CALIBRATION AND MODIFICATIONS OF THE MAGNETIC FLOAT PYCNOMETER

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TECHNICAL REPORT AFML—TR—74—16

APRIL 1974

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT—PATTERSON AIR FORCE BASE, OHIO 45433

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AFML-TR-74-16

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FOREWORD

This report was prepared in the Polymer Branch (MBP) of the Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers", Subtask No. 73400465 "Polymer Bulk Properties and Morphology", with Dr. M. T. Gehatia acting as subtask scientist. Coauthor was Dr. D. R. Wiff, University of Dayton, Research Institute.

The report covers research conducted from November 1971 to July 1972.

This report was released by the authors in October 1973.

This technical report has been reviewed and is approved.

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ABSTRACT

An automatic "hands-off" magnetic float pycnometer developed in this laboratory was applied in preliminary research to determine the partial specific volume of polymer in solution. During this phase of the research it became obvious that the original calibration was not adequate. To improve this technique a few modifications have been made, by adding a new digital ammeter and by replacing part of the homemade electronics with a commercial phase lock-in amplifier. Then a new comprehensive calibration was performed and all parameters required to characterize the apparatus and the float were determined. Finally, partial specific volume of the polymer polystyrene in cyclohexane was investigated by applying the new magnetic float pycnometry and also by using the conventional technique. The results obtained from both methods were in excellent agreement. The instrument will significantly shorten experimental time and result in cost reduction.

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INTRODUCTION

Today many important Air Force and space vehicles require applications of polymeric materials. This is due to the recently achieved high strength and the inherent light weight of synthetic bulk polymers. The future is expected to bring even stronger, lighter weight polymeric materials with improved physical properties due to better control of molecular level morphology. It is well known (References 1,2) that the molecular weight (MW) and molecular weight distribution (MWD) greatly affect the physical properties of the solid polymers and especially the strength, flexibility, modulus, and craze formation. Since conventional determination of MWD requires a tedious process of fractionation and determination of MW for each fraction, a new method was developed in this laboratory based on equilibrium sedimentation with the ultracentrifuge. This method leads to the determination of the entire MWD from a single experiment. In this way it significantly shortens the experimental time and ultimately causes cost reduction (References 3-8).

Determination of MWD also requires knowledge of the partial specific volume, V_p, of the polymer in the solution under consideration. This parameter is derived from pycnometric experiments. Since conventional pycnometry is a rather tedious procedure and in the case of volatile solvents unreliable, an improved technique of Magnetic Float Pycnometry was developed in this laboratory (References 9, 10). This new fully automated "hands-off" type instrument was designed to measure differences in density of solutions to $\pm 1.0 \times 10^{-7}$ g/cc with a temperature control of ±0.0001°C over a long time interval.

After this instrument was applied in polymer research, it was evident that modifications were necessary and especially the technique of calibration had to be improved. These modifications and the new way of calibration are the subject of this report.

SECTION II

MAGNETIC FLOAT PYCNOMETER

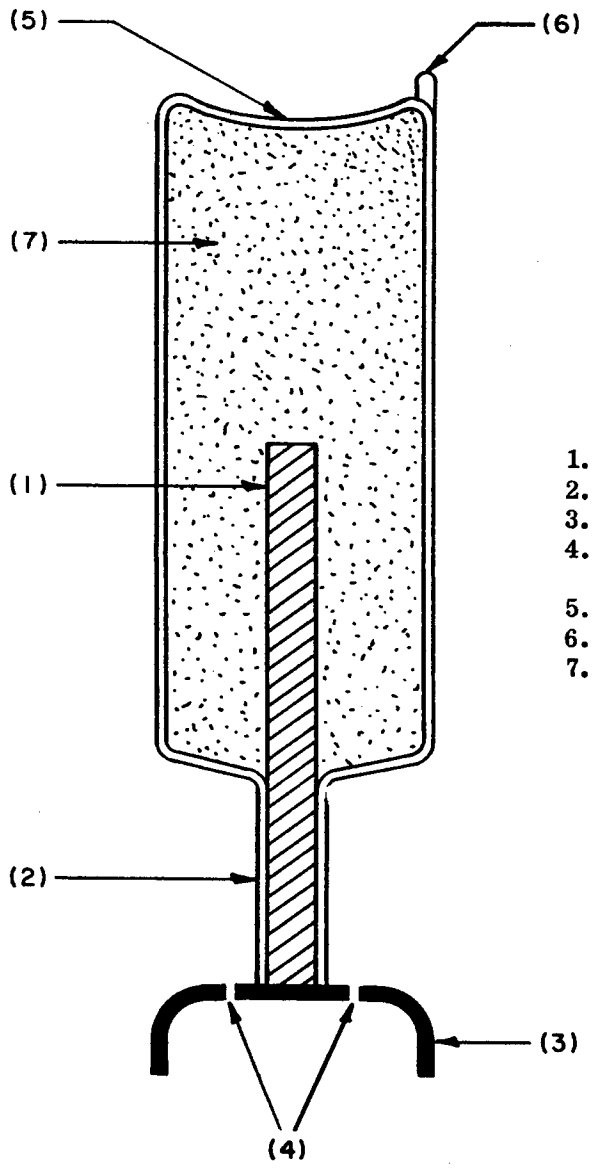
The detailed physical description of the magnetic float and the theory of its operation are discussed in References 9, 10.

The float (see Figure 1) was fabricated from pyrex glass with a stem and opaque base on its lower end. After a permanent rod magnet had been inserted, the float was sealed to enclose air for an approximate maximum buoyancy. This buoyancy can also be adjusted (decreased) by wrapping platinum wire around the stem. The float is inserted into a couette containing the liquid under consideration. The couette is placed inside a solenoid coil as shown in Figure 2 and the float is in a slightly buoyant state being vertically stable on the axis of the solenoid.

To achieve final buoyancy adjustment a controlled electrical current is passed through the solenoid coil. The electrical current is controlled with the help of four digitized dials each representing a decade of refinement. The current generates magnetic forces which pull the float down. The dial readings can be recorded. A schematic of the magnetic float system is shown in Figure 2.

To stabilize the float, a horizontal beam of light is used which passes through the center of the couette near to its bottom and impinges on a photocell. This generates an additional current in the solenoid slightly enhancing the magnetic force. The increased total force pulls the float down until its opaque lower part blocks the light beam and interrupts the additional force. After a short period of oscillations the lower opaque end becomes stable near to the middle of the light beam's cross section.

A special ammeter indicates the photoelectric current. It proved to be convenient to have an initial intensity (float not interrupting the light beam) at 80% of the meter's full scale deflection and to stabilize the float at 60% of this initial deflection.



