THE EFFECT OF FREE VOLUME ON THE RADIATION ACCELERATION OF CREEP IN POLYCARBONATES

by

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Department of Chemical Engineering
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Cambridge 39, Massachusetts
May 19, 1967

Professor Edward N. Hartley
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Professor Hartley:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled "The Effect of Free Volume on the Radiation Acceleration of Creep in Polycarbonates," in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Signature redacted

Andrew H. Goldsmith

Acknowledgements

The author wishes to express his sincere appreciation to Professor A. S. Hoffman, who suggested both the subject of this thesis and the general method of attack. In addition, the author would like to thank Mr. Robert Mayer, whose assistance, especially on the creep apparatus and experiments, was invaluable.

Mr. Kenneth Wright of the M.I.T. High Voltage Laboratory was responsible for the set-up of irradiation apparatus and for the operation of the Van de Graaff generator.

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I. Summary

With the increase in commercial applications of radiation, there has come enhanced interest in the study of polymer -- radiation interaction. Prior to 1959, all experiments were of the before radiation and after radiation type. In 1959 however, Mokulskii et. al. (3,4,5,6) conducted studies of the dynamic properties of polymers while they were undergoing irradiation.

One of the discoveries resulting from this work was that in several polymers, at least, there was an increase in creep rate during irradiation. These studies were continued in 1966, by Bell (7), Hoffman (8), and Mayer (28) and it was found that the phenomena extended to other polymer systems. In a preliminary study Mayer found that the radiation acceleration of creep in polycarbonates was preceeded by an induction period and the the length of this induction period was affected by quenching the samples into liquid nitrogen from above their glass temperature.

This seemed to tie in with decay period phenomena in support of a hypothesis connecting creep acceleration with the interrelation of gas generation and the amount of free volume in the sample.

In this thesis an attempt was made to investigate the effect of free volume by varying it in the following manner. Polycarbonate samples were equilibrated at 160°C. (15°C. above the glass transition) and then were quenched into constant temperature baths of different temperatures. Density measurements indicated how much of an effect the different quenchings had. Samples which had been treated in this manner were then used in irradiated creep tests.

The results seem to indicate two things. First, that the induction period was not affected by quenching and secondly that more effectively

quenched samples had higher initial elongations and higher creep rates after the initiation of radiation accelerated creep.

However, one sample was run which did not have the same induction period as the others. There does not seem to be a clear explanation for this, except for the possibility of equipment difficulties which were being experienced.

II. Introduction

A. Effect of Irradiation

1. General

During the last few decades synthetic polymeric materials have become increasingly important. There has been a simultaneous growth in commercial radiation applications and in space research. Since the unusual properties of polymeric materials are suited to these areas, the consequences of radiation incidence on plastics is of extensive interest. Several books describing general types and mechanisms of radiation effects have been written (1,2).

Prior to the 1960's most experimental work consisted of exposing the subject material to radiation, removing it from the radiation, and determining the change in properties. The first investigation of mechanical characteristics during irradiation was carried out in the Soviet Union by Mokulskii, et. al. (3,4,5,6), using nuclear reactor radiation. In studies with polyvinyl chloride, polymethylmethacrylate, polyisobutylene, polystyrene, and polytetraflouroethylene, Mokulskii, et. al., found that during irradiation all samples exhibited an enhabced creep rate. In 1966, Bell (7) examined the behavior of several polymer systems, polystyrene, polymethylmethacrylate, and polyvinylchloride--acetate copolymer, during irradiation with three and eight MEV electrons (beta particles). The work on polymethylmethacrylat was elaborated on under a project headed by Hoffman (8). In all cases an accelerated rate of creep was found for the duration of the irradiation.

2. Creep During Irradiation

The following results were usually found in studies of creep rate during irradiation (see Figure 1). In Region I (stress but no radiation) the sample underwent the normal glassy creep expected for that kind of material. At Time "1" the electron beam was turned on. There followed an induction period before the creep rate increased. In polystyrene the creep rate became constant, whereas in polyvinylchloride--acetate copolymer and polymethylmethacrylate it continued to accelerate (9). At Time "2" the electron beam was turned off and in Region III the creep rate decayed over periods ranging from instantly to a matter of minutes. Removal of the stress occurred at Time "3", and was followed by very small amounts of elastic recovery, especially in the case of polymethylmethacrylate (10), which is shown in Figure 2.

3. Irradiation in the Absence of Stress.

In their investigations, both Bell and Hoffman irradiated samples in the absence of significant stress. It was found that under these conditions the samples underwent expansion. In the case of polystyrene (11) the expansion leveled off after a given amount of radiation.

When Hoffman examined polymethylmethacrylate in this manner, he found expansion at constant rate with one exception. One sample irradiated at high temperature and low beam current leveled out after several minutes of irradiation (12). Expansion after irradiation had ceased was found in one case with polymthylmethacrylate (13). Bell reported similar delays in the decay of polyvinylchloride--acetate

FIGURE 1: GENERAL EFFECT OF RADIATION ON CREEP

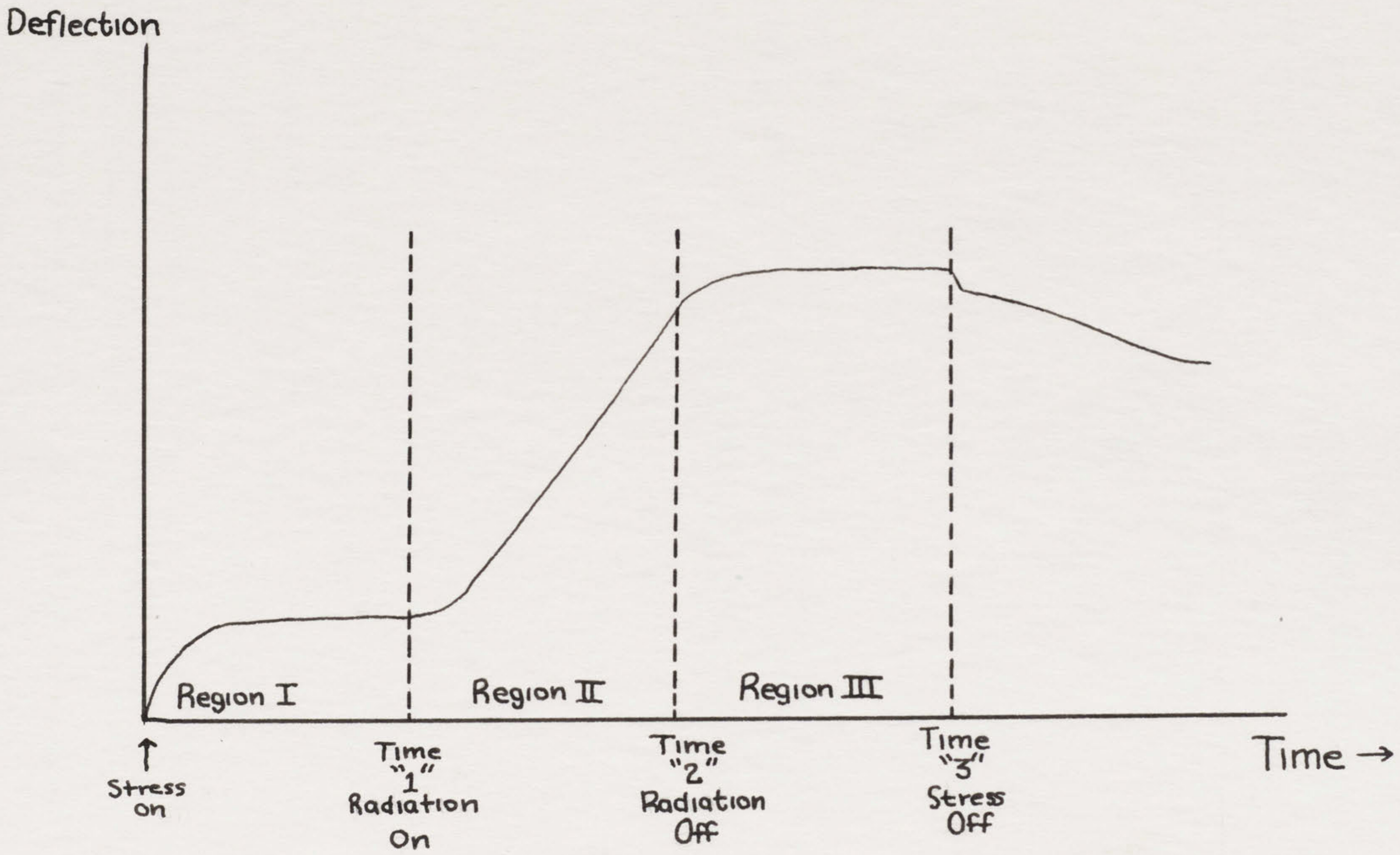
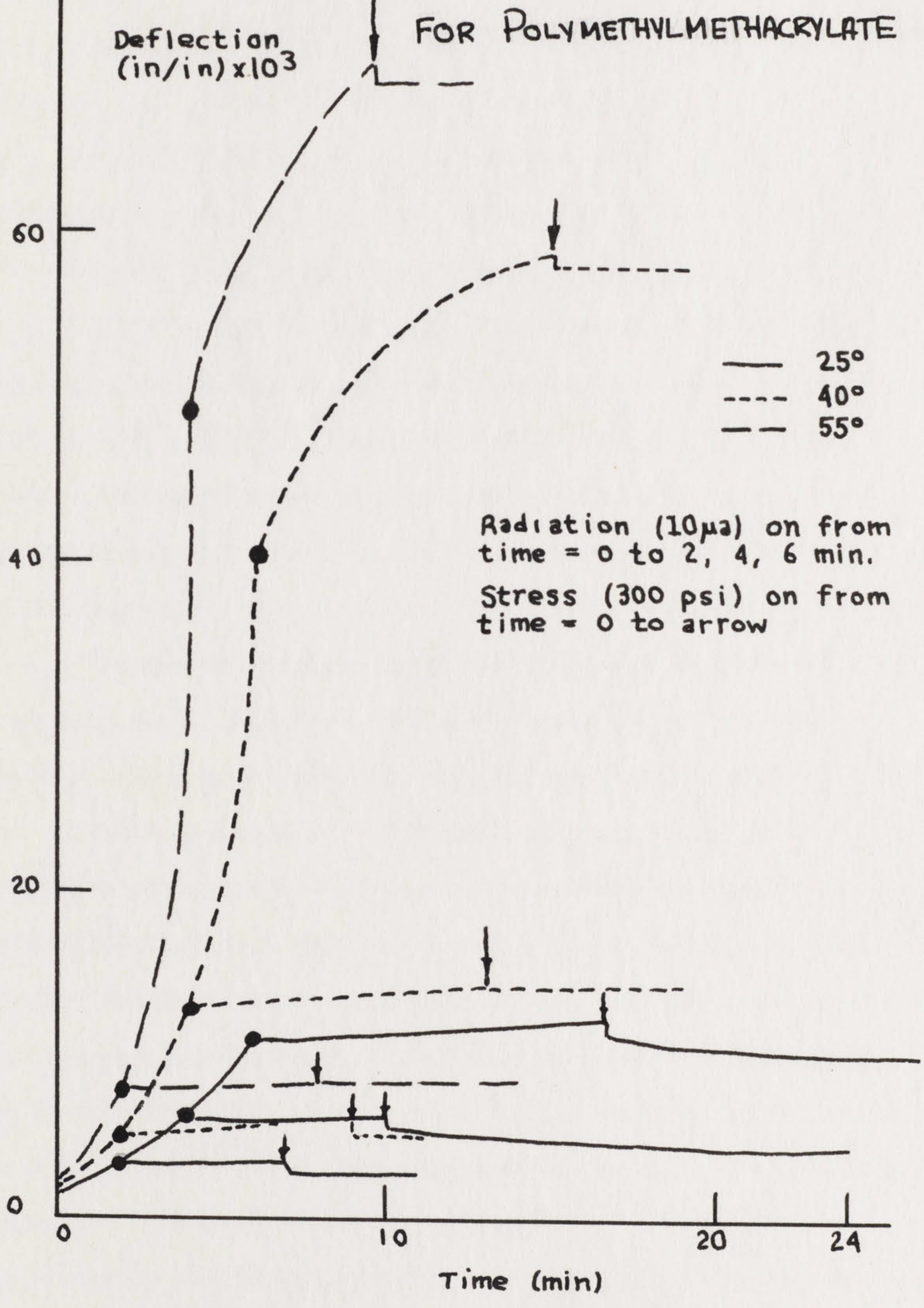


FIGURE 2: RADIATION CREEP AND CREEP RECOVERY (10) FOR POLYMETHYLMETHACRYLATE



Radiation (10μa) on from time = 0 to 2, 4, 6 min.

Stress (300 psi) on from time = 0 to arrow copolymer as well as in polymethylmethacrylate.

