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PHASE BEHAVIOR OF SODIUM STEARATE IN ANHYDROUS CYCLOHEXANE

BY

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On completion of this work I wish to express my sincerest thanks to Dr. R. F. Sessions, professor of chemistry, Georgia School of Technology, formerly professor of chemistry at the University of Richmond, for his suggestion of the problem, for supplying parts of the apparatus and aiding in its installation, and for his most valuable aid and guidance in prosecution of the problem that was given generously under unfavorable circumstances. His great personal interest and his many kindnesses will not be soon forgotten. I also wish to express my sincere thanks to Dr. J. Stanton Pierce, whose interest and cooperation made possible this work. My thanks also to Dr. R. B. Irby for his cooperation and his many valuable suggestions. To Dr. W. E. Trout, Jr. go my heartfelt thanks for his interest, suggestions, and many kindnesses, which aided materially in the completion of this work. The original suggestion of this problem was made to Professor Sessions by Dr. J. W. McBain, Director of the National Chemical Laboratories, Poona, India, formerly professor of chemistry at Stanford University. The ideas of Dr. McBain and his students have been freely drawn upon and due acknowledgment is made at this time.

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I INTRODUCTION

Soap solutions, aqueous and non-aqueous, are characteristic in that they form colloidal systems at certain concentrations, the properties of which are influenced by temperature and pressure. Application of the Gibbs phase rule to such systems makes possible the location of the various phases of a particular system and hence enables phase diagrams to be constructed. For systems of soap-hydrocarbons such as are found in fuels, beauty preparations, greases, medical preparations, etc., a phase diagram would show very readily the most satisfactory composition for the conditions desired. (1)

The colloidal nature of these systems accounts for such properties as swelling, gelation, viscosity change, opalescence, detergency, solubilization, etc. Although these properties are exhibited by different colloid systems, many of them can be shown to obey the fundamental laws of physical chemistry. The application of the Gibbs phase rule is important in this connection and for this reason phase studies of the

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(1) K. S. Mysels, Ind. Eng. Chem. <u>41</u>, 1435, (1949).

soaps have been made over a long period of time. However, the studies have generally been restricted to soap-water systems with only slight attention paid to the equally important soap-hydrocarbon systems. Within recent years, the absence of information about such systems has been realized and partial studies of the existing phase relationships have been made.

An incomplete study of the phase relationships existing for the system sodium stearate-cyclohexane has been made by Smith and McBain and the probable phase diagram drawn (2). However, their work gives only a partial picture of the phase relations in this system and much of the diagram is tentatively delineated because of incomplete data. The present work is a continuation of the study of this system.

The specific purpose of this investigation was to investigate the phase relationships of the system sodium stearate-cyclohexane at high soap concentrations above 50°C. and to locate on a phase diagram as accurately as possible the boundaries of any phases encountered.

As a secondary purpose of the investigation, the techniques of the experimental method used were studied, special emphasis being given to the properties and correct use of vitreous silica springs.

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(2) G. H. Smith and J. W. McBain, J. phys. and colloid chem. 51, 1189, (1947).

II HISTORICAL

Man probably first discovered soap when he observed that the grease soaked ashed from the fire he had used to cook his food had the property of lathering slightly when rubbed on his body with some water and removing the accumulated dirt from his skin. As early civilization developed wood fire ashes were used for the necessary cleaning purposes, and they have been used for cleaning purposes by the people of ancient civilizations until fairly recent times (3). The early Romans learned of soap from the Gallic tribes to the north and Plinius notes this fact, which is the earliest recorded mention of soap. Cakes of crude soap and the remains of a soap factory were found in the ruins of Pompei, so it is evident that the early Romans had learned how to manufacture soap(4).

From the early civilizations and down through the periods of history, the use of soap became more widespread as civilization was developed. The method of manufacture, however, reached a certain point in development and then stopped. It had become an art based on trial and error, necessitating much skill and was regarded as a closely guarded secret by each

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(3) C. R. A. Wright, Fixed Oils, Fats, Butters, and Waxes: Their preparation and properties, 2nd edition, C. Griffin & Co., London, 670, (1903).

(4) J. Lewkowitsch, J. of Soc. Chem. Ind., 26, 590, (1907).

manufacturer. In 1741, Geoffroy discovered that soap yielded a fatty material when decomposed with a mineral acid. This fatty material differed in its solubility in alcohol from that of known oils and fats, but this fact was passed unnoticed and it was not until 1811, when an analysis of soap was made by Chevneul, that the true nature of soap was discovered. The fact that soap was found to consist of the alkali salts of the fatty acids obtained by saponification of fats and oils had hardly any effect at all on the art of soap manufacture, although it did lead the way for the development of the candle industry (5).

The findings of Chevneul were forgotten until Krafft and coworkers verified his conclusions in a series of experiments and they went even further. They concluded that the hydrolysis of soap could reach completion, if one of the two components of the normal salt was removed. This postulate was later disproved by J. Lewkowitsch, however (6). Krafft and Wiglow also observed during their studies of soaps that finished soap was colloidal in nature (7).

The observation of Merklen in 1906 (8) marked the first real attempt to place the soap industry inside the realm of science. He made studies of soaps at various stages of manufacture and reached the following conclusions:

1. Commercial soap did not have a definite composition, but had a variable composition depending on the nature of the fatty acids,

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(5) J. Lewkowitsch, J. of Soc. Chem. Ind., 26, 590, (1907).
(6) J. Lewkowitsch, J. of Soc. Chem. Inc., 26, 590, (1907).
(7) F. Krafft and H. Wiglow, Ber. 28, 2573 (1895).
(8) Merklen, Etudes sur la Constitution des Savons du Commerce dans ses Rapports avec la Fabrication, (Marseille, 1906).

the composition of the nigre, for settled soaps, and the temperature at which the soap boiling was conducted. The effect of pressure could be neglected, since the soap was always boiled at atmospheric pressure.

2. The finished soap behaved like a colloid.
3. The adsorption of water by the colloid soap was a function of the nature and structure of the colloid, the nature of the solvent, the nature of the salts and alkali present, and the temperature at which the soap was boiled.

These observations lead Lewkowitsch to conclude that the manufacture of soap was "governed by the laws of mass action, the phase rule, and the modern chemistry of colloids" (9), and from this point on the knowledge of the chemistry of soap advanced rapidly.

Although it had been observed previously that aqueous solutions of soaps and other substances possessed colloidal properties, it was not until 1912 that an attempt was made to investigate the properties of such solutions. Because of the simplicity of the chemical nature of soaps and convenience to study from various points of view, McBain and Taylor began a study, continued by McBain and others, of the properties of soap solutions. In their first investigations (10) it was discovered that aqueous soap solutions possessed electrolytic as well as colloidal properties. Conductivity measurements of these soap solutions showed that instead of decreasing with increasing concentrations, the conductivity increased. This marked the discovery of the "colloidal electrolyte" as it was called by McBain. However, neither this single experiment nor previous ones of conduct-

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(9) J. Lewkowitsch, J. Soc. Chem. Ind., 26, 590, (1907).

(10) J. W. McBain, E. C. V. Cornish, and R. C. Bowden, J. Chem. Soc. 105, 2042, (1912).

ivity measurements (11) were enough to claim proof of the discovery of a whole new class of colloids, and there was also the possibility that the abnormal conductivity could be due to hydrolysis of the soap to form hydroxide ions. The proof that soaps existed in aqueous solutions as colloidal electrolytes had to be shown by comparison of different kinds of physico-chemical data, any one of which could be explained by some other hypothesis.

In 1920 it was shown by C. S. Salmon through the determination of the concentration of potassium and sodium ions in soap solutions and gels, using E. M. F. measurements, that the high conductivity was not due to hydrolysis of the soap (12) and further evidence of this was obtained by McBain and Martin (13) by observing that in concentrated soap solutions the hydrolysis amounts to only a fraction of a percent and even in 0.01 N solutions it amounts to but 6.6%. These experimenters added palmitic acid to a solution of sodium palmitate and found that the solution was still alkaline, verifying earlier conclusions that acid soap is formed in which all fatty acid is sorbed or combined (14). Solutions to which alkali was added gave about the same alkalivity as the added alkali, since the added alkali repressed the hydrolysis equilibrium of the soap.

The osmotic activity of soap solutions, determined from freezing point data, indicated that the same sort of association occurred between the soap molecules, since the numerical values obtained (15, 16, 17) were

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(11) J. W. McBain and M. Taylor, Ber. 43, 321, (1910).
(12) C. S. Salmon, J. Chem. Soc., 113, 530, (1920).
(13) J. W. McBain and H. E. Martin, J. Chem. Soc. 107, 957, (1914).
(14) J. W. McBain and T. R. Bolam, J. Chem. Soc. 111, 825, (1918).
(15) J. W. McBain and C. S. Salmon, J. Amer. Chem. Soc. 42, 426, (1920).
(16) J. W. McBain, M. E. Laing, A. F. Titley, J. Chem. Soc. 112, 1279, (1919).
(17) J. W. McBain and M. Taylor, Zeitsch. physikal Chem. 76, 179, (1911).

only about half of what they should have been for a solution of a non-electrolyte. This, along with the conductivity measurements, was the evidence on which McBain based his original conclusions for the existence of the colloidal electrolyte. However, in addition to the above, further substantiating evidence was obtained from viscosity measurements of soap solutions in 1908 (18) and from ultra microscopic observations of the formation of soap curd by Zsigmondy and Bachmann (19).

A colloidal electrolyte may be considered a salt in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle which exhibits equivalent conductivity comparable to that of a true ion and which may amount to several times that of the simple ions from which it was derived. On the other hand, the osmotic activity may be less than that of a non electrolyte. For soaps, these electrolytes exhibit true reversible reproducable equilibrium in all solutions and a definite transition from typical simple electrolyte through colloidal electrolyte to neutral colloid may be observed in all of its stages. The transition from crystalloid to colloid is observed not only in passing from salts of the lower fatty acids to the higher, but may be exhibited by one of the higher members merely upon change of temperature and concentration.

While continuing the investigation of soap solutions it was observed by M. E. Laing that aqueous solutions of Sodium oleate could exist in the three physical states of sol, gel, and curd at the same temperature and

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(18) A. Mayer, G. Schaeffer, and E. F. Terraine, Compt. rend. 146, 484, (1908).

(19) R. Zsigmondy, and W. Bachmann, Kolloid Zeitschr. 11, 145, (1913).

soap concentration (20). The physical properties of the sol and gel were found to be identical except for rigidity and elasticity and the curd, or neutral soap, was a sol or gel from which part of the soap had been abstracted through the formation of white curd fibers. That the curd was hydrated and was influenced by the vapor pressure of the mother liquor had been observed previously (21). Further study of the hydration of curd fibers led McBain and Salmon to conclude that the hydration of the curd may depend only on the vapor pressure of the mother liquor, since previous experiments indicated such a likelihood (22). If this were true, then the phase relationships existing for the systems of soap-water could easily be determined. That the phase rule is directly applicable to a soap system has been shown (23, 24), since a colloidal solution in which true reversible equilibria subsists behaves as a single phase toward external equilibria. This would apply to any colloidal soap system.

From this point on, it was possible to study the phase changes in soap systems and thus make possible the construction of phase diagrams over the entire range of temperatures and compositions, provided the experimental means were available. Any one experimental method could not give sufficient data for construction of a complete phase diagram, but a combination of several different methods was usually found necessary (25, 26). The vapor pressure method of W. W. Lee has been very successful for studying the phase behavior of soaps at very high soap concentrations,

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(20) M. E. Laing, J. Chem. Soc. <u>113</u>, 1506, (1920).
(21) J. W. McBain and M. Taylor, J. Chem. Soc. <u>112</u>, 1300, (1919).
(22) J. W. McBain and C. S. Salmon, J. Am. Chem. Soc., <u>42</u>, 426, (1920).
(23) J. W. McBain and A. J. Burnett, J. Chem. Soc., <u>115</u>, 1320, (1922).
(24) J. W. McBain and R. D. Vold, M. J. Vold, J. Am. Chem. Soc. <u>60</u>, 1866, (1938).
(25) R. D. Vold and R. H. Ferguson, J. Am. Chem. Soc., <u>60</u>, 2066, (1938).
(26) R. D. Vold, J. phys. chem. <u>43</u>, 1226, (1939).

one of the most difficult areas to study (27).

It is a well known fact that soap has no definite melting point, but goes through a process of gradual melting until it is finally converted into a liquid. However this is not observed for salts of carboxylic acids which have less than about eight carbon atoms in the chain/ This partial melting was first observed by Thiessen who tried to explain it as dimensional melting or melting of the crystal lattice in different dimensions to account for the large density changes observed (28).

In order to add to the completeness of the phase diagram for sodium palmitate-water, Vold and Vold (29) found that dilatometric and MICROSCOPIC ~~miscropic~~ evidence indicated the anhydrous soap had at least five successive phase changes between 79° and 300°C. which they regarded as successive stages of melting. These points of phase change in the anhydrous soap also served to indicate where a phase change would be likely to extend over into the binary system. Further work showed that all saturated sodium soaps pass through a sequence of mesomorphic states between room and melting temperature (30).

Non-aqueous Systems

In contrast to the aqueous soap systems, there has been very little investigation of soaps in non aqueous medid. One of the earliest observations made was by Gabel when he noted that sodium stearate and sodium palmitate were colloids in quinoline (31). Several years later M. E. Laing

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(27) J. W. McBain and W. W. Lee, Oil and Soap, 20, 17-25 (1943).
(28) W. Gallay and I. E. Puddington, Can. J. Research, 21B, 202, (1943).
(29) R. D. Vold and M. J. Vold, J. Am. Chem. Soc. 61, 808, (1939).
(30) R. D. Vold, J. Am. Chem. Soc. 63, 2915, (1941).
(31) Gabel, Diss. Magdeburg (1906) from J. Chem. Soc. 111, 440, (1918).

noted that potassium eleate acted as a true electrolyte in anhydrous alcohol at its boiling point with only moderate conductivity and gave no indication of any colloid present, but solutions of potassium oleate in alcohol solidified to a white curd on cooling and sodium oleate in alcohol became a gel when cooled (32). However, in 1924 M. E. Laing and J. W. McBain concluded that although soaps form true molecular solutions at the boiling point of alcohol, they will only form gels in alcohol solutions if water is present (33).

The first real attempt to investigate non aqueous lyophilic colloids was made by Fisher in 1919 (34). He studied the behavior of some soaps in non aqueous solvents and described the properties of the gels formed, but it was not until 1932 that gel formation by soaps in non aqueous media was investigated (35).

The behavior of different soaps in organic media varies with the metal, the chain length of the hydrocarbon, and the solvent. E. Neyman found that nickel and cobalt palmitates formed gels which liquified on shaking or warming, whereas stable jellies were formed in light petroleum and thixotropy or something similar was observed for some of the heavy metal soaps (36). Other investigators, studying sodium soaps in forty different organic solvents, found that the soaps do not dissolve in the majority of solvents at room temperature, but swell on heating to give clear mobile solutions near the boiling point of the solvent. On cooling these solutions, it was observed that the nature of the soap solvent

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(32) J. W. McBain, British A. A. S., 3rd Report on Colloid Chemistry, 4, (1920).
(33) M. E. Laing and J. W. McBain, Kolloid Z., 35, (1924).
(34) M. H. Fisher, Chem. Eng. 27, 184, (1919).
(35) J. W. McBain and W. L. McClatchie, J. Phy. Chem. 36, 2567, (1932).
(36) E. Neyman, Kolloid Z. 77, 270, (1936).

system determined whether the soap remained in solution, crystallized out, formed a pseudo gel, or formed a true gel (37).

One of the more intensively studied soaps is aluminum dilaurate. It has been found that this soap swells to a gel in cyclohexane without greatly disturbing the structure of the soap, but a system of 40% aluminum dilaurate in benzene forms a gel, the x-ray diffraction pattern of which indicates that the original crystallites of soap have disappeared with the probable formation of micelles of oriented soap layers. It was concluded that the gel formation with cyclohexane does not affect the bulk of the soap crystallites and must be a surface phenomenon or a partial disintegration accompanied by the disappearance of the most amorphous crystallites or arrangement of the gross particles with respect to each other, leaving the fine structure of the particles, as revealed by x-rays, still unchanged (38). Evidence that aluminum dilaurate forms an association colloid in benzene has been advanced by McBain and Working (39). Ordinary soaps in water are the best examples of association colloids, for in them the ions and molecules associate spontaneously with the formation of micelles, or colloidal particles, which are in true reversible equilibrium with the ions and molecules from which they form. A characteristic of these colloids is that the apparent molecular weight is a function of concentration and temperature. Observing that the osmotic pressure measurements indicated rapid association with increasing concentration and that there was an increase

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(37) M. Prasad, G. S. Hattiangdi, B. K. Wagle, J. Colloid Sci. <u>2</u>, 467, (1947).

(38) S. S. Marsden, Jr., K. J. Mysels, G. H. Smith, J. Colloid Sci. <u>2</u>, 265, (1947).

(39) J. W. McBain and E. B. Working, J. phys. chem. <u>51</u>, 974, (1947).

in relative viscosity with increased temperatures, as well as a dependence of structural viscosity upon concentration and time, the investigators were forced to conclude that an association colloid was formed.

It is now recognized that solutions of stable colloids, such as soap systems, form true phases in the sense of Gibbs and the available evidence agrees well with the view that soap molecules associate to form colloidal particles which then stick together in loose aggregates, enmeshing and immobilizing large tracts of solvent; further, the colloidal particles are not original soap but something that results from the interaction of soap and solvent (40). That the methods used for determining phase changes of soap-water systems are applicable to soap-hydrocarbon systems, has been demonstrated by Shreme and Doscher, and Vold (41, 42).

A systematic survey of the phase rule behavior of soaps in organic solvents has been made and it was concluded that colloid systems are formed, in many instances in the absence of ions, as shown by the occurrence in these systems of jellies, gels, liquid crystalline phases, and syneresis (43). An extension of this work was made with the viewpoint of correlating the solubility behavior of a typical soap with the physical and chemical properties of the solvent and further investigation of the phase relations in soap-hydrocarbon systems. It was found that the nature, number, and space relationships of the polar groups of solvent molecules, the polority of the solvent, and the size and shape of the

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(40) K. J. Mysels, J. Colloid Sci. 2, 375, (1947).
(41) G. W. Shreme, Ph.D. Dissertation, Stanford University, (1946).
(42) T. M. Doscher and R. D. Vold, J. Colloid Sci. 1, 299, (1946).
(43) R. D. Vold, C. W. Liggett, and J. W. McBain, J. phys. chem. 44, 1058 (1940).

solvent molecules had an important influence on the solubility of a typical soap. Further observations were made on the phase behavior of the systems and solubility curves determined, many of which exhibited sharp breaks, sometimes attributed to micelle formation (44).

The first systematic study of the phase relationships of a soap-hydrocarbon system was made by Doscher and Vold (45). They studied the phase relations of the system sodium stearate-cetane over the complete range of temperature and composition and constructed a partial phase diagram from the data obtained. An attempt was also made to correlate the observed effects with the internal structure of the phases.

However, Smith and McBain in 1947, realizing the lack of data, available on soap-hydrocarbon systems, investigated the phase behavior of sodium stearate in twelve different hydrocarbons with special emphasis on cyclohexane and toluene. From their observations, they were able to construct partial phase diagrams of these two systems (sodium stearate-cyclohexane and sodium stearate-toluene), and since the solubility behavior of the soap in the various hydrocarbons was similar in each case, they postulated that the general phase behavior of sodium stearate and any one of the solvents studied would give a phase diagram of the same type as that for the system sodium stearate-cyclohexane. They further observed that all phase changes were reversible and that they obeyed the Gibbs phase rule, that the solubility of the soap was the same in all of the pure hydrocarbons, and they describe the existing phases in the anhydrous hydrocarbon systems, i. e., (1) a white opaque gel that exhibits

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(44) C. M. Leggett, R. D. Vold, and J. W. McBain, J. phys. chem. 46, 429, (1942).

(45) T. M. Doscher and R. D. Vold, J. Colloid Scil, 1, 299, (1946).

limited swelling with temperature, (2) a golden, translucent liquid crystalline phase, (3) a white, wax-like, semi-translucent liquid crystalline phase, (4) isotropic solution, and (5) an isotropic jelly which has unlimited swelling and passes into solution without any observed transition (46).

Sorption and desorption isotherms for the system sodium stearate-cyclohexane were determined by Shrene for 40, 50, 80, and 110°C. using the McBain-Baker sorption balance, but he observed no change of phase and he noted that for the 110 degree isotherm the sorption-desorption was reversible above 85% relative vapor pressure. It was also observed that the amount of cyclohexane taken up by the soap increased with temperature, varying from 3% at 40°C. to 33% at 110°C. (47). However isobaric curves constructed by Smith and McBain from Shreve's isothermal data showed that a marked change in the affinity of the soap for the cyclohexane occurred between 80 and 110°C., which they assumed to be the transformation to the liquid crystalline phase at 98°C. which they had observed for all anhydrous systems containing below 45 - 50% of soap. This however could have been due to the transformation to a liquid crystalline phase which systems containing more than 50% soap undergo at 90°C. This phase was described by Smith and McBain as translucent, white, wax-like in appearance, and was observed to transmit light. The fact that the white, wax-like, liquid crystalline phase had a vapor pressure lower than the golden liquid crystalline phase seems to bear this out since the association of soap and solvent is stronger than for the golden liquid-crystalline phase.

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(46) G. H. Smith and J. W. McBain, J. phys. chem. 51, 1189, (1947).
(47) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

The present work is a continuation of the study of the system sodium stearate-cyclohexane, in which the region of high soap concentration is investigated very thoroughly for any phase changes. The method used is that of vapor pressure measurement using the McBain-Bakr sorption balance. This method is similar to that used by Shreve for soap-hydrocarbon systems (48).

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(48) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

III MATERIALS USED

Cyclohexane

The cyclohexane used was obtained from Eastman Kodak Company- White label No. 702. Prior to use it was dried over Drierite for 24 hours and a filtered portion was redistilled and the middle portion was finally distilled into ampoules under vacuum conditions. For the method used see, "Experimental Procedure."

Sodium Stearate

The soap used was prepared by neutralizing stearic acid with sodium ethylate and drying at 105° C. The soap was kept in a vacuum dessictor over P_2O_5 for several months prior to use. The analysis of the sodium stearate gave the following results:

1. The soap was examined by Dr. R. F. Sessions for alkali and free acid and none was found to be present.
2. Using the McBain Split Analysis Method the soap was found to be 100% soap.

Results of Analysis

	1	2	3	Average
(a)	99.69	100.8	99.65	100.04
(b)	101.2	101.35	100.1	100.88
(c)	100.5	101	99.93	100.44

(a) by excess H SO
(b) by fatty acid
(c) correction for occlusion

Method of Analysis:

About 700 mg. of soap is weighed on a tared watch glass and by means of a brush all of the soap is removed from the watch glass into a 250 ml. beaker. The weighing is made rapidly as the soap adsorbs water from the atmosphere.

To the soap sample about 50 ml. of hot distilled water is added. Usually the soap dissolves at once, but if it does not, then it is heated until it does. The fatty acid of the soap is separated by adding 0.1 N sulfuric acid until about 2.5 milliequivalents are present in excess. In order to minimize occlusion of the mineral acid, the soap solution should be at about 100° C. when the acid is added.

After having become thoroughly cool, the fatty acid is filtered through a previously wetted filter paper. It is then carefully washed free of the excess mineral acid and the filtrate containing the excess mineral acid is titrated with sodium hydroxide to the phenolphthalein end point. This enables the alkali content of the soap to be calculated.

The fatty acid on the filter paper is washed into a suitable erlenmeyer flask with hot neutral 95° alcohol. Caution should be exercised as the fatty acid may clog the filter paper if it becomes cool between additions of alcohol. When the fatty acid is slow to dissolve the alcohol may be heated to boiling and the hot vapors allowed to fall on the acid, then hot alcohol added. This procedure is repeated until the fatty acid is dissolved. The filter paper is rinsed with hot alcohol to make certain that all of the fatty acid is removed.

The filtrate is then titrated, while hot, to the phenolphthalein end point with sodium hydroxide. After the end point is reached the filter paper is added to check for completeness of extraction of the fatty acid; if the solution fades, more sodium hydroxide is added, it will seldom be more than one drop.

A blank is run on the filter paper to check for sorbed carbon dioxide.

Of many methods available for soap analysis (46, 47) the one described above was found to be the most satisfactory

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(46) Snell, F. D. and Biffen, F. M., Commercial Methods of Analysis, p. 381, McGraw-Hill, N. Y., N. Y. (1944)
(47) Scott, W. W., Standard Methods of Chemical Analysis, 5th Edition, D. Van Nostrand Company, New York, p. 2029 (1939)

and most accurate by the author. Several other methods of analysis were tried on a commercial brand of sodium stearate of high purity to acquire the technique and give a comparison as to its accuracy.

The results show that titrational and other indarterminate errors were very small, if any at all. This is seen by comparison of (a) and (b) in the table above.

It was observed during the practice analysis that the difference between the percent soap for (a) and (b) was greatly influenced by the size of the sample used. An increase in temperature, before the addition of the H_2SO_4 decreased the average deviation of the analysis.

Using different weights of soap for analysis and precipitating the fatty acid at approximately the same temperature revealed that the differences in the soap percentages as found by (a) and (b) were a linear function of the weight of the sample. Assuming this difference to be due to occlusion of H_2SO_4 during the decomposition of the soap, it is seen from Figure 1 that the weight of H_2SO_4 occluded is a linear function of the weight of the sample used. It was also found that by heating the soap solution during the fatty acid precipitation, the occlusion of H_2SO_4 was reduced. Analysis of the decomposed soap for $SO_4^{=}$ ion using Ba^{++} ion as a preciptating agent gave very poor results since the precipitated barium soap gave high results.

Positive evidence was obtained of the occlusion of H_2SO_4 although not quantitative. It was concluded that quantitative results could not be obtained by any gravimetric method. The results of the titrations are accepted as purity of the soap used.

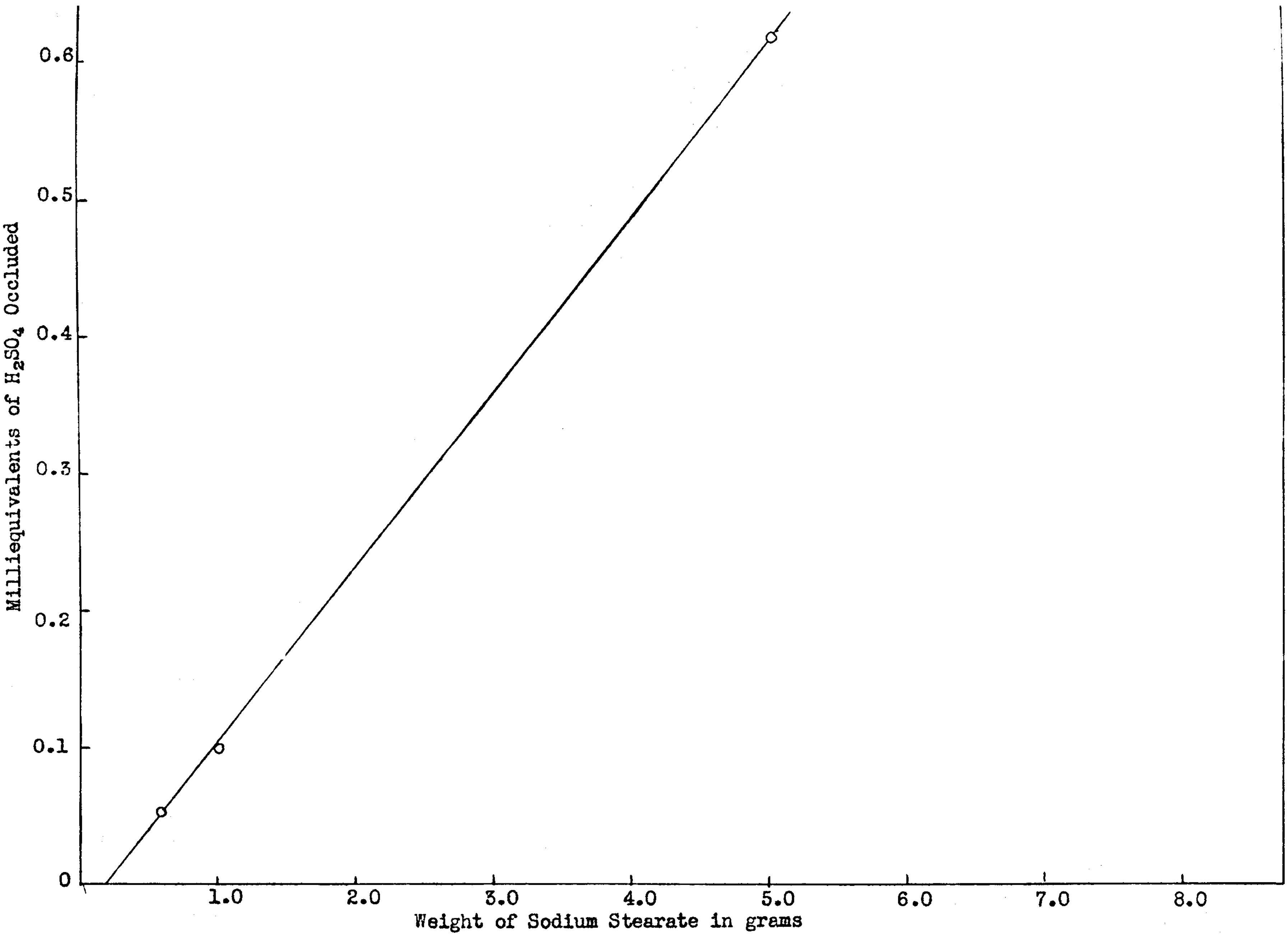

Figure 1
Occlusion of H_2SO_4 by Stearic Acid

TABLE 1

THE OCCLUSION OF SULFURIC ACID BY STEARIC ACID USING THE MCBAIN SPLIT ANALYSIS METHOD

Wt.	Sodium Stearate (in grams)	Vol. H_2SO_4 (in ml.)	Vol. NaOH (in ml.)	Calculated % of stearic acid
1.	5.0181	4.44	(a) 27.60	(a) 99.2
			(b) 28.43	(b) 107.0
2.	1.0143	48.47	(a) 13.74	(a) 98.37
			(b) 18.86	(b) 104.3
3.	0.5868	49.29	(a) 21.67	(a) 99.96
			(b) 11.02	(b) 105.4

	Difference in Titrations (a) and (b) in Milliequivalents	Sulfuric Acid Occluded IN Mg.
1.	1.236	30.31
2.	.197	4.83
3.	.104	2.54

(a) by titration of excess H_2SO_4
(b) by titration of fatty acid

Normality of reagents used

	1	2	3
H_2SO_4	7.480	0.1193	0.1193
NaOH	0.6148	0.1831	0.1831

The soap used was prepared by Dr. R. F. Sessions and was of high purity. This soap was used for each of the three determinations above.

All of the soap solutions were only moderately warm when decomposed with H_2SO_4 . Temperature valves were not recorded.

IV EXPERIMENTAL

An important characteristic of the phase diagrams for soap-hydrocarbon systems is the probable existence of many heterogeneous regions just as in the phase diagrams for soap-water systems. McBain has shown that the phase rule is found to apply to the equilibria among the various phases of soap-hydrocarbon systems. (51)

It is thus possible for one soap phase containing a definite amount of hydrocarbon to be in equilibrium with another soap phase containing a different percentage of hydrocarbon. Both phases are in equilibrium with a hydrocarbon vapor phase above them. The two condensed phases are mechanically separable, bounded by an interface, and physically distinguishable in every sense as required by the phase rule. By applying the phase rule to a colloidal system, then under the above described circumstances the boundaries of the regions of heterogeneity may be established.

