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Evaluation of the force constants of non-polar gases from viscosity data

Charles Warren Keller

EVALUATION OF THE FORCE CONSTANTS OF
NON-POLAR GASES FROM VISCOSITY DATA

BY

CHARLES WARREN KELLER

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1959

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(signature) (advisor)   *(signature)*

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I. INTRODUCTION

Studies of the intermolecular forces and potential energy functions have been largely of a theoretical nature. Various empirical statements representing these theories have been developed and tested. Of these, the Lennard-Jones (6-12) potential is one of the more realistic and has become the most favored when dealing with non-polar molecules.

The values of these "force constants" or the values of the Lennard-Jones (6-12) potential parameters, have been determined from both diffusion and viscosity data. Although these "force constants" can be determined from diffusional measurements as well as viscosity data, the literature is predominately filled with values of force constants which were determined from viscosity measurements. Until recently, there has been little diffusional data reported over a sufficient temperature range to evaluate force constants for gas pairs. Recent work has indicated that the values of the force constants, when determined from diffusion and viscosity data, are not in good agreement.

Much viscosity data are obtained under dynamic or
flow conditions at pressures exceeding atmospheric.

The purpose of this investigation was to evaluate
the force constants of certain selected non-polar gases
at atmospheric pressure from viscosity data obtained
using a rolling ball viscometer. It was believed that
the force constants, evaluated from viscosity measurements
in this manner, would be more nearly comparable with
those calculated from diffusional data and hence, would
be in better agreement. The gases used in this inves-
tigation were air, argon, carbon dioxide and helium.

II. LITERATURE REVIEW

In the review of the literature concerning the intermolecular force constants, only the following items pertinent to this thesis will be considered: (1) intermolecular forces of non-polar gases, (2) calculation of intermolecular forces of non-polar gases, and (3) measurement of viscosity of gases.

Intermolecular Forces of Non-Polar Gases

It is a known phenomenon that molecules of substances attract each other when they are widely separated and set up forces of repulsion when they are brought into proximity. Therefore, the forces of interaction between spherical non-polar molecules are a function of the separation distance between such molecules. These forces may be divided into two catagories, (1) short range forces, and (2) long range forces.

Short Range Forces. In the field of intermolecular forces, the short range forces are existent when the molecules are in proximity and their electron orbits overlap. These forces are highly directional and of

considerable magnitude. At the present time, these forces
have not been evaluated analytically for even the most
elementary cases[32].

Long Range Forces. Whereas the short range inter-
molecular forces could not be treated by quantum mechanics,
long range forces may be handled very satisfactorily by
such methods. These forces are of an electrical nature
and vary inversely as powers of the molecular separation
distance. Three types of forces, dispersion, electro-
static and induction, are all integrated into the long
range forces. These are thoroughly discussed by
Hirschfelder, Curtiss and Bird[9].

Dispersion Forces. Dispersion forces result
mainly from the interaction of instantaneous dipoles
created in neutral symmetrical molecules by the
motion of the orbital electrons.

Electrostatic Forces. Electrostatic forces are
those set up by the interaction of the various multi-
pole moments existing in a molecule.

Induction Forces. Induction forces are created
when a charged particle interacts with a neutral
molecule and induces into that molecule a dipole
moment.

Potential Energy of Interaction. For convenience,
the potential energy of interaction is used to describe

intermolecular forces rather than the force of interaction. These functions may be stated as follows[7]:

$$F(r) = - \frac{d\phi}{dr} \quad ; \quad \text{and} \quad \phi(r) = \int_r^\infty F(r)dr \quad (1)$$

where   F = force of interaction between two spherically shaped non-polar molecules

        r = intermolecular separation

    $\phi(r)$ = potential energy of interaction.

Development of Potential Functions. Most potential functions have been developed on the basis of a spherical non-polar molecule and the long range forces have been found to be mainly those of dispersion. By a mathematical combination of the terms representing the attractive and repulsive forces existing, potential models have been developed and related to the intermolecular separation. Once these relations have been developed, and the collision integrals evaluated, the parameters or force constants of the potential functions may be determined from experimental data on transport properties.

Lennard-Jones Potential. Of the expressions developed for potential functions, possibly the most realistic is that referred to as the Lennard-Jones potential. It is expressed as

$$\phi(r) = 4e \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (2)$$

where   e = depth of potential well and represents maximum energy of attraction

    σ = low velocity collision diameter or value of (r) for which ϕ = 0.

The value of σ is also the distance of closest ap-
proach of two molecules which collide with zero
initial relative kinetic energy. The inverse twelfth
power term in equation (2) represents the repulsive
interaction between the molecules while the sixth
power attraction term is representative of the induced
dipole reaction. These powers, it should be noted,
may vary with the type of substance used. The
parameters for this potential e and σ have the
dimensions of energy and length respectively. For
each substance under consideration, these values are
constants, being related to the chemical nature of
that substance. Figure 1 is a pictorial represen-
tation of some of the spherically symmetrical
empirical potential functions which have been
developed.

Rigid Elastic Spheres. Because of its simplic-
ity, the model of the rigid elastic spheres is often
used for exploratory calculations. This function
represents a rigid elastic or impenetrable sphere of
diameter σ, and the values of the potential may be
represented as follows:

$$\phi\,(r) = \infty \qquad r < \sigma$$
$$\phi\,(r) = 0 \qquad r > \sigma \tag{3}$$
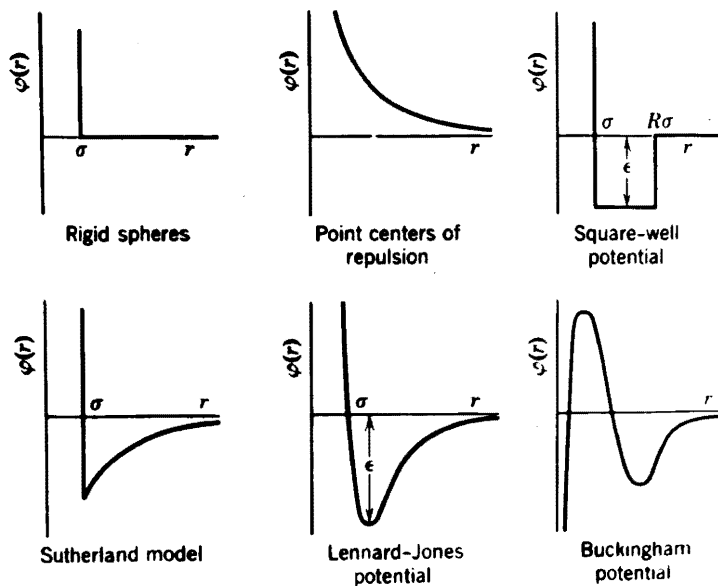
Figure 1. Spherically Symmetrical Potential Functions

Hirschfelder, Joseph O., Charles F. Curtiss and R. Byron Bird: "Molecular Theory of Gases and Liquids," p. 30. John Wiley and Sons, New York, N. Y., 1954.

Point Centers of Repulsion. The potential
represented by the "point centers of repulsion" is one
in which each molecule is considered to exist at
a single point. This repulsion is represented by the
equation

$$\phi(r) = ur^{-v} \tag{4}$$

where   u = a constant

v = index of repulsion.

This function may be used where it is necessary to
use a differential of the potential.

Square Well Potential. The square well potential
model is one which represents rigid spheres of a
diameter σ surrounded by an attractive core whose
strength is represented as e which extends to
separations Rσ. In this model, therefore, both
attractive and repulsive forces are considered. This
model has been found useful in calculations involving
complex molecules as the three adjustable parameters
allow for considerable lattitude. The square well
potential may be represented by equation as follows:

$$\phi(r) = \infty \qquad r < \sigma$$
$$\phi(r) = -e \qquad \sigma < r < R\sigma \tag{5}$$
$$\phi(r) = 0 \qquad r > R\sigma$$

The Sutherland Model. The Sutherland model has

been found to be a fairly realistic model for use. It

is based on the potential represented by rigid spheres

of a diameter of σ which attract each other according

to an inverse power law. This is represented by the

equations

$$\phi(r) = \infty \qquad r < \sigma$$
$$\phi(r) = -ur^{-\beta} \qquad r > \sigma \qquad (6)$$

where   u = a constant

β = a constant for which the collision
          integrals may be evaluated.

The collision integrals for the values of β equal to

four, six and eight have been tabulated[34].

The Buckingham Potential. The Buckingham

potential is a four-parameter function which includes

the more complex induced dipole reactions as well as

estimating the repulsive forces existing in the system.

It is a more realistic statement than the Lennard-Jones

potential, but is also more difficult to handle

numerically. This potential does not lend itself to

calculations made from transport properties in that

it is unrealistic in the sense that it goes to -∞

at the origin. It may be represented mathematically

as follows:

$$\phi(r) = v\exp(-ur) - wr^{-6} - w'r^{-8} \qquad (7)$$

where   u, v, w and w' = constants.

Calculation of Intermolecular Forces of Non-Polar Gases

In the various intermolecular potential functions, the force constant e is evaluated as e/k, where k is Boltzmann's constant. The statement of e/k has the dimensions of degrees Kelvin while the dimensionless expression kT/e is referred to as the reduced temperature. This constant may be evaluated both from diffusion and viscosity data.

Evaluation of Force Constants from Diffusion Data.

Hirschfelder, Curtiss and Bird[11] present the equation for calculation of the first approximation of the coefficient of diffusion in a binary mixture as follows:

$$(D_{12})_1 = 0.0026280 \frac{\sqrt{T^3 (M_1 + M_2)/2M_1 M_2}}{P \, \sigma_{12}^2 \, \Omega_{12}^{(1,1)} (T_{12}^+)} \tag{8}$$

where

D_{12} = diffusion coefficient, in square centimeters per second

P = pressure, in atmospheres

T = temperature, in degrees Kelvin

T_{12}^+ = kT/e_{12}

M_1, M_2 = molecular weights of species 1 and 2, in grams

σ_{12}, e_{12}/k = molecular potential energy parameters characteristic of 1-2 interaction, in Angstroms and degrees Kelvin, respectively.

Experimentally obtained values of the diffusion coefficient
at different temperatures may be substituted into this
equation and the value of the force constant calculated.
The function $\Omega_{12}^{(1,1)}$ has been evaluated and tabulated[16]
for various reduced temperatures. The actual solution
requires a trial and error method of approach.

Evaluation of Force Constants from Viscosity Data.
Hirschfelder, Curtiss and Bird[10] present an equation for
the calculation of the first approximation of the coeffi-
cient of viscosity for a pure gas as follows:

$$(\mu)_1 \times 10^7 = 266.93 \frac{\sqrt{M\,T}}{\sigma^2 \; \Omega^{(2,2)+}(T^+)} \tag{9}$$

where μ =   viscosity, in grams per centimeter
                     per second

          T =   temperature, in degrees Kelvin

          T^+ =   reduced temperature = kT/e

          M =   molecular weight, in grams

          σ =   collision diameter, in Angstroms

      e/k =   potential parameter, in degrees Kelvin

$\Omega^{(2,2)+}$ =   collision integral at T^+.

The function $\Omega^{(2,2)}$ has been computed and tabulated[16]
for various reduced temperatures. Experimentally
determined viscosities at different temperature levels
may then be inserted and the force constants evaluated[14]
by a trial and error method.

Measurement of Viscosity of Gases

Webster[39] defines viscosity as "that property of a body in virtue of which, when flow occurs inside it, forces arise in such a direction as to oppose the flow." Therefore, if a "body" can be subjected to a known force and the opposition to this force evaluated, the viscosity of the "body" may be determined. The units of viscosity are expressed in relation to length, mass and time. Physical measurement of resistance forces in terms of these variables may be mathematically related to the viscosity.

General Methods of Measurement of Gaseous Viscosity. A number of methods have been developed along with the necessary equipment for the relation of the viscosity of gases to the variables of length, mass and time. In all cases, a known force is applied to the gas. From its resistance to the applied force, the viscosity is calculated. Among the methods used for such determinations are (1) capillary flow method, (2) ultrasonic viscometer method, (3) oscillating disk method, (4) rotating cylinder method, (5) rolling ball method, and (6) falling ball method.

Capillary Flow Method. The capillary flow method for determination of gaseous viscosities requires measuring the quantity of gas that will

flow through a capillary tube of known cross sectional
area during a specific time period. The conditions
of the gas with relation to temperature and pressure
are known. This provides the necessary data to
relate the volume to the mass of gas passing through
the tube. These physical measurements may then be
mathematically related to the viscosity. The equipment
shown in Figure 2 used by Rigden[30] is a typical
type used for viscosity coefficient evaluation by the
capillary flow method. Two capillary tubes are placed
in series and joined to the ends of a wide-limbed
U-tube containing oil, the whole forming a closed
system. The two oil-gas surfaces are originally at
different levels, and in progressing toward equilibrium
conditions, the gas is forced through the capillaries.
Measurement of oil movement rate is related to the
flow rate of the gas and the difference in the level
of the oil surfaces determines the driving pressure.

The capillary flow method was one of the first
used in the determination of fluid viscosities. The
large number of correction factors that must be
applied has limited its use in more recent experi-
mental work. Another disadvantage in the method is
that the equipment is necessarily large. Therefore,
maintenance of the system at a constant temperature

te aspirator   Dry air
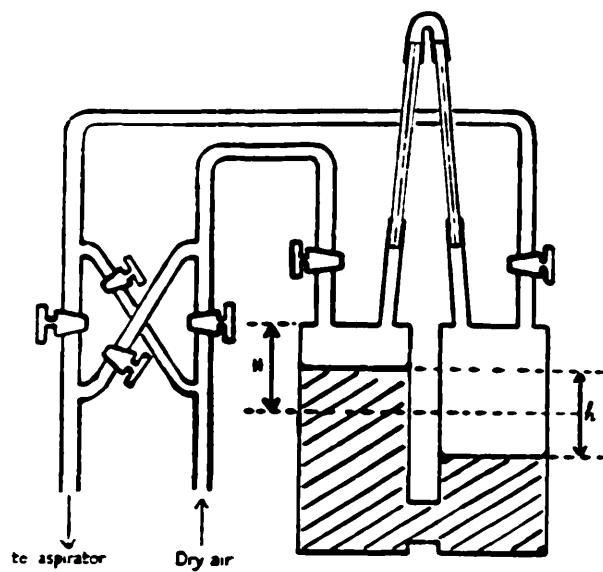
Figure 2. Capillary Viscometer

Rigden, P. J.: Viscosity of Air, Oxygen, Nitrogen,
    Phil. Mag., 25, 962 (1938).

requires a large thermostatic unit and overall size may become prohibitive.

Ultrasonic Viscometer Method. In recent years, a method has been developed for measuring fluid viscosities using ultrasonic vibrations[38]. The instrument is sold under the trade name of the "Ultra-Viscoson." This unit provides an instantaneous and continuous viscosity measurement using ultra-high frequency sound waves. The viscometer consists of a small sensing element or prove immersed in the fluid to be tested, and an electronic computer. The vibration rate of a thin alloy-steel blade in the end of the probe is determined by the viscosity of the fluid being tested. This method is extremely useful for process work where a continuous reading of viscosity for a fluid stream is required.

Oscillating Disk Method. Numerous investigators[22,23,25,35] have made experimental gaseous viscosity determinations by the oscillating disk method. The principle involved is as follows: A circular disk is suspended in the gas so as to lie horizontally and is given a small torsional oscillation in its own plane. The rate at which the oscillations diminish measures the viscosity of the surrounding gas. Several materials of construction

have been used for this disk with Sutherland and

Maass[36] using silver while Kestin and Pilarczyk[25]

used ground quartz. In each case, the disk is

suspended between two disks of the same material in

order to increase the viscous drag. The oscillation

amplitude may be measured by optical means and the

general method used by both Sutherland and Maass[37]

and Kestin and Pilarczyk[25] is the most common.