B. Mechanisms of Creep Acceleration

The mechanism leading from irradiation to increase in creep rate or expansion in the absence of stress is not well understood. Bell discussed various possibilities, among them the mechanism proposed by Mokoulskii, et. al. (6), and concluded that the most likely seemed to be one connected with the evolution of gases (14).

It is usually accepted that below the glass transition temperature molecular motions are restricted to short segments of chains. The mobility of the short segments is greatly limited by the presence of other nearby segments. Now if free volume is defined by the difference between the actual volume of the sample and the volume of the segments themselves, the free volume so defined can be divided into a disperse free volume and a "void" volume, to account for the fact that some of this free volume may exist in the form of tiny bubbles, which do not contribute to the space that each segment sees.

The disperse free volume is that which is important to the jumping of the segments. Obviously the greater the disperse free volume, the more room there is available for movement, and hence for two samples of the same material at the same temperature it would be expected that the sample with the higher disperse free volume would have the higher rate on creep tests. For further information on free volume and its effect on segmental motion, it is dealt with quite extensively in a book by Meares (15).

Since the initial "non-dynamic" irradiation studies were made in the 1940's and 1950's, it has been known that the irradiation of organic polymers leads to the evolution of gases. Bell hypothesized that when gases were evolved in the polymeric system of interest the gases increased the mobility of the polymer segments. One point which is unexplained by this theory per se, is that diffusion calculations have indicated (16) that for most of the polymers examined it would take several hours for the gas generated by the irradiation to diffuse out. Therefore one would expect the accelerated creep rate to persist instead of decaying in a period of minutes.

In extending the gas generation-free volume theory, Hoffman suggested that the gas diffuses to either microcrazes or microvoids and hence the diffusion equations are not applicable. Pointing out another possibility, he suggested that the act of generating gas along the chain was the push needed by the chain for movement (17).

Mokulskii (6) proposed that creep acceleration was governed by a mechanism of molecular activation resulting from the radiation. Because of the time scales involved, Bell (18) concluded that this mechanism was highly unlikely. An activated site would have a lifetime on the order of a fraction of a second. This is not in agreement with the experimental observation of decay periods of several minutes duration.

In reviewing the work of Bell and Hoffman, no reference has been made thus far to the nature of the radiation involved. In part, Bell used eight MEV electrons from the Van de Graff gererator in the Lawrence Radiation Laboratory in Livermore, California. The remainder of his work was accomplished with three MEV electrons from the Van de Graaff generator located in the MIT High Voltage Laboratory. Bell found no appreciable differences in the data from the two electron sources, indicating that the phenomenon is not dependent on the energy of the radiation. Should any question arise as to the definition of terms involving radiation, the reader is directed to two references already mentioned, Charlesby (1) and Chapiro (2).

C. Polycarbonate

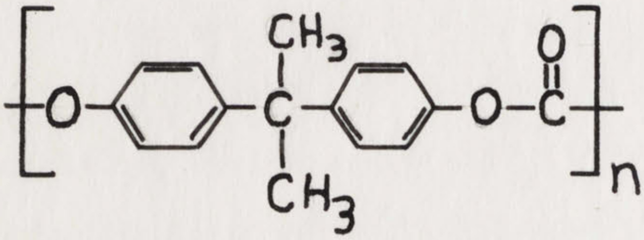
Polycarbonates are relatively new plastics available on a semi-commercial scale since about 1957. The particular carbonate used in this work is poly-(4,4'-dioxydiphenyl-2,2-propane carbonate), often referred to as bisphenol-A polycarbonate. This polymer is prepared by reacting bisphenol-A (4,4'-dihydroxyphenol-2,2-propane) with phosgene in the presence of a hydrogen chloride acceptor.

There are two very good sources of information regarding the general properties of polycarbonates (19,20)to which reference can be made in the event of questions. Figure 3 shows the structure of the bisphenol-A polycarbonate. This particular carbonate is referred to as "polycarbonate" in the remainder of this paper.

Polycarbonate is thermoplastic, but has good heat resistance. It is highly resistant to oxidative degeneration below 160°C. As a result of the high aromatic content, it is very resistant to burning, evolving carbon dioxide, and in thicknesses greater than 0.040 inch is considered self--extinguishing. It is noted for good light transmission, a high index of refraction, and good dimensional stability.

There are several drawbacks to bisphenol-A polycarbonate. One of these is that it has a tendency to craze or crack under tensile strains of over 0.75%, which corresponds to an ASTM stress of 2,000 psi. It also has a tendency to absorb water during processing,

FIGURE 3: BISPHENOL-A
POLYCARBONATE



this having an adverse effect on properties.

Chemically it is stable to water and dilute acids; it is insoluble in aliphatic hydrocarbons. It undergoes slow decomposition in the presence of strongly alkaline substances. For a more complete list of physical properties see Table 1. Table 2 lists the solubility data.

Bisphenol-A polycarbonate is resistant to radiation, as would be expected. From Figure 3, it may be seen that there are two main chain aromatic rings per repeating unit. It is known that these resonant ring structures are quite stable to radiation and tend to induce stability in adjoining atoms through their ability to "spread" energy over several atoms (21,22). It has been found (23,24) that the main effect that high energy electrons have on polycarbonate structure at room temperature is that of chain scission (as opposed to cross-linking).

The G value for gas evolution (Gdefined here as the number of molecules of gas evolved per 100ev absorbed) has been determined to be 2.9 (23,25). In addition (25), the composition of the gas evolved was found to be 60% CO, 39% CO_2, and 1% H_2. Table 3 lists the effect on properties of irradiation of bisphenol-A polycarbonate with two MEV electrons.

D. Effect of Quenching on Free Volume

The free volume of a polymer sample may be affected by "freezing" it in a non-equilibrium state. That is, if a polymer sample is heated above T_g and allowed to come to thermal equilibrium there, it will be in an expanded state commensurate with it's thermal properties.

However if it is now cooled below its glass transition temperature, it will not necessarily be in an equilibrium state. If it is cooled quickly, it will not have sufficient time to contract to an equilibrium value before it reaches the glass temperature. At the glass temperature gross molecular motions cease and only short segmental jumps can occur, "freezing" the material in a non-equilibrium expanded state. This expanded state is obviously of lower density and hence contains more free volume than the equilibrium state.

This procedure of quenching has been used to vary density by several experimenters in the past. Whitney (26) quenched two materials into ice water and liquid nitrogen. He found that he could vary the density of polystyrene from 1.050 to 1.052 grams per cubic centimeter and that of polymethylmethacrylate from 1.194 to 1.197 gram per cubic centimeter. In working with polyvinylchloride, Ke (27) determined the density of quenched material to be 0.959 gram per cubic centimeter; the density of material cooled at 0.1°C. per minute to be 0.973; and the density of material cooled at the intermediate rate of 1.0°C per minute to be 0.961. In Ke's data the effect of non-equilibrium crystallization is undoubtedly responsible for a large part of the density differences. Whitney's data is undoubtedly more typical of non-crystalline polymer systems.

E.~~D.~~ Preliminary Radiation Study of Polycarbonate

A pilot study was conducted with polycarbonate by Mayer (28) to determine whether and if so, to what extent, radiation acceleration of creep existed in this material. The resulting data (see Figure 4)

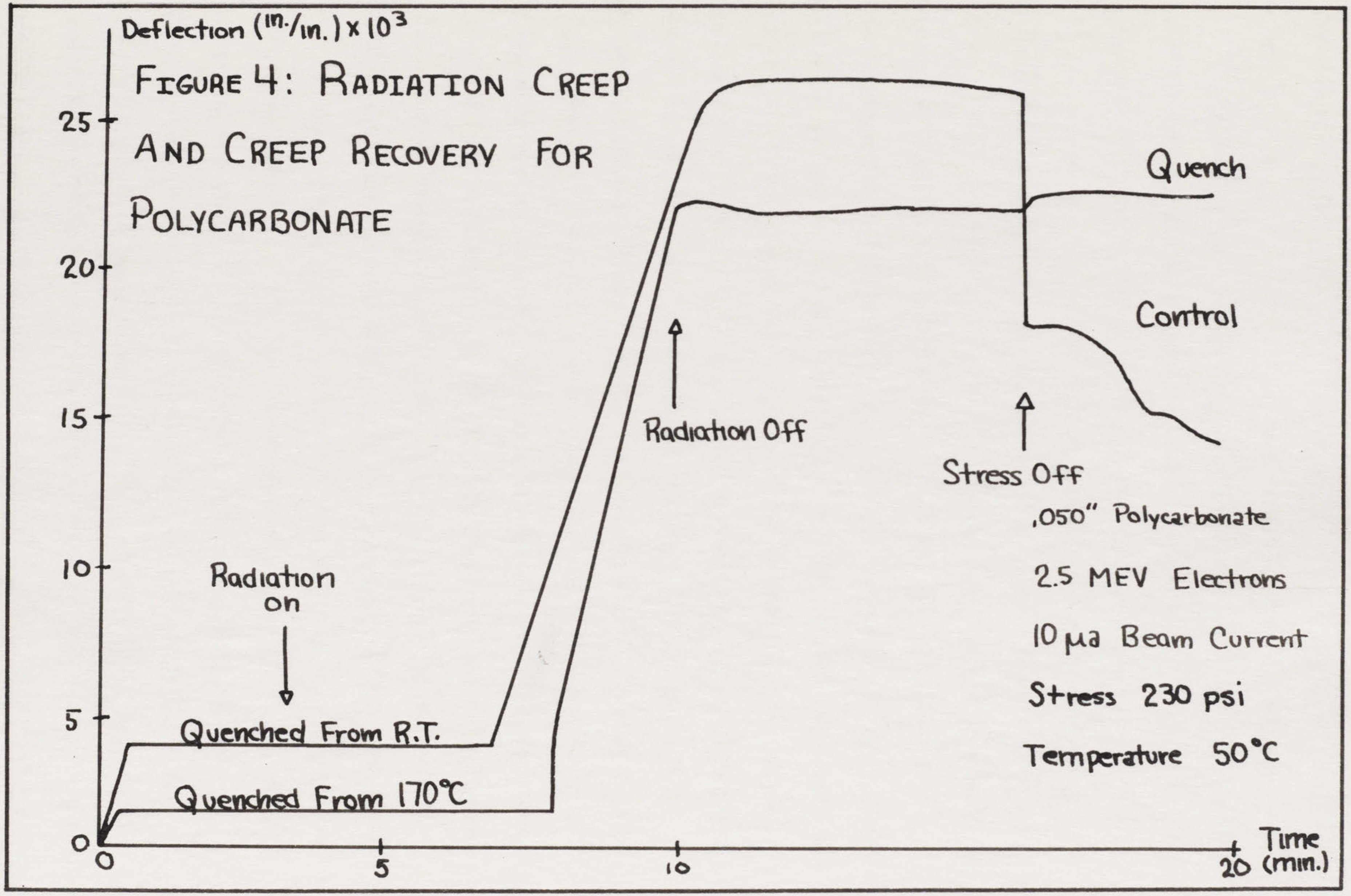


FIGURE 4: RADIATION CREEP AND CREEP RECOVERY FOR POLYCARBONATE

indicates that the effect is quite pronounced. However the radiation creep curve displayed several characteristics unique to polycarbonates.

For instance, during the induction period polycarbonate exhibited only the creep typical of non-irradiated polycarbonate samples. During this period there was absolutely no acceleration effect whatsoever.

The decay period was present but was comparitively short. Barker (29) measured the diffusion rate of O_2 in polycarbonate and arrived at a value of $D = 8 \times 10^{-8}$ cm.^{2} per second at 50°C. Hoffman estimated that the average diffusivity of the gases evolved in polymethylmethacrylate was $D = 2 \times 10^{-9}$ cm.^{2} per second (30). Since G values for gas evolution are similar, 1.9 for polymethylmethacrylate versus 2.9 for polycarbonate (31), and the geometry of the samples was similar, it would be reasonable to assume that if they absorbed energy at the same rate, gases would build up at the same rate. Polymethylmethacrylate and polycarbonate have about the same density (32). Hence for incident electron beams of the same current it is reasonable to assume that they absorb energy at about the same rate (33). Therefore the conclusion arrived at by Hoffman (30), that diffusion is not rapid enough to explain the decay rate found in polymethylmethacrylate irradiation studies, would also apply to polycarbonates.

As a part of his exploratory study, Mayer (28) heated a sample of polycarbonate to 170°C. and then quenched it to -195°C. (liquid nitrogen temperature). The results of the subsequent radiation study are shown in Figure 4. The control sample shown there was quenched from room temperature to -195°C. As it may be seen, the induction period was longer, the decay to normal creep rates was almost instantaneous, and there was little recovery. No attempt was made to determine the extent of the effect of the quenching on the polycarbonate density.

