# INVESTIGATION OF DENSITY OF VAPORS IN EQUILIBRIUM WITH LIQUIDS

# T H E S I S

## INVESTIGATION OF DENSITY OF VAPORS IN EQUILIBRIUM WITH LIQUIDS

**The methyl-ether liquid-vapor equilibrium at the critical temperature.**

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SUBMITTED

TO

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## INTRODUCTION

The characteristic of a liquid to endeavor, at all times, to be in equilibrium with its own vapor gives rise to the phenomenon of vapor pressure. If the liquid is in an open vessel exposed to the atmosphere, ebullition will set in when the vapor pressure has reached a value of one atmosphere. However if the liquid be entirely enclosed and then heated above its normal boiling point no bubbles will result, but evaporation will take place silently and inconspicuously with the result that the amount in the vapor phase will increase with a rise in temperature. Finally a remarkable occurrence takes place. The meniscus dividing the two phases disappears and no longer can any distinction be made between vapor and liquid. The temperature at which this transformation occurs for any substance is called the critical temperature and the corresponding pressure and volume are known as the critical pressure and critical volume.

The first time that this phenomenon had been observed and recorded was in 1822 by Cagniard de la Tour, (Ref. #1). Since that time many experimenters such as Sir William Ramsay, (Ref. #2) and M. Jamin, (Ref. #3) have observed the same occurrence and made definite measurements on the critical pressure and volume of many substances. However there is still room for investigation of the visible phenomenon attending the transformation as well as for studying the effects of varying amounts of liquid relative to the space of the container, especially when moderately large amounts of liquid are utilized (20-30 c.cs.).

The large number of references given below refer to workers who have expressed divergent views with regard to the explanation of the phenomena observed, (Ref. #4). Furthermore little work of very recent date is recorded.

With this in view the following work was carried out as an introduction to a systematic and detailed investigation for the future. Consequently this initial investigation was from the start somewhat exploratory. The observations made in one line of endeavor invariably served as a guide to the next procedure with a view to a closer investigation of some particular phenomenon. Consequently the results have been arranged in the order which they were obtained. Although the report is by no means complete in itself, yet it does seem to yield information which would serve as a useful guide to further investigation of a more detailed character capable of theoretical interpretation.
The investigations throughout were made on methyl ether, chosen because of its relative ease of preparation and moderately low critical pressure.

## APPARATUS

### General

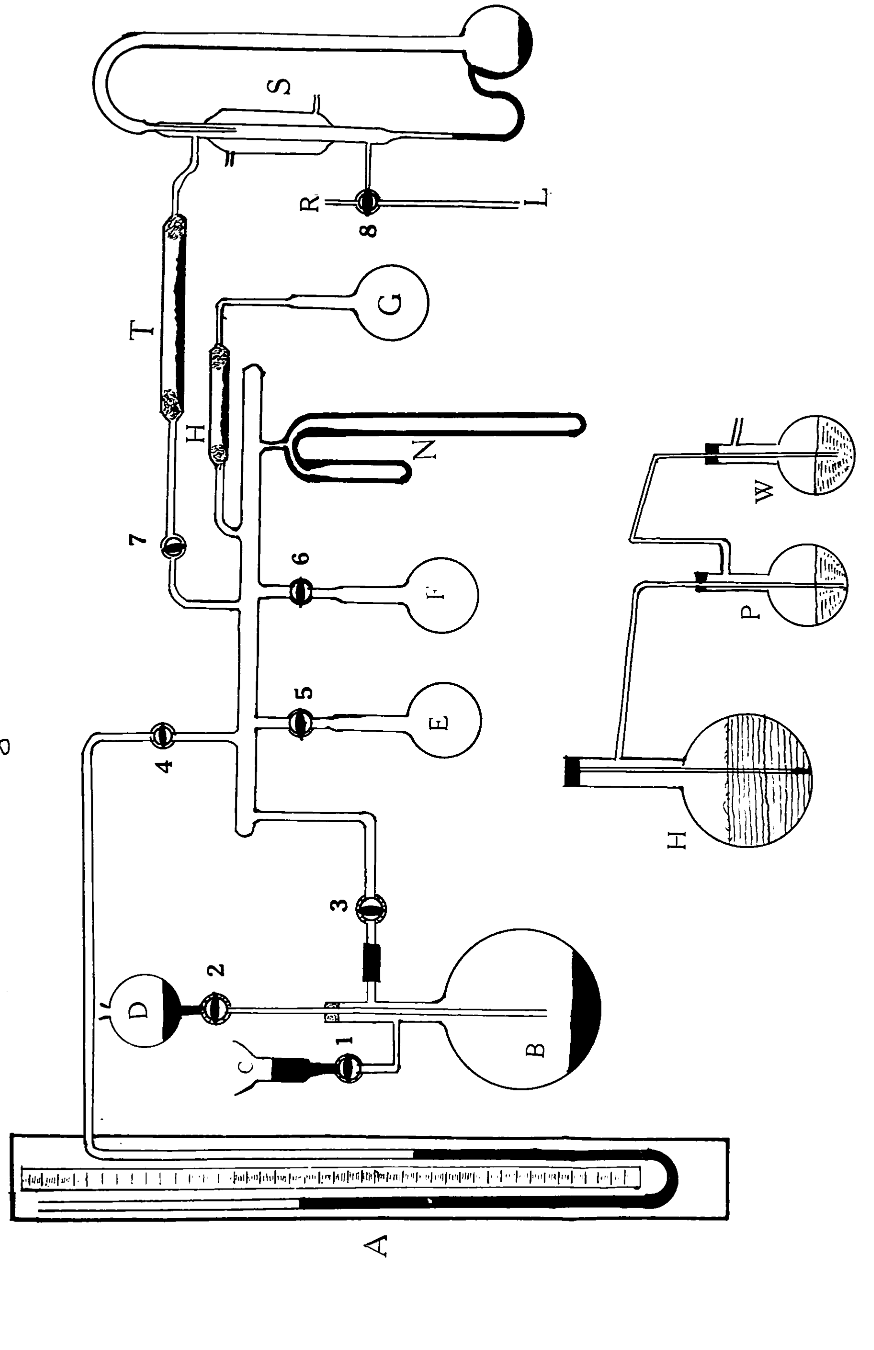
The apparatus utilized consisted essentially of two units. The one was for preparing and purifying the methyl ether. The other was for maintaining the high pressure tube at definite temperatures and at the same time was arranged so as to protect the operator from the effects of a possible explosion.