In these methods, a small mirror is attached to the

rod suspending the oscillating disk. Light from

a fixed source is reflected by this mirror on to a

scale. Time measurements are made over a number of

oscillations, and the error introduced by the timing

device may be greatly reduced. This apparatus is

especially effective for investigating gaseous

viscosities at greatly reduced temperatures as the

portion of the equipment containing the gas sample and

disk are relatively small. They may therefore be

immersed in a Dewar flask containing liquid air or

some other coolant. Figure 3 illustrates the appara-

tus used for measuring gaseous viscosity by the

oscillating disk method.

Rotating Cylinder Method. A modification of

the oscillating disk method is one in which the disks
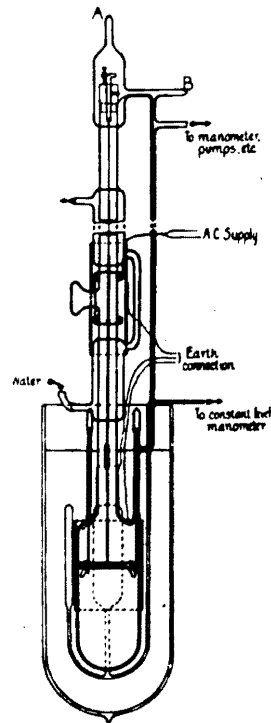
FIG. 1. *Apparatus for measuring the viscosity of gases over a large temperature range.*

Figure 3. Apparatus for Measurement of Gaseous
Viscosity over a Large Temperature Range
by the Oscillating Disk Method

Sutherland, B. P. and O. Maass: Measurement of the
Viscosity of Gases over a Large Temperature
Range, Can. J. Research, 6, 429 (1932)

are replaced by rotating concentric cylinders.
Investigators[1,4,6,21,24,28] have utilized this
apparatus for determinations of gaseous viscosity.
Figure 4 illustrates the apparatus used by Bearden[2]
and is essentially the same as the others. The
inner cylinder is driven at a constant speed by the
drive motor while the outer cylinder is suspended
from a small torsional wire. When the inner cylinder
is in motion, the viscous action of the gas between
the cylinders serves to cause an angular deflection
in the outer cylinder. Hence, oscillation of the
outer cylinder takes place. By measurement of the
oscillation amplitude and time for completing one
cycle, the viscosity of the gas may be determined.
The equipment is necessarily large, thus precluding
its immersion in a thermostatic bath. Experimental
determinations are therefore limited to temperatures
which may be maintained in the room where the
apparatus is located. However, the greatest dis-
advantage of the equipment is that it is complex
and a number of correction factors are required in
the calculations. Among these are corrections for the
characteristics of the torsion wire which may change
with time, and corrections made necessary by
variations in the speed of the rotating cylinder.
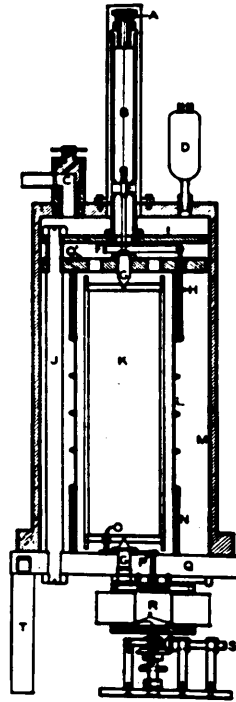
FIG. 1. Cross section of apparatus. *A*, adjustable torsion
wire support; *B*, torsion wire; *K*, inner cylinder rotating
on centers *G*; *L*, suspended cylinder; *N*, guard cylinders;
M, bell jar; *R*, magnetic drive.

Figure 4. Cross Section of Rotating Cylinder Viscometer

Bearden, J. A.: A Precision Determination of the
Viscosity of Air, Phys. Rev., <u>56</u>, 1024 (1939)

Rolling Ball Viscometer. A more recent devel-
opment in laboratory type viscometers is the rolling
ball viscometer. In this unit, a ball of known
diameter is allowed to roll through an inclined
precision bore tube. The time required for the ball
to traverse a specific distance is measured. Hubbard
and Brown[20] in their investigations of this
instrument obtained data indicating that viscosity could
be accurately determined when the fluid flow around
the rolling ball was in the laminar region. In
using this method, the instrument was standardized
with a fluid of known viscosity. From the results
of this standardization, values for the resistance
factor and Reynold's number were calculated. These
values were plotted on logarithmic graph paper for
a series of determinations at different inclination
angles. The plot resulted in a straight line of
slope -1.0 when the fluid flow around the ball was
in the laminar region. A break in the curve and a
change in the slope resulted when the turbulent flow
region was encountered. Hubbard and Brown[20] also
determined a dimensionless calibration curve which
has been derived to a good approximation from a simple
approximate treatment of the problem in terms of the
hydrodynamics of viscous fluids by Lewis[29].

Kiyama and Makita[26,27] and Bicher and Katz[3]
used this method for determinations at elevated
temperatures and pressures. The advantages of the
rolling ball viscometer are numerous. In experimental
determinations, only two variables are involved--
roll time of the ball and inclination angle of the tube.
There are no correction factors to be applied as in
other methods of viscosity determination. Because
of the relatively small size of the equipment
involved, determinations of viscosity may be made
at elevated temperatures and pressures. This is not
possible with other types of viscometers as equipment
could not be constructed to withstand the necessary
pressures and temperatures.

Falling Ball Viscometer. A modification of the
rolling ball viscometer is the falling ball type,
used mainly for liquids. As in the rolling ball
viscometer, the time required for the ball to pass
through a specific distance while immersed in the
fluid is measured. This information combined with
the angle of inclination of the tube may be used to
calculate the fluid viscosity. This method could be
utilized for both gases and liquids, but its use
with gases would result in extremely limited
applications. Clearance between the ball and tube

would be minimized. The ball would of necessity
be extremely light in weight. For viscous liquids,
this method is one of the best available. It has
been used by Wobser and Muller[40] to measure
viscosities in the range from one to one million
centipoises.

III. EXPERIMENTAL

The experimental section of this thesis will be composed of the following sections: (1) purpose of investigation; (2) plan of experimentation; (3) materials; (4) apparatus; (5) method of procedure; (6) data and results; and (7) sample calculations.

Purpose of Investigation

The purpose of this investigation was to evaluate the force co stants of certain selected non-polar gases at atmospheric pressure from viscosity data obtained using a rolling ball viscometer. It was believed that the force constants, evaluated from viscosity measurements in this manner, would be more nearly comparable with those calculated from diffusional data and hence, would be in better agreement. The gases used in this investigation were air, argon, carbon dioxide and helium.

Plan of Experimentation

The plan of experimentation that was followed involved the following steps: (1) choice of a method for viscosity measurement, (2) design of equipment, (3) measurement of viscosities, (4) calculation of viscosities, and (5) calculation of force constants.

Choice of a Method for Viscosity Measurements. Several methods were available for the measurement of gaseous viscosities. It was decided to utilize the rolling ball method as developed and correlated by Hubbard and Brown[20]. The decision was based upon simplicity of the equipment, and the fact that application of numerous correction factors was not required to calculate the viscosity of the fluid. Four common non-polar gases were chosen for study: air, argon, carbon dioxide and helium.

Design of Equipment. The second phase of the experimental work was concerned with design of a viscometer tube based upon the principle of the rolling ball viscometer. This tube was designed to allow the gas within the tube to be maintained at constant temperature during experimental determinations.

Measurement of Viscosities. The third phase of the experimental work was concentrated upon the actual physical

measurements to determine viscosities of the gases.
This involved a series of tests at various temperatures.
Measurements were taken in such a manner that the angle
of inclination was varied throughout each series.

Calculation of Viscosities. Calculating the
viscosities of the gases under study comprised the fourth
phase of the experimental work. These calculations
followed the method developed by Hubbard and Brown[20],
and utilized successfully by Kiyama and Makita[26,27].

Calculation of Force Constants. The final phase of
experimental work involved calculating force constants
for the gases. The methods presented by Hirschfelder,
Curtiss and Bird[14] and Strunk[34] were used to evaluate
the individual force constants.

Materials

The list of materials used in the experimental work
may be found in Appendix B.

Apparatus

The standard apparatus used in the experimental work
is listed in Appendix C. Specially designed equipment will
be discussed and information pertinent to its design and
construction is presented in this section of the thesis.

Viscometer Tube. The viscometer tube used for the
experimental work was of special design as shown in
Figure 5. The equipment was fabricated by Fisher
Scientific Company. All glass in the assembly is pyrex.

Stopcocks. Stopcocks were utilized for control of
gas entry into the tube and to seal the tube from the
atmosphere. The standard stopcock fittings used are
listed in Appendix C.

Viscometer Mounting Board. A mounting board was
constructed such that the viscometer could be originally
mounted in a level position. One end of the board could
be elevated a desired distance by a jackscrew arrangement.
This arrangement consisted of two steel plates, 2-1/2 x
1-7/8 x 1/4-inches, drilled and tapped for a standard
3/8-inch bolt, attached to the end of the viscometer
board. Two 3/8-inch hexagonal head bolts, three inches
long,,served as jackscrews. The configuration of the
board is shown in Figure 6. Figure 7 is a photograph
of the mounting board with the viscometer tube installed.

Viscometer Tube Mounting Brackets. Mounting
brackets for the viscometer tube were fabricated
from two standard laboratory clamps. These clamps
were reduced in length and silver soldered to a
brass plate drilled to accept three 1/8-inch flat
head wood screws. Figure 8 illustrates the con-
struction of the tube mounting bracket.

FEMALE GLASS
JOINT ₮ 24/40
WITH HOOKS

RUBBER
STOPPER

15/64" LUCITE R D

TOP VIEW

3⅛"   ¾"   12"   ¾"   3⅛"

7"

A

1½"

A

½"

SIDE VIEW

PRECISION BORE
GLASS TUBE
0.3855"±0.0002"
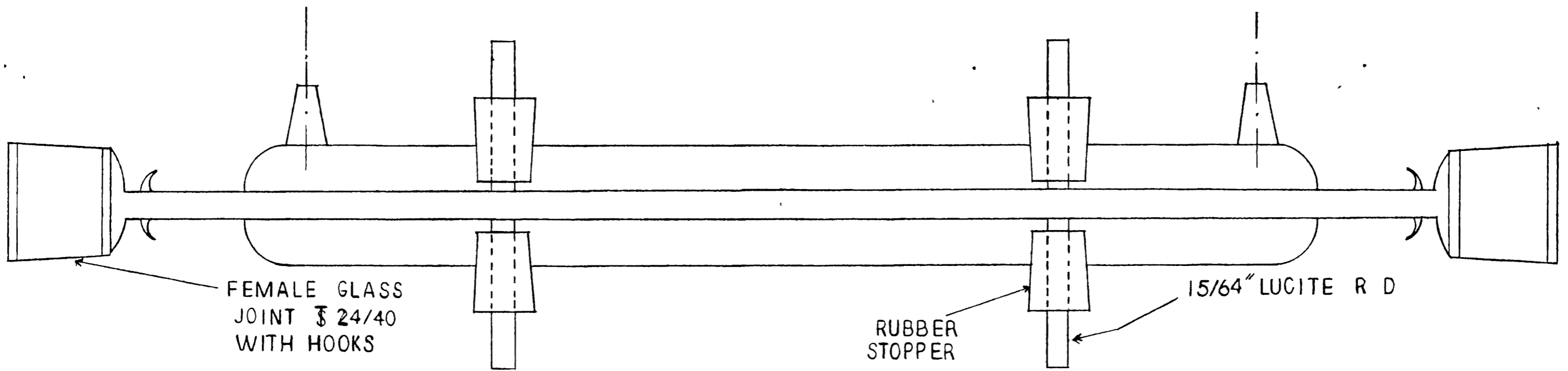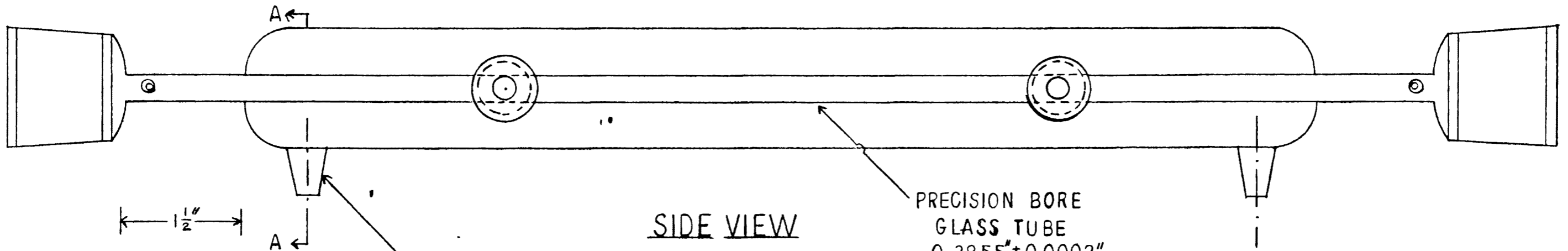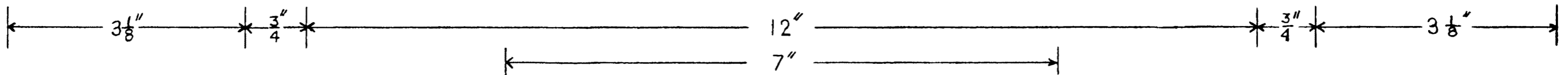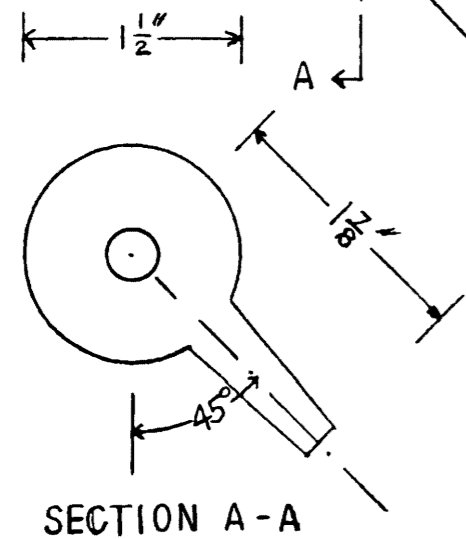
1/2" CONDENSER TYPE
JACKET OUTLET

45°

SECTION A-A

DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

VISCOMETER TUBE

SCALE 3/4"= 1 INCH	DATE 4/6/59	CASE NO: 59
DRAWN BY: WK		FILE NO: 490
CHECKED BY: mRS 4/20/59		FIGURE NO. 5
APPROVED BY: mRS 4/20/59		SHEET NO· 1 of 1

STEEL PLATE
$2\frac{1}{2}'' \times 1\frac{7}{8}'' \times \frac{1}{4}''$
DRILLED AND
TAPPED FOR
STD: $\frac{3}{8}''$ BOLT