III. Apparatus

A. Creep Experiments

1. Mechanical Apparatus

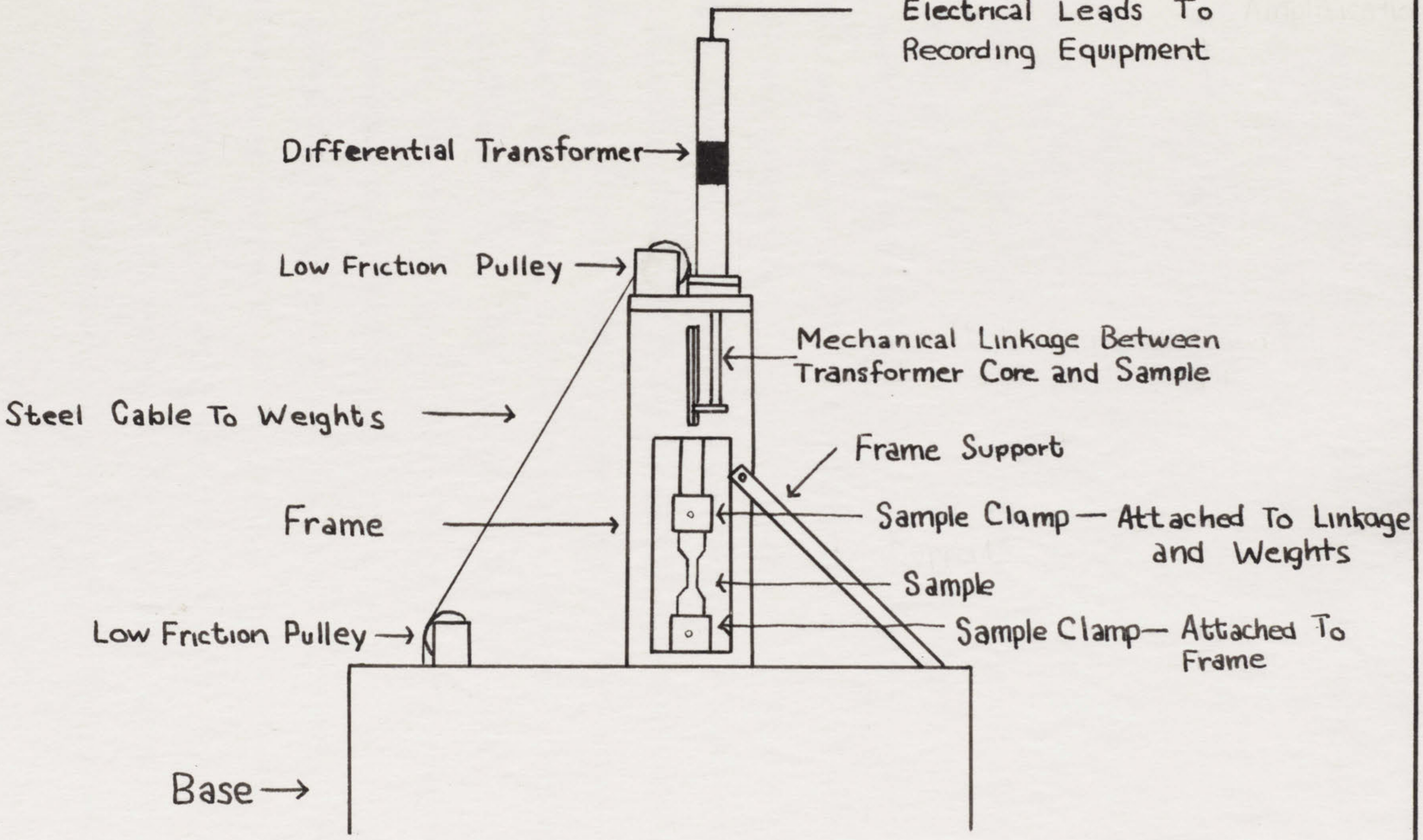
In essence, the creep experiments consisted of suspending the sample from a fixed object, attaching a weight to the free end, and measuring the sample length as a function of time. The slope of such a plot at any time is its creep rate at that time. The basic apparatus for measuring the creep rates of different samples is depicted in Figure 5.

The stress is applied to the sample by means of a braided steel cable which passes around two low friction pulleys to a weight pan. A spring attached to the cable ensures no slack in the cable and maintains constant tension (at a very low value) in the system.

In order to apply stress during irradiations (when the radiation hazard makes it impossible to be in the experimental chamber), a pneumatic system which could be controlled from the electronic console area was used. This system consisted of a pneumatic cylinder below the weight pan coupled to an air supply in the control room. A remotely controlled solinoid valve in the gas line just before the cylinder made it possible to raise or lower the weights quickly. The time for a complete stress change was less than one second. The stress application was found quite smooth and experiments by Bell (34) with a load cell indicated that the friction of the pulleys was not significant and that reproducibility was very good.

The sample clamps were those used by Bell. These clamps

FIG. 5: CREEP APPARATUS



were tightened with a torque wrench so as to give reproducible results with all samples. Details of construction and dimensions of the clamps are found in Bell's thesis (35).

2. Radiation Source and Control

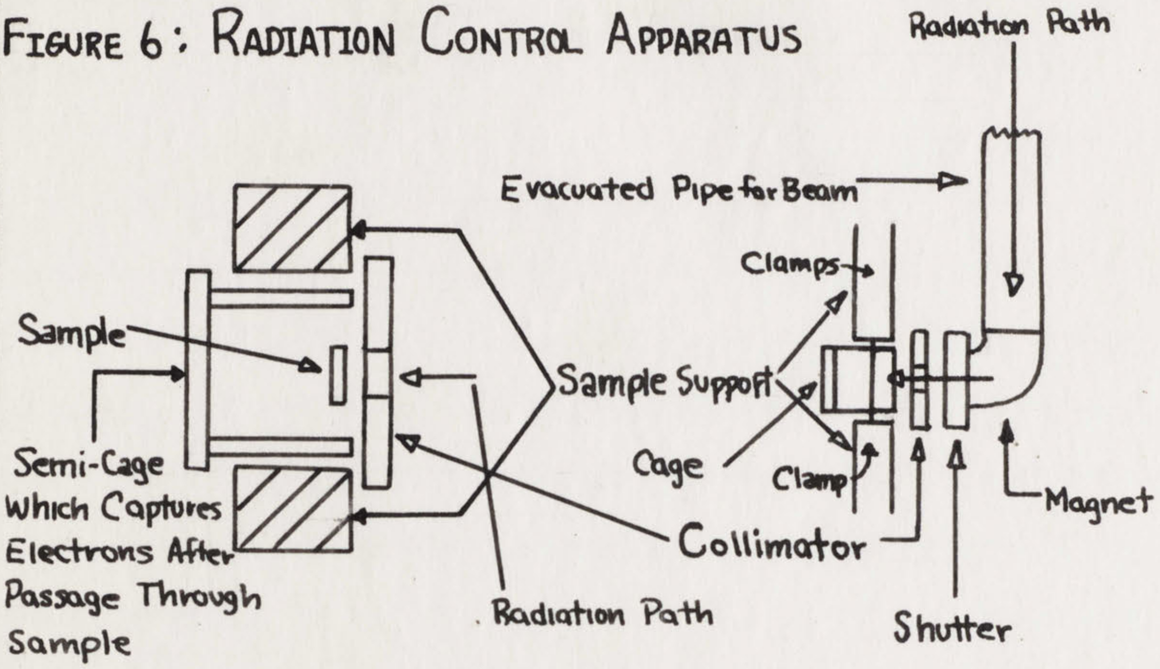
The radiation used in this thesis consisted of three MEV electrons from the Van de Graaff generator located in the High Voltage Laboratory (Building N10) of the Massachusetts Institute of Technology.

The electron beam entered the experimental chamber vertically through the ceiling and was turned ninety degrees by a large magnet, making the beam horizontal. Just prior to reaching the sample, the beam passed through a 3/8 inch aluminum block with a 3/4 inch diameter hole in the center. This restricted the area of the sample which was subjected to radiation. Due to spreading of the beam after passing through the aluminum block, the area of effective radiation was about one inch in diameter. A side view of the electron beam path is shown in Figure 6B. The shutter depicted just after the magnet enabled the beam to be stopped and started cleanly.

Behind the sample another aluminum block was mounted, this one with extensions perpendicular to the face so as to form a semi-cage, as shown in Figure 6A. The purpose of this was to measure the beam current passing through the sample. The perpendicular extensions made it possible to absorb most of those electrons scattered by the sample.

The beam energy was measured on the Van de Graaff control console and varied between 2.5 and 3.0 MEV. The variation was due to

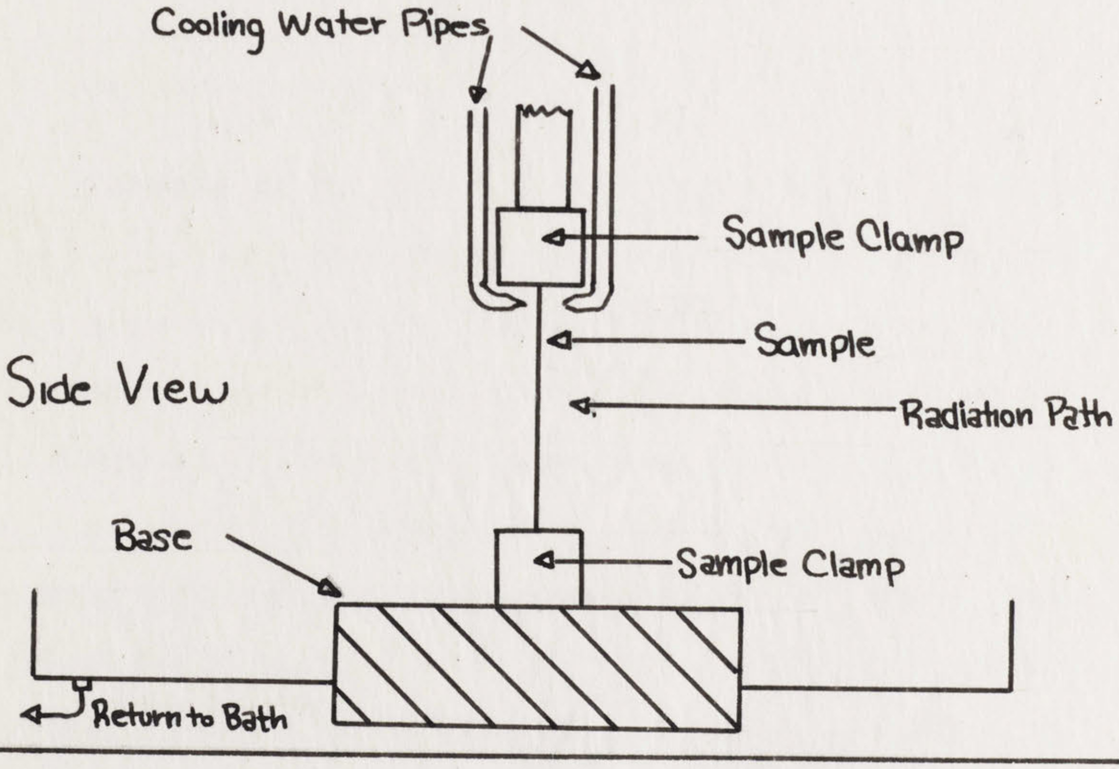
FIGURE 6: RADIATION CONTROL APPARATUS



A. TOP VIEW

B. SIDE VIEW

FIGURE 7: SAMPLE COOLING SYSTEM



the daily operating characteristics of the Van de Graaff generator.

3. Temperature Control

Throughout the experimentation, sample temperature was regulated in the following manner. Water at the desired temperature was allowed to flow uniformly down both faces of the sample by two tubes (one on each side) near the top of the sample. The ends of the tubes were flattened in an attempt to obtain as uniform flow as possible across the sample. Figure 7 (on the preceeding page) contains a general picture of the cooling system.

The water for the tubes was supplied by a large constant temperature bath equipped with both heating and refridgeration units. After contact with the sample, the water was caught in a plastic tray and returned to the constant temperature bath. With this temperature control apparatus the water temperature was controlled to within 0.5°C.

4. Electronic Equipment

Elongation of the sample during a creep test results in movement of the core of a differential transformer. This core movement causes a variation in the output of the differential transformer. A demodulator compares the voltage and phase of the output signal of the differential transformer to the voltage and phase of the going in and sends a d.c. signal which is proportional to the core movement to a digital integrating voltmeter. The d.c. signal from the demodulator is averaged over a given time period by the voltmeter and is then displayed digitally on the front of the voltmeter. In addition the averaged value is recorded by an on-line printer. By knowing the calibration curve for the system (voltage on digital voltmeter versus core displacement) and the rate at which the on-line printer prints, one can obtain a plot of sample elongation versus time. This system is shown in Figure 8.

