# INVESTIGATION
OF THE
# DENSITY OF A VAPOR

# AN INVESTIGATION OF THE DENSITY OF A VAPOR IN EQUILIBRIUM WITH A LIQUID NEAR THE CRITICAL TEMPERATURE.

A Thesis

by

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# C O N T E N T S.

# I N T R O D U C T I O N.

The realization that the state of all existent matter could be classified under three general heads was a notable advance in the study of science. The further realization that the state of matter was dependent upon the conditions of temperature and pressure in which it found itself was an equally notable step. With the lapse of time, man has drawn up laws and rules based upon comprehensive experimental data which enable him to predict with accuracy the behavior of a system composed of matter in any one of the three states. His generalizations have extended, even to systems of any two or all three of the states.

Of the three possible transitions, probably that between liquid and gas presents one of the most interesting and fruitful subjects for study. A liquid presents a few clearly definable properties which are not evident in a gas, yet a liquid can be made to become a gas of the same chemical constitution by suitably altering the temperature or the imposed pressure. The reverse procedure is likewise as readily accomplished. Since the state is so completely a product of the temperature and pressure, our terms "familiar liquids" and permanent gases are ascribed to certain chemical substances only because the imposed conditions, generally met with, favor that particular state.

Any liquid will create above itself an atmosphere of its own vapor, which if allowed to take place in a confined and otherwise evacuated space, will slowly fill all the available room and exert a pressure on the container dependent for its magnitude only upon the temperature of the liquid. An increase in temperature will cause the pressure exerted, known as vapor pressure, to become greater. When this pressure has become equal to one atmosphere, equivalent to the weight per square millimetre at the bottom of a mercury column 760 mm. high, the temperature is termed, the boiling point. Unconfined, the liquid would exhibit ebullition at this temperature, and under the influence of a constant inflow of heat, would completely change over into the gaseous state. In a totally closed system, all at the same temperature, the two states would remain in contact at equilibrium indefinitely. The effect of increasing the temperature still further, now becomes of interest. The liquid volume finds itself subject to two opposing forces, the loss due to conversion into vapor, and the gain caused by thermal expansion. Of necessity this will result in a lowering of the liquid density and a consequent rise in the vapor density. The increasing temperature has another important effect, insofar as it lowers the surface tension of the liquid. Since surface tension may be considered as being responsible

for the well known visible line of demarcation between liquid and gas, it is to be expected that this line or meniscus will be influenced perceptibly by the increasing temperature. Finally, a temperature can be reached where the meniscus will become indistinct and vanish. The contents will present an appearance of complete homogeneity and will visibly resemble a similar container full of either liquid or gas at normal pressure and temperature. By lowering the temperature, the meniscus will reappear and the various changes will take place in the reverse order. The temperature at which this transition occurs has been termed the critical temperature. It is of peculiar interest because the properties of either phase are converging, slowly at first and rapidly toward the last. It should be evident that a complete understanding of the alterations which take place, leading up to and accompanying this transformation, is necessary to compile a satisfactory theory regarding the liquid-gas transition.

It is now more than a century since the observance of the critical phenomenon was first reported, during that time numerous investigations have been directed with the object of supplying a more complete and satisfactory explanation for its occurrence.

The working conditions have been complicated by the high pressures encountered, and small containers have been necessarily employed to sustain this pressure.

The author has completed an investigation upon the behavior of the liquid and gaseous densities of methyl ether in the region of the critical temperature by a new method, displaying a precision and directness not encountered in any of the previous work.

## HISTORICAL INTRODUCTION.

Since Caignard de la Tour's[1] discovery in 1822, that a liquid sealed in a tube would completely disappear at some definite temperature and would reappear upon cooling, investigators have been endeavoring to learn more about this peculiar transformation. Two explanations were advanced almost immediately to account for the critical phenomenon.

(i) The surface tension of a liquid decreases with a rise of temperature and if this diminution continued, it would be possible to arrive finally at a temperature where the surface tension had fallen to zero. There would be no capillarity and no surface of demarcation existent, in other words the liquid and gas would be visibly indistinguishable and mutually miscible in all proportions. Whether this means that they are physically identical or not, does not follow directly.

(ii) As the temperature rises, the vapor density increases and the liquid density decreases, thus it is conceivable for the two to have finally the same density. Ramsay[2] and later Jamin[3], postulated this latter theory to account for the critical phenomenon.

Andrew's[4] classical experiments upon carbon dioxide in the region of the critical temperature showed that even several degrees above the critical temperature,

the effect of compression did not result in a uniform alteration of volume between certain pressure limits. This was rather surprising because during this irregularity no liquid visibly separated out. Furthermore, gaseous carbon dioxide at a temperature of 50°C. and under a pressure of 150 atmospheres, altered its volume with alterations in pressures in the accepted manner of a gas, yet when cooled to 20°C. it exhibited all the properties of a liquid, without, at any time, having visibly altered its state. In Andrew's own words, he says, "A liquid and a gas are only distant stages of a long series of continual physical changes".

Cailletet and Colardeau[5] seemed to believe that the liquid state persisted after the critical point had been exceeded. To substantiate this theory, Cailletet and Hautfeuille[6] experimented with iodine in the tube along with the carbon dioxide. Iodine has the property of not being soluble in carbon dioxide vapor, but is soluble in the liquid. Above the critical temperature, that portion of the tube previously occupied by the liquid, retained its violet color, while the upper part of the tube remained colorless. This provided fairly substantial qualitative proof of the hypothesis.

The theory of Ramsay[2] and Jamin[3], that the liquid state continued past the critical temperature

was further substantiated by the work of Cailletet and Hautfeuille[6] upon the behavior of the pressure-temperature curve above the critical temperature. It was found that the curve depended for its slope in this region upon the relative amount of liquid which occupied the tube. This variation was believed to have been possible only if the liquid continued to exist as such, after the meniscus had vanished. The theory required only that the densities had to be equal, which in no way prevented the two phases from still being physically different. Jamin[3] went so far as to say that the liquid might even become less dense than the vapor and displace the latter at the top of the tube. Cailletet,[7] after many trials, did not get any indication of such a condition as postulated by Jamin.

It might be interesting to consider briefly how Cailletet and later S. Young[8] conducted their experiments to determine the density of the liquid and gaseous aggregates existing at the critical point. The liquid was enclosed in a small bore glass tube, one end of which was sealed off, and the other end connected to a high pressure pump. A thread of mercury was used to trap the liquid and to communicate the pressure. The mass of liquid employed was predetermined and remained constant throughout the experiment. The volume which this liquid occupied was readily determined by

having the tube calibrated, and the total volume available could be altered at any time by moving the mercury column up or down. At the critical temperature the meniscus disappeared at a position in the tube dependent upon the relative space occupied by the liquid, in comparison to the total space. By decreasing the volume of the total space, the meniscus was made to vanish almost exactly at the top of the tube. Conversely, by increasing the total volume, the meniscus was made to vanish at the bottom of the space. In the first case the density of the liquid was computed, in the second case, the density of the vapor. However, once the meniscus had vanished, no further measurements could be made. The disappearance of the meniscus at any time, was and still is, a difficult condition to define under the best of circumstances, and varies considerably with the illumination. The meniscus moves up or down very rapidly for slight temperature alterations near the critical temperature. It is best to bear these two facts in mind when considering the quantitative results obtained by such methods for the density of either liquid or gas.

Cardoso and Coppola[13] might be mentioned as having done fairly accurate determinations upon the density and pressure of methyl ether up to the critical temperature. They made their measurements in an

accurately calibrated tube, and by a comparison of the volumes occupied by the two phases, arrived at densities for both liquid and vapor up to about .5°C. from the critical temperature. They have drawn the usual parabolic density-temperature curve but have made no attempt to experimentally justify the extrapolation.

Almost all the workers mentioned, have drawn up density-temperature curves for the liquid and vapor from the data obtained. The general shape of these curves have been similar in all cases, i.e., a parabola with the apex at the critical temperature. The exact nature of this parabola in the region of its apex had in no case been determined experimentally. Its shape had been inferred, but never proven. Admittedly, measurements had been made very close to this region, but very close seems hardly good enough when it is considered that densities are known to have been changing at the rate of 4 or 5% per .1°C.

This short-coming has been realized to be of some significance and a serious handicap in the physical explanation of the phenomena. Several workers[14] have tackled the problem experimentally with varying degrees of success. Many more have theorized and speculated concerning it and have supported their hypotheses by elaborate mathematical proof. To mention but a few

would be to include the names of Shaposhinkov[9] and J. Havlickek[10] . A very few have done extensive determinations concerning the densities of the liquid and gaseous phases past the critical temperature. Since this paper deals with the author's attempt to do the same thing, the methods and results of these immediately previous workers will be reviewed in some detail.

The investigation by Galitzine[19] followed much the same procedure, and yielded the same general results as the preliminary work carried on by the author. Galitzine found that when using ethyl ether, the temperature at which the meniscus disappeared, $T_c$, was not the same as the temperature at which it reappeared $T_c'$, and that $T_c - T_c'$ had a positive and constant value, uninfluenced by the relative mass of the material under observation. Not only was the temperature different, but also the position in the tube which the meniscus took up for any temperature below the critical temperature was governed by whether that temperature was approached from above or below. Galitzine seemed convinced from the observations that the density in the upper part of the tube containing the ether, was considerably less than the density in the lower part, for even 6 or 7 degrees after complete homogeneity was apparent to the eye. This density difference, he claimed,

was about 20% and that it maintained itself indefinitely. Small traces of impurities, notably air, were thought to be responsible, but experimental tubes with definitely greater quantities of air included showed no difference to those tubes which were carefully filled to exclude air.

Several years later, Traube[21] and Teichner[22] attacked the same problem in a slightly different manner than had any of the previous workers. Since all the former density determinations had depended for their evaluation upon the position of the meniscus and since the meniscus became indistinct and disappeared just at the stage where the measurements were of the greatest significance, it was a logical diversion to determine the density in some other manner. The simplest and most direct method possible, was employed. Small glass floats, one to two millimetres in diameter , of known density, were enclosed within the experimental tube along with the material under observation. The effective density of each float was determined, and each float was individually distinguishable, so that at a glance it could be identified with its correct density value. Traube included 8 of these small glass bubbles in each tube. The heaviest had a density of about .678, and the lightest, .422, the intermediate ones varied from one another by about .035. The liquid-vapor system under investigation was carbon-tetrachloride. A less dense

system than this could not have been satisfactorily used, because lighter floats than those having an effective density of .422 would not have withstood the pressure. Teichner increased the number of floats to 15, thereby decreasing the gap between floats by a half. Both experimenters used a vapor heating bath composed of some high boiling liquid whose temperature was controlled by adjusting the pressure on it. The tube containing the floats and the carbon tetrachloride was placed within a second tube and surrounded by a clear oil, both tubes were then lowered into the vapor bath, which was surrounded by a thick felt packing supplied with small observation slits. From these precautions it is evident that both Traube and Teichner realized the necessity of removing the possibility of slight temperature fluctuations. Whether they were equally successful in obtaining a constant and equal temperature throughout the length of the bomb ( 16 to 20,cms. ) has not been recorded, nor did they seem to have any device to detect such an equality, had it been present. Traube and Teichner, alike found a density difference of considerable magnitude between the upper and lower parts of the tube, after the critical temperature had been exceeded. Even after a lapse of many minutes, the density difference persisted with only a slight diminution.

The obvious uncertainty was that when a float, or floats of known density were at the top of the container, the surrounding medium was of a greater density, but how much greater could not be accurately determined. Conversely, a float, or floats resting on the bottom must have been surrounded by a medium of lesser density, but how much less was not subject to computation. Floats which remained suspended in the tube were justly considered as having exactly the same density as the surroundings, a situation which demanded a very delicate control of temperature. The necessary gaps between the density values of successive floats was also a weakness which prevented any continuous determinations from being made.

Gouy[24] had predicted, many years before, that the gravitational attraction should create an appreciable gradation in density from top to bottom of a tube, 10 to 20 cms. long, containing a gas whose density was of an order of magnitude comparable to that obtained at the critical temperature. His calculations showed, however, that the actual difference, although definite, would not be nearly as great as was obtained by Teichner or Traube.

Villard[25] put two very small thermometers inside a tube containing liquid ethylene. One thermometer had its mercury bulb at the bottom of the tube, the other

at the top. Upon heating just beyond the critical temperature, ( very low in this case, about 9°C.), the two thermometers registered a difference in temperature of almost 3°C., the top one being the warmer. Villard interpreted this as meaning that evaporation was still taking place from the indistinguishable molecular aggregate in the bottom of the tube. The difference seems unreasonably large to have been caused in this manner, and furthermore the maintainance of such a temperature difference is contrary to natural laws. The author would be inclined to believe that poor thermostating was the explanation.

F. B. Young[20], after a careful consideration of the results of previous workers, decided that the marked differences of density were to be attributed to the presence of a small percentage of impurity in the substance assumed to be pure. This would serve to reopen the controversy between Traube's liquidogenic and Andrew's classical theories, and to make additional experimental material relating to the critical phenomena of pure substances highly desirable.

Young's procedure for filling the experimental tubes with pure substances was exceedingly precise and has been treated at great length in his account of the work. The actual density figures at the critical temperature were obtained by arranging to have two tubes,

in one of which the meniscus vanished exactly at the bottom, and in the other exactly at the top. Equality of density was not obtained in this manner, but for tubes in which the meniscus disappeared about midway, equality of density was claimed. The method of determination in this last case was to have a number of close parallel lines set up behind the tube and to observe them through the contents. When the lines showed no discontinuity any place throughout their length, it was assumed that the density throughout the tube was uniform. Furthermore, the behavior and distribution of the opalescence was construed to prove certain facts about the distribution of densities. Gaseous impurities were credited with retarding, rather than assisting, the formation of opalescence, and the rapidity with which the opalescence spread throughout the tube was hence a measure of the purity. Young believed that with the disappearance of the fog there vanished simultaneously all density differences and since impurities delayed the spread of the fog as well as shortened its duration, he concluded that gaseous residuals were entirely responsible for the differences in density reported by previous experimentalists. It might be well to note also that Young considered density equilibrium to have become established throughout the tube during the lapse of a

few minutes, ( he mentions 10 in one place ) following an alteration in temperature. He ascribed even this lag to the time required for thermal conduction through the glass wall and into the centre of the contents.

P. Hein[23] conducted his investigations of the subject in an analogous manner to Teichner and Traube. His results, however, were not in exact accord with theirs. Hein mentions the addition of a thermocouple to the heating apparatus in such a manner that the upper and lower junctions were near the respective ends of the bomb. He does not state how sensitive it was, nor to what extent it was used. The liquids investigated were carbon tetrachloride, sulphur dioxide and carbon dioxide. In each case the material was exhaustively purified and added to the experimental tube in an air-free condition. For purposes of comparison, other tubes were filled with the same liquids, but were not freed from air as the previous ones. In general, the results indicated that the density difference was due to the included air. Hein discovered that rapid stirring within the bomb, performed magnetically, offset any effect which slight inclusions of air might have. In other words he showed that gaseous impurities only retarded equilibrium, and because of this retardation, a density difference had been obtained. This conclusion

would be valid only if no temperature gradient had existed throughout the length of the bomb, a point which he does not make clear.

Of more recent date was the investigation by Schroer[11], who managed to derive denisty readings completely around the temperature-density curve, but found that instead of a regularly curving apex, the parabola became flattened. The work was done on ethyl ether in an apparatus not materially different from that used by Cailletet almost half a century previous. A device was added for stirring the contents of the tube magnetically and the pressure was altered during the measurements. By this latter modification in procedure, Schroer contrived to proceed completely around the end of the parabola and got density readings which he interpreted as being, at one time for the liquid and at another time for the gas. In the author's opinion, the results were somewhat influenced by the pressure manipulation, which would account for the flattening of the curve;

Callendar's[12] work on water at the critical temperature was published coincidentally with the paper of Schroer's. To quote Callendar's own words in regard to Van der Waal's equation, he says; "The representation given by the formula of the conditions at the critical point have been accepted as a matter of course, although it was very hard to verify this experimentally. The

whole theory, in fact, lacked experimental proof. To obtain this, it would be necessary to examine the properties of the liquid right up to the critical point. According to Van der Waal's theory, when the meniscus vanished, the density of the liquid became equal to the density of the vapor."

Callendar's main work was directed at determining the relationship of the latent heats of the two phases just at the critical temperature. His density determinations were not any more precise than those of Schroer's upon ethyl ether. Callendar used small quartz bombs filled to different degrees of fullness with water. The quartz was necessary because of the corrosive action of water and steam upon glass at high temperatures and pressures. He mentions that the water could be detected rising in the tube after the meniscus had disappeared, unfortunately the technique for this was not made very clear.

Even a cursory examination of the short review provided here is sufficient to show that the results, obtained over a considerable number of years, have been at variance amongst themselves. Very often the interpretation, by different men, of the same results has not been the same. In general, two main divisions seem to have developed: (i) those who have clung to Andrew's

classical theory and endeavored to explain the phenomena by reference to his pressure-volume isothermals, and; (ii) those who have believed, like Traube, that an intermediate formation of "liquidons" and "gasons" must be necessary.

To say conclusively that one or other of the theories is incorrect would be sheer folly in the face of such conflicting evidence. The author submits this account in the hope that it will serve to show clearly how the density of a liquid and of its saturated vapor converge at the critical temperature. The weak spots of previous experimental procedures have been bridged wherever possible. The theoretical deductions arising from the results will be treated later.