$21\frac{1}{4}''$

$32\frac{3}{8}''$

$1\frac{1}{4}''$

$31\frac{5}{32}''$

$\frac{1}{8}''$

$1\frac{1}{2}''$

$\frac{3}{4}''$

$4\frac{15}{16}''$

$1\frac{1}{2}'' \times 1\frac{1}{2}''$ ANGLE IRON

$1\frac{1}{2}''$

$4\frac{15}{16}''$

$4\frac{1}{4}''$

$4\frac{1}{4}''$
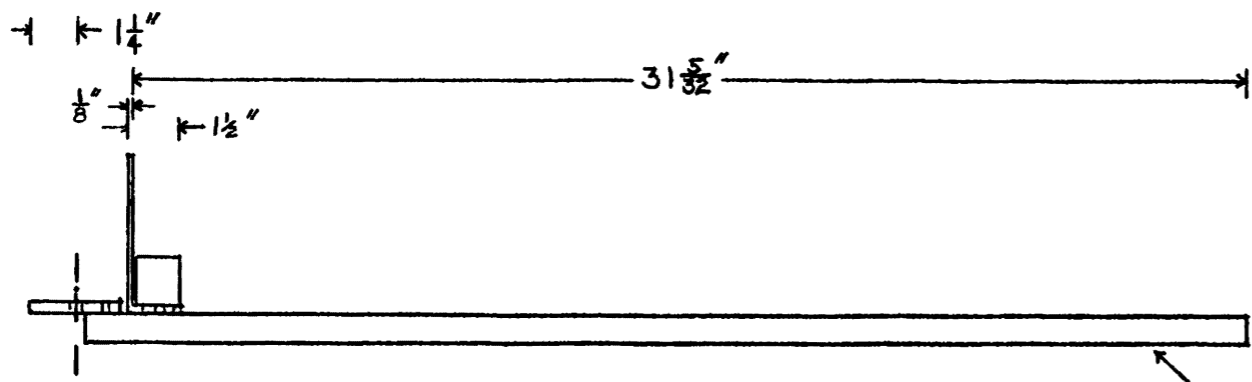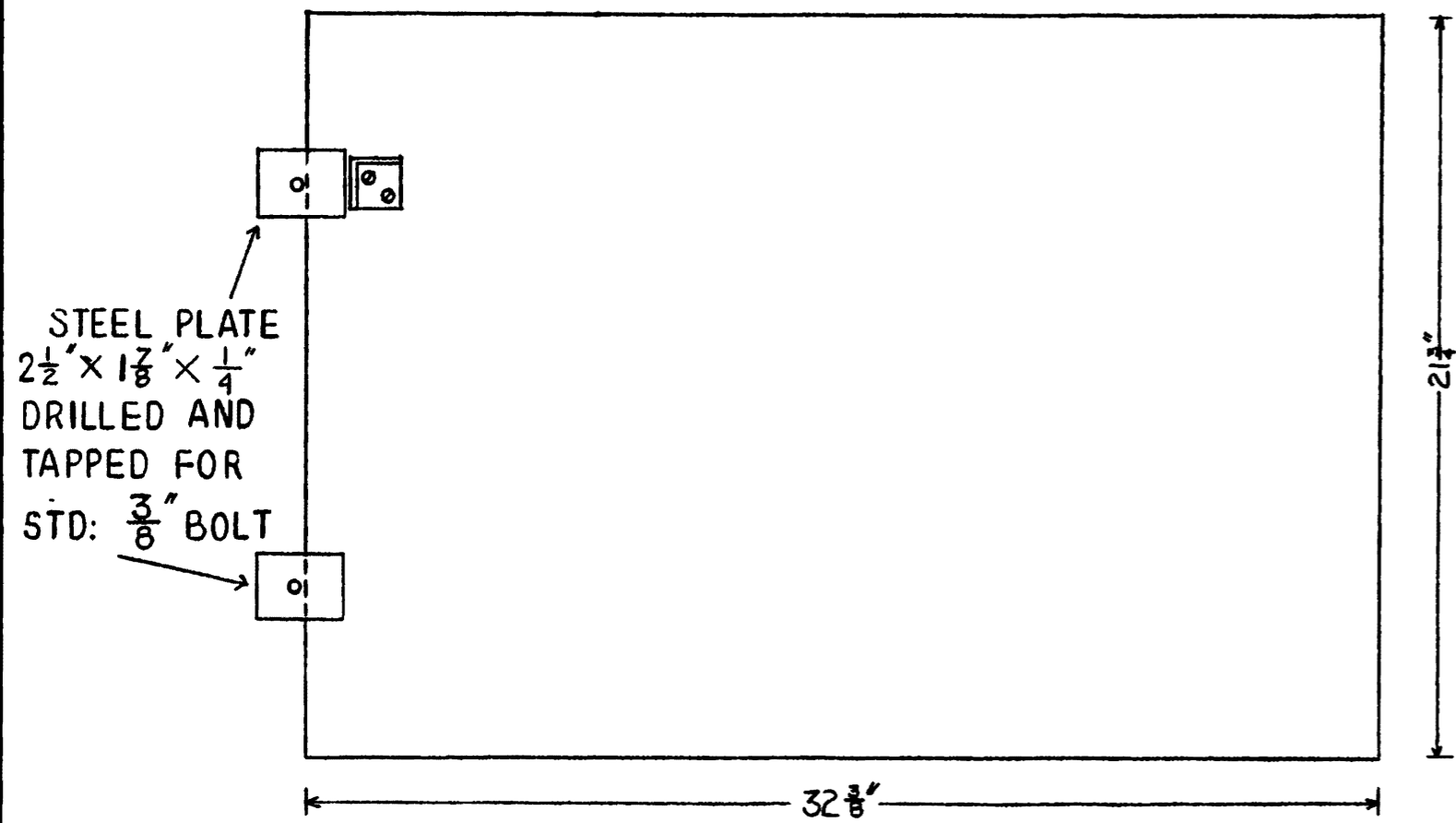
BOARD CONSTRUCTED OF
$3/4''$ PLYWOOD
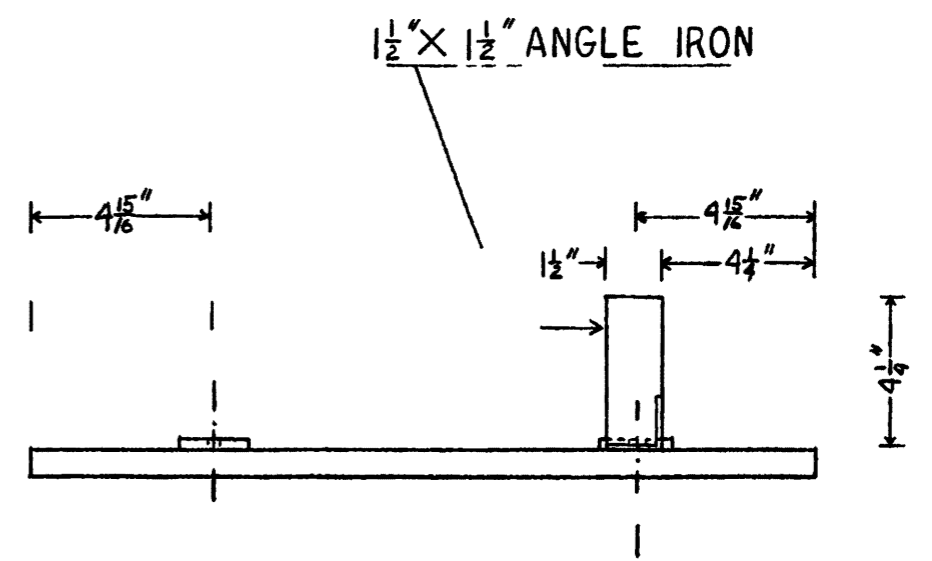
DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

VISCOMETER
MOUNTING BOARD

SCALE: $3/16'' = 1''$	DATE 4/7/59	CASE NO: 59	
DRAWN BY: CWK		FILE NO: 490	
CHECKED BY: MRS	4/30/59	FIGURE NO: 6	
APPROVED BY: MRS	4/30/59	SHEET NO: 1 of 1	

Figure 7. Viscometer Mounting Board

Figure 8. Viscometer Tube Mounting Bracket

Elevation Reference Mark. An elevation reference
mark was constructed from angle iron and is illustrated
in Figure 9. A small black dot in the center of the
white cross served as a standard reference point at
which to measure the elevation of the board. This
elevation was utilized in determining the inclin-
ation angle of the viscometer tube.

Method of Procedure

To determine the viscosities of gases utilizing the
equipment designed, the following procedures were developed.

Measurement of Constants. Certain constant values
which entered into viscosity calculations were measured
prior to initiation of experimental tests.

Measurement of Ball Diameter. The diameter of
the ball used for experimental determinations was
measured with a micrometer. A series of five
measurements were taken and the arithmetical average
diameter used in the calculations.

Measurement of Ball Density. The density of the
steel ball was determined by calculation. The ball was
weighed on an analytical balance. Dividing the weight
by the volume calculated from the diameter yielded
the density of the ball.

Figure 9. Elevation Reference Mark

Measurement of Roll Distance. The distance
through which the roll of the ball would be timed was
measured with the cathetometer. The viscometer tube
was placed in a vertical position, and the distance
between the centers of the lucite rods determined.
The roll distance was found to be 17.720 centimeters.

Measurement of Distance from Elevation Reference
Mark to Pivot Point. To determine the angle of
inclination of the viscometer, the distance between
the elevation reference mark and the pivot point
was required. The pivot point was the end of the
viscometer mounting board which was not elevated.
This distance is a fixed value and was used in all
calculations for the angle of inclination. Measure-
ment with the cathetometer showed this to be
79.135 centimeters.

Leveling of Apparatus. Before installing the vis-
cometer tube on the mounting board, it was necessary to
level all of the equipment. It is essential that the
line of sight of the cathetometer be parallel to the plane
of the viscometer mounting board when the board is in its
level position.

Leveling the Viscometer Mounting Board. The
viscometer mounting board was placed on top of the
laboratory desk, the area where the experimental

apparatus was to be utilized. Using a hand level, no discrepency was noted in the plane of the board. The reference plane for all measurements was the one occupied by the viscometer mounting board in this position.

Leveling the Cathetometer. The plane of the viscometer mounting board had now been established. The cathetometer was adjusted at this time so that the line-of-sight of the telescope was parallel to that plane. The base of the cathetometer was adjusted with the three leveling screws until a hand level placed on the base ring indicated the unit was level. This procedure was pursued until the hand level placed at any position on the base ring indicated no discrepency in level. The telescope of the cathetometer was then leveled. The hand level was placed along the telescope tube and adjustments made until the bubble in the hand level indicated satisfactory positioning. Shims were placed under the telescope supports to maintain the telescope in the desired position.

Mounting of the Viscometer Tube. Mounting of the viscometer tube was accomplished by placing it in the viscometer tube mounting brackets. The bracket clamp set screws were then tightened to hold it firmly in place.

The tube was supported at each end in the area between the point of insertion of the rubber stoppers containing the lucite rods and the cooling jacket outlets.

Insertion of the Ball into the Tube. To insert the ball into the system, a tube of paper was rolled and inserted into the viscometer. The ball was then passed through into the precision bore tube. This prevented the ball from contacting the fittings which were coated with stopcock grease. Contamination of the ball with grease would greatly affect the results obtained.

Leveling the Tube. The viscometer tube was mounted exactly parallel to the plane of the mounting board utilizing the cathetometer. The steel ball was placed in the viscometer where one pair of lucite rods adjoin the precision bore tube. The telescope of the cathetometer was focused on the ball. The height of the telescope was adjusted until the image of the ball was exactly centered in the cross hairs of the scope. The ball was then moved to the point at which the other pair of lucite rods adjoined the precision bore tube. The telescope of the cathe-tometer was refocused on the ball. If the image was not exactly centered in the cross hairs, the tube was not level. Adjustments in placement of the viscometer

were made until the ball was exactly centered in the cross hairs of the telescope at any position in the precision bore tube. At this point the tube was level. No further adjustment was made throughout the experimental investigations.

Attachment of Viscometer to a Gas Source. The viscometer was attached to the gas source by a length of one-half inch rubber tubing. The gas outlet from the cylinder was regulated by means of a Matheson "Two Stage" automatic gas regulator and delivery pressure was adjusted to approximately three pounds per square inch, gage. Gas was delivered into the viscometer through a standard straight stopcock with a four millimeter bore. This permitted isolation of the viscometer tube from the gas regulator when necessary.

Attachment of the Viscometer to the Manometer. The discharge end of the viscometer tube was fitted with a three-way stopcock with two tubes on one side. One tube was connected to a mercury manometer. The second leg of the manometer was open to the atmosphere as it was desired to operate the equipment at atmospheric pressure. The manometer related the pressure differential between the gas within the tube and the surrounding atmosphere.

Venting Gas to the Atmosphere. In filling the
viscometer tube with gas, it was necessary to vent
gas to the atmosphere. The second tube of the
stopcock was used for this purpose and for relief
of excess pressure in the viscometer.

Connection to the Constant Temperature Bath. The
viscometer was connected to the circulating pump of the
constant temperature bath by two lengths of one-half inch
rubber tubing. The pump discharge entered the elevated
end of the viscometer.

Operation of the Constant Temperature Bath.
The constant temperature bath was attached to the
viscometer tube and approximately two and one-half
gallons of distilled water added. The "Micro Set
Thermoregulator" was inserted and connected to the
control unit by means of the cable and socket
provided. The ground lead was attached to properly
grounded conduit, and the unit connected to a source
of 110 volt, alternating current. The bath was placed
in operation by rotating the power switch on the
control box. The desired controlled temperature
was set by rotating the adjusting magnet on the
"Thermoregulator" unit. The bath operated at three
heating levels, low, medium and high. These provided
100, 200 and 400 watts respectively. Operation of the

bath was not possible unless one of these elements was in use. The circulation pump would not function unless this condition existed. Temperature control was enhanced at lower temperatures by use of the permanently installed cooling coil in the bath. Potable water was circulated through this coil to provide continual cooling. Proper adjustment of this flow allowed the unit to "cycle." The periods during which the heating unit was operating would be approximately equal to the periods when it would be inoperative. This provided a more positive control on the temperature in the bath. The unit would not control automatically at a temperature below 23 degrees Centigrade. Any determinations below that temperature were made with the unit adjusted so that heat input was equal to heat removed by the cooling water. The automatic regulator did not function in this range. Constant observation and adjustment was necessary for a period of time before the temperature would remain steady.

Filling Viscometer Tube with Gas. It was necessary that all traces of alien gas be removed from the viscometer tube to assure that the viscosities measured would be for the pure gas.

Use of Vacuum Pump. The first step in the
removal of alien gas from the viscometer was to apply
a vacuum to the system for a period of ten minutes.
The vacuum connection from a laboratory type vacuum
pump was attached to the atmospheric vent of the
viscometer. The stopcock was adjusted so that the
system back to the gas regulator was under vacuum.
After a ten minute period, the vent stopcock was
closed and gas admitted to the viscometer. The valve
at the regulator was closed and the vent valve opened
to again evacuate the entire system. The vacuum was
applied about one minute at this time. The vent valve
was closed and gas again admitted to the tube. The
valve at the regulator was closed and vacuum applied
to the system by opening the vent valve. This pro-
cedure was repeated at least six times for each filling
of the tube with a different gas.

Flushing the Tube. The vacuum pump was removed
from the system and gas allowed to flow through the
viscometer tube into the atmosphere. After a ten
minute period, the vent to the atmosphere was closed
and the gas inlet stopcock closed. The gas sample
was contained within the viscometer tube. This
procedure was always performed at a temperature below
the desired operating temperature to compensate for

expansion of the gas as the temperature increased. When the enclosed gas was vented, pressure in the viscometer was greater than the atmosphere. Therefore, air would not enter the tube when the vent was opened. ,

Changing the Gas in the Viscometer. It was desirable to change the sample of gas in the viscometer in certain instances. The procedure used was the same as for introduction of a new gas. In some cases, only the latter portion of the procedure, allowing the gas to flow freely through the system, was used.

Inclination of the Tube. The inclination of the tube was accomplished by elevating one end of the viscometer mounting board with the two jackscrews. The viscometer tube was mounted so that the precision bore tube was parallel to the plane of the mounting board. Thus, when the board was inclined at a specific angle, the tube was at the same angle.

