Corrections:

Page 22 and 23

Pipette instead of(pysette)

Page 29

Warren De Sorbo instead of (Warren De Sabo)

Elasticity of Silicic Acid Gel

This Thesis is presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for degree of Bachelor of Arts (A.B), major in chemistry.

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INTRODUCTION

"Ceiinosssttuu, id est, Ut tensio sic vis" (9)

When Robert Hooke published his "Description of Helioscopes" in 1676 the quotation above appeared on page 31- translated - "The power of any Spring is in the same proportion with the tension therein." He formulaged his theory from experimental results.

It remained for Young, nearly a century and half later, to interpret Hooke's results in the generalized sense known today. Young defined the modulus, now known by his name, as the ratio of the force, causing elongation or compression, over the increment of expansion or contraction produced by it.

When a portion of matter is under the influence of a force tending to change its shape or size, it is said to be under <u>stress</u> while the accompanying distortion or volume change is called the <u>strain</u>.

A mixture of silicate, acid, and water trangresses, with elapse of time, into a jelly-like substance called 'gel' Its specific properties depend upon the previous history and age of the gel.

To find the characteristic behavior of the elasticity of silicic acid gel, with consideration of the usual variables, is the essence of this research.

$$\text{Elasticity} = \frac{\text{stress}}{\text{strain}}$$

HISTORICAL:

Investigation of the properties of a number of materials, i.e., coiled spring drawn out, stretching of a suspended wire, sagging of a beam between supports, led Robert Hooke in 1676 to enunciate his now famous law. Within the specified limits of an elastic body, the stress is proportional to the strain.

The varied number of experiments by countless observers have led to the establishment of Hooke's law as an experimental fact. Continued experiments of this phenomenon gave rise to hypothesis and later to a mathematical theory of elasticity.

Boscovitch, Poisson, Cauchy and Navier were the pioneers in the mathematical analysis of internal forces. It is with due respect that I mention here some of the greatest men who were responsible not only for a clearer understanding of the properties of a solid through mathematical treatment, but also for their great contributions to higher calculus. It was through the efforts of Cauchy, Green, Stokes, Maxwell, Thomson and others that every branch of science today can postulate and interpret results by means of mathematical analysis.

Correlation and an understanding of the fundamental concepts of matter soon led to a mathematical theory independent of the origin of stress. Having once established Hooke's law, independent of the origin of stress, the properties of a solid can be determined from very little data.

Over 1,000,000 years ago the first silicic acid gel was formed. Oxides of silicon formed colloidal solutions which under the proper conditions settled out in jelly-like mass. Dehydration and latter crystal formation changed the gel into Quartz and derivatives. Yet to-day all the properties and characteristics of the gel are not fully known.

That silicic acid gel was elastic was one of the first things observed. It was noticed that the gel when pressure (limited) was applied, would change shape but return to normal with release of the pressure.

Little work was done on the elastic properties of gels before the 19th century. Some of the pioneers were Villari, Rontgen, Russner, Lemdal and others. Their investigations were mainly qualitative in nature.

In 1919 (6) it was noticed that a definite musical note was produced when test tubes of silicic acid gel were struck. Further investigation showed that the frequency of vibration is determined by the properties of the gel. Decrease in concentration of silica (in-crease in acid concentration) produces an increase in vibration.

A rather ingenious method was devised by Freundlich & Leifris (5) to determine the relative measurement of the elastic modulus and elastic limit of sols and gels. A particle suspended in the gel was displaced by a magnetic force. The particle size being constant, the elastic displacement, X, and the distance, r, from the from the magnet are connected by the relation $xr^2 = K$ (constant). The elastic modulus is then expressed as $1/xr^2$.

The most intensive work on the elasticity of silicic acid gels was done by Prasad (13). A rod shape gel, removed from its container, was fastened by one end to a table, its other end, in a verticle position, was free. A piece of paper, with a mark to serve as reference, was placed near the top of the free end. By means of a leather throng, a small aluminum pan, in which weights were placed, was fastened to the free end. All precautionary measures were taken to reduce to a minimum the effect of the weight of the throng and pan, as well as, other variable factors. The compression was determined with a Kalthetometer, a microscope which can be moved vertically with the help of a round graduated screw, reading to .0005cm. calipers were used to measure the cross section and length of gel from the supported end to the free end. The load on the free end was continuously increased by the addition of 1 gm. weights. Inspection of the graph showed that the first part of the curve obeyed Hooke's law. As the weights increased the elastic boundary was overstepped and the gel broke. The elasticity was figured according to the following formula:

$$E = \frac{4\ mgl^3}{3\ a^4d}$$

In order to give you an idea of the results obtained by Prasad (13) the following table was taken from the Kolloid Z.

Table 1.

No. of runs	Time	Silicic Acid	Other Phase	Elasticity
1	28hrs. 15'	2.18g	54.82	1.834×10^5
1	39 " 0'	2.18g	48.82	2.844×10^5
2	47 " 30'	2.18g	44.82	5.955×10^5
1	52 " 0'	2.18g	36.32	8.901×10^5
2	48 " 0'	2.18g	32.32	14.330×10^5

From his elasticity values, Prasad (13) calculated the velocity sound would have through silicic acid medium by means of the formula $V = \sqrt{\frac{E}{D}}$ where V = Velocity, E = elasticity, D = density.

Although the following does not pertain directly to silicic acid gels, I thought it would be of interest to describe briefly a method used by Sheppard and Sweet (15) to measure the elasticity of gelatin gels. The jelly formed in a cylindrical split jacket mold, was placed in the torsion machine invented by Sheppard. A worm drive, operated either by hand, or a constant speed electric motor, rotated the base at a constant angular speed twisting the jelly cylinder. The circular base was graduated in degrees. The test cylinder also carries a circular graduated scale. Briefly, a lever arm moved along a scale to measure the difference in the two readings.

Using an entirely different method, Kroger and Fischer (10) at University of Leipzig measured the elastic properties of silicic acid gels by the bending rod method. Rectanular bars of gel were placed on 2 horizontal, parallel copper amalgam supports. Weights were placed on the gel causing it to sag or bend. The amount of bending or displacement was measured by the optical lever (20). By use of this method, it was found that equally old gels have about the same elasticity.

The reason for such a long historical account seems justified if the reader has acquired at least one of the following:

(1) A clearer understanding of elasticity.

(2) Become acquainted with methods of measurement and their results.

(3) An idea which might be of practical value in research.

THEORETICAL

Interatomic forces define the relationship between atoms and molecules from which matter is constructed. Any change of the external forces on a body may, or may not, cause a deformation of structure, but; its influence is transmitted to the molecules and atoms. When displaced molecules tend to regain their normal position, the body is said to be in a condition of strain.

Nearly every phase of industry is primarily interested in equilibrium conditions. Equilibrium is the resultant of all existing forces while a condition is the particular mode of the force. The probing into effect of conditions on materials and searching to find a correlating relationship forms the basic foundation of Progress.

The property of regaining the original shape when the former conditions are restored is known as elasticity. Because of the specific characteristics of matter within known limits, all material shows elastic properties although the range of elasticity may vary greatly with the material.

Deformation designates the change in the shape of a body caused by the application of external forces. " The deformation accompanying tension, compression, and shear are known respectively as elongation shortening and detrusion" (4).

The resultant internal force that resists the change produced by an external force is called stress. Victor

THEORETICAL CONT'D.

analysis of this resultant applies the name of normal stress to the normal component and shearing stress to the tangent component unit stress is defined to be stress per unit area which may be expressed in pounds per square inch (lbs./ in ^{2}), tons per square foot (tons/ft.^{2}), kilograms per square centimeter (kg/cm^2), and the like. (4).

Within the limit of elasticity, the ratio of stress to strain is known as the modulus of elasticity or Young's Modulus. Expressed matematically Young's Modulus for compression, or expansion is written

$$E = \frac{S}{E} = \frac{F/A}{e/l}$$

F = applied force
A = area
e = change in length
l = length
S = stress
E = strain

The shear formula written symbolically is :

$$E = \frac{\text{Unit shearing stress}}{\text{Unit detrusion}} = \frac{F/A}{a/l} = \frac{Fl}{aA}$$

F = force applied.
A = area
a = detrusion
l = length or height

The modulus of shear elasticity may be called the Modulus of rigidity. (19).

A body undergoing some deformation is under strain, whil e a body subjected to an external force is under stress.

MISCELLANEOUS

A. Formation:

Silicia gel is usually prepared by adding silicate (water glass) to an acid solution and allowing to stand. Hydrolysis of some silicon compounds, silicon tetrachoride, silicon sulfide, ethyl silicate and others produce a jelly. The jelly may also be produced by dialysis of silica sol. (18).

B. Composition:

Variation of the ratio of silicate to acid to water determines most of the specific properties of silica gel. The following references may be of use if you are interested. (1), (18), (16), (11), (2).

C. Chemical Properties:

"The freshly formed oxide consists of crystalline centers of cristobalite" (16). The increase of viscosity, caused by initial growth of crystals, prevents free movement of atoms and molecules. The previous history of the gel determines to a marked degree the gel characteristics.

D. Elasticity:

A freshly prepared gel seems to possess the same order of magnitude as that of gelatin. Under certain conditions the gel will vibrate, producing a musical note when struck.

E. Gel, theory of structure:

(1) Micillar theory assumes a discontinuous granular

MISCELLANEOUS CONT'D.

solid phase dispersed in a liquid phase- Frankenheim (1835) (1).

(2) Filbrillar theory differs from the Micillar theory in that the solid phase is assumed to be continuous - Van Bemmelen (1898) (1)

(3) Liquid-liquid theory was proposed by Ostwald (1) who suggested that the gel was the limiting case of a viscous liquid.

(4) Solid solution theory, supported by Procter (1914), (1), is as the name signifies a solid solution.

(5) Poly-silica condensation theory has been proposed by Hurd (7) to explain the mechanism for the assumed formation of the fibrillar structure.

F. Hydration and Dehydration of Silicic Acid Gel.

Van Bemmelen (17), first one to make a systematic and exhaustive investigation, studied the effect of dehydration and hydration on the properties of the gel. The results of his work brought to light the possibilities of silica gel in industry. This stimulus led to further investigation by many workers.

G. Syneresis:

While the gel is aging, the structure contracts with the expulsion of H2O.

H. Uses of:

Activated silica is rapidly replacing some of the absorbing agents, charcoal, clay, filters, finely divided metals and the like, in industry. Silica seems to have

MISCELLANEOUS CONT'D.

an infinity for nearly all vapors. Hospitals, Drug Companies, Cable Manufacturers, Gasoline Crackers, the navy and many other concerns use silica to take moisture out of air. But its use is not limited to just acting as water absorber.

I. Other Properties:

Although I am not going to mention the numerous other properties of silica gel even briefly, I think it would be of interest to the reader to become acquainted with the different aspects and uses of silica. The list of references under the bibliography may prove helpful. Look also in the chemical abstracts, a resume of nearly all work done by investigators as well as reference to original.

APPARATUS:

In the research lab. was a machine devised by Dr. Hurd (head of the Chemistry Department) to study the elastic properties of silicic acid gel. Perhaps a diagram will be clearer than a word description, for this reason a diagram is shown on the following page.

After gelation occurred, the steel wire was twisted by E, producing a torque in C, thus setting up a stress in the gel. The amount of strain was measured by light reflected from mirror to a scale.

A few measurements were made with the apparatus but because a number of factors, strain, amount of stress and the like, were beyond too accurate control and only relative measurements could be obtained without controlled calibration.

The a dhesion force between brass and silica gel is appreciable but to find out what material had more or less adhension force than brass a number of tests were made. Cylinders were made from glass, aluminum, balsa, rubber fiber composition, bakelite, iron. For cylinders of the same size the adhesion force seemed to decrease in the following order: brass- glass- rubber fiber composition- iron- aluminum-balsa.

Diagram Number 2, shows method which was devised by the writer with criticism and suggestions given by my roommate, Franklin Connor, an electrical engineer. The ball bearings permitted movement of the steel rod while at the same time held it in a verticle position.

APPARATUS CONT'D.

The pulley E made from masonite, served as a lever arm. Weights attached to the silk thread produced a torgue in the cylinder, thus, setting up a stress in the gel. Light reflected from the mirror to a graduated scale measured the amount of strain produced.

By a mathematical treatment of the forces involved it was possible to find the shear elasticity by the by the following formula;

$$E = \frac{T}{4\pi\theta L}\left(\frac{b^2 - a^2}{a^2\ b^2}\right)$$

The derivation of the above formula will be given later. Although it was possible to find the elasticity and the way the elasticity changed with time, I still was not satisfied. It meant measuring b, a, and L and taking the average value of each, everytime a different gel was used. It may appear to be easy but try it without expensive equipment. An error of .001 of an inch in any one measurement would throw the results in error by more than 5%. Also the starting friction of the bearings under different weight loads had to be calibrated. It was of the utmost importance that the apparatus remain in a verticle position without moving during the run. There were also a number of minor snags to overcome.

Improvements were made, kinks were straightened out, everything which might produce a sizable error was

APPARATUS CONT'D.

reduced to a minimum and taken into consideration in the calculation. Yet I was not satisfied. There are plenty of ways that elasticity might be measured but it costs money to construct the apparatus. I had nearly given up hope of trying to obtain a better method when, in every day terminology, I was struck by an idea. The result of which is shown in diagram number 3.

Material used:

(1) Rolled brass tubing, made by G.E., height 7", inside diameter 2.750", thickness ¼".

(2) Brass cylinder, made by G.E., height 6", outside diameter 1.240".

(3) Pivots made from steel drill rod, ¼" stock.

(4) Brass plate, form bottom of tubing, 6" by 4" by ¼".

(5) Brass plate, used for top, cut in form of circle, 3¼"X ¼"

(6) Threaded piece of drill rod, screw head, notched at other end to serve as pivot slot.

(7) Masonite wheel, lever arm, 1.437" by ½"

(8) Mirrors, cut from microscope slides and silvered 1" by 3/10".

(9) Brass plugs to act as pivot holders were brazened into small cylinder.

(10) Scale, made from graph paper divided into tenths.

(11) Lens, to focus light beam, for a length 20"

(12) Small rectangular platform with leveling screws.

(13) Pulleys- a 3" wheel pressed over drill rod with pivot ends.

APPARATUS CONT'D.

Material used continued.