1. Permanent Magnet
2. Stem
3. Opaque base
4. Holes to prevent air bubbles
5. Concavity
6. Protrusion
7. Sealed air space

Figure 1. Cross Section of the Float

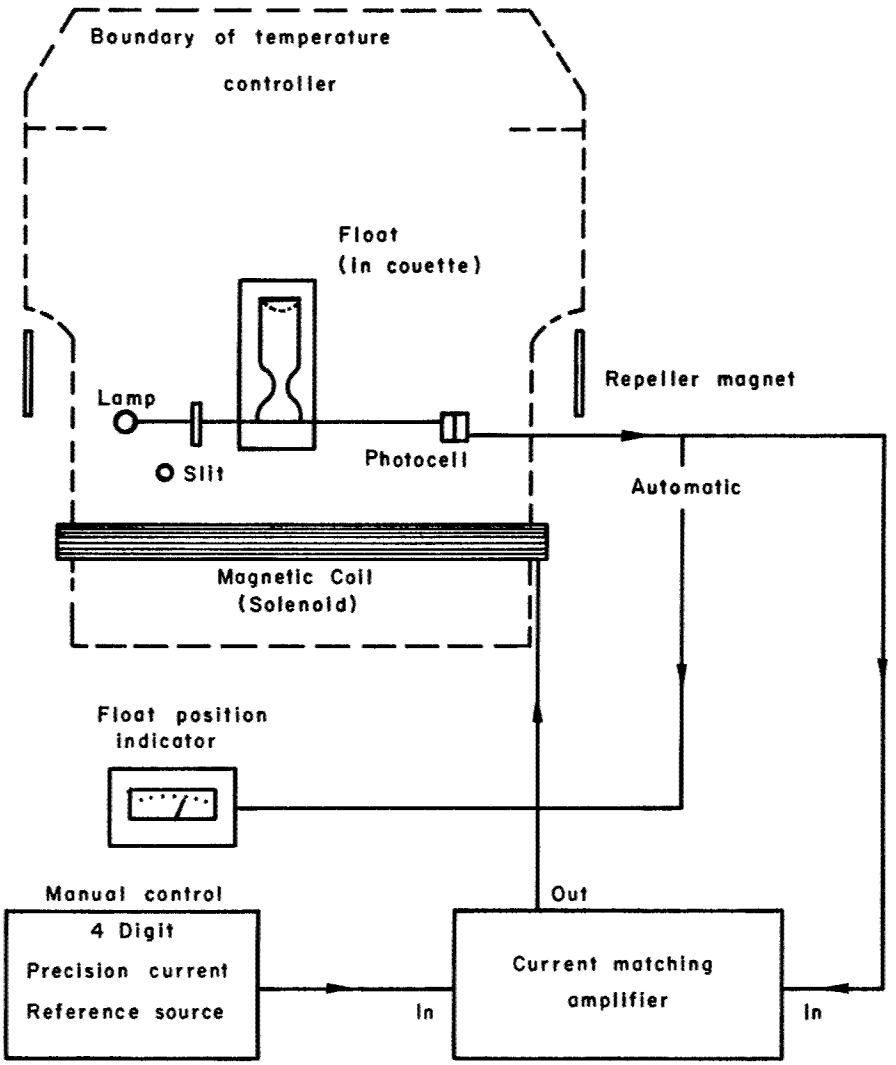


Figure 2. Schematic of Magnetic Float System with Emphasis on the Vertical Stabilization Control

SECTION III

OPERATING EQUATIONS

The theory of pycnometry used in this work was first derived by Lewis and Randall (Reference 11) and the operating equations for a magnetic float are given in the previous report (Reference 9).

According to these original derivations, the vector sum of forces acting on a float at equilibrium must be zero, i.e.,

$$M_F (1-V_F\rho) + m_{Pt} (1-V_{Pt}\rho) + fR = 0 \qquad (1)$$

Here the quantities V_F and V_{Pt} are the reciprocal of the densities of the float (F) and platinum (Pt), respectively. That is, the reciprocal of the density has units of volume per unit mass or equivalent in nature to the partial specific volume of a polymer in solution V_p. It is only for the esthetic symmetry of the equations that this equivalence is used. M_F and m_{Pt} are the masses (or weights) of the float and platinum, respectively. ρ is the density of the liquid under consideration. R is proportional to the amount of current introduced with the decade dials and f is the conversion factor for obtaining an active mechanical force from the value for R.

This equation is based on an assumption that the additional force generated by the photoelectric current is minute and can be neglected. This assumption proved to be wrong. As a result a new digital ammeter was built into the system which would indicate the total actual current D flowing through the solenoid coil. Finally, Equation 1 was substituted by a new expression:

$$M_F(1-V_F\rho) + m_{Pt} (1-V_{Pt}\rho) + f_{FD}D + K_F = 0 \qquad (2)$$

Here f_{FD} is a new parameter converting D into a mechanical force, K_F is a constant dependent upon the instrument and the float used.

Equation 2 may also be written in the form

$$(M_F + m_{Pt} + K_F) + f_{FD}D = (V_F + V_{Pt})\,\rho \tag{3}$$

In a set of liquids such as polymer in solution with slightly varying concentrations, the same float with the same amount of platinum around the stem can be used to determine all the densities ρ_n and corresponding current D_n. If one of these densities, e.g., the solvent density, ρ_o with corresponding current D_o, is known, then Equation 3 reduces to a simple difference equation

$$f_{FD}(D_n - D_o) = (V_F + V_{Pt})\,(\rho_n - \rho_o) \tag{4}$$

or

$$\frac{f_{FD}}{V_F + V_{Pt}} = \frac{\rho_n - \rho_o}{D_n - D_o} \tag{5}$$

In this case only the constants f_{FD}, V_F and V_{Pt} must be, "a priori", known. In a general case, however, M_F, m_{Pt} and K_F must also be predetermined. Determination of m_{Pt} is a simple procedure involving weighing under standard clean analytical conditions. Therefore, the calibration of the instrument and float reduces to determination of the following five constants M_F, V_F, V_{Pt}, f_{FD} and K_F.

Because of the high degree of sensitivity characterizing the magnetic float pycnometer, the buoyancy factor $(1-V\rho)$ used in absolute molecular weight determinations could be measured with a precision of $\pm 1.0 \times 10^{-4}$ and the partial specific volume V_p to $\pm 1.0 \times 10^{-2}$ cc/g. It is obvious that the calibration of the parameters mentioned above must accordingly be determined very precisely because in the analysis of $(1-V\rho)$ the experimentalist is dealing with differences of differences (see Lewis and Randall Reference 11).

SECTION IV

CALIBRATION OF FLOAT'S MASS (M_F)

M_F could not be determined by weighing the float with a regular balance. Because of the magnetic rod inside the float, the weight was greatly dependent upon various magnet materials present in the balance itself and in the surrounding laboratory. The position and location of the float also greatly influenced the results. In order to obtain a meaningful quantity for this weight, the float was inserted in the pycnometer and located in its position of equilibrium along the solenoid axis and at the regular (60%) height described at the end of Section II. To make this positioning possible, a special table as shown in Figure 3 was constructed over the instrument with a two-pan balance located on top. A thread was suspended from the arm of this balance where a pan was usually attached. This thread passed through two holes (one made in the bottom of the balance and the other in the table's top) down to where the float was located on the solenoid's axis. The length of the thread was adjusted so that the float (enclosed in a specifically constructed net) was precisely located at the 60% height when in equilibrium. Then the thread plus net, with and without the float, was weighed. This provided the quantity M_F which expresses the effective weight of the float located in its fixed position at equilibrium. No current whatsoever was flowing through the solenoid during the weighing.