Angle of Inclination Measurement. The viscometer inclination angle was determined by measuring the vertical displacement of the reference point on the elevation reference mark (Figure 9) with the cathetometer. Used as a base was the reading taken with the viscometer mounting board at a zero angle

of inclination. The following equation was used
to calculate the inclination angle of the viscometer
tube:

$$\sin \theta = \frac{E_f - E_o}{79.135} \tag{10}$$

where θ = angle of inclination, in degrees

E_f = final elevation of reference point, in centimeters

E_o = original elevation of reference point, in centimeters

79.135 = distance from pivot point to elevation reference mark, in centimeters.

<u>Method of Moving the Ball in the Tube</u>. It was
necessary to move the ball to the upper end of the inclined
tube after each experimental roll. This was accomplished
using an electromagnet capable of controlling the ball
movement from outside the viscometer jacket. The ball
was positioned in the tube by this magnet. When the
switch on the magnet was released, the ball was free to
roll.

<u>Method for Timing the Roll of the Ball</u>. The time
required for the ball to traverse the distance between the
two lucite rods was measured. An electric timer capable
of timing to tenths of a second was employed. The timer
was started when the ball passed the first set of lucite
rods and stopped as it passed the second set. It was

necessary to account for various fluctuations in the roll time due to friction and other forces, and in the ability of the observer to determine the exact moment of passage of the ball. Therefore, a series of tests were made at a single angle of inclination. At first, forty tests were made at each angle, and a cumulative time recorded. It was noted that the average time computed from thirty determinations was, in every case, the same as for forty. Therefore, the number of tests at each angle was reduced to thirty. The time was recorded as a cumulative value for the series. The arithmetical average was used as the time for a single test. The electric timer could be read only to the nearest tenth of a second and estimated to the nearest five hundredths of a second. The time was averaged and determined to the nearest one hundredth of a second. It was assumed that an error in the measurement of the time of plus or minus 0.05 seconds was made and the probable error in the timing was found to be plus or minus 0.03 seconds. The calculations for this error are shown in Appendix E.

Determination of Viscosities. Viscosity measurements require that the viscometer be standardized with a fluid of known viscosity. In this experimental work, air was chosen to be the standard. The viscosity coefficient μ has been calculated with the following equation[3,20,26,27,40]:

$$\mu = b\ Z\ \sin\theta\ (\rho_o - \rho) \qquad (11)$$

where μ = viscosity coefficient, in grams per centimeter-second

        b = instrument constant, in square centimeters per square seconds

        Z = roll time, in seconds

        θ = angle of inclination of tube, in degrees

        ρ_o = density of the ball, in grams per cubic centimeter

        ρ = density of the gas, in grams per cubic centimeter.

Equation 11 is satisfied only when the flow of gas through the crescent shaped area between the tube and ball is in the streamline flow region.

Calibration of Viscometer. Hubbard and Brown[20] demonstrated a definite correlation between the resistance factor and the Reynold's number when the ball is rolling at uniform velocity. The resistance factor may be determined from the following equation:

$$\text{Resistance factor} = \frac{5\pi g}{42} \times \frac{(D + d)^2}{L^2 d} \times \frac{\rho_o - \rho}{\rho} \times Z^2 \sin\theta \qquad (12)$$

where   g = acceleration of gravity, in centimeters per second per second

        D = diameter of the tube, in centimeters

        d = diameter of the ball, in centimeters

        L = distance of roll, in centimeters

        ρ_o = density of the ball, in grams per liter

        ρ = density of the gas, in grams per liter

        Z = time of the roll of the ball over distance L, in seconds

        θ = angle of tube inclination, in degrees

The comparable value for Reynold's number may be calculated from the following equation:

$$\text{Reynold's number} = \frac{Ld^2}{(D + d)} \times \frac{\rho}{\mu Z} \tag{13}$$

where

L = distance of roll, in centimeters

d = diameter of the ball, in centimeters

D = diameter of the tube, in centimeters

ρ = density of the gas, in grams per cubic centimeter

μ = viscosity of the gas, in grams per centimeter per second

Z = time of roll of the ball through distance L, in seconds.

The resistance factor plotted against the Reynold's number on a logarithmic scale yields a straight line with a slope of -1.0 when the flow is in the laminar region. This line is no longer straight where flow is changing from laminar to turbulent. It curves until it reaches a certain smaller slope in the turbulent region. The correlation between the resistance factor and the Reynold's number is obtained for a gas of known viscosity by measuring the roll time of the ball and the viscometer inclination angle. The constant b in equation 11 may then be utilized to compute the viscosities of the other gases.

Experimental Calibration Procedure. Air was chosen as the medium with which to standardize the viscometer. The viscosity of air was assumed to be

1,819 x 10^{-7} grams per centimeter-second at 20 degrees
Centigrade[1,18,24]. The viscometer was filled with
air by the procedure outlined and allowed to reach
the desired temperature. Ten tests were performed
at different inclination angles, and the roll time
determined at each angle used for individual calculations.

Gas Density Determination. The density of the
gas within the viscometer tube was calculated by the
following equation:

$$\rho = \rho_{(STP)} \times \frac{273}{T} \times \frac{P}{760} \tag{14}$$

where ρ = density of the gas, in grams per
cubic centimeter

$\rho_{(STP)}$ = density of the gas at 273 degrees
Kelvin and 760 millimeters of
mercury

T = temperature of the gas, in
degrees Kelvin

P = pressure of the gas, in
millimeters of mercury.

Correlation Curve Determination. The values of
the resistance factor and Reynold's number for these
tests were calculated using equations 12 and 13
respectively. Plotted on a logarithmic scale as
shown in Figure 10, the values yielded a straight
line with a slope of -1.0 .

Calculation of Instrument Constant. The instru-
ment constant for the viscometer was determined
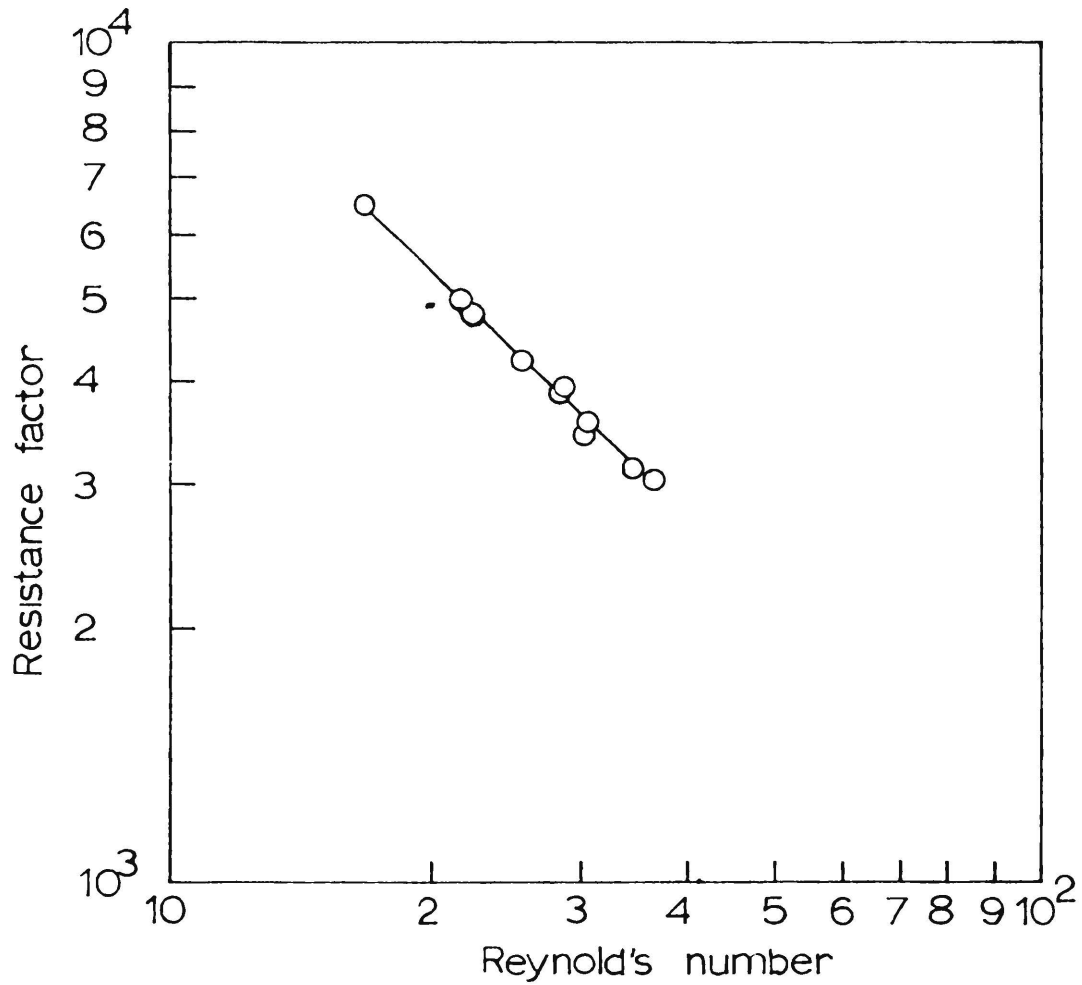
FIGURE 10   RESISTANCE FACTOR - REYNOLD'S
NUMBER CORRELATION WITH AIR AT 20°C

through substitution in equation 11 of the values for the viscosity coefficient, roll time, sine of the inclination angle and difference between the densities of the ball and gas. Values of the instrument constant b were obtained for each of the ten tests and the arithmetical average determined. The instrument constant was evaluated as 3.50×10^{-7} square centimeters per square seconds. This value was used in all subsequent calculations.

Viscosity Determinations. Viscosity determinations were performed at three temperature levels for each gas. The temperatures chosen were 27, 44.2 and 73.2 degrees Centigrade. At least eight tests were made at each temperature level, varying the inclination angle between individual tests. The procedures followed were identical to those presented earlier in this section of the thesis for measuring the roll time and inclination angle. The viscosity coefficient for each test was calculated using equation 11. The arithmetical average of these determinations was used as the viscosity of the gas at the specified conditions.

Calculation of Force Constants. The values of the force constants e/k and the collision diameter σ were determined from experimental viscosity data in the manner outlined by Hirschfelder, Curtiss and Bird[13] and as modified by Strunk[34].

Data and Results

The viscosity coefficients for four non-polar gases--
air, argon, carbon dioxide and helium--were obtained
experimentally at three temperature levels of 27, 44.2
and 73.2 degrees Centigrade.

Viscosity Coefficients. The experimental values for
the viscosity coefficients are presented in Table I. All
coefficients are based on measurements at a pressure of
one atmosphere. Coefficients were obtained from the
literature for air at both 20 and 27 degrees Centigrade.
The experimental data from the viscosity determinations
are recorded in Appendix D. Appendix E contains a discussion
of errors in the viscosity measurements and how the results
were influenced by these errors.

Potential Parameters. In addition to determining
viscosity coefficients over a range of temperatures, the
evaluation of the parameters for the Lennard-Jones
potential from the actual viscosity data was attempted.
The Lennard-Jones model was chosen as it is considered to
be one of the most realistic for non-polar gases. The
potential parameters presented in Table II were calculated
by the method developed and outlined by Hirschfelder,
Curtiss and Bird[13]. The errors in the potential
parameters were evaluated and discussed in Appendix E.

TABLE I

Experimental Viscosities of
Air, Argon, Carbon Dioxide and Helium
at One Atmosphere of Pressure

Gas	Temperature °C	Viscosity X 10^{-7} gm per cm-sec
Air[1]	20.0	1,819 ± 2
Air[2]	27.0	1,851 ± 2
Air	44.2	1,870 ± 40
Air	73.2	1,990 ± 40
Argon	27.0	2,160 ± 50
Argon	44.2	2,240 ± 50
Argon	73.2	2,400 ± 50
Carbon Dioxide	20.0	1,520 ± 30
Carbon Dioxide	27.0	1,530 ± 30
Carbon Dioxide	44.2	1,570 ± 30
Carbon Dioxide	73.2	1,730 ± 40
Helium	27.0	1,950 ± 40
Helium	44.2	1,990 ± 50
Helium	73.2	2,030 ± 40

(1) Bearden, J. A.: A Precision Determination of the Viscosity of Air, Phys. Rev. 56, 1023-40 (1939).

(2) Johnston, Herrick L., and Kenneth E. McCloskey: Viscosities of Several Common Gases Between 90° Kelvin and Room Temperature, J. Phys. Chem., 44, 1038-1058 (1940).

TABLE II

Lennard-Jones Potential Parameters for

Air, Argon, Carbon Dioxide and Helium

over Various Temperature Ranges

Gas	Temperature Range °C	Force Constant e/k °K	Collision Diameter σ in Å
Air	27.0 to 44.2	--------	----------
Air	44.2 to 73.2	67 ± 283	3.83 ± 1.30
Air	27.0 to 73.2	--------	----------
Argon	27.0 to 44.2	67 [a]	3.79 [a]
Argon	44.2 to 73.2	114 [a]	3.56 [a]
Argon	27.0 to 73.2	91 ± 159	3.66 ± 0.81
Carbon Dioxide	27.0 to 44.2	--------	----------
Carbon Dioxide	44.2 to 73.2	--------	----------
Carbon Dioxide	27.0 to 73.2	163 ± 73	4.07 ± 0.31
Helium	27.0 to 44.2	--------	----------
Helium	44.2 to 73.2	--------	----------
Helium	27.0 to 73.2	--------	----------

a   The error in calculation of k_μ was so large that it precluded calculation of error for these values. These calculations are discussed in Appendix E.

Sample Calculations

The sample calculations presented cover the following phases of the computations: (1) calculation of the gas density, (2) calculation of the tube inclination angle, (3) calculation of the resistance factor, (4) calculation of the Reynold's number, (5) evaluation of the instrument constant, (6) calculation of the gas viscosity, (7) calculation of the force constant e/k, and (8) calculation of the collision diameter.