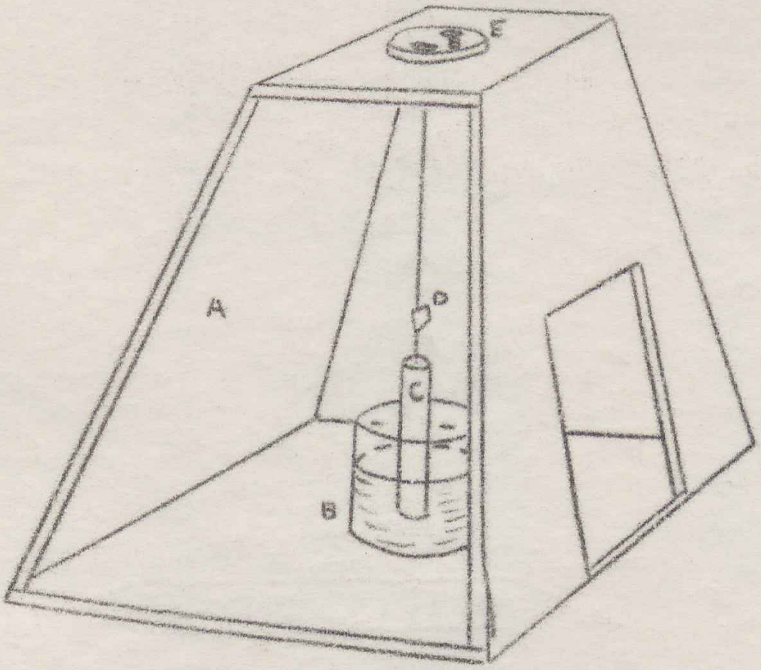
(14) Pans made from wire mesh with sides turned up.

(15) Celluloid placed in bottom of each pan.

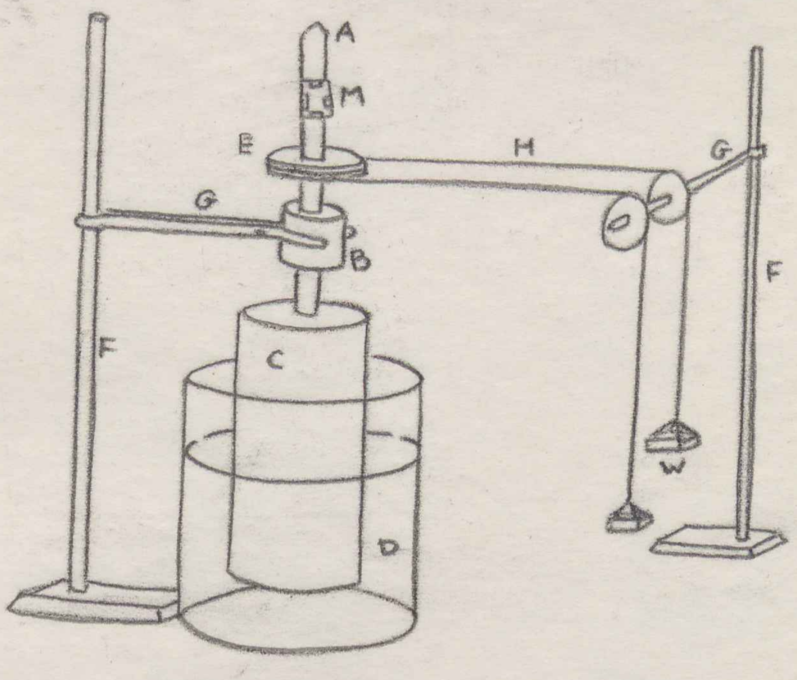
(16) Silk cord to go around wheel, over pulleys, weights attached to ends.

All work was carefully measured--placed in lathe for centering and truing--exceptional care taken in construction--all joints were brazened. At this time, thanks is given to Mr. Sommerman, Machinist, for his assistance in construction.

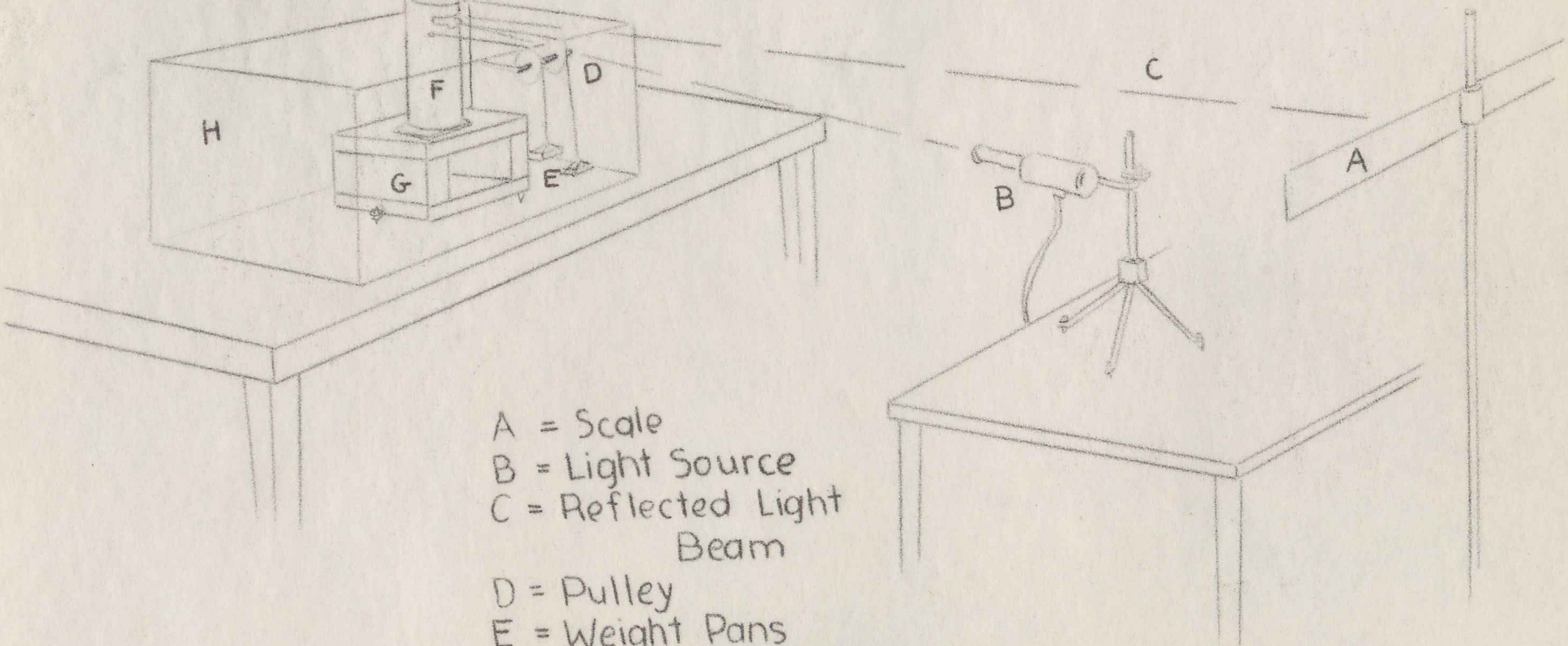
I think the diagrams along with material used are self-explanatory.



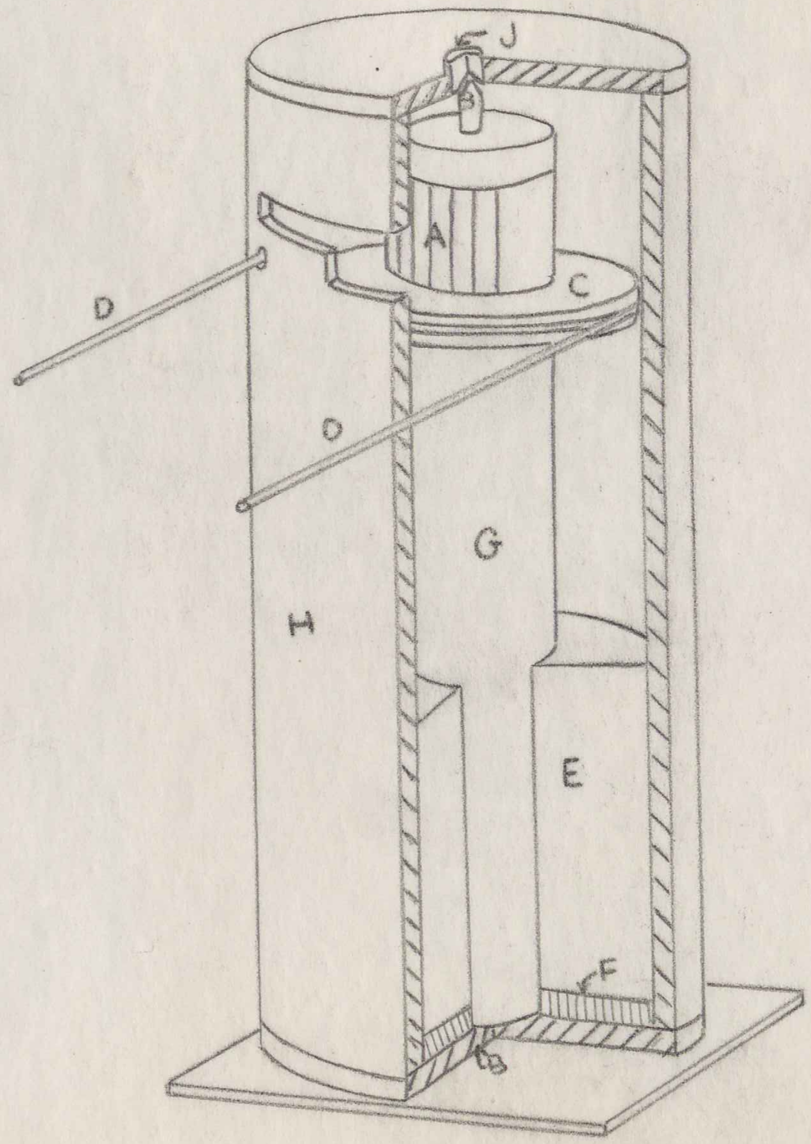
A = Trapezoid Frame
B = Glass Beaker of Silicic Acid
C = Brass Cylinder
D = Reflecting Mirror
E = Graduated Lever Arm



A = Steel Rod
B = Ball Bearing Holder
C = Cylinder
D = Glass Beaker of Silicic Acid
E = Pulley
F = Standard
G = Holders
H = Silk Cord
W = Weights and Pans
M = Mirror

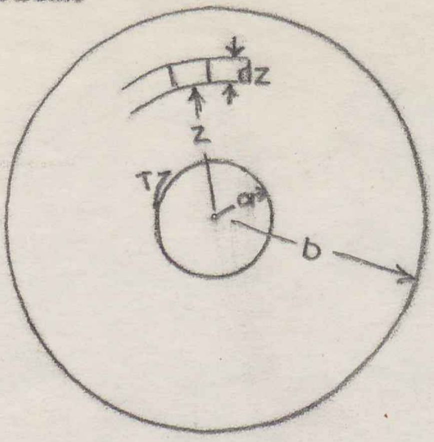


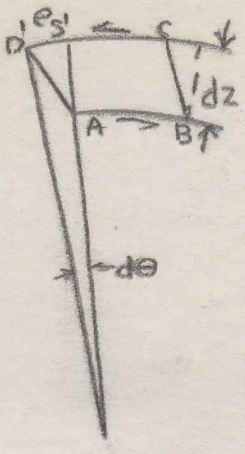
A = Scale
B = Light Source
C = Reflected Light Beam
D = Pulley
E = Weight Pans
F = Elasticity Machine
G = Adjustable Platform
H = Glass Water Bath

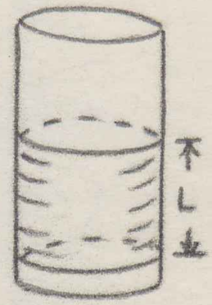


A - Mirror
B - Pivots
C - Wheel
D - Silk Cord
E - Gel
F - Mercury
G - Inside Cylinder
H - Outside Cylinder
J - Adjustable Pivot Holder

Derivation:







Given:

Torque - T - force x lever arm

b - radius (inside) of larger cylinder

a - radius (outside) of smaller cylinder

x - distance from center of d-area upon which force acts

e_s - shearing unit-strain

L - height of gel

s_s - unit- stress

The d-area, ABCD, subjected to shear is considered a layer sliding a relative amount to the layer in front of it.

Hence:

$$\tan d\theta = \frac{e_s}{x} = E_s$$

$$\sum \text{area of shear} = 2\pi xL$$

$$s_s = \frac{F_x}{A} = \frac{T/x}{2\pi xL} = \frac{T}{2\pi x^2 L}$$

$$E_s = \frac{s_s}{e_s} = \frac{Tdx}{2\pi e_s x^2 L}$$

$$e_s = \frac{Tdx}{2\pi x^2 L E_s}$$

$$\tan d\theta = \frac{Tdx}{2\pi E_s x^3 L} = d\theta \text{ (in radians)}$$

$$\theta = \int_a^b \frac{T}{2\pi E_s L}\frac{dx}{x^3} = \frac{T}{2\pi E_s L}\left(\frac{-1}{2x^2}\right)\Bigg|_a^b = \frac{T}{4\pi E_s L}\left(\frac{b^2 - a^2}{a^2 b^2}\right)$$

$$\therefore E_s = \frac{T}{4\pi\theta L}\left(\frac{b^2 - a^2}{a^2 b^2}\right)$$ where θ is measured in radians.

EXPERIMENTAL PROCEDURE:

The reaction between acetic acid and sodium silicate is of such a nature that a gel is formed. The sodium silicate used was the "E" Brand produced by the Philadelphia Quartz Co. Distilled water was used to dilute Glacial Acetic Acid to 0.155N.- titrated against standard Na OH. The normality of sodium silicate, after dilution with distilled water, was 1.327N. when titrated against standard H_2SO_4 using M. O. as indicator.

The HAc and distilled H_2O were measured volumetrically by burettes -- the silicate by pysette.

When the acid and silicate had reached the same temperature, they were mixed by pouring back and forth.

To measure PH of each solution, the Quinhydrone electrode was used. The equilibrium between Hydroquinone and Quinone shifts with change in PH or hydrogenion concentration. A platinum wire placed in a solution containing Hydroquinone acquises a potential depending on the ratio of oxidized to the reduced form which is a measure of PH.

The PH was determined by measurement of the potential of the Quinhydrone electrode in combination with a standard saturated calomel half cell. If desirous of further information see Daniels.(23).

The potential was measured by a Leeds and Northrup instrument designed for PH measurement.

The time of 'set' was determined by a method developed by Hurd and Miller. A pointed glass rod 9cm. long and 3 mm in diameter is inserted into gel at about 15° to

Experimental Procedure cont'd.

vertical. The gel is 'set' if the rod does not topple. As soon as the acid and silicate were thoroughly mixed, 100cc of the solution, measured by pysette, was placed in the apparatus of the remaining solution, 50cc was set aside to test for 'time of sets', the rest placed in a beaker for PH measurement.

I was fortunate to have the use of the 'dark room', a room used for developing pictures, in order to cut out reflected light.

The apparatus was placed against one wall, the scale against the opposite wall.

The scale was made from graph paper divided into tenths of an inch. By making use of the hair line in the lens of the light source, it was possible to read to a fiftieth and estimate to a hundredth of an inch.