To describe a system completely the phase rule states that the number of phases plus the number of independent variables, which must be

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(51) G. H. Smith and J. W. McBain, J. phys. and colloid chem., 51, 1189, (1947).

prescribed to determine the physical state of a system, must exceed the number of components by two. This is the ordinary statement of the phase rule in which three variables function to fix the state of the system considered. For the system concerned the three variables to be considered are temperature, pressure, and composition. Equilibrium is a necessary prerequisite for application of the phase rule.

When the phase rule is applied to a system of two components having three phases, the system is a univariant one, (it has one degree of freedom). This means that the system may be completely defined by specifying only one of the three independent variables on which its state depends. Therefore for a given temperature, the simultaneous presence of two condensed phases must fix the pressure and give definite compositions for each of the coexisting phases. It is easily seen from the phase diagram (Figure 31) that the two phases can exist together over a considerable portion of the total compositions. Therefore even though the percentage of hydrocarbon in each phase cannot change, the total composition of the system can change until one phase has replaced the other, and during such a change in overall composition the vapor pressure must remain constant. It is therefore possible to determine the area of heterogeneity by measuring the range of total composition where the pressure remains constant.

An experimental method which enables the simultaneous measurement of overall composition and vapor pressure has been developed and used successfully for soap-water systems (52, 53, 54). The vapor pressure

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(52) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).
(53) J. W. McBain and W. W. Lee, Oil and Soap, 20, 17, (1943).
(54) R. D. Vold, J. phys. chem., 43, 1213, (1939).

method used in this investigation is similar to that used for the soap-water systems.

The sample to be studied is left in an atmosphere of constant vapor pressure and vapor is sorbed (55) or evolved until the vapor pressures of the sample and the surrounding atmosphere are equal, the change in composition of the sample being measured by means of a vitreous silica spring. When a small increment of pressure resulted in a large change of composition, regions of heterogeneity could be located as being within that range of composition that would show regions of zero slope in the curve. At a constant temperature, by varying the vapor pressure, isothermal curves could be plotted and the location of regions of zero slope determined and distinguished from the intervening regions where a single condensed phase is present and the vapor pressure and composition vary continually.

Knowing the location of regions of zero slope for several temperatures as obtained from several isotherms the heterogeneous regions could be determined on a temperature composition phase diagram. Determination of these areas by other methods shows good agreement with the vapor pressure method. In fact, no single method used could give sufficient data for the construction of a complete phase diagram, and it is necessary to use several methods of approach. For that part of the phase diagram involving a very high percentage of soap, the vapor pressure method is necessarily used since at high soap concentration all other methods give data of doubtful significance or fail completely. (56)

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(55) N. K. Adam, The Physics and Chemistry of Surfaces, (See footnote on p. 253) 3rd edition, Oxford University Press, London, (1941).

(56) R. D. Vold, J. phys. chem., 43, 1213, (1939).

The method of obtaining the relative vapor pressure values was an indirect one. The equilibrium temperatures of the two thermostats were observed and the vapor pressure corresponding to these temperatures determined from an accurately drawn graph of vapor pressure plotted against temperature. (See appendix for error in calculating vapor pressure.) The vapor pressure data for the graphs was obtained from Landolt-Bornstein, Physikalish-Chemische Tabellen. (57)

For each set of data obtained at a definite temperature a plot was made of relative vapor pressure as ordinate against composition as absiassa, the relative vapor pressures being expressed as percent saturation, i. e., the actual vapor pressure of the system (as determined by the temperature of the lower thermostat) as compared with the saturation vapor pressure which the pure liquid would exert if at the temperature of the sample in the upper thermostat.

Small temperature changes always occur in the upper and lower thermostats of the apparatus with a corresponding change in vapor pressure but for a given phase the relative vapor pressure is almost unaffected by these changes, also the idealized requirements of Raoults law are approximated by the isothermal plot. For these reasons relative vapor pressure is used. (58)

The overall composition was determined from the zero weight of the soap sample, measured just prior to exposure to the hydrocarbon vapors. All weight changes, as indicated by change in length of the silica spring, were attributable to sorption or desorption of the hydrocarbon. From a knowledge of these two factors the composition of the soap could be determined.

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(57) Landolt-Bornstein, Physikalish-Chemische Tabellen, 5th edition, Vol.II, , 1369, Berlin, (1923).

(58) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

THE APPARATUS

The distinguishing characteristic of the apparatus is a connected double thermostat, each capable of being maintained at a different temperature. One thermostat controls the temperature of the sample and the other controls the temperature of the liquid reservoir. The single tube in the connected thermostats is called the McBain and Bakr sorption balance. (59)

The construction and use of this apparatus while not difficult requires certain techniques. Therefore a section describing the construction and use of the components follows:

1. The thermostat (Figure 17)

The thermostat consists of a large glass pyrex tube 36 inches in length and 2.36 inches in diameter. The tube contains a cork 1 inch thick located 13 inches from the bottom which fits snugly against the side of the tube and around the sorption tube contained in the thermostat. Small bits of asbestos distributed uniformly over the cork surface and an asbestos rope coiled around the sorption tube and pressed snugly down on the cork provide additional insulation to insure complete separation between the two thermostats. A pyrex tube 1.96 inches in diameter is also contained in the lower thermostat. This provides a support for the separator to prevent its possible slippage and provides further insulation for the lower thermostat.

The tube has two separate Nichrome heating wires wound around its exterior so that each thermostat may be heated independently. Each heating

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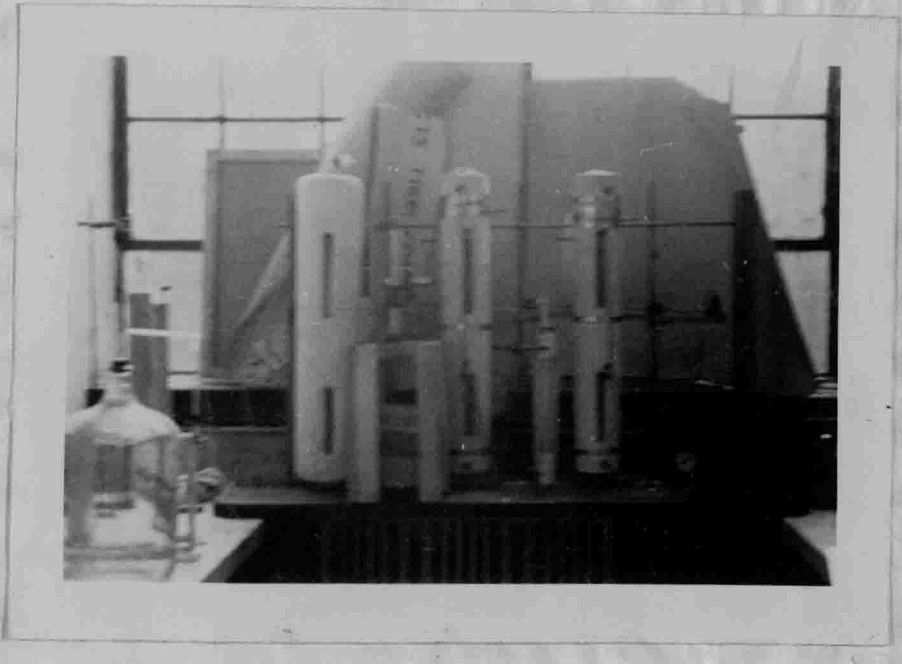
(59) J. W. McBain and A. M. Bakr, J. Am. Chem. Soc. 48, 690, (1926).

Figure 17

The Apparatus

(a) The Voltage Transformerswith an annealing oven for silica springs also shown.



(b) The Thermostats.

wire begins at the end of the tube and terminates at the separator. Covering the Nichrome heating wire is a layer of thick corrugated asbestos paper supplemented by an inch thick layer of magnesia asbestos pipe insulation.

In order that observations made be made of the spring, sample, and temperature, the upper thermostat has two rectangular slits diametrically opposite, 10 inches in length and one inch wide, cut through the asbestos and magnesia layers. The sides of the slit are reinforced with stiff asbestos board and the exposed heating wires covered with a piece of pane glass (the size of the slit).

The lower thermostat has a similar single slit 9 inches in length in line with one of the slits in the upper thermostat beginning 8 inches below it. This lower slit enables observations to be made of the reservoir temperature.

The bottom of the double thermostat contains a tightly fitting plug of asbestos 2 1/2 inches long and the top is sealed with a similar plug.

The two separate chambers in the tube can thus be heated and thermostated independently. The ends of the heating wires are connected to variable voltage transformers which are manually controlled and these in turn are connected to a small Raytheon voltage stabilizer which eliminates fluctations in the incoming power supply and insures a constant source of AC voltage. In a thermostat of this design, changes in room temperature can cause temperature fluctuations in the thermostats with resulting changes in relative vapor pressure. Under the experimental conditions these temperature fluctuations were very small, affecting the relative vapor pressure by about 0.6% at low pressures and 0.4% near saturations. The room containing the thermostats was poorly ventilated and partially underground with the result that the room temperatures remained approximately constant and was slow to be influenced by external temperature changes. The normal temperature fluctuation of the thermostats was plus or minus one degree centigrade, however severe weather conditions produced greater fluctuations but usually required a longer period of time, so that with care the variable voltage transformers could be reset to compensate for the temperature change and equilibrium allowed to be reestablished before making spring length measurements. Near saturation the composition of the soap was greatly affected by small changes in temperature as is easily seen from an isothermal curve. So sensitive was the composition of the soap to small temperature changes that the heating effect of the light bulb used to illuminate the spring caused an observable change in the length of the spring when measurements were being made. However the temperature of the thermostats was observed to remain approximately the same from about 3 pm to 9 am (an 18 hour period) so that most of the measurements made near saturation are reasonably reliable since 24 hours or longer was allowed for equilibrium and spring measurements were usually made before 9 am.

The single sorption tube in the two thermostats, the upper thermostat at the temperature of the isotherm being studied and the lower thermostat at the desired temperature of the hydrocarbon reservoir, must have a temperature gradient along the tube at the separator between the two thermostats. For connected thermostats of this design the gradient has no effect since it varies only between the reservoir temperature and the temperature of the isotherm. If the temperature at the area of the separator were greater than the temperature of the sample then the sample would be heated by convection currents, and if the temperature were less than the temperature of the reservoir then vapor would condense.

Since an indirect method is used to measure the relative vapor pressure, it is necessary to know precisely the temperature of the sample and of the hydrocarbon reservoir. This is done by placing carefully calibrated thermometers as close as possible to the wall of the sorption tube in each thermostat. In the lower thermostat the thermometer was passed through a small hole in the separator (which served as its support) and located between the wall of the sorption tube and the separator support, touching the sorption tube. In the upper thermostat, the thermometer was attached to a rigid piece of thin wire and lowered to a position on the sorption tube slightly below the sample, the wire being held in fixed position by insertion of the asbestos plug in the top of the tube and looping the end of the wire about the uppermost metal band encircling the insulation jacket.

To determine the exactness of the indirect method experiments were performed by Shreve (60) to determine whether the thermometers on the outside of the sorption tube at the positions mentioned above indicate the actual temperatures of these same positions inside the sorption tube. His results indicated that the temperatures inside and outside the sorption tube at the same level were different by less than 0.5°C.

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(60) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

2-The Sorption or vapor pressure tube (Figure 2)

This part of the apparatus consists of a sealed pyrex glass tube 30 1/2 inches long and .98 inches in diameter (inside). The top part of the tube contains a silica spring supporting a platinum bucket containing soap and above the nichrome wire supporting the spring an evacuated spherical glass container full of copper foil. According to R. D. Zentner this technique will prevent damage to the soap sample during the sealing on of the sorption tube, since it has been found necessary to incorporate in the sorption tube some device which will shield the sample from the high temperatures involved (61). The lower end of the tube contains an ampoule of the hydrocarbon used and serves as a liquid reservoir.

A pyrex tube about 48 inches long is sealed at one end and blown out to hemispherical shape; in the process the glass is made somewhat thicker than the wall of the tube. After careful annealing and cooling the tube is cleared with dichromate-sulfuric acid cleaning solution and rinsed thoroughly with distilled water several times. When the tube is completely dry it is broken carefully and evenly 29 inches from the sealed end and the shorter piece of tubing is constricted to an opening about 1/8 - 1/4 inch in diameter and 1 1/2 inches in length, the thickness of the glass composing the hourglass like constriction being 3 times that of the tubing thickness. Care must be exercised in the annealing of this constriction or the glass may crack when heat is reapplied and the whole tube spoiled. When the constriction is cool a mark is made 1 1/2 inches from its center and the tube carefully broken at this point. The break,

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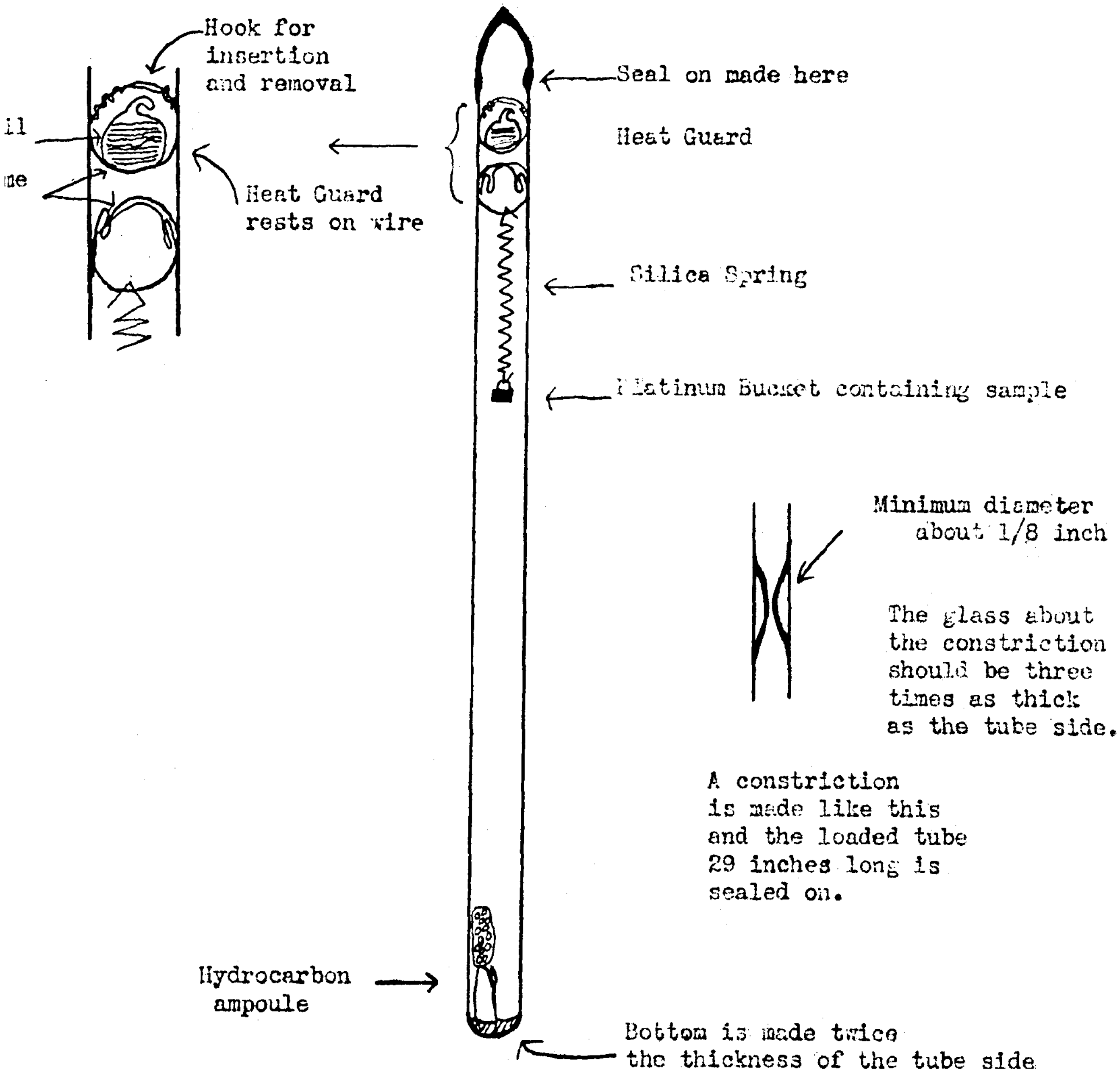
((61) R. D. Zentner, J. phys. and colloid chem. 51, 972, (1947).

Figure 2

The Sorption Tube Assembly
(Scale 1:5 inches)



if not even, is smoothed off and the longer end of the constriction sealed to a hyvac line.

Into the 29 inch tube is carefully placed a previously prepared ampoule of the hydrocarbon. The ampoule has a very thin walled bottom and a thin walled piece of tipped tubing (where the side arm was sealed off from the distilling fork) which are easily broken. To avoid damage to the ampoule the tube is placed horizonally on a table and the ampoule (the thin walled tip projecting upward) placed just inside the tube and pushed carefully to the bottom with a length of small glass tubing. The tube is tilted and removed to a clamp near the hyvac line, care being taken to keep the tube always leaning so that the ampoule will not hit the side of the tube and become broken during the loading and sealing on. A piece of nichrome wire is made into a loop which presses tightly against the side of the tube and a previously calibrated silica spring with a load consisting of a small platinum bucket containing the soap sample is centered on the loop and the looped wire and load pushed down into the tube with a piece of glass tubing which just fits inside the longer tube until the lower part of the loop is 25 1/2 inches from the bottom of the tube. Twisting the jug serves to center the spring should it be displaced from the center of the loop during the loading. It is important that the spring be in a vertical position after the tube is sealed otherwise it may scrape the side of the tube during the isotherm studies and cause loss of the soap sample or breakage of the spring. Another loop of nichrome wire is made and inside the loop is placed a pyrex glass container filled with copper foil; this container having been evacuated to a pressure of about 10^{-6} mm Hg. The container is large enough so that it fits snugly inside the sorption tube and is supported by the loop of wire. It should have about 1/8 inch clearance all around to speed evacuation. This is pushed down into the tube until it is just above the loop supporting the spring. It should be as close as possible, but not touching since the position of the "heat guard" may shift, causing the spring to be displaced from the vertical. The tube is now carefully sealed on to the constriction. To avoid introducing any additional moisture into the sorption tube when the seal on is made, the necessary blowing should be done through a drying tube. The two ends which are sealed together should be fire polished before the seal on is made, since small splinters of glass may be dislodged during the seal on and cause breakage of the spring or fall into the soap sample and cause increased extension of the spring resulting in an error in the calculation of the dried soap. After the seal on and elimination of any leaks present, the system is evacuated to the lowest possible pressure obtainable. The evacuation should be begun slowly to avoid loss of soap thrown out into the air stream. For the two tubes used in this investigation, the evacuation was as follows: a cenco hyvac pump was allowed to evacuate the system for 1 1/2 hours, after which time a Todd mercury diffusion pump was put into operation. One and one half hours later the pressure as determined by a Mc Leod gauge was 10^{-5} mm Hg. After 8 hours of evacuation tube 3 was sealed off at a pressure of $7x10^{-6}$ mm Hg. An oxygen fed torch with a yellow flame was used to heat the sorption tubes and the tubing of the hyvac line after the pressure had reached a value of 10^{-5} mm. This facilitated the removal of occluded gases from the glass and aided in removing moisture from the soap sample. The soap was in no way affected by the heat applied around it. If the hydrocarbon ampoule has a leak in it or has been damaged in the loading or sealing on, the evaporation of the hydrocarbon during evacuation will cause solidification of the ampoule contents or its complete disappearance. In such a case the tube must necessarily be removed and reloaded. The possibility of damage to the spring by splinters of glass is very great during its removal. In the removal of the tube from the hyvac line, water vapor may condense around the spring on the side of the tube and the spring swing against the side of the tube and become stuck in which case heat is applied until the water has evaporated and the spring swings clear. The spring should never be pulled once it becomes stuck, because of the danger of its breakage, nor should the spring be allowed to make contact with the sharp broken end of the tube for this usually severs the delicate silica fiber.

When the tube is evacuated as completely as possible it is sealed off as follows: the center of the constriction is heated very slowly and uniformly, the heat of the flame being gradually increased until the glass is dull red in color; that is, just viscous enough to cause the tube to be forced together by the external pressure. The constriction should be collapsed for about one inch at its center and a small hot flame applied at the center of the collapsed area while applying downward pressure to the sorption tube. The tube is then pulled free and its end carefully annealed. The tube is now mounted on a ring stand and the length of the spring measured at the observed temperature with a cathetometer. Before the tube is installed in the thermostat the hydrocarbon is removed from the ampoule as follows: the end of the tube containing the ampoule is immersed in a dry ice-acetone freezing mixture and the ampoule contents frozen solid. This takes a couple of hours because of the good vacuum. A powerful magnet is carefully brought against the tube on the side to which the ampoule leans when in a near vertical position and the ampoule lifted several inches, then the magnet removed, allowing the ampoule to strike the bottom of the tube. Usually this must be repeated several times before the thin walled bottom of the ampoule is broken. As the tube warms up to the temperature of the room the hydrocarbon melts and flows into the bottom of the sorption tube. The prepared tube is then placed in the thermostat. (See figure 2.)

The platinum buckets and the soap samples used in the investigation are weighed very accurately on a sensitive balance before loading the tube and the weight checked just before the tubes are installed in the thermostat to make sure that none of the soap was lost from the bucket while preparing the tube. Since the weighings are usually made some distance from the room containing the hyvac line and some time prior to insertion of the spring in the tube it was found convenient to protect the samples from moisture and drafts which might blow the soap from the buckets. This was accomplished by supporting the platinum buckets on a small glass hook which was inserted in a cork stoppering a 50 ml-Erlenmeyer flask. Thus the buckets were handled only with glass hooks during the weighings and their surfaces kept free from foreign matter such as grease and dust.

The Ampoule

The hydrocarbon ampoule consists of two sections sealed together, one section containing small clean steel spheres and the other the hydrocarbon. A piece of pyrex glass tubing 1/2 inch in outside diameter and

5 inches long is sealed at one end and pulled out to a small point at the other end. Another piece of tubing of the same diameter is pulled out to a slowly tapering point and sealed off at a distance 7/8 inches from the point where the tube begins to taper off. The two sections are then joined, leaving one open end for each section. One-half inch from the junction of the two sections on the side of the tapering tube a T seal is made with a tube 3/16 inches (outside) diameter and 2 1/2 inches long. The end of the section is sealed off and blown out into a thin walled bubble which is then flattened on one side so that the flat part is diagonal to the length of the tube. The top section is filled with small grease free steel spheres to a height of 2 inches and then sealed off. The ampoule is then sealed on to a vacuum distillation flask. The hydrocarbon is distilled into the evacuated ampoule. A portion of material in the ampoule is distilled out so that only vapors of hydrocarbon are above it when it is sealed off. At the point where the seal off is made the glass top should project inward toward the taper and should be almost flush with the top section of the ampoule; otherwise the tip will almost always be broken when preparing the sorption tube.

Operation of the Apparatus

The thermostats are placed on ring stands and tied to the stand with small strips of metal which encircle the jacket at each end and the center. Additional support is provided by two short rods clamped to the stand and providing a V shaped clamp. Since the jackets are rather soft this clamp cannot be too tight, so a wide strip of metal tied to the stand with wire holds the thermostat in the V shaped clamp or wedge.

Directly behind the upper slit in each thermostat is a 60 watt light bulb which provides illumination when the spring measurements and temperature observations are made. A small flashlight is very convenient to use for temperature observations of the hydrocarbon reservoir.

To obtain the temperatures of the ovens surrounding the soap and the hydrocarbon reservoir, mercury thermometers were employed. These thermometers were calibrated against a Bureau of Standards thermometer (B and S. No. 92725) between the range of 20 to 100, and corrections applied at the time of temperature observations. The range of the thermometers was 250°C. in each case and they were graduated in units of one degree centigrade.

The sorption tubes were installed in the thermostats as follows: Loops of friction tape were securely fastened to the top of the sorption tube and the tube was carefully lowered into a supported thermostat containing a cork separator, separator support, and thermometer for the liquid reservoir. After the tube was safely lowered into the thermostat the friction tape was removed and small asbestos twine coiled about the tube and pressed down on the cork separator. The thickness and effectiveness of the separator were then farther increased by small bits of asbestos until light passed into the bottom of the tube could not be viewed from above around the edge of the separator. After placing the thermometers in the upper thermostat the asbestos plug was inserted and the manually controlled voltage transformers set for the desired isotherm temperature.

An increase in the voltage applied to the heater of the liquid reservoir serves to increase the relative vapor pressure within the sorption tube. As the vapor pressure is increased the heat transfer between the separator of the two thermostat chambers increases and the voltage transformer controlling the temperature of the upper chamber must be turned back to compensate for the increased temperature. At high relative vapor pressures the voltage transformers must be carefully manipulated to cause a very small change in temperature, otherwise too large a change in pressure results and an insufficient number of points are obtained to plot accurately the isotherm.

The spring length measurements are made with a cathetometer or traveling microscope resting on a stable platform placed in front of the thermostats. This same instrument was used for spring calibrations, calibration of the McLeod guage, and all other measurements requiring an accurate determination of length. The cathetometer included lock and pinion focusing with a three way focus; fine adjustment and complete with spirit level as furnished by the Precision Tool and Instrument Company of Surrey, England. The vernier reading was accurate to 0.02 mm., having a vertical travel of 25 am. For horizontal displacement, it was equipped with a horizontal sweep controlled by lock and screw. Cross hairs in the field of vision facilitated focusing upon a horizontal line. In all measurements of spring length, the tips of the hooks on both ends of the silica spring were used to focus upon. The cathetometer was placed in exactly the same position in front of the thermostats for each measurement of spring length. This enabled any possible error in focusing to be kept constant. Measurements must be made rapidly because of the slight heating effect caused by the light source located behind each thermostat. As a rule measurements were made for a given vapor pressure after 24 hours, since usually this was the time required for equilibrium. At very low relative vapor pressures equilibrium was established more rapidly and no change in the length of the spring could be detected after 12 hours. At pressures near saturation 36 hours or more were required.

The sample of soap used should occupy only about 3/4 of the available volume of the platinum buckets used, since changes in the composition of the soap may cause some of the soap to be lost from the bucket, necessitating removal of sorption tube from the thermostats to determine the weight of soap lost.

The samples should be carefully watched at pressures near saturation, since vapor may condense on the spring to give an erroneous reading or a slight change in temperature may occur and cause the upper chamber to be cooler than the lower with the result that vapor condenses in the upper chamber on the sample and spring to overload it, causing the sample to be suspended out of sight or possible breakage of the spring. The vapor pressure should not be lowered by large amounts when the soap is in a hydrocarbon rich phase since the soap may froth out of the bucket.

Before the investigation was begun it was observed that the power supply was cut off occasionally because of storms, repairs, accidents, etc. If the power supply were cut off for several hours during the absence of the author and then cut on without his knowledge he would unknowingly obtain inaccurate measurements of the spring length due to interference of the equilibrium process. To avoid unreliable data an electric clock was installed in the laboratory and connected to the same electric outlet that supplied the voltage stabilizer. Whenever the clock was observed to have stopped this indicated that any measurements made were of doubtful accuracy. Checks of the temperatures and data obtained previously determined whether any measurements made were used or whether they were disregarded for measurements made after equilibrium was definitely established (usually 24 hours later).

The McBain-Bakr Silica Spring

The silica spring is the most fundamental part of the apparatus and it should therefore be considered in some detail. Named after its inventors, (62) the McBain-Bakr Sorption balance is a thin fiber of fused silica wound in the shape of a helix. These balances possess great sensitivity and near perfect elasticity and are strong enough for ordinary laboratory use. These favorable characteristics make their use in certain sorption experiments very convenient. Obviously their use is a study such as the sorption of hydrogen on nickel would not be practical. Although the sorption balance has been widely used and studied, (63, 64, 65, 66) no detailed description of the use of the balance has appeared in the literature. In this investigation the balance and its use was considered only as it applied to the study being made.

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(62) J. W. McBain and A. M. Bakr, J. Am. Chem. Soc. 48, 690, (1926).
(63) J. W. McBain and A. M. Bakr, J. Am. Chem. Soc. 48, 690, (1926).
(64) J. W. McBain and R. F. Sessions, J. Am. Chem. Soc. 56, 1-4, (1934).
(65) J. W. McBain and R. F. Sessions, J. Colloid Sci. 3, 213, (1948).
(66) J. S. Tapp, Can. J. Research, 6, 584, (1932).

The near perfect elasticity possessed by the springs is due to the fact that the elastic properties of quartz crystals, one of the most perfectly elastic substances known, are carried over to the silica glasses (67). It is seen from figures 3 and 4 that the elastic response is linear over a wide range, but the points fall off of the curve as the elastic limit is approached and the spring is greatly distorted; not conforming to the assumptions of the mathematical treatment that the pitch of the spring should be small (68).

A balance of almost any desired sensitivity and strength may be made by proper selection of the fiber thickness, the diameter of the spiral, and the number of turns composing the spiral.

The strength and sensitivity are each interdependent. For increased sensitivity the strength will be decreased and a very strong spring will not be very sensitive. However, a spring of large diameter consisting of many turns of a fiber of large diameter will give a spring of great strength and sensitivity. With practice, springs of any desired strength and sensitivity may be made. The sensitivity desired is determined by the experiment. For the investigation of soaps, the sensitivity desired is about 1 mm per mg. Springs of great sensitivity rapidly approach the elastic limit and hence limit the load which may be applied. In an investigation such as this a spring of great sensitivity would probably be carried out of range of the cathetometer during a phase change and exceed the elastic limit, causing it to break.

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(67) J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 6, C(part 2) 252, Longmans, Green and Co., London, (1947).

(68) J. W. McBain and A. M. Bakr, J. Am. Chem. Soc. 48, 690, (1926).

