1965

# The effect of molecular weight on the compressibility of bisphenol a polycarbonate

Allan L. Holmstrom
*Lehigh University*

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June 4, 1965

Dear Dr. Moyle,

Indeed our letters did cross in the mail. I presume you understood my anxiety as the semester drew to a close. I did, however, finish on time and as of about ten minutes ago was cleared finacially for Graduation.

I do want to personally thank you for all you have done for me, you've been most kind and I appreciate it.

Enclosed is the copy of the report you requested. In a seminar I gave for the Materials Research Group, the only question that came up of consequence was whether the strain on the sample was isotropic. It would be isotropic I believe if the Poisson ratio where 0.5, however, I believe it has a value more like 0.25. It may be more appropriate to therefore call the bulk modulus the "apparent" bulk modulus to keep the terminology clean. - The solution to the above I guess is to suspend a spherical sample in an incompressible fluid and make compressibility measurements; but, we'd never do it on our budget. - If you have any comment I'd be interested in hearing it.

I'm leaving for North Carolina Sunday morning and hope to be able to rent a house in short order so we can have our things moved down. I can see a big month of indicision coming up.

Please say Hello to your family from us.

Sincerly,

Al Holmstrom

# THE EFFECT OF MOLECULAR WEIGHT ON THE COMPRESSIBILITY OF BISPHENOL A POLYCARBONATE

by Allan L. Holmstrom

A Research Report
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Master of Science

Lehigh University
Bethlehem, Pennsylvania
1965

# CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

May 20 1965
(date)

Morton P. Moyle
(Professor in Charge)

(Head of the Department)

# Acknowledgements

I wish to express my appreciation to Dr. Morton P. Moyle, my advisor, who offered invaluable advice and encouragement to me; to Joseph Hojsak for his part in constructing the apparatus; and to fellow students who were so willing to give assistance when needed.

Thanks are also in order to General Electric Company's Polycarbonate Research and development Department, the Polymer Corporation of Pennsylvania, Westlake Plastic Company, Cadillac Plastic Company, and Dow Chemical Company for donating samples of the material used in this project,as well as data on physical properties.

Finally, to my wife, Marilyn, who shared in the successes and failures of the work, my thanks for typing this report.

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## Abstract

The compressibilities of Lexan ~~130-112~~ 101-112 and Lexan ~~101-112~~ 130-112, having average molecular weights of ~~40~~ 35,000 and ~~35~~ 40,000, respectively, have been investigated over the pressure range from ~~14.7~~ atmospheric to 30,000 psia. and over the temperature range from 50°F to 350°F.

The ~~C~~ompressibility of Lexan above the glass transition temperature 295°F, ~~(295°F)~~ was found to be independent of molecular weight; ~~but~~ however, below 200°F ~~the higher~~ the polymer with average molecular weight 40,000 ~~material~~ exhibited a compressibility 25 percent higher than the polymer with [illegible] molecular weight [illegible] ~~lower molecular weight material~~.

A modified van der Waal's equation of the form

$$(P+40,000)(V-0.6487)=20.8T$$

was ~~shown~~ found to represent the experimental P-V-T ~~values~~ data obtained from the compressibility measurements within ± [illegible] %.

Differentiation and Rearrangement of the Tait equation ~~into terms of bulk~~ yields a relationship between bulk modulus K and pressure; a plot of [illegible] shows a discontinuity at about 15,000 psi. when ~~plotted~~, indicating ~~the~~ a pressure-induced transition ~~of Lexan~~ from a rubbery material to a glassy material in the 300°F to 350°F range.

# MISSING

# PAGES

## Background

There is very little data in the literature on the compressibility and P-V-T relationships for polymers. The majority of data reported has consisted primarily of temperature-volume relationships; very little attention has been given to the equally important pressure-volume relationships.

The fabrication of polymers utilizing extruders and injection molding equipment, requires that the polymer be formed under conditions which are often 10-20,000 psi. and 100-300°C above their normal conditions of use. An urgent practical need for P-V-T work on polymers is thus created in relating proper mold size at fabricating conditions to the proper size of the finished product at its normal conditions.

The need for this type of work does not end on a practical basis, however, for it is hoped, that when enough P-V-T data has been accumulated, a general equation of state for polymeric materials will be formulated.

It is the object of this work to explore the P-V-T relationships for the bis-phenol A polycarbonate with particular attention to the effect of molecular weight on P-V-T behavior and to illustrate some of the information that can be obtained directly from a P-V-T investigation.

Compressibility data on high polymers have been reported by a number of investigators (   ).

## Introduction

An exhaustive search of the literature failed to reveal any data concerning the effect of molecular weight on the compressibility of linear high polymers has not been adequately established to date. Spencer and Gilmore have reported equilibrium P-V-T data for Polystyrenes (9,11) having molecular weights of 321,000 and 360,000; Calculations ~~show that the compressibility of~~ indicate that the higher molecular weight ~~sample is greater than~~ polystyrene is more compressible than that of the low molecular weight ~~sample~~ material for external pressures ~~greater than~~ above 14,000 psi. Below 14,000 psi. external pressure there ~~appears to be~~ the data shows no statistically significant effect of molecular weight.

No other published data offers information from which a further relationship may be derived for compressibility as a function of molecular weight. ~~Spencer and Gilmore do~~ also ~~offer equilibrium P-V-T data at one temperature and one molecular weight~~ and for polymethyl methacrylate, ethyl cellulose, cellulose acetate butyrate, and polyethylene ~~at~~ at a single ~~temperature~~ molecular weight level.

~~The main purposeof Spencer and Gilmore's work was to develop an equation of state for the polymers they worked with. The type of equation~~ They have proposed ~~was~~ a modified van der Waal's equation of state for polymers of the form

$$(P + \pi)(V - \omega) = \frac{RT}{M}$$

here P is the pressure, V the volume and $\pi$ the "internal" ressure, $\omega$ the volume at 0°K, R the gas constant, T the bsolute temperature and M the molecular weight of the nteraction unit which in many cases is the monomeric repeat nit.

Dynamic compressibility data on several polymers in he frequency range of 0.1 cps. to 60 kc/sec. has been reported ~~published~~ by Heydemann.(4) Polyesters having different side groups which alter~~s~~ the molecular weight appear to show a decrease in compressibility with increasing molecular weight. Of course, this is different than increasing molecular weight by increasing the degree of polymerization. Simha has pointed out that isothermal or isobaric volume changes are brought about by two mechanisms, one instantaneous and the other time dependent.(8) Dynamic data does not take into account the time dependency that can be substantial in viscoelastic materials.

Weir has proposed an equation of the virial type (13) having 12 constants to describe the P-V-T relationships of a number of materials. ~~Teflon over a range of 100°C.~~ Although ~~this is an excellent equation for accuracy, its usefulness is very limited since derivatives of the equation cannot be used in the prediction of other thermodynamic~~ coefficients, its size prohibits quick ~~calculation on anything less than a computer, and its temperature range is quite restricted~~.

An equation of state has been proposed for rubber through thermodynamic reasoning and the statistical model of the rubber molecule. The form of the equation is:

$$\tau = \frac{g\,\nu\,R\,T}{V}\left(1 - \frac{2M_c}{\text{Mol. Wt.}}\right)\left[\frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2\right]$$

where $\tau$ tension, g is a correction factor, $\nu$ is number of moles of segments present and corresponds to the n in the ideal gas equation, $M_c$ is the average molecular weight of a segment, $l$ extention length and $l_0$ is the original unstretched equilibrium length.(3) As indicated, this equation is remarkable similar to the ideal gas equation and has been found to be well suited to rubber.

Recently, Wood of the National Bureau of Standards has shown that the Tait equation, proposed to relate the variables of pressure and volume for sea water, is useful for high polymers (14). The Tait equation

$$\frac{V_0 - V}{V_0} = c \log_{10}(1 + P/b)$$

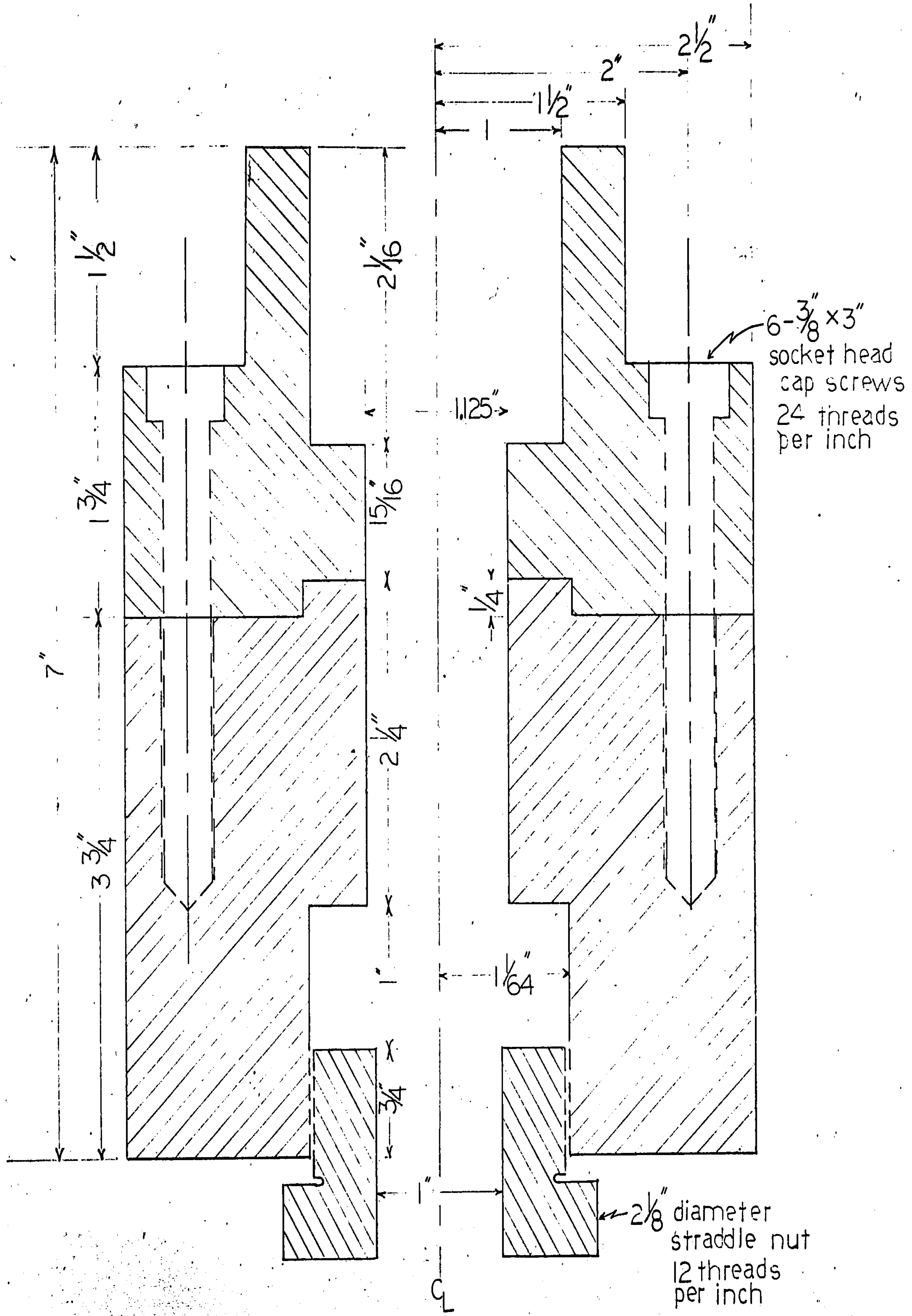
where V is the volume, P is the pressure, $V_0$ the volume at zero pressure, b and c being constants, is not very useful in this general form, however, rearranging it into the bulk modulus, K, and plotting it against pressure, P, it has been found to predict the second order transition pressure when the polymer is above the glass transition temperature. Second order transition is defined as the point where a polymer changes from a glassy state to a rubbery state, or vice versa. The glass transition temperature is the second order transition temperature under a pressure of one atmosphere.

## Equipment

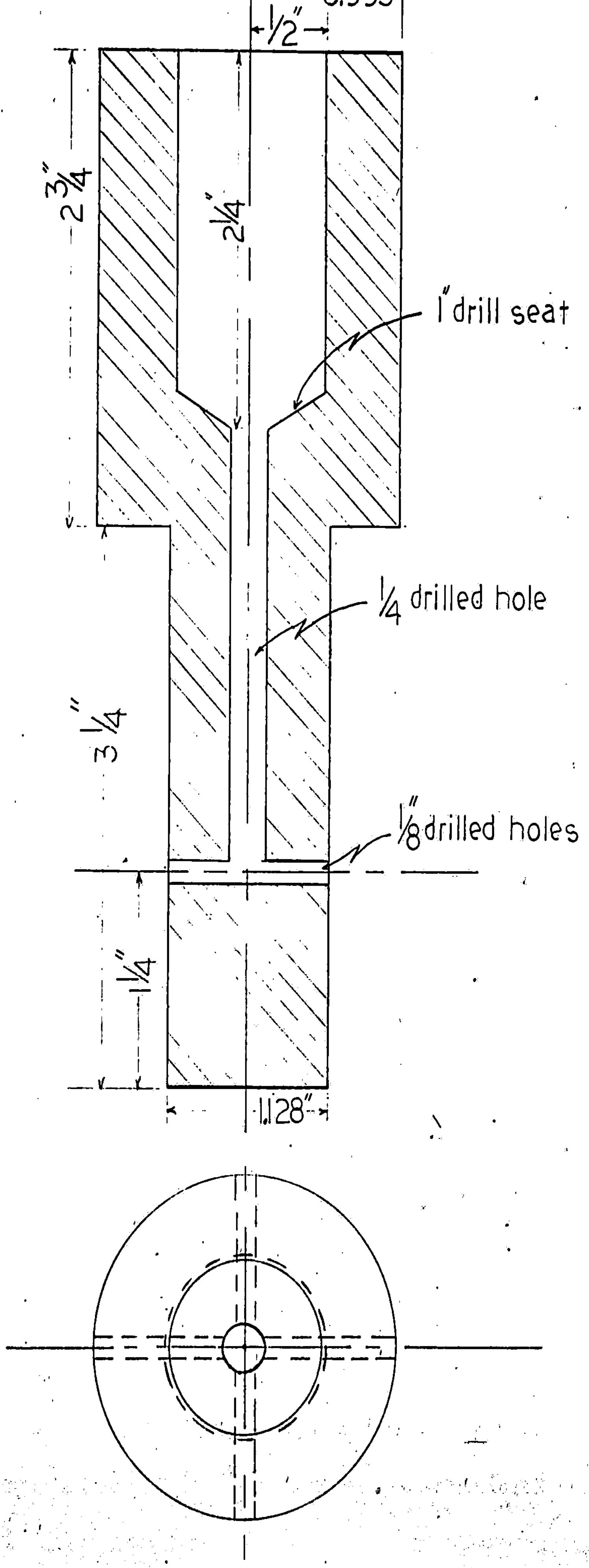
To obtain P-V-T and compressibility ~~data requires constant temperature, constant pressure,~~ volume measure~~ments.~~ For ~~this purpose~~ A ~~a~~ compression chamber was constructed from 4140 steel consisting of three basic parts: cylinder, plunger, and bottom plate (figure 1).

~~The cylinder was turned down in two pieces to the dimensions~~ shown in Figure 1. The reason ~~for two pieces~~ was to allow the equipment to be modified to handle a liquid polymer seal if the need arose. After ~~the cylinder was~~ heat treated ~~to harden it~~, the inner surface [illegible] was honed out to a diameter of 1.135 inches.

~~In~~ Figure 2 shows ~~the specifications for~~ the plunger. ~~are given.~~ The top of the plunger ~~is~~ [illegible] bored ~~to a one-inch diameter~~ so that to allow ~~for~~ a ~~piston to force~~ molten polymer [illegible] down ~~the~~ a central d~~rilled~~ channel ~~and~~ to the outer surface of the plunger to form ~~to form the~~ a liquid polymer seal. ~~referred to.~~ The lower part of the plunger, having the smallest diameter, was then plated with hard chrome and polished to a~~bout~~ 1.135 inches in diameter. Cylinder and plunger were then worked together with a small quantity of valve grinding compound until a close fit was obtained, but not so tight as to restrict vertical movement of the plunger in the cylinder. ~~The plunger was not hardened so that it can easily be worked to modify it for a polymer seal piston.~~



CYLINDER
Figure 1



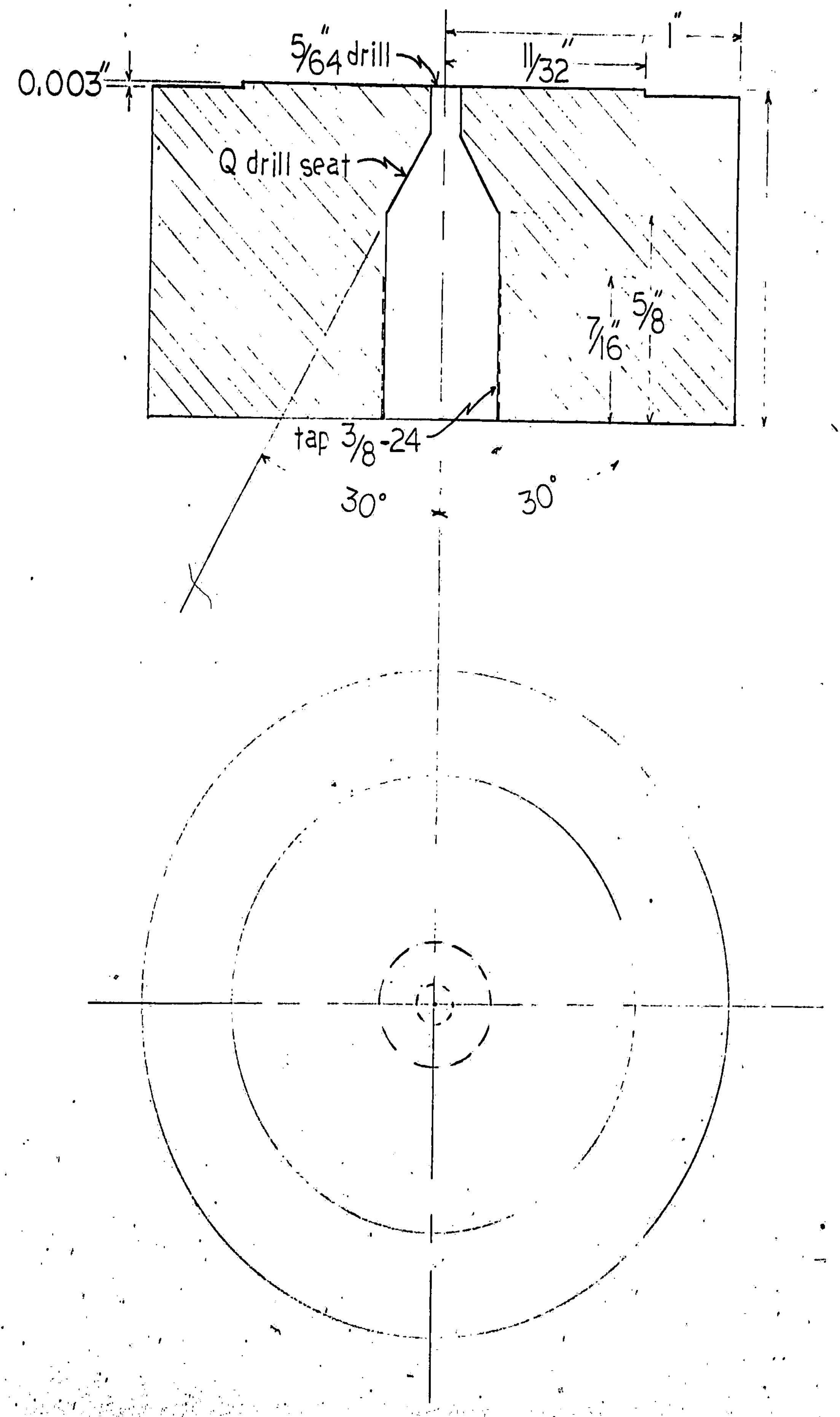
PLUNGER
Figure 2

a plate

At the bottom of the cylinder ~~is a plate, shown in Figure 3, which~~ retain~~s~~ed the thermocouple mounting arrangement shown in Figure 4. A 0.003 inch layer was removed from the edges of the face of thebottom plate to reduce the surface area acting on the lead washer seal between this plate and the bottom face of the cylinder.

an ~~The thermocouple~~, Aero Research Instrument Company, iron constantan thermocouple, model T-91-M-4AJ8A16, was used to measure [illegible] ~~has a 0040 inch diameter 304 stainless steel sheath with iron-constantan thermocouple wire and MgO insulation.~~ The hot junction was ~~is~~ integrally welded to the end of the sheath. The soapstone and steel ~~follower are standard high pressure fittings made by the American Instrument Company. Epoxy resin was used at the tip since it is an adequate filler as well as an insulator~~.