Methyl ether is a gas at ordinary temperatures and pressures and it liquifies at -20° C to a transparent liquid with a density of very nearly 0.5. It is very soluble in water and also dissolves in concentrated sulfuric acid to the extent of about fifty volumes of gas to one volume of acid. However, the addition of small amounts of water to sulfuric acid saturated with methyl ether results in the immediate liberation of most of the dissolved ether. This property proved of value in storing quantities of ether between time of preparation and time of requirement. Furthermore this method of liberation effectively removed any alcohol vapors which might have arisen from the primary preparation.

The methyl ether was generated by the addition of concentrated sulfuric acid to methyl alcohol in equal proportions by volume. This addition had to be carried out very carefully or the heat generated would have resulted in the loss of great quantities of the product.

The alcohol (about 200 c.cs.) was placed in a 500 c.cs. pyrex distilling flask and cooled thoroughly in a mixture of ice and water.

Diagram IA



The 200 c.cs. of sulfuric acid which was to be used was also cooled in the same bath and then added in about 25 c.cs. portions and evenly mixed and cooled between additions. When the whole amount of the acid had been added in this way the flask was fitted with a cork stopper, thermometer and delivery tube which dipped beneath the surface of 50 c.cs. of concentrated sulfuric acid (P) and thence to another container with another 50 c.cs. of sulfuric acid (W). (See diagram 1B).

The reaction vessel was then carefully heated until lively effervescence resulted and the heating continued until the temperature rose to about 135° C. When absorbing vessel #1 had become saturated; as evidenced by the appearance of bubbles in #2 a fresh lot of acid was moved into the #1 position. The acid thus saturated was ready for the extraction and purifying train. The purifying train served also to deliver the methyl ether into the required tubes.

Description

As shown in diagram 1A, at the extreme left there is a mercury manometer (A) with one tube open to the atmosphere and capable of registering pressures from zero up to 2 atmospheres. (B) is a 500 c.cs. distilling flask with an extra side arm introduced and connected to the small reservoir (C). (D) is a dropping funnel which enters (A) through a cork. (E, F & G) are 50 c.cs. round bottom flasks connected to the main line as shown. (H) is a phosphorous pentoxide drying tube introduced between (G) and the system. (S) is a Langmuir pump connected through another phosphorous pentoxide tube (T) to the system.

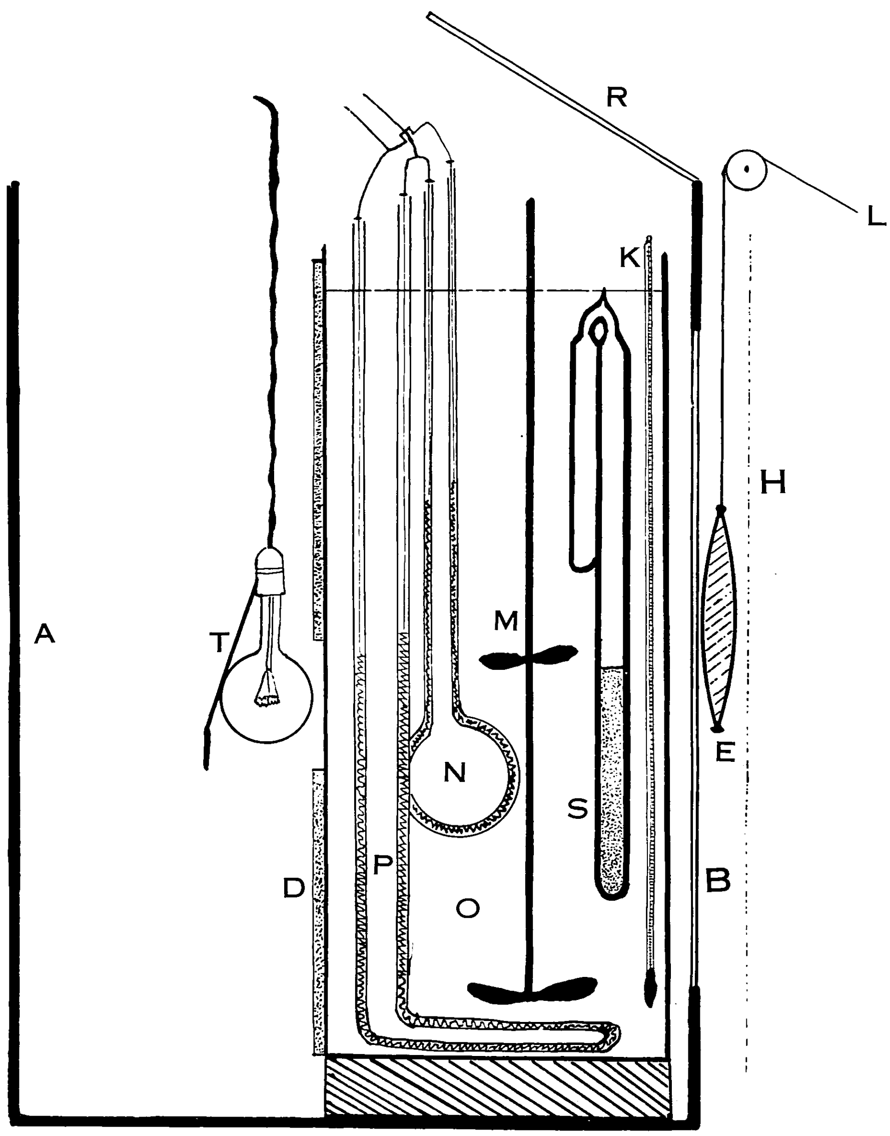



Diagram 2

(L) leads to a motor driven High-Vac pump and (R) opens to the atmosphere. (N) is the thick walled pyrex U-tube which was made to withstand a pressure of 60 atmospheres.

(1, 2, 3, 4, 5, 6 & 7) are ground-glass, one-way stop-cocks and (8) is a two-way stop-cock.