In this case the weight on the balance $W = M_F$. In addition, it should be mentioned that the table was constructed from heavy wood timbers only and the balance was sufficiently above the top of the solenoid so that the iron in the balance would have a negligible effect on the float's mass.

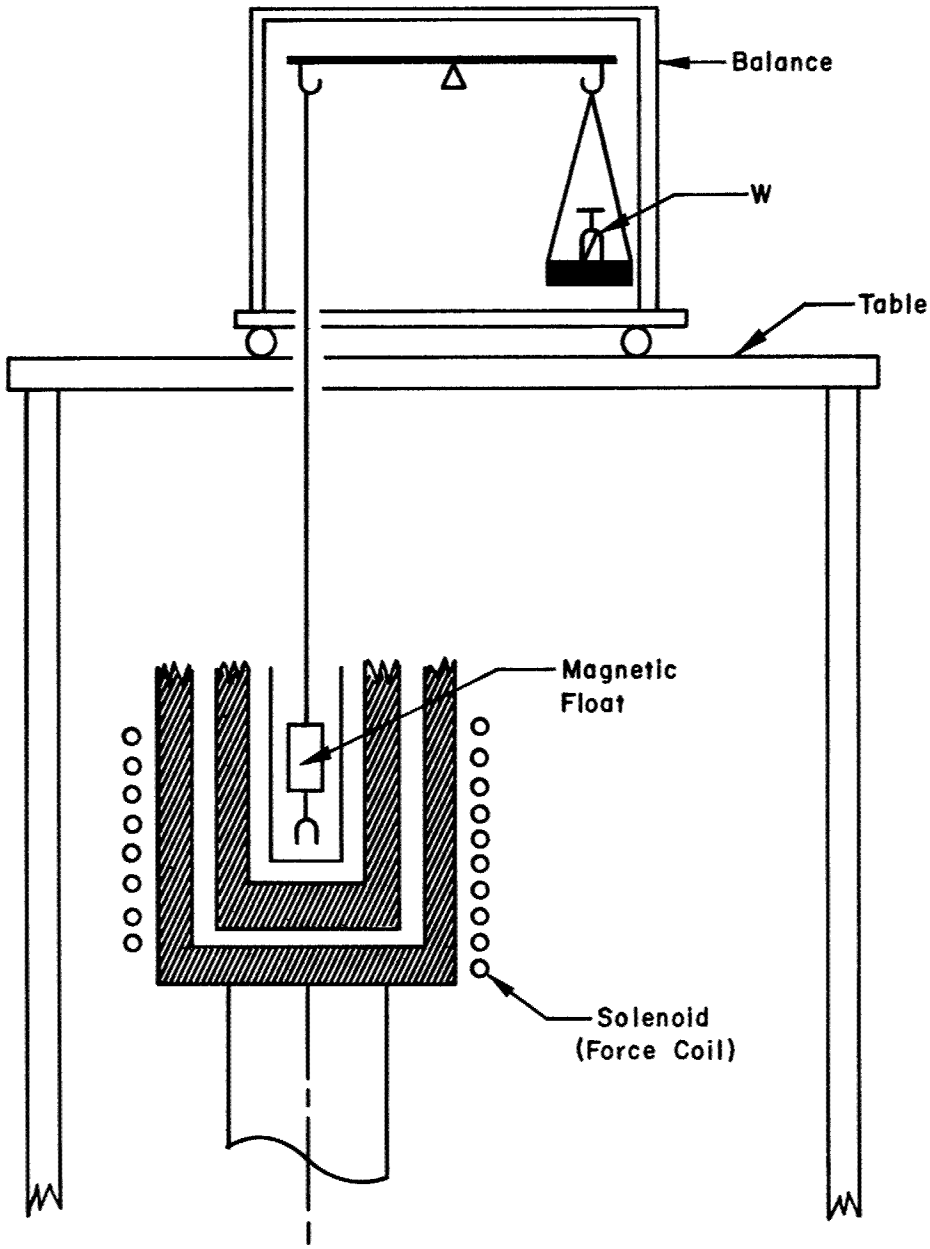


Figure 3. Schematic of Apparatus Used for Calibrating the Magnetic Floats

SECTION V

CALIBRATION OF PARAMETERS f_{FD} AND K_F

The experimental arrangement consisted of the float suspended by a thread and located inside the inner temperature chamber at its equilibrium position along the solenoid axis (See Figure 3). To determine this equilibrium position the light beam was activiated with the usual starting deflection of 80% full scale on the indicating ammeter. Then the vertical position of the float was varied by changing the length of the suspending thread until the float's bottom opaque section interrupted the light beam thereby causing the ammeter to read 60% of the initial full intensity setting.

After this vertical position was determined, the light source was turned off. The float was then tared again to equilibrium on the balance located high above the magnetic float chamber. Electric current was introduced into the solenoid only by incrementing the digital decade dials as discussed in relation to Equation 1. The initial value of R was 0.0000. R was incremented in steps of 0.100 until the maximum setting of 3.000. At each incremental step, the magnetic forces acting on the float and caused by the increased current in the solenoid, were counter-balanced by adding weights W_n to the balance pan opposing the pan from which the float was suspended by the thread. A digital meter was incorporated into the system which indicated the total current (D) flowing through the solenoid coils. With each additional increment of R more current flowed through the solenoid and the corresponding magnitude was indicated by the digital meter readings for D as discussed in relation to Equation 2.

If the light was on, the total current D would be the sum of the currents controlled by R and the photoelectric current caused by the light source. In this case, however, the light source was disconnected. It was expected that R and D would be identical, however, this was not the case. Typical data obtained by this process is shown in Table I.

Usually 90 to 100 readings were recorded, i.e., at least three sets of data such as in Table I, were averaged in order to obtain f_{FD} and K_F.

Determination of these parameters involved a Gauss least squares fit to the formula

$$W_n = f_{FD} D_n + K_F \tag{6}$$

The applicability of this linear expression can be easily verified by noting the linearity of the resulting plot of W_n versus D_n in Figure 4.

Table I. Data Used in the Determination of the Parameters f_{FD} and K_F.