By constructing the pans out of wire mesh, it was not very difficult to make them of identical weight. The friction of each pulley and the pulleys in combination with the pivoting cylinder were calibrated.

The distance between the mirror and the scale (74.55") was carefully measured and checked. The light source, reflecting mirror and zero reading on scale were so placed as to be in a straight line. This was necessary in order that the angle of deflection would give the correct value of the angle through which the gel was twisted.

Once the solution was placed in the apparatus and a few routine details taken care of, it was only necessary to place weights on the pan, record the time and measure the deflection. Well, it was almost as simple as that.

Experimental Procedure cont'd.

Perhaps by looking at the diagrams under the title apparatus again, the general procedure will be clearer.

EXPERIMENTAL RESULTS:

The criterion of elasticity is the ability of a body to regain its original shape. The elastic limit is the maximum unit stress to which a body can be subjected and still regain the original form with removal of the stress.

A deformation becomes plastic, when the elastic limit has been exceeded and no complete recovery, with release of stress.

There is no distinct transgression between viscosity and elasticity or plasticity. After mixing, the viscosity of the solution gradually increases to a point where that property is now thought of as plasticity or elasticity. Yet it is possible for a gel to show all 3 properties simultaneously.

Because of the relationship of the 3 properties along with their intermediate transgressions, it is not possible to give a sharp distinction between any two of them.

Although I will mention the high points and some information which the data and graphs do not show, analysis of the data and curves is the best criterion of the results obtained.

(1) Silicic acid gel has elasticity.

(2) The stress-strain relationship obeys Hooke's law as long as the elastic limit is not exceeded.

(3) Elastic deformation, plastic deformation, elastic flow and plastic flow all coexist under certain conditions.

EXPERIMENTAL RESULTS CONT'D.

(4) In some cases the elastic deformation was followed by a plastic flow or deformation which gradually slowed until a point was reached which was not exceeded with elapse of time even though the elastic limit had been over stepped. With release of the stress, the elastic recovery was followed by elastic after effect and, as time went on, with nearly complete recovery of original conditions or shape.

(5) In most cases, after the elastic-limit had been overstepped, the plastic flow proceeded at a constant rate until the stress was removed.

(6) It was noticed that if the stress more than exceeded the elastic-limit the plastic flow (moving slightly faster than in the preceeding case) was constant but every so often the deflected light shultered back and forth within a very short range, then continue on as before.

(7) Elasticity, or Young's Modulus increases with time and eventually approaches a constant limit.

(8) There seems to be no direct relationship between the elasticity and PH.

(9) Gels of PH, around 6, were capable of being deformed to a greater extent and still return to original shape, than, gels whose PH was not in this neighborhood.

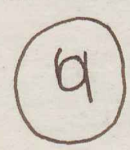
(10) As a rule, the alkaline gels showed greater plasticity than elasticity characteristics.

EXPERIMENTAL RESULTS CONT'D.

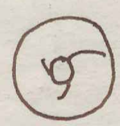
(11) Measurements made by Hurd's machine showed the following characteristics:

(a) The gel structure when too much stress was applied broke in patterns which differed with PH.

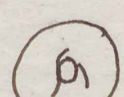
(b) The alkaline gels, in most cases, never had the same pattern twice even though identical solutions were used. The following is a typical pattern:



(c) As the PH decreased into the acid side, a definite pattern, reproducable within the limit of experimental errors, became apparent. Example:



(d) As the PH decreased still lower, the pattern of breakage seemed to be a combination of the above two. Example:



Calculations:

$$E_s = \frac{W}{D} K \qquad K = 2.3245$$

$$= \frac{2.3245W}{D} \quad \text{grams/ inch.}^2$$

Calculation of max. possible error:

(1) of K $\quad K = \dfrac{(1.219\ .002\%)(2.60\ .006\%)(b^2\ .00001\%\ a^2\ .00001\%)}{4\pi^2(1.29 \pm .002\%)(b^2\ a^2 \pm 1\times10^{-10}\%)}$

error of K = $\sqrt{(.002)^2\ (.006)^2\ (.002)^2} = .007\%$

(2) of $\frac{W}{D}$ $\quad \frac{W}{D} = \dfrac{(\text{grams}\ .005\%)}{(\text{inches}^2\ .01'')}$

It is noticed at once that the error in calculation is principally determined by the amount or size of deflection.

For very small deflections the error is large and it decreases as the amount of deflection increases.

Therefore the maximum possible error will be left in the following form:

$$E_s = \frac{W\ K}{(D \pm .01'')}$$

With consideration of the errors involved, the elasticity of the gel, 2 hours after gelation by rod method, is given below.

Run # 2	E_s =	127..4	grams/inch2
# 3	" =	253 .3	"
# 4	" =	282 7.1	"
# 5	" =	348 5.4	"
# 6	" =	102 1.0	"
# 7	" =	180 12.	"
# 8	" =	333 12.	"
# 9	" =	141 17.	"
# 10	" =	339 34.	"
# 11	" =	906 91.	"

MISCELLANEOUS OBSERVATIONS:

(1) It was noticed in some of the acid gels but more so in the alkaline gels that the pitch varied with aged gel. As the gel became older, the note seemed to reach a maximum, then fall to a minimum, later to be followed by an increase. Unfortunately no data was taken, it was merely a curiosity observation. Perhaps it would be of interest to check this phenomenon to see if this really does take place.

(2) Being interested mainly in what happens when the gel is under strain, by observing between crossed Pollariods, it was found that the reflected light at nearly right angles to the transmitting beam is plane pollarized. Also the reflected light at about 60° to transmitting beam is partially pollarized, upon showing the above observations to Dr. Langmiur, he proposed that the mere fact of plane polarized light in reflected beam suggests a crystalline network of almost uniform structure. This phenomenon might lead to interesting possibilities. I suggest something of the following nature might be easily carried out. Warren De Sabo conducted a research on the amount of transmitted light and the amount of reflected light by means of photo electric cells. Use a similar hook up but place a pollaroid lens between the gel and photo electric cell. By this means the time when extinction is reached can easily be determined. Such a determination might give an added clue to the

MISCELLANEOUS OBSERVATIONS: cont'd.

internal structure of silicic acid.

(3) Since viscosity and elasticity are related, I was interested in finding a simple way to obtain viscosity measurements. A number of ideas were thought of, some correlated the general principles of the methods now used to measure viscosity, others were too impractical; but, most of all, I didn't have the time to spend since I already had a research problem over which I was pulling my hair out. To answer a question, how is the elasticity effected if there is a change in any of the conditions, under which the gel is formed, I changed at least one of the conditions radically. After mixing the silicate and acid in the usual manner, ½ of the solution was placed in a beaker to set undisturbed the remaining solution, placed in an erlenmeyer flask, was stirred rapidly (3600 R.P.M.) by a stirrer attached to a small electric motor. The following data observed:

(1) The solution became gradually more viscous. The part of the solution near the top of the erlenmeyer thickened into a jelly-like mass before the solution in the beaker formed a gel.
(2) After stirring the solution twice as long as it took the gel in the beaker to set, the resulting thickened mass behaved like heavy grease.
(3) Upon standing, it did not dry up as rapidly (only about one-third as fast) as the gel in the beaker.

MISCELLANEOUS OBSERVATIONS; cont'd.

(4) Its elasticity was more like that of rubber in certain respects.

I discussed the above phenomena and its possibilities with Dr. Langmium who later suggested to Dr. Hurd a method for experimenting. Briefly, it was as follows: Take 6 or more samples of a gel which normally sets in about ½ hour. Sample number one is stirred for the first five minutes (0 to 5) and then allowed to set; sample number two stirred for the next five minutes (5 to 10), sample number three (10 to 15); sample number four (15 to 20), sample number five (20-25), sample number six (25 to 30). Each sample after being stirred for five minutes, is allowed to set. In this way, by varying time of mixing, it is possible to find the effect of stirring upon the setting of gel. I might also suggest to study the effect of stirring upon elasticity, plasticity, viscosity and the like as this was what I had in mind when I talked with Dr. Langmiur.

(4) It is a well known fact that any increase in the work that an electric motor must do decreases the speed of revolution. By putting a resistance across the electric field, it is possible to regulate the speed of the motor. I suggest that a stroboscope be used to insure a means to keep the speed uniform or constant. A voltmeter and ammeter is connected in the circuit. Knowing the voltage and current, the

MISCELLANEOUS OBSERVATIONS; cont'd.

amount of power put in the motor is calculated by P = iV. By plotting P against T the viscosity can be determined also how the viscosity changes after the gel is set. This method of determing viscosity is fairly simple to measure. Why not conduct a research along this line ? It might prove worthwhile.

METHODS WHICH MIGHT BE USED TO DETERMINE ELASTICITY.

(1) The most common method for determination of elasticity of gels is by perfected tension or torsion machines. These types of machines are expensive but plasticity, elasticity and combination deformation can be rapidly determined. A highly perfected machine of this sort was used by Baker (22) in his study of fruit jellies.

(2) The most generalized method is by the bending of test rods. This method is rather limited because the gel must be fairly ridged before determinations of this sort can be made.

(3) Measuring the velocity of sound through the gel the elasticity may be found by means of the formula $V = \sqrt{\frac{E}{D}}$ where V is velocity of sound, E, Elasticity and D, density of gel. Although this method is mentioned in a number of books as a possibility, none of them tell how it may be done; except, knowing the elasticity the velocity of sound in the medium may be calculated. But, the elasticity is what we want to determine.

I propose the following methods for determining the elasticity in absolute units.

(a) A thin slice of gel is placed between the plates of a condenser as illustrated below.

METHODS, cont'd.

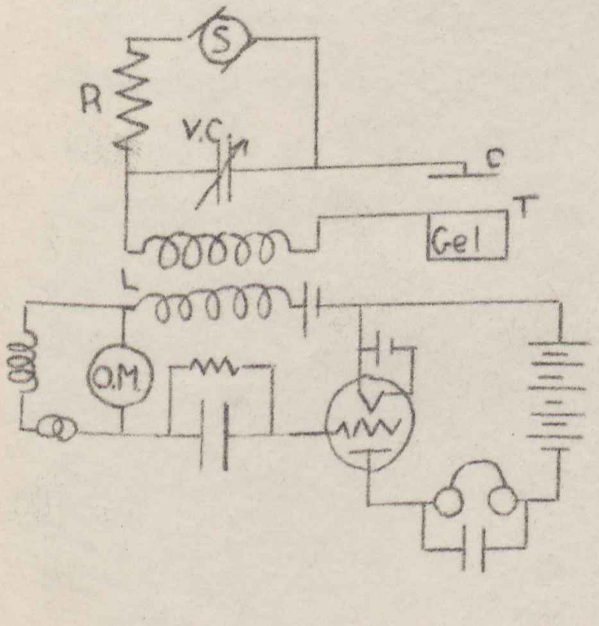
Electromotive force applied to the condenser will produce a slight change in thickness and a corresponding change in the length of the gel slice. Using an alternating electromotive force, a periodic increase and decrease in these dimensions will be produced.
If the frequency of the alternating current corresponds to the frequency of one of the possible modes of vibration of the gel, resonance will be set up which will rupture the gel. This phenomenon is known as the Piezoelectric effect.
(b) A cylinder of gel is fastened, by one end, to the table in a vertical position. To the free end is fastened a piece of tinfoil to serve as a conducting material. A short distance above the tinfoil is a copper plate, held by a suitable support, connected to a changeable frequency circuit. The tinfoil and the copper plate serve as the plates of a condenser. An alternating current sent through the condenser will cause a periodic force to exist between the plates. If the frequency of the periodic force coincides with the frequency of one of the possible modes of vibration of the gel the resonance set up will rupture the gel.
Either (a) or (b) might be used equally well, the only difficulty of any great importance is the building of

Methods, cont'd.

the changeable frequency circuit. A circuit which might be used is shown below. For information on circuit look in any book on frequency oscillators.

(4) A rather simple method for determining the elasticity of the gel may be obtained by dropping a ball from a fixed height on to the gel. The height of the rebound is a measure of the elasticity. A calibrated scale can be used and in this way an approximate measure of elasticity be found. The ball may be made from plastic or any other suitable material.

(5) For determination of the elasticity and plasticity with respect to time the apparatus used for this thesis proved to be rather simple in construction and satisfactory in results. Although invented by the writer to make elasticity measurements it can also be used to study the plasticity, elastic flow and plastic flow of gels.



L = Inductance
R = Resistance
V.C.=Variable Condenser
(S)= Generator
C = Copper plate
T = Tinfoil

O.M. Calibrated Oscillator meter

SUMMARY

(1) The first part of this thesis was developed, mainly, to familiarize the reader with a fundamental concept of elasticity.

(2) The apparatus, with diagrams, was explained and discussed in regard to measurement of elasticity.

(3) The equation used to calculate the elasticity, $E_g = \frac{T}{4 \pi \theta L} \frac{(b^2 - a^2)}{(a^2\ b^2)}$ was derived and developed.

(4) How the measurements were taken was discussed under experimental Procedure.

(5) That there is plasticity and plastic flow as well as elasticity and elastic flow, and how each changes with the age of the silicic acid gel was expanded upon under Experimental Results.

(6) By use of the derived equation the elasticity of the gel was calculated.

(7) A number of observations, not connected directly with elasticity determinations, were recorded and discussed.

(8) Different methods which might be used to find the elasticity of silica gels were examined.

(9) From the experimental data curves were drawn.

(10) Silicic acid gel has high elasticity but low tensile strength.

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(19) The fundamental idea and the formulae were taken from (4).

(20) Any Good Book on Optics will give a clear description.