In diagrams (2) & (3) are shown a vertical cross section through, and a front elevation, respectively, of the heating bath.

(A) is a large sheet metal tank about 3 feet high 2 feet wide and 18 inches from front to back. One of its faces has a large plate glass window insert (B) through which the observations were made. Set inside the tank is a 3 gallon pyrex glass straight-walled vessel almost filled with glycoline (O). Surrounding the pyrex vessel is a layer of heavey corrugated cardboard (D) to act as a heat insulator with openings cut opposite the lights and in front. (P) and (N) are heating units placed inside pyrex tubing and together drawing about 10 amperes at full capacity. (M) is a stirrer driven by a motor. (E) is a large lens of about 4 inches diameter mounted in a frame and connected to a cord (L) which extends forward to the operator at a distance of 7 feet. By means of a cathetometer and this lens the temperature readings could be taken on the thermometer. (K). The cathetometer also served to measure liquid levels in the high pressure tube (S). (R) is a wooden deflector to guard against oil splattering in case of an explosion. Similarily, a wire screen (H) is stretched across the front with a small vertical opening cut directly in front of the lens, this screen is also used as a precautionary

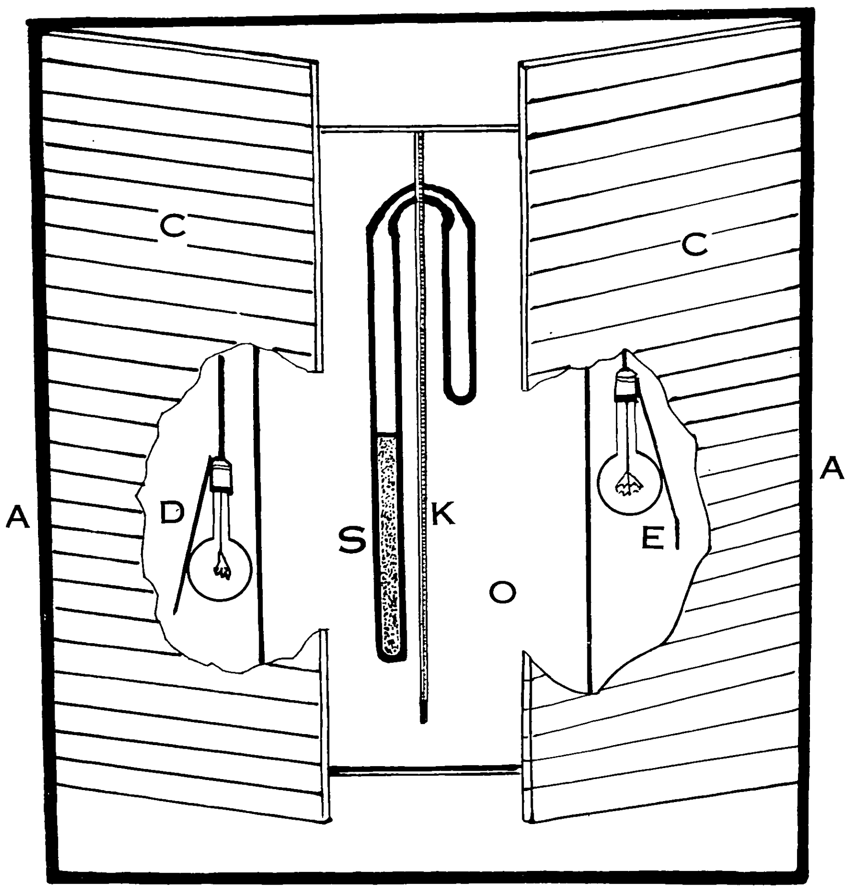



Diagram III

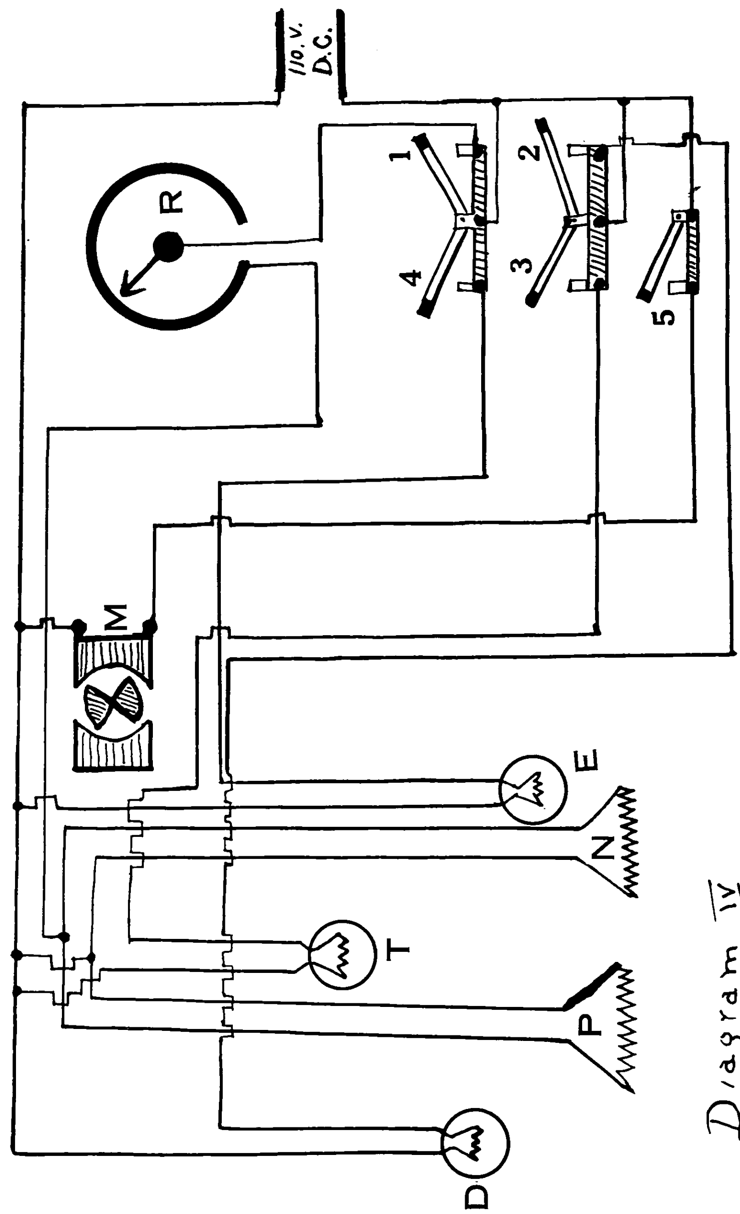



Diagram IV

measure. A 150 watt electric light bulb (T) and reflector is placed at the rear of the bath to aid in observing the meniscus level.

