COLLOIDAL & ELASTIC PROPERTIES
OF
META STYRENE & RUBBER

SOME COLLOIDAL AND ELASTIC PROPERTIES OF META STYRENE AND RUBBER.

Thesis

by

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PART I.

INTRODUCTION.

In the following pages an account is given of an investigation of the colloidal properties of meta styrene. Meta styrene is a colloid that swells and disperses yielding lyophilic sols not with water but with organic liquids. From the work on proteins, soaps, tannins and other substances we now have considerable knowledge of the properties of colloidal solutions where water is the dispersion medium, that is to say, hydrophilic colloids. But the class of lyophilic colloids of which meta sytrene is an example, that is organophilic colloids,has, to date, received scant attention. This is due, no doubt, to the fact that they are not as important as the hydrophilic sols which are of particular interest due to their close association with life processes.

The organophilic colloids are, however, of sufficient importance to justify their investigation. To this category of colloids belong both natural and synthetic rubber, balata, gutta percha, the cellulose esters and the heavy metal salts of the fatty acids. A number of synthetic products such as polymerized vinyl ester, cyclopentadiene and cinnamylidene-fluorene have recently been prepared and we may expect this list to be greatly extended in the near future. It is therefore desirable for us to have some knowledge of the properties of the solutions of such products, some of which already have found wide application in industry and others will in all probability do so.

There are points of theoretical interest to colloid chemists which can be investigated best through the organophilic colloids. As an instance, there is the question of correlation of the chemical structure of the colloid and liquids that swell the colloid and those that precipitate it. from solutions. As water is always the dispersion medium in hydrophilic sols, this point cannot be taken up at all in their examination. Disturbing factors due to ionization of the dispersion means are largely eliminated in organophilic sols so that a comparison of some of the properties of these solutions with those of hydrophilic sols may shed light on the part that ionization plays in the latter case.

In selecting meta styrene as a typical organophilic colloid, a deliberate attempt was made to obtain the most stable kind of a system possible. Meta styrene is a synthetic, saturated hydrocarbon and it can be obtained in a state of purity by polymerizing styrene prepared from cinnamic acid. This can be done by simply allowing styrene to stand,when it spontaneously polymerizes. It was originally thought that it was a homogeneous substance but evidence to the contrary was found in the course of this work. The solid meta styrene swells and disperses in other hydrocarbons and halogen derivatives such as benzene, toluene, chloroform and carbon tetrachloride. In a system of this sort,changes in the properties of the solution due to chemical reactions involving the disperse phase are reduced to a minimum and such a solution appears to be most satisfactory for detecting changes in the sol that may be caused by solvation, desolvation, formation of net-works or similar phenomena.

HISTORICAL REVIEW.

It will be convenient for future reference to review the facts previously established about the state of aggregation of meta styrene and other polymers of styrene. We shall first consider the high polymer of styrene known as meta styrene.

Simon(1) in 1839 appears to have been the first to remark on the polymerization of styrene. He stated that under the influence of light and heat, styrene is transformed into a tough, jelly-like mass. The author assumed that this was an oxidation process, although he gave no evidence to support this view.

In 1845 J. Blythe and A.W.Hofmann(2) reported experiments that showed that the polymerization of styrene involved no combination with oxygen. A sample of styrene was floated in a small beaker on mercury and then enclosed by an inverted beaker containing oxygen. After several months the styrene had become tough and elastic but there was no diminution in the oxygen volume.

An analysis of the polymerized product gave results for a hydrocarbon ($C_8 H_8$) so these workers concluded that the process was one of molecular rearrangement and not of oxidation.

These authors confirmed the results of Simon(3) concerning the effect of light and heat in accelerating the polymerization. A sample of styrene exposed to sunlight for three weeks in the summer and a second sample heated to 200°C. for several hours both became highly viscous. But a sample which had been kept by Liebig in the dark for 5 years was still a mobile liquid.

The fact that the process of polymerization of styrene is a reversible one was mentioned in the same paper. Some of the solid polymerization product which these authors were the first to designate as "meta styrene" was heated in a small flask by a spirit lamp. By careful distillation not a trace of residue was left in the retort and the liquid that distilled was nothing else but pure styrene.

The next research published on meta styrene appeared in 1866 when M. Bertholet(4) reported the results of his work. He showed that styrene may polymerize in a solution as well as in the pure state; for meta styrene was observed to form when a solution of styrene in toluene was heated to 200° for some time.

Other means than light and heat were indicated to catalyze the polymerization. Sulphuric acid was stated to cause styrene to polymerize to give a compound which becomes liquid at 300° but does not regenerate styrene. Iodine dissolved in styrene with the evolution of hydrogen iodide and a polymerized gummy mass resulted. The alkali metals had no effect on styrene.

Twelve years later, Krakau(5) studied the polymerization of styrene and agreed with the previous investigators with regard to the formation of meta styrene. But his product on distillation decomposed into styrene and a dimer which was identical with the liquid di styrene that Erlenmeyer(6) had isolated from the mixture of products obtained when cinnamic acid was heated with hydrogen chloride at 150°. The occurrence of this dimer in the distillation products of meta styrene has not been confirmed by later workers.

Krakau also states that traces of iodine, bromine and sulphur retard the process of polymerization in styrene.

The first studies of the rate of the polymerization process was made by G. Lemoine(7) in 1897. He used a vacuum distillation procedure to separate styrene from meta styrene.

At room temperature in the dark, the polymerization is very slow as only 5% of meta styrol was formed in the course of one year. Light and heat speed up the reaction and an equilibrium is reached between the styrene and the polymer at percentages which depend on temperature and pressure when the amount of light is constant.

When catalyzed by light, the polymerization reaction proceeds rapidly at first and then slows down. Lemoine explained this fact by showing that the only wave lengths that are active in catalyzing the change are those which are easily absorbed by meta styrene. A layer of styrene 4 m.m. thick was shown to absorb the ultra violet and part of the violet end of the spectrum almost completely. A sample of styrene placed inside of such a layer of meta styrene and allowed to stand in sunlight showed no polymerization after several months.

This author observed that a sample of styrene that had been exposed to sunlight and then placed in the dark showed no further polymerization.

The temperature coefficient for the reaction calculated by Goldberg(8) from Lemoine's data gives between 3° and 35°.

$$\frac{K_{T+10}}{K_T} = 1.34$$

Krönstein(9) makes a distinction in general between two types of polymerization. The term "Euthymorphous" is applied to a process where the polymer is built up "directly" from the monomer. By "mesomorphous" he designates a polymerization where the monomer aggregates to some sort of intermediate compound which then reacts with more monomer to give the high polymer.

The polymerization of styrene is considered to belong to the second type. The period between the first observable rise in viscosity to the formation of a gel corresponds to the first stage of his mesomorphous polymerization and the intermediate substance is called "Poly styrene". The subsequent hardening of the polystyrene corresponds to the second part of the process.

It is difficult to see how this nomenclature helps the situation. If the "poly styrene" is precipitated with alcohol it gives meta styrene and styrene. And the "poly styrene" can be made by swelling meta styrene in styrene. So the view that the formation "poly styrene" represents any definite compound is not justified.

In 1909, Hans Stobbe(10) in conjunction with G. Posnjak published the first of a series of five papers on the subject of meta styrene. These authors were the first to recognize clearly the colloidal nature of meta styrene sols. They state that the properties of the substance shown in swelling, high viscosity of its solution, precipitation by alcohol, amorphous form, and the fact that it fails to raise the boiling point of a solvent, place it in the same category as rubber, starch, dextrin, etc.

These workers prepared "pure" meta styrene by twice precipitating the "crude" meta styrene from a benzene solution by alcohol. It is described as a white, odorless, amorphous solid which can easily be pulverized. It was soluble in benzene, toluene, styrene, molten naphthalene, nitro benzene and carbon tetra chloride. By swelling pure meta styrene with suitable proportions of styrene, gels were prepared with the varying properties ascribed by previous workers to meta styrene.

Pure meta styrene was shown to be a saturated derivative, as in a carbon tetrachloride solution it did not decolorize either bromine or alkaline permanganate.

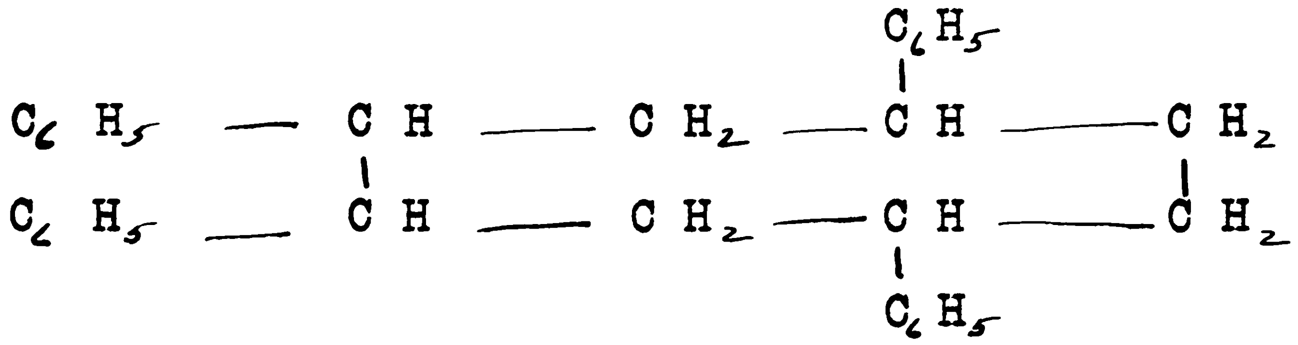
A formula was proposed for the polymer which considers the following facts known about the substance:

1. It is formed by the union of an unknown number of styrene molecules.

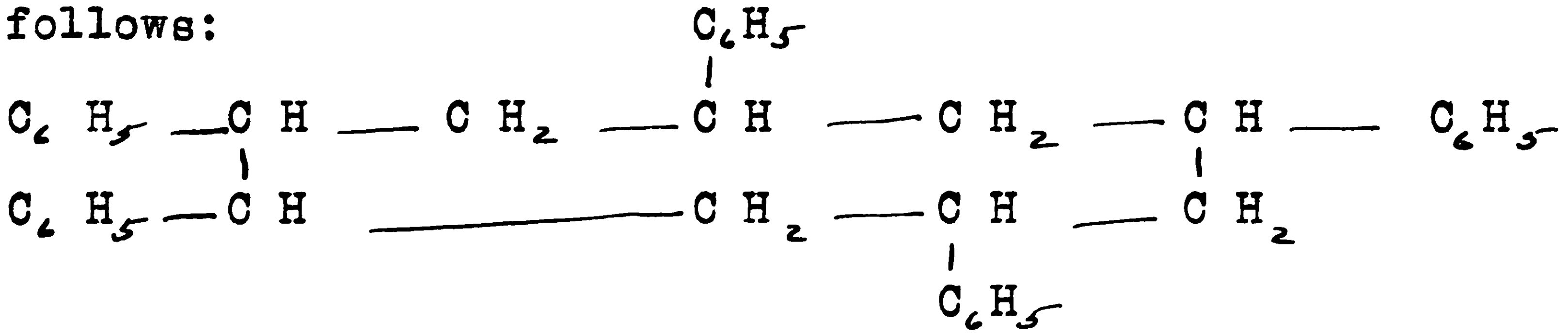
2. On heating to 320°, it is decomposed into styrene. The ease with which this reverse reaction is effected is taken to indicate that the styrene arrangement of the carbon atoms is not changed during the polymerization.

3. Meta styrene is saturated.

In case an even number of styrene molecules, as four polymerize, the formula is written:



and an odd number of styrene molecules are arranged as follows:



Stobbe and Posnjak next conducted some experiments on the rate of the polymerization under various conditions. They estimated the percent. of meta styrol in a styrene solution by comparing the viscosity of the solution with the viscosity of solutions of known concentration.

They showed that a sample of styrene that had been kept for some time in the dark polymerized much faster when exposed to light than a freshly distilled sample. Ultra violet light was found to polymerize styrene so rapidly that a layer of solid styrene was precipitated where the light entered the solution.

In 1915 Stobbe(11) adopted the change in refractive index caused by polymerization as a means of following the reaction. By this method the results of his previous paper were verified and the several new facts were established.

The polymerization of a freshly distilled sample was slower at the start than it was later, after some meta styrene had been formed. That is to say, the reaction is auto catalytic.

A sample that has been placed in the light and then removed to a dark place continues to polymerize much faster than a sample that had never been exposed to light. This is referred to as a "Photo chemical after effect".

If some styrene is heated and then cooled it polymerizes faster than a sample that has never been heated. This is "thermal after effect".

This same author(12) reported that the refractive index of a 5% benzene solution of styrene was raised from n_{c}^{20} = 1.49883 to 1.49994 when exposed to sunlight in a quartz tube for 230 days. On the other hand, the index of refraction of a 5% meta styrol solution was lowered from 1.50125 to 1.50116 by the same treatment.

Stobbe concludes that an equilibrium is reached in the reaction:

$$\text{Monomer} \rightleftarrows \text{Polymer}$$

The light here plays the same part as it has been observed to play in the equilibrium:

$$\text{Labile isomer} \rightleftarrows \text{Stable isomer}$$

This latter phenomenon has been studied by Stobbe and Wilson(13) with the stereo isomeric nitro benzol desoxybenzoins and by Stoermer(14) with a series of stereo isomeric ethylenic bodies.

In a very recent paper on the chemistry of high molecular organic compounds Staudinger(15) refers to work done on meta styrene apparently contained in a thesis that has not as yet been published as a journal article. He mentions that a polymer obtained by treating styrene with stannic chloride can be separated by treatment with solvents into fractions having different molecular weights and giving sols of different viscosities. The fractions with the lowest molecular weights give the solutions with the lowest viscosities.

He further points out that the temperature at which the styrene is polymerized effects in a marked manner the molecular weight and the viscosity of the meta styrene.

The higher the temperature used, the lower are the molecular weights and viscosities of the resulting polymers. Work of a similar nature was carried out independently in the course of the present investigation and our results agree with those of Staudinger in so far as the two experiments are strictly comparable.

Staudinger states that if a sample of meta styrene, which has been made by polymerization at low temperatures without the aid of a catalyst, is heated, the viscosity of a solution prepared from this substance is low. Further, reagents such as Cl_2, Br_2, O_3 and HNO_3 cause a reduction in the viscosity of the solution. These changes are attributed to the breaking down of a very large molecule into smaller ones.

This author makes an interesting classification of organic colloids. The first group is called "Association Colloids" and the system colloidal sugar in benzene is an example. Here, the forces holding the individual molecules together in a colloid particle are the same forces that hold molecules together in a crystal. All colloids of this kind are lyophobic and form molecular solutions in suitable solvents.

The lyophilic colloids are composed of immense molecules, all the atoms of which are held together by the same kind of primary valency. The colloidal particle merely consists of a single molecule. The lyophilic sols are further divided into "Eukolloids" and "Hemi" colloids.

The eukolloids are substances having a very high average molecular weight, about 20,000. They give solutions of high viscosity which are very sensitive to heat and reagents. On heating or on treatment with suitable chemicals the viscosity of the solutions is lowered due to depolymerization of the large molecule into smaller ones.

The hemi colloids are distinguished from the eukolloids in that they are composed of molecules with a molecular weight of from 2000 to 10,000. They are stable to heat and to reagents.

Th the eukolloid class Staudinger assigns meta styrene that has been polymerized at room temperatures. Meta styrene prepared at high temperatures is placed in with the hemi colloids.

LOWER POLYMERS OF STYRENE

The researches published on the subject of meta styrene have been in good agreement but such is not the case in the matter of lower polymers of styrene. There are two bi molecular compounds of styrene mentioned in the literature. One is a solid melting at 124° and the other a liquid boiling at 312° .

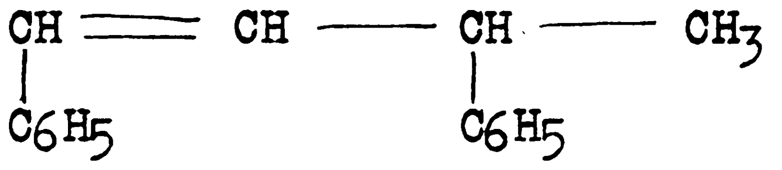
The solid di styrane was first prepared by Engler and Leist(16) by heating calcium cinnamate. From the mixture of products obtained, a solid hydrocarbon was isolated which gave an analysis and molecular weight that corresponded to the formula C_{16} H_{16}. W. Miller(17) repeated Engler's experiment and found the same material. Radziszewski(18) made the substance by passing vapours of styrene di bromide over hot lime. Lieberman(19) distilled β Truxillic acid and obtained the compound in a pure state with a melting point of 124°. On the addition of bromine, the solid di bromide, C_{16} H_{16} Br_2 which melted at 238° was formed. Finally, Stobbe and Posnjak(20) prepared the solid dimer by the method of Engler and Leist and spent considerable effort in deducing a structure for it.

When Emil Erlenmeyer(21) synthesized the molecule by the method of Lieberman he was struck by the similarity of the smell of the substance with the odour of stilbene. An investigation by Erlenmeyer showed conclusively that the product that had been thought by previous workers to be di styrene, C_{16} H_{16} was stilbene, C_{14} H_{12}.

Stobbe(22) accepted the identity of solid di styrene and concluded that there is but one dimer of styrene, the liquid boiling at 312°.

The liquid di styrene was first described by E. Erlenmeyer(23) who made it by heating cinnamic acid with an aqueous solution of hydrobromic acid at 170°. It was a colorless liquid with a boiling point of 312°. Fittig and Erdman(24) prepared the substance by boiling styrene with 50% sulphuric acid and made the dibromide, $C_{16} H_{16} Br_2$, which was a solid melting at 102°. Königs and Mai(25) obtained the product in a good yield by the action of a mixture of acetic and sulphuric acids on styrene at room temperature.

Stobbe and Posnjak(26) succeeded in reducing the di styrene by heating it for eight hours at 250° with hydrogen iodide and phosphorus. The compound formed was 1.3 di phenyl butane. This and other considerations led them to fix the structure of the dimer as:



$$\underset{C_6H_5}{CH} = CH - \underset{C_6H_5}{CH} - CH_3$$

It may be concluded that no polymers of molecular weight intermediate between the dimer and the high polymer meta styrene have ever been shown to exist. The dimer has not been shown to form from the monomer and there is no evidence that an intermediate stage in the polymerization of styrene to meta styrene.

PREPARATION OF META STYRENE

Meta styrene was prepared in the present investigation by causing styrene to polymerize under three different sets of conditions. The product obtained in each case showed that the physical, colloidal and elastic properties of the one depend to a very marked degree on the process used to prepare the meta styrene.

The sample of meta styrene used in most of the experiments described on the following pages was prepared by allowing some styrene, purchased from Kahlbaum, to polymerize by standing four years. The resulting product was a hard, very tough, transparent, glassy solid. When dissolved in chloroform and precipitated by the addition of ethyl alcohol it was transformed to a white, opaque, tough, fibrous mass which could not be pulverized. It resembled reprecipitated cellulose acetate very strongly in physical form. This product will hereafter be denoted as the "cold polymer" and unless otherwise stipulated, this is the product used in the experiments.

A second variety of meta styrene used was prepared by heating styrene, prepared from cinnamic acid, for forty-eight hours at 140° under a reflux. The product was a very brittle, transparent solid full of air holes. It could easily be pulverized to a powder. This meta styrene will be referred to as the "140° polymer".

The third product used was made by heating styrene obtained from cinnamic acid, in a closed vessel at 180° for twenty hours. This material was even more brittle than the 140° polymer and was readily pulverized. It contained but few bubbles and was in the form of transparent plates about one-eighth of an inch thick. This sample will be called the "180° polymer".

MOLECULAR WEIGHTS OF THE META STYRENE PREPARATIONS.

The molecular weights of the cold 140° and 180° polymers were found by the depression of the freezing point method using benzene as the solvent. The usual procedure was followed: A suitable amount of the solid was weighed out and placed in 20 c.c. of benzene in the inner tube of a freezing point apparatus. After solution had taken place, the freezing point of the solution was measured several times reading the temperature on a Beckman thermometer to .001°. The freezing point of the same sample of benzene was taken immediately after and the difference of the two taken as ΔT. The molecular weight of the solution was then calculated from the equation:

$$m = \frac{100 K_F W}{\Delta T W'}$$

where m = molecular weight of solute
K_F = freezing point constant of solvent
W' = weight of dissolved substance
W = weight of solvent
ΔT = observed lowering of freezing point

<u>Molecular Weight of Cold Polymer.</u>

A solution of .328 grams of the cold polymer in 100 c.c. of benzene gave the following results:

Freezing point of solution	3.960°
(on Beckman scale)	3.960°
	3.960°
av. =	3.960°
Freezing point of benzene	3.960°
	3.961°
	3.960°
av. =	3.960°

A solution of 2 grams of meta styrene in 100 c.c. of benzene likewise produced no observable lowering of the freezing point. A lowering of the freezing point of .002° degrees certainly is observable so from this measurement, the molecular weight of the cold polymer must be over 50,000. But Nernst(27) has shown that the lowering of the freezing point of colloidal solutions is not a theoretically sound method of determining molecular weights so this result may be accurate.

Staudinger(28) gave the molecular weight of the cold polymer as 21,000 but he did not mention how he arrived at this figure.

Molecular Weight of 140° polymer:-

Weight of meta styrene 1,0000 gr.
Weight of benzene 17.5800 gr.
$\Delta T = .145°$
$m = 1920$
Calculated for 20 C_8H_8 2080 19 C_8H_8 = 1976

Molecular Weight of 180° polymer:-

Weight of meta styrene 1.0000 gr.
Weight of benzene 17.5800 gr.
$\Delta T = .128°$
$m = 2180$
Calculated for 21 C_8H_8 2184

It will be shown later that these polymers are not homogeneous but are mixtures of molecules of varying size. So these molecular weights represent an average of all the molecules present. The fact is apparent, however, that at room temperatures, styrene polymerizes to give a much larger aggregate than it does at high temperatures.

VISCOSITY OF BENZENE SOLUTIONS OF META STYRENE.

Corresponding to the large difference in molecular weight,a very great difference in the viscosity of the solutions of the different meta styrene preparations was observed. The cold polymer with the high molecular weight gives sols of high viscosity, while the heat polymers give solutions of low viscosity. The viscosities of different concentrations of the cold polymer are given in Table I., those of the 140° polymer in Table II, and those of the 180° polymer in Table III. All three are shown graphically in Fig. I.

The various solutions described here were made by weighing a definite amount of meta styrene into 100 c.c. of pure, dry benzene. The sols were kept in glass stoppered bottles and allowed to stand for two weeks before the readings were taken. During this period, they were shaken slightly every day.

In view of the recent work of Hatschek(29), Herschel and Buckley(30) and others, it may be advisable to define what is meant by the "visoosity" of a solution. All measurements of viscosity recorded were made with the aid of either of the three Ostwald viscosity pipettes, the constants of which are given below.

	Time of Flow (Benzene)
Viscos~~c~~imeter #1	65.0 sec.
" #2	56.8 "
" #3	77.2 "

To determine the viscosity of a sol, five c.c. of the sol was measured into the lower bulb of the viscos~~c~~imeter by means of a pipette and allowed to come to the temperature of the water bath in which the viscos~~c~~imeter was clamped in a vertical position. The level of the liquid was then raised above the higher mark and the time taken by the liquid to flow between the two marks on the instrument was noted by means of a stop watch. The relative viscosity is the ratio:

$$\frac{\text{Time of flow of sol}}{\text{Time of flow of solvent}}$$

Unless otherwise stated, all measurements were made at 25 .01°C.. Concentrations are expressed as grams of solute per 100 c.c. of solvent. The time of flow is noted throughout in seconds.

Table I. Viscosity-Concentration Relation for cold
Polymerized Meta Styrene in Benzene.

The meta styrene used was purified by precipitating it by ethyl alcohol from a chloroform solution four times. The product was dried out at room temperature in air. The benzene was thiophene free and had been dried over phosphorus pentoxide.

Viscos~~c~~imeter #1 was used.

Concentration	Time of Flow	Relative Visoosity
.0102	69.8	1.064
.0246	76.6	1.167
.0500	89.0	1.357
.0735	102.4	1.561
.1004	119.4	1.820
.1262	136.8	2.085
.1510	155.0	2.363
.1762	177.0	2.698
.2054	200.6	3.058
.2250	224.0	3.414
.2532	242.4	3.695
.3022	287.8	4.478
.3490	351.6	5.359
.4016	433.0	6.601
.5600	651	9.924

Table II. Viscosity-Concentration Relation of Solutions of 140° Polymer in Benzene.

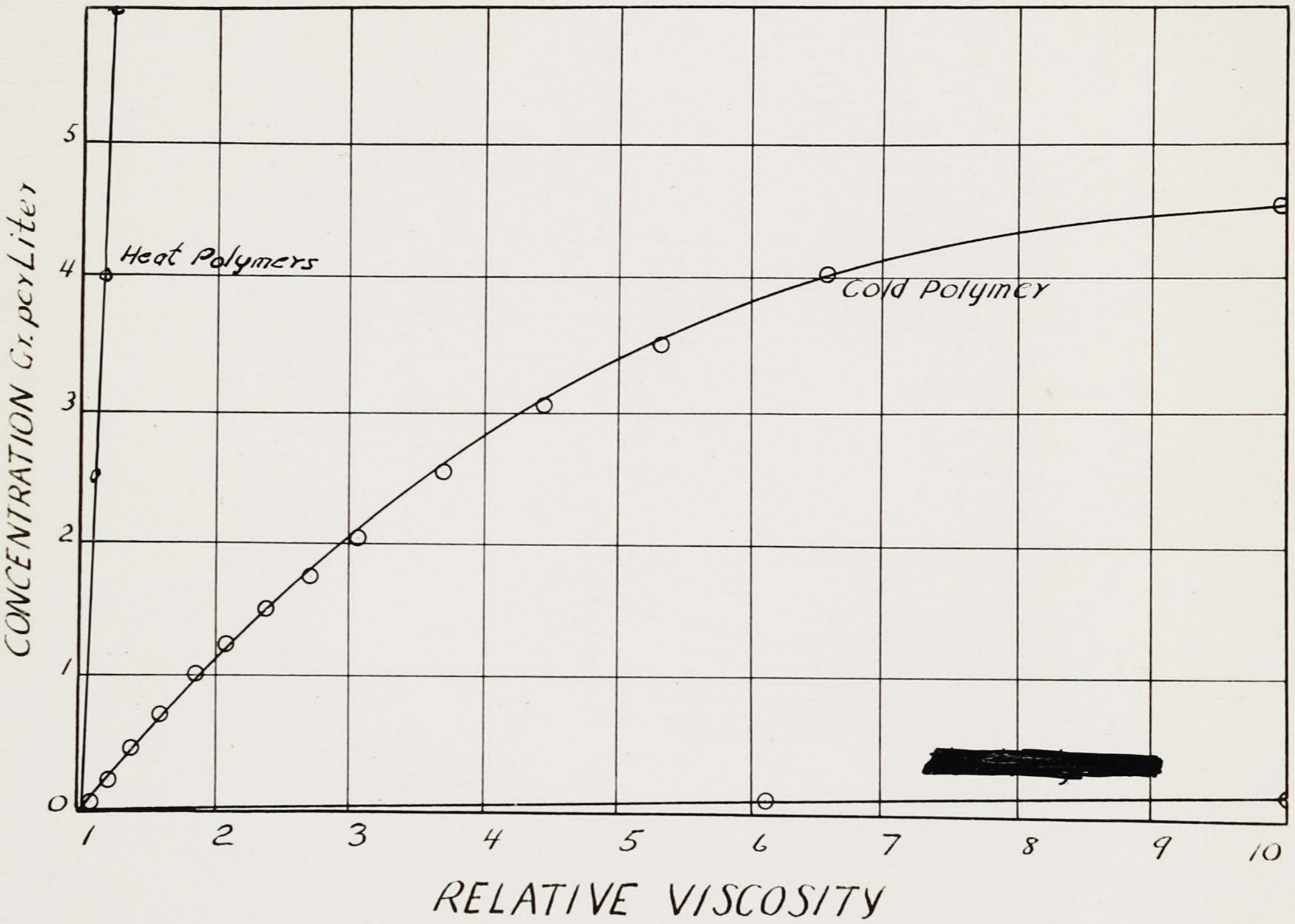
Viscos~~o~~imeter #3

Concentration	Time of Flow	Relative Viscosity
.0500	77.4	1.003
.1000	78.5	1.017
.1500	79.6	1.031
.2000	80.8	1.034
.3000	83.8	1.085
.4000	86.6	1.122

Table III. Viscosity-Concentration Relation of Solutions of 180° Polymer in Benzene.

Temperature = 25°
Viscos~~o~~imeter #3

Concentration	Time of Flow	Relative Viscosity
.0500	77.3	1.001
.1000	77.6	1.005
.1500	78.7	1.018
.2000	79.8	1.034
.3000	81.8	1.059
.4000	84.0	1.089



[redacted]

FIGURE I.

SEPARATION OF META STYRENE INTO FRACTIONS DIFFERING IN THEIR DEGREE OF POLYMERIZATION.

That both the 140° and 180° meta styrene are heterogeneous substances is evident from their behaviour when treated with suitable solvents. For a detailed discussion of the solubility of meta styrene in organic liquids, the reader is referred to a later section on that subject. But at the present time it may be stated that there exists a number of organic liquids that we have found are just on the border line between swelling agents and precipitants for the cold polymer. Such a group includes di ethyl ether, acetone and ethyl oxalate. Since the solubility of a polymer increases as the degree of polymerization decreases, it was anticipated that these liquids would be solvents for the heat polymers.

When an attempt was made to dissolve the heat polymers in ether, acetone and ethyl oxalate, the meta styrene swelled and part of it went in solution. But there remained a white, insoluble residue that was not swollen by the liquid. If the test tubes containing the solutions were allowed to remain quiet for several days, a white powder settled to the bottom of the tubes. The addition of further quantities of the solvent in question caused no change but the addition of a small amount of benzene caused the white powder to go into solution almost immediately.