(21) Hurd- Head of Chemistry Department- Union College

(22) Baker, G. Fruits Products J. 17 329-30 (1938)

CALIBRATION OF APPARATUS

#1 Calbration of pulley on left

#2 Calibration of pulley on right

#3 Calibration of both pulleys and cylinder

#1

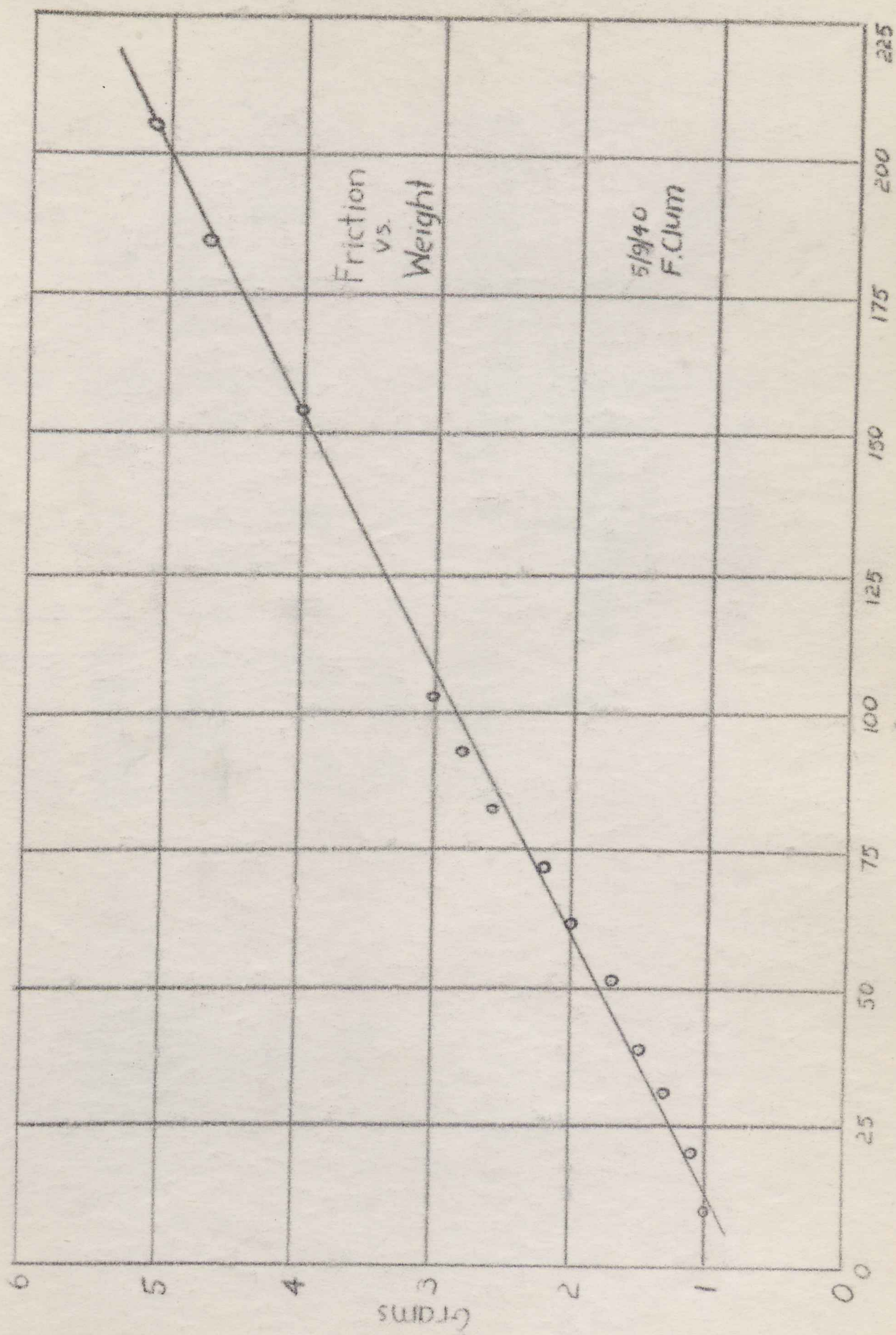
Pan	Weight	Friction
1g	1.4	.4 g.
10	11.4	.4
15	15.4	.4
20	20.4	.4
30	30.5	.5
40	40.6	..6
50	50.8	.8
60	60.9	.9
70	70.9	.9
80	80.9	.9
90	91.0	1.0
100	101.2	1.2

#2

Pan	Weight	Friction
10g	10.7 g	.7 g
20	20.7	.7
30	30.8	.8
40	40.9	.9
50	51.0	1.0
60	61.2	1.2
70	71.2	1.2
80	81.3	1.3
90	91.3	1.3
100	101.5	1.5

#3.

Pan	Weight	Friction
10g	11.0g	1.0g
20	21.1	1.1
30	31.3	1.3
40	41.5	1.5
50	51.7	1.7
60	62.0	2.0
70	72.2	2.2
80	82.6	2.6
90	92.8	2.8
100	103.	3.0
150	154.	4.0
180	184.7	4.7
200	205.1	5.1


Friction
vs.
Weight
5/9/40
F. Clum
Grams
Grams
0
25
50
75
100
125
150
175
200
225
0
1
2
3
4
5
6

CALIBRATION OF APPARATUS cont'd.

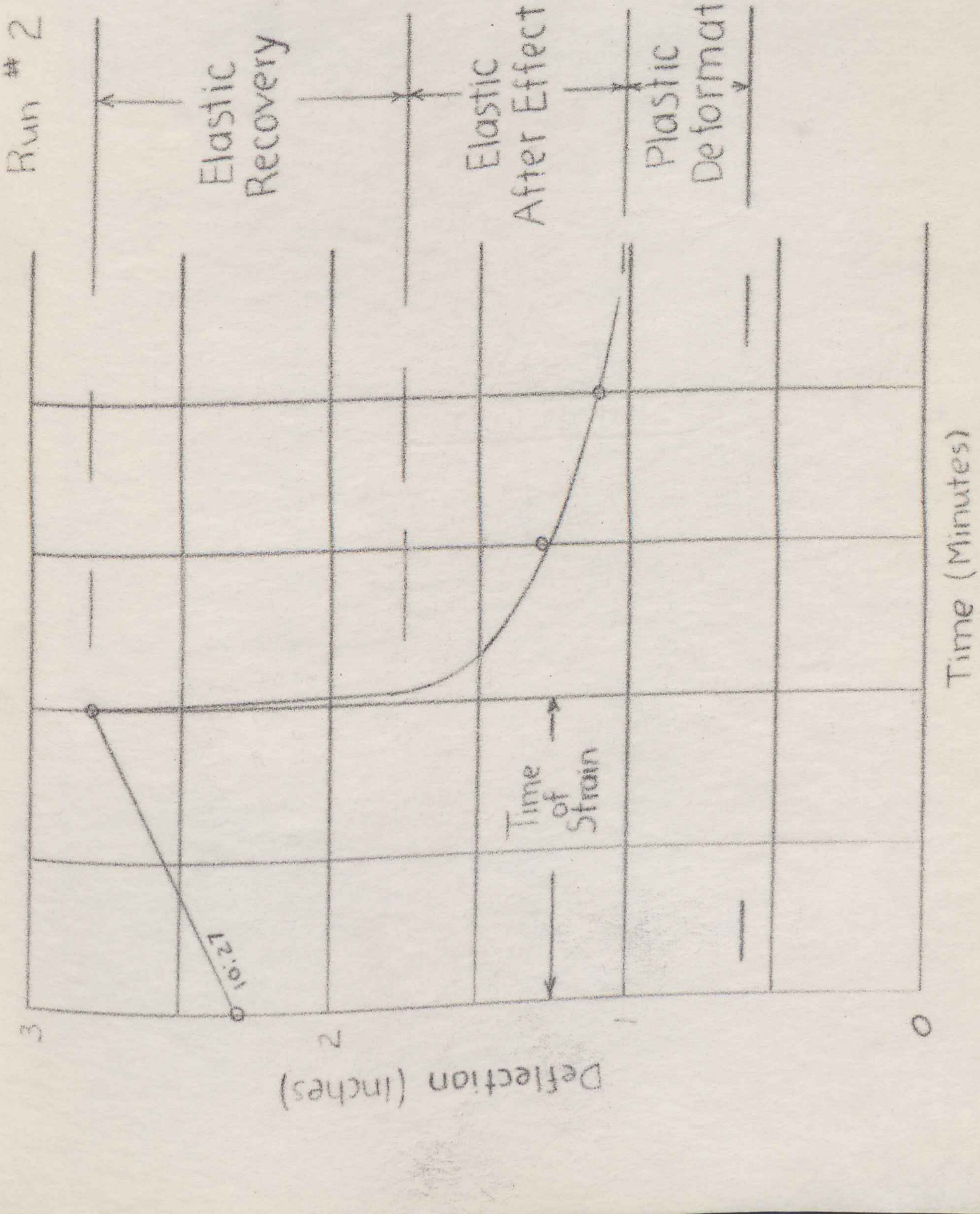
Run # 2

Silicate	150cc	time mixed	8:30P.M.
HAC	45.7cc	time set	9:00 P.M.
water	104.3	temp.	23° C

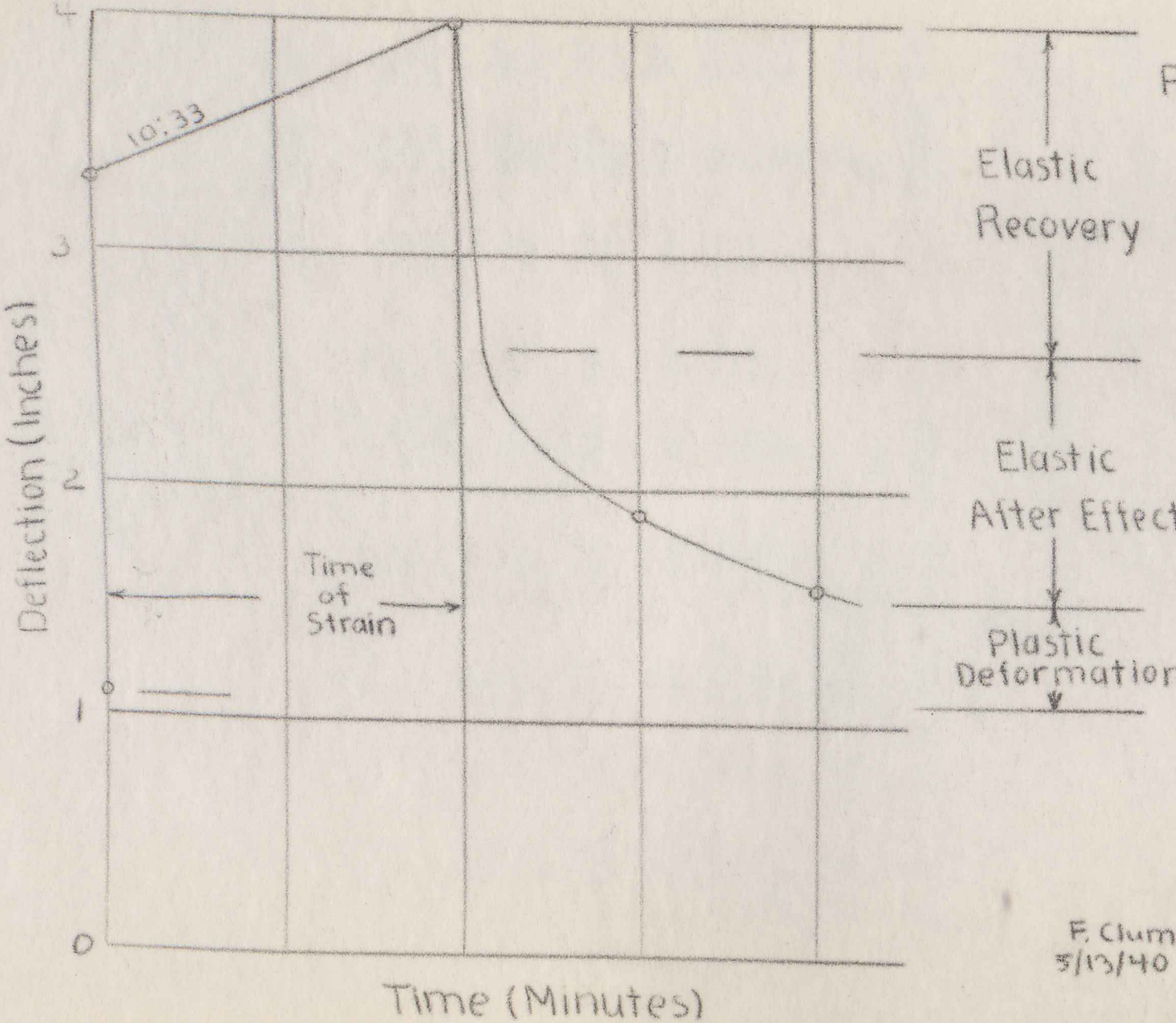
Amount of solution used 200cc

PH 4.8

Time	Weight	Def.	Time	Weight	Moved	Time	Weight	Lag.
10:22	20	1.0"	10:25	20	1.5"	10:26	0	.6"
:27	40	2.3	:29	40	2.8	10:30	20g	2.1
						:31	0	1.5
						:32	0	1.1
10:33	60	3.3	10:35	60	4.0	10:35	40	3.4
						:35½	20	2.7
						:36	0	1.9
						:39	0	1.6
10:40	80	4.2	10:42	80	5.0	:42	80	4.4
						:45	0	2.5
10:45	100	5.4	10:47	100	6.1			
:47	120	6.6	10:48	120	7.0			
:48	140	7.7	:49	140	7.9	10:49	40	5.4
:50	170	8.4	:51	170	9.0			
:51	210	10.0	:51½		8			
:52	250	11.0	:54	250	11.5			
:54	300	12.9	:54½		broke			


Run # 2
Elastic Recovery
Elastic After Effect
Plastic Deformation
Time of Strain
10.27
Deflection (inches)
3
2
1
0
Time (Minutes)

F. Clum
5/13/40



Run # 2
Deflection (Inches)
4
3
2
1
0
10:33
Time of Strain
Elastic Recovery
Elastic After Effect
Plastic Deformation
Time (Minutes)

F. Clum
5/13/40

CALIBRATION OF APPARATUS cont'd.

