AN ABSOLUTE VISCOMETER FOR LOW TEMPERATURES AND MEDIUM HIGH PRESSURES

AN ABSOLUTE VISCOMETER FOR LOW TEMPERATURES AND MEDIUM HIGH PRESSURES : VISCOSITY OF NITROGEN GAS DOWN TO VERY LOW TEMPERATURES

Pavel HESOUN, Dipl. Ing.

A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Engineering

McMaster University

March 1970

MASTER OF ENGINEERING (1970)
(Mechanical Engineering)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: AN ABSOLUTE VISCOMETER FOR LOW TEMPERATURES AND MEDIUM HIGH PRESSURES : VISCOSITY OF NITROGEN GAS DOWN TO VERY LOW TEMPERATURES

AUTHOR: Pavel HESOUN, Dipl. Ing. (Tech. University of Prague)

SUPERVISOR: Dr. Brian Latto

NUMBER OF PAGES: ix, 144

SCOPE AND CONTENTS:

A new two-capillary absolute viscometer for the measurements of the viscosity of gases down to cryogenic temperatures and for moderate pressures up to 200 atm has been developed and described in this thesis.

An experimental determination of the absolute viscosity of nitrogen at atmospheric pressure and in the temperature range 97.41-297.88°K is also reported. The maximum error of the smoothed data is believed to range from ±1% at highest temperatures to ±1.6% at the least favourable lowest temperatures.

Data obtained in this work and those of previous workers have been correlated using integral equations postulated by Chapman-Enskog collision theory of dilute gases.

Furthermore, viscosity measurements have been carried out for nitrogen at 42 and 84 atm and are presented in the thesis to confirm the applicability of the viscometer for high pressure work.

ACKNOWLEDGEMENT

The writer wishes to acknowledge the helpful advice received from Dr. B. Latto with regard to numerous discussions on the design, theoretical and experimental aspects of the research project. It is especially appreciated by the writer that the advice and instruction, which protected him from making unnecessary misjudgements and unreasonable assumptions, was presented in a form which made it possible to carry out independent research.

The writer wishes also to acknowledge the assistance of both Mr. D. Crookes and the Engineering workshop in the manufacturing of the apparatus.

TABLE OF CONTENTS

Chapter

Appendices

LIST OF ILLUSTRATIONS

Photograph

Figure

LIST OF TABLES

NOMENCLATURE

Unless othervise defined in the text, the symbols used in this work have the following meanings:

Capital letters

Q	mass flow rate
V	volume flow rate
ΔP	pressure drop
L	mean free path, mercury thread length
G	weight
Re	Reynolds number
N	factor of safety, design factor
T	absolute temperature in °K

Small letters

d	inside capillary diameter
l	capillary length
p, P	absolute pressure
r	radius
g	gravitational constant
m	Hagenbach correction factor
n	Couette correction factor, number
t	temperature in °C
v	velocity, mercury pellet volume
h	height of manometer column, pellet meniscus
k	Boltzmann constant

Greek symbols

α	coefficiet of thermal expansion
ε	max. potential energy of attraction
σ	low velocity collision diameter, principal stress
$\Omega^{(l,s)}$	collision integral
η	absolute viscosity
ρ	density
λ	length parameter of Couette correction
τ	time, sheer stress
Δ, δ	difference, differentiation sign
Σ	sum

Subscripts

m	relating to mean value or mercury or Hagenbach correction factor
n	relating to Couette correction factor
o	relating to 0 °C
a	relating to atmospheric conditions
e	relating to equivalent value
M	relating to modified value
w	relating to water
t	relating to constant temperature
p	relating to constant pressure

Subscripts (1) and (2) refer to the upstream and downstream capillary, respectively.

CHAPTER I

INTRODUCTION

Accurate experimental viscosity data furnish a worthwhile contribution to the study of interrelationship between various transport coefficients of gases and intermolecular models as postulated by different theories. The theory is merely a method of describing certain phenomena which can be refined or replaced by a new one when it is no longer reliable. To justify such changes in a theoretical approach to the problem, experimental proof is important.

Although the viscometry of gases has provided one of the best verifications of the Chapman-Enskog kinetic theory for simple dilute gases, the Lennard-Jones (6-12) intermolecular potential function, often used to evaluate the collision integrals $\Omega^{(1,s)}$, has not proved to be quite adequate to meet the requirements of advanced molecular physics. In order that improved potential functions be made available, sufficiently accurate experimental data of the transport coefficients, especially that of viscosity of simple gases over broad temperature range are required.

An initial survey of the available data has shown that the absolute viscosity for the more common gases, like nitrogen or argon, are not only sparse but also unreliable. The most reliable sets of viscosity data for nitrogen are those by Johnston et al. /8/[+] and by Clarke and Smith /17/ which deviate by about 3% at 114 °K and even much more if extrapolated towards liquifying point at atmospheric pressure. This is not really satisfactory for nitrogen which has high theoretical and practical importance.

Apparently, very little work has been carried out on viscosity of a large number of gases at high pressures and low temperatures which are necessary as a background for the development of a universal theory for fluids. Attempts are currently being made to produce a universal model which would bridge the gap between low and high density theories developed for dilute gases and liquids, respectively. Presently, the Enskog's theory of dense gases gives still the best non-empirical equations for expressing the effect of pressure on gas viscosities.

Values for viscosity of gaseous substances are also of practical importance in applied mechanics such as fluid dynamics and heat transfer in fluids, entering directly into Reynolds, Schmidt and Prandtl criteria.

Considering the aspects presented above, the main objectives of this research are outlined as follows:

/1/ To develope an absolute viscometer suitable for gases at low and medium densities and to prove its value at moderate pressures

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[+] Reference number

/2/ To carry out an experimental study on the low temperature viscosity for dilute nitrogen

An approach to these objectives is reported in this thesis.

CHAPTER II

LITERATURE SURVEY

1. Low Pressure Region

There are about twenty sets of experimental data available for the viscosity of nitrogen at low pressures but only those by Johnston et al. /8/ and Clarke and Smith /17/ involve more than five experimental points in the low temperature region. Vogel /9/, Trautz and Baumann /31/ and Vasilesco /7/ contributed to a lesser extent by data taken at widely separated temperatures.

The first report on the viscosity of nitrogen below the ice-point temperature was by Vogel /9/ in 1914, who employed two types of secondary oscillating-disk viscometers to obtain the viscosity of twenty common gases. Both viscometers were basically of the same design and differed only in dimensions. The oscillating disk was installed in a glass vessel, which was located in a large Dewar flask containing a liquid constant temperature bath. The measurements were carried out at fixed point temperatures given by liquid air, liquid oxygen, ether-carbonacid mixture and ice-point and accounts for the wide separation of the data along the temperature scale. The viscosities at 81.6°K and 273.1°K were obtained for nitrogen at pressures 310 and 746 mm of mercury, respectively.

Both apparatus were first calibrated using air at ice-point temperature (273.15°K) and the measurements evaluated using the Coulomb-Maxwell theory for oscillating viscometers. The viscosity of the calibrating air at 273.15°K was taken as $\eta_0=1.724\cdot10^{-4}$ poise and was based on thorough analysis of previous absolute viscosity measurements which had been obtained mostly in the latter part of the 19th century. This value agrees with similar data, quoted in the literature up to this date, to better than ±0.5%. The absolute viscosity of nitrogen at 273.1°K measured by Vogel and given as $\eta_0=1.678\cdot10^{-4}$ poise, however, is 0.94% higher than the results of latest correlations /3/which casts certain doubts on the dependability of Vogel's results,even at lower temperatures. The lack of viscosity data available in 1914 prevented Vogel from correlating most of his low temperature experimental results.

In 1929, Trautz and Baumann /31/ reported experimental viscosity data of several gases and gas mixtures, obtained by means of a secondary single capillary transpiration viscometer, calibrated using dry air. The viscosity of nitrogen was obtained at fourteen different temperatures ranging from 195 to 583°K. The formula given by Millikan, relating the reference dry air viscosity values to the calibrating temperature t°C, $\eta_{air,t} = 1823.8 - 4.93 \cdot 10^{-8} \cdot (23 - t)$ poise$\cdot 10^{7}$, was used by Trautz and Baumann to calculate their reference viscosities. This formula, which appears to have served as a standard for most of the works in the United States and Canada /8/ before 1940, gives the reference air viscosity as about 0.5% lower than that given by Vogel, which is generally accepted as a standard in Europe. The comparison of the viscosities obtained by Trautz and Baumann with those by Vogel should, therefore, be made only after recalculation of the results to the same reference viscosity. This has not been done, however, in the correlation of this work as there is not sufficient information available to judge the reference air viscosity values used in the past since it is difficult to assess their relative accuracy.

In the introductory paper by Trautz and Weizel /35/ describing the apparatus and experimental method used there is no attempt to estimate the overall accuracy of the experiments.

Johnston et al. in 1940, reported consistent sets of low temperature viscosity data on several gases including nitrogen. The results were obtained using a secondary oscillating disk viscometer which included certain refinements, when compared with that of Vogel, especially in the measurement and control of temperature. Use of bath temperature control permitted the viscosity measurements at series of points over the temperature ranging from 90 to 300°K at pressures which varied from 500 to 760 mm of mercury. Liquid oxygen was used for the temperature bath for 90°K and a freezing mixture of dichlordifluoromethane was used for 118°K. Between 130 and 150°K, the dichlordifluoromethane bath was cooled using liquid air and kept at required temperature in a Dewar flask. Above 150°K the bath temperature was controlled using a thermostat which gave temperature regulation better than ±0.05 degree when used in connection with an accessory cryostat. With the help of this temperature control, the viscosity of nitrogen was measured at fifteen points, roughly uniformly distributed over the above mentioned temperature range.

The apparatus constants were determined using dry air at temperatures close to 296.1°K. Reference dry air viscosity at this temperature was taken as $\eta_o = 1.833 \times 10^{-4}$ poise and is based on the absolute air viscosity values of previous works correlated by Johnston. This standard is about 0.5% higher than that given by Millikan's equation but is in very good agreement with the standard accepted in Europe. Vogel's reference viscosity value $\eta_o = 1.724 \times 10^{-4}$ for air at 273.1°K corresponds to 1.832×10^{-4} poise for air at 296.1°K.

Johnston took two or three viscosity readings at each temperature and the averages of these readings were used in correlations presented in this present work. The deviations of Johnston's viscosities from his smooth curves are better then ±0.17 % and consequently this set of data is one of the best as far as the precision and reproducibility are concerned. Very careful analysis has been reported by Johnston on the accuracy of his experiment,resulting in the conclusion that, with account taken of the chance deviations, the inaccuracies in the smoothed experimental data are not greater than±0.7% in the most unfavourable cases at temperatures at about 90°K, and do not exceed ±0.3% in values at 300°K. Johnston's error analysis is not absolute, but relates to the relative values, with air taken as a standard. The inaccuracy of the standard is not discussed.

Johnston's data on nitrogen are in a good agreement with the results by later investigators but they tend to higher values at very low temperatures as compared with the absolute measurements by Clarke and Smith /17/ carried out in 1967 and with the absolute measurements presented in this thesis. The deviation of the data below 120°K is so pronounced that it can be explained only by a temperature dependent systematic error from a source not known to Johnston, which might have occured in his work at very low temperatures. The conclusions of correlation, presented in chapter VII of this thesis, only confirm this suspicion.

In 1945, Vasilesco /7/ presented several sets of gas viscosity data over the broad temperature range of 90 to 1600°K.

An absolute Poiseuille type viscometer using platinium capillaries was first used to determine viscosity value of dry air, which was found to be $\eta_0 = 1.720 \cdot 10^{-4}$ poise at 273.1°K, based on an average of about twenty runs at the same temperature. Viscosity values of other gases were then obtained by means of the same viscometer but were evaluated and presented as values relative to zero viscosity of each gas. The standard dry air viscosity,as measured and used by Vasilesco,is 0.23 % lower then Vogel's standard and consequently is close to the average value of standards accepted in Europe and in the United States. The viscosity of nitrogen at ice-point temperature in Vasilesco's work is $\eta_0 = 1.6637 \cdot 10^{-4}$ poise and is only 0.12 % higher than that resulting from the correlation presented in chapter VII of this work. Considering low temperature character of the correlation, only viscosities at 90.2, 194.76 and 273.1°K were included to further comparisons. As it is apparent from Vasilesco's publication, the viscosities at 90.2 and 194.76°K were obtained in 1937 by Fortier using a transpiration absolute viscometer very similar to that used by Vasilesco. For this reason and since the two viscosity data under discussion were first published by Vasilesco, they are usually attributed to him in various publications /3/, /11/. This assumption has been also included in the correlation of this thesis.

The experimental points by Vasilesco are in excellent agreement with the smoothed data of this present work, showing deviations less than ±0.3% over the whole temperature range where comparison was possible.

Vasilesco estimated that his viscosity values are accurate to ±0.15% with respect to assumed values of ice-point viscosities of gases concerned. However, no attempt to assess an absolute inaccuracy of the reference ice-point viscosities has been reported.

In Vasilesco's apparatus, a constant pressure was maintained between the capillary ends as compared to Trautz's system which used a constant volume of gas which was passed through capillary by consequently decreasing pressure produced by mercury piston. Steady state flow systems are considered to be more reliable as there is no necessity to introduce any form of hydrostatic head correction /33/.

The most recent study on viscosities of several gases at low temperatures, including nitrogen, is that by Clarke and Smith /17/, published in 1968. The results were obtained by a capillary flow technique in a temperature range from 114 to 374°K and related to nitrogen viscosity at ice-point temperature taken as $\eta_0 = 1.665 \cdot 10^{-4}$ poise. Presentation of the experimental results by Clarke and Smith in relative form, however, has nothing in common with the absolute character of the experiment, but is, like in Vasilesco's case, a matter of arbitrary choice or convenience. The constant volume transpiration system derives a driving power from pressure difference created between two vessels which are connected by a capillary. The resulting variable pressure drop over the capillary is read several times during each run in order to evaluate integral-type working equation obtained by integration of Poiseuille equation over the finite time of an experimental run.

The capillary tube was located in a fluid bath that was thermostatically controlled to ±0.1 centigrade at any specific temperature. Temperature conditions were measured using a gas thermometer which was considered to be accurate to ±0.1 centigrade. The degree of temperature control suggests that an error in temperature estimate could not influence the accuracy and precision of experimental viscosities by Clarke and Smith to too large extent. In spite of that, the mean of at least five individual measurements was presented as the viscosity value at each temperature. This resulted in the deviation of viscosity values of less than ±0.25% from smooth curves fitted to the data using a method of least squares.

The good precision of the data, as presented by Clarke and Smith, does not indicate the experimental precision as defined by statistical analysis. The experimental scatter of the results treated in this manner is smaller since averaging of data taken at a given temperature partially eliminates the influence of random errors and cannot be compared directly to the case when only one reading is taken at each temperature. The possible experimental error, as claimed by the authors, can be greater than ±1% only at the lowest temperatures.

A comparison, made by Clarke and Smith, of their nitrogen viscosity data with those by Johnston et al. /8/ has shown a discrepancy below 170°K where the latter data are up to 3% higher, within the range where comparison is possible. This discrepancy approaches about 5% if Clarke's data are extrapolated to 90.2°K. As a similar discrepancy was also observed for argon, an assumption of systematic error in Johnston's or Clarke's data or in both seems to be a logical explanation of the disagreement.

Concluding Comments on Low Pressure Nitrogen Viscosity Data

/1/ The available low temperature viscosity data are sparse even for simple common gases such as nitrogen, which is one of the most investigated of the gases.

/2/ There is a 3% discrepancy between the most reliable sets of low temperature nitrogen viscosity data, i.e. those obtained by Johnston et al. /8/ and those by Clarke and Smith /17/ in the region where comparison is possible.

/3/ To improve the depth of knowledge of thermophysical properties of simple gases, any accurate investigation of viscosities at cryogenic temperatures can be considered as a significant contribution.

/4/ An application of absolute capillary method seems to be the most suitable for the low temperature viscometry.

2. High Pressure Region

It is not the intention to present any detailed study in this thesis of the viscosity of nitrogen at high pressures and low temperatures. Consequently only a brief historical survey is included. A survey of the low temperature viscosity measurements for nitrogen is shown in the P-T diagram, Figure 1.

The first report on high pressure viscosity measurement of nitrogen at low temperatures was that by Ross and Brown /27/, published in 1957. An absolute constant volume one capillary viscometer was located in a high pressure vessel which was immersed to a liquid bath, thermostatically controlled at a required temperature. The driving force of the test gas was produced by two spring bellows, connected by a capillary tube. At the beginning of each run, the capillary was displaced from its neutral position and consequently one bellow compressed and the other expanded. The viscosity values were evaluated from the working equation, expressing the viscosity as a function of the geometrical dimensions of the apparatus and the time necessary for the capillary to return to its neutral position.

The viscosity of nitrogen at pressures up to 682 atm were measured at temperatures ranging from 223.15 to 348.15°K. The accuracy of the results was estimated by the authors to be within ±1% with an experimental precision ±0.5%.

In 1963, Goldman /22/ published a paper covering work carried out exclusively on nitrogen viscosity at high pressures and low temperatures. Having developed a constant volume one capillary viscometer, Goldman measured the nitrogen viscosities at 194.7, 211.9 and 298.2°K, respectively, at pressures up to 120 atm. The test gas was forced through the capillary by a pressure difference created by oil column of a huge U-tube manometer. The viscosity data were found to agree relatively well with those obtained by Ross and Brown and could be correlated using a formula of Enskog's theory for dense gases so that the experimental points did not deviate from smooth curves more than ±3%. No error estimate of the experimental method was reported in Goldman's paper.

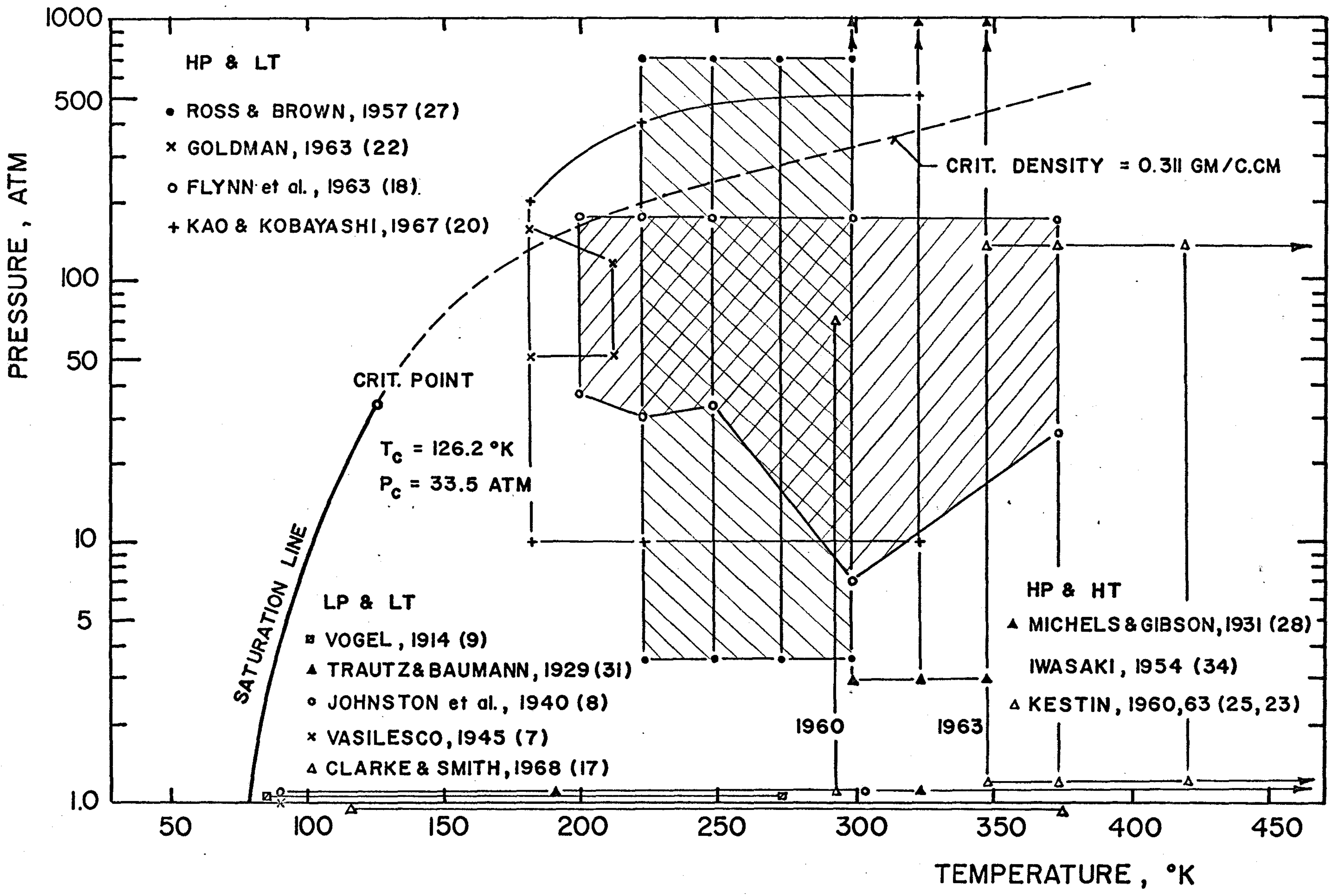


Figure 1. Graphical P - T Presentation of Available Nitrogen Viscosity Data.

In 1963, Flynn et al. /18/ published viscosity data for dense nitrogen and other gases in the temperature range of 194.6 to 373.1°K and pressures up to 177 atm. In an absolute one capillary viscometer of a good design, a steady state flow of gas was maintained through a capillary by means of two-plunger injector which could be driven at different speeds by electric motor with variable reduction gear. This system provided a constant pressure drop over the capillary during the test run and the possible effect of variable hydrostatic head, which occures with some systems, was thus eliminated. The viscosities were calculated using a modified form of Poiseuille equation, presented in appendix A1. The experimental procedure consisted in measuring Poiseuille viscosities for a series of mass flow rates at each temperature. The viscosity was then obtained by extrapolating Poiseuille viscosities to zero mass flow rate. The method gave an absolute measurements of viscosity and, furthermore, the semi-empirical Hagenbach correction factor was eliminated.

The viscosity data by Flynn et al. represents one of the most reasonable set available. Even so, the estimated experimental accuracy within ±0.1% as reported, does not appear to be realistic.

The best high pressure data on helium and nitrogen viscosities and their mixtures are those by Kao and Kobayashi /30/

which were published in 1967. Using a primary one capillary viscometer equipped with a double plunger volumetric pump. which maintained a steady state flow of the test gas in the capillary, the viscosity of nitrogen was measured over four isotherms in a 183.15 to 323.15°K temperature range and at pressures from 10 to 500 atm. The maximum probable error in calculated viscosities was estimated to be ±0.137 %. Precision of the results is excellent. Extensive comparison of the results with existing data was also reported.

Concluding Comments on Low Pressure Nitrogen Viscosity Data

/1/ All four sets of viscosity data for nitrogen at high pressures were obtained using absolute capillary methods and are generally of good accuracy.

/2/ The best available data of Kao and Kobayashi /30/ are in agreement to those by Flynnet al. to within 0.3 % over the whole temperature range. The data by Ross and Brown /27/ are about 8 % lower over their lowest isotherm and Goldman's data /22/ at high pressures are about 2 % higher.

/3/ Owing to excellent absolute data by Flynnet al. and Kao and Kobayashi, high pressure nitrogen viscosities at low temperatures are well described. Only the very low temperature region, where the major discrepancies occur, is open to a more thorough investigation.

CHAPTER III

VISCOMETER SELECTION AND DESIGN CONSIDERATIONS

1. Viscometer Principle

There are several ways to obtain the viscosities of fluids experimentally. These can be clasified to two categories:

/1/ A body is moved in a fluid and the viscous drag is measured and analysed to obtain the fluid viscosity.

/2/ The fluid is transpired through a restriction and its viscosity evaluated on the basis of measured force-flow relationship.

The former method includes the oscillating disk, oscillating sphere, rotating cylinder, falling sphere and rolling ball. The latter approch includes methods based on the transpiration of a fluid through a capillary tube or through an annular space.

A viscometer based on any of these principles can basically be used to give absolute viscosity which can be calculated directly from the dimensions of the apparatus and the data obtained from the measurements.

Only few absolute determinations of viscosity, however, for which a high degree of accuracy can be claimed, have been made using the drag-type viscometers, as the theory has not been, for most of them, adequately developed. The drag-type viscometers are usually used for determining relative viscosities by reference to certain standard fluids. Usually a better precision is attainable with viscometers designed specially for relative measurements. This apparently higher precision, as compared to absolute methods, is partly due to simplification in design and partly due to elimination of errors made in the measurements of the geometrical dimensions of parts of absolute viscometers, such as capillary diameters. The accuracy of the secondary viscometers, on the other side, depends on the accepted value of the viscosity of the calibrating fluid which often differs in different works.

The theory for a capillary flow viscometer based on Poiseuille law is considered to be the most reliable of all the viscometers. Therefore, capillary or transpiration type viscometers are frequently used for both absolute and relative determination of viscosity. The most accurate sets of gas viscosity data at various densities have mainly been obtained using absolute capillary viscometers of various design. All the methods described above, however, have been used for accurate determination of gaseous viscosities at elevated pressures.

Considering all the methods described above, the choice is largely a matter of convenience. For this work, it was decided to use an absolute two capillary viscometer since:

/1/ It was essential to obtain an absolute viscometer for use at cryogenic temperatures.

/2/ The theory of capillary viscometer is well developed

/3/ Kinetic energy and Couette correction terms are eliminated in the working equation devised for transpiration system using two capillaries in series (see app. A1.) thus maintaining the apparatus a fully absolute viscometer.

/4/ A viscometer based on the same principle had already been successfully used in our laboratory for gas refrigerants /13/ and was believed to be applicable even to extended pressure and temperature range.

Having chosen the type of viscometer, a steady state flow through a capillary system was considered most suitable for an absolute measurements. If constant pressure drops are maintained over the capillaries, there is no need for hydrostatic correction ar correction concerning errors from integration of the governing parameters over the time of experiment.

In a constant volume viscometer, the most accurate means of exerting a driving force to the test gas seems to be a calibrated two-plunger injector /18/, /20/ having plungers driven in opposite directions by a geared synchronous motor run by a constant frequency power supply.

The injector may, however, give rise to errors due to time of development of a steady state flow in a transpiration system and errors from flow instabilities caused by imperfect synchronization of both plungers. As similar injectors also require extremely precise workmanship and would certainly become the most expensive part of the whole project a more suitable principle was sought to be used.

It was finally decided to employ an open-circuit transpiration system using a constant head of a test gas as a source of transpiration driving power. This method, which was used for some high pressure viscometers, has proved to have several positive features:

/1/ Lower complexity and cost of the instrument

/2/ Remarkable flexibility of desired flow rates, variable by only controlling the main throttle valve. This, in connection with interchangable capillaries, permits the use of the viscometer for both low and high pressure measurements at optimal conditions.

/3/ No limitations of application at low temperatures as observed with enclosed viscometers using mercury piston to produce a driving power.

/4/ No need to thermostat a viscometer cell and any kind of injecting system separately at very low temperatures.

The volume flow rate of the test gas was measured after the expansion to atmospheric pressure using a precise volume displacement volumeter, manufactured by "Brooks Instrument Co." , irrespective of the immediate test pressure in the viscometer cell.

2. Technological Aspects

In spite of previous application of two capillary low pressure viscometer in our laboratory, only limited amount of experience from previous work could be used for present work and no auxiliary instrumentation at all. An intended application of the viscometer at high pressures and cryogenic temperatures has revealed several sources of both physical and technological difficulties which have made the design and performance of the apparatus only vaguely similar to the previous one.

In high pressure work, leaks are often causes of principle difficulties and are crucial in the viscometry where only small flow rates are dealt with. Cryogenic temperatures give rise to special sources of troubles of this sort,as there is a strong tendency for leaks to increase in magnitude with decreasing temperature which makes detection difficult. Furthermore, repeated low temperature cycling can cause leaks to appear in materials during the operational period of the apparatus. Very often leaks occur at joints, connectors and seals. Obviously, the use of materials with different coefficients of thermal expansion must be kept to a minimum. Also the loss of ductility of certain materials at cryogenic temperatures is another difficulty.

An attempt was made to predict and therefore avoid all possible difficulties, as given above. Extreme care was devoted to assembling the parts of the viscometer, especially the joints and connectors. The only major change in the original design was in the type of joints that were used between the capillary tubes and the end chambers. The original joints were a type of Swagelok[+] connectors having Teflon seals which failed at temperatures below 100°K due to unsufficient elasticity and large shrink at those temperatures.

3. Limits of Application

It is believed that there is no general way leading to the "best" design of the capillary viscometer in question.Several limiting factors have been introduced already by the choice of the basic design pattern of the viscometer and materials

[+] Trade name of tube fittings

involved.

The transpiration system of the viscometer was composed of two high precision bore "Veridia" glass capillaries connected to metal chambers of the viscometer cell,which was located in the high pressure vessel,as described in detail in chapter IV of this thesis. The glass capillary tubes can be easily removed from their joints and replaced by ones of different bore,whenever it is required. Glass was preferred to metal for the following reasons:

/1/ Ease in selecting a tube with the most uniform inner bore

/2/ Ease in calibrating, checking and cleaning

"Veridia" capillaries, which are manufactured with different nominal bores ranging from 0.25 to about 2. mm, are cut and supplied with lengths about 60 cm. Considering this, the nominal design length of the long and short capillary was chosen as 52 cm and 32 cm, respectively.

A high pressure three limb oil-in-glass differential manometer for the measurement of the pressure drops which had a limb length of 30 cm, was specially designed for the purpose. Considering the manometer oil of specific gravity of 0.826, the maximum measurable pressure drop over the capillaries was restricted to a certain practical limit. To some extent the physical dimensions were intuitive but had to comply with certain flow limitations.