The explanation of the phenomenon is that the meta styrene consisted of a mixture of a number of molecules of varying size. The solvents used, ether, acetone, and ethyl oxalate, were able to peptize the smaller molecules but the higher polymerized aggregates were insoluble and remained as the powder. The benzene added dissolved them.

The rapidity with which the solution became clear after the addition of benzene leads to the conclusion that the material comprising the powder was not very highly polymerized. For it takes considerable time for benzene to swell and dissolve the high molecular meta styrene polymerized at room temperature even when it is finely divided. It appears probable that the material insoluble in ether, acetone and ethyl oxalate was but slightly more polymerized than the soluble fraction. If this reasoning is correct the material polymerized at 140° and at 180° is heterogeneous but the size of the individual molecules does not vary greatly.

FRACTIONAL PRECIPITATION OF META STYRENE.

We were unable to find solvents that would dissolve part of the cold polymerized meta styrene and leave a residue of highly polymerized material. But, nevertheless, evidence has been obtained that this polymer, like the heat polymers, is composed of molecules varying within a narrow range in their size.

The first evidence in favor of this view came as a result of fractionally precipitating a solution of meta styrene and collecting successive fractions. The fractions were thoroughly dried under the same conditions and the viscosity of their solutions was found to differ. The experimental details follow.

A sol of cold polymerized meta styrene was made by dissolving 1.5 grams in 100 c.c. of benzene. Anhydrous ethyl alcohol was added very slowly to 100 c.c. of the sol with continual shaking. After 42.8 c.c. had been added a slight white turbidity appeared. The solution was then allowed to stand for 24 hours and the precipitate settled in the bottom of the containing vessel. The solution was decanted off and more alcohol added and the process was repeated until precipitation was complete. The precipitates were collected separately and dried with a vacuum pump. Solutions were made of the fractions in benzene of the same concentrations (.328 grams per 100 c.c. of benzene) and the viscosity of these solutions taken. The results are tabulated below.

Table IV. Viscosity of Meta Styrol Fractions. The precipitates from the third, fourth and fifth precipitations were dissolved together.

Viscos~~p~~imeter #2

Total c.c. of Alcohol added.	Time of Flow	Relative Viscosity
42.8	307.2	5.40
43.24	300.6	5.29
44.24 45.75 48.75	131.2	2.31

FRACTIONAL DIFFUSION OF META STYRENE

Further evidence as to the heterogeneous condition of cold polymerized meta styrene was obtained by fractionally diffusing the material. A sample of meta styrene weighing 2.17 grams was placed in a bottle and 100 c.c. of benzene added. After part of the meta styrene had dissolved the liquid was poured off and 50 c.c. of fresh benzene added. The solution poured off was precipitated by ethyl alcohol and the precipitate dried under vacuum, The following fractions were collected in this manner.

Fraction 1.	Weight (dry)	.42	grams
Fraction 2.	" "	.74	"
Fraction 3.	" "	.56	"

Solutions of the same concentration were made of all the fractions by dissolving the proper amount in benzene to give a concentration of .328 grams per 100 c.c. of benzene.

The viscosities of these fractions are given in Table V.

Table V. Viscosities of Meta Styrene Fractions obtained by Diffusion.

Viscos~~c~~imeter #1.

Fraction	Time of Flow	Relative Viscosity
1	321.6	4.90
2	332.2	5.07
3	346.9	5.27

It is seen that the fractions collected last have the highest viscosity.

This corresponds with the theory that, in the original substance, there exist aggregates with different sizes and that those which are composed of the largest number of combined molecules are the least soluble and would be found in the largest proportions in the last part of the meta styrene to dissolve. Sols composed of the largest aggregates are the ones that have the highest viscosities.

The separation of the polymers by this method is not so sharp as by the precipitation method. Undoubtedly much of the high polymer dissolved in the first fractions. But there is enough of a difference in the rate at which the highest and lowest aggregates become peptized to effect a rough separation by this procedure.

The lowest relative viscosity obtained for any fraction either by precipitation or by diffusion was 2.31 . While this is considerably lower than that of the original substance, still it is far higher than that of the heat polymers (1.09) which had molecular weight of about 2000. It therefore appears likely that no considerable amount of material exists in the cold polymerized meta styrene with a low molecular weight; but that this cold polymerized material is comprised of molecules of very large dimensions that vary over a comparatively restricted range.

FRACTIONAL PRECIPITATION OF RUBBER.

The method described for the fractional precipitation of meta styrene was extended to the case of rubber. The rubber hydrocarbon was obtained free from proteins and resins by the following purification process.

A sample of ribbed smoked sheet was extracted five times with mixtures of 70 parts of acetone and 30 parts of petrol ether. The rubber was allowed to stand in this extracting liquid at room temperature for two days before the solvent was poured off and a fresh portion added. This procedure removed all resins from the crude rubber.

After this extracted rubber was dried it was allowed to swell in benzene, care being taken not to shake the mass of swollen material. Under these conditions the rubber hydrocarbon diffuses into the benzene leaving behind a skeleton composed of protein material. The benzene was then decanted off and the pure caoutchouc was precipitated by ethyl alcohol and placed in a vacuum desiccator for two weeks to dry.

A solution of this material was made by adding .76 grams of the sample to 100 c.c. of benzene. This solution was fractionally precipitated in the manner previously described, the precipitate dried and solutions of the same concentration (.328 grams per 100 benzene cc.) were made. The following table presents the viscosities of these solutions.

Table VI. Viscosity of Precipitated Rubber Fractions.

Viscos~~o~~imeter #2

Fraction		Time of Flow	Relative Viscosity
Fraction 1	(.48 gr)	149.4	2.63
" 2	(.20 gr)	91.0	1.62
" 3	(.07 gr)	82.0	1.46

It appears then that rubber as well as meta styrene is composed of aggregates of different degrees of polymerization. The relatively low viscosities of all the fractions is probably due to the fact that when the rubber was diffused out of the protein, only about 50%

of the hydrocarbon was extracted. The remainder stayed with the protein and it cannot be removed without danger of getting part of the protein in solution. The fraction of rubber that was not obtained in solution was the more insoluble and hence, the most highly polyermized part. And the fraction of the original hydrocarbon that was collected in the solution was the lower polymerized and less viscous part.

FRACTIONAL DIFFUSION OF RUBBER.

Attempts to fractionate the rubber hydrocarbon by a diffusion process similar to the one employed in the case of meta styrene met with questionable success.

Four samples of smoked sheet from which the resin but not the protein had been removed were allowed to diffuse into benzene and the fractions were collected in two different ways. In the first two experiments, the benzene was poured off and the rubber precipitated immediately and allowed to dry in air in a dark place. After the fraction last obtained was dry, solutions of all the fractions were made by dissolving .328 grams in 100 c.c. of benzene and their viscosities measured at the same time. The results of these two experiments are shown below.

Table VII. Experiment 1. Viscosimeter #2.

Fraction	Time of Flow	Relative Viscosity
1.	256.0	4.51
2	293.6	5.17
3	309.2	5.44

Table VIII. Experiment 11. Viscosimeter #2.

Fraction	Time of Flow	Relative Viscosity
1	169.8	2.92
2	281.0	4.32
3	278.0	4.28

These results show that the fractions that diffused out last have the highest viscosities. But this might be explained by other reasoning than the assumption that the latter fractions consisted of a higher polymer. The different fractions were allowed to dry in air for different periods of time. The first one was exposed to the atmosphere about a month longer than the last one. So it was possible that the first samples were oxidized during this time sufficiently to lower their viscosity the amount found.

In the next two experiments, the fractions were collected in a manner that precluded the possibility of oxidation. Instead of precipitating the benzene solution as soon as it was siphoned off the rubber, it was placed in a dark brown bottle, fitted with a ground glass stopper and removed to a dark cupboard. When all the fractions had been collected in this manner, they were all precipitated at the same time and dried together in a high vacuum desiccator. Solutions of .328 grams of the samples in 100 c.c. of benzene were then made and the viscosities of the solutions measured on the same day.

Table IX. Experiment III Viscos¢imeter #1

Fraction	Time of Flow	Relative Viscosity
1	336.8	5.18
2	371.4	5.69
3	377.1	5.80
4	250.0	3.85
5	244.4	3.76

Table X. Experiment IV. Viscos¢imeter #1

Fraction	Time of Flow	Relative Viscosity
1	335.0	5.15
2	292.8	4.50
3	359.2	5.53
4	208.2	3.20
5	252.2	3.88

If fraction #2 of experiment IV is considered an error, it is seen that the viscosity of the fractions 1, 2 and 3 gradually rises; and the viscosity of the last two fractions is considerably lower than any of the others. This may be due to part of the protein going into solution as it has been shown that traces of impurities lower the viscosity of a rubber sol considerably.

These experiments show that the rubber hydrocarbon is not homogeneous (complicating factors, however, not present in the case of meta styrene, make a separation of the polymer into regular fractions by diffusion a matter of difficulty)

EFFECT OF THE TEMPERATURE AT WHICH THE MEASUREMENT IS MADE ON THE VISCOSITY OF A META STYRENE SOL.

While the time of flow of a meta styrene sol through a viscosimeter varies with the temperature at which the measurement is made, it was found that the ratio of the time of flow of the sol to the time of flow of the solvent at the same temperature is a constant that does not vary with the temperature.

This experiment was conducted with a sol of the cold polymerized meta styrene that had been purified by precipitation from a chloroform solution by alcohol. The material was dried at 80° and .328 grams were then dissolved in 100 c.c. of benzene to give the solution used.

To measure the viscosity at different temperatures, a constant temperature bath was adjusted at the desired temperature and the viscosimeter, containing 5 c.c. of the sol, was clamped in the bath. After allowing 15 minutes for the sol to reach the temperature of the bath, the time of flow of the sol through the viscosimeter was taken and checked. At each temperature a new sample of the sol was used.

The results of the experiment are shown in Table XI. Viscosimeter #3 was used in all cases. The figures in the third column, representing the time of flow of benzene at different temperatures, were calculated from the measurements of the absolute viscosity of benzene given in Landolt-Börnstein, 3rd Edition, p.46. The temperature-viscosity curve was plotted and the values at the desired temperature then interpolated. Knowing the time of flow of benzene through the viscosimeter at 25° and the absolute viscosity at any temperature, the time of flow at any temperature could be calculated.

TABLE XI.

Temperature °C.	Time of Flow (Sol)	Time of Flow Benzene	Relative Viscosity
6.8	361.4	102.7	3.52
13.5	325.0	92.3	3.52
18.7	301.2	85.1	3.54
25.0	274.2	77.2	3.53
29.8	257.0	72.8	3.53
35.0	242.1	68.0	3.56
43.7	216.3	61.0	3.54
50.0	200.1	56.8	3.52

Figure II shows the time of flow of the sol plotted against the temperature.

THE SURFACE TENSION OF META STYRENE SOLS OF VARIOUS CONCENTRATIONS.

The instrument used to measure the surface tension of the meta styrene sols was an apparatus of the Du Noüy type supplied by the Central Scientific Company. It has been fully described by the inventor(31).

Briefly it consists of a loop of platinum wire

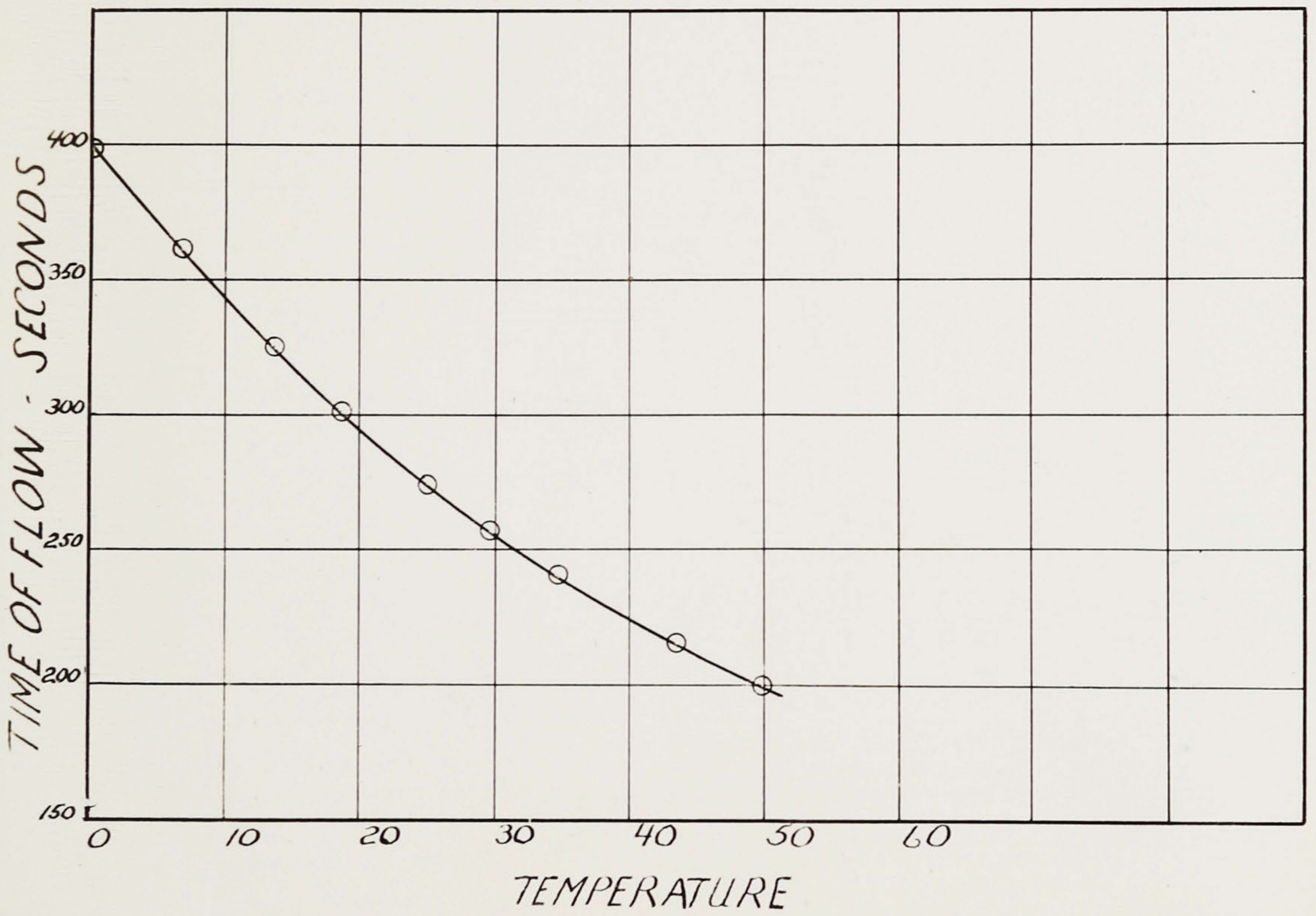

TIME OF FLOW - SECONDS
400
350
300
250
200
150
0
10
20
30
40
50
60
TEMPERATURE

FIGURE II.

which is pulled out of the surface of a liquid by force applied to a lifting arm through a torsion wire. A pointer attached to the wire gives the angular distortion of the wire necessary to pull the loop out of the liquid.

The instrument was calibrated before use by placing known weights in the loop and reading the angular distortion of the wire necessary to just raise the loop. A curve correlating these two measurements was plotted. Then, knowing the circumference of the loop, the surface tension of a liquid could be calculated from a measurement of the angular distortion of the wire when the loop left the liquid.

By this method, a value of 76 dynes per cm. was obtained for the surface tension of water at 18° and 32.8 dynes per cm. for benzene at the same temperature. These measurements agree as well as could be expected with the value for water of 74.12 dynes /cm. and of benzene, 29.98 dynes /cm. both of which were determined by the capillary tube method (Landolt-Börnstein).

In the following table are given the values for the surface tension of sols of meta styrene in benzene. All measurements were made at 18°C.

TABLE XII.

Concentration (Grams of meta styrene per 100 c.c. of benzene)	Angular displacement of wire.	Surface tension (Dynes per cm.)
0	47.2	32.8
.0140	47.1	32.7
.1503	47.3	32.9
.2250	47.2	32.8
1.0000	47.1	32.7

It is seen that, within the concentrations mentioned, the addition of meta styrene to benzene produces no measurable affect on its surface tension.

THE EFFECT OF ULTRA VIOLET LIGHT ON THE PROPERTIES OF A META STYRENE SOL.

Exposure of a solution of meta styrene in benzene to ultra violet light for varying periods of time was found to lower the viscosity of the solution. After the solution has been exposed a certain length of time, further exposure causes no further decrease in viscosity.

The following table gives the results obtained when a solution of .328 grams of meta styrene per 100 c.c. of benzene was exposed to the light emitted by a quartz mercury vapour lamp. Fifteen c.c. of the sol was placed in a small quartz container fitted with a stopper and then placed 6 cm. away from the lamp. The sol was allowed to remain there for an appropriate period of time and its viscosity was then measured at 25° . A new sample of the

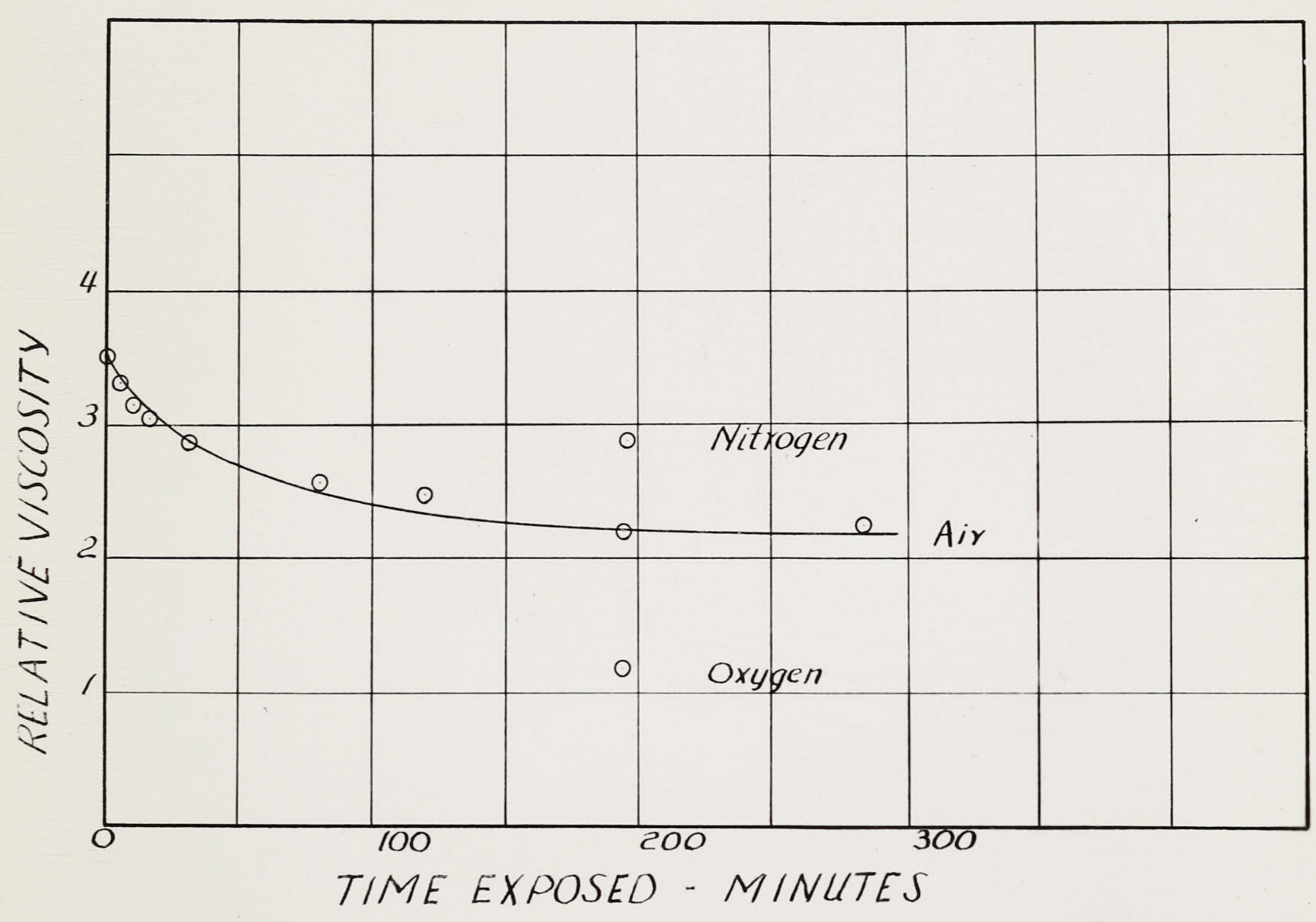

4
3
2
1
RELATIVE VISCOSITY
Nitrogen
Air
Oxygen
0
100
200
300
TIME EXPOSED - MINUTES

FIGURE III.

sol was used for each experiment and the volume of the liquid as well as the distance from the lamp were kept constant. The same quartz container was used throughout.

TABLE XIII.

Viscos~~c~~imeter #3 used,

Time exposed. (Minutes)	Time of Flow.	Relative Viscosity
0	270	4.49
5	254	3.30
10	241.6	3.13
16	235.6	3.05
31	220.0	2.85
80	199.0	2.58
120	191.5	2.48
195	169.8	2.20
280	172.0	2.22

Figure III represents the above results graphically.

In the above experiments, no attempt was made to control the constitution of the atmosphere above the sol. It was found, however, that this was an important factor. When the air above the solution in the quartz was displaced by nitrogen, the viscosity of the solution was decreased less than when the air was present. But when oxygen was the residual gas, the viscosity decreased far more than in either of the above mentioned cases as the figures in the next table show.

TABLE XIV.

Gas	Minutes Exposed	Time of Flow	Relative Viscosity
Air	195	169.8	2.20
Nitrogen	195	217.4	2.87
Oxygen	195	93.2	1.20
	0	270	4.49

The fact that the viscosity of the solution is decreased considerably in the absence of oxygen shows that the primary cause of the decrease in viscosity is not oxidation.

At the same time that the viscosities of the sols mentioned in Table XIV were taken, their freezing points were also measured. The freezing points of the sols that had been exposed to ultra violet light in the presence of nitrogen and air were exactly the same as the freezing point of the solvent.

But the sample exposed to ultra violet light for 195 minutes in the presence of oxygen showed a marked depression of the melting point.

The following were the readings taken:

Concentration of sol .328 grams in 87.9
Grams of benzene
Melting point of benzene 3.616
(on Beckmann) 3.618
3.616
3.616
3.616

Melting point of sol.	3.596
	3.600
	3.600
	3.600
	3.600

= .016°

The average molecular weight calculated is 1140.

It would appear that the explanation for the action of ultra violet light on meta styrene sols is that the highly polymerized material is catalytically depolymerized, in part at least by ultra violet light. Both ultra violet light and oxygen act as catalysts in promoting this change.

Considerably difficulty was encountered at the beginning of this work on the action of ultra violet light by the solutions turning a faint yellow or brown when they had been exposed for some time. The coloration was more pronounced in the specimens that had been subjected to the action of the rays for the longest periods of time and it was at first thought that it was due to oxidation of meta styrene.

The observation that benzene alone gave the coloration precluded this possibility. The cause was finally narrowed down to traces of thiophene in the benzene. The amount of this impurity required to cause the color was extremely small and it is probable that at least a delicate qualitative test for thiophene might be worked out on this basis.

It is interesting that no appearance of color was noted when the atmosphere above the solution was oxygen; but the color did appear in every experiment when nitrogen or air was used.

THE EFFECT OF FREEZING A META STYRENE SOL ON ITS VISCOSITY.

When a meta styrene sol was frozen and then allowed to melt, no change in the appearance of the liquid was noticeable. That is, no solid meta styrene separated out on freezing or on melting. The viscosity of the sol immediately after melting was exactly the same as before it was frozen and no change in viscosity took place on standing for several days.

But if the solution is sepatated from the solid as the latter melts, the fractions separated in this manner differ widely in their viscosity. These experiments were conducted on a sol in benzene of the concentration .328 grams of meta styrene in 100 c.c. of solvent. Thirty-five c.c. of the sol were placed in a large test tube and immersed in an ice bath until the whole mass was solid. The length of time that the sol was allowed to remain frozen was found to have no effect on the results.

In the first experiment the sol was separated into two nearly equal portions on thawing, fraction 1 being the part that became liquid first.

The viscosities of the fractions are shown below.

TABLE XV.

Viscosimeter #1

Sample	Time of Flow	Relative Viscosity
Original sol	270.6	4.15
Fraction 1	258.4	3.97
" 2	278.6	4.28

The observation that there was considerable difference in the viscosity of the two portions led to experiments in which the sol was separated into five approximately equal fractions as it melted. The results of three similar experiments are tabulated below. The same original sol and viscosimeter #1 were used in all.

TABLE XVI.

Experiment 2.

Fraction	Time of Flow	Relative Viscosity
Original sol	270.6	415
1	256.4	3.94
2	402.0	6.17
3	264.0	4.06
4	255.0	3.92
5	221.2	3.40

TABLE XVII.

Experiment 3.

Fraction	Time of Flow	Relative Viscosity
Original sol	270.6	4.15
1	288.2	4.43
2	315.4	4.85
3	343.6	5.27
4	214.4	3.29
5	204.0	3.14

TABLE XVIII.

Experiment 3.

Fraction	Time of Flow	Relative Viscosity
Original sol	270.6	4.15
1	312.8	4.80
2	330.0	5.08
3	322.0	4.95
4	239.0	3.68
5	237.0	3.65

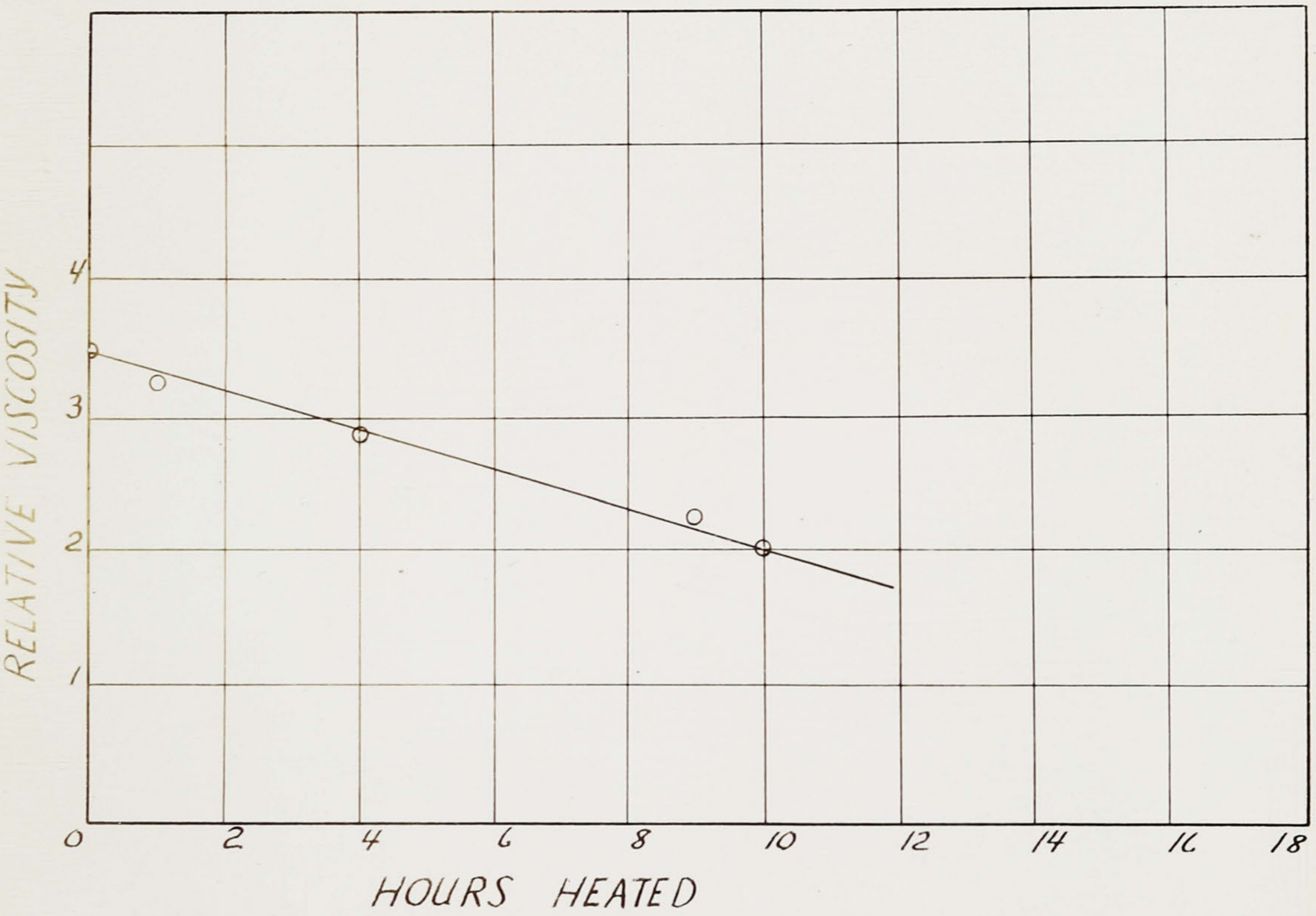
The experiments cannot be expected to check exactly because no attempt was made to control the rate of melting.

It is seen that the first three-fifths of the material that melts contain a higher concentration of meta styrene than the last two-fifths.

This phenomenon can be explained by assuming that the solid meta styrene separates out on freezing in a very fine state of subdivision. Then the first portions of benzene that become liquid peptize a large amount of the meta styrene before the rest of the benzene melts. This would account for the high viscosity of the first fractions and the low viscosity of the latter fractions.

THE EFFECT OF HEATING SOLID META STYRENE ON THE VISCOSITY OF META STYRENE SOLS.