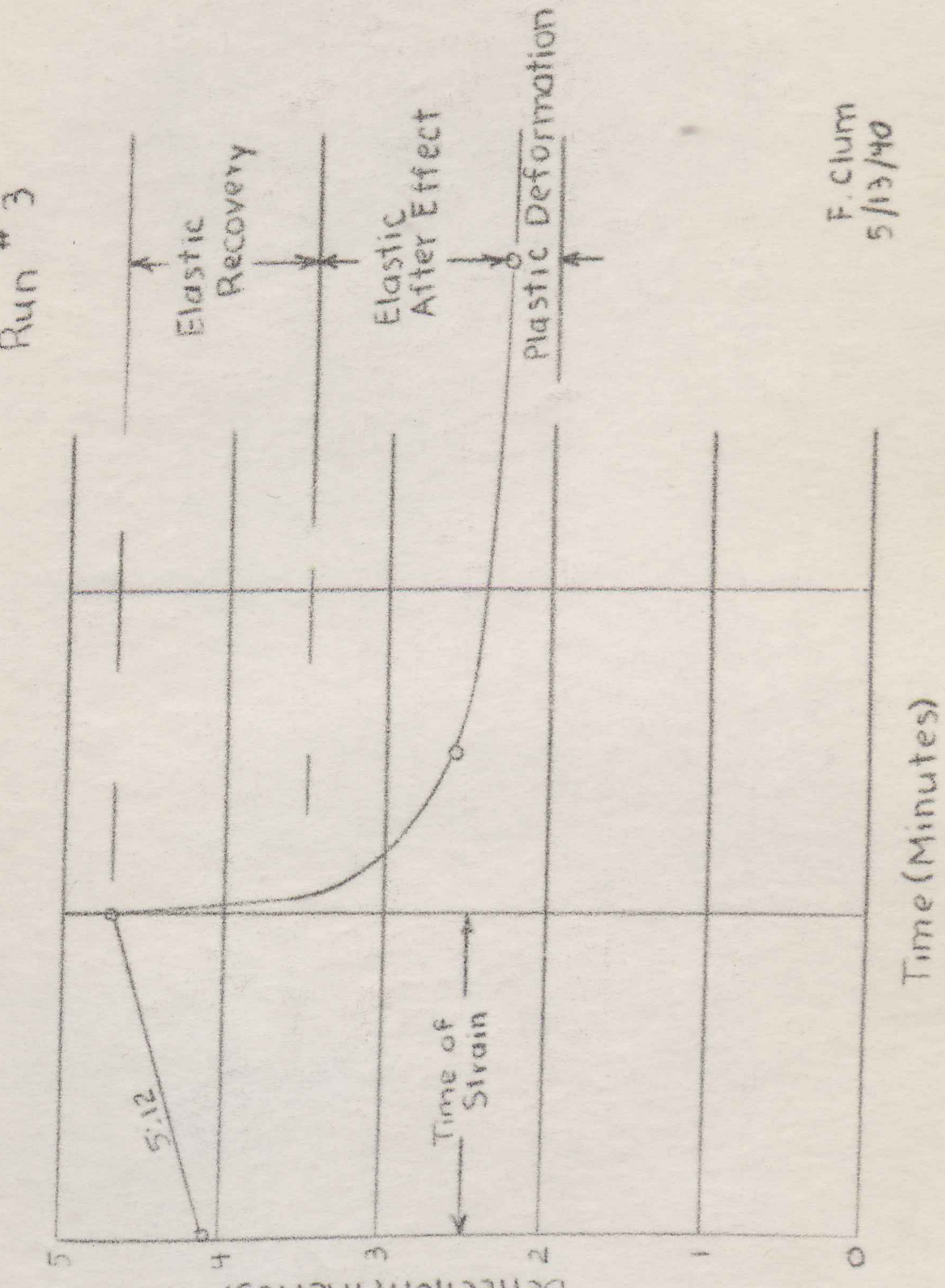
Run # 3.

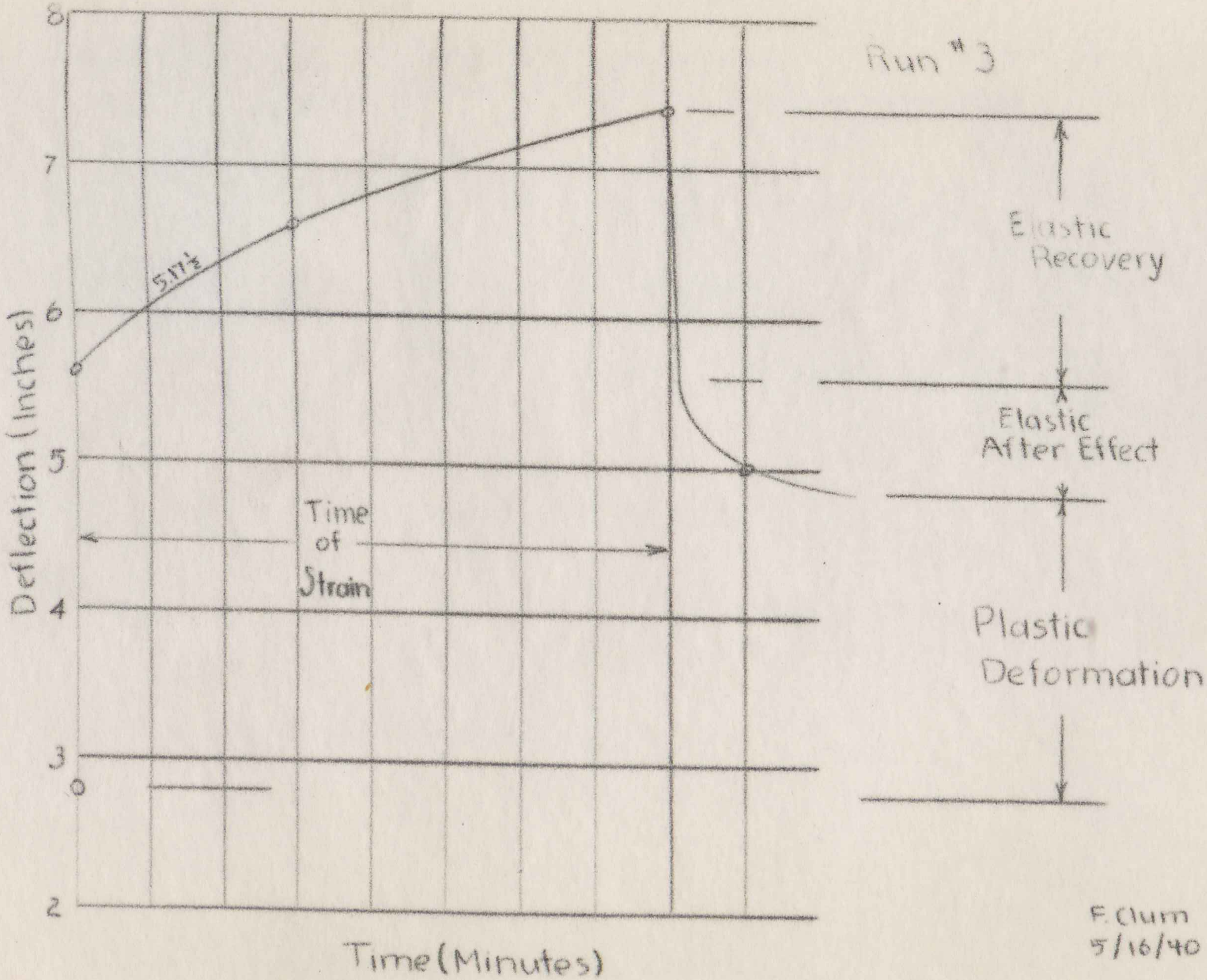
Silicate	150cc	time mixed	3:30
HAC	65.4cc	time set	4:30
Water	84.6cc	temp.	24°c

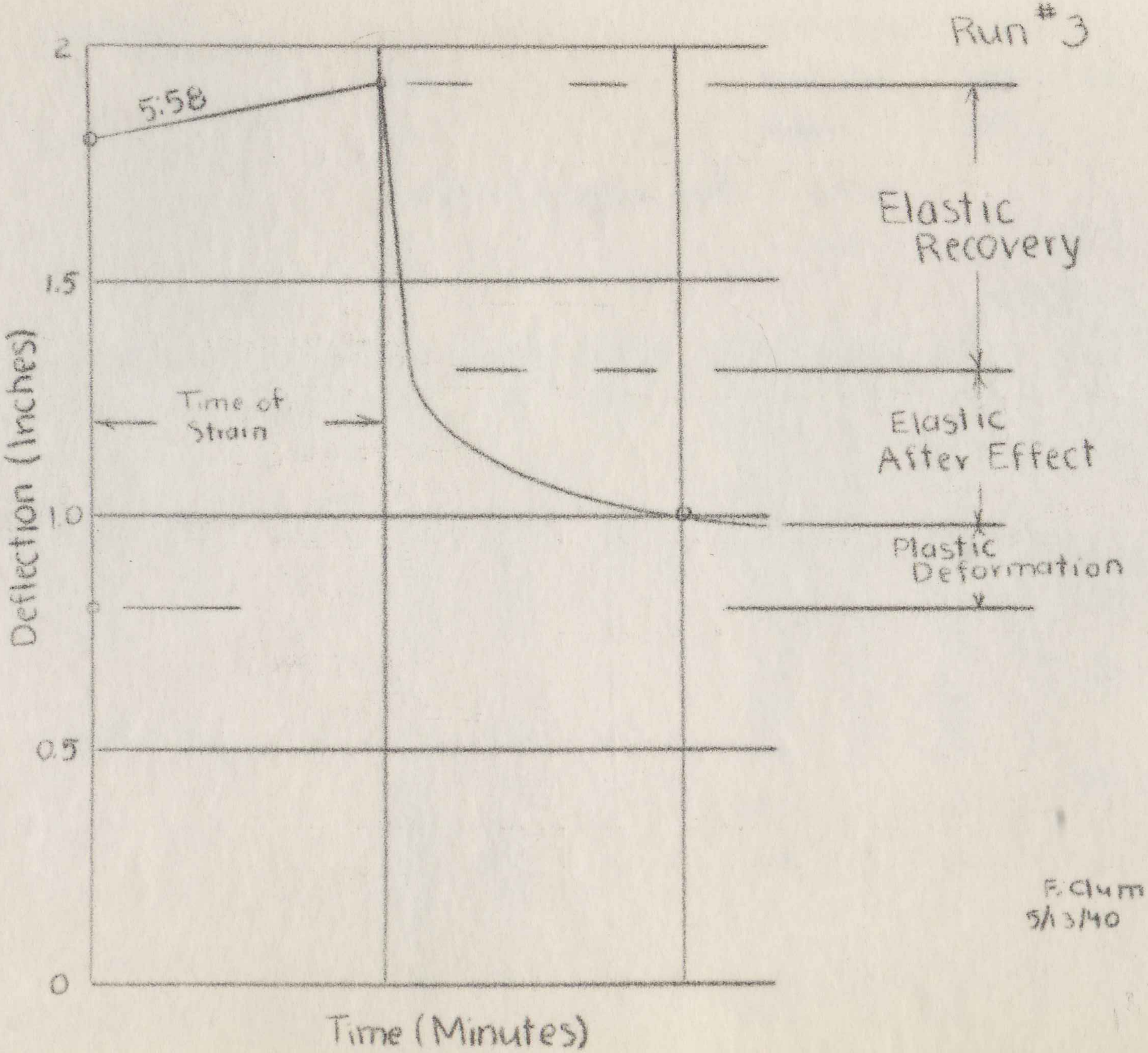
Amount of solution used 100cc

PH 4.6

time	weight	def.	time	weight	Moved	time	weight	lag.
4:45	5g	.25"	4:48	5g	.25"			
:50	15	.5				4:51	10	.4
						:53	0	.2
:54	30	.9						
:55	40	1.4	4:58	40	1.7	:58	0	.8
:58	50	1.8	:59	50	1.9	:59	0	1.0
5:00	70	2.3	5:01	70	2.5	5:02	20	1.7
						:02	0	1.2
5:03	90	2.8	:04	90	3.2	:04	40	2.4
						:05	0	1.6
:05	50	2.3						
:06	100	3.3	:07	100	3.6	:07	50	2.9
						:07	0	2.0
:08	50	2.6						
:12	150	4.1	:13	150	4.7	:13	100	3.1
						:13½	0	2.6
						:15	0	2.3
5:15½	100	3.6	:16	100	3.8			
:16½	150	4.5	:17	150	4.8			
:17½	200	5.6	:21	200	6.6			
			:26	200	7.4	5:27	100	6.2
						:27½	0	5
:28	100	5.9						
:28½	200	7.2						


Run # 3
Elastic Recovery
Elastic After Effect
Plastic Deformation
F. Clum
5/13/40
5:12
Time of Strain
Deflection (Inches)
Time (Minutes)
0
1
2
3
4
5


Run # 3
8
7
6
5
4
3
2
Deflection (Inches)
Time (Minutes)
5.17½
Time of Strain
Elastic Recovery
Elastic After Effect
Plastic Deformation
F. Clum
5/16/40


Run # 3
5:58
Time of Strain
Elastic Recovery
Elastic After Effect
Plastic Deformation
Deflection (Inches)
2
1.5
1.0
0.5
0
Time (Minutes)
F. Clum
5/13/40

CALIBRATION OF APPARATUS cont'd.

Run # 4

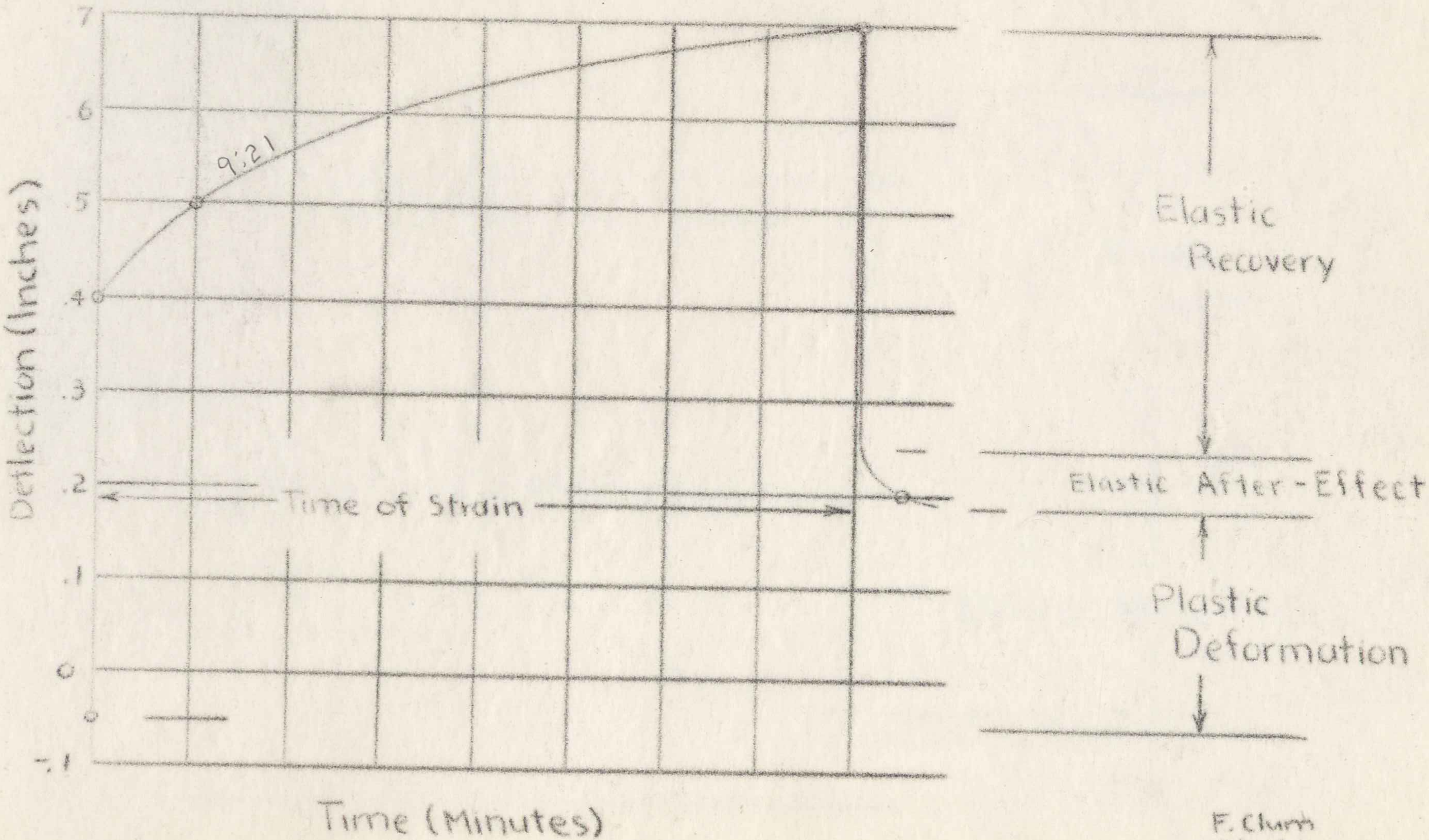
Silicate	150cc	Time Mixed	5:40 P. M.
NAC	75cc	Time Set	7:00 P. M.
Water	75cc	Temp.	23° C