The theory of Van der Waal's, regarding the transition from liquid to gaseous states, postulates an absolute continuity; this conclusion is based on the complete parallelism of pressure-volume isothermals at, and in the vicinity of the critical temperature. These isothermals, whether on the liquid or vapor side of the critical temperature isothermal, show an inflection at the critical pressure, but are supposed to be indistinguishable from one another as the isothermals approach the critical temperature. Later investigations, notably those of Traube and Teichner, have cast some doubt upon the continuity theory, particularly in regard to its

aspect of equal density of vapor and liquid at the critical temperature. Adherents of the continuity theory, notably Kamerlingh Onnes[26], attributed the discrepant experimental observations to the inflection in the pressure-volume curve at the critical temperature where minute differences in hydrostatic pressure, or temperature, or contamination by traces of a second component might cause variations within the containing vessel, sufficient to account for the observations.

There have been a number of entirely independent investigations involving critical temperature-pressure regions which point to a discontinuity of state at the critical temperature. It has been observed that the solubility of substances decreases markedly as the critical temperature is approached and reaches a zero value in its neighborhood, which cannot be accounted for by a change of concentration of the solvent.[27]

Recently, the velocity of a chemical reaction has been shown to increase regularly with the temperature and then fall to zero value when the critical temperature was reached.[28] Kamerlingh Onnes has determined the dielectric constant of a system through the critical temperature-pressure region. A discontinuity which he has not interpreted seems to be obvious from the data which he has determined.

The above references are given as evidence that in spite of the apparent continuity of the pressure-volume isothermals, a definite discontinuity must exist at the critical temperature. The solubility, velocity of reaction and di-electric discontinuities might be explained by a regional orientation which may exist in the liquid state, the disappearance of which may greatly influence the so called, critical temperature. The suddeness of the disappearance of such a regional orientation with slight temperature changes has already been proven by a dissertation of Nernst's[29].

Apart from this, the existence of a liquid and vapor density difference persisting beyond the critical temperature becomes more or less obvious from the observation that the critical temperature (disappearance of meniscus) can be observed in tubes containing various relative amounts of material under examination. On the basis of the continuity of state of Van der Waal's, the following calculation will show that the critical phenomenon should be observable only when the tube is filled with the material under inspection to an extent which will conform to a single, definite critical density value.

Suppose:

W = weight of material.

V = volume of tube.

$V_g$= volume of gas, and $d_g$= density of gas.

$V_l$= volume of liquid, and $d_l$= density of liquid.

$d_c$= density of contents at the critical temperature.

Under all conditions:

$$(V - V_g)d_l + V_g d_g = W.$$

Hence; $$V_g = \frac{W - Vd_l}{d_g - d_l}$$

As T approaches $T_c$, then $d_c$ approaches $\frac{d_g + d_l}{2}$

and $W \doteqdot d_c V$.

Substituting these special conditions in the general equation, we get;

$$V_g = \frac{d_c V - d_l V}{d_g - d_l}$$

$$= \frac{\left[\left(\frac{d_g - d_l}{2}\right) V\right] - Vd_l}{d_g - d_l}$$

$$= \frac{V}{2}\left[\frac{d_g - d_l}{d_g - d_l}\right]$$

Hence; $$V_g = \frac{V}{2}$$

It is seen that the writer is inclined to question the continuity of state in the absolute sense in which Van der Waal advanced it. The discrepancies indicated by solubility and velocity of chemical reaction experiments cannot be controverted. The discrepancy existing between liquid and vapor densities, inferred by the above calculation, and indicated by the above described experiments of Traube and Teichner, can be made to conform to the continuity theory, only on the basis of experimental influences involving a vertical temperature gradient, the presence of an impurity, or a pressure gradient based on gravitational attraction. From the point of view of the inflection in the pressure-volume isotherm which gives $dP/dV = 0$, it is admitted that the slightest variation in experimental conditions would tend to bring about an observed variation in density.

One of the objects of the work described herein, was to eliminate such variations as might be caused by a temperature gradient, or contamination by an impurity; at least to evaluate their influence where a complete removal was prevented by experimental exigencies. The first step in this direction was the adoption of a technique for determining the absolute densities in both liquid and vapor phase independently, under conditions where true equilibrium existed.

PRELIMINARY EXPERIMENTAL WORK.

In October of 1930, the present investigation was commenced. No program was definitely planned except that the behavior of some liquid was to be observed just below, at, and above the critical temperature. The liquid chosen was methyl ether because of its relative ease of preparation and because of the moderate pressure and temperature associated with the critical phenomenon. It should be clearly understood that the trend which the investigation finally took was suggested by the observations taken in the early stages, and as the work progressed, the field broadened and took on a novelty and interest which could not have been predicted at the start.

Much of the same apparatus was used as is described later on in this account. The methyl ether preparation and purification train was considerably simpler and the purity of the product was correspondingly lower. The heating bath was provided with two less electric heating coils, no thermocouple and no magnet.

The investigation was directed so as to detect if possible, any density increase due to gravity at the bottom of a column of gas whose density was very high. This vapor of high density was provided by the liquid methyl ether near its critical temperature. It was planned to use the liquid itself as a manometer. To do this, a U-tube of heavy walled pyrex glass was made with an internal diameter of about 1 cm., having one arm of the U about

three times as long as the other. The longer arm was roughly 20 cms. in length. A quantity of methyl ether was distilled into the tube and the latter sealed off. The tube was then placed in the oil bath and heated to near the critical temperature. It was hoped that by observing the difference in the levels of the liquid in each arm, to be able to compute roughly the extra weight of the vapor in the long arm. However other agencies appeared to be at work in governing the liquid levels because in all the many observations made at various temperatures only slightly removed from the critical temperature, the level in the short arm was always lower than that in the long arm. At the time this behavior was very mysterious, but in the light of later work it was readily seen that a very slight temperature gradient throughout the oil bath might have caused the peculiar results.

In order to make the most of an idea which had proven a failure, the U-tube was removed and inverted so that all the liquid collected in the long arm; the tube was then replaced in the oil bath in this position. Observations at many temperatures were made in the hope of finding some regular behavior exhibited by the meniscus. It was thought that our choice of a wide bore tube would reduce to a minimum the time required for equilibrium to become established between liquid and vapor. Repeated observations through a cathetometer revealed that as much as thirty to forty minutes was required for the meniscus to become

stationary, after arriving at some maintained temperature. The closer this temperature became to the critical temperature the less was the time required for equilibrium. This shows, I believe, why experimenters who have worked with relatively fine bore tubing to contain the liquid under observation, have obtained consistent results for the critical temperature, although it is problematical whether anything like equilibrium was established at any point previous to the critical temperature.

Quite by accident it was observed that the equilibrium level of the meniscus for some definite temperature on the way up was not the same as the equilibrium level of the meniscus when the identical temperature was approached from above; providing that the temperature had been raised to, or through, the critical temperature between the two observations. At first this was believed to be merely a coincidence, but after getting exactly the same behavior in a second tube; straight this time, of about 16 inches in length and of the same diameter as the previous U-tube; even when long periods of time were allowed for equilibrium to come about, it was made evident that whatever the cause, the results were capable of repetition. Of further interest was the rather surprising observation that the difference in the equilibrium meniscus level for a series of definite temperatures, depending upon the direction of approach to these temperatures, was roughly a constant.

For example;

| Temperature. | Meniscus level when temperature was approached from below. | Meniscus level when temperature was approached from above. | Difference. |
|---|---|---|---|
| 125.5°C. | 3.30 cms, | 2.70 cms. | .60 cms. |
| 126.2°C. | 2.90 cms. | 2.35 cms. | .55 cms. |
| 126.7°C. | 2.75 cms. | 2.20 cms. | .55 cms, |
| 127.1°C. | 2.60 cms. | 2.05 cms. | .55 cms. |

The absolute value for the temperature in the above table, was probably a fraction of a degree in error because the thermometer was destroyed before it could be standardized.

All of the usual opalescent phenomena were observed accompanying the critical temperature. In tubes filled with liquid to different extents, the fog intensity varied only slightly. In all cases the fog was obviously composed of innumerable, fine droplets, individually discernable in the proper light which were present throughout the length of the tube in the region of the critical temperature. In tubes having different proportions of liquid to total internal volume, the meniscus disappeared at widely different places in the tube, but regardless of where it disappeared , it always first reappeared at the bottom. No amount of care in heating or cooling could alter this procedure. The moment that the meniscus flashed into view, the droplets in the cloud descended slowly, the meniscus rose rapidly and at the same time small globules ascended through the liquid, giving the impression of a two directional

rain, directed at the meniscus.

At this stage in the investigation it was decided to try enclosing a float of some kind within the bomb, and seeing how it behaved. The floats tried in different bombs were large, glass elongated cylinders with hemispherical ends, about 6 cms. long and 6 or 7 mms. in diameter. A small amount of methyl ether was sealed in each float to help compensate for the high external pressure to which they were subjected. In this manner, floats with an effective density of from .35 to .40 were constructed. By this means it was hoped to detect a density gradient existing between the bottom and the top of the liquid near the critical temperature. This gradient would be expected, if at this temperature the liquid assumed some of the properties of a gas. All the observations showed that once the float sank through the meniscus, it continued all the way down to the bottom. No measurements could be made closer than five degrees to the critical temperature because floats of a sufficiently low density could not be constructed that would stand the pressure.

At this point, the idea was conceived of continuing the measurements with the floats, except that they would be suspended from a quartz spiral whose extension would give a means of calculating the fraction of the weight of the float not being held up by the buoyant effect of the surrounding medium. It was hoped to be able to either suspend two or three floats in one bomb at different positions, or else move the one suspension to various locations. The latter alternative was chosen.

The technical difficulties at first seemed a barrier to the realization of the scheme. In the first place the diameter of the containing vessel could not be increased beyond about 14 mms. and continue to give any degree of safety against explosion. This meant that something new in the way of spirals had to be developed if they were to be used in such a confined space and still give the required degree of accuracy. Secondly, the moving device had to be compact and capable of adjustment from outside the bomb. Magnetism was the only conceivable way of effecting this since the bomb had to be completely sealed off.

With this rough plan of attack as a guide, the following work was commenced. Failure, in one form or another, beset the work continually. New technique had to be developed, new ideas tried out and even new machinery designed and constructed to perform operations incapable of being executed by manual skill.

## DESCRIPTION OF APPARATUS.

1. The Quartz Spirals. (15) (Preliminary Note.)

Where there arises the need for making weight determinations under conditions of high pressure, limited space and high temperature, requiring the accuracy of an analytical balance, the quartz spirals described here serve admirably. There are several properties of quartz which make it exceedingly well suited to the task.

(i) Its great tensile strength enables comparatively fine fibres to hold relatively large weights.

(ii) Its low thermal expansion makes any temperature correction negligible .

(iii) Its hardness causes the finished spiral to have a definite "no load" length, to which it returns exactly even after being extended to three times its normal length for a period of three or four weeks.

(iv) An added feature is that over the entire range of use, the extension bears practically a straight line relationship to weight. (Exemplary case will be cited later on)

In order that the spirals should be of any service in the work at hand, the diameter had to be not more than 6 mms.; the length, not more than about 4 cms.; the total weight capacity, at least .4 grs. and the minimun weight detection, .0002 grs. for a .05 mm. extension. By experiment, it was found that the quartz fibre had to be .1 mm. (plus or minus .01 mm.) in diameter to sustain the load required. It was further found that because of the small

spiral diameter, upwards of one hundred turns would be needed to give the prescribed sensitivity. This meant that about forty turns of fibre per cm. of spiral length was necessary. Uniformity in the diameter of the fibre was found to be an important factor since a spiral wound from fibre of varying size, ( .1 $\pm$.03 mm.) gave a total weight capacity corresponding to the weakest portion of its length and a sensitivity much impaired by the useless, thicker portions.

Looking back over these prerequisites, it was little wonder that the preparation of fibres and the winding of these fibres into suitable spirals, could not be accomplished by hand methods, depending solely upon the skill of the worker.

PREPARATION OF FIBRES.

The molten quartz was drawn out to the desired size by a device operated by a falling weight. A piece of quartz rod was firmly tied to the end of a strong cord, which in turn, passed over three pulleys in such a manner as to give a horizontal pull upon the quartz. The moving portion was held in check by a foot operated catch, which upon release allowed the quartz rod to move away rapidly from a similar rod, mounted firmly about ten inches above the level of the desk. The operator directed an oxy-gas hand-torch flame downward upon the quartz and an oxy-blast-lamp on the desk heated the lower side. At the moment that the foot pedal was depressed, the hand-torch was removed and

simultaneously the blast lamp was pulled back by a mechanical device; about one second later, the release operated and the moveable piece of quartz receded quickly for a distance of twelve feet, leaving in its wake, the fine fibre. After a little practice with regard to the correct amount of quartz to be made molten and after some experiments upon adjusting the weight employed, nicely uniform fibres were obtained. Since only four or five feet of fibre was needed for a spiral, the uneven portions at each end of the original twelve feet could be discarded. In this way, fibres not varying more than .01 mm. from the desired .1mm were obtained.

THE WINDING MECHANISM.

To dispense with the tedious and inexact process of winding these fibres by hand, a machine was designed and constructed by the author from Erector parts, to perform the task more easily and more precisely. The device automatically revolved the rod around which the fibre was wound and at the same time advanced the rod horizontally so as to give the resultant spiral a uniform but adjustable pitch. There was maintained on the fibre a friction tension, which could be conveniently altered, if desired, during the course of the winding.

The essential parts of the machine are shown in the accompanying sketch. (Fig. 1a).

The power was supplied by a small, 6 volt, D. C. electric motor (A), which revolved at about 3200 r.p.m.

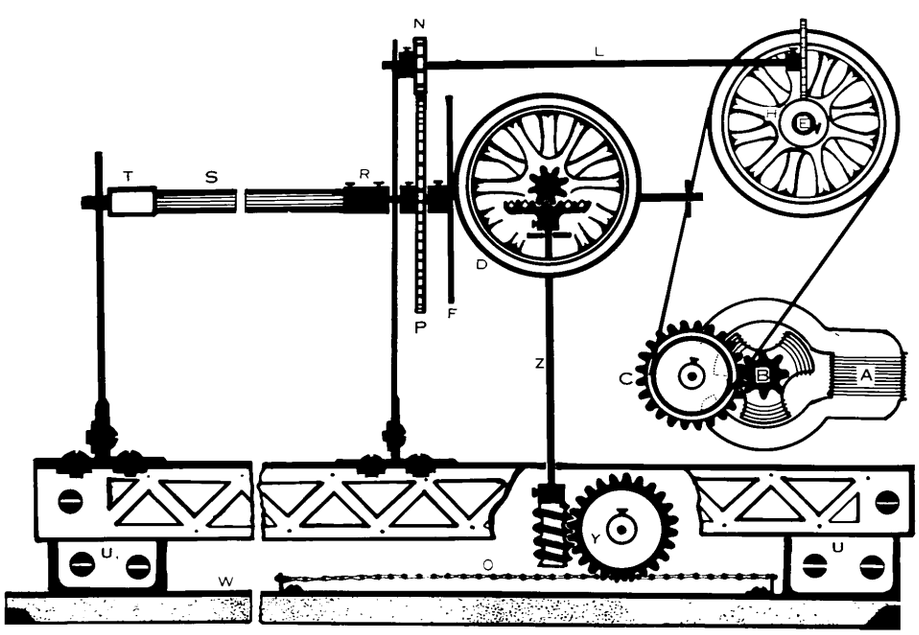


FIG. 1a

(Length, about 18 in.; height about 10 in.)

A pinion (B), on the motor shaft, engaged the flat gear (C) which in turn, through a pulley and belt, caused the shaft (E) to revolve with a speed reduction of nine to one, relative to the motor. This shaft, by means of the worm gear (H) further reduced the speed twenty-five times and conveyed the power through a right angle to the shaft (L), which by a pinion and large flat gear, caused the chuck (R) to revolve at about 4 r.p.m. A 7" by $\frac{1}{4}$" carbon rod (S) was held in the chuck and kept in line by the free bearing (T) at the opposite end. Directly behind the large gear and turning with the chuck shaft was a three inch flat steel disk (F), one face of which was covered with a sheet of thin cardboard, against this disk was pressed a three inch wheel with a narrow friction rim (D), mounted on a shaft at right angles to the previous one. By means of the pinion and crown gear, the movement of this shaft was communicated to a vertical one (Z), extending down through the platform of the machine, The shaft (Z) had a worm gear attached to its lower end which meshed with the flat gear (Y)mounted on a short shaft placed at right angles to the longitudinal axis of the machine. The lower part of the gear (Y) meshed with a chain which was securely fastened level with the base and parallel to the longitudinal axis of the machine. As the chuck revolved, the system of gears just described, caused the sprocket in contact with the chain to advance along its length at a speed determined by

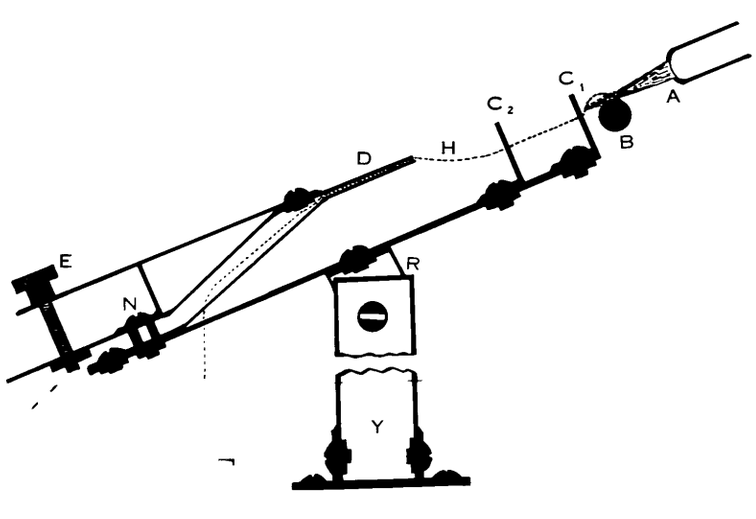


FIG. 1b.