Calculation of the Gas Density. For experimental test number 29 using air, the density of the air was calculated as follows:

$$\rho = \rho_{(STP)} \ x \ \frac{273.0}{T} \ x \ \frac{P}{760.0} \tag{14}$$

where $\rho_{(STP)}$ = 1.293 gm/liter[5]

T = 293.0 °K

P = 735.8 mm Hg

then

$$\rho = (1.293)\frac{(273.0)(735.8)}{(293.0)(760.0)} \tag{15}$$

$$\rho = 1.166 \ gm/liter \tag{16}$$

Calculation of the Tube Inclination Angle. For experimental test number 29, the angle of inclination of the viscometer tube was calculated from equation 10 as follows:

$$\sin \theta = \frac{E_f - E_o}{79.135} \qquad (10)$$

where
$$E_f = 4.515 \text{ cm}$$

$$E_o = 1.650 \text{ cm}$$

then
$$\sin \theta = \frac{(4.515 - 1.650)}{79.135} \qquad (17)$$

$$\sin \theta = 0.03620 \qquad (18)$$

$$\theta = 2° \ 4' \qquad (19)$$

Calculation of the Resistance Factor. For experimental test number 29, the resistance factor was calculated as follows:

$$\text{Resistance factor} = \frac{5\pi g}{42} x \frac{(D + d)^2}{L^2 d} x \frac{\rho_o - \rho}{\rho} x Z^2 \sin \theta \qquad (12)$$

where
$$g = 980 \text{ cm/sec/sec}$$

$$D = 0.979 \text{ cm}$$

$$d = 0.953 \text{ cm}$$

$$L = 17.720 \text{ cm}$$

$$\rho_o = 7807 \text{ gm/liter}$$

$$\rho = 1.17 \text{ gm/liter}$$

$$Z = 1.88 \text{ sec}$$

$$\sin \theta = 0.03620$$

$$\text{Resistance factor} = (366)(0.0125)(6690)(3.53)(0.03620) \qquad (20)$$

$$\text{Resistance factor} = 3910 \qquad (21)$$

Calculation of the Reynold's Number. For experimental

test number 29, the Reynold's number was calculated as

follows:

$$\text{Reynold's number} = \frac{Ld^2}{(\quad + d)} \times \frac{\rho}{\mu\,Z} \qquad (13)$$

where

L = 17.720 cm

d = 0.953 cm

D = 0.979 cm

ρ = 1.17 gm/liter

μ = 1,819 x 10^{-7} gm/cm-sec

Z = 1.88 sec

then

$$\text{Reynold's number} = \frac{(17.720)(0.953)^2}{(0.979 + 0.953)} \times \frac{(1.17)}{1,819 \times 10^{-7}(1.88)} \qquad (22)$$

$$\text{Reynold's number} = 28.4 \qquad (23)$$

Evaluation of the Instrument Constant. The instrument

constant evaluated from the data for experimental test

number 29 was determined by rearranging equation 11 to read:

$$b = \frac{\mu}{z \sin \theta \, (\rho_o - \rho)} \qquad (24)$$

where

μ = 1,819 x 10^{-7} gm/cm-sec

z = 1.88 sec

$\sin \theta$ = 0.03620

ρ = 1.17 gm/liter

ρ_o = 7807 gm/liter

and

$$b = \frac{1,819 \times 10^{-7}}{531} \qquad (25)$$

$$b = 3.43 \times 10^{-7} \qquad (26)$$

<u>Calculation of the Gas Viscosity.</u> For experimental test number 58, the viscosity of the carbon dioxide was calculated as follows:

$$\mu = b\, Z \sin\theta\, (\rho_o - \rho) \tag{11}$$

where
$$b = 3.50 \times 10^{-7}\ cm^2/sec^2$$
$$Z = 1.83\ sec$$
$$\sin\theta = 0.03170$$
$$\rho_o = 7807\ gm/liter$$
$$\rho = 1.63\ gm/liter$$

therefore

$$\mu = (3.50 \times 10^{-7})(1.83)(0.03170)(7806) \tag{27}$$

$$\mu = 1{,}590 \times 10^{-7}\ gm/cm\text{-}sec \tag{28}$$

<u>Calculation of the Force Constant e/k.</u> The calculation of the force constant e/k for argon between the temperatures of 44.2 and 73.2 degrees Centigrade was made as follows:

Evaluate a quantity k_μ as developed by Hirschfelder[13]

$$k_\mu = \left[\frac{\mu(T_2)}{\mu(T_1)}\right]_{exptl} \left[\frac{T_1}{T_2}\right]^{0.5} \tag{29}$$

where $\mu(T_2)$ = experimental viscosity at temperature T_2, in grams per centimeter per second

$\mu(T_1)$ = experimental viscosity at temperature T_1, in grams per centimeter per second

T_1 = temperature of viscosity determination, in degrees Kelvin

T_2 = temperature of viscosity determination, in degrees Kelvin

Substituting the following values for argon:

$$\mu(T_2) = 2,400 \times 10^{-7} \text{ gm/cm-sec}$$
$$\mu(T_1) = 2,240 \times 10^{-7} \text{ gm/cm-sec}$$
$$T_1 = 317.2 \text{ °K}$$
$$T_2 = 346.2 \text{ °K}$$

equation 29 becomes

$$k_\mu = \frac{(2,400 \times 10^{-7})}{(2,240 \times 10^{-7})} \left[\frac{317.2}{346.2}\right]^{0.5} \tag{30}$$

$$k_\mu = (1.07)(0.957) \tag{31}$$

$$k_\mu = 1.02 \tag{32}$$

The value of e/k may then be determined by a trial and error solution of the following equation[12]:

$$k_\mu = \left[\frac{\Omega^{(2,2)}(T_1^+)}{\Omega^{(2,2)}(T_2^+)}\right]\left[\frac{F_\mu^{(3)}(T_2^+)}{F_\mu^{(3)}(T_1^+)}\right] \tag{33}$$

where $T_1^+ = kT_1/e$

$\Omega^{(2,2)}(T_1^+)$ = collision integral for T_1^+

$\Omega^{(2,2)}(T_2^+)$ = collision integral for T_2^+

$F_\mu^{(3)}(T_2^+)$ = function for calculating the third approximation of the viscosity coefficient for T_2^+

$F_\mu^{(3)}(T_1^+)$ = function for calculating the third apprximation of the viscosity coefficient for T_1^+

The values for the collision integrals and third approximation functions have been calculated and tabulated by Hirschfelder, Curtiss and Bird[16,17].

In the trial and error solution, the first assumption for a value of e/k for argon was 124. This yielded:

$$T_1 = 317.2 \ ^\circ K$$

$$T_2 = 346.2 \ ^\circ K$$

$$e/k = 124.0 \ ^\circ K$$

$$T_1^+ = 2.558 \ ^\circ K$$

$$T_2^+ = 2.792 \ ^\circ K$$

From the tables in Hirschfelder, Curtiss and Bird[16,17] the following values for the collision integrals were obtained:

$$\Omega^{(2,2)}(T_1^+) = 1.0860$$

$$\Omega^{(2,2)}(T_2^+) = 1.0589$$

$$F_\mu^{(3)}(T_1^+) = 1.0025$$

$$F_\mu^{(3)}(T_2^+) = 1.0030$$

Substituting into equation 33:

$$k_\mu = \frac{(1.0860)(1.0030)}{(1.0589)(1.0025)} \tag{34}$$

$$k_\mu = 1.0261 \tag{35}$$

The value of k_μ for a value of e/k of 124 is not identical to that calculated in equation 32. Therefore, further assumptions were made for the value of e/k until equation 33 was an identity with equation 29. In this instance, a value of 114 will yield a solution of equation 33 which is identical to equation 32.

Calculation of the Collision Diameter. Once the

value of e/k has been determined, the collision diameter

may be evaluated[14] as follows:

$$\sigma^2 = \frac{266.93\sqrt{M\ T_1}\ \ F_\mu^{(3)}(T_1^+)}{[\mu(T_1) \times 10^7]\ \Omega^{(2,2)}(T_1^+)} \tag{36}$$

where σ = collision diameter, in Angstroms

  M = molecular weight of the gas, in grams

  T_1 = temperature of viscosity determination, in degrees Kelvin

  $\mu(T_1)$ = viscosity of gas at temperature T_1, in grams per centimeter per second

  $F_\mu^{(3)}(T_1^+)$ = function for calculating the third approximation of the viscosity coefficient for T_1

  $\Omega^{(2,2)}(T_1^+)$ = collision integral for T_1^+

Substituting the following values for argon into equation 36:

$$M = 39.94\ \text{gm}$$
$$e/k = 114\ °K$$
$$T_1 = 346.2\ °K$$
$$T_1^+ = 3.037$$
$$F_\mu^{(3)}(T_1^+) = 1.0035$$
$$\Omega^{(2,2)}(T_1^+) = 1.0357$$
$$\mu(T_1^+) = 2,400 \times 10^{-7}\ \text{gm/cm-sec}$$

the solution is obtained where

-58-

$$\sigma^2 = \frac{(266.93) \ \overline{/13,830} \ (1.0035)}{(2,400 \times 10^{-7} \times 10^7)(1.0357)} \tag{37}$$

$$\sigma^2 = 12.67 \ \overset{\circ}{A}{}^2 \tag{38}$$

$$\sigma = 3.56 \ \overset{\circ}{A} \tag{39}$$

IV. DISCUSSION

The discussion section of this thesis will be concerned with the following items: (1) discussion of results, (2) recommendations, and (3) limitations.

Discussion of Results

The discussion of results falls into the following catagories: (1) comparison of experimental gas viscosities with previous investigations, and (2) comparison of experimentally determined force constants with previous investigations. Included is a discussion of discrepencies which appear and postulates as to their source.

Comparison of Experimental Gas Viscosities with Previous Investigations. The experimentally determined viscosities for air, argon, carbon dioxide and helium were found to differ from values determined by previous investigators. Table III lists the viscosities of air determined in this investigation with viscosity coefficients from literature sources. Table IV compares the experimental viscosities of argon with values from the

TABLE III

Comparison of the Experimental Values

for the Viscosity of Air with

Previous Investigations

Temperature °C	Viscosity Experimental X 10^{-7} gm/cm-sec	Viscosity by Previous Investigations gm/cm-sec	Variation %
20.0	----------	1,819 X 10^{-7}[1]	----
27.0	1,850 ± 40	1,841 X 10^{-7}[1]	0.54
44.2	1,870 ± 40	1,924 X 10^{-7}[2] [a]	2.75
73.2	1,990 ± 40	2,057 X 10^{-7}[2] [a]	3.31

(1) Hirschfelder, Joseph O., R. Byron Bird, and Ellen L. Spotz: The transport properties for non-polar gases, J. Chem. Phys., 16, 968-981 (1948).

(2) Lange, Norbert Adolph (Editor): "Handbook of Chemistry," p. 1662. Handbook Publishers, Inc., Sandusky, Ohio, 1956. 9 ed.

a Graphical Interpolation

TABLE IV

Comparison of the Experimental Values

for the Viscosity of Argon with

Previous Investigations

Temperature °C	Viscosity Experimental X 10^{-7} gm/cm-sec	Viscosity by Previous Investigations gm/cm-sec	Variation %
27.0	2,160 ± 50	2,233 X $10^{-7(1)a}$	3.31
44.2	2,240 ± 50	2,327 X $10^{-7(1)a}$	3.57
73.2	2,400 ± 50	2,510 X $10^{-7(1)a}$	4.38

(1)   Lange, Norbert Adolph (Editor):   "Handbook of Chemistry," p. 1662.   Handbook Publishers, Inc., Sandusky, Ohio, 1956.   9 ed.

a   Graphical Interpolation

literature while Table V presents viscosities of carbon
dioxide. Table VI contains experimental values of helium
viscosity compared with previous investigations.

Comparison of Experimental Values for Air
Viscosity with Previous Investigations. Table III
contains experimentally determined values for the
viscosity coefficient of air compared with values
found in the literature. As the equipment was cal-
ibrated with air at 20 degrees Cent'grade, no exper-
imental value was obtained at this temperature.
With each temperature increase, the per cent deviation
from previous investigations became greater. It
should be noted that the results of the experimental
work are all lower than values from previous inves-
tigations. A theory will be presented as to the
cause of this deviation.

Comparison of Experimental Values for Argon
Viscosity with Previous Investigations. Table IV
compares the experimentally determined viscosity
coefficients for argon with results from previous
investigations. The per cent variation between
experimental values determined by the rolling ball
method and values taken from the literature increases
with temperature. It should be noted that in all
cases, the experimental values are lower than the

TABLE V

Comparison of the Experimental Values
for the Viscosity of Carbon Dioxide
with Previous Investigations

Temperature °C	Viscosity Experimental X 10^{-7} gm/cm-sec	Viscosity by Previous Investigations[1][a] gm/cm-sec	Variation %
20.0	1,520 ± 30	1,480 X 10^{-7}	-2.36
27.0	1,530 ± 30	1,515 X 10^{-7}	-1.19
44.2	1,570 ± 30	1,610 X 10^{-7}	2.55
73.2	1,730 ± 30	1,786 X 10^{-7}	2.97

(1) Lange, Norbert Adolph (Editor): "Handbook of Chemistry," p. 1663. Handbook Publishers, Inc., Sandusky, Ohio, 1956. 9 ed.

a   Graphical Interpolation

TABLE VI

Comparison of the Experimental Values

for the Viscosity of Helium with

Previous Investigations

Temperature °C	Viscosity Experimental X 10^{-7} gm/cm-sec	Viscosity by Previous Investigations[1][a] gm/cm-sec	Variation %
27.0	1,950 ± 40	2,026 X 10^{-7}	3.65
44.2	1,990 ± 50	2,112 X 10^{-7}	5.96
73.2	2,030 ± 40	2,237 X 10^{-7}	9.26

(1)   Lange, Norbert Adolph (Editor):   "Handbook of Chemistry," p. 1663.   Handbook Publishers, Inc., Sandusky, Ohio, 1956.   9 ed.

a   Graphical Interpolation

values from the literature. This variation will be
discussed later in this section of the thesis.

Comparison of Experimental Values for Carbon
Dioxide Viscosity with Previous Investigations.
Table V presents the experimental viscosities of
carbon dioxide determined by this experimental work
compared with values from the literature. It will
be noted that the determinations at temperatures of
20 and 27 degrees Centigrade yield viscosity
coefficients higher than values from the literature.
Determinations at higher temperatures followed the
pattern of air and argon, and yielded results between
two and three per cent below the literature values.
The cause for the variation at the two lower
temperatures will be discussed under the heading of
equipment problems. The variation of the determinations
at higher temperatures will be discussed with those
noted for the other gases.

Comparison of Experimental Values for Helium
Viscosity with Previous Investigations. Table VI
presents a comparison of the experimental viscosity
coefficient for helium with values from previous
investigations. The experimental deviation from the
previously determined coefficients was greatest for
helium. The range was from three per cent at 27 de-
grees Centigrade to nine per cent at 73.2 degrees

Centigrade. In all cases, the experimentally deter-
mined coefficient is lower than the values from the
literature. Helium followed the pattern of air,
argon and carbon dioxide in that the per cent
variation from past results increased with an
increase in temperature.

Viscosity Deviation with Increase in Temperature.
It was noted for each gas that an increase in tem-
perature resulted in increased deviation from
previously determined viscosities. The experimental
values were lower than those of other investigations.
Experimental results were reproducible, so further
consideration was given to the source of these
variations. It was assumed that since results could
be reproduced, the method and procedure developed
was satisfactory. As discussed previously in this
section, viscosities for air, argon and carbon
dioxide exhibited similar deviations. The deviations
for the viscosity of helium was about three times
that of the other gases. Experimental determinations
were taken at different angles of inclination and
roll times, and agreement was exhibited between
the individual results. Sufficient ime was allowed
for the temperature of the gas in the tube to reach
equilibrium with the fluid in the viscometer jacket.

In each case, the measured viscosity was lower
than anticipated at the temperature existing
in the equipment. If it were possible that
the steel ball did not reach the temperature
of the surrounding gas, then cooling of the
gas could take place at the surface of the
ball as it passed through the tube. If this
were true, results would yield a viscosity
coefficient for a lower temperature than
that of the bulk of the gas. Thermal con-
ductivities of the gases were investigated
and are listed in Table VII. The thermal
conductibity of air, argon and carbon dioxide
are approximately the same while that for
helium is six times greater. From this
information, one could conclude that if the
gas around the ball were being cooled at the
moment of passage, helium would be affected
to a much greater extent than the other
gases. Verification of this assumption
was not possible due to equipment failure.

TABLE VII

Thermal Conductivity of Gases

at

Various Temperatures

Gas	Temperature °C	Thermal Conductivity X $10^{5(1)}$ g-cal/(sec)(sq cm)(°C/cm)
Air	0.0	5.572
Air	100.0	7.197
Argon	0.0	3.88
Argon	100.0	5.087
Carbon Dioxide	0.0	3.393
Carbon Dioxide	100.0	5.06
Helium	0.0	33.60
Helium	100.0	39.85

(1) Lange, Norbert Adolph (Editor): "Handbook of Chemistry," p. 1544. Handbook Publishers, Inc., Sandusky, Ohio, 1956. 9 ed.