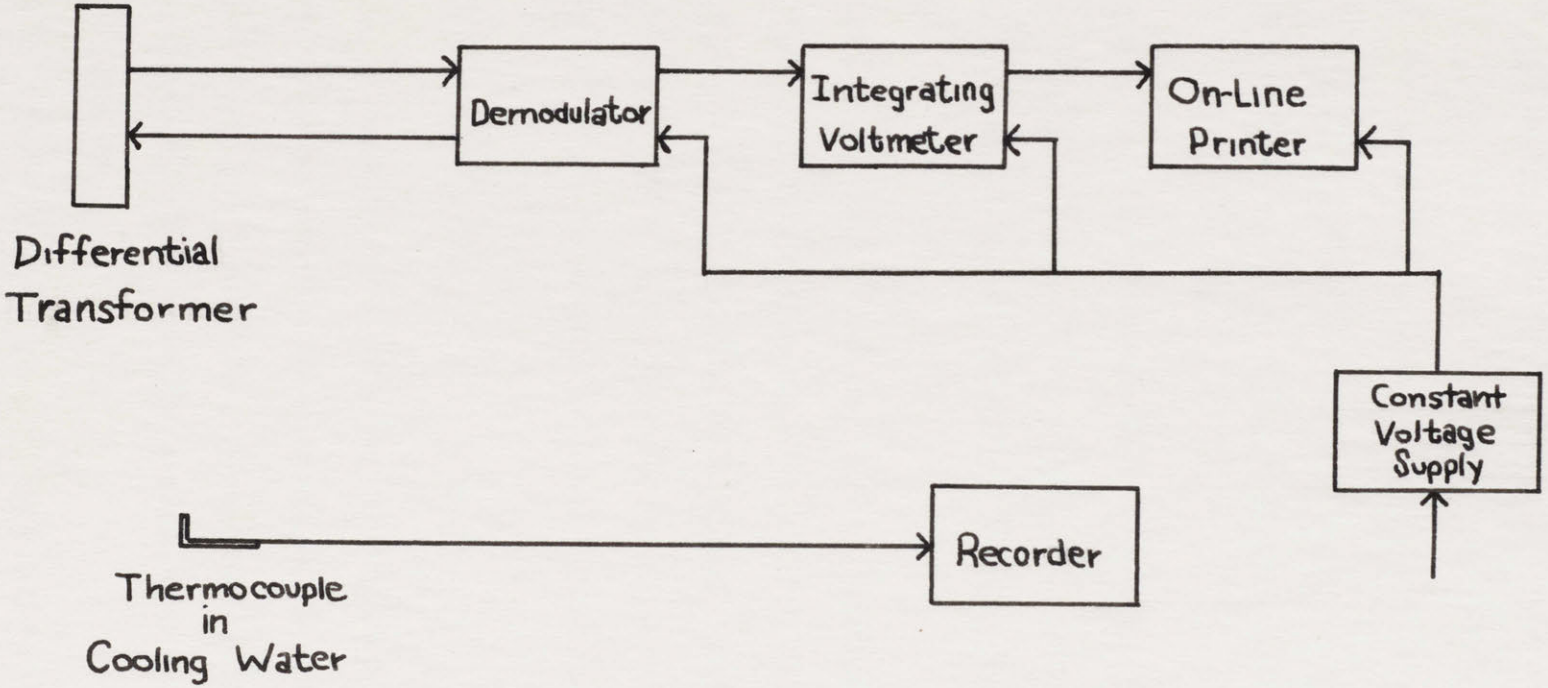
The differential transformer used here is manufactured by Kavlico Electronics. According to specifications it has a temperature range from -65°F. to 300°F. The null position is constant to within 0.001 inch over this range. In addition, it has a radiation tolerance of 4.3×10^{17} n. per cm.^{2} (e greater than 1 MEV). This differential transformer was unit number 91130, size C. After part of the experimental work had been completed an intermittent short was detected in this unit.

The Kavlico differential transformer was then replaced by one from the Automatic Timing and Control Company of King of Prussia, Pennsylvania. This transformer was not shielded to radiation. However it was felt that the amount of radiation (gamma rays) that would strike and penetrate the transformer was small.

The demodulator used in this experimentation is an Automatic Timing and Controls Company demodulator. During the earlier part of the experimental work the demodulating unit was faulty due to several defective transistors and resistors. A new demodulator was provided by Lawrence Radiation Laboratories. Because of irregularities encountered during the calibration testing, a third demodulator was also used. All demodulators were of the same model and size. The calibration will be discussed further in the Experimental Procedure section.

The output signal from the demodulator was transmitted to

FIGURE 8: ELECTRONIC EQUIPMENT



a Dymec Integrating Digital Voltmeter (Model 2401 B). This voltmeter averages the signal over some predetermined period and then displays the result digitally on the face. In addition, the averaged result is sent to an on-line printer for recording. An averaging period of one second was used throughout this work. With a sample period of one second, operating on the one volt scale, the voltmeter error was less than 0.1 mv.

The printer was a Hewlett Packard Model H37-562A on-line printer. It has two printing speeds, fifty times per minute and a much higher rate. Throughout this work the fifty times per minute rate was used.

The recorder used to record cooling water temperature was a Leeds and Northrup Speedomax H recorder with a 0-300°F. temperature span. It was operated with a chart speed of ten inches per minute.

A Sola transformer and a Sorenson voltage regulator (Model 1001) were used to provide 115 volt (within 0.1%) power to the system.

B. Density Determining Apparatus

In an effort to measure quantitatively the effects of different degrees of quenching, a method of accurate density determination suitable for polycarbonate was attempted. This method depended upon the difference in coefficient of cubic expansion between glassy polymers and organic liquids.

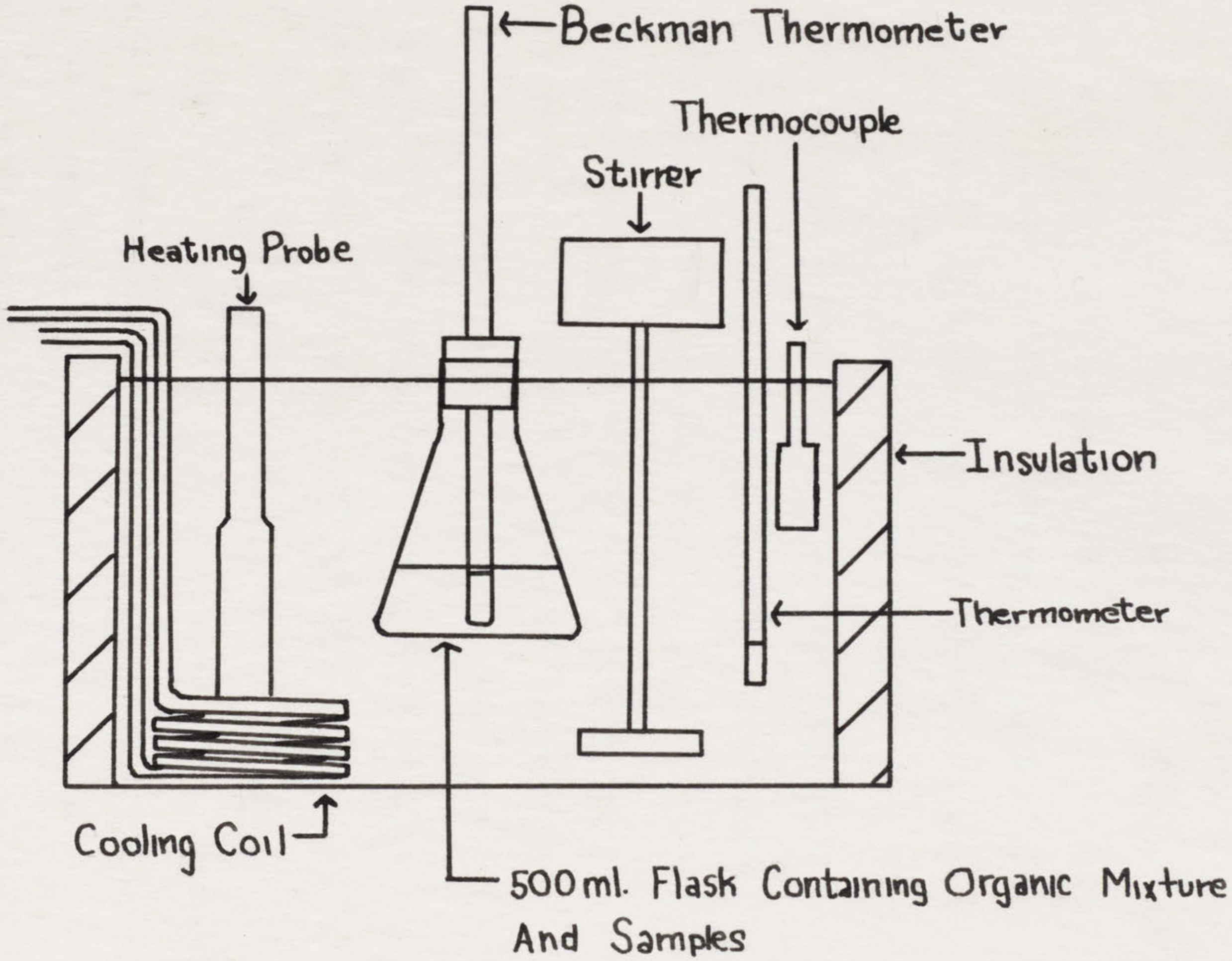
In essence the temperature of a mixture of organic liquids with a polycarbonate sample in it was lowered until the polycarbonate began to rise, at which point the density of the polycarbonate is just slightly different then the liquid density. If the density of the liquid mixture is known as a function of temperature, then the density of the polycarbonate at that temperature can be evaluated quite accurately. The apparatus used in these determinations will now be discussed. The apparatus is shown in Figure 9.

A 500 milliliter wide mouth flask was used to contain the organic mixture and the sample. This sample flask was immersed to a point about one inch above the organic liquid level in a twenty liter insulated water bath. This bath was equipped with a stirrer, temperature controller, and a 450 watt heater. In addition, the bath contained a copper coil constructed from about two feet of 3/8 inch copper tubing through which cooling water from the tap was run at varying rates. The higher the rate, the more rapidly the temperature of the twenty liter bath decreased.

The bath temperature was read on a three inch, 30°C. immersion thermometer with 0.1°C. graduations. With a magnifying glass the bath temperature could therefore be read to a one -hundreth of a degree ± 0.02°C. The temperature of the organic mixture was measured with a Beckman thermometer. This thermometer has graduations every 0.01°C and therefore maybe read to 0.001°C. ± 0.0015°C. with a magnifying glass.

Several liquid mixtures were tried in this apparatus. They will be discused in the Experimental Procedure section.

FIGURE 9: DENSITY DETERMINING APPARATUS



IV. Experimental Procedure

A. Sample Preparation

All samples were prepared from a sheet of "LEXAN" polycarbonate provided by the General Electric Company. This sheet was 8 inches wide, 11 inches long, and 0.010 inch in thickness. In order to remove any orientation incurred during fabrication, this sheet was annealed before use.

During the annealing process, the sample sheet was placed between two glass plates separated by four 0.020 inch separators. The surfaces of the glass plates were coated with a special Teflon spray coating to prevent the polycarbonate sheet from adhereing.

The sample sheet was maintained at 140°C. for twenty hours. It was held at this temperature, just below glass transition, in order to relax the more extreme stresses which had caused severe buckling in previous annealing attempts. The temperature was then increased to 157°C. and held there for $3\frac{1}{2}$ hours. During the final stage, the temperature was maintained at 164°C. for 23 hours. Examination of the annealed sheet between crossed polarizers (birefringence studies) revealed no apparent stress concentrations.

The sheet was then covered by protective tape, whose adhesive was of a polymeric nature and hence was unlikely to penetrate the polycarbonate sheet. The protective tape was used in an effort to prevent contamination of the sheet by oil in later handling and fabrication.

After application of the tape, the sheet was divided into rectangles 3 inches by 3/4 inch with a pair of scissors. Samples to be used in creep studies were then brought to the shape and dimensions shown in Figure 10 in a milling operation.

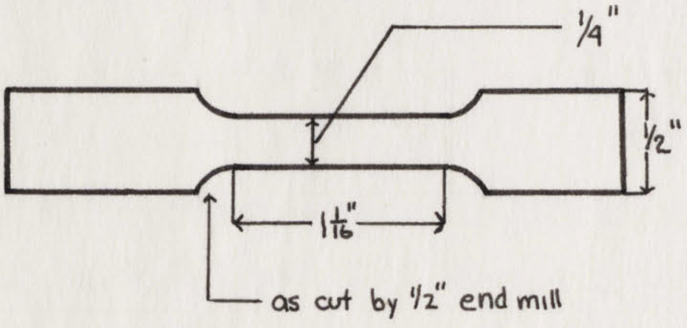
First, the rectangles were clamped between two rectangular blanks and brought down to just above the required size by milling. This manoeuvre evened out the sides and ensured square corners on the rectangles. The products of this step were then inserted into another blank for milling to the final shape. The samples were milled to accuracy on one side and then were milled to the desired shape.on the other side. It was this 'turning over' step which made square corners important. These samples were then ready for either quench treatment or creep testing, although of course, the protective tape was removed first.