Diagram of the tension and guide device, mounted on the same base with the wind-mechanism and placed at right angles to the plane of Fig. 1a, in a position opposite the carbon rod (S).

the radial position of the friction drive, and thereby carry along the whole machine at a uniform, but adjustable rate of speed. ($U_1$ & $U_2$) were steel skids which supported the machine and slid in the grooved track (W).

Figure 1 b shows the tension and guide device. (A) was a small air-blast gas burner constructed of pyrex, (B) was the revolving carbon rod around which the fibre was wound. ($C_1$ & $C_2$) were plates with narrow vertical slits through which the fibre (H) passed. (D) was the friction plate bearing against a similar plate beneath, and (E) was the tension adjusting screw. (N) was a pivot around which the upper part of the tension plate could be revolved to allow of convenient threading of the fibre. (R) was another pivot which permitted the elevation or partial rotation of the entire guide so as to assure correct alignment at all times. (Y) was a firm steel upright which was securely fastened to the wooden base and supported the guide and tension mechanism.

The burner supplying the heat required to soften the quartz thread was mounted on a retort stand and held in position by a clamp. The exact position and intensity of this flame required a great amount of study and trial before it was correctly placed. It had to be of sufficient intensity to soften and yet not appreciably weaken the fibre, for in the latter case the tension would cause the fibre to thin out and snap. A very hot flame directed at

not quite the correct angle was also useless because once the quartz touched the carbon rod no amount of heat on it would then cause it to become permanently bent. The best results were obtained when the peak of the blue inner cone of the flame just touched the fibre about two mms. in advance of the carbon rod, and when the axis of the flame, if produced, would pass down the centre of the oncoming fibre. Many other arrangements were tried but none met with as good success as that just described.

When the spiral was completed, it and the rod were removed from the machine, the spiral was slipped off the rod and neat rings formed at each end.

The process of calibration consisted of suspending the spiral from a solid support and measuring, with a cathetometer, the length from the upper tip of the top ring to the lower tip of the bottom ring. This length for any spiral was termed the "normal length". Then small calibrated weights were suspended on it and the length measured as before. The weight in grams divided by the extension in millimetres was called the "sensitivity". The sensitivity when multiplied by the fraction of a millimetre to which the cathetometer was capable of measuring accurately (.05 mm. in our case) gave the"limit of detection" for the spiral in question. Two and one half times the normal length multiplied by the sensitivity gave the"maximum load" for any spiral.

To illustrate that the extension was linear, consider the following example;

Spiral #6022

| Load | Sensitivity |
|---|---|
| .4165 grs. | .00449 grs. per mm. |
| .3270 " | .00449 " " ". |
| .1670 " | .00449 " " ". |

A total of about fifty spirals were wound on this machine by the author, and besides those used in the work described in this paper, a considerable number were donated to Mr. C. A. Winkler to carry out his experiments in connection with the critical temperature.

2. The Bomb. (See A, Fig. 2.)

The heavy walled pyrex tubing was supplied in three-foot lengths; each length could be made into two finished bombs. The first step was to apply the oxy-gas flame to the middle of the three-foot length and allow the glass to fall in, and to finally obtain two elongated test tubes. Care had to be observed to insure uniformity of thickness and regularity of contour around the closed end in order to give maximum strength. A slight depression was made in the wall at a point fourteen inches from the closed end, (just below (B)). A piece of thin walled pyrex tubing was then selected which just fitted snugly within the bomb tubing but which came to rest against the constriction

at (B). A piece of this tubing three-eighths of an inch in length was fitted with a glass pulley, made from capillary tubing, which revolved freely upon a glass shaft fastened at both ends to the upper edge of the ring. Upon the lower edge of the ring were two glass guides, one at the centre and the other at the edge.

A thin wire nail was fitted loosely into a very thin walled pyrex sheath, and the sheath allowed to extend a short distance past both ends of the nail (E). This particular design prevented the nail from tipping away from the interior wall of the bomb at the end opposite to which the magnet was applied. A small glass hook on one end completed this unit.

The counterweight (W) was a piece of capillary tubing, adjusted in size so that its weight was almost equal to that of (E). A closed hook at the top of it, and an open hook at the bottom completed this part.

The float (D) was blown from pyrex glass, its shape was very uniform and of such design as to best resist high pressures without collapsing. The volume was made as near to one cubic centimetre as possible and its weight kept between .4 and .5 grams. A neat open hook was sealed to the top of it. The task of accurately determining the volume of the float presented a great difficulty for some time. A small specific gravity bottle was constructed with a wide mouth closed by a ground glass stopper and a capillary overflow from the opposite end. The float itself

was weighed, and the weight corrected for the buoyant effect of air. The specific gravity bottle was weighed full of distilled water at a known temperature, and again full of water with the float included within it. In this way a consistent determination of the volume of the float could be obtained.

A fine silk thread was tied to the glass-sheathed nail (E), then threaded up through the outside guide on (B), thence over the pulley and down through the centre guide to the counterweight (W). The length of the thread was such that with the nail about one inch from the bottom of the bomb, the counterweight (W) was against the saddle (B). The open hook of the float (D) was slipped into the ring at the bottom of the calibrated spiral (C), and the hook carefully closed, using a small flame. Similarily the hook on the bottom of the counterweight (W) was connected to the top ring of the spiral. The whole suspension was then carefully lowered into the bomb.

The bomb was then clamped in an upright position and immersed in water up to the level of (B). At a point two inches above (B) a uniform constriction was made in the tube, leaving only a narrow aperture. This procedure was followed because the silk thread had to be kept cool while it was only about one inch removed from molten glass. Furthermore it was desired to leave as little dead-space as possible above the saddle. A short piece of pyrex tubing was then sealed on to the open end of the bomb and connected to the filling device. (See page 41 Fig. 1, item T.)

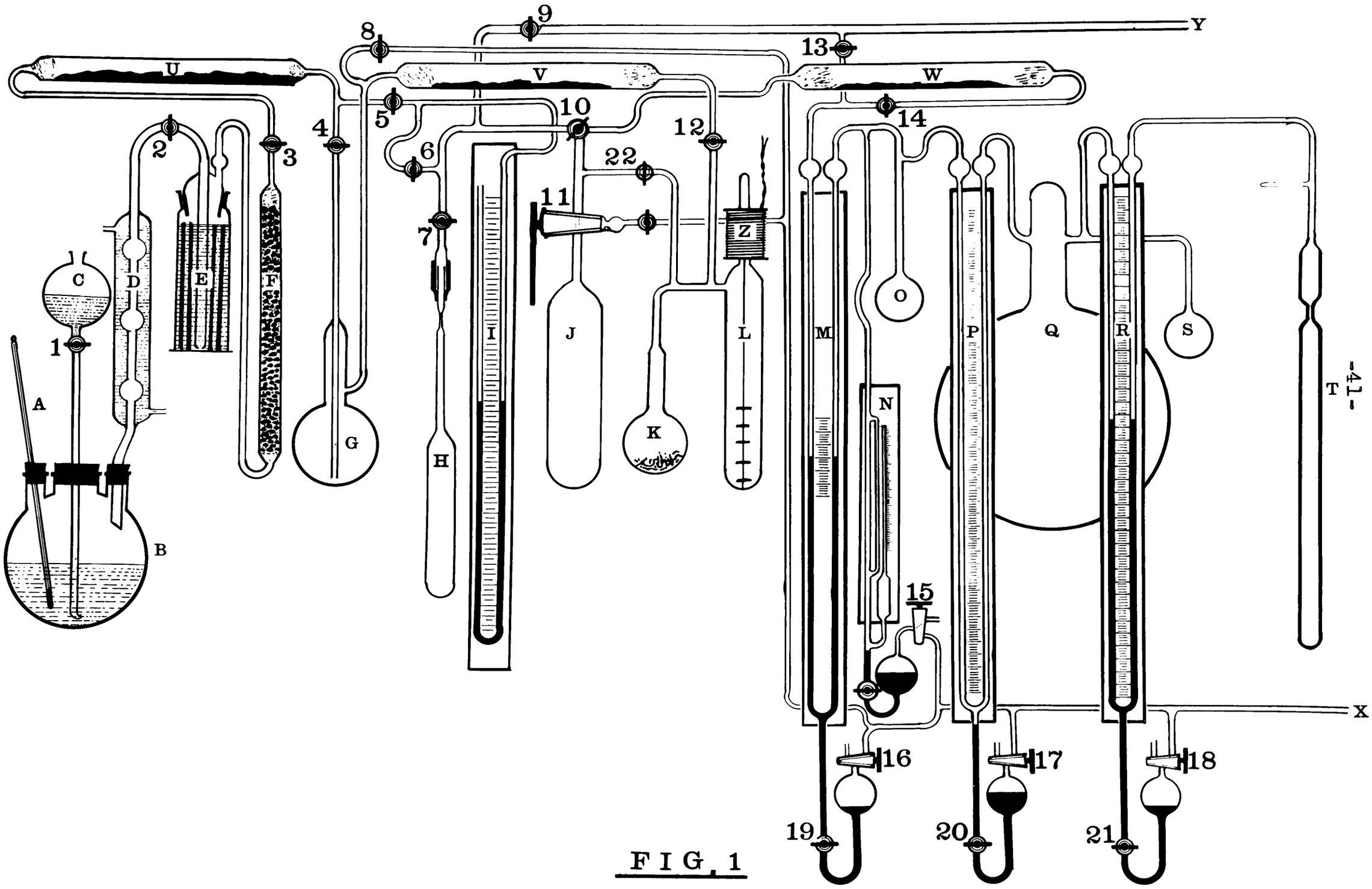
U
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FIG. 1

3. The methyl ether preparation and purification train

With reference to figure 1., page 41 , the apparatus may be divided roughly into three sections, the divisions being based upon the use of each section.

(i)(Commencing at the left) From (A) to (G) was designed for the preparation and crude purification of the ether.

(ii) From (H) to (L) was used for further refinement and delivery to storage bombs, as well as for introducing the ether back into the system from storage when desired.

(iii) The section (M) to (S) served to admit measurable quantities of pure ether to the finished bomb without the danger of contamination with air or stop-cock grease.

(B) was a one litre pyrex flask fitted with a 0 to 360°C. thermometer (A), a dropping funnel (C) and a water cooled condenser (D). (E) was a bubbler packed with glass rods and filled with concentrated sulphuric acid. Tubes (F) & (U) were supplied with calcium chloride lumps and phosphorous pentoxide, respectively. (G) was a 300 cc. pyrex flask.

In operation, 500 ccs. of concentrated sulphuric acid was added to (B), stop-cocks #2,3 & 4 were opened and a refrigerant (-80°C.) was placed around (G). Stop-cock #5 was turned so as to connect the system to the mercury manometer (I). A bunsen burner was placed under (B) and stop-cock #8, which communicated with the water

vacuum line, was manipulated so as to maintain a negative pressure of about 4 cms. of mercury as registered on (I). When the thermometer (A) reached 130°C., the methyl alcohol in (C) was admitted, drop by drop, to (B) through the glass valve #1. The temperature was kept steady and the pressure maintained as described. Liquid methyl ether collected in (G).

The water condenser (D) served to return any unused alcohol to the reaction chamber, as well as small quantities of water. The sulphuric acid bubbler (E) at first absorbed all the methyl ether which came over, but soon became saturated and then behaved as a drying agent and as a remover of alcohol vapor. The tower (F) acted as a further dryer, as also did (U). 250 ccs. of methyl ether could be prepared in this way in about three hours time. It will be observed that the arrangement of the dehydrators and alcohol removers was such as to protect the very active one, phosphorous pentoxide, from rapid hydration. The ether was now ready for fractional distillation and subsequent storage.

Stop-cocks #4,3 & 2 were closed and #12 was opened, the refrigerant was transferred from around (G) to (L), and the methyl ether slowly distilled from (G) to (L), passing through the phosphorous pentoxide drying tube (V). The container (L) had about ½ the capacity of (G), and was fitted with an electro-magnetically operated glass stirrer. When (L) was about ¾ full, stop-cock #12 was

closed, the refrigerant was replaced about (G) and also around (K). An empty dewar flask was set around (L) and the stirrer started. The methyl ether very slowly distilled , without bumping, into (K). The flask (K) contained about 4 grams of sodium wire, which it was thought would take out the last traces of water and alcohol. The last portion (15 ccs.) in (L) was allowed to escape each time. From (K) the ether was distilled into (J). The remainder of the ether which had been left in (G) was now put through (L) and (K), as previously described, and finally added to that already in (J). Stop-cock #11 was capable of resisting high pressures because its barrel was held in place by a vacuum, as illustrated.

The storage bomb (H) was made from ordinary glass tubing and could have any desired capacity from fifty ccs. down to ten ccs. It was fitted inside the glass tubing just below #7, and the joint made air-tight by a section of rubber tubing wired in place. Stop-cocks # 6 & 7 were opened and #11 was closed, #10, a two-way valve, was turned so as to connect (J) with (H). Vacuum was applied by opening #9, which communicated with (Y), the high vacuum line. When (I) registered a good vacuum, #9 was closed and the contents of (J) was allowed to warm up to about $0^{o}C$. This served to create a pressure of about two atmospheres in (J), which greatly speeded up the filling of the bomb (H). A momentary opening of #11 returned the pressure in (H) to atmospheric, which was again reduced, as before,

to a vacuum. After about three repetitions of alternate vacuum and pressure, the refrigerant was placed around (H) and the stop-cock #11 carefully adjusted so as to maintain a pressure in (H) of about one atmosphere, as read on the manometer (I). Fifty ccs. of ether could be transferred in this way, from (J) to (H) in about four minutes.

When (H) was four-fifths full of liquid, valve #11 was closed and stop-cock #9 opened, the cooling mixture was left around (H) and a flame applied to the constriction in the neck of the bomb. The constriction collapsed and the bomb was removed, and could be kept until needed at room temperature. Other bombs were placed in position and filled as before until the supply in (J) became exhausted.

Methyl ether, prepared exactly as described here, was supplied to Dr. E. W. R. Steacie[16] and Mr. H. A. Reeve[17] for experiments upon thermal decomposition rates. About two hundred ccs. was also used by Mr. C. A. Winkler[18] for his work on critical phenomena. The author used another six hundred ccs. in the work described by this paper. Roughly, about one litre of the liquid methyl ether has been handled by means of these storage bombs without a single mishap of any kind. Previously, methyl ether had been stored dissolved in concentrated sulphuric acid and liberated when desired by the addition of water; the method was wasteful and cumbersome, and the regenerated ether had to be exhaustively dried.

The section of the apparatus on the right of the diagram consisted,essentially, of three mercury seals, (M,P & R). (P & R) had carefully calibrated scales extending their full length, while (M) had only a short section of rough scale at its central point. Each branch of the U in every seal was topped by a twenty-five cc. bulb in order to prevent mercury from being forced through the system when one or other of the seals was pulled out while a difference of pressure existed on opposite sides of it. Even with this precaution, under pressure differences of more than ten cms. of mercury, the seal could not be successfully withdrawn. Stop-cocks #16,17 & 18 were of the two-way variety, one lead communicated with the water-vacuum line (X), while the other opened to the atmosphere. Stop-cocks #19,20 & 21 were ordinary one-way valves which were necessary to arrest the upward or downward motion of the mercury at the will of the operator. The length of the arms of each mercury seal was roughly 120 cms. and the height from the mercury level in the reservoir to a point half way up the U, was 76 cms. The mercury was carefully cleaned and dried, and its level was never allowed to fall below any one of the stop-cocks #19,20 & 21.

(N) was a McLeod gauge, capable of measuring pressures down to .0002 mm. of mercury. (O) was a fifty cc. pyrex flask, (Q) was a pyrex round bottom flask of roughly six litres capacity. It was planned at first to use this calibrated volume for introducing accurate quantities of

gaseous methyl ether to the bomb, but in practice it was never used as such. The small bulb (S) was intoduced to enable the gaseous methyl ether which had been accumulated in (Q) to be condensed, thus allowing the mercury seal (R) to be pulled out without forcing a slug of mercury out of (R) over into (T).

The thick walled pyrex glass bomb, described heretofore (page 38 ) was sealed to the system in the position (T). The interior details of the bomb have been omitted in Fig.1.

All the mercury seals were drawn out, stop-cock #14 was closed and #13 opened, thereby connecting the system from (M) to (T) with a Langmuir mercury pump backed up by a mechanical high vacuum pump. The evacuation was allowed to continue for a period of four or five hours, at the end of that time the pressure had been reduced to about .0003 mm. of mercury. The seal (M) was raised to the position shown in the diagram, and the extent of the vacuum was tested occasionally over a period of two hours to detect, if possible, any leaks. Very little trouble was encountered in making the system air-tight, and on several occasions, the pressure did not alter appreciably even when left for twenty-four hours.