$W \times 10^2$			$R \times 10^1$	$D \times 10^1$		
1	2	3	1,2, & 3	1	2	3
0.27	0.27	0.29	1.00	1.27	1.17	1.24
0.52	0.50	0.57	2.00	2.33	2.20	2.37
0.76	0.72	0.84	3.00	3.32	3.13	3.41
0.98	0.95	1.05	4.00	4.23	4.05	4.30
1.17	1.17	1.26	5.00	5.08	5.05	5.16
1.39	1.39	1.47	6.00	6.12	6.08	6.07
1.64	1.62	1.70	7.00	7.11	7.08	7.08
1.85	1.87	1.95	8.00	8.12	8.11	8.11
2.08	1.87	1.95	9.00	9.14	9.10	9.12
2.32	2.33	2.43	10.00	10.15	10.13	10.13
2.56	2.59	2.69	11.00	11.16	11.13	11.13
2.79	2.83	2.94	12.00	12.17	12.14	12.17
3.05	3.06	3.19	13.00	13.20	13.15	13.18
3.28	3.30	3.43	14.00	14.20	14.18	14.19
3.52	3.54	3.67	15.00	15.22	15.20	15.20
3.76	3.77	3.91	16.00	16.23	16.21	16.21
4.00	4.02	4.15	17.00	17.24	17.21	17.22
4.24	4.25	4.39	18.00	18.25	18.23	18.23
4.48	4.48	4.63	19.00	19.26	19.24	19.24
4.71	4.71	4.86	20.00	20.26	20.18	20.15
4.95	4.49	5.09	21.00	21.28	21.20	21.14
5.16	5.18	5.33	22.00	22.29	22.22	22.19
5.42	5.41	5.58	23.00	23.30	23.23	23.20
5.67	5.64	5.82	24.00	24.31	24.27	24.23
5.92	5.90	6.06	25.00	25.32	25.27	25.24
6.04	6.14	6.30	26.00	26.33	26.28	26.25
6.37	6.38	6.55	27.00	27.34	27.28	27.24
6.62	6.61	6.80	28.00	28.35	28.39	28.25
6.85	6.84	7.04	29.00	29.35	29.29	29.26
7.09	7.08	7.27	30.00	30.36	30.31	30.29

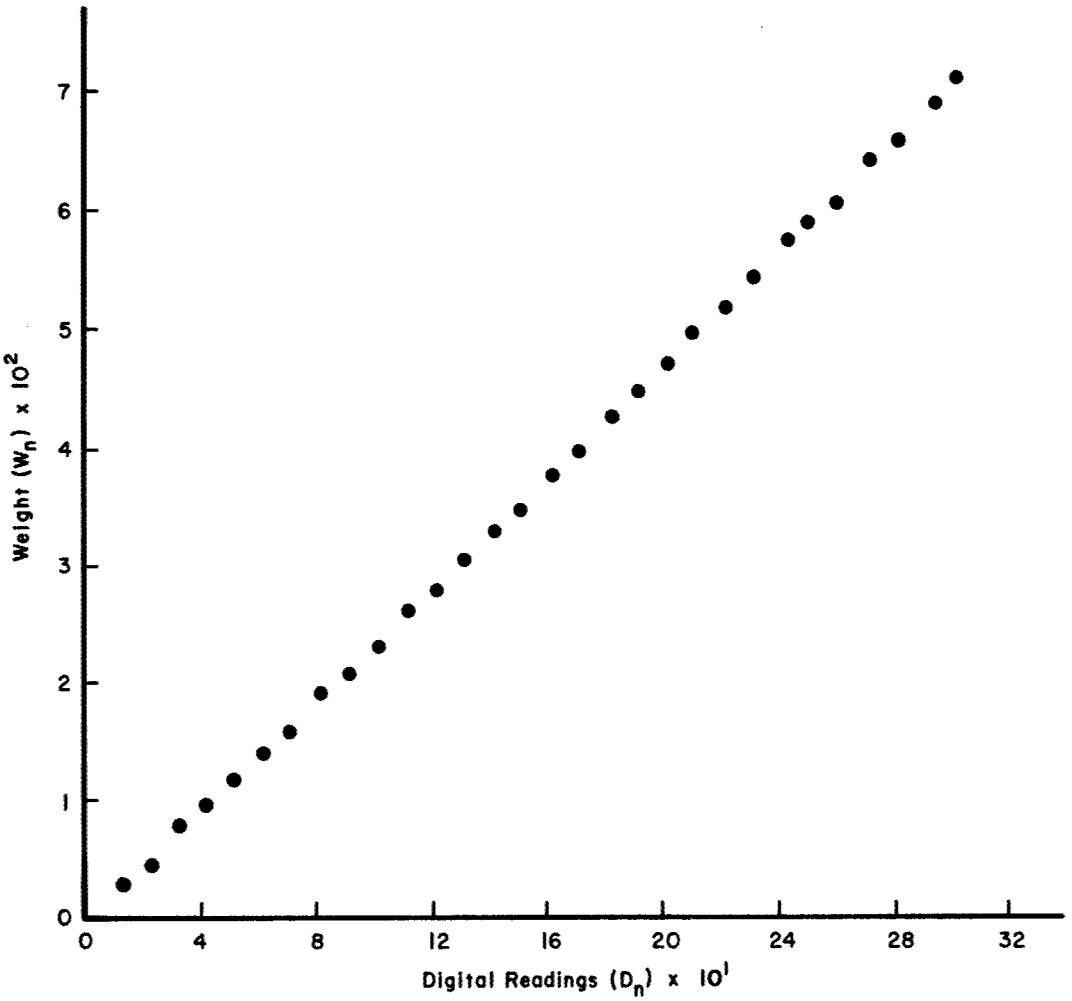


Figure 4. Plot of Data Used in the Least Squares Determination of f_{FD} and K_F

SECTION VI

MEASUREMENT OF FLOAT'S VOLUME (v)

Since the reciprocal of the floats density, $V_F = v_F/M_F$ where v_F is the float's volume, and M_F is the float's weight, which was already measured, the determination of the float's reciprocal density, V_F, reduced to the measurement of v_F. For this purpose a conventional pycnometer was fabricated (See Figure 5).

Bidistilled and degassed water was added to this pycnometer and the magnetic float was inserted. The excess of water was removed from the pycnometer through the central capillary when the lid with ground glass periphery was inserted. It has to be borne in mind that the volume is temperature dependent, and therefore, the float has to be calibrated for a desired temperature. In the following case the calibration temperature was 35°C. The pycnometer with the magnetic float were inserted into a constant temperature bath at 35°C. While attaining thermal equilibration more expanding water flowed out from the pycnometer through the central capillary. Then the pycnometer was throughly dried on its outside and weighed. A similar procedure was repeated in a case when only water without magnetic float was inserted into the pycnometer. Also, the weight of the empty pycnometer with and without the float was measured. All these measurements were accomplished on the same balance. In addition, during these weighings the position of the float within the pycnometer and the position of the pycnometer on the pan were kept unchanged.