In Figure 5 the details of the dynamometer used to measure the pressure are shown. A Tinus-Olson Testing Machine was used to calibrate the dynamometer so that the strain as read by an SR-4 strain indicator, could be directly related to the pressure exerted on the polymer sample. Since the dynamometer was ~~would be~~ subjected to a temperature gradient ~~it was desirable to examine~~ the effect of the temperature gradient on the dynamometer was investigated. ~~As a result~~, an independent system was constructed by placing two strain gages on the supporting beam of the press. This part of the press was always at room temperature. The dynamometer was then calibrated against this second system at room temperature,



BOTTOM PLATE
Figure 3

# SCHEMATIC DIAGRAM OF BOTTOM PLATE THERMOCOUPLE MOUNTING

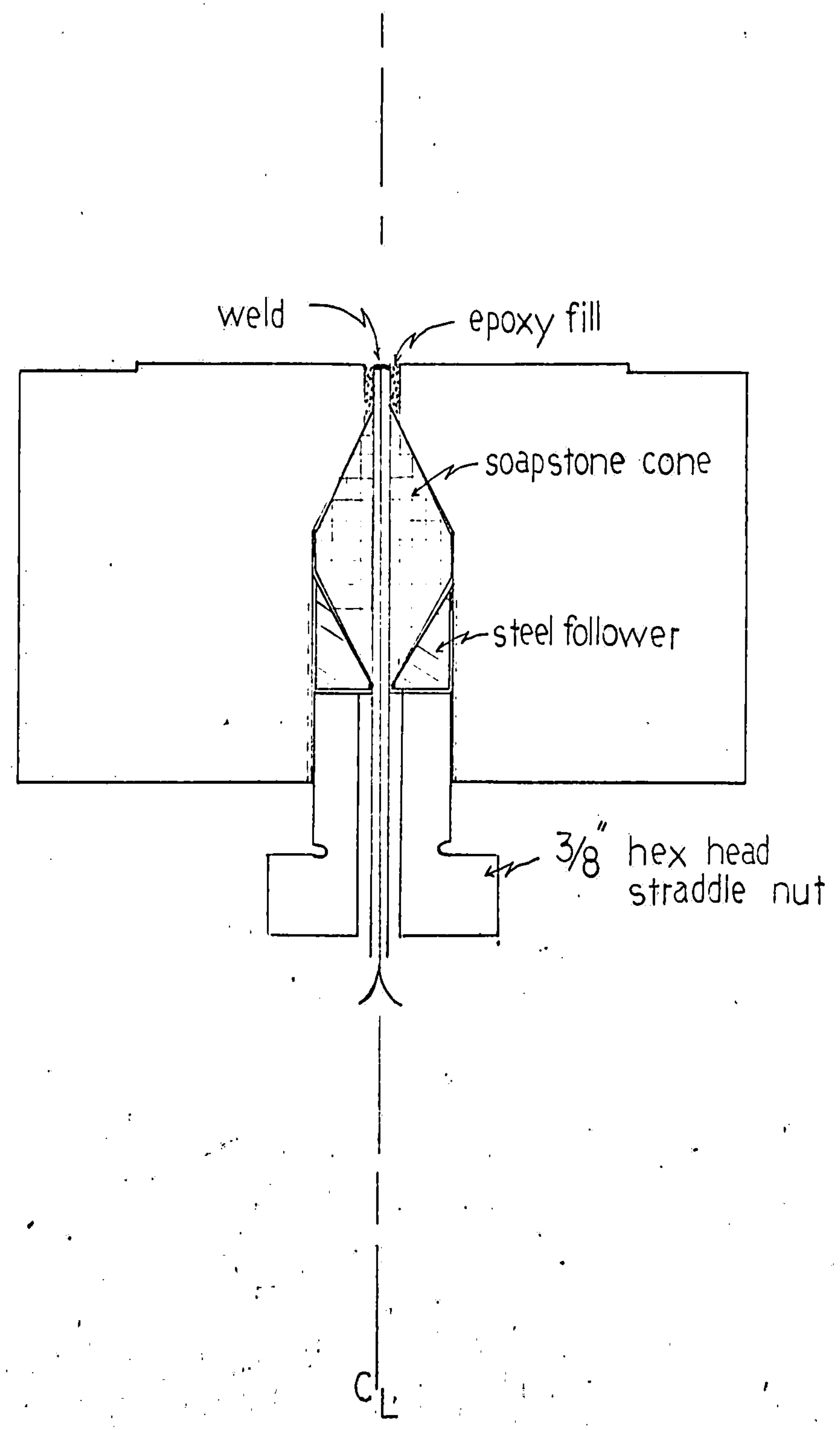
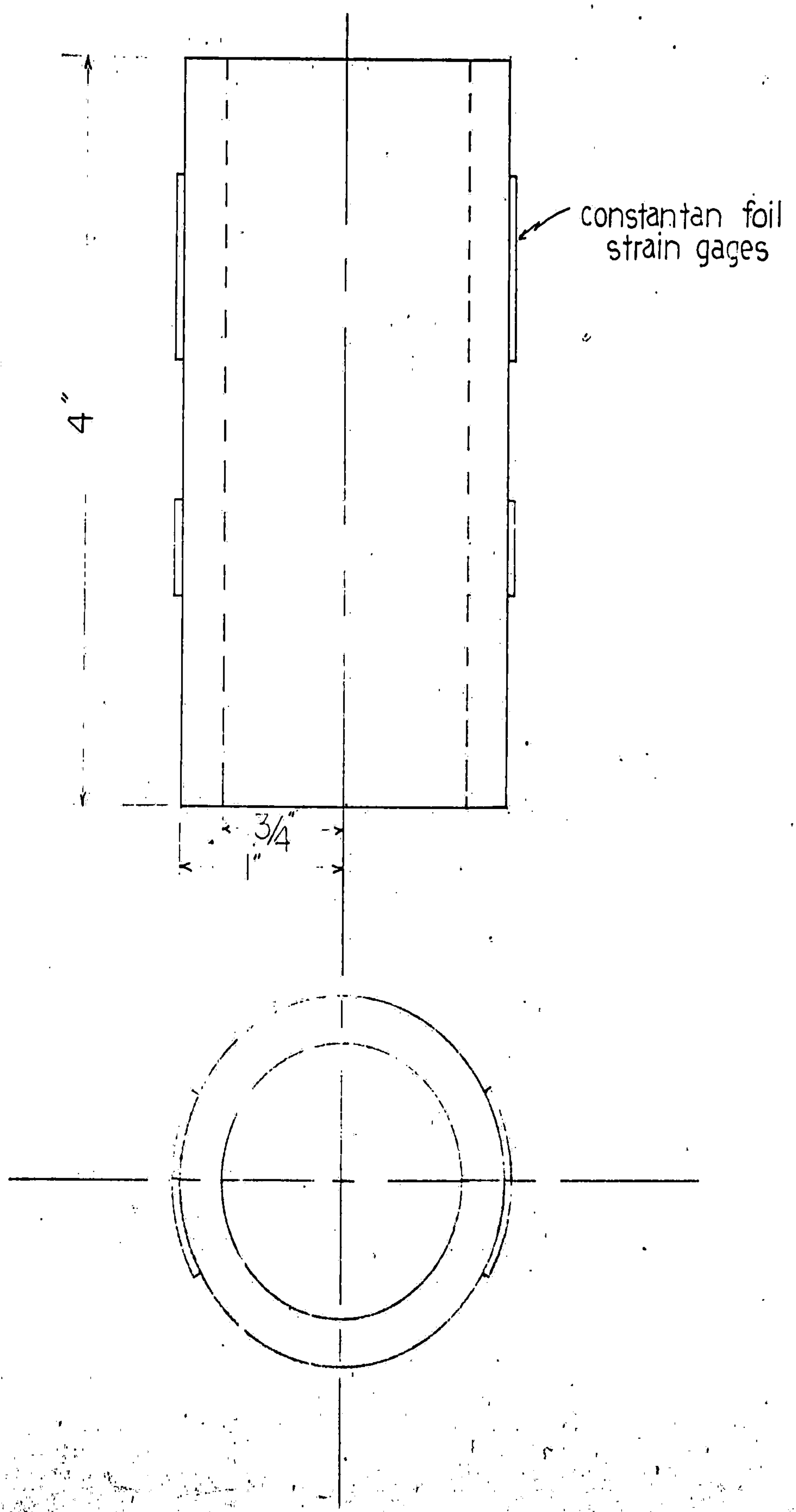


Figure 4



DYNAMOMETER

Figure 5

and with a 250°F gradient. In Figure 6 the results are plotted; it can be seen that the zero point is translated, however, the slope is constant which indicates that the true pressure was recorded.

Figure 7 shows the strain versus pressure calibration curve. The actual calibration curve used was plotted on a 2 feet by 4 feet graph.

Heat was applied to the cylinder by two five inch Chromalox band heaters, each capable of delivering 825 watts. In addition, Briskeat flexible heating tape has been placed around the upper part of the plunger and around the two inch straddle nut to decrease the temperature differential between, for example, the plunger in contact with the sample, and the plunger in contact with the surroundings. This reduce~~s~~d the temperature gradient in the plunger and bottom plate and prevent~~s~~ed excessive "heat leak" in the axial direction.

One inch thick asbestos pipe insulation encased the bulk of the cylinder. A sheet of aluminum foil was placed on the outside of the insulation and served to reduce radiation losses at higher temperatures and restrict convection currents around the cylinder.

A Wheelco on-off controller was used to control the temperature. When the controller ~~is~~ was off, a two position relay switch ~~is~~ was unactivated and allow~~s~~ed a Variac to feed power to the heaters in the amount of about 85 percent

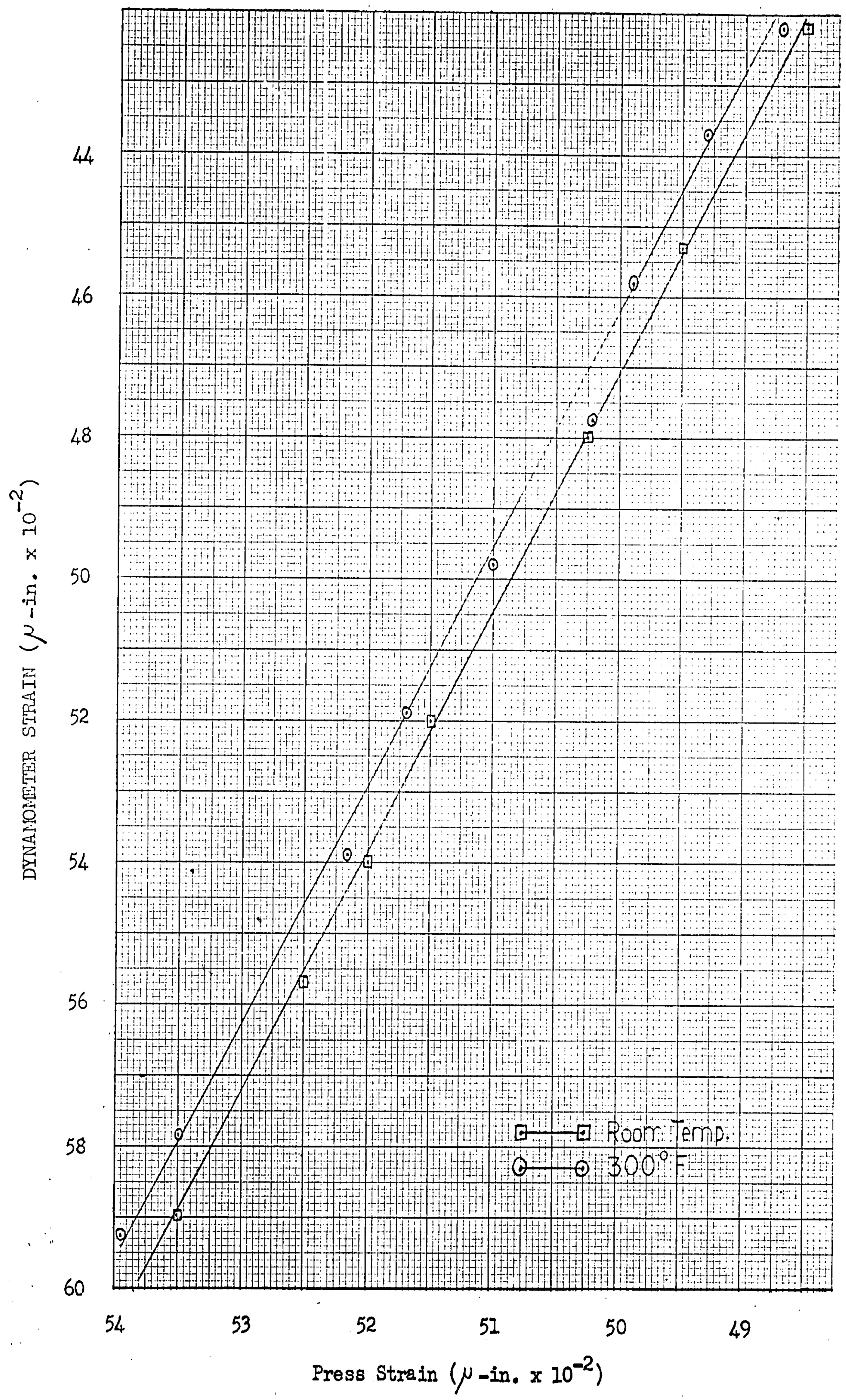

DYNAMOMETER STRAIN ($\mu$-in. x $10^{-2}$)
44
46
48
50
52
54
56
58
60
54
53
52
51
50
49
Press Strain ($\mu$-in. x $10^{-2}$)
Room Temp.
300° F

Figure 6

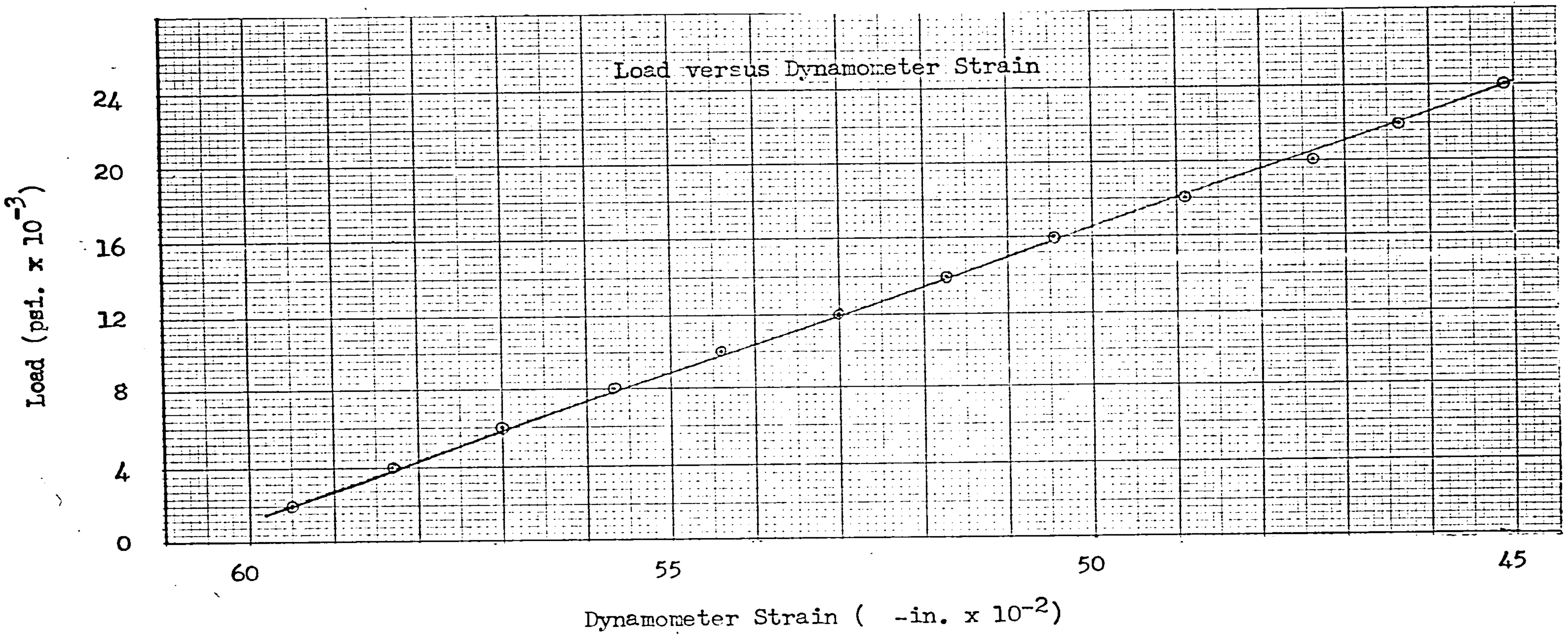

Load versus Dynamometer Strain
Load (psi. x 10^-3)
0
4
8
12
16
20
24
60
55
50
45
Dynamometer Strain ( -in. x 10^-2)

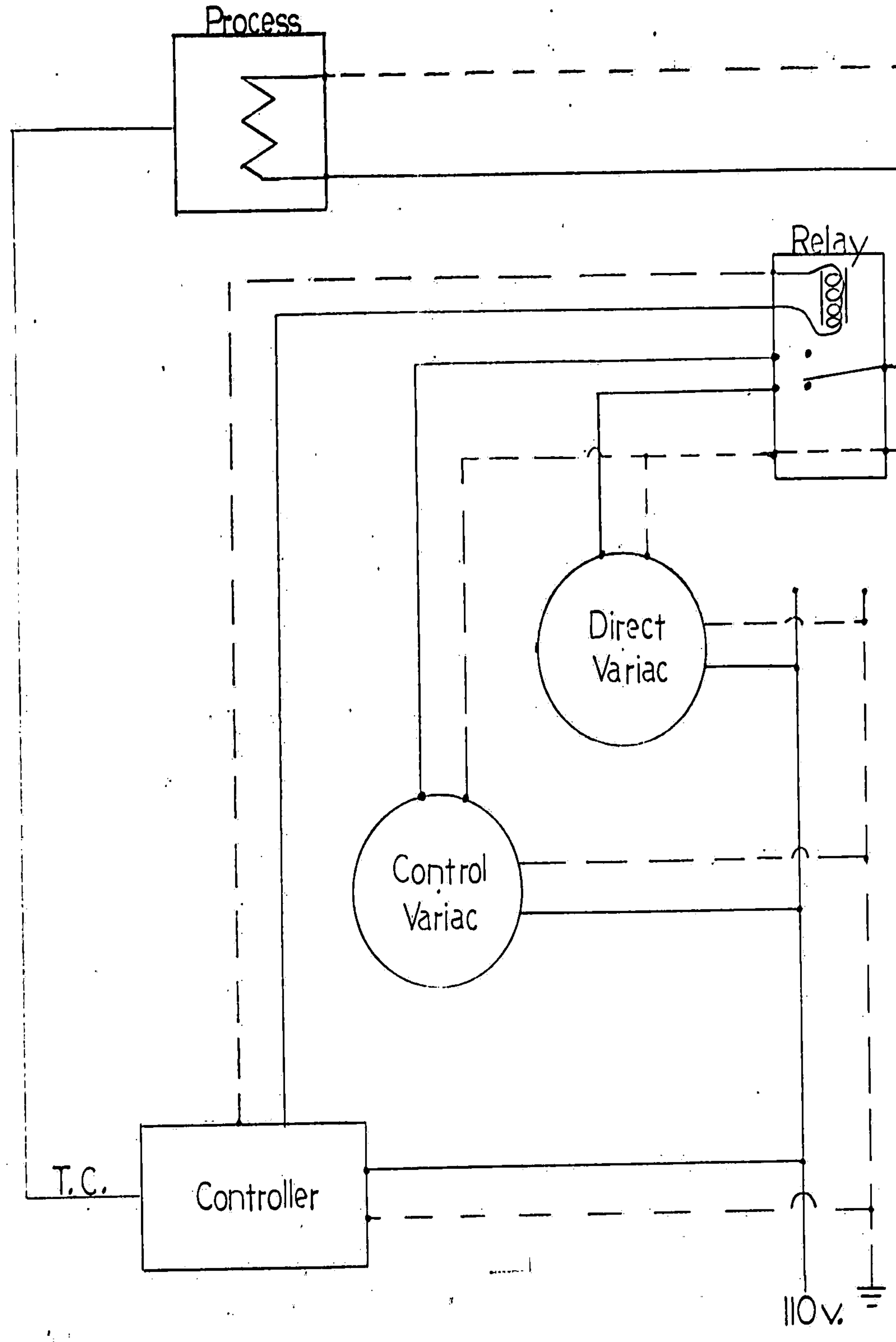
Figure 7

needed to maintain the set point. ~~When the controller goes~~ was ~~on it activates~~ d ~~the relay and permits~~ ed ~~another Variac to supply power of about 110 percent of that needed to maintain the set point.~~ The surface temperature of the cylinder between the two band heaters was used as the control temperature and this arrangement ~~will~~ controlled the sample temperature to within ±2°F. ~~A wiring diagram of the control and heating elements is contained in Figure 8.~~

Besides the thermocouple in the bottom plate there ~~are~~ were thermocouples at the bottom and top of the cylinder, between the two heating bands, ambient, and one down the center channel of the plunger. These thermocouples yielded a profile of the temperature of the entire cylinder and ~~the~~ millivolt readings were printed out on a six point Speedomax recorder with a 10 millivolt range. A portable potentiometer was used to ~~make~~ take accurate measurements of the temperature of the sample through the bottom plate thermocouple. The potentiometer ~~will~~ read the thermocouple in contact with the sample to ±½°F accuracy.