If the cold polymerized meta styrene was subjected to temperatures of about 95° for any considerable length of time it was found that the viscosity of a



<u>FIGURE IV.</u>

solution made from the material was considerably lower than that made from a sample that had not been so treated.

The material used in this experiment was a sample of the cold polymerized material that had been purified by reprecipitation from a benzene solution by alcohol four times. The product was then thoroughly dried in air. Samples of this meta styrene were then placed in an electrically heated air oven which was kept at a temperature of 95° throughout. At appropriate intervals pieces of the meta styrene were taken out and allowed to cool. Solutions in benzene were made of a concentration of .328 grams in 100 c.c. of benzene. The viscosities were measured in visco~~s~~imeter #3 at 25°C.

The next table shows the results.

TABLE XIXI

Hours heated	Time of Flow	Relative Viscosity
0	268.4	3.487
1	255.0	3.251
4	223.8	2.873
9	177.2	2.295
10.0	159.0	2.060

When the length of time of heating is plotted against the relative viscosity, as in Fig.IV, it is seen that the decrease in viscosity is a linear function of the time.

THE EFFECT OF BOILING A BENZENE META STYRENE SOL ON ITS VISCOSITY.

The effect on the viscosity of boiling a meta styrene sol has been determined for a large number of sols. In the case of the first one examined, the viscosity of the sol immediately after the boiling was stopped was lower than that of the original sol. On standing, the viscosity of the solution increased until it had reached a constant value about 10 hours later. All attempts to repeat these experiments with new sols have been unsuccessful as every other sol showed a slight decrease in viscosity on boiling and this new value did not alter with time. The experiments with the first sol will be described first.

The material used in these experiments had a history previous to the time used that was impossible to duplicate in the time at our disposal. A quantity of cold polymerized material was reprecipitated from a chloroform solution four times by ethyl alcohol and then allowed to stand in a chloroform solution for five months (March to August 1926). The solution was kept during this time in a dark glass bottle in a dark closet. In August, the meta styrene was precipitated from the solution by alcohol and dried in air. 3.2800 grams of the substance were then dissolved in 1 litre of purified, dry benzene and this latter solution was kept in a dark glass bottle. It was three months old when these experiments were started.

Fifty c.c. of the sol was then placed in a 150 c.c. Pyrex erlenmeyer and connected to a reflux condenser by means of a cork protected by tinfoil. Later , the flask was sealed directly through glass to the condenser but this did not alter the results. The boiling was conducted by placing the flask on an electric hot plate so adjusted that the liquid boiled at a moderate rate. When the boiling was stopped, the contents of the flask were cooled in a stream of cold water without removing the condenser. When cold, the flask was removed and tightly stoppered with a cork protected by tinfoil. Samples of the liquid were taken out from time to time and their viscosity measured at 25°C,

It was found, as previously mentioned, that the viscosity immediately after boiling had ceased was lower than that of the original sol. This decrease was small but it was observed consistently. The value which the viscosity finally reached depended on how long the sol had been boiled. The longer it was boiled, the more viscous it became on standing. It took longer for a sol that had been boiled for a long time to reach equilibrium than one that had been boiled for a shorter period of time.

The results of experiments in which the sol was boiled for various periods of time are given in the following tables. By the figures in the column headed "Time" is meant the number of hours elapsed between the time when the boiling was stopped and when the viscosity was measured.

TABLE XX.

Experiment I

Sol boiled for 15 minutes.

Relative viscosity of original sol = 5.07

Viscos~~c~~imeter #1

Time	Time of Flow	Relative Viscosity
.25	322	4.91
.75	323	4.92
3.87	339	5.17
5.80	341	5.22
24.0	340	5.21

TABLE XXI.

Experiment IA. This is a duplication of Experiment I.

Sol boiled for 15 minutes.

Relative viscosity of original sol = 5.07

Viscos~~c~~imeter #2.

Time	Time of Flow	Relative Viscosity
.45	278.2	4.90
1.16	279.0	4.91
2.40	281.2	4.95
3.07	292.6	5.14
4.40	294.2	5.18
11.00	296.0	5.21
24.00	296.2	5.21

TABLE XXII.

Experiment II.

Sol boiled 30 minutes

Relative viscosity of original sol = 5.07

Visco~~s~~imeter #2.

Time	Time of Flow	Relative Viscosity
.45	268.2	4.72
1.50	272.4	4.80
2.92	274.6	4.83
6.66	314.	5.53
8.66	313.	5.51

TABLE XXIII.

Experiment IIA. This is a duplication of Experiment II.

Sol boiled 30 minutes.

Relative viscosity of original sol = 5.07

Visco~~s~~imeter #2.

Time	Time of Flow	Relative Viscosity
.75	267	4.70
12.5	310.8	5.47
15.0	310.8	5.47

TABLE XXIV.

Experiment III.

Sol boiled 120 minutes.

Relative viscosity of original sol = 5.07

Visco~~s~~imeter #2.

Time	Time of Flow	Relative Viscosity
.10	325.6	4.95
1.16	325.6	4.95
6.00	362.4	5.52
8.00	397.4	6.06
25.10	397.0	6.06

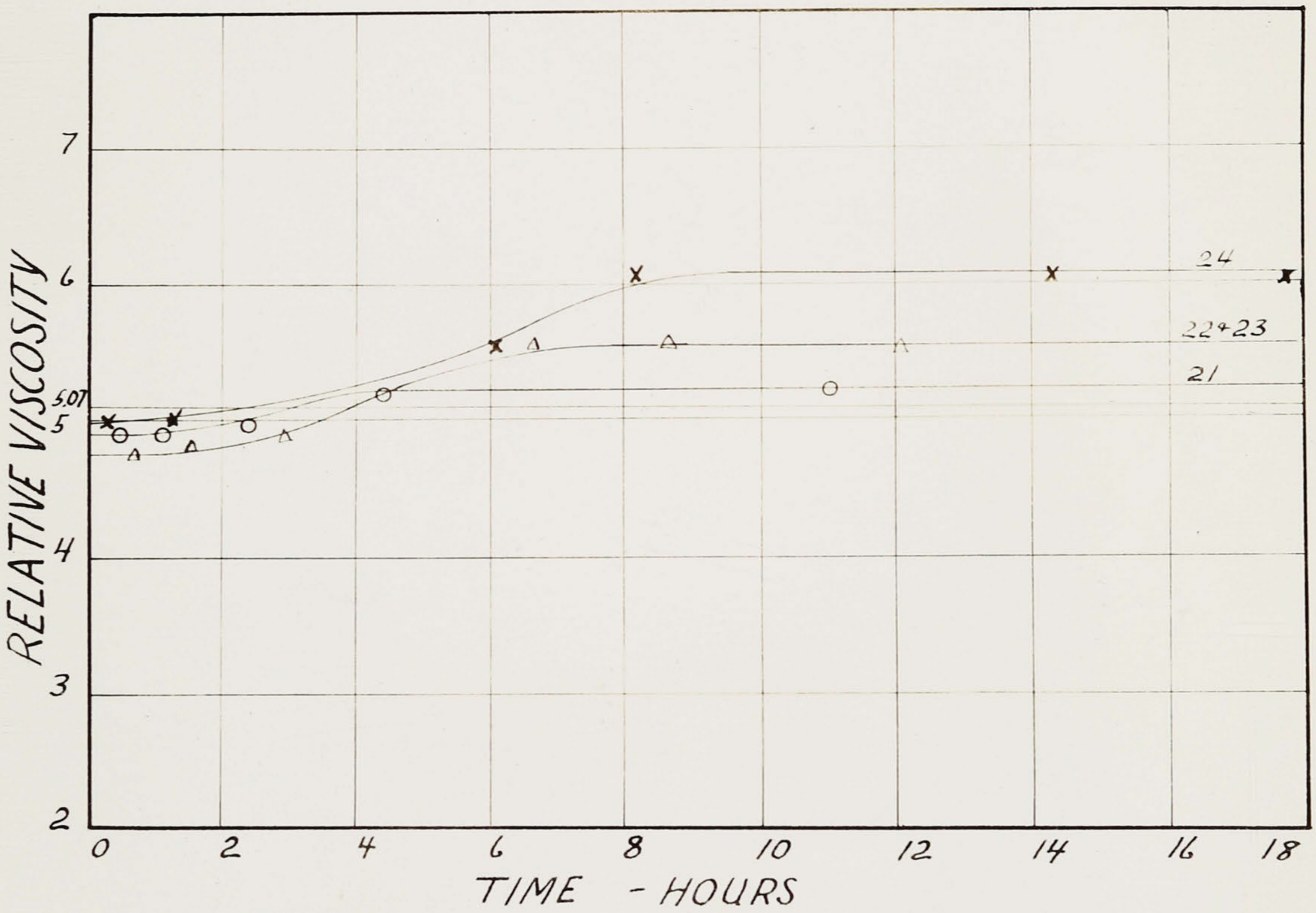

RELATIVE VISCOSITY
TIME - HOURS
7
6
5.07
5
4
3
2
0
2
4
6
8
10
12
14
16
18
24
22+23
21

FIGURE V.

Experiment IV. A solution was boiled for eight hours. When boiling was stopped, it was found that a solid gel of meta styrene had separated. Twelve hours later the gel had not changed in appearance and the relative viscosity of the solution around the gel was 6.44 .

The figures tabulated in Tables XXI, XXII, XXIII and XXIV are plotted in Fig. V. The experiments indicate that boiling this sol caused the meta styrene to polymerize to a material that gave a more viscous solution. When boiling was continued long enough, as in Experiment IV, the meta styrene actually became so highly polymerized that it was insoluble in benzene. An explanation for the observed initial drop in viscosity is offered by the observation that strenuous shaking actually lowered the viscosity of the sol. This question will be considered in a following section on the changes caused by shaking a sol.

It was desired to extend the experiments just described but all of that sol was used up. A new sol of the same concentration was prepared in the same manner that the old one had been made except that the meta styrene used had not been allowed to stand for five months in chloroform. When this sol was boiled it was found that a small decrease in viscosity resulted and this value did not alter with time.

Thinking that the age of the solution might be the factor that determined its behaviour when boiled, the new sol was allowed to stand for three months. At the end of this time it was boiled again but no change in its properties could be observed. The viscosity still dropped below the original value and remained there. Table XXV gives the value of the viscosity of different samples of the same sol when boiled for different periods of time.

TABLE XXV.

Viscosimeter #3.

Hours boiled	Time of Flow	Relative Viscosity
0	274.2	3.55
1	267.6	3.46
2	268.0	3.47
4	260.0	3.37
9	259.0	3.36

There seems to be no simple relation between the amount when the viscosity is lowered and the length of time the solution is boiled. But even prolonged boiling does not produce a very marked change.

EFFECT OF BOILING SOLS OF META STYRENE IN OTHER SOLVENTS.

The influence of the temperature at which a sol is boiled was investigated by boiling sols of meta styrene in toluene and xylene as well as in benzene. It was found that boiling a sol of which the dispersion medium has a high boiling point caused a greater decrease in the viscosity than was caused in the case of a lower boiling solvent. The new value for the viscosity did not change when the solution was allowed to stand.

The sols used in these experiments were prepared by dissolving .328 grams of the same sample of meta styrene in 100 c.c. of the solvent in question.

In the results below, the relative viscosity is the ratio of the time of flow of the sol to the time of flow of the solvent in the particular sol.

Experiment I.

Solvent - Benzene (Boiling point = 80°).

Sol boiled 5.5. hours.

Relative viscosity of original sol = 3.43

" 15 minutes after boiling = 3.32

" 20 hours after boiling = 3.33

Experiment II.

Solvent - Toluene (Boiling point = 111°).

Sol boiled 5.5 hours

Relative viscosity before boiling = 3.02

" 15 minutes after boiling = 2.53

" 20 hours after boiling = 2.52

Experiment III.

Solvent - Xylene (Boiling point = 140°).

Sol boiled 5.5 hours

Relative viscosity before boiling = 3.00

" 15 minutes after boiling = 1.73

" 20 hours after boiling = 1.73

EFFECT OF BOILING A BENZENE SOLUTION OF THE HEAT POLYMERIZED META STYRENE.

Solutions of both the 140° polymer and the 180° polymer in benzene were boiled for five hours and practically no change in the viscosity of the sol was observed.

The solutions used were of the concentration of .4000 grams of meta styrene in 100 c.c. of benzene. All measurements were made with viscos~~o~~imeter #3.

Experiment I.

180° meta styrene.

Relative viscosity before boiling 1.08
" 15 minutes after boiling 1.07
" 20 hours after boiling 1.07

Experiment II.

140° meta styrene

Relative viscosity before boiling 1.12
" 15 minutes after boiling 1.10
" 20 hours after boiling 1.11

The fact that meta styrene when heated in the dry state gives solutions with low viscosities must be attributed to depolymerization. The decrease in viscosity observed in the experiments just described, where the value immediately after boiling does not alter with time, would appear to be due to the same cause.

Why the first sample of meta styrene should polymerize and the second sample depolymerize when heated to the same extent is a question that cannot be answered at the present state of our knowledge. Another sol is now being made that is expected to show the same behaviour when boiled as was shown by the first one and it is hoped that further experiments will throw some light on the situation.

THE CHANGES IN THE VISCOSITY OF META STYRENE SOLS CAUSED BY MECHANICAL AGITATION.

Mechanical agitation was found to cause the viscosity of meta styrene sols to drop. The influence of the rate of agitation, the length of time the sol was agitated and the concentration of the sol were investigated in this connection and each was found to be an important factor. It is most convenient to discuss each of these factors separately.

Influence of the rate of agitation of a sol on the change in viscosity produced.

That the viscosity of a meta styrene sol is lowered on shaking was first demonstrated by shaking a 100 c.c. bottle containing a sol as vigorously as possible by hand. The sol used was the same one described in the paragraph preceding Table XXV. After thirty minutes shaking the relative viscosity of the sol had decreased from 3.14 to 3,07 (Viscos~~o~~imeter #2). This change corresponds to a difference in the times of flow of 4.2 seconds. In all of these shaking experiments, the viscosity of the sol was measured immediately after shaking was stopped and at intervals up to 48 hours later. In no case did the viscosity alter at all with time so this point will not be mentioned again.

The impossibility of gaining quantitative knowledge about the effect of shaking a sol so long as the personal factor was so important led to the construction of several mechanical contrivances to do the work. It was found that it required very severe mechanical agitation to produce any lowering of the viscosity.

To give some idea of the velocity of shaking required to produce an effect, several of the unsuccessful forms of apparatus are described.

Apparatus #1. consisted of an arm which was fastened by a bearing at one end and held a small glass bottle containing the sol at the other. Between the two ends, a cam was attached which was actuated by a motor and vibrated the arm to which the sol was attached at the rate of 105 oscillations per minute. During each stroke, the jar containing the sol travelled 44 cm. A sol was shaken in this machine for three hours and it had the same viscosity at the end of the experiment as it had at the start.

Apparatus #2 was made by bolting a board on the flywheel of an electric motor that revolved at a rate of

1000 R.P.M. A 100 c.c. bottle containing the sol was fastened to the board lengthwise so that the centre of the flywheel coincided with the centre of the bottle. When the system moved rapidly, the sol was thrown against the walls of the bottle but not violently enough to cause any decrease in viscosity in 2 hours.

Apparatus #3 was effective in reducing the viscosity. All subsequent measurements refer to this machine. It consisted of a connecting rod, three feet long, which was fastened at one end to a crank shaft and at the other to the top end of an arm. This arm was two feet long and the bottom end was fastened to a base by a bearing. The crank shaft was driven by a motor so that it revolved at the rate of 550 R.P.M. when the machine was in operation. The sol was fastened to the middle of the connecting rod in a special type of container.

The container for the sol was made by sealing off one end of an eight inch length of glass tubing of one inch bore. The other end was closed with a tight fitting cork protected by tinfoil. The tube was heated in a flame and the glass pushed in by a sharp carbon rod so that the inside of the tube contained twenty glass posts that acted as baffling plates.

These experiments show that vigorous agitation is required to lower the viscosity of a sol and that even long continued moderate shaking produces no effect.

Influence of the length of time a sol is shaken on the change in viscosity produced.

The decrease in viscosity of a sol was found to be roughly proportional to the length of time it was shaken. This effect was shown by two sols of different concentration.

Apparatus #3 and Viscosimeter #3 were used. The results are here tabulated to show the effect observed. Each measurement was made on a fresh sample of sol.

TABLE XXVI.

Experiment I.

Sol contained .328 grams of the meta styrene in 100 cc. of benzene.

Minutes shaken	Time of Flow	Drop (seconds)
0	274.2	-
10	273.8	0.4
45	272.0	1.8
90	268.2	3.8

TABLE XXVII.

Experiment II.

Sol contained .144 grams of meta styrene in 100 cc. of benzene.

Minutes shaken	Time of Flow	Drop (seconds)
0	274.2	-
5	274.0	.2
13	273.7	.3
30	272.0	1.7

Effect of concentration of sol on change in viscosity caused by shaking.

The viscosity of concentrated solutions, having a high viscosity, is lowered more by mechanical agitation than dilute sols.

In the previous experiments the shaking machine was run at a rate of 550 R.P.M. In the present experiments it went at 615 R.P.M.

In the tabulation of results below the figures in the column headed "Concentration" refers, as usual, to the number of grams of meta styrene dissolved in 100 c.c. of benzene.

TABLE XXVIII.

Concentration	Time of Flow of Original Sol.	Time of Flow (Secs.) after 30 min. shaking.	Drop (Secs.)
.05	104.4	103.4	1
.075	120.6	118.8	1.8
.144	175.4	173.4	2
.176	219.6	217.6	2
.205	236.8	234.6	2.2
.235	300.2	296.0	4.2
.349	421.4	416.6	4.8
.45	934.0	922.0	12.0

These experiments on shaking were originally started to find out whether the initial drop in viscosity caused by boiling a sol could be explained on the basis of the agitation caused by boiling. This discussion refers only to the cases where the viscosity was observed to increase when the sol was allowed to stand after boiling.

The thought was that if the cause of the lowering observed after boiling was due to agitation, then severe shaking at room temperature ought to cause a similar effect.

It does not appear probable that the agitation that the sol receives due to the formation of bubbles could lower the viscosity as it is not vigorous enough. But the increased kinetic energy of the solvent molecules at high temperatures might be sufficient to cause them to bombard the colloidal micelles with much violence that a decrease in viscosity would result.

The final high viscosity of the sol together with the observation that when boiled for eight hours, part of the meta styrene became insoluble in benzene was interpreted to mean that the meta styrene became more highly polymerized. It now appears that the high viscosity of the solution is due not only to the presence of a higher polymer. The sol required to be allowed to stand for some considerable time before it became highly viscous. While standing, there must take place some process which could not occur while ebullition was in progress owing to the sol being in a state of agitation. This process may be either solvation, the formation of some sort of gel structure or possibly a combination of both.

THE EFFECT OF SMALL AMOUNTS OF CERTAIN SUBSTANCES ON THE VISCOSITY OF META STYRENE SOLS.

Among the effects that have been observed on introducing small amounts of electrolytes into colloidal solutions is the so-called "Electro Viscous Effect". Kruyt and de Jong(32) have reported that the viscosity of agar and starch sols is markedly decreased by the addition of electrolytes such as H Cl, K Cl, etc. in concentrations of one milli mole per liter. Kruyt and Eggink(33) have observed the effect with organophilic sols. Using a rubber in benzene sol, these authors found that a number of electrolytes lowered the viscosity of the sol when introduced in concentrations of one milli mole per liter.

Smoluchowski (34) has shown on theoretical considerations that the viscosity of a colloidal solution would be lowered if the charges on the particles were decreased or neutralized. The previously mentioned workers explained their results by saying that the colloid micelle absorbed one of the ions of the electrolyte added and thus the charge on the micelle was lowered. Whitby and Jane(35) made a careful study of the electro viscous effect in rubber using very carefully dried material but found that even under these conditions, acids, bases and salts lowered the viscosity of the sol. Organic bases were found, even in the absence of water, to lower the viscosity of the sol to an extent proportional to the dissociation constant of the base in water. The effect was therefore judged to be electro viscous.

The recent work of Humphrey and Jane(36) on the sign of the charge on rubber micelle brings this explanation into question because these authors state that when a dry sol was examined it was found that the rubber micelle had no charge on it. When water was present, the rubber particles were observed to have charges of both signs. But the electro viscous effect in rubber is the same for both wet and dry sols.

No suitable explanation for the so-called "Electro viscous" phenomenon appears to be at hand. Hence it was decided to investigate the effect with meta styrene sols with the hope of shedding more light on the situation.

The results of these experiments are, in brief, that there exists no electro viscous effect in meta styrene sols. Of the number of electrolytes tried, only ferric bromide had any appreciable effect on the viscosity of the sol and this reagent caused precipitation.

There follows a more thorough account of the materials and methods employed and the results obtained.

<u>Materials:-</u> The meta styrene used in these experiments was a sample of styrene prepared by Kahlbaum that had spontaneously polymerized by three years standing. This product was dissolved in chloroform and precipitated by

ethyl alcohol five times to remove any trace of unchanged styrene. The resulting material was thoroughly dried in a vacuum desiccator over $Ca\ Cl_2$ for a period of two weeks.

The benzene used to make up the sol was Kahlbaum's product. It was shaken with concentrated sulphuric acid several times to remove traces of thiophene and then washed with aqueous sodium carbonate solution. The benzene layer was separated and dried by allowing to stand two weeks with powdered calcium chloride, after which it was distilled through a dry glass system into a dry container.

The alcohol used in introducing inorganic salts was commercial ethyl alcohol which had been dried over calcium chloride and fractionated. Only the fraction boiling at 78° was taken.

The various materials added to the sols were samples of Kahlbaum's products and were not further purified.

All of these measurements were made on the same sample of meta styrene sol. It was made up by dissolving 3.2800 grams of meta styrene in one liter of benzene. The resulting solution was kept in a dark brown glass stoppered bottle. It had a relative viscosity of 5.00 (Benzene = 1)

METHOD OF INTRODUCING REAGENTS.

The method adopted for introducing small known amounts of reagents was a slight modification of the one

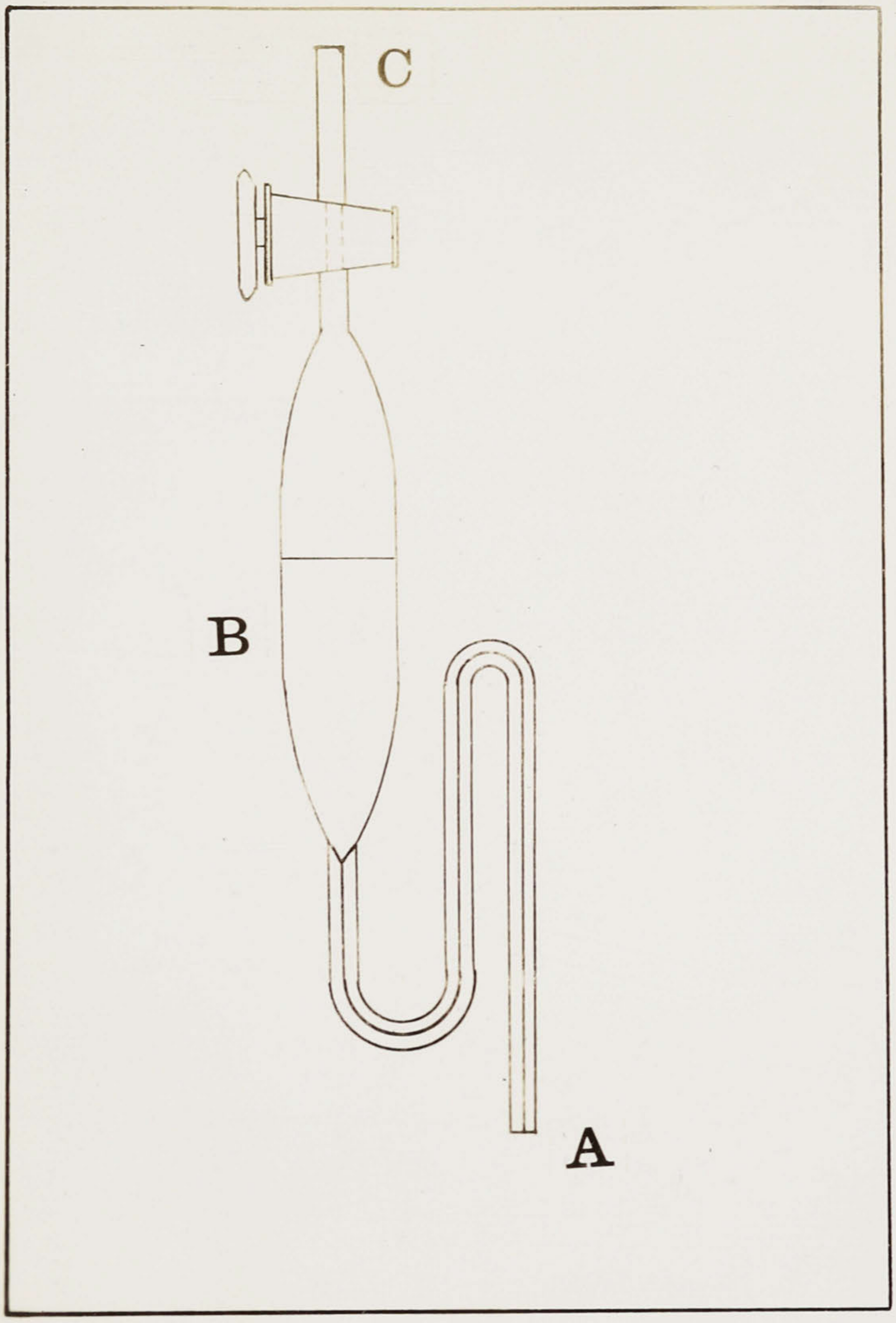


FIGURE VI.

described by R.S.Jane(37). Ten cubic centimeters of the sol were measured into 100 c.c. glass stoppered bottles and to these samples was added a solution of the impurity ether in benzene or in alcohol. Benzene was used wherever the substance it was desired to add was soluble in that liquid.

Solutions of reagents were made of such concentration so that 10 drops added to 10 c.c. of the meta styrene sol would give a concentration of the reagent of about 5 milli moles per liter. To this end, concentrated solutions were prepared by dissolving a known weight of the substance in question in benzene and progressively diluting this solution until the proper concentration was reached.

The actual addition of the solution to the sol was made with the aid of the apparatus shown in Fig.VI.

Suction was applied at C and the solution drawn into B through A. Then by opening the stop-cock the solution was allowed to flow back through the capillary tube and drop off the ground tip A.

If the liquid was brought to the same level in B each time, the first ten drops that came off of A were found to be of the same weight. Drops of benzene taken in this manner weighed .0285 grams.

A sample calculation of the whole process may serve to make the method clear:

It is desired to add aniline to 10 c.c. samples of meta styrene sols up to a concentration of 1 milli mole per liter.

3.5088 grams of aniline were weighed outand dissolved in 50 c.c. of benzene. This solution is 7.416% by weight aniline and may be denoted as solution A.

10 c.c. of solution A are diluted with 50 c.c. of benzene to give solution B which is 1.236% by weight aniline.

20 c.c. of solution B are then diluted with 20 c.c. of benzene to give solution C which contains .618% by weight of aniline.

Each drop of solution C weighs .0285 grams. Five drops will weigh .1425 grams. This amount of solution C will contain .0008806 grams of aniline.

Now 10 c.c. of a solution containing one millimole per liter of aniline will contain .000931 grams. (Mol.wt. aniline = 93.10)

So five drops of solution C added to ten c.c. of meta styrol sol will produce a concentration of aniline of

$$\frac{.0008806}{.000931} = .946 \text{ milli moles per liter.}$$

The addition of one drop of solution C will give a concentration of $\frac{.946}{5} = .189$ milli moles per liter and so forth.

After the impurity had been added to the sol, the solution was gently shaken and allowed to stand over night. Five c.c. of the sol were then introduced into an Ostwald viscosity pipette and the viscosity measured at 25°C.

The effect of at least one of each of the following classes of substances has been determined: organic acids and bases, inorganic salts, organic solvents and precipitants. The results are tabulated below. All concentrations of reagents are given in milli moles per liter.

Since the reagents were added in benzene solution, it was first necessary to determine the change in viscosity produced by the addition of pure benzene.

TABLE XXIX.

Effect of pure benzene.

Drops of Benzene added. (each drop = .0285 gr.)	Relative viscosity
0	5.00
4	4.86
8	4.75
12	4.68
16	4.67

Effect of Acids. TABLE XXX.

Di chlor acetic.

No. of drops of C_6H_6 solution.	Concentration	Relative Viscosity
0	0	5.00
2	1.52	4.94
4	3.04	4.88
8	6.08	4.74
16	12.16	4.67

This experiment was repeated twice and checked well within limits of experimental error.

TABLE XXXI.

Formic acid.

No. of drops of C_6H_6 solution	Concentration	Relative Viscosity
0	0	5.00
1	.28	4.94
2	.56	4.92
3	.84	4.89
4	1.12	4.87
5	1.40	4.84

Effect of Organic Bases.

TABLE XXXI.

Piperidine.

No. of drops of C_6H_6 solution	Concentration	Relative Viscosity
0	0	5.00
2	.75	4.92
4	1.50	4.90
6	2.25	4.87
8	3.00	4.75

TABLE XXXII.

Aniline.

No. of drops of C_6H_6 solution.	Concentration	Relative Viscosity
0	0	4.97
1	.53	4.94
2	1.06	4.93
3	1.59	4.90
4	2.12	4.89
5	2.65	4.87

TABLE XXXIII.

Di methyl aniline.

No. of drops of C_6H_6 solution.	Concentration	Relative Viscosity
0	0	5.00
1	.34	4.96
3	1.02	4.92
5	1.70	4.88

Effect of Solvents.

TABLE XXXIV.

Nitro benzene.

No. of drops of C_6H_6 solution	Concentration	Relative Viscosity
0	0	5.00
1	.21	4.95
2	.42	4.93
3	.63	4.89
4	.84	4.88
5	1.05	4.86

Effect of Precipitants

TABLE XXXV.