Equipment Problems. One problem en-
countered in the use of the viscometer was
the measurement of the viscosity of carbon
dioxide at lower temperatures. Of necessity,
the viscometer was operated at angles of
inclination from about one to one and one-
half degrees. Below these particular

angles, friction between the ball and glass was suffi-
cient to cause erratic time measurements within a
single test. This resulted in a very narrow oper-
ating range for carbon dioxide determinations. The
problem could be alleviated by using a steel ball
of a greater diameter, reducing the ratio of the
diameters of the tube to the ball. In turn the
value of the Reynold's number would be reduced to
a point such that the instrument would operate in the
laminar flow region over a wider range of inclination
angles. This is especially important in measurement
of the viscosity of gases more dense than air and
having viscosity coefficients below that of air.
Equation 13 relates Reynold's number as directly
proportional to the density of the gas and inversly
proportional to the viscosity coefficient of the
gas. In the case of carbon dioxide, these factors
combine to greatly reduce the operating range of the
instrument.

Comparison of Experimentally Determined Force Con-
stants with Previous Investigations. The values of the
force constants were found to differ from values reported
by previous investigators. Table VIII presents the values
of the force constants calculated from the experimental
data as compared to results from other investigations.

TABLE VIII

Comparison of Force Constants from Experimental Data

with Values from Previous Investigations

Gas			Force Constants Experimental	Force Constants Previous Investigations [1]
Air	e/k	°K	67 ± 283	97
	σ	Å	3.83 ± 1.30	3.617
Argon	e/k	°K	91 ± 159	124
	σ	Å	3.66 ± 0.81	3.418
Carbon Dioxide	e/k	°K	163 ± 73	190
	σ	Å	4.07 ± 0.31	3.996
Helium	e/k	°K	----------	6.03
	σ	Å	----------	2.70

(1) Hirschfelder, Joseph O., R. Byron Bird, and Ellen L. Spotz: The Transport Properties for Non-Polar Gases, J. Chem. Phy., 16, 974 (1948).

For helium, it was not possible to obtain values of the
constants from the experimental data. This was attributed
to the discrepencies in the experimental viscosity data.
For air and carbon dioxide, the force constant could be
obtained over one temperature range. For argon, a constant
was obtained for each temperature range with considerable
variation between the individual values. With a value of
the force constant over each temperature range available
for argon, the method used by Strunk[34] was applied to
the data.

Re-evaluation of Force Constants for Argon.

Re-evaluation of the force constants for argon was
based on the premise that the assumption of the
exponent of one-half for the temperature factor in
equation 29 does not hold over the complete tempera-
ture range in question. The first step in the pro-
cedure was evaluation of the following functions:

$$\frac{\mu_2}{\mu_1}\left[\frac{T_1}{T_2}\right]^{0.5} = \frac{\Omega_1}{\Omega_2} \tag{40}$$

$$= 1.0108 \tag{41}$$

$$\frac{\mu_3}{\mu_2}\left[\frac{T_2}{T_3}\right]^{0.5} = \frac{\Omega_2}{\Omega_3} \tag{42}$$

$$= 1.0237 \tag{43}$$

$$\frac{\mu_3}{\mu_1}\left[\frac{T_1}{T_3}\right]^{0.5} = \frac{\Omega_1}{\Omega_3} \qquad (44)$$

$$= 1.0348 \qquad (45)$$

Comparison of the above values was made to the ratios tabulated in Table IX. These values were calculated using equation 33. It was noted that for the exponent of 0.5, there was no agreement between values for the force constant. By trial and error solution, the exponent of 0.4425 was found to yield results exhibiting the least variation between force constants over the individual temperature ranges. In this case, the following relationships exist:

$$\frac{\mu_2}{\mu_1}\left[\frac{T_1}{T_2}\right]^{0.4425} = \frac{\Omega_1}{\Omega_2} \qquad (46)$$

$$= 1.01405 \qquad (47)$$

$$\frac{\mu_3}{\mu_2}\left[\frac{T_2}{T_3}\right]^{0.4425} = \frac{\Omega_2}{\Omega_3} \qquad (48)$$

$$= 1.02885 \qquad (49)$$

$$\frac{\mu_3}{\mu_1}\left[\frac{T_1}{T_3}\right]^{0.4425} = \frac{\Omega_1}{\Omega_3} \qquad (50)$$

$$= 1.04335 \qquad (51)$$

Comparing the above values to Table IX, the constants were evaluated as shown in Table X. The arithmetical

TABLE IX

Ratios of Collision Integrals for Values

of the Force Constant e/k

e/k °K	Collision Integral Ratios		
	$\dfrac{\Omega_1}{\Omega_2}$	$\dfrac{\Omega_2}{\Omega_3}$	$\dfrac{\Omega_1}{\Omega_3}$
110	1.0146	1.0238	1.0388
115	1.0154	1.0246	1.0404
120	1.0150	1.0260	1.0414
125	1.01615	1.02647	1.0431
130	1.0166	1.0271	1.0441
140	1.0175	1.0277	1.0470
145	1.0179	1.0294	1.0477

TABLE X

Evaluation of Force Constant e/k from

Collision Integral Ratios

e/k °K	$\frac{\Omega_1}{\Omega_2}$	e/k °K	$\frac{\Omega_2}{\Omega_3}$	e/k °K	$\frac{\Omega_1}{\Omega_3}$
108	1.0142	140	1.0290	127	1.0437
	1.0141		1.0289		1.0434
107	1.0140	139	1.0288	126	1.0433
e/k = 107 °K[a]		e/k = 139 °K[a]		e/k = 126 ± 150 °K	

Average e/k = 124 °K[a]

a. The error in the calculation of the value of μ_2/μ_1 is so large as to preclude the calculation of the errors for these values. The calculations are discussed in Appendix E.

average of the three constants was determined. The numerical value of e/k as calculated by this method was 124 degrees Kelvin. This value is greatly in error and the magnitude of the error may not be determined. This error is discussed in Appendix E. The collision diameter was calculated using equation 36 and found to be 3.12 Angstroms, a lower value than that reported by Hirschfelder, Bird and Spotz[19]. Again, it was not possible to evaluate the error in this calculation as no error in the measurement of e/k was determined. This method was not applicable to data for air, carbon dioxide or helium.

Equipment Failure. Two equipment failures were experienced. The first was the appearence of a small hole in the junction of the precision bore glass tube to the viscometer jacket. This resulted in leakage of water into the tube. The leak did not become extensive until a vacuum was applied to the system. The viscometer was returned to the manufacturer for repairs. The process of sealing the hole reduced the diameter of the precision bore tube at one point to less than the ball diameter. A small brass insert was placed in the tube to prevent the ball from reaching the constricted area. This in no way affected the measurements taken. The final failure of

the equipment occurred when attempts were made to check some of the data. The calculations had been completed and discrepencies noted in the values of the viscosity coefficients. It was decided to confirm the previous determinations. At this time, the vacuum was applied to the system as before. A compound fracture occurred in the precision bore tube at the point where it had been constricted in the repair process. It was presumed that a stress point existed causing this failure. It was not possible to conduct further experimental tests.

Recommendations

The recommendations to be presented are ones which have evolved in the process of conducting the experimental viscosity determinations. They are concerned with the method of construction of the viscometer as this was the primary source of problems encountered in the experimental work.

Method of Heating the Steel Ball. To insure thermal equilibrium between the steel ball and surrounding gas, a method for direct heating of the ball should be incorporated into future designs. One of the following methods would possibly prove satisfactory for this purpose.

Induction Heating. The steel ball could
be heated by an induction heating unit surround-
ing the glass tube. The ball could be posi-
tioned in the heater and current applied to
generate the heat. This system has a disadvan-
tage in that the exact temperature of the ball
would not be known. If the ball were over-
heated, the problem of cooling the ball would be
the same as that of heating it in the existing
equipment. After heating the ball, sufficient
time would have to be provided to allow the ball
to reach equilibrium with the surrounding gas
in the tube.

Heating the Steel Ball Outside the
Viscometer. One procedure which appears to be
practical is that of heating the steel ball
prior to its insertion into the viscometer.
This method has been used by previous inves-
tigators for the determination of the viscosity
of liquids. In this case, the viscometer tube
may be open to the air and the ball inserted
directly into the tube. With a gas, the ball
would be allowed to reach equilibrium immersed
in a bath at the same temperature as the gas in
the viscometer tube. The ball would then be

inserted into the viscometer for the viscosity deter-
minations. This procedure would require modification
of the viscometer design to permit the ball to be
injected without introduction of an alien gas. This
could be accomplished by the use of an "air lock"
system. The ball would be introduced from the "air"
into a chamber of the viscometer through which gas is
flowing under pressure. The gas in this instance
would be the same as that in the viscometer. The
ball would be placed in this chamber and isolated
from the atmosphere. It would then be allowed to
pass into the viscometer proper. This would require
fabrication of special stopcocks having sufficient
bore diameter to pass the steel ball. The ball
could thus be preheated to the desired temperature,
and injected into the viscometer without introduction
of an undesirable gas.

Diameter Ratios. It is recommended that if future
experimental tests are performed using a rolling ball
viscometer, the ratio of the diameter of the tube to the
diameter of the ball be decreased. For this experimental
work the diameter ratio was 1.0271. This was too large
for determination of the viscosity of carbon dioxide at
all but a narrow range of inclination angles. Decreasing
this "tube to ball" ratio results in a decreased Reynold's

number at any specific angle. This permits operation in
the laminar flow region over a much wider range of inclin-
ation angles.

Electric Timing of Roll Time. It is recommended that
a system of timing by photoelectric methods be investigated.
The breaking of a beam of light by the passage of the ball
could be used to activate the timing system and the values
of time should be more consistent. It is also recommended
that a timer of increased accuracy be used with an apparatus
of this nature in that a considerable portion of the error
in the time measurement comes from inability to read the
timer to the nearest one hundredth of a second. Another
method which should be investigated is that of surrounding
the glass tube with a wire coil of such magnitude that
when a ball made of a magnetic material passes through the
coil, the increase in magnetic permeability of the system
with respect to the earth's magne ic field will result in
the generation of a small current in the coil. Amplified,
this small pulse could be used to activate the timing
system. The coils would of necessity be watertight, or else
some non-conducting medium such as transformer oil would
have to be used in the heating jacket.

Instrument Constant Determinations. The instrument
constant for the viscometer should be determined at each
operating temperature. This type of calibration will
eliminate the error introduced by the expansion of the
ball due to temperature elevation.

Limitations

The experimental work presented in this thesis was limited to the measurement of the viscosity coefficient and calculation of the force constants for air, argon, carbon dioxide and helium.

Temperature Limits. Determinations were conducted at 27, 44.2 and 73.2 degrees Centigrade. These specific temperatures were chosen as diffusion data was available from the work of Strunk[31] at these conditions. The constant temperature bath used in the experimental work would not control automatically at temperatures below 25 degrees Centigrade. The upper limit of its operation was 99 degrees Centigrade.

Pressure Limit. All experimental determinations were made with a pressure of approximately one atmosphere existing in the viscometer.

Purity of Gases. All experimental determinations were made with the tube filled with pure gas. No determinations of the viscosity of mixtures was attempted.

Angle of Inclination Limit. Viscosity determinations were made with the viscometer operating between the inclination angles of 34 minutes and three degrees and 15 minutes. At angles lower than 34 minutes, the friction between the ball and the glass caused exceedingly erratic readings. The upper limit of three degrees and 15 minutes was the maximum elevation that could be obtained.

V. CONCLUSIONS

The evaluation of the force constants for the non-polar gases air, argon, carbon dioxide and helium from viscosity coefficients determined with a rolling ball viscometer led to the following conclusion:

1. Due to errors in the measurement of the viscosity of the gases, no conclusive results were obtained for the values of the force constants for air, argon, carbon dioxide or helium.

VI. SUMMARY

The objective of this investigation was to evaluate the force constants for the non-polar gases air, argon, carbon dioxide and helium from experimental viscosity data over a temperature range of 27 to 73.2 degrees Centigrade. The viscosity coefficients for these gases were determined experimentally using a rolling ball viscometer. The error in the measurements was evaluated at approximately two per cent, and the values differed from results of previous investigators by an amount greater than this error. Discrepencies in the experimental viscosity data or basic theory precluded the determination of force constants over all the temperature ranges studied for air, carbon dioxide and helium. No conclusive results were obtained in the evaluation of the force constants.

VII. APPENDICES

The nomenclature used in the thesis is listed in Appendix A. Appendix B contains a list of materials used for the experimental work. The apparatus used in the experimental procedures is listed in Appendix C. The data taken during the experimental determinations of the viscosity coefficients are listed in Appendix D. Appendix E contains a discussion of the error in the calculations and the methods used to evaluate these errors.

APPENDIX A

Nomenclature

The nomenclature used in this thesis is as follows:

b = instrument constant

D = diameter of viscometer tube

D_{12} = diffusion coefficient

d = diameter of the steel ball

E_f = final elevation of reference point

E_o = original elevation of reference point

e = depth of potential well and represents maximum energy of attraction

e/k = molecular potential energy parameter

F = force of interaction between two spherically shaped non-polar molecules

$F_\mu^{(3)}(T_1^+)$ = function for calculation of the third approximation of the viscosity coefficient at temperature T_1

g = acceleration due to gravity

k = Boltzmann's constant

L = distance of roll of the ball

M = molecular weight of the gas

P = pressure of the gas

r = intermolecular separation distance

T = temperature of the gas

T_1^+ = reduced temperature = kT_1/e

T_{12}^+ = kT_{12}/e

u = a constant

v = a constant

w = a constan

w' = a constant

Z = roll time of the ball

Greek Letters.

β = a constant for which the collision integrals may be evaluated

θ = inclination angle of the viscometer tube

μ = viscosity coefficient

$\mu(T_1)$ = viscosity coefficient at T_1

ρ = density of the gas

ρ_0 = density of the steel ball

σ = collision diameter

$\phi(r)$ = potential energy of interaction

$\Omega^{(2,2)}(T_1^+)$ = collision integral at T_1^+

Subscripts.

1, 2, and 3 = first, second and third determinations of viscosity

12 = represents 1-2 interaction of molecules

STP = standard temperature and pressure

APPENDIX B

Materials

This appendix contains a list of the materials used
in the performance of the experimental work for this thesis:

Air. Compressed, oil pumped. Specifications:
Air 99.9 per cent, with 20.9 per cent oxygen, 79.1
per cent nitrogen, and 0.1 per cent argon. The dew
poin is -75 degrees Fahrenheit as a maximum. The
air contains trace amounts of other rare atmospheric
gas, but no carbon dioxide. Obtained from The
Matheson Company, Inc., P. O. Box 966, Joliet, Illi-
nois. Used for standardization medium in the viscom-
eter.

Argon. Compressed. Specifications: Argon with
minimum purity of 99.995 per cent containing less than
7 ppm of oxygen, 5 ppm of hydrogen and 50 ppm of
nitrogen with a dew point around -90 degrees Fahren-
heit. Obtained from The Matheson Company, Inc.,
P. O. Box 966, Joliet, Illinois. Used as a medium for
determination of the viscosity of argon.

Carbon Dioxide. Compressed, Bone Dry. Specifications: Carbon Dioxide, Bone Dry with a minimum purity of 99.8 per cent with 0.05 per cent nitrogen, 0.009 per cent oxygen, 0.000 per cent sulfur dioxide, 0.000 per cent hydrogen sulfide, 0.000 per cent carbon monoxide, and 0.0025 per cent water. Obtained from The Matheson Company, Inc., P. O. Box 966, Joliet, Illinois. Used as a medium for determination of the viscosity of carbon dioxide.