The Reynolds number of a flow and the development length of the velocity profile at the entrance of the capillary offer the limits of particular importance. Validity of Poiseuille law is strictly limited to conditions of laminar flow described when $Re_{crit} \leqq 2000$ for smooth circular tubes. With respect to Flynn's /18/ experimental finding, however, that the Hagenbach correction factor m (see app. A1) for square ended capillary becomes an unpredictable function of mass flow rate, the value of $Re = 1500$ was used as working limit of acceptable flow conditions.

According to Bousinesq /1/, the effect of the entrance extends over a tube length $x_{1\%}$ and is given by

$$x_{1\%} = 0.065 \times Re \times d \qquad /1/$$

where d is the bore of the capillary. At this length, the ratio of the maximum to the average velocity is to be within 1 % of the constant value which would occur in very long tube and it was assumed that the disturbances due to entrance effect had become negligible. It was arbitrarily decided that the ratio of the development length $x_{1\%}$ to the capillary length should not excess 25 %.

An analysis of the main parameters governing the flow in the transpiration system has been done for nitrogen over the required pressure and temperature range with regard to the above mentioned limiting criteria. For the purpose of estimation, the Hagen-Poiseuille equation was used in the form

$$Q = \frac{\pi\ d^4\ \rho\ g\ \Delta P}{128\ \eta\ l} \qquad /2/$$

to calculate the mass flow rate Q as a function of pressure and temperature, assuming constant pressure drop of 10 cm of oil (S.G. 0.826) over the short capillary, given as the possible maximum by the manometer design. The density and assumed viscosity values for nitrogen were taken from gas tables /3/. The equation 2. is discussed in appendix A1. of this work.

In Figures 2. - 5., the dependence of mass flow rate and Reynolds number are given over the temperature range 100 to 400°K at isobaric conditions for pressures 1, 10, 40 and 100 atm, respectively. Nominal capillary diameters of 0.3, 0.4 and 0.5 mm were considered in the calculations.

For this viscometer, the Reynolds number Re = 1500 was found to be reached before the accepted limit of the development length for all capillary diameters. The prevailing criterion was then

$$Re = \frac{\rho\ \bar{v}\ d}{\eta} = \frac{4\ Q}{\pi\ d\ \eta} \leqq 1500 \qquad /3/$$

and it was used to determine the minimum temperature for which a capillary of given bore, having a constant pressure over it, can be used at each nominal pressure.

The maximum allowable pressure drops as a function of pressure and temperature were also obtained graphically from Figures 2.- 6. and are shown in Figures 6., 7. and 8. for capillary diameters 0.3, 0.4 and 0.5 mm, respectively. The latter figures were employed to choose approximate sizes of removable capillaries used for the present work.

It is apparent from the graphs that it is not reasonable to use a given capillary diameter over too wide pressure and temperature range due to both theoretical and practical difficulties which may arise.

This study on the applicability of the viscometer was based on the physical properties of nitrogen gas and cannot be used accurately for other gases with different densities and viscosities.

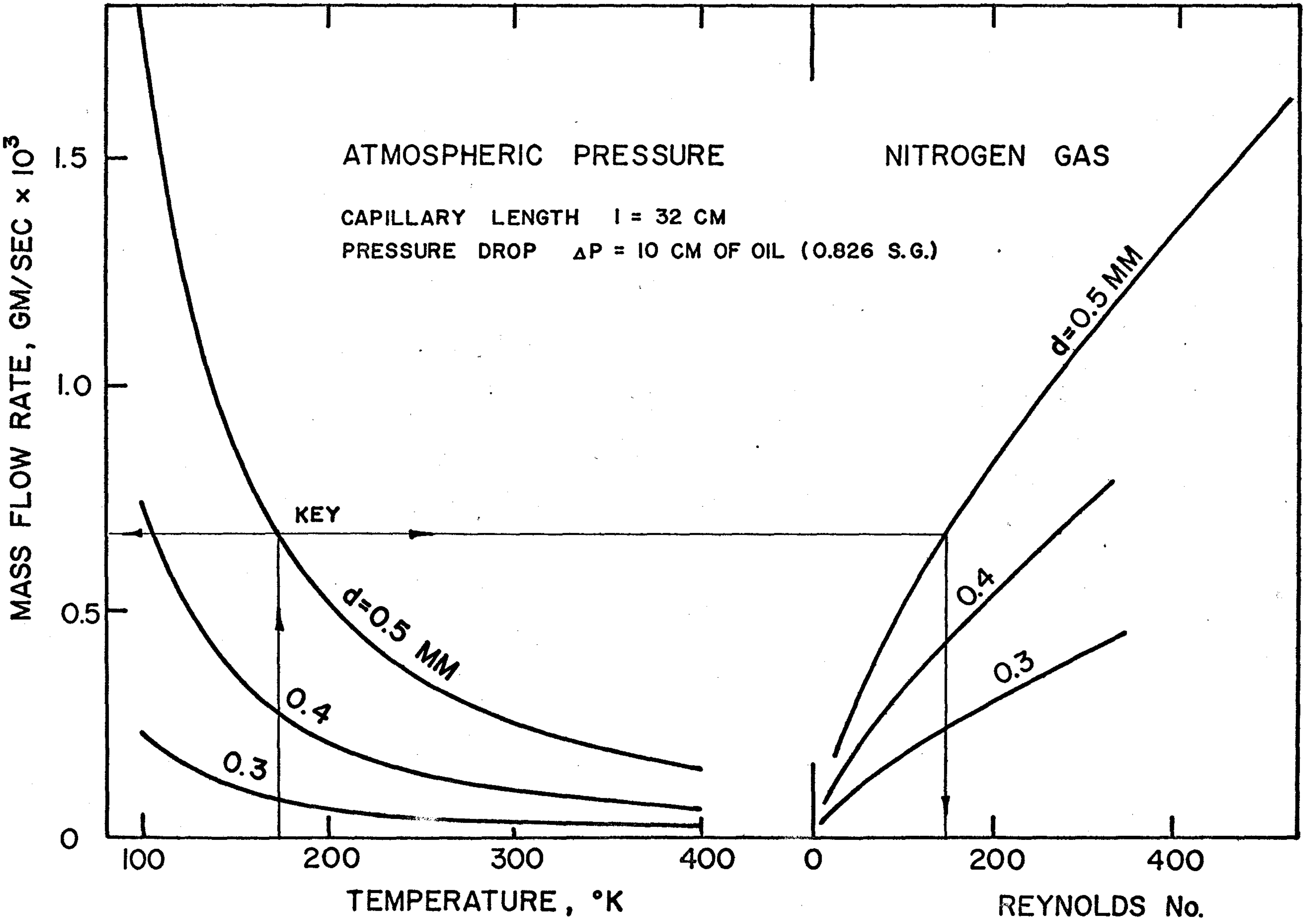


Figure 2. Mass Flow Rate versus Temperature and Re for Different Capillary Diameters and Specified Conditions at Atmospheric Pressure.

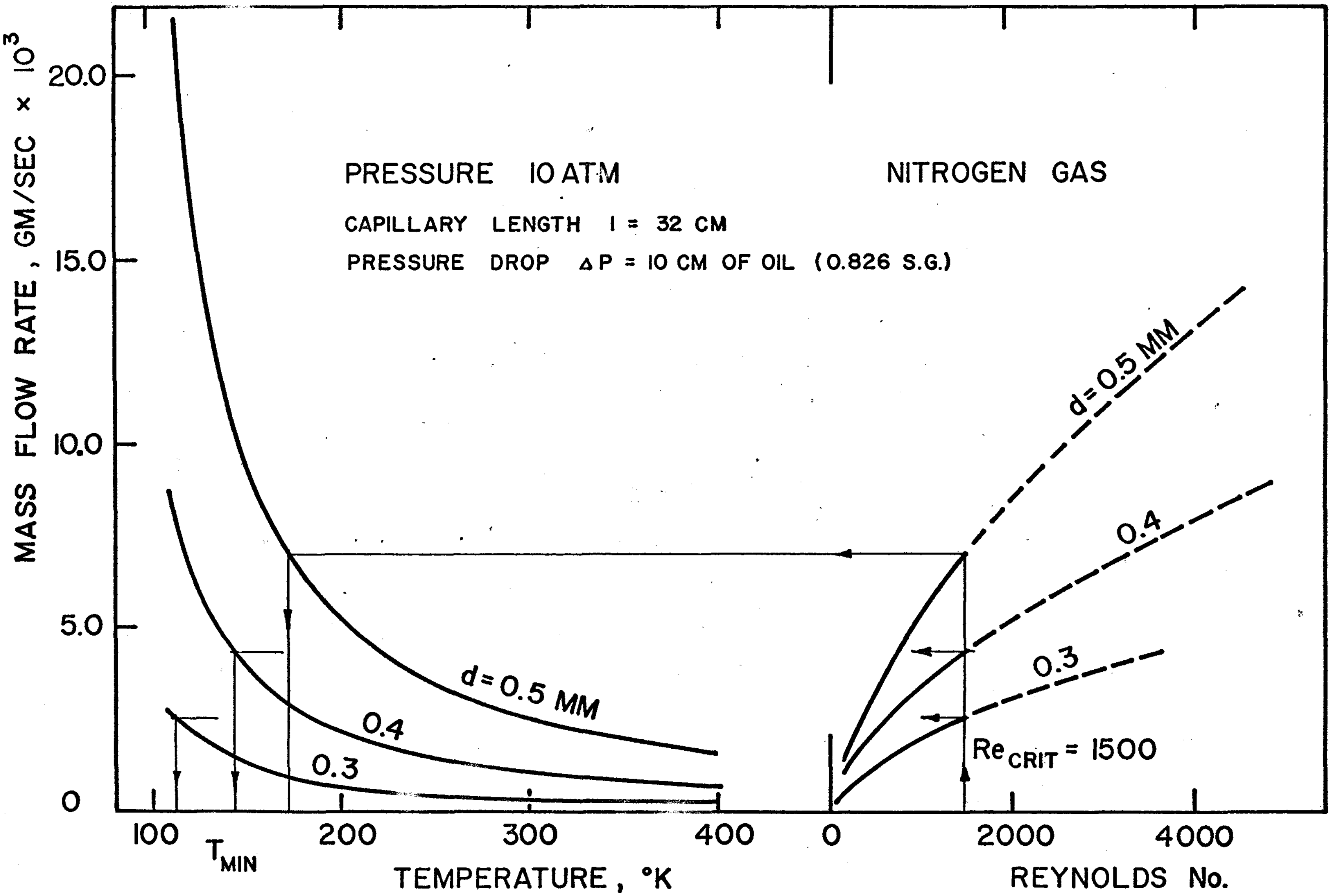


Figure 3. Mass Flow Rate versus Temperature and Re for Different Capillary Diameters and Specified Conditions at 10 atm.

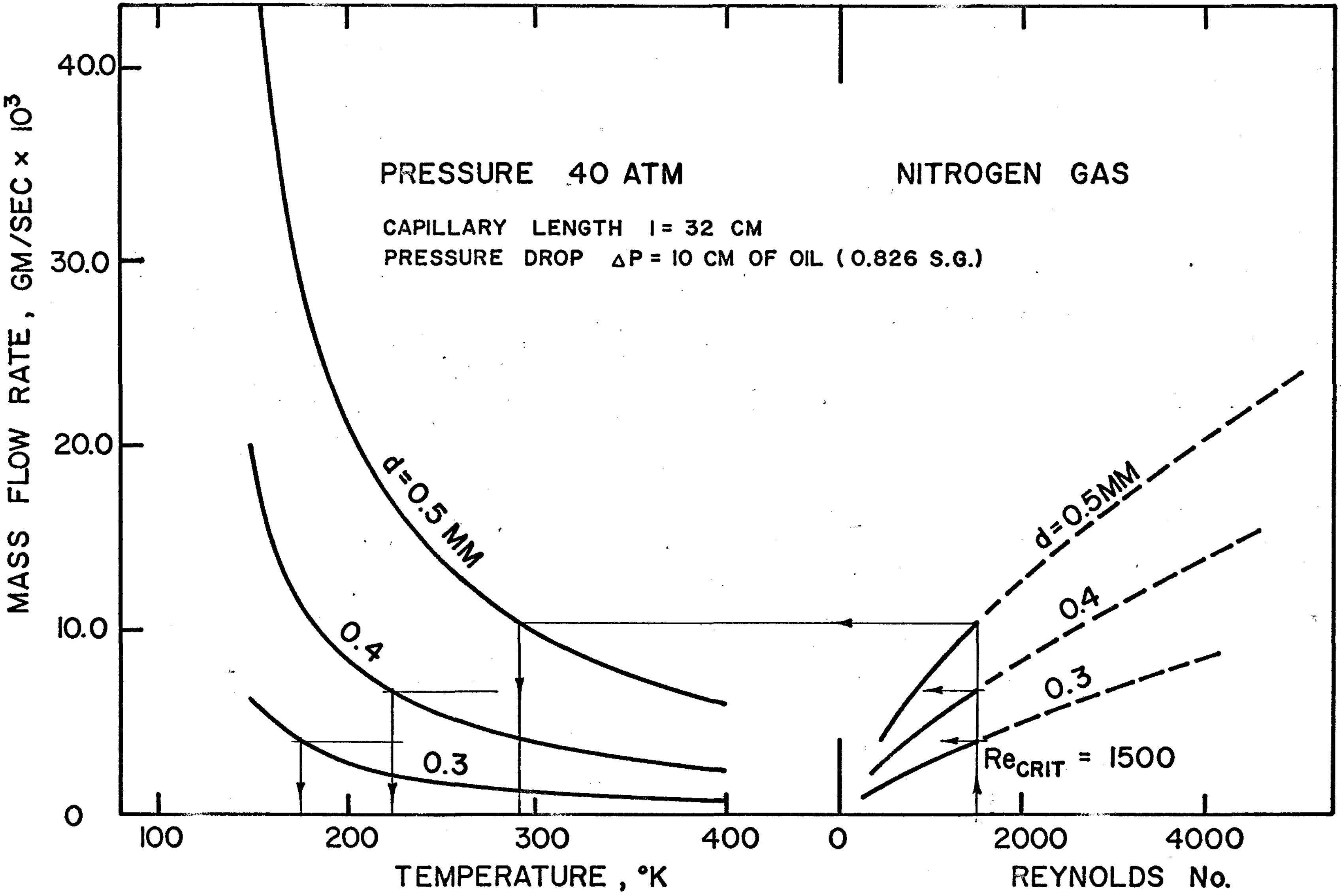


Figure 4. Mass Flow Rate versus Temperature and Re for Different Capillary Diameters and Specified Conditions at 40 atm.

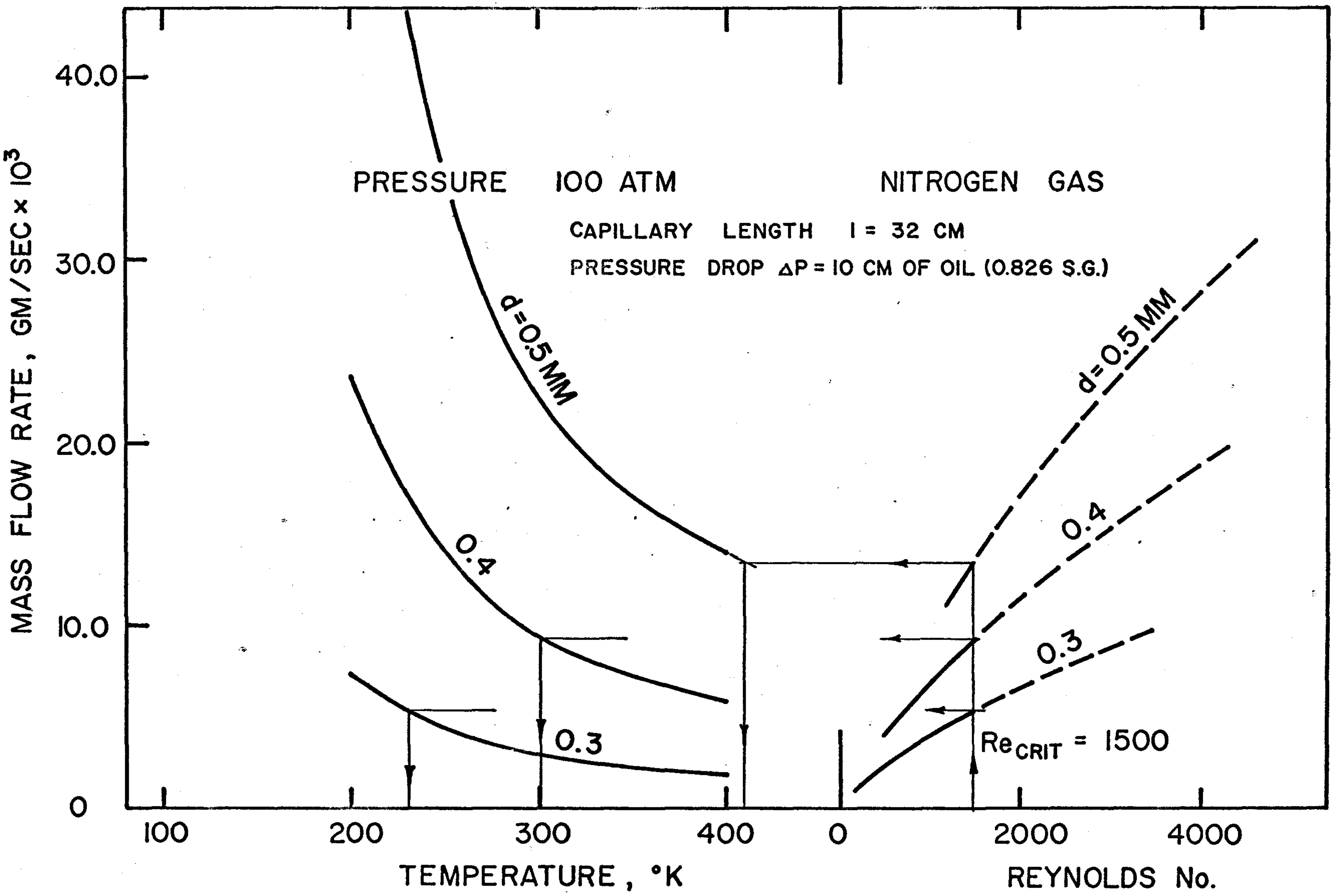


Figure 5. Mass Flow Rate versus Temperature and Re for Different Capillary Diameters and Specified Conditions at 100 atm.

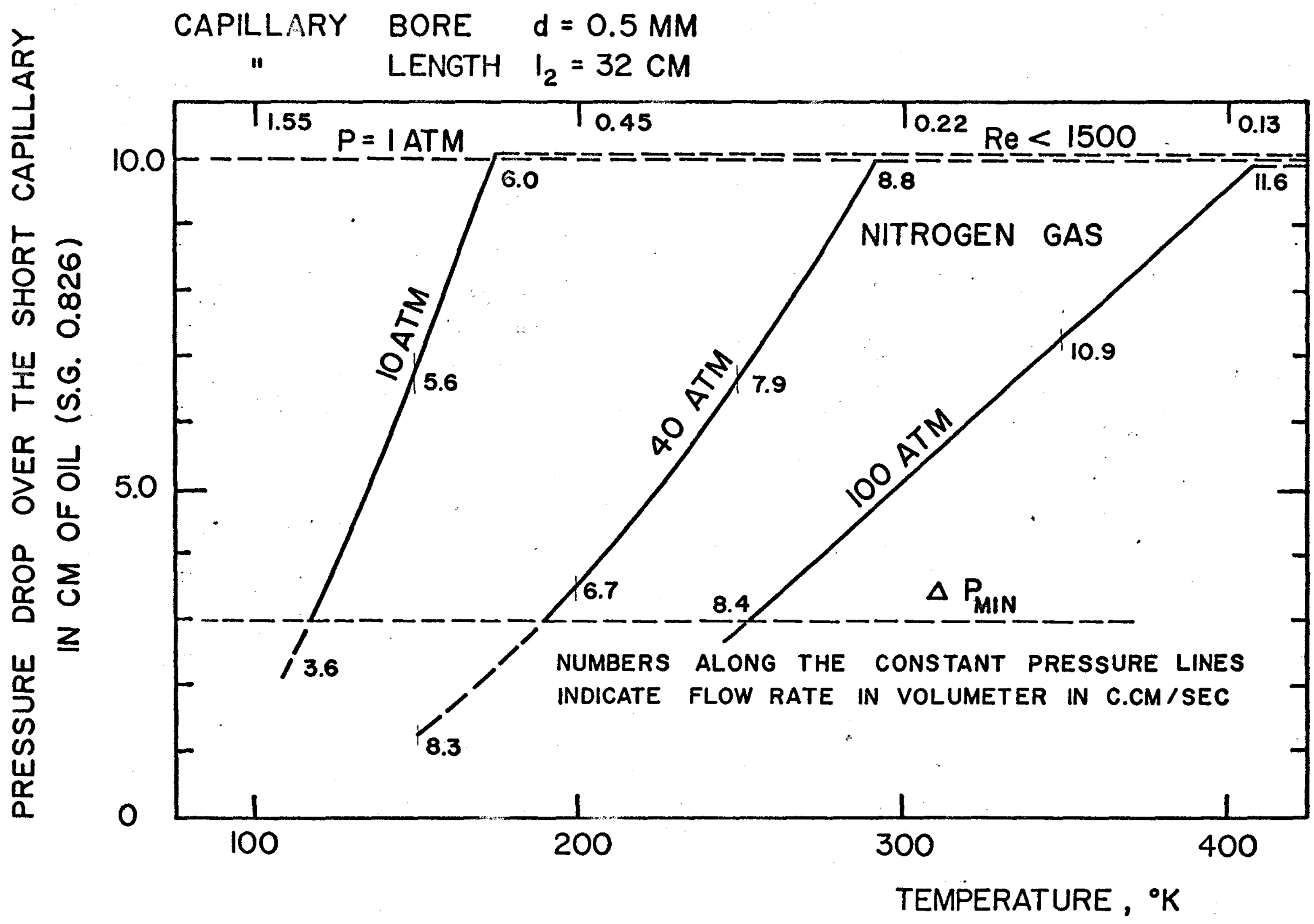


Figure 6. Pressure Drop over the Short 0.5 mm Nominal Diameter Capillary with a Reynolds No. = 1500.

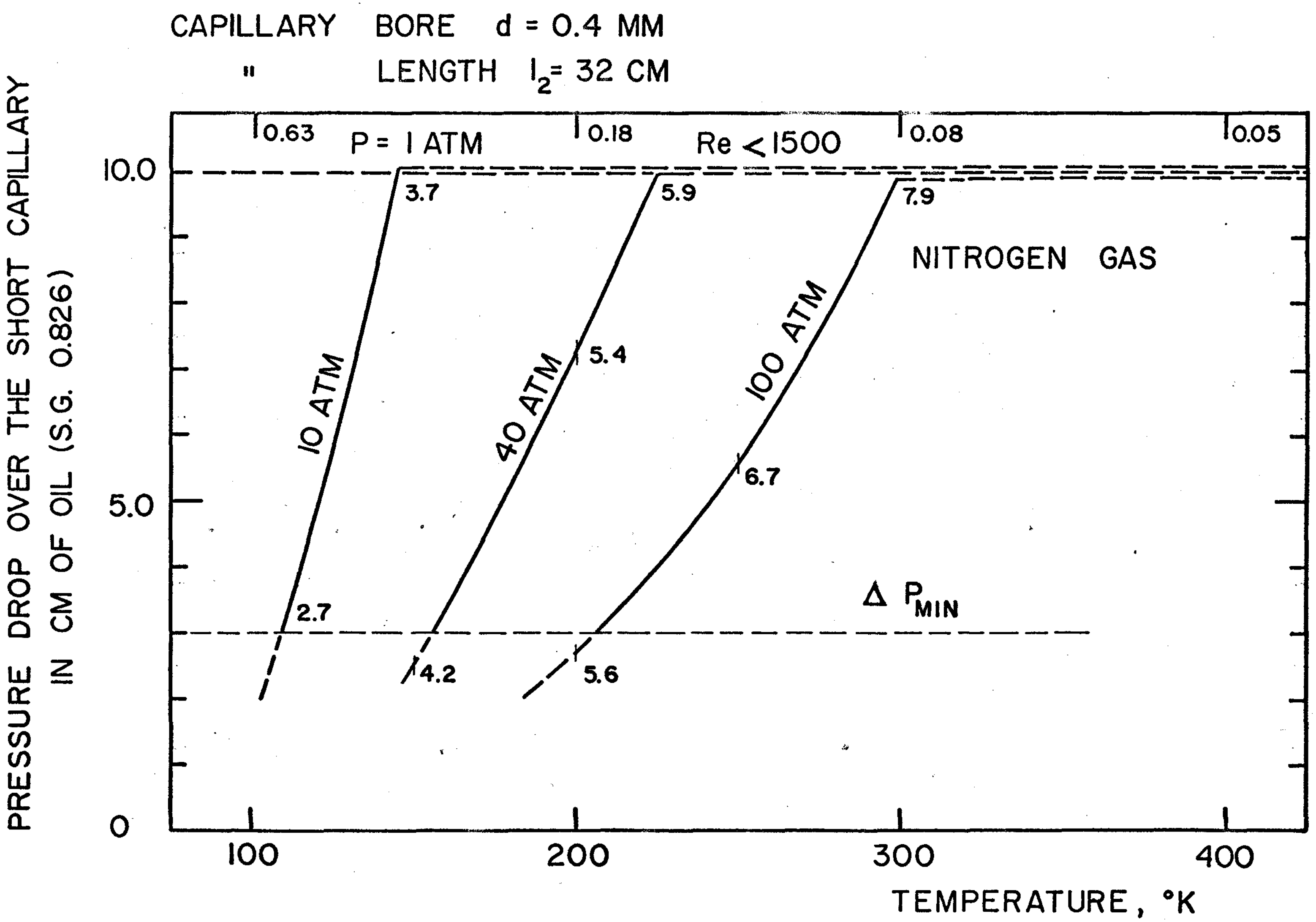


Figure 7. Pressure Drop over the Short 0.4 mm Nominal Diameter Capillary with a Reynolds No. = 1500.

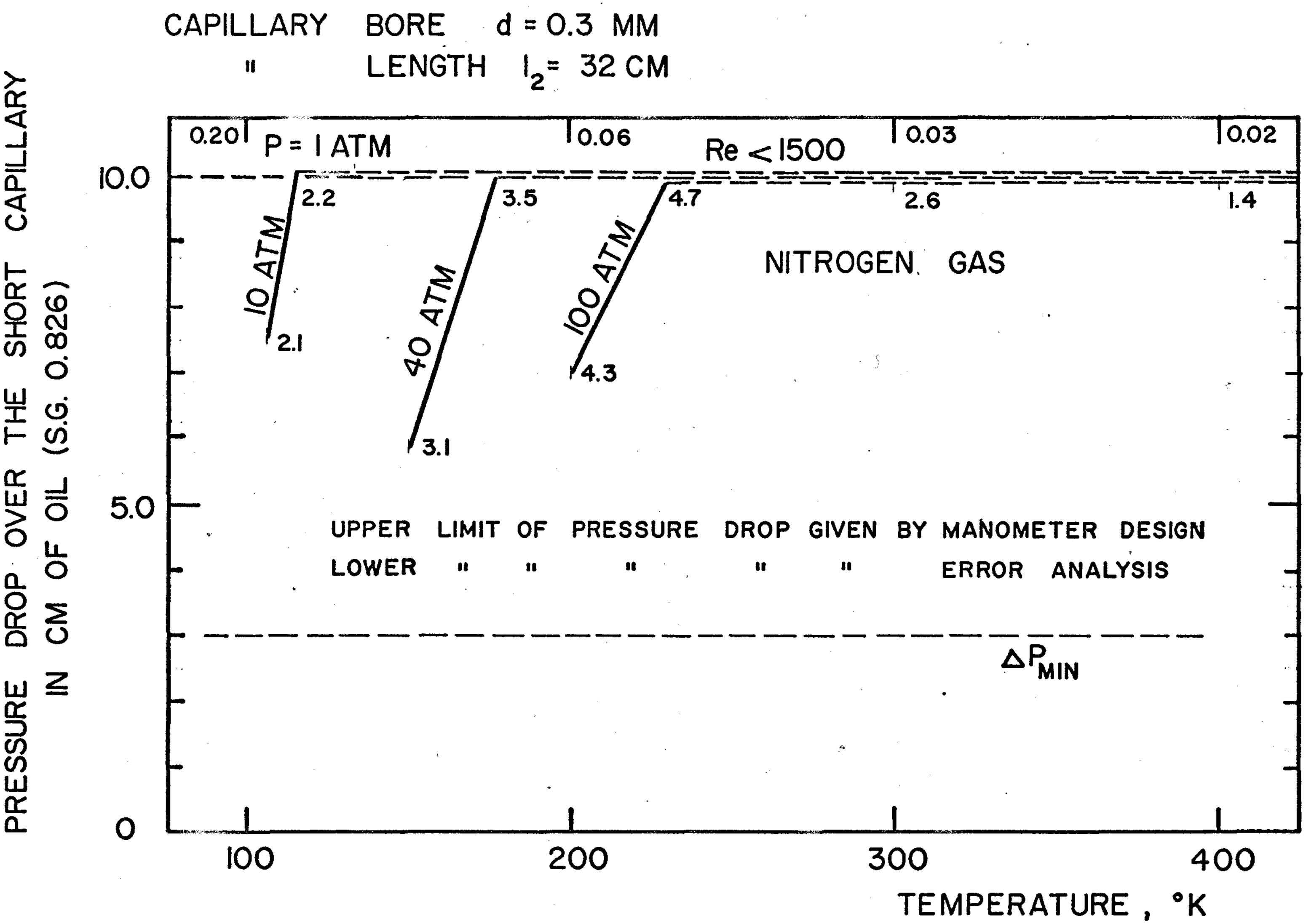


Figure 8. Pressure Drop over the Short 0.3 mm Nominal Diameter Capillary with a Reynolds No. = 1500.