Pressure was applied to the sample ~~with~~ via a hydralic press having a 60,000 psi. capacity. Hydralic leakage was ~~very small~~ imperceptible and thus did not pose a problem in maintaining steady pressure.

Volume changes were indicated by a dial micrometer which measured the distance the plunger traveled as the



TEMPERATURE CONTROL WIRING DIAGRAM

Figure 8

sample was compressed.

~~See~~ Figure 9 shows ~~for~~ a schematic diagram of the compression cylinder~~, and Figure 10 for the view of the assembled apparatus and control equipment~~.

Calculation of the compressibility of the plunger and the temperature effects on the plunger and cylinder will yield ~~about 1 percent~~ a maximum error of ±1% under the most extreme conditions. ~~Hence~~, This factor ~~is~~ was ignored ~~since the accuracy of the data will only be ±1 percent due to errors in pressure and compression measurements~~.

## SCHEMATIC DIAGRAM OF ASSEMBLED COMPRESSIBILITY APPARATUS

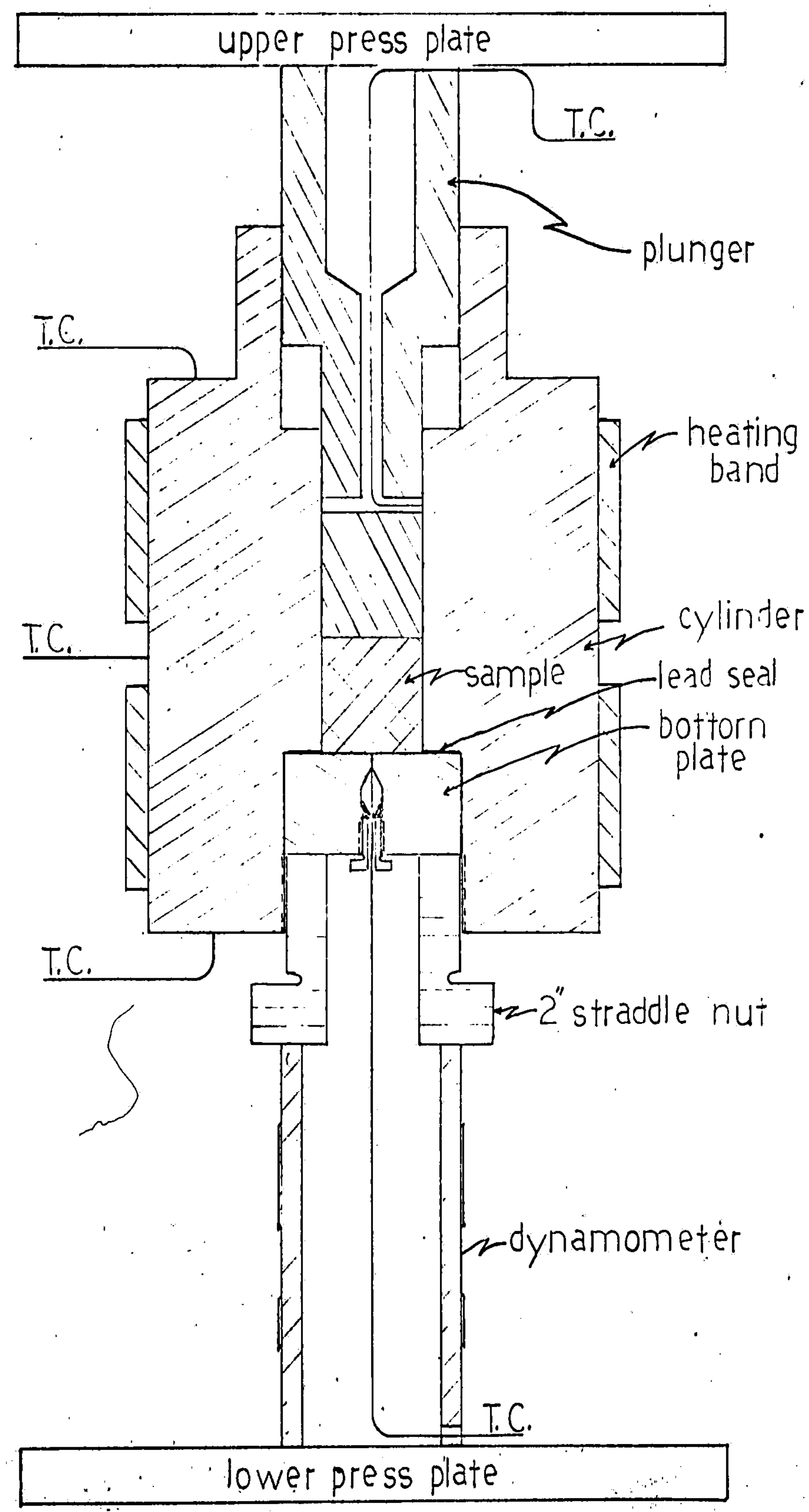


Figure 9

ASSEMBLED APPARATUS

Figure 10

## Procedure

Test specimens were prepared by carefully machining them from one and a half inch extruded rods of the sample material. The diameter of the specimen was 1.135 inches. This diameter produced a snug fit in the cylinder requiring the help of the hydralic press to fully seat it, yet, without the problem of having the leading edge of the cylinder scraping material off the sides of the specimen.

Drying of the specimen was necessary to remove absorbed moisture which would yield a weight slightly higher then that of the dry specimen. Twelve hours at 175°F proved to be sufficient drying condition. After removing from the drying oven the specimen was kept in a desicator until it was placed in the compressibility apparatus.

Careful measurements with a micrometer determined the initial volume of the speciman. The weight of the specimen was obtained from an analytical balance.

When the apparatus had been assembled containing the specimen, the setpoint of the controller was set at a desired temperature and the system allowed to achieve thermal equilibrium. At the equilibrium temperature a desired pressure was applied to the plunger by the hydralic press. When the volume became constant, as indicated by the dial micrometer showing that the plunger had stopped its forward progress, temperature, pressure, and volume readings were recorded. A new pressure was then set and when equilibrium readings were obtained they were recorded. When the entire range of pressure had been examined a new temperature was assigned and the procedure repeated.

The increments used were as follows:

1. Pressure: 3,000 psi. intervals over the range of 0 to 30,000 psi.
2. Temperature: 50°F intervals from room temperature to 350°F.

Identical procedure was used for both samples Lexan 130-112 and Lexan 101-112, a polycarbonate prepared from bisphenol-A having weight average molecular weights of 40,000 and 35,000, respectively.

At the end of a run the specimen was removed and examined for thermal damage and weighed to determine if any weight was lost.

Water acts as a catalyst for the decomposition of polycarbonates. Because of the long times the sample was required to be at a temperature and the fact that it is difficult to keep small amounts of water from the sample, the maximum workable temperature was 350°F. Above this temperature decomposition occured too rapidly to reliable evaluate the properties of the material.

## Equipment Test

Spencer and Gilmore's P-V-T work with five polymers made it possible to test the apparatus to see if the results obtained would be consistent with the work already performed. Since polymethyl methacrylate and polystyrene samples were available, and had been examined by Spencer and Gilmore, they were both tested in this apparatus.

The equation Spencer and Gilmore suggested for polystyrene was:

$$(P + 27,000)\ (V - 0.882) = 11.6T$$

Since the equation was obtained from data having temperatures of 100 to 300°F above the second order transition temperature, the equation can only be applied above this transition temperature. Thus, 200°F was chosen for the comparison and the equation is plotted in Figure 11 at this temperature.

To obtain the volume as a function of pressure, one must first know the starting volume of the sample. If the room temperature volume is determined from micrometer measurements, the initial volume at an elevated temperature can be calculated by adding to the room temperature volume a volume contribution from thermal expansion. For an amorphous material where there are no preferential thermal expansion directions due to crystal considerations this volume can be determined utilizing the fact that the coefficient of thermal expansion will be the same in three dimensions.

Once the initial volume has been determined, the volume at any pressure is the initial volume less the decrease in volume by compression. In Table I are listed the volumes predicted by Spencer and Gilmore's equation for selected pressures, and the results this equipment produces. The experimental points are also plotted in Figure 11.

Data for polymethyl methacrylate derived in an analogous manner to those for polystyrene are given in Table II. Spencer and Gilmore's equation for polymethyl methacrylate was:

$$(P+31,300)(V-0.735)=12.05T$$

These results are plotted in Figure 12. Equilibrium time was considered to be approximately three and a half hours for both materials.

In both cases the experimental results are seen to be in agreement with the predictions of the equations. What deviation does exist arises from two sources: one, the work of Spencer and Gilmore was carried out at a temperature about 200°F higher; and two, this work and Spencer and Gilmore's work only claim one to two percent accuracy due to normal experimental errors.

## TABLE I.

### Polystyrene

At 200°F $$V = \frac{(11.6)\ (366)}{(P+27,000)} - 0.822$$

| Pressure (psi.) | Volume (cc/g) |
|---|---|
| 0 | 0.9795 |
| 5,000 | 0.9549 |
| 10,000 | 0.9369 |
| 15,000 | 0.9232 |
| 20,000 | 0.9125 |
| 25,000 | 0.9038 |
| 30,000 | 0.8966 |

Experimental Results Sample weight = 23.833g.

| Pressure (psi.) | Height (in) | Volume ($in.^3$) | Volume (cc/g) |
|---|---|---|---|
| 0 | 1.3840 | 1.4028 | 0.9646 |
| 3,100 | 1.3680 | 1.3866 | 0.9534 |
| 6,510 | 1.3532 | 1.3716 | 0.9431 |
| 10,060 | 1.3416 | 1.3598 | 0.9351 |
| 12,300 | 1.3340 | 1.3521 | 0.9297 |
| 21,820 | 1.3175 | 1.3354 | 0.9182 |
| 29,820 | 1.3036 | 1.3216 | 0.9087 |

## TABLE II.

### Polymethyl methacrylate

At 200°F

$$V = \frac{(12.05)\ (366)}{(P + 31{,}300)} - 0.734$$

| Pressure (psi.) | Volume (cc/g) |
|---|---|
| 0 | 0.8750 |
| 5,000 | 0.8550 |
| 10,000 | 0.8408 |
| 15,000 | 0.8293 |
| 20,000 | 0.8200 |
| 25,000 | 0.8123 |
| 30,000 | 0.8060 |

Experimental Results

Sample weight = 26.650 g.

| Pressure (psi.) | Height (in) | Volume (in.$^3$) | Volume (cc/g.) |
|---|---|---|---|
| 0 | 1.4027 | 1.4218 | 0.8743 |
| 2,950 | 1.3862 | 1.4050 | 0.8639 |
| 5,820 | 1.3720 | 1.3906 | 0.8551 |
| 10,550 | 1.3598 | 1.3783 | 0.8476 |
| 14,760 | 1.3498 | 1.3682 | 0.8414 |
| 18,260 | 1.3396 | 1.3572 | 0.8349 |
| 21,800 | 1.3309 | 1.3490 | 0.8296 |
| 25,850 | 1.3207 | 1.3387 | 0.8232 |
| 30,470 | 1.3128 | 1.3306 | 0.8183 |

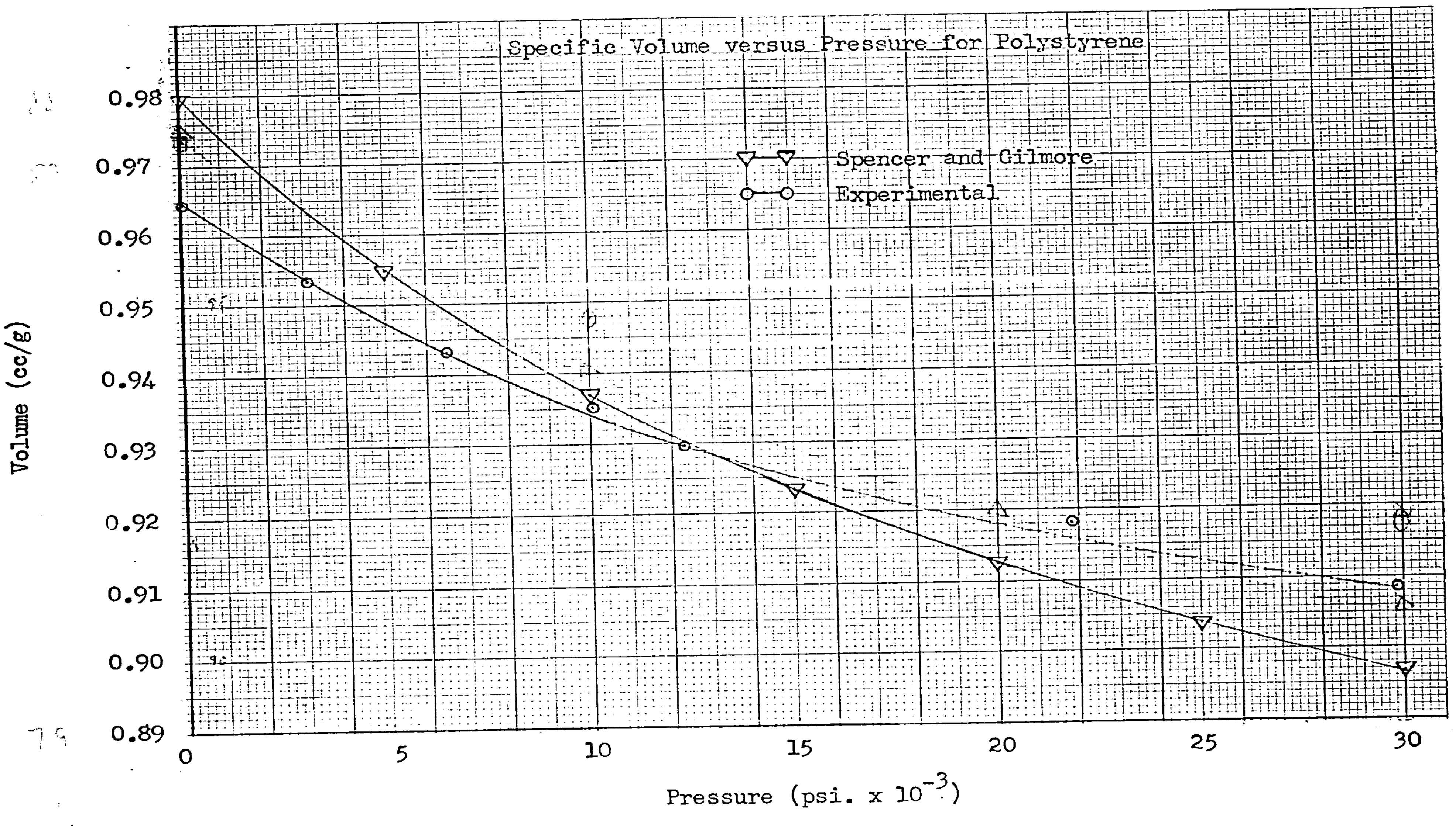

Specific Volume versus Pressure for Polystyrene
Spencer and Gilmore
Experimental
Volume (cc/g)
0.98
0.97
0.96
0.95
0.94
0.93
0.92
0.91
0.90
0.89
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 11

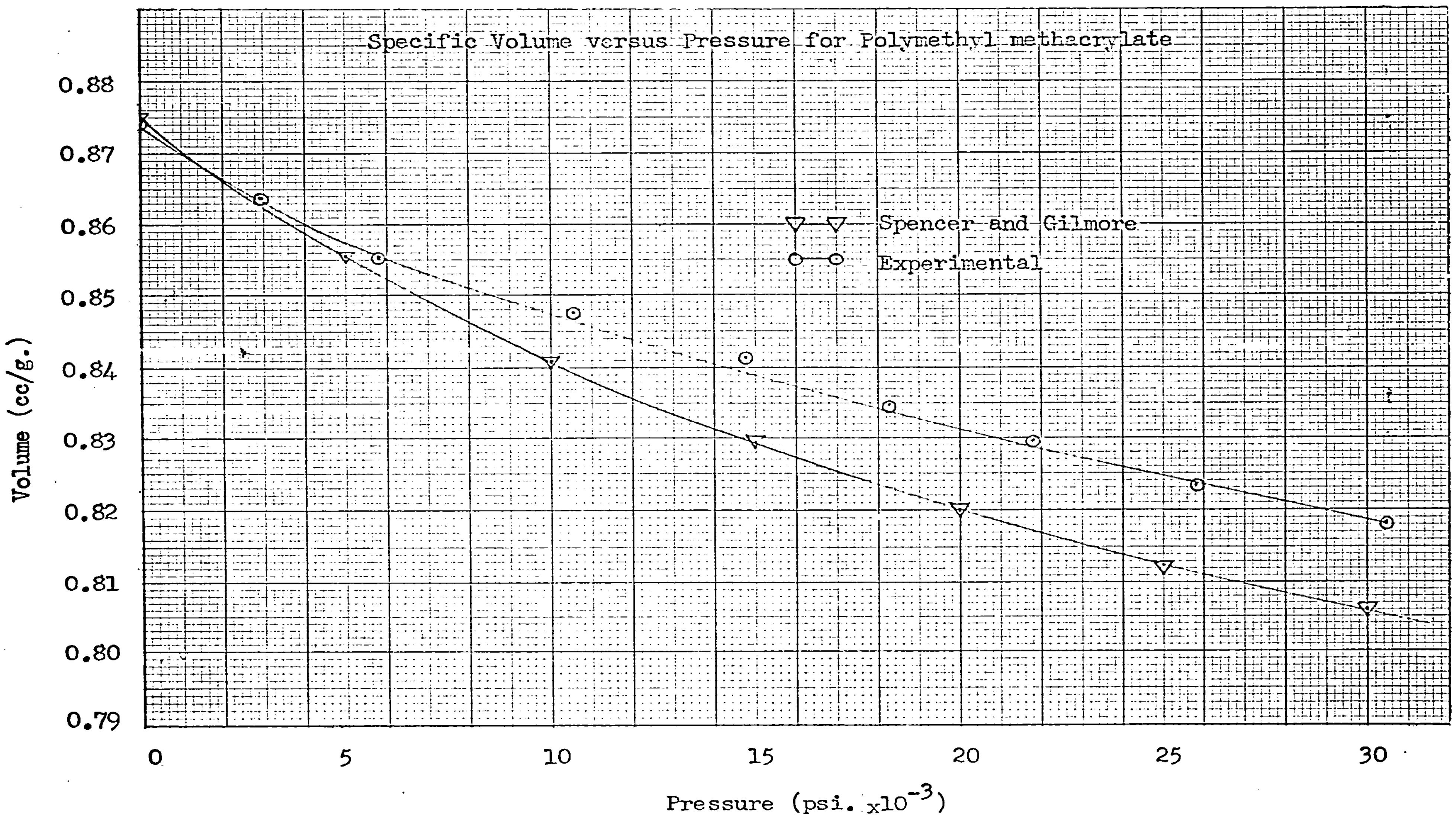

Specific Volume versus Pressure for Polymethyl methacrylate
Spencer and Gilmore
Experimental
Volume (cc/g.)
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
0.80
0.79
0
5
10
15
20
25
30
Pressure (psi. x10^-3)

Figure 12

## Results

The compressibility ($\beta$) is defined as $-\frac{1}{V_o}\frac{\partial V}{\partial P}$ where $V_0$ is the volume at zero pressure and $\partial V$ and $\partial T$ are differential changes in volume and temperature, respectively. $V_0$ can be obtained by extrapolating a plot of volume versus pressure, however, the difference between the volume at zero pressure and the volume at one atmosphere is so small that we can use the volume at one atmosphere without introducing appreciable error. Furthermore, $\frac{\partial V}{\partial P}$ can be approximated quite well by $\frac{\Delta V}{\Delta P}$ as long as the straight line relationship implied by these finite difference quantities closely approximates the actual curve. Then, at constant temperature, compressibility may be calculated by evaluating the volume of a sample at several pressures.

$$\Delta V = V_b - V_a,\quad \Delta P = P_b - P_a,\quad V_1 \text{ volume @ one atm.},\quad \beta = -\frac{1}{V_1}\frac{\Delta V}{\Delta P}$$

The data collected from this experimental work is tabulated in Tables III through IX. They include readings every 50°F from 50°F to 350°F, each through a pressure range of 30,000 psi. The values of compressibility are plotted against the average pressure $((P_b+P_a)/2)$ in Figures 13 through 19.