Distilled Water. Purified by the distillation unit in the Chemical Engineering Department of the University of Missouri School of Mines and Metallurgy. No information is available on the purity. Used for a heat transfer medium in the constant temperature bath.

Helium. Compressed. Specifications: Helium minimum purity 99.99 per cent with a dew point around -60 degrees Centigrade or -76 degrees Fahrenheit. In trace quantities the following gases are present:

	Maximum	Minimum
Carbon Dioxide	0.000768%	0.000395%
Argon	0.000079	0.000019
Hydrogen	0.000031	0.000030
Nitrogen	0.002808	0.000718
Methane	0.000002	0.000000

Obtained from The Matheson Company, Inc., P. O. Box 966, Joliet, Illinois. Used as a medium for determination of the viscosity of helium.

APPENDIX C

Apparatus

The following apparatus was used in the experimental work for this thesis:

Adaptor. For gas cylinder with outlet connection number 580 to adapt a gas regulator with inlet connection number 590. Obtained from The Matheson Company, P. O. Box 966, Joliet, Illinois. Used to connect the gas regulator to the cylinder of compressed argon.

Adaptor. For gas cylinder with outlet connection number 320 to adapt to a gas regulator with inlet connection number 590. Obtained from The Matheson Company, P. O. Box 966, Joliet, Illinois. Used to connect the gas regulator to the cylinder of carbon dioxide.

Analytical Balance. Voland Analytical Balance, Model 640-D, Serial number M-18033, sensitivity of 0.1 milligram, from Voland & Sons., Inc., New Rochelle, N. Y. Obtained from E. H. Sargent & Co., Chicago, Illinois. Used to determine the weight of the steel ball.

Clamps. CASTALOY Extension with rubber sleeves, small size, eight inches long, over all; the jaws will grip objects up to 1-1/2 inches in diameter. Catalog number 5-731. Manufactured by the Fisher Scientific Company, New York, N. Y. Used in the fabrication of the viscometer tube mounting brackets.

Gas Regulator. Automatic, two stage, for pressure delivery of 5 to 50 pounds per square inch. Catalog number 8, with number 590 inlet connection. Obtained from The Matheson Company, P. O. Box 966, Joliet, Illinois. Used to regulate the pressure and flow of the gas from the cylinder into the viscometer tube.

Bulk Tape Eraser. "Jiffy-Rase," with momentary on-off switch, Model P-30, 110 to 130 volts, Serial J-4995. Manufactured by the Rason Manufacturing Company, Brooklyn, N. Y. Used as an electromagnet to position the steel ball in the viscometer tube.

Cathetometer. With telescope. Range of reading from zero to 90 centimeters to the nearest 0.005 centimeter. MSM Serial number 16470. Manufactured by Wm. Gaertner & Co., Chicago, Illinois. Obtained on loan from the Physics Department of the University of Missouri School of Mines and Metallurgy. Used to measure the elevation of the reference point to determine the inclination angle of the viscometer.

Constant Temperature Circulating System.
Precision, range 50 to 210 degrees Fahrenheit with a
control sensitivity of plus or minus 0.02 degrees
Fahrenheit. Circulating rate is five gallons per
minute at zero head and two gallons per minute at
six feet of head. Heating capacity is 450 watts at
115 volts, 60 cycle alternating current, single
phase. Capacity is two and one-half gallons. Serial
number Г-3, Catalog number 66600. Manufactured by
the Precision Scientific Company, 3737 W. Cortland
Street, Chicago 47, Illinois. Used to maintain the
viscometer and contents at a constant temperature.

Level. Hand type, nine inches long, cast
aluminum construction. Manufactured by Mayes Bros.
Tool Mfg. Co., Port Austin, Michigan. Used to level
the viscometer board and cathetometer base.

Manometer. Standard Clean Out, 24 inch. Man-
ufactured by The Meriam Instrument Co., Cleveland,
Ohio. Used to compare the gas pressure in the vis-
cometer with atmospheric pressure.

Micrometer. One inch maximum reading, smallest
division 0.001 inches, Serial number 1911, USIM 843.
Manufactured by the Lufkin Company. Used to measure
the diameter of the steel ball used in the viscometer.

Steel Ball. Chrome plated ball, nominal diameter of 0.375 inches. Manufacturer unknown. Used in viscometer tube for experimental viscosity determinations.

Stopcock. Straight with S plugs, pyrex brand glass, 4 mm bore. Catalog number 14-560. Obtained from Fisher Scientific Company, 2850 S. Jefferson, St. Louis 18, Missouri. Used as viscometer inlet valve.

Stopcock. Three-way with two tubes on one side, pyrex brand glass, 4 mm bore. Catalog number 14-597. Obtained from Fisher Scientific Company, 2850 S. Jefferson, St. Louis 18, Missouri. Used as a viscometer vent valve and manometer inlet valve.

Thermoregulator. Micro Set, range 50 to 220 degrees Fahrenheit, Catalog number 62537. Manufactured by The Precision Scientific Company, 3737 W. Cortland Street, Chicago 47, Illinois. Used as a control element in the constant temperature circulating system.

Timer. Precision "Time-It," zero to 9999.9 seconds in tenth of a second intervals. Operates on 115 volt, 60 cycle alternating current drawing 5 watts. Manufactured by the Precision Scientific Company, 3737 W. Cortland Street, Chicago 47, Illinois. Used to time the roll of the ball in the viscometer.

Vacuum Pump. Cenco-Hyvac, motor driven, "guaranteed to attain an ultimate pressure in connection with a leak-proof system of 0.3 micron of mercury pressure. At its normal operating speed of 350 rpm, it has a free air displacement of 10 liters per minute." Unit driven by a 1/8 horsepower motor operating on 110 volt, 60 cycle alternating current, single phase, 2.4 amperes, 1785 revolutions per minute, with a 40 degree Centigrade temperature rise. Catalog number 91105-A. Manufactured by Central Scientific Company, 1700 Irving Park Blvd., Chicago, Illinois. Used to evacuate the viscometer prior to introduction of the gas to be studied.

APPENDIX D

Experimental Data

This appendix contains the experimental data and
selected calculated values in Table XI through Table XXVIII.
The data in Tables XI through XIV were taken prior to
the first failure of the glass tube and were not used
in any of the calculations.

TABLE XI

Experimental Data for Determination of the Viscometer

"Instrument Constant" Using Air at

20.0 °C and 735.0 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination o '		Viscosity μ X 10^7 m/cm-sec	Instrument Constant b X 10^7 s cm/sq sec	Reynold's Number	Resistance Factor
1	0.930	0	40	1,819	-------	7.55	22,641
2	1.280	0	56	1,819	-------	13.02	10,472
3	1.735	1	15	1,819	-------	16.39	8,963
4	2.085	1	31	1,819	-------	19.59	7,538
5	2.580	1	52	1,819	3.311	31.11	3,697
6	2.865	2	4	1,819	3.558	37.13	2,883
7	3.420	2	28	1,819	3.550	44.21	2,427

TABLE XII

Experimental Data for Determination of the Viscometer

"Instrument Constant" Using Air at

20.0 °C and 736.3 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination		Viscosity $\mu \times 10^7$ gm/cm-sec	Instrument Constant $b \times 10^7$ sq cm/sq sec	Reynold's Number	Resistance Factor
		°	'				
8	1.470	1	4	1,819	3.429	14.61	7,605
9	1.850	1	20	1,819	3.687	20.10	5,140
10	2.275	1	39	1,819	3.789	24.99	4,024
11	2.865	2	4	1,819	3.639	30.21	3,465
12	3.230	2	20	1,819	3.627	33.85	3,113
13	3.665	2	39	1,819	3.547	37.66	2,852
14	4.500	3	15	1,819	3.364	43.83	2,428
15	1.270	0	55	1,819	3.732	13.75	7,425

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TABLE XIII

Experimental Data for Determination of the Viscometer

"Instrument Constant" Using Air at

20.0 °C and 736.8 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination ° '		Viscosity $\mu \times 10^7$ gm/cm-sec	Instrument Constant $b \times 10^7$ sq cm/sq sec	Reynold's Number	Resistance Factor
16	1.160	0	50	1,819	3.061	10.28	12,100
17	1.880	1	22	1,819	3.752	18.07	6,346
18	2.365	1	43	1,819	3.146	21.56	5,616
19	3.050	2	12	1,819	3.695	32.61	3,161

TABLE XIV

Experimental Data for Determination of the Viscosity
of Carbon Dioxide at 27.0 °C and 724.2 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
20	2.235	1	37	2.00	1,551
21	2.245	1	38	2.00	1,558
22	1.855	1	21	2.32	1,493
23	1.200	0	52	3.62	1,507
24	3.100	2	15	1.45	1,559
25	2.455	1	47	1.95	1,661
26	1.455	1	3	3.17	1,601
27	2.120	1	32	2.18	1,603
28	1.345	0	57	3.42	1,560

TABLE XV

Experimental Data for Determination of the Viscometer

'Instrument Constant" Using Air at

20.0 °C and 735.8 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination ° '		Viscosity $\mu \times 10^7$ gm/cm-sec	Instrument Constant $b \times 10^7$ sq cm/sq sec	Reynold's Number	Resistance Factor
29	2.865	2	4	1,819	3.427	28.42	3,911
30	2.140	1	33	1,819	3.504	21.72	5,004
31	1.705	1	14	1,819	3.436	16.96	6,535
32	2.505	1	49	1,819	3.525	25.57	4,227
33	3.035	2	12	1,819	3.494	30.71	3,550
34	3.715	2	41	1,819	3.404	36.60	3,058

TABLE XVI

Experimental Data for Determination of the Viscometer

"Instrument Constant" Using Air at

20.0 °C and 735.0 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Viscosity $\mu \times 10^7$ gm/cm-sec	Instrument Constant $b \times 10^7$ sq cm/sq sec	Reynold's Number	Resistance Factor
35	3.445	2	30	1,819	3.479	34.66	3,159
36	2.725	1	58	1,819	3.546	27.95	3,844
37	2.160	1	34	1,819	3.559	22.24	4,812
38	2.870	2	5	1,819	3.640	30.21	3,465

TABLE XVII

Experimental Data for Determination of the Viscosity of Carbon Dioxide at 27.0 °C and 737.2 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
39	3.030	2	11	1.61	1,683
40	2.340	1	41	1.97	1,591
41	3.695	2	40	1.35	1,720
42	2.915	2	6	1.60	1,609
43	2.255	1	37	2.07	1,611
44	2.775	2	00	1.68	1,609

TABLE XVIII

Experimental Data for Determination of the Viscosity
of Carbon Dioxide at 27.0 °C and 44.2 °C
and 736.8 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
		Temperature = 27.0 °C			
45	2.775	2	00	1.71	1,636
46	2.310	1	40	2.02	1,610
47	2.825	2	2	1.64	1,599
48	2.695	1	57	1.80	1,674
49	2.105	1	31	2.17	1,577
50	2.710	1	57	1.74	1,623
		Temperature = 44.2 °C			
51	2.710	1	57	1.77	1,651
52	3.420	2	28	1.45	1,711

TABLE XIX

<u>Experimental Data for Determination of the Viscosity</u>
<u>of Carbon Dioxide at 44.2 °C and 726.2 mm Hg Pressure</u>

Test No	Reference Mark Elevation cm	Angle of Inclination °	Angle of Inclination '	Roll Time sec	Viscosity μ X 10^7 gm/cm-sec
53	3.180	2	18	1.51	1,657
54	2.470	1	47	1.92	1,637
55	3.135	2	16	1.52	1,644
56	2.320	1	40	1.99	1,594
57	1.660	1	12	2.68	1,535
58	2.510	1	49	1.83	1,585
59	1.280	0	55	3.51	1,551
60	0.805	0	34	6.17	1,715
61	1.420	1	1	3.18	1,559
62	1.760	1	16	2.41	1,465
63	1.475	1	4	3.09	1,574
64	1.810	1	18	2.47	1,543

TABLE XX

Experimental Data for Determination of the Viscosity
of Carbon Dioxide at 20.0 °C and 739.3 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination		Roll Time sec	Viscosity μ X 10^7 gm/cm-sec
		°	'		
65	1.235	0	53	3.69	1,577
66	1.665	1	12	2.57	1,477
67	1.200	0	52	3.52	1,458
68	1.330	0	57	3.28	1,506
69	1.395	1	00	2.97	1,430
70	2.185	1	34	2.06	1,554
71	1.720	1	14	2.54	1,508
72	1.300	0	56	3.55	1,593

TABLE XXI

Experimental Data for Determination of the Viscosity of Carbon Dioxide at 44.2 °C and 73.2 °C and 743.0 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
Temperature = 44.2 °C					
73	1.595	1	9	3.00	1,652
74	1.765	1	16	2.61	1,590
75	1.675	1	12	2.78	1,607
76	1.525	1	6	3.06	1,611
Temperature = 73.2 °C					
77	1.420	1	1	3.71	1,819
78	1.840	1	19	2.71	1,722
79	1.500	1	5	3.40	1,761
80	2.260	1	38	2.18	1,701
81	1.860	1	20	2.68	1,721
82	2.360	1	42	2.13	1,735
83	2.120	1	32	2.40	1,757
84	2.330	1	41	2.15	1,730

TABLE XXII

Experimental Data for Determination of the Viscosity of Helium at 27.0 °C and 747.9 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
85	3.310	2	23	1.66	1,896
86	2.810	2	2	2.00	1,940
87	2.840	2	3	2.00	1,960
88	2.840	2	3	2.01	1,970
89	3.075	2	13	1.84	1,953
90	2.825	2	2	2.00	1,950
91	2.635	1	54	2.14	1,946
92	2.910	2	6	1.94	1,948

TABLE XXIII

Experimental Data for Determination of the Viscosity

of Helium at 44.2 °C and 745.9 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination ° '		Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
93	2.875	2	4	1.81	1,796
94	3.555	2	34	1.60	1,962
95	2.950	2	8	1.98	2,016
96	3.475	2	30	1.64	1,978
97	3.760	2	43	1.53	1,985
98	3.225	2	20	1.82	2,026
99	3.545	2	33	1.60	1,957
100	3.210	2	19	1.78	1,972
101	2.510	1	49	2.32	2,010
102	1.595	1	9	2.92	-----
103	3.115	2	15	1.84	1,983
104	3.425	2	28	1.67	1,973
105	3.595	2	36	1.58	1,960
106	3.865	2	47	1.50	2,000

TABLE XXIV

Experimental Data for Determination of the Viscosity of Helium at 73.2 °C and 740.1 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
107	2.795	2	1	2.10	2,026
108	3.400	2	27	1.71	1,961
109	2.955	2	8	1.99	2,029
110	2.685	1	56	2.20	2,039
111	3.145	2	16	1.86	2,019
112	2.845	2	3	2.07	2,033
113	2.990	2	9	1.97	2,038
114	3.245	2	20	1.81	2,027

TABLE XXV

Experimental Data for Determination of the Viscosity

of Argon at 27.0 °C and 44.2 °C

and 734.0 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination		Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
		°	'		
Temperature = 27.0 °C					
115	3.565	2	34	1.78	2,189
116	2.995	2	10	2.09	2,160
117	3.180	2	18	1.96	2,150
118	3.460	2	30	1.80	2,149
119	2.905	2	6	2.15	2,155
120	3.340	2	25	1.86	2,149
121	3.500	2	31	1.78	2,149
122	3.775	2	43	1.67	2,174
Temperature = 44.2 °C					
123	3.775	2	43	1.73	2,253
124	3.415	2	28	1.89	2,233
125	3.065	2	13	2.14	2,263
126	3.325	2	24	1.94	2,231
127	2.905	2	6	2.25	2,260
128	3.145	2	16	2.05	2,225
129	3.525	2	33	1.84	2,238
130	3.785	2	44	1.72	2,245

TABLE XXVI

Experimental Data for Determination of the Viscosity
of Argon at 73.2 °C and 732.7 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity μ X 10^7 gm/cm-sec
131	3.625	2	37	1.92	2,407
132	4.005	2	53	1.73	2,390
133	3.570	2	34	1.95	2,401
134	2.910	2	6	2.43	2,440
135	3.535	2	33	1.97	2,402
136	3.690	2	40	1.88	2,393
137	3.830	2	46	1.80	2,378
138	3.450	2	29	2.01	2,393

TABLE XXVII

Experimental Data for Determination of the Viscosity
of Air at 73.2 °C and 732.7 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination		Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
		°	'		
139	3.050	2	12	1.90	2,000
140	3.220	2	19	1.80	2,000
141	3.075	2	13	1.86	1,974
142	2.775	2	00	2.10	2,011
143	3.110	2	15	1.85	1,985
144	3.370	2	26	1.69	1,965
145	2.930	2	6	1.98	2,002
146	3.200	2	18	1.78	1,971

TABLE XXVIII

Experimental Data for Determination of the Viscosity
of Air at 44.2 °C and 735.3 mm Hg Pressure

Test No	Reference Mark Elevation cm	Angle of Inclination °	'	Roll Time sec	Viscosity $\mu \times 10^7$ gm/cm-sec
147	2.995	2	10	1.80	1,860
148	3.355	2	25	1.65	1,910
149	2.875	2	4	1.89	1,875
150	2.540	1	50	2.14	1,876
151	2.735	1	58	1.98	1,869
152	3.075	2	13	1.75	1,857
153	2.790	2	1	1.94	1,868
154	2.885	2	5	1.86	1,852

APPENDIX E

Appendix E contains a discussion of the error in the experimental determinations and the methods used to evaluate these errors.