CHAPTER IV

DESCRIPTION OF EQUIPMENT AND INSTRUMENTATION

General Arrangement. The reader is referred to drawings given in Figures 10.- 13. and photographs in Figures 20.- 26., for more detailed information on the design and technology of non standard parts used in the assembly. Both the high pressure and low pressure experimental set-up differ only in few details and are described simultaneously.

The flow diagram shown in Figure 9. is used as a reference in further description of functional aspects of both basic and auxiliary equipment.

The gas under test is supplied from gas bottle 25 to the high pressure vessel via a silica gel dryer 22 at a pressure controlled by regulators 23 and 24, which are selected according to required experimental conditions. It is also intended to install an additional dry-ice or liquid nitrogen cold trap in series with the dryer for better elimination of water vapour and other substances which might block the inlet pipe or vessel connectors during high pressure tests. A stainless steel high pressure vessel together with the viscometer cell was kept at the required temperature,

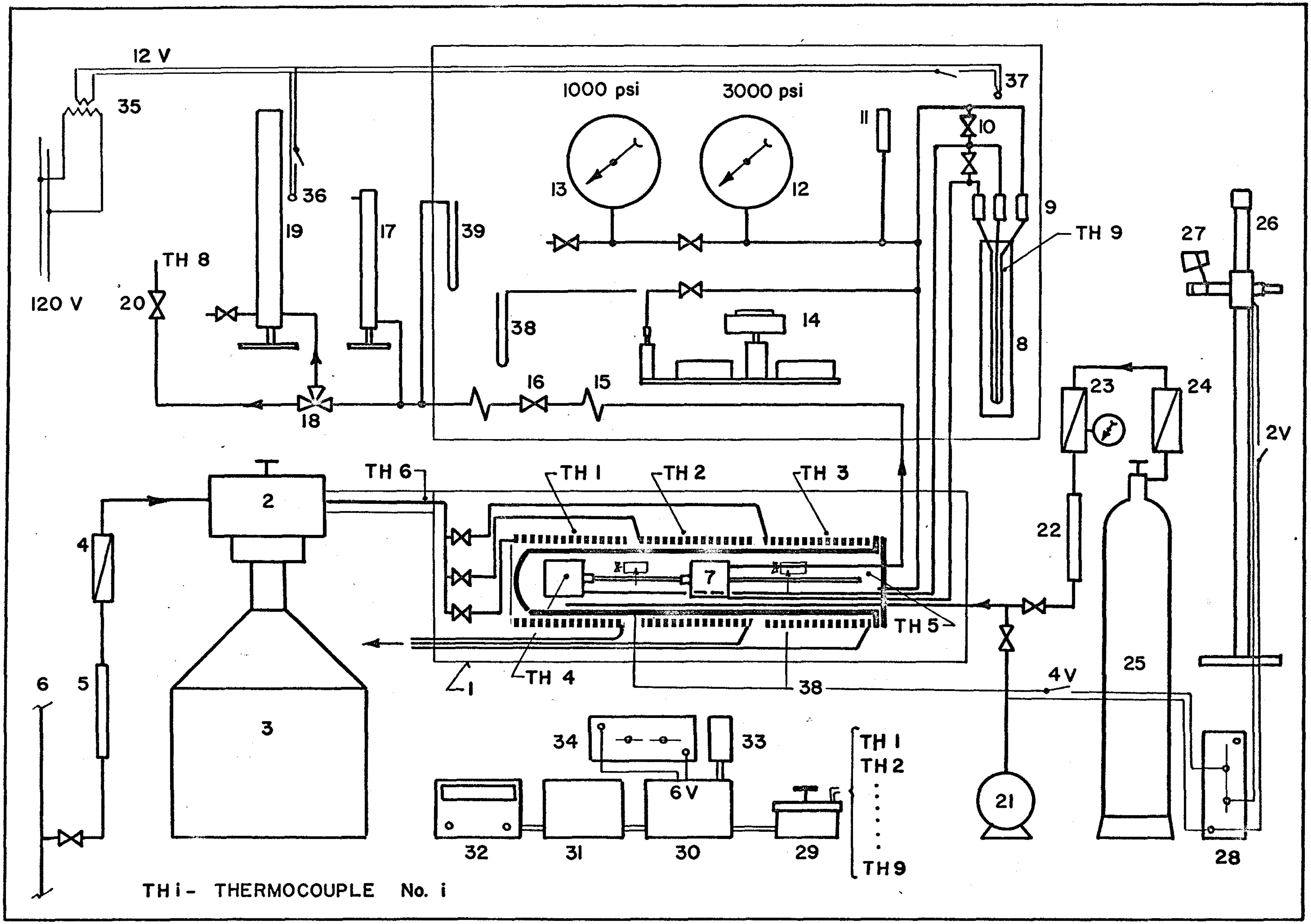


Figure 9. Flow Diagram.

Legend for Flow Diagram

1. Insulating Jacket with Heat Exchanger
2. Coolant Delivery System
3. Liquid Nitrogen Dewar Vessel
4. "Watts" Model M-0125 Air Pressure Regulator
5. Silica Gel Dryer
6. 20 lbf/sq in Air Pressure Line
7. Viscometer Cell with High Pressure Vessel
8. High Pressure Three Limb Differential Manometer
9. Manometer Oil Trap
10. Manometer Bypass Valve
11. "Republic" I9 637B-12-1/8-2 Release Valve Set for 2600 psi
12. "Weksler" Type AA3 High Pressure Gauge, 0 - 3000 psi
13. "Weksler" Type AA3 " " " , 0 - 1000 psi
14. "Chandler" No.23-1 Portable Standard Dead Weight Tester, 50 - 3000 psi, Pressure Intervals 0.1 psi
15. Test Gas Heat Exchanger
16. "Whitey" Type 21 RF2 Micro-regulating Valve
17. "Brooks" Type 1211 1355 Flowmeter with Laboratory Type R2-15-AA Tube with Stainless Steel and Carboloy Float, respectively, used as a temporary meter for high pressure tests
18. Three Way Glass Valve
19. "Brooks" VOL-U-METER Calibrator Model 1053, Capacity 70 c.cm, used for low pressure tests
20. Discharge Control Clamp
21. "Edwards" Vacuum Pump

22. High Pressure Silica Gel Dryer
23. "Matheson" Low Pressure Regulator Model 70, 0 - 30 psi, used for low pressure tests
24. "Matheson" Model 11 High Pressure Regulator, 0 - 30 psi, used for low pressure tests

    "Harris" Model X87 High Pressure Regulator, 0 - 2000 psi, used for high pressure tests
25. Test Gas Bottle
26. "Griffin and George" Cathetometer
27. Cathetometer Spot Light
28. 6V Battery
29. Thermocouple Multiswitch Box
30. "Guildline" Model 9461A Potentiometer
31. "Guildline" Model 9460 Photocell Galvanometer Amplifier
32. "Guildline" Model 9461A Galvanometer
33. "Guildline" 1.01859 V Standard Cell
34. 6V Battery
35. 120/12 V Transformer
36. VOL-U-METER Illumination Light
37. Manometer Illumination Light
38. Mercury U-tube Manometer, used for low pressure tests
39. Oil U-tube Manometer for Pressure Measurement in the VOL-U-METER

and stabilized pressure and temperature of the test gas before it entered the capillaries. The test gas entered the upstream (long) capillary tube directly from the vessel plenum and then passed to an intermediate chamber and entered the downstream (short) capillary. After passing through an exit chamber, the test gas was lead via a microregulating throttle valve 15 to the low pressure displacement Volumeter 19 and then to the atmosphere. Heat exchangers 15 in the exit line brought the test gas to room temperature from any experimental condition.

Pressure drops over the capillaries were measured using a high pressure three limb differential manometer 8, located on the instrument panel. Oil traps were fitted in the manometer lines to avoid oil getting into the line, in the event of a manometer blow-out. The absolute pressure in the vessel plenum was measured using a U-tube mercury manometer 38 for low pressures, and a highly accurate dead weight gauge 14, sensitive to 1 psi, for the high pressure runs. Two standard Burdon-type gauges 1000 psi (13), and 3000 psi (12), were used to indicate the pressure.

The viscometer cell and high pressure vessel were kept at a given temperature by passing an appropriate fluid through the heat exchanger coils, located in an insulating box 1 . Direct evaporation of liquid nitrogen in the heat exchanger coils was used for the low temperature work described in this thesis. The temperature distribution along the viscometer cell was hand-controlled by manipulating the valves supplying the separate coils of the heat exchanger. This simple arrangement worked dependably and produced good results. It is not, however, suitable for use in viscosity measurements when a constant temperature must be kept for a long period, such as for the high pressure measurements over isotherms.

A high precision system was used to measure the thermocouple outputs. This system was composed of "Guildline" Model 9461A Potentiometer together with Model 9460 Photocell Galvanometer Amplifier and Model 9461A Galvanometer. Location of the thermocouples is shown in Figure 9.

The Viscometer Cell and High Pressure Vessel are shown in detail in Figures 10. and 25. The brass end chambers are connected by 1/4" O.D. stainless steel tubes to the outside Swagelok connectors. The whole viscometer cell set-up does not have to be perfectly rigid or aligned as flexible rubber capillary conectors used allow for some misalignment. The connectors also allow for variations of capillary outside diameter, which is not guaranteed by the manufacturer and vary widely about a 6 mm nominal value. The grip exerted by the elastic properties of rubber connecting tubes is replaced, at very low temperatures when rubber

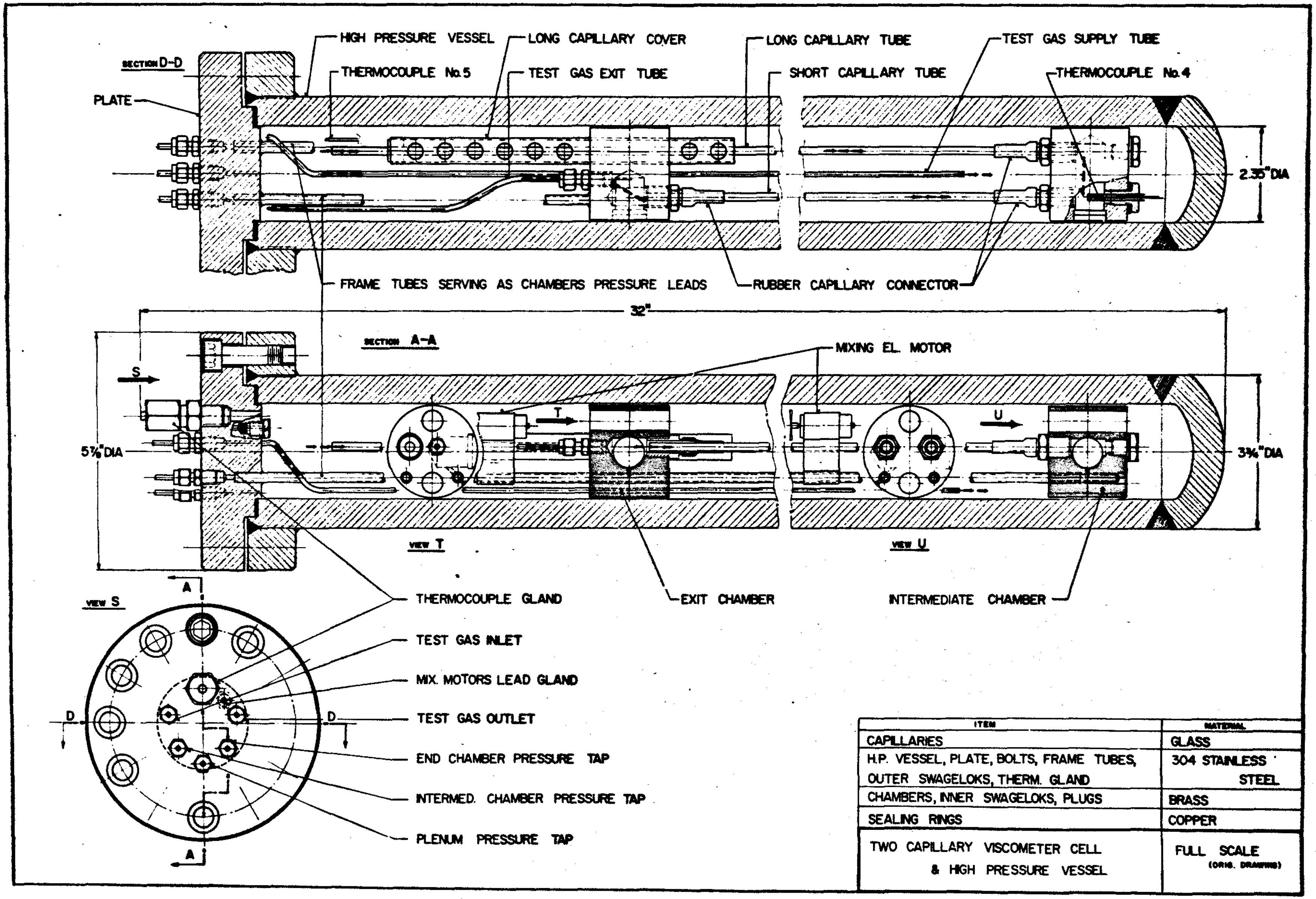
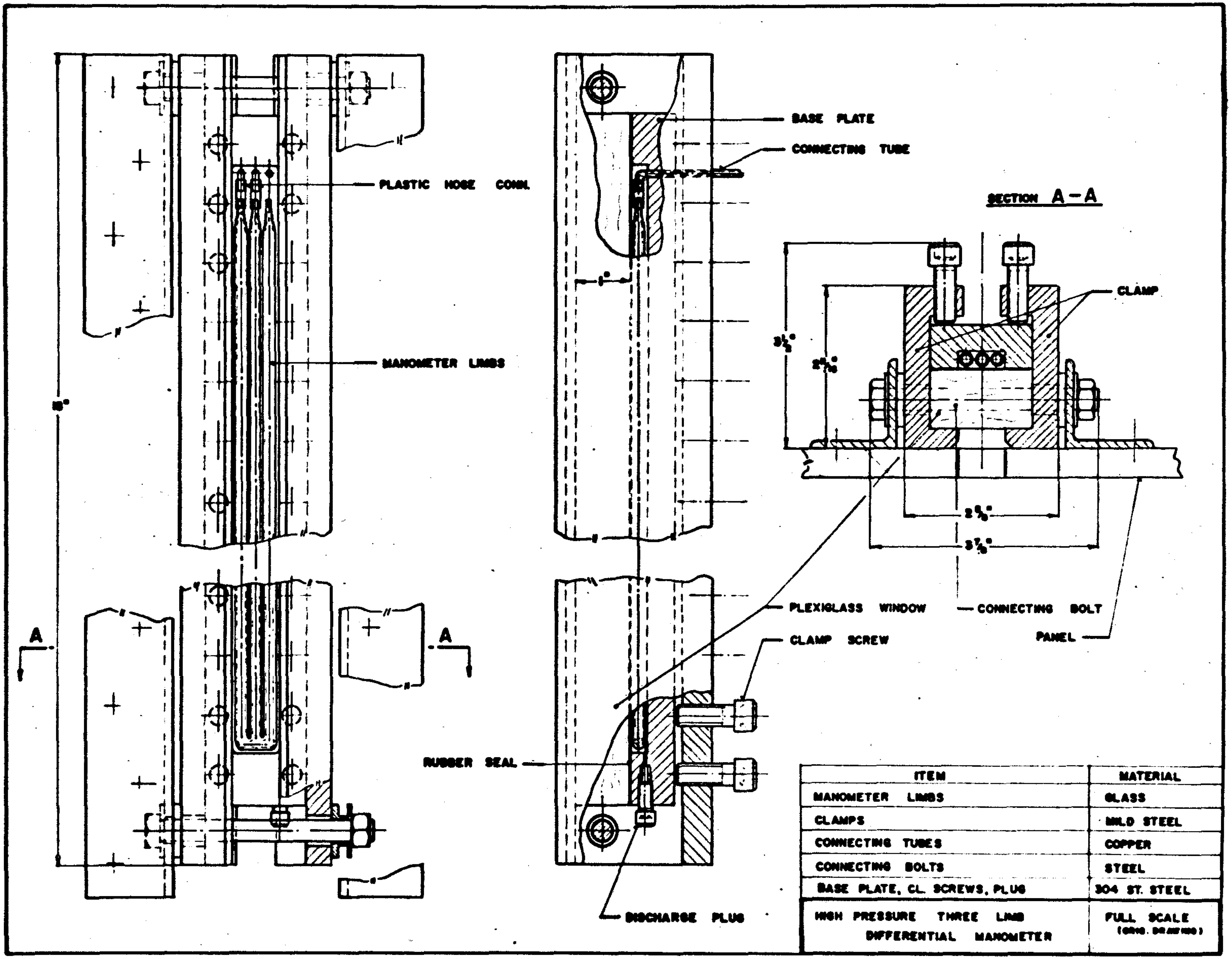


Figure 10. Two Capillary Viscometer Cell and High Pressure Vessel.



ITEM	MATERIAL
MANOMETER LIMBS	GLASS
CLAMPS	MILD STEEL
CONNECTING TUBES	COPPER
CONNECTING BOLTS	STEEL
BASE PLATE, CL. SCREWS, PLUG	304 ST. STEEL
HIGH PRESSURE THREE LIMB DIFFERENTIAL MANOMETER	FULL SCALE (ORIG. DRAWING)

Figure 11. High Pressure Three Limb Differential Manometer.

becomes brittle, by pressure due to thermal contraction. No signs of cracking were detected after the connectors had several times been subjected to the temperature of liquid nitrogen.

Mixing motors, which are installed inside the vessel, could not be used at the very low temperatures but did help in establishing a uniform temperature at about 250°K and higher. All metal joints of the viscometer cell were done using eutectic soft solder, recommended for application at low temperatures. All outer connectors, located in the vessel plate, are stainless steel Swageloks, having pipe threads sealed with teflon tape.

The shapes of cavities of the end chambers were designed such that they are geometrically similar, with respect to location of the capillary exits. Identical flow patterns in both chambers is a necessary condition for the equality of the Hagenbach correction factors, which was assumed in derivation of the working equation in appendix A1.

The High Pressure Differential Manometer is shown in Figures 11. and 25. An oil-in-glass three limb manometer is fitted to a stainless steel back plate and is read through a transparent plexiglass window. The window is sealed to the face of the back plate using 1/32" rubber gasket and is held in place by means of 32 screws located in two steel clamps.

The high precision bore 1/8" I.D. glass tubes of the manometer limbs are about 30 cm long, and were filled with an oil, 0.826 S.G., as the manometer fluid to about 20 cm.

Two of the three limbs are connected, by means of short plastic tubes, to copper lines, which are soldered in the back plate. The third limb is open to the manometer chamber, which is at the working pressure in the high pressure vessel. Both the capillaries and glass manometer tubes are thus not subjected to high pressure.

An overpressurizing of the manometer, as a result of incorrect control of the apparatus, can result only in a blow-out of the oil, either into the oil traps or to the manometer chamber. To cope with the latter problem, a discharge plug has been included into manometer design which makes it possible to clean the manometer without the necessity of dismantling the body. In the case of a blow-out, which is almost unavoidable over a long period, ether was found to be a good solvent for the oil residue for both the oil traps and the manometer chamber.

The manometer, attached to the control panel, is separated from the viewing position by a heavy metal frame with a 1/2" plexiglass window. Also, the cathetometer is equipped with 1/8" aluminium guard. In spite of satisfactory performance during high pressure tests, as described in appendix A6., these safety devices are very important for all high pressure tests,due to the unpredictable behaviour and ageing of plexiglass when submitted to an external load If the manometer is to stay in use for a long period of time, a block of tempered glass instead of plexiglass might be better and more reliable.

<u>Temperature Control Equipment</u> consists basically of the insulating jacket with heat exchanger and the coolant supply equipment.

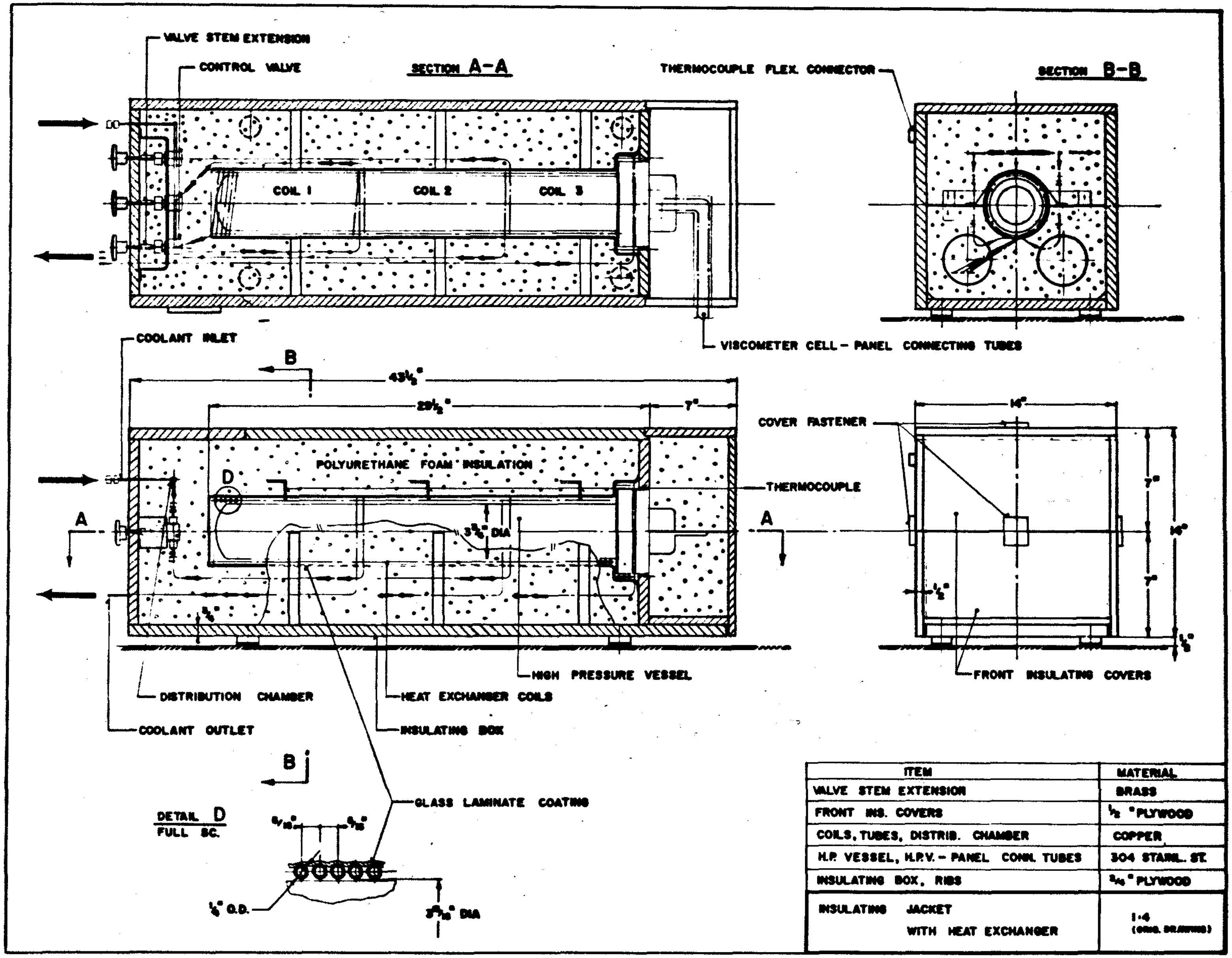
The high pressure vessel is located in the heat exchanger and tightly fits to the 1/4"O.D. copper tube coils. As shown in Figure 12. and photographs in Figures 26. and 27., each of the three coils can be controlled separately by means of the control valve CV, located on a tube connecting the distribution pipe DP with the entrance of each coil. The heat exchange media is supplied via a single supply tube and leaves the system by three separate discharge lines. The heat exchanger and pertinent tubing are located in a wooden box and insulated using low conductivity polyurethane foam. The photograph shown in Figure 27. had been taken before the inner space was filled with foam. In order to obtain the temperature distribution along the viscometer length, a thermocouple was attached to the middle of each coil. A knowledge of temperature distribution along the heat exchanger is particularly important when the coils are used directly as a coolant evaporator, which was the case. If an auxiliary constant temperature bath was used, however, to supply the secondary coolant to the heat exchanger, improved temperature control would be expected, since the coolant and the test gas could be kept at a required temperature. Whereas, the present system uses liquid nitrogen for cooling, and coil temperatures generally differ from that required in the viscometer cell.

The coolant delivery equipment, shown in Figure 13., was designed primarily to work in two possible ways, as follows:

/1/ Liquid nitrogen can be used directly as a coolant and forced into the heat exchanger by pressure regulated dry compressed air.

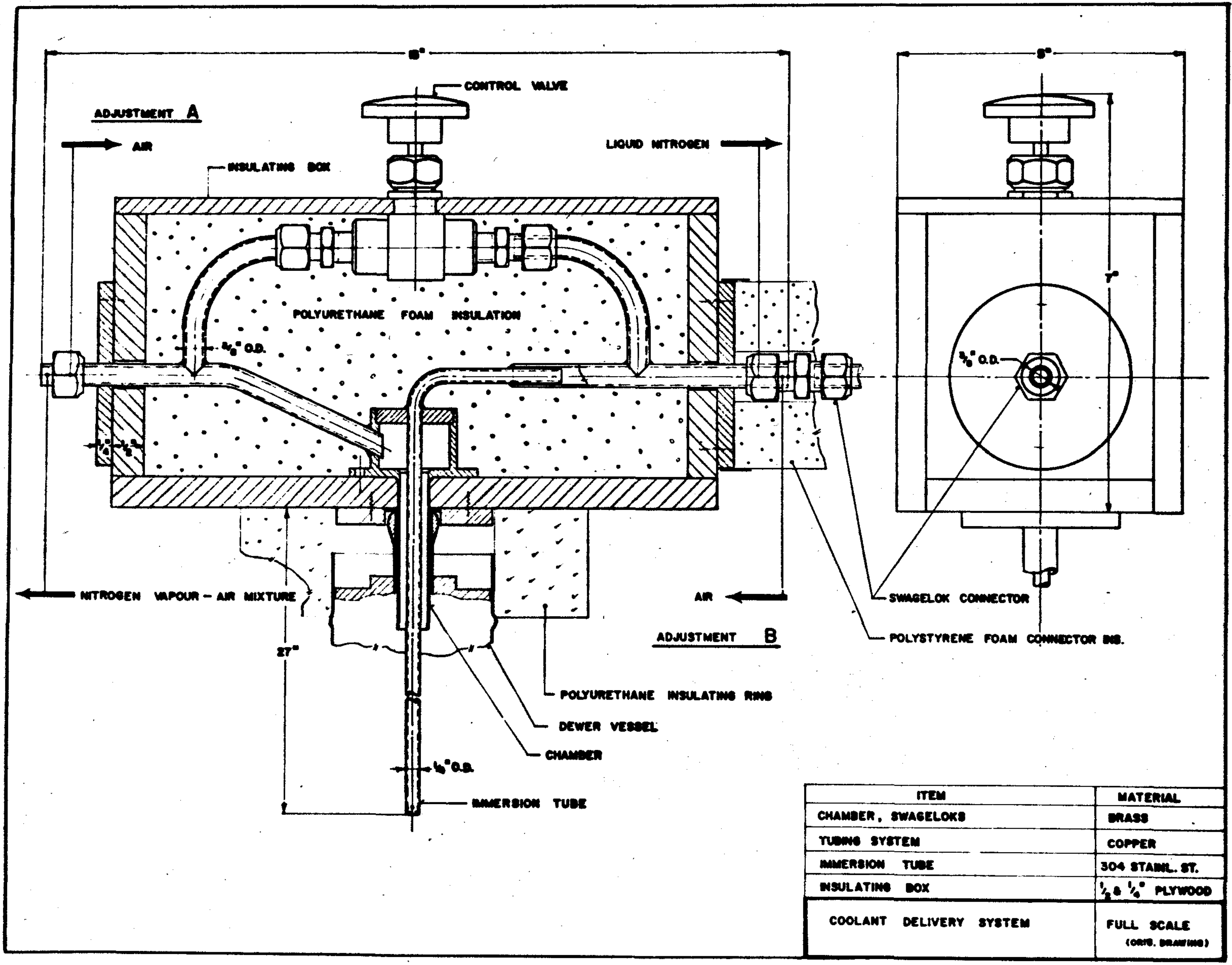
/2/ Dried air can be brought to the Dewar vessel beneath liquid nitrogen level via centrally located immersion tube, thus producing a nitrogen vapour-air mixture as a coolant. The coolant temperature can be controlled by additional mixing with the air, which bypasses the mixing chamber via a control valve.

The latter configuration has not been used during test runs due mainly to the large time constant of the system, and the necessity to design and install a cold trap into the



ITEM	MATERIAL
VALVE STEM EXTENSION	BRASS
FRONT INS. COVERS	½ " PLYWOOD
COILS, TUBES, DISTRIB. CHAMBER	COPPER
H.P. VESSEL, H.P.V. - PANEL CONN. TUBES	304 STAINL. ST.
INSULATING BOX, RIBS	3/4 " PLYWOOD
INSULATING JACKET WITH HEAT EXCHANGER	1:4 (ORIG. DRAWING)

Figure 12. Insulating Jacket with Heat Exchanger.