Diagram (3) shows the appearance of the apparatus as viewed from in front with only those details inserted which are incapable of being shown in diagram (2). As before, (A) is the sheet metal tank, ( S & K ) are the high pressure tube and thermometer respectively while (O) is the oil bath. (D & E) are two 150 watt electric light bulbs. (D) is so placed as to illuminate to best advantage the tube in a transverse manner and (E) makes the reading on the thermometer visible. The control of these lights was essential for viewing the proceedings and each was connected to separate switches placed close to the operator. (C & C) are two 1 inch wooden shields placed to serve as a precaution against flying glass.

Diagram (4) represents in a schematic manner the wiring arrangement. (P & N) are the heating coils connected in parallel with each other and in series through (R), a variable resistance capable of carrying up to 10 amperes, the whole being controlled by switch #1. (D, T & E) are the three bulbs individually controlled by switches (2, 3 & 4). (M) is the stirrer motor with its switch #5. (R) and the five switches were mounted together in a unit close to the operator and along with the cord for raising or lowering the lens permitted of complete control and observation at a distance.

Manipulation of Apparatus

A quantity of water was added to (D) and (C) was filled with the ether-saturated sulfuric acid prepared as previously described, tap #1 was turned so as to allow the contents of (C) to flow into chamber (B). Taps # 7 & 8 were turned so as to permit connection of system with motor driven High-Vac pump. Bulb (E) was surrounded with a solid carbon dioxide and acetone mixture contained in a Dewar flask. Tap #5 was turned so as to connect (E) with the system. Tap #4 was opened thereby connecting the manometer with the main line and enabling the degree of evacuation to be followed. Tap #3 was now cautiously opened and the reduced pressure immediately resulted in a rapid evolution of gas from the contents of (B). This was allowed to continue for some time until a large part of the air in (B) had been driven out when #3 was again closed and the vacuum reestablished in the system. Then #7 was closed and #3 opened and the manometer closely watched. If the mercury level fell on the right hand side and then began to slowly climb it indicated that condensation of the ether was progressing in (E). Usually the alternate manipulation of #7 and #3 was required several times before this took place because of the difficulty met with in having the ether vapor condense rapidly enough in the presence of much air. However when condensation was progressing nicely about 10 c.cs. of liquid could be obtained in 15 minutes. When effervescence lagged in (B) the introduction of small amounts of water from (D) through #2 revived the evolution of the ether. When about 40 c.cs. of ether had been liquified in (E), tap #3 was closed and taps #6 & 7 were opened until the manometer registered in almost complete vacuum. Then the Dewar was transferred to surround the flask (F) and the tap #7 closed, as (E) warmed up, the liquid in (E) vaporized and recondensed in (F). This distillation was carried on until only 5 or 10 c.cs. remained in (E), when #6 was closed and #7 opened thereby allowing the remainder in (E) to escape through the pump. This procedure was deemed necessary to reduce the impurities as much as possible. The ether in (F) was now distilled over into (G) passing on its way over the phosphorous pentoxide contained in (H) to remove any small amounts of water still present. From (G) the ether was ready for enclosure in the tube (N). In subsequent work numerous tubes were substituted for (N), the one drawn being only the first one used but in all cases the procedure was indentical. The tube (N) was surrounded with the refrigerant and the ether distilled in until the tube was almost filled. When this had been done the total efforts of the High-Vac pump and the Langmuir were called upon to reduce the pressure as far as possible and the ether in the tube was allowed to evaporate slowly into the system until the desired level was obtained in (N). This precaution served to prevent the presence of any air above the liquid level in (N) which might influence its future behavior. With this evaporation still going on and when the desired level had been reached the tube (N) was carefully sealed off at the constriction in the thick walled pyrex tubing connecting it to the main line. The tube containing its charge of ether was now ready for observation and could be transferred to the heating bath. (See diagrams 2 & 3).

EXPERIMENTAL PROCEDURE AND RESULTS

1. The tube was first mounted in the thermostat, in a vertical position with the extremities of the U-tube upwards. The behavior of the liquid levels were noted under various rates of temperature change. Particular care was taken in a 10° temperature region just below the critical temperature to record the levels in the two arms accurately. In the following table are given the results of one run picked out from a time-temperature graph. Many more observations than are given were made in each run.

| TIME in min. | TEMPERATURE | $\frac{dT}{dt}$ | LEVEL IN SHORT ARM | LEVEL IN LONG ARM |
|---|---|---|---|---|
| 0 | 29.1°C | | 6.95c.ms. | 8.65c.ms. |
| 15 | 54.0° | 1.48° per min. | 3.40 | 12.15 |
| 30 | 75.0° | | 2.90 | 12.60 |
| 35 | 81.0° | | 2.85 | 12.7 |
| 55 | 104.0° | | 3.55 | 12.1 |
| 75 | 121.4° | .04° per min. | 4.1 | 8.75 |
| 85 | 122.2° | | 3.8 | 8.1 |
| 95 | 122.4° | | 3.85 | 7.8 |
| 100 | 122.4° | | 3.85 | 7.8 |
| 265 | 122.4° | 0° per min. | 5.35 | 6.35 |
| 275 | 123.0° | | 5.10 | 6.20 |
| 285 | 123.5° | | 4.85 | 6.05 |
| 305 | 124.1° | | 4.45 | 5.50 |
| 320 | 125.0° | .035° per min. | 3.85 | 4.80 |
| 335 | 125.7° | | 3.20 | 4.10 |
| 350 | 125.8° | | 2.85 | 3.75 |
| 360 | 126.1° | | Meniscus vanished. | |
| 385 | 126.3° | | Milky fluorescence in bottom of tube. | |
| 400 | 127.1° | | | |
| 410 | 126.1° | cooling .13° per min. | Tube clear. | |
| 415 | 125.2° | | Meniscus reappeared. | |

A study of this table reveals a few interesting facts.