Denoting

W_1 = weight of pycnometer + float + water

W_2 = weight of empty pycnometer + float

W_3 = weight of empty pycnometer without float

W_4 = weight of pycnometer + water without float,

$W_5 = W_1 - W_2$ indicates weight of water in pycnometer surrounding the float, and $W_6 = W_4 - W_3$ is the weight of water present in the pycnometer

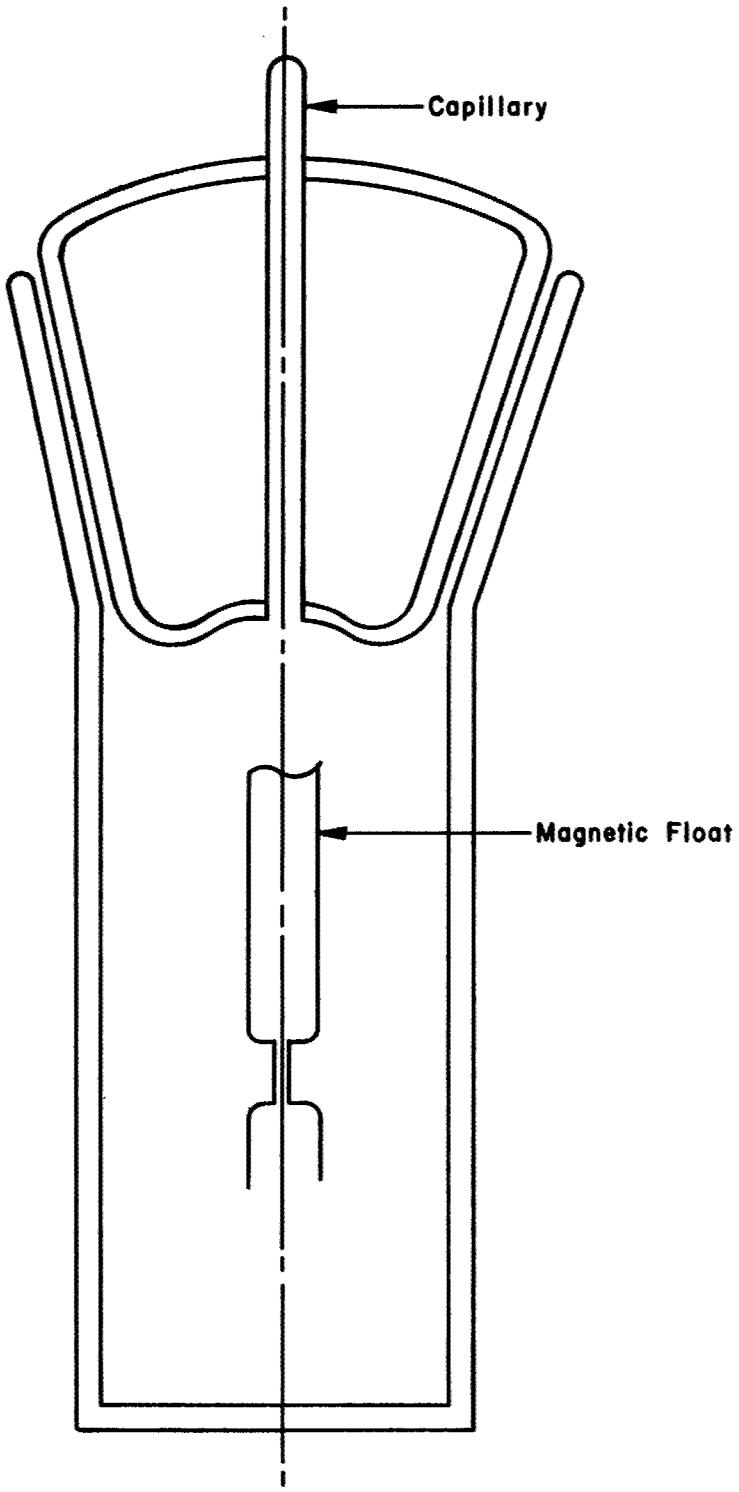


Figure 5. Pycnometer Used for Measurement of the Float's Volume

without the float. It is obvious that $W_6 - W_5 = W$ is the weight of water which occupies the volume of float at 35°C.

Knowing the density of water at 35°C the volume of water resulting in the weight W which is equal to volume of the float, v_F, can be calculated.

Finally, the reciprocal of the density of the float at 35°C could be determined as $V_F = v_F/M_F$. The results can be found in Table II.

Table II. Data Associated with Determining the Volume, Reciprocal Density, etc. of the Float.

Nomenclature	Measured Quantity
M_F = Mass of Float	27.1418g.
v_F = Volume of Float	36.7104cm^3
V_F = Reciprocal of Float Density	1.348071cm^3/g
ρ_F = Density of Float	0.74180g/cm^3
K_F = Constant for a given float (Magnet in float)	0.0180g
f_{FD} = Conversion factor of digital reading to force	2.34040×10^{-2}g/reading
f_{FR} = Conversion factor of dial reading to force	2.35602×10^{-2}g/reading

SECTION VII

DENSITY OF PLATINUM

The density of platinum (Pt) is frequently recorded as 21.45g/cm^3. This quantity is, however, not an invariable constant. It changes from sample to sample according to way of production and processing. The density of Pt wires differs from the density of Pt bars or foils and has to be determined independently for each batch. The precise determination of Pt density was found to be a great difficulty due to the variation in wire diameter, the inherent high density of platinum, etc.

A. Method of Successively Adding Pt Weights to the Float

In order to determine this density, platinum wire was wrapped around the float so as to make it bouyant at 35°C in degassed double distilled water while the digital dials were set on values required to balance forces as expressed by Equation 2 already indicated above

$$M_F(1-V_F\rho_{water}) + m_{Pt}(1-V_{Pt}\rho_{water}) + f_{FD}D + K_F = 0 \qquad (7)$$

Then successively small known platinum weights were added to the concavity in the upper part of the float and the current D flowing through the solenoid was readjusted for each weight to attain a new equilibrium.

The resulting differential expression is:

$$\Delta m\ (1-V_{Pt}\rho_{water}) = f_{FD}\Delta D \qquad (8)$$

The variation of ΔD is

$$\delta(\Delta D) = \delta(\Delta m)\ \frac{(1-V_{Pt}\rho_{water})}{f_{FD}} + (\Delta m)\frac{\delta(1-V_{Pt\ water})}{f_{FD}}$$

$$(\Delta m)\ \frac{(1-V_{Pt}\rho_{water})\ \delta\ f_{FD}}{f_{FD}^2} \tag{9}$$

Therefore we can estimate the experimental error in determining

$(1-V_{Pt}\rho_{water})$

by

$$\left|\frac{\delta(1-V_{Pt}\rho_{water})}{(1-V_{Pt}\rho_{water})}\right| \leq \left|\frac{\delta(\Delta D)}{\Delta D}\right| + \left|\frac{\delta(\Delta m)}{\Delta m}\right| + \left|\frac{\delta f_{FD}}{f_{FD}}\right| \tag{10}$$

Reasonable estimates of individual errors are $\delta(\Delta D)/\Delta D \sim 3.0 \times 10^{-3}$; $\delta f_{FD}/f_{FD} \sim 1.0 \times 10^{-4}$; $\delta(\Delta m)/\Delta m \sim 6.0 \times 10^{-4}$.