A milling speed of 700 rpm and a low feed rate constituted the milling conditions. No more then 0.020 inch was taken off on any one cut. The milling head used was a ½ inch, 4 fluted, high speed end mill. It was stored in acetone when not in use, in an effort to prevent sample contamination with oil. During the entire milling procedure no cutting oil or liquid coolant of any sort was used.

B. Quench Treatment

In attempting to vary the density (and hence the free volume) of samples, a quench treatment was employed. Reduced to basics, the treatment consisted of heating a sample to some temperature above T_g, holding it there until it reached equilibrium, and then cooling it at different rates to below glass transition. The procedures used in this treatment, whose theoretical implications were discussed in

FIGURE 10: SAMPLE DIMENSIONS



sample thickness is 0.010"

the Introduction, will be discussed below.

A constant temperature hot air oven was used as the heat source. A large slab of aluminum stabilized the temperature of the oven; that is, the slab of aluminum prevented the sample temperature from dropping appreciably until the sample was removed from the oven, instead of beginning to decrease the instant the oven door was opened.

The samples were placed on standard glass microscope slides, which, in turn, were placed on the aluminum plate. After the samples had come to equilibrium (usually about thirty minutes was allowed) at the oven temperature, they were ready to be quenched. The oven temperature was kept at 160°C., or about fifteen degrees above glass transition.

The quenchings were accomplished very simply. When it was desired to quench a sample, the glass slide with the sample on it was tilted over the correct temperature bath and the sample slide quickly in.

Two constant temperature bathes were used in the quenchings. These were liquid nitrogen and dry ice--ethanol. According to the Handbook of Physics and Chemistry (36) the bath temperatures are the following:

liquid nitrogen	-195.8°C.
dry ice--ethanol	-72°C.

All quenched samples were allowed a minimum of three to five minutes in the low temperature bath. In an effort to avoid oil contamination, the sample was not touched by hand at any time.

C. Creep Tests

1. Calibration

Each differential transformer was calibrated before use. This was accomplished by inserting a barrel micrometer into the apparatus, positioned in such a way so as to move the core of the differential transformer by measured amounts. By noting the voltage at each extension and the amount of the extension, calibration plots were constructed. These calibration plots are shown in Figures 11 and 12. Note the difference in level of output voltage between the Kavlico and the ATC (Automatic Timing and Control Company) differential transformers.

When the Kavlico differential transformer was used the demodulator setting was kept at 400, for the ATC differential transformer a setting of 500 was employed. The correct settings were utilized on the appropriate calibrations.

The slope of the calibration curve for the Kavlico differential transformer over its linear range (approximately +54mv. to -21 mv.) was 6.91×10^{-4} inches per millivolt. The same calibration curve, but for the ATC differential transformer, was of slope 27.5×10^{-3} inches per volt over a range of at least 2.4 volts to -2.4 volts.

2. Creep Measurement

Before making creep studies, all of the electronic equipment was allowed a minimum of two hours to warm up. In addition the circulating bath was turned on so as to permit it to reach its equilibrium temperature. The pneumatic system for changing sample

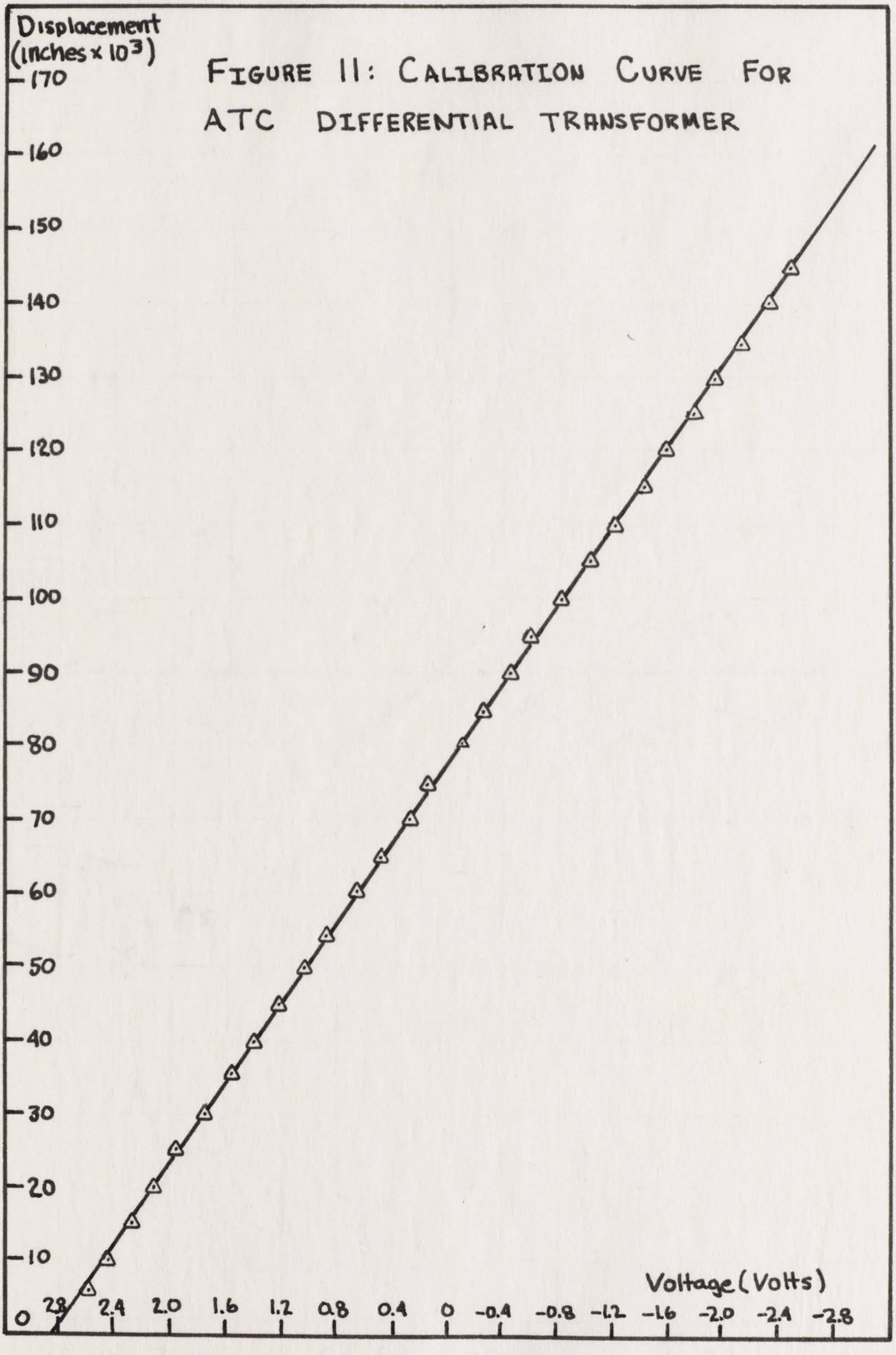


FIGURE 11: CALIBRATION CURVE FOR ATC DIFFERENTIAL TRANSFORMER

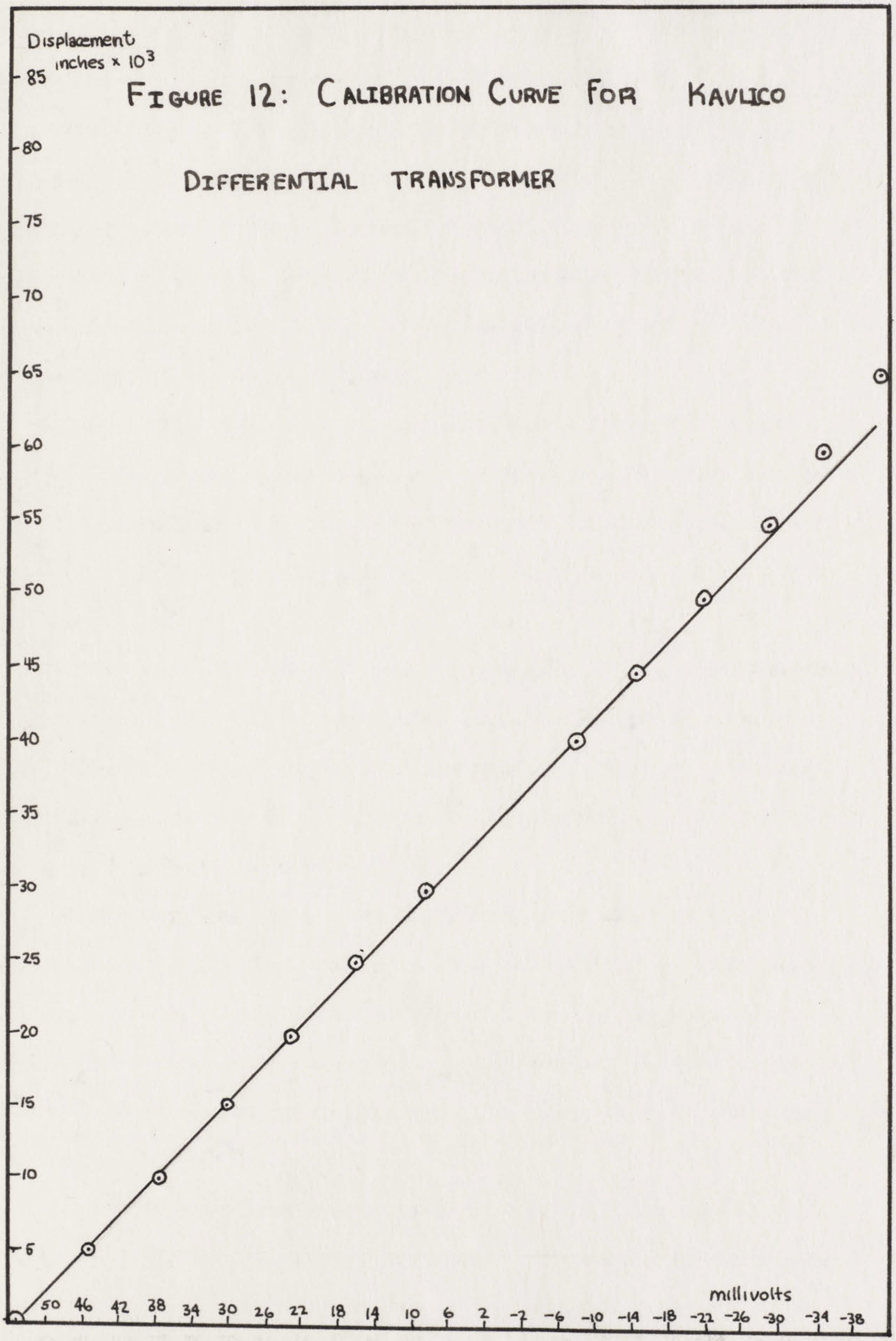


FIGURE 12: CALIBRATION CURVE FOR KAVLICO DIFFERENTIAL TRANSFORMER

stress was pressurized. Simultaneously the radiation beam control apparatus was set up by the High Voltage Laboratory staff.

The creep apparatus was then carefully lined up with the shutter so that the 3/4 inch hole in the collimator block was centered. In order to test the beam alignment, a glass slide was then placed where the sample would normally go and was briefly irradiated. The resulting discoloration pattern indicated whether or not the beam was uniform and correctly aligned.

Once this was completed satisfactorily, the apparatus was ready for the sample. The sample was centered in two sample clamps, one at each end, and the clamps were tightened using a torque wrench set at 12 inch pounds. The sample (and clamps) were then mounted in the creep apparatus.

The two cooling water tubes (see Figure 7) were then positioned so as to provide a uniform water flow on both sides of the sample over the entire necked region of the sample. At this point the semi-cage (see Figure 6B) was positioned and the electrical connections for measuring beam current attached.

The differential transformer was then adjusted so that it would remain within its linear range for the duration of the experiment. Finally the steel cable was given a pull to ensure tautness, the cooling water temperature and position was checked, and the electrical connections were examined for shorts. The experiment was then ready for running.

If the experiment was to measure radiation acceleration of creep, a timer and the printer were started at the instant of stress application. After one minute, the irradiation was begun and this point was noted on the printer. At the end of the desired irradiation period the beam was turned off, the point again being noted on the printer. At the conclusion of a given time period, the stress was removed. After several minutes, the printer was turned off and the experiment concluded. The irradiated sample was removed from the clamps and placed in an appropriately labelled envelope.

D. Density Determinations

1. Via Binary Liquid Mixtures

From Figure 13 it may be seen that in the water-glycerol system, a composition change of 1% corresponds to an indicated density change of 0.0027 grams per cubic centimeter. Hence care was taken to ensure that loss of the more volatile component was minimized during storage and use. Even so, no solution was used if it was more than five days old. All solutions were prepared on a Mettler platform balance. This balance was considered accurate to within 0.2 gram. Since about 400 grams of fluid were prepared each time, the compositions were correct to within 0.05%. The glycerol used in both cases was MALLINCKRODT Analytical Reagent Glycerin. All water used was distilled.