When the testing of the system for leaks was being conducted, one of the methyl ether storage bombs of 35 or 40 cc. capacity was placed in a refrigerant (-20°C.) for five minutes, then removed, wrapped in a towel, and the

tip broken off. The open end was then inserted below stop-cock #7 and held there in the manner described previously. The contents was allowed to distill over into (J) and held in readiness. The phosphorous pentoxide drying tube (W) was replaced by a fresh one every time a new bomb was to be filled. When the system, to the right of (M), had been found capable of maintaining its vacuum, stop-cock #10 was turned so as to connect (J) with (W), stop-cocks #13 and 14 were opened and the small volume from #11 over to (M) was evacuated thoroughly. Stop-cock #13 was then closed and #11 was opened until the pressure, as indicated on (M), was about one atmosphere. The evacuation was then repeated, followed by the building up of the pressure as described. This process was performed about six times to be sure that whatever pressure did remain, was due to methyl ether gas and not air.

Mercury seals (P & R) were raised to their mid-point and (M) was drawn out, a refrigerant (-80°C.) was placed around (O) and the ether in (J) was caused to distil slowly into (O). When about twenty-five ccs. of liquid had collected in (O), the distillation was stopped and about five ccs. of liquid was allowed to evaporate out of (O) into the pump system (Y). The seal (M) was immediately returned to its position, as shown in the diagram. All the precautions described were to preclude the possibility of introducing any air into the carefully evacuated

system.

The mercury seal (P) was drawn out and the refrigerant around (O) was removed, and the pressure in (Q) was allowed to build up to about eighty cms. of mercury, as registered on (R). The mercury in (P) was then forced up into position by pressure applied to the atmosphere lead of stop-cock #17. Simultaneously,the refrigerant was returned to (O). Another dewar flask, containing a refrigerant, (-80°C.) was placed around (S) to reduce the pressure in (Q) to such a value that the seal (R) could be withdrawn. The refrigerant was then placed around (T), and the seal (R) immediately drawn down. When the desired amount of ether had been condensed in (T), the seal (R) was again raised. By means of the oxy-gas flame, the bomb (T) was sealed off at the constriction, and removed from the system.

4. The Heating Bath.

The accompanying diagram, Fig 2., page 50 , represents the arrangement of the heating apparatus, with the bomb in position. The actual container, (not shown in the diagram) was a pyrex glass jar, eighteen inches high and eight inches in diameter. The jar contained three gallons of glycoline which served as the heating medium. A certain amount of detail has been omitted from the drawing so as not to confuse with the really essential features,

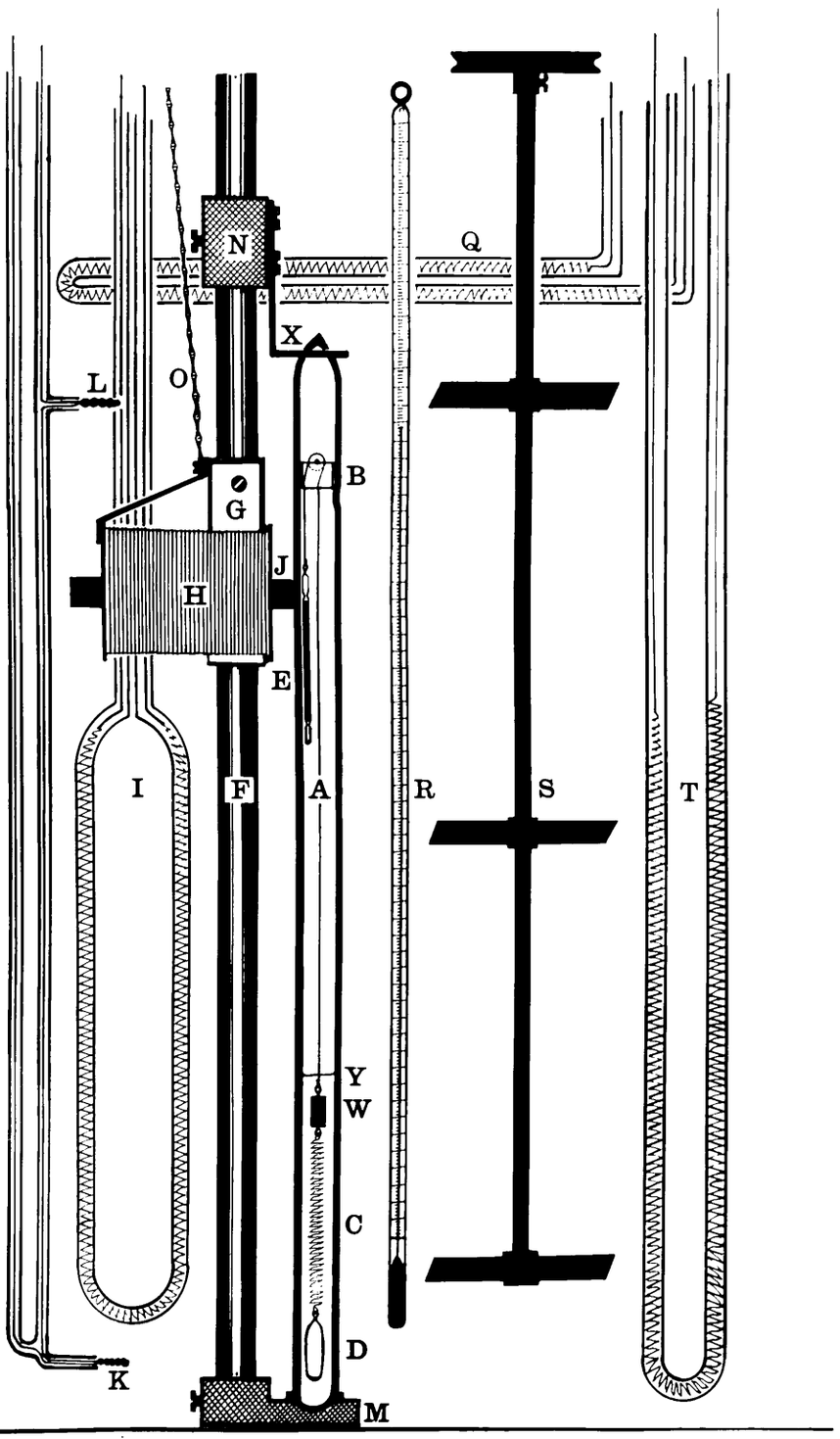



FIG. 2

furthermore, some of the parts have been slightly misplaced in order that all may be shown more clearly.

The thick walled pyrex glass bomb (A), contained the methyl ether, with the meniscus level at (T), it was securely set in a pocket in the wooden base (M) and held at the top by the heavy copper strip (X) which had a hole drilled in it large enough to fit over the tip and rest firmly on the shoulder of the bomb. This copper strip was in turn bolted to the collar (N), which was set-screwed to the heavy brass rod (F). This particular arrangement allowed for the easy removal of the bomb and yet assured that when in position it would be held rigidly in place. Great care was taken to be sure that the bomb was absolutely vertical and that nothing altered this in the process of heating.

The brass shaft (F), $\frac{3}{4}$ inch in diameter, had a keyseat cut its entire length, the brass collar (G) was fitted with a key which allowed the free vertical movement of (G) but restricted its rotation upon the shaft to almost zero. Attached to the collar (G) was an electromagnet (H), wound upon a hollow brass spool provided with brass ends. Through the brass spool was inserted a solid wrought iron core (J) which fitted closely but yet had free longitudinal movement within the spool. The correct length of the core was such, that with the bomb in position, about three-eighths of an inch more of the core projected from the spool at the end remote

from the bomb than from the end next to the bomb. The purpose of this was to insure that the pole-piece was kept in direct contact with the exterior of the bomb throughout the latter's entire length by means of the natural spring created by the core endeavoring to centre itself in the electro-magnetic field. This may seem like a superfluous refinement, but until it was adopted all sorts of difficulties were encountered in getting a firm grip upon the nail.

The chain (O) was fastened to (G) and proceeded upward and over a suitable sprocket mounted upon a shaft, and thence to a counterweight outside the bath. The shaft had a pulley over which ran a belt that extended back to another pulley and crank situated beside the operator. By turning the crank one way or the other, the magnet device could be raised or lowered at the will of the experimenter, and when the electro-magnet was turned on, the nail within the bomb, followed along, thereby placing the float (D) at any desired position between the upper and lower extremities of its movement.

The heaters (I & T) were connected in parallel with each other and in series with a suitable rheostat which could be adjusted to vary the current from one to nine amperes. Since the temperature control was entirely manual, a switch was connected <u>across</u> the rheostat leads, and when the temperature was observed to be falling

slightly, this switch was closed for four or five seconds thus raising the current flowing through (I & T) to a maximum for that length of time. When the switch was reopened the original flow of current was resumed. This dispensed with the difficulty of resetting the rheostat at the correct position after each restoration of temperature. With a little practice, the temperature control became a comparatively easy matter and needed to be checked not oftener than once every five or ten minutes. This amount of attention served to maintain the temperature to within one-twentieth of a degree of the desired value at all times.

The heater (Q) was on a separate switch and had its own controlling rheostat. (L & K) were the upper and lower junctions of an alumel-chromel thermo-couple. Actually (L & K) were exactly duplicated by a second set of similar junctions connected in series with those shown, the purpose being to give greater sensitivity. The carefully insulated leads from the thermo-couple were connected to a lamp and scale galvanometer. This device readily detected differences in temperature between the upper and lower junctions of the order of .01 degrees. Using this as a detector, the current necessary to maintain any desired temperature was correctly proportioned between (Q) and the double unit (I & T), so that the galvanometer registered no deviation. Taking no precautions, i.e. without operating (Q), the top of the

bath would become, from one to two tenths of a degree cooler than the bottom. The position of the junction (K) was not as close to the heater (I) as the drawing would indicate. Actually, both (K) and (L) were situated very close to the top and bottom of the bomb respectively, while heaters (I & T) were removed as far as possible from each other and from the bomb. A fourth heater (not shown) was also in the bath, but was used only in conjunction with (I & T) to raise the temperature fairly rapidly in the early stages of the heating, but was never used to maintain a temperature.

The thermometer (R) had a temperature range of 0 to 200°C., graduated in fifths, and was calibrated against a standard thermometer over the range of 100 to 150°C. The stirrer (S) occupied a central position in the bath, was of a sturdy construction involving double bearings top and bottom and was driven by a belt from a variable speed motor. The stirrer blades were about three inches long from tip to tip and were rotated at a brisk rate of speed to eliminate, as far as possible, any stagnant oil. Directly behind the bomb, but outside the glass containing vessel was a vertical row of four, one hundred watt, frosted mazda bulbs which provided a good clear illumination throughout the length of the bomb.

The whole bath was thermally insulated with asbestos and rested upon a fifty pound slab of slate. The entire unit was housed within a sheet-steel tank, 2½ feet high

2 feet wide and 1½ feet from front to back. The front face of the tank was inset with a plate-glass window, 23 inches high and 7 inches wide. Outside of this window were two wooden wings, securely fastened in such a manner as to leave only a sufficiently wide slit to make the bomb and thermometer visible. Ten feet back from this was a tough fibre-board screen, 7 feet high, and 7 feet across, firmly fastened in an upright position. A plate-glass window, 2 feet long and 6 inches wide was set in this screen at approximately the same level as the window in the tank. Behind the screen were all the electrical controls; the cathetometer, for measuring the spiral extension; the telescope for observing the thermometer; and the operator. Both the cathetometer and the telescope were especially constructed to give a high magnification at the distance for which they were used.

The apparatus as herein described has given good satisfaction for about 300 hours of actual operation. The factor of reliability was of great importance because the operator could not safely approach the heater to carry out any adjustments, alterations or repairs while the temperature was up. It required from 5 to 6 hours for the temperature to fall from 130°C. to room temperature, and about fifty minutes to recover the previous temperature.

## EXPERIMENTAL PROCEDURE.

The experimental procedure was not unduly complicated and did not greatly alter from the first bomb to the last. In the main, two types of determinations were attempted on each bomb.

(i) The density was measured from the upper to the lower limit of movement of the suspension while the bomb and its contents were maintained at some definite temperature. Obviously, this sort of measurement provided very little information when the meniscus level disappeared above the highest position to which the float could be raised.

(ii) The density, above and below the position at which the meniscus disappeared was determined at a succession of different temperatures, these temperatures first being approached from below and then from above.

Some of the first bombs tried were not correctly filled, i.e., they had too high a proportion of liquid for the available space, which resulted in the meniscus rising above the float, even at the latter's upper extremity of movement. At first it was not appreciated that slight variations in temperature throughout the length of the bomb would result in erroneous density values. For this reason, a number of determinations were incorrect, and to definitely show that the error was due to this cause, the temperature gradient was removed and finally reversed, which resulted in a corresponding alteration in density. The importance of removing this gradient will be shown in some detail in the following results.

Since all the weight measurements depended upon the length of the spiral which was measured by optical means, it was necessary to check up on any possible optical distortion brought about by the various layers of glass between the spiral and the eye. No correction was found to be necessary.

In all the bombs, the following data had to be compiled before the parts were assembled.

(i) The volume of the glass float. (V)

(ii) The weight of the float. (W)

(iii) The sensitivity of the spiral. (S)

(iv) The normal length of the spiral. (N)

With this information it was possible to determine the density of the medium surrounding the float at any time. The length of the spiral from tip to tip was measured by the cathetometer, say X mms. From this was subtracted the normal length,N, and the result multiplied by the sensitivity of the spiral,S. The product was subtracted from the weight of the float,W, and divided by the volume of the float,V, the result of this division gave the density. In abbreviated form it may be expressed as;

$$d = \frac{W - (X-N)S}{V} .$$

Consider an example; Bomb #13, Spiral #6043, Float #120a, Temperature 127.1°C., Float at top.

Top of spiral------ 25.510 cms.

Bottom of spiral--- 18.080 cms.

Extension------ 74.30 mms.

Extension ---- 74.30 mms. (X)

Normal ------- 39.15 mms. (N)

35.15 mms.

Sensitivity -- .00447 (S)

.15711 grs.

Weight of float ------ .3773 grs. (W)

Hence .3773 - .1571 = .2202 grs.

And $d = \frac{.2202}{.8691} = .2533$

The cathetometer readings could be checked repeatedly to .05 mms., but since two readings had to be made for each density determination, the limit of error might be considered as .10 mms. An alteration of this extent in the cathetometer reading would change the density value in the previous example by .0005.

In all the following tables of results, the densities have been determined as heretofore described. The particular conditions existing at the time of measurement are designated as is also the position of the float within the bomb. The results are collected into groups discriminated by the bomb from which they were obtained. In many cases the bomb was removed from the heater and replaced therein, between succeeding tables, while other bombs were investigated in the meantime.

# EXPERIMENTAL RESULTS.

## BOMB # 4.

Specifications: Spiral # 117877b.

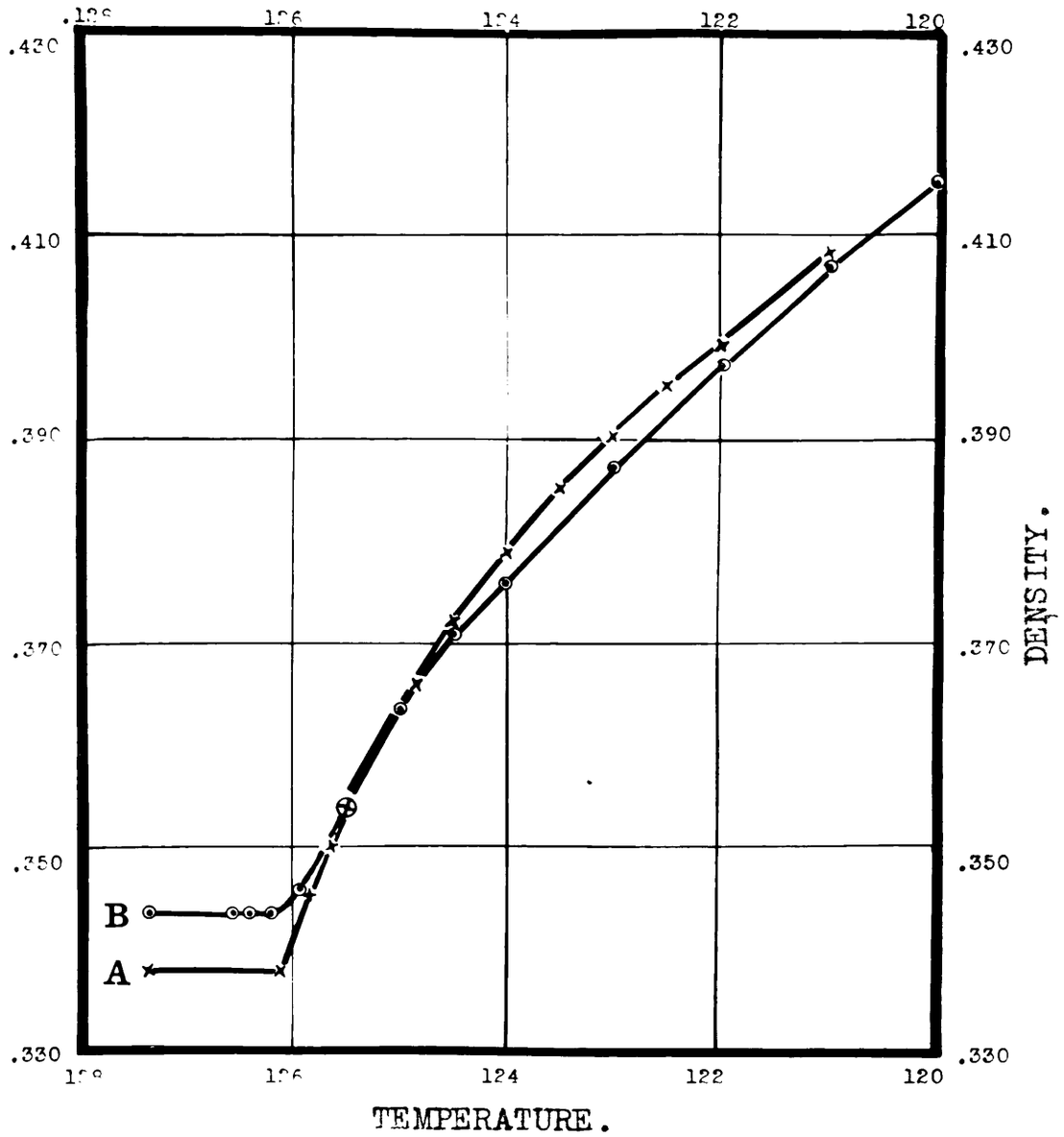
Float # 120b.