From these plots it can be seen that at low temperatures, well below the glass transition temperature, the Lexan 130-112, the higher average molecular weight material is more compressible than the Lexan 101-112 of lower average molecular weight. This trend continues until

## TABLE III.

Lexan at 50°F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure P (psi.) | Pressure Increment $\triangle P$ (psi.) | Volume Change $\triangle V$ (in.$^3$ x10$^3$) | Compressibility $\beta = -1/V(\triangle V/\triangle P)$ (psi.$^{-1}$ x10$^6$) | $1/\beta$ |
|---|---|---|---|---|---|---|
| | ✓ | Lexan 101-112 | 1/V = 0.7220 | ✓ | | |
| 0 1.3850 | 5,120 | 2,560 | 5,120 | 7,222 | 1.020 | 9.804 |
| 5,120 1.3778 | 9,120 | 7,165 | 4,090 | 4.999 | 0.882 | 11.337 |
| 9,120 1.3728 | 12,420 | 10,815 | 3,210 | 4.444 | 1.001 | 10.00 |
| 12,420 1.3684 | 16,610 | 14,515 | 4,190 | 4.747 | 0.821 | 12,180 |
| 16,610 1.3636 | 20,140 | 18,375 | 3,530 | 5.252 | 1.078 | 9.276 |
| 20,140 1.3583 | 24,160 | 22,150 | 4,020 | 6.514 | 1.172 | 8.532 |
| 24,160 1.3518 | 27,230 | 25,695 | 3,070 | 4.494 | 1.049 | 9.533 |
| 27,230 1.3473 | 31,390 | 29,310 | 4,160 | 7.020 | 1.216 | 8.22 |
| 31,390 1.3403 | | | | | | |
| | | Lexan 130-112 | 1/V = 0.7220 | | | |
| 1.3850 | | | | | | |
| 4,720 1.3798 | 7,710 | 6,215 | 2,990 | 5.151 | 1.244 | .8169 |
| 9,780 1.3705 | 15,330 | 12,555 | 5,550 | 9.393 | 1.223 | .817 |
| 15,330 1.3638 | 19,080 | 17,205 | 3,750 | 6.666 | 1.288 | .776 |
| 19,080 1.3573 | 22,130 | 20,605 | 3,050 | 6,464 | 1.526 | .655 |
| 21,800 1.3473 | 26,970 | 24,385 | 5,170 | 9.999 | 1.396 | .716 |
| 26,970 1.3414 | 29,660 | 28,315 | 2,690 | 5.959 | 1.606 | .623 |

TABLE III. CONT.

| P(a) | P(b) | $\bar{P}$ | $\triangle P$ | $\triangle V$ | $\beta$ | 1/β |
|---|---|---|---|---|---|---|
| | | | Lexan 130-112 1/V = 0.7220 | | | |
| /.3850 | | | | | | |
| 3,380/.3767 | 7,990 | 5,685 | 4,610 | 8.282 | 1.288 | .776 |
| 7,990/.3709 | 11,390 | 9,690 | 3,400 | 5.858 | 1.244 | .804 |
| 11,390/.3657 | 14,610 | 13,000 | 3,220 | 5.151 | 1.157 | .864 |
| 14,610/.3571 | 19,225 | 16,917 | 4,615 | 8.585 | 1.346 | .743 |
| 19,225/.3425 | 26,700 | 22,962 | 7,475 | 14.645 | 1.418 | .705 |
| 26,700/.3348 | 30,280 | 28,490 | 3,580 | 7.676 | 1.548 | .646 |

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## TABLE IV.

Lexan at 100°F

| Pressure a (psi.) | Pressure b (psi,) | Average Pressure $\bar{P}$ (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ (in.$^3$)X$10^3$ | Compressibility $-1/V(\Delta V/\Delta P)$ (psi.)$^{-1}$X$10^6$ | | |
|---|---|---|---|---|---|---|---|
| | | Lexan 101-112 1/V = 0.7180 | | | | | |
| 1.3928 | | | | | | | |
| 2,150 1.3921 | 7,150 | 4,640 | 4,980 | 6.943 | 1.001 | 10.6 | |
| 7,130 1.3918 | 9,680 | 8,405 | 2,550 | 3.345 | 0.942 | 10.615 | |
| 9,680 1.3913 | 13,490 | 11,585 | 3,810 | 4.663 | 0.879 | 11.376 | 0 |
| 13,490 1.3910 | 15,720 | 14,605 | 2,230 | 3.345 | 1.077 | 9.285 | |
| 15,720 1.3905 | 19,530 | 17,625 | 3,810 | 4.460 | 0.840 | 11.905 | |
| 19,530 1.3900 | 23,600 | 21,565 | 4,070 | 5.068 | 0.894 | 11.186 | |
| 23,600 1.3895 | 26,970 | 25,285 | 3,370 | 5.271 | 1.123 | 8.905 | |
| 26,970 1.3888 | 30,925 | 29,948 | 3,955 | 6.538 | 1.187 | 8.425 | |
| | | Lexan 130-112 1/V = 0.7162 | | | | | |
| 1.3963 | | | | | | | |
| 2,280 1.3939 | 6,500 | 4,390 | 4,220 | 2.438 | 0.422 | 2.369 | |
| 6,500 1.3901 | 9,000 | 7,750 | 2,500 | 3.750 | 1.077 | .929 | |
| 9,000 1.3853 | 12,300 | 10,515 | 3,030 | 4.815 | 1.141 | .876 | |
| 12,030 1.3807 | 15,420 | 13,735 | 3,390 | 4.612 | 0.976 | 1.025 | |
| 15,420 1.3744 | 18,000 | 27,210 | 3,580 | 6.335 | 1.270 | .787 | |
| 18,000 1.3683 | 21,200 | 19,600 | 3,200 | 6.087 | 1.366 | .732 | |
| 21,200 1.3619 | 24,900 | 23,050 | 3,700 | 6.740 | 1.307 | .765 | |
| 24,900 1.3553 | 27,750 | 26,325 | 2,850 | 6.487 | 1.634 | .612 | |
| 27,750 1.3492 | 31,150 | 29,450 | 3,400 | 6.087 | 1.285 | .778 | |

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TABLE V.

Lexan at 150°F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure $\bar{P}$ (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ (in.$^3$ x 10$^3$) | Compressibility $\beta = -1/V(\Delta V/\Delta P)$ (psi.$^{-1}$ x10$^6$) | |
|---|---|---|---|---|---|---|
| Lexan 101-112 1/V = 0.7138 | | | | | | |
| 0 | 5,410 | 2,705 | 5,410 | 8.058 | 1.063 | 9.407 |
| 5,410 | 7,730 | 6,750 | 2,320 | 6.234 | 1.991 | 5.022 |
| 7,730 | 11,230 | 9,480 | 3,500 | 5.017 | 1.023 | 9.775 |
| 11,230 | 15,075 | 13,152 | 3,845 | 4.581 | 0.850 | 11.765 |
| 15,075 | 19,380 | 17,227 | 4,305 | 5.757 | 0.955 | 10.471 |
| 19,380 | 21,970 | 20,675 | 2,590 | 3.953 | 1.099 | 9.099 |
| 21,970 | 24,420 | 23,195 | 2,450 | 3.801 | 0.898 | 11.136 |
| 24,420 | 27,360 | 25,990 | 2,940 | 5.119 | 1.242 | 8.052 |
| 24,420 | 30,900 | 27,660 | 6,480 | 10.389 | 1.144 | 8.741 |
| Lexan 130-112 1/V = 0.7138 | | | | | | |
| 2,310 | 8,010 | 5,160 | 5,700 | 8.565 | 1.073 | .932 |
| 8,010 | 10,450 | 9,230 | 2,440 | 8.159 | 2.384 | .419 |
| 10,450 | 13,330 | 11,890 | 2,880 | 5.980 | 1.482 | .675 |
| 13,330 | 18,160 | 15,745 | 4,830 | 12.467 | 1.842 | .543 |
| 18,160 | 21,360 | 19,760 | 3,200 | 6.082 | 1.356 | .735 |
| 21,360 | 27,170 | 24,265 | 5,810 | 10.846 | 1.333 | .750 |
| 27,170 | 29,410 | 28,290 | 2.240 | 4.967 | 1.582 | .632 |

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TABLE VI.

Lexan at 200°F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure $\bar{P}$ (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ ($in^3 x 10^3$) | $\beta$ = $-1/V(\Delta V/\Delta P)$ ($psi.^{-1} x 10^6$) | |
|---|---|---|---|---|---|---|
| | | Lexan 101-112 | 1/V = 0.7098 | | | |
| 0 | 3,050 | 1,525 | 3,050 | 7.800 | 1.816 | 5.507 |
| 3,050 | 6,350 | 4,700 | 3,300 | 4.511 | 0.970 | 10.309 |
| 6,350 | 9,650 | 8,000 | 3,300 | 4.815 | 1.036 | 9.653 |
| 9,650 | 12,570 | 11,100 | 2,920 | 5.17 | 1.257 | 7.955 |
| 12,570 | 16,130 | 14,350 | 3,560 | 5.372 | 1.072 | 9.328 |
| 16,130 | 19,030 | 17,580 | 2,900 | 6.791 | 1.662 | 6.017 |
| 19,030 | 22,150 | 21,590 | 3,120 | 6.943 | 1.580 | 6.329 |
| 22,150 | 25,570 | 23,860 | 3,420 | 5.423 | 1.126 | 8.880 |
| 25,570 | 28,550 | 27,060 | 2,980 | 7.197 | 1.714 | 5.834 |
| 25,570 | 31,530 | 28,550 | 5,960 | 13.481 | 1.497 | 6.680 |
| 28,550 | 31,530 | 30,040 | 2,980 | 6.284 | 1.606 | 6.227 |
| | | Lexan 130-112 | 1/V = 0.7099 | | | |
| 3,460 | 7,100 | 5,330 | 3,740 | 5.271 | 1.000 | 1.00 |
| 7,100 | 10,680 | 8,890 | 3,580 | 7.044 | 1.397 | .716 |
| 10,680 | 14,950 | 12,815 | 4,270 | 6.740 | 1.120 | .895 |
| 14,950 | 18,550 | 16,750 | 3,600 | 7.450 | 1.468 | .681 |
| 18,550 | 24,460 | 21,505 | 5,910 | 8.109 | 0.973 | 1.028 |
| 24,460 | 26,180 | 24,320 | 3,720 | 8.818 | 1.682 | .595 |
| 26,180 | 30,560 | 28,370 | 4,380 | 9.883 | 1.601 | .625 |

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## TABLE VII.

Lexan at 250°F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure P (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ (in.$^3$ x$10^3$) | Compressibility $\beta = -1/V(\Delta V/\Delta P)$ (psi.$^{-1}$x$10^6$) | |
|---|---|---|---|---|---|---|
| | | | Lexan 101-112 $1/V = 0.7058$ | | | |
| 0 | 2,130 | 1,065 | 2,130 | 5.473 | 1.813 | 5.512 |
| 2,130 | 5,820 | 3,975 | 3,690 | 7.450 | 1.425 | 7.018 |
| 5,820 | 10,300 | 8,060 | 4,480 | 8.109 | 1.271 | 7.868 |
| 10,300 | 14,100 | 12,200 | 3,800 | 7.146 | 1.328 | 7.530 |
| 14,100 | 17,650 | 15,875 | 3,550 | 7.298 | 1.452 | 6.887 |
| 17,650 | 21,520 | 19,585 | 3,870 | 8.970 | 1.636 | 6.112 |
| 21,520 | 25,900 | 23,710 | 4,380 | 9.274 | 1.495 | 6.689 |
| 25,900 | 29,550 | 27,725 | 3,650 | 7.602 | 1.471 | 6.798 |
| 17,650 | 25,520 | 21,585 | 7,870 | 18.240 | 1.637 | 6.109 |
| | | | Lexan 130-112 $1/V = 0.7059$ | | | |
| 2,450 | 6,740 | 4,595 | 4,290 | 8.413 | 1.384 | .722 |
| 6,740 | 10,750 | 8,745 | 4,010 | 7.450 | 1.312 | .762 |
| 10,750 | 13,740 | 12,245 | 2,990 | 6.639 | 1.567 | .638 |
| 13,740 | 19,110 | 16,425 | 5,370 | 9.477 | 1.246 | .803 |
| 19,110 | 22,440 | 20,775 | 3,330 | 7.602 | 1.612 | .620 |
| 22,440 | 25,820 | 24,130 | 3,380 | 7.805 | 1.629 | .613 |
| 25,820 | 30,275 | 28,048 | 4,455 | 9.376 | 1.485 | .673 |

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# PAGES

TABLE VIII.

Lexan at 300°F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure $\bar{P}$ (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ (in.$^3$ x10$^3$) | Compressibility $\beta = -1/V(\Delta V/\Delta P)$ (psi.$^{-1}$x10$^6$) | |
|---|---|---|---|---|---|---|
| | | Lexan 101-112 | 1/V = 0.7018 | | | |
| 3,050 | 5,640 | 4,345 | 2,590 | 16.015 | 4.341 | |
| 5,640 | 10,000 | 7,820 | 4,360 | 19.157 | 3.085 | |
| 10,000 | 13,380 | 11,690 | 3,380 | 8.818 | 1.831 | |
| 13,380 | 17,630 | 15,505 | 4,250 | 10.947 | 1.808 | |
| 17,630 | 19,380 | 18,505 | 1,750 | 4.663 | 1.871 | |
| 19,380 | 24,670 | 22,025 | 5,290 | 10.541 | 1.399 | |
| 24,670 | 28,550 | 26,610 | 3,880 | 7.298 | 1.321 | |
| 19,380 | 23,480 | 21,430 | 4,100 | 9.122 | 1.563 | |
| | | Lexan 130-112 | 1/V = 0.7019 | | | |
| 350 | 2,880 | 1,615 | 2,530 | 20.576 | 5.708 | .175 |
| 2,880 | 6,150 | 4,515 | 3,270 | 16.826 | 3.611 | .277 |
| 6,150 | 9,630 | 7,890 | 3,480 | 13.532 | 2.729 | .366 |
| 9,630 | 13,990 | 11,810 | 4,360 | 20.525 | 3.304 | .303 |
| 13,990 | 19,110 | 16,550 | 5,120 | 8.616 | 1.181 | .847 |
| 19,110 | 21,600 | 20,355 | 2,490 | 10.136 | 2.857 | .350 |
| 21,600 | 25,300 | 23,450 | 3,700 | 8.869 | 1.683 | .594 |
| 25,300 | 29,360 | 27,330 | 4,060 | 7.247 | 1.253 | .798 |

## TABLE VIII. CONT.

| P(a) | P (b) | $\bar{P}$ | $\Delta P$ | $\Delta V$ | $\beta$ | |
|---|---|---|---|---|---|---|
| Lexan 130-112 $1/V = 0.7009$ | | | | | | |
| 1,660 | 4,150 | 2,905 | 2,490 | 14.342 | 4.037 | .248 |
| 4,150 | 7,950 | 6,050 | 3,800 | 16.015 | 2.954 | .339 |
| 7,950 | 10,550 | 9,250 | 2,600 | 10.440 | 2.815 | .458 |
| 10,550 | 13,800 | 12,175 | 3,250 | 7.602 | 1.640 | .610 |
| 13,800 | 16,550 | 15,175 | 2,750 | 7.196 | 1.834 | .545 |
| 16,550 | 19,420 | 17,985 | 2,870 | 6.791 | 1.658 | .603 |
| 19,420 | 22,560 | 20,990 | 3,140 | 8.565 | 1.912 | .523 |
| 22,560 | 25,610 | 24,085 | 3,050 | 6.943 | 1.595 | .627 |
| 25,610 | 29,730 | 27,670 | 4,120 | 7.45 | 1.267 | .789 |

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TABLE IX.