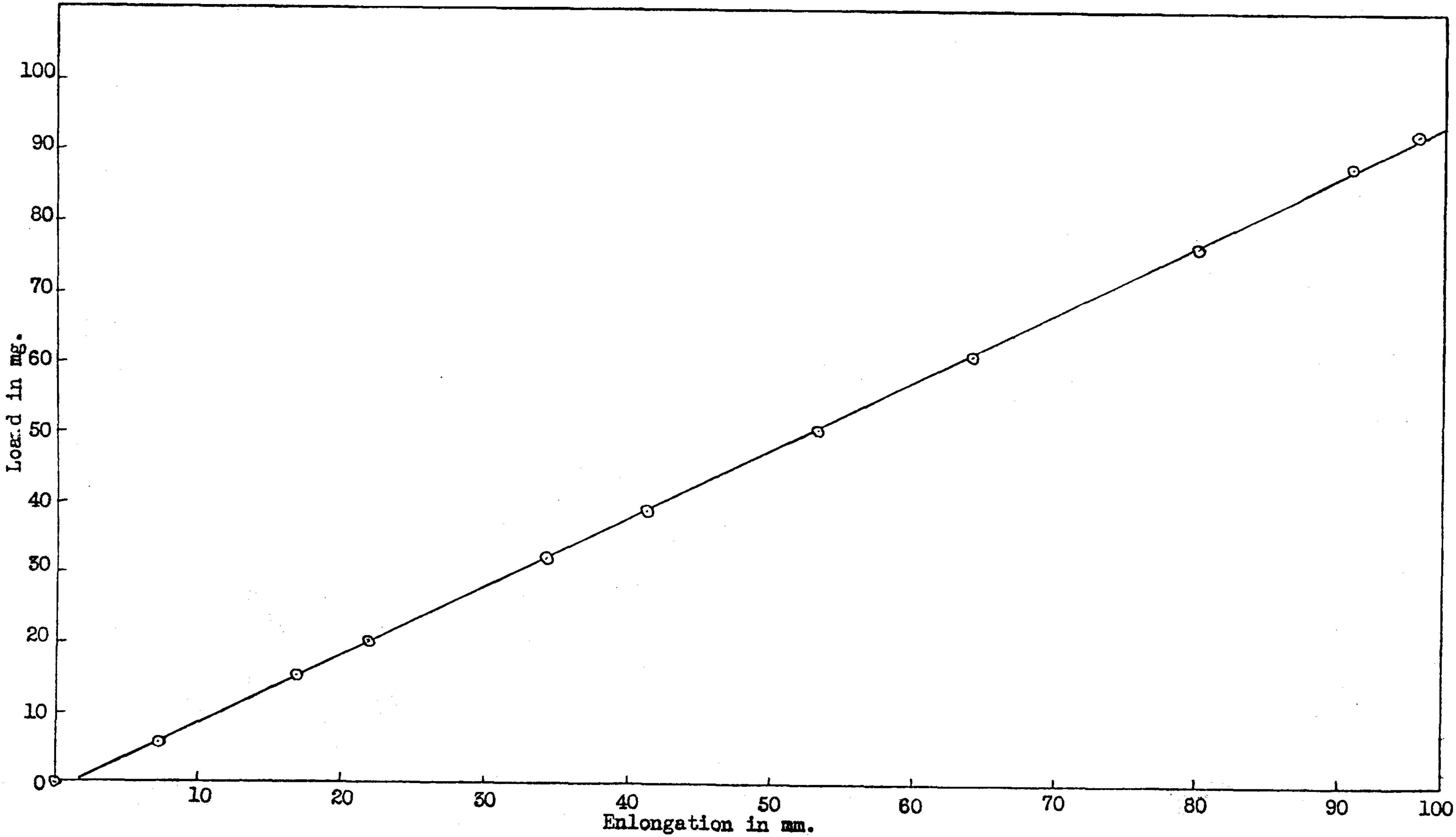

Figure 3
Enlongation vs Load
Spring Al

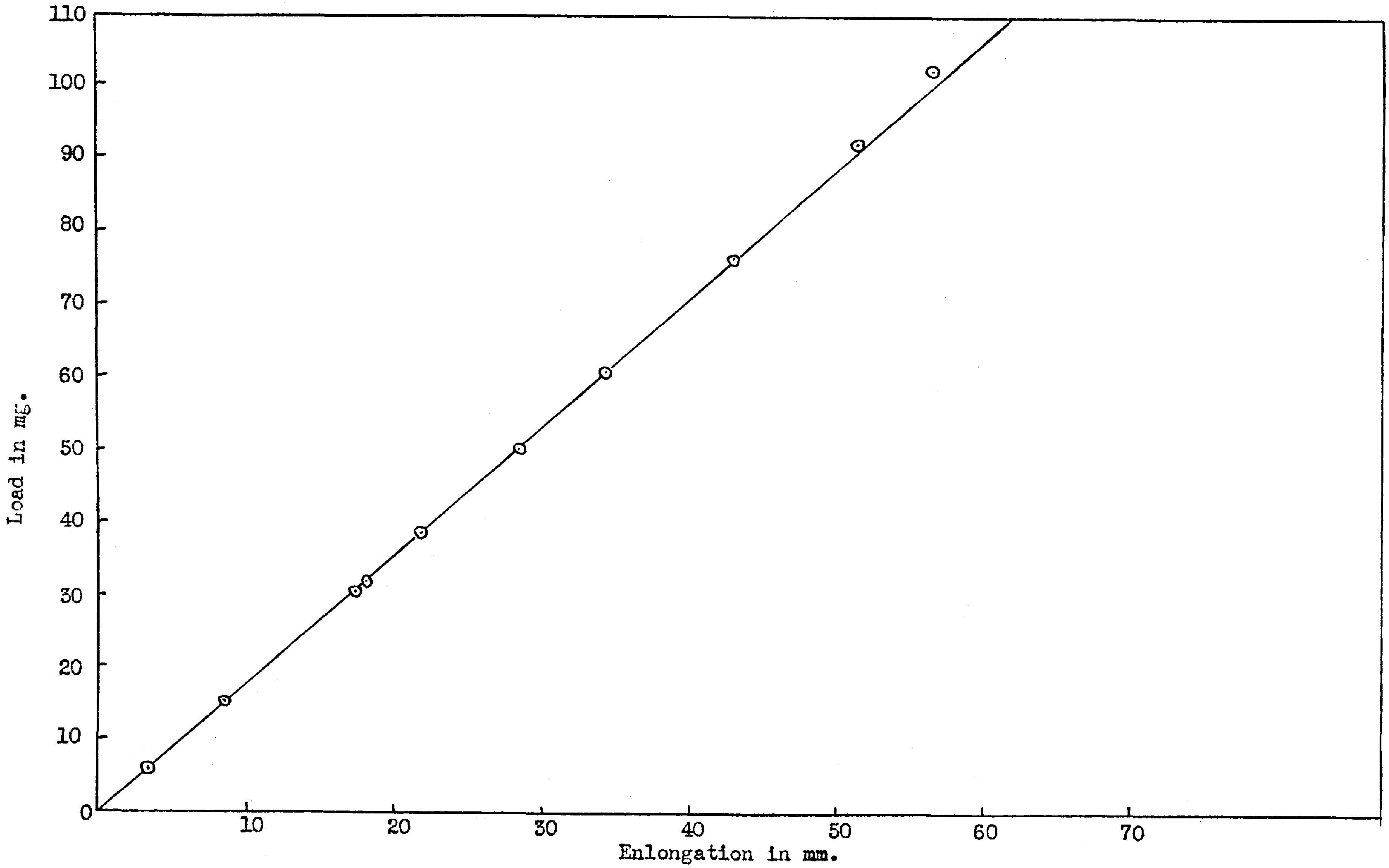

Figure 4
Enlongation vs Load
Spring S112

Although the springs suffer permanent enlongation when exposed to water vapor at high temperatures and relative pressures, no organic vapor has yet been found that cuases this phenomenon at any relative pressure. It has also been observed that plastic flow, if it occurs, is not detectable after years of suspension in organic vapors (69). McBain and Sessions show that springs exposed to certain organic vapors change upon subsequent exposure to air (70). Sessions and Reid (71) point out that under the conditions mentioned above it is doubtful that springs can be used for further experiments due to variation in the zero length as experimental conditions vary. Therefore, new springs should be used for each experiment.

The silica spring possesses two undesirable characteristics. With an increase in temperature, the spring decreased in length and also the sensitivity decreases. These changes, although small, are of importance in the method used to calculate the weight on the spring and shall be considered in detail elsewhere in this thesis.

Construction of the spring

Although the springs used in this investigation were supplied by Dr. R. F. Sessions, many springs were made by the author in order to learn the correct technique of their manifacture and thus add to the completeness of the study.

To make a spring of a definite sensitivity is almost impossible, but with a fair amount of experience, a spring of approximately the

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(69) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

(70) J. W. McBain and R. F. Sessions, J. Colloid Sci. 3, 213, (1948).

(71) R. F. Sessions, and W. E. Reid, Jr., a paper presented before the Georgia section of the A. C. S. meeting in minature (1949). To be published.

desired sensitivity may easily be made.

The silica fiber of the spring is made from a small piece of fused silica rod. A small section of the rod (5 mm) is heated to white incandescence, removed from the flame and quickly pulled out to arms length. This must be done very rapidly, since the melting point of the substance is very sharp and a course fiber may result if the action is too slow. If the fiber is pulled while the silica is still in the flame, it will be course at the ends and too fine at the center. A test for the uniformity may be made by drawing the cool fiber between the thumb and index finger; this also serves to indicate the courseness of the fiber. Measurements with a micrometer at each end of the fiber and along its length give its exact diameter and the uniformity of this diameter may be checked with a microscope.

The fibers produced should be straight and of uniform diameter, about one meter in length. Most of the springs made were formed from fibers about 0.013 mm in diameter.

A fiber meeting the above specifications is now ready to be fashioned into a spring. An Alundum rod 1/2 inch in diameter and 12 inches long, one end supported loosely in a one inch cork and the other end passing through a similar cork and projecting beyond it one inch, is mounted so that the rod may be turned freely without jerking or sliding back. The end of the rod projecting from the cork is mounted slightly below the horizontal end to give the spring the desired pitch. Carbon rods have formerly been used for fashioning the spring, but after slight use they become pitted and must be discarded, otherwise the springs become so difficult to remove from the rod that they are usually broken, and it becomes difficult to obtain springs with coils of uniform diameter and closeness. With a refractorie such as Alundum this difficulty is avoided.

With a small piece of gummed paper, about one inch of the silica fiber is fastened to the Alundum rod at a point near the highest end, as though it were going to be fastened along the length of the rod, and the projecting fiber allowed to hang down on the front side of the mounting. With a moderate flame the fiber is formed at right angles to the rod. A hook is then made on the hanging end of the fiber and on this is placed a small weight of about 20 mg. The rod is now twisted a few degrees as though the fiber were going to be wound about the rod cold. A small hump appears and it is at this point that the flame is applied. The proper type of flame to use is often hard to obtain. After experimenting with different types of flames the author made a small hard torch from pyrex glass which when used with compressed air produced a flame of the exact type desired. It was very small, came to a fine point, and produced the desired temperature. The rod is turned a slight amount causing a hump to appear, and the flame held close to the hump on the fiber, causing it to be softened and pulled against the rod by the weight mentioned above. The flame is held at one fixed point after the first hump appears, which is usually on a horizontal diameter of the rod, and the rod turned very slowly. If it is turned too fast, then hexagonal shaped coils will result. The flame should always be held so that its tip is directed at the rod, since the rod absorbs most of the heat produced, otherwise the fiber will be pulled out and be too fine, causing the spring to be ruined. The temperature of the flame used was such that with careful use of the torch this danger was easily avoided. In several cases when the flame was not directed at the rod, the fiber was pulled out, with the result that some parts of the spring usually broke while being removed from the rod or when a weight was placed on it.

As the rod is slowly revolved, perfectly round coils are fused on the rod, if all goes well, and the coils formed are almost touching. The latter is dependent upon the horizontal position of the rod, which may be adjusted as the spring is fused on to make the pitch of the spring as small as possible. (Compare J. S. Tapp, Can. J. Research, 6, 584, (1932).

When all but the last several inches of the fiber are fused about the rod, the operation is halted, the weight removed from the fiber, and the fiber broken off about one inch from the rod with tweezers. The gummed paper used to support the fiber initially is moistened and removed and any glue or paper fragments are burned off and the rod removed from one end of its support by sliding it back through the other end. The spring is now gently blown towards the clear end with compressed air, being helped along the rough spots by lifting it over them with a glass hook, until the unwound portion projects over the free end. The flame is applied at the midpoint of the projection and a small hook is made by bending back toward the rod the outer end of the projecting fiber with tweezers. The rod and spring are removed from the support and the spring completely removed from the rod. The removal of the spring from the rod is one of the most delicate operations of the whole procedure and unless done very carefully the spring will usually be broken, but if the spring is broken it need not necessarily mean a complete loss, since the salvaged portion, it it contains about 15 turns, can make a satisfactory spring.

A second hook is made at the other end of the spring and the spring supported by a small glass hook. Springs are always handled with tweezers or glass hook and the hands should never be used.

The finished spring is now examined under stress to make sure that it has no kinks or weak spots and that it is symmetrical. A 100 mg. weight is next suspended from the spring and the spring aggitated. This insures that the spring will be capable of withstanding sudden changes in tension. A rough measurement is then made with a cemtimeter rule of the length of the spring and the 100 mg. weight removed and the spring again measured. This gives a rough measure of the sensitivity of the spring. Many of the springs made for this study had sensitivities of about one mm per mg.

The springs are annealed for 24 hours at a temperature of 325 degrees C. while under a tension of 30 mg. before being used for experimental work in order to relieve strains and to avoid plastic flow (72).

Elastic Response of Silica Springs

In this and the following discussions of the various properties of silica springs, it will be necessary to use graphs and data pertaining to actual springs. The springs most studied were those used in the sorption tubes, and in most cases the data and graphs used will refer to these springs.

As seen from the graphs (figures 3 and 4), the springs conform to Hooke's law, that the enlongation produced is proportional to the applied force.

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(72) G. W. Shreve, Ph. D. Dissertation, Stanford University, (1946).

For a sensitive spring (A-1), this law is obeyed from loads of 0 to 80 mg, but at loads greater than 80 mg. the points are seen to fall slightly off the curve, indicating that the law is not obeyed precisely as the spring approaches its elastic limit and becomes greatly deformed. For a spring of small sensitivity (S-112) the points do not fall on the curve for loads greater than 65 mg. indicating that springs of small sensitivity have a low elastic limit due to their rigidness. This small load range and low sensitivity makes their use undesirable in the investigation considered since the load must be known as accurately as possible, and if linearity is assumed, then for a spring of about 0.5 mm/mg we would have an error of about 2% for loads greater than 65 mg. In general, we may say that springs of sensitivity from 0.5 to 1 mm/mg, and of good construction, will obey closely Hooke's law from 0 to 65 mg and linearity may be assumed without introducing any error.

This seems to contradict the popular assumption that very sensitive springs are not essential to such a study as this when a large sample is used. It is true that for a spring of low sensitivity the limit of detection (73) would be made small and for a large sample the error of detection (later described) would be decreased, but the error introduced by the assumption of linearity would cause an error of large magnitude when the composition of the soap was calculated.

The error of detection is the possible error caused by the inability of the cathetometer used to measure the exact length of the spring. The cathetometer used was accurate to 0.002 cm. so that the total possible

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(73) J. S. Tapp, Can. J. Research, <u>6</u>, 584 (1932).

error of detection was 0.004 cm. For a load of 25 mg. and a spring of about 1 mm/mg sensitivity this represents and error of 0.16% or an error in weight of 0.04 mg. which is usually small enough to be neglected. For a load of 52.90 mg. consisting of 24.00 mg of soap and cyclohexane, a 0.02 mg change in weight (representing an 0.08% error of detection) would represent a change in soap composition of 0.08%.

It is necessary to calibrate the springs used over a wide range of loads in order to determine whether the response of the spring is linear over the range of loads expected to be used in the experiment, but if the gain in weight need not be known accurately, then linearity may be assumed. Figure 18 shows the elastic response of the two springs used in this investigation. It is seen that the response is linear of loads up to about 80 mg.

Effect of temperature on zero length and sensitivity

Silica glass has one of the smallest coefficients of expansion of any known substance (0.000000449) and is very unusual in some of its properties. For example above 1200 degrees it contracts and upon being cooled from 1500 to 1200 degrees it expands (74).

The small coefficient of expansion of the silica glass makes it suitable for use in experiments at high temperatures, but when a fiber is pulled from a fused silica rod and fashioned into ahelix, it is found that the helix contracts with increase in temperature, instead of expanding as would normally be expected.

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(74) H. F. Roscoe and C. Schorlemmer, A Treatise on Chemistry, Revised Edition, 914, Vol. I, McMillan and Co., London, (1911).

This unusual property of the springs makes necessary their calibration over the range of temperatures expected to be used in the experiment. The decrease in the length of the spring with temperature depends upon the enlongation of the spring or its load and it is therefore necessary to make calibration curves for each spring over the entire temperatures range with several different loads. Combination of these calibration curves will then enable the experimenter to determine exactly the decrease in the length of the spring for a given temperature and load.

The method of calibrating the springs is as follows:

A piece of pyrex tubing about 46 cm long and 5 cm in diameter is wound with Nichrome heating wire and the wire connected to a variable voltage transformer which is manually controlled. This should be connected to a voltage stabilizer to prevent fluctuations in the AC current and resulting fluctuations in the temperature. The bottom of the tube is stoppened with a large cork and the tube then supported upright in a well lighted place, free from drafts. The back of the tube should be covered with asbestos paper to protect the tube from any possible drafts which will cause sudden temperature changes and further protection from sudden temperature changes is obtained by shielding the apparatus with a large sheet of asbestos paper about 20 inches high. A small goose-necked lamp lighting the tube diagonally from the side insures adequate illumination. A large cork which just fits the top of the tube is fitted with two glass hooks. One of these hooks is made very long and supports the spring, and a calibrated thermometer is suspended from the other hook which is about 1/2 inch from the hook supporting the spring.

The stoppered tube prevents air currents inside the tube from bouying up the spring, causing inaccurate measurements to be made. Although it is possible that with such a crude apparatus some movement of air in the tube does occur, its effect on the spring should be small provided the exterior of the tube were free from sudden drafts, for which purpose the asbestos paper shields are used.

The voltage transformer is set for the desired temperature with the unloaded spring supported in the tube close to the stem of the thermometer. After thermal equilibrium is established, usually about an hour, the length of the spring is measured, with a leveled cathetometer. By correct manipulation of the spring, the two reference points can usually be made to be in the same plane so that no refocusing is necessary after the first focus is made, thus increasing the accuracy of the measurements.

Three measurements of the spring length are made, the average value being accepted as the accurate value of the spring length. For the unloaded spring where the decrease in length is very small, this is sometimes difficult to do, as the calibration curves will show. For the springs used the decrease in length per 10 degrees increase in temperature was about 0.002 cm, and the cathetometer used was accurate only to 0.002 cm. This explains the multitude of points on the curves 5 and 6.

After the measurement of the zero length, the spring is removed and a small weight of about 25 mg is placed on the spring and when thermal equilibrium is established the spring length is measured. This is repeated for loads of about 50, 75, and 100 mg. , etc. The temperature of the calibration tube is then raised a definite amount and the whole process repeated. For the springs used in this investigation, measurements were made at 10 degrees intervals from 50 to 150 degrees Centigrade for various loads. The curves 5 through 11 are the various calibration curves for the two springs used.

As seen in figures 5 and 6 the points are widely scattered due to the difficulty mentioned above, but a linear relation is indicated. Figures 7 and 8 show more clearly this linear relation, but there is still a scattering of the plotted points. Figures 9 and 10 represent the most accurate data obtained in the calibration. The plotted points seem to indicate that the decrease in the length of the spring with increased temperature is not a straight line function at all. If the graphs are carefully studied it will be seen that the points fall about the curve in such a manner as to indicate that a line connecting the points would form a slight curve, the curve for figure 10 bending one way and the curve bending another way for figure 9.

It is probably that if the curves are not straight lines and have only a very small curvature over the range considered (50-150 degrees c.), then a combination of all factors would result to form a curve which appears to be a straight line.

The slope of each of the calibration curves was determined and a plot was made of slope against load for each spring. As seen from figure 12 the resulting curves were not straight lines which indicated that the contraction in length of the springs for a given temperature change was not directly proportional to the load on the spring.

The temperature coefficient or change in length of the spring per degree centigrade is, of course, negative, and its numerical value is

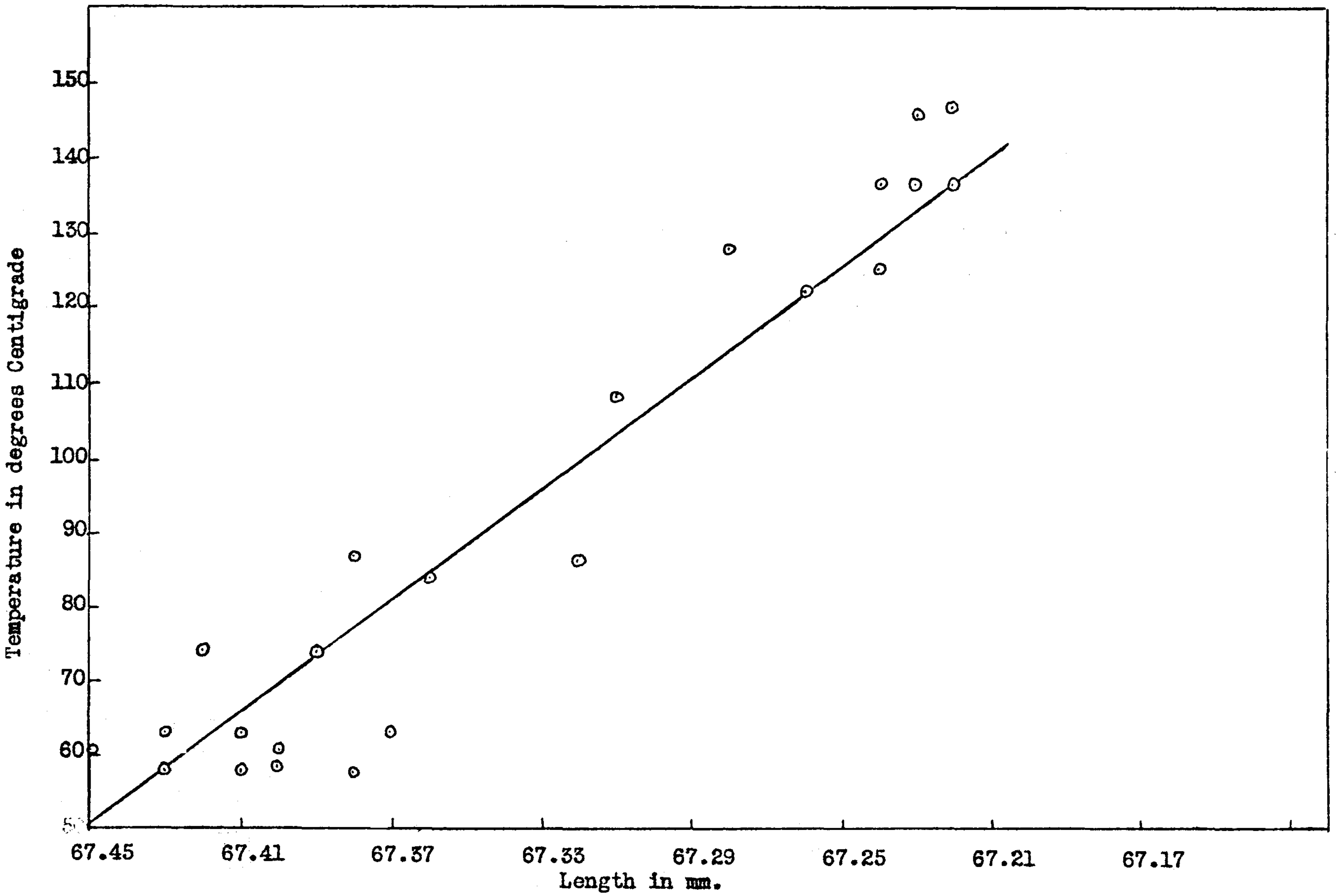

Figure 5
Length vs Temperature - Spring 2
Load; 0 (zero length)

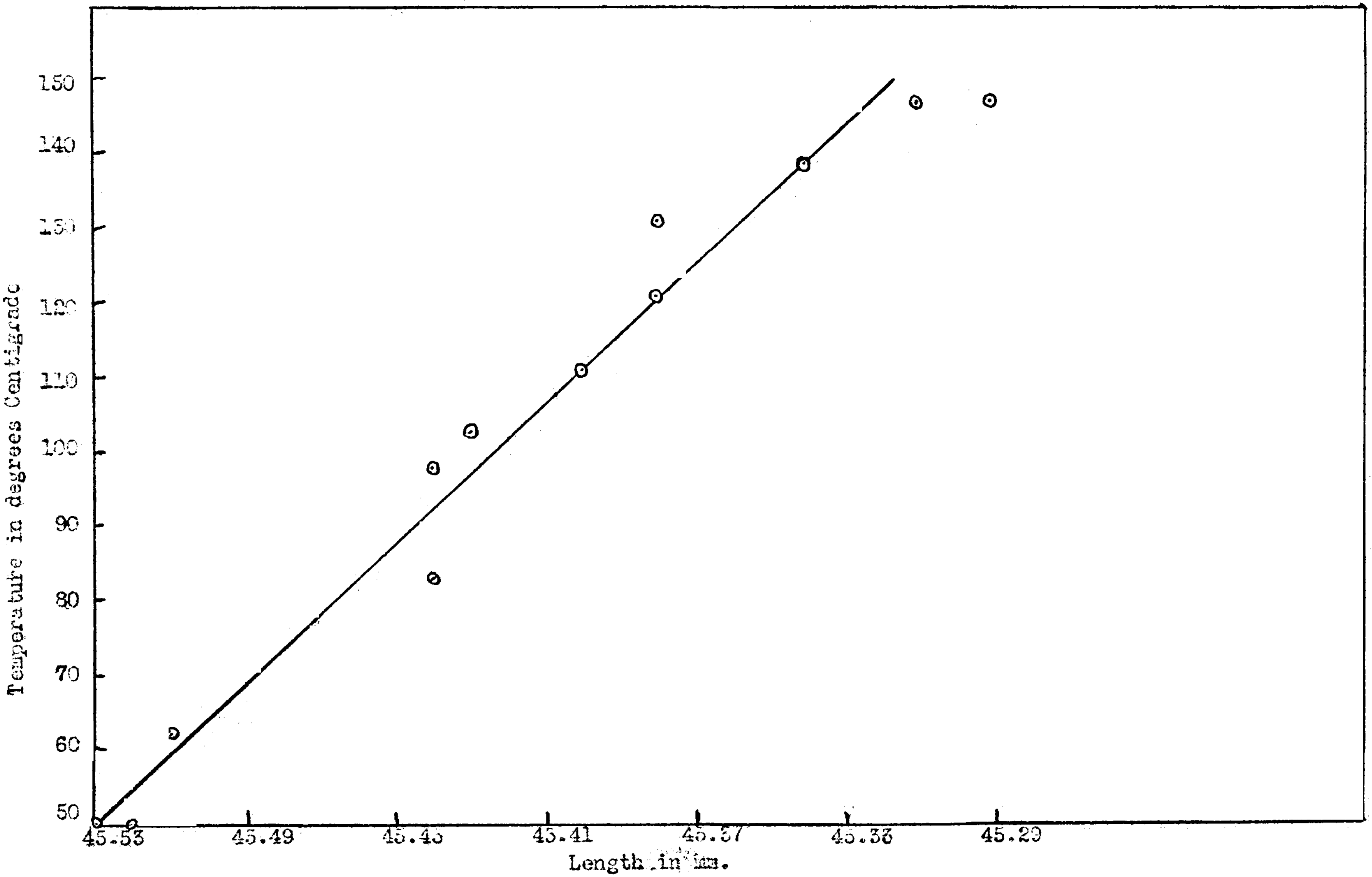

Figure 6
Length vs Temperature- Spring 3
no load- zero length

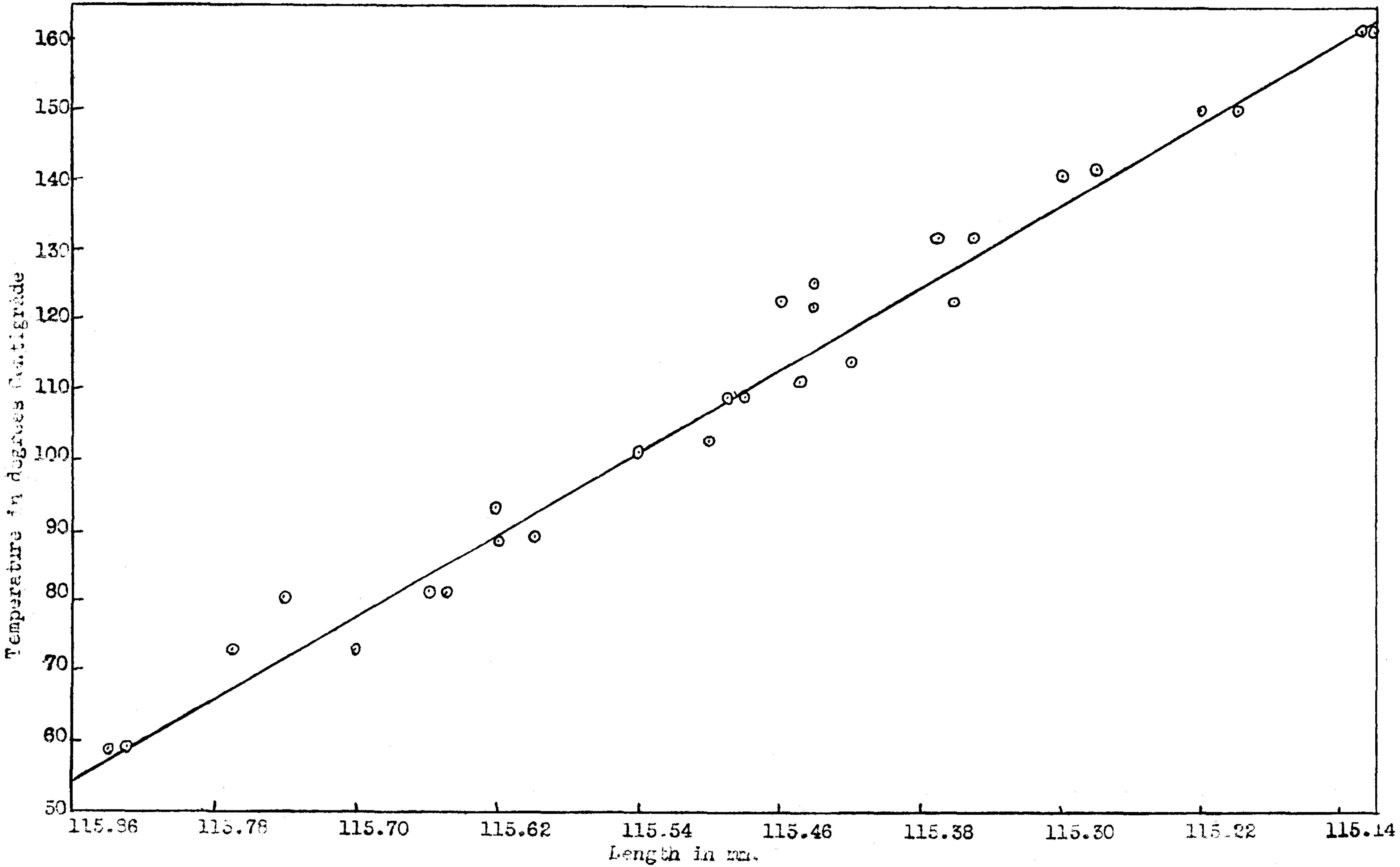

Figure 7
Length vs Temperature- Spring 2
Load: 50.9 mg.