This bomb contained too much liquid, which resulted in the meniscus rising almost to the top of the bomb before disappearing. In all these determinations, the bottom of the bath was undoubtedly hotter than the top by about one-fifth of a degree. This vertical temperature gradient was not detected until later. Bomb # 4 was the first one to successfully yield density values above the critical temperature.

TABLE # 2.

| Temperature. | Density. |
|---|---|
| 127.35°C. | .3378 |
| 126.10 | .3378 |
| 125.85 | .3467 |
| 125.65 | .3503 |
| 125.50 | .3540 |
| 124.85 | .3661 |
| 124.50 | .3724 |
| 124.00 | .3788 |
| 123.50 | .3856 |
| 123.00 | .3904 |
| 122.50 | .3954 |
| 122.00 | .3993 |
| 121.00 | .4085 |

The float was about two cms. above the bottom of the bomb.




GRAPH # 1.

A. Corresponds to TABLE # 2.

B. Corresponds to TABLE # 3.

BOMB # 4. (Continued)

TABLE # 3.

| Temperature. | Density. | |
|---|---|---|
| 127.35°C | .3438 | @ |
| 126.55 | .3438 | |
| 126.40 | .3438 | |
| 126.20 | .3434 | |
| 125.90 | .3446 | |
| 125.50 | .3541 | @ |
| 125.00 | .3643 | |
| 124.50 | .3710 | @ |
| 124.00 | .3763 | @ |
| 123.00 | .3873 | @ |
| 122.00 | .3975 | @ |
| 121.00 | .4074 | |
| 120.00 | .4151 | |

The float was at its upper extremity of movement, i.e., about 25 cms. higher up in the bomb than in Table # 2.

(@ indicates an exact check with a previous or subsequent run.)

These results are plotted as temperature against density in GRAPH # 1.

It will be observed that the densities at the top and bottom are very nearly the same up to the critical temperature, but above that, the density at the bottom is less than at the top. The absolute temperature values recorded above may be slightly in error because the thermometer employed was destroyed before it could be standardized.

BOMB # 5.

Specifications: Spiral # 6014.
Float # 121.

This bomb had less liquid than # 4, but no density determinations were obtained because the glass failed to withstand the pressure. The whole bath was very thoroughly wrecked.

BOMB # 7.

Specifications: Spiral # 6021a.

Float # 122.

The amount of liquid was still less than in either # 4 or # 5, but again the meniscus rose above the float before disappearing.

TABLE # 4.

| Temperature. | Density. |
|---|---|
| 127.8°C. | .3042 |
| 126.4 | .3026 |
| 126.2 | .3026 |
| 126.0 | .3026 |
| 125.9 | .3117 |
| 125.8 | .3183 |
| 125.7 | .3231 |
| 125.5 | .3305 |
| 125.3 | .3380 |
| 125.0 | .3449 |
| 124.7 | .3502 |
| 124.4 | .3567 |
| 124.1 | .3615 |

Temperatures approached from above.

Float at the bottom.

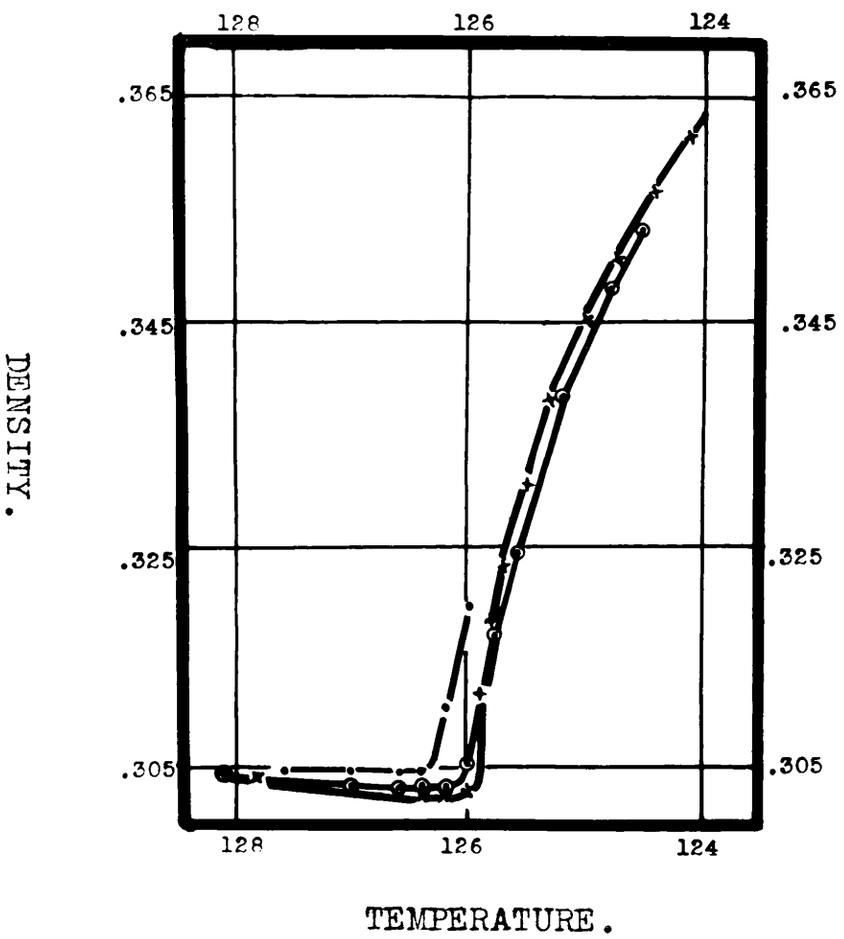
TABLE # 5.

| Temperature. | Density. |
|---|---|
| 124.5°C. | .3528 |
| 124.8 | .3479 |
| 125.2 | .3384 |
| 125.6 | .3244 |
| 125.8 | .3169 |
| 126.0 | .3051 |
| 126.2 | .3030 |
| 126.4 | .3030 |
| 126.6 | .3030 |
| 127.0 | .3030 |
| 128.1 | .3040 |

Temperatures approached from below.

Float at the bottom.

See GRAPH # 2.




GRAPH # 2.

+ Corresponds to TABLE # 4.

⊙ Corresponds to TABLE # 5.

• Corresponds to TABLE # 8.

BOMB # 7. (Continued)

TABLE # 8.

| Temperature. | Density. |
|---|---|
| 116.4°C. | .1315 |
| 118.0 | .1386 |
| 118.3 | .1400 |
| 119.1 | .1437 |
| 120.1 | .1483 |
| 121.0 | .1564 |
| 121.2 | .1582 |
| 122.7 | .1704 |
| 123.6 | .1792 |
| At this point the meniscus touched the bottom of the float. | |
| 126.0 | .3196 |
| 126.2 | .3104 |
| 126.4 | .3047 |
| 126.6 | .3047 |
| 127.0 | .3047 |
| 127.6 | .3047 |

Temperatures approached from below.

Float at its upper limit of movement.

See GRAPH # 2. (Only last part of Table # 8 is plotted)

BOMB # 8.

Specifications: Spiral # 6019.

Float # 123.

In this bomb the amount of liquid was still less than in any of the previous ones. The meniscus disappeared just below the float when the latter was at its upper limit.

TABLE # 12.

| Temperature. | Density. |
|---|---|
| 118.7°C. | .1423 |
| 118.9 | .1427 |
| 119.9 | .1491 |
| 120.9 | .1560 |
| 121.7 | .1628 |
| 122.6 | .1693 |
| 124.1 | .1872 |
| 125.0 | .2058 |
| 125.2 | .2083 |
| 125.4 | .2173 |
| 125.6 | .2244 |
| 126.1 | .2619 |
| 126.2 | .2678 |
| 126.4 | .2678 |
| 126.5 | .2678 |
| 128.0 | .2678 |

Float at its upper limit, and above the meniscus at all times.

Temperatures approached from below.

TABLE #13.

| Temperature. | Density. |
|---|---|
| 128.0°C. | .2678 |
| 126.8 | .2678 |
| 126.2 | .2678 |
| 125.8 | .2327 |
| 125.7 | .2287 |
| 125.6 | .2240 |
| 125.4 | .2167 |
| 125.1 | .2081 |
| 123.4 | .1821 |
| 122.6 | .1716 |
| 121.3 | .1613 |
| 120.4 | .1541 |
| 119.4 | .1470 |
| 118.2 | .1421 |

Float was at its upper limit, and above the meniscus at all times.

Temperatures approached from above.

See GRAPH # 3.

BOMB # 8. (Continued)

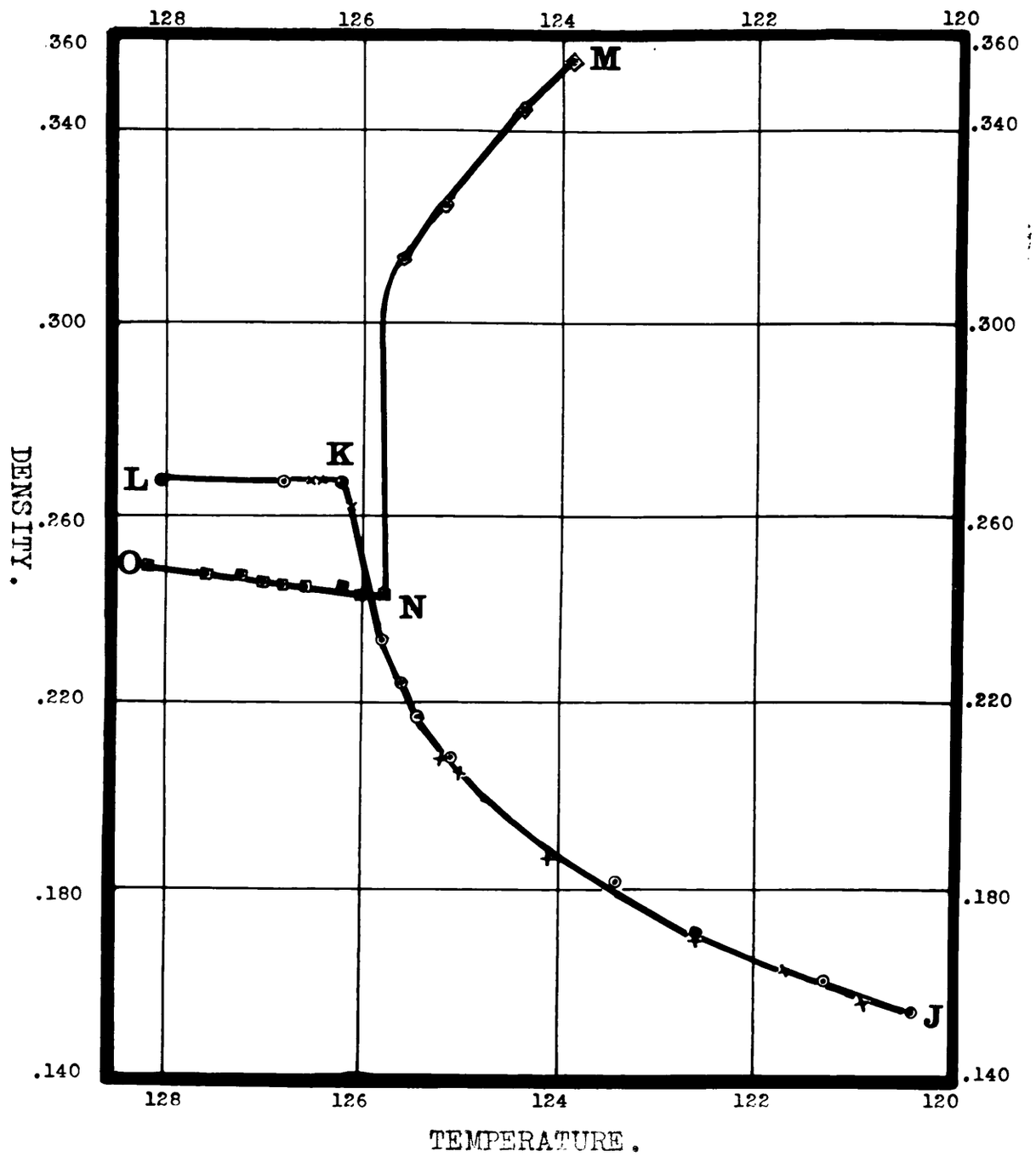
TABLE # 15.

| Temperature. | Density. |
|---|---|
| 123.1°C. | .3665 |
| 123.9 | .3549 |
| 124.4 | .3455 |
| 125.2 | .3250 |
| 125.6 | .3045 |
| 125.8 | .2436 |
| 125.9 | .2427 |
| 126.0 | .2432 |
| 126.2 | .2449 |
| 126.4 | .2449 |
| 126.6 | .2449 |
| 126.8 | .2453 |
| 127.0 | .2460 |
| 127.2 | .2470 |
| 127.6 | .2474 |
| 127.8 | .2483 |
| 128.2 | .2489 |
| 128.7 | .2498 |
| 129.3 | .2513 |
| 129.6 | .2524 |
| 129.9 | .2524 |

Float at bottom.

Temperatures approached from below.

See GRAPH # 3.




GRAPH # 3.

Curve, JKL corresponds to TABLES # 12 & 13.

Curve, MNO corresponds to TABLE # 15.

## BOMB # 9.

Specifications: Spiral # 6022.

Float # 125.

The amount of liquid in bomb # 9 was still less than in any of the preceeding bombs. The meniscus disappeared several centimetres below the float at the latter's upper limit of movement.

TABLE # 17.

| Temperature. | Density. |
|---|---|
| 118.4°C. | .1440 |
| 120.9 | .1600 |
| 122.5 | .1724 |
| 124.1 | .1926 |
| 125.9 | .2467 |
| 126.0 | .2655 |
| 126.1 | .271 |
| 126.4 | .271 |
| 127.0 | .271 |
| 128.7 | .271 |
| 130.9 | .270 |
| 133.3 | .270 |

Float above meniscus at all times.

Temperatures approached from below.

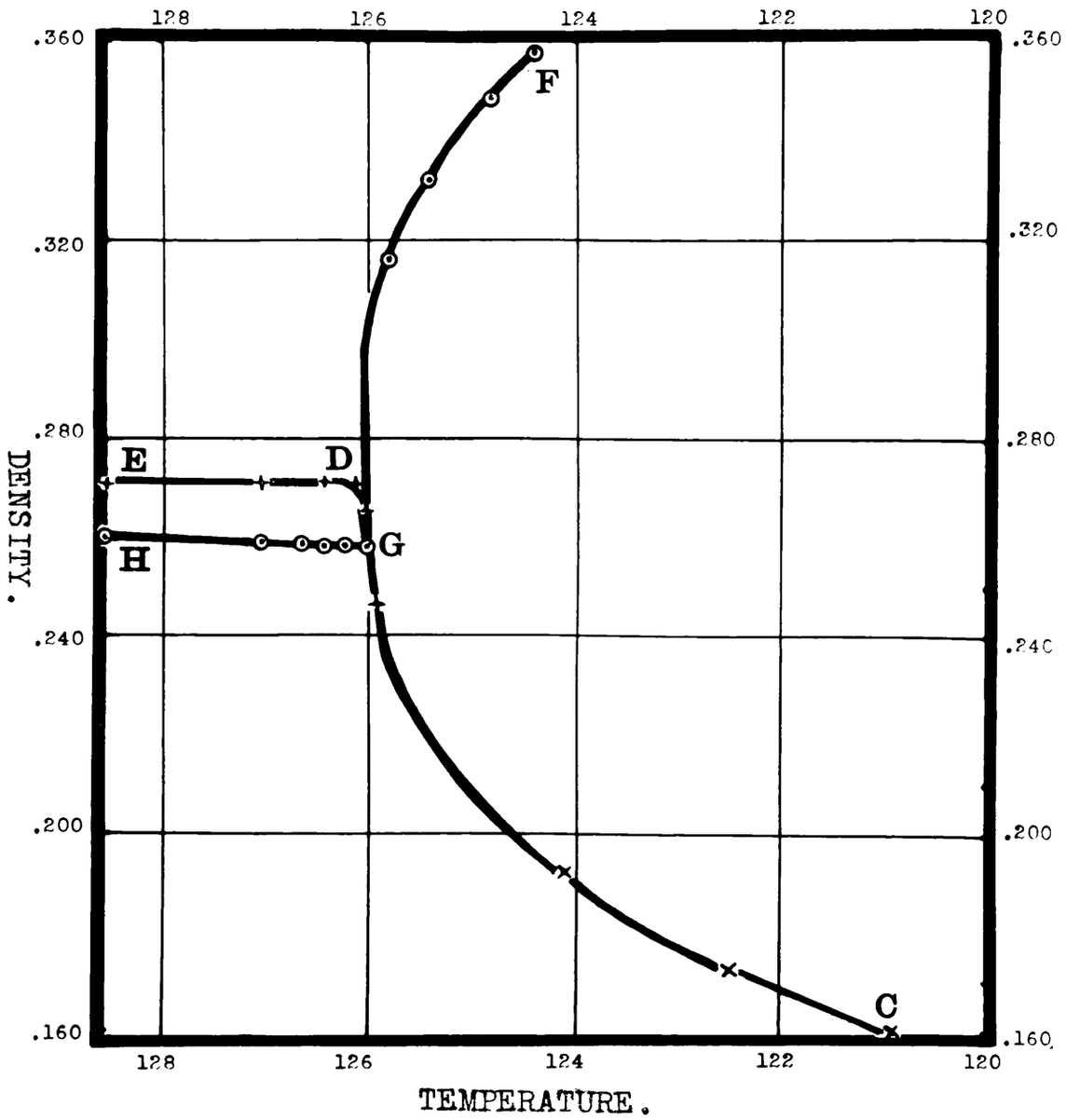
TABLE # 18.

| Temperature. | Density. |
|---|---|
| 124.4°C. | .3580 |
| 124.8 | .3491 |
| 125.4 | .3323 |
| 125.8 | .3161 |
| 126.0 | .2585 |
| 126.2 | .2585 |
| 126.4 | .2585 |
| 126.6 | .2596 |
| 127.0 | .2596 |
| 129.7 | .2616 |
| 130.9 | .2629 |

Float below meniscus at all times.