ITEM	MATERIAL
CHAMBER, SWAGELOKS	BRASS
TUBING SYSTEM	COPPER
IMMERSION TUBE	304 STAINL. ST.
INSULATING BOX	1/2 & 1/4" PLYWOOD
COOLANT DELIVERY SYSTEM	FULL SCALE (ORIG. DRAWING)

Figure 13. Coolant Delivery System.

the compressed air line, after a standard silica gel dryer had proved to be inefficient.

Flow Measurement was achieved by a direct volume displacement method using a high precision "Brooks" VOL-U-METER Calibrator Model 1053 with a total capacity of 70 cm^3 suitable for low volume flow rates from 1 to 120 cm^3/min, which is the range for low pressure viscosity measurements. The displacement of the frictionless mercury ring - sealed piston in a precision glass tube was observed and the time required for this displacement measured using a stop watch. The mass flow rate could thus be determined since the pressure and temperature within the Volumeter were measured simultaneously.

The test gas, discharging from the open viscometer circuit to the atmosphere, was led into the Volumeter by switching the three way glass valve 18 for the required time period. The discharge throttling clamp 20 was adjusted to create a discharge line pressure equal to that observed when using the Volumeter. This was done to decrease the back pressure effect which might disrupt steady state conditions in the transpiration system after the Volumeter has been put into operation. Hand control of the three way valve is not considered to be adequate for higher mass flow rates associated vith high pressure tests and another control arrangement was suggested for this case.

As the mass flow rates of the high pressure runs of this work were beyond the range of the Volumeter available, a standard flowmeter 17, Type 21 RF 2, manufactured by "Brooks Instr.", with a laboratory Type R2-15-AA tube was temporarily installed for those experimental runs. Stainless steel and carboloy floats were employed, respectively, for different flow rates required.

This flowmeter was used as a supplementary equipment since a primary displacement Volumeter with required volume was not available at the time of high pressure tests. The accuracy of high pressure data is lower due to unsufficient precision of the flowmeter as compared with that obtained using the primary Volumeter. This does not signify, however, that the data are worthless.

<u>Temperature Measurement Equipment</u> is described in appendix A5. in the discussion of thermocouple callibration. Location of the thermocouples is shown in Figure 9.

Photograph of the experimental apparatus is shown in Figure 20. The volumeter is located on the left hand side of the panel sill, the dead weight gauge is in the center.

The viscometer cell is firmly connected to the panel instrumentation and is kept constantly in the same position. When access to the viscometer cell is required to check or replace the capillaries, the insulating box with the high pressure vessel is slid back and the viscometer cell supported by wooden blocks, as shown in Figure 23.

The 1/8" O.D. tubes, connecting the panel with the stainless steel Swageloks of the vessel plate, which is submitted to low temperatures, are made of stainless steel. Moreover, pressure lines at the rear of the panel are made primarily of 1/8" O.D. copper tubes connected by means of brass Swageloks.

CHAPTER V

EXPERIMENTAL PROCEDURE

The entire system was first assembled but the viscometer cell was left out of the pressure vessel, as shown in Fig. 23., and metal parts thoroughly cleaned by ether. The capillary tubes were cut to required lengths and cleaned with chromic acid, water, acetone and ether in turn. The tubes were then attached to the chamber connectors with short lengths of rubber tubing, as shown in Figure 10. With the plugs of the intermediate chamber put in place and tightened, the capillary system could then be tested for leaks.

The free end of the long capillary was first connected by a plastic hose to a U-tube filled with mercury, the pressure tap of the vessel plenum was plugged and the throttle valve closed. The resulting constant volume system was then pressurized to six times the maximum expected operating pressure drop over the capillaries and the change of pressure observed for several hours. A fall in pressure indicates a leak in the system and can be estimated from the ratio of pressure change. After the viscometer had proved leakproof, the viscometer cell was inserted into the pressure vessel, the plate bolts were tightened and the front insulating covers put in place. The leak test did not include the high pressure vessel. A small leak in the vessel plate gasket, however, cannot be of any influence on the open circuit viscometer with the flowmeter located downstream of the viscometer cell.

Before use, the viscometer was thoroughly evacuated using a vacuum pump 21, Figure 9., and filled with the test gas at a predetermined pressure. The differential manometer release valves 10 needed to be opened during all pressure changing procedures to relax the excessive pressure differences which might blow out the manometer oil. The valve on the line connecting the viscometer with the U-tube manometer or the dead weight gauge must be closed during evacuation of the viscometer to avoid the penetration of mercury or gauge oil to the pressure lines.

During the actual measurements, liquid nitrogen was brought into the heat exchanger and its flow rate hand-controlled separately for each heat exchanger coil. The throttle valve was adjusted to achieve the required pressure drop over the capillaries when the experimental temperature was close to the required value. As soon as both thermocouples, located in the viscometer cell, showed that an acceptable temperature equilibrium was established, the temperature readings were taken followed by connecting the volumeter into the viscometer circuit. During the time when the volumeter piston traversed the predetermined height, the pressure drops were measured several times. After a period ranging from 90 to 200 sec, according to experimental temperature, a time reading was taken and the temperature within the viscometer measured again to allow the estimation of the average test temperature. All other important readings such as atmospheric conditions etc., as listed in the appendix A3., were taken after each run.

Apart from good insulation of the heat exchanger and temperature-relaxing effects within the vessel, it took a considerable care to establish the temperature equilibrium simultaneously with an acceptable temperature distribution. The system was usually run for at least four hours before the apparatus was sufficiently stabilized to take any valid experimental readings. A good stability of the system during the tests results in a decrease of the experimental scatter of the viscosity.

CHAPTER VI

OPERATIONAL TEST OF THE VISCOMETER

1. Precision Test at Different Mass Flow Rates

The equation governing a flow in the viscometer has been derived assuming that both the Hagenbach and Couette correction factors would be eliminated. However, it has been observed many times in viscometry that at least some of the simplifying assumptions made in the theoretical derivation of working equations may be violated under the conditions prevailing in practical measurements.

In the present case it was assumed that there was flow similarity at the ends of both capillaries. This assumption was checked by a series of experiments carried out at different mass flow rates. Five readings were taken for a given mass flow rate, which was varied systematically from 0.145 to 0.283×10^{-3} gm/sec at the temperature of 294.88 °K and atmospheric pressure. The resulting calculated viscosities indicated no particular divergence trend if plotted versus mass flow rate, as shown in Figure 14. As this is the only isothermal viscosity run for nitrogen where the flow was varied in the systematic manner, an attempt has been made to determine the values of Hagenbach correction factors of both capillaries using a graphical extrapolation of the Poiseuille viscosities to zero mass flow rate. Because of the sensitivity of this type of plot on the Hagenbach correction terms, the trend of the data was obscured by the experimental scatter. However, similar experiment will be repeated at higher pressures where an influence of kinetic energy correction is more pronounced.

The experimental values of this test were assessed using a statistical approach to indicate precision of the apparatus at perfect temperature equilibrium. The standard deviation of a set is taken as

$$\mathrm{STDEV} = \sqrt{\sum_{i=1}^{n} \frac{(\eta_i - \eta_{mean})^2}{n}} \qquad /4/$$

where η_{mean} is a mean arithmetic value of a set of n measurements.

The fractional mean deviation is taken as

$$\mathrm{FMDEV} = \frac{1}{n} \sum_{i=1}^{n} \frac{\eta_i - \eta_{mean}}{\eta_{mean}} \times 100, \quad \% \qquad /5/$$

The scatter of the viscosities for the isothermal test is small when compared to the scatter of the actual runs carried out over the temperature range, such as that shown in Figure 17. This indicates, to some extent, the effect of random

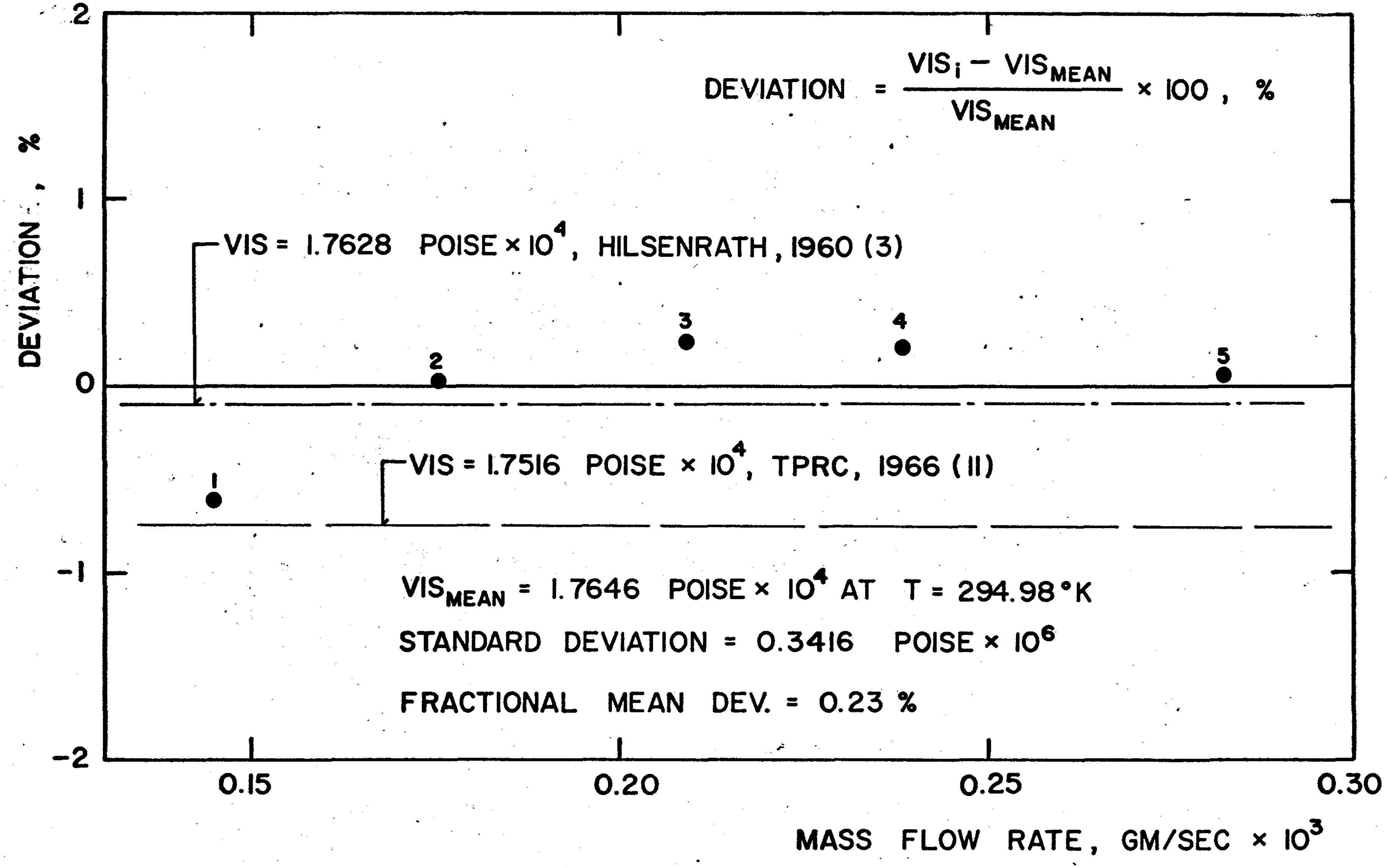


Figure 14. Experimental Scatter of Nitrogen Viscosity Measurements Taken at Different Mass Flow Rates for Low Pressure and Constant Temperature.

errors due to control of the viscometer temperature.

The average of the five test points is 0.74 % above the viscosity recommended by TPRC /11/ but only 0.1 % above that correlated by Hilsenrath /3/, as shown in Figure 14.. This may possibly indicate a small systematic error of this present work.

2. Effect of Instability of Mass Flow Rate on Viscometer Performance

The working equation of the viscometer is based on the form of Hagen-Poiseuille law which assumes the steady state operation of the system. It is rather difficult to determine whether a stability has been achieved in an experimental run. There is always the possibility of small perturbations in the flow which can be indicated by fluctuations of pressure drops. This present viscometer has shown good stability and maintained a steady-state flow, since the pressure drops over the capillaries did not fluctuate more than ±0.01% during the five isothermal test runs, described above. Furthermore, the fluctuations did not exceed ±0.1% during other experimental runs when they was possibly influenced by temperature instability. The small and slow oscillations are believed not to have any measurable effect on the accuracy of the results, but can certainly influence the experimental precision.

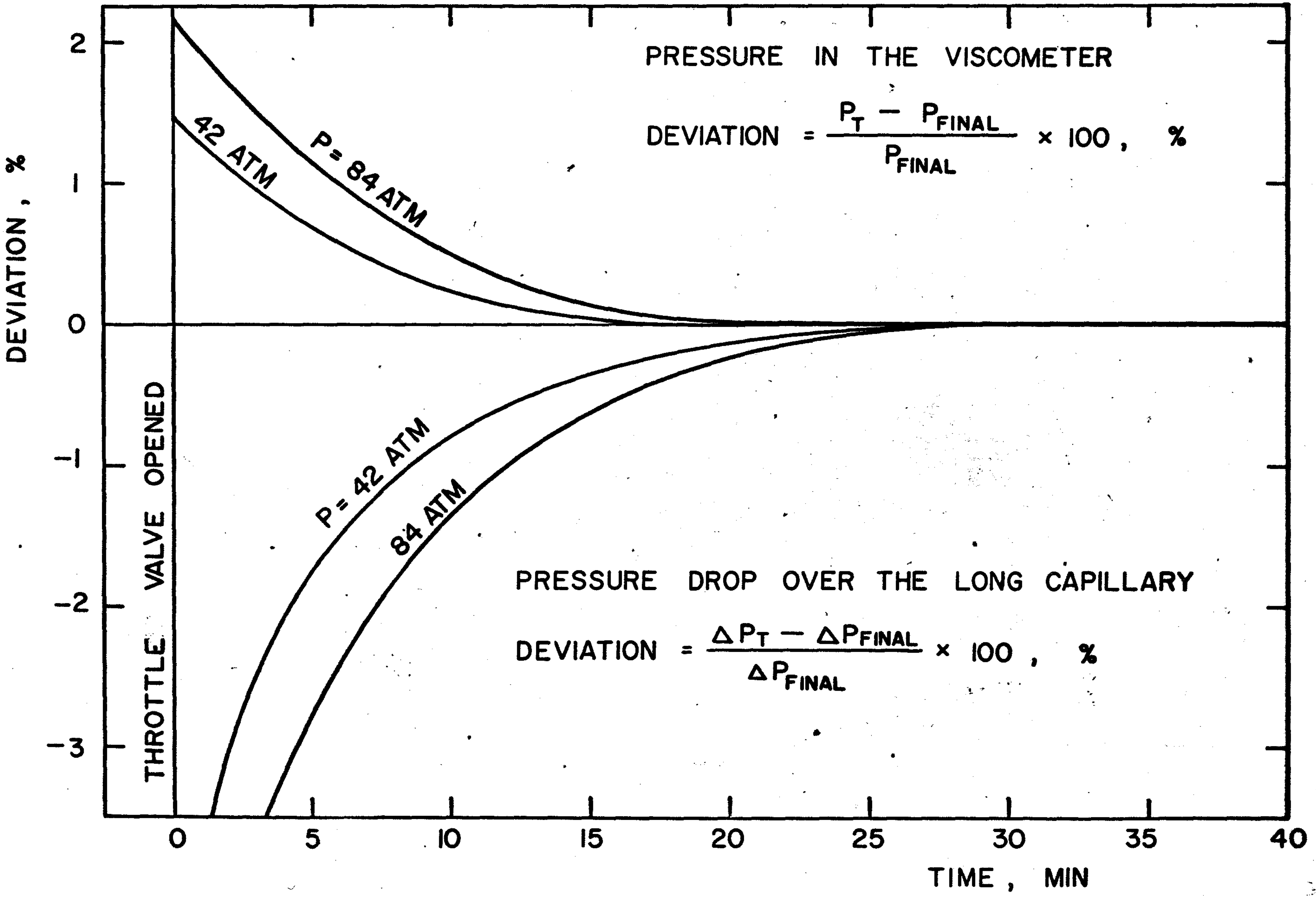


Figure 15. Time for Establishment of Steady State Flow Conditions in the Viscometer at Different Operating Pressures.

During low pressure tests, only a small stabilization time, of only several seconds after the throttle valve adjustement, was observed. This quick response, due mainly to the "narrow band" low pressure regulator and small capacity of the transpiration system, was not observed during high pressure runs when a considerable time was required for the relaxation process. This unwanted dynamic behaviour was caused by response characteristic of the simple high pressure regulator which was employed for high pressure experimental runs. The downstream pressure of the regulator is conditioned by the mass flow rate and any re-adjustment of the throttle valve is followed by a pressure relaxation within the system. A plot of the transient characteristic for nominal pressures of 42 and 84 atm is shown in Figure 14.

A possible method of controlling the pressure fluctuation is to use the dead weight testor as a feed-back regulator, or to use a better spring pressure regulator.

CHAPTER VII

RESULTS AND DISCUSSION

1. Results

Experimental absolute viscosity values for dilute nitrogen, measured in this work over the temperature range from 97.41 to 294.88°K,which are presented in Table 1., were correlated using a semi-theoretical data smoothing approach,based on Enskog's collision theory for dilute gases and the results correlated to those by other investigators, as listed in Table 2.

Also viscosities of nitrogen were measured at pressures of 42.28 and 83.99 atm and at room temperature, using a standard rotameter to estimate the flow rate, which possibly gives less accurate results than the Volumeter used for the low pressure tests.

2. Data Smoothing

It was decided not to use any of empirical correlations, which often produce good but physically unjustified fit of an experimental data.

Presently, the rigorous kinetic theory of gases provides the best mathematical expressions relating the theoretical conclusions with experiments. The viscosity of a dilute gas can be calculated from the equation

$$\eta = 266.93 \frac{\sqrt{M \;\; T}}{\sigma^2 \; \Omega^{(2,2)*}} , \qquad (\text{gm/cm sec}) \; 10^7 \qquad /6/$$

provided that a suitable intermolecular potential function has been found to calculate the collision integrals $\Omega^{(2,2)*}$. In the equation M is the molecular weight, T is the absolute temperature in °K and σ is the low-velocity collision diameter in Å which is the distance at which the intermolecular potential is zero.

In this work, since nitrogen is a non polar gas, the collision integrals based on the Lennard-Jones (6-12) potential function were used because this empirical potential has been found to accurately describe the force interaction between molecules of simple gases. The L-J(6-12) potential was used in a form

$$\varepsilon(r) = 4 \;\; \varepsilon \;\; \left[(\sigma/r)^{12} - (\sigma/r)^{6} \right] \qquad /7/$$

In this equation, which defines the potential energy of interaction between two molecules at distance r, ε is maximum energy of attraction and σ is the low-velocity collision diameter.

The results of this theory, however, are applicable only to dilute gases, which can be defined as those whose properties are completely determined from the mechanism of binary collisions between the gas molecules. A study by Childs and Hanley /19/, analysing the dependence of mean free path of gas molecules on pressure and temperature, had shown that nitrogen may be considered as a dilute gas over relatively broad pressure range and its absolute viscosity is, therefore, independent of density.

The collision integrals $\Omega^{(2,2)*}$ which were used in all the the calculations of this work were obtained from Hirschfelder's work /29/ which tabulates $\Omega^{(2,2)*}$ as a function of the reduced temperature $T_{6-12} = T/(\varepsilon/k)_{6-12}$, where ε/k_{6-12} is the energy parameter of the L-J (6-12) potential function, k is the Boltzman constant.

Unfortunately, there appears to be no unique value for the length parameter σ and energy parameter ε/k_{6-12} which will result in a perfect fit of experimental data over a wide temperature range. This may be due to the inadequacy of the molecular model or the sensivity of this approach to the experimental accuracy, but is more likely to be due to the former reason.

Hirschfelder /29/, using certain available viscosity data for nitrogen at that time, obtained values of L - J potential parameters of $\sigma = 3.681$ Å and $\varepsilon/k_{6-12} = 91.46$°K. The parameters, when used to generate temperature dependent

TABLE 1. EXPERIMENTAL LOW TEMPERATURE ABSOLUTE VISCOSITY DATA OF THIS WORK (1969-70) FOR NITROGEN

LOW PRESSURES

TEMPERATURE, °K	VISCOSITY, POISE*10^4	CAPILLARIES NO.
97.41	.6623	1, 3
123.42	.8283	1, 3
142.28	.9675	1, 3
155.11	1.0292	1, 2
179.78	1.1902	1, 2
219.15	1.3896	1, 2
251.57	1.5434	1, 2
262.38	1.6184	1, 2
292.02	1.7449	1, 3
294.88	1.7644	1, 2

HIGH PRESSURES

ABSOLUTE PRESSURE 42.28 ATM

293.97, °K	1.824, POISE*10^4	1, 3

ABSOLUTE PRESSURE 83.99 ATM

294.88	1.983	1, 3

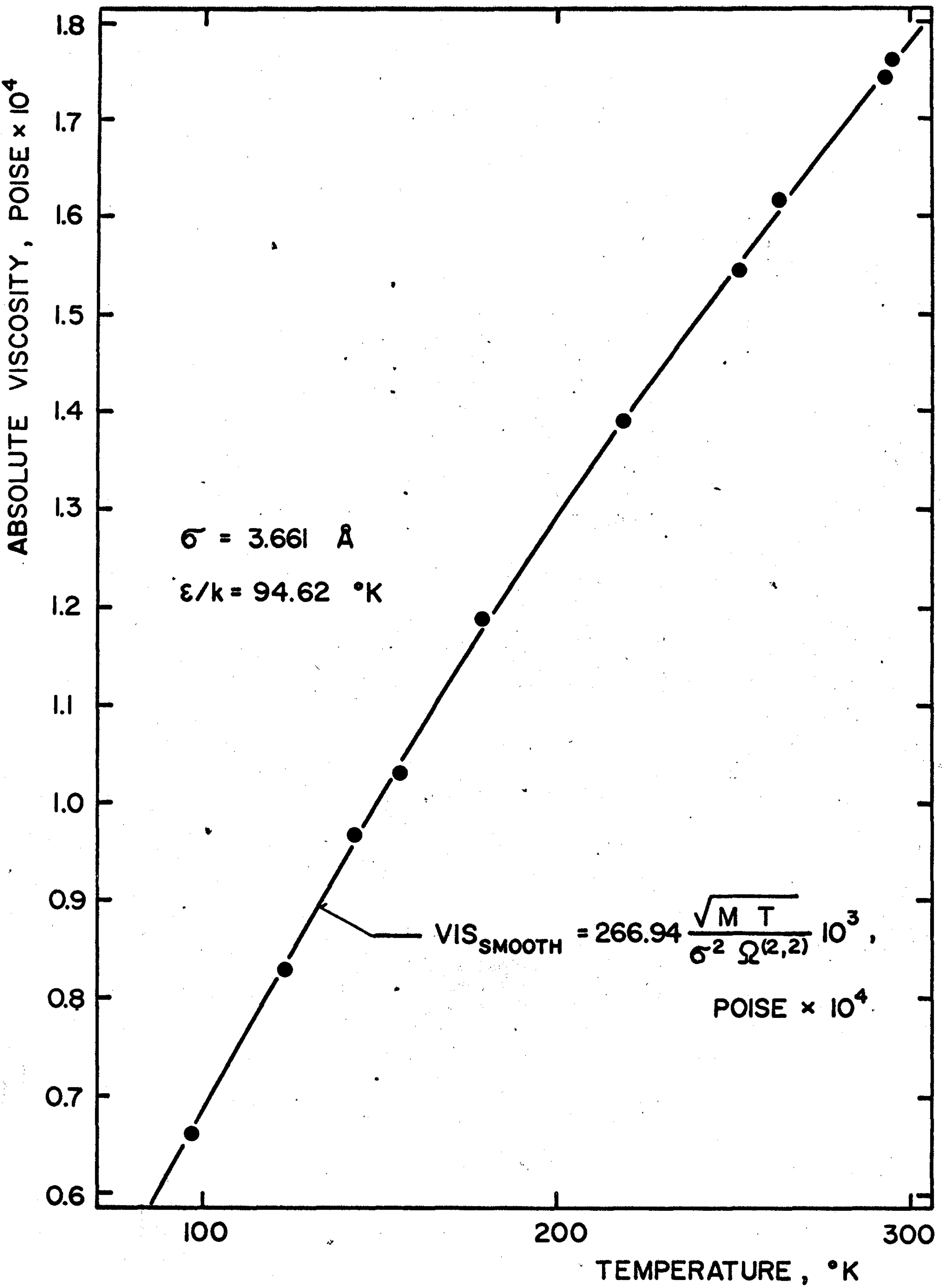


Figure 16. Experimental Low Pressure Nitrogen Viscosity Data of this Work Fitted to a Curve Based on the Collision Theory.

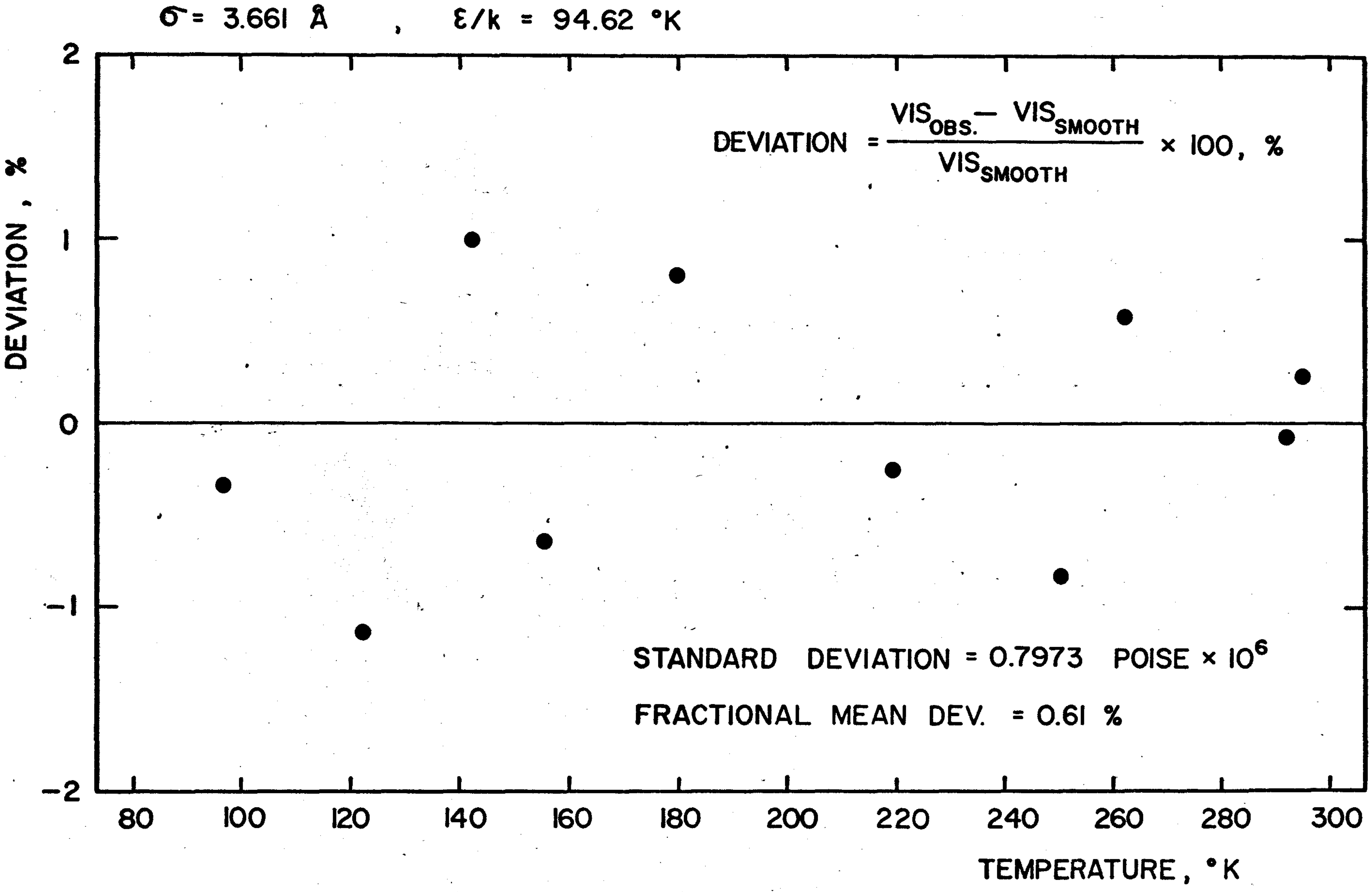


Figure 17. Deviations of the Experimental Low Pressure Viscosity Data of this Work from the Smooth Curve for Nitrogen.

nitrogen viscosity data reproduce the experimental data extremely well within the reduced temperature range given approximately by

$$1.2 < T^*_{6-12} < 6.5 \quad ,$$

as found by Childs and Hanley /19/, but show systematic deviation as much as -4.5 % at $T^*_{6-12} = 14.5$ which is the maximum value for the experimental data.

A smooth curve given in a general form by equation 6. was first fitted to the experimental data of this work and the potential parameters $\sigma = 3.661$ Å and $\varepsilon/k_{6-12} = 94.62$ °K were found to give an optimal fit. A graphical comparison of the computed viscosities with the experimental values is shown in Figures 16. and 17. . Only one point lies more then 1 % from the smooth curve. A fractional mean deviation and a standard deviation of the fit were found to be 0.61 % and 7.973 poise$\times 10^7$, respectively. Both types of deviation were used as statistical means for evaluation of the experimental precision and are basically defined by equations 4. and 5. . The trend of the experimental data is in good agreement with the generated curve.

The departures of the experimental results by other investigators from the smoothed curve, based on the data of this work , were computed and are plotted in Figure 18. .