(i) The liquid levels in the two arms did not reach the same level even when ample time was given for equilibrium to become established. The level in the long arm was always higher. This observation was borne out in every run that was made.

(ii) The levels decreased more or less regularly with a constant rate of heating.

(iii) The fluorescence observed around the critical temperature was limited to that locality in which the liquid was last present.

(iv) The meniscus disappeared upon heating and reappeared upon cooling at quite different temperatures, although the rates of heating and cooling were extremely slow.

(v) When the temperature was kept constant just below the critical temperature the difference in level between the two arms became less but did not vanish even after 160 minutes. The results recorded in the above table were repeatedly obtained in different runs, at least to the extent that the above five conclusions were found to be correct.

It was realized that there was possibly a certain lag between the temperature of the bath and the temperature effective within the tube and that this lag operated in opposite directions upon heating. and cooling. If appreciable, this might account for the fourth result above.

To investigate this, a glass tube open at one end and of the same thickness as the one which contained the ether, was inserted in the bath with its open end two or three inches above the level of the oil in the bath. A thermometer was inserted inside and surrounded with oil. The same thermometer as was used in the bath previously was left as before. The temperature of the bath was now raised at different rates and the reading on the two thermometers recorded simultaneously. Later the one was checked against the other to insure uniformity of calibration.

TABLE OF RESULTS

| TIME | TEMPERATURE OF BATH | TEMPERATURE IN TUBE | Corrected for calibration difference. |
|---|---|---|---|
| 0 | 119.4°C | 118.0°C | |
| 1 | 120.3° | 118.9° | |
| 2 | 121.4° | 120.0° | |
| 3 | 122.4° | 121.0° | Rate of heating |
| 4 | 123.4° | 122.0° | 1°/min. |
| 5 | 124.4° | 123.0° | |
| 6 | 125.4° | 124.0° | Average lag |
| 8 | 127.4° | 126.0° | |
| 10 | 129.3° | 127.8° | 1.4°C |
| 0 | 114.4°C. | 114.2°C | |
| 2 | 115.0° | 114.9° | Rate of heating |
| 4 | 115.7° | 115.4° | 0.3°/min. |
| 6 | 116.3° | 116.1° | |
| 8 | 117.0° | 116.7° | Average lag |
| 10 | 117.6° | 117.3° | |
| 12 | 118.2° | 118.1° | 0.2°C |
| 13 | 118.5° | 118.3° | |

At rates of heating equivalent to a rise in temperature of 0.1°C or less per minute, the lag proved to be negligible. From this experiment it may be concluded that any lag in temperature cannot account entirely for the difference in temperature between meniscus disappearing or reappearing.

The observations with regard to the difference in level between the liquid levels will be discussed later on.

Another type of experiment was next undertaken. The tube containing the methyl ether was now inverted and replaced in the bath. The temperature was raised as rapidly as possible to a point two degrees above the critical temperature and held for several minutes. The bath was then allowed to cool to 115°C and heating commenced again more slowly and observations taken. The preliminary heating was merely to bring about an even distribution of material in both arms. The level of the liquid above the bottom of the tube in the long arm was measured in centimetres and time and temperature recorded simultaneously throughout the range of temperatures in the neighborhood of the critical temperature.

The following is a table chosen from the several hundred observations made to illustrate the general behavior observed. Later on, another series of observations were made on a straight tube and in every respect verified these results.

| TIME | TEMPERATURE | LEVEL | APPEARANCE | |
|---|---|---|---|---|
| Min. | Degrees Centigrade | cms. | Of Meniscus | Of Cloud |
| 0 | 119.8 | 10.8 | | |
| 15 | 122.2 | 9.8 | | |
| 33 | 125.4 | 7.85 | | |
| 45 | 126.9 | 6.10 | Quite distinct | Faint |
| 46 | 127.0 | 6.30 | Meniscus almost gone | Distinct |
| 47 | 127.1 | 6.50 | Meniscus gone | Heavy |
| | Immediate cooling | | | |
| 48 | 127.0 | 6.45 | " " | " |
| 49 | 126.7 | 6.50 | " " | very heavy |
| 50 | 126.8 | 3.50 | " " | " " |
| 54 | 126.8 | 3.50 | " " | " " |
| 57 | 126.7 | 3.50 | " " | " " |
| | Heating again | | | |
| 59 | 127.0 | 1.85 | " " | " " |
| 62 | 127.8 Cooling | ---- | All clear | All clear |
| 63 | 127.8 | ---- | " " | " " |
| 70 | 126.9 | ---- | " " | " " |
| 71 | 126.8 | ---- | " " | Very slight haze |
| 77 | 126.25 | 1.3 | Very faint | " " " |
| 79 | 126.10 | 1.6 | Clearer | Cloud gone |
| 82 | 126.10 | 2.1 | Quite clear | " " |
| 87 | 126.10 | 2.4 | Distinct | " " |
| 114 | 126.10 | 2.95 | " | " " |
| 124 | 126.10 | 2.95 | " | " " |

A brief review of the results brings forth some interesting details. The ether was heated from 20°C to 127.10° with an average rate of heating over the last 18° of .15° per minute. The meniscus disappeared at 127.0°C at a height of 6.50 cms. from bottom and a heavy cloud took its place while the temperature remained fairly steady from 126.9° to 126.7°C. Over this range the cloud remained unchanged at 3.5 cms. over a time interval of 7 minutes. When the temperature was raised rapidly to 127.8°, the cloud vanished at 127.1° with a surface height of 1.85 cms. Immediately cooling was allowed at the average rate of 0.1° per minute. A very slight haze appeared at 126.8° and continued down to 126.25° when it vanished and at 126.15° the meniscus was first distinct enough to measure at a height of 1.60 cms. Now for a period of 45 minutes the temperature was held steady at 126.10°. The level of the meniscus rose steadily at first and then slowed up and remained constant at 3 cms.