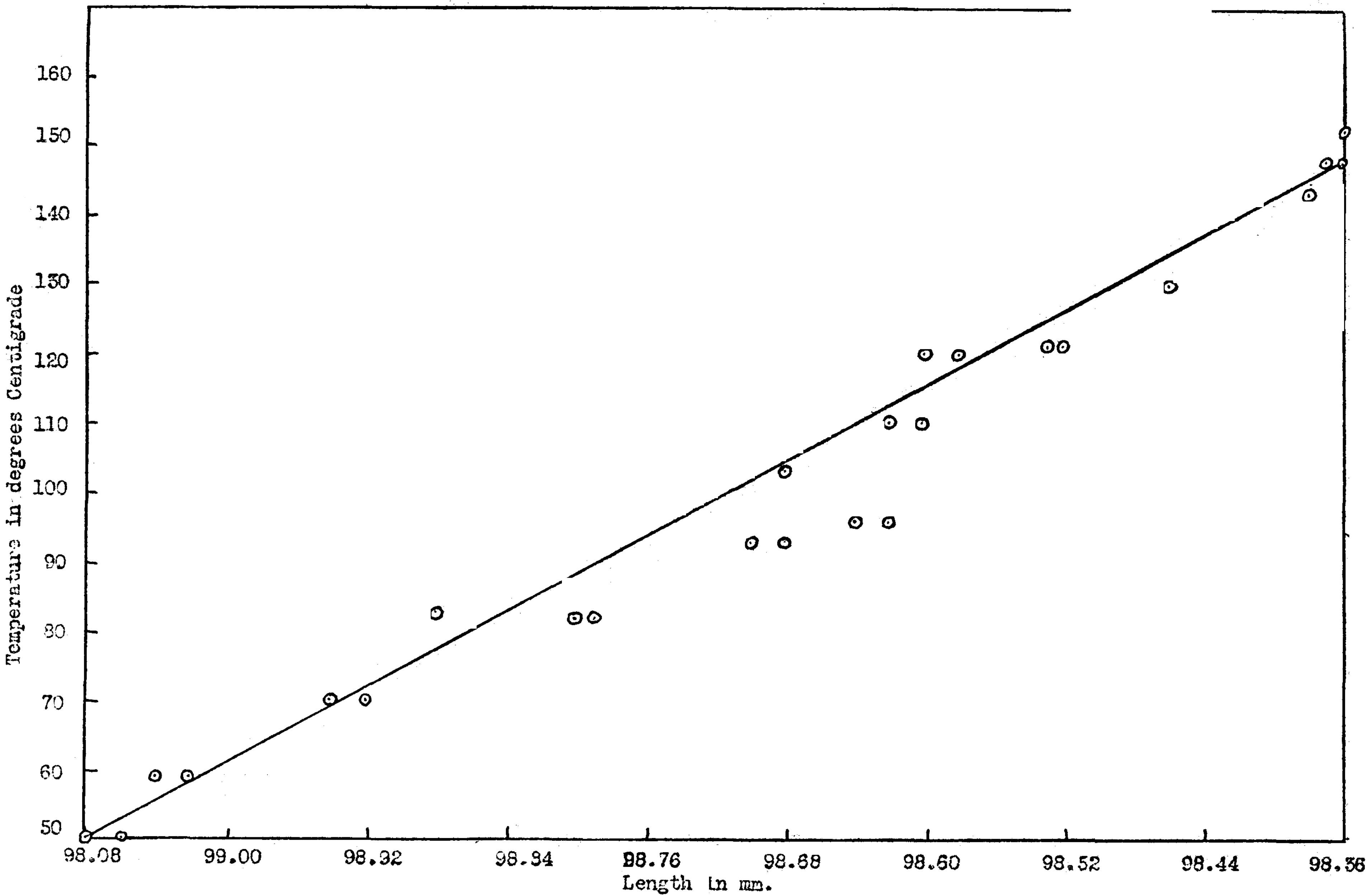

Figure 8
Length vs Temperature- Spring 3
Load 50.9 mg.

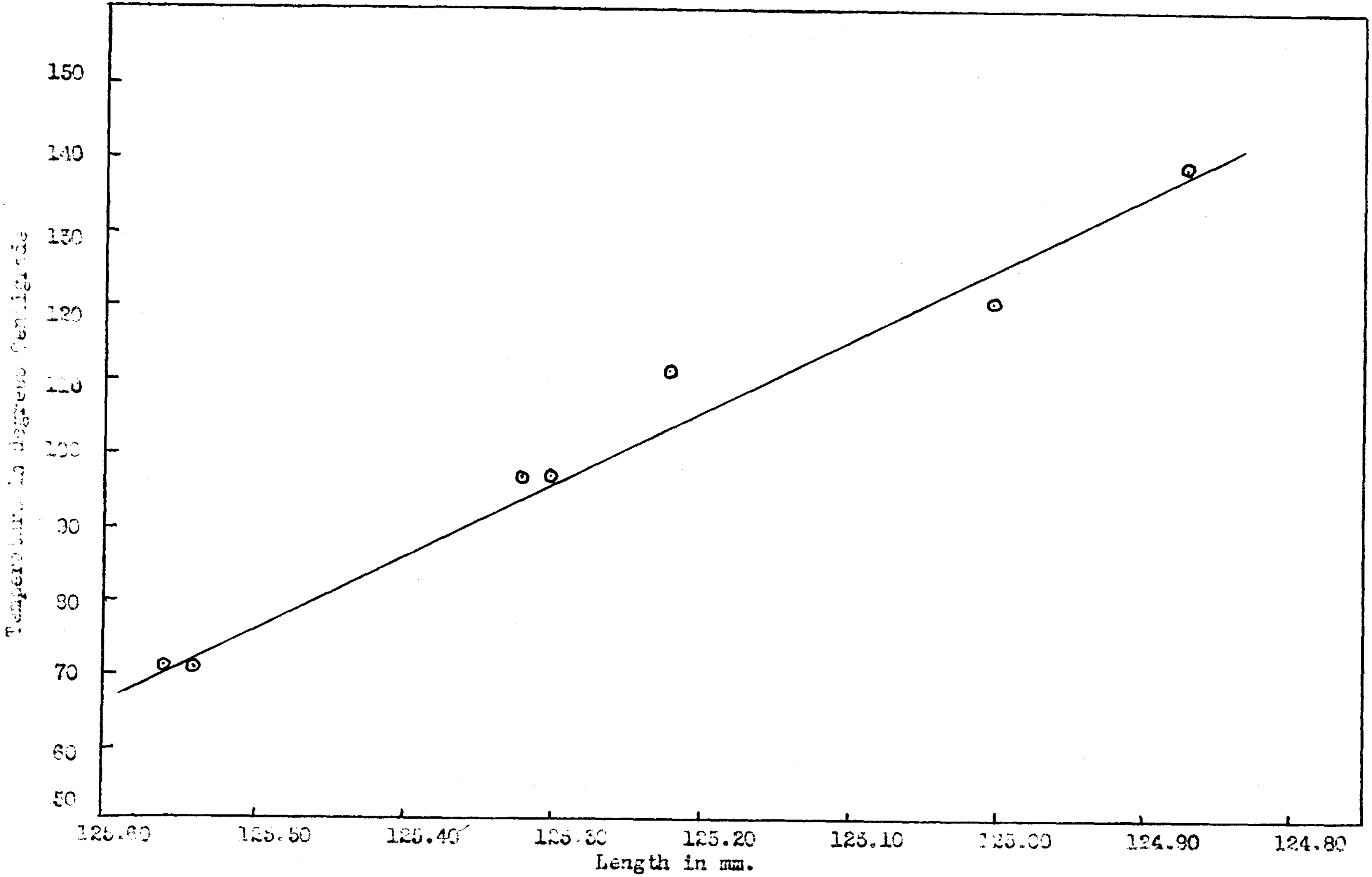

Figure 9
Length vs Temperature - Spring 3
Load 77·1 mg.

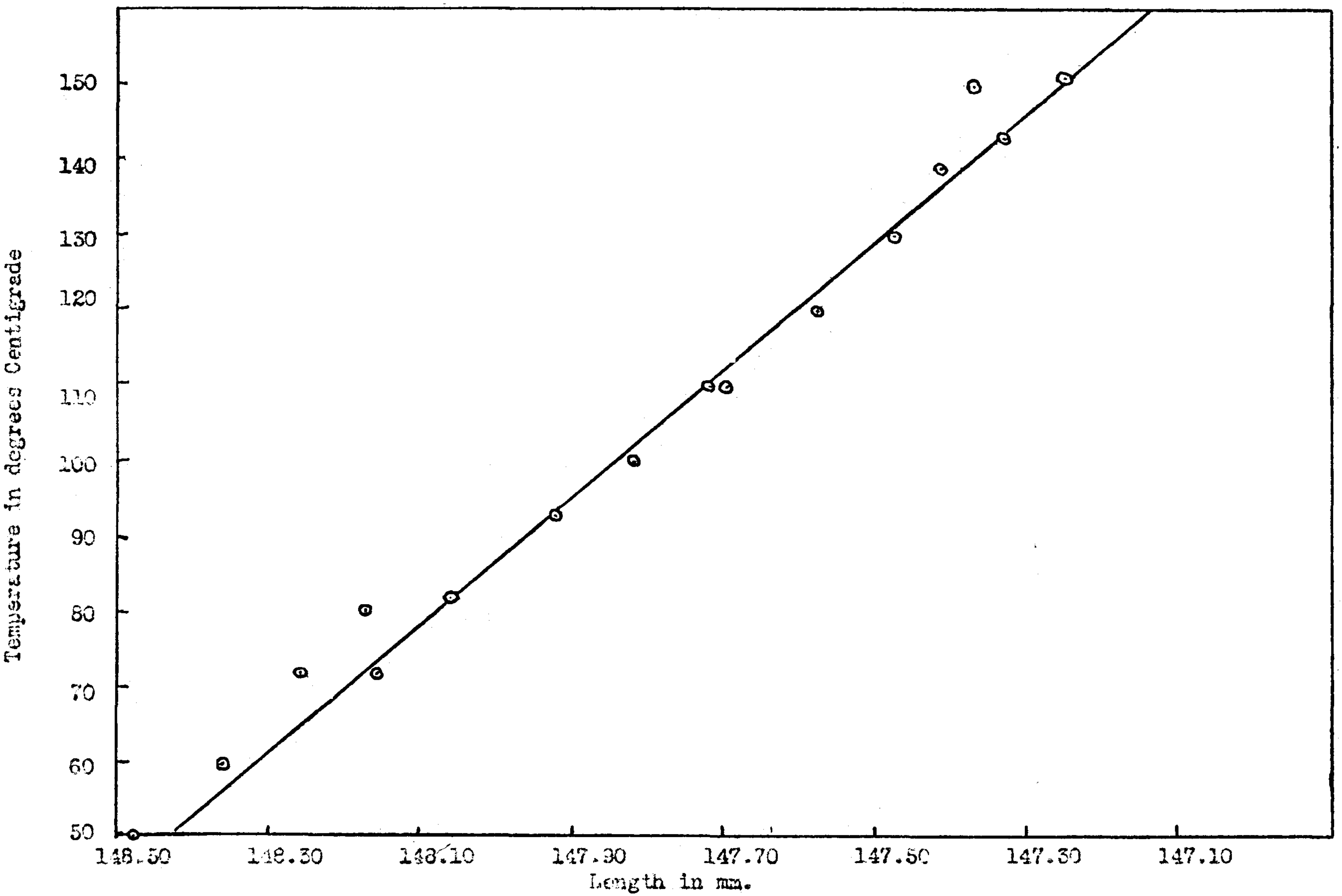

Figure 11
Length vs Temperature- Spring 3
Load: 99.6 mg

determined by the sensitivity of the spring and the suspended load. The effect of the load on the temperature coefficient is shown by the data in table II. For springs less sensitive than the ones used, the values would be much smaller. For example, a spring of small sensitivity(about 0.3 mm/mg), with no load, would show no change in length for a 10 degree temperature rise, when measured with a cathetometer capable of being read to 0.002 cm.

The temperature coefficients were obtained from the calibration curves and are therefore subject to the same errors which influence the accuracy of these curves.

TABLE II

Load(mg)	Temperature Coefficient (cm/deg. C.) Balance 2	Balance 3
0	-0.00027	-0.0002
50.9	-0.00066	-0.00075
77.1	-0. ——	-0.00093
99.6	-0.00125	-0.0012

Sensitivity is defined as the displacement caused by unit weight, that is, $\frac{\text{enlongation}}{\text{load}}$. With silica springs this is influenced by the construction of the spring, the temperature, and the load on the spring.

The factors which determine the sensitivity of the spring itself are;

1. The length of the spring or the number of turns comprising the spiral.
2. The thickness of the fiber used.
3. The diameter of the spring.
4. The closeness and uniformity of the turns of the spiral.

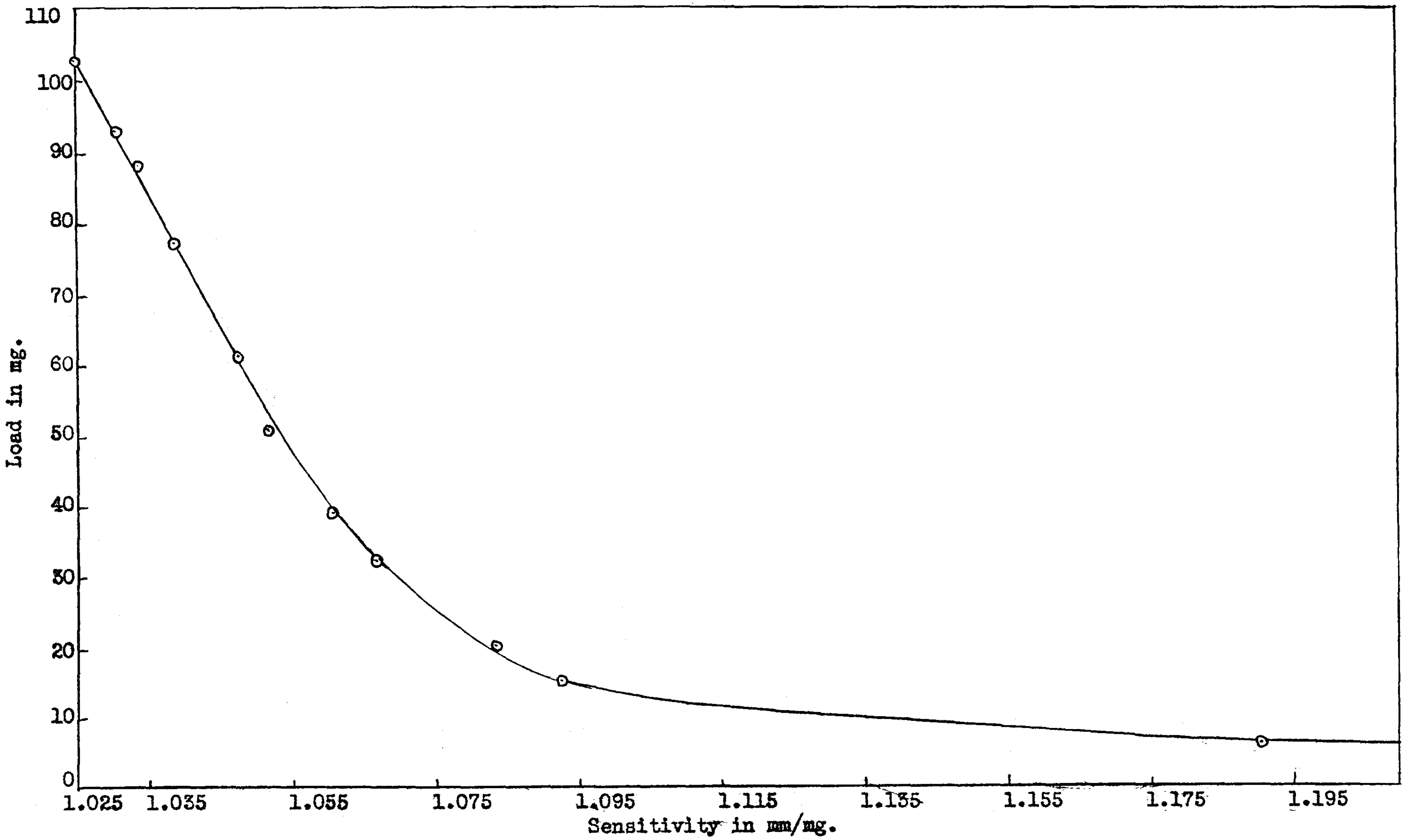

Figure 13
Sensitivity vs Load
Spring A1 - Temperature 25°C.

When a load is suspended from a spring, the spiral undergoes twisting, stretching, and bending. The enlongation is therefore due largly to the twisting of the fiber comprising the spiral, or the stress is a shearing stress. Now Hooke's law states that $\frac{\text{stress}}{\text{strain}}$ = a constant or $\frac{\text{load}}{\text{enlongation}}$ = a constant. For a shear type of strain the constant is called the modulus of rigidity. Since the above is true, then we may say $\frac{\quad}{\text{sensitivity}}$ = modulus of rigidity. We are applying Coulomb's theory of the twisted cylinder, which applies only to bodies of circular symmetry twisted about the symmetrical axis to the helix. This may be done provided the pitch of the helix is small, for which case the effects are the same. (75)

We therefore see that sensitivity $= \frac{a^2 l}{GI}$, but $I = 1/2\ MR^2$ for a cylinder, where R = the radius of the fiber, so that sensitivity $= \frac{2a^2 l}{GMR^2}$, where a = radius of spring, l = the length of the fiber, G = a constant, involving the modulus of rigidity, and M = the mass of the fiber.

From this relationship we see that the four above conditions must hold true.

The effect of temperature on spring sensitivity is very small. Tables V and VI show the change in sensitivity for springs 2 and 3 for different temperatures at different loads. The average change in sensitivity being about -0.001 mm/mg per 10° temperature rise. The values given in Table V and VI were obtained from the calibration curves, which accounts for the regular variation, since linearity was assumed for the calibration curves. Although the change in sensitivity with temperature is small, it is important that the change be known accurately. The

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(75) M. Scott, Mechanics, Statics and Dynamics, 128-132, McGraw-Hill, N. Y., N. Y., (1949).

sensitivity should be carried to the nearest thousandth (0.001)mm/mg when calculating the change in soap composition. This is accurate enough, since an enlongation of 5.713 cm. gives a weight difference of 0.02 mg. when the sensitivities are 0.948 mm/mg and 0.9484 mm/mg and this would amount to only about an 0.08% error in calculating the soap composition.

The sensitivity also varies with the load as is seen from Figure 13. The variation is somewhat regular for loads from 40 to 100 mg, but is by no means linear. The pronounced variation for small loads was due to weak sections in the fiber which caused the spring to be distorted. When the small weights were added the spring began to straighten out, causing large apparant changes in sensitivity.

The change in sensitivity with load, (Table III) although small, accounts for a change in sensitivity of 0.01 mm/mg when the load varies from 43 to 65 mg. Were this change neglected, it would represent an error of 0.5 mg, or 2.0% when calculating the composition of the soap. Figure 14 shows the variation in sensitivity with load for springs 2 and 3. It is obvious from these graphs that this variation is not a straight line function. Several curves are drawn for each spring to show the effect of temperature on the sensitivity.

From the above it must be concluded that the McBain- Bakr Sorption Balance is a very delicate instrument, capable of extreme accuracy when used correctly. Balances of the sensitivity used in this investigation are capable of detecting extremely small changes in weight; an amount equivalent to only 0.08% change in soap composition. The smallest detectable change in weight is defined as the fraction of a millimeter to which the cathetometer is capable of detecting, divided by the sensitivity expressed as mm/mg (76). For the springs used, the limit of detection was 0.02 mg.

Although, as previously stated, the springs have been used and studied for some years, there has never appeared in the literature any detailed description of the correct method of their use. However, the author is aware of the information contained in theses, of students working under Professor McBain, on file in the library of Stanford University. Two of theses, namely "Sorption of Gases and Vapors" by R. F. Sessions and "Phase Equilibria of Soap Systems" by G. W. Shreve were examined.

One of the prerequisites for proper use of the sorption balance is a study of the corrections necessary to be applied in order to arrive at values representing the highest degree of accuracy. The following summary describes the method employed to determine the exact composition of the soap.

A silica spring of about 1 mm/mg sensitivity is calibrated with no load and with several loads of about 20 mg. difference over the entire temperature range to be used in the experiment, measurements being made of the spring length at about 10° intervals.

Graphs of length vs. temperature are then made for each load used. At present linearity must be assumed, due to the limit of accuracy of the cathetometer measurements. From the plots of length against temperature, the sensitivities are determined for each load at several different

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(76) J. S. Tapp, Can. J. Research <u>6</u>, 584, (1932).

Data used to plot Sensitivity vs Length Curves

Figures 15 and 16

Temperature 50°C.

TABLE III

Spring 2

Load (mg.)	Sensitigity (mm/mg.)	Enlongation (mm.)
50.0	0.9503	48.37
53.0	0.9499	50.34
56.0	0.9493	53.16
60.0	0.9485	56.91
70.0	0.9465	66.26
80.0	0.9440	75.52

TABLE IV

Spring 3

Load (mg)	Sensitivity (mm/mg.)	Enlongation (mm.)
43.0	1.0552	45.37
45.0	1.0544	47.45
48.0	1.0532	50.55
50.9	1.0520	53.55
53.0	1.0515	55.73
55.0	1.0503	57.77
57.0	1.0496	59.83
60.0	1.0484	62.90
65.0	1.0464	68.02

TABLE V

Change in sensitivity of Spring 2 with temperature

Temperature (°C.)	Load (mg)	Observed length (mm)	zero length (mm)	enlongation (mm)	Sensitivity (mm/mg.)
50	50.9	115.82	67.45	48.37	0.9502
	99.6	160.91		93.46	0.9383
60	50.9	115.75	67.43	48.32	0.9493
	99.6	160.79		93.36	0.9373
70	50.9	115.68	67.40	48.28	0.9485
	99.6	160.66		93.26	0.9363

TABLE VI

Change in sensitivity of Spring 3 with temperature

Temperature (°C.)	Load (mg)	Observed length (mm)	zero length (mm)	enlongation (mm)	Sensitivity (mm/mg.)
70	50.9	98.93	45.49	53.44	1.050
	77.1	125.56		80.07	1.0385
	99.6	148.20		102.71	1.031
80	50.9	98.86	45.47	53.39	1.049
	77.1	125.46		79.99	1.0375
	99.6	148.07		102.60	1.030
90	50.9	98.78	45.44	53.34	1.048
	77.1	125.36		79.92	1.0365
	99.6	147.95		102.51	1.029

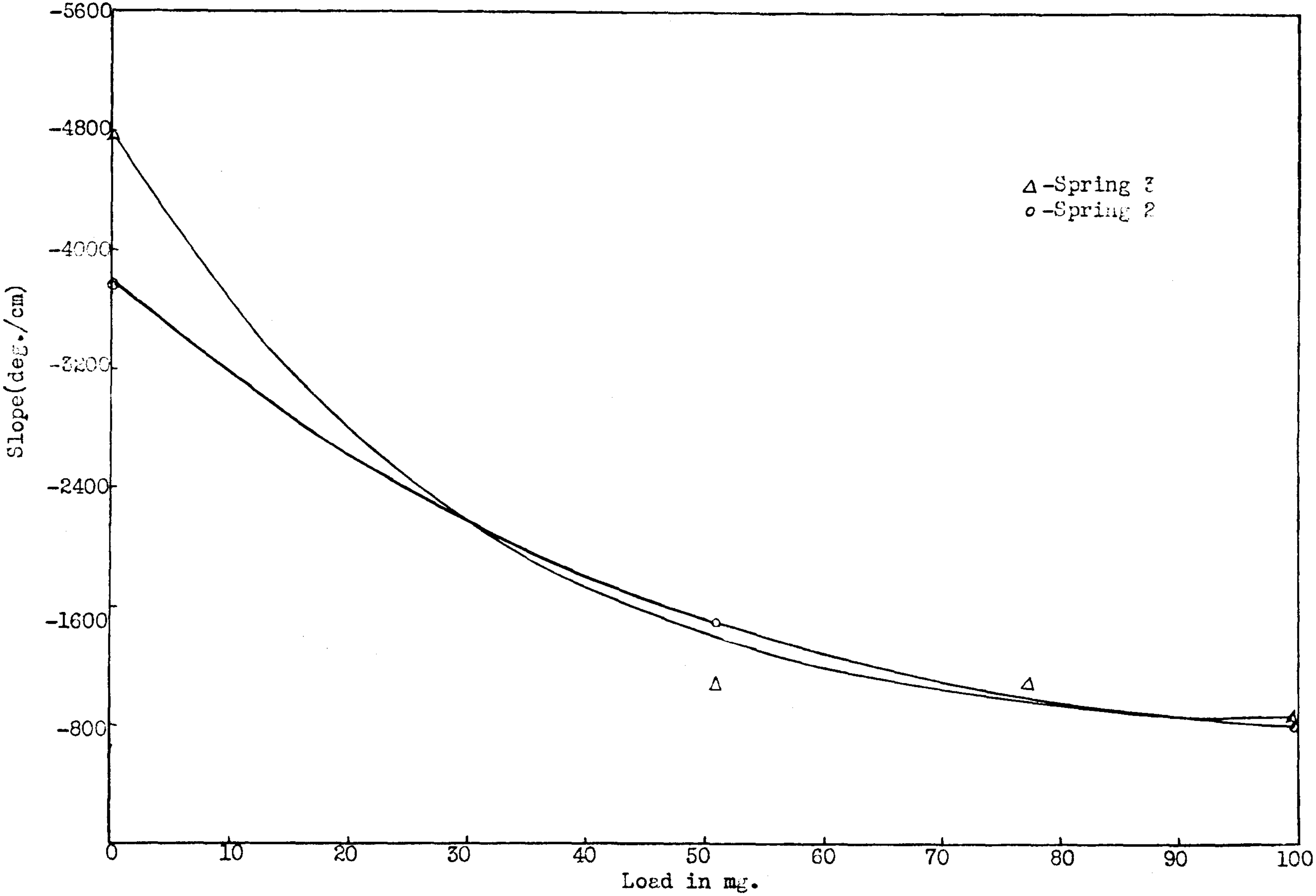

Figure 12
Load vs Slopes of Calibration Curves

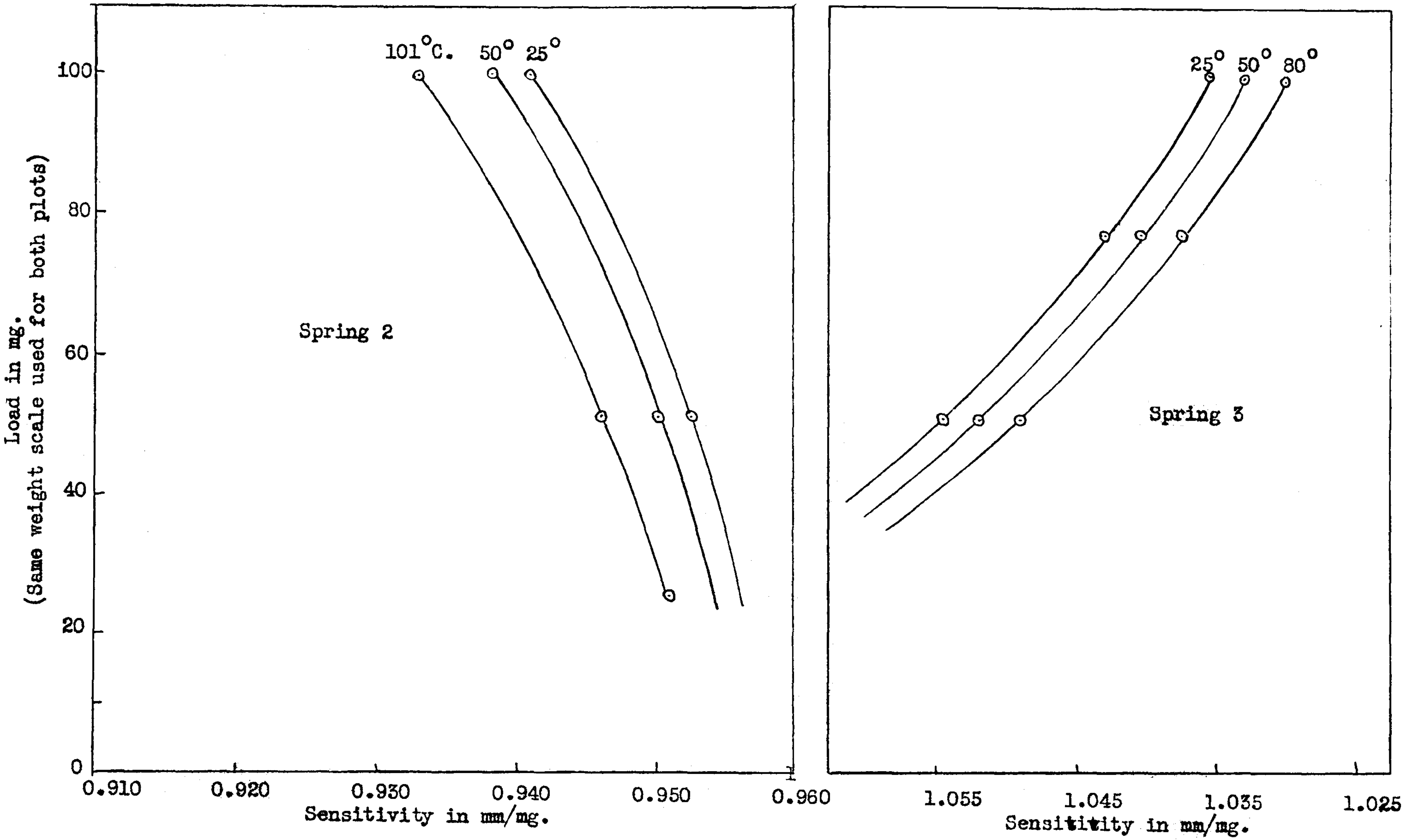

Figure 14
Sensitivity vs Load
(for several temperatures)

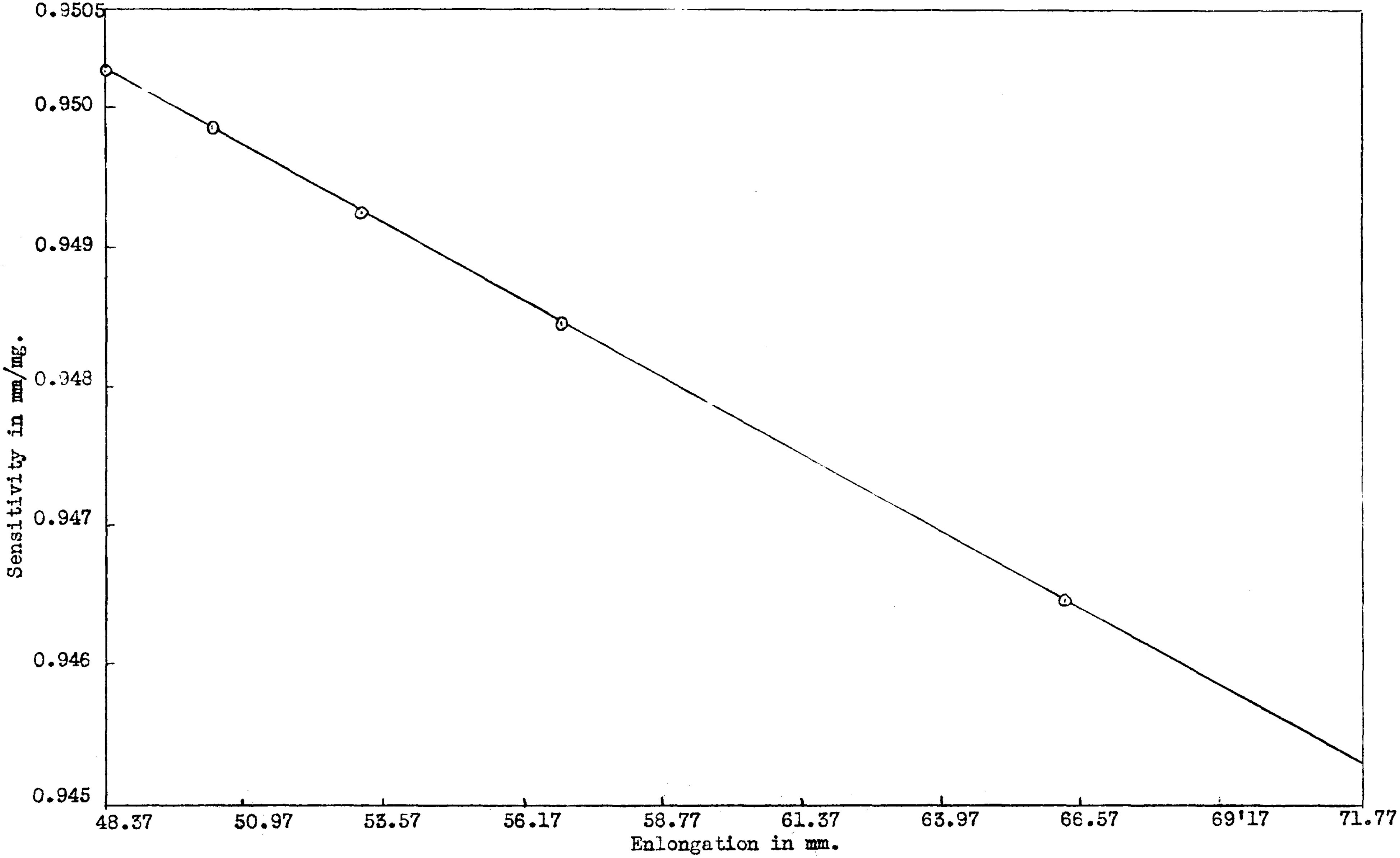

Figure 15
Sensitivity vs Length-Spring 2
Temperature 50°C.