Ethyl alcohol.

No. of drops of C_6H_6 solution	Concentration	Relative Viscosity
0	0	4.98
1	.32	4.94
2	.64	4.92
3	.96	4.90
4	1.28	4.85
5	1.60	4.83

Effect of Inorganic Salts.

The inorganic salts used were added to the sol by means of an alcoholic solution because of the low solubility of the salts in benzene. A control experiment on the effect of drops of alcohol was therefore necessary.

The meta styrene sol used in these measurements was a different one than the sol used in the preceding one.

TABLE XXXVI.

Effect of alcohol.

No. of drops of Alcohol	Relative Viscosity
0	3.55
5	3.40
10	3.31

TABLE XXXVII.

Effect of mercuric bromide.

No. of drops of alcoholic soln.	Concentration	Relative Viscosity
0	0	3.55
5	.95	3.40
10	1.90	3.31

TABLE XXXVIII.

Effect of ferric bromide.

No. of drops of alcoholic soln.	Concentration	Relative Viscosity
0	0	3.55
5	1.1	2.50
10	2.2	2.40

The large decrease in the viscosity caused by the ferric bromide solution was due to the fact that part of the meta styrene had been precipitated by the reagent and was visible as a solid in the bottom of the jar. Consequently, the remaining solution had a lower concentration of meta styrene than the original and a lower viscosity.

This result is not to be confused with the electro viscous effect where the viscosity decreases and no precipitation takes place.

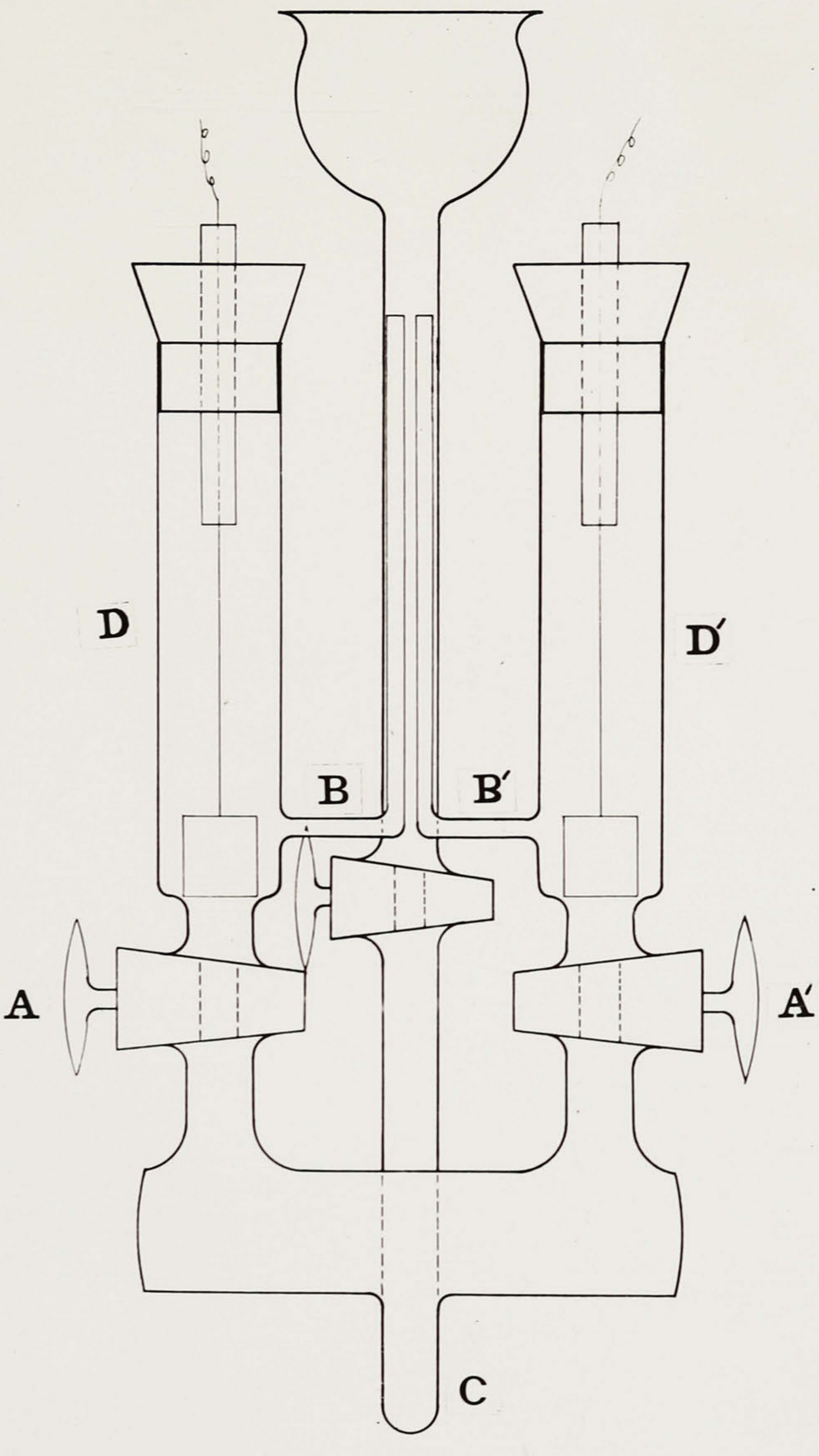


FIGURE VII.

Since there is no electro viscous effect with meta styrene, a saturated hydrocarbon colloid, and the effect is pronounced with rubber, an unsaturated hydrocarbon, the opinion may be ventured that the decrease in viscosity observed by the addition of some reagents into the rubber sol is caused primarily by the unsaturated character of the rubber. The compounds that produce the greatest electro viscous effect, say the tertiary amines, very readily form additional compounds and it is plausible that the addition of these molecules to the free valencies of the rubber aggregate may disintegrate it to some extent and cause the decrease in viscosity observed.

CATAPHORESIS EXPERIMENTS.

The precipitation of meta styrene from solution by ferric bromide indicates that the meta styrene micelle has a negative charge on it. Cataphoresis experiments, however, failed to show the presence of such a charge.

Since the meta styrene sol is colorless, an indirect method of observing its migration had to be used. The apparatus used in the present case was adopted because of its simplicity and because it was found to give good results with silver, ferric hydroxide and arsenous sulphide hydrosols.

The apparatus is shown diagramatically in Fig.VII. It consists of the familiar U tube fitted with stop-cocks A, to separate the part containing the solvent from the part containing the sol. The small tubes B B' are merely used as a gauge to tell when the level of liquid in both of the electrode chambers is the same.

Before use, the entire apparatus was very carefully cleaned, rinsed and dried, and the apparatus was then placed in a constant temperature bath regulated to 25 .01°C. The sol was then introduced up to the top of the stop-cocks A A' through the tube C. These cocks were then closed and benzene was added to the electrode chambers D D' until the liquid covered both electrode and the levels in B B' coincided. The electrodes were then attached to a 110 volt D.C. circuit and the cocks A A' opened. The total distance from one electrode to another was 15 cm. When the experiment had run for a suitable length of time, the current was turned off, cocks A A' were closed and the solutions in chambers D and D' were removed by means of a small pipette. These solutions were then evaporated in weighed glass dishes.

Various concentrations of sol were used in these experiments, all of which had been prepared from carefully dried materials. The time for which the current was left on varied from 24 to 48 hours. In none of our experiments did enough of a residue appear to say that any migration had taken place. There was always a faint trace of residue visible in the bottom of the glass evaporating dish, but it never weighed more than .0002 grams.

In this connection the experiments of Humphrey and Jane(38) on the sign of the particle charge in rubber sols are of interest. These authors conclude that when the materials are dry there is no charge on the rubber micelle. When water was present, they observed particles with charges of both signs.

The probable reason, therefore, why the meta styrene sols examined showed no migration in an electric field is that the meta styrene micelles have no charge on them.

SWELLING OF META STYRENE IN ORGANIC LIQUIDS.

Quantitative measurements on the swelling of meta styrene are impossible to make because of the circumstance that meta styrene goes into solution at its surface long before the interior of the solid has become swollen to anywhere near its maximum extent. Nevertheless, a series of qualitative experiments have been conducted with the object of establishing some sort of relationship between the structure of the colloid and the liquid that will peptize it.

The tests described below were made by placing pieces of meta styrene of approximately the same size in test tubes and adding equal quantities (about 5 c.c.) of the liquid in question. The tubes were allowed to stand at room temperature and their appearance noted from time to time. A description of the results observed are given below.

HYDROCARBONS.

Aromatic hydrocarbons, benzene, toluene, xylene and styrene, swell and disperse meta styrene very rapidly.

Aliphatic hydrocarbons, octane, propane, amylene and pentane do not swell meta styrene at all but act as precipitants (See a later section on precipitation).

The terpenes carophyllene and pinene swelled meta styrene very slightly if at all.

ALCOHOLS.

The aliphatic alcohols, methyl, ethyl, isopropyl, iso butyl, amyl, hexyl, secondary octyl and di acetone are precipitants for meta styrene.

Cumic alcohol was found to be a swelling agent.

HALOGEN SUBSTITUTED COMPOUNDS.

Chloroform, bromoform, ethyl, propyl and butyl iodides, carbon tetrachloride, acetylene tri chloride and ethylidine di chloride are swelling agents.

The chlorinated aromatic hydrocarbons, such as chloro and bromo benzene and bromo naphthalene are also swelling agents.

Di chlorohydrin is not a swelling agent, but tri bromohydrin is.

ALDEHYDES.

The lower aliphatic aldehydes such as acetaldehydes are precipitants but as the length of the carbon chain is increased, the aldehydes begin to swell meta styrene. Heptaldehyde produced solution.

Benzaldehyde was found to be a good swelling agent for meta styrene and salicylaldehyde a poor one.

KETONES.

Acetone produces no swelling with meta styrene, ethyl methyl ketone slight swelling and di ethyl ketone is a fair swelling agent.

ETHERS.

Di ethyl, iso amyl and normal butyl ethers produce no swelling.

The aromatic ethers such as anisole readily dissolve meta styrene.

ACETALS.

Methylal, ethylal and acetal dissolve meta styrene and the solutions show a blue cloudiness.

ACIDS.

Formic, acetic, proprionic, butyric, heptylic and caprylic acids are non-swelling agents.

ESTERS.

Ethyl and methyl acetates, ethyl oxalate and ethyl malonate produce only very slight swelling. Butyl acetate, amyl acetate, ethyl butyrate, ethyl sebacate and ethyl oleate are fair swelling agents. Aceto acetic ester caused no swelling.

Ethyl benzoate is a good solvent for meta styrene and so is nitro benzene.

ANHYDRIDES.

Acetic anhydride is a precipitant.

AMIDES.

Formamide causes no swelling.

AMINES.

Di ethyl amine is a good swelling agent.

Aniline, methyl, di methyl, ethyl and di ethyl aniline were found to be swelling agents. Their solvent power increases as the length of the chain increases.

Pyridine and piperidine are very good solvents.

NITRILES.

Aceto and proprionitriles were found not to swell meta styrene at all.

SULPHUR COMPOUNDS.

When the oxygen in a compound, such as alcohol, which does not swell meta styrene, is replaced by a sulphur atom, we get a swelling agent. Thus, ethyl and methyl mercaptan and carbon disulphide are solvents. So also is phenyl iso thiocyanate and thio phenol.

It is seen that the following generalizations can be drawn concerning solvent power. Meta styrene, a hydrocarbon containing a benzene nucleus, dissolves in other hydrocarbons and, in general in liquid of non polar character. In an homologous series, the solubility of meta styrene is lowest in the lowest members of the series and it increases as the molecular weight increases.

The swelling relations of meta styrene are similar in many respects to those of rubber, another polymerized hydrocarbon. But whereas meta styrene is derived from a benzenoid hydrocarbon, rubber is a polymer of a straight chain compound. Hence we find rubber soluble in such straight chain compounds as hexane, pentane, octane and ether in which meta styrene is insoluble.

The cellulose esters are compounds of a polar nature and they are soluble in general in polar compounds. Again, broadly speaking, it is found that liquids that are good solvents for the cellulose esters are poor swelling agents for rubber and meta styrene, and the converse is true that liquids that swell rubber and meta styrene swell the cellulose esters little, or not at all.

A more complete account of the relation between the structure of a colloid and the structure of liquids that swell it has recently been given by Whitby(39). This summary includes a discussion of meta styrene.

DEGREE OF SOLVATION IN META STYRENE GELS.

The results of some quantitative experiments on the degree of solvation of meta styrene sols may be of interest in that they give some idea as to what may be the degree of solvation of the disperse material.

These experiments were conducted by allowing pieces of meta styrene to swell in the liquid in question until the whole mass was just about to go into solution. Part of the solid gel was then cut off, placed in a weighing bottle and weighed. The material was then thoroughly dried in a high vacuum desiccator and the weight of the solid meta styrene was ascertained.

In this way the following values were found:

Solvent	Grams of solvent taken up by 1 gm.of Meta Styrene.
Chloroform	9.22
Bromoform	4.71
Benzene	4.82
Toluene	3.44
Xylene	2.79

It does not appear probable that the meta styrene in solution is solvated to a much greater extent than in these experiments with the massive material, because if the degree of swelling is but slightly increased, the material goes into solution, and were swelling to continue after dispersion had taken place, we should expect that the viscosity of meta styrene sols would alter considerably with time. But this is not true. This last argument is valid, of course, only if viscosity is caused to any extent by solvation, as Hatschek(40), Whitby(41) and others contend it may be.

The values observed for meta styrene, which must be taken as approximate minimum values, are intermediate between the measurements of McBain(42) on nitro cellulose, (100% maximum) and those of Whitby on rubber (2000-4000%).

PRECIPITATION POWER OF SEVERAL ORGANIC LIQUIDS.

To correspond to the swelling measurements, it was desirable to investigate quantitatively the relative precipitating power of a number of organic liquids with special reference to homologous series. In these tests a sol of .328 grams of meta styrene in benzene was used throughout.

Five c.c. of this sol were pipetted into a 100 c.c. erlenmeyer and the precipitant was added drop by drop with continual agitation until a faint permanent milkiness was discernible. With a little practice it was found that the measurements could be repeated within 1%.

The numbers after the names of the following materials are the number of c.c. of that liquid necessary to cause coagulation of 5 c.c. of the meta styrene - benzene sol.

ACIDS

Acetic	5.02
Propionic	20.20
Butyric	16.00
Heptylic	9.15

ANHYDRIDES

Acetic	7.35

HYDROCARBONS

Pentane	6.13
Octane	5.75
Amylene	16.0

ESTERS

Ethyl formate	3.94
Methyl acetate	25.50
Ethyl acetate	- swelling agent
Ethyl butyrate	"

ALCOHOLS

Methyl alcohol	1.25
Ethyl "	1.95
Butyl "	2.93
Amyl "	3.14
Hexyl "	3.24
Octyl "	4.20

KETONES

Acetone	21.60
Methyl ethyl ketone -	swelling agent

ETHERS

Di ethyl	35.00
butyl	17.00
Di benzyl	swelling agent
Benzyl-ethyl	"

In the case of the alcohols, precipitating power decreased as the length of the carbon chain increased. The same conditions appear to prevail with the esters. But the ethers, acids and hydrocarbons do not fit in with such a general scheme. In these compounds, the reverse seems to be true so far as these measurements go.

VISCOSITY OF META STYRENE SOLS IN DIFFERENT SOLVENTS.

With the object of obtaining some information as to the role played by solvation on the viscosity of meta styrene sols, the viscosity of a number of sols of meta styrene in a variety of solvents was determined. The scheme was to find which sols were the most viscous and, by precipitation tests on the same sols, to determine which were the most highly solvated. The results of the precipitation tests are reported in the next section.

All of the sols, the viscosity of which is reported here, were made by dissolving .328 grams of meta styrene in 100 c.c. of the solvent. The liquids used were, for the most part, Kahlbaums best grade. These were used without further purification. Where chemicals of less certain purity were employed, they were first purified, usually by distillation.

The sols were three weeks old when measured. All measurements were made at 25° in viscos~~p~~imeter #3.

The following table shows the results.

TABLE XXXIX.

Solvent	Time of Flow of solvent	Time of Flow of sol.	Relative Viscosity Solvent = 1
Ethyl iodide	34.2	79.5	2.320
Chloroform	42.0	133.8	3.262
Methylal	42.4	89.2	2.104
Butyl iodide	57.5	167.2	2.912
Acetal	58.5	94.4	1.784
Carbon tetrachloride	63.0	194.0	3.080
Toluene	70.8	214.0	3.023
Bromoform	71.6	177.2	2.477
Benzene	77.0	270.2	3.518
Xylene	78.8	249.4	3.369
Anisole	110.8	358.0	3.231
Nitro benzene	167.6	395.0	2.357
Ethyl benzoate	204.0	496.8	2.817
Methyl aniline	222.0	675.6	3.040
Di ethyl aniline	227.6	610.6	2.710
Ethyl aniline	229.2	673.5	2.940
Aniline	397.0	943.0	2.376
Butyl aniline	402.5	937.6	2.322

In the above table the sols are arranged in the order of the viscosity of the solvents. They are retabulated below in the order of the relative viscosity of the sols.

TABLE XL

Solvent	Relative Viscosity
Acetal	1.784
Methylal	2.104
Ethyl iodide	2.320
Butyl aniline	2.322
Nitro benzene	2.357
Aniline	2.376
Bromoform	2.477

TABLE XL. Cont'd.

Solvent	Relative Viscosity
Di ethyl aniline	2.710
Ethyl benzoate	2.817
Butyl iodide	2.912
Ethyl aniline	2.940
Toluene	3.023
Methyl aniline	3.040
Carbon tetrachloride	3.080
Anisole	3.231
Chloroform	3.262
Xylene	3.369
Benzene	3.518

It is seen clearly from Table XXXIX and XL that while the time of flow of sols with different dispersion media differs greatly, the relative viscosity of the sol with respect to the solvent does not vary over nearly as wide a range. There is, apparently, no precise relation between the viscosity of the solvent and the viscosity of the sol; although there appears to be a tendency for a more viscous solvent to give sols with a higher relative viscosity.

STUDIES OF THE PRECIPITATING POWER OF SEVERAL ORGANIC LIQUIDS ON SOLS OF META STYRENE DISPERSED IN DIFFERENT SOLVENTS.

The precipitating power of a single precipitant on sols of a given colloid in different solvents has been used as an index by which the relative degree of solvation of the colloid in different solvents can be compared. This scheme has been used in particular in investigating nitro cellulose sols(43). The reasoning is that highly solvated sols have a large amount of solvent associated with the micelle and that a smaller amount of precipitant is required to cause flocculation than in the sase of sols where the degree of solvation of the colloid is lower and there is a larger amount of free solvent.

In the present investigation a number of different precipitants were applied to a series of sols of meta styrene in different solvents. The method used for determining precipitating power was the same as the one previously described. The results show that precipitation is not a satisfactory method of determining the relative degree of solvation in different liquids. For if this method of determining the relative "solvent power" of a number of liquids for a given organophilic colloid is correct, it is to be expected that different precipitants will place a number of liquids in the same order as regards "solvent power".

In the following table of results, the numbers given refer to the number of c.c. of the precipitant required to precipitate 5 c.c. of the sol in question.

The sols used were the same one as described in the preceding section on viscosity.

TABLE XLI.

Solvent used to make the sol.	Precipitants Ethyl Alcohol	 Acetic Acid	 Acetic Anhydride	 Octane	 Methyl Formate
Chloroform	2.30	3.82	6.48	10.40	8.49
Bromoform	1.78	3.45	8.50	6.40	12.57
Benzene	1.91	4.94	7.52	5.62	10.78
Toluene	1.80	4.78	7.40	5.16	10.54
Xylene	1.60	4.00	6.78	4.10	10.00
Ethyl iodide	1.90	4.22	8.07	7.50	12.40
Butyl iodide	1.65	4.02	6.84	5.70	10.84
Aniline	2.45	0.78[x]	1.80[x]	insol.	9.17
Methyl aniline	2.87	1.18[x]	8.40[x]	5.50	12.64
Ethyl aniline	2.68	1.60[x]	8.00[x]	7.14	12.30
Butyl aniline	1.98	2.25[x]	8.20[x]	6.30	11.56
Di ethyl aniline	2.45	1.34[x]	7.50[x]	5.92	11.15
Acetal	0.32	0.67	3.40	0.46	2.50
Methylal	0.69	0.73	1.09	3.12	1.85
Ethyl benzoate	2.30	3.56	6.75	6.90	9.80
Nitro benzene	2.64	3.60	6.42	4.84	9.25
Anisole	2.40	4.51	7.21	6.60	11.10
Carbon tetrachloride	1.56	3.93	5.70	4.04	9.55

[x] Reaction takes place. These results are not reliable.

In Table XLII the numbers given are the order in which that sol appears when a comparison is made of the precipitating power of the precipitant on the 18 different sols. That is to say, the figure 12 opposite chloroform and under ethyl alcohol means that eleven other of the sols required less ethyl alcohol to cause precipitation than the chloroform sol.

TABLE XLII.

Solvent used to make the sol.			Precipitants		
	Ethyl Alcohol	Acetic Acid	Acetic Anhydride	Octane	Methyl Formate
Chloroform	12	11	6	17	3
Bromoform	6	8	18	12	17
Benzene	9	18	13	8	10
Toluene	7	17	11	6	9
Xylene	4	13	8	4	8
Ethyl iodide	8	15	15	16	16
Butyl iodide	5	14	9	9	11
Aniline	14	3	2	-	4
Methyl aniline	18	4	17	7	18
Ethyl aniline	17	6	14	15	15
Butyl aniline	10	7	16	11	14
Di ethyl aniline	15	5	12	10	13
Acetal	1	1	3	1	2
Methylal	2	2	1	2	1
Ethyl benzoate	11	9	7	14	7
Nitro benzene	16	10	5	5	5
Anisole	13	16	10	13	12
Carbon tetrachloride	3	12	4	3	6

When tabulated in this way it is seen that the information obtained from any one precipitant is not collaborated by all the others. An inspection of the table shows a large number of inconsistencies and it will suffice to point out a few of the striking ones.

The chloroform sol was the most difficult to precipitate with octane but only two others were more readily flocculated by methyl formate.

The carbon tetrachloride sol was the twelfth easiest sol to coagulate with acetic acid but the fourth with acetic anhydride and the third with alcohol.

The chloroform sol was more easily coagulated than the chloroform sol by alcohol but the reverse is true with methyl formate.

The toluene sol was more easily coagulated by octane than the ethyl benzoate sol but the reverse is true with acetic acid.

About the only point on which all the precipitants agree is that the methylal and ethylal sols are the easiest to precipitate and it is noteworthy that these two gave the sols of lowest viscosity. The analogy fails, however, when applied to ethyl iodide.

There exists one point on which the results are fairly concordant. That is if it requires less of one precipitant than of any other to cause coagulation in one sol, that precipitant will be the best for all the other sols. It may be clearer to tabulate the results of such a comparison as in Table XLIII. In this record, sols of aniline and the substituted anilines are omitted.

The dielectric constant of the precipitant is given under "e".

TABLE XLIII.

		Order of precipitating power.				
Precipitant	e	1	2	3	4	5
Ethyl alcohol	27	13	0	0	0	0
Acetic acid	9.7	10	12	1	0	0
Octane	1.94	0	1	9	1	2
Acetic anhydride	20.5	0	0	3	9	1
Methyl formate		0	0	0	2	11

Thus, in the thirteen sols examined, ethyl alcohol was the best precipitant in every case, acetic acid the second best in twelve cases, octane the third best in nine cases, acetic anhydride the fourth best in nine cases and methyl formate was the poorest in eleven cases.

The precipitating power of a liquid does not vary as its dielectric constant and there appears to be no physical property of the precipitants that varies in the same way that their precipitating power does so it is not possible to predict on this basis whether or not a liquid will make a good precipitant.

THE EFFECT OF THE CONCENTRATION OF META STYRENE IN A BENZENE SOL ON THE AMOUNT OF A PRECIPITANT REQUIRED TO CAUSE FLOCCULATION.

As was shown before, a small increase in the concentration of a meta styrene sol causes a large increase in the viscosity of the sol. If the increase in viscosity observed is to be accounted for by saying that in a sol of high viscosity a large amount of the solvent is associated with the meta styrene in such a manner that it is not free to move, it should be true that a different amount of precipitant should be required to cause precipitation in the case of a viscous sol and a non-viscous sol because the amounts of free solvent differ in both cases.

This has been the subject of investigation with both the cold polymerized meta styrene, where the viscosity rises rapidly with concentration, and the heat polymer, where an increase in concentration causes but little rise in viscosity.

In Table XLIV, the figures in the colum headed "c.c. alcohol" refer to the number of c.c. of alcohol required to cause a permanent precipitate to appear in 5 c.c. of the sol. Concentration is given in terms of grams of meta styrene in 50 c.c. of benzene and the relative viscosity is the time of flow of the original sol compared with the time of flow of benzene.

TABLE XLIV.

Sample	Concentration	c.c.alcohol	Relative Viscosity
Cold polymer	.025	1.91	1.357
"	.075	1.86	2.363
"	.100	1.83	3.058
"	.200	1.74	6.601
140° material	.025	2.65	1.003
"	.075	2.52	1.031
"	.100	2.47	1.034
"	.200	2.37	1.122
180° material	.025	2.78	1.001
"	.075	2.63	1.018
"	.100	2.52	1.034
"	.200	2.47	1.089

It is seen that as the concentration of meta styrene in the sol increases, the amount of alcohol required to cause precipitation decreases slightly regardless of whether or not the viscosity rises to any extent.

SOLUBILITY AND PRECIPITATION RELATIONSHIPS BETWEEN THE COLD POLYMERIZED META STYRENE AND THE HEAT POLYMERIZED MATERIAL.

Precipitation:

It was noted in the preceding experiment that it required less alcohol to precipitate the cold polymerized meta styrene from a benzene solution than either of the heat polymers. The experiment has been extended to include other precipitants with the results shown in Table XLV.

All of the sols used had a concentration of meta styrene of .200 grams in 100 c.c. of benzene. Tests were made, as before, on 5 c.c. samples.

TABLE XLV.

Precipitant	Cold polymer	140°	180°
Ethyl alcohol	1.83	2.47	2.52
Ethyl formate	3.60	4.40	4.92
Acetic acid	4.44	5.35	5.75
Octane	5.93	7.40	7.85
Acetic anhydride	7.50	9.35	10.50

These results are seen to be consistent with each other. The cold polymer was the easiest to precipitate with each precipitant, the 140° polymer next and the 180° polymer the hardest in every case. The effectiveness of the precipitants is in the order shown in the table for all sols.

Solubility:

Both the 140° and 180° polymers were found to be soluble in all of the liquids that dispersed the heat polymer. But there exist two points in which there is a difference in the solubility of the two kinds of polymers.

The heat polymers are swelled and dispersed very rapidly in a good meta styrene solvent such as chloroform, benzene, etc. While it takes about two days for the cold polymer to swell and disperse in benzene, the heat polymers will swell and disperse in an hour.

Some liquids that are put on the border line between precipitants and solvents for the cold polymer will dissolve all or part of the heat polymers. Acetone, di ethyl ether and ethyl oxalate swell and disperse the part of the heat polymers but leave a residue of unswollen material consisting of higher polymerized material. Methyl ethyl ketone dissolves the heat polymers completely but petrol ether swells them hardly at all.

DISCUSSION.

Suspensoid systems in general may be classified as either lyophilic or lyophobic colloids and the results of these experiments have definitely placed sols of meta styrene in the class of neutral lyophilic colloids along with rubber, the cellulose esters and the undissociated soaps. The properties of the lyophobic colloids have been practically completely understood by the recognition of two factors of supreme importance: their large specific surface and the existence of a difference of electric potential between the colloid particle and the medium in which it is dispersed. A consideration of these two properties of lyophobic sols explains why such systems should exist, why they should be stable and why they should break down under a given set of conditions. But in the neutral, lyophilic sols, the electric charge is absent and adsorption of other than solvent molecules plays a very minor role in determining their characteristics. So we must look to other sources for an understanding of these systems.

The chief points of interest about lyophilic sols may be briefly summarized as follows:

1. Why are they formed in preference to true solutions?
2. What is the cause of their high viscosity?
3. What is the mechanism of their coagulation?

The mechanism of the formation of solid gels is of interest in systems where gels are formed. But as meta styrene sols do not set to gels, this need not concern us here.

Various answers have been given to the first question in the literature during the past few years. Staudinger(44) has advanced a theory that has, at least, the advantage of extreme simplicity. This author makes the suggestion that the process of forming a lyophilic colloid solution is exactly the same as the formation of a true solution. The only difference between the two is that in the true solution the molecules are small and in the colloid solution, the molecules are very large.

Although this view may appear attractive on first thought, particularly in the author's original language, it proves unsatisfactory from at least two aspects. If colloid solutions consist merely of huge molecules in solution, then we should expect that some of the largest molecules that have been synthesized should show colloidal properties. But some very large molecules have been built up by known methods, showing no trace of colloidal properties. Conspicuous among these compounds are the conjugated amino acids and tannins prepared by Emil Fischer. On the other hand, there exist molecules of comparatively low molecular weight, such as the soaps and the pentacyclo pentadiene made by Staudinger and Bruson(45), that do yield colloidal solutions.

Another objection to the theory mentioned above lies in the fact that some substances give true solutions in one class of solvents and colloid solutions in another. An example of this behaviour is to be found in the soaps, which give true solutions in alcohol but colloid sols in water. It is apparent that any successful theory of the formation of lyophilic sols must consider the important part played byb the solvent.