Lexan at 350 °F

| Pressure a (psi.) | Pressure b (psi.) | Average Pressure $\bar{P}$ (psi.) | Pressure Increment $\Delta P$ (psi.) | Volume Change $\Delta V$ ($in^3 x 10^3$) | Compressibility $\beta = -1/V(\Delta V/\Delta P)$ ($psi^{-1} x 10^6$) |
|---|---|---|---|---|---|
| | | | Lexan 101-112 $1/V = 0.6980$ | | |
| 1.4327 | | | | | |
| 1,900 1.4110 | 5,270 | 3,585 | 3,370 | 21.691 | 4.493 |
| 5,270 1.3937 | 8,440. | 6,855 | 3,170 | 17.282 | 3.806 |
| 8,440 1.3784 | 11,650 | 10,045 | 3,210 | 15.356 | 3.131 |
| 11,650 1.3668 | 13,950 | 12,900 | 3,210 | 11.555 | 3.507 |
| 13,950 1.3576 | 17,800 | 15,875 | 3,850 | 15.255 | 2.766 |
| 17,800 1.3392 | 21,000 | 19,400 | 3,200 | 12.366 | 2.698 |
| 21,000 1.3295 | 26,600 | 23,800 | 5,600 | 9.680 | 1.207 |
| 26,600 1.3238 | 28,300 | 27,450 | 1,700 | 5.676 | 2.331 |
| 21,000 1.3084 | 28,300 | 24,650 | 7,300 | 15.356 | 1.468 |
| | | | Lexan 130-112 $1/V = 0.6979$ | | |
| 1.4329 | | | | | |
| 490 1.4119 | 3,130 | 1,810 | 2,640 | 20.982 | 5.548 |
| 3,130 1.3959 | 6,150 | 4,640 | 3,020 | 15.964 | 3.689 |
| 6,150 1.3767 | 10,480 | 8,315 | 4,330 | 19.208 | 3.097 |
| 10,480 1.3625 | 14,100 | 12,290 | 3,620 | 14.190 | 2.736 |
| 14,100 1.3487 | 17,360 | 15,730 | 3,260 | 13.785 | 2.952 |
| 17,360 1.3389 | 21,770 | 19,565 | 4,410 | 9.832 | 1.556 |
| 21,770 1.3312 | 25,000 | 23,385 | 3,230 | 7.754 | 1.676 |

TABLE IX. CONT.

| P(a) | P(b) | $\bar{P}$ | P | V | $\beta$ |
|---|---|---|---|---|---|
| | | Lexan 130-112 $1/V = 0.6973$ | | | |
| 1.4341 | | | | | |
| 9,000 1.4226 | 11,660 | 10,330 | 2,660 | 11.500 | 3.014 |
| 11,600 1.4088 | 14,620 | 13,640 | 2,960 | 13.836 | 3.265 |
| 14,620 1.3954 | 18,000 | 16,310 | 3,380 | 13.380 | 2.760 |
| 18,000 1.3840 | 21,420 | 19,710 | 3,420 | 11.352 | 2.314 |
| 21,420 1.3761 | 24,330 | 22,875 | 2,910 | 7.906 | 1.896 |
| 24,330 1.3696 | 27,200 | 25,765 | 2,870 | 6.487 | 1.576 |
| 27,200 1.3618 | 30,860 | 29,030 | 3,660 | 7.805 | 1.487 |

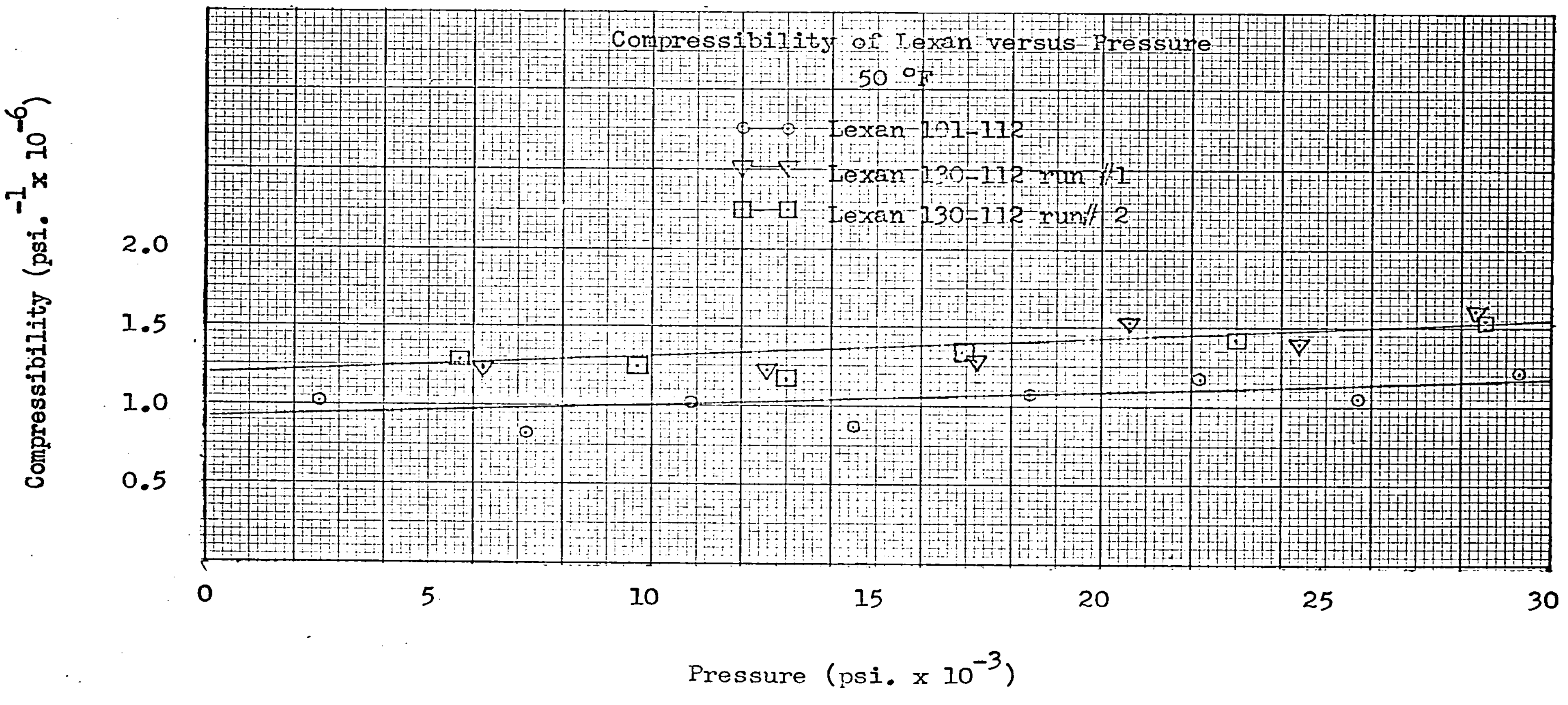
Compressibility of Lexan versus Pressure
50 °F
Lexan 101-112
Lexan 130-112 run #1
Lexan 130-112 run # 2
Compressibility (psi.$^{-1}$ x $10^{-6}$)
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 13

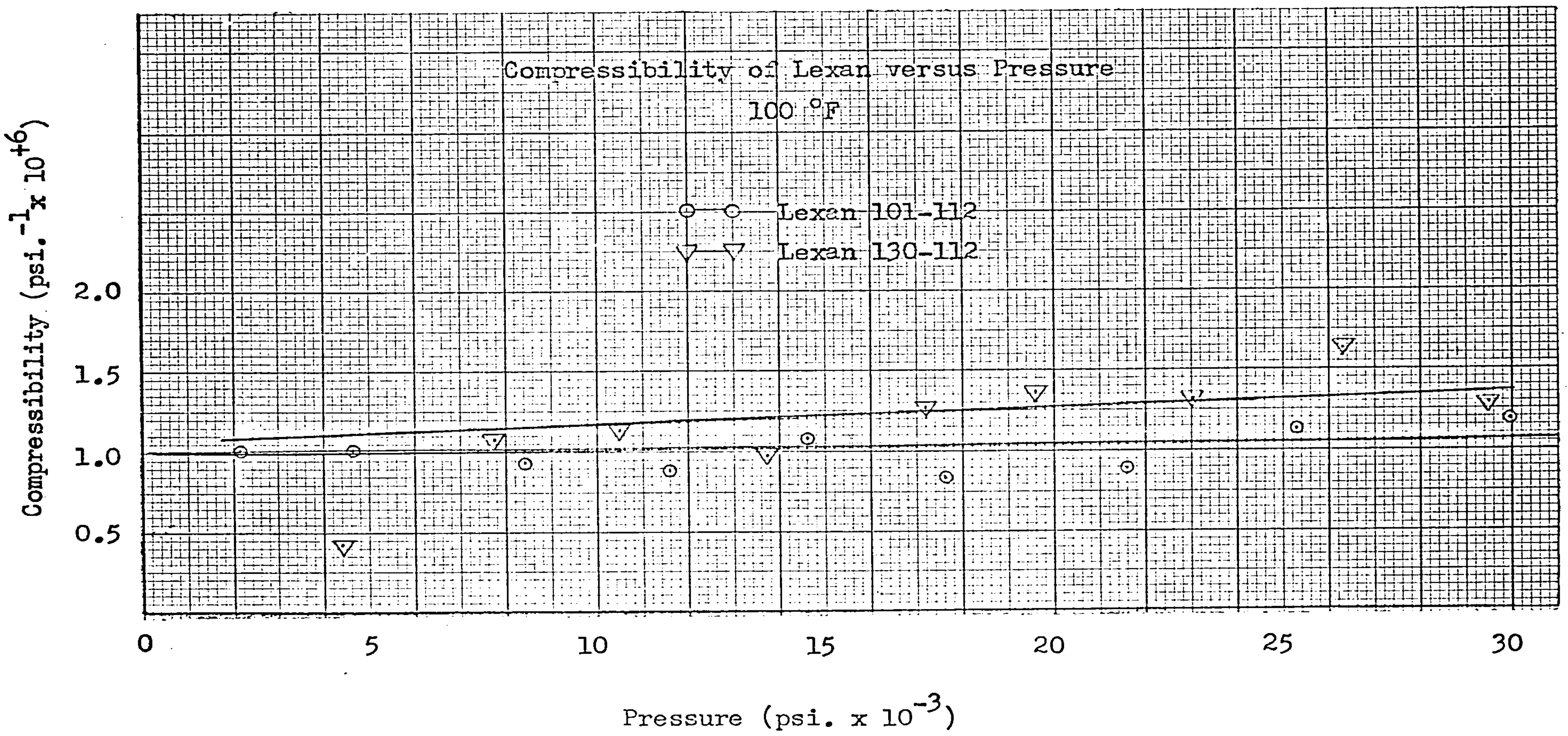
Compressibility of Lexan versus Pressure
100 °F
Lexan 101-112
Lexan 130-112
Compressibility (psi.$^{-1}$ x $10^{+6}$)
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 14

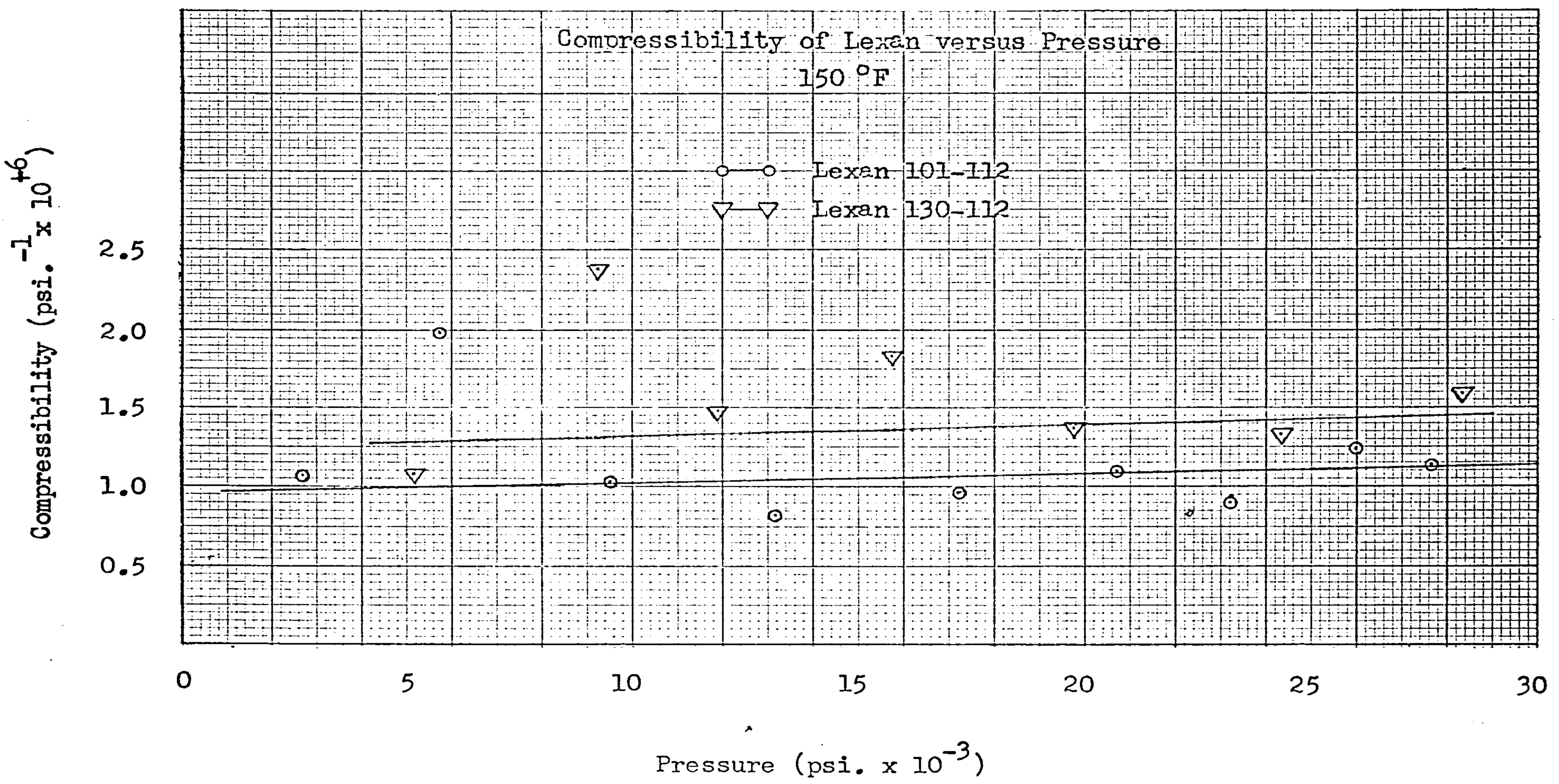
Compressibility of Lexan versus Pressure
150 °F
Lexan 101-112
Lexan 130-112
Compressibility (psi.$^{-1}$ x 10$^{+6}$)
2.5
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
Pressure (psi. x 10$^{-3}$)

Figure 15

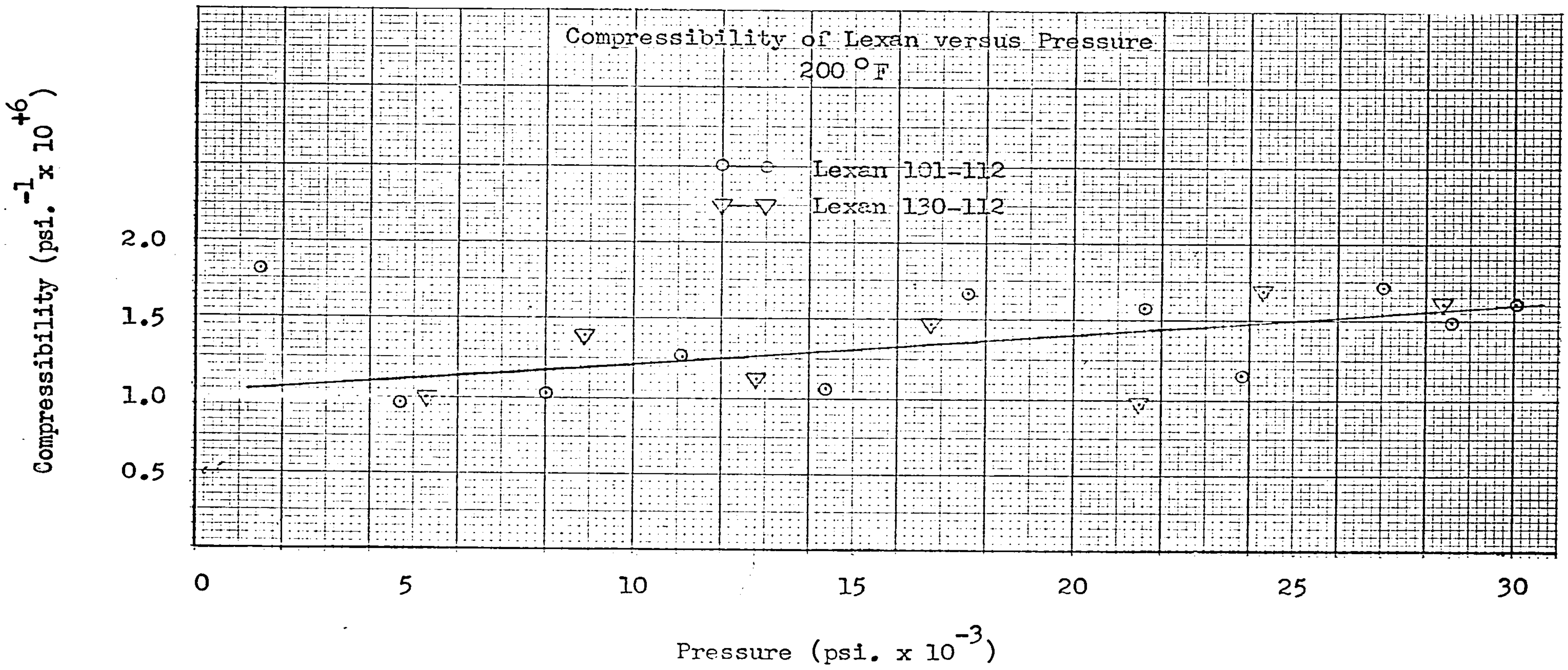
Compressibility of Lexan versus Pressure
200 °F
Lexan 101-112
Lexan 130-112
Compressibility (psi.$^{-1}$ x $10^{+6}$)
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 16

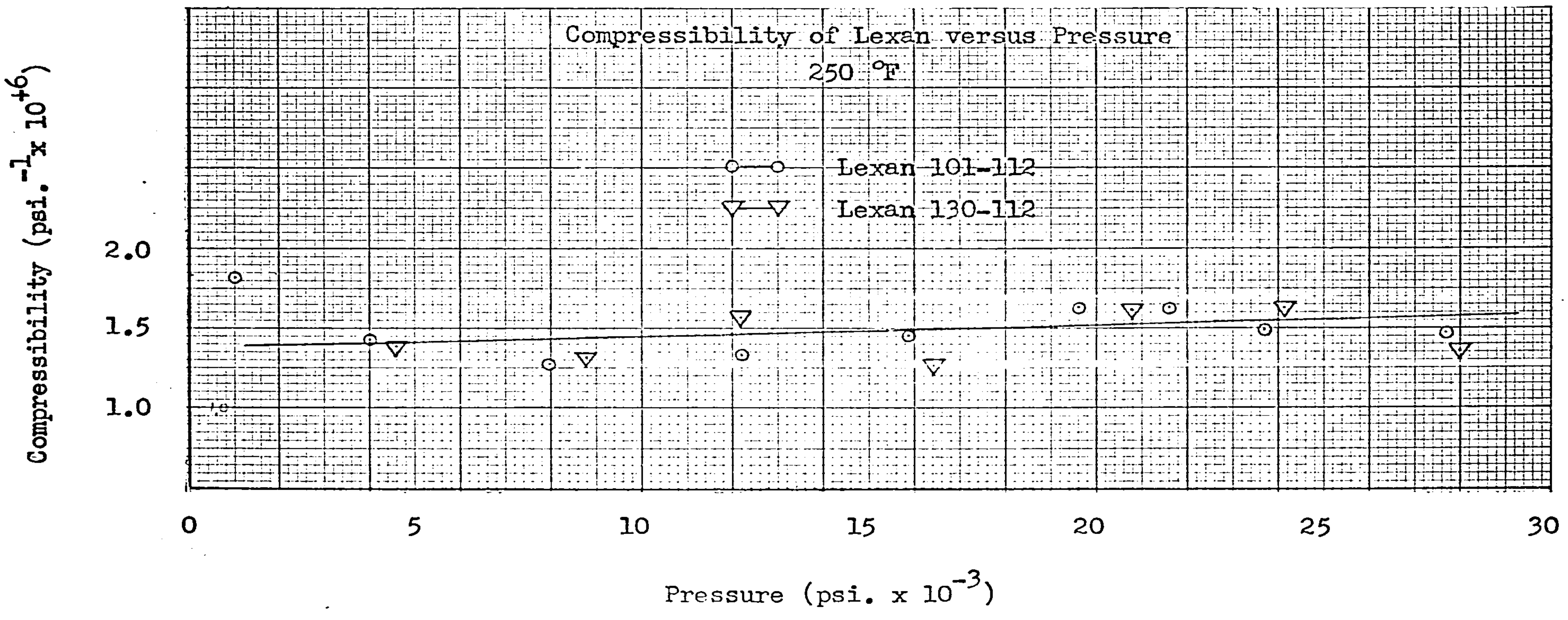
Compressibility of Lexan versus Pressure
250 °F
Lexan 101-112
Lexan 130-112
Compressibility (psi.$^{-1}$ x 10$^{+6}$)
2.0
1.5
1.0
0
5
10
15
20
25
30
Pressure (psi. x 10$^{-3}$)