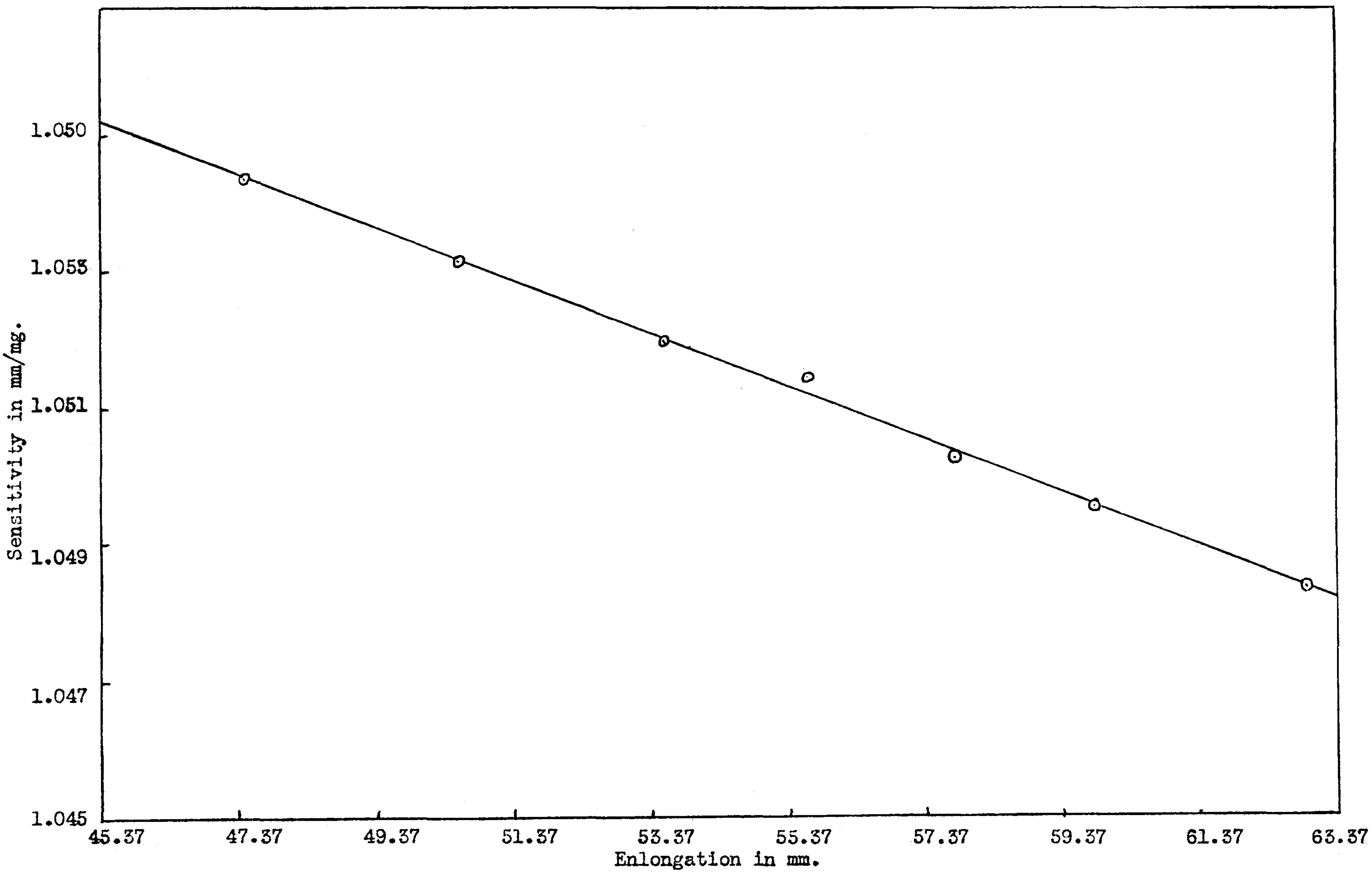

Figure 16
Sensitivity vs Length- Spring 3
Temperature: 50°C.

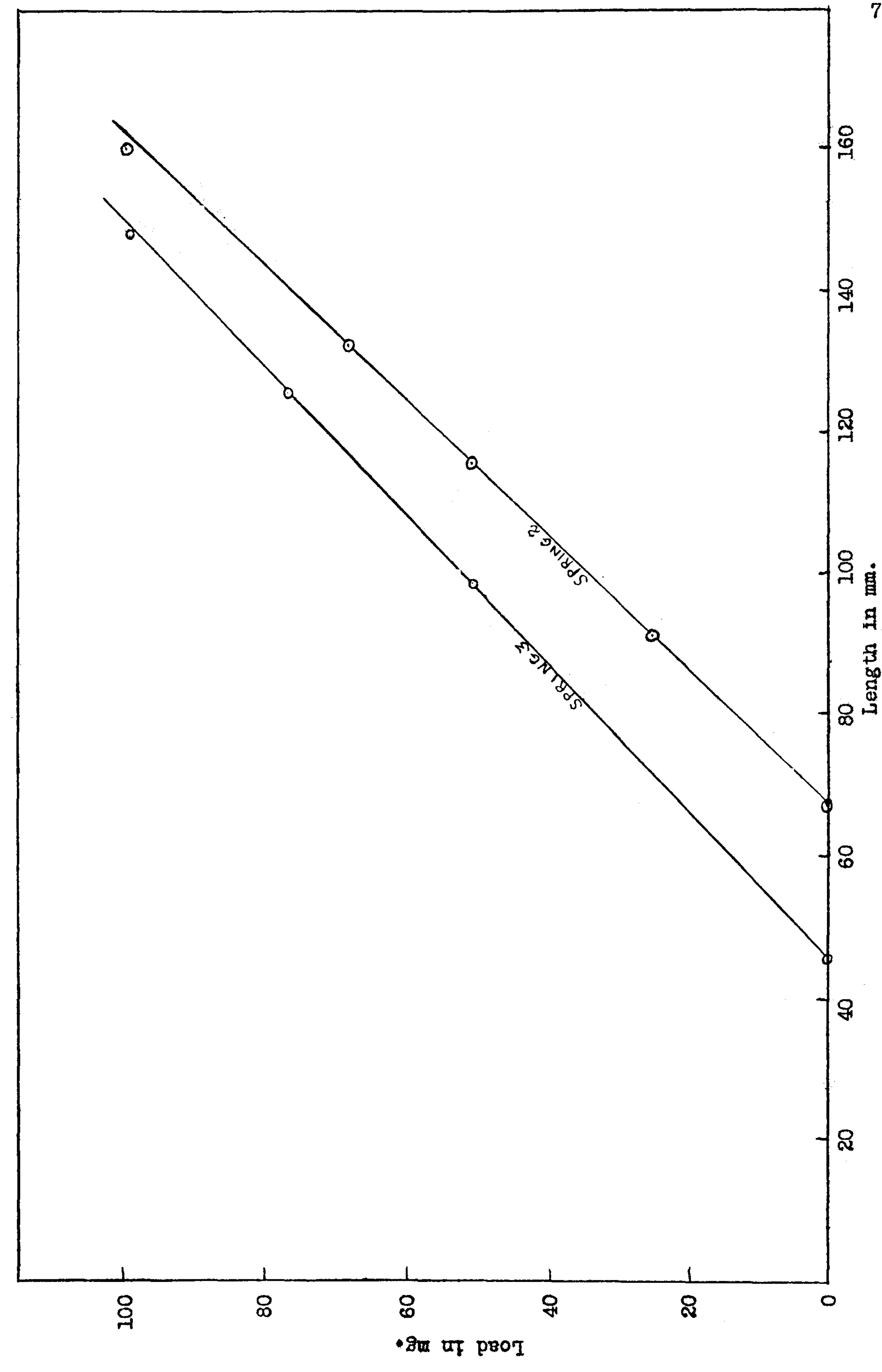

Figure 18
Length vs Load- Spring 2 and Spring 3
Temperature:101 degrees C.

temperatures. This establishes the variation of sensitivity with temperature. This need be done only for a small number of values, since the length vs temperature plots insure linearity.

A plot of sensitivity against load is now made for each spring. After the shape of the curve has been determined, a blow up of the curve is made, using the values for loads expected on the balance during the experiment. On the blow up, the sensitivity isplotted against the enlongations instead of the loads (which are equivalent), to enable the plot to be used for experimental observations. This is shown in figures 15 and 16. It is necessary to change the sensitivity units on the plot as the temperature changes.

From the above described plot, the sensitivity is determined for a particular spring enlongation by inspection of the graph and this is divided into the length of the spring (observed length minus the zero length) at the observed temperature. This gives the weight of the total load on the spring. From this is subtracted the weight of the platinum bucket and the difference is the weight of soap plus hydrocarbon. Dividing this difference into the weight (vacuum) of the soap sample used gives the percent soap.

Preparation of the Sorption Balance

1. Sorption balance No. 3
    Spring used: no. 2
        Sensitivity: 0.952 mm/mg at 25°C.
        Zero length: 154.26 - 37.06 = 117.20 mm at 25°C.
    Weights of load components:
        Platinum bucket: 28.9 mg.
        Soap sample in air: 23.5 mg.
        Soap sample in vacuum: 23.28 mg.

Detectable limit of percent soap: 0.09%

Sorption Started: 8 July, 1949

The tube was evacuated for 5 hours at 25°C. and 10^{-5} mm Hg.

2. Sorption balance No. 4

Spring used: no. 3

Sensitivity: 1.0585 mm/mg. at 25°C.

Zero length: 110.74 - 21.48 = 89.26 mm at 25°C.

Weights of load components:

Platinum bucket: 25.0 mg.

Soap sample in air: 16.3 mg.

Soap sample in vacuum: 16.18 mg.

Detectable limit of percent soap: 0.12%

Sorption started: 8 July, 1949

The tube was evacuated for 6 hours at 25°C. and 10^{-5} mm Hg.

(It will be noted from 1 and 2 above that although spring 3 is more sensitive than spring 2 the detectable limit of percent soap is smaller for spring 2. This was due to the fact that balance 3 contained 7.1 mg. more of soap than balance 4 and this larger soap sample enabled small changes in soap composition to have a greater effect on the spring length than the soap sample in balance 4.)

3. Soap- The sodium stearate was prepared as described on page 16.

4. The lengths of the springs were measured at 25°C. before breaking the ampoules of cyclohexane, in order to determine the weight of the soap in vacuum. After breaking the ampoules the tubes were then installed in the thermostats and allowed to remain at the isotherm temperature for two days before making spring length measurements. The first

isotherm was run at 50° and at first the springs showed no apparent change in weight, but were the same length as they were at 25°, before sorption was begun. This was because the spring length had decreased during the 25° temperature increase, and the weight of the sorbed cyclohexane had caused an enlongation of the spring exactly equal to the contraction caused by the temperature change.

A typical calculation of the determination of the percent soap and the relative vapor pressure may be found in the appendix.

V EXPERIMENTAL RESULTS

This section includes a brief discussion of the more important aspects of particular isotherms. The isotherms (Figures 19 - 30 and Figure 32) are presented along with the data from which they were constructed.

Isotherms were run at temperature intervals of 5 degrees from 50 to 100 degrees Centigrade and one was run at 110 degrees. In experiments of this nature, where so many factors can influence the results obtained, it is usually necessary to perform the experiment in duplicate, since the results obtained from using only one sorption tube would be questionable as there would be no way to check on the reliability of the results unless the experiment were repeated. When the experiment is performed in duplicate, however, each apparatus serves as a check on the other.

In this investigation, two isotherms were run simultaneously, in two separate apparati for each isotherm temperature. On each isothermal graph is plotted separately the isotherms run with each individual apparatus, designated Balance 3 and Balance 4.

The lowest relative vapor pressure obtainable for each isotherm was determined by the room temperature, as the apparatus used was not fitted with cooling tubes to lower the temperature of the reservoir below that of the room. Due to this fact, the lowest relative vapor pressure obtainable for the 50 degree isotherm was about 38%. As the isotherms were run at higher temperatures, lower pressures could be obtained. If any phase changes occurred below the lowest pressure obtained, then they could easily have been skipped, but the shape of the curves indicate that no phase transitions were skipped due to this fault in the apparatus.

As seen from the graphs, the isotherms run with each apparatus are not identical, as they should be, however the isotherms run with Balance 3 agree very well with those obtained by Shreve (77). For low vapor pressures, the two isothermal curves agree very nicely, but at higher pressures the soap sample in Balance 4 is observed to take on more cyclohexane. At isotherm temperatures above 90 degrees C. this difference between the two isotherms begins to disappear and the results from both balances are almost identical. The two tubes were examined carefully and all thermometers checked, but no reason for the difference in the isotherms of the two different tubes could be found. It is suggested that this difference was due to a cold spot in the top of Balance 4. This causing condensation of cyclohexane at high relative vapor pressures with the result that near saturation pressures were obtained before the reservoir temperature indicated such pressures. The 50, 55, and 60 degree isotherms run with Balance 4 indicates that this is a probable

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(77) G. W. Shreve, Ph. D., Doc. Dissertation, Stanford University, (1946).

explanation.

The 50° Isotherm (Figures 19 and 20; Tables VII and VIII)

This was the first isotherm run and it was the lowest temperature maintained for any isotherm.

The first reading made with balance 3 was made at a temperature of 55° due to a miscalculation of the necessary setting of the voltage transformer, but th e temperature was adjusted after 24 hours and the tube allowed to stand at 50° for a period of 24 hours before the next reading was made.

A fault inherent in the apparatus was made obvious from the first isotherm, and that was the inability to reach saturation pressures without condensation of hydrocarbon vapor on the spring; thus voiding any possible readings made. The extreme sensitivity of vapor pressure to very small changes in temperature when near saturation made small changes in relative vapor pressure difficult, since the manually controlled voltage transformers regulating the temperature of the thermostats was not sufficiently sensitive to regulate the temperature closer than one degree and even a change of one degree required some skill in their use. The inability to reach saturation pressures is characteristic of most of the isotherms run, but in several cases saturation was reached or approached very closely.

The importance of making readings when equilibrium has been established is noted from these two 50° isotherms. Many of the readings made for the first isotherm(Figure 19) were made at 10 and 12 hour intervals. This was insufficient time for equilibrium to be established, especially at saturation pressures. It is noted that points are plotted at pressures greater than saturation for each balance. There was,atthe time of the reading, no apparent condensation of vapor in the upper thermoatat. This indicates that equilibrium was not established when the observations were made and that the apparent pressure was caused by a sudden change in temperature. When desorption was begun the amount of cyclohexane sorbed increased instead of decreasing for balance 4, which verifies the above conclusion. Further external temperature changes caused an increase in relative vapor pressure (refered to henceforth as RVP) as the temperature of the hydrocarbon reservoir was lowered ; these values are plotted as sorption values on the curve. That the point at 72.84 % soap for balance 3 is not a reliable value may be seen by comparison of isotherms run with this balance at higher temperatures.

Due to the unreliability of the points plotted near saturation for the first isotherm it was decided to rerun this isotherm, noting especially the sorption of cyclohexane at high pressures. These values are presented in Figure 20(Table VIII). Although the data is presented as the 50° isotherm , Table VIII will show that many points are plotted which were not obtained at the isotherm temperature of $50\underline{+}1°$. These values are included to get a more complete picture of the isotherm, especially the desorption curve of balance 4. A drop of cyclohexane was observed on the platinum bucket of balance 4 at saturation so no reading was taken, but the shape of the curve indicates that saturation was reached .

The dates on which the readings were made are included with the data for the two 50° and the 55° isotherms to show how time influences the hysteres curves. Comparison of these values shows that time has a

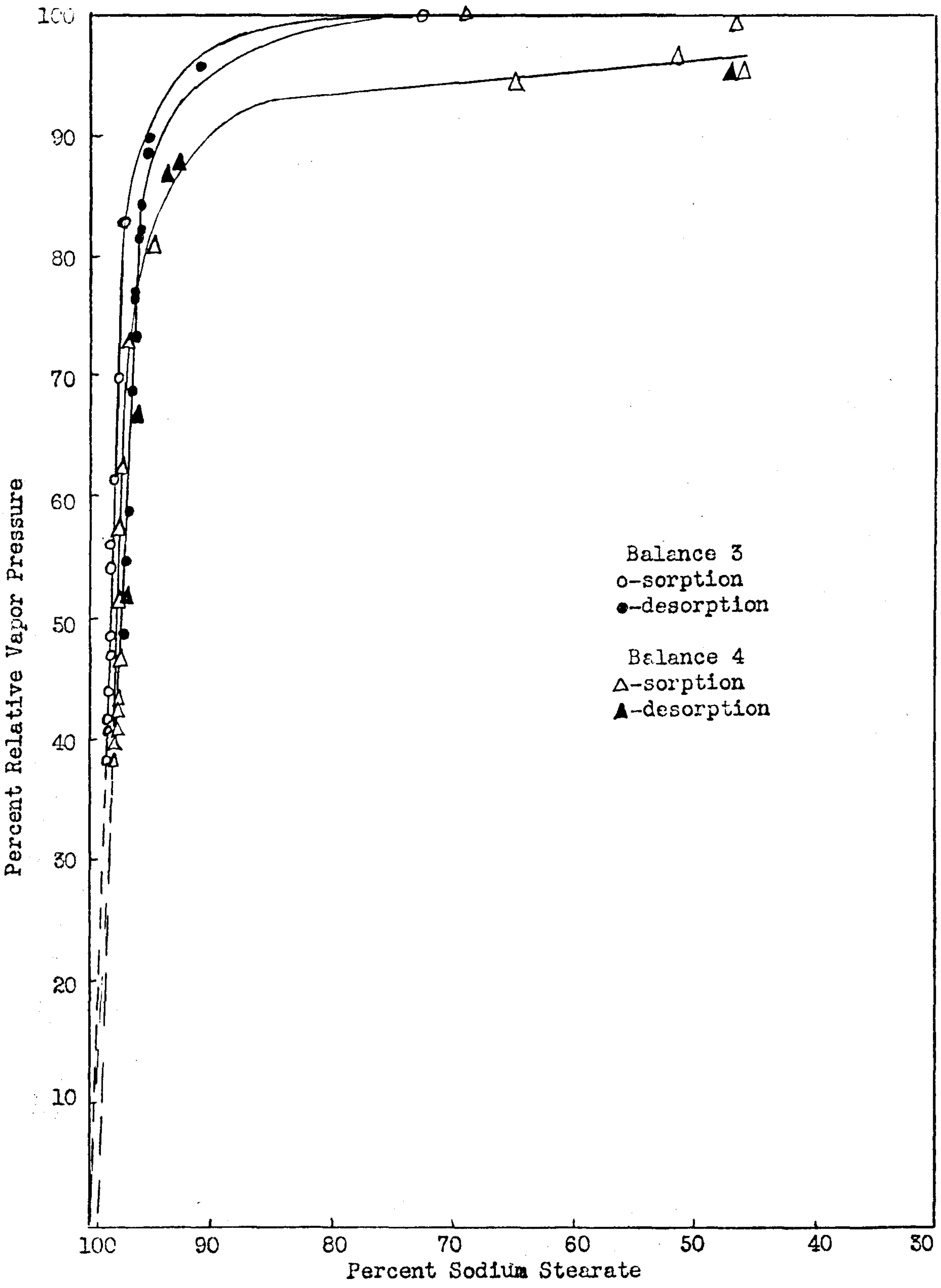


Figure 19
The 50° Isotherm(a)

Table VII

The 50^b Isotherm(a)

Balance 3

Date	Spring Length (cm)	Temperature		Percent Soap	RVP
Sorption		Top	Bottom		
7/11/49	11.739	55.5	27.2		
7/12	11.736	49.8	26.2	98.50	38.39
7/14	"	49.5	27.3	98.50	40.83
7/15	11.736	49.0	27.2	98.50	4137
7/16	"	49.5	29.0	"	43.86
7/16	11.738	"	29.2	98.41	44.31
7/18	11.742	49.2	30.5	98.19	47.53
7/18	"	49.5	31.2	98.19	48.47
7/19	11.738	"	33.7	98.41	54.06
7/19	11.742	50.5	35.2	98.19	56.04
7/20	11.744	49.5	36.5	98.11	61.25
7/21	11.748	50.5	40.4	97.94	69.60
7/22	11.762	50.8	45.4	97.38	82.97
7/22	11.764	51.7	46.4	97.25	82.58
7/23	12.296	49.5	49.6	7284	100.3
Desorptic					
7/24	11.810	51.0	49.6	90.89	95.61
7/26	11.800	50.7	47.1	95.73	88.55
7/27	"	50.3	45.4	95.73	84.19
7/27	11.808	49.1	45.8	95.37	89.77
7/28	11.796	51.2	45.6	95.87	82.21
7/28	11.792	51.0	43.6	96.04	76.84
7/29	11.794	50.5	44.6	95.95	81.47
7/29	11.786	50.5	42.9	96.32	76.41
8/1	11.788	47.5	39.2	96.24	73.08
8/1	11.776	50.9	40.4	96.76	68.48
8/2	11.772	49.5	35.4	96.92	58.22
8/2	11.768	50.3	34.6	97.08	54.78
8/3	11.764	49.5	31.2	97.24	48.39

Balance 4

Date	Spring Length (cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption					
7/12/49	8.932	50.5	26.5	98.24	38.10
7/14	8.934	"	27.6	98.12	40.70
7/15	8.937	49.5	26.7	97.94	39.70
7/15	8.940	50.5	28.7	97.82	42.13
7/16	8.940	49.5	27.7	"	41.51
7/16	"	49.2	28.2	"	42.99
7/18	8.942	49.7	30.4	97.71	46.62
7/19	"	50.2	33.0	"	51.29

Table VII
(continued)

Balance 4

Sorption					
7/20	8.942	50.5	35.7	97.71	57.14
7/20	8.944	51.5	38.8	97.59	61.97
7/21	8.954	52.7	43.8	97.00	72.73
7/23	8.991	50.5	44.8	94.90	82.05
7/24	9.646	49.5	49.6	69.24	100.4
Desorption					
7/26	9.838	50.9	49.3	64.18	94.95
7/27	10.316	49.7	48.5	54.19	96.17
7/27	10.801	49.1	48.8	46.78	99.04
7/28	10.846	50.1	48.6	46.20	95.00
7/28	10.764	49.0	47.5	47.26	95.00
7/29	9.032	50.5	46.6	92.88	87.55
7/29	9.016	50.0	45.8	93.64	86.44
8/1	8.994	48.8	42.8	94.73	80.64
8/2	8.968	49.8	38.8	96.14	66.67
8/3	8.956	49.0	32.2	96.89	51.54

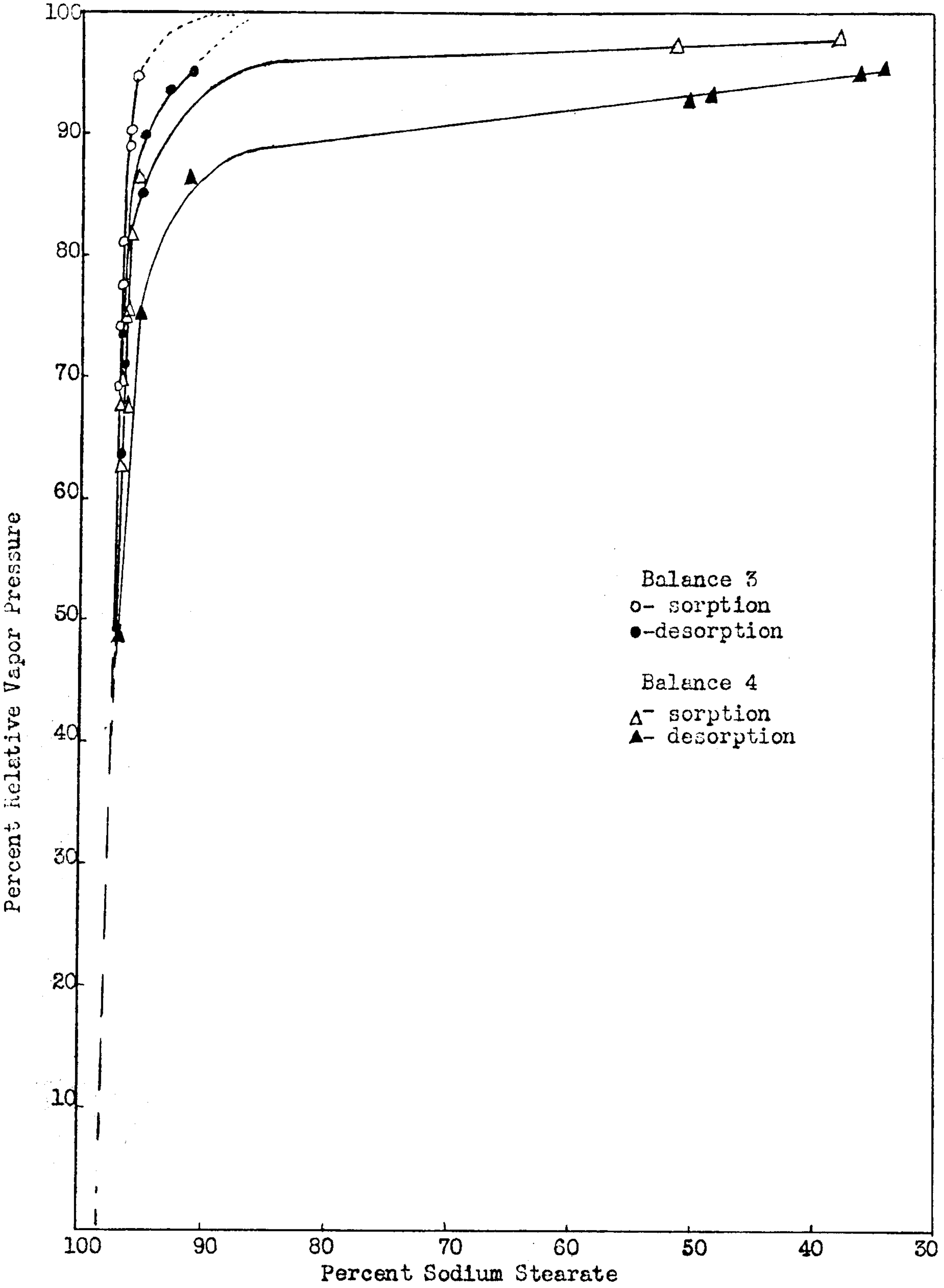


Figure 20
The 50° Isotherm(b)

Table VIII

The 50° Isotherm(b)

Balance 3

Date	Spring Length(cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption					
8/3/49	11.760	49.8	39.6	96.92	69.10
8/4	11.774	51.0	42.6	96.84	73.97
8/5	11.778	49.6	42.6	96.64	77.59
8/6	11.782	49.5	43.6	96.48	81.10
8/7	11.787	49.3	44.6	96.28	84.41
8/8	11.798	48.5	45.6	95.80	90.29
8/9	11.794	51.0	47.6	96.00	88.90
8/10	11.804	50.8	48.6	95.57	92.27
Desorption					
8/12	11.778	48.7	40.5	96.64	73.54
8/17	11.820	51.5	48.6	94.90	89.83
8/18	11.922	50.0	48.6	90.87	95.10
8/19	11.876	"	48.1	92.64	93.61
8/20	11.822	50.3	47.2	94.83	89.71
8/21	11.816	49.2	44.6	95.06	85.15
8/22	11.810	49.6	45.0	95.33	85.12
8/23	11.792	50.2	41.6	96.09	73.43
8/24	11.790	50.7	41.2	96.16	71.09
8/24	11.782	49.5	37.3	96.52	63.40
8/25	11.770	51.0	32.6	97.00	48.93

Balance 4

Date	Spring Length(cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption					
8/4	8.960	49.5	36.8	96.60	62.00
8/4	8.958	50.8	39.8	96.71	67.39
8/5	8.962	49.5	38.8	96.48	67.29
8/6	8.960	49.8	39.8	96.60	69.66
8/7	8.962	50.1	41.8	96.48	74.22
8/8	8.966	49.7	41.8	96.25	75.34
8/9	8.973	50.7	44.8	95.91	81.46
8/10	8.984	50.8	46.6	95.29	86.15
8/11	10.490	48.7	47.8	51.28	97.08
8/12	11.622	48.3	47.6	37.95	97.64
Desorption					
8/17	11.832	48.7	47.1	36.22	94.75
8/18	12.110	48.5	47.1	34.13	95.30
8/19	10.680	48.9	46.8	48.43	93.05
8/20	10.566	47.6	45.7	50.11	92.54
8/21	9.062	48.6	44.4	91.26	86.13
8/24	8.990	50.5	42.8	95.07	76.05
8/26	8.958	49.6	31.7	96.83	48.45

great influence on the points plotted. The sorption curve for balance 3 in Figure 20 tends to approach saturation at 94 % soap , but the data obtained for both the 50° isotherms is not reliable near saturation. This is very obvious from the desorption curves of balance 3. Temperature fluctuations did not allow equilibrium to be established, and the points plotted above 90 % RVP cannot be considered accurate.

The 55° Isotherm (Figure 21; Table IX)

Temperature fluctuations caused the curve for balance 3 to be somewhat distorted near saturation, however the desorption values fall very close to the sorption curve which indicates that for this balance the isotherm was reversible. The sorption curve for balance 4 shows that more cyclohexane is sorbed at a higher temperature and the desorption curve shows clearly that saturation was not reached (compare Figure 21). Hysteresis, although less than for Figure 20, is most apparent near the sharp bend in the curve. Had more time been allowed for desorption near 80% RVP, the hysteresis would probably habe been less.

For this isotherm, as with the 50° isotherm and most of the others at higher temperatures, it will be noted that exterpolation of the curves back to zero vaypr pressure gives a soap composition of only about 93% instead of 100% as would be expected. This is probably due to the fact that the soap was not allowed to dry as completelyas possible before beginning each isotherm. This will be discussed later.