Temperatures approached from below.

See GRAPH # 4.




GRAPH # 4.

Curve, CDE corresponds to TABLE # 17.

Curve, FGH corresponds to TABLE # 18.

BOMB # 9. (Continued)

The unusual nature of the results, as found in tables # 17 and # 18, where the medium of greater density occurred above that of a lower density, required some further investigation. First of all, had a state of equilibrium been attained in the time allowed, and secondly, how would stirring, within the bomb, affect the densities? The following is a sample result of many that were obtained.

TABLE # 20.

| Temperature. | Distance of float from the bottom of the bomb. | | Density. |
|---|---|---|---|
| 127.8°C. | 3 cms. | (After one hour) | .2604 |
| 127.8 | 3 " | (After stirring) | .2604 |
| 127.8 | 3 " | (More Stirring ) | .2604 |
| 127.8 | 25 " | | .2674 |

These results show that the peculiar density values were not transitory nor caused by poor distribution of the material within the bomb.

The cause was obviously a permanent one, and the next probable cause to be investigated was the temperature distribution throughout the height of the oil bath.

BOMB # 9. (Continued)

It was at this stage of the work that the thermocouple (LK) and the heater (Q), (see Fig. 2), were added to the oil bath. With the aid of these units, the decrease in temperature existing from the bottom to the top of the oil was detected and finally removed. The following tables show how this correction radically altered the nature of the results, even in the very first attempt when the equalization of temperature was not as perfect as might have been desired. Later on, the equalization was vastly improved and checked by additional thermocouples in various places throughout the bath.

TABLE # 21.

| Temperature. | Density. (1) | Density. (2) | |
|---|---|---|---|
| 126.3°C. | .2128 | .2122 | |
| 126.5 | .2170 | | |
| 126.7 | .2202 | .2192 | |
| 126.9 | .2255 | | Float at a position above the visible meniscus. |
| 127.1 | .2296 | .2296 | |
| 127.3 | .2338 | | Temperature equalized throughout the bath. |
| 127.9 | .2432 | .2449 | |
| 128.9 | .2523 | .2535 | |
| 129.9 | .2583 | | Temperatures approached from below. |
| 131.1 | .2618 | .2606 | |
| 132.1 | .2638 | .2624 | |
| 135.0 | .2662 | .2648 | |

Density.(2) above represents values obtained on a different day.

BOMB # 9. (Continued)

TABLE # 22.

| Temperature. | Density. (1) | Density. (2) | |
|---|---|---|---|
| 128.9°C | .2662 | .2635 | |
| 127.3 | .2634 | | Float was above the visible meniscus. |
| 126.9 | .2613 | .2620 | |
| 126.7 | .2606 | | |
| 126.3 | .2384 | .2345 | Temperature was equalized. |
| 125.9 | .2220 | .2190 | |
| 124.9 | .2008 | .1977 | Temperatures were approached from above. |

TABLE # 23.

| Temperature. | Density. | |
|---|---|---|
| 125.9°C. | .3406 | |
| 126.3 | .3332 | |
| 126.7 | .3207 | |
| 127.1 | .3138 | |
| 127.9 | .2967 | |
| 128.9 | .2854 | |
| 131.1 | .2772 | |
| 132.3 | .2742 | |
| 135.1 | .2722 | |

Float near the bottom of the bomb.

Temperature equalized.

Temperatures approached from below.

TABLE # 24.

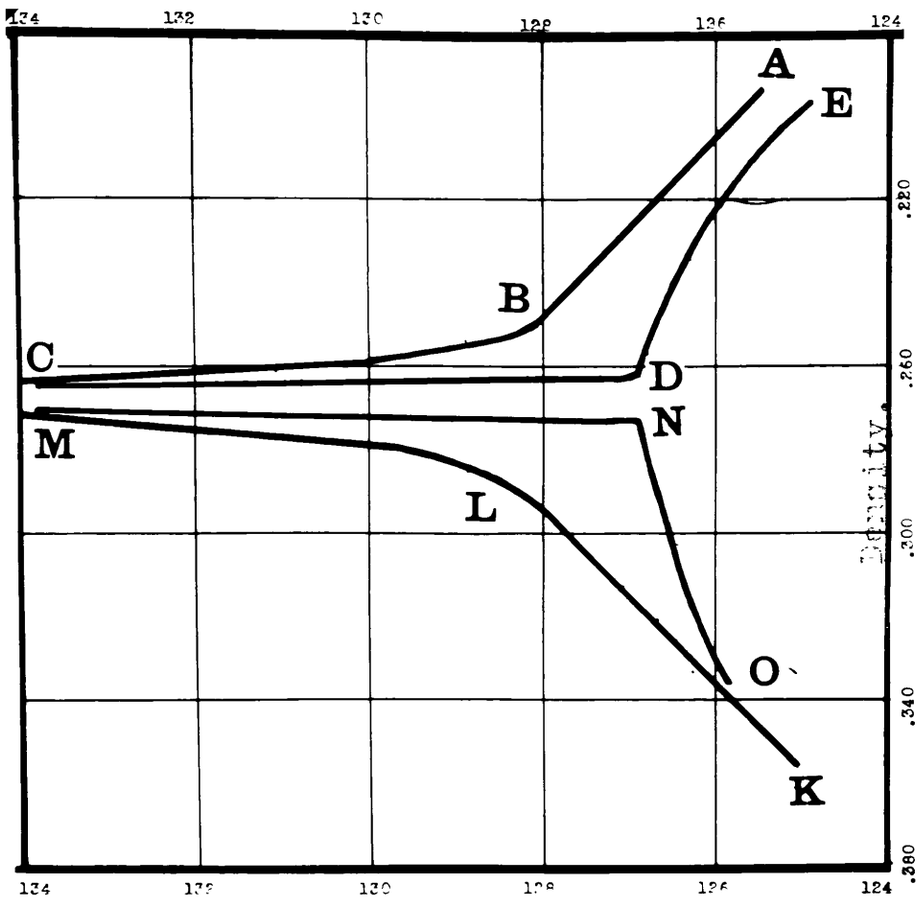
| Temperature. | Density. |
|---|---|
| 128.9°C. | .2722 |
| 126.9 | .2722 |
| 126.5 | .3020 |
| 126.3 | .3168 |
| 126.1 | .3288 |
| 125.9 | .3367 |

Float near the bottom of the bomb.

Temperature equalized.

Temperatures approached from above.

See GRAPH # 5.




Temperature.

GRAPH # 5.

Curve ABC corresponds to Table # 21.

Curve CDE corresponds to Table # 22.

Curve KLM corresponds to Table # 23.

Curve MNO corresponds to Table # 24.

BOMB # 9. (Continued)

To show how the temperature gradient from bottom to top of the bath affected the densities, the following determinations were made. By a suitably placed electric heating coil, the previously existing gradient was removed and then reversed.

TABLE # 25.

Float was near the bottom of the bomb.

| Temp. | Top of bath warmer than bottom by 1/10° C. Density. | Temperature equalized throughout the bath. Density. | Bottom of bath warmer than top by 1/10° C. Density. |
|---|---|---|---|
| 127.1°C. | .3192 | .3085 | .2954 |
| 127.9 | .3063 | .2939 | .2790 |
| 128.9 | .2923 | .2819 | .2736 |
| 132.3 | .2777 | .2742 | .2690 |

TABLE # 27.

Float was in the upper part of the bomb.

| Temp. | Top of bath warmer than bottom by 1/10° C. Density. | Temperature equalized throughout the bath. Density. | Bottom of bath warmer than top by 1/10° C. Density. |
|---|---|---|---|
| 127.1°C. | .2567 | .2476 | .2572 |
| 127.9 | .2574 | .2546 | .2622 |
| 128.9 | .2600 | .2598 | .2650 |
| 132.3 | .2639 | .2652 | .2677 |

BOMB # 9. (Continued)

The distribution of densities throughout the length of the bomb at any one temperature was now investigated.

The numbers appearing under the heading,"position", denote the cathetometer reading corresponding to the upper tip of the float. The bottom of the bomb, on the same scale, is equivalent to a reading of - 1.2 cms.

TABLE # 31.

Temperature = 127.1°C.
Temperature equalized throughout the bath.
Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 22.6 cms. | .2421 |
| 20.5 | .2560 |
| 18.4 | .2724 |
| 16.2 | .2847 |
| 12.1 | .2925 |
| 7.6 | .2930 |
| 2.0 | .2934 |

The preceeding table, and the four following tables form an interesting group.

BOMB # 9. (Continued)

TABLE # 32.

Temperature = 128.9°C.

Temperature equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 22.3 cms. | .2578 |
| 19.6 | .2594 |
| 18.1 | .2629 |
| 16.6 | .2736 |
| 16.3 | .2745 |
| 11.9 | .2790 |
| 8.6 | .2796 |
| 2.7 | .2805 |

TABLE # 33.

Temperature = 126.7°C.

Temperature equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 22.6 cms. | .2384 |
| 20.2 | .2454 |
| 18.1 | .2713 |
| 16.1 | .2867 |
| 12.5 | .2985 |
| 9.2 | .3009 |
| 5.7 | .3004 |
| 2.2 | .3006 |

Note:

In bomb # 9 the meniscus disappeared at a height of about 18 cms. from the bottom of the bomb at a temperature of 126.9°C.

BOMB # 9. (Continued)

TABLE # 34.

Temperature = 125.5°C.

Temperature equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 22.1 cms. | .2178 |
| 21.0 | .2253 |
| 19.7 | .2290 |
| 18.6 | .2329 |
| 16.6 | .3201 |
| 12.7 | .3305 |
| 10.9 | .3326 |
| 8.6 | .3363 |
| 5.7 | .3358 |
| 1.8 | .3360 |

TABLE # 35.

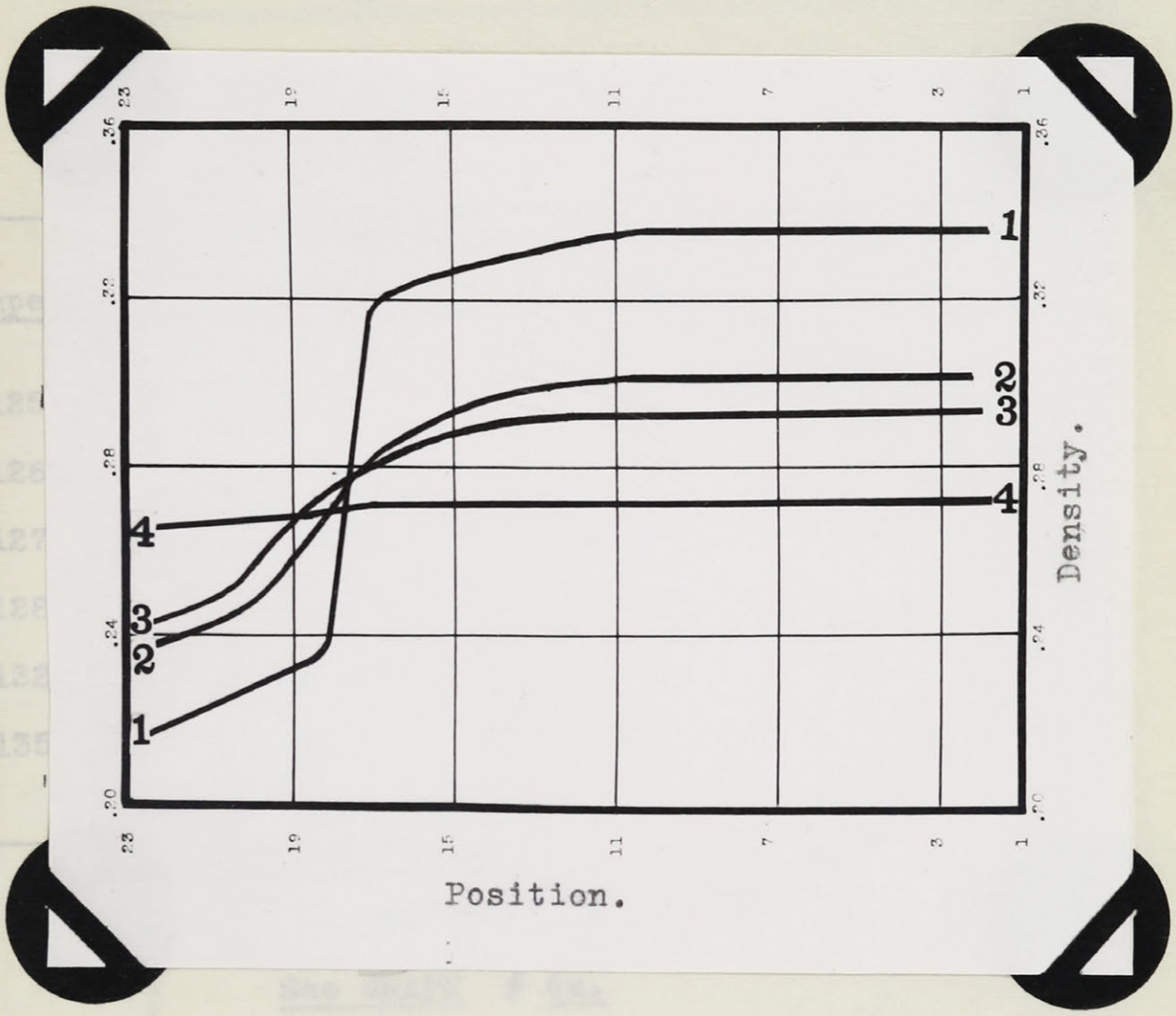
Temperature = 135.1°C.

Temperature equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 23.2 cms. | .2657 |
| 20.6 | .2685 |
| 17.0 | .2713 |
| 15.5 | .2713 |
| 12.2 | .2729 |
| 8.8 | .2725 |
| 5.4 | .2720 |
| 1.6 | .2727 |

The results of the previous five tables ( #'s 31 to 35 inclusive) have been plotted on GRAPH # 6.




GRAPH # 6.

Curve # 1 corresponds to Table # 34.

Curve # 2 corresponds to Table # 33.

Curve # 3 corresponds to Table # 31.

Curve # 4 corresponds to Table # 35.