Figure 17

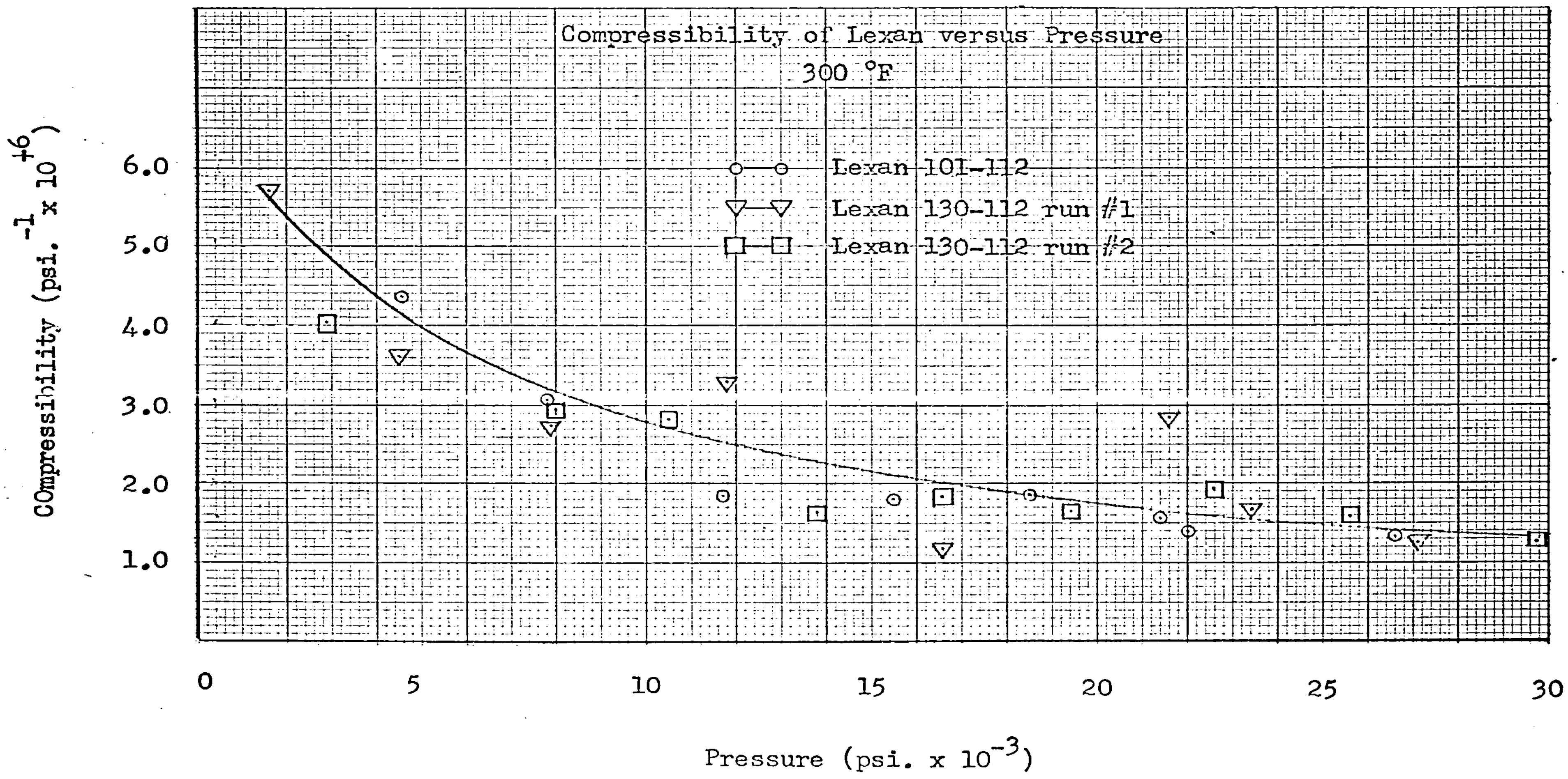
Compressibility of Lexan versus Pressure
300 °F
Lexan 101-112
Lexan 130-112 run #1
Lexan 130-112 run #2
COmpressibility (psi.$^{-1}$ x 10$^{+6}$)
6.0
5.0
4.0
3.0
2.0
1.0
0
5
10
15
20
25
30
Pressure (psi. x 10$^{-3}$)

Figure 18

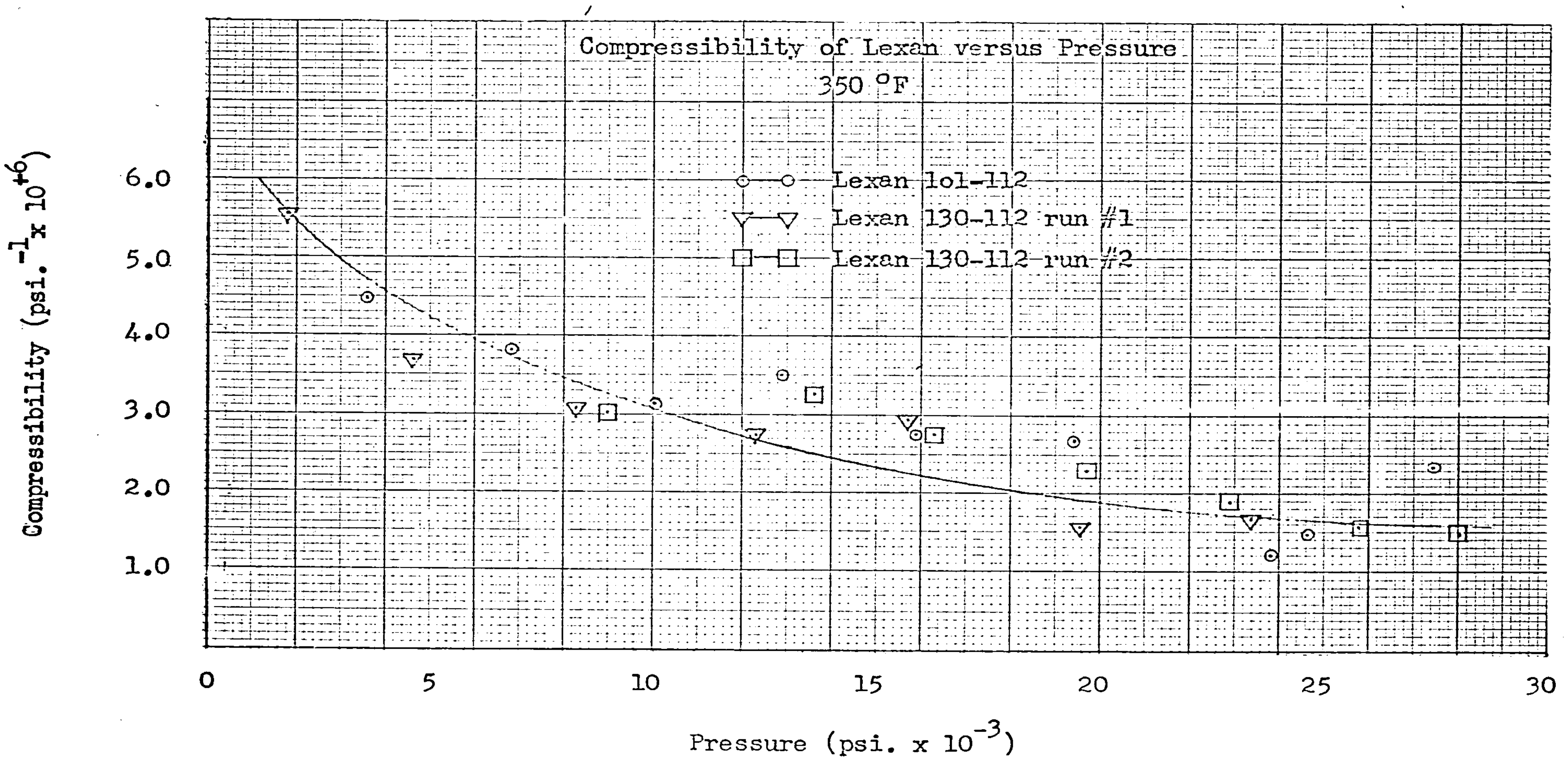
Compressibility of Lexan versus Pressure
350 °F
Lexan 101-112
Lexan 130-112 run #1
Lexan 130-112 run #2
Compressibility (psi.$^{-1}$ x $10^{+6}$)
6.0
5.0
4.0
3.0
2.0
1.0
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 19

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about 200°F where they become indistinguishable from each other. At 295°F the second order transition temperature is exceeded and the result is a departure from the straight line relations of the lower temperatures to a condition where the material is highly compressible up to about 10,000 Psi. (in the case of the 300°F run) trailing off and approaching the compressibility values obtained below the glass transition temperature. As the temperature is increased the higher compressibilities extend out to higher pressure. Note, however, that even at 350°F the material approaches a compressibility value close to that at lower temperature.

Spencer and Gilmore proposed the modified van der Waal's equation of the form $(P+\pi)\ (V-\omega) = RT$. It is necessary to calculate two constants; $\pi$, the internal pressure in psi., and $\omega$, the specific volume at absolute zero temperature. If the density at one temperature, and the volume coeffcient of expansion, $\frac{dV}{dT}$, are known under equilibrium conditions, then $\omega$ can be calculated. From Schnell's thermal data on the bisphenol A polycarbonate we find the specific volume to be 0.8852 cc/g. at 200°C and the volume coefficient of expansion to be $5.0 \times 10^{-4}$ cc/g.°K. The specific volume is then:

$$\omega = 0.8852 \ \text{cc/g} - \left[5.0 \times 10^{-4} \ \text{cc/g}^{\circ}\text{K} \ (473^{\circ}\text{K})\right]$$

or $\omega = 0.6487$ cc/g.

Since there are two mechanisms responsible for the volume coefficient, i. e., change due to thermal energy of the molecule and the change due to the configuration of the molecule or the change in position of molecular segments, there is some question as to which value of the coefficient to use, the instantaneous value or the equilibrium value. Because the values dealt with here are all equilibrium values, it seems consistant to use the equilitrium coefficient of volume expansion.

Rearranging the proposed equation,

A $P = \frac{RT}{(V-\omega)} - \pi$ at constant temperature. Differentiating with respect to volume,

$$\left(\frac{dP}{dV}\right)_T = \frac{-RT}{(V-\omega)^2}$$

B $$\sqrt{(V-\omega)^2} = (V-\omega) = \sqrt{-RT\left(\frac{dV}{dP}\right)_T}$$

Rearranging A and substituting equation B

C $$\pi = \sqrt{-RT\left(\frac{dP}{dV}\right)_T} - P$$

Thus, for constant temperature measurements, $\pi$ may be evaluated directly without extrapolating values.

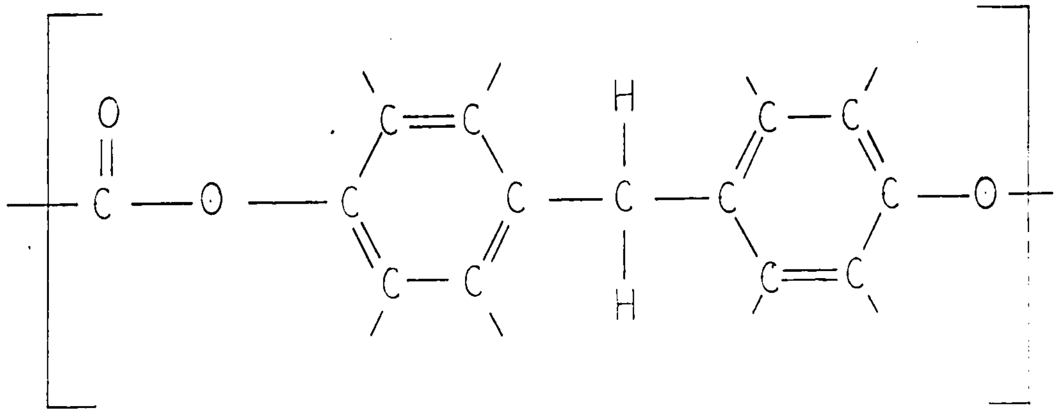
In the unique set of units used for this equation R=1206/M, where M is defined as the monemeric "Interaction unit." Since the bisphenol A polycarbonate unit has no side groups it seems reasonable to assume that M is the weight of the repeat unit, in which case:

$$R=1206/226=5.34$$

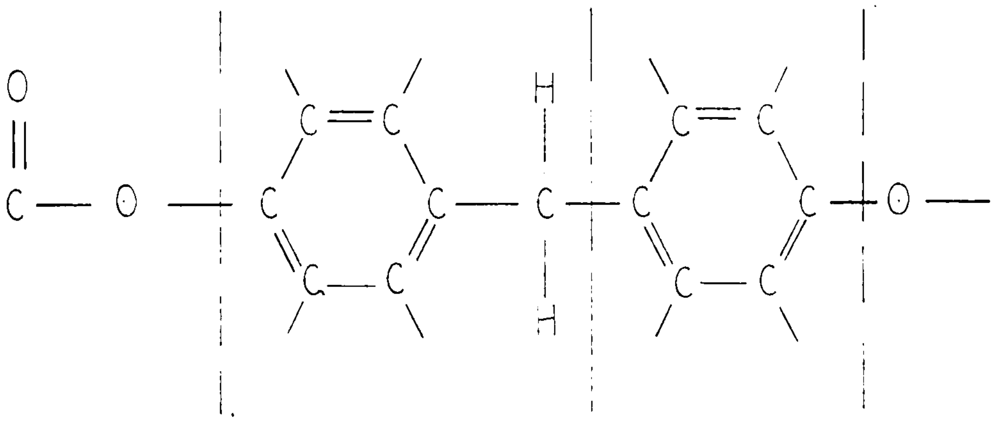
The other possibility, see Figure 20, is that a group about the size of a benzene ring acts as the interaction unit in which case we can predict:

$$R=1206/78=15.5$$

## POSSIBLE INTERACTION UNITS



Bisphenol A Polycarbonate Repeat Unit



Benzene Ring Interaction Unit Approximation

Figure 20

## TABLE X.

| $\overline{P}$ (psi.) | $\Delta P/\Delta V$ (psi./in.$^3$) x $10^{-5}$ | $-T\Delta P/\Delta V$ ($^\circ$K psi./in.$^3$) x $10^{-8}$ | | $\sqrt{-T\Delta P/\Delta V}$ x $10^{-4}$ | |
|---|---|---|---|---|---|
| | Lexan at 300°F (423°K) | | | | |
| 27,600 | 5.531 | 2.339 | 3,826 | 1.530 | 1.95 |
| 24,085 | 4.394 | 1.858 | 3.040 | 1.364 | 1.74 |
| 22,025 | 5.018 | 2.122 | 3.472 | 1.458 | 1.86 |
| 18,000 | 4.226 | 1.787 | 2.924 | 1.337 | 1.71 |
| 15,175 | 3.821 | 1.616 | 2.644 | 1.272 | 1.62 |
| 11,690 | 3.833 | 1.621 | 2.652 | 1.621 | 1.63 |
| 9,200 | 2.491 | 1.053 | 1.723 | 1.027 | 1.31 |
| 4,500 | 1.944 | 0.822 | 1.345 | 0.907 | 1.16 |
| | Lexan at 350°F (450°K) | | | | |
| 29,030 | 4.688 | 2.109 | 3.450 | 1.454 | 1.86 |
| 25,765 | 4.425 | 1.991 | 3.257 | 1.412 | 1.81 |
| 23,050 | 3.788 | 1.704 | 2.788 | 1.306 | 1.67 |
| 19,710 | 3.013 | 1.355 | 2.217 | 1.165 | 1.49 |
| 15,875 | 2.524 | 1.136 | 1.858 | 1.066 | 1.36 |
| 12,290 | 2.551 | 1.148 | 1.878 | 1.072 | 1.37 |
| 10,045 | 2.330 | 1.003 | 1.641 | 1.002 | 1.28 |
| 6,855 | 1.834 | 0.825 | 1.350 | 0.910 | 1.16 |
| 3,585 | 1.554 | 0.699 | 1.144 | 0.837 | 1.07 |

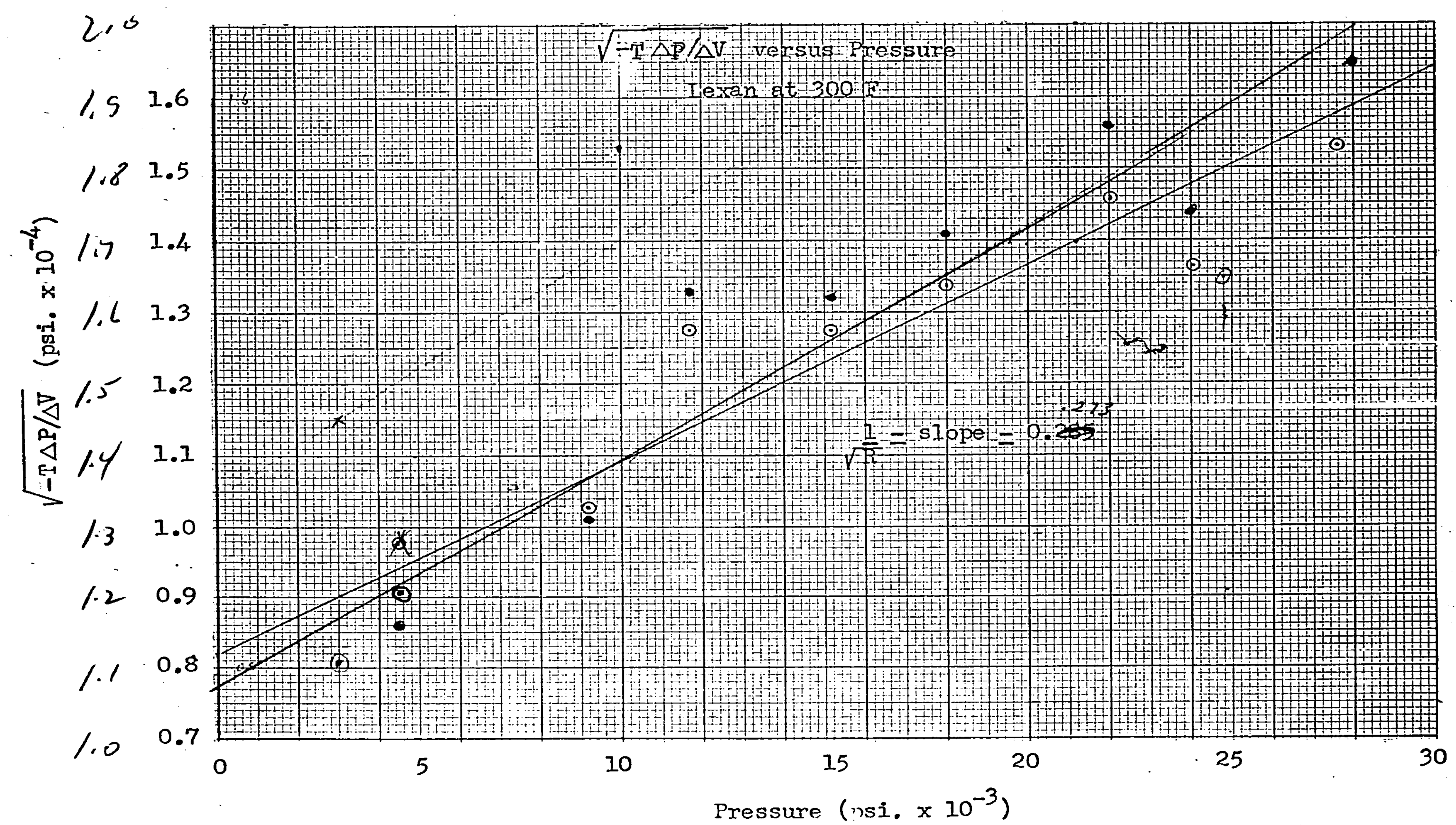

$\sqrt{-T\Delta P/\Delta V}$ versus Pressure
Lexan at 300 F
$\frac{1}{\sqrt{R}}$ = slope = 0.~~255~~
.273
$\sqrt{-T\Delta P/\Delta V}$ (psi. x $10^{-4}$)
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 21