The 60° Isotherm (Figure 22; Table X)

The sorption and desorption curves for balance 3 are seen to be identical, showing no hysteresis. Temperature fluctuations were very small for this and all other isotherms up to 90°, since they were run during the winter months and the data near saturation pressures is therefore more accurate. Hysteresis is only very slight for balance 4,

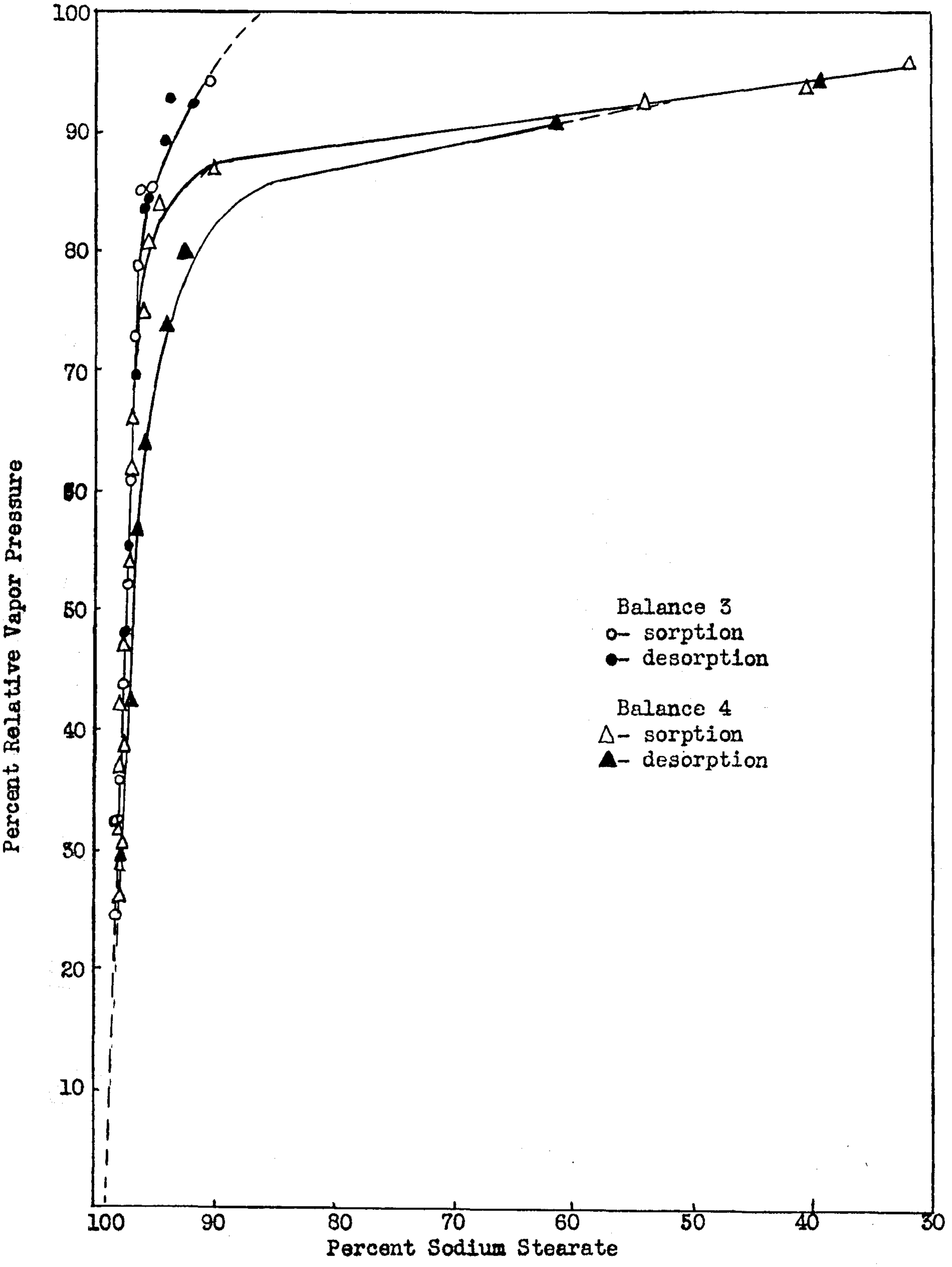


Figure 21
The 55° Isotherm

Table IX

The 55° Isotherm

Balance 3

Date	Spring Length(cm)	Temperature		Percent	RVP
		Top	Bottom	Soap	
Sorption					
9/11/49	11.750	55.7	21.5	97.73	24.94
9/11	11.754	54.5	26.1	97.53	32.18
9/12	11.754	"	28.4	"	35.81
9/13	11.762	"	32.9	97.20	43.53
9/14	11.762	55.2	37.4	97.20	52.00
9/15	11.768	55.0	41.4	96.92	60.90
9/16	11.778	54.5	45.6	96.52	72.87
9/17	11.786	54.0	47.3	96.16	78.53
9/19	11.794	54.6	50.4	95.76	85.53
9/22	11.804	55.0	50.8	95.33	85.14
9/23	11.932	54.5	52.7	90.34	94.01
9/ Desorption					
9/25	11.848	54.7	52.5	93.57	92.79
9/29	11.892	54.0	51.9	91.83	92.31
9/30	11.836	54.0	50.9	94.02	89.10
10/1	11.802	54.2	49.6	95.41	84.40
10/3	11798	54.5	49.7	95.68	83.91
10/7	11.784	54.3	44.7	96.28	69.43
10/9	11.762	54.4	31.9	97.20	48.04
10/11	11.750	54.5	25.0	97.73	30.60
10/12	"	"	23.5	"	28.70
10/8 (not used)	11.776	53.8	39.6	96.60	57.74

Balance 4

Date	Spring Length(cm)	Top	Bottom	Percent Soap	RVP
Sorption					
9/10	8.938	54.8	21.7	97.65	25.86
9/11	8.934	55.3	24.2	97.82	28.77
9/12	8.936	55.0	26.2	97.71	31.73
9/13	8.940	54.5	28.9	97.53	36.44
9/14	8.940	55.1	32.7	97.53	42.28
9/15	8.942	55.5	35.4	97.41	46.95
9/16	8.946	55.6	38.8	97.18	54.08
9/17	8.952	54.8	41.3	96.83	61.37
9/18	8.958	55.2	44.0	96.54	65.54
9/19	8.972	54.6	46.6	95.74	74.45
9/22	8.978	55.8	49.8	95.46	80.66
9/23	9.028	56.0	51.0	94.99	83.83
9/26	9.082	54.7	50.8	90.19	86.83
9/27	10.340	55.1	52.8	53.72	92.28
9/29	11.400	55.8	53.8	39.98	93.35
9/30	12.492	55.6	54.3	31.60	95.45
Desorption					
10/1	11.562	54.8	53.1	39.39	93.77
10/3	9.952	"	51.8	61.34	90.31
10/5	9.032	55.8	49.6	92.35	79.82
10/6	9.004	56.0	47.9	93.91	73.95
10/7	8.972	55.6	43.0	95.68	63.94

Table IX
(continued)

Balance 4

Date	Spring Length(cm) Desorption	Temperature Top	Temperature Bottom	Percent Soap	RVP
10/8	8.964	54.7	39.8	96.25	56.43
10/9	8.947	54.8	32.4	97.18	42.19
10/10	8.944	54.8	30.2	97.30	38.44
10/11	8.938	54.3	24.7	97.59	30.57
10/12	8.934	54.4	23.7	97.82	29.20

but is noticeable at about 60% RVP.

The 65, 70, and 75° Isotherms (Figures 23, 24, and 25; Tables XI, XII, and XIII)

These three isotherms are almost identical. It is to be noted that with an increase in temperature more cyclohexane is sorbed and the shape of the curve changes gradually. The sharp break noted for balance 4 in the 50° isotherm has changed to a more gradual curve.

Hysteresis is not apparent for the 65 and 70° isotherms and is only slightly noticable for the 75° isotherm. The point at about 37% RVP for balance 4 for the 70° isotherm on the sorption run must be due to an error in reading the cathetometer, since it can be explained no other way.

The 80, 85, and 90° Isotherms (Figures 26, 27, and 28; Tables XIV, XV, and XVI)

The 80 and 85° isotherms are almost exactly alike in appearance, however the 85° isotherm shows much more hysteresis. This is especially noticeable for balance 4. In Figure 26 it will be noted that hysteresis extends over a very large part of the isotherm. This hysteresis is greater than that shown for any of the pervious isotherms run with this balance and it is seen to extend from about 30% RVP to the maximmm RVP reached. This may have been due to failure to allow sufficient time for equilibrium. The higher isotherm temperature requires a larger change in temperature to cause a small change in vapor pressure. This would require a longer time for equilibrium to be established and as a result the hysteresis would be more noticeable. The large temperature difference between the room temperature and the isotherm temperature lowers slightly the maxinum RVP that can be obtained for spring length measurements since this large temperature difference causes greater heat loss through the windows in the upper thermostat

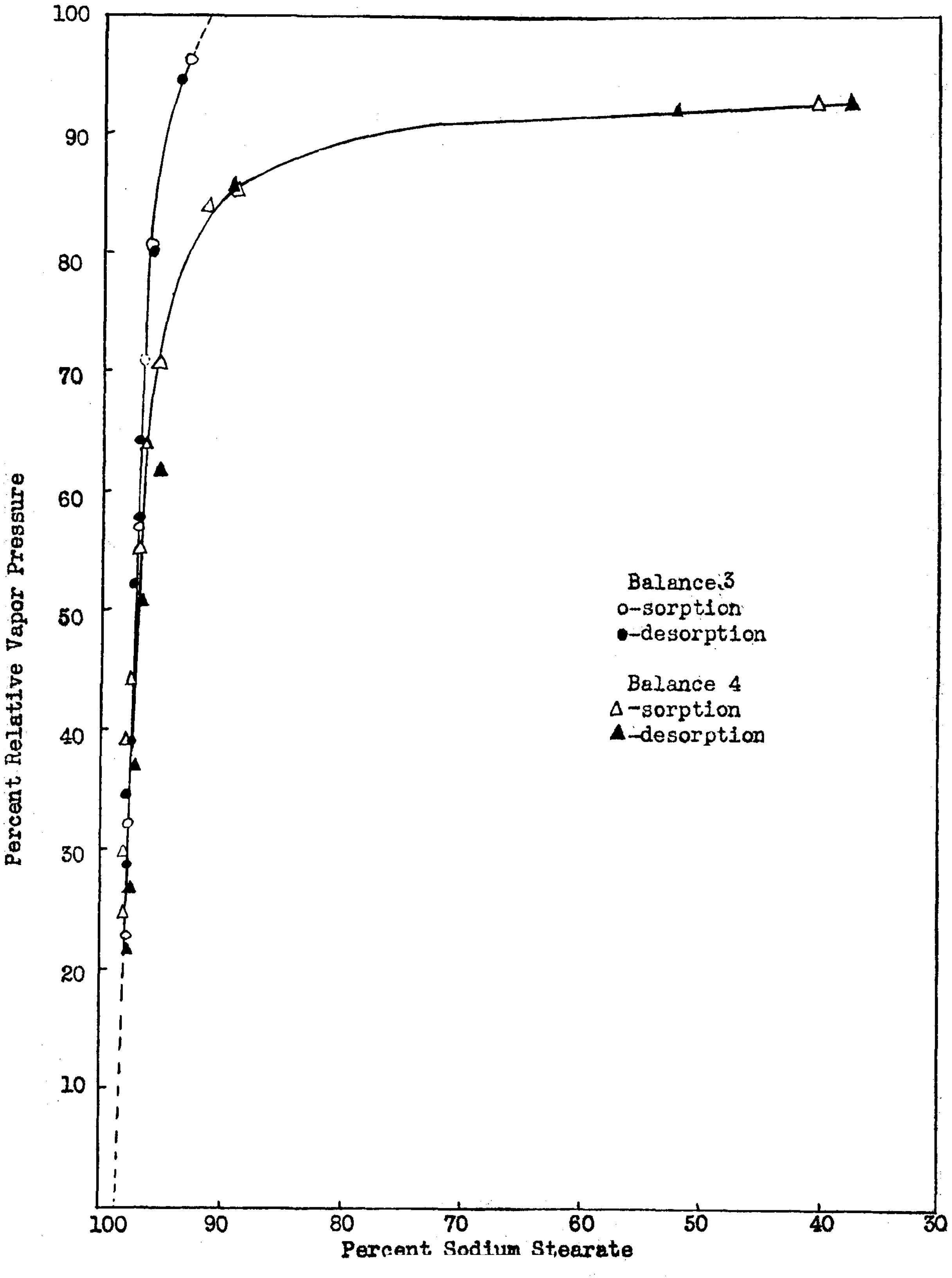


Figure 22
The 60° Isotherm

Table X

The 60° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C.		Percent Soap	RVP
	Top	Bottom		
Sorption				
11.742	60.6	23.2	97.90	22.96
11.744	60.5	30.7	97.81	32.22
11.760	59.0	43.9	97.12	57.14
11.786	59.3	53.1	96.04	80.48
11.864	60.0	58.9	92.90	96.10
11.756 (not used)	58.5	39.4	97.32	48.90
11.772 (not used)	58.7	48.9	96.64	70.88
Desorption				
11.846	59.5	57.9	93.60	94.45
11.788	60.5	54.2	95.96	80.05
11.772	60.0	47.7	96.64	63,90
11.774	59.8	46.3	96.56	60.73
11.764	60.3	45.4	96.96	57.58
11.754	60.6	43.1	97.41	52.42
11.742	60.3	35.2	97.90	38.82
11.742	61.0	33.0	"	34.59
"	60.0	27.5	"	28.57
11.736	59.5	20.7	98.35	21.16

Balance 4

Spring Length (cm)	Temperature, °C.		Percent Soap	RVP
	Top	Bottom		
Sorption				
8.928	60.0	23.7	98.12	23.90
"	60.2	28.7	"	29.64
8.932	60.0	35.1	97.88	38.96
8.938	60.7	38.8	97.53	43.94
8.948	60.0	43.8	96.94	55.06
8.956	"	47.8	96.54	63,90
8.978	60.2	51.1	95.40	70.52
9.052	59.5	54.5	91.41	83.86
9.104	61.0	56.4	88.90	84.96
11.364	60.0	57.9	40.25	92,47
12.104	59.7	59.7	34.12	100.00
Desorption				
11.680	60.0	57.8	37.38	92.47
10.432	59.8	57.4	52.09	91.87
9.102	59.2	54.7	89.00	85.29
8.980	60.0	46.8	95.29	61.56
8.954	59.0	40.8	96.65	50.67
8.942	59.0	32.9	97.35	36.93
8.936	60.4	26.5	97.71	26.67
8.932	59.5	21.0	97.88	21.43

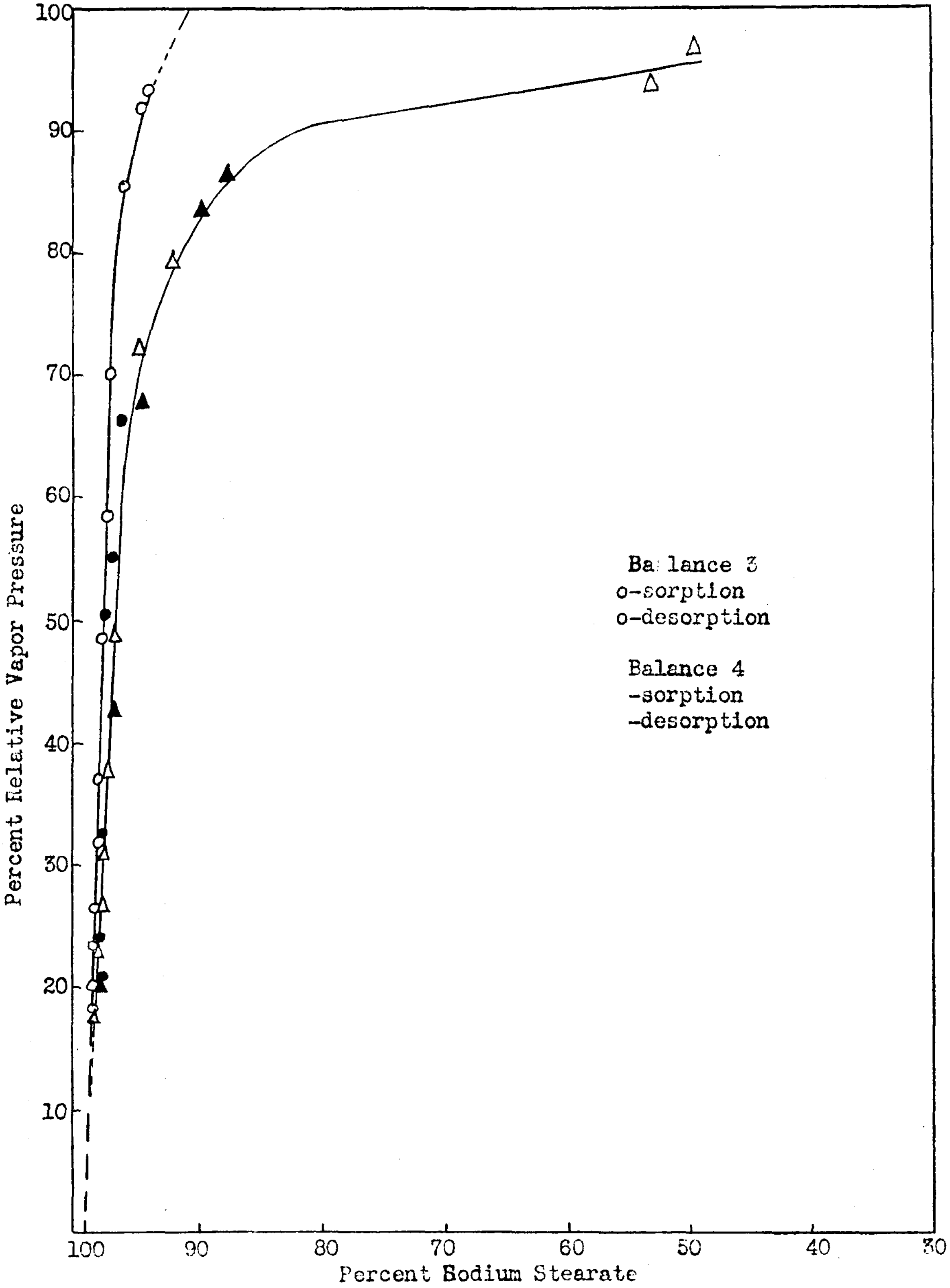


Figure 23
The 65° Isotherm

Table XI

The 65° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption				
11.724	64.5	21.4	98.60	18.31
11.726	65.3	27.4	98.52	23.29
11.728	65.5	30.3	98.44	26.40
11.734	65.7	35.1	98.19	31.91
11.736	64.3	37.5	98.10	36.83
11.740	65.5	45.6	97.90	48.50
11.748	64.7	49.6	97.32	58.37
11.754	64.0	53.9	97.08	69.98
11.776	64.5	60.8	96.16	85.16
11.808	65.7	63.1	94.83	91.49
11.826	64.0	61.9	94.10	93.00
Desorption				
11.778	65.4	53.7	96.08	66.24
11.764	64.7	48.9	96.88	55.54
11.746	65.5	46.0	97.65	50.43
11.744	64.5	34.4	97.73	32.45
11.736	64.5	27.2	98.10	24.00
11.740	"	24.2	97.90	20.89

Balance 4

Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption				
8.924	65.5	21.7	98.06	18.03
8.928	65.7	24.7	97.82	20.43
8.930	66.0	27.2	97/71	22.78
8.934	64.5	29.7	97.53	26.67
8.936	64.0	32.8	97.41	30.93
8.938	66.0	39.3	97.29	37.34
8.944	64.0	44.3	96.94	48.53
8.954	64.0	47.0	96.54-	53.95
8.980	64.2	54,9	95.01	71.97
9.034	65.0	58.2	92.25	78.82
10.350	65.0	63.0	53.42	93,45
10.588	66.0	65.0	49,62	96,63
Desorption				
9.124	65.4	61.0	87.93	86,21
9.082	65.0	59.8	89.89	83.40
8.994	66.0	54.9	94.45	67.72
8.944	65.0	41.8	96.94	42.58
8.924	64.0	23.7	98.06	19.86

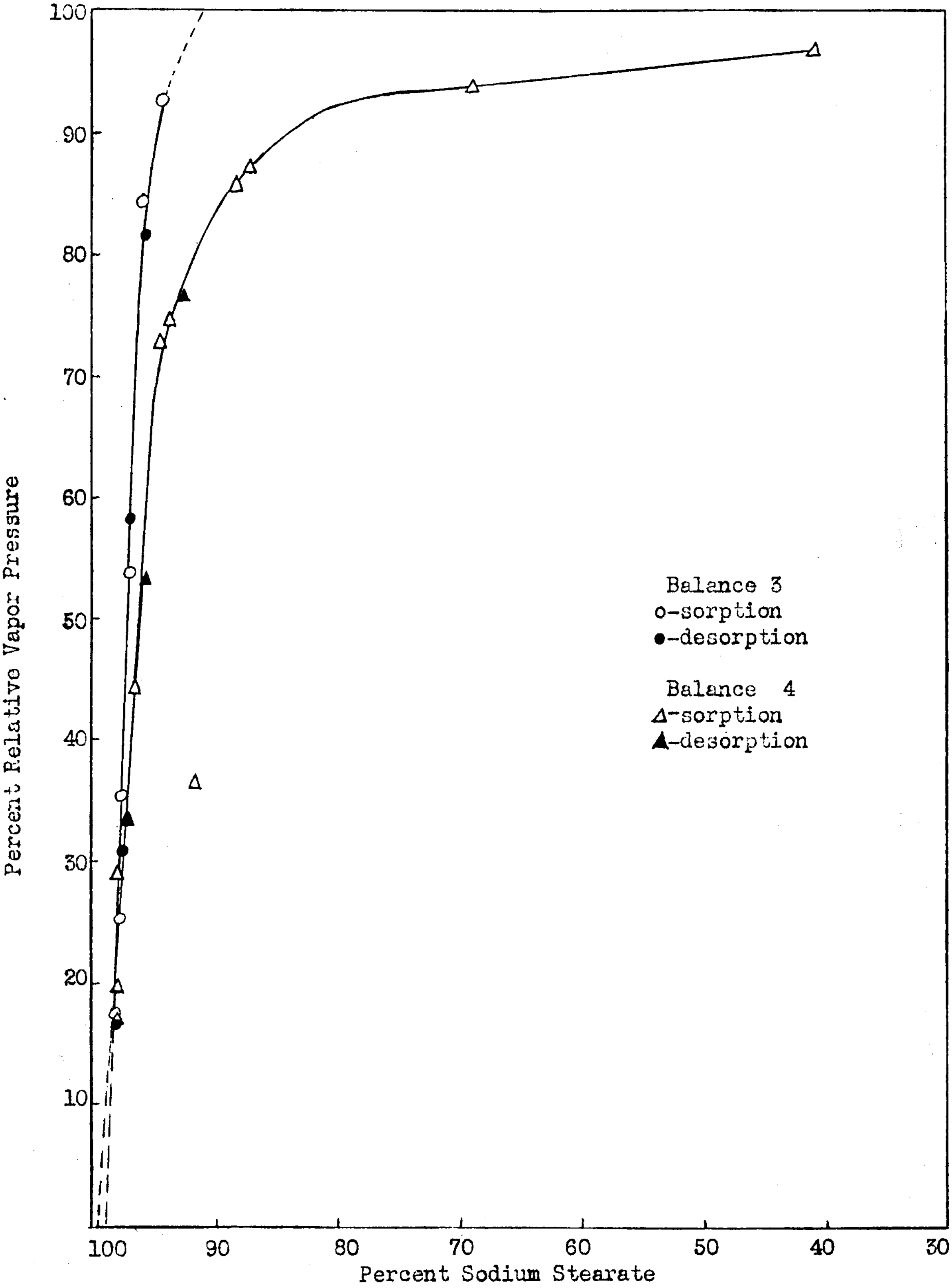


Figure 24
The 70° Isotherm

Table XII

The 70° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption				
11.726	69.5	24.2	98.27	17.67
11.736	69.7	32.4	97.79	25.19
11.742	70.7	43.6	97.57	37.91
11.748	69.0	51.3	97.28	53.82
11.776	"	63.9	96.12	84.35
11.812	68.5	66.3	94.63	92.64
Desorption				
11.784	70.9	64.8	95.76	81.54
11.754	70.5	54.8	97.04	58.18
11.742	69.5	37.5	97.57	30.96
11.726	69.8	24.2	98.27	16.88
Balance 4				
Sorption				
8.920	70.0	23.9	98.24	17.19
8.928	71.0	27.7	97.76	19.82
8.926	69.8	35.8	97.88	28.81
9.038	70.2	43.6	91.98	36.46
8.944	71.0	47.9	96.89	44.39
8.982	70.3	60.8	94.84	72.53
8.994	71.0	62.2	94.23	74.29
9.106	69.7	65.0	88.51	85.45
9.126	70.1	66.0	87.60	87.13
9.632	69.0	67.0	69.26	93.51
11.264	70.0	69.0	41.21	96.86
Desorption				
9.018	71.0	63.0	92.99	76.43
8.962	69.0	50.9	95.91	53.05
8.934	"	38.9	97.47	33.21
8.920	71.0	24.4	98.24	16.96

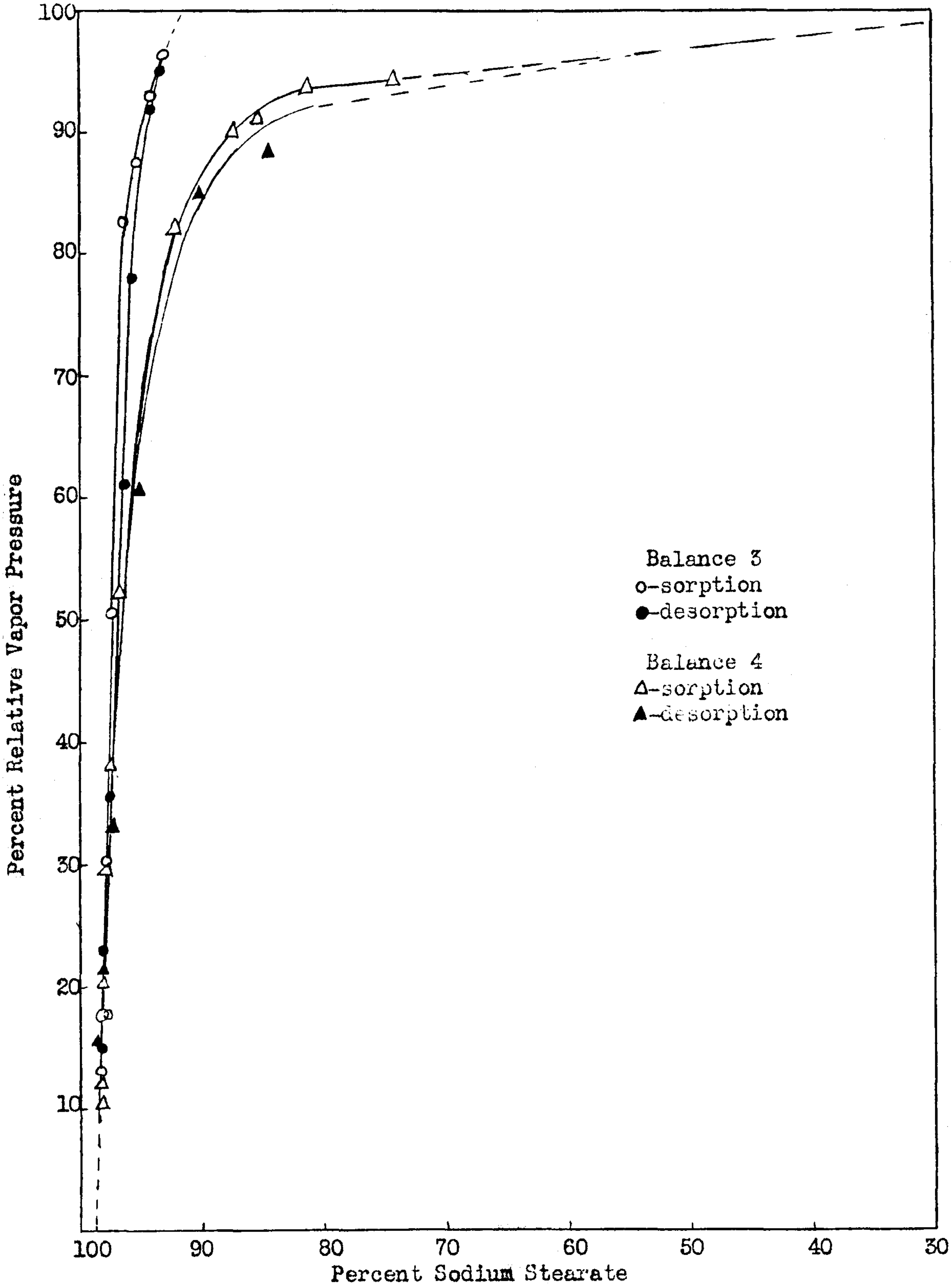


Figure 25
The 75° Isotherm

Table XIII

The 75° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C. Top	Temperature, °C. Bottom	Percent Soap	RVP
Sorption				
11.718	75.5	22.2	98.31	13.14
11.720	74.5	28.0	98.23	17.86
11.730	75.3	41.6	97.82	30.17
11.738	75.8	55.6	97.45	50.54
11.768	75.0	69.1	96.20	82.73
11.792	75.5	71.4	95.17	87.48
11.816	"	73.2	94.21	93.05
11.844	74,5	73.4	93.08	96.49
11.				
Desorption				
11.840	74.2	72.7	93.27	95.33
11.820	73.8	71.2	94.06	91.86
11.784	75.5	67.8	95.53	77.90
11.766	"	60.7	96.26	61.05
11.738	75.0	45.6	97.45	35.48
11.730	75.5	34.7	97.82	22.87
11.720	75.0	24.2	98.23	14.76

Balance 4

Spring Length (cm)	Temperature, °C. Top	Temperature, °C. Bottom	Percent Soap	RVP
Sorption				
8.916	74.0	16.7	98.18	10.52
8.916	75.3	20.2	98.18	12.13
8.920	76.0	32.1	97.94	20/24
8.926	74.3	40.3	97.59	29.54
8.932	75.7	47.9	97.30	38.10
8.944	76.2	57.0	96.60	52.35
9.026	74.3	68.3	92.30	81.99
9.128	"	71.0	87.27	89.89
9.168	75.0	72.0	85.52	91.05
9.270	76.0	73.8	81.35	93.45
9.466	75.9	73.9	74.25	94.05
Desorption				
9.190	76.0	72.0	84.58	88.28
9.064	76.3	71.0	90.24	84.47
8.968	75.0	60.0	95.12	60.44
8.930	75.7	44.3	97.41	33.03
8.926	74.9	32,8	97,59	21.61
8.916	74.2	24.9	98.18	15.62