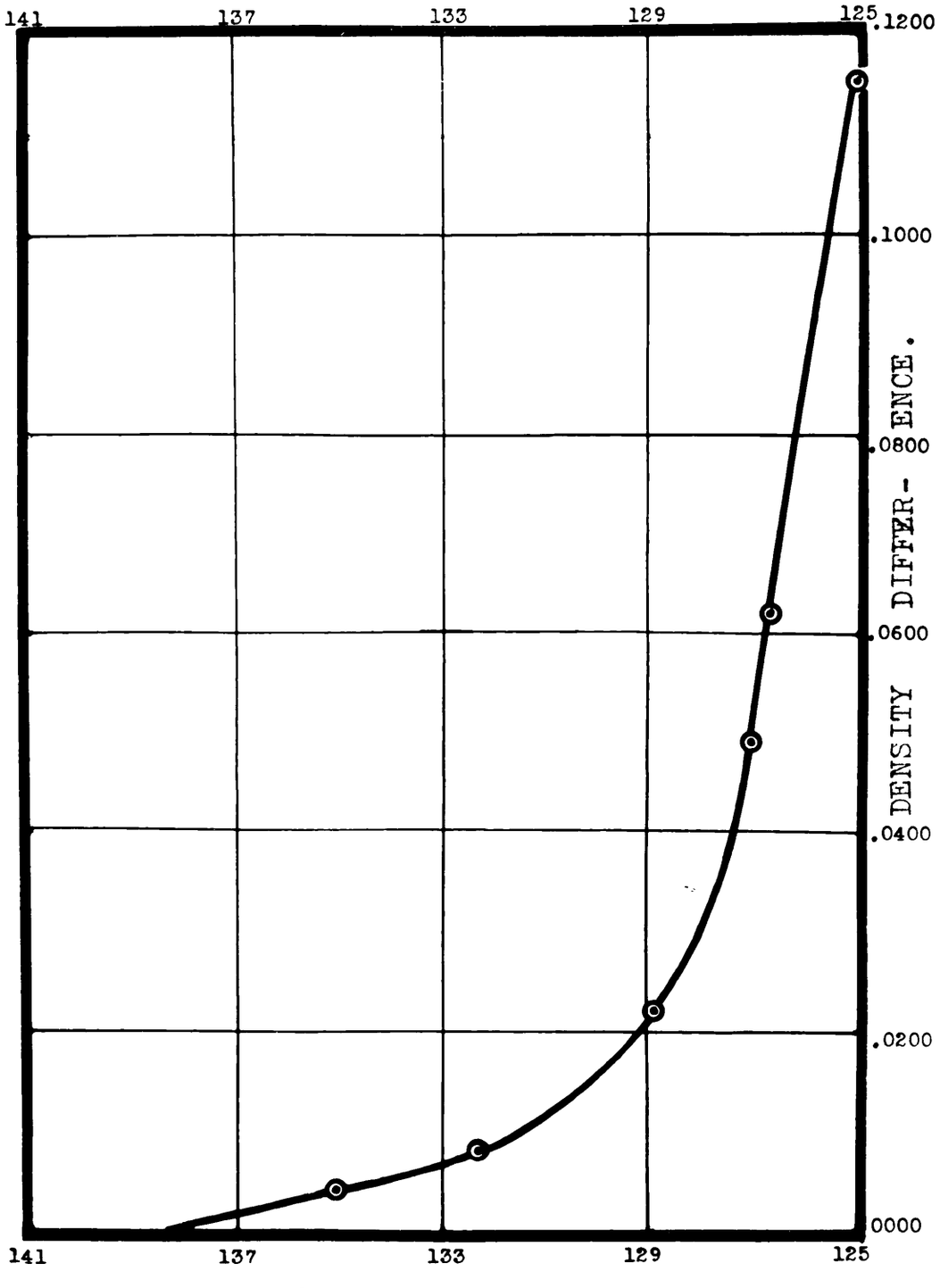
The graphical representation of Table # 32 fits into the above graph correctly, but has been omitted in order not to cause undue confusion of lines.

BOMB # 9. (Continued).

TABLE # 36.

| Temperature. | Density at 22 cms. | Density at 2 cms. | Difference. |
|---|---|---|---|
| 125.5°C. | .2200 | .3360 | .1160 |
| 126.7 | .2390 | .3010 | .0620 |
| 127.1 | .2450 | .2940 | .0490 |
| 128.9 | .2580 | .2800 | .0220 |
| 132.3 | .2650 | .2730 | .0080 |
| 135.1 | .2680 | .2720 | .0040 |

See GRAPH # 6a.


141
137
133
129
125
.1200
.1000
.0800
.0600
.0400
.0200
.0000
DENSITY DIFFER- ENCE.
TEMPERATURE.

GRAPH # 6a.

## BOMB # 10.

Specifications: Spiral # 6036.

Float # 200.

The amount of liquid was still less than in any previous bomb. The meniscus fell considerably when the bomb was heated slowly in the region of the critical temperature.

### TABLE # 49.

Temperature. = 125.5°C.

Temperature was equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 22.9 cms. | .2023 @ |
| 20.4 | .2023 @ |
| 16.4 | .2015 |
| 9.6 | .2046 |
| 7.2 | .3476 |
| 3.5 | .3494 |
| 1.2 | .3498 @ |

### TABLE # 43.

Temperature = 127.1°C.

Temperature was equalized throughout the bath.

Contents of bomb well stirred.

| Position. | Density. |
|---|---|
| 23.8 cms. | .2286 @ |
| 20.5 | .2283 |
| 17.3 | .2298 |
| 14.0 | .2298 |
| 9.9 | .2350 |
| 7.0 | .2376 |
| 4.8 | .2429 |
| 3.6 | .2512 |
| 2.9 | .2593 |
| 1.1 | .2871 @ |

@ These values were checked repeatedly in later determinations.

BOMB # 10. (Continued)

TABLE # 37.

Temperature = 127.9°C.

Temperature was equalized throughout the bath.

Contents of bomb was well stirred.

| Position. | Density. |
|---|---|
| 24.0 cms. | .2339 |
| 20.5 | .2354 |
| 17.8 | .2339 |
| 16.4 | .2350 |
| 14.1 | .2342 |
| 11.5 | .2342 |
| 7.9 | .2346 |
| 4.8 | .2368 |
| 3.0 | .2459 |
| 2.1 | .2489 |
| 1.0 | .2526 |
| " | " |

TABLE # 38.

Temperature = 128.9°C.

Temperature was equalized throughout the bath.

Contents of bomb was well stirred.

| Position. | Density. |
|---|---|
| 23.8 cms. | .2362 |
| 21.4 | .2368 |
| 18.4 | .2362 |
| 14.0 | .2362 |
| 7.8 | .2357 |
| 4.0 | .2379 |
| 2.8 | .2403 |
| 0.9 | .2429 |
| " | " |

BOMB # 10. (Continued)

TABLE # 39.

Temperature = 132.3°C.

Temperature was equalized throughout the bath.

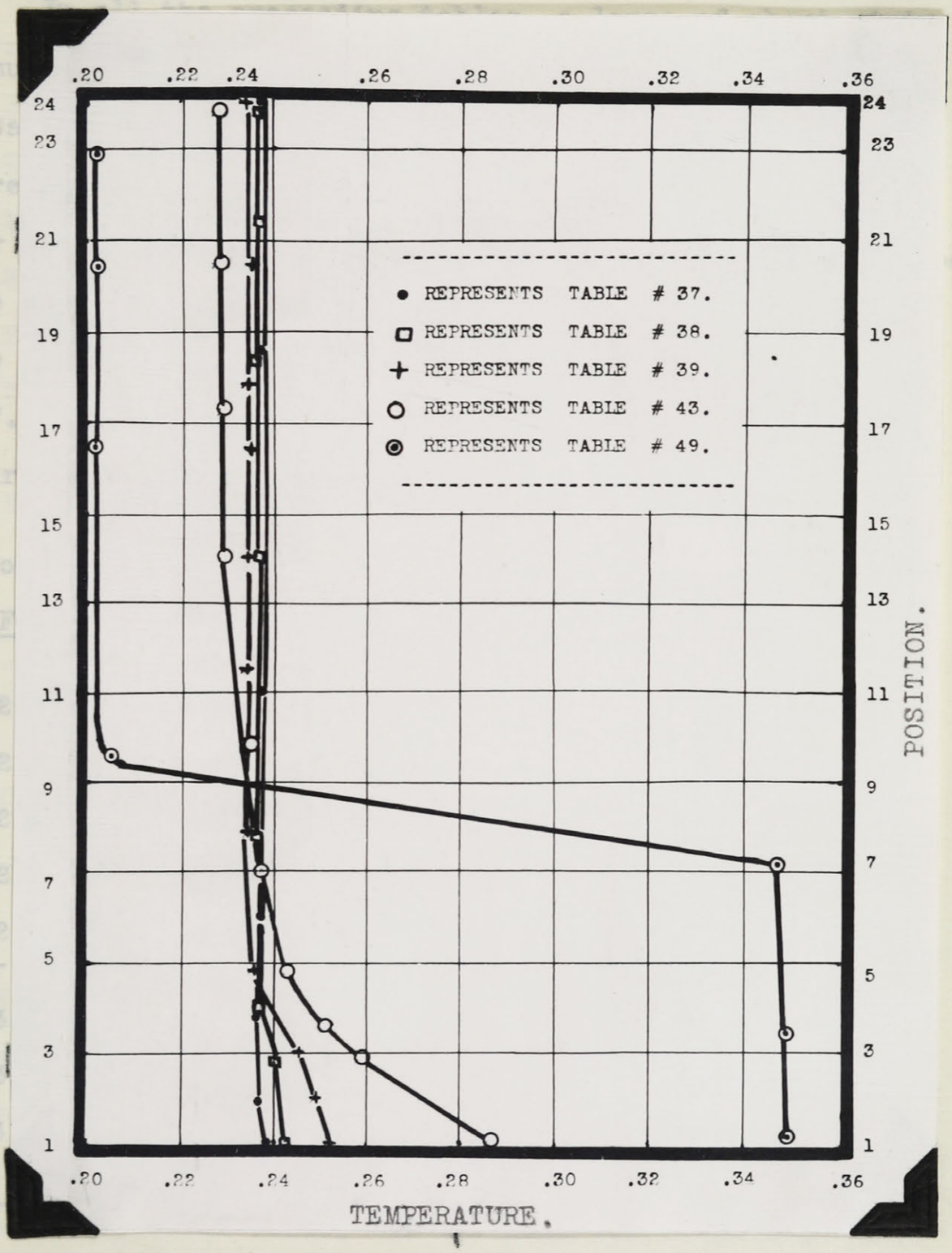
Contents of bomb was well stirred.

| Position. | Density. |
|---|---|
| 24.0 cms. | .2368 |
| 18.5 | .2365 |
| 11.0 | .2368 |
| 5.9 | .2368 |
| 3.9 | .2368 |
| 1.9 | .2376 |
| 1.0 | .2387 |

See GRAPH # 7 for TABLES # 37, 38, 39, 43 & 49.

Note:

In bomb # 10 the meniscus disappeared at a height of about 4 cms from the bottom of the bomb at a temperature of 126.9°C.


.20 .22 .24 .26 .28 .30 .32 .34 .36
24 23 21 19 17 15 13 11 9 7 5 3 1
REPRESENTS TABLE # 37.
REPRESENTS TABLE # 38.
REPRESENTS TABLE # 39.
REPRESENTS TABLE # 43.
REPRESENTS TABLE # 49.
POSITION.
TEMPERATURE.

GRAPH # 7.

BOMB # 10. (Continued.)

In all the preceeding tables, a lapse of about sixty minutes was allowed after any given temperature had been obtained, before the corresponding density measurements were made. Whether sufficient time had been allowed for equilibrium to have become established was problematical. The results of the first attempt to settle this question are given below. The two temperatures chosen, 125.5 and 127.1°C., were definitely on opposite sides of the temperature at which the visible meniscus vanished.

TABLE # 44.

| Position of Float. | Temperature. | Time. | Density. |
|---|---|---|---|
| 2.4 cms. | 125.5°C. | 0 min. | .3490 |
| 2.4 | 125.5 | 15 | .3490 |
| 2.4 | 125.5 | 55 | .3490 |
| 2.5 | 125.5 | 65 | .3493 |
| 2.0 | 125.5 | 70 | .3493 |
| 23.4 | 125.5 | 72 | .2028 |
| 23.3 | 125.5 | 77 | .2023 |
| 23.4 | 125.5 | 90 | .2023 |

The contents of the bomb was given a thorough stirring between each of the above determinations.

BOMB # 10. (Continued)

TABLE # 44a.

| Position of Float. | Temperature. | Time. | Density. |
|---|---|---|---|
| 23.5 cms. | 127.1°C. | 0 min. | .2181 |
| 23.6 | 127.1 | 10 | .2226 |
| 23.7 | 127.1 | 18 | .2253 |
| 23.6 | 127.1 | 26 | .2267 |
| 23.8 | 127.1 | 35 | .2282 |
| 1.0 | 127.1 | 40 | .2868 |
| 23.6 | 127.1 | 50 | .2286 |
| 1.0 | 127.1 | 60 | .2868 |
| 23.7 | 127.1 | 80 | .2286 |

The contents of the bomb was given a thorough stirring between each of the above determinations.

The two temperatures, 125.5 and 127.1°C., in the immediately previous tables, were each approached from below. This meant that after the temperature had been established, the density in the lower part of the bomb decreased with the passage of time, and the density in the upper part increased to an equilibrium value. If the same two temperatures were approached from above, then the passage of time would cause the densities, in the lower and upper regions of the tube, to approach their equilibrium value from the opposite direction to that in the previous example.

BOMB # 10. (Continued)

The results obtained with bomb # 9 showed that the equilibrium density values, determined above the temperature at which the meniscus disappeared, depended for their magnitude upon the direction from which the temperature was approached.

( See tables 21 to 24, inclusive; page 72 ).

( See graph # 5 ; page 74 ).

The period of observation was not longer than thirty minutes for any one temperature.

Whether, given more time, the equilibrium density would become the same regardless of the direction of approach was next investigated.

TABLE # 50.

| Position. | Density. | |
|---|---|---|
| 23.0 cms. | .2057 | Temperature = 125.5°C. approached from 132.3°C. |
| 18.9 | .2057 | |
| 15.1 | .2065 | Temperature equalized throughout the bath. |
| 10.7 | .2061 | Contents of bomb was well stirred. |
| 9.2 | .2061 | |
| 5.4 | .3476 | TABLE # 50 is to be compared with; |
| 1.0 | .3498 | TABLE # 49, page, 82 & TABLE # 44, page, 86 |

BOMB # 10. (Continued).

TABLE # 48.

| Position. | Density. | |
|---|---|---|
| 22.3 cms. | .2335 | Temperature = 127.1°C. approached from 132.3°C. |
| 17.0 | .2331 | ---------- |
| 9.0 | .2335 | Temperature equalized throughout the bath. |
| 4.9 | .2338 | ---------- |
| 2.3 | .2402 | Contents of bomb was well stirred. |
| 1.0 | .2500 | |

TABLE # 48 is to be compared with;

TABLE # 43, page, 82.

& TABLE # 44a, page, 87.

It will be observed that TABLE # 50, agrees with TABLE # 49 & 44, much more closely than does TABLE # 48 agree with TABLES # 43 & 44a.

At a temperature of 127.1°C., no meniscus nor cloud were visible, regardless of the direction of approach. At 125.5°C., a clearly defined meniscus was visible under the conditions imposed by either mode of approach.

The two particular temperatures used as illustrations above were not unique in any way. Instead of 125.5°C., any temperature below the critical temperature might have been substituted, and instead of 127.1°C., any temperature above the critical temperature and not beyond 132.3°C., could have been used to give the same general result.

BOMB # 10. (Continued)

In other words, it appears that if the differences exhibited between tables 48 and 44a, are due to an equilibrium lag, then the mere presence of a meniscus is sufficient to almost completely remove this lag.

After sundry experiments with several other bombs, and after completely rebuilding the heating bath, Bomb # 10 was again placed in the heater. The chief object was to see if the results already recorded here could be repeated. Again the question of whether enough time had been allowed for equilibrium to have become established was revived and to endeavour to finally settle this point, the following results were derived.

TABLE # 52.

| Time. | Density at 23 cms. above the bottom. | Density at 1 cm. above the bottom. |
|---|---|---|
| 0 min. | .2346 | Temperature = 132.3°C. Temperature was equalized throughout the bath. Contents of bomb was well stirred. |
| 5 | .2354 | |
| 10 | .2354 | |
| 15 | .2354 | |
| 18 | | .2373 |
| 25 | | .2373 |

BOMB # 10. (Continued).

TABLE # 51.

| Time. | Density at 23 cms. | | Density at 1 cm. |
|---|---|---|---|
| 0 min. | .2109 | | |
| 3 | .2170 | | |
| 8 | .2226 | | |
| 13 | .2240 | | |
| 18 | .2256 | | |
| 23 | .2267 | | |
| 28 | .2271 | | |
| 43 | .2275 | | |
| 58 | .2278 | | |
| 73 | .2275 | | |
| 88 | .2286 | | |
| 103 | .2290 | | |
| 118 | .2290 | | |
| 133 | .2304 | | |
| 148 | .2309 | | |
| 163 | .2317 | - | |
| 178 | .2317 | - | |
| 193 | .2317 | - | |
| 208 | .2317 | - | |
| 223 | .2317 | - | |
| 228 | | | .2507 |
| 233 | | | .2507 |

Temperature = 127.1°C.

Temperature equalized throughout the bath.

No stirring, except after 208 minutes.

## BOMB # 11.

Specifications: Spiral # 6041.
Float # 120.

This bomb contained slightly less material than any of the previous ones.

The only information derived was that the density of the liquid was .3483, and the density of the vapor .2030 at 125.5°C.

The spiral suspension suffered damage after about five hours of use which made it impossible to obtain any further readings.

## BOMB # 12.

Failed to hold the pressure, and thoroughly wrecked the heating bath.

All the preceeding results have been in agreement as far as the existence of a density difference between top and bottom is concerned. The fact that slight temperature differences between the top and bottom of the bomb brought about such pronounced alterations in the magnitude of the density difference (see page 75 ) made it advisable to check upon this phase of the work.

A second, double unit, thermocouple with moveable upper junctions was inserted in the bath. By means of this addition various regions along the entire length of the bomb was investigated and compared with a point opposite the bottom of the bomb. It was found that under conditions of heating arranged to give uniform temperature throughout, the galvanometer showed no deflection while the upper junctions were moved from a position an inch under the surface of the oil down to about three inches from the bottom of the bomb. This shows quite conclusively that the heating of the bomb was uniform when the galvanometer gave no deviation from the zero mark. A temperature difference of one tenth degree brought about a deflection of three centimeters on the galvanometer scale.