35°

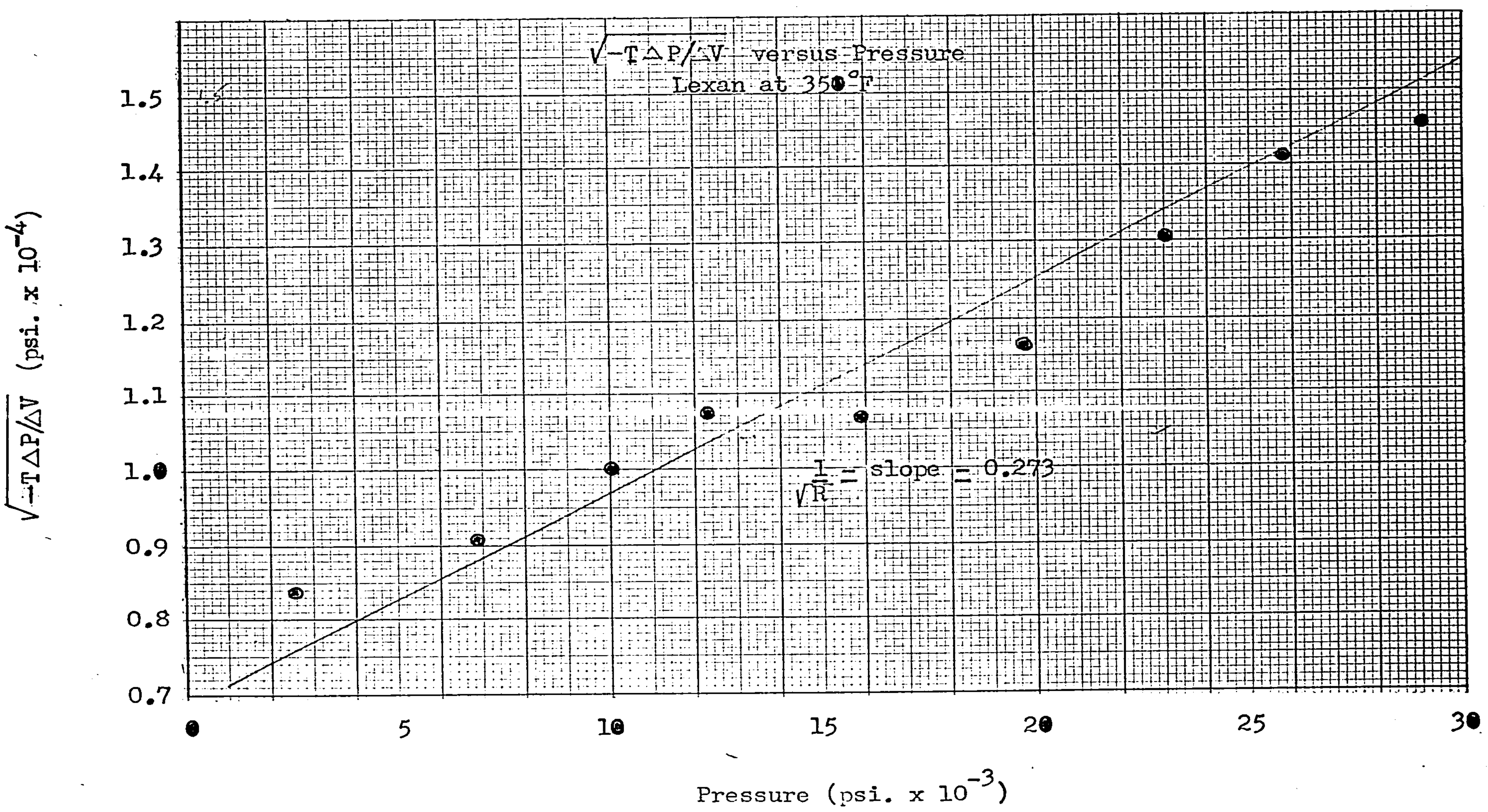

$\sqrt{-T\Delta P/\Delta V}$ versus Pressure
Lexan at 350°F
$\frac{1}{\sqrt{R}}$ = slope = 0.273
$\sqrt{-T\Delta P/\Delta V}$ (psi. x $10^{-4}$)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 22

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Taking equation C and dividing by $\sqrt{R}$

$$\pi/\sqrt{R} = \sqrt{-T\left(\frac{dP}{dV}\right)_T} - P/\sqrt{R}$$

For small intervals $\left(\frac{\Delta P}{\Delta V}\right)_T$ may replace $\left(\frac{dP}{dV}\right)_T$ and P then becomes $\bar{P}$, the average pressure over the interval.

D $$\pi/\sqrt{R} = \sqrt{-T\left(\frac{\Delta P}{\Delta V}\right)_T} - \bar{P}/\sqrt{R}$$

Plotting $\sqrt{-T\frac{\Delta P}{\Delta V}}$ versus $\bar{P}$ enables R to be calculated emperically from the slope of this plot.

In Table X a number of points are listed for the 300°F and 350°F runs. The points are plotted in Figures 21 and 22 and the least squares line is shown. R, evaluated from the slope, shows that approximately 3 groups the size of the benzene group constitute the "interaction unit" since R = 12.9.

It should be noted that one equation of this type will not describe the P-V-T relationships both above and below the second order transition temperature. Because our main interest is in determining quantities such as mold size, the equation of interest should then describe the material above this transition temperature as has been started.

In Table XI the resulting values of $\pi$ are listed. $\pi$ was found to have an average value of 26,602. The final form of the equation is:

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## TABLE XI.

Calculation of $\pi$ for Lexan at 300°F

| $\sqrt{RT\Delta P/\Delta V}$ (psi.) | $\bar{P}$ (psi.) | $\pi$ (psi.) |
|---|---|---|
| | For Lexan 101-112 | |
| 29,750 374[illegible] | 4,345 | 25,415 ~ 33,000 |
| 35,300 | 7,820 | 27,480 |
| 45,810 | 11,690 | 34,120 |
| 46,120 | 15,505 | 30,615 |
| 45,320 | 18,505 | 26,815 |
| 52,390 | 22,025 | 30,365 |
| 53,980 62800 | 26,610 | 27,370 36[illegible] |
| | For Lexan 130-112 | |
| 25,920 | 1,615 | 24,305 |
| 32,680 | 4,515 | 28,165 |
| 37,570 | 7,890 | 29,680 |
| 47,800 | 23,450 | 24,350 |
| 55,380 | 27,330 | 27,050 |
| | | |
| 30,810 | 2,905 | 27,905 |
| 36,010 | 6,050 | 29,960 |
| 36,900 | 9,250 | 27,650 |
| 48,400 | 12,175 | 36,250 |
| 45,800 | 15,175 | 30,625 |
| 48,090 | 17,985 | 30,105 |
| 45,180 | 20,990 | 24,190 |
| 49,050 | 24,085 | 24,965 |
| 55,000 | 27,670 | 27,330 |

$\sum$ all $\pi$ = 593,610

average $\pi$ = 28,267

## TABLE XI. CONT.

### Calculation of $\pi$ for Lexan at 350°F

| $\sqrt{RT\Delta P/\Delta V}$ (psi.) | $\bar{P}$ (psi.) | $\pi$ (psi.) |
|---|---|---|
| | For Lexan 101-112 | |
| 30,400 | 3,585 | 26,815 |
| 32,620 | 6,855 | 25,765 |
| 37,100 | 10,045 | 27,055 |
| 34,000 | 12,900 | 21,100 |
| 38,300 | 18,875 | 19,425 |
| 38,690 | 19,400 | 19,290 |
| 57,990 | 23,800 | 34,190 |
| | For Lexan 130-112 | |
| 27,030 | 1,810 | 25,220 |
| 33,140 | 4,640 | 28,500 |
| 36,190 | 8,315 | 27,875 |
| 38,490 | 12,290 | 26,200 |
| 37,040 | 15,730 | 21,310 |
| 51,010 | 19,565 | 31,545 |
| 49,180 | 23,385 | 25,795 |
| | | |
| 36,650 | 10,330 | 26,320 |
| 35,410 | 13,640 | 21,950 |
| 38,310 | 16,310 | 22,000 |
| 41,830 | 19,710 | 22,120 |
| 46,260 | 22,875 | 23,385 |
| 50,720 | 25,765 | 24,655 |
| 52,200 | 29,030 | 23,170 |

$\sum$ all $\pi$ = 523,675

average $\pi$ = 24,937

$$(P+26{,}602)(V-0.6487)=12.9T$$

Plotting the above equation with the data obtained experimentally reveals the fact that the equation does not satisfactorily represent the data, in fact, it deviates from the experimental values by as much as seven percent of the total volume. As a result the variable parameters $M$, the interaction unit, and $\pi$, the internal pressure, were adjusted to yield a good fit. The final value of $M$ was chosen to yield a value of $R=20.8$, and the final value of $\pi$, the internal pressure, was 40,000. The resulting adjusted equation is:

$$(P+40{,}000)(V-0.6487)=20.8T$$

In Table XII the experimentally determined volumes at various pressures are tabulated. In Figures 23 and 24 the adjusted equation is plotted along with the experimental points to compare the fit obtained.

The Tait equation:

I $\quad \frac{V_o-V}{V_o}=c\ \mathrm{Log}\ (1+P/b)$ is not particularly useful in this form. Differentiating for the $\frac{\partial V}{\partial P}$ we obtain the following expression:

$$\text{II} \qquad \frac{\partial V}{\partial P}=-V_o\,(0.4343c)\,\frac{1}{b+P}$$

upon rearranging,

## TABLE XII.

### Experimental Pressure - Volume Equilibrium Values

Cross-sectional area of cylinder = 1.0136"

| Pressure (psi.) | Sample Height (in.) | Sample Volume (in$^3$) | Specific Volume (cc/g) |
|---|---|---|---|
| Lexan 101-112 at 300°F | | Sample weight = 27.197 g. | |
| 0 | 1.4056 | 1.4248 | 0.8584 |
| 3,050 | 1.3860 | 1.4048 | 0.8464 |
| 5,640 | 1.3702 | 1.3888 | 0.8369 |
| 10,000 | 1.3513 | 1.3697 | 0.8253 |
| 13,500 | 1.3426 | 1.3609 | 0.8199 |
| 17,630 | 1.3318 | 1.3499 | 0.8133 |
| 19,380 | 1.3272 | 1.3452 | 0.8105 |
| 24,670 | 1.3168 | 1.3347 | 0.8042 |
| 28,550 | 1.3096 | 1.3274 | 0.8001 |
| Lexan 130-112 at 300°F | | Sample weight = 26.821 g. | |
| 0 | 1.4054 | 1.4245 | 0.8704 |
| 2,880 | 1.3820 | 1.4008 | 0.8559 |
| 6,150 | 1.3655 | 1.3841 | 0.8458 |
| 9,630 | 1.3521 | 1.3705 | 0.8373 |
| 13,990 | 1.3419 | 1.3601 | 0.8310 |
| 19,110 | 1.3333 | 1.3514 | 0.8256 |
| 21,600 | 1.3233 | 1.3413 | 0.8196 |
| 25,300 | 1.3146 | 1.3325 | 0.8142 |
| 29,360 | 1.3075 | 1.3253 | 0.8097 |
| Lexan 130-112 at 300°F | | Sample weight = 27.034 g. | |
| 0 | 1.4074 | 1.4265 | 0.8648 |
| 1,660 | 1.3902 | 1.4091 | 0.8541 |
| 4,150 | 1.3761 | 1.3948 | 0.8454 |
| 7,950 | 1.3603 | 1.3788 | 0.8358 |
| 10,550 | 1.3500 | 1.3684 | 0.8296 |
| 13,800 | 1.3420 | 1.3603 | 0.8246 |
| 16,550 | 1.3349 | 1.3531 | 0.8202 |
| 19,420 | 1.3282 | 1.3463 | 0.8161 |
| 22,560 | 1.3198 | 1.3377 | 0.8109 |
| 25,610 | 1.3129 | 1.3308 | 0.8068 |
| 29,730 | 1.3056 | 1.3234 | 0.8022 |

TABLE XII. CONT.

| Pressure | Sample Height | Sample Volume | Specific Volume |
|---|---|---|---|
| Lexan 101-112 at 350°F | | Sample weight = 27.197 g. | |
| 0 | 1.4234 | 1.4328 | 0.8633 |
| 1,900 | 1.4086 | 1.4277 | 0.8601 |
| 5,270 | 1.3872 | 1.4061 | 0.8472 |
| 8,440 | 1.3701 | 1.3887 | 0.8367 |
| 11,650 | 1.3550 | 1.3734 | 0.8276 |
| 13,950 | 1.3436 | 1.3619 | 0.8205 |
| 17,800 | 1.3285 | 1.3461 | 0.8111 |
| 21,000 | 1.3163 | 1.3342 | 0.8039 |
| 26,600 | 1.3068 | 1.3246 | 0.7981 |
| 28,300 | 1.3012 | 1.3189 | 0.7946 |
| Lexan 130-112 at 350°F | | Sample weight = 26.821 g. | |
| 0 | 1.4234 | 1.4428 | 0.8815 |
| 3,130 | 1.3971 | 1.4161 | 0.8653 |
| 6,150 | 1.3812 | 1.3999 | 0.8553 |
| 10,480 | 1.3623 | 1.3808 | 0.8436 |
| 14,100 | 1.3483 | 1.3666 | 0.8350 |
| 17,360 | 1.3347 | 1.3528 | 0.8266 |
| 21,770 | 1.3250 | 1.3430 | 0.8205 |
| 25,000 | 1.3173 | 1.3352 | 0.8158 |
| Lexan 130-112 at 350°F | | Sample weight = 27.034 g. | |
| 0 | 1.4149 | 1.4342 | 0.8694 |
| 9,000 | 1.3695 | 1.3881 | 0.8415 |
| 11,600 | 1.3586 | 1.3771 | 0.8348 |
| 14,620 | 1.3459 | 1.3642 | 0.8269 |
| 18,000 | 1.3327 | 1.3508 | 0.8189 |
| 21,420 | 1.3215 | 1.3395 | 0.8120 |
| 24,330 | 1.3137 | 1.3316 | 0.8073 |
| 27,200 | 1.3073 | 1.3251 | 0.8033 |
| 30,860 | 1.2986 | 1.3163 | 0.7979 |

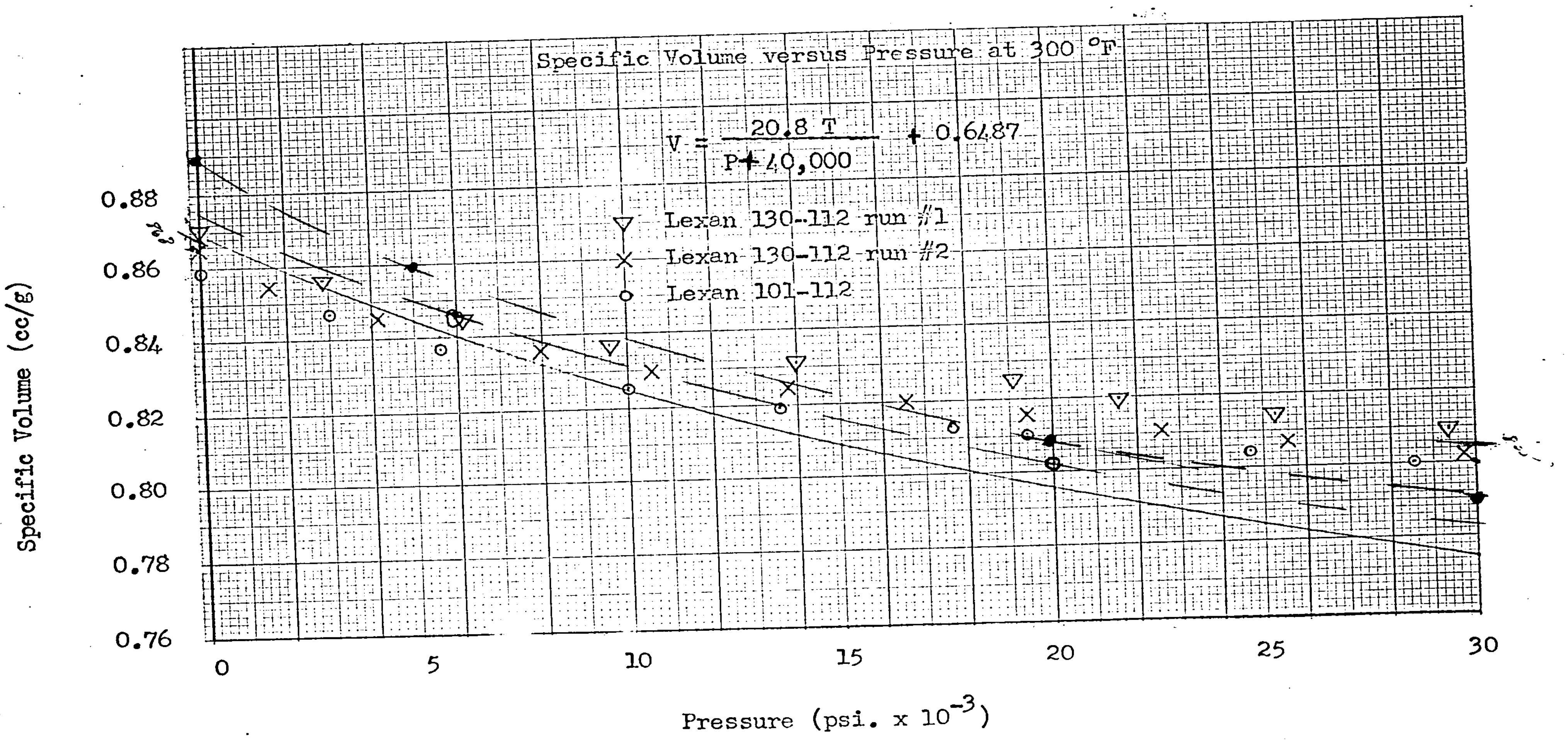
Specific Volume versus Pressure at 300 °F
V = 20.8 T / (P + 40,000) + 0.6487
▽ Lexan 130-112 run #1
× Lexan 130-112 run #2
○ Lexan 101-112
Specific Volume (cc/g)
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0
5
10
15
20
25
30
Pressure (psi. x 10^-3)

Figure 23

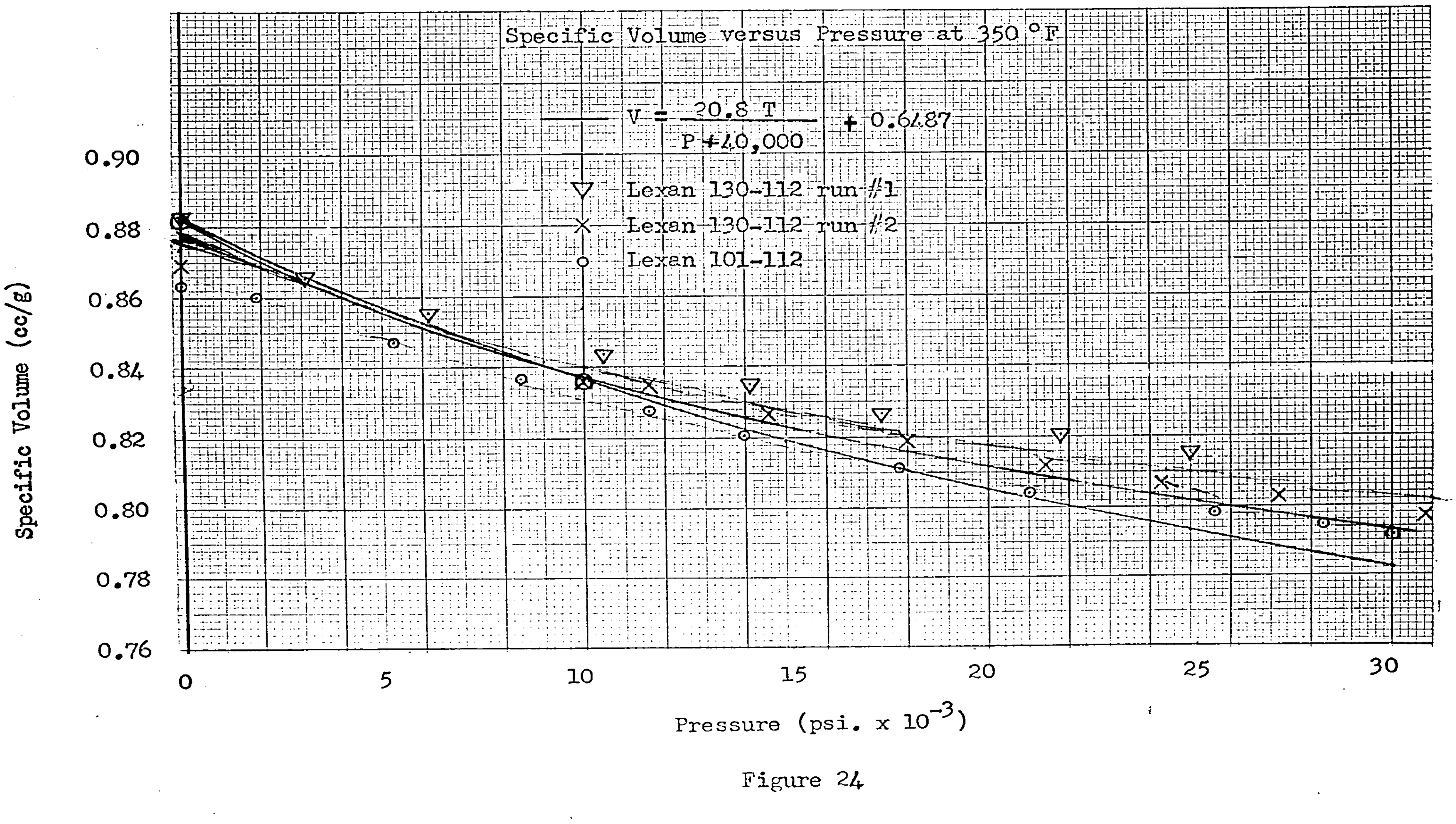
Specific Volume versus Pressure at 350 °F
V = 20.8 T / (P + 40,000) + 0.6487
Lexan 130-112 run #1
Lexan 130-112 run #2
Lexan 101-112
Specific Volume (cc/g)
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
0
5
10
15
20
25
30
Pressure (psi. x 10^-3)

Figure 24

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## TABLE XIII.