The result is that

$$\frac{\delta(1-V_{Pt}\rho_{water})}{(1-V_{Pt}\rho_{water})} \sim 4.0 \times 10^{-3} \tag{11}$$

Because of the very small numerical value of the product $V_{Pt}\rho_{water}$, the quantity $(1-V_{Pt}\rho_{water})$ is approximately unity and therefore

$$\delta(1-V_{Pt}\rho_{water}) \sim 4.0 \times 10^{-3}.$$

Experimentally, the average value of $(1-V_{Pt}\rho_{water})$ was found to be 0.946 ± 0.004. This precision was not accurate enough to determine the density of platinum. The result would be a loss of at least one significant figure in determining ρ_{Pt} from the above number.

B. Determination of Pt Density With Conventional Pycnometry

This method also proved to be unsuccessful. Due to the inherent high density of platinum and the corresponding small associated volume, a large amount of wire had to be inserted in the pycnometer. In spite of this, the weight of the volume of water displaced by the platinum wire was inadequate to provide precise results. Instead of water ($\rho_{water} \sim 1.0 g/cm^3$), mercury ($\rho_{Hg} \sim 13.6 g/cm^3$) was used as a medium to be displaced by the platinum wire. Unfortunately, air pockets appeared in the pycnometer. This was attributed to the fact that the mercury did not "wet" the platinum surface. To obtain acceptable results the following technique was used.

C. Method of Density Measurements With Two Dissimilar Floats

In order to obtain the density of platinum, two calibrated floats each of different densities were independently made null for bouyancy and respective digital readings obtained. Letting the respective floats be designated 1 and 2, we have

$$(M_2-M_1) - (M_2V_2-M_1V_1)\rho_o + (m_2-m_1) - (m_2-m_1)\rho_o V_{Pt} + f_2D_2 - f_1D_1 + K_2 - K_1 = 0 \quad (12)$$

Here $M_2 - M_1$ = Difference in masses of the floats

$M_2V_2 - M_1V_1$ = Difference in volumes of the two floats. These were measured by conventional pycnometry discussed in the previous section.

ρ_o = density of liquid in the couette. In this case degassed, bidistilled water was used.

$m_2 - m_1$ = difference in platinum masses required to make each independent float almost bouyant in the liquid of density ρ_o.

f_2, f_1 = previously determined conversion functions for float 2 and float 1, respectively.

D_2, D_1 = Digital readings at which the respective floats were made just bouyant. f_2D_2 and f_1D_1 being the corresponding forces.

$K_2 - K_1$ = the difference between the constants found for each float, analogous to some unknown constant external magnetic field. This is only present when current passes through the magnetic coil. It might be some self-induction or an external magnetic field caused by the current lighting the light source. This has not been checked since it has always been a constant off-set.

Performing the experiment in this manner, the density of the platinum wire used was $\rho_{Pt}^{35^\circ} = 17.73234 g/cc$.

SECTION VIII

EXPERIMENTAL VERIFICATION

In order to verify the overall performance including calibration of this new apparatus, a narrow fraction of polystyrene, MW = 160,000, obtained from the Pressure Chemical Company, Pittsburgh,Pennsylvania, and dissolved in spectral grade cyclohexane, was investigated with the conventional and the magnetic float pycnometer at 35°C.

Conventional pycnometry used in this laboratory applies a glass pycnometer shaped in the form of a banana, shown in Figure 6 and described in Reference 12. The solution under consideration (about 40cc) is inserted into the pycnometer and exposed to a constant temperature of 35°C ± 0.01°C. The excess of liquid is removed from the end capillary in the left arm, the height of the liquid in the other arm attains the scribe mark. Then the capillaries are sealed by capping the arms with teflon caps. The pycnometer is removed from the constant temperature bath, dried, and weighed. A pycnometer filled with bidistilled and degassed water is weighed, as well as an empty pycnometer. The weight of water is necessary to calibrate the pycnometer's volume: In this way densities of solutions with various concentrations can be determined.

The buoyancy parameter is evaluated with the aid of the Lewis-Randall theory (Reference 11), where

$$(1-V_p\rho) = \left(\frac{dm}{dw_1}\right)\left(\frac{w_2}{m}\right) \qquad (13)$$

w_1 is weight fraction of polymer, w_2 is the equivalent weight fraction of water in solution under investigation and V_p is the partial specific volume of the polymer in solution. Having $(1-V_p\rho)$ determined,one can also evaluate the partial specific volume V_p (see Table III and Figure 7).