TABLE 2. EXPERIMENTAL LOW TEMPERATURE ABSOLUTE VISCOSITY DATA OF OTHER INVESTIGATORS USED IN THE CORRELATION FOR DILUTE NITROGEN

	TEMPERATURE, °K	VISCOSITY, POISE*10^4
VOGEL,1914(9)	81.60	.5600
	273.15	1.6780
TRAUTZ+BAUM.,1929(31)	195.65	1.2730
	196.85	1.2750
	232.75	1.4640
	235.25	1.4650
	289.25	1.7280
	290.95	1.7350
JOHNSTON,1939(29)	90.17	.6314
	118.26	.8164
	130.82	.8924
	140.98	.9547
	155.56	1.0418
	169.40	1.1225
	184.72	1.2100
	200.16	1.2982
	215.75	1.3808
	229.88	1.4535
	245.19	1.5313
	260.13	1.6030
	273.21	1.6650
	285.08	1.7195
	300.05	1.7849
VASILESCO,1945(7)	90.20	.6156
	194.76	1.2600
	273.10	1.6637
CLARKE+SMITH,1967(12)	114.35	.7660
	134.40	.9000
	152.50	1.0120
	176.00	1.1540
	200.90	1.2960
	225.70	1.4310
	252.30	1.5620
	272.45	1.6610
	299.10	1.7860

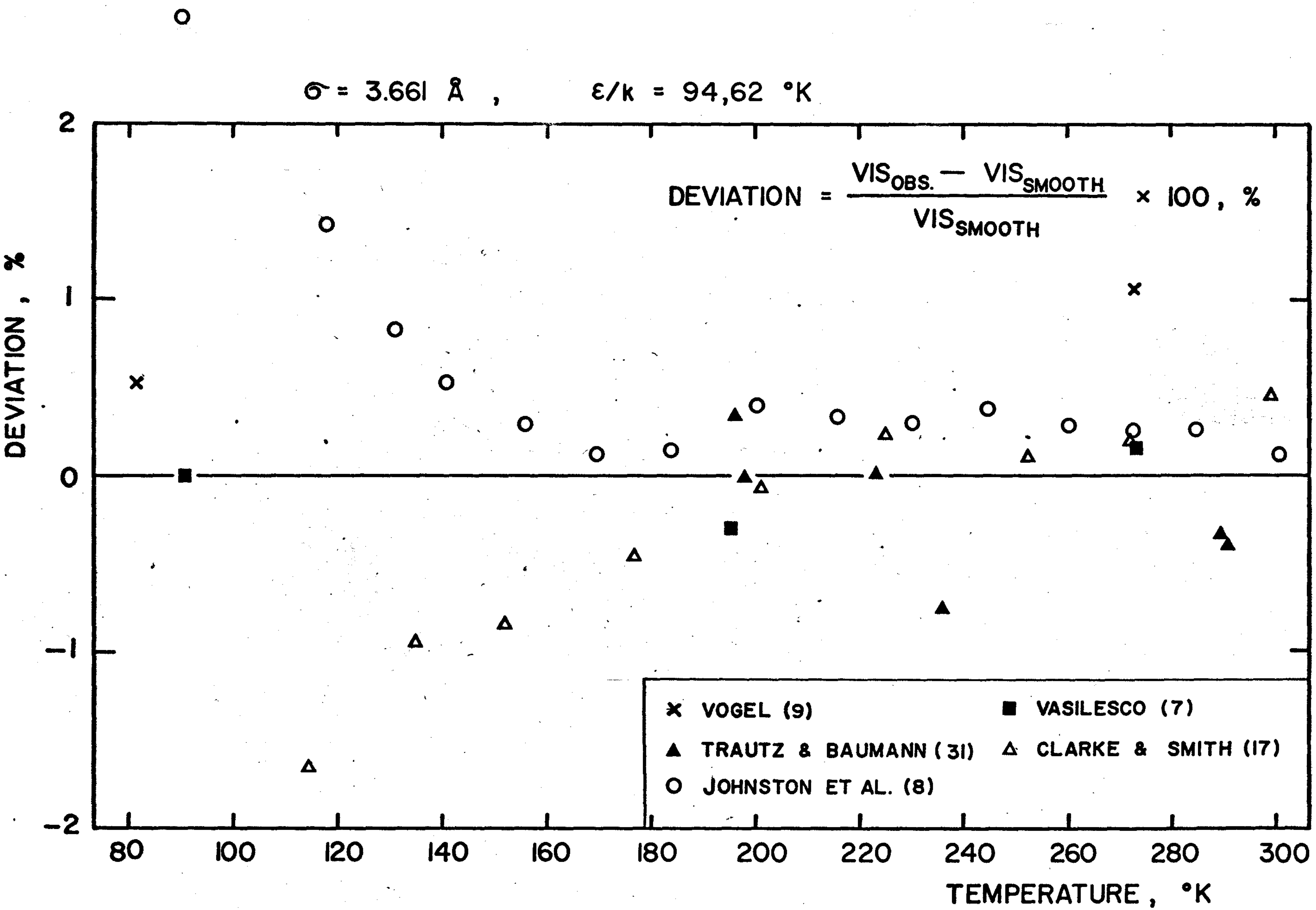


Figure 18. Deviations of the Experimental Low Pressure Viscosity Data from the Smooth Curve Fitted to the Data of this Work for Nitrogen.

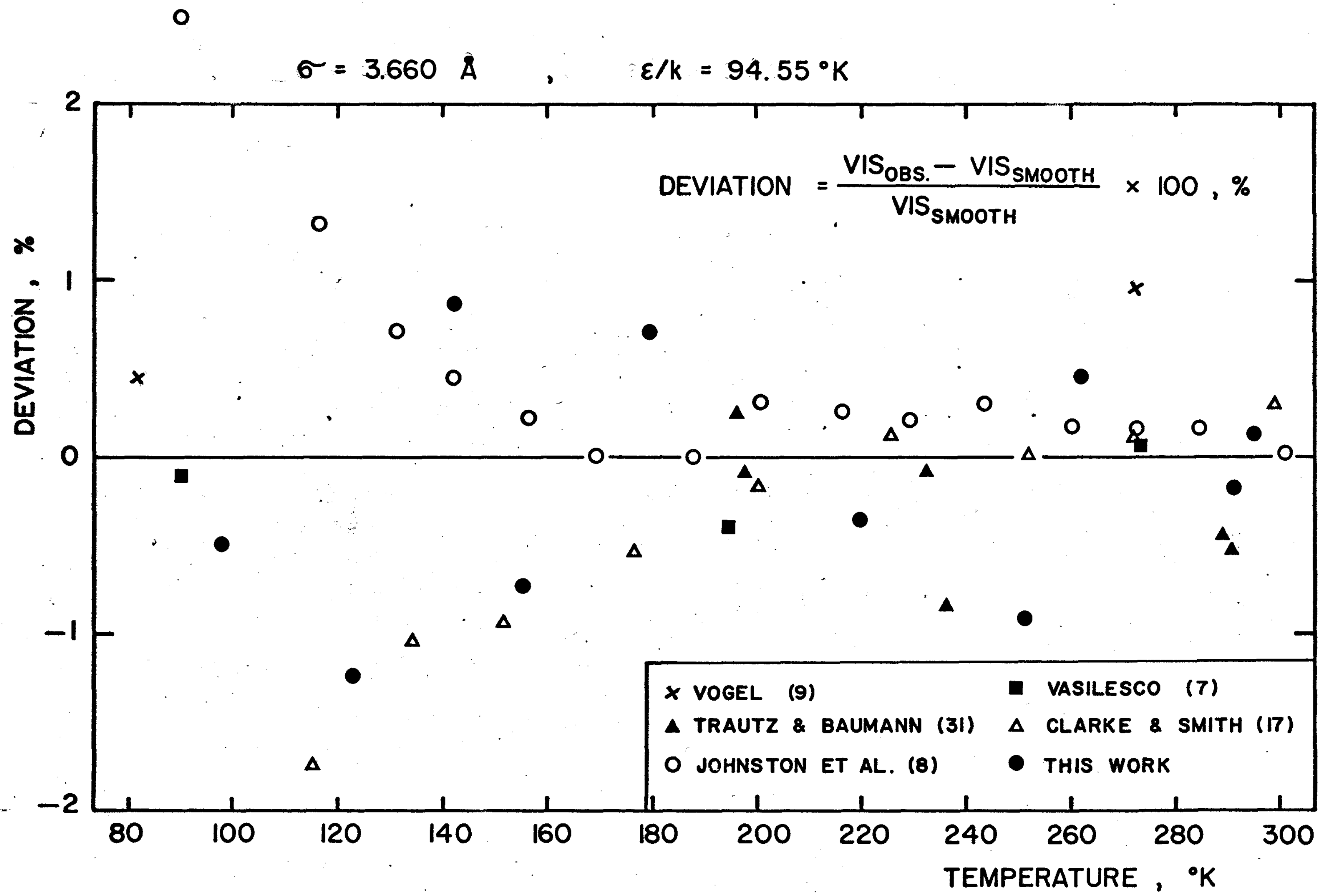


Figure 19. Deviations of the Experimental Low Pressure Viscosity Data from the Smooth Curve Fitted to Combined Data for Nitrogen.

The data at temperatures above 170°K are in relatively good agreement with the results of this work and seem to confirm the error estimation given in app. A2. A systematic deviation of Johnston's data from those of Clarke and Smith, mentioned in the literature survey of this work, appears below 170°K.

Contrary to the doubts expressed by Clark /17/ as to validity of the theory used by Johnston /8/ for his oscillating-disk experiments, the results of this work do not agree with either of Johnston, or Clarke and Smith but lie somwhere between their values and are in good agreement with the low temperature viscosity points presented by Vogel and Vasilesco, respectively.

An attempt has been made to obtain the smoothed low temperature viscosities for dilute nitrogen, based on all information available, and the combined data of all the works, listed in Tables 1. and 2., were treated together and correlated using a semi-theoretical fit based on the collision theory. The resulting smoothed curve gave potential parameters of the L - J (6-12) potential of $\sigma = 3.660$ Å and $\varepsilon/k_{6-12} = 94.55$°K. The deviation plot of the combined data from the smooth curve is shown in Figure 19. . A fractional mean deviation and a standard deviation of this fit are 0.51 % and 7.09919 poise$\cdot 10^7$, respectively. No corrections were applied to bring the results obtained using secondary methods, which were based on the dry air viscosity, to a standard conditions.

It is obvious from the comparison of deviation plots shown in Figures 17. and 18. that the smoothed nitrogen viscosity data of this work lie about 0.1 % below those of the combined works over the whole temperature range.

The parameters of L - J (6-12) potential, which were presented in this chapter, are not claimed to be optimal values for dilute nitrogen despite relatively good agreement with the experiments, even at the highest temperatures. These values were used to correlate the nitrogen low temperature viscosity data by the best non-empirical means presently available. The parameters were computed by the direct search optimization method using CDC 6400 digital computer.

3. Previous Correlations

Two recent correlations of nitrogen viscosity data were used for comparison in the low temperature region.
A graphical comparison of the viscosity data for dilute nitrogen by Hilsenrath /3/ together with those by TPRC /11/ and the smoothed data recommended in this work are presented in a deviation plot in Figure 20..

The correlation by TPRC was based on a purely empirical approach using polynomials of 3rd order to fit the experimental data. At low temperatures a fitted polynomial very

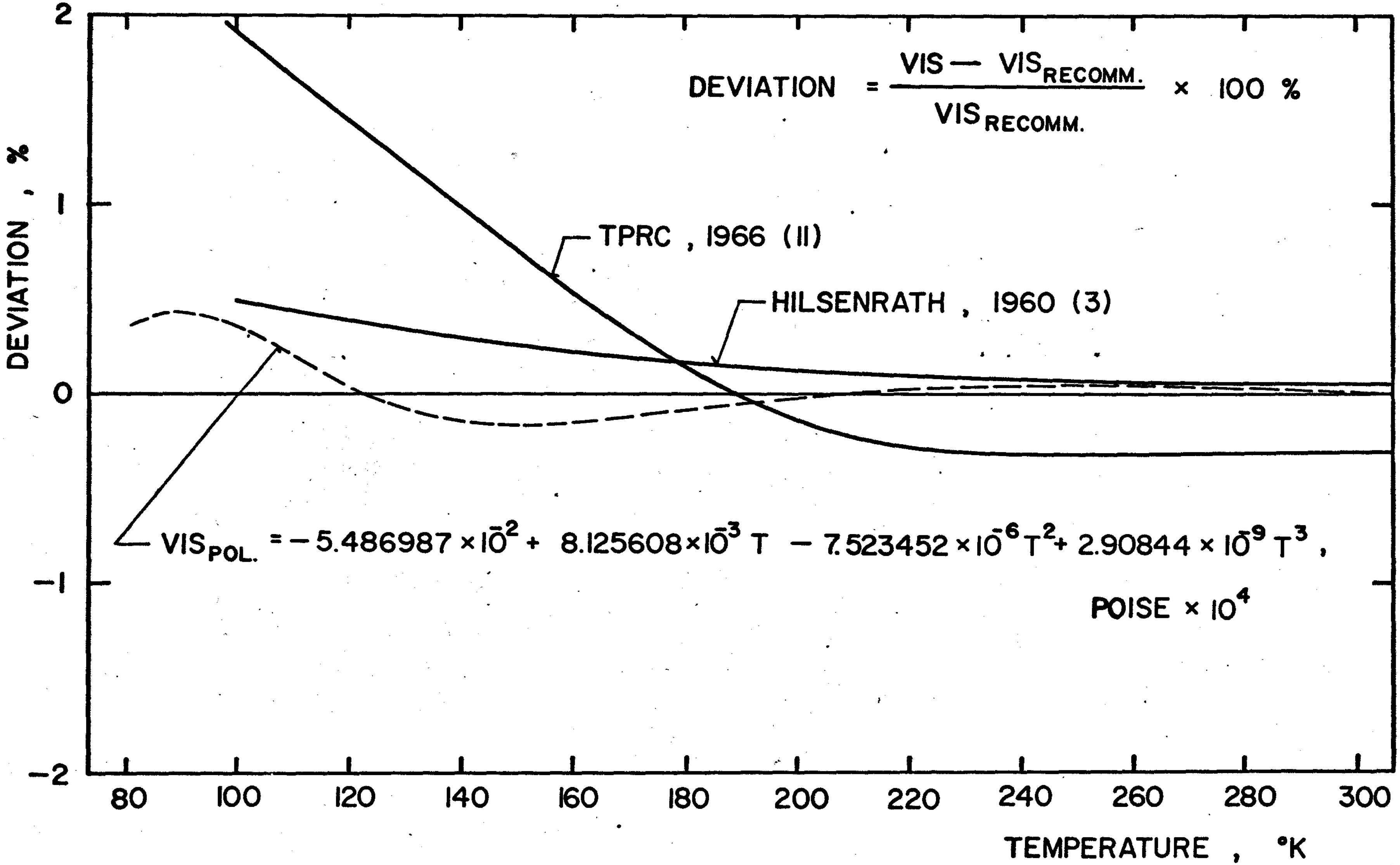


Figure 20. Deviations of Available Correlated Low Pressure Nitrogen Viscosity Data from the Smoothed Recommended Data.

nearly follows Johnston's data which were considered to be of reasonably good precision.

Hilsenrath used Hirschfelder's potential parameters of $\sigma = 3.681$ Å and $\varepsilon/k_{6-12} = 91.46$ °K to calculate the viscosity values for nitrogen at low temperatures. His values are in very good agreement with the correlations of this work, for room temperatures, but show a systematic positive departure as the temperature decreases. The deviation is caused by the influence of the most recent data obtained by Clarke and Smith, and those of this work, which could not be considered in Hilsenrath's correlation.

A polynomial of 3^{rd} order was fitted to the combined data treated in this work and is presented in the deviation plot given in Figure 20.. The fluctuation of this fully empirical plot is obvious.

The high density viscosity values, listed in Table 1. for pressures $p = 42.28$ and 83.99 atm,were found to be 0.3 % and 3.5 % higher then those interpolated from Hilsenrath's correlation /3/.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

1. Experimental Results

/1/ Experimental absolute viscosities of dilute nitrogen were measured in the temperature range from 97.41 to 294.88°K and correlated with the contradictory previous results. On the basis of the correlation, based on the theoretical work of Enskog, a set of data was recommended for the absolute viscosity of dilute nitrogen at low temperatures and is given in Table 3.

/2/ The viscosity of nitrogen at 273.15°K was found to be $\eta_0 = 1.6617$ poise$\times 10^{4}$, which is consistent with the recommended values and agrees, within the experimental accuracy, with the values $\eta_0 = 1.6625$, given in Hilsenrath s correlation, and with the value $\eta_0 = 1.6645$, which is the mean of direct experimental determinations at standard conditions.

/3/ Estimated accuracy of the smoothed data of this work is ±1.0% at the ice-point temperature and ±1.65%

TABLE 3. RECOMMENDED VALUES OF ABSOLUTE VISCOSITY OF DILUTE NITROGEN IN LOW TEMPERATURE REGION

TEMPERATURE, °K	VISCOSITY, POISE*10^4
80.00	.5456
90.00	.6149
100.00	.6833
110.00	.7506
120.00	.8169
130.00	.8804
140.00	.9446
150.00	1.0065
160.00	1.0670
170.00	1.1259
180.00	1.1831
190.00	1.2393
200.00	1.2935
210.00	1.3472
220.00	1.3995
230.00	1.4511
240.00	1.5014
250.00	1.5505
260.00	1.5993
270.00	1.6469
273.15	1.6617

at the least favourable condition corresponding to a temperature of 100°K. The recommended viscosity values are believed to have an accuracy of better than ±1.0% over the whole temperature range.

2. Experimental Apparatus

/1/ The viscometer has proved to be suitable for use at low pressures and moderate pressures of up to 100 atm.

/2/ The experimental scatter is primarily larger than for a one-capillary viscometer due to more complex difference-form of the working equation involving more variables which are influenced by random errors. The fractional mean deviation of five experimental readings, taken at perfect temperature equilibrium, was 0.23 % whilst that of ten individual measurements taken over the temperature range was 0.61 % with all but one point within ±1.0 %. However, the accuracy is felt to be better than that possible with a secondary or single capillary apparatus.

/3/ Comparing the experimental precision of this work with that by Clarke and Smith /17/ , where all experimental points lie within ±0.25 % from the empiric smooth curve, it must be considered that each of viscosity values, presented by these investigators, represent the mean of five to ten individual measurements at the same temperature and that the influence of random errors, which are the primary cause of experimental scatter, were to a great extent eliminated by this averaging.

/4/ It is suggested that improved precision may be obtained by using a constant temperature bath for the coolant fluid. This would enable the viscometer to be held and used at a given temperature for larger period and thus guarantee an improved stability.

/5/ An improvement of pressure control, as used during the verification measurements at high pressures, would decrease the time constant of the system and accelerate experimental procedure. The derivation of a control signal from the dead weight gauge might be one of the principles of improved pressure regulation.

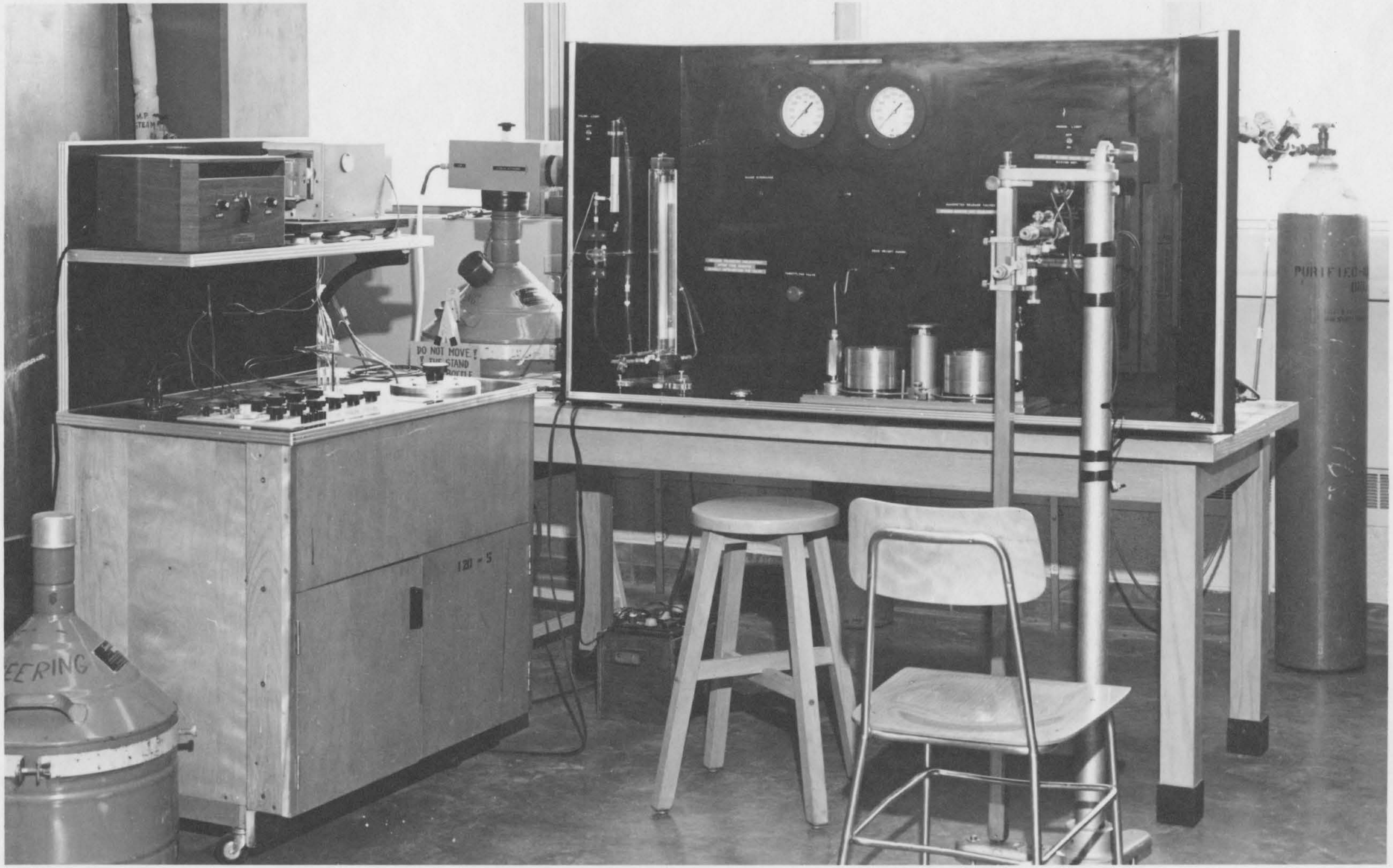


Figure 21. Experimental Apparatus

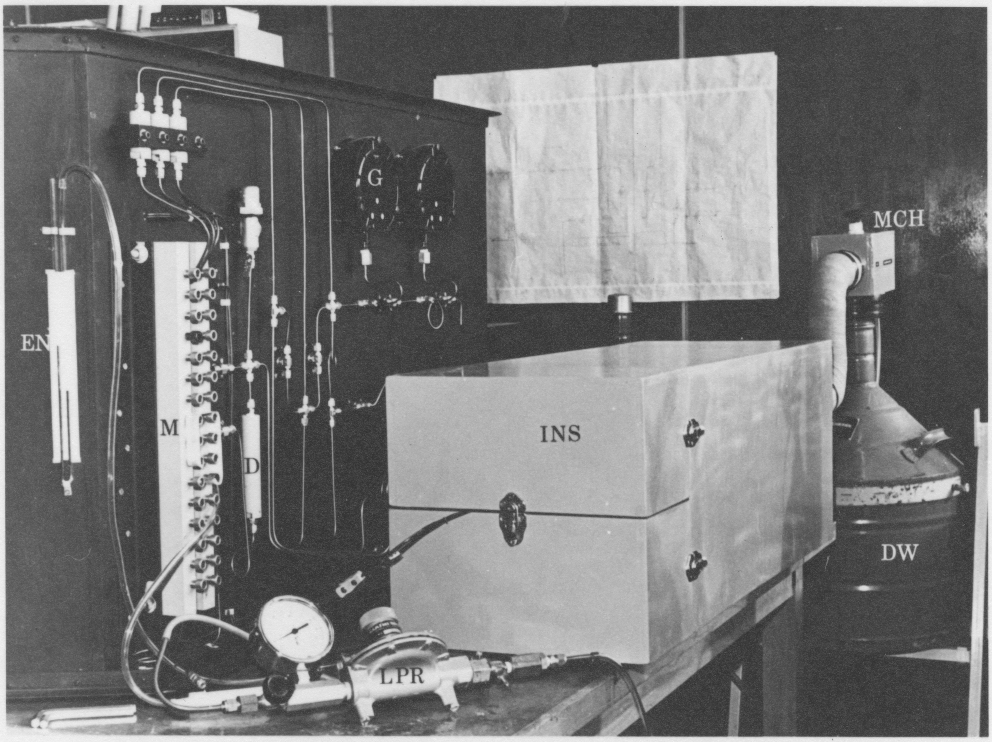


Figure 22. Rear View of Experimental Apparatus.

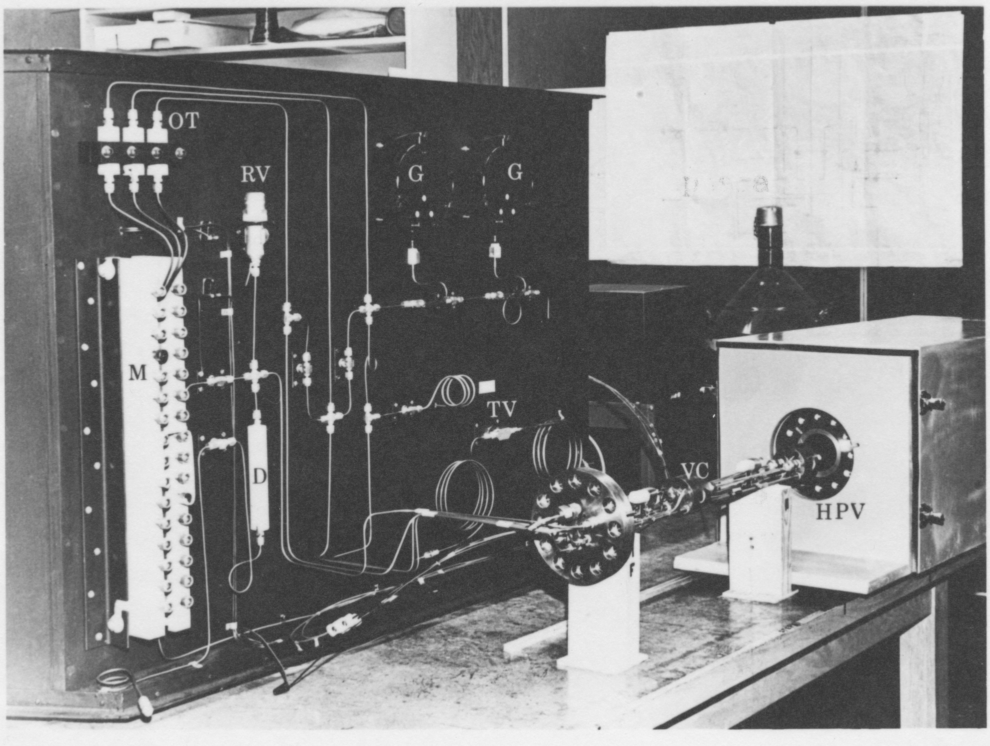


Figure 23. Rear of Control Panel with Viscometer Cell.

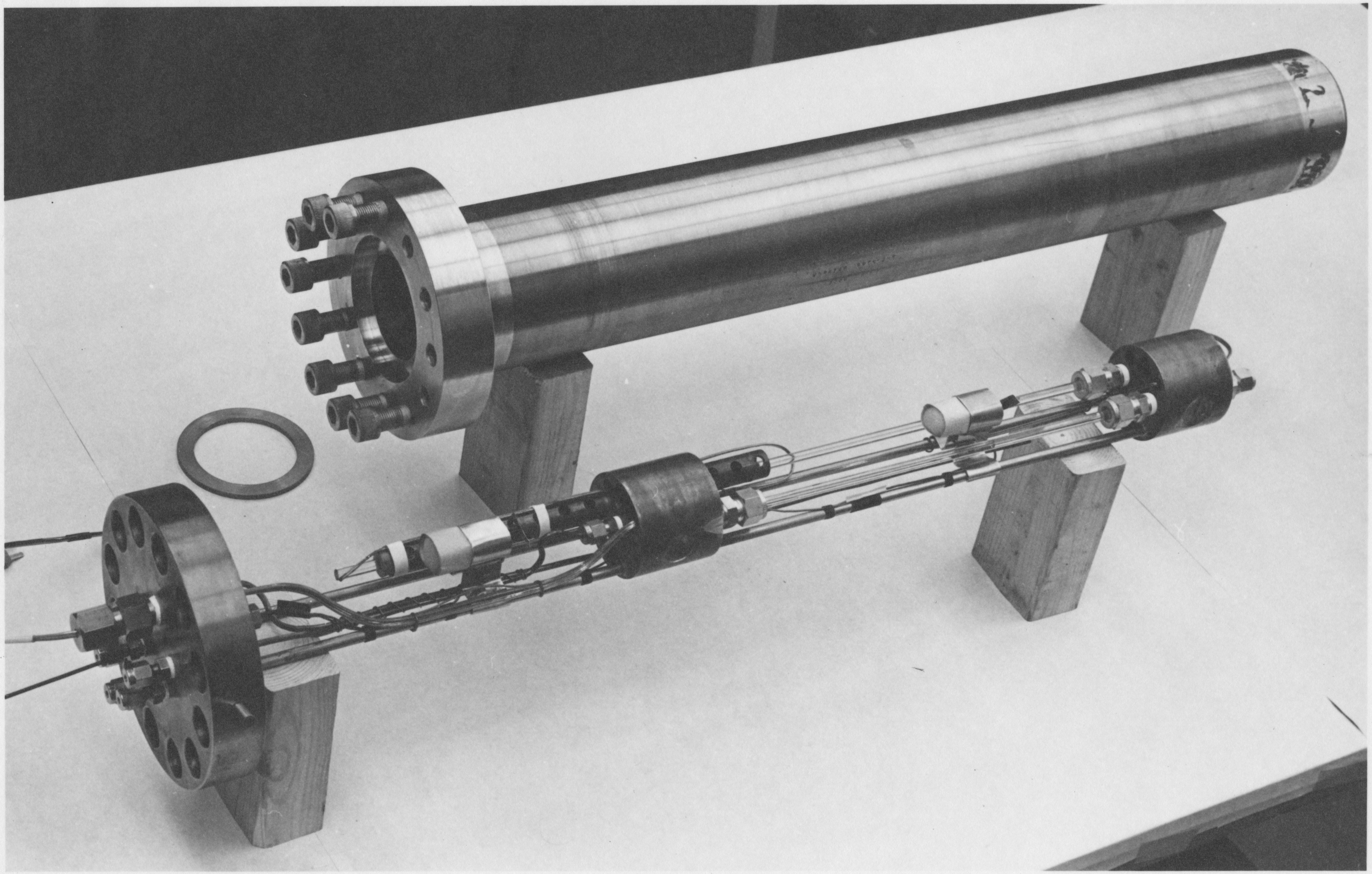


Figure 24. Viscometer Cell and High Pressure Vessel.