This peculiarity of the meniscus in slowly altering its position with time as the temperature was maintained constant was further investigated and yielded the following information. The temperature was quickly raised to 126.10° and held at this value for forty minutes, the meniscus meanwhile dropped in level from a height of 7.5 cms. to about 4.5cms. and then remained steady. The temperature was then rapidly raised to 128° and held for 10 minutes, whereupon cooling was allowed down to 126.6°, a value which was maintained rigidly for 18 minutes without the slightest trace of a cloud or meniscus. The temperature was now lowered to exactly 126.40° and held for 24 minutes with absolutely no sign of any cloud or meniscus. Again at 126.30° over a period of 15 minutes there was no sign of a liquid. Upon further cooling to 126.2° no change was visible over a period of 17 minutes but at the end of this time a very faint meniscus could be detected about o.25 cms. above the bottom of the tube and showed no tendency to increase in magnitude or density during the time of observation. This temperature may be taken as the highest value corresponding to the re-appearance of liquid from vapor upon cooling and checks very well with previous and subsequent determinations. Now it will be noted that, as previously recorded, the meniscus persisted and apparently had reached an equilibrium level at a temperature somewhat higher than 126.2°C when this value was approached from the lower side. All these conditions were repeated and special care taken to detect if this peculiarity was manifested again. With this in view the temperature was rapidly raised from room temperature up to 126.2°C and maintained for about an hour with level noted every five minutes. This, repeated at the same final temperature, except that it was brought to this temperature from 115°C instead of from room temperature yielded the same result. This difference in procedure had no other effect than to alter slightly the first level measurement and in no appreciable manner did it alter the final level attained. Several determinations of this sort were made each time using a different final temperature but everytime approaching it from below. Then the liquid was raised above its critical temperature and allowed to cool down to the same temperatures as were previously observed but approached in the opposite direction.

The results of this are best expressed in a graph. {Page 28}

This tube was now removed and the weight of the contents determined as well as the total internal volume of the tube. From this data the vapor density at the critical temperature was found to be 0.21. This value has essentially very little meaning because more or less liquid could have been employed and presumably the critical temperature would have been the same and obviously the vapor density would have been more or less depending on the amount of liquid.

With a view to determining the actual density just before and after the critical temperature a number of glass floats were employed and enclosed in the tube with the ether. Because of the terrific pressures generated and because we wished to use floats of a good size to overshadow the effects of regional density fluctuations the manufacture of these floats presented a difficulty. Only two floats out of a large number made were serviceable. These utilized small quantities of methyl ether inside themselves to partially compensate the exterior pressure but obviously a float could never be made of this type to float in the gaseous phase.

The information gained from these two was that a temperature of 120.45°C the ether had a density of 0.39 and at 122.25°C the ether had a density of 0.31.

Now as it so happened one of the tubes used in the density determination had a higher proportion of liquid to available space than had been utilized previously. This led to some peculiar observations. As the temperature was raised the level of the liquid rose steadily and continued to rise right up to the moment that the meniscus vanished. This occurred at a temperature of 125.9°C and at a distance of about 2cms. from the top of the tube without any trace of a cloud formation at any time. After the temperature had been held at 127.5°C for several minutes it was dropped back to 125.9°C but tube remained absolutely clear over total time of observation. As the temperature was eased back to 125.7°C a milkiness began to appear at the top of the tube. This rapidly increased in intensity and remained as long as the temperature was kept constant. A slight increase in temperature to 125.8°C lessened the intensity and a lowering to 125.60°C increased the intensity again and yielded a maximum at 125.65°C. At 125.5°C the meniscus reappeared at a position slightly higher than that at which it had previously disappeared and all trace of cloud vanished at 125.4°C. These results may be briefly summarized:

(i) In a tube having a high proportion of liquid to available space, the level rose continually with increase in temperature.

(ii) No cloud formed upon heating past critical temperature but cloud did form upon cooling past the critical temperature and this cloud occupied the space finally occupied by the vapor.

(iii) The critical temperature seemed to be appreciably lower than when a similar determination was made on a tube filled to a lesser extent.

With these apparently discordant results in mind a redetermination of the behavior in a less filled tube was repeated. This time a different tube and a different sample of ether were employed. In every respect these last determinations confirmed the previous observations on the inverted U-tube containing a small proportion of liquid to available space.

The following is a table of the results obtained showing the final equilibrium level reached at the various temperatures depending on direction of approach.

In the following table, recording time, temperature and liquid level in a straight tube under similar conditions to the inverted U-tube where in every case the temperature was approached from beneath.

| TIME | TEMPERATURE | LEVEL IN cms. |
| --- | --- | --- |
| 0 min. | 125.2°C | 3.80 |
| 2 " | 125.2 | 3.60 |
| 4 " | 125.2 | 3.50 |
| 5 " | 125.2 | 3.45 |
| 8 " | 125.2 | 3.40 |
| 10 " | 125.2 | 3.35 |
| 15 " | 125.2 | 3.35 |
| 20 " | 125.2 | 3.30 |
| 25 " | 125.2 | 3.30 |
| 0 " | 125.6 | 3.30 |
| 5 " | 125.6 | 3.20 |
| 10 " | 125.6 | 3.20 |
| 15 " | 125.6 | 3.10 |
| 20 " | 125.6 | 3.10 |
| 0 " | 126.2 | 3.00 |
| 2 " | 126.2 | 3.00 |
| 4 " | 126.2 | 2.95 |
| 7 " | 126.2 | 2.90 |
| 15 " | 126.2 | 2.90 |

| TIME | TEMPERATURE | LEVEL IN cms. |
| --- | --- | --- |
| 0 min. | 126.7°C | 2.80 |
| 4 " | 126.7 | 2.75 |
| 6 " | 126.7 | 2.75 |
| 0 " | 127.1 | 2.70 |
| 5 " | 127.1 | 2.60 |
| 10 " | 127.1 | 2.60 |

The following is a table recording, as before, time, temperature and liquid level except that the same temperatures were approached from above.