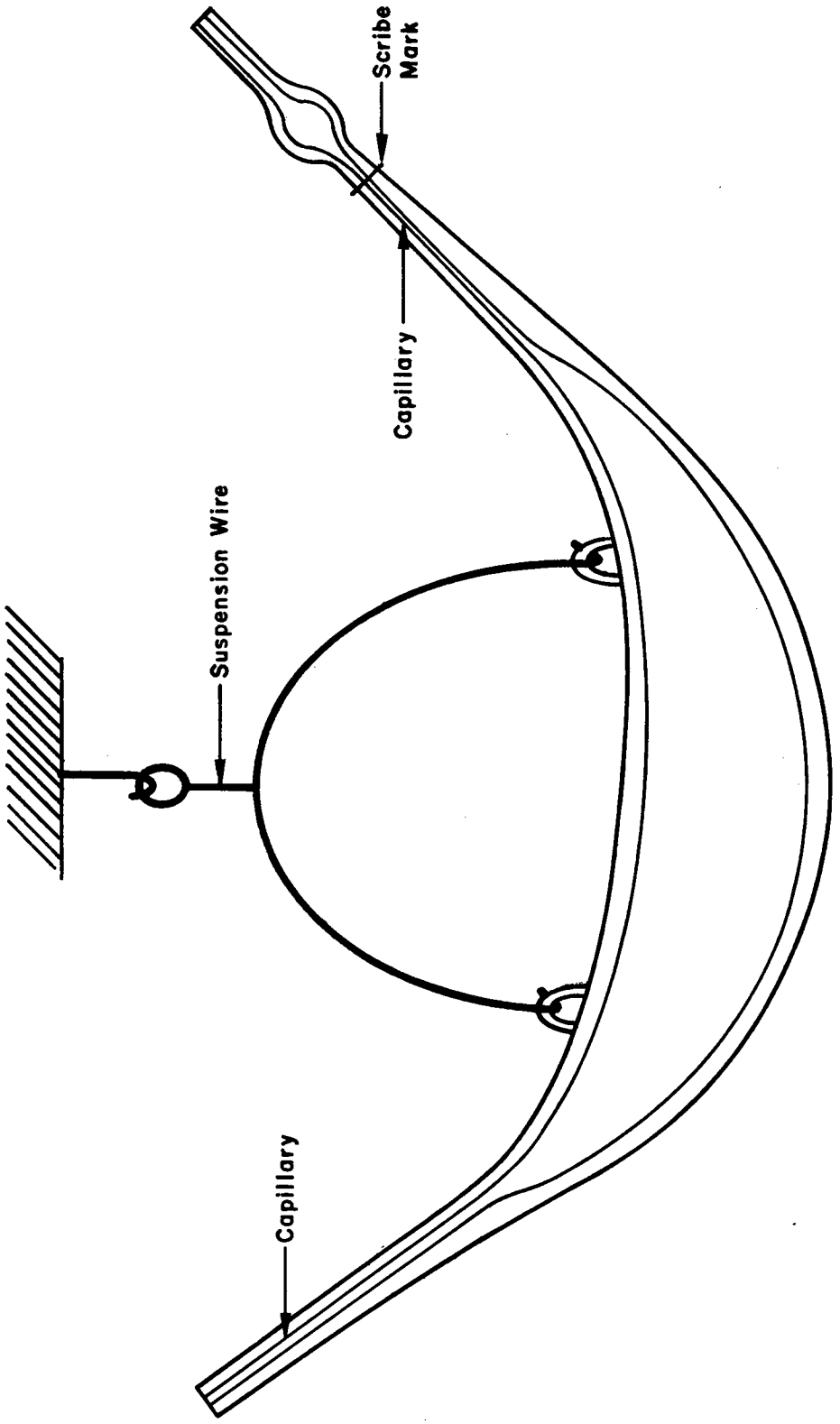


Figure 6. Pycnometer Used for Conventional Measurements of Liquid Densities

Table III. Data Obtained by Conventional Pycnometry for Determining V_p of Polystyrene (MW=160,000) in Spectral Cyclohexane at 35°C.

No.	C(%)	m	ρ	1/ρ	w_1	w_2	dw/dw_1	w_2/m	1-Vρ	V	1/V
0	0.00000	40.63150	0.7640513	1.308813	0.0000000	1.0000000	11.505	0.02461145	0.28315	0.93822	1.0658
1	0.20251	40.65283	0.7644524	1.308126	0.0020251	0.9979749	11.505	0.02454872	0.28243	0.93867	1.0653
2*	0.22542	40.65653	0.7645220	1.308007	0.0022542	0.9977458	11.505	0.02454085	0.28234	0.93870	1.0653
3	0.40739	40.67778	0.7649216	1.307324	0.0040739	0.9959261	11.505	0.02448330	0.28168	0.93908	1.0649
4	0.58698	40.69833	0.7653080	1.306664	0.0058698	0.9941302	11.505	0.02442681	0.28103	0.93945	1.0645
5*	0.67787	40.70935	0.7655152	1.306310	0.0067787	0.9932213	11.505	0.02439787	0.28070	0.93962	1.0643
6	0.83998	40.72904	0.7658968	1.305659	0.0083998	0.9916002	11.505	0.02434591	0.28010	0.93994	1.0639
7	0.97875	40.74646	0.7662131	1.305120	0.0097875	0.9902125	11.505	0.02430180	0.27959	0.94021	1.0636

$\rho^{35°C}_{water} = 0.9940426\ g/cm^3$; $H = 1-V = \frac{w_2}{m} \cdot \frac{dm}{dw_1}$

$v^{35°C}_{pycnometer} = 53.17920\ cm^3$; $V = \frac{1}{\rho}(1-H)$

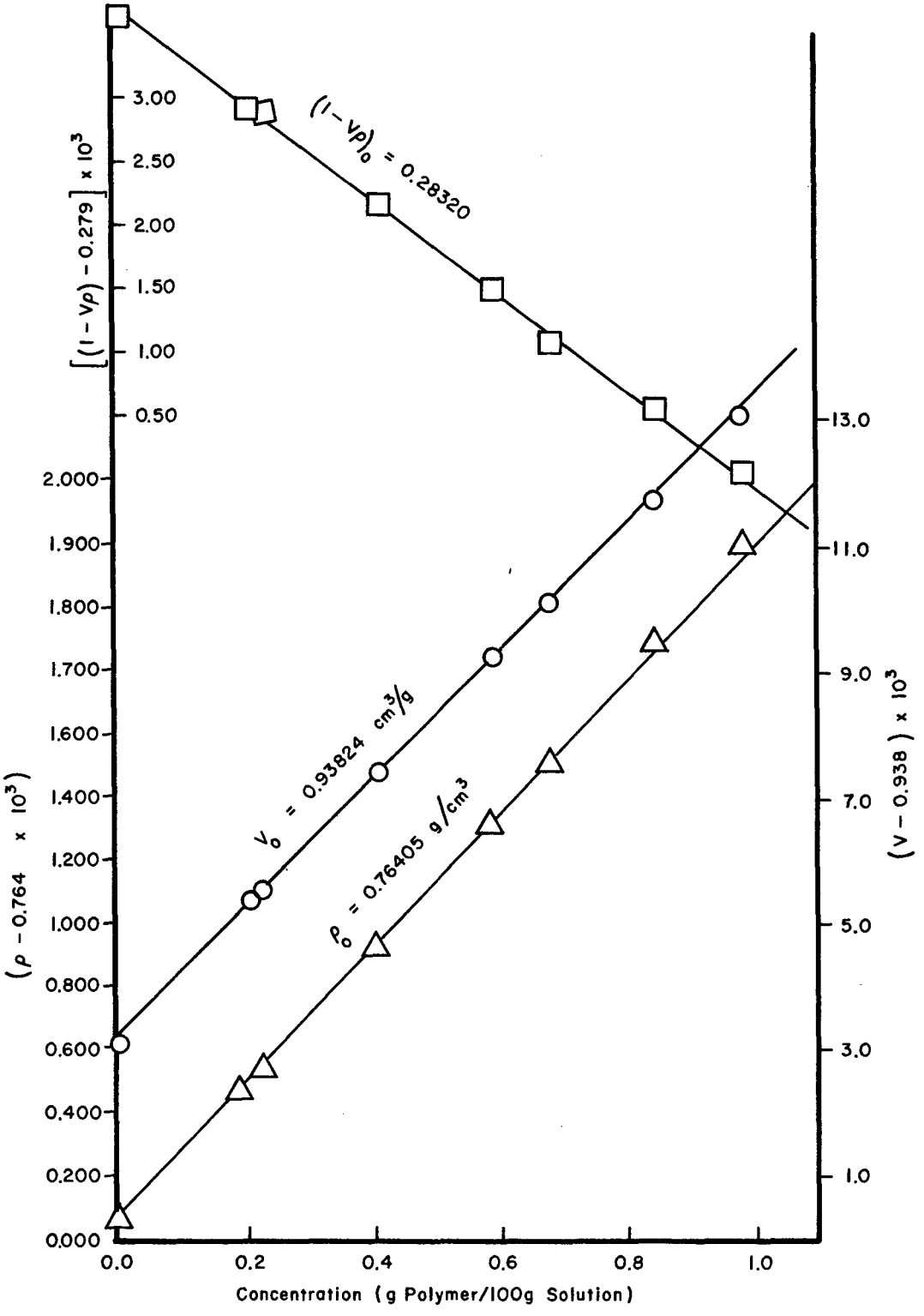


Figure 7. Results from Conventional Pycnometry of Polystyrene (MW = 160,000) in Spectral Cyclohexane at 35°C

The density measurements with the magnetic float pycnometer provided the results given in Table IV. After computations were performed the desired quantities $(1-V\rho)$, ρ, and V extrapolated to zero concentration were obtained. These are presented on Figure 8.