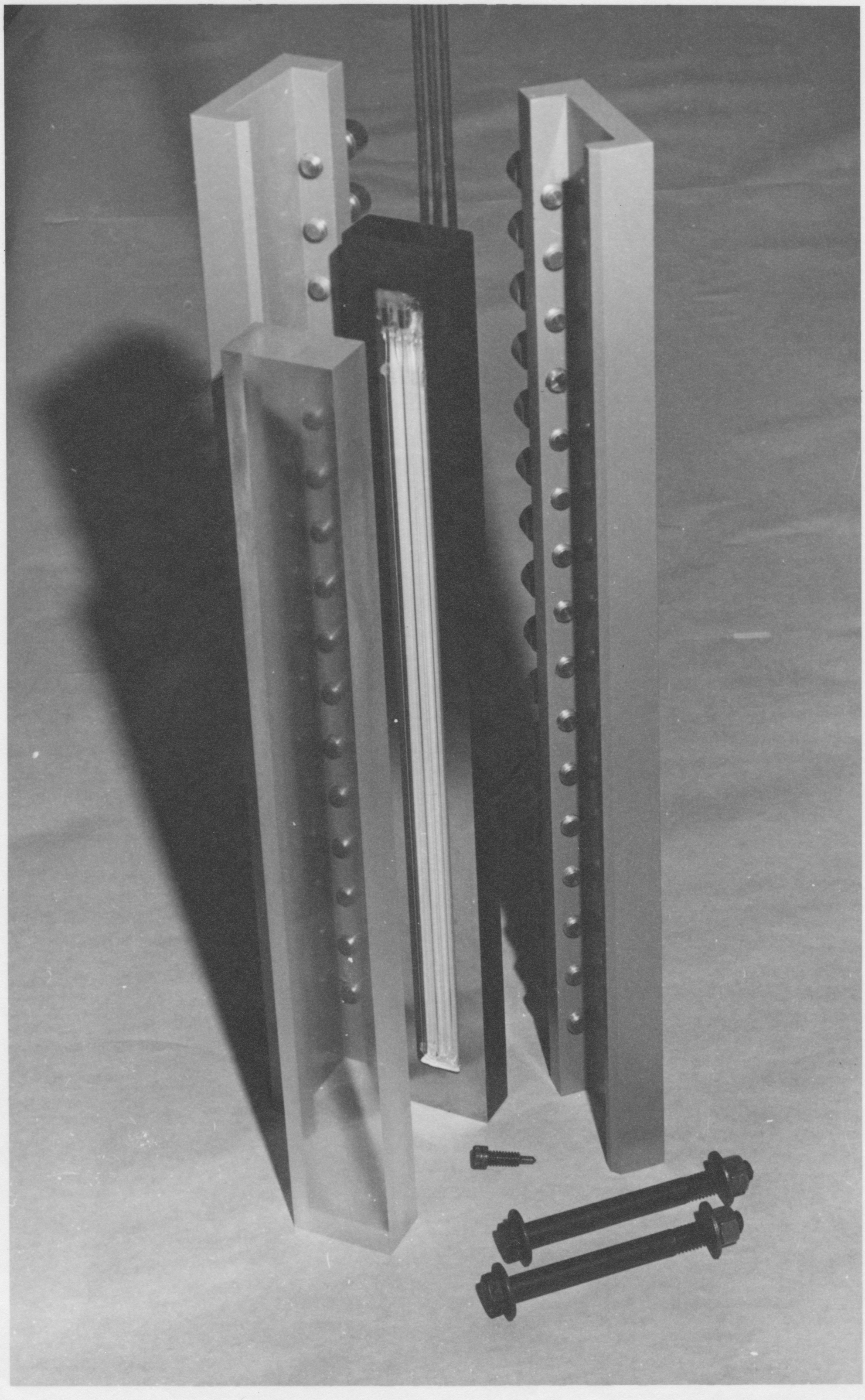


Figure 25. Exploded View of High Pressure Differential Manometer.

Figure 26. Coolant Supply and Control System.

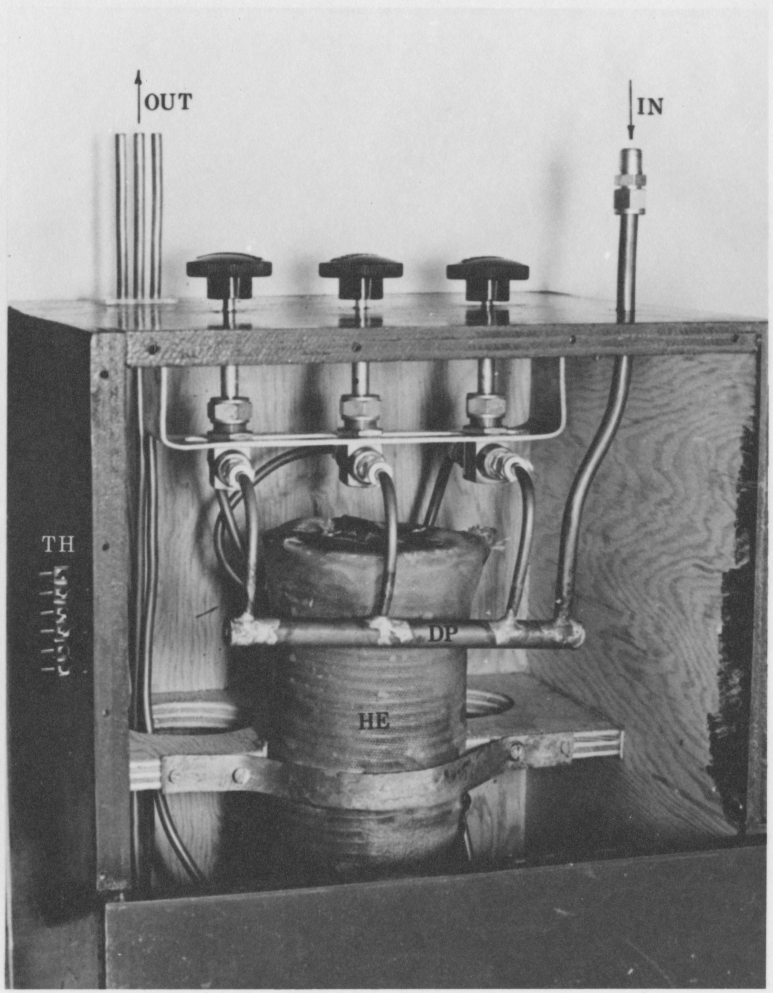


Figure 27. Coolant Distribution System.

APPENDIX A1.

A1. GENERAL THEORY AND WORKING EQUATION

The absolute methods used for the measurements of the viscosity of Newtonian fluids have been derived on the basis of Newton's hypothesis, defined by mathematical expression

$$F = \eta \frac{dv}{dx} \qquad /8/$$

where F is a force exerted by the fluid per unit area of a plane parallel to the direction of motion, dv/dx is a velocity gradient along the distance normal to the plane and constant of proportionality η is an absolute viscosity. The limits of applicability of the Newton's hypothesis determine the limits of the viscometry method based on this hypothesis. The Reynolds criterion imposes an upper limit on the velocity gradients which may be employed. The methods do not apply to non Newtonian fluids such as colloidal solutions or heterogeneous systems. Further limits of application of absolute viscometry methods for Newtonian fluids are less general and vary from one method to another.

The law of viscous flow of fluids in capillaries was first successfully formulated by Poiseuille in 1890, and sumarized in the empirical equation

$$V = k \frac{\Delta P \ d^4}{l} \qquad /9/$$

where ΔP is a pressure drop over a capillary of length l, inside diameter d, and V is a volume flow rate of a fluid. Constant k was presented as one which was characteristic of a given fluid at a given temperature. Hagenbach in 1845, obtained above equation theoretically and showed that the constant k was $k = \pi/128 \times \eta$ where η is an absolute viscosity of a fluid. The equation for an isothermal laminar flow for a Newtonian fluid flowing in a smooth circular tube can be written as

$$\eta = \frac{\pi d^4 \ \rho \ g \ \Delta P}{128 \ Q \ l} \qquad /10/$$

and is often referred to as the Hagen-Poiseuille or Poiseuille Equation. In this formula, Q is the mass flow rate of a fluid (gm/sec), d is the internal diameter and l is the length of the tube (cm), ρ is the density of a fluid at the mean pressure in the tube (gm/cm^3), g is the acceleration due to gravity (cm/sec^2), ΔP is the pressure drop along the tube (gf/cm^2) and η is the absolute viscosity of a fluid in (gm/cm sec), (i.e. poise).

Both experimental and theoretical investigation have shown that the simple Poiseuille equation is inadequate to describe laminar flow in a tube of finite length. Allowing for entrance and exit effects, the Poiseuille equation can be modified to obtain

$$\eta = \frac{\pi d^4 \rho \ g \ \Delta P \ (1+8L/d)}{128 \ Q \ (1+\lambda)} - \frac{m \ Q}{8 \pi (1+\lambda)} \qquad /11/$$

where the first term in the equation is often referred to as the Poiseuille viscosity. The corrections involved are as follows:

/1/ The Kinetic Energy Correction , $m\ Q\ /\ 8\pi\ (1+\lambda)$. It was first observed by Hagenbach that the pressure difference, when measured between chambers situated at the ends of a tube, is created only partly by viscous resistance. Actually, part of the effective pressure is converted into kinetic energy to be dissipated in the exit chamber and part is dissipated in establishing a parabolic velocity gradient within transient length of the capillary tube.

There is a considerable amount of contradictory data and conclusions in the literature concerning the magnitude of the dimensionless K.E. correction factor m , sometimes referred to as Hagenbach correction factor. Different investigators have proposed constant values of m ranging from greater than 1.0 to zero. The conclusions, that with capillaries having belled ends, m could be considered zero was stated by some investigators, but contradicted by the others. Some other investigators reported that m is not a constant but varies with the Reynolds number.

That m is a constant, within a certain experimental error, seems to have been proved at flow rates corresponding to Reynolds number from 50 to 1500, in an extensive experimental study by Wellman et al. in 1964 /33/. The magnitude of $m = 1.12$, recommended by Boussinesq /1/ for square-end capillaries seems to be confirmed by some experimental findings, but an influence of the geometry of the exit chambers may introduce an additional uncertainty into the value of m for different viscometers. For example Flynn et al. /18/, found that m varied from 0.88 to 1.70 for his high pressure viscometer, having evaluated the coefficients for sixteen different isotherms.

The main advantage of the two capillary viscometry method is that K.E. term is eliminated and the error due to uncertainty in m reduced to the smaller one resulting from a possible difference in K.E. factors of two geometrically identical capillaries.

/2/ The Couette Correction. The fluid entering a capillary must flow in a converging stream from the wide entrance chamber to acquire its velocity. The differences in velocity between adjacent streamlines of the flow involve the expenditure of energy to overcome viscous resistance which may be expressed by a lengthening of the capillary tube by a quantity λ, which is usually taken as $\lambda = n \times d$, where n is a constant estimated to range from 0 to 3, /36/, for different capillary end shapes. The value of $n = 0.6$, based on recent investigations, is often accepted for a capillary tube having squared ends. With a two capillary viscometer the Couette correction is largely eliminated and there is no need to discuss it in detail.

/3/ Slip Correction. In derivating the Poiseuille equation no slip of the fluid at the capillary wall is assumed. In practice, this condition might not be strictly true. The slip effect may be significant if the mean free path L of the gas molecules becomes comparable with the size of the tube. Assuming L to be mean value along the tube, the slip correction $(1 + 8\ L/d)$, based on Knudsen flow theory, was introduced /5/ to allow for the slip along the wall. In the atmospheric pressure measurements, the mean free path of nitrogen is about $L \simeq 8. \times 10^{-6}$ cm at 75 mm Hg and 0°C /3/, the slip correction takes on the value of $(1 + 8\ L/d) = (1 + 8 \times 8 \times 10^{-6} / 0.05) = 1.0012$ for the 0.5 mm capillary diameter. The correction, which is 0.12 % at 0°C would be much lower at low temperatures and was neglected in the present low temperature work. The slip correction formula is not really rigorous but seems to be adequate to estimate the magnitude of the slip effect. The mean free path decreases very rapidly with increase in pressure and consequently the slip correction factor becomes negligible at high pressures for even high temperatures.

When using the series capillary apparatus we deal with two equations

$$\eta = \frac{\pi d_1^4 \rho_1 g \Delta P_1}{128 Q_1 (l_1 + n_1 d_1)} - \frac{m_1 Q_1}{8\pi (l_1 + n_1 d_1)} \qquad /12/$$

$$\eta = \frac{\pi d_2^4 \rho_2 g \Delta P_2}{128 Q_2 (l_2 + n_2 d_2)} - \frac{m_2 Q_2}{8\pi (l_2 + n_2 d_2)} \qquad /13/$$

where subscripts 1 and 2 refer to long and short capillary, respectively. On the assumption that K.E. factors m_1 and m_2 are very nearly equal i.e. $m_1 \simeq m_2 = m$, as well as Couette correction factors $n_1 \simeq n_2 = n$, we can treat both equations simultaneously to eliminate both K.E. and Couette correction. Neglecting the slip correction term and allowing for thermal expansion or contraction of the material of the capillaries, the resulting working formula for the series two capillary apparatus is in the form

$$\eta = \frac{\pi d_1^4 \; g \; (1 + 3\alpha \Delta t)}{128 \; Q \; (l_1 - l_2)} \left[\Delta P_1 \rho_1 - \left(\frac{d_2}{d_1}\right)^4 \Delta P_2 \; \rho_2 \right] \qquad /14/$$

where α is the coefficient of thermal expansion of the capillary material in 1/°C, $\Delta t = t - t_{calibr.}$ is a difference between actual viscometer temperature during the run and that at the time of calibration of the capillaries in °C, and ρ_1 and ρ_2 are the mean densities at the mean pressures p_{1m} and p_{2m} existing in the capillaries which are

$$p_{1m} = p_a + \Delta P_{ent} - \Delta P_1 / 2 \qquad /15/$$

$$p_{2m} = p_a + \Delta P_{ent} - \Delta P_1 - \Delta P_2 / 2 \qquad /16/$$

p_a is the atmospheric pressure, ΔP_{ent} is the excess of a pressure in the viscometer plenum over the atmospheric pressure, ΔP_1 and ΔP_2 are pressure drops along the two capillaries.

The working equation 14. was derived assuming that the correction factors m and n , respectively, are very much the same for both capillaries and that no significant error was thus introduced. This assumption is of basic importance and its justification is further discussed, in view of relative error,in appendix A2.

More detailed information on the actual use of working equation 14. and the physical units used are given in the low pressure and high pressure sample calculations in appendix A3.

APPENDIX A2.

A2. ERROR ANALYSIS

1. Measurements Obtained at Atmospheric Pressure.

It is often difficult to calculate accurately the experimental error, which is a sumation of three basic error groups: /1/ random errors /2/ systematic errors and /3/ human errors. During all experimental procedures checks were made continuously to eliminate unnecessary mistakes. To decrease the probability of the occurence of systematic errors, calibrations were done with extreme care, including all necessary corrections in the expressions used. Care was taken when making repeated leakage tests of the pressure lines and transpiration system of the viscometer.

The "most probable" relative error in the viscosity, calculated in this appendix, is considered to define the experimental accuracy of this work. The error analysis is based on the simultaneous treatment of both systematic and random errors. The "accuracy" is defined as the relation between a given value to that of a given absolute standard and is considered "high" if the net systematic error is small. Accuracy is not, in principle, a statistical term as is the precision, which is given its quantitative measure by statistical methods and is related to the reproducibility of the measurements and the scatter of the experimental results. The experimental precision attained in this work is discussed separately in chapters VI and VII of this thesis.

It is worthwhile noting that there is only a vague relationship between accuracy and precision and that they are not usually interchangable. Obviously, high accuracy implies high precision. However, high accuracy is not guaranteed by perfect precision.

The following analysis has been done for nitrogen but can be applied to any gas of similar physical properties, provided the physical properties are known to the same degree of accuracy.

There are several factors which limit the accuracy of the viscosity values obtained by the capillary method:

/1/ The reliability of the Hagen-Poiseuille equation

/2/ The accuracy of the actual measurements

/3/ The accuracy of the subsidiary data required for the viscosity estimation

Provided the basic assumptions are adhered to, the Hagen-Poiseuille equation is considered very reliable. It is important, however, to consider the possible discrepancy in viscosity measurements obtained on two different types of viscometers which utilize two different theoretical concepts. This underlines the necessity of accurate absolute viscosity measurements. This approach can give experimental viscosity values which agree with the physical definition of viscosity.

Groups /2/ and /3/ will not be discussed separately but brought together for each assessment.

For a precise error analysis it is necessary to analyze the working equation

$$\eta = \frac{\pi\, d_1^4 \; g \quad (1 + 3\alpha\,\Delta t)}{128 \quad Q \; (l_1 - l_2)} \left[\Delta P_1\, \rho_1 - \left(\frac{d_2}{d_1}\right)^4 \Delta P_2\, \rho_2\right] \qquad /17/$$

Denoting the term in brackets as ΔP_M and the difference in the capillary lengths as Δl we get

$$\eta = \frac{\pi\, d_1^4 \; (1 + 3\alpha\,\Delta t)}{128 \quad Q \quad \Delta l} \quad \Delta P_M \qquad /18/$$

The "most probable" method, allowing for certain degree of compensation of invidual variable deviations, may be represented by the equation

$$d\eta = \sqrt{\sum_{i=1}^{J} \left(\frac{\partial \eta}{\partial x_i} \times dx_i\right)^2} \qquad /19/$$

where $d\eta$ is a deviation (absolute error) in viscosity, dx_i is a deviation in the i-th of J variables of the working equation.

Partially differentiating equation 18. and putting the results into the form of equation 19. and then dividing the whole expression by η, we get

$$\frac{d\eta}{\eta} = \sqrt{4\left(\frac{d\ d_1}{d_1}\right)^2 + \left(\frac{dg}{g}\right)^2 + \left(\frac{d\ \Delta P_M}{\Delta P_M}\right)^2 + \left(\frac{dQ}{Q}\right)^2 + \left(\frac{d\Delta l}{\Delta l}\right)^2}\ , \qquad /20/$$

neglecting the coefficient of linear expansion and for the sake of simplicity considering ΔP_M to be independent of d_1.

Particular values of each component of the last equation can be estimated as follows:

<u>The Capillary Diameter Errors [d(d)/d] .</u> The diameter of each capillary tube was measured using a gravimetric method and calculated from the equation

$$d^2 = \frac{4\ W_m}{l_e\ \rho_m} \qquad /21/$$

where W_m is the weight of mercury thread and l_e is the effective length of the thread (see appendix A4.) Hence, the relative error in a diameter is given by,

$$\frac{d(d)}{d} = \frac{1}{2}\sqrt{\left(\frac{dW}{W}\right)^2 + \left(\frac{dl_e}{l_e}\right)^2 + \left(\frac{d\ \rho_m}{\rho_m}\right)^2} \qquad /22/$$

The weight of the mercury threads was measured with a "Mettler" balance with a maximum reading of 160 gm and an accuracy of 0.001 gm. To minimize the error in the measurement of the capillary diameters, the calibrations were done with approximate coarse tube lengths. The capillaries were cut and faced after calibration. The difference between "full length" average diameter and the actual average diameter of the "net" length as used in the viscometer, has been analysed on the basis of the known diameter variation over the coarse capillary length, and for each capillary used was found to be negligible. Diameter variation along each capillary was obtained prior to final calibration by the short pellet method. The coarse capillary tube lengths at the time of calibration were approximately 60 cm. For the nominal diameter of 0.5 mm the weight of mercury thread was of the order of 1.5 gm. Therefore,

$$\frac{dW_m}{W_m} = \pm 0.067\ \%$$

The capillary lengths were measured using a "Griffin and George" cathetometer equipped with a "Beck" microscope, provided with a double hairline. The smallest division of the cathetometer was 0.001 cm, therefore, the accuracy of a length measurements of $l_1 = 52$ cm for the long and

l_2 = 32 cm for the short capillary was estimated to be

$$\left(\frac{dl_e}{l_e}\right)_1 = \pm 0.002\ \% \quad , \quad \left(\frac{dl_e}{l_e}\right)_2 = \pm 0.003\ \%$$

The density of the mercury was obtained from table F4. of the "Handbook of Chemistry and Physics" /4/. The uncertainty is given as one unit in the last significant place of the listed density values, which would introduce an inaccuracy of only about 0.001%. Therefore, the resulting capillary diameter errors are, from equation 22.,

$$\left(\frac{d(d)}{d}\right)_1 = \left(\frac{d(d)}{d}\right)_2 = \pm 0.034\ \%$$

In the majority of cases the diameter reproducibility was found to be within this tolerance.

Acceleration due to Gravity [dg/g] . The acceleration due to gravity was estimated and given by the Dept. of Energy Mines and Resources as 980.3941 cm/sec^2, for Hamilton and vicinity,(coordinates: latitude 43° 15.5' N, longtitude 79° 52.2' W, hight above sea level of 316 feet) and is claimed to be accurate within ± 0.0001 %.

Mass Flow Rate [dQ/Q] . The rate of flow was measured by means of "Emerson" displacement volumeter and its value is dependent upon three main factors related by the equation:

$$Q = \frac{V}{\tau} \rho \qquad /23/$$

where V is the volume of the test gas transpired through the capillary system within time interval τ and ρ is the density of the test gas in the volumeter.

The relative error in Q, using equation 23., is

$$\frac{dQ}{Q} = \sqrt{\left(\frac{dV}{V}\right)^2 + \left(\frac{d\tau}{\tau}\right)^2 + \left(\frac{d\rho}{\rho}\right)^2} \qquad /24/$$

The accuracy of the indicated volume of the flowmeter is claimed, by the manufacturer, to be

$$\frac{dV}{V} = \pm 0.2 \%$$

A mechanical stop watch, which was used for the timing, has a certificate attesting the accuracy for short time periods as being ±0.2 sec. Allowing for reaction time of an operator, estimated to be 0.1 sec, we can estimate the accuracy of the time measurements for time periods about 120 sec long, as

$$\frac{d\tau}{\tau} = \frac{0.3}{120} \times 100 = \pm 0.25\ \%$$

Densities of gases at room temperatures are usually well known. The density of nitrogen gas was found by interpolation of the data correlated and recommended by Hilsenrath /3/ which are quoted to have an accuracy of ±0.1 %. Both the temperature and pressure of the test gas in the volumeter were measured very accurately and the uncertainty of these state variables was included in calculation by considering the relative error in the density to be ±0.15 %. Therefore, the error in the mass flow rate , from equation 24., is

$$\frac{dQ}{Q} = \pm 0.35\ \%$$

Error in the Capillary Lengths Difference $[d\, \Delta l/\Delta l]$

The absolute error of the cathetometer used was ±0.001 cm. The capillary lengths l_1 and l_2 were measured separately, with this uncertainty, and then the difference $\Delta l = l_1 - l_2$ was calculated. The relative error of Δl , assuming that the deviations of l_1 and l_2 are of opposite sign, is for the capillary lengths used

$$\frac{d\, \Delta l}{\Delta l} = \pm \frac{dl_1 + dl_2}{l_1 - l_2} = \pm \frac{0.002}{20} \times 100 = \pm 0.01\ \% \qquad /25/$$

Error in the Modified Pressure Difference $\left[d\,\Delta P_M/\Delta P_M\right]$.

It is apparent that for the term

$$\Delta P_M = \left[\Delta P_1\,\rho_1 - \left(\frac{d_2}{d_1}\right)^2 \Delta P_2\,\rho_2\right] = \left[\Delta P_{M1} - \Delta P_{M2}\right] \qquad /25/$$

it is not sufficient to calculate relative error by the procedure used so far. First of all, the relative errors of the modified pressure drops ΔP_{M1} and ΔP_{M2} must be evaluated and only then the relative error of the difference $\left[\Delta P_{M1} - \Delta P_{M2}\right]$ can be calculated for the true modified pressure values observed during the measurements.

The pressure drops over the capillaries ΔP_1 and ΔP_2 were calculated from the equations

$$\begin{aligned} P_1 &= h_1\ \rho_{oil}\ \rho_w \\ P_2 &= h_2\ \rho_{oil}\ \rho_w \end{aligned} \qquad /27/$$

where h_1 and h_2 are the heights of oil columns read on the differential manometer using the "Griffin and George" cathetometer, $\rho_{oil} = 0.826$ is a specific gravity of red oil used in the manometer, ρ_w is water density at manometer temperature.

The relative errors in ΔP_{M1} and ΔP_{M2}, obtained by the above method, are

$$\frac{d\,\Delta P_{M1}}{\Delta P_{M1}} = \sqrt{\left(\frac{dh_1}{h_1}\right)^2 + \left(\frac{d\,\rho_{oil}}{\rho_{oil}}\right)^2 + \left(\frac{d\,\rho_w}{\rho_w}\right)^2 + \left(\frac{d\,\rho_1}{\rho_1}\right)^2} \qquad /28/$$

$$\frac{d\,\Delta P_{M2}}{\Delta P_{M2}} = \sqrt{\left(\frac{dh_2}{h_2}\right)^2 + \left(\frac{d\,\rho_{oil}}{\rho_{oil}}\right)^2 + \left(\frac{d\,\rho_w}{\rho_w}\right)^2 + \left(\frac{d\,\rho_2}{\rho_2}\right)^2 + 4\left(\frac{d(d_1)}{d_1}\right)^2 + 4\left(\frac{d(d_2)}{d_2}\right)^2} \qquad /29/$$

The absolute error of the cathetometer, for length differences, was indicated above as ±0.002 cm. It was observed that the oil meniscus in the differential manometer could not be located better then to ±0.002 cm, so that when the pressure differential measurements are done, another absolute error of ±0.004 cm must be included. Knowing the total absolute error of ±0.006 cm, the relative errors of both column heights h_1 and h_2 can be calculated, assuming the approximate values of $h_1 = 17$ cm and $h_2 = 10$ cm , which are controlled by the manometer design. That is,

$$\frac{dh_1}{h_1} = \pm\frac{\Delta h}{h_1} = \pm\frac{0.006}{17}\,100 = \pm 0.035\ \%$$

$$\frac{dh_2}{h_2} = \pm \frac{\Delta h}{h_2} = \pm \frac{0.006}{10} \; 100 = \pm 0.06 \;\%$$

The water densities were taken from the "Handbook of Chemistry and Physics" /4/, the accuracy of these tables being better then ±0.001 %. An uncertainty in oil specific gravity ρ_{oil} may be considered to be given by a unit change in the last significant decimal place which results in the relative error of ± 0.12 %.

Errors in the test gas densities depend not only on the accuracy of the particular gas tables, which was ±0.1% for nitrogen tables used, but also, to a great extent, on the accuracy of pressure and temperature estimation. Gas pressure was measured very accurately and the error thus introduced may be neglected. If it is assumed that the uncertainty in temperature estimation in the low temperature region has a constant values of say ±0.3, 0.4 and 0.5 centigrade, respectively, we may find the relative error in the density to be temperature dependent, as shown in Figure 28. This temperature dependence results from the variable slope of the density vs. temperature function. It is apparent that the relative arrors of the modified pressure differences ΔP_{M1} and ΔP_{M2} , as well as the resulting error, will be temperature dependent too.