It will be noted that heretofore the density alterations brought about by any particular set of temperature conditions was treated separately. In other words, let us say that the bottom of the bath was made warmer than the top by $1/10^{o}$, then the effect of this had been noted at several different average temperatures, the bath was then cooled down, the liquid state allowed to reappear and after an intermission of several hours, the process was repeated with, let us say, the temperature equalized throughout.

The following tabulation of results shows the way in which a succession of temperature differentials affected the density distribution within the bomb. That is to say, a temperature one degree above the point at which the meniscus vanished was maintained and the temperature gradient successively altered. Of the three possible conditions , i.e., warmer at the bottom, equalized, and warmer at the top, all were tried in every possible manner ofsuccession. Complete cycles were performed in different orders to see what the effect would be. By a consideration of the time values it will at once be evident between what stages the liquid was allowed to reappear in the bomb.

Bomb. # 9.

| Time | Position | Density | |
|---|---|---|---|
| 0 Min. | bottom | .2752 | |
| 4 " | top | .2749 | |
| 14 " | bottom | .2736 | Temp. = 127.9° C. |
| 19 " | bottom | .2718 | Bottom 1/5 ° warmer. |
| 29 " | bottom | .2705 | |
| 39 " | bottom | .2692 | |
| 44 " | top | .2705 | |

From the conditions existing as described immediately above, the temperature was made equal top and bottom. The temperature on the thermometer was still 127.9°.

| Time | Position | Density |
|---|---|---|
| 0 Min. | bottom | .2687 |
| 6 " | top | .2683 |
| 30 " | top | .2683 |
| 40 " | bottom | .2683 |

This was the first hint that the densities, once brought to equality top and bottom, would not shift back to the usual density difference when the temperature gradient along the bomb was removed. The stability of this one-way shift was investigated more fully.

| Time | Position | Density | |
|---|---|---|---|
| 15 Min. | top | .2561 | |
| 25 " | top | .2572 | |
| 30 " | bottom | .2856 | Temp. 127.9° C. |
| 45 " | top | .2552 | Temp. equalized. |
| 60 " | top | .2544 | |
| 65 " | bottom | .2828 | |
| 75 " | top | .2546 | |
| 85 " | bottom | .2821 | |
| 100 Min. | bottom | .2874 | |
| 105 " | bottom | .2884 | |
| 107 " | top | .2486 | Temp. 127.9° C. |
| 122 " | top | .2486 | Top 1/10° warmer. |
| 125 " | bottom | .2869 | |
| 135 " | bottom | .2875 | |
| 145 " | bottom | .2888 | |
| 160 Min. | bottom | .2803 | |
| 165 " | top | .2544 | Temp. 127.9° C. |
| 175 " | bottom | .2798 | Temp. equalized. |
| 180 " | bottom | .2801 | |
| 200 Min. | bottom | .2752 | |
| 205 " | top | .2611 | Temp. 127.9° C. |
| 225 " | top | .2643 | Bottom 1/15° warmer. |
| 240 " | top | .2661 | |
| 255 " | bottom | .2687 | |

The following procedure was carried out with the object of finding if anything could induce the density difference to reappear once equality had been obtained. More time than previously was allowed under equalized temperature conditions and finally a slight excess temperature at the top was employed.

For about one hundred minutes the temperature was maintained at 127.9° with the bottom 1/10° warmer. The density, top and bottom, became equal.

| Time | Position | Density | |
|---|---|---|---|
| 100 Min. | bottom | .2683 | |
| 115 " | top | .2676 | |
| 120 " | bottom | .2681 | |
| 123 " | bottom | .2692 | Temp. 127.9° C. |
| 125 " | top | .2678 | Temp. equalized. |
| 145 " | top | .2683 | |
| 150 " | bottom | .2685 | |
| 160 " | bottom | .2683 | |
| 165 " | top | .2681 | |
| 175 " | top | .2683 | |
| 185 Min. | bottom | .2742 | Temp. 127.9° C. |
| 195 " | top | .2558 | Top 1/15° warmer. |

This was not carried any farther at this time, but it served to show that by means of even a slight excess temperature at the top for ten minutes there was affected a redistribution of densities which 75 minutes at equal temperature failed to do.

| Time | Position | Density | |
|---|---|---|---|
| 10 Min. | bottom | .2879 | |
| 15 " | top | .2495 | Temp. 127.9° C. |
| 95 " | top | .2544 | Temp. equalized. |
| 100 " | bottom | .2825 | |
| 170 Min. | top | .2696 | Temp. 127.9° C. |
| 175 " | bottom | .2696 | Bottom 1/10° warmer. |
| 190 Min. | top | .2683 | |
| 210 " | bottom | .2699 | |
| 220 " | bottom | .2720 | |
| 245 " | bottom | .2738 | Temp. 127.9° C. |
| 265 " | top | .2637 | Top 1/20° warmer. |
| 280 " | top | .2631 | |
| 295 " | top | .2631 | |
| 310 " | bottom | .2770 | |
| 311 Min. | bottom | .2749 | |
| 325 " | bottom | .2695 | Temp. 127.9° C. |
| 330 " | top | .2682 | Temp. equalized. |
| 345 " | bottom | .2678 | |

The following table is an account of the result of prolonged heating at 127.9°, temperature equalized, and accompanied by vigorous stirring within the bomb.

| Time | Position | Density | |
|---|---|---|---|
| 60 Min. | bottom | .2899 | |
| 90 " | bottom | .2865 | |
| 105 Min. | bottom | .2865 | |
| 120 " | bottom | .2865 | |
| 150 " | bottom | .2865 | Continuous stirring. |
| 153 " | top | .2576 | |
| 160 Min. | top | .2585 | |
| 165 " | top | .2590 | |
| 180 " | top | .2606 | |
| 195 " | top | .2618 | |
| 210 " | top | .2627 | |
| 225 " | top | .2634 | |
| 235 " | top | .2646 | |
| 240 Min. | bottom | .2798 | |
| 255 " | bottom | .2814 | |
| 260 " | bottom | .2814 | |
| 270 " | top | .2611 | Continuous stirring. |
| 280 " | top | .2618 | |
| 290 " | bottom | .2805 | |
| 305 " | top | .2632 | |
| 345 " | top | .2646 | |

| Time | Position | Density | |
|---|---|---|---|
| 10 Min. | bottom | .2888 | |
| 33 " | bottom | .2805 | |
| 73 " | bottom | .2775 | |
| 118 " | bottom | .2722 | Temp. 127.9° C. |
| 136 " | bottom | .2694 | Bottom 1/10° warmer. |
| 138 " | top | .2673 | |
| 140 " | bottom | .2673 | |
| 145 Min. | top | .2668 | |
| 146 " | bottom | .2668 | Temp. 127.9° C. |
| 172 " | top | .2668 | Temp. equalized. |
| 173 " | bottom | .2668 | |

Now the temperature of the whole bath was slowly lowered, being careful to maintain equal temperature top and bottom all the time.

| Time | Temp. | Density at bottom | |
|---|---|---|---|
| 183 Min. | 127.9 | .2668 | |
| 188 " | 127.7 | .2668 | |
| 190 " | 127.5 | .2668 | |
| 192 " | 127.3 | .2668 | |
| 195 " | 127.1 | .2668 | |
| 198 " | 126.9 | .2668 | |
| 201 " | 126.7 | .2668 | |
| 205 " | 126.5 | .2668 | |
| 207 " | 126.4 | .2668 | (Heavy fog) |
| 209 " | 126.3 | Fog obscured view. | |

A note on the nature of the fog.

Under the conditions imposed in the foregoing table, the formation and disappearance of the fog presented a remarkable sight. The tube remained perfectly clear down to 126.5°, at 126.4° a mist flashed into view throughout the entire length of the bomb. The intensity was uniform and the distribution complete. As the temperature dropped, the mist increased in intensity, and at 126.3° entirely concealed every trace of the spiral and float. Suddenly a clear spot appeared immediately at the bottom of the bomb. This clear spot swept upward at about 1 cm. per second. Simultaneously a clear region fell, with equal rapidity, from the top. The clear regions met about 12 cms. above the bottom and revealed a sharp meniscus. The whole dissipation of the fog occupied not more than 15 seconds. It will be noted that the temperature of the reappearance of the meniscus was about ½ of a degree lower than that temperature at which it disappeared.

To more clearly show the exact nature of the previous 6 pages of results, a brief summary is here appended.

1. Temp. 127.9°C.

(i)
Bottom 1/5° warmer than the top.
Density difference = 0.
Time = 44 minutes.

---

(ii)
Temp. 127.9°C.
Temperature equalized.
Density difference = 0.
Time = 40 minutes.

---

2. Temp. 127.9°C.

(i)
Temperature equalized.
Density difference = .0275
Time = 85 minutes.

---

(ii)
Temp. 127.9°C.
Top 1/10° warmer.
Density difference = .0402
Time = 45 minutes.

---

(iii)
Temp. 127.9°C.
Temperature equalized.
Density difference = .0257
Time = 20 minutes,

Temp. 127.9°C.

(iv) Bottom 1/15° warmer than the top.

Density difference = .0026

Time = 55 minutes.

---

3. Temp. 127.9°C.

(i) Bottom 1/10° warmer.

Density difference = 0.

Time = 100 minutes.

---

Temp. 127.9°C.

(ii) Temperature equalized.

Density difference = 0.

Time = 75 minutes.

---

Temp. 127.9°C.

(iii) Top 1/15° warmer.

Density difference = .0184.

Time = 10 minutes.

---

4. Temp. 127.9°C.

(i) Temperature equalized.

Density difference = .0281

Time = 100 minutes.

Temp. 127.9°C.

(ii) Bottom 1/10° warmer.

Density difference = 0.

Time = 75 minutes.

---

Temp. 127.9°C.

(iii) Top 1/20° warmer.

Density difference = .0139

Time = 120 minutes.

---

Temp. 127.9°C.

(iv) Temperature equalized.

Density difference = 0

Time = 35 minutes.

---

5. Temp. 127.9°C.

Temperature equalized.

Density difference = .0173

Time = 345 minutes.

Almost continuous stirring.

---

6. Temp. 127.9°C.

(i) Bottom 1/10° warmer.

Density difference = 0

Time = 140 minutes.

---

(ii)

Temp. 127.9°C.

Temperature equalized.

Density difference = 0

Time = 28 minutes.

---

(iii)

Temp. 127.9°C. to 126.4°C.

Temperature equalized.

Density difference = 0

Time = 26 minutes.

---

## C O N C L U S I O N.

An apparatus has been constructed which has successfully served to measure the density existing in any part of a sealed tube containing material below, at, or above the critical temperature. No previous workers in this field have managed to design or construct a similar machine, nor one which gave nearly the same accuracy or versatility of determination. An important factor in the success of the apparatus was the development of a mechanical device for making compact and very accurate quartz spirals. All of the previously doubtful factors, such as vertical temperature gradients, impurities, and gravitational influences, have been either eliminated or accounted for in the experimental work.

A definite difference in density between the bottom and top of the contents of the bomb has been found above the temperature at which any visible line of demarcation could be noted. There apparently still existed a region in which the densities altered rapidly for very small differences in position of the float, and this region corresponded very closely to the position at which the meniscus was last visible.

Above or below this position, no marked density fluctuations were detectable over distances of several centimetres. This fact more or less rules out the assumption that the density differences obtained were brought about through gravitational influences. As would be expected, the absolute density values were different in different bombs, depending upon the proportion of liquid to available space. Furthermore, on raising the temperature several degrees above the critical temperature, the density difference between the upper and lower portions, decreased, and with subsequent lowering of the temperature, increased, but did not reach nearly the original values. The above results have been obtained time and again in the same bomb and in different bombs, and may be looked upon in the nature of a generalization. Taking them alone into account, the conclusion might well be drawn that there is a definite difference between the liquid and vapor state which persists above the temperature at which the meniscus vanishes. Involved in this equilibrium of so called "gasons" and "liquidons" of Traube, there is a resistance effect which gives rise to the above mentioned hysteresis. This would be apparent without specifying the exact nature of the "gasons" and "liquidons" except as a terminology to

indicate a definite discontinuity between the liquid and gaseous states, be it due to association or the still more speculative idea of a difference in molecular volume.

It may be pointed out that asymtotically, the hysteresis effect pointed to infinite time for final equilibrium, as measured, and this adds a further complication to any theoretical elucidation. On top of this came the experiments involving the maintenance of a temperature differential. When the lower medium was kept at even one-tenth of a degree warmer than the top, (all above the critical temperature) the upper portion of the tube, not only became equal in density to the bottom but actually exceeded it by a very appreciable amount. After once this equality had been reached, the restoration of a uniform temperature throughout the length of the bomb could not reestablish the usual density difference, nor could it alter in the slightest, the complete uniformity of the density, even when maintained for prolonged periods of time. On the contrary, upon making the top as little as one-fifteenth of a degree warmer than the bottom, the complete uniformity was at once destroyed and the density in the lower portion of the bomb exceeded that in the upper.

It is possible to suggest that with a temperature differential in which the bottom was warmer, the dense medium above must have been in continuous gravity diffusion with the medium below and thus brought about an intermixing which reduced the lag in equilibrium that might be assumed to have been the fundamental cause of any density differences so far observed. However, a little reflection precludes the possibility of such a simple explanation. The performance of continuous stirring upon the medium, equivalent to a mechanical mixing, failed to accomplish any semblance of equalization of densities, even over prolonged periods of time. This failure is contrary to the simple explanation advanced above.

The work described has to be analysed from two different viewpoints, the classical and predominating hypothesis of a continuity of state and the hypothesis of a definite discontinuity in property as most radically advanced by Traube's theory of gasons and liquidons. On the basis of the classical theory, starting with a medium at the critical temperature but at a pressure much above the critical pressure, reduction of pressure leads to a continuous increase in volume until the critical pressure is reached, then the inflection in the isothermal may be represented mathematically by $dV/dP = -\infty$. On the classical theory, when a liquid

in equilibrium with its vapor is heated up, the density of the former decreases and the density of the latter increases until at the critical temperature, $d\rho_1/dT = -\infty$ and $d\rho_2/dT = +\infty$, where $\rho_1$ is the density of the liquid and $\rho_2$ is the density of the vapor. These plus and minus infinities involved in the compressibility-pressure relationships and in the density-temperature gradients can be interpreted from an experimental point of view, that true equilibria are not reached except at infinite time. By analogy, consider an unopposed chemical reaction where the velocity - time gradient becomes asymtotic and is therefore never definitely reached. The question arises, are the phenomena recorded above interpretable in this sense? Is the density difference between the vapor and the liquid above the critical temperature due to some resistance effect? If so, then this resistance effect is not due to a viscosity phenomenon in the ordinary sense of the word. The mechanical stirring to which the medium was subjected without any noticeable differences, the time experiments which showed no observable trend of density equalization are in support of this view. Then in dealing with infinities, may the resistance toward equilibrium become infinite? One experiment seems to show that this is not the case. On heating the medium to a considerable

amount above the critical temperature, the density differences diminished. Upon the reverse process, the density differences did not revert to the same values, but a definite density difference was found and therefore in the reverse direction, a change definitely opposed to a continuity of state was observed.

On the other hand, a temperature gradient in the medium, in line with the above $d\rho/dT$ variation brought about an equalization of density which seemed to be irreversible. Hence we have two apparently contradictory pieces of experimental evidence as to the nature of the phenomenon being one due to a lag effect or a definite discontinuity between the liquid and gaseous states. Further experimentation must be carried out in this connection.

In spite of what has just been said, the preponderance of evidence as given by the experimental results is against the classical theory. The difference in density is obviously not due to a gravitational effect. The difference in density is apparently not due to a viscosity effect. The density difference cannot be due to an impurity effect in the sense that the impurity was originally distributed between the vapor and the liquid, because unquestionably, the amount of impurity that could have been present could not have influenced

the density as measured, to an appreciable extent, even had it been concentrated at one point in the medium. This is not saying that the impurity might not have promoted a lag in the establishment of the equilibrium.

The last sentence above, involves what may be said against the classical theory. Granted what is doubtful in view of the experiments recorded, that there is a lag which only infinite time would dispel, the question remains before us; a lag between what? The mere acceptance of a lag of equilibrium of density which is not due to a temperature gradient, a gravity effect, nor the mass influence of an impurity, implies an equilibrium between two distinct and different states of matter and one which persists above the critical temperature.

In the light of further experimentation, this view may be modified, but at present it can be claimed that the results obtained above point to an as yet unexplained difference between the liquid and gaseous states of aggregation which is not dependent solely upon, pressure-volume-temperature data.

It is obvious that further experimentation is required. The task is by no means an easy one because the results are so much a product of the experimental conditions. A start has been made here and a great number of the technical difficulties have been overcome. It is

believed that the generalizations with regard to the data contained above will not be altered, but this further experimental work may give the additional information which will answer the question of the existence of a true continuity of state.

Experiments must be performed with systematic variation of the average density of the medium in the bomb. Experiments must be carried out in which the medium is taken through various temperature differentials and time cycles. The definite generalizations established with regard to the behavior of methyl ether at the critical temperature must be substantiated by experiments with other substances. In other words the experiments described have indicated the necessity of further work, and of even greater importance, they have pointed out the ways and means of going about the work. It may require several years to accumulate sufficient data upon which to base a substantial theory. It is premature, therefore, to offer theoretical explanations which would be of necessity, highly speculative.

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