A different explanation of the process of swelling and solution of lyophilic colloids has been suggested by Arsem(46), Whitby(47) and McBain(48). These workers believe that the colloidal particle consists not of one huge molecule but of a number of smaller molecules which are held together to form an aggregate by some sort of residual valency forces. Arsem has stated this theory about as clearly as it can be put. "When a crystalline substance goes into solution, it seems permissible to assume that the lattice-forming residual valence bonds are separated and appropriated by the superior combining power of the solvent molecules so that the crystal structure is entirely broken down and the molecules individually dispersed. In a gel, however, some of the residual valences function permanently as lattice bonds while others remain free and can hold or release molecules of the free phase in accordance with surrounding conditions. Swelling, then, is the result of the combination of the molecules of a fluid with the free valences of a gel lattice".

This conception appears to be quite sufficient to explain swelling and sol formation in meta styrene. The liquids in which it forms sols are those which resemble it in chemical structure most and which may be assumed to have sufficient attractive force to separate and saturate some of the valence bonds that hold the solid material together. No liquid has been found, however, that has sufficient attractive force to disperse meta styrene into its ultimate molecules as alcohol does for the soaps.

McBain(49) has recently expressed the opinion that the best solvents for lyophilic colloids are those which yield sols with the lowest viscosities. It is confusing to speak of relative solvent power when referring to a colloid such as rubber or meta styrene. For if meta styrene will dissolve in a liquid, it will dissolve in it in all proportions. Either you can dissolve a small chip of meta styrene in a liter of say, benzene, or you can dissolve a drop of benzene in a large block of meta styrene. And solutions of all intermediate concentrations may be prepared. In the case of crystalloids, solubility has a definite quantitative significance but this is entirely lacking in the colloids.

McBain is likely confused himself as to just what he means by solvent power when speaking of colloids. His final criterion of a good solvent is that it gives a solution with a low viscosity, which appears to be begging the question a bit. What is probably meant by a good solvent is one that swells a colloid rapidly and, by the use of which, concentrated solutions may be prepared that will have a low enough viscosity so that they may be conveniently handled.

It was shown in the present work that poor swelling agents, that is liquids that swell the colloid slowly, may yield sols with very low viscosities. As an instance, methylal and ethylal swell meta styrene so slowly that it takes weeks for the colloid to go into solution. Yet these sols have by far the lowest viscosities of any prepared, and according to McBain's criterion, ethylal and methylal are the best solvents of the liquids examined for meta styrene.

It would seem advisable then to describe the property of a solvent in terms of precisely what we mean; to say that it swells and disperses a colloid rapidly or slowly, or that it yields sols with high or low viscosity. There is no relationship of general application between the two properties.

One of the most frequently quoted attempts to correlate the viscosity of a lyophilic sol with the concentration of the disperse phase was made by Arrhenius(50). His rule is that the logarithm of the relative viscosity of a sol is proportional to the concentration of the disperse phase.

Mathematically formulated it is;

$$\log \frac{n}{n_0} = K\ C$$

where η = viscosity of the sol

η_0 = viscosity of the solvent

K = a constant

C = concentration of disperse phase.

It is most convenient to compare our results of viscosity concentration figures of meta styrene in benzene with the above formula by calculating the value for K at several concentration. This is done below.

Conc. gr/100 c.c.	log n/n_o	K
.0102	.0269	2.63
.0500	.1326	2.64
.0753	.1934	2.57
.1262	.3191	2.53
.2054	.4854	2.37
.3022	.6511	2.14
.4016	.7483	1.87
.5600	.9967	1.78

The viscosity concentration relation for meta styrene cannot be expressed by this equation. Deviations from this equation are, moreover, the rule rather than the exception. The proteins give a "constant" which increases with increasing concentration while the nitro cellulose sols studied by Baker(51) as well as those examined by McBain(52) gave constants that varied in the same direction as those for meta styrene. Hatschek (53) points out that the constants obtained with different specimens of rubber may vary in either direction.

Hatschek (54) has developed an equation which expresses the relation between viscosity and concentration in an emulsion. To derive his expression, he assumes that the volume concentration of the disperse phase is so high that the particles assume a polyhedral shape due to close packing.

Then in Hatschek's own words: "If the system is sheared, the polyhedra are deformed and, above a certain limiting velocity, they may not have time to return to their original shape under the influence of interfacial tension, so that the whole of the shear takes phase in the layers of continuous place parallel to the plane of shearing. In this case, the viscosity of the emulsion is given by the formula:

$$n^1 = \frac{n}{1-\sqrt[3]{f}}$$

where n is the viscosity of the continuous phase and f the ratio: volume of disperse phase/total volume".

The difficulty in applying this equation to lyophilic sols lies in the determination of the volume of the disperse phase. It is generally conceded that the disperse phase in such sols is solvated but there exists no independent method of measuring the degree of solvation. The formula has been tested by Trevan(56) and found experimentally to hold for the type of system for which it was designed.

The question arises as to whether or not a lyophilic colloid may be assumed to have become so highly solvated that the conditions described above prevail. That is to say, can the high viscosity of lyophilic sols be explained by their degree of solvation?

In the absence of any independent method of measuring degree of solvation, Hatschek's equation may be used to calculate the degree of solvation necessary to account for the viscosity of the sol.

By re-arranging the equation we have:

$$f = \left(\frac{n' - n}{n'}\right)^3$$

Knowing f the ratio volume of disperse phase/total volume and the concentration by weight of the sol, we can calculate the solvation factor. This has been done and the results for several concentrations of meta styrene are shown below.

% Conc. of Sol. by Weight	Relative Viscosity	f. (%)	Ratio f/c
.0569	1.357	1.7	29
.1140	1.820	9.1	50
.1720	2.363	19.2	111
.2340	3.058	32.8	139
.2880	3.695	38.8	135
.3970	5.359	53.8	135
.4560	6.601	61.3	134

It is seen that the ratio f/c is a constant when over 32% of the volume of the sol is composed of disperse phase. At lower concentrations, it is not fair to expect this ratio to be constant because it was specified in the derivation of the equation that the emulsion must be a concentrated one for the conditions of shear assumed to hold true.

Then, at concentrations where the equation does apply, it is necessary to assume that one gram of meta styrene occupies a volume of 135 c.c. in the sol in order to account by the solvation theory for the high viscosity of the sol. This is at least ten times as great as our direct sorption experiments point to and is three times as high as any sorption measurements on any colloid have ever indicated. Until a method is discovered by which we can actually measure the true degree of solvation in a sol, we have no positive evidence that meta styrene is or is not solvated to the extent indicated above. But in the absence of such a method, we must say that the evidence that we have on the degree to which colloids may be swollen makes it improbable that meta styrene is solvated in a sol to an extent that would account for its high viscosity.

This conclusion may be confirmed from another point of view. It is known from osmotic pressure experiments(56A) and other work that molecules of a solute in a true solution have associated with them a number of solvent molecules; that is, they are solvated. The degree to which they are solvated has been shown to be greatly influenced by a change in temperature, being lower at higher temperatures.

The increase in the relative viscosities of emulsoid sols at low temperatures has been very generally ascribed to an increase in the degree of solvation of the disperse phase. This explanation has been offered by Martin and Chick(57) to explain the very high relative viscosity of their sodium caseinate sol at low temperatures and Hatschek (58) has indicated that it is of universal application.

We have shown, however, that the relative viscosity of a meta styrene sol is absolutely independent of temperature between the limits of 6.8° to 50°. If we are to assume that the high viscosity of the sol is due to its high degree of solvation, then we are forced to say that a change in temperature produces no change in the degree of solvation. This conclusion is not in harmony with the facts that have been established about solvation and it therefore seems very probable that the high viscosity of meta styrene sols is not due to solvation of the disperse phase.

The task before us is then to explain why the viscosity of a meta styrene sol obeys Hatschek's equation in the region where it may be expected to apply and at the same time is independent of temperature. It may be stated that no view has been yet brought forward that can reconcile the two experimental facts.

It appears to the writer that a combination of the theory of McBain that high viscosity is caused by the presence in the liquid of ramifying aggregates together with the further assumption that these aggregates form a definite continuous net-work which encloses particles of solvent might be at least partially successful in solving the problem. The aggregates forming the structure, which is thought of as resembling a cell wall, may be considered as being swollen to about the same extent that we have observed the solid material to swell, absorbing about ten times its weight of solvent. The cell walls are therefore elastic and as they are continuous and enclose droplets of the solvent, they closely resemble the emulsion system which was mathematically treated by Hatschek to derive his equation.

The conditions for shear would therefore be the same and the same relation is assumed to hold between concentration and viscosity as with emulsions. But in speaking of volume concentration in our meta styrene system in connection with Hatschek's equation, we must consider the total volume enclosed by our cell walls as being the effective volume of our disperse phase. But in reality, only the outer skin of the cells consists of meta styrene and the bulk of the cells consists of solvent which is held there through purely mechanical means and is in no way attached to the meta styrene.

The relative viscosity of the meta styrene sol is independent of temperature because although the degree of solvation of the meta styrene may alter with temperature, the effect on the volume of the cell is small. The volume of the disperse phase is practically independent of temperature, so the viscosity of the sol is also.

It is clearly recognized by the author that the above discussion is hypothetical in character. It has no direct experimental evidence in its favor and no similar system has ever been demonstrated. But the properties of meta styrene sols appear to be unique and demand an unique explanation. And since the structure of any lyophilic colloid sol has never been satisfactorily explained by any theory, there can be no serious harm done by advancing this hypothesis. It is recommended by the fact that it appears to explain the facts known about the viscosity of meta styrene sols.

The coagulation of meta styrene sols by various organic liquids which act as precipitants indicates that coagulation is a phenomenon which primarily concerns the solvent and the precipitant and in which the colloid micelle plays little part. It was shown in the experimental part on coagulation that no relation exists between the precipitating power of a number of precipitants on a variety of sols prepared with different solvents other than that good precipitants for the colloid in one solvent will be good precipitants for the colloid in any other solvent.

This is taken to mean that the process of coagulation by a precipitant is that first the molecules of precipitant become solvated by the free solvent and then further quantities of the precipitant solvate themselves at the expense of the micelles, causing them to precipitate. The force with which the micelle holds on to its solvating molecules is weak in comparison with the force with which the precipitant attracts them.

That good precipitants retain this property in any solvent is considered to mean that a molecule that tends to attract strongly any kind of a molecule that will peptize meta styrene will attract strongly all kinds of molecules that peptize meta styrene.

The properties of solutions of the heat polymers of meta styrene may be accounted for on the basis of the views developed for the high polymer. The low polymers are of molecular dimensions much nearer to the size of the solvent molecules than to the aggregates of the high polymer. They may be considered, therefore, to resemble the solvent in constitution to a greater degree than the high polymer. According to the principle that a colloid will swell and dissolve most readily in a solvent that resembles it most chemically, we may expect that the low polymers of meta styrene will be more easily soluble in a given liquid than will be the high polymer. This we find to be true.

The free affinity valencies of the low polymer are completely saturated by solvent molecules so they do not join together to form a network. Therefore, they have low viscosities.

The low polymers are assumed to have an attractive force for solvent molecules of the same kind of magnitude as the molecules of a precipitant. It will therefore take more of a precipitant to coagulate a solution of the low polymer than is required to coagulate a similar solution of the high polymer because in the former case the precipitant must compete with the colloid for solvent molecules, and the competition is strong, In the case of the high polymer, the precipitant solvates itself at the expense of the colloid with almost no opposition. So it will take a large number of precipitant molecules to tear away from the low polymer enough solvent to cause coagulation.

PART II.

INTRODUCTION.

The observation that meta styrene, which at room temperature is a hard inelastic solid, could be converted into a very elastic material by warming it to about 80° led to an investigation of its elastic properties. The object of the work was to gain some knowledge as to the conditions that must prevail for elastic properties to exist and to study the effect of such factors as temperature on elastic properties.

A very great amount of attention has been given to the elastic properties of vulcanized rubber because of its commercial significance. But rubber is an elastic colloid which exhibits complicating features that make it difficult to recognize the essential features of elasticity. It would appear that a fuller understanding of the phenomenon in rubber may be obtained from the study of such a system as meta styrene where the elastic properties can be created, altered or destroyed at will by varying the colloid by various controllable factors.

It was observed that the time that a piece of meta styrene was allowed to remain stretched altered its retractive powers markedly. An investigation was carried out to see if this was true of rubber also and the results of these experiments are included in this section.

The author very gladly expresses his indebtedness to Mr. Thomas N. White of the Physics Department of McGill University who made the X-ray spectographs mentioned here.

THE EFFECT OF TEMPERATURE ON THE EXTENSIBILITY OF META STYRENE.

It can be roughly shown that an increase in the temperature of meta styrene renders the material elastic, by plunging a piece of it into boiling water. The substance can then be drawn out to several hundred ~~per~~ cent. of its original length.

The present experiments were carried out in order to ascertain at what temperature the substance began to become elastic and to what extent it would stretch under a constant load at different temperatures. A description of the procedure follows.

Preparation of test pieces: Test pieces of uniform thickness were prepared by evaporating a solution of meta styrene in styrene to dryness at 95°. The evaporation was carried out in a shallow flat trough made of aluminum foil. The trough was glued to a flat surface and the foil could be easily peeled off the meta styrene when evaporation was complete.

Lower boiling solvents, such as chloroform and benzene were found to be unsatisfactory as it was impossible to get sheets of meta styrene free from bubbles when using them. The transparent sheet of meta styrene thus prepared

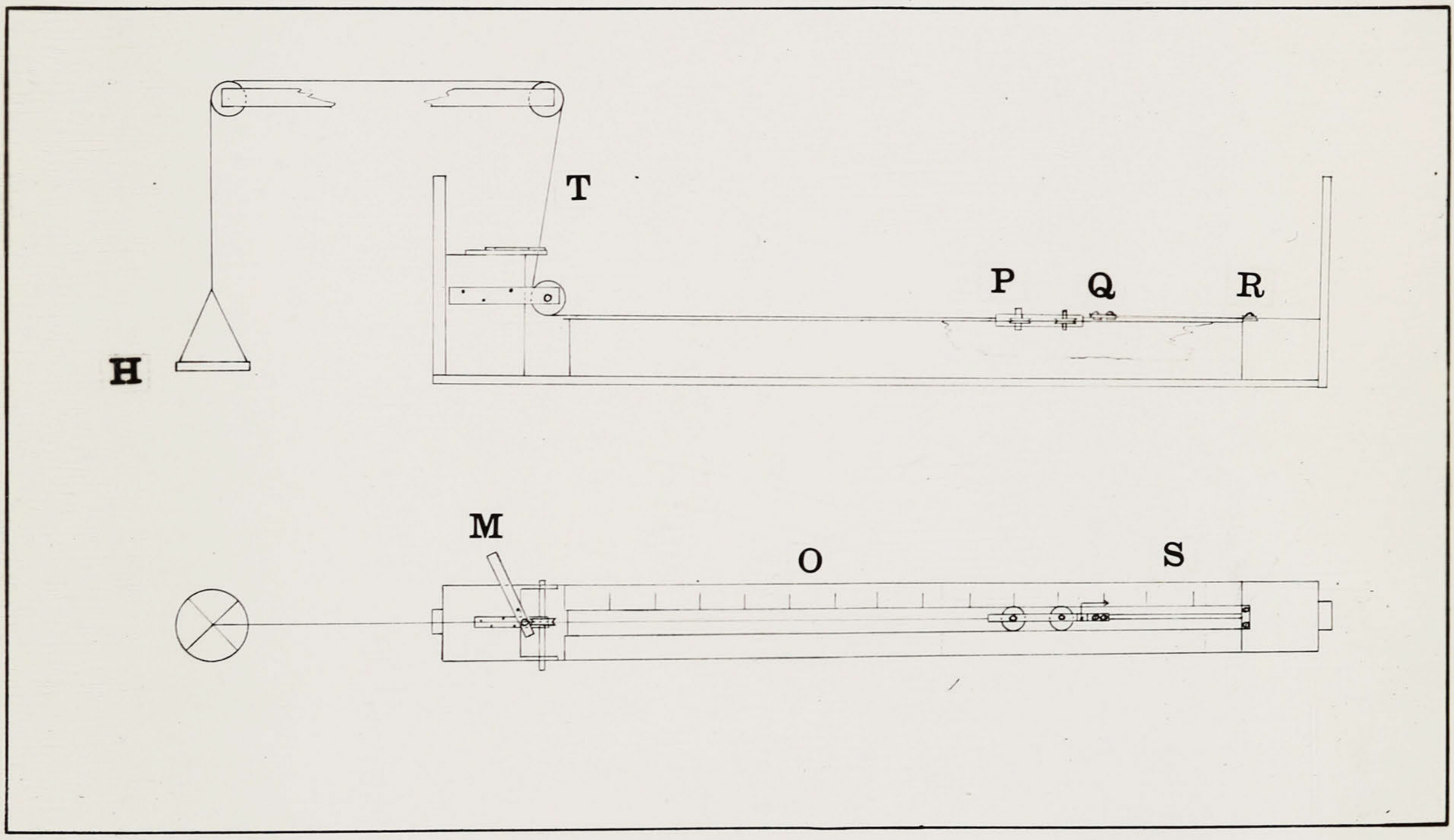


FIGURE VIII.

was placed over a piece of milli meter ruled paper and strips 5 mm. wide were cut off. The thickness of the strips was determined by a micrometer and found to vary from .5 to 1 millimeters. The exact determinations of each test strip are given with the data.

Apparatus: The apparatus used throughout these experiments is shown in Fig. VIII. It consisted of a small car P fitted with flanged wheels so that it could run up and down a track, one rail of which was formed by a metal meter ruler O. The test piece S was placed in the grips R, Q and tension sould be applied by weights in the pan H acting through a cord running through a pulley system as indicated. A pointer attached to the car indicated the position of the end of the grip Q on the scale. M is a device for clamping the cord so that the strip could be held at any position indefinitely.

The whole machine was immersed in a water bath, the temperature of which could be regulated by means of gas burners, and two stirrers kept the temperature in the bath uniform.

A ten gram weight in the pan was just sufficient to allow for frictional losses innthe machine. All loads indicated are in addition to this 10 grams.

To measure the elongation produced by a given weight at different temperatures, a test piece was gripped as indicated above and a 75 gram weight placed in the pan.

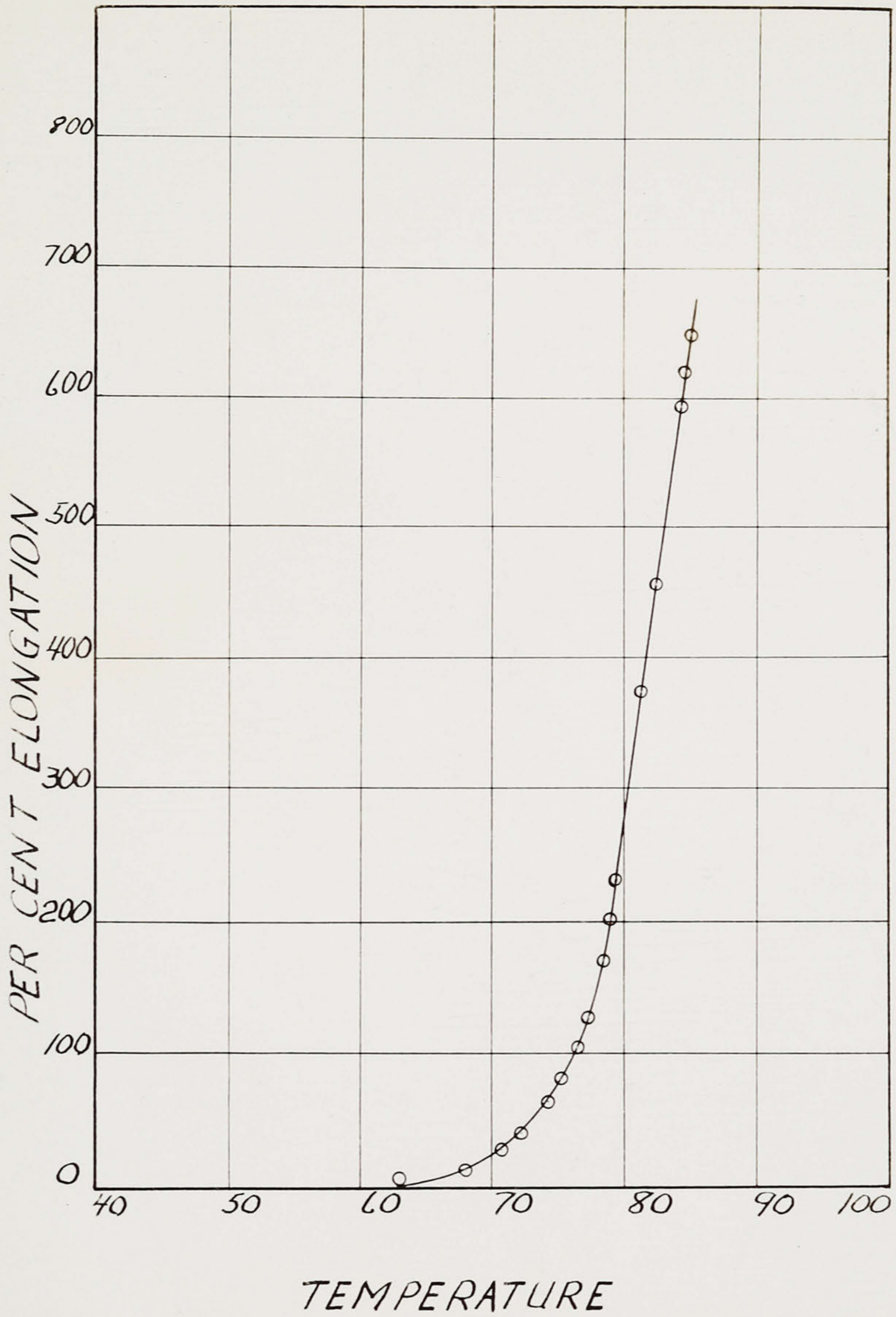

800
700
600
500
400
300
200
100
0
PER CENT ELONGATION
40
50
60
70
80
90
100
TEMPERATURE

FIGURE IX.

The temperature of the bath was then raised at such a rate that it required 45 minutes to bring the temperature from 13° to 85°, and the position of the pointer noted over a range of temperatures. The results are shown below.

TABLE XLVI.

Experiment 1.

Load 75 grams. Cross section of strip = 1.92 sq.m.m.

Temperature	Length	Δ	% Elongation
13	3.6 cm.	0	0
20	3.6 "	0	0
25	3.6 "	0	0
35	3.6 "	0	0
43	3.65"	.05	1.39
48	3.65"	.05	1.39
53	3.65"	.05	1.39
58	3.70"	.1	2.79
63	3.80"	.2	5.57
68	4.0 "	.4	11.10
71	4.5 "	.9	25.70
72	5	1.4	39.0
73	6	2.4	66.7
75	6.5	2.9	80.5
76	7.	3.4	94.5
76.5	7.5	3.9	100.8
77	8	4.4	122.
77.5	8.8	5.2	144.
78.7	11	7.4	205.
79.5	12	8.4	234.
81.	13.5	9.9	274.
84	25.	21.4	595.
84.5	26.	22.4	623.
85	27.	23.4	650.
85.3	28.	24.4	678.

This experiment was duplicated and the results found to agree. The following table shows the measurements and the results are shown graphically in Fig. IX.

TABLE XLVII.

Experiment II.

Load 75 grams. Cross section = 1.87 sq.m.m.

Temperature	Length	△	% Elongation.
15	3.76 cm.	0 cm.	0
46	3.76	0	0
50	3.78	.02	.53
60	3.8	.04	1.06
65	3.9	.14	3.7
69.5	4.3	.56	14.9
73	5.0	1.24	33.0
74.5	6.0	2.24	59.5
76	7.0	3.24	86
78	9.2	5.44	145
79	12.0	8.24	219
79.7	14.0	10.24	272
80.2	16.0	12.2	325
81	18.0	14.2	380
82	20.0	16.2	430
83	22.0	18.2	485
84.5	28.0	24.2	645

THE EFFECT OF LOWERING THE TEMPERATURE ON THE EXTENSION OF META STYRENE.

The observation has been made that a load of 75 grams caused a great extension of meta styrene when the temperature was raised sufficiently. Qualitative experiments had shown that if a piece of meta styrene that had been so stretched was cooled rapidly while extended, it became hard and inelastic and remained extended. Material thus treated, however, is in a state of strain for when placed in hot water again, it snaps back to nearly its original length.

The purpose of these experiments was to find out whether or not the stretched material tended to contract

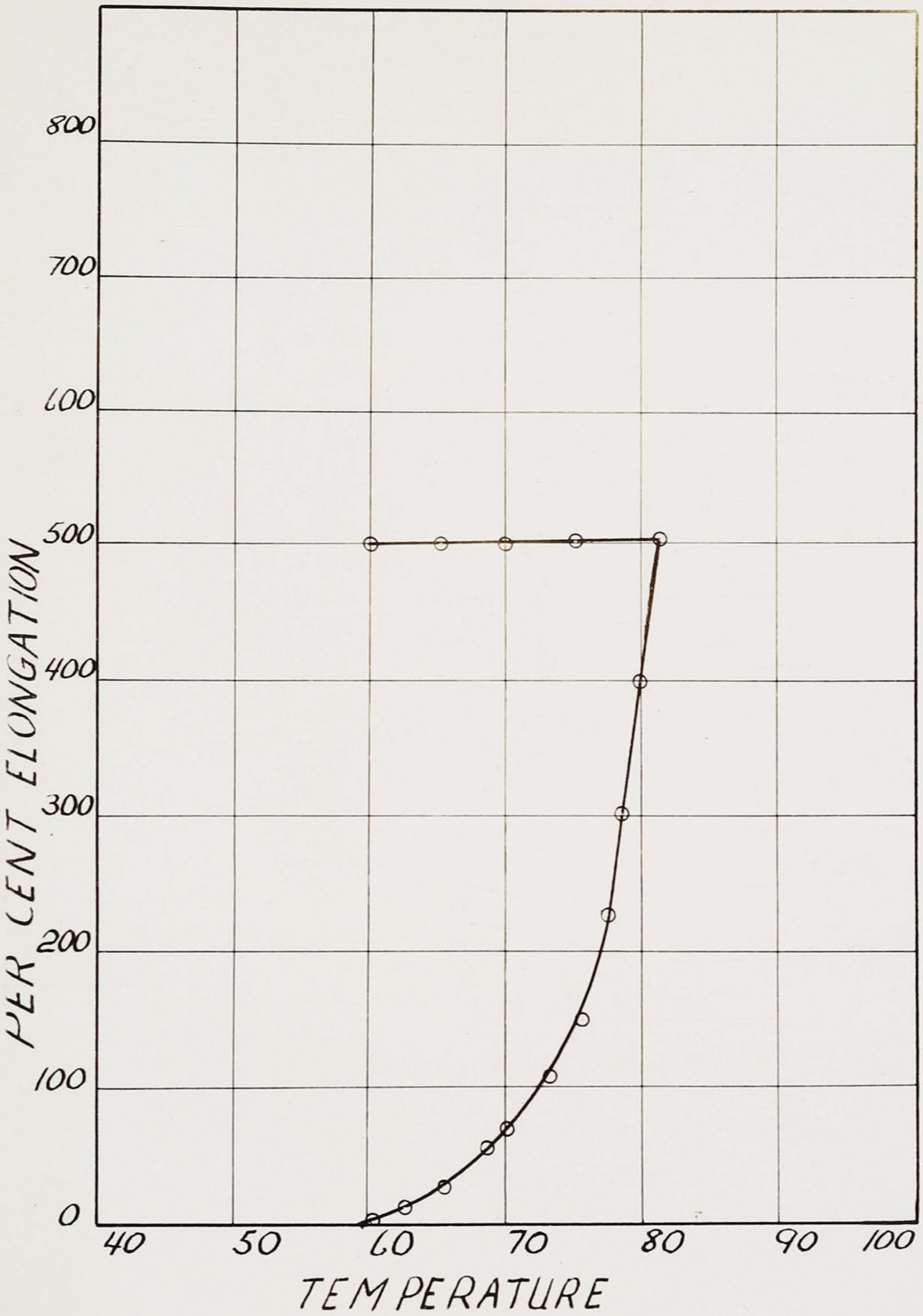

PER CENT ELONGATION
800
700
600
500
400
300
200
100
0
40
50
60
70
80
90
100
TEMPERATURE

FIGURE X.

when cooled and whether material that had been so treated would become elastic at the same temperature as the original substance.

A strip of meta styrene was placed in the stretching machine and a 75 gram load placed on the pan. The temperature was raised until the meta styrene had stretched 500% and the temperature was allowed to drop. The figures in Table shpw that there was no tendency for the material to contract when cooled similar to its ability to stretch when heated. The data is plotted in Fig. X.

TABLE XLVIII.

Experiment III.

Load, 75 grams. Cross section 2.02 sq.m.m.