Table IV. Data Obtained by Magnetic Float Pycnometry for Determining V_p of Polystyrene (MW=160,000) in Spectral Cyclohexane at 35°C.

No.	%C	ρ	w_1	w_2	$f_{FD} \times 102$	w_2/ρ	$(1-V\rho)$	V	1/V
1	0.0000	0.76405	0.0000000	1.00000	0.76765	1.30881	0.2838	0.9372	1.0670
2	0.2637	0.76463	0.0026369	0.99736	2.90912	1.30437	0.2829	0.9378	1.0663
3	0.5398	0.76522	0.0053982	0.99460	5.07867	1.29976	0.2819	0.9384	1.0656
4	0.7169	0.76561	0.0071689	0.00283	6.51567	1.29678	0.2813	0.9388	1.0653
5	0.9058	0.76601	0.0090579	0.99094	7.99013	1.29364	0.2806	0.9392	1.0647

$d\rho/dw_1 = 0.2169$; $(1-V\rho) = (w_2/\rho)\ (d\rho/dw_1)$

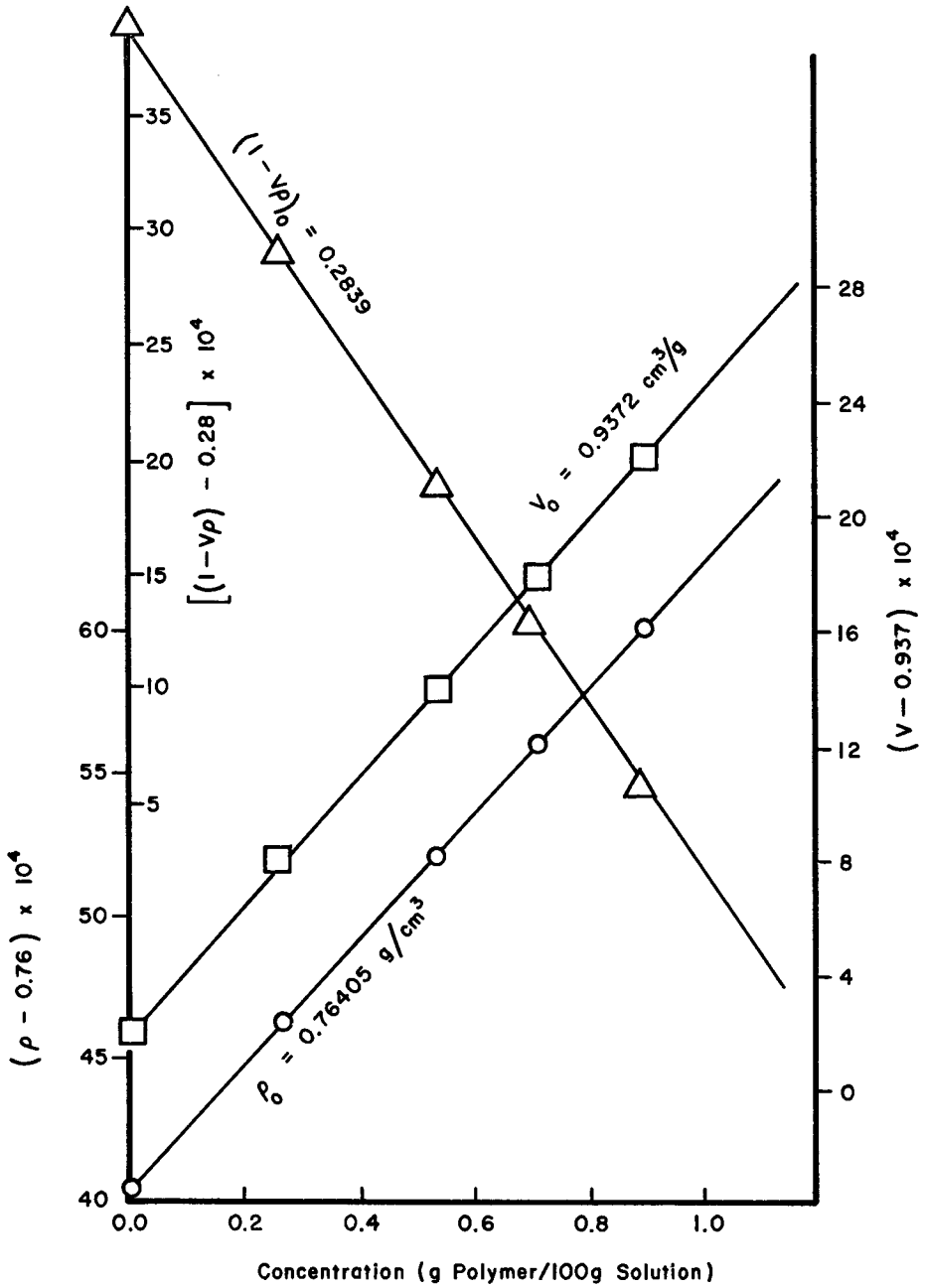


Figure 8. Results from Magnetic Float Pycnometry of Polystyrene (MW = 160,000) in Spectral Cyclohexane at 35°C

SECTION IX

CONCLUSION

Since the results obtained from both techniques agree very well (see Figures 7 and 8) the performance and calibration of the magnetic float pycnometer has been verified.

This new instrument was obtained as result of a long experimental development. Many of its electronic components were made in a temporary way in order to make them easily replaceable and modifiable. These components frequently require repairs and cause break-downs of the instrument. In order to make the Magnetic Float Pycnometer fully and reliably operational these nonstandard components must be replaced by commonly available solid state units.

This instrument has proved useful in significantly shortening the experimental time required to establish the molecular weight scale for MWD determinations. A hands-off experiment is used instead of the conventional tedious process. Cost reduction is also accomplished.

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UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
CALIBRATION AND MODIFICATIONS OF THE MAGNETIC FLOAT PYCNOMETER

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Report, November 1971 to July 1972

5. AUTHOR(S) *(First name, middle initial, last name)*
Donald R. Wiff
Matatiahu T. Gehatia

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1974	28	12

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 7340	
c. Task No. 734004	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

An automatic "hands-off" magnetic float pycnometer developed in this laboratory was applied in preliminary research to determine the partial specific volume of polymer in solution. During this phase of the research it became obvious that the original calibration was not adequate. To improve this technique a few modifications have been made, by adding a new digital ammeter and by replacing part of the homemade electronics with a commercial phase lock-in amplifier. Then a new comprehensive calibration was performed and all parameters required to characterize the apparatus and the float were determined. Finally, partial specific volume of the polymer polystyrene in cyclohexane was investigated by applying the new magnetic float pycnometry and also by using the conventional technque. The results obtained from both methods were in excellent agreement. The instrument will significantly shorten experimental time and result in cost reduction.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pycnometer						
Magnetic Float						
Partial Specific Volume						
Polystyrene						
Molecular Weight						
Molecular Weight Distribution						
Density of Liquids						
Polymers						

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