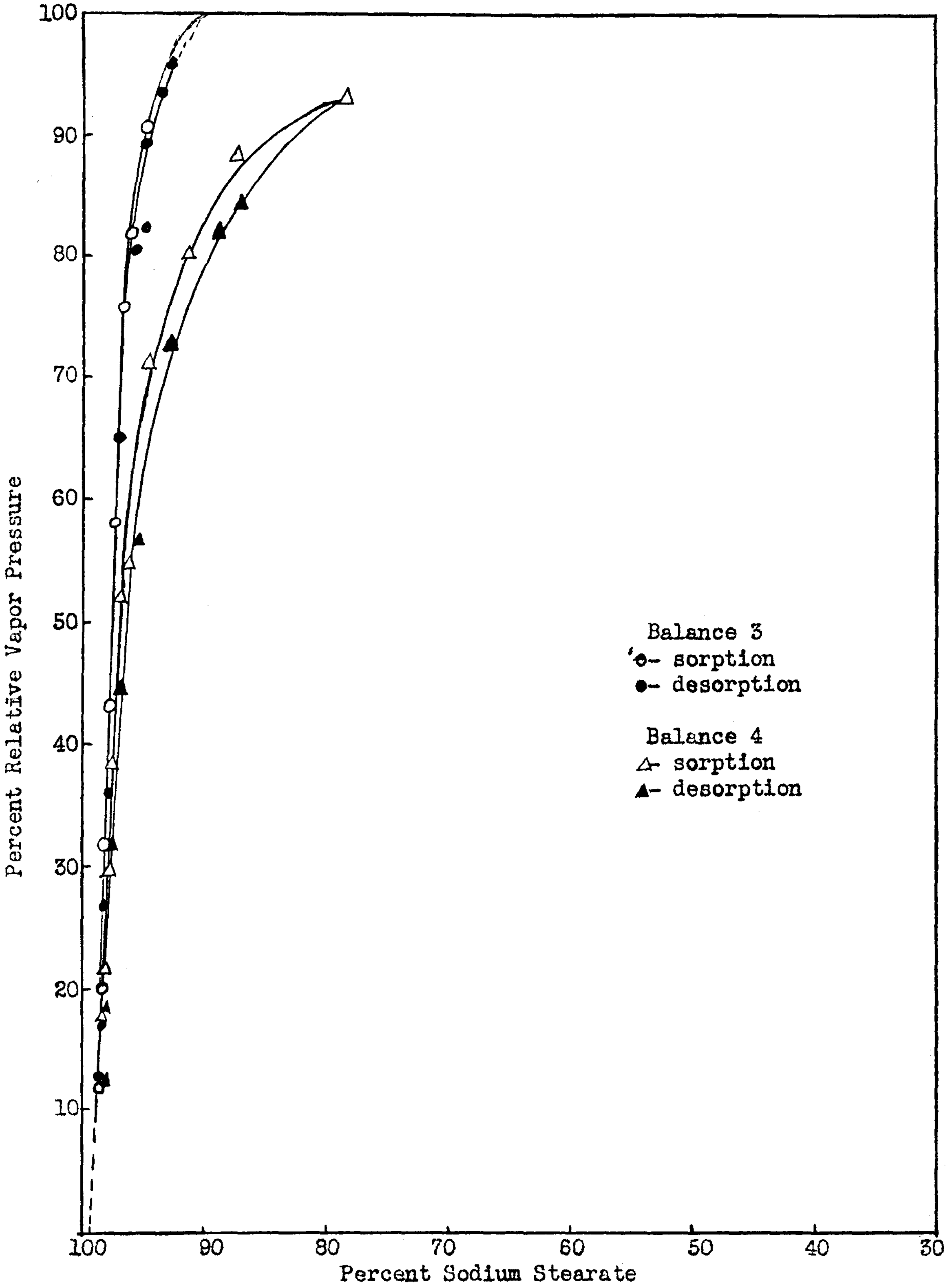


Figure 26
The 80° Isotherm

Table XIV

The 80° Isotherm

Spring Length (cm)	Balance 3 Temperature, °C. Top	 Bottom	Percent Soap	RVP
Sorption				
11.716	80.2	23.2	98.56	12.06
11.720	79.5	34.4	98.35	20/00
11.724	"	45.6	98.19	31.68
11.732	"	54.5	97.86	43.29
11.744	"	62.9	97.32	58.36
11.764	80.5	71.7	96.48	76.20
11.778	80/3	73.7	95.88	81.82
11.806	79.5	76.50	94.65	90.69
11.832	"	77.2	93.61	93.42
11.850	80.5	79.0	92.97	95.62
Desorption				
11.804	79.5	73.2	94.83	82.47
"	"	75.7	"	89.32
11.784	79.2	72.3	95.64	80.52
11.760	79.3	65.9	96.64	65.01
11.736	79.5	49.4	97.69	35.89
11.728	80.0	42.6	98.02	26.76
11.720	79.1	30.2	98.39	17.04
11.714	79.0	23.2	98.64	12.50
11				
	Balance 4			
Sorption				
8.912	80.0	23.7	98.36	12.43
8.916	79.7	31.5	98.12	17.69
8.918	80.0	36.7	98.00	21.62
6.924	"	44.8	97.65	29.60
8.928	"	51.5	97.47	38.38
8.938	80.1	60.0	96.89	51.75
8.952	81.0	63.5	96.14	54.45
8.982	79.7	69.0	94.51	71.29
9.042	80.2	73.0	91.26	80.16
9.126	80.0	75.7	87.32	88.11
9.278	80.3	77.8	78.39	92.91
Desorption				
9.134	81.0	75.3	86.99	84.16
9.096	80.5	74.0	88.71	81.94
9.010	80.1	70.0	92.88	72.78
8.960	79.7	62.2	95.46	56.60
8.938	80.5	56.0	96.89	44.36
8.932	79.3	45.8	97.24	31.40
8.920	79.1	31.9	97.88	18.28
8.914	80.0	24.2	98.24	12.70

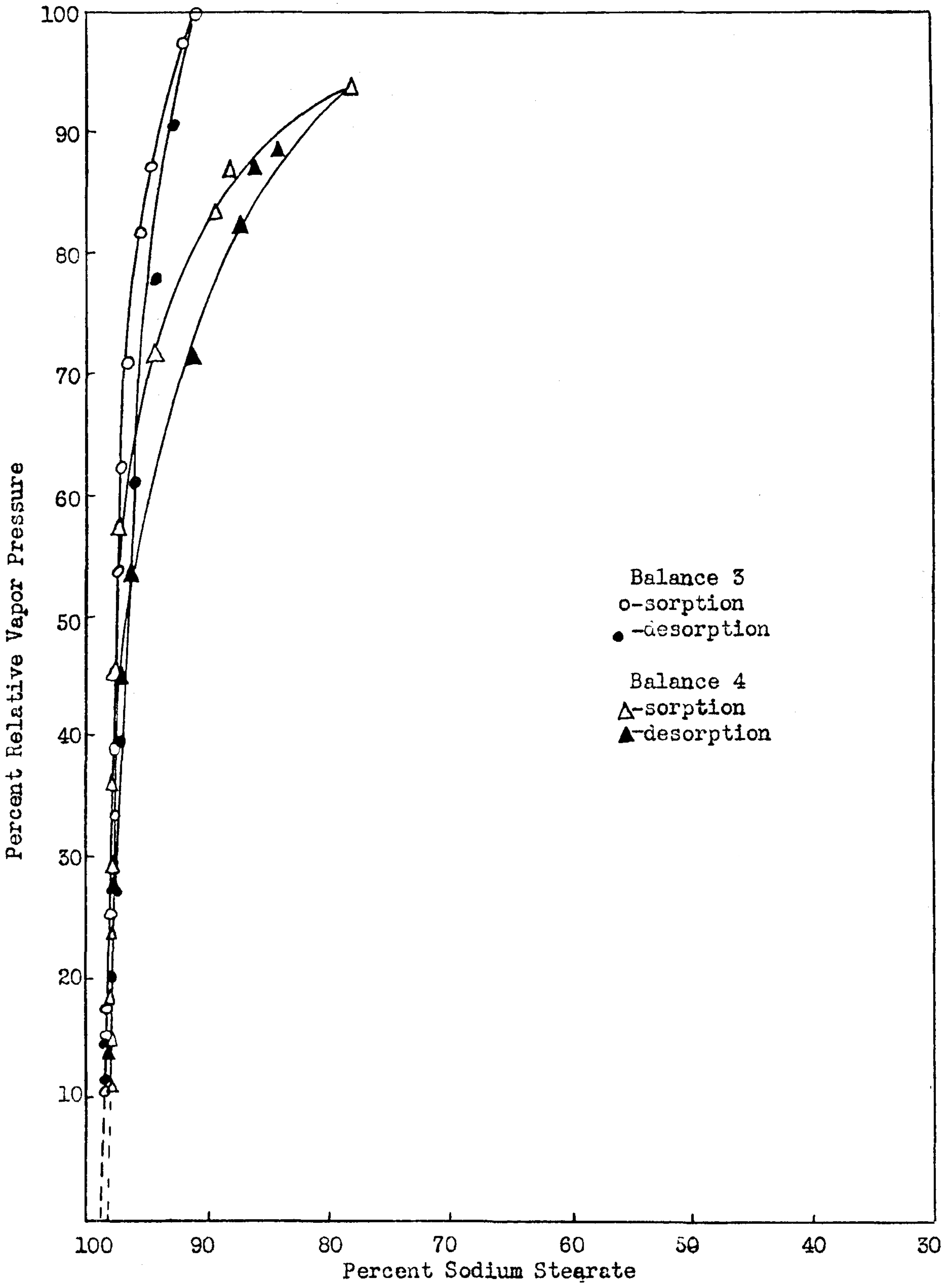


Figure 27
The 85° Isotherm

Table XV

The 85° Isotherm

Balance 4

Spring Length (cm)	Temperature, oC. Top	Bottom	Percent Soap	RVP
Sorption				
8.908	84.6	23.7	98.48	10.76
8.910	85.1	30.9	98.36	14.68
"	85.0	35.7	"	17.87
8.912	86.0	43.8	98.24	23.71
8.918	"	48.8	97.88	28.88
8.922	85.0	55.2	97.65	37.70
8.928	"	60.3	97.35	45.01
8.942	"	67.0	96.54	56.84
8.982	85.8	74.8	94.40	71.40
9.078	85.0	78.9	89.44	83.18
9.102	85.0	80.3	88.32	86.77
9.344	84.1	82.0	78.32	93.59
Desorption				
9.182	86.0	82.0	84.40	88.54
9.152	84.5	79.8	86.11	86.82
9.120	84.7	78.0	81.88	87.51
9.002	85.1	74.0	93.15	71.28
8.944	85.0	65.0	96.42	53.13
8.936	"	60.0	96.89	44.66
8.918	86.0	47.6	97.88	27.42
8.914	84.8	36.9	98.12	18.72
8.912	85.0	29.7	98.24	13.92
8.910	84.8	25.7	98.36	11.74

Balance 3

Spring Length (cm)	Temperature, oC. Top	Bottom	Percent Soap	RVP
Sorption				
11.708	84.5	23.2	98.64	10.59
11.710	84.5	31.2	98.56	15.03
11.714	85.0	35.1	98.35	17.40
11.720	84.5	44.1	98.10	25.18
11.730	84.7	51.6	97.65	33.33
11.730	84.5	55.8	97.65	39.06
11.736	"	64.8	97.40	53.53
11.742	85.0	69.7	997.16	62.32
11.756	84.5	73.2	96.56	70.82
11.780	84.4	77.8	95.57	81.65
11.794	84.5	80.0	94.98	87.06
11.864	84.8	83.8	92.20	97.44
11.888	84.5	84.7	91.29	101.2

Table XV
(Continued)

The 85° Isotherm

Spring Length (cm)	Balance 3 Temperature, °C. Top	 Bottom	Percent Soap	RVP
Desorption				
11.848	84.9	81.8	92.82	90.83
11.806	84.5	76.2	94.48	77.88
11.768	84.0	68.2	96.04	60.95
11.744	"	60.9	97.05	39.52
11.730	84.5	46.2	97.65	27.29
11.722	"	41.4	98.02	22.59
11.710	85.5	31.2	98.56	14.83
"	84.7	25.2	98.56	11.54
11.708	84.0	23.2	98.64	10.71

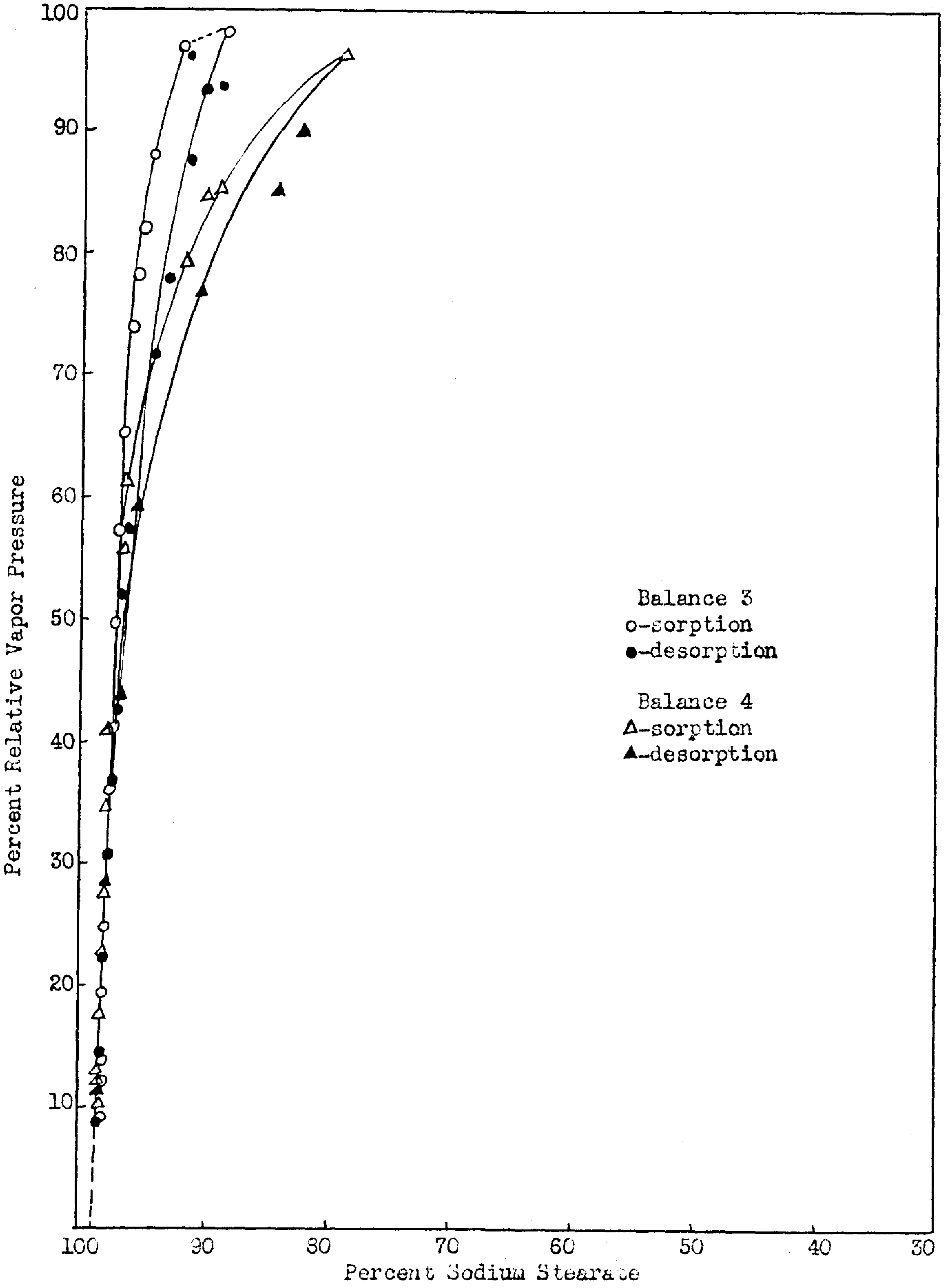


Figure 28
The 30° Isotherm

Table XVI

The 90° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption				
11.704	89.0	22.9	98.52	9.27
11.708	"	28.7	98.35	12.08
"	89.2	32.7	"	14.09
11.706	90.7	41.9	98.44	19.44
11.712	90.9	48.3	98.19	24.90
11.720	90.0	57.7	97.81	36.17
11.724	90.5	61.8	97.65	41.00
11.728	90/2	67.1	97.49	49.45
11.736	90.5	71.7	97.12	57.20
11.742	"	75.8	96.88	65,30
11.754	"	80.1	96.36	74.20
11.770	89.0	80.4	95.72	78.12
11.780	89.6	82.6	95.30	81.97
11.798	90.2	85.6	94.56	87.94
11.856	89.4	88.2	92.05	96.81
Desorption				
11.868	89.2	87.8	91.58	96.37
11.946	90.2	88.0	88.72	93.77
11.954	89.3	88.5	88.42	97.94
11.910	89.8	87.5	90.02	93.69
11.876	89.5	84.7	91.29	87.56
11.828	90.5	81.6	93.34	77.80
11.804	90.4	78.8	94.33	71.50
11.758	89.1	70.7	96.20	57.41
11.746	89.3	67.7	96.72	51.86
11.734	90.7	63.1	97.24	42.66
11.726	90.3	58.6	97.57	36.71
11.718	89.5	53.0	97.94	30.83
11.712	89.2	44.3	98.19	22.28
11.704	90.3	34.4	98.52	14.64
11.700	90.5	24.0	98.73	9.30

Table XVI
(continued)
The 90° Isotherm

Spring Length (cm)	Balance 4 Temperature, °C.		Percent Soap	RVP
	Topp	Bottom		
Sorption				
8.900	89.7	25.7	98.60	10.31
8.904	90.0	29.5	98.36	12.02
8.900	89.2	31.0	98.60	13.16
8.902	89.5	38.5	98.48	17.68
8.904	89.0	44.6	98.36	22.71
8.906	90.9	50.8	98.30	27.37
8.908	"	57.2	98.18	34.39
8.914	91.0	62.0	97.82	40.79
8.932	90.8	71.0	96.83	55.45
8.936	90.7	74.0	96.60	61.21
9.032	90.5	82.3	91.62	79.30
9.058	89.0	83.0	90.14	84.58
9.080	90.7	85.0	89.10	85.32
9.322	89.6	87.8	78.89	96.31
Desorption				
9.244	89.7	86.0	82.01	90.10
9.190	89.0	83.2	84.23	85.21
9.050	89.2	80.0	90.54	76.79
8.952	89.0	71.4	95.74	59.06
8.928	"	62.5	97.06	43.75
8.908	89.7	51.2	98.18	28.67
"	"	38.7	"	17.65
8.898	90.7	29.2	98.72	11.71
"	"	22.7	"	8.73

and hence the cyclohexane condenses an the silica spring more readily at pressures close to saturation, thus voiding any possible measurements.

In Figure 27 (Table XV), it is seen that a RVP of 101.2 was reached. No vapor condensation was abserved so it is assumed that this was caused by a sudden temperature change and since the soap composition is about where it should be for 100% RVP, the point is plotted as such. The soap composition for balance 4 was, as usual, much less than that for balance 3 at the highest RVP reached.

The 90° isotherm (Figure 28) shows a large amount of hysteresis for balance 3; more so than for any previous isotherm with this balance. An almost horizonal portion is apparent at the highest RVP reached, but insufficient data was obtained to indicate clearly any possible phase change. The hysteresis curve for balance 4 shows that for the area in question some change may have occured, but more data will have to be obtained for proof of this.

The 95° Isotherm (Figure 29; Table XVII)

This was the first isotherm in which a definite phase change was observed, both graphically and visually.

Balance 3 does not show this phase change very clearly. The necessary flat portion indicating a phase change is change is absent, probably because too large an inrrement of pressure was taken before the phase area was reached. The highest RVP obtained (before condensation of vapor on the spring) corresponded to a soap compostition of about 78%. The desorption curve is seen to be a straight line above 80% RVP. If it is considened that the soap has a great affinity for cyclohexane in this probable phase area, then the desorption would be very slow and the time requred for the soap to become "Gel--Crystal and

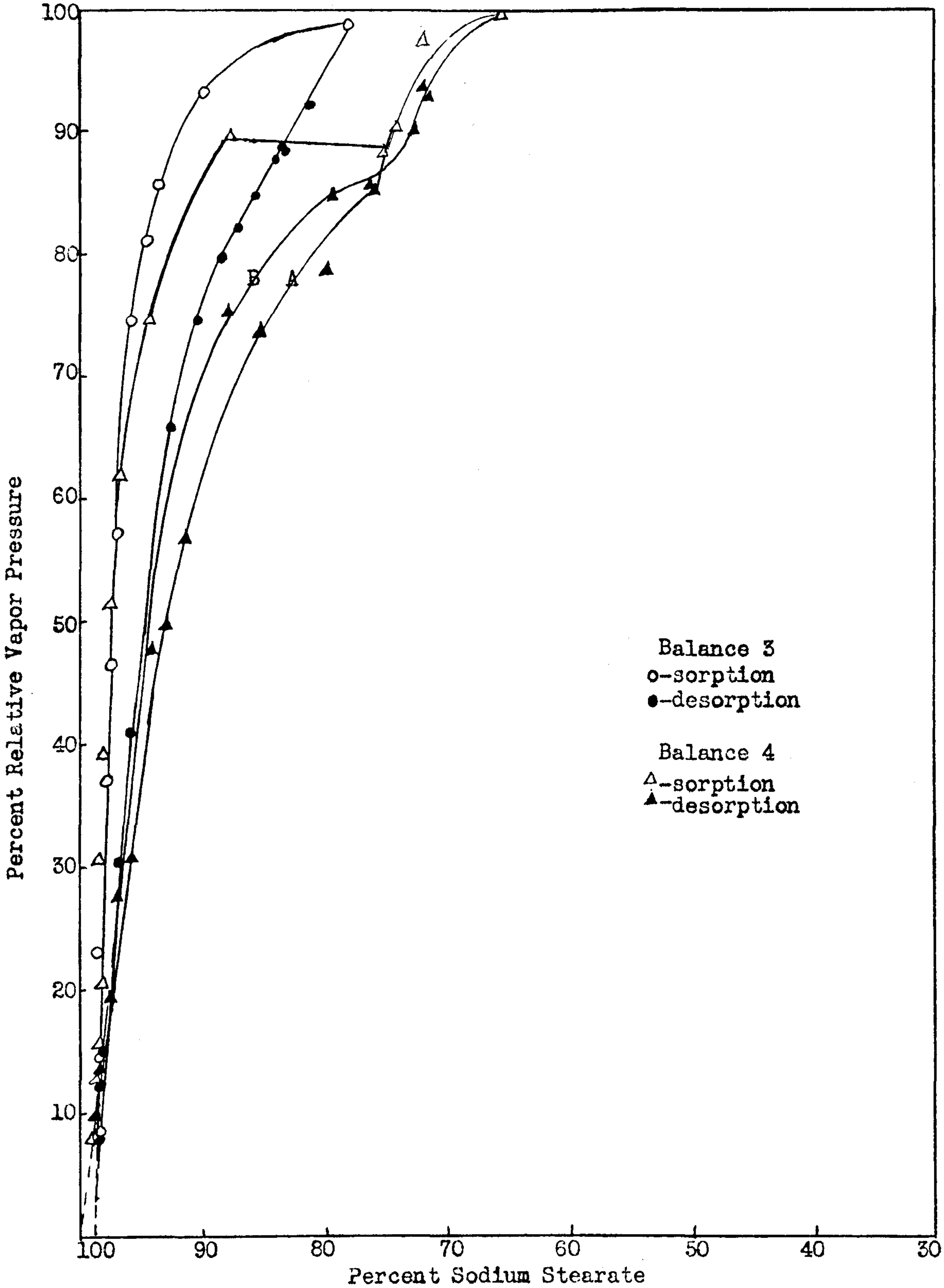


Figure 29
The 95° Isotherm

Table XVII

The 95° Isotherm

Balance 3

Spring Length (cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption				
11.694	93.7	24.4	98.77	8.68
11.696	95.0	36.8	98.69	14.18
11.700	95.7	48.8	98.52	22.16
11.714	94.5	62.0	97.90	36.96
11.722	94.7	68.8	97.52	46.40
11.734	95.0	75.2	97.04	56.56
11.764	95.0	84.4	95.76	74.45
11.790	94.5	86.9	94.67	80.98
11.814	95.0	90.2	93.72	85.67
11.911	"	92.5	89.92	93.39
12.280	94.5	93.9	78.04	98.49
Desorption				
12.173	95.0	92.0	81.12	92.07
12.104	94.5	90.0	83.23	88.39
12.084	95.5	90.7	83.89	87.83
12.090	94.8	90.5	83.68	88.65
12.032	95.5	89.5	85.59	84.61
11.990	95.8	88.5	87.09	81.90
11.956	95.5	87.2	88.28	79.57
11.898	95.5	84.2	90.37	74.01
11.842	95.2	80.3	92.60	65.73
11.759	94.1	64.8	95.96	40.99
11.738	94.0	56.3	96.84	30.50
11.720	95.4	42.4	97.61	17.42
11.711	94.7	33.4	98.02	12.44
11.703	95.4	23.2	98.35	7.84
11.706	94.7	22.0	98.23	7.56

Balance 4

Spring Length (cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption				
8.890	95.4	23.7	99.03	8.00
8.898	94.7	33.7	98.60	12.62
8.894	94.5	38.9	98.78	15.54
8.894	94.0	45.8	98.78	20.67
8.896	94.7	57.0	98.66	30.67
8.906	95.7	64.8	98.12	39.21
8.916	94.7	72.0	97.41	51.56
8.928	94.9	78.0	96.77	61.77
8.976	95.5	85.0	94.18	74.65
9.106	94.0	90.0	87.74	89.76
9.426	95.7	91.2	75.15	88.08

Table XVII
(Continued)
The 95° Isotherm

Balance 3

	Spring Length (cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Desorption					
	9.402	94.7	89.0	75.96	85.33
	9.292	95.7	87.0	79.90	78.58
	9.164	94.7	83.5	85.20	73.51
	9.029	95.7	76.0	91.52	56.74
	8.998	94.7	70.8	93.04	49.42
	8.944	94.7	58.5	95.91	30.76
	8.915	"	44.3	97.59	19.11
	8.902	95.1	32.7	98.30	12.02

Additional Points

	Spring Length (cm)	Temperature Top	Temperature Bottom	Percent Soap	RVP
Sorption					
	9.458	94.2	90.5	74.12	90.09
	9.520	95.7	94.8	72.17	97.40
	9.743	96.2	96.0	65.72	99.40
Desorption					
	9.524	95.7	93.3	71.91	93.68
	9.544	94.7	92.0	71.43	92.89
	9.504	94.7	91.0	72.65	90.04
	9.390	94.7	89.0	76.39	85.33
	9.300	95.0	89.0	79.59	84.58
	9.116	94.7	84.3	87.32	75.11
	8.969	94.0	69.0	94.34	47.51
	8.922	95.7	54.8	96.89	27.63
	8.892	94.2	35.4	98.90	13.69
	8.890	95.7	26.9	99.02	9.41

Sol" would be very great. However, if readings were made regularly over small intervals of time, a straight line would be obtained until the phase of definite vapor pressure were passed through and the curve would then be slightly curved as the vapor pressure or the sample depended upon the amount of cyclohexone sorbed. The desorption curve becomes curved at about 87.5% soap so it is assumed that the boundries of the probable phase region are between 78- 87.5% soap.

Balance 4 shows a sharp break at 90% RVP between 87.74 and 75.15% soap. This is the type of curve that should be obtained for a phase change when the phase rule applies. The desorption curve marked A was obtained by returning to the lowest RVP obtainable after the flat horizoral portion of the curve was obtained. The values are given in Table XVLL. It was decided to investigate further this isotherm with balance 4 and these values are given in the table as "additional points".

The pressure was raised to 90% RVP and the isotherm contiuned from this point. The shape of this curve above 90% RVP is to be noted since other isotherms which show a probable phase change exhibit this type of curve on the boundry of lowest soap composition. The desorption curve B does not follow the same path as the desorption curve A. This is due to the fact that the curve was begun at a different point and also a fewer number of points were obtained. Once the two desorption curves are beyond the probable phase area they are identical. This shows the importance of time and pressure on the desorption values obtained in the phase area. On both desorption curves, regardless of the vapor pressure, it is seen that points are located at about 79.5% soap.

Observation of the soap sample in balance 3 showed that a distinct and definite change in the sample had accured slightly beyond the highest RVP reached. The sample appeared swollen. It was waxy in appearance and district crystals had formed. The crystals on the surface on the sample (those visible) were long and they tapened to a point. They were very white in color and translucent. This was observed when the sample was at an RVP at which cyclohexane condensed on the spring and the soap composition was less than about 75%. This was apparently the tip of the white waxy liquid-crystalline phase.

The 101° Isotherm (Figure 30; Table XV111)

This isotherm does not show any flat portions, but it is evident that some change occured in the soap between 86.9 and 74.9%.

Both balances show the same type of curve as that obtained for the 95° isotherm after the phase change. Both balances have points plotted on the sorption curve at about 80% soap which show that it is possible that two phase areas were encountered between 86.9 and 74.9% soap and that the tip which seperates them is between about 81.5-79.5% soap. The desorption values obtained for balance 4 indicates that these values may have been obtained in a phase area where desorption is extremely slow. From the shape of the curves at about 75% soap it is concluded that a phase change occured between 79-75% soap.

The 110° Isotherm (Figure 32) Table XIX

This isotherm like many others, shows no hysteresis, although the readings were made at irregular intervals of time for balance 3. The isotherm is apparently completely reversible over its entire range of vapor pressure.