Temperature	Length	Δ	% Elongation
15	3.63	0	0
50	3.63	0	0
55	3.63	0	0
60	3.80	.17	.46
65.5	4.5	.87	24.0
68.5	5.6	2.0	55.
73	7.5	3.9	107.
75.5	9.0	5.4	148
77	11.	7.4	204
77.5	13.	9.4	259
79	16	12.4	342
80	19	15.4	425
81	21	17.4	479
81.5	22	18.4	505
81.5	22	18.4	505
79	22	18.4	505
75	22	18.4	505
70	22	18.4	505
60	22	18.4	505
40	22	18.4	505

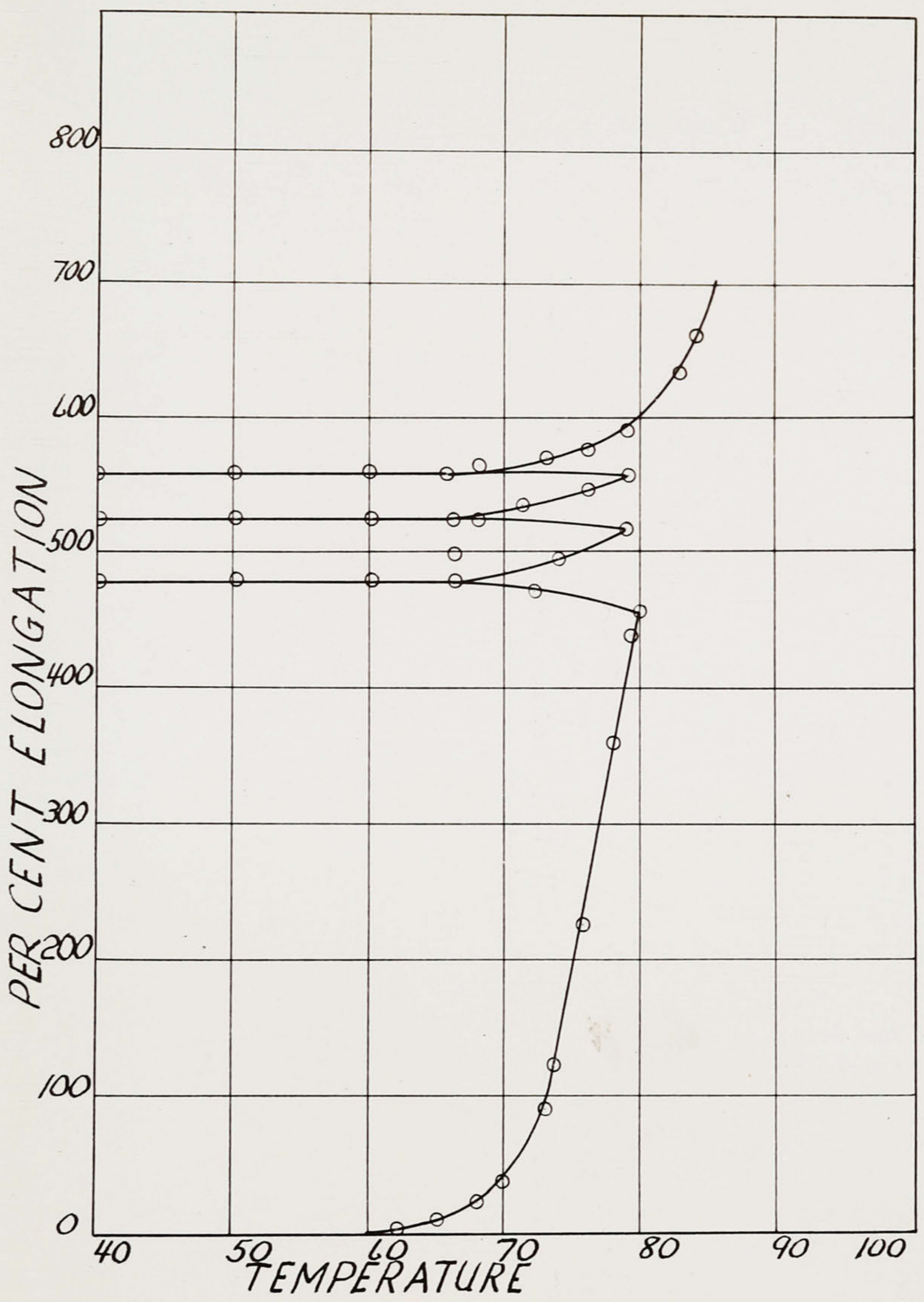

800
700
600
500
400
300
200
100
0
PER CENT ELONGATION
40
50
60
70
80
90
100
TEMPERATURE

FIGURE XI.

In Experiment IV the test piece was first stretched and then cooled as described in Experiment III. After cooling, however, the temperature was again raised and it was found that the material began to extend at the same temperature as the original meta styrene. But at the same temperature, it assumed a higher elongation than did the original material. If this is again cooled and then heated, still higher values can be obtained for the elongation.

Table XLIX shows the results obtained and they are plotted in Fig.XI.

TABLE XLIX.

Experiment IV.

Load, 75 grams. Cross section - 2.05 sq.m.m.

Temperature	Length	Δ	% Elongation.
Heating 10	3.7 cm.	0	0
55	3.7	0	0
60	3.8	.1	2.7
65	4.1	.4	10.8
68	4.5	.8	21.7
70	5.0	1.3	35.2
72	6.5	2.8	75.6
73	7.0	3.3	89.4
75	11	7.3	197
77	15	11.3	306
78	17	13.3	360
80	20.6	16.9	457
Cooling 75	20.6	16.9	457
73	20.8	17.1	463
72	21.0	17.3	467
70	21.2	17.5	473
68	21.4	17.7	478
64	21.5	17.8	481
40	21.5	17.8	481

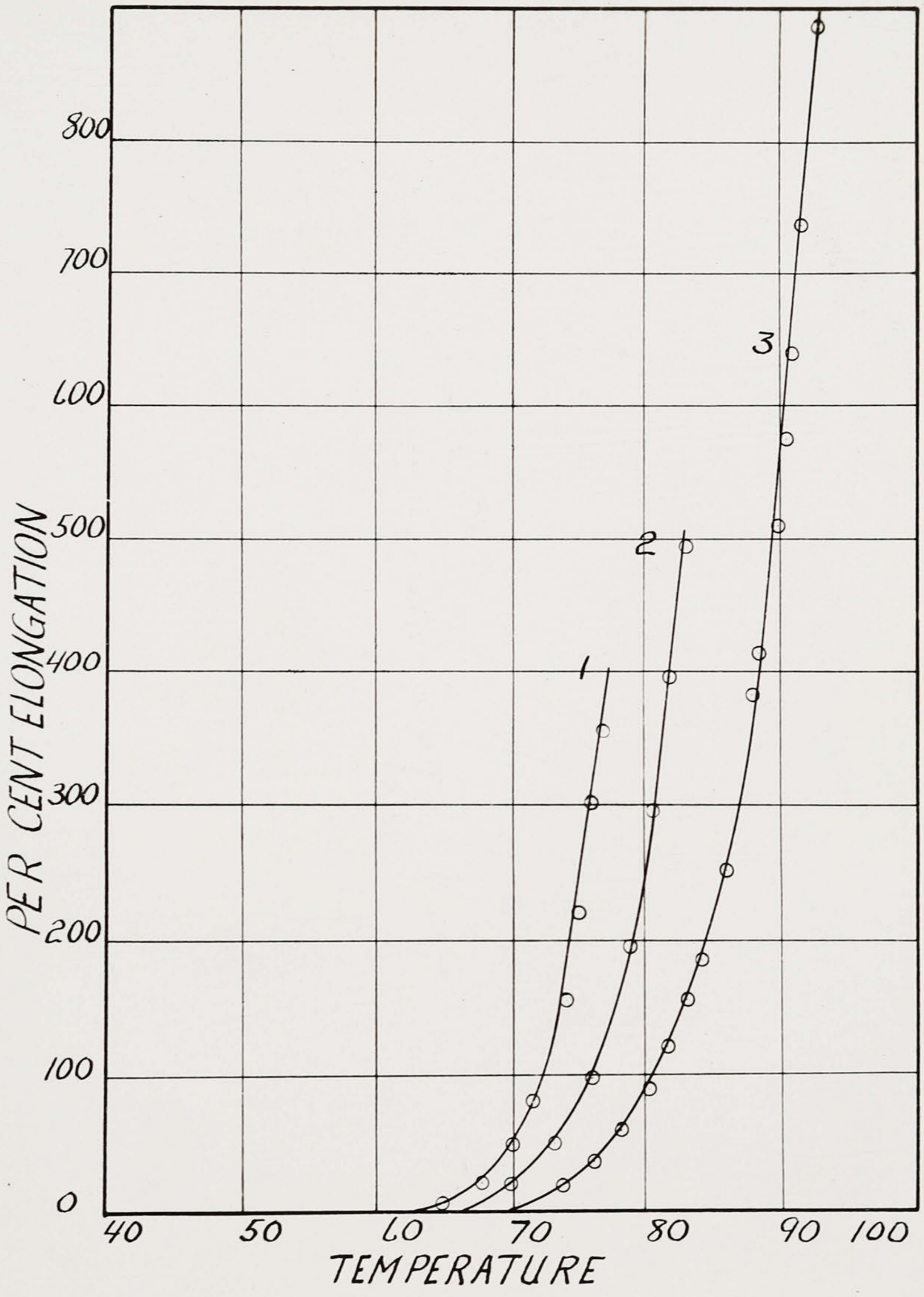

PER CENT ELONGATION
800
700
600
500
400
300
200
100
0
40
50
60
70
80
90
100
TEMPERATURE
1
2
3

FIGURE XII.

TABLE XLIX Cont'd.

Temperature		Length	Δ	% Elongation
Heating	45	21.5	17.8	481
	67	21.5	17.8	481
	70	21.7	18	487
	74	22	18.2	495
	77	22.4	18.7	505
	79	23	19.3	523
Cooling	76	23	19.3	523
	74	23.2	19.5	528
	50	23.2	19.5	528
Heating	60	23.2	19.5	528
	69	23.4	19.7	533
	76	24	20.3	549
	78	24.2	20.5	554
	79	24.4	20.7	560
Cooling	74	24.4	20.7	560
	25	24.0	20.7	560
Heating	35	24.4	20.7	560
	62	24.4	20.7	560
	68	24.7	21	569
	74	25	21.3	575
	77	25.2	21.5	581
	79	25.5	21.8	590
	80.3	26.	22.3	604
	83	27.2	23.5	635
	84	282.	24.5	662
	Broke			

EFFECT OF VARYING THE TENSION ON THE TEMPERATURE AT WHICH META STYRENE BECOMES EXTENSIBLE.

It was found that a large load put on the meta styrene strip caused it to draw out at a slightly lower temperature than when a small load was used. The data follows for loads of 35 and 120 grams and Fig.XII gives the curves for 35, 75 and 120 gram loads.

TABLE L.

Experiment V.

Load = 35 grams   Av. cross section 1.95 sq.m.m.

Temperature	Length	Δ	% Elongation.
40	3.1 cm.	0	0
66	3.2	.1	3.2
74	3.7	.6	19.3
78	5.0	1.9	64.4
81.5	7.0	3.9	125
84	9.0	5.9	190
86	11	7.9	255
88	15	11.9	384
89	17	13.9	448
90	19	15.9	514
91	22	18.9	610
92	29	25.9	835
93	33	29.9	965
93.5 Broke	36	32.9	1059

Experiment VI.

Load = 120 grams   Av. cross section 1.89 $m.m.^2$

Temperature	Length	Δ	% Elongation
40	3.7	0	0
62	3.7	0	0
62.3	3.8	.1	2.7
68	4.5	.8	21.6
70	5.6	1.9	51.4
72	6.6	2.9	78.5
74	9.5	5.8	156
75	12	8.3	224
76	15	11.3	305
76.9 Broke	17	13.3	360

THE RATE OF EXTENSION OF META STYRENE UNDER DIFFERENT TENSIONS AT A CONSTANT TEMPERATURE

An attempt was made to measure Young's modulus of elasticity for meta styrene at different temperatures but it was found impossible to do so because there was apparently no definite limit to which even a small tension would cause the material to extend if the force was allowed to act for a sufficient length of time, although it was found that a large tension caused the extension of the material more rapidly than did a small one, as might be expected. The following tables show the rate at which the same strip of meta styrene stretched under different loads. The original test piece had an average cross section of 2.13 sq. m.m.

TABLE LI.

Experiment VII.

Load 5 grams. Temperature 95°

Time (sec.)	Length (cm.)
0	6
10	8
30	9
55	10
110	11
160	12
210	13
255	14
315	15
370	16
420	17
490	18
560	19
660	20

TABLE LII.

Experiment VIII.

Load 15 grams. Temperature 95°

Time (sec.)	Length (cm.)
0	8.5
10	10
30	15
38	16
50	17
63	18
80	19
103	20
150	21
190	21.5

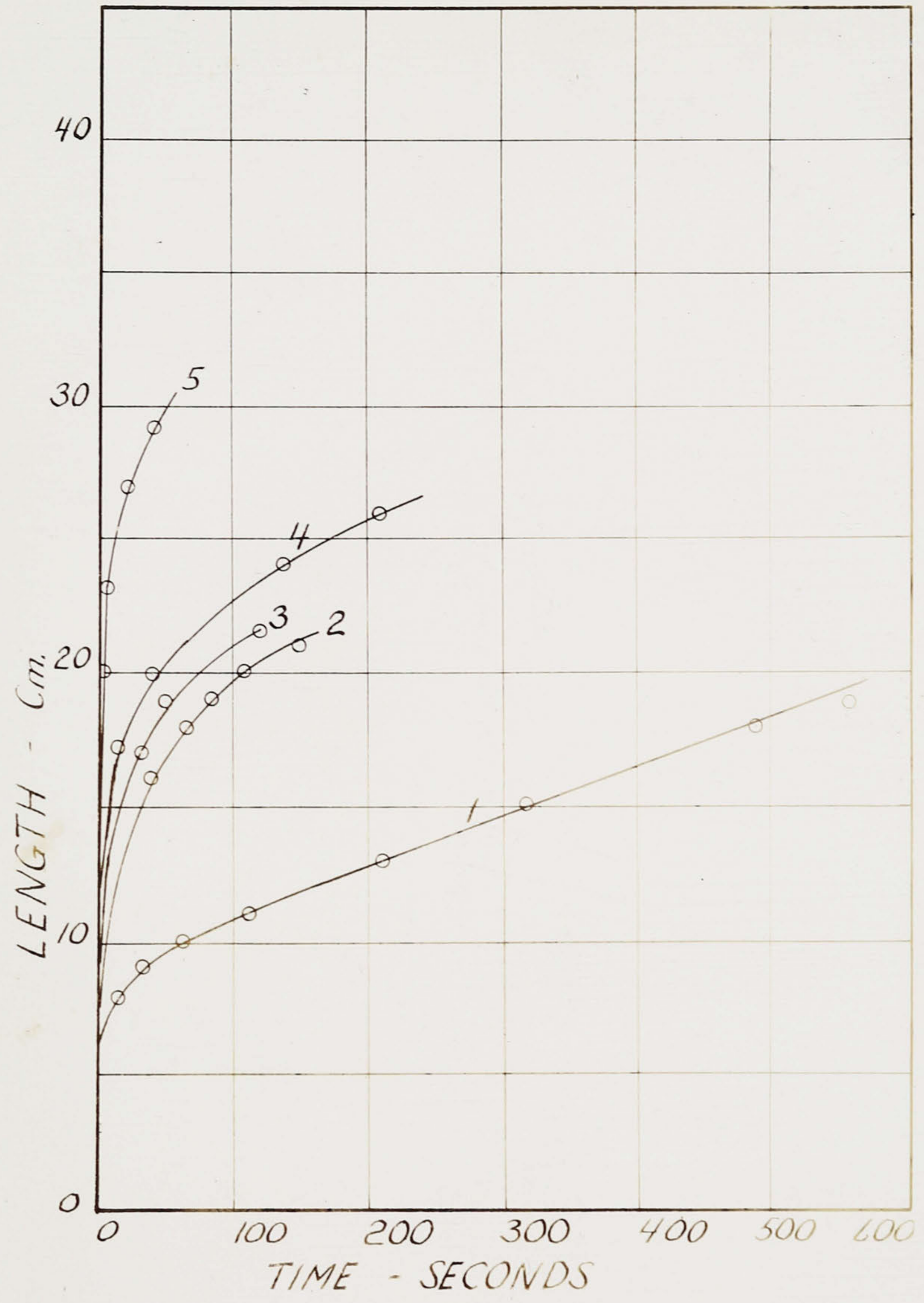

40
30
20
10
0
LENGTH - Cm.
5
4
3
2
1
0
100
200
300
400
500
600
TIME - SECONDS

FIGURE XIII.

TABLE LIII

Experiment IX.

Load 25 grams. Temperature 95°

Time (sec.)	Length (cm.)
0	7.4
10	11
22	14
33	17
43	19
70	20
120	21.5

TABLE LIV

Experiment X.

Load 35 grams. Temperature 95°

Time (sec.)	Length (cm.)
0	7
2	12
15	17
24	19
39	20
65	22
110	23
135	24
175	25
210	26

TABLE LV.

Experiment XI.

Load 45 grams. Temperature 95°

Time (sec.)	Length (cm.)
0	9
5	20
26	27
39	29

The results of these tests are plotted in Fig.XIII. The loads to which the curves refer are:

Curve 1	5 grams
2	15 "
3	25 "
4	35 "
5	45 "

It is evident that all the curves are of the same form. The initial extension is rapid and then the rate slows down after reaching a certain extension. The period of rapid extension appears to be the longer the greater the load.

THE TEMPERATURE AT WHICH META STYRENE THAT HAS BEEN STRETCHED AND THEN COOLED CONTRACTS.

It has been previously shown that meta styrene that has been stretched and then cooled is inelastic and that on warming it does not contract if the tension that caused the original extension is still allowed to remain. In the present experiment the stretched and cooled material was caused to contract under no load by raising the temperature and the temperature at which it contracted to a given leggth was noted.

TABLE LVI.

Experiment XIA.

Retraction after stretching - no load.

Original length 3.5 cm. Av.cross section 2.08 mm.^{2}

Temp.	Length	Δ	% Elongation
18	27.9	24.4	698
50	27.9	24.4	698
53	27.7	24.2	693
59	27	23.5	674
62	26	22.5	643
63.6	25	21.5	615
65	24	20.5	587

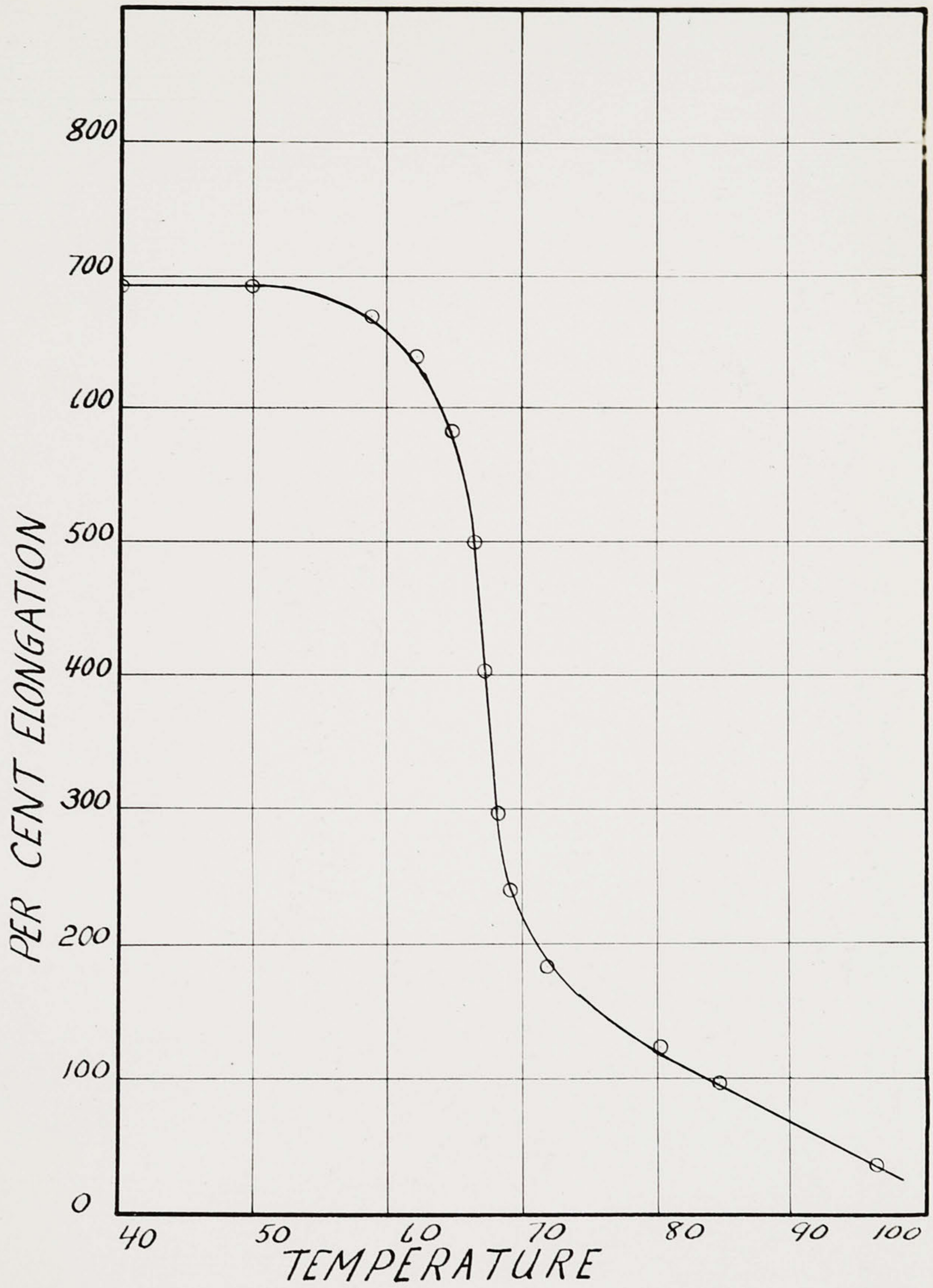

PER CENT ELONGATION
800
700
600
500
400
300
200
100
0
40
50
60
70
80
90
100
TEMPERATURE

FIGURE XIV.

TABLE LVI Cont'd.

Temp.	Length	Δ	% Elongation
65.5	23	19.5	557
66	22	18.5	530
66.3	21	17.5	500
67	20	16.5	472
67.3	19	15.5	444
67.5	18	14.5	415
68	17	13.5	386
68.5	14	10.5	300
69.5	12	8.5	242
71	11	7.5	214
72	10	6.5	185
76.5	9	5.5	157
81	8	4.5	128
85	7	3.5	100
91	6	2.5	71.5
97	5	1.5	43

The results of Experiment XIA are shown in Fig. XIV. There is a narrow range of temperature over which the meta styrene does most of its contracting which corresponds to the temperature range at which the material becomes elastic. The shape of the lower part of the S shaped curve is due to the conditions under which the experiment was carried out. At relatively small elongations, the meta styrene requires considerable time, as will be shown later, to contract to its equilibrium position at a given temperature. During the experiment, the temperature of the bath was being pregressively raised so that the meta styrene did not have sufficient time to contract as much as it could have at the temperature indicated. Hence the values given for the temperature at the lower end of the curve are too high.

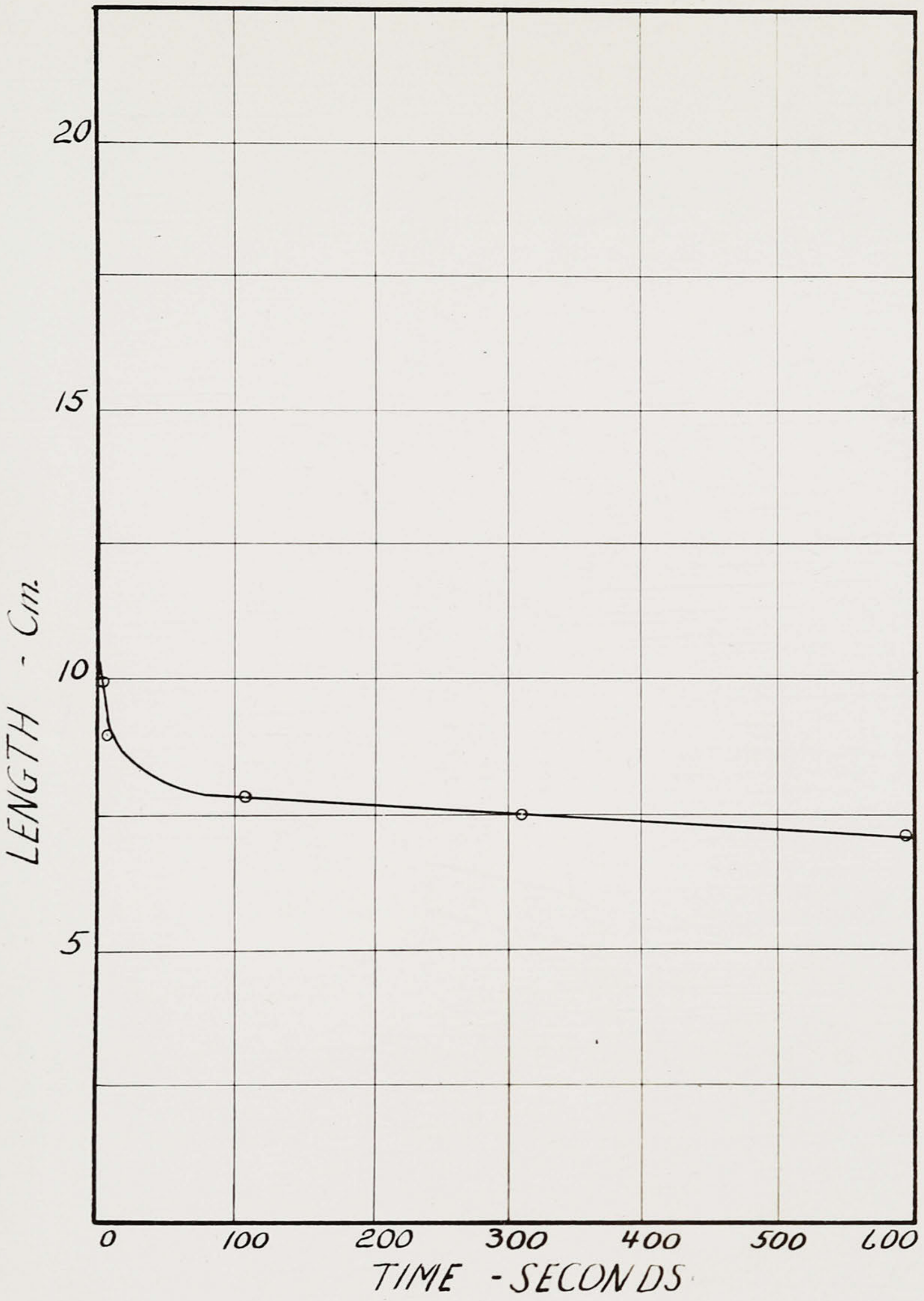


FIGURE XV.

ELASTIC AFTER EFFECT IN META STYRENE

The phenomenon of "elastic after effect", that is the slow retraction which follows the initial rapid contraction of the stretched material when released is well known in the case of rubber. Indications of a similar behaviour were seen in the experiment just described with meta styrene and this experiment was conducted to measure it.

A strip of meta styrene 6 cm. long was placed in water at 95° and stretched to 22.5 cm. It was then allowed to contract under no load and the time that the strip took to contract over successive intervals was recorded.

Under "time" in Table LVII are listed the number of seconds the strip required to contract to the length opposite it.

TABLE LVII.

Experiment XII.

Time (sec.)	Length (cm.)
0	20
0	18
0	16
0	14
0	13
0	12
0	11
1	10
7	9
102	8
310	7.5
900	7

The curve for this table is shown in Fig. XV.

The length of time the meta styrene was allowed to remain in the hot water while stretched was found to influence its ability to contract profoundly. The longer it remained in an extended condition, the poorer became its elastic properties.

A series of experiments was conducted in which a strip of meta styrene 2 cm. long was stretched to 11 cm. at 95°. It was then allowed to remain at this temperature for various periods of time and the rate of retraction on release was measured. The following figures show the results of these tests.

TABLE LVIII.

Experiment XIII.

Material stretched and released immediately.

Length (cm.)	Time (sec.)
12	
3	0
2.5	30
2.0	200

TABLE LIX

Experiment XIV.

Stretched material remained extended for 5 minutes.

Length (cm.)	Time (sec.)
12	
5	0
4	5
3.5	55
3.2	165
✗3.1	200
2.8	470

✗ Interpolated to compare with length at 200 seconds in Experiments XIII, XV, XVI and XVII.

TABLE LX

Experiment XV.

Stretched material remained extended for 10 minutes.

Length (cm.)	Time (sec.)
12	
5.5	0
5	10
4	95
3.5	200
3.2	500

TABLE LXI

Experiment XVI.

Stretched material remained extended for 90 minutes.

Length (cm.)	Time (sec.)
12	
8	0
7	8
6	35
5	200
4.5	450

It was shown that heating alone did not cause the meta styrene to lose its elastic properties by heating a strip of meta styrene to 95° for 2 hours before it was stretched. It was then stretched and allowed to contract immediately and it was found to be as elastic as the material that had not been previously heated for a,long time before stretching. For a large permanent after set, it is necessary to heat the meta styrene while it is extended.