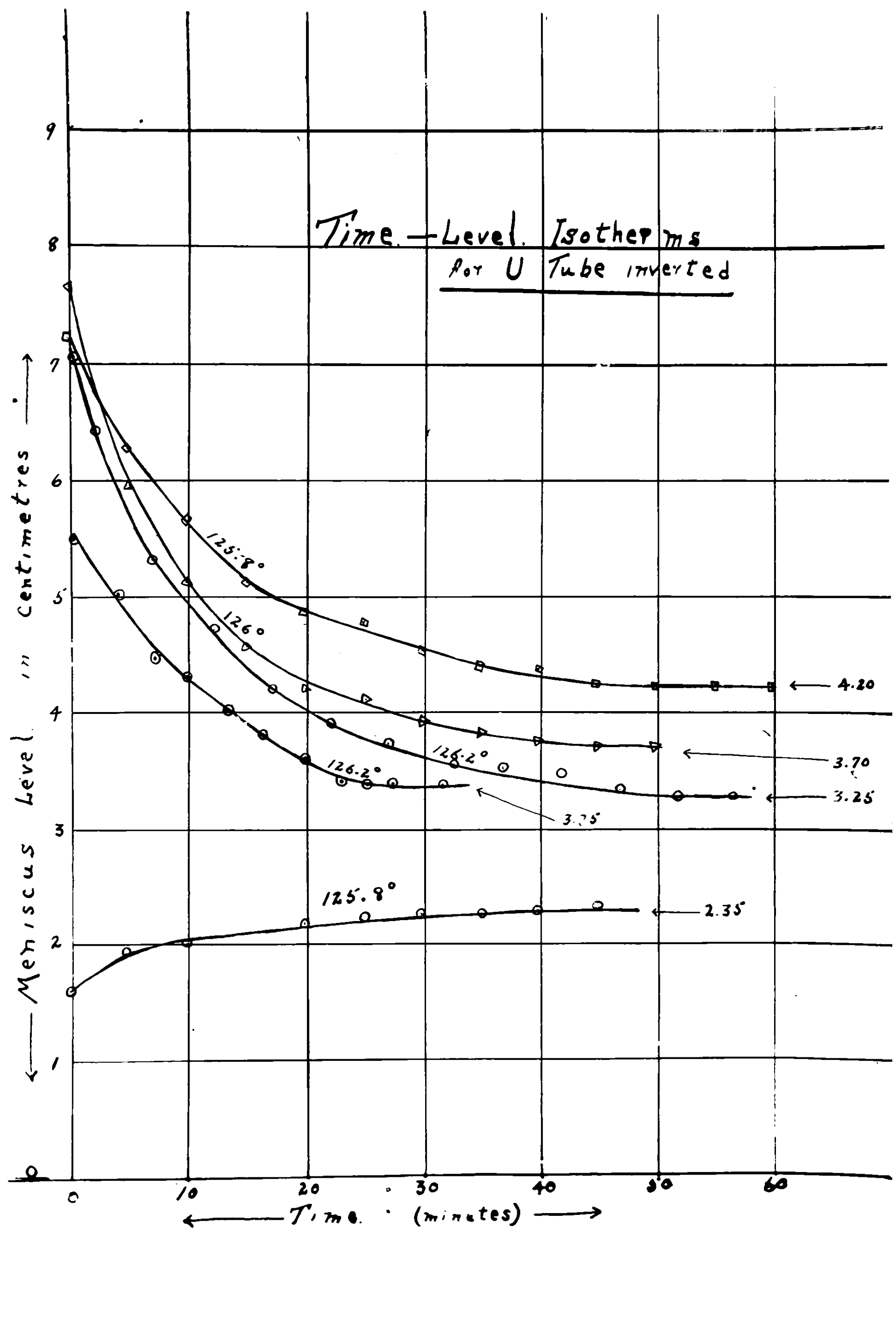
| TIME | TEMPERATURE | LEVEL IN cms. |
| --- | --- | --- |
| 0 min. | 127.1°C | 1.95 |
| 5 " | 127.1 | 2.05 |
| 10 " | 127.1 | 2.05 |
| 15 " | 127.1 | 2.05 |
| 20 " | 127.1 | 2.05 |
| 0 " | 126.7 | 2.15 |
| 5 " | 126.7 | 2.20 |
| 10 " | 126.7 | 2.20 |
| 15 " | 126.7 | 2.20 |
| 0 " | 125.6 | 2.45 |
| 5 " | 125.6 | 2.50 |
| 10 " | 125.6 | 2.55 |
| 15 " | 125.6 | 2.55 |
| 20 " | 125.6 | 2.55 |

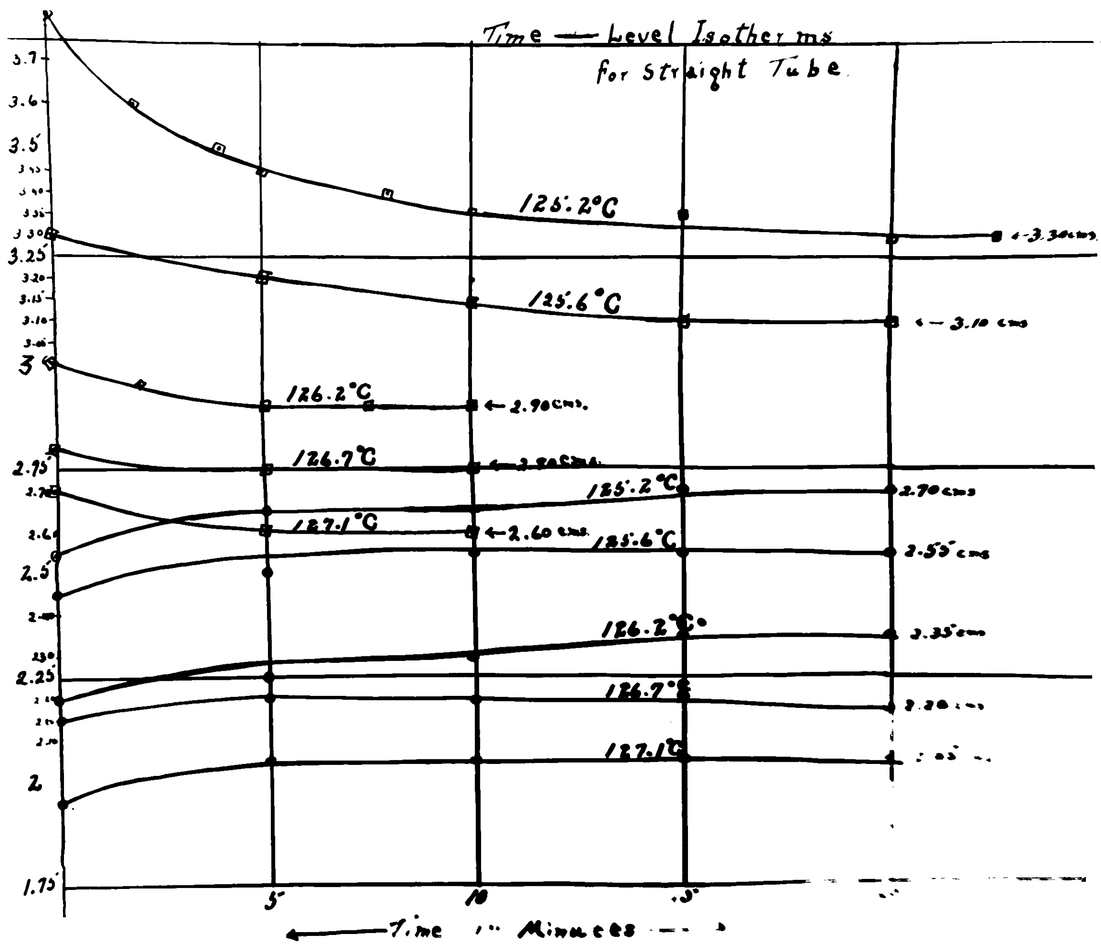
| TIME | TEMPERATURE | LEVEL IN cms. |
|---|---|---|
| 0 min. | 125.2°C | 2.55 |
| 5 " | 125.2 | 2.65 |
| 10 " | 125.2 | 2.65 |
| 15 " | 125.2 | 2.70 |
| 20 " | 125.2 | 2.70 |