A 500 milliliter wide mouth flask was filled to a depth of about one and one-half inches, equivalent to between 275 and 300 grams of fluid. The temperature of the bath was set to just above the desired range, and the samples were put in the bottom of the flask. The system was then allowed to equilibrate. When the bath and the flask were at about the same temperature, as indicated by a 0 to 50°C. thermometer in the flask, where the Beckman is in Figure 9, the thermocontroller was switched off and cooling water turned on. In attempts with a glycerol-ethanol system, a Beckman $5\frac{1}{2}$°C range thermometer was used. However, with the water-glycerol solutions, a 50°C. thermometer with 0.1°C. graduations was more than sufficiently accurate. When the sample was positioned on the bottom it was examined carefully for air bubbles. If any were seen, the sample was swirled around until it was free of bubbles. With density measurements of this order, the presence of visable air bubbles would certainly have distorted the results.

The temperature at which a sample became buoyant was recorded. When correlated with the known density-composition-temperature data for the solution in use, the density of the sample was known at that temperature. By using the known value for the coefficient of linear expansion, 3.9×10^{-5} per °F. (37), of polycarbonate, the density was corrected to 25°C. The calculation of the volumetric coefficient of expansion from the linear coefficient is made in Appendix B.

Figures 13 and 14 are plots of density versus temperature for several glycerol-water mixtures (38). Note that by measuring the temperature difference in the buoyancy points of two samples being tested simultaneously, one can get a more accurate measure of their density difference. Since the plots are straight lines, $dD/dT = k =$ a constant. Therefore $D_2 - D_1 = k(T_2 - T_1)$. Since over short composition ranges k is independent of composition, the calculation of density differences will not be affected by slight composition errors. Hence in all experiments an annealed "control" was run in addition to the treated samples.

There are two basic sources of error which affect the accuracy

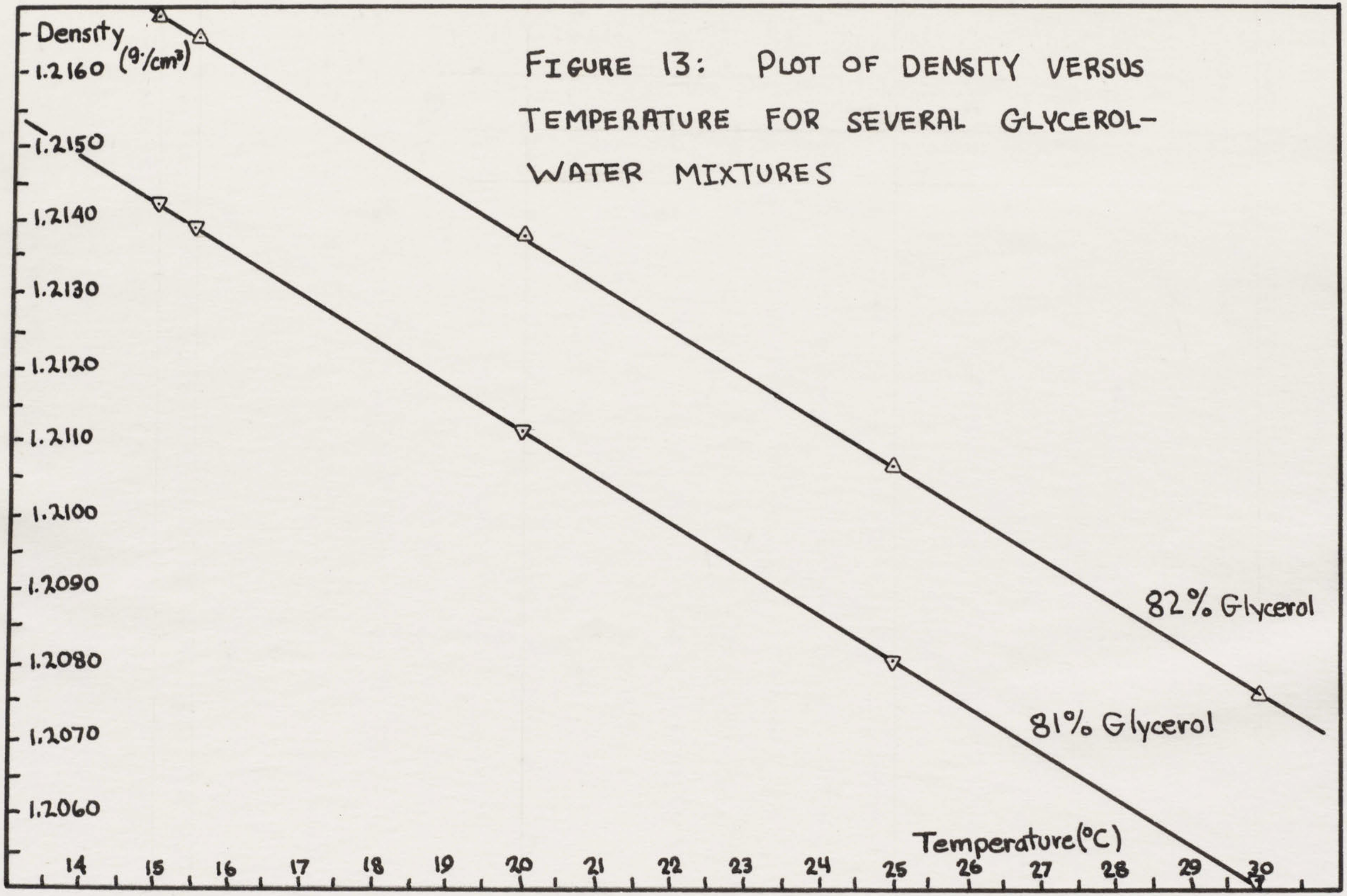


FIGURE 13: PLOT OF DENSITY VERSUS TEMPERATURE FOR SEVERAL GLYCEROL-WATER MIXTURES

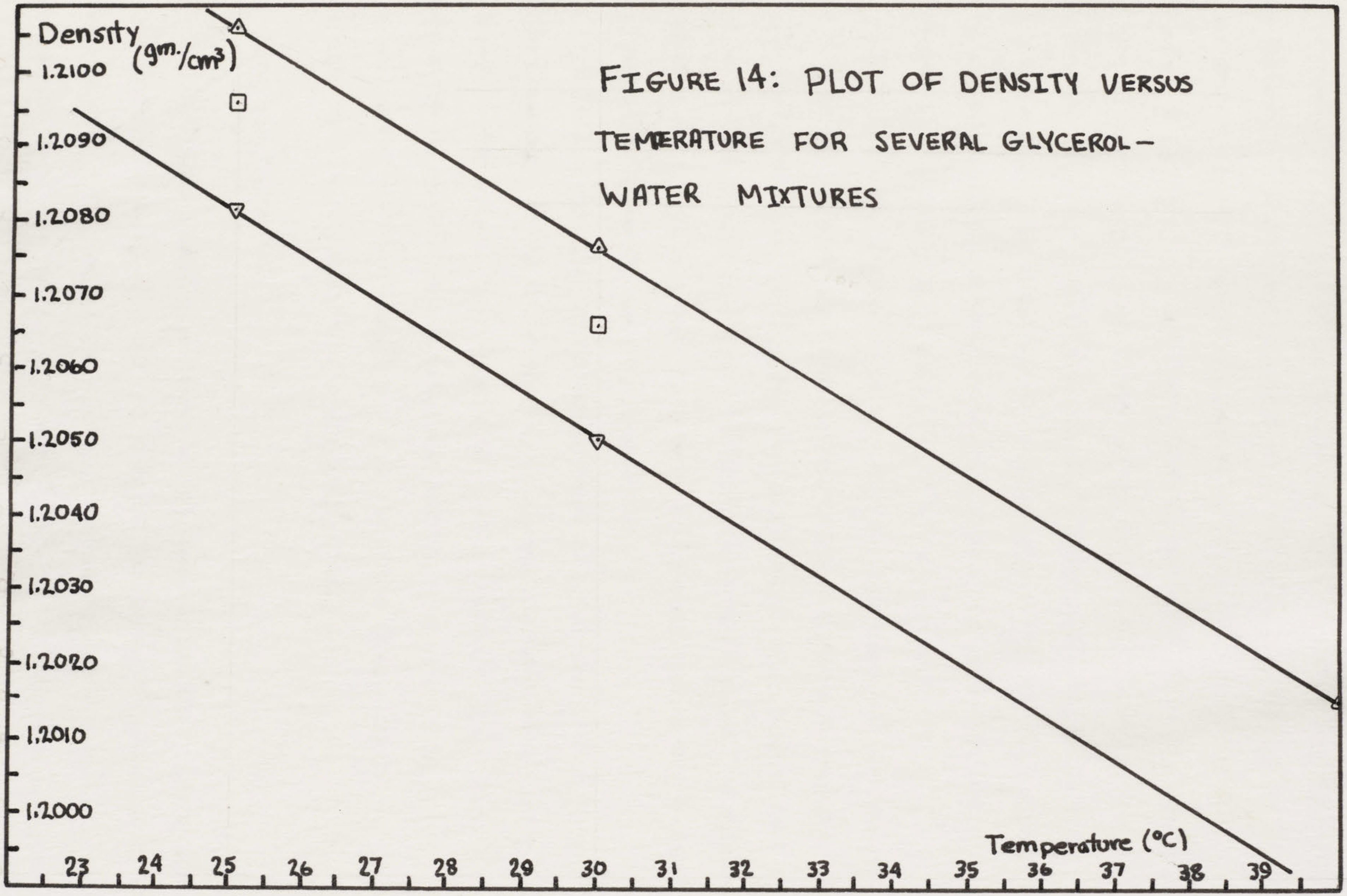


FIGURE 14: PLOT OF DENSITY VERSUS TEMPERATURE FOR SEVERAL GLYCEROL-WATER MIXTURES

of this method. One is the exactness with which an observer can determine the buoyant point of a sample. This observation is complicated by the fact that as a sample approaches neutral buoyancy it is more greatly affected by convection currents and thermal gradients. In addition, if the test fluid has a high viscosity the sample may not begin to move appreciably until it is well past the temperature at which it has this neutral buoyancy. The other basic source of error lies in the accuracy with which the density versus temperature data is known for different mixtures of the binary test fluid.

In general, the selection of a binary liquid system to determine the density of polycarbonate samples was dictated by three restraints. The first was that the density data for the binary system must be already available. The second constraint was that the polymer-solvent interactions were to be kept to a minimum. The other major consideration was to have a system whose viscosity was sufficiently low.

Two systems were found for polycarbonate, but both had a major drawback. In the glycerol-ethanol system, viscosities of suitable mixtures were quite high, about 504 centipoises (39). The interaction of water with polycarbonate was the draw back to the glycerol-water solution, whose viscosity was about 50 cp. These problems will be discussed in the Discussion section.

2.~~B~~ Immersion Tests

Densities were also measured by the immersion method. Basically, the samples were weighed in air and then totally immersed in mediums of known density. The mediums used in this work were water and ethanol. During this work care was taken to work with dry samples. When weighed dry after immersion several weights were taken over several minutes to determine if the weight was constant. When ethanol was used as the immersing medium reproducibility was excellent. When water was used there was intermal reproducibility (samples densities stayed in same order and spacing) but the absolute value varied somewhat.

In this experimentation, a Mettler balance accurate to 0.0001 gram within 0.0001 gram was used. At no time was the sample touched by hand. Immersed weights were made on a hook of copper wire. A sample calculation of density by this method is to be found in Appendix C.

The ethanol used in this work was U.S.I. Pure ethyl alcohol, U.S.P.--N.F. Reagent Quality. The water was distilled.

V. Results

A. Creep Experiments

Four experimental runs were made, one on the Kavlico differential transformer and three on the ATC differential transformer. The creep experiment monitored by the Kavlico transformer, called Run A, is shown in Figure 15. The three experiments using the ATC differential transformer are shown in Figure 16 and are labeled B, C, and D.

The sample used in Run A was untreated, having only been annealed and then milled. Run B was made with a sample quenched from 160°C. into an ethanol-dry ice bath (-72°C.). The sample used in Run C was quenched from 160°C. into a liquid nitrogen bath and the sample of Run D was cooled from 160°C. at the rate of 0.2°C. per minute. The conditions of each run are shown in Table 4.

Table 4; Conditions During Creep Experiments

Run	Temperature (°C.)	Thickness (.001 inch)	Energy (MEV)	Stress (psi)	Time Irradiation Begun	Ends (min)	Stress Off at (min.)
A	26.2	10	3	1148	.82	15	15
B	26.2	10	3	1148	1.0	13	14
C	26.6	10	3	1148	1.0	12	13
D	26.7	10	3	1148	1.0	12	13

In all four runs the beam current was approximately 10 microamperes.