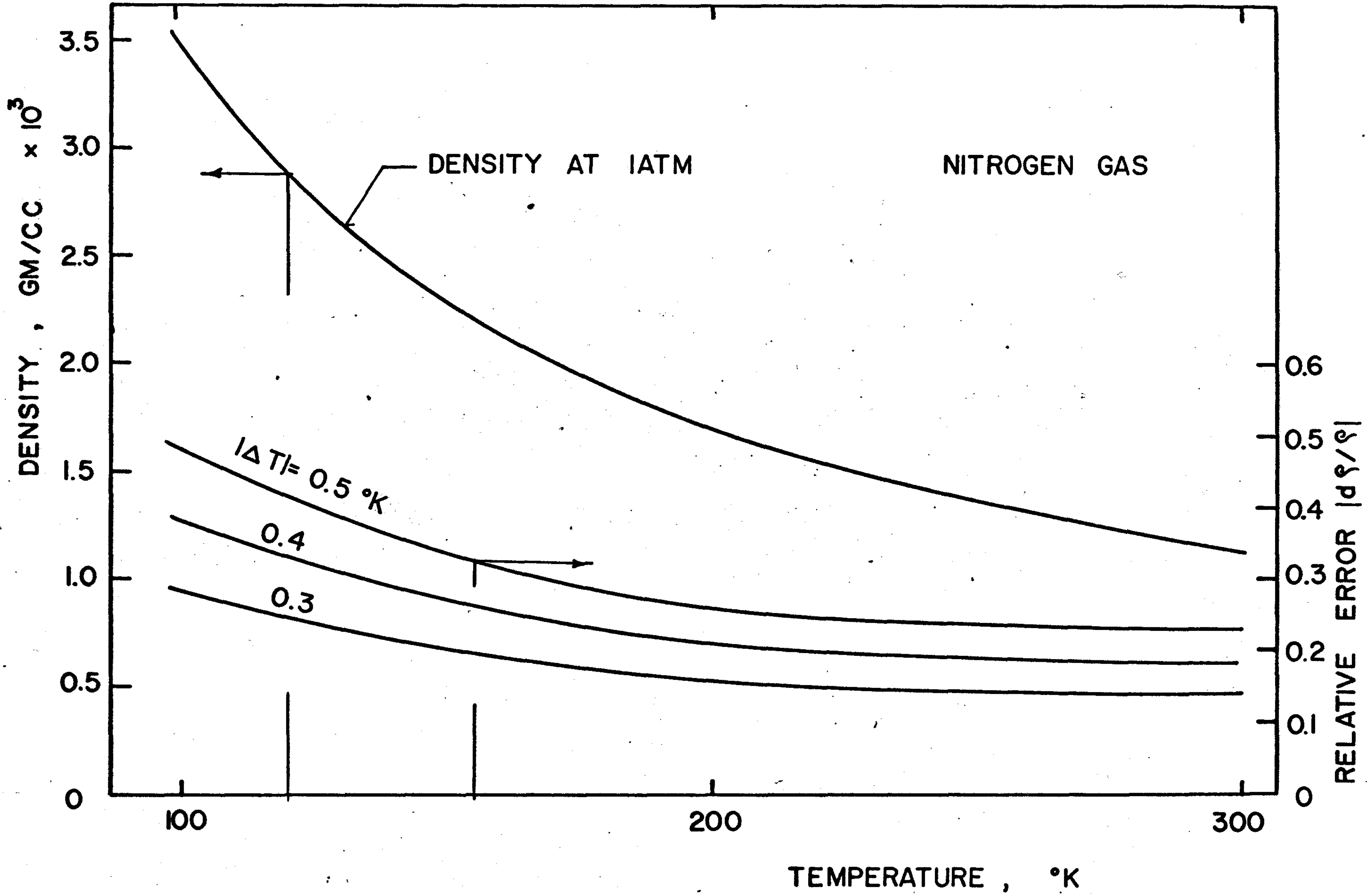


Figure 28. Relative Error in Nitrogen Density due to Uncertainty in Temperature Estimate $|\Delta T| = 0.3$, 0.4 and 0.5 °K

Assuming the value of ±0.3 centigrade to be the error in temperature measurements, the relative errors in modified pressure drops were calculated from the equations 28. and 29. and are listed in Table 4. for several temperatures ranging from 100 to 273.15°K.

TABLE 4. ERROR IN MODIFIED PRESSURE DROPS

T, °K	$\frac{d\,\Delta P_{M1}}{\Delta P_{M1}}$	$\frac{d\,\Delta P_{M2}}{\Delta P_{M2}}$	$\pm\left\lvert\frac{d\,\Delta P_{M}}{\Delta P_{M}}\right\rvert$
273.15	±0.19	±0.28	±0.86
240	0.19	0.28	0.86
200	0.20	0.29	0.90
160	0.23	0.30	1.00
140	0.25	0.32	1.06
120	0.28	0.34	1.17
100	0.31 %	0.37 %	1.30 %

It is apparent that the error in ΔP_M due to errors in the modified pressure drops ΔP_{M1} and ΔP_{M2}, calculated assuming the maximum pressure drops over the capillaries, is not a straightforward sum of the errors in individual modified pressure drops, but a more complex effect. The error in ΔP_M was numerically evaluated from the equation

$$\left|\frac{d\,\Delta P_M}{\Delta P_M}\right| = \left|\frac{\left(1 \pm \frac{d\Delta P_{M1}}{\Delta P_{M1}}\right)\Delta P_{M1} - \left(1 \pm \frac{d\Delta P_{M2}}{\Delta P_{M2}}\right)\Delta P_{M2}}{\Delta P_{M1} - \Delta P_{M2}} - 1\right| 100 \qquad /30/$$

for the typical values of ΔP_{M1} and ΔP_{M2}. The above equation suggests that the relative error in ΔP_M may be different for each possible combination of the signs of the relative errors in the modified pressure drops. The maximum absolute values of the relative errors $|d\,\Delta P_M / \Delta P_M|$ at several gas temperatures are listed in Table 4..

With the knowledge of all components of equation 20., we can obtain the final errors in the viscosity $d\eta/\eta$. The errors are listed in Table 5.

TABLE 5. OVERALL EXPERIMENTAL ERROR

T, °K	$\frac{d\eta}{\eta}$	$\frac{d\eta}{\eta}$ loc.	$\frac{d\eta}{\eta}$ res.
275.15	± 0.93	± 0.08	± 1.01
240	0.93	0.09	1.02
200	0.97	0.12	1.09
160	1.07	0.16	1.23
140	1.12	0.20	1.32
120	1.23	0.24	1.47
100	1.35 %	0.30 %	1.65 %

It should be noticed that, an error in the measurement of test gas temperature will not only increase the uncertainty in gas density and thus in the obtained viscosity value, but will introduce an uncertainty in the location of a measured point on temperature scale. Errors in viscosity due to uncertainty in the relative position of η with respect to temperature, i.e. the location, given by $d\eta/\eta_{loc.}$ were calculated, assuming the inaccuracy in temperature estimate of ±0.3 centigrade, on the basis of previously measured viscosity values. The errors which are temperature dependent, are larger at low temperatures, due to increase of the temperature coefficient of viscosity $(\partial\eta/\partial T)_{p=1\ atm}$ and the decrease of the viscosity value with decreasing temperature. Errors due to uncertainty in the location of the experimental viscosities $d\eta/\eta_{loc.}$ were supposed to be additive to the final error $d\eta/\eta$. The resulting error $d\eta/\eta_{res.}$ in absolute viscosity measurements of this work were obtained by the sumation of those two components and are listed in Table 5. for several temperatures in the low temperature range.

It was stated above that the method used to estimate "most probable" error allows for the statistically probable partial compensation of errors in the different variables of the relatively complex working equation. The simultaneous error analysis, assuming the severest contribution of each error, has yielded the final assessment of errors in the viscosity measurements which are about twice as large as those given in Table 5. However, the comparison of the viscosity values obtained at room temperatures, as reported in chapter VI, has shown an excellent agreement with the previous works and any extreme combination of the systematic errors does not seem to be probable.

Experimental scatter of the results suggests that even the assumptions which were made for random error components were not unrealistic and that the error $d\eta/\eta_{res.}$ in table 5. can be considered as the final uncertainty of the realistic smooth curves fitted to the experimental data of this work.

In deriving the working equation in appendix A1., a simplifying assumption, concerning the compensation of the end effects with both capillaries, was made assuming that the correction factors are equal, i.e. $m_1 \simeq m_2 = m$, and $n_1 \simeq n_2 = n$. An attempt to assess the magnitude of a possible error introduced by this assumption was done as follows:

To investigate an influence of the K.E. correction, we start with a simplified form of modified Poiseuille equations

$$\eta = \eta_1 - \frac{m_1 \; Q}{8 \pi \, l_1} \qquad /31/$$

$$\eta = \eta_2 - \frac{m_2 \; Q}{8 \pi \, l_2} \qquad /32/$$

where the subscripts 1 and 2 refer to the long and short capillary, respectively, and η_1 and η_2 are the Poiseuille viscosities. A simplified form of the working equation, obtained on the assumption that $m_1 \simeq m_2 = m$, and following the same procedure as given in appendix A1., is then

$$\eta = \frac{\eta_1 \; l_1 - \eta_2 \; l_2}{l_1 - l_2} \qquad /33/$$

If the correction factors are different for both capillaries and $m_1/m_2 = k$ is their ratio, equation 33. will give error in the viscosity results. This error depends again on the capillary dimensions and the flow rate within the transpiration system, and it is not tangible to solve the problem in its general form. Considering the viscometer adjustment as described in the sample calculation in app. A3., we can find that for an estimated value for $m_1 = 1.12$, the magnitude of the whole K.E. term for the long capillary is about 0.3 % of the η viscosity value. Equations 31. and 32. can then be rewritten as

$$\eta = \eta_1 - 0.003 \times \eta$$

$$\eta = \eta_2 - 0.003 \times \eta \times k \; \frac{l_1}{l_2}$$

since the mass flow rate is the same for both capillaries.

Calculating the Poiseuille viscosities η_1 and η_2 from above equations for different valus of k and substituting them into the simplified working equation 33., we recieve a different viscosity value η as compared with that when the assumptions, $m_1 \simeq m_2 = m$ and consequently $k = 1$, would be satisfied. The error in viscosity due to difference in K.E. correction factors was calculated as $d\eta/\eta_m = 100(\eta_k - \eta_{k=1})/\eta_{k=1}$ and is listed, against $100\,(m_1 - m_2)/\,m_2 = 100\,(k - 1)$ values for $k = 1.05$, 1.1 and 1.2 , in Table 6.

TABLE 6. EXPERIMENTAL ERROR DUE TO UNSATISFIED ASSUMPTIONS OF WORKING EQUATION AT LOW PRESSURES

100 (k-1)	$\frac{d\eta}{\eta_m}$
5	0.04
10	0.08
20 %	0.12 %

100 (j-1)	$\frac{d\eta}{\eta_n}$
5	0.00
10	0.01
20 %	0.03 %

Deriving the working equation and assuming that the Couette factors for both capillaries have the ratio $n_1/n_2 = 1/j$, we end up with an expression having $[l_1 - l_2 + n_1(d_1 - j \cdot d_2)]$ instead of the simple difference of the capillary lengths $(l_1 - l_2)$. Assuming the value of n equal 0.6 , the errors due to difference in the Couette correction factors were calculated and listed in Table 6. for j values of 1.05, 1.1 and 1.2 , for the dimensions of the capillaries used for the low pressure tests.

The $d\eta/\eta_m$ error values in Table 5. were obtained on the basis of analysis of a particular example viscosity run but their magnitude will not be too different at other temperatures and for similar gases unless the viscometer dimensions or flow rate are changed significantly.

Both error values $d\eta/\eta_m$ and $d\eta/\eta_n$ are relatively small compared to possible variations in correction factors for both capillaries, but not so negligible as to make the careful approach to the viscometer design and capillary ends performance unimportant.

These errors have not been used when assessing the accuracy of this experimental work since the deviation of the k and j coefficients from the unity, could not be reliable estimated. An approximate analysis has shown that the m correction factors varied for different test runs and were generally above the recommended values. The ratios of the K.E. factor k , however, did not differ from unity by more than 7 % within a particular low pressure run.

2. Measurements Obtained at High Pressures.

The principal sources of errors for high pressure measurements are the same as those at atmospheric pressure. As the assessed particular errors in the variables, which are substituted to the working equation, are of the same magnitude, the overall accuracy of the experimental data at low pressures, as stated in Table 5., can be basicaly applied to the high pressure data for steady-state, steady-flow conditions in the transpiration system.

It is necessary to make sure, however, that the smaller capillary diameters, proposed for high pressure experiments, be estimated to a sufficient degree of precision. This may call for a more accurate scale than that used for the gravimetric calibration of larger capillaries. The accuracy of the nitrogen density tables used /3/ is not thought to be different at high pressures but this will not necessarily be the case for other gases.

TABLE 7. EXPERIMENTAL ERROR DUE TO UNSATISFIED ASSUMPTIONS OF WORKING EQUATION AT HIGH PRESSURES

100 (k-1)	$\frac{d\eta}{\eta_m}$
5	0.4
10	0.8
20 %	1.6 %

Following the same procedure as for low pressures, the error in viscosity due to possible uncertainty in K.E. correction factors was calculated for the high pressure measurements at $p = 42.28$ atm, described in appendix A3., and listed in Table 7. In this example, the K.E. term for the long capillary reaches about 3% of the resulting viscosity and is, due to higher mass flow rate, much more significant than that for the low pressure test. This is also the case for the possible influence of uncertainty in the equality of K.E. correction factors on the resulting error in the viscosity. The measurements at $p = 42.28$ atm was done using relatively large capillaries having a bore of 0.5 mm. The mass flow rate, therefore, exceeded the maximum value which should be expected for capillaries of smaller nominal diameter which are scheduled for the high pressure measurements. The error values in Table 4. are thus somewhat exaggerated.

A3. SAMPLE CALCULATION

1. Low Pressure Measurements.

The nitrogen viscosity reading taken on 30th Nov. 1969, at the test temperature of $T = 219.15°K$ was chosen arbitrarily to illustrate a typical calculation. The readings of the variables used in the working equation 14. were as follows:

Pressure Readings. The atmospheric pressure at 0.55 A.M., read on the barometer with built-in correction for nonstandard conditions was $p_a = 753.7$ mm Hg at 0°C. The density of mercury at 0°C is 13.5955 gm/cm^3 /4/, therefore, $p_a = 753.7 \times 13.5955 = 1024.69$ gf/cm^2. The pressure head between the viscometer plenum and the ambient conditions was $\Delta P_{ent} = 52.0$ mm Hg at $t_a = 20.5°C$. The mercury density at this temperature is 13.5450 gm/cm^3, therefore, $\Delta P_{ent} = 52.0 \times 13.5450 = 70.43$ gf/cm^2. Two pressure drops readings were taken during 2min 54.3sec time period of the volumeter run,

$\Delta P_2 = 10.413$ $\Delta P_1 = 16.737$, cm of oil

$\Delta P_2 = 10.411$ $\Delta P_1 = 16.720$, cm of oil

Specific gravity of the manometer oil used is 0.826 and the density of water at 20°C is 0.9981 gm/cm^3 /4/. The average pressures drops over the capillaries are then

$$\Delta P_2 = 10.412 \times 0.826 \times 0.9981 = 8.58397 \quad , \quad gf/cm^2$$

$$\Delta P_1 = 16.7285 \times 0.826 \times 0.9981 = 13.79148 \quad , \quad gf/cm^2$$

The mean capillary pressures, using equations 15. and 16., are

$$p_{1m} = p_a + \Delta P_{ent} - \Delta P_1/2 = 1088.22 \quad , \quad gf/cm^2$$

$$p_{2m} = p_a + \Delta P_{ent} - \Delta P_1 - \Delta P_2/2 = 1077.04 \quad , \quad gf/cm^2$$

<u>Temperature Readings.</u> The thermocouple readings taken just before and after the volumeter run and the resulting temperatures were

TABLE 8. TEMPERATURES DURING LOW PRESSURE SAMPLE RUN

Thermocouple No.	4	5	8	9
EMF before the run, mV	-1.930	-1.927	0.778	0.817
EMF after the run	-1.927	-1.930	0.778	0.817
Average EMF$_{obs.}$	-1.928	-1.928	0.778	0.817
Calibration correct.	-0.009	-0.012	0.005	-
Corrected EMF $_{tab.}$	-1.937	-1.940	0.783	0.817
Temperature /11/, °C	-53.97	-54.03	19.90	20.5

Thermocouples No.4 and 5 were located inside the viscometer cell and their average temperature t = -54°C (219.15°K) was considered as a reference temperature for this run.

APPENDIX A3.

The temperature of the nitrogen in the volumeter was $t_8 =$ 19.90°C (293.05°K). The temperature $t_9 = 20.5$°C (303.65°K) was identical with the ambient temperature and had only a little influence on the differential manometer readings.

Densities. Mean gas densities in the capillaries were calculated so that the density ρ_t at the reference temperature and p=1atm was found first by interpolation from the tables /3/ and corrected to true mean capillary pressures using an equation of the state. Then

$$\rho_1 = \rho_t \frac{p_{1m}}{1032.25} = 1.56069 \times 10^{-3} \frac{1088.22}{1032.25} = 1.64532 \times 10^{-3} \ \mathrm{gm/cm^3}$$

$$\rho_2 = \rho_t \frac{p_{2m}}{1032.25} = 1.56069 \times 10^{-3} \frac{1077.04}{1032.25} = 1.62841 \times 10^{-3} \ \mathrm{gm/cm^3}$$

The density of the gas in the volumeter is a function of the temperature $t_8 = 19.90$°C and the pressure inside the calibrated volume $p_v = p_a + \Delta P_{back} = 1024.69 + 3.3 = 1027.99$ gf/cm^2 , where ΔP_{back} is the excess of pressure in the volumeter over the atmospheric pressure. In this case, $\Delta P_{back} =$ 4.0 cm of oil (S.G. = 0.826) = 3.3 gf/cm^2. The density is then

$$\rho_v = \rho_{t8} \frac{p_v}{1032.25} = 1.16573 \times 10^{-3} \times \frac{1027.99}{1032.25} = 1.16058 \times 10^{-3} \ \mathrm{gm/cm^3}$$

where ρ_{t8} is the interpolated density at t_8 and 1 atm.

Mass Flow Rate. The volumeter piston indicated the displacement $V = 70.0\ \text{cm}^3$ in the time $\tau = 2$ min 54.3 sec = 174.3 sec. The mass flow rate is given by

$$Q = \frac{V}{\tau}\ \rho_v = \frac{70.0}{174.3}\ 1.16058\times10^{-3} = 0.46609\times10^{-3}\ ,\quad \text{gm/sec}$$

Absolute viscosity. The dimensions of the capillaries used for the run were:

No. 1 $l_1 = 52.113$, $d_1 = 0.0500056$, cm

No. 2 $l_2 = 32.388$, $d_2 = 0.0501960$, cm

Using gravitational constant of $g = 980.3941\ \text{cm/sec}^2$, as discussed in appendix A2., and a coefficient of thermal expansion of the capillaries of $\alpha = 3.3\times10^{-6}\ 1/{}^\circ\text{C}$, the absolute viscosity can be calculated from the working equation 14. as

$$\eta = \frac{\pi\ 0.0500056^4\ \ 980.3941\ \left(1{+}3\ 3.3(-54.0-24.0)\right)}{128\times0.46609\times10^{-3}\ (52.113 - 32.388)}\ 10^{-3}\times$$

$$\left[13.7948\times1.64532 - \left(\frac{0.0501960}{0.0500056}\right)^4\times8.58379\times1.62841\right] = 1.3896\times10^{-4},\quad \text{gm/cm sec}$$

Considering the estimated error, we conclude that the experimental absolute viscosity of nitrogen at $T = 219.15\,{}^\circ\text{K}$

and atmospheric pressure is

$$\underline{\underline{\eta = (1.3896 \pm 0.0147)\,10^{-4}}}\,, \quad \text{poise}$$

Reynolds Number. For the flow in a given capillary, Re is approximately

$$Re = \frac{w\ d\ \rho}{\eta} = \frac{4\ Q}{\pi\ d\ \eta} = \frac{4\times 0.46609\times 10^{-3}}{\pi\times 0.05\times 1.39\times 10^{-4}} \simeq 85$$

which is well below the critical value for a tube. The development length for laminar flow is only $x_{1\%} = 0.065 \times Re \times d = 0.065 \times 85 \times 0.05 = 0.28$ cm and is only about 0.7% of the short capillary length.

2. High Pressure Measurements.

The evaluation of the nitrogen viscosities at high pressures was done using basicaly the same procedure as that for the low pressures and will be briefly illustrated by the reading taken on 8th February, 1970, with $T = 293.97°K$ and the absolute pressure $p = 42.28$ atm.

Pressure readings. The atmospheric pressure at 10.00 A.M. was $p_a = 745.0$ mm Hg at 0°C, that is 1012.86 gf/cm^2. The pressure head in the viscometer plenum, measured using the dead weight gauge, was found to be $\Delta P_v = 607.0$ psi $= 42633.0$ gf/cm^2. The reference absolute pressure in the viscometer

$p = \Delta p_v + p_a = 42633.0 + 1012.86 = 43645.86$ gf/cm^2 = 42.282 atm.

The observed mean pressure drops along the capillaries were

$$\Delta P_2 = 5.2825 \quad , \quad \Delta P_1 = 8.425 \quad , \quad \text{cm of oil}$$

Since the specific gravity of the manometer oil is 0.826 and the water density at ambient temperature of t= 23.0°C is 0.9978 gm/cm^3, the pressure drops are

$$\Delta P_2 = 5.2825 \ 0.826 \ 0.9978 = 4.35375 \quad , \quad \text{gf/cm}^2$$

$$\Delta P_1 = 8.425 \ 0.826 \ 0.9978 = 6.94374 \quad , \quad \text{gf/cm}^2$$

Consequently the pressure drops are negligible compared to the reference pressure and the mean capillary pressures are then

$$p_{1m} \simeq p_{2m} = p_m = p = 43\,645.86 \text{ , gf/cm}^2$$

Temperature Readings. The corrected values of thermocouple readings converted to degrees are :

TABLE 9. TEMPERATURES DURING HIGH PRESSURE SAMPLE RUN

Thermocouple No.	4	5	8	9
Temperature, °C	20.85	20.85	22.0	23.0

The reference temperature was t = 20.85°C (293.97°K), the temperature of the nitrogen in the flowmeter t_8 = 22.00°C (295.15°K) and the differential manometer temperature was t_9 = 23.0°C (296.15°K).

Densities. The density of nitrogen at p_m = 42.282 atm and a reference temperature T = 293.97°K, cross-interpolated from the gas tables /3/, was $\rho_1 \simeq \rho_2 = \rho = 49.4910 \times 10^{-3}$ gm/cm^3 The density in the flowmeter at $t_8 = 22.00$°C and a pressure $p_v = p_a + \Delta P_{back} = 1012.86 + 3.3 = 1016.26$ gf/cm^2, where ΔP_{back} is the pressure head between flowmeter and ambient pressure, was $\rho_v = 1.14441 \times 10^{-3}$ gm/cm^3.

Mass Flow Rate. A "Brooks" flowmeter, tube size R-2-15-AA with a stainless steel float, was used in this case as an alternative to the displacement volumeter, to measure the volume flow rate. For the float position at h = 149.2 mm, the equivalent volume flow rate, obtained from the calibration curve was $V_{air} = 266.0$ cm^3/min .
The mass flow rate of the nitrogen, using the recommended correction factor for the instrument, was therefore,

$$Q = V \ \rho_v/60 = V_{air}\sqrt{\frac{\rho_{air}}{\rho_v}} \ \rho_v/60 = 5.19632 \times 10^{-3}, \quad \text{gm/sec}$$

where $\rho_{air} = 1.20018 \ 10^{-3}$ gm/c.cm is the reference dry air for the "Brooks" calibration curve.

Absolute Viscosity. The short capillary, No.3, was used in this case, which had dimensions of $l_2 = 32.275$ and $d_2 = 0.0501869$ cm. The experimental absolute viscosity of nitrogen at T = 293.97°K and pressure p = 42.28 atm, calculated from the working equation, is therefore,

$$\eta = \frac{\pi\ 0.0500056^4\ \ 980.3941}{128 \times 5.19632 \times 10^{-3}\ (52.113-32.2754)} \left[6.94374 - \left|\frac{0.0501869}{0.0500056}\right|^4 \times 4.35375 \right] 49.491 \times 10^{-3} = \underline{\underline{1.8242 \times 10^{-4}}}\ , \quad \text{poise}$$

The thermal expansion term was negligible for this temperature.

Reynolds Number for the given flow in a capillary

$$\mathrm{Re} = \frac{4\ \ Q}{\pi\ d\ \eta} \simeq 725$$

The development length was therefore,

$$x_{1\%} = 0.065 \times \mathrm{Re} \times d = 0.065 \times 735 \times 0.05 = 2.35\ \text{cm}$$

which is about 7.3% of the short capillary length, and is well within the allowable limit.

APPENDIX A4.

A4. CAPILLARY CALIBRATIONS

Since the capillary diameter is raised to the fourth power in the working equation and the uncertainty in its evaluation effects the error in viscosity significantly, it is important to determine the bore diameter with the highest precision. But since a perfectly uniform bore is one of the basic assumptions of validity of Poiseuille law, it is also essential to have a capillary with little or no elipticity or conicality over its length. The second condition is of great importance due to lack of any reliable method enabling an estimation of the systematic error in viscosity caused by irregularities in the bore.

The viscometer was designed for straight glass "Veridia" capillaries having high precision bores ranging from diameters of 0.25 to about 2mm. It was, therefore, possible to calibrate the tubes using a "mercury thread" method which, in previous works, has proved to be adequately accurate and convenient. The selection of the capillaries and the calibration procedure was as follows:

/1/ Several thoroughly cleaned capillary tubes of the required nominal bores were first checked by passing a small mercury pellet along the tubes and observing its variation in length, which indicated the tube diameter fluctuation.

/2/ Two capillaries having the most uniform bore were chosen and after being cleaned again by soaking them in chromic acid and then rinsing with distilled water, alcohol and then ether. The mean diameter of each capillary was then obtained gravimetrically by putting a long thread of mercury along the entire length of the capillary. This procedure, called the "long pellet method", was repeated several times, mainly to decrease the influence of weighing error.

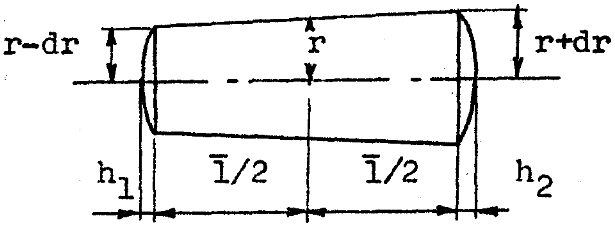
/4/ The capillaries were then cut to the design lengths and faced. The uniformity of the tube bores was sufficient to consider the mean diameter obtained for the rough tube lengths to be the same for shorter design lengths.

The theory for both "short pellet" and "long pellet" calibration methods is straightforward. Considering a short mercury pellet of weight G, mean diameter $d = 2r$, a length between the wetted surfaces of $\bar{l}$, and a depth of each meniscus h_1 and h_2, we can obtain the diameter at a certain location from the equation,

$$G = v \times \rho_m = \pi r^2 \times le \times \rho_m \qquad /34/$$

where $v = \pi r^2 \times le$ is the volume of an equivalent cylinder, $le = \bar{l} + (h_1 + h_2)/2$ is the length of an equivalent cylinder.

This is based on the assumption that in a good capillary a small pellet has the form of a right circular cone capped at each end by a spherical segment. The volume of such a pellet is then,



$$v = \pi r^2 \left[\left(1 + \frac{(dr)^2}{3r^2}\right) \times \bar{l} - \frac{dr}{r} (h_1 - h_2) + \left(1 + \frac{(dr)^2}{r^2}\right) \times \frac{h_1 + h_2}{2} + \frac{h_1^3 + h_2^3}{6\, r^2} \right] \qquad /35/$$

In practice dr/r , h_1^3 , h_2^3 and $h_1 - h_2$ are small compared to $\bar{l}$ and we can neglect them. Then

$$v = \pi r^2 \times \bar{l} + \frac{\pi r^2}{2} (h_1 + h_2) = \pi r^2 \times \left(\bar{l} + \frac{h_1 + h_2}{2}\right) = \pi r^2 \times l_e \qquad /36/$$

where l_e is a length of an equivalent cylinder defined by equation 34.

As soon as the variation of the capillary diameter is known over its length L , the volume of a capillary bore is

$$V_b = \int_0^L \pi r^2 \times dL = \frac{\pi d_m^2}{4} \qquad /37/$$

from which the mean capillary diameter d_m can be evaluated. The procedure was refined by Fisher /12/ such that the integral equation 37. is substituted by an expression including the integrals

$$\int_0^L l_e^2 \times dL \quad \text{and} \quad \int_0^L dL/l_e \quad ,$$

which are easier to evaluate accurately. The volume of a small pellet v was also excluded and replaced by a larger volume of a long mercury thread V .

Since, in any case, the procedure involves the need for a graphical or numerical integration which is a probable source of errors which are difficult to assess, the "short pellet" method was used only for capillary checks during the selection of the best tubes.

The mean capillary diameters were calculated from the expression

$$G = V \times \rho_m = \pi\, d^2/4 \times L_e \times \rho_m \qquad /38/$$

which is basicaly identical with that of equation 34. , except that V and G are the volume and weight and $L_e = (h_1 + h_2)/2$ the equivalent length of the long thread. The reasoning for the use of the equivalent length is similar to that described above. It is apparent, that an error due to idealized meniscus shape is very small since in this case, the meniscus heights h_1 and h_2 are small compared to the length of the long cylindrical thread part of length L .

There are other methods for calibrating a capillary which are mentioned in the literature, such as a method based on the measuring the electrical resistance of the long thread instead of weighing it, also there is a X-ray technique, and a method which employs the use of probes to sense the ends of a mercury pellet. These methods were tried by Latto /2/ but none of them were sufficiently accurate.