Amount of solution used 100cc

PH 4.4

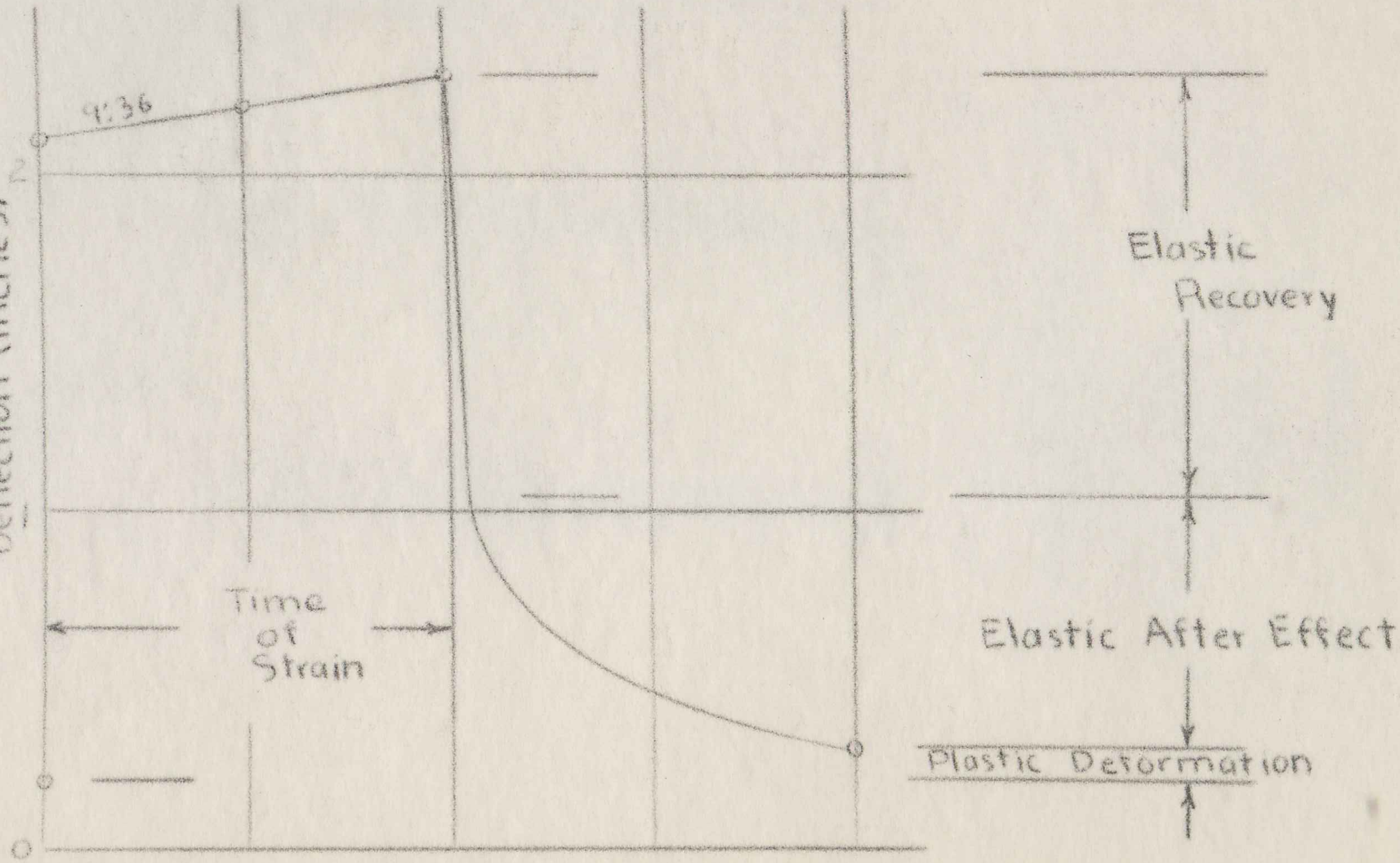
to left							to right						
Time	Weight	Def.	Time	Weight	Moved		Time	Weight	Lag.		Time	Weight	Moved
7:55	20	.20	7:58	20	.30		7:59	0	0	L	8:02	10	.1
							8:04	0	0	R	8:05	20	.2
							:06	0	0	R	8:08	30	.3
							:09	0	.05	R			
							:11	0	.05	R			
8:12	20	.15	8:14	20	.20	L	8:14	0	.05	L			
			8:15	20	.20	R	8:19	0	.05	R	8:15	20	.15
8:19	30	.2	8:23	30	.3	L	:23	0	.05	L			
			8:26	30	.3	R	:28	0	.05	R	8:24	30	.25
8:29	40	.3	:31	40	.4	L	:31	0	.1	L			
							:33	0	.05	L			
			8:36	40	.4	R	:37	0	.1	R	8:34	40	.3
							:40	0	.05	R			
8:43	50	.35	:45	50	.45	L	:45	0	.1	L			
							:50	0	.05	L			
			:57	50	.6	R					8:50	50	.35
			9:20	50	.9	R	9:20	0	.05	R			
9:21	100	.4	:22	100	.5	L							
			:29	100	.7	L	:29	0	.2	R			
9:31	200	1.1	9:34	200	1.3	L							
			:35	200	1.4	L							
			:36	200	1.5	L							
9:36	300	2.1	:37	300	2.2	L							
			:38	300	2.3	L	9:40	0	.3	L			
9:40	400	3.5					9:45	0	1.2	L			

Run # 4



F. Clum
5/18/40

Run #4



F. Clum
5/18/40

CALIBRATION OF APPARATUS cont'd.

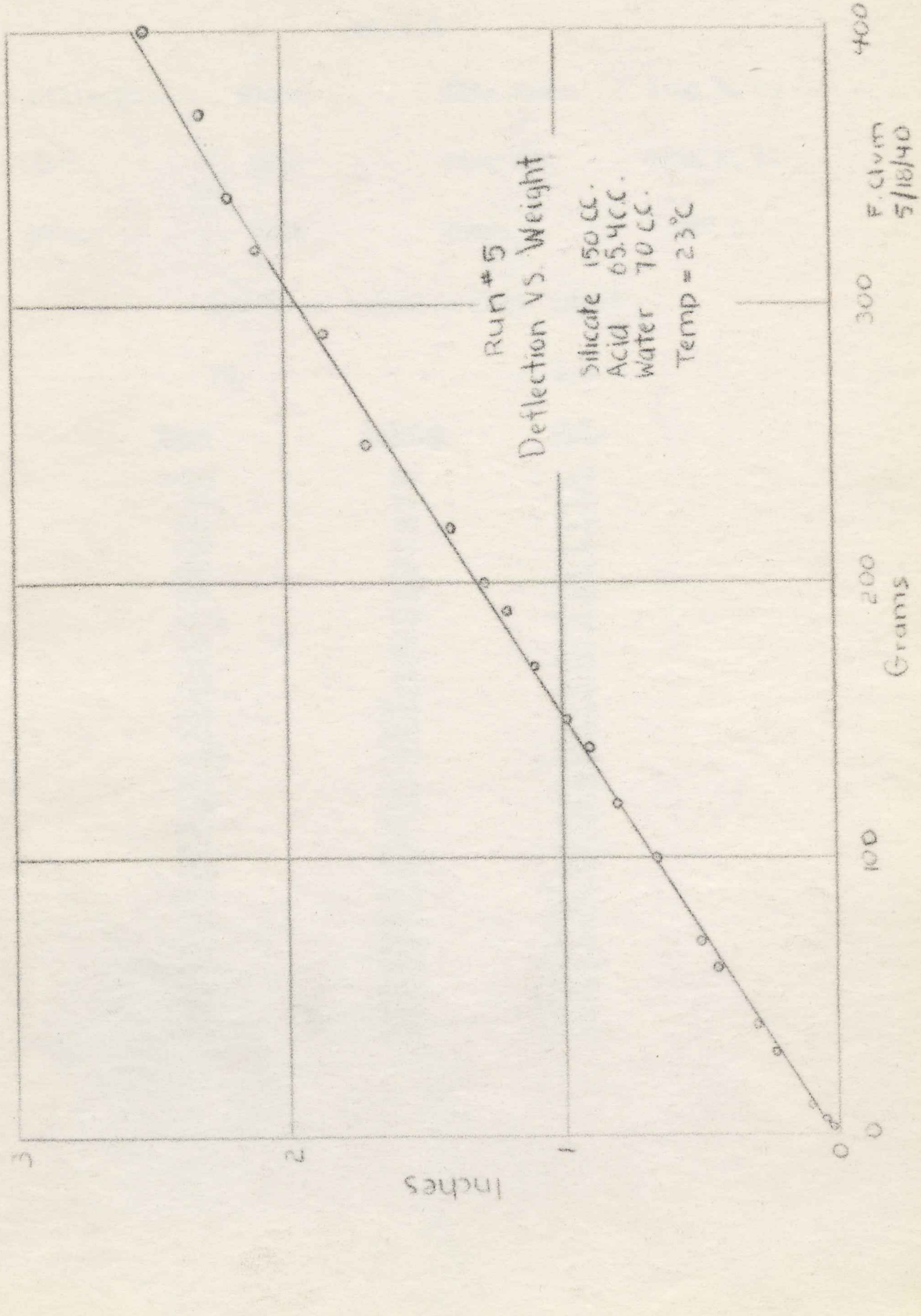
Run #5

Silicate	150cc	Time Mixed	11:20 A. M.
HAC	65.4	Time Set	12.13 P. M.
Water	84.6	Temp.	23° C

Amount of solution used 100cc

PH 4.6

Time	Weight	Def.
2:00	2	.02
:03	5	.05
:05	10	.10
:06	20	.18
:08	30	.23
:09	40	.3
2:10	50	.38
:10½	60	.44
:11	70	.5
:15	100	.65
:16	120	.80
:17	140	.9
:18	150	.98
:19	170	1.1
:20	190	1.2
:21	200	1.28
:22	220	1.4
:23	250	1.7
:24	290	1.85
:25	320	2.1
:26	340	2.2
:27	370	2.3
:28	400	2.5


Run # 5
Deflection VS Weight
Silicate 150 cc.
Acid 65.4 c.c.
Water 70 cc.
Temp = 23°C
5/18/40
Grams
0
100
200
300
400
Inches
0
1
2
3

CALIBRATION OF APPARATUS cont'd.

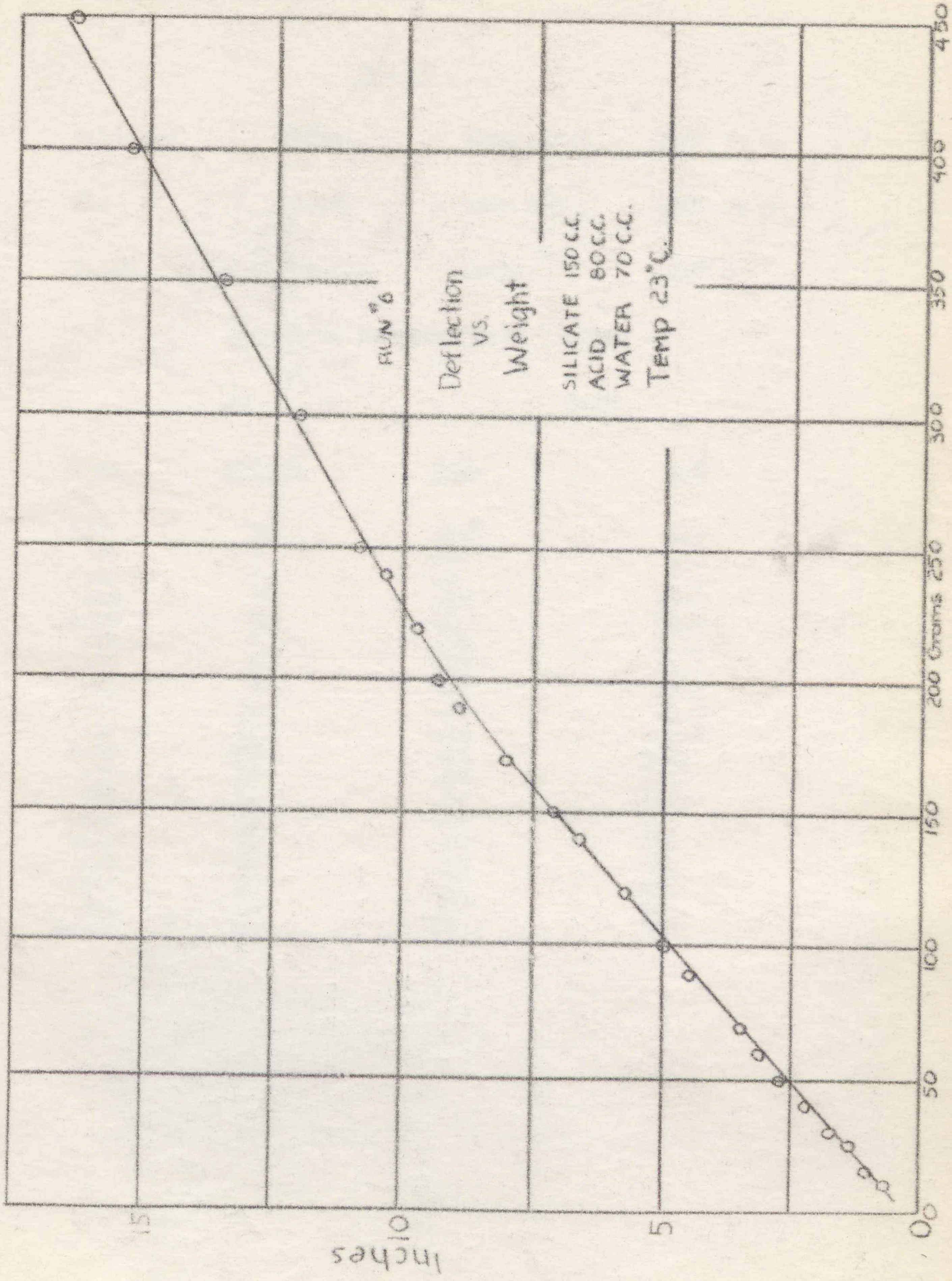
Run # 6

Silicate	150cc	Time mixed	3:00 P. M.
HAC	80cc	Time Set	4:22 P. M.
Water	70cc	Temp.	23° C

Amount of solution used 100cc

PH 4.3

Time	Weight	Def.
5:28	10	.7
:28½	15	1.0
:29	20	1.3
:35	25	1.5
:36	30	1.7
:37	40	2.2
:37½	50	2.7
:38	60	3.1
:39	70	3.5
:42	90	4.4
:43	100	4.9
:44	120	5.7
:44½	140	6.6
:45	150	7.1
:46	170	8.0
:47	190	8.9
:48	200	9.3
:49	220	9.7
:50	240	10.3
:51	250	10.8
:52	300	12.0
:53	350	13.5
:54	400	15.3
:55	450	16.4
5:56	500	17.5


RUN #6
Deflection
vs.
Weight
SILICATE 150 c.c.
ACID 80 c.c.
WATER 70 c.c.
Temp 23°C.
Inches
0
5
10
15
Grams
0
50
100
150
200
250
300
350
400
450

CALIBRATION OF APPARATUS cont'd.