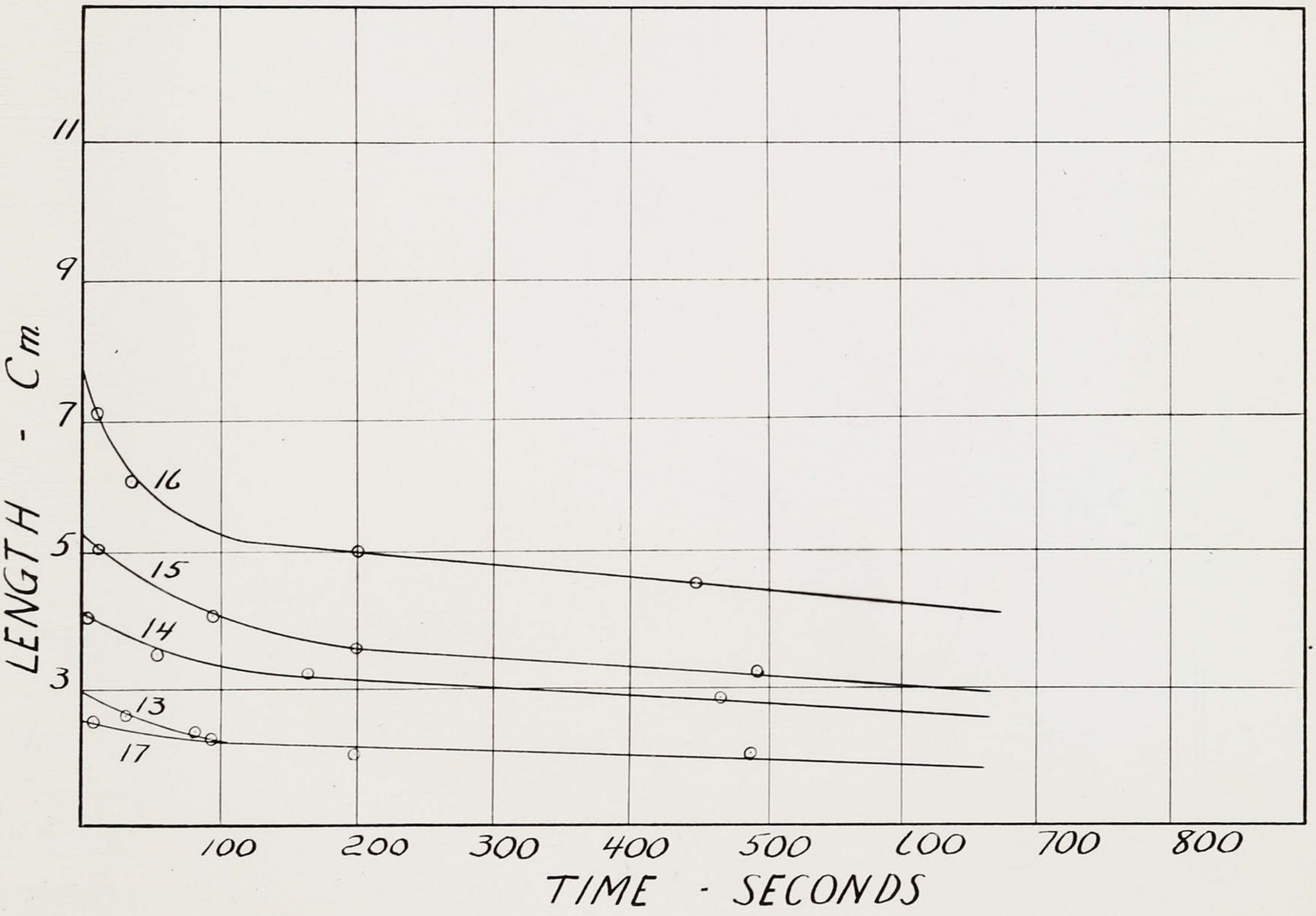

11
9
7
5
3
LENGTH - Cm.
16
15
14
13
17
100
200
300
400
500
600
700
800
TIME - SECONDS

FIGURE XVI.

TABLE LXII

Experiment XVII.

Meta styrene heated at 95° for 2 hours before stretching. Released immediately after stretched.

Length (cm.)	Time (sec.)
12	
3	0
2.5	5
2.3	80
2.0	230

The curves for Experiments XIII - XVII are given in Fig.XVI. The numbers on the curves refer to the numbers of the experiments.

After each of the experiments on stretching meta styrene was completed, the strip was drawn out as far as possible to see how great an elongation could be obtained. Some fifty strips were treated in this way and the greatest elongation ever obtained was 1500%. Several samples broke between 1300 and 1500% but the majority broke at about 1000% elongation.

SOME ELASTIC PROPERTIES OF RUBBER.

Although the elastic properties of rubber have been the subject of innumerable investigations, there exists no account of the influence of the temperature at which the extension is made on the contracting power of the rubber - particularly the amount of "set".

By "set" is meant the permanent deformation shown by a piece of rubber when stretched and then released. It is small in vulcanized rubber but very appreciable in the raw material.

It has been observed that the amount of "set" in meta styrene depended to a great extent on the length of time the stretched material was heated so similar tests were conducted with rubber.

The influence on the amount of "set" in rubber of the amount of stretch and the temperature at which the extension was made was investigated. It was also observed that the amount of "set" could be influenced by the thermal history of the rubber after release.

The first experiments described are those in which the length of time a stretched piece of rubber was allowed to remain in a bath at a given temperature was varied.

A piece of smoked sheet (the same stock was used in all experiments) about 7 cm. long and .5 cm. wide was fastened in the testing machine previously described so that 4 cm. of it was between the grips. The rubber was then stretched to 12 cm. at 48° and allowed to remain there for different lengths of time. The strip of rubber was then cut off at both ends next to the grips and allowed to contract at room temperature until it had reached a constant length. This process took about 10 days.

It was found that on heating the strips at 100° that had been allowed to come to equilibrium in this manner,

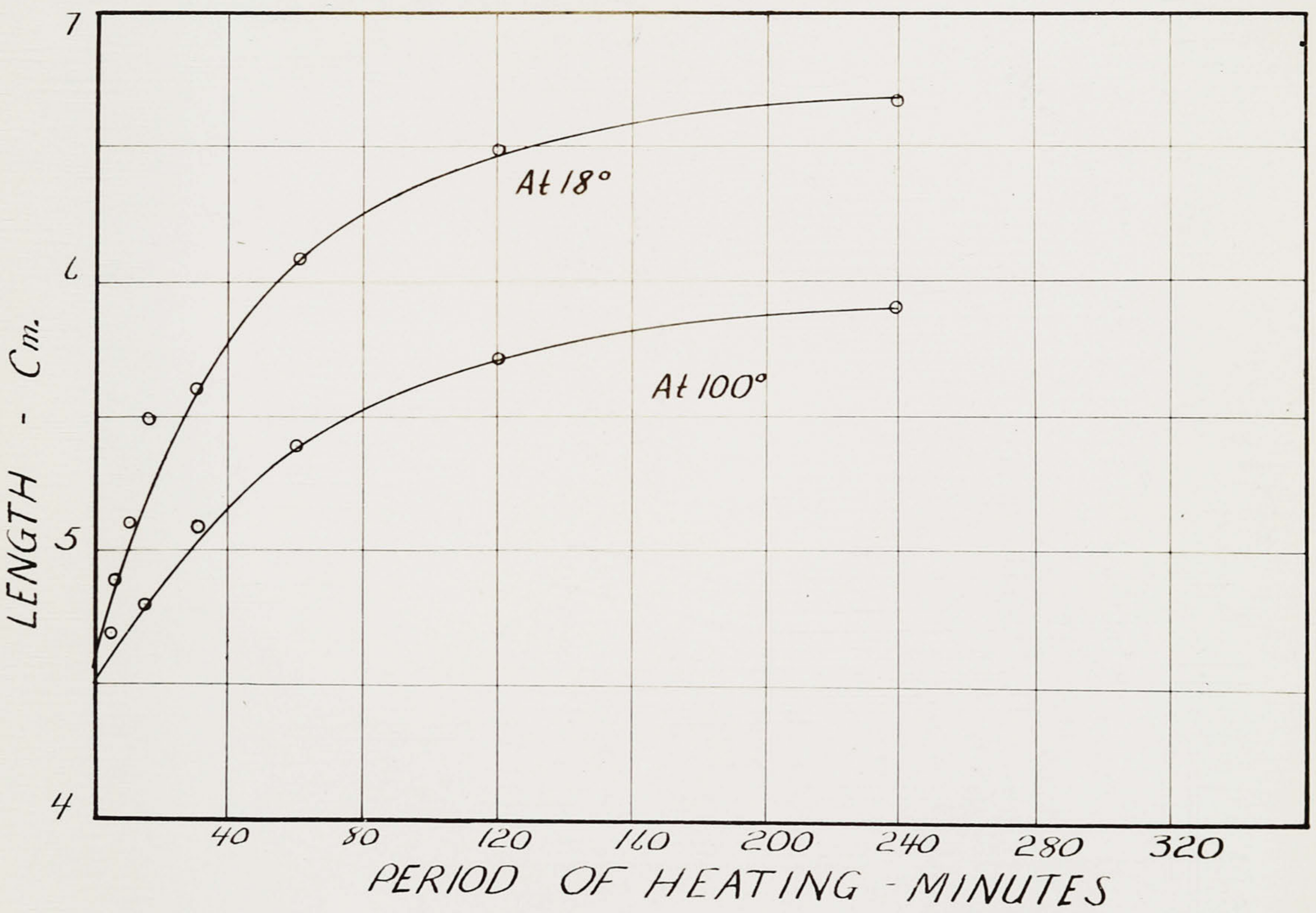

7
6
5
4
LENGTH - Cm.
At 18°
At 100°
40
80
120
160
200
240
280
320
PERIOD OF HEATING - MINUTES

FIGURE XVII.

they contracted further and reached a new length. Further heating caused no further contraction.

The results of these experiments are given in Table LXIII.

T is the time in minutes that the stretched strip of rubber was allowed to remain in the 48° bath.

L is the length to which the material contracted at room temperature.

L' is the length to which the strip contracted on being heated for 1 hour at 100°.

TABLE LXIII.

Experiment XVIII.

Strips of rubber 4 cm. long stretched to 12 cm. at 48°. Left in bath extended for time T.

T. (min.)	L	L'
5	4.9	4.7
10	5.1	4.7
15	5.5	4.8
30	5.6	5.1
60	6.1	5.4
120	6.5	5.7
240	6.7	5.9

Fig. XVII shows the amount of set plotted as a function of the time the sample was kept stretched at 48°. The upper curve refers to the values reached at room temperature and the lower one to the values reached at 100°.

The effect of the temperature at which the stretching was carried out on the amount of set in rubber was the subject of the following study. Strips of rubber 4 cm. long

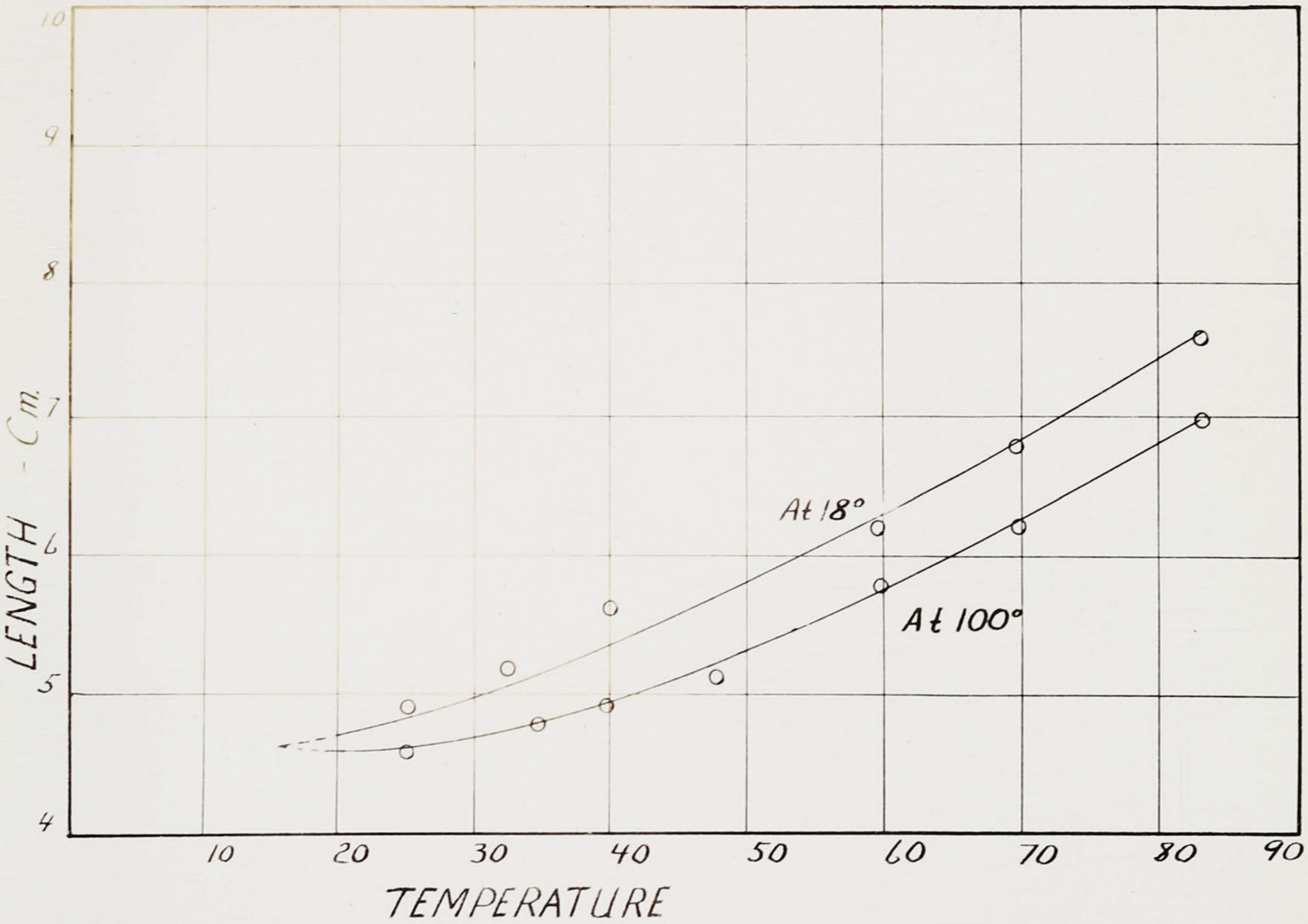


FIGURE XVIII.

were stretched to 12 cm. and allowed to remain for 30 minutes in baths at different temperatures. As before, the amount of set at room temperature and at 100° was determined. In the next table, L represents the length to which the rubber contracted at room temperature and L' the length reached at 100°. The temperatures refer to the temperature at which the stretching was done.

TABLE LXIV.

Experiment XIX.

Original length of rubber strip, 4 cm.
Stretched to 12 cm. and allowed to remain
stretched for 30 minutes.

Temp.	L	L'
20	4.7	4.6
25	4.9	4.6
35	5.2	4.8
40	5.9	4.9
48	5.6	5.1
60	6.2	5.8
70	6.8	6.2
83	7.6	7.0

The results in Table LXIV. are plotted in Fig. XVIII. The top curve again gives the values reached at room temperature and the bottom curve the lengths to which the rubber contracted at 100°.

It was found that the length to which a 4 cm. strip of rubber was stretched at 48° had much to do with the resulting amount of set, both at room temperature and at 100°. The results of experiments carried out on the effect are given below.

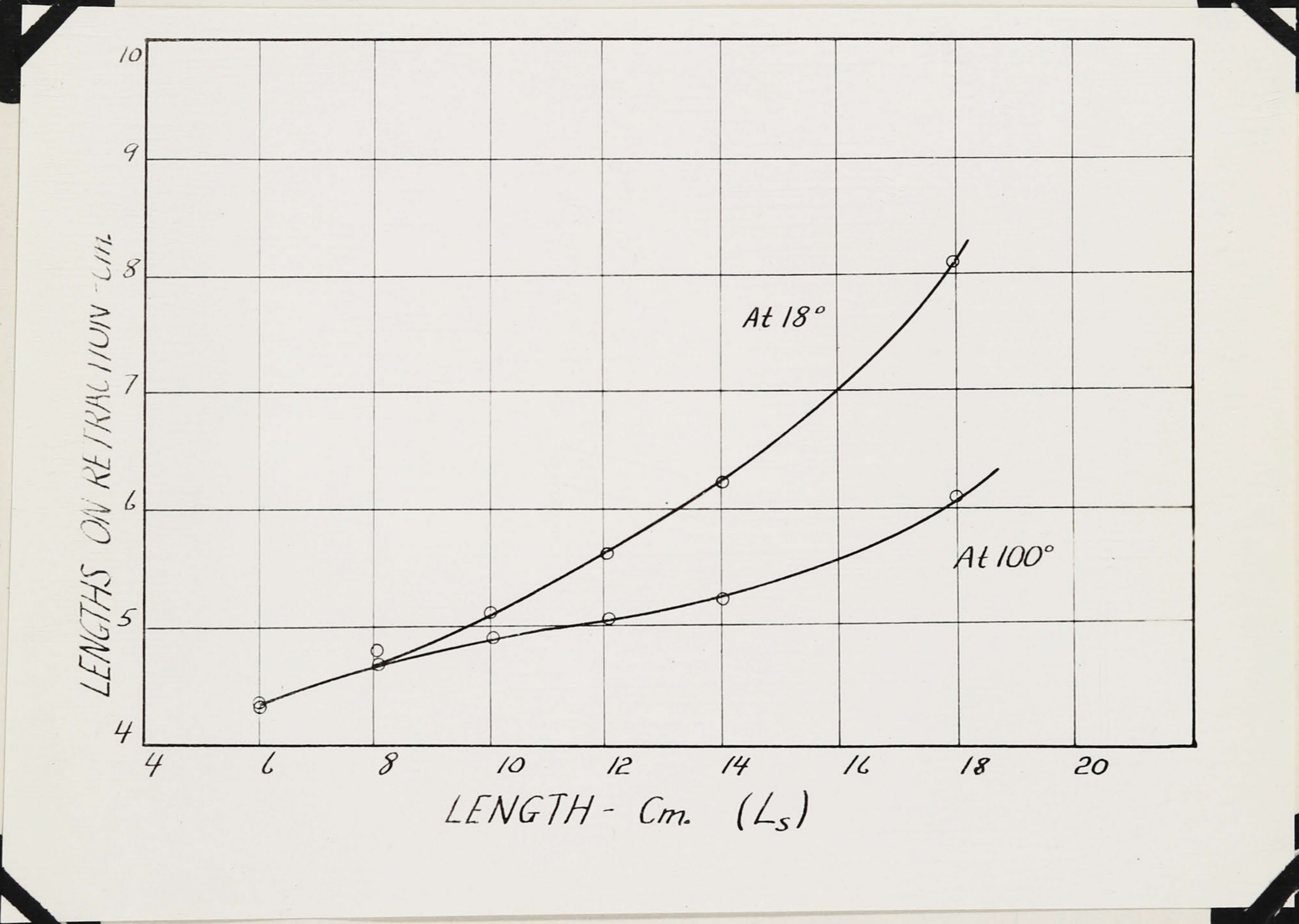

10
9
8
7
6
5
4
4
6
8
10
12
14
16
18
20
LENGTHS ON RETRACTION - Cm.
LENGTH - Cm. (L$_s$)
At 18°
At 100°

FIGURE XIX.

L_s represents the length to which the 4 cm. length was stretched, L the length to which it was contracted at room temperature and L′ the length reached at 100°.

TABLE LXV.

Experiment XX.

Strips of rubber 4 cm. long were stretched to various lengths at 48° and llowed to remain at that temperature for 30 minutes.

L_s	L	L′
6 cm.	4.3 cm.	4.3 cm.
8	4.8	4.7
10	5.1	4.8
12	5.6	5.1
14	6.2	5.2
18	8.1	6.1
20	9.7	Used for X-ray work

Fig.XVIV. shows this experiment in a graphical form, the upper curve referring to room temperature values and the lower one to lengths reached at 100°.

DISCUSSION OF RESULTS.

COMPARISON OF ELASTICITY IN RUBBER AND IN META STYRENE.

Meta styrene may be said to exhibit the same elastic properties that raw rubber does as far as it has been investigated. Certain features that are obscure in rubber are shown to an exaggerated extent by meta styrene but the essential phenomenon seems to be the same. In the following discussion, a comparison of the properties of rubber and meta styrene will be made with the object of making this contention clear.

It has been shown (Fig. X) that below 75° meta styrene is but slightly elastic but that it shows an enormous increase in elasticity when the temperature is slightly raised. Below 58° the material is not elastic at all.

The elastic properties of rubber show the same sensitivity to temperature but the temperature ranges corresponding to the ones mentioned above for meta styrene are different. Meta styrene in the region say of from 60° to 75° corresponds to rubber at room temperature; both materials are now moderately elastic. Meta styrene above 75° becomes very elastic and Feuchter(60) has recently shown that rubber may be drawn out to enormous lengths (up to 10,000% elongation) at high temperatures.

The shape of the temperature-elongation curve for rubber is the same as for meta styrene except that the temperature interval 30° - 40° correpponds to the 65°- 75° interval for meta styrene.

Katz(61) and also Hock have also shown that rubber becomes a hard, brittle inelastic solid when cooled in carbon dioxide-ether mixture. In this state, rubber resembles meta styrene at room temperatures.

The relation to the stress applied and the temperature at which rubber becomes very elastic - the "melting line" as Feuchter expresses it - has not as yet been investigated. So no comparison can be made with the results here presented for meta styrene (Fig.XII.)

In meta styrene, the temperature at which the material began to extend was lowered about 5° for an increase in tension of 400%. The probability is that the change in the "melting point" of rubber with change in tension is also very small or else Feuchter would have been unable to repeat his experiments where the stretching force was applied by hand and therefore was not exactly constant.

As mentioned before if meta styrene is stretched while heated, and then cooled while extended, it remains extended and will contract again even months later if it is warmed up to its "melting point". An exactly similar phenomenon has been known for some time in rubber(62) and has been the subject of recent extended investigation by Feuchter(63).

An interesting difference in the behaviour of the two materials when "racked", that is stretched while above the "melting point" and then cooled, will be discussed in a later paragraph on the X-ray examination of the two substances. Rubber when "racked" shows clear crystal interference spots on the plate while meta styrene so treated shows none.

It was recognized as early as 1805 and reported by Gough(64) that stretching raises the temperature of rubber. This interesting fact has been rediscovered several times since and in 1857 Joule (65) made a quantitative study of it. Hence it is now called the Joule Effect.

A similar examination of meta styrene will be made in the near future and it is hoped to add the results of this study as an appendix to this thesis.

It was seen that the amount of "set" in meta styrene increased as the length of time it was kept extended was increased (Fig. XV). The same conditions were found to prevail in rubber (Fig. XVII).

Enough has been said, it is believed to show that the general character of the elasticity in the two substances, rubber and meta styrene, is the same. The interesting question arises as to whether or not many lyophilic colloids might not show elasticity at suitable temperatures. This will be the object of future investigation.

THE VISCOUS AND PLASTIC NATURE OF RUBBER.

THE NATURE OF "SET".

Although the fact has long been known that raw rubber does not return exactly to its original length after stretching, this feature has been studied only with the object of correlating the amount of "set" shown by a piece of raw rubber and the properties of the vulcanized material(66). The amount of "set" has been chosen arbitrarily as the percent. deviation from the original length, one, or in some cases ten, minutes after release. These measurements afford no idea as to the magnitude of the permanent set as this can be measured only several weeks after the sample has been released.

A view of the cause of "set" will be developed here that is satisfactory in explaining the complicated phenomena previously reported in this communication. This view will first be stated as briefly as possible and then it will be applied to explain our observations.

For the purpose of exactness, it will be well to present definitions of what we mean by "plasticity" and "viscosity". The definitions used are quoted from Bingham(67) " Only by the behaviour of materials under shearing stresses are we enabled to distinguish between a fluid and a solid." If a body is continuously deformed by very small shearing forces, it is a liquid, whereas if the deformation stops increasing after a time, it is a solid. Liquids are said to be"viscous" and their movement under stress is referred to as "viscous flow". Solids are said to be "plastic" and their movement under stress is described as "plastic flow".

Rubber at room temperature is here suggested as consisting of two phases, one a liquid, viscous phase, and the second a solid, plastic phase. Further, it is assumed that the solid phase is composed of a whole series of compounds with melting points ranging from room temperature up to around 90° - aggregates of polymerized isoprene which differ in their degree of polymerization.

It is not considered that these aggregates differing in their degrees of polymerization have sharp melting points, but rather the opposite that the only criterion that we can apply to tell whether they are solid or liquid is whether they are plastic or viscous.

Referring to Fig. XVIII, the effect of temperature on the amount of set both at room temperature and at 100° is shown.

The total set is thought of as being due to two factors:- the viscous flow of the liquid phase and plastic deformation of the solid. An increase in temperature would increase the amount of both of these deformations and we take as the amount of set the sum of these two.

When the temperature of the system is raised, part of the solid material melts and flows under the stress applied. When the strip of rubber is allowed to contract at room temperature this material that was melted solidifies and becomes plastic; and the rubber will cease to contract after the elastic forces tending to pull the solid aggregates together is less than the yield value for the plastic material. If, now the temperature is again raised above the melting point of this plastic material the forces tending to bring the solid aggregates together are able to do work and the rubber contracts more.

Hence we observe that the set at 100° is smaller than at room temperature (20°) except for the sample that was stretched at 20° and allowed to contract at the same temperature. In this latter case no solid material melted during the length of time the rubber was stretched and hence no material solidified and prevented the rubber from contracting as far as it could when it was allowed to stand at room temperature.

The relations between the length of time the stretched rubber was allowed to stand at 48° and the resulting set are given in Fig. XVII. At this temperature the viscosity of the viscous phase already present would have diminished and a definite amount of the solid phase would become viscous, and the rapid rise in the amount of set corresponds to the viscous flow in the rubber. When this has had time to reach equilibrium, the amount of set is constant.

The lower set observed at 100° is again due to the solid which had melted at 48° and had become solid again at room temperature thus preventing the rubber from contracting. When this material is again melting, the rubber contracts further.

The fact that for small periods of stretching the value for the set at 100° approaches the value for the set at room temperature points to the conclusion that the initial deformation is due to the viscous flow of material that is liquid at room temperature; and that the solid phase that melted at 48° is highly viscous and takes longer to flow than the material that is already viscous at the room temperature.

Fig. XIX. shows the amount of deformation in similar rubber strips when they are extended to different lengths for the same period of time at 48°. The amount of set is plotted against the strain. As, however, stress is not proportional to strain in rubber above small elongations but increases more rapidly than the strain, the curve is not a straight line. The lower portion of the curve where the extensions are relatively small does approximate to a straightmline and when extrapolated, it indicates that an extremely small amount of flow will take place when a very small stress is applied. This is the necessary condition for viscous flow (see Bingham, loc. cit. p. 217). At small elongations then, the set is caused by viscous flow of liquid phase.

It is evident that the amount of set at 100° is not lower than the amount at room temperature until the elongations exceed 7 cm. A consideration of the conditions of the experiment will explain this. The test pieces of rubber were allowed to remain extended for thirty minutes. Fig. XVII shows clearly that even at 12 cm. elongation, the flow was to a large part still due to viscous flow of material that is liquid at room temperature during this period of time. The solid phase that melted at 48° will be more highly viscous, of course, than the original liquid phase and the flow of this material will be much slower than the liquid with greater fluidity. It is only when a sufficiently great stress is applied that this highly viscous material flows to any appreciable extent during the 30 minutes allowed. When this stress is reached, the melted material is deformed and when the rubber is brought to room temperature, it solidifies and prevents retraction by the mechanism suggested before.

The above theory has been useful in interpreting the results observed by the writer. Possibly it will fall down when more is known about "set". But it is believed that it does indicate that a study of the nature of the permanent deformation in rubber with particular reference to distinguishing plastic and viscous flow in the material may throw a considerable amount of light on the long debated question as to the constitution of rubber. This represents a new method of attack on the problem and it is thought that it warrants an extended investigation.

THE ELASTIC PROPERTIES OF THE HEAT POLYMERS.

Strips of the heat polymerized samples of meta styrene were prepared by the method described for the cold polymer; but the strips were so brittle and had such low tensile strength that they could not be tested accurately. A few rough measurements were made, however, to compare their properties with the cold polymer. Both the specimens polymerized at 140° and the one made at 180° showed almost identical behaviour.

The heat polymers became soft at 40° and readily extensible at 47°. At higher temperatures they are very readily drawn out but their contracting power is poor. At 72° a piece of material 1 cm. long was drawn out to 9 cm. On release it contracted to 7.0 cm. and remained there. At 89° a piece 1 cm. long was drawn out to 15 cm. and it contracted to 12 cm. on release. At 100° the heat polymers can be drawn out to thin threads representing several thousand percent. elongations, but they have almost no power of retraction.

The fact that the elastic qualities of heat polymerized meta styrene are very much inferior to those of the cold polymerized material is significant in view of the fact that the molecular weight of the former is very much lower than that of a latter, and points to the important conclusion that the possession of good elastic properties by an organic colloid is dependent on a very high molecular weight.

ELASTICITY IN META STYRENE GELS.

Meta styrene becomes elastic not only on heating but also on the incorporation of a suitable proportion of a swelling agent. If the swelling agent used is volatile, the gel becomes tough on exposure to the atmosphere due to evaporation of the swelling agent. But if a non-volatile swelling agent is used, a material may be produced with elastic properties comparable with those of rubber and the gel does not harden when exposed to air for long periods of time. Several of the most satisfactory specimens will be described. They were prepared by adding a suitable amount of the non-volatile swelling agent to a concentrated chloroform solution of meta styrene and evaporating off the chloroform. The proportions of materials in the gels was found by dissolving part of the gel in chloroform, precipitating the meta styrene with alcohol and weighing the dried meta styrene.

A gel containing 65% by weight of tri o cresol phosphate was slightly sticky but could be extended some 600% without breaking.

A gel consisting of 34% ethyl oleate could be stretched 500% and it returned to its original length within ten minutes after release. The initial contraction was larger and was followed by a period of "creep".

A variation in the method of preparing the gels gave the best ones obtained. A gel containing what was known to be an excessive amount of ethyl oleate was first prepared and this material was allowed to stand in ethyl alcohol for several hours. The material after this treatment was white and opaque due to precipitation of the meta styrene. But on standing for a day, the alcohol evaporated off and ethyl oleate in the gel swelled the meta styrene so that the gel was transparent.

This material contained 50% by weight of ethyl oleate and could be stretched 1300% without breaking. Its retractive power was particularly good as a piece thus extended showed practically no "set" after a few minutes.

X-RAY EXAMINATION OF STRETCHED META STYRENE AND RUBBER.

The fact that unstretched rubber gives an X-ray spectograph that is typical of amorphous solids and liquids has been known for a long time. Figure XX is a picture of unstretched smoked sheet. Early in 1925, Katz(68) reported that Hevea caoutchouc when stretched above 100% gives an X-ray diagram that is typical of a crystal, ie. sharp interference points appear. Figure XXI shows the results obtained with a strip of smoked sheet stretched 500%. During the past two years numerous articles have appeared dealing with this aspect of rubber, an excellent summary of which is given by Clark(69).

Hauser(70)mentions that if rubber is stretched when warm and cooled while it is in this extended condition, it remains extended and in this state it gives strong interference points. Since meta styrene can be extended in the same manner, it was thought of interest to examine it with the aid of the X-ray spectograph. Figure XXII shows a picture of unstretched meta styrene. It is remarkably similar to the results obtained with unstretched rubber. Figure XXIII shows the results obtained with the same sample of meta styrene elongated to 1300%. There appears to be no orientation of the molecules of this substance when stretched to form a crystal lattice that will cause the diffraction of X-rays. A large number of samples of meta styrene prepared in various ways and stretched to different degrees, were photographed but the results were the same as shown in Figure XXIII.