The resulting plots of deflection versus time were characterized according to the following items;

1) Initial elongation upon application of stress
2) Induction period

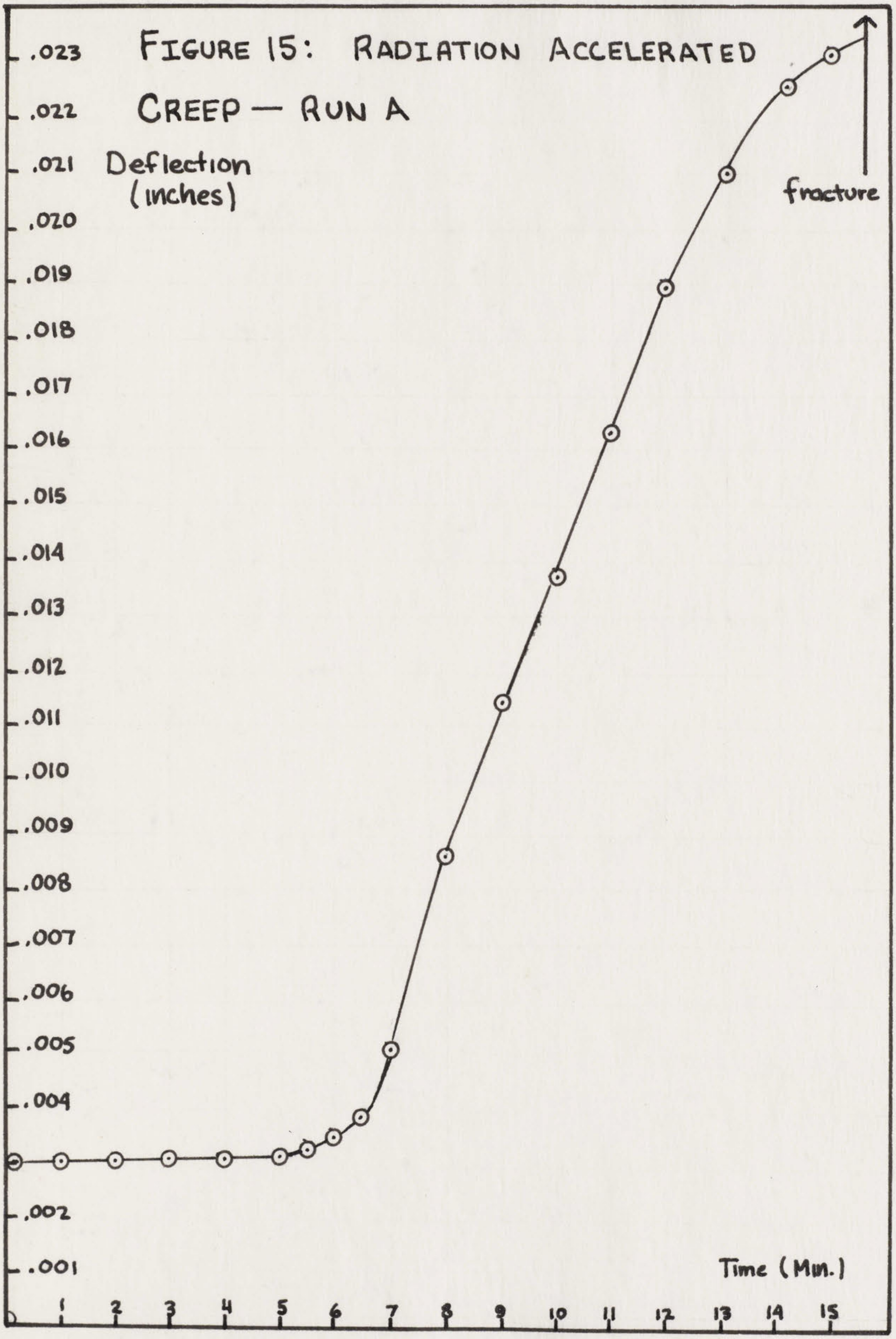


FIGURE 15: RADIATION ACCELERATED CREEP — RUN A

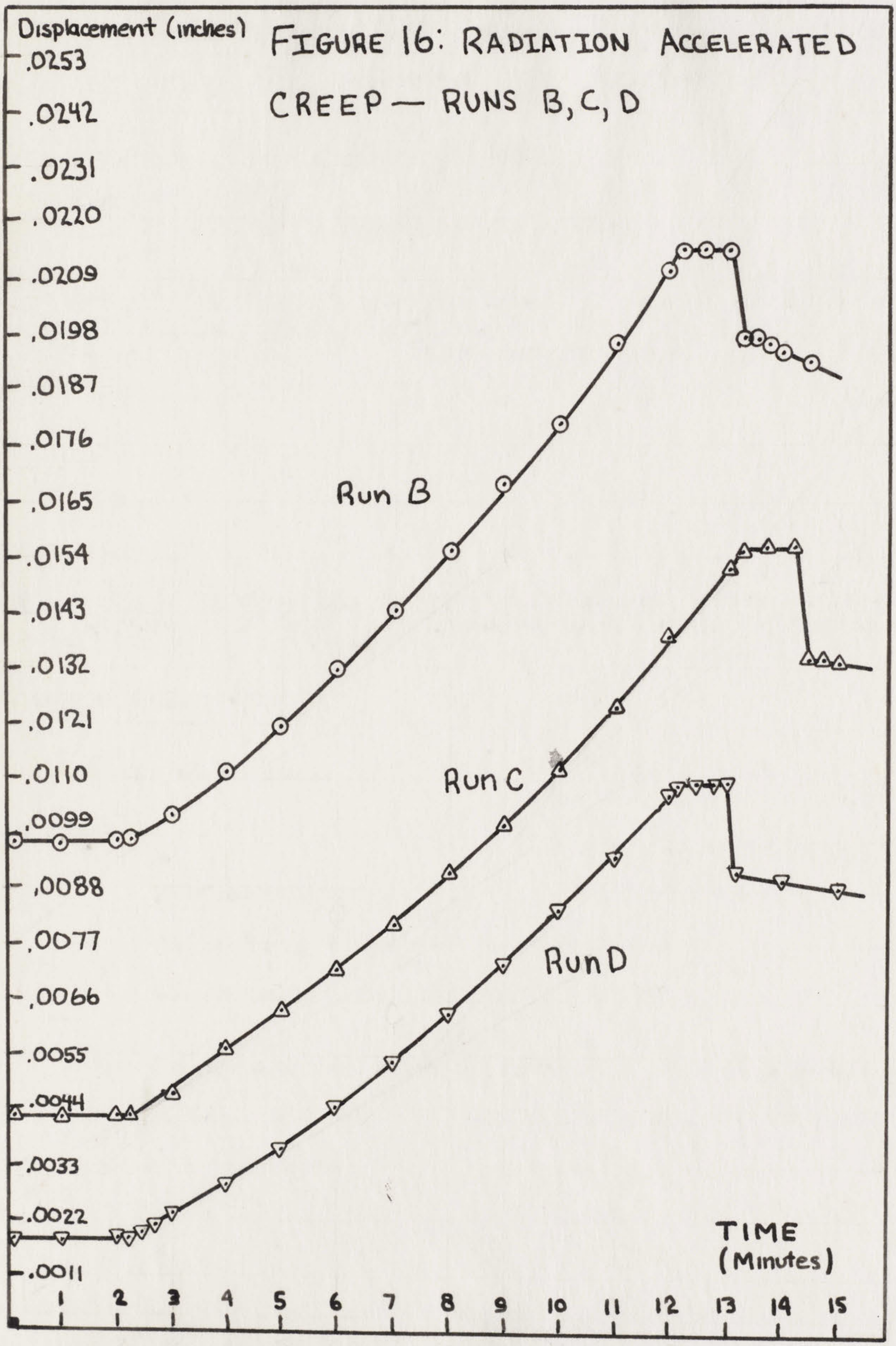


FIGURE 16: RADIATION ACCELERATED CREEP — RUNS B, C, D

3) Creep rates after 1.5, 3, 7, and 11.5 minutes of irradiation

4) Instantaneous recovery when the stress was removed

The values for these items are listed in Table 5.

Table 5: Characterization of Creep Curves

Run	Initial Elongation (.001 in.)	Induction Period (min.)	Creep Rate After -- Minutes of Irrad.				Instantaneous Recovery (.001 in.)
			1.5	3.0	7.0	11.5	
			(0.001 inch per minute)				
A	3.0	4.2	---	---	2.55	---	fractured
B	9.7	1.2	.633	,855	1.17	1.62	1.7
C	4.2	1.2	.633	.770	.962	1.43	2.2
D	1.7	1.2	.634	.686	.922	1.20	1.7

Note: In Run C the stress was applied several times due to a delay in demodulator operation. The electronic drift during these runs was negligible.

B. Density Measurements

1. Ethanol Displacement

	Density (corrected to 25.0°C)
Annealed sample	1.2026 gm./cm.^{3}
Sample quenched from 160° to -195°	1.1990
Sample quenched from 160° to -72°C	1.1978

These measurements were conducted at 70.9°F., at which temperature the density of ethanol is 0.7882 (<u>40</u>). The densities were corrected to 25°C. by use of the equation:

$$D_T = D_{T_0}\left[1-\alpha(T-T_0)\right] \qquad (1)$$

which is the defining equation for volumetric coefficient of expansion.

The value of the volumetric coefficient of expansion used was that calculated in Appendix B of 2.1 x 10^{-4} per °C. A sample calculation is given in Appendix C.

2. Water Displacement

	Density (corrected to 25.0°C.)
Annealed sample	1.2123 gm/cm.^{3}
Sample quenched from 160° to -195°	1.2100
Sample quenched from 160° to -72°C	1.2096

These densities were measured at 74°F., at which temperature the water density was 0.9976 (41), and corrected to 25°C. in the same manner as were the ethanol displacement densities. The samples were not equilibrated with water prior to the density measurements.

3. Binary Liquid Mixture

	Density (corrected to 25.0°C.)
Annealed sample	1.2089 gm./cm.^{3}
Sample quenched from 160° to -195°	1.2083

These densities were measured and corrected as described in the Experimental Procedure section on density measurement via binary liquid systems. These samples were equilibrated for three days in a solution consisting of 76% glycerol and 24% water, and then tested in a solution composed of 81% glycerol and 19% water.

C. Immersion Tests

These were conducted during the search for a suitable binary liquid mixture for use in the density determinations. They were conducted in a very simple manner. A sample was weighed, and then immersed in the trial liquid for a given amount of time. At the end of the immersion period they were removed and weighed after having been wiped dry of the test liquid. Any weight changes and the duration of the test were then noted.

In an experiment of this nature with carbon disulfide, the polycarbonate sample increased its weight 38% in a 45 minute period. In addition the sample became cloudy.

In a test with water, a faulty balance was used for the initial measurement. However after three days immersion the sample was weighted and placed in a vacuum oven. After two days in the vacuum at 50°C., the weight was found to have decreased by 0.26%. This seems reasonable, since Christopher and Fox (42) state 1) that 24 hour immersion testing indicated a weight increase of 0.2% and 2) the equilibrium value at 73°F is 0.35%.

After 17 hours immersion in carbon tetrachloride, the weight was found to have increased by 4%. In addition, the samples were quite brittle.

Neither glycerol nor ethanol had any apparent effect after several days immersion.

D. Expansion in Absence of Stress

Although not strictly applicable to this thesis, an untreated sample was irradiated in the absence of significant stress. The beam current was 10 microamperes, the beam energy was 3 MEV, and the sample was 0.010 inch in thickness. In contast to the behavior found in other polymers, no expansion was detected after 10 minutes of irradiation. A point change in deflection occurred when there was an irregularity in the operating behavior of the Van de Graaff, but no gradual deflection at all was evident. Since only one run was attempted and since the accelerator was not operating well, there is a possibility that this result is not meaningful. Another possibility which exists, is that the starting friction of the mechanism was not overcome except during the one point.

I. Discussion

A. Densities

There were considerable variations in the densities found by the three methods. However, there are several possible reasons, all based on the fact that water interacts with polycarbonate.

Since the samples used in the binary liquid work were pre-equilibrated with water, it seems quite possible that water absorption is responsible for both the relatively high density values and the small difference between the annealed and quenched samples.

By the very nature of the quenching process, the quenched sample is not in an equilibrium state. Because at room temperature it is so far below its glass transition, the return to equilibrium would be expected to be slow. However plasticizers tend to decrease the glass transition, enhancing molecular motion, so it is possible that the presence of water within the polymer accelerated its return to an equilibrium state. In addition the presence of water dissolved in the polymer would account for part of the difference in density between the ethanol immersion values and the binary liquid values. If the polymer were saturated with water (0.35%) the density could at most have been increased 0.004 gram per cubic centimeter, a value which would make the ethanol displacement and binary liquid mixtures much more comparable in value.

The values resulting from the water displacement method are much harder to rationalize. That the densities are even higher then those reported for samples equilibrated in water makes them seem highly suspect. This is especially true in light of the fact that an error in the binary liquid system will tend to report values greater than the correct value (since a sample may not rise at the instant it is buoyant). These facts, coupled with the low reproducibility of the water immersion method, indicate that one should have little confidence in this technique.