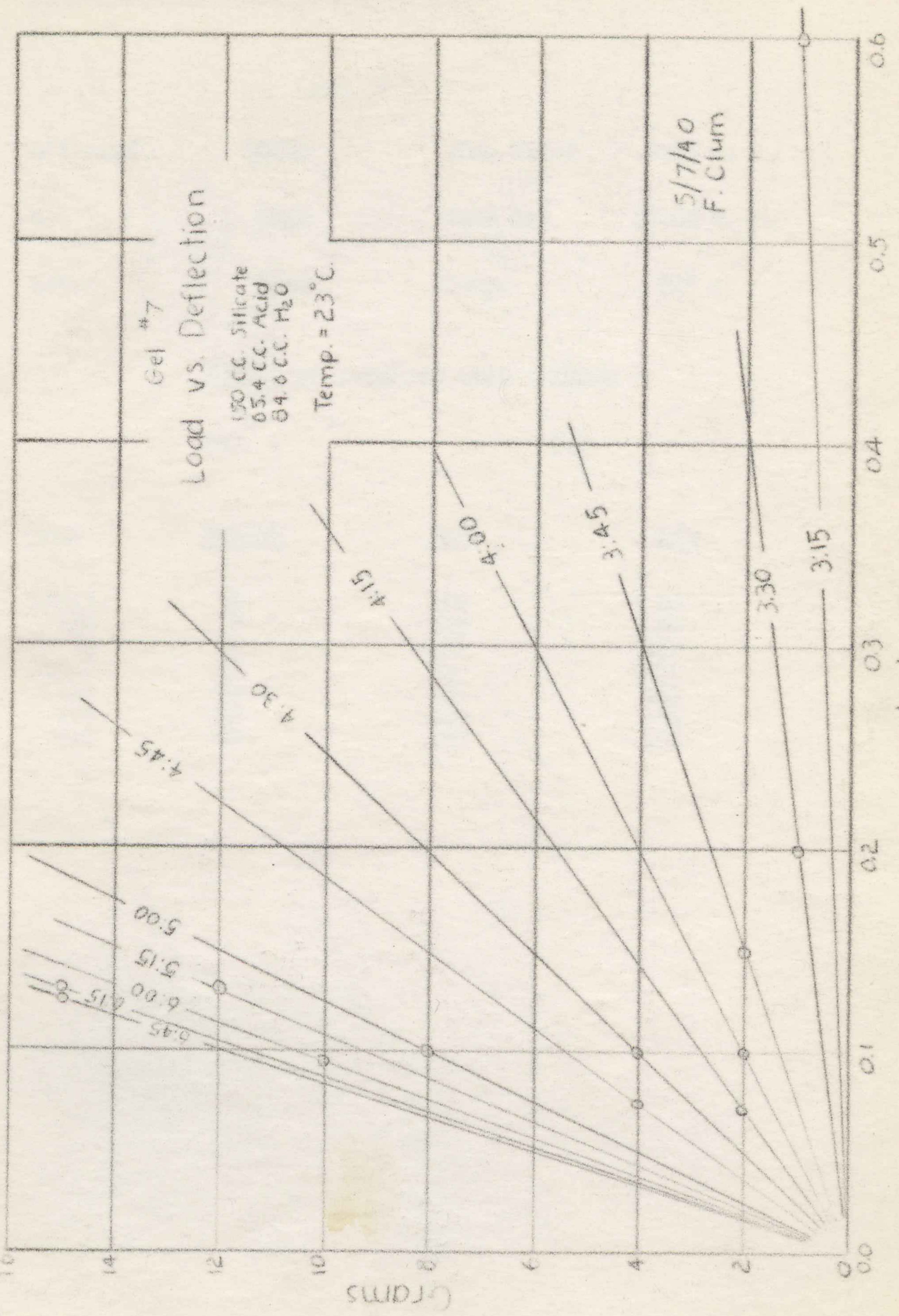
Run #7

Silicate	150cc	Time mixed	1:55 P. M.
HAC	65.4cc	Time Set	2:58 P. M.
Water	84.6cc	Temp	25° C

Amount of solution used 100cc

PH 4:56

Time	Weight	Def.	W/D
3:05	1g	.65"	1.5
:15	1	.5	2.0
:30	1	.2	5.0
:45	2	.15	13.3
4:00	4	.2	20.0
:15	6	.22	27.3
:30	6	.15	40.0
:45	6	.11	54.5
5:00	12	.15	80.0
:15	12	.14	85.6
6:00	15	.14	107.
:15	25	.22	114.
:45	25	.20	125.
7:30	30	.22	136
8:00	30	.22	136
:30	50	.36	139
9:00	30	.20	150
:30	30	.20	150
10:00	30	.20	150


Gel #7
Load vs. Deflection
150 c.c. Silicate
63.4 c.c. Acid
84.6 c.c. H2O
Temp. = 23°C.
5/7/40
F. Clum
3:15
3:30
3:45
4:00
4:15
4:30
4:45
5:00
5:15
6:00
6:15
6:45
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Inches
0
2
4
6
8
10
12
14
16
Grams

CALIBRATION OF APPARATUS cont'd.

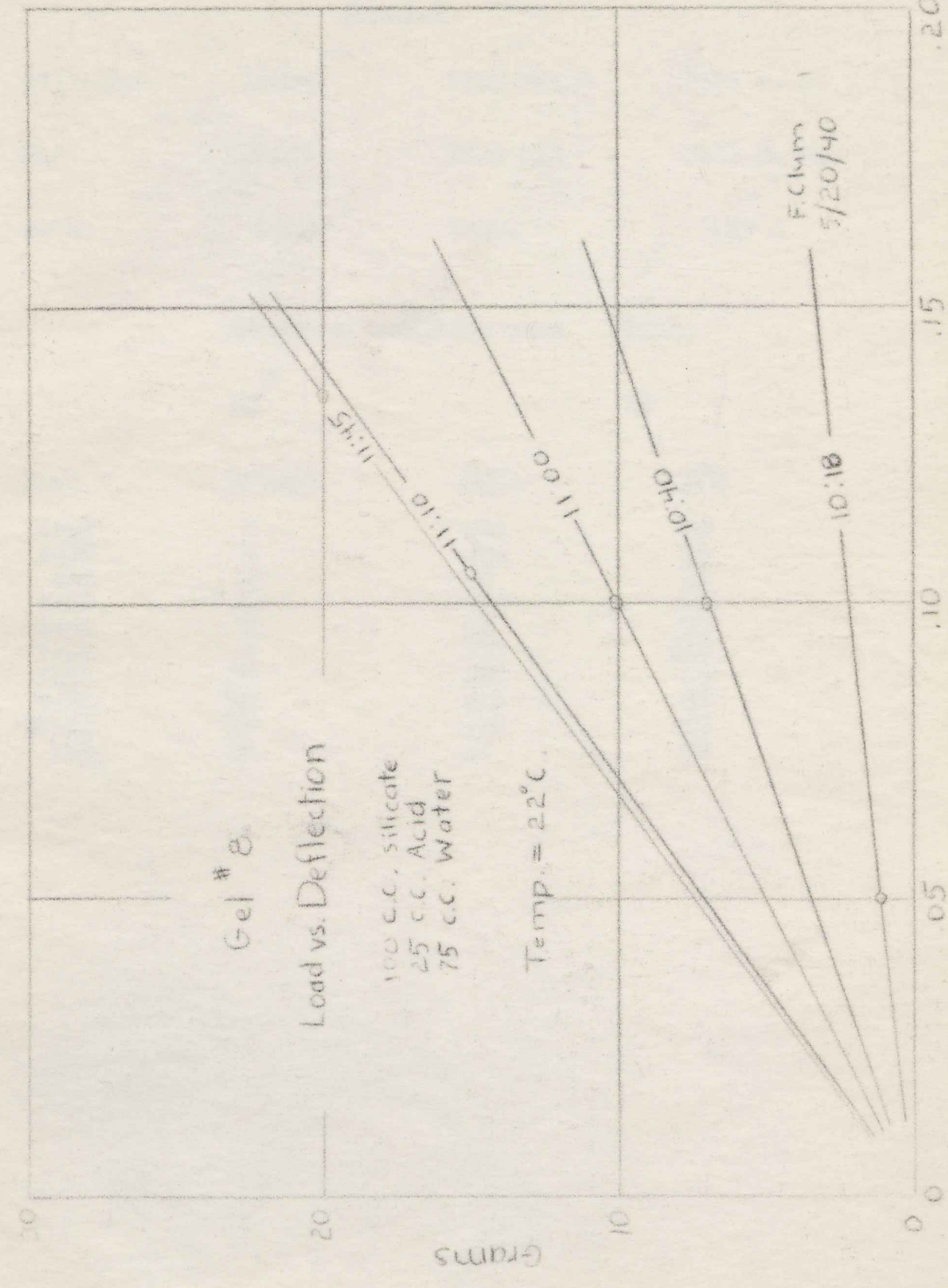
Run #8

Silicate	100cc	Time Mixed	9:32 P. M.
HAC	25cc	Time Set	10:03 P. M.
Water	75cc	Temp.	23° C

Amount of solution used 100cc

PH 5.3

Time	Weight	Def.	W/D
10:18	1	.05	20
:40	7	.10	70
10:53	15	.15	100
11:00	10	.1	100
:10	30	.21	143
:30	20	.14	143
:45	40	.27	145


Gel # 8
Load vs. Deflection
100 c.c. silicate
25 c.c. Acid
75 c.c. Water
Temp. = 22°C.
11:15
11:10
11:00
10:40
10:18
F.Clum
5/20/40
Grams
0
10
20
30
Inches
0
.05
.10
.15
.20

CALIBRATION OF APPARATUS, cont'd

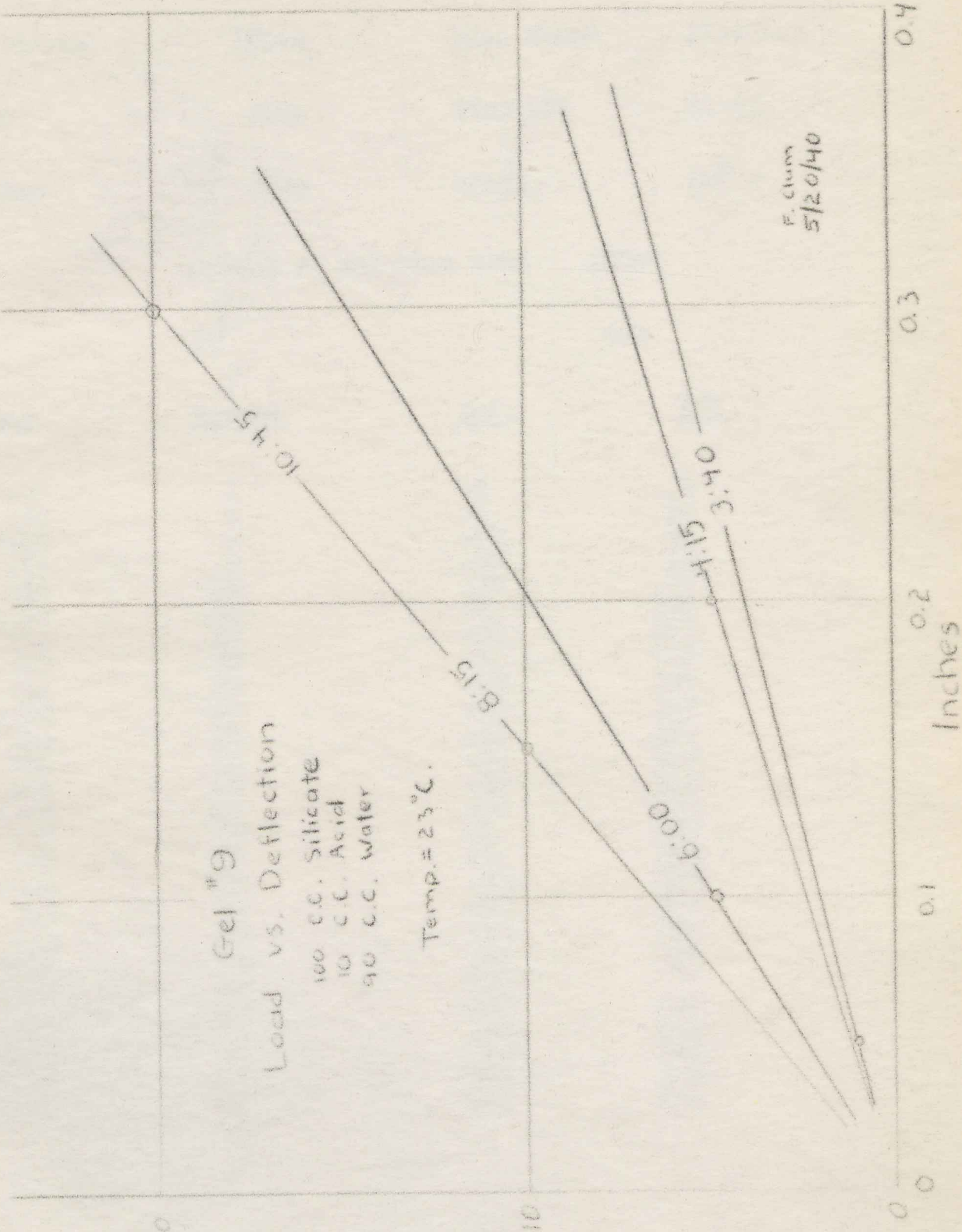
Run # 9

Silicate	100cc	Time Mixed	3;12 P. M.
HAC	10cc	Time Set	3:20 P. M.
Water	90cc	Temp.	23° C

Amount of Solution used 100cc

PH 10

Time	Weight	Def.	W/D
3:40	1	.05	20
4:00	1	.04	25
:15	5	.2	25
5:20	5	.08	62
6:00	5	.1	50
7:45	5	.05	100
8:15	10	.15	67
9:10	10	.15	67
10:10	10	.15	67
:45	20	.3	67



Gel #9
Load vs. Deflection
100 c.c. Silicate
10 c.c. Acid
90 c.c. Water
Temp. = 23°C.
10:45
8:15
6:00
4:15
3:40
F. Clum
5/20/40
Inches
Grams
0
0.1
0.2
0.3
0.4
0
10
20

CALIBRATION OF APPARATUS, cont'd.