It had never been shown in a satisfactory manner that the pure rubber hydrocarbon showed a diffraction pattern on stretching. Since raw rubber, with which the effect was observed, contains protein material in amounts ranging up to 8% and since gelatin(71) has been shown to give a diffraction pattern on stretching up to 100%, it was thought that the crystal interferences observed in raw rubber might be due to the protein it contained.

A benzene solution of protein and resin free rubber was prepared by the method described earlier(page 28) and strips of rubber were prepared by evaporating off the solvent. This material when stretched gave no X-ray interference points. Another sample of protein and resin free rubber that had been standing for some time in a drawer showed two interference spots on extension up to 300% (Figure XXIV) and very clear interferences on "racking" to 1800% (Figure XXV). The first sample of pure rubber prepared probably contained some solvent as it is very difficult to remove the last traces of a swelling agent from rubber. Clark(72) has shown that even small amounts of a swelling agent in rubber will prevent the stretched material from giving X-ray interference points.

It would appear, then, that some difference exists between the stretched rubber and the stretched meta styrene. But in the present state of our knowledge of the subject, it is impossible to say just what this difference is.

Figure XXVI. is a picture of the tri o cresol phosphate gel of meta styrene stretched 500%. No interference spots are visible and it is noticeable that a new ring has made its appearance inside of the one caused by meta styrene.

A recent paper by Hunemorder(73) has just arrived in which the author reports the results obtained on taking X-ray spectographs of stretched meta styrene. The author states that meta styrene when stretched to "about 4000%" gives no interference points but the "amorphous ring" becomes slightly elliptical.

Hunemorder describes his material as "meta styrene polymerized by long standing". But he speaks later of swelling his material in ether. Now, meta styrene that has been polymerized at room temperatures does not swell at all in ether. It appears likely that his sample of meta styrene was polymerized by heating.

In conclusion it may be said that the cold polymerized meta styrene has not yet been extended above 1500%. And at this elongation, its X-ray diffraction pattern is the same as for the unstretched material.

These prints are the same size as the negatives. They were taken with the K_α rays from copper (λ = 1.57 Angstrom units). The specimen was placed on the slit and the plate 5.5 cm. away from the slit.

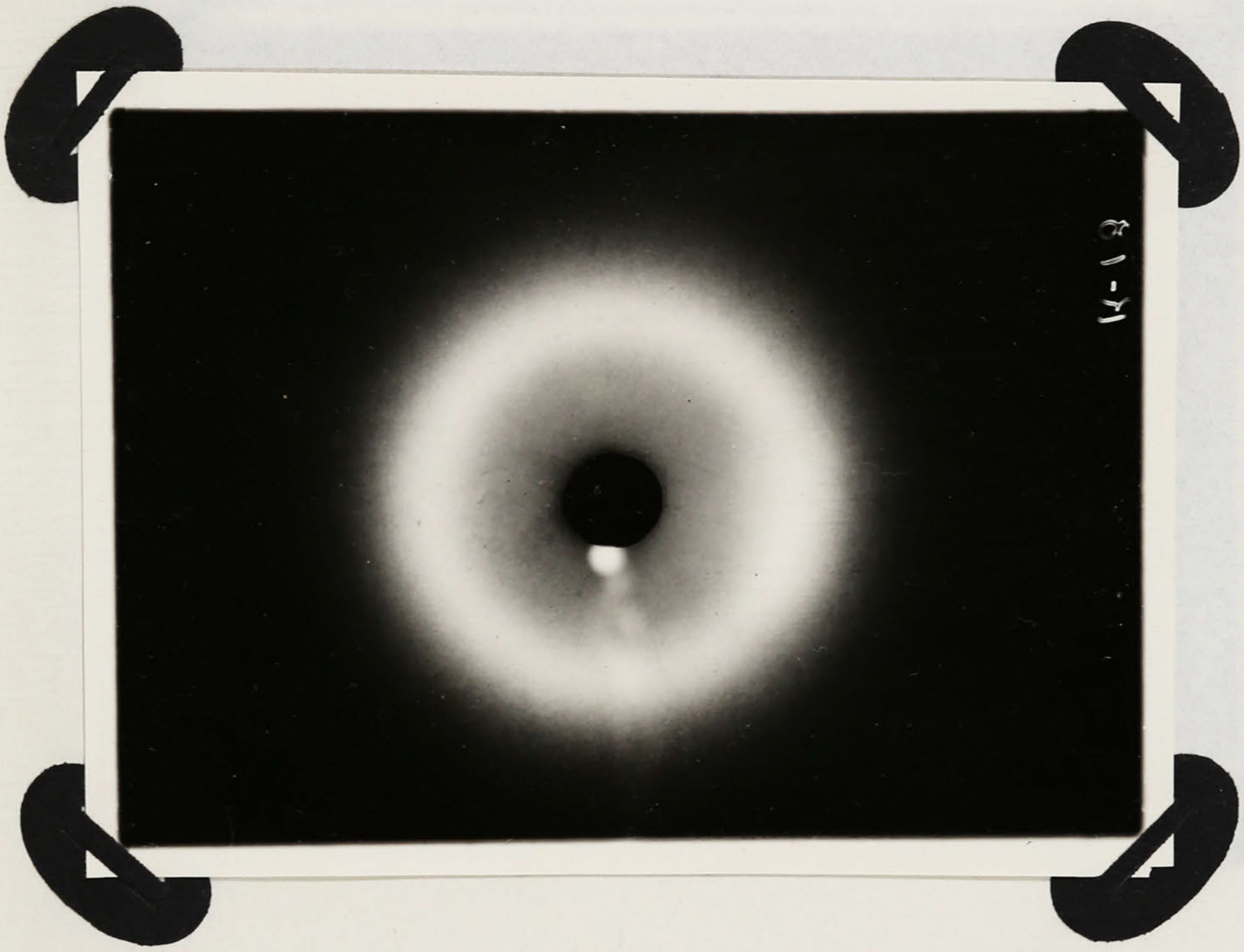


FIGURE XX.

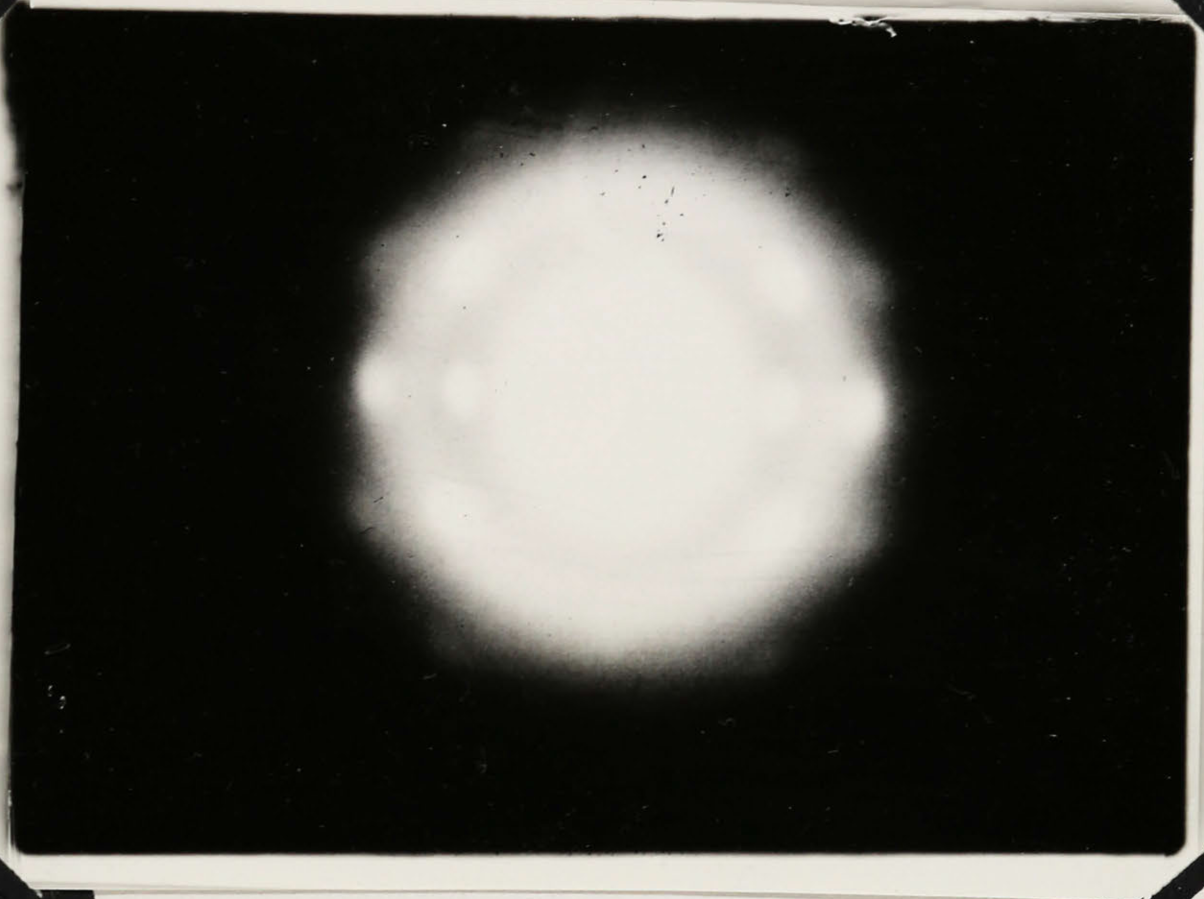


FIGURE XXI.

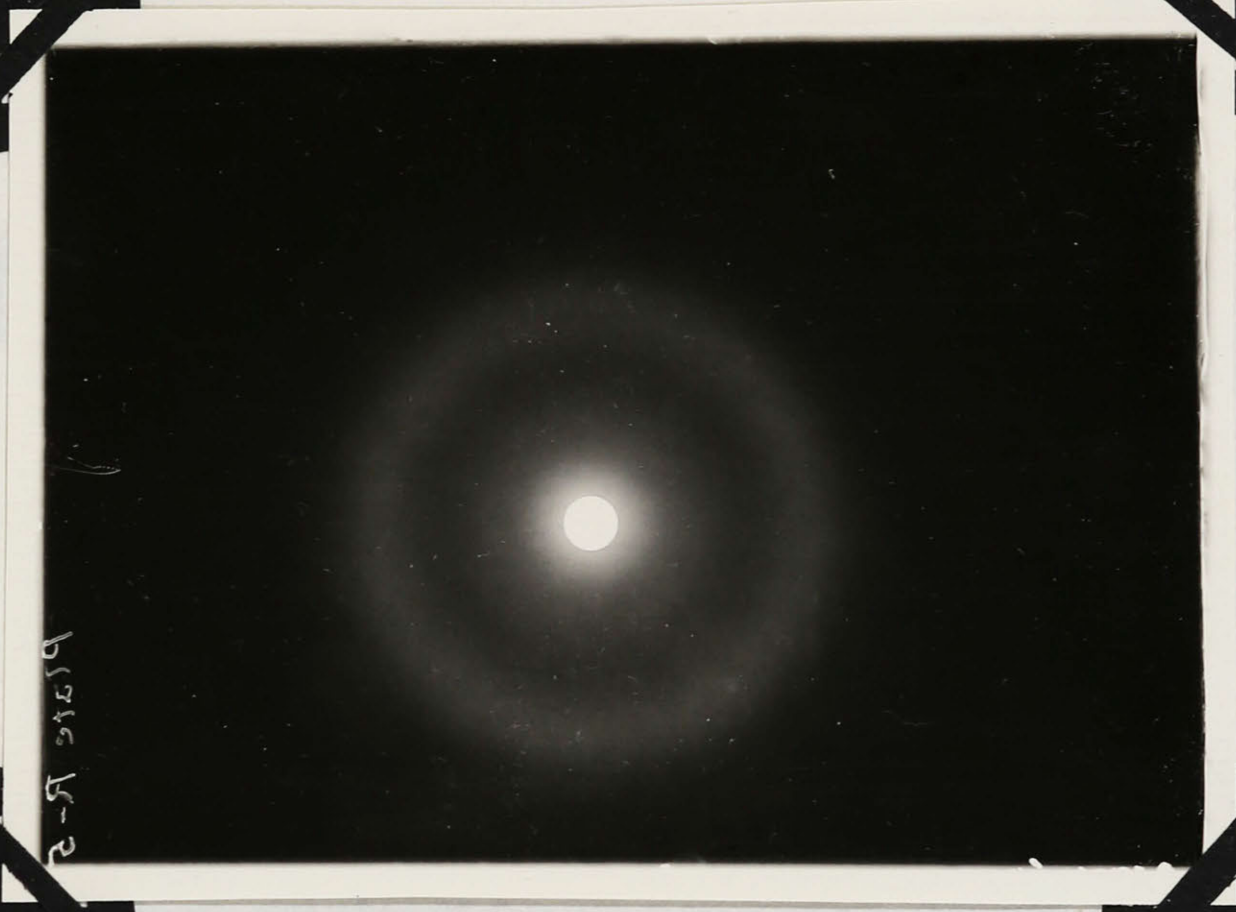


FIGURE XXII.

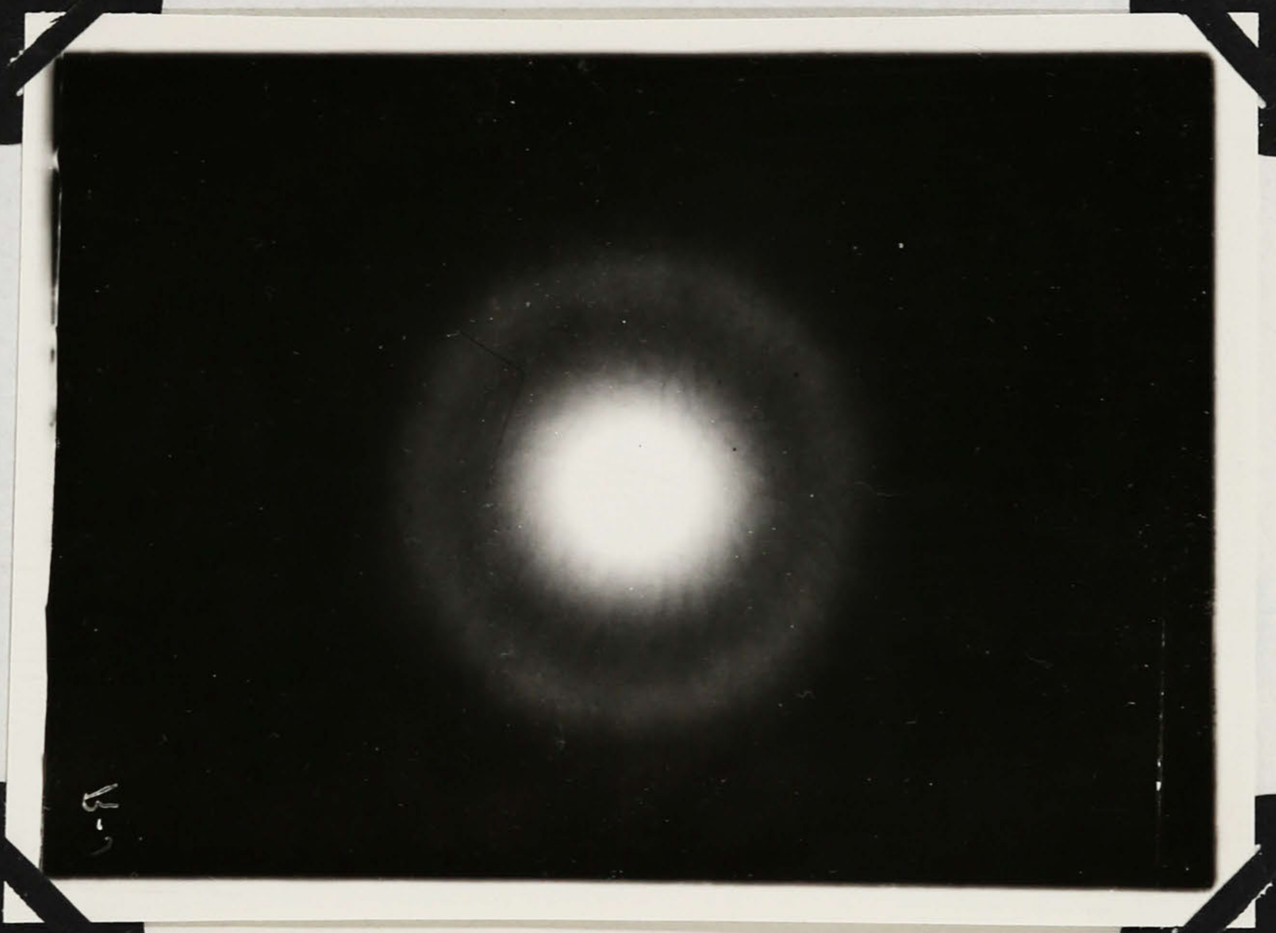


FIGURE XXIII.

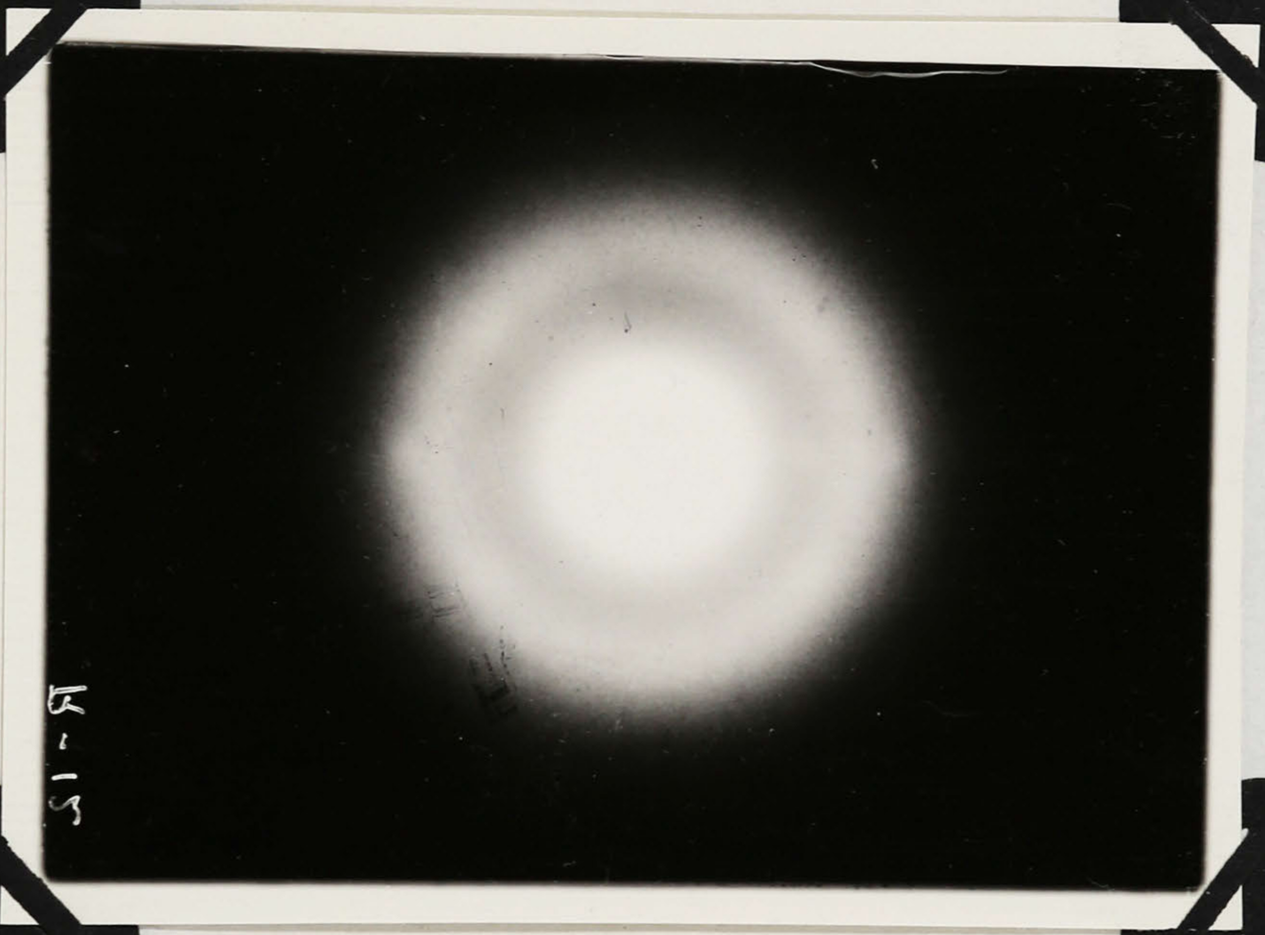


FIGURE XXIV.

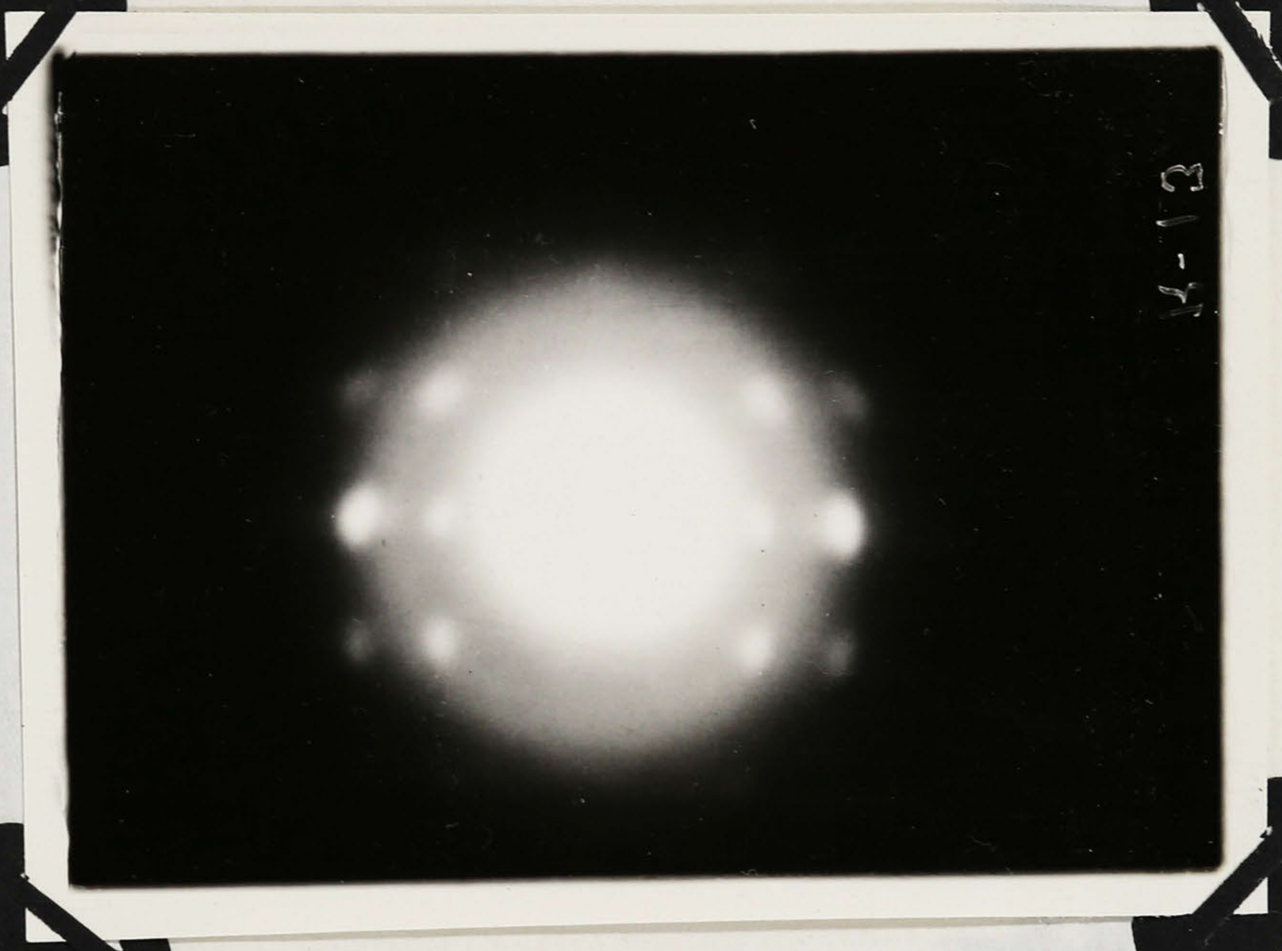


FIGURE XXV.

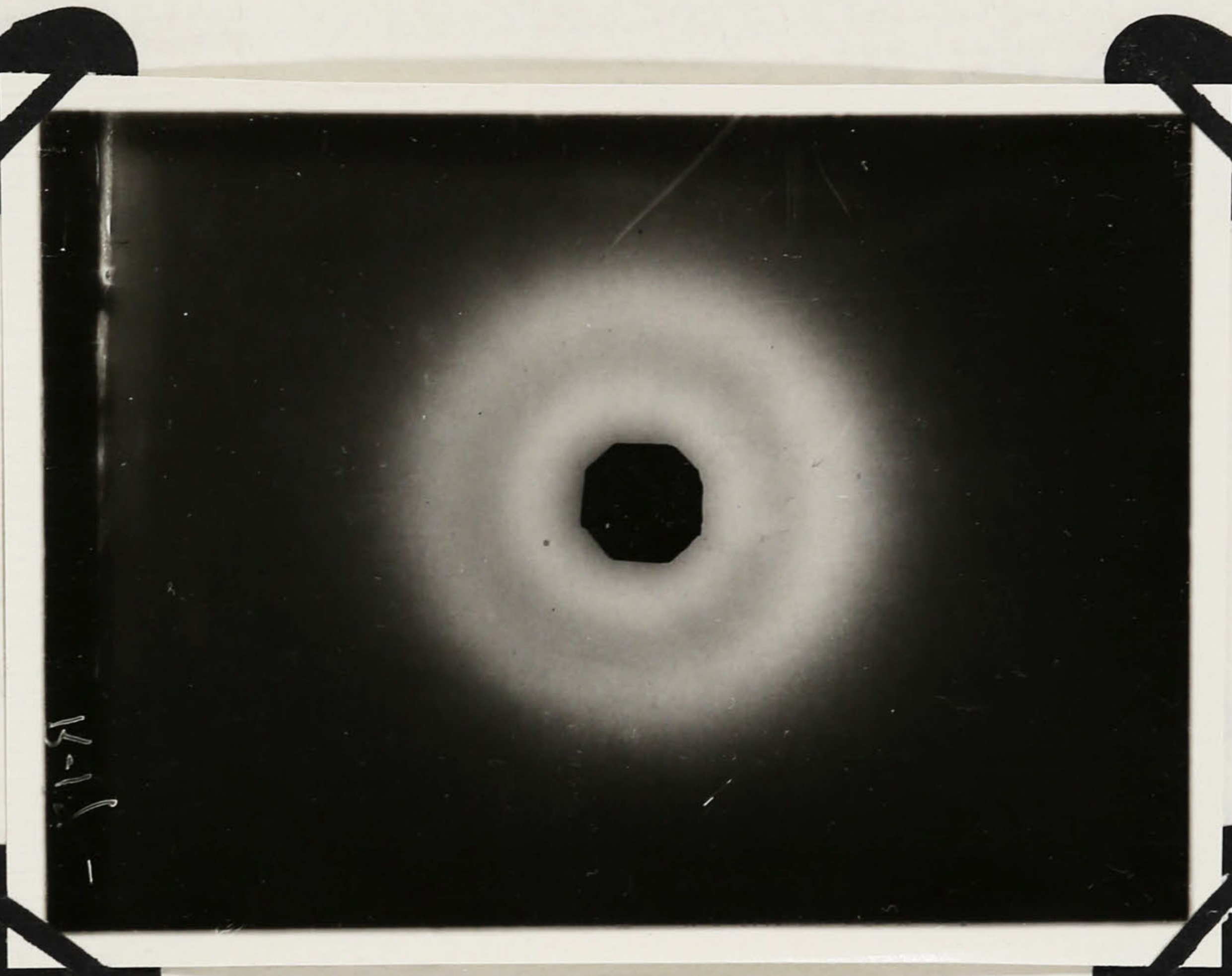


FIGURE XXVI.

SUMMARY

1. The molecular weight and the colloidal and elastic properties of meta styrene have been shown to depend on the temperature at which the styrene is polymerized.
2. Meta styrene and rubber have been shown to be heterogeneous.
3. The relative viscosity of meta styrene sols increases rapidly as the concentration of meta styrene increases. A suggestion has been made to account for the high viscosity of meta styrene sols.
4. The relative viscosity of a meta styrene sol has been shown to be independent of the temperature at which the viscosity is measured.
5. The surface tension of a meta styrene sol has been shown to be the same as the surface tension of the solvent.
6. The meta styrene micelle does not migrate in an electric field.
7. The effect of heat, reagents, freezing, exposure to ultra violet light and mechanical agitation on the viscosity of meta styrene sols has been investigated.
8. A correlation has been made between the chemical constitution of meta styrene and liquids that swell or precipitate the colloid. Precipitation tests by a number of precipitants on sols in a variety of dispersion means have ~~been~~ shown that

the amount of a precipitant that may be added to a sol without causing precipitation can not be regarded as an index of the degree of solvation of the sol.

9. The viscosity of meta styrene sols in various dispersion means has been reported.

There is no strict parallelism between the viscosity of the solvent and the viscosity of the sol.

10. An investigation has been made of the elastic properties of meta styrene and a comparison has been made between this colloid and rubber.

11. The phenomenon of "set" in raw rubber has been studied and a view has been advanced to explain this aspect of rubber.

12. Some elastic gels of meta styrene have been described.

13. X-ray spectograph studies have been made of meta styrene and of rubber.

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