On the other hand, the ethanol immersion determination seems quite dependable. The weights of the dry and immersed samples are easily reproducible. In addition, interaction with water, if any at all, is very small.

By all three methods of measurement, the sample with highest density was the annealed one, as expected. However both methods (a sample quenched in ethanol-dry ice was not tried in the binary liquid mixture) applied to the two quenched samples indicated that the sample quenched in dry ice-ethanol (-72°C) was in a more expanded state then the sample quenched in liquid nitrogen (-195°C).

This indicates that the sample quenched in liquid nitrogen did not cool as rapidly as the one quenched in the ethanol-dry ice bath. The only reasonable explanation for this behavior is to assume that as soon as the hot sample contacted the liquid nitrogen it was covered by a layer of gaseous nitrogen in the form of very small bubbles and that this layer served as an effective insulator. Effective enough, in fact, to permit the sample quenched in ethanol-dry ice to cool more rapidly.

B. Effect of Quenching on the Radiation Acceleration of Creep

It seems undenyable that quenching did affect the radiation acceleration of creep. In all density determinations the sample quenched in ethanol-dry ice had the lowest density and hence the highest free volume. Considera highest free volume. Considering the three samples treated on the same day, run on the same day, with the same electronic equipment, the sample with the highest free volume had 1) the highest initial elongation and 2) the highest creep rate at any given time, except initially, when all were equal. The sample quenched in liquid nitrogen, with the next highest specific volume was the next highest in all the same categories. Run D, the annealed sample was the lowest in all of these categories.

However, in all three cases the induction period was of the exact same length, 1.2 minutes. This is a sharp contrast to the prediction that the sample with highest free volume should have the highest induction period.

So far in this discussion, Run A has been ignored. The sample used in Run A was cut from the same part of the annealed polycarbonate sheet as were the samples of runs B,C, and D. Runs B, C, and D were conducted about two weeks after RunA. The only difference in the sample history between samples A and D is the second annealing experienced by the D sample.

There were major differences in the equipment used to monitor the two sets of runs. Run A was conducted with a different demodulator and differential transformer. Both components were later found to contain intermittent shorts, and had been replaced by the time of runs B,C, and D. Nonetheless, it is difficult to envision any mechanism through which the nature of the electronic equipment could affect the time delay involved in the induction period.

In an attempt to correlate the creep rates shown in Runs B, C, and D, a plot of -ln(creep rate) versus specific volume of the polymer was made. If the polymer follows a relation like equation (2)

$$\eta = A e^{-B\vartheta_p} \qquad (2)$$

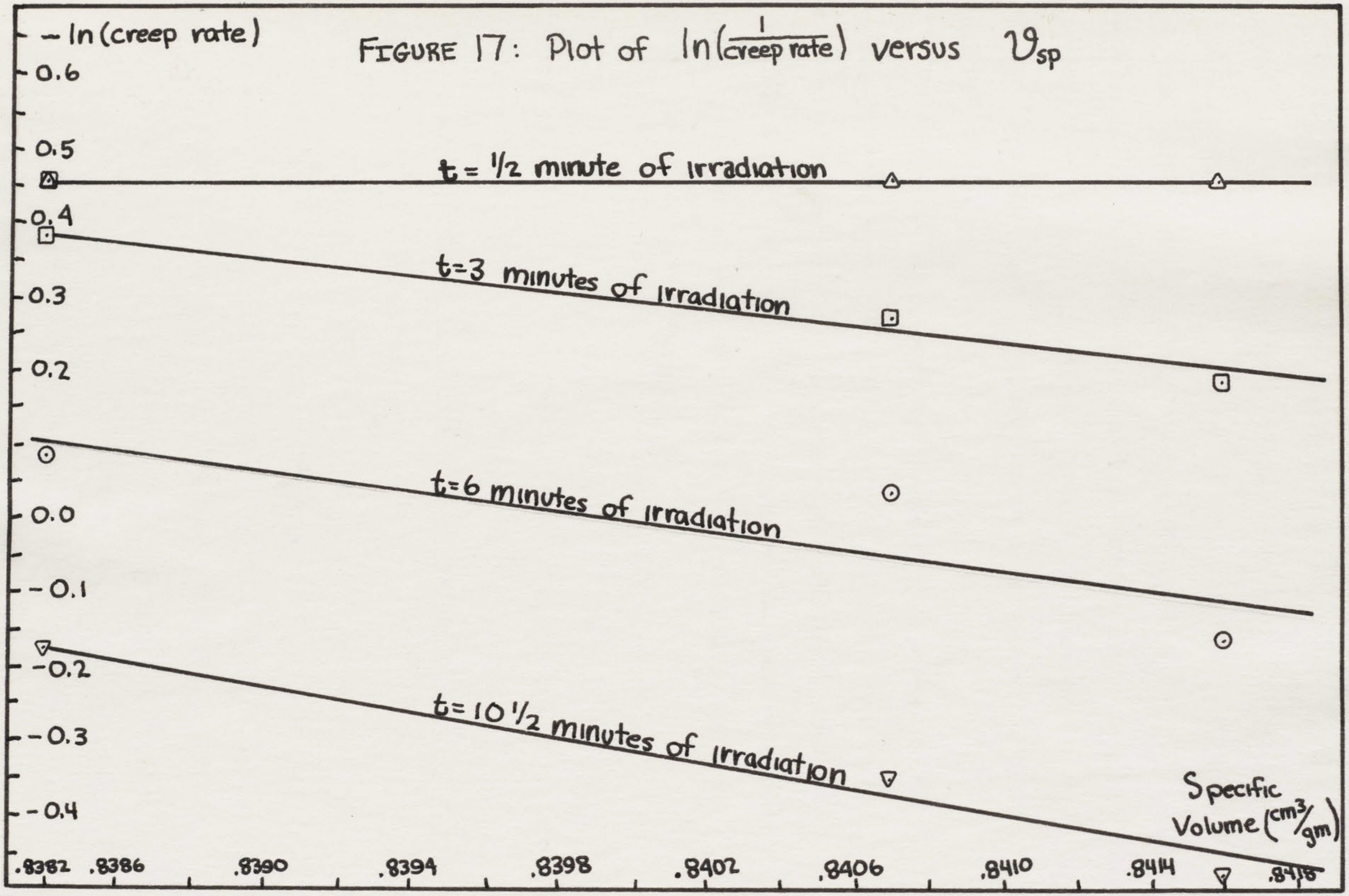
then the plot for any given time should be a straight line whose slope is related to B. ϑ_p is a measure of the free volume present in a polymer compared to its free volume at glass transition temperature. The specific volume of the polymer (which is 1/density) should be proportional to ϑ_p. In addition, the creep rate should be proportional to $1/\eta$. By assuming that the density of the samples irradiated is the same as that of the samples whose density was measured in the ethanol immersion test, this plot was prepared and is shown in Figure 17.

Although it is difficult to decide with only three different density materials, there does seem to be an almost linear relationship among the points. However there appears to be a definite 'downward' trend at increasing specific volumes.

There is some question as to whether the variations in the radiation creep curves are due to the effect of varying amounts of free volume (what sort is varied, dissolved or microvoid?), or if they might be due to other non-equilibrium quenching effects, such as the degree of crystallinity. Indeed, it seems that the curves do show effects which would be expected if this were the case. In all cases the more effectively quenched material possesed the higher initial elongation and higher creep rates. It is known that polycarbonate can have a very small degree of crystallinity, although it is usually amorphous.

Therefore there are two major things which are yet to be determined. First, what is the reason for the variation between Runs

FIGURE 17: Plot of $\ln\left(\frac{1}{\text{creep rate}}\right)$ versus ϑ_{sp}



B, C, and D and Run A as well as Mayer's two experiments. Is this to sample history or equipment differences? Secondly, what is the effect of quenching on the behavior of polycarbonate in general. All effects found on the radiation accelerated creep curves might be due to changes in the basic properties of the polycarbonate and not related to the mechanism of radiation accelerated creep at all, except in the sense that radiation effect magnified the creep differences to the extent that they were visable.

To attempt to theorize about the acceleration mechanism on the basis of these experiments (which seem to contradict Mayer's) is futile due to the variance and the unknown side effects of quenching. It can only be said that the lack of a change in the induction periods (although they were all different than Run A) throws doubt upon the mechanism discussed in the Introduction.

VII. Recommendations

Obviously more radiation runs should be made in an attempt to decide what the large variation between sets of runs was due to. Do all 0.010 inch samples annealed a second time in a hot air oven display a 1.2 minute induction period, independent of the rest of their history? It would also be desirable to run samples with different densities to see how valid the correlation of equation (2), pictured in Figure 17 is.

With respect to this work, the side effects of quenching merit further study. Non-irradiated creep tests of long duration and sufficiently high stress levels would reveal whether quenched polycarbonate samples have significantly higher creep rates in general then annealed samples. The free volume theory of glass transitions would definitely predict this. Stress-strain curves from the Instron tester might also reveal other basic effects of quenching. Ultimate property testing with the Instron tester might also reveal which type of free volume was most affected by the quenching. In, addition, x-ray studies might indicate if the crystallinity has been increased by the annealing process.

One way to avoid the problems associated with quenching would be to presaturate the sample with gas, either by storage under high pressure gas atmospheres or pre-irradiation under no stress. Another method, one which would avoid the skin effects of quenching, would be to cool the sample under very high pressure.from above its glass transition to below it. The stress would have been transmitted throughout the sample, instead of being concentrated at the surface.

Appendix A: Tables

Table 1 Properties of Bisphenol-A Polycarbonate (43)

Density	1.20 gm./cm.^{3}
Glass Temperature	145°C.
Softening Range	190°C--230°C.
Melt viscosity (315°C.)	4,000 poises
Crystallinity	amorphous to x-rays
ASTM Tensile Strength (73°F.)	8,000--9000 psi
Specific heat	0.30
Brittle Temperature	less then -215°C.

Table 2 Solubility Data on Bisphenol-A Polycarbonate ~~(43)~~(44)

Good Solvents:	sym-tetrachloroethane
	methylene chloride
	cis-1,2-dichloroethylene
	chloroform
	1,1,2-trichlorothane
Weak Precipitants:	acetone
	ethyl acetate
	toluene
	carbon tetrachloride
	nitromethane
Strong Precipitants:	aliphatic hydrocarbons
	alcohols
	monochlorides
	carbon disulfide

Table 3 Effect of Irradiation on Bisphenol-A Polycarbonate (<u>45</u>)

	original	final	dose
Tensile Strength	12,000psi	14,000psi	30mrad.
Elongation	150%	180%	20mrad.
Softening (initial)	225°C.	213°C	20mrad.

Appendix B: Calculation of Volumetric Coefficient of Expansion from the Linear Coefficient of Expansion

Suppose one starts with a unit volume, and each rectilinear dimension expands by the amount ΔX, if x is the initial length.

then the fractional change in volume is

$$\frac{(x+\Delta x)^3 - x^3}{x^3} = \frac{x^3 + 3x^2\Delta x + 3x\,\Delta x^2 + \Delta x^3 - x^3}{x^3}$$

since initially a unit volume was selected

$$= 3\Delta X + 3(\Delta x)^2 + (\Delta x)^3$$

If the change in length is per degree temperature then ΔX is the linear coefficient of expansion and

$$3\Delta x + 3(\Delta x)^2 + (\Delta x)^3 = \alpha = \text{volumetric coefficient of expansion}$$

for polycarbonate linear coefficient of expansion

$$\Delta x = 3.9\times10^{-5}/°F \quad (46)$$

since $\Delta x \ll 1$

$$\alpha = 3\Delta X = 3(3.9\times10^{-5})/°F$$

$$= 3(3.9\times10^{-5})(1.8)\ /°C$$

$$\alpha = 2.1\times10^{-4}\ /°C$$

or

$$\alpha = 2.1\times10^{-4}\ \frac{cm^3/cm^3}{°C}$$

Appendix C: Sample Calculation of Density

weight of annealed dry sample	0.4617gm.
weight of annealed sample immersed in alcohol	0.1437gm.
temperature of ethanol	70.9°F = 21.6°C.
density of ethanol at that temperature	0.7882 (40)

$$D = \text{mass}/\text{volume}$$

$$= \frac{\text{weight}}{\left(\frac{\text{weight} - \text{weight immersed}}{\text{density of alcohol}}\right)}$$

$$= \frac{(0.4617)(0.7882)}{(0.4617-0.1437)}$$

$$D = 1.2031 \text{ gm.}/\text{cm}^3 \quad \text{at } 21.6°\text{C}$$

Correcting to 25°C. with equation 1

$$D_T = D_{T_0}\left[1-\alpha(T-T_0)\right]$$

$$= (1.2031)\left[1-(2.1\times10^{-4})(25-21.6)\right]$$

$$D = 1.2026 \quad \text{at } 25°\text{C}.$$

α was obtained from appendix B

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