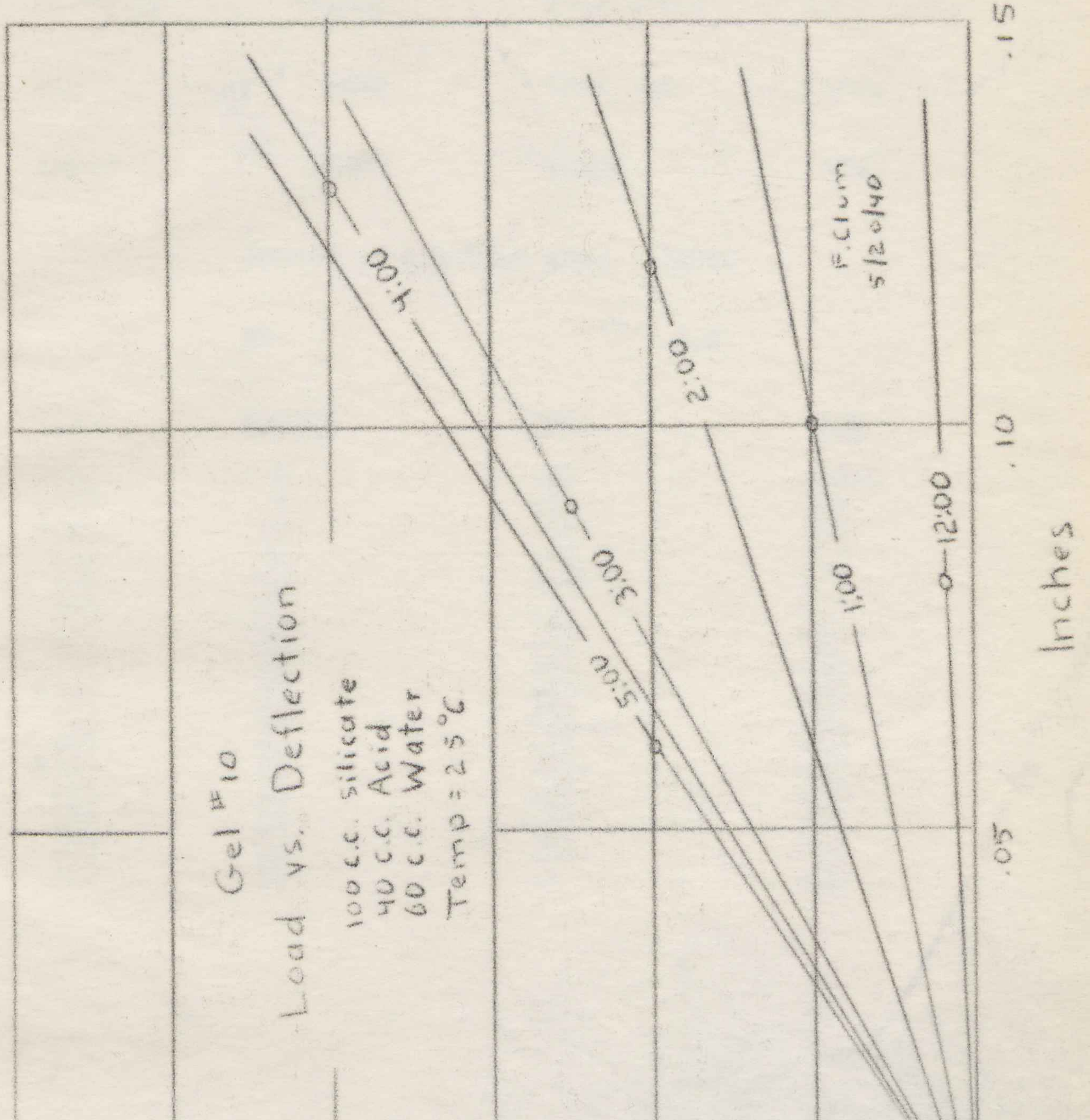
Run # 10

Silicate	100cc	Time Mixed	11:00A.M.
HAC	40cc	Time Set	11:28
Water	60cc	Temp.	25° C

Amount of solution used 100cc

PH 4.8

Time	Weight	Def.	W/D
11;35	1	.5	2
:45	1	.1	10
12:00	2	.08	25
:15	5	.08	62
:30	10	.15	67
1:00	10	.1	100
:15	10	.08	125
:30	15	.1	150
:45	25	.15	166
2:00	20	.12	167
:15	20	.11	180
:30	20	.10	200
:45	20	.09	222
3:00	25	.09	255
:30	30	.1	300
:45	30	.1-	310
4:00	40	.13-	320
:15	30	.09	330
:30	40	.15	266
5:00	20	.06	334
6:00	30	.09	334
7:30	30	.09	334
8:45	35	.14	250
9:45	30	.14	214
10:30	30	.15	200
11:00	60	.31	194


Gel #10
Load vs. Deflection
100 c.c. silicate
40 c.c. Acid
60 c.c. Water
Temp = 25°C
4:00
5:00
3:00
2:00
1:00
12:00
Grams
0
10
20
30
40
50
60
Inches
0
.05
.10
.15

CALIBRATION OF APPARATUS, cont'd.

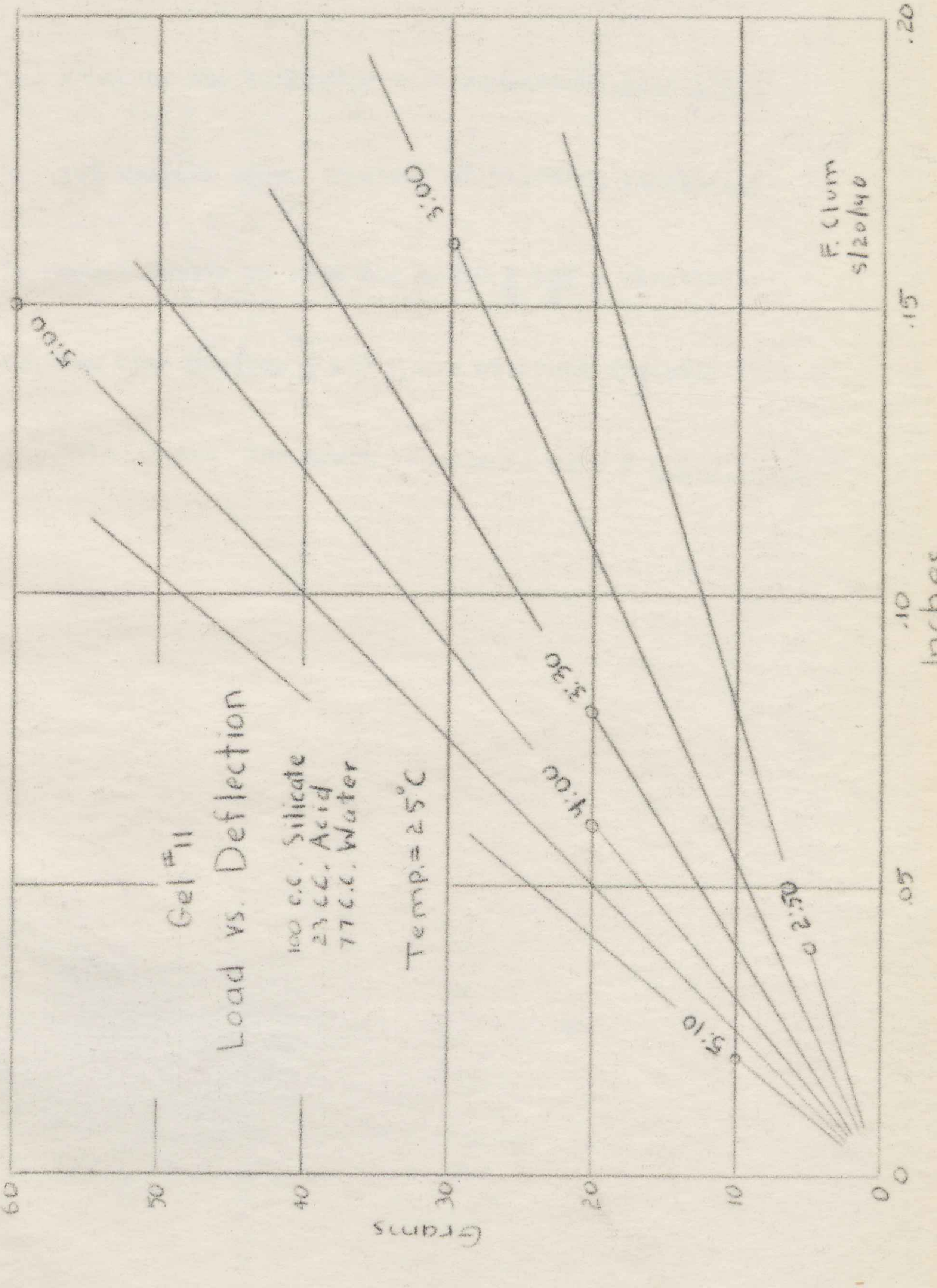
Run # 11

Silicate	100cc	Time Mixed	2:27 P. M.
HAC	23cc	Time Set	2:30½ P. M.
Water	77cc	Temp.	25° C

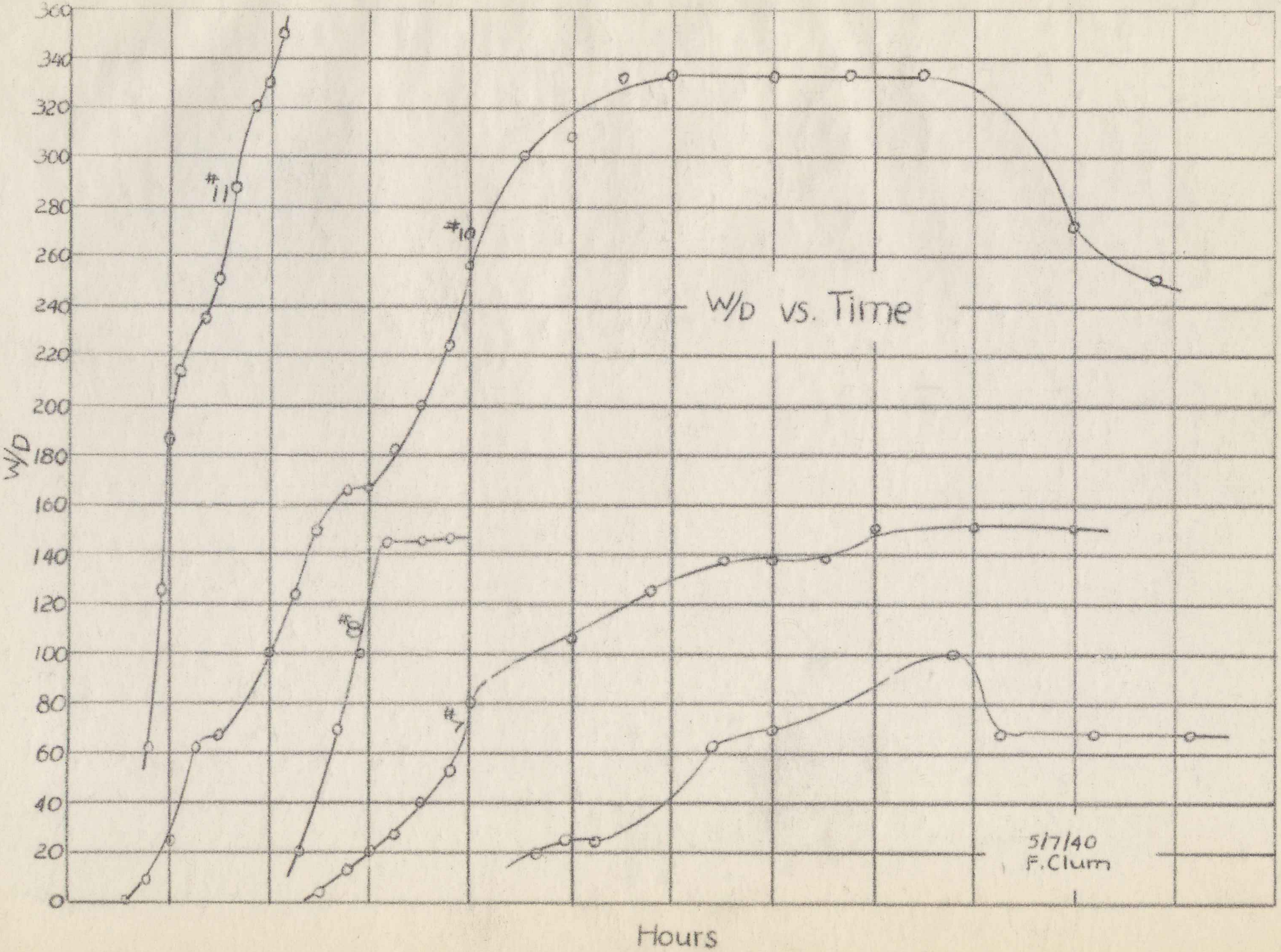
Amount of solution used 100cc

PH 5.8

Time	Weight	Def.	W/D
2:45	5	.08	62.5
2:50	5	.04	125
3:00	30	.16	187
:10	30	.14	214
:20	20	.09-	230
:30	20	.08	250
:40	20	.07	286
:50	20	.06	330
4:00	20	.05-	350
:10	60	.17	352
:30	40	.10	400
5:00	60	.15-	400
:10	10	.02	430
:30	60	.20	300
:40	60	.20	300
:50	30	.1	300


Gel #11
Load vs. Deflection
100 c.c. Silicate
23 c.c. Acid
77 c.c. Water
Temp. = 25°C
F. Clum
5/20/40
5:00
3:00
3:30
4:00
2:50
5:10
Grams
Inches
0
10
20
30
40
50
60
.05
.10
.15
.20

The graph on the following page represents <u>elasticity</u> plotted against time. Instead of plotting <u>elasticity</u>, it seemed better to plot the ratio $\frac{W}{D}$ ($\frac{WK}{D}$ = elasticity) against time because <u>W</u> and <u>D</u> are obtained directly from the data sheet. The graph represents runs # <u>7,8,9,10,11</u>


W/D vs. Time
W/D
Hours
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
#11
#10
#8
#7
5/7/40
F.Clum