Probable Error in Time. The measurement of the time of roll was one of the most critical measurements to be taken. It was assumed that the time of roll could be measured to plus or minus 0.05 seconds. Each determination of viscosity utilized 30 readings of the roll time. The probable error in the time was evaluated as follows:

$$r = \pm\ 0.6745 \sqrt{\frac{d_1^2 + d_2^2 + --- + d_n^2}{n - 1}} \qquad (52)$$

where
r = probable error in the time

d = deviation from the mean

n = number of measurements

Substituting in this equation, the probable error in the time was evaluated as follows:

$$r = \pm\ 0.6745 \sqrt{\frac{30(0.05)^2}{29}} \qquad (53)$$

$$r = \pm\ 0.6745\ (0.0503) \qquad (54)$$

$$r = ^+ 0.03\ \text{seconds} \qquad (55)$$

Probable Error in the Ball Diameter. The probable error in the ball diameter was based on the measurement of the ball with a micrometer. The deviations from the mean

diameter were determined and equation 52 utilized to evaluate
the probable error in the measurement. The diameter was
measured to be 0.3753, 0.3754, 0.3752, 0.3751 and 0.3753
inches. The mean value of the diameter is 0.3753 inches.
The probable error in the diameter is as follows:

$$r = \pm 0.6745 \sqrt{\frac{2(0.0001)^2 + (0.0002)^2}{4}} \qquad (56)$$

$$r = \pm 0.6745 \sqrt{2 \times 10^{-8}} \qquad (57)$$

$$r = \pm 0.0001 \text{ inch} \qquad (58)$$

Percentage Error in the Ball Density. The per cent
error in the density of the ball was evaluated as follows:

$$\rho_o = \frac{\text{weight}}{\pi d^3 / 6} \qquad (59)$$

where   weight of ball = 3.5410 $\pm$ 0.0002 grams

diameter of ball = 0.3753 $\pm$ 0.0001 inch

$$\text{error in weight} = \frac{(0.0002)(100)}{(3.5410)} = 0.004 \% \qquad (60)$$

$$\text{error in diameter} = \frac{(0.0001)(100)}{(0.3753)} = 0.03 \% \qquad (61)$$

Using the following equation

$$P = \sqrt{(p_1 n_1)^2 + (p_2 n_2)^2 + \text{---}} \qquad (62)$$

where   P = per cent error in derived quantity

p = per cent error in measured quantity

n = exponent to the measured quantity as it
appears in the derived quantity.

then the per cent error in the ball density is

$$P = \left[(0.004)^2 + (3 \times 0.03)^2\right]^{0.5} \quad (63)$$

$$P = (8 \times 10^{-3})^{0.5} \quad (64)$$

$$P = 0.09 \% \quad (65)$$

Error in the Gas Density. The density of the gas was calculated using equation 14. The error in this calculation stemmed from the measurement of the temperature and pressure of the gas. The value of the density at standard temperature and pressure was assumed to be exact and contain no error. The error in the density of the gas was derived as follows:

$$\text{pressure} = 735.8 \pm 0.1 \text{ mm Hg}$$

$$\text{temperature} = 293.0 \pm 0.1 \text{ °K}$$

$$\text{error in pressure} = \frac{(0.1)(100)}{735.8} = 0.01 \% \quad (66)$$

$$\text{error in temperature} = \frac{(0.1)(100)}{293.0} = 0.03 \% \quad (67)$$

$$P = \sqrt{(0.01)^2 + (0.03)^2} = 0.03 \% \quad (68)$$

Error in Sine of Angle of Inclination. The sine of the angle of inclination was calculated using equation 10. The error in this measurement was evaluated as follows:

$$\sin \theta = \frac{E_f - E_o}{79.135} \quad (10)$$

at about two degrees inclination,

$$\Delta E = 2.775 \pm 0.005 \text{ cm}$$

$$79.135 \pm 0.020 \text{ cm}$$

the per cent error in these values is

$$\text{error in } \Delta E = \frac{(0.005)(100)}{(2.775)} = 0.2 \% \quad (69)$$

$$\text{error in } 79.135 = \frac{(0.020)(100)}{(79.135)} = 0.02\% \quad (70)$$

and the per cent error in the sine of the angle is

$$P = [(0.02)^2 + (0.2)^2]^{0.5} = 0.2 \% \quad (71)$$

Error in the Instrument Constant. The error in the instrument constant was evaluated at a time of 2.00 seconds. The arithmetical average of the time for the ten determinations of the constant was 2.04 seconds. The constant as calculated using equation 24 was examined for error as follows:

$$\mu = 1,819 \times 10^{-7} \pm 0.1 \%$$
$$Z = 2.00 \pm 0.03 \text{ sec} = 1.5 \%$$
$$\sin \theta = 0.03490 \pm 0.2 \%$$
$$\rho_0 = 7807 \pm 0.09 \%$$
$$\rho = 1.166 \pm 0.03 \%$$

with the expression for the error then

$$P = [(0.1)^2 + (1.5)^2 + (0.2)^2 + (0.09)^2 + (0.03)^2]^{0.5} \quad (72)$$
$$P = 1.5 \% \quad (73)$$

The instrument constant was evaluated as 3.50×10^{-7}. This error when applied to the constant gives a value of $3.50 \pm 0.05 \times 10^{-7}$.

Error in the Viscosity Measurement. The viscosity as

calculated by equation 11 was subject to error as follows:

Per cent errors in the measured quantities

$$Z = 1.5 \%$$

$$\sin \theta = 0.2 \%$$

$$b = 1.5 \%$$

$$\rho_o = 0.09 \%$$

$$\rho = 0.03 \%$$

Per cent error in the derived quantity

$$P = [(1.5)^2+(0.2)^2+(1.5)^2+(0.09)^2+(0.03)^2]^{0.5} \quad (74)$$

$$P = 2.1 \% \quad (75)$$

Identical calculations were carried out for times of from

1.5 to 2.75 seconds and the per cent error was found to

vary from 2.5 per cent at the former to 1.9 per cent at

the latter. These per cent errors were applied to the

values of the viscosities in Table I.

Error in Calculation of k_μ. The error in the calculation

of the value of k_μ as expressed in equation 29 was calculated

utilizing the following percentage errors already calculated:

$$\text{error in } \mu(T_2) = 2.1 \%$$

$$\text{error in } \mu(T_1) = 2.1 \%$$

$$\text{error in } T_1 = 0.03 \%$$

$$\text{error in } T_2 = 0.03 \%$$

therefore

$$P = [(2)(2.1)^2 + (2)(0.03/2)^2]^{0.5} \quad (76)$$

$$P = 3.0 \% \quad (77)$$

Error in Calculation of Force Constant e/k. The error of three per cent in the value of k_μ will have a great effect upon the error of the force constant. The value of k_μ is near one. The change in k_μ as calculated from equation 33 is very small for variations in the value of e/k. This has the effect of necessitating a very large change in e/k to bring about a three per cent change in the value of k_μ. In the case of the force constants listed in Table II, only three of the errors could be evaluated. Those are listed in that table. The other two could not be determined. The limiting factor was the lack of collision integral listings at reduced temperatures of less than 0.30. The method utilized for the calculation of error in the value of the force constants was to use the force constant listed in Table II and the value of k_μ from which it was calculated. The value of k_μ was decreased or increased by three per cent. By trial and error, equation 33 was evaluated using assumed values of e/k until the value of k_μ thusly calculated agreed with the value which had been increased by three per cent. This value of e/k was then subtracted from the original value and this difference presented as the error. For example, in the case of carbon dioxide at 317.2 degrees and 346.2 degrees Centigrade, the force constant was calculated to be 163 degrees Kelvin. Upon applying a three per cent variation to the value of k_μ, the force constant was evaluated as 90 degrees Kelvin.

The difference was 73 degrees Kelvin. This would then be
expressed as 163 ± 73 degrees Kelvin, or an error of 45
per cent. The other errors were of even a greater magni-
tude. This demonstrates that the force constants calcu-
lated from the experimental data have no significance
due to the errors in the measurement of the viscosities.
The calculations carried on by the method of Strunk[34]
likewise have no significance except to demonstrate that
it was possible to obtain a unique solution of this type
with the data for argon.

Error in the Collision Diameter. The error in the
collision diameter was determined for each of the gases
where it was possible to determine the error in the force
constant e/k. The procedure utilized the values of the
reduced temperature determined by the original calcula-
tions and that for the calculation of the error in the
force constant. The values of the collision integrals
were determined for each reduced temperature and the per
cent error in those values entered into the calculation
of the collision diameter. For carbon dioxide at 317.2
and 346.2 degrees Kelvin, the following calculations were
made:

$$\text{reduced temperature } T^+ = 2.124$$

$$\text{reduced temperature } T^+ = 3.847 \text{ (with error)}$$

$$\Omega^{(2,2)} = 1.152$$

$$\Omega^{(2,2)} = 0.978 \text{ (with error)}$$

$$\text{error in } \Omega^{(2,2)} = \frac{1.152 - 0.978}{1.152}(100) = 15 \text{ \%} \qquad (78)$$

Applying the same procedure to the evaluation of the factor $F_\mu^{(3)}(T^+)$, the per cent error was found to be 0.30. All of these factors were then utilized in the solution of the error in the collision diameter from equations 36 and 62. The errors in the factors in equation 36 were as follows:

$$M = 0.01 \%$$
$$T_1 = 0.03 \%$$
$$F_\mu^{(3)}(T_1^+) = 0.30 \%$$
$$\Omega^{(2,2)}(T_1^+) = 15 \%$$
$$\mu = 2.0 \%$$

Applying equation 62, the results were as follows:

$$P = [(0.01/4)^2+(0.03/4)^2+(0.3/2)^2+(15/2)^2+(2/2)^2]^{0.5} \quad (79)$$
$$P = 8 \% \quad (80)$$

This is the error in the calculation of the collision diameter. Similar calculations were made for each collision diameter where the error in e/k was known.

Error from Expansion of the Steel Ball. The error introduced by the expansion of the steel ball was calculated as follows:

$$\alpha_b = 12.2 \times 10^{-6} \text{ ppm expansion per °C}$$
$$\text{Original Diameter} = 0.3753 \pm 0.0001 \text{ inch}$$
$$\Delta T = 53.2 \text{ °C}$$
$$\text{Diameter Expansion} = d\,\alpha_b\,\Delta T \quad (81)$$
$$= (0.3753)(12.2 \times 10^{-6})(53.2) \quad (82)$$
$$= 0.0002 \text{ inch}$$

At 73.2 °C, the diameter = 0.3755 inch

Because of this expansion, the instrument constant should
be determined for each temperature at which the instrument
will operate. The expansion will have the effect of
altering the instrument constant as the ball will take
a longer time to complete its roll than when it was at
the lower temperature.

Error in Ball Density with Increase in Temperature.
As the temperature of the ball increases, the density will
decrease as illustrated by the following equation:

$$\rho_s = \frac{-3 \, \alpha_b \, \Delta T}{1 + 3\alpha_b \Delta T} \, (\rho_{so}) \tag{84}$$

where
$$\alpha_b = 12.2 \times 10^{-6}/°C$$
$$\Delta T = 53.2 \, °C$$
$$\rho_{so} = 7807 \text{ grams per liter}$$

then
$$\rho_s = \frac{(-3)(12.2 \times 10^{-6})(53.2)(7807)}{1 + 3(12.2 \times 10^{-6})(53.2)} \tag{85}$$

$$\rho_s = -19 \text{ g/liter} \tag{86}$$

Therefore, the per cent error in the density is

$$\text{error} = \frac{(19)(100)}{7807} = 0.24 \, \% \tag{87}$$

This error is approximately three times greater than the
error in the density as calculated at room temperature, but
when applied in equation 74 for the calculation of the
error in the viscosity, it is negligible compared to the
errors in the time and instrument constant.

Error in Diameter Ratio Due to Ball Expansion. The
expansion of the ball will decrease the diameter ratio
as follows:

$$\text{diameter ratio change} = \frac{\Delta(D - d)}{(D - d)_1} \qquad (88)$$

$$(D - d)_1 = 0.0102 \text{ inch}$$

$$(- d)_2 = 0.0100 \text{ inch}$$

$$\text{diameter ratio change} = \frac{(0.0100 - 0.0102)}{0.0102}(100) = 2\% \qquad (89)$$

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IX. ACKNOWLEDGMENTS

X. VITA

The author of this thesis was born on June 30, 1929 in Springfield, Missouri.

The Elementary and High School education of the author was obtained at the Greenwood Training School at Southwest Missouri State College in Springfield, Missouri. His High School education was completed in May 1947. He then entered Southwest Missouri State College in June 1947 and was enrolled until September 1948. At this time, he transferred to the University of Missouri School of Mines

and Metallurgy in Rolla, Missouri. He completed his
requirements for a Bachelor of Science Degree in Chemical
E gineering in May 1951.

Upon graduation, the author accepted a position with
the Oak Ridge National Laboratory, Oak Ridge, Tennessee.
While employed there, he was engaged in the development
of nuclear reactors for the production of commercial
electrical power. He resigned from this position in
October 1953 to accept an appointment to U. S. Naval
Officers Candidate School at Newport, Rhode Island.

The author was stationed at the Officer Candidate
School until April 1954. He was commissioned as an
Ensign in the United States Naval Reserve and ordered to
the Bureau of Ordnance in Washington, D. C. for active
duty. At his release from active duty in August 1957, he
held the rank of Lieutenant (junior grade), and was pro-
moted to the rank of Lieutenant in October 1958.

Upon his release from active duty, he returned to the
University of Missouri School of Mines and Metallurgy to
complete the requirements for a Master of Science degree
in Chemical Engineering. He served as a Graduate Assistant
in Chemical Engineering for the school year 1957-58, and
as an Instructor in Chemistry during the 1958-59 school
year.

Charles Warren Keller