The calibration set-up is shown in Figure 32. . A pellet of "triple distilled"mercury was introduced into the capillary CP which had a plastic tube at each end and was held in a steel jig. The arrangement was then immersed into a bath of glycerin GB . This was done since the glycerine has the same refractive index as that of the capillary glass. The length of the pellet was then checked by means of horizontally positioned "Griffin and George" cathetometer CT which was equipped with "Beck" microscope. The short pellet was then moved over the capillary length

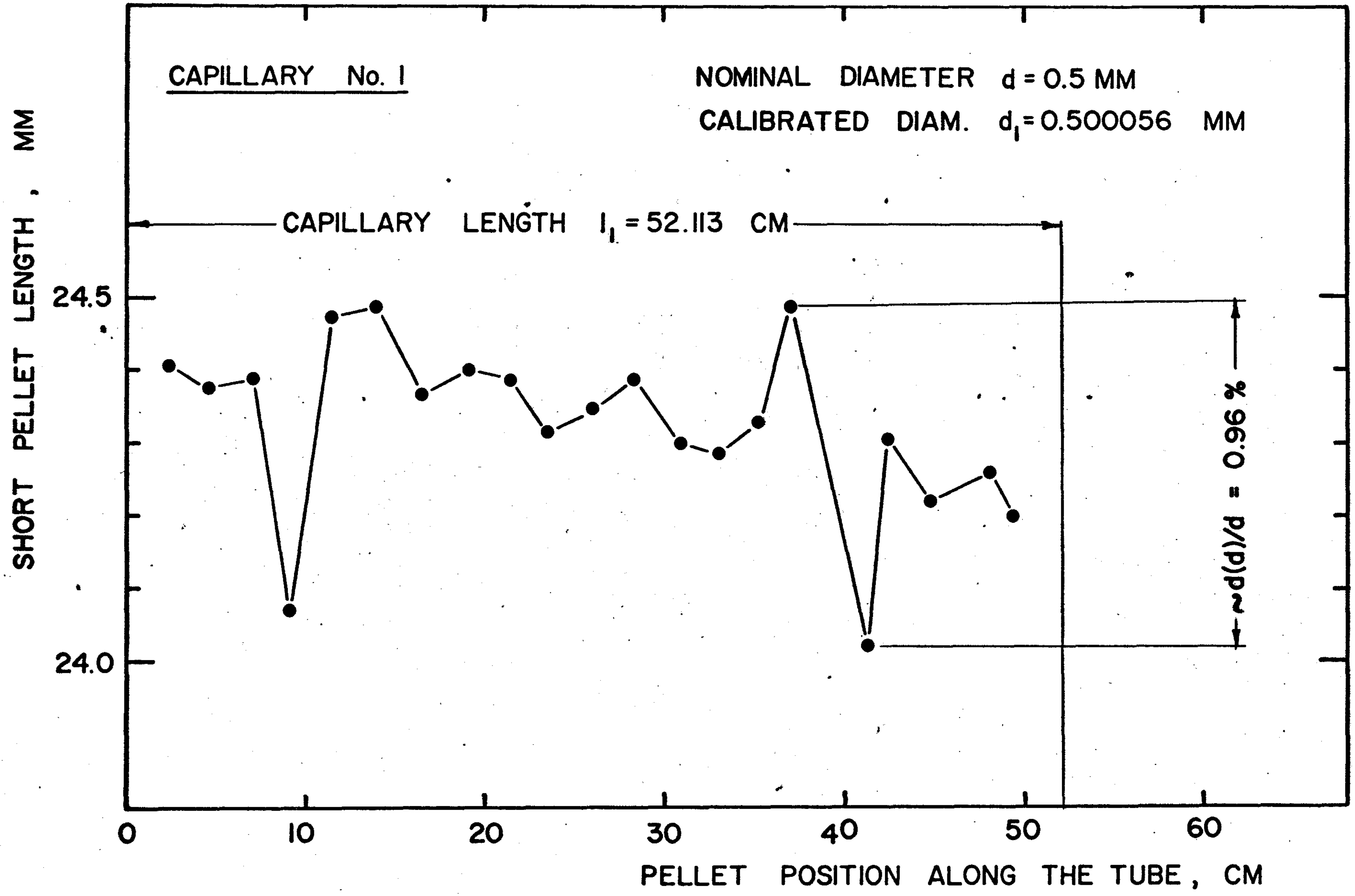


Figure 29. Small Mercury Pellet Calibration Curve for No.1 Capillary.

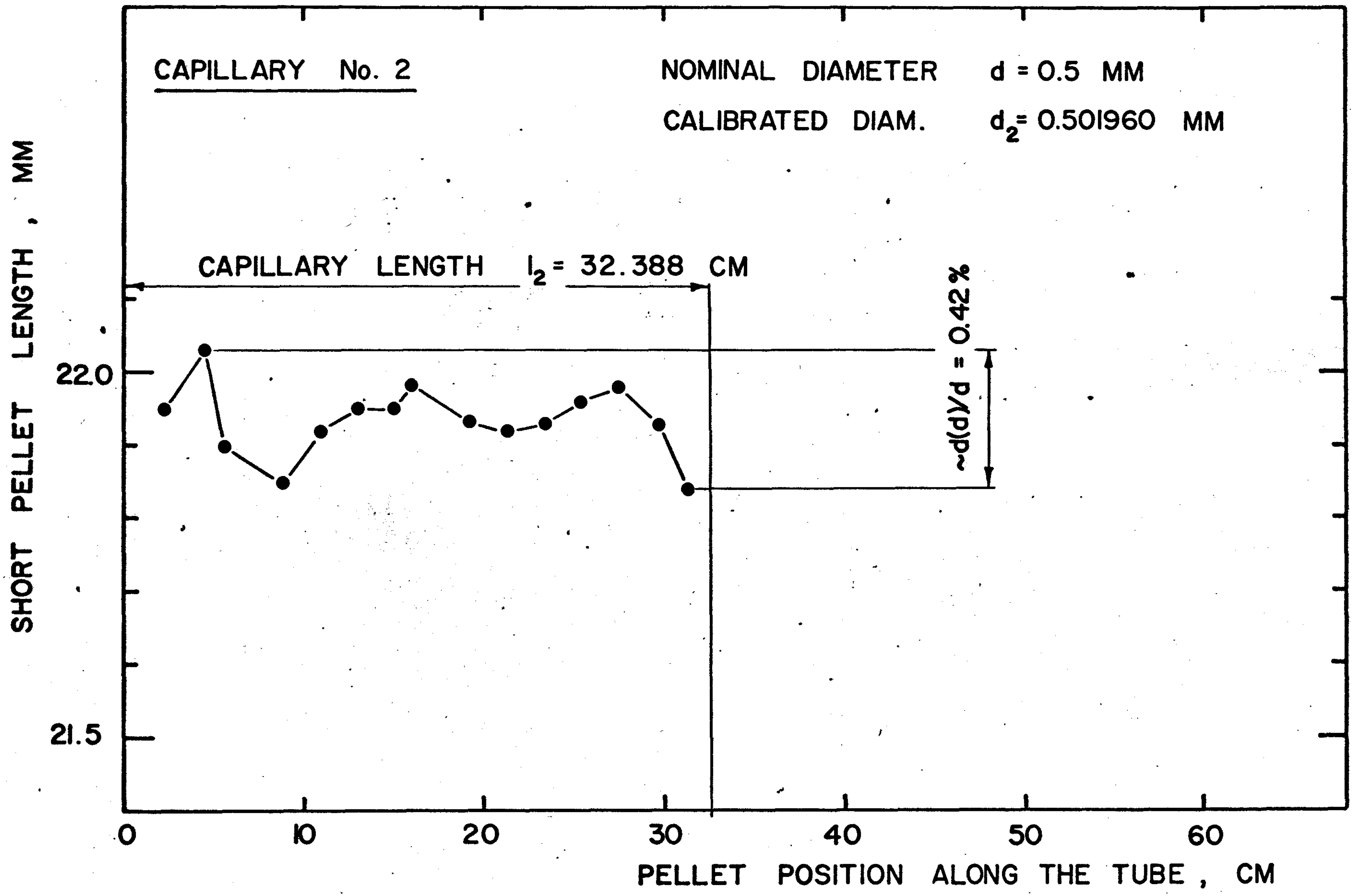


Figure 30. Small Mercury Pellet Calibration Curve for No.2 Capillary.

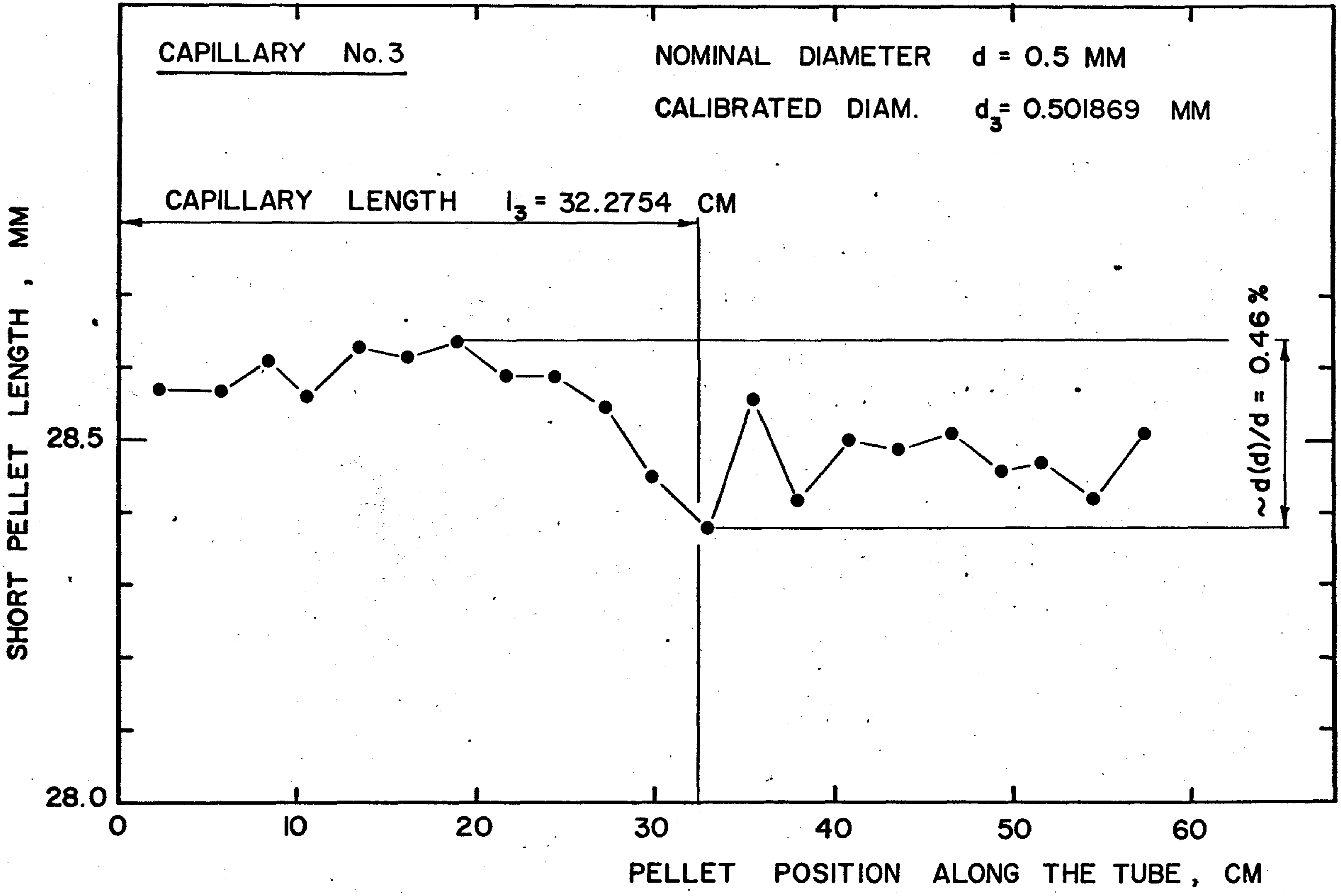


Figure 31. Small Mercury Pellet Calibration Curve for No.3 Capillary.

so that each new pellet position overlapped the old position.

The bath was not used for repeated large pellet calibrations but the arrangements and procedure were basically the same. The large pellet was extracted and weighed after each reading, the procedure being repeated at least five times to minimize the weighing error. Latto /2/ made a check to observe whether the possibility of an air being trapped between the pellet and the tube wall would have any effect on the calibration precision, and concluded it to be negligible.

Calibration graphs for each of the tubes used are given in Figures 29. , 30. and 31.. The diameters obtained from the large pellet calibration are also included in the figures as well as the capillary lengths.

Three capillaries of the nominal diameter of 0.5 mm were used during the experiments. Capillaries No.1 and No.2 had been used in one of the previous low pressure viscometers in this laboratory, and were only refaced and recalibrated. No.3 capillary was used after No.2 had been broken during a seal replacement.

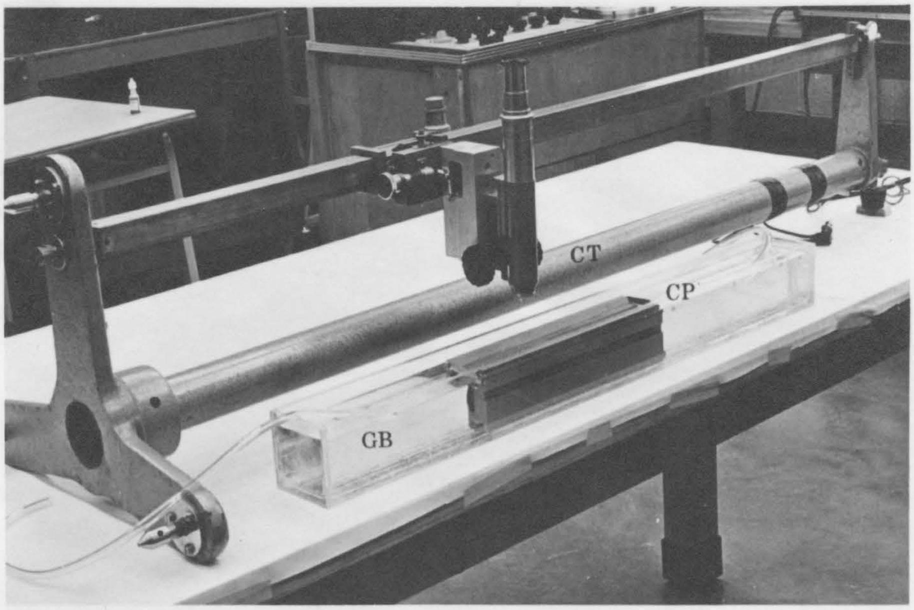


Figure 32. Capillary Calibration Equipment.

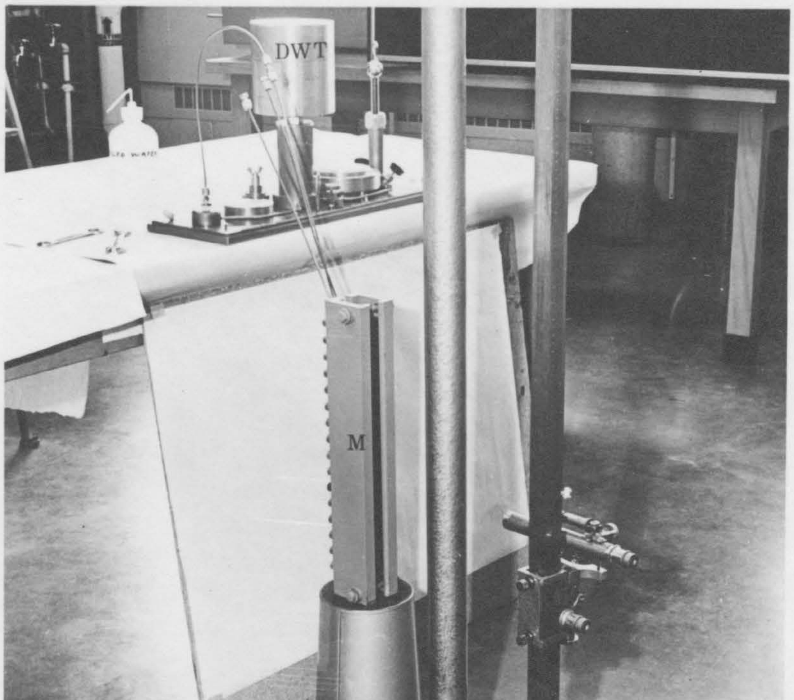


Figure 33. Pressure Test of Differential Manometer.

APPENDIX A5.

A5. THERMOCOUPLE CALIBRATIONS

The temperature coefficient of the viscosity of gases at low pressure $(\partial\eta/\partial T)_p$ has a positive sign over the entire region of temperatures used and becomes greater with decreasing temperature. A given value of uncertainty in temperature has, therefore, greater influence on the overall accuracy of the viscosity estimation at low temperatures than in the middle and higher temperature region. This uncertainty is emphasised by a similar trend of gas densities, as discussed in the error analysis of this work. Adequate attention has been, therefore, given to both choice and calibration of the temperature measurimg equipment used.

With respect to the laboratory equipment, the secondary thermocouple measurement appeared to be most reasonable to use. Powell et al. /16/ attempted to evaluate the suitability of some commercially available thermocouple wires, such as cobalt, gold or constantan versus copper or "normal" silver, for low temperature use. Gold or cobalt is reported to have much larger sensitivity than constantan but this advantage is offset by larger inhomogeniety voltages which cause approximately the same relative error. For this reason it is necessary to spot-calibrate each thermocouple used even when they are all made from a given batch. This precaution is also necessary for constantan below 80°K. Above 80°K, which happens to be approximately the minimum design temperature of the viscometer, constantan has proved to be much more reliable. Furthermore, the regularity of the deviation curves for constantan wires of different lots, led Powell to the conclusion, that it is acceptable to construct a complete recalibration table for any new thermocouple by calibration at a few fixed points, followed by a linear interpolation of the deviations from the appropriate reference table. For these reasons "copper-constantan" thermocouples were used all of which were compared at the reference temperatures of melting ice and the boiling point of liquid nitrogen at atmospheric pressure. The most important thermocouples, No.4 and 5 , which were used to measure temperatures inside the viscometer cell, and No.8, used in the volumeter, were then accurately calibrated against a "Thermo-Electric" copper-constantan thermocouple No.705 and also at fixed temperatures of liquid nitrogen, ice melting point and boiling water. The cold junctions were kept at 0°C both during calibration and actual use. The deviations of the emf. of the thermocouples from the N.B.S. (Circular No.561) copper-constantan thermocouple tables are shown in Figure 34. .

Since the lower limit of the reference table is 80°K, the range had to be extrapolated below the temperature of liquid nitrogen which was used as the low temperature reference point. Both the N.B.S. and Powell's copper-constantan thermocouple characteristic curves are reasonably parallel over their common temperature range. Similarity in shape was, therefore, postulated even for lower temperatures and the N.B.S. table graphically extrapolated by the smooth curve, parallel with that by Powell. The numerical coordinates of the extrapolated curve,that were used as a reference for the deviation plot given in Figure 34. are listed in Table 10.

TABLE 10. EXTENTION OF N.B.C. COPPER-CONSTANTAN THERMOCOUPLE CONVERSION TABLES

C	0	1	2	3	4	5	6	7
-190	-5.379	-5.395	-5.411	-5.427	-5.443	-5.460	-5.477	-5.492

Extrapolated →

The N.B.S. reference table, having a reference junction at 0°C, was used despite the necessity of extrapolation , since Powell's low temperature tables present values of thermoelectric potential differences for a reference temperature at 0°K and must be recalculated for any other reference point.

The mutual comparison of all eight thermocouples used in the viscometer has shown that the greatest differences were about 0.004 mV (0.25 centigrade) at the liquid nitrogen

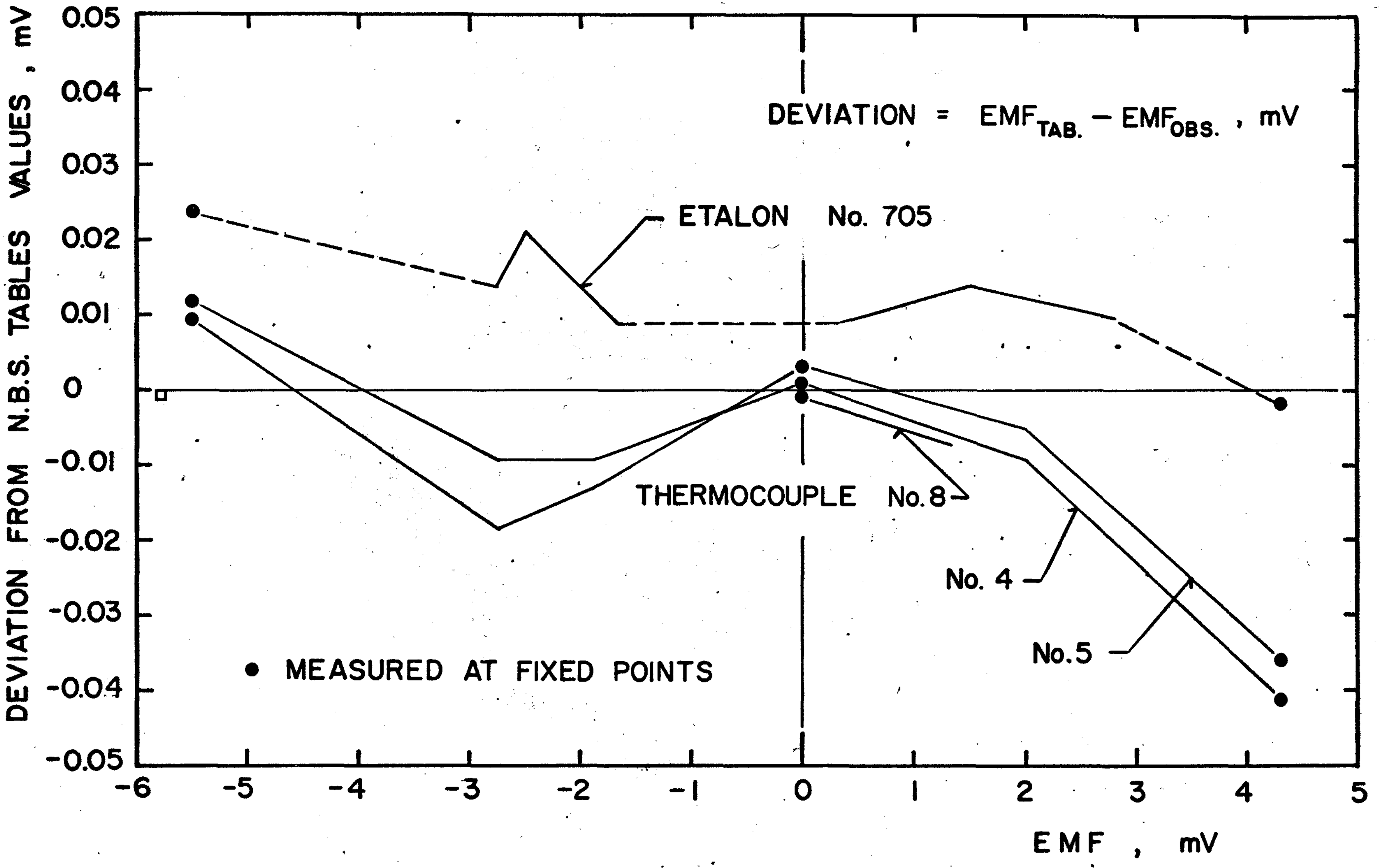


Figure 34. Thermocouple Calibration Curves

temperature. Only the most important thermocouples were, therefore, calibrated individually as described above. The calibration against No. 705 thermocople was done at several random temperatures over its calibrated temperature range from -112 to 150°F. The calibration at fixed points was also applied to thermocouple No.705 and its range thus broadened for the future use. The final set of calibrated points and emf. deviations are,

Temperature		Deviation in mV	
-112	°F	0.014	
-100		0.021	
-50		0.009	
50		0.009	
100		0.012	
150		0.010	
77.28	°K	0.022	Fixed points
372.82		-0.002	

The last two temperatures refer to the boiling point of liquid nitrogen /32/ at atmospheric pressure p_a= 753.3 mm Hg, measured at the time of calibration, and the boiling point of distilled water /4/ at p_a= 750.0 mm Hg.

The high precision "Guidline Instr." Potentiometer Type 9160 together with Type 9461A Galvanometer and

Type 9460 Photocel Galvanometer Amplifier, was used for both the thermocouple calibration and the temperature measurements. The systematic error of the thermocouple calibration is , therefore, believed to be very close to that of the No.705 copper-contstantan thermocouple, which was calibrated by "Thermo-Electric, Ltd.", Canada, with reference to N.B.S. Standard Thermocouples APHSSP-992/1 for -112, -100 and -50°F and APH-1421 for 50, 100 and 150°F. The uncertainty of the N.B.S. Standard Thermocouples APHSSP-992/1 and APH-1421 are, according to Thermo-Electric certificate, ±0.1 and ±0.06 centigrade, respectively.

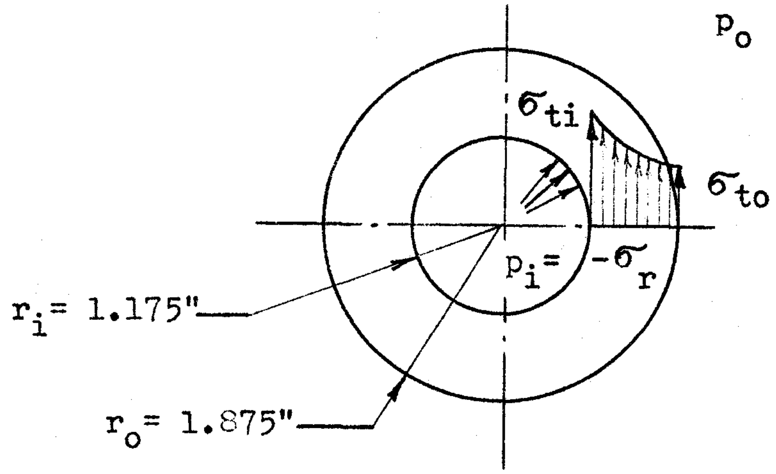
APPENDIX A6.

A6. HIGH PRESSURE STRUCTURAL AND LEAK TESTS

Dimensions of the pressurized parts of the viscometer were estimated using appropriate theories of failure. The parts were carefuly designed and the most important components were given structural and leak tests, in accordance with pertinent safety regulations. With respect to the internal location of the high pressure system, relatively large factors of safety were considered in order to decrease the probability of any kind of mechanical failure. The design pressure for the system was set at 3000 psi.

High Pressure Vessel (see Figures 10. and 25.) has the largest volume of pressurized gas and may be subjected to temperatures as low as -320°F. 304 austenitic stainless steel was chosen for the material for the vessel, cover and the bolts, since /1/ this material has a high resistance to various types of corrosion /2/ and it does not exhibit low temperature brittlenes but remains ductile over the range of temperatures to be used /32/. Due to the latter property it was not necessary to pressure test the vessel at the intended low temperature conditions.

The vessel is not expected to be subjected to sudden loads or mechanical impacts. Principal stress of the vessel of following dimensions,



are given by Lame's formulae for thick-shell cylinder:

Tangential Stress

$$\sigma_{ti} = \frac{p_i\,(r_o^2 + r_1^2) - 2\,p_o\,r_o^2}{r_o^2 - r_i^2} \qquad (6850 \text{ lb/sq in}) \qquad /39/$$

$$\sigma_{to} = \frac{2\,p_i\,r_i^2 - p_o\,(r_o^2 + r_i^2)}{r_o^2 - r_i^2} \qquad (3850 \text{ lb/sq in}) \qquad /40/$$

Radial Stress

$$\sigma_r = -p_i \quad \text{at} \quad r = r_i \qquad (-3000 \text{ lb/sq in})$$

$$\sigma_r = -p_o \quad \text{at} \quad r = r_o \qquad (-15 \text{ lb/sq in})$$

Longitudinal Stress

$$\sigma_1 = \frac{p_i\, r_i^2 - p_o\, r_o^2}{r_o^2 - r_i^2} \qquad (1920 \text{ lb/sq in}) \qquad /41/$$

where p_i and p_o are pressures inside and outside the cylinder. Numerical values of principle stresses, calculated for the vessel, are given in brackets after each equation.

Allowing for the ductile behaviour of the stainless steel, the factor of safety was calculated from the maximum shear stress theory as

$$N = (s_y/2)\,/\,\tau_d = 3.56 \qquad /42/$$

where $s_y = 35 \times 10^3$ lb/sq in is the yield stress of 304 stainless steel, and $\tau_d = (\sigma_{max} - \sigma_{min})/2 = (\sigma_{ti} - \sigma_r)/2 =$ 4925 lb/sq in is the maximum shearing stress in the high pressure vessel wall.

The vessel was tested by "Crane Corp.", Hamilton, Ontario, Canada by subjecting it to an internal oil pressure of 6000 psi (which is twice the design pressure) for six hours. A test certificate for the vessel was issued by the test laboratory.

High Pressure Differential Manometer. The back plate and side clamps of the manometer (see Figure 11.) were designed to withstand a line pressure of 1500 psi. The transparent front window was originally intended to be made of tempered glass, however a cheap and more accessible plexiglass plate was used. In spite of that it is believed that the manometer in its present form can be used up to the maximum pressure of 3000 psi. If this should be the case, however, the manometer would have to be pressure tested using compressed gas at 6000 psi.

Figure 33. shows a photograph of the manometer whilst undergoing a pressure test in which a dead weight tester was used to produce the high pressure. The manometer was filled with distilled water and pressurized by oil pumped from the dead weight tester. A cathetometer was focused on the oil-distilled water interface which was located in one of the manometer limbs and leakages and internal volume changes were thus indicated by a change in level of the interface. A structural test, at 3000 psi (i.e. twice the design pressure) , was followed by six hour leak test at 2500 psi. No leakages occured after a thin rubber gasket was used between the front window and the manometer body, and a torque about 150 lb in applied to the clamp bolts. The upper limit of the dead weight tester is 3000 psi and the test could not be extended to find the failure

pressure limit.

Originally, silicon rubber coating was tried as a seal for the window-back plate contact surface, but this did not prove to be suitable. A thin rubber gasket 1/32" thick appeared to be satisfactory and proved to be perfectly leakproof.

Auxiliary Equipment. The connecting tubes, valves etc., were chosen for a working pressure of up to 3000 psi. The manometer oil traps and high pressure silica gel dryer were made in the main Engineering workshop of McMaster University, and were pressure tested to 3000 psi in the same way as that used for the manometer.

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