,
"The Viscosity of Gases under High Pressure", Chemical Inst., Kyoto Tech. University, Japan, 1952.

8. Hubbard, R. W. and C. G. Brown,
"The Rolling Ball Viscometer", Ind. and Eng. Chem., 15, 212, 1943.

9. Wellman, E. J.,
"Viscosity Determination of Several Fluorinated Hydrocarbon Vapours with a Rolling Ball Viscometer", Ph.D. thesis, School of Mechanical Engineering, Purdue University, 1955.

10. Kinser, R. E.,
"Viscosities of Several Fluorinated Hydrocarbon Compounds in the Vapour Phase", M.Sc. thesis in Mechanical Engineering, Purdue University, 1956.

11. Kamien, C. Z., and O. W. Witzell,
"Effect of Pressure and Temperature on the Viscosity of Refrigerants in the Vapour Phase", ASHRAE Trans., Vol. 65, No. 1693, pgs. 663-674, 1959.

12. Lilios, N.,
"The Viscosity Determination of Several Liquid Refrigerants at Atmospheric Pressure", M.Sc. thesis in Mechanical Engineering, Purdue University, 1957.

13. McCullum, R. G.,
"High Temperature Viscosity Measurements of Fluorinated Hydrocarbon Compounds in the Vapour Phase", M.Sc. thesis in Mechanical Engineering, Purdue University, 1958.

14. Tsui, C.Y.,
"Viscosity Measurement for Several Fluorinated Hydrocarbon Vapours at Elevated Pressures and Temperatures", M.Sc. thesis in Mechanical Engineering, Purdue University, 1959.

15. Willbers, O.J.,
"Viscosity Measurements for Several Fluorinated Hydrocarbon Vapours at Low Temperatures", M.Sc. thesis in Mechanical Engineering, Purdue University, 1961.

16. Riley, V. J.,
"The Viscosity of Liquid Freon - 11 and Freon - 12 at Temperatures to -110°C", M.Sc. thesis in Mechanical Engineering, Purdue University, 1963.

17. Eisele, E. H. III.,
"The Determination of the Dynamic Viscosity of Several Freon Compounds at Temperatures in the Range 200°F to - 200°F", M.Sc. thesis in Mechanical Engineering, Purdue University, 1965.

18. Gordon, D. T.,
Private Communications - Graduate Student, Purdue University, 1967.

19. Witzell, O. W. and J. W. Johnson,
"The Viscosities of Liquid and Vapour Refrigerants", A paper presented at ASHRAE Semi-annual Meeting, January 25-28, Chicago, 1965.

20. "Liquid Density and Viscosity of Freon 114-B2", E.I. DuPont de Nemours and Co. Inc., Publication No. (X-50A).

21. Lewis, H. W., " Calibration of the Rolling Ball Viscometer", Anal. Chem. 25, pp. 507-8, 1953.

22. Johnson, J. W., "A Correlation of the Viscosity of Fluorinated Hydrocarbon Compounds in the Liquid and Vapour Phases", M.Sc. thesis in Mechanical Engineering, Purdue University, 1962.

23. Reid, R. C. and T. K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill Book Co., 1958.

24. Barr, G., "A Monograph of Viscometry", Oxford University Press, 1931.

25. Dinsdale, A. and F. Moore, "Viscosity and Its Measurements", Chapman and Hall Ltd., London, 1962.

26. "Properties of Commonly Used Refrigerants", Air-Conditioning and Refrigeration Institute, 1957 edition.

27. "Handbook of Fundamentals, American Society of Heating, Refrigerating and Air Conditioning Engineers, 1967 edition.

28. "Preliminary Thermodynamic Properties of Freon - 14, E.I. Du Pont de Nemours & Co. Inc., Copyright 1961, (T-14).

29. "Thermodynamic Properties of Freon - 21", E. I. Du Pont de Nemours & Co. Inc., Copyright 1939, (T-21).

30. "Thermodynamic Properties of Freon - 22", E. I. Du Pont de Nemours & Co. Inc., Copyright 1964, (T-22).

31. "Thermodynamic Properties of Freon - 115", E.I. Du Pont de Nemours & Co. Inc., (T-115).

32. Benning, A. F. and McHarness, "Thermodynamic Properties of Freon - 113", E. I. Du Pont de Nemours & Co. Inc., (T-113A).

33. Albright, L. F. and J. J. Martin,
"Thermodynamic Properties of Chlorotrifluoromethane",
Ind. and Eng. Chem., 44, 188, January 1952.

34. Latto, B.,
"The Viscosity of Steam at Atmospheric Pressure",
Technical Report No. 16, University of Glasgow, U.K.,
1965.

35. Chavet, I.,
"Gas Flowmeter for Continuous Operation",
J. Scientific Instruments, Vol. 39, 1962.

36. Black, R. M. et. al.,
"A Flowmeter for Measuring Very Low Rates of Helium Gas
Flow", J. Sc. Inst., Vol. 41, page 345, 1964.

37. Veprek, J. A.,
"A Thermistor Flowmeter", J. Sc. Inst., Vol. 40, page 66,
1963.

38. Levy, A.,
"The Accuracy of the Bubble Meter Method for Gas Flow
Measurement", J. Sc. Inst., Vol. 41, page 449, 1964.

39. Harrison, P. and I.F. Darroch,
"Air Flow Measurement by the Soap Film Method", NEL
Report No. 302, Ministry of Technology, U.K., 1967.

40. Baker, H. et. al.,
"Temperature Measurement in Engineering", Vol. II,
John Wiley & Sons, Inc., 1961 edition.

41. "Thermophysical Properties Research Centre Data Book",
Vol. 2, Purdue University, 1967.

42. Hillsenrath, J. et. al.,
"Tables of Thermodynamic and Transport Properties of Air,
....., Nitrogen, etc.", Pergamon Press, 1960.

43. "Temperature, Its Measurement and Control in Science and
Industry", Reinhold Publishing Corporation, 1941.

44. Schultze, H.,
Ann. Physik, V.5., page 147, 1901.

45. Fisher, W.,
"The Coefficients of Gas Viscosity", Phys. Rev. Vol. 28,
page 73, 1909.

46. Carr, N. L.,
"The Viscosity of Gas Mixtures at High Pressures",
Ph.D. thesis, Illinois Inst. Tech. 1952.

47. Latto, B.,
Private Communication, McMaster University, 1968.

48. Innes, M.J.S.,
Chief, Gravity Division, Department of Energy, Mines
and Resources, Ottawa, Private Communication, 1967.

49. Knudsen
Annalytic Physik (4), Vol. 28, page 75, 1909.

50. "Handbook of Chemistry and Physics" 45th Edition, Chemical
Rubber Publishing Co., 1964 - 1965.