No flat portions were observed for the isotherm that was run

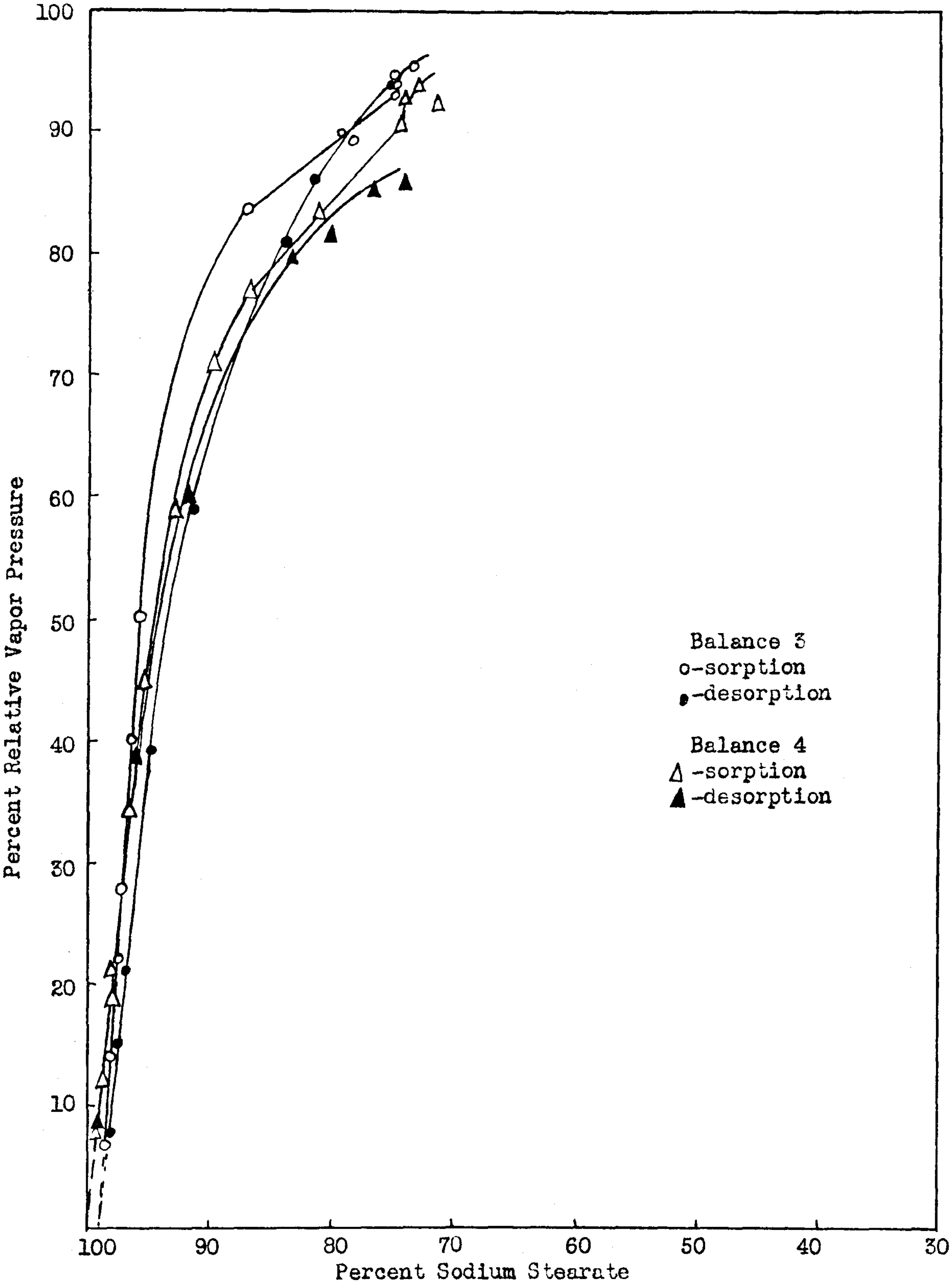


Figure 30
The 101° Isotherm

Table XVIII

The 101° Isotherm

Balance 3

	Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption					
	11.700	101.5	24.2	98.35	6.92
	11.708	100.5	40.4	97.98	13.99
	11.719	101.3	52.7	97.53	22.07
	11.724	101.0	59.1	97.28	27.76
	11.740	101.0	69.7	96.64	40.07
	11.760	101.2	76.8	95.76	50.04
	11.986	100.0	93.6	87.09	83.68
	12.225	100.8	97.0	79.48	89.89
	12.260	102.0	97.7	78.49	89.09
	12.380	100.3	98.2	75.19	94.68
	12.380	101.1	98.5	75.19	92.94
12	12.389	100.8	98.3	74.95	93.41
	12.454	101.0	99.2	73.32	95.37
Desorption					
	12.390	100.3	97.7	74.93	93.16
	12.152	101.3	95.3	81.63	84.81
	12.089	"	93.6	83.68	80.89
	11.868	100.5	81.8	91.47	59.24
	11.782	101.5	69.2	94.87	38.88
	11.735	100.0	50.7	96.84	21.15
	11.719	100.2	42.4	97.53	15.24
	11.706	101.2	26.3	98.10	7.65

Balance 4

	Spring Length (cm)	Temperature, °C. Top	Bottom	Percent Soap	RVP
Sorption					
	8.887	100.9	26.7	99.02	7.94
	8.894	101.7	37.2	98.60	11.94
	8.905	101.7	51.9	98.00	21.17
	8.926	100.1	64.2	96.83	34.05
	8.946	101.7	73.5	95.63	44.54
	8.998	100.0	81.0	92.88	58.54
	9.065	100.7	88.2	89.59	70.68
	9.125	101.8	92.1	86.76	76.64
	9.158	101.7	93.0	85.34	78.55
	9.258	100.7	94.0	81.14	83.08
	9.440	101.3	97.5	74.60	90.22
	9.450	100.9	98.0	74.25	92.51
	9.488	101.7	99.2	72.98	93.62
	9.508	101.5	99.0	72.36	93.59
	9.545	100.7	99.7	71.21	92.11

Table XVIII
(continued)
The 101° Isotherm

Spring Length (cm)	Balance Temperature, °C. Top	Balance Temperature, °C. Bottom	Percent Soap	RVP
Desorption				
9.449	101.7	97.0	74.22	87.91
9.280	100.7	93.2	80.30	81.20
9.374	101.7	95.7	76.83	84.84
9.200	100.2	92.0	83.57	79.65
9.018	100.7	82.3	91.88	59.70
8.938	100.7	68.0	96.14	38.12
8.902	100.9	48.1	98.18	18.66
8.884	100.0	26.7	99.20	8.12

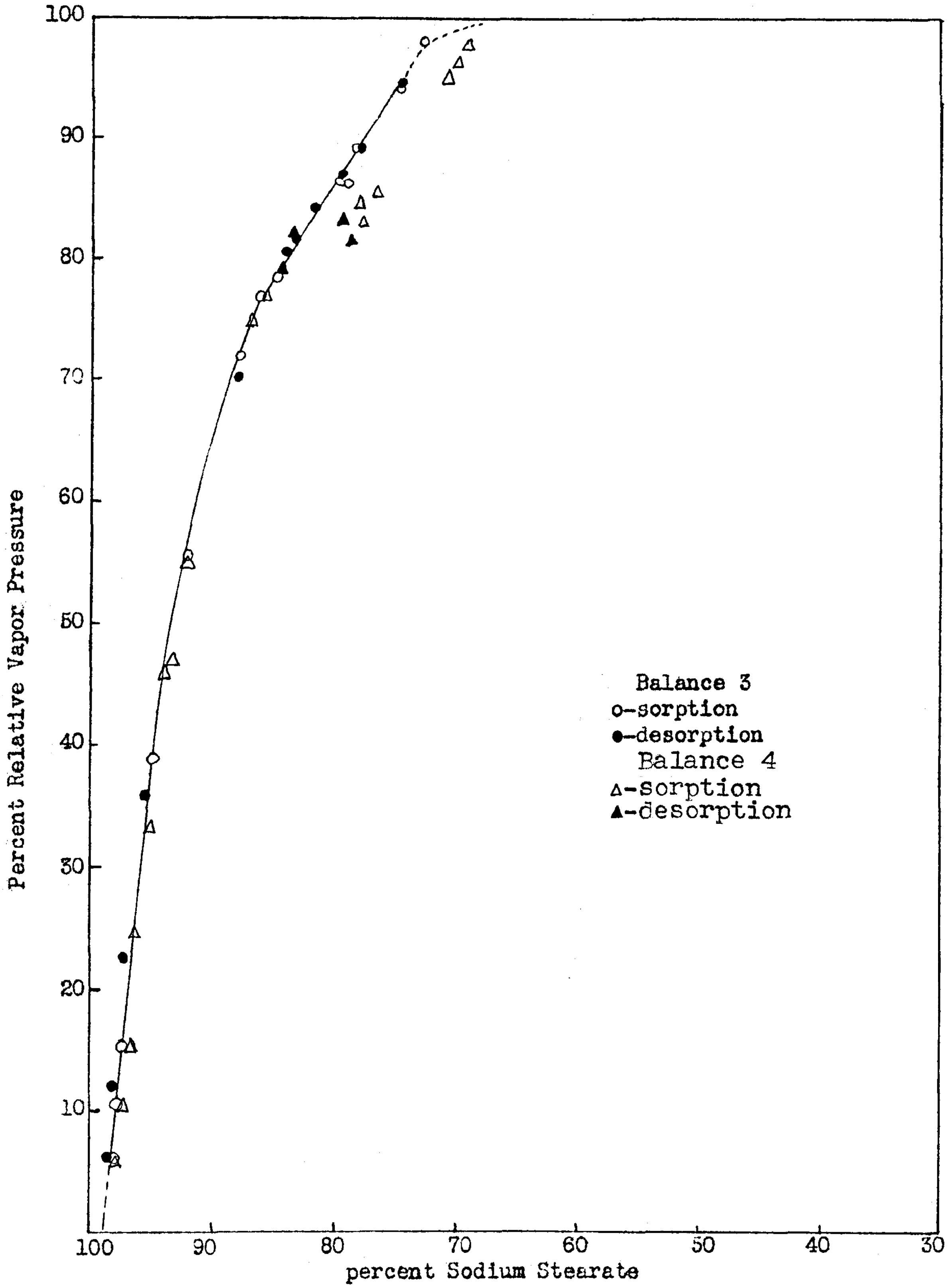


Figure 32
The 110° Isotherm

Table XIX

T
The 110° Isotherm

Balance 3

Spring Length (cm)	Temperature, °C.		Percent Soap	RVP	HOurs between readings
	Top	Bottom			
Sorption					
11.692	110.0	25.5	98.35	5.92	
11.704	109.0	38.5	97.82	10.40	14
11.712	109.8	48.6	97.45	15.22	11
11.726	110.8	59.9	96.88	22.16	15
11.772	111.0	76.8	94.94	39.12	12
11.840	110.4	88.5	92.13	55.59	10
11.958	111.0	98.2	87.78	71.97	16
12.000	110.2	100.0	86.32	76.99	21
12.042	111.0	101.4	84.93	78.53	11
12.204	110.8	105.2	79.84	86.52	18
12.226	109.8	104.4	79.21	86.26	24
12.256	109.9	105.2	78.36	89.29	18
12.388	110.7	108.5	74.76	94.02	12
12.468	110.8	110.0	72.77	97.69	47
Desorption					
12.392	109.9	107.5	74.66	94.50	22
12.270	110.6	106.0	77.96	89.18	47
12.212	111.0	105.2	79.62	87.06	18
12.132	110.5	103.4	81.97	84.12	24
12.084	"	102.2	83.47	81.47	11
12.066	"	101.9	84.04	80.59	13
12.042	110.3	100.7	84.93	78.56	11
11.950	"	97.0	88.05	70.88	14
11.752	"	73.5	95.76	35.85	19
11.718	110.8	60.5	97.20	22.69	42
11.696	109.3	41.9	98.15	11.84	20
11.686	111.0	25.9	98.60	5.92	19

Table XIX
(Continued)
The 110° Isotherm

Balance 4

Spring Length (cm)	Temperature, °C. Top	Temperature, °C. Bottom	Percent Soap	RVP	Hours betw een readings
8.872	110.2	25.7	97.88	5.69	
8.882	109.0	38.5	97.29	10.46	12
8.890	110.4	50.6	96.83	16.24	20
8.902	109.7	61.9	96.19	24.67	53
8.922	109.8	71.0	95.12	33.43	19
8.958	109.7	82.0	93.20	47.07	50
8.950	110.7	82.0	93.63	45.88	24
8.980	110.3	87.8	92.09	54.87	22
9.091	109.2	98.0	86.85	74.85	73
9.112	109.0	99.0	85.88	77.20	22
9.126	108.7	99.0	85.29	77.91	47
9.308	110.7	104.0	78.13	84.65	24
9.144	109.7	100.5*	84.54	79.04	51
9.318	109.4	102.0	77.75	83.13	21
9.230	108.9	101.0*	81.02	81.71	73
9.520	109.1	107.0	71.00	95.02	46
9.546	109.2	107.6	70.23	96.37	29
9.572	108.7	107.8	69.47	97.86	22
9.266	109.2	102.0*	79.67	83.33	22
9.292	109.4	102.5*	78.70	81.53	19
9.354	109.0	103.0*	76.47	85.71	25

NO complete desorption isotherm was obtained due to lack of time before the deadline for the completion of this work.

Values marked with an asterisk(*) are desorption values.

with balance 3, but from the points plotted it is seen that no phase change occurs between about 88-78% soap whereas previous isotherms show a phase change somewhere within this soap composition.

DISCUSSION

As has been emphasized elsewhere in this thesis, the points plotted near saturation for the individual isotherms are greatly influenced by temperature fluctuations and such points are somewhat unreliable, but are approximately where indicated. This fault of the apparatus is unfortunate since at the temperatures at which phase changes were encountered the soap percentages were those which were reached only when the relative vapor pressure was near saturation. This made definite establishment of the phase boundries somewhat difficult. Further, the difficulty in causing a small change in RVP with the voltage transformers made the exact location of the flat horizonal portion of the sorption-desorption curves a tedious procedure, especially for the desorption curves where the desorption is extremely slow.

Contrary to the statements of Shreve and of Smith and McBain, it was found that the isotherms were completely reversible when sufficient time was allowed for equilibrium to be established. Shreve found that only the 110° isotherm was reversible and this only above 85 % RVP, but this author has shown this isotherm to be completely reversible over its entire range of RVP. All of the isotherms obtained are ~~were~~ perfectly reversible, i.e., the 60, 65,70, 110, and parts of other isotherms, when sufficient time is allowed for the establishment of equilibrium. Included with the data for the 50, 55, and 110 isotherms are the dates on which the readings were made or the time between readings to show the influence of time on the points plotted. The hysteresis, which is apparent for many of the isotherms, is due to the fact that insufficient time was allowed for equilibrium to be established. Comparison of the aforementioned data makes this fact obvious and inspection of those isotherms which show a phase change further supports this conclusion.

Many of the isotherms show that when the sorption and desorption curves are exterpolated back to zero vapor pressure the soap composition is about 99 % instead of 100 % as would be expected. This could be due to the fact that the soap was not allowed to dry as completely as possible under the circumstances, it could be due to an error in determining the weight of the soap sample, moisture in the soap sample, etc. If this behavior were due to an error in determining the weight of the soap sample, then the percent soap should return to the same point for each isotherm and should be different for each balance. This is not the case. The isotherms that were run with each balance, when exterpolated back to zero vapor pressure, give , in most cases , about the same soap composition for each balance. Further, the soap percentage is 100 % in some cases, showing that whatever the cause of this behavior, it is not constant. It is suggested that this behavior may be due to the inability of the soap to become as completely dry as possible under the existing conditions. The soap sample was, in most cases, allowed to dry at the lowest RVP obtainable at the temperature of the next isotherm to be run (a 5^{o} temperature interval) for two days before beginning the isotherm, but in some cases three or four days were allowed for drying and the sopp composition was still about 99% when the curve was exterpolated back to zero RVP. Due to lack of time (the total year and one half being allotted to obtaining the maximum number of possible isotherms) it was impossible to subject yhe cyclohexane to liquid air temperatures, since this would require dismanteling the thermostat after each isotherm. The time involved in such an operation would have been prohibitive.

Figure 31 is a reproduction in part of the proposed phase diagram of the anhydrous system sodium stearate-cyclohexane which Smith and McBain have drawn for this system. Their diagram is based on data which they obtained by visual observayions of sealed tubes containing different percentages of soap. Observations of these samples at different temperatures enabled them to locate definitely certain areas which are the solid lines connecting the closed circles. The dashed lines indicate approximately the boundries which they could not locate definitely. No attempt has been made to show how the phase transitions of the anhydrous soap extend into the system, but the temperatures at which these transitions occur are indicated on the temperature axis with square symbols. The horizonal dashed line at 90° indicates the point at which the samples changed to the white waxy liquid-crystalline phase. This was observed for samples containing more than 50% soap, and samples containing more than 85 % soap were observed to undergo the transitions of the anhydrous soap. The solid line connecting the points at 98° indicates the point at which samples containing less than 50 % soap wefe transformed into the golden liquid-crystalline phase.

The data obtained from the isotherms previously described show

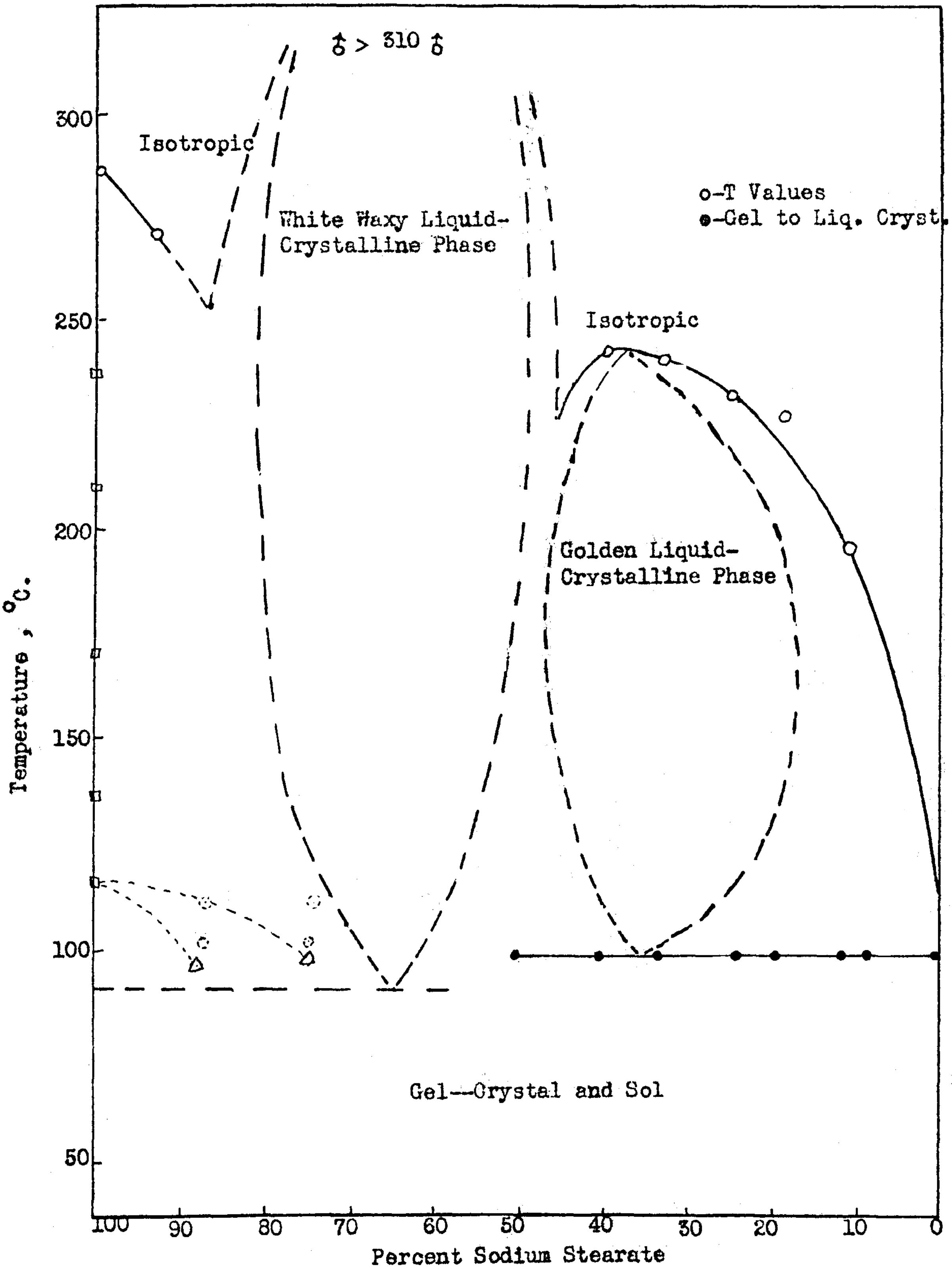


Figure 31
Phase Diagram of the System:
Sodium Stearate-Cyclohexane

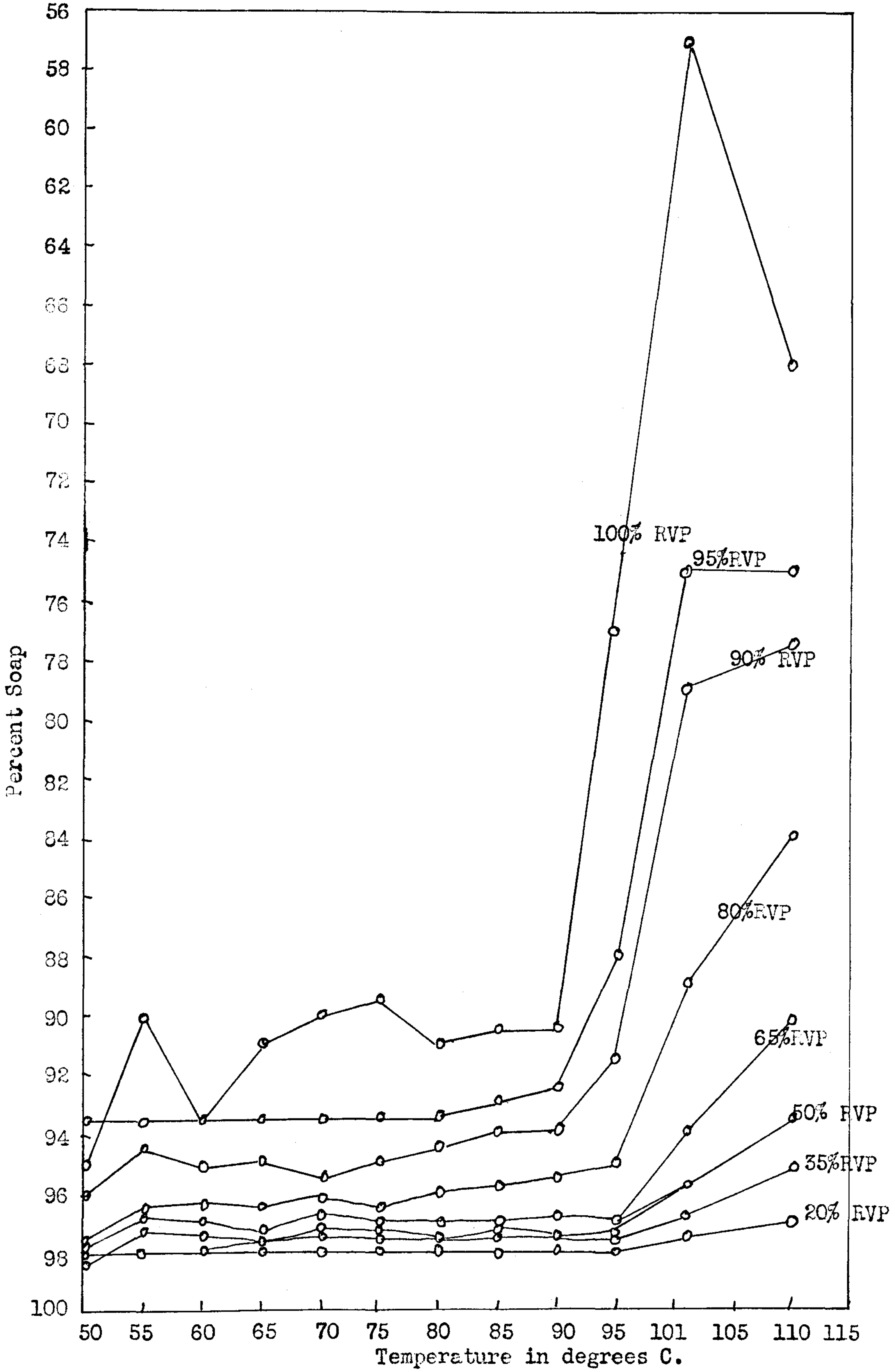
that below about 90° the system is " Gel--Crystal and Sol" as Smith and McBain have predicted. At 95° the first evidence of a phase change was obtained. This may correspond to the curd-curd transition or possibly to the curd-subwaxy transition. The definite location of the phase boundries cannot be established due to lack of additional information, but the available evidence would seem to indicate that this transition is the extension of the curd-subwaxy transition into the system. No flat portions were obtained for the 101° isotherm, but the desorption curve for balance 4 indicates that some transition may have occured; this is further indicated by the shape of the curves at the higher RVP's. Since the 101° isotherm was obtained so near the deadline for the completion of this work, anxiety to include this information in the thesis may have caused a"skipping" of the phase change. This possibility has been pointed out by Shreve and other authors.

Submission of the thesis at this time prevents the establishment of sufficient points to completely establish this area, however the points obtained appear to be located on the curd-subwaxy boundries. The points obtained are plotted on the phase diagram and dashed lines connected from them to the transition at 114° to show how this transition probable extends into the system.

Smith and McBain have shown that the phase rule applies to this system, but the observations of Shreve on soap-water systems in which the transition to a single undevided phase, observable as "flats", was observed has not been previously demonstrated as applicable to soap-hydrocarbon systems. It is clearly shown by the 95° isotherm that just as with soap-water systems the phase transitions observable as "flats " a pply also to soap-hydrocarbon systems.

Isobaric graphs by Smith and McBain, constructed from the isothermal data of Shreve, show that between 80 and 110° there is a large change in the affinity of the sodium stearate for cyclohexane. Figure 33 is a similar isobaric graph. Due to the unreliability of the data obtained at saturation, the isobar at 100% RVP must be viewed with reservation. It is clearly seen however that the affinity of the soap for cyclohexane greatly increases between 95 and 101°. Smith and McBain postulate that this is due to the transition at 98° and the data presented adds further confirmation to this postulate.

The limitations, corrections necessary, improvements, etc., of the experimental method used and also of the apparatus have been discussed previously in other sections of this thesis.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58
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64
66
68
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72
74
76
78
80
82
84
86
88
90
92
94
96
98
100
Percent Soap
50
55
60
65
70
75
80
85
90
95
101
105
110
115
Temperature in degrees C.
100% RVP
95%RVP
90% RVP
80%RVP
65%RVP
50% RVP
35%RVP
20% RVP

Figure 33

The Data for the Isobaric Curves of Figure 33

Temperatures:	50	55	60	65	70	75	80	85	90	95	101	110
% Soap at 20% RVP:	98	98	98.3	98	98	98	98.2	98	98	98.5	97.5	97
" at 35% RVP:	98	97.8	97.8	98	97.5	97.7	98	97.5	97.5	97.7	96.8	95.2
" at 50% RVP:	98.3	97.3	97.5	97.7	97.2	97.3	97.5	97.3	97.5	97.5	95.8	93.5
" at65% RVP:	97.8	96.8	97	97.3	96.8	97	97	97	96.8	97	94	90.2
"at 80% RVP:	97.5	96.5	96.3	96.5	96.2	96.5	96	95.8	95.5	95	89	84
"at 90% RVP:	96	94.5	95	95	95.5	95	94.5	94	94	91.5	79	77.5
"at 95% RVP:	95	90	93.5	93.5	93.5	93.5	93.5	93	92.5	88	75	75
"at 100%RVP:	95	90	93.5	91	90	89.5	91	90.5	90.5	77	55	68

SUMMARY

The anhydrous system sodium stearate-cyclohexane has been studied from 50 to 110°C. using the method of vapor pressure measurement and a total of 13 isotherms were obtained.

From 50 to about 90°C. the system is "Gel—Crystal and Sol" as has been previously been predicted. Phase changes were observed at 95° and above which are belaived due to the extension of the curd-subwaxy transition into the system. The probable boundries of this phase region are sketched on the phase diagram for this system and the points obtained are plotted.

The transition to a single undevided phase observable as "flats" has been demonstrated as applicable to soap-hydrocarbon systems.

Contrary to previous statements by various authors, it has been shown that the isotherms are perfectly reversible when sufficient time is allowed for equilibrium.

Isobaric graphs are presented which show that between 95 and 101°C. there is asudden change in the affinity of sodium stearate for cyclohexane which supports the postulate of Smith and McBain that this is due to the transition at 98°C.

The techniques of the experimental procedure have been studied and the limitations, improvements, etc. are discussed.

The correct use of silica springs has been studied and corrections have been established for slight variations in spring sensitivity which enable extremely accurate measurements to be made.

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APPENDIX

I-A Typical Calculation of Percent Sodium Stearate

Balance 4
Isotherm Temperature= 50°C.

(a) observed length of spring= 9.646 cm.
(b) zero length of spring at 50°C. = 4.553 cm.
(c) enlongation (a-b) = 5.093 cm.
(d) the sensitivity for this enlongation and temperaturea as determined from Figure 16 = 1.053 mm/mg.
(e) c + d = load on the balance in mg. ,or

$$\frac{50.93\text{mm}}{1.053\ \text{mm/mg}} = 48.37\ \text{mg.}$$

(f) subtraction from (e) of the weight of the platinum bucket gives the weight of the soap plus the cyclohexane sorbed, or;

$$50.93\ \text{mg.} - 25.00\ \text{mg.} = 23.37\ \text{mg.}$$

(g) the weight of the soap sample used divided by (f) gives the percent soap , or:

$$\frac{16.18\ \text{mg.}}{23.37\ \text{mg.}} \times 100 = 69.24\ \%$$

II- A Typical Calculation of Percent Relative Vapor Pressure

The temperatures of the upper and lower thermostats were determined by observing the thermometers contained therein. The correct temperature values were obtained by reference to the calibration curve of each thermometer. The vapor pressure was determined for the corrected temperature of both the upper and lower thermoststs from an accurately drawn graph of vapor pressure vs temperature. The percent relative vapor pressure was then determined by dividing the vapor pressure existing at the temperature of the upper thermostat into the pressure at the temperature of the lower thermostat and multiplying this value by 100.

The calculations are as follows:

(a) temperature of the upper thermostat = 50.2°C.

(b) temperature of the lower thermostat or hydrocarbon reservoir = 48.7°C.

(c) corrected temperature for (a) = 49.7°C.

(d) corrected temperature for (b) = 48.5°C.

(e) vapor pressure of cyclohexane at the temperature (c) = 266 mm

(f) " " " " " " " (d) = 254 mm

(g) percent relative vapor pressure = $\frac{f}{e} \times 100 = \frac{254\ \text{mm}}{266\ \text{mm}} \times 100 = 95.59\ \%$ RVP

III- Some Errors which influence the above Calculations

The errors which influence the accuracy of this experiment have been discussed in other sections of the thesis. This section is included to show how the errors previously mentioned were calculated.

(a) For I above:

1. The possible error due to the assumption of linear response of the silica spring:

From Figure 18 it is seen that the point located at 99.6 mg is off the curve for spring 2 by an amount equivalent to 2 mm, or that the enlongation is 2 mm less than would be expected if linearity were assumed. The percent error due to the assumption of linearity would therefore be $\frac{2}{95} \times 100$ or 2.11 % for a load of 99.6 mg.

2. The possible error due to neglect of sensitivity change with temperature:

For balance 4 the spring sensitivity is 1.042 mm/mg at 110°C. and 1.055 mm/mg at 50°C. for an enlongation of 49.80 mm. This enlongation divided by each of the aforementioned sensitivities gives loads of 47.79 mg and 47.20 mg respectively.

This gives an error in the calculation of the load at 110°C. of $\frac{0.59}{47.79} \times 100 = 1.24$ %. Calculating the percent soap as done in I above gives 71.00 % soap for the 47.79 mg load and 72.88 % soap for the 47.20 mg load . Neglect of the sensitivity change with temperature would thus cause an error of 1.88 % soap for the enlongation considered.

3. The possible error in calculating the percent soap (for the same conditions as in I above):

weight (vacuum) of soap sample used = 16.18 mg.

sensitivity of spring = 1.055 mm/mg

vernier reading accurate to 0. 02 mm

total possible error in observing spring length = 0.04 mm

1 mg	gives	an	enlongation	of	1.055 mm
0.4 mg	"	"	"	"	0.42 mm
0.04 mg	"	"	"	"	0.04 mm

When the percent soap is 69.24 % , then the weight of soap plus hydrocarbon is 23.37 ± 0.04 mg. Since $\frac{16.18}{23.41} \times 100 = 69.12$ % soap, then the percentage of soap is thus shown to be accurate to within ± 0.12 %.

(b) For II above:

1. The probable error in determining the vapor pressure from the graphs:

From 0 to 82°C. the vapor pressure of cyclohexane could be determined accurately to within about 0.5 mm and at temperatures greater than 82°C. to within about 3-5 mm, depending on the temperature. At 20°C. the vapor pressure is 77 mm and at 110°C. it is about 1688 mm. The error at 20°C. would be $\frac{0.5}{77} \times 100 = 0.65$ % and at 110°C. the error would be $\frac{3}{1688} \times 100 = 0.18$ %.

2. The probable error in relative vapor pressure as the temperature varies.

(a) isotherm temperature = 110°C.

vapor pressure of cyclohexane at 110°C. = 1688 mm

" " " " " 30°C. = 122 mm

" " " " " 31°C. = 127 mm

relative vapor pressure at 30°C. = 0.0723

" " " " 31°C. = 0.0770

percent error in relative vapor pressure for a one degree difference = 6.50 %.

difference in percent relative vapor pressure for a one degree difference = 0.47 %.

(b) for a higher relative vapor pressure at the same isotherm temperature;

vapor pressure at 102°C. = 1375 mm

" " " 103°C. = 1410 mm

relative vapor pressure at 102°C. = 0.8146

" " " " 103°C. = 0. 8353

difference in relative vapor pressure = 0.0207 (as percent = 2.07 %)

percent error in relative vapor pressure for a one degree difference = 2.54 %.

For an isotherm at lower temperature this error is smaller.In the above calculation it is assumed that the temperature of the upper thermostat remains constant, but if the lower thermostat temperature changes one degree , then it is to be expected that both thermostats undergo a change of one degree. In this case the error is much smaller. For example, if the isotherm temperature were 70°C. and the lower thermpstat was at a temperature of 30°C. , then the percent error in the relative vapor pressure caused by a one degree temperature change would be only 0.58 % as calculations similar to the above will show.

AUTOBIOGRAPHY

I, Walter Edward Reid, Jr., was born November 19, 1924, in Richmond Virginia. I attended the local elementary and high schools of Henrico County, graduating in 1940 from Dumbarton Junior High School and in 1942 from Glen Allen High School. Upon completion of high school, I became employed by The Bodeker Drug Company, but shifted in 1944 to work more essential to the war effort, and worked for the 1353 service unit of the War Department, an Ordinance repair depot, until my enrollment in Richmond college in 1945. As an undergraduate, I served for two years as laboratory assistant in analytical chemistry. In June of 1949 I received the Bachelor of Science degree.

Upon completion of my undergraduate work I accepted a Fellowship of the Research Corporation of America, which enabled me to continue my studies as a graduate student. At present I am a candidate for the Master of Science degree. This thesis is submitted in a partial fulfilment of the requirements of the Master of Science degree.