### Pressure versus Bulk Modulus

| 300°F | | 350°F | |
|---|---|---|---|
| Pressure $\bar{P}$ (psi.) | Bulk Modulus K $1/\beta$ = psi.x$10^{-5}$ | Pressure $\bar{P}$ (psi.) | Bulk Modulus K $1/\beta$ = psi.x$10^{-5}$ |
| | Lexan 101-112 | | |
| 4,345 | 2.304 | 3,585 | 2.226 |
| 7,820 | 3.241 | 6,855 | 2.627 |
| 11,690 | 5.461 | 10,045 | 3,194 |
| 15,505 | 5.531 | 12,900 | 2.851 |
| 18,505 | 5.345 | 15,875 | 3.615 |
| 22,025 | 7.148 | 19,400 | 3.706 |
| 26,610 | 7.570 | 23,800 | 8.285 |
| 21,430 | 6.398 | 27,450 | 4.290 |
| | | 24,650 | 6.812 |
| | | 23,050 | 5.426 |
| | Lexan 130-112 | | |
| 1,615 | 1.752 | 1,810 | 1.802 |
| 4,515 | 2.769 | 4,640 | 2.711 |
| 7,890 | 3.664 | 8,315 | 3.229 |
| 11,810 | 3.027 | 12,290 | 3.655 |
| 16,550 | 8.467 | 15,730 | 3.388 |
| 20,355 | 3.500 | 19,565 | 6.427 ← |
| 23,450 | 5.942 | 23,385 | 5.966 |
| 27,330 | 7.981 | | |
| | | | |
| 2,905 | 2.477 | 10,330 | 3.318 |
| 6,050 | 3,385 | 13,640 | 3.063 |
| 9,250 | 3.552 | 16,310 | 3.623 |
| 12,175 | 6.097 | 19,710 | 4.321 |
| 15,175 | 5.452 | 22,875 | 5.274 |
| 17,985 | 6.031 | 25,765 | 6.345 |
| 20,990 | 5.230 | 29,030 | 6.725 |
| 24,085 | 6.270 | | |
| 27,670 | 7.893 | | |

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III $$-\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right) = \frac{0.4343c}{b+P} = \beta$$

where is the compressibility. Taking the inverse of equation III,

IV $$K = 1/\beta = \frac{b}{0.4343c} + \frac{P}{0.4343c},$$ we obtain an equation of a straight line for the bulk modulus, K. Obviously, plotting the bulk modulus, K, against the pressure P, should yield a straight line by which the constant C could be evaluated from the slope of the plot and b could be calculated from the intercept. Note, however, that the equation predicts only one straight line. What happens if there is a discontinuity, i. e., a change in slope and a change in intercept from a certain group of points? The obvious conclusion is that the K versus P relationship or mechanism has changed. It is this result that is of importance to us here since it allows one to approximate the second order transition pressure for a material above the glass transition temperature.

In Table XIII the bulk modulus and corresponding pressures are tabulated for all points obtained on the Lexan above the second order transition temperature. Figures 25 and 26 contain plots of bulk modulus versus pressure for temperatures of 300 and 350°F, respectively. In both figures it can be seen that there is a discontinuity at about 15,000 psi. It is about this pressure where the material changes from its

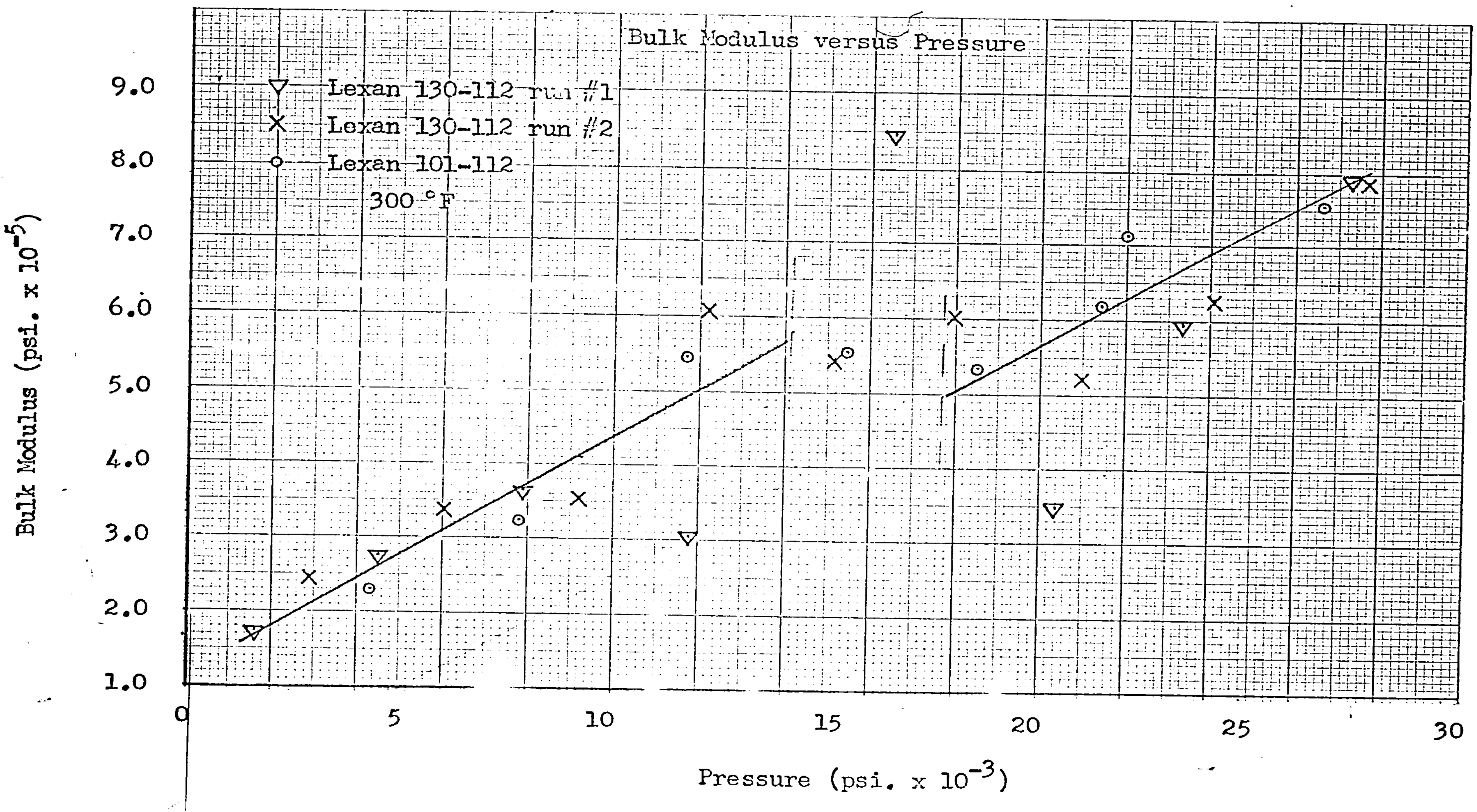
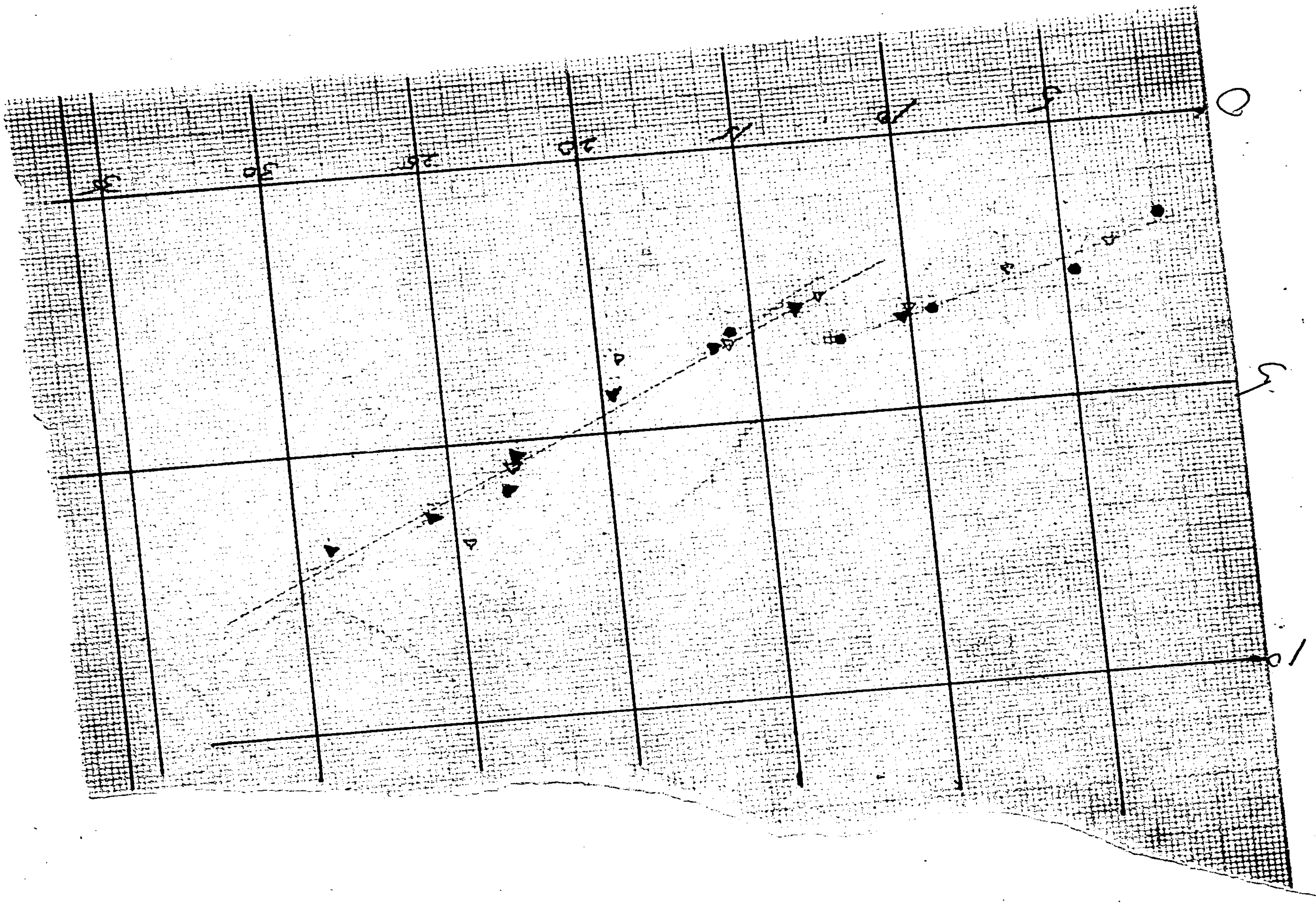

Bulk Modulus versus Pressure
▽ Lexan 130-112 run #1
X Lexan 130-112 run #2
○ Lexan 101-112
300 °F
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Bulk Modulus (psi. x $10^{-5}$)
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 25


35
30
25
20
15
10
5
0

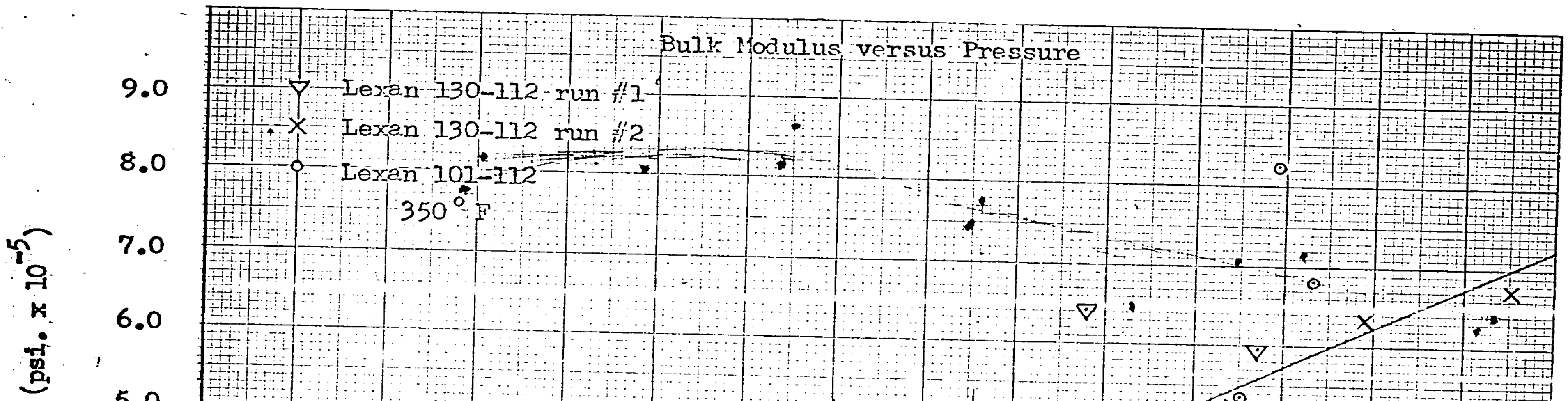

Bulk Modulus versus Pressure
▽ Lexan 130-112 run #1
× Lexan 130-112 run #2
○ Lexan 101-112
350 °F
Bulk Modulus (psi. x $10^{-5}$)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5
10
15
20
25
30
Pressure (psi. x $10^{-3}$)

Figure 26

rubbery state to its glassy state. To exactly pinpoint the transition pressure several points obtained near this pressure are needed to eliminate the range of uncertainty.

## Discussion of Results

The experimental work performed on Lexan tends to substantiate the prior work performed on high molecular weight amorphous polymers. The compressibility is readily seen to be a function of more than one mechanism as proposed by Simha. One mechanism is that of molecular size due to thermal energy acting similar to a molecule in a lattice sight. This mechanism is predominate at lower temperatures and accounts for the difference in the compressibility with average molecular weight. As the temperature increases each molecule becomes more mobile and begins to acquire enough agility to actually rearrange segments of itself to make itself small under increasing pressure. With increasing temperature the molecule tends to become larger; with increasing pressure to become smaller. For Lexan, a temperature of about 200°F gives the molecule enough mobility so that the difference in compressibility with different molecular weight samples approaches zero.

Of course, above the glass transition temperature the type of mechanism that predominates is that of molecular rearrangement. In the lower pressure ranges above this temperature the large effects of this mechanism are clearly demonstrated with values of compressibility four to five times that at the lower temperatures.

The possibility of a change in state with increasing pressure is substantiated when the data is applied to the Tait relationship. There is no question that there are two lines formed each having a different slope and intercept which can only indicate that some internal change of mechanism has occured. In this case, a change from a rubbery state at low pressures to a glassy state at high pressures.

The inability of the derived van der waal's equation to satisfactorily fit the data demonstrates the superficial nature of the model. The model is far too simple to accurately represent the complex interaction of a polymeric material. The adjusted equation of this type was able to approximate the volume-pressure relationship sufficiently for engineering applications. In the cirtical pressure range, i. e., 10,000 to 20,000 psi. where the majority of Lexan is processed, the accuracy of the equation is quite good. At higher temperatures the fit could be improved.

Molecular weight has been shown to have a negligible effect on the P-V-T properties at elevated temperature. This does not imply, however, that a Lexan polymer of extremely high molecular weight (or low molecular weight) will follow this equation. This equation was developed for the commercially obtainable grades of bisphenol A polycarbonate. These grades generally include average molecular weights of 32,000 to 42,000. Outside this weight range the properties of the material make it difficult to fabricate and hence these extremes are used only for very special applications. Generally speaking, the equation derived here, and those developed earlier by Spencer and Gilmore, should be valid if the material is within ±15 percent of the molecular weights tested, which includes most of the commercially available materials.

Observed, but not investigated during the course of the experiment, was a "hysteresis effect" on the volume of the sample depending on whether or not the volume at a point was taken while increasing the pressure or decreasing the pressure. The volume of the polymer sample during a decreasing pressure run was found to be from 30 percent to 40 percent of the total volume change due to 30,000 psi. greater than at a corresponding point during an increasing pressure measurement. A similar run was made on a cylindrical sample of brass and the difference had a maximum of 4 percent difference based on the total volume change over the entire pressure range. The polymer molecule which tends to rearrange itself upon compression and become smaller apparently does not contain sufficient energy to extend itself when part of the pressure is released to attain the state achieved with increasing pressure measurement. It does exhibit a "memory" since it returns to its original volume when all pressure is removed.

## Conclusions

From the P-V-T data gathered in this project the following conclusions can be drawn.

1.) For temperatures above the glass transition temperature the compressibility of commercially available Lexan is essentially independent of molecular weight.

2.) Combined with the work of Spencer and Gilmore on polystyrene, one may deduce a trend that indicates that most commercial high molecular weight amorphous polymers will have compressibilities independent of molecular weight at temperatures above the second order transition temperature.

3.) At temperatures well below the glass transition temperature the Lexan having the highest average molecular weight had a compressibility higher than the compressibility for the lower molecular weight material. The difference averages to approximately 25 percent.

4.) The modified van dar Waal's equation $(P+40,00)(V-0.6487)=20.8T$ will describe the behavior of the bisphenol A polycarbonate above the glass transition temperature.

5.) It has been verified that at temperatures above the glass transition temperature, the Tait Equation, when rearranged in a form relating the bulk modulus to the pressure, will indicate a pressure at which Lexan changes from a rubbery material to a glassy material. This second order transition pressure was found to be about 15,000 psi. for temperatures between 300 and 350°F.

## Nomenclature

$b$ - constant

$c$ - constant

$g$ - stress-strain correction factor constant

$K$ - bulk modulus

$l$ - stretched length

$l_o$ - unstretched length

$M$ - molecular interaction unit

$M_c$ - molecular weight of a ropeat unit

$P$ - pressure (psi.)

$R$ - gas constant

$T$ - temperature (absolute)

$v$ - number of moles of molecular interaction segments

$V$ - volume (cc/g)

$V_o$ - volume at zero pressure

$V_1$ - volume at one atmosphere pressure

$\beta$ - compressibility (psi.$^{-1}$)

$\pi$ - "internal" pressure constant (psi.)

$\tau$ - tension

$\omega$ - volume at zero degrees Kelvin

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## Vita

The author was born in Jamestown, New York, on May 6, 1940. He graduated from Jamestown High School in June, 1958.

He enrolled in Bucknell Universities' five year engineering program for the B.A. and B.S. degrees in Chemical Engineering and was graduated in June, 1963.

In the fall of 1963 he entered Lehigh University to pursue a course of study leading to the Master of Science Degree in Chemical Engineering.