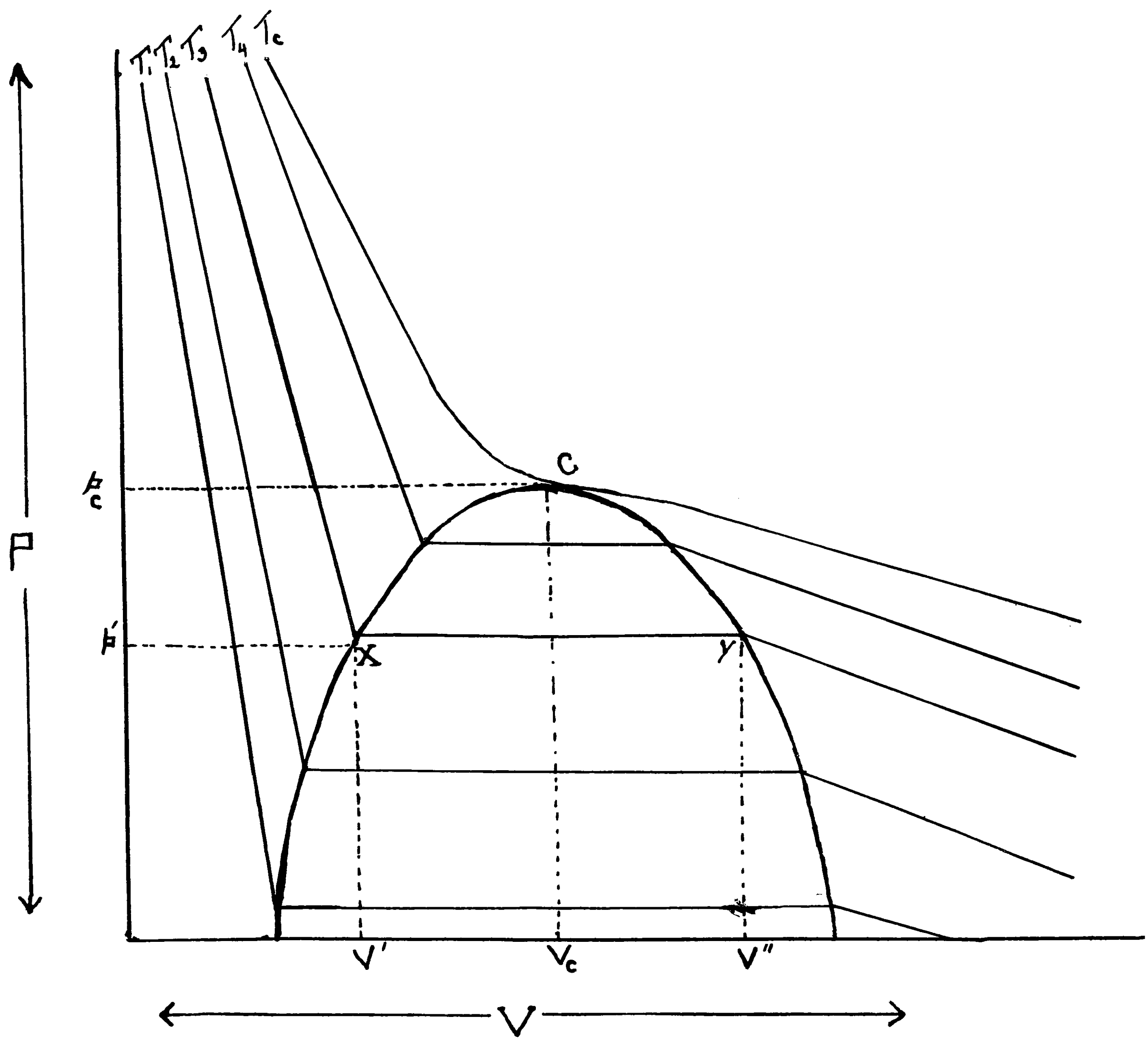
It will be noted that these observations are in complete agreement with those made on the inverted U-tube. The equilibrium values from the two preceeding tables are summarized in the following table.

| TEMPERATURE | LEVEL with rising temperature | LEVEL with falling temperature. | DIFFERENCE |
|---|---|---|---|
| 125.2°C | 3.30 cms. | 2.70 cms. | 0.60 cms. |
| 125.6 | 3.10 " | 2.25 " | 0.55 " |
| 126.2 | 2.90 " | 2.35 " | 0.55 " |
| 126.7 | 2.75 " | 2.20 " | 0.55 " |
| 127.1 | 2.60 " | 2.05 " | |

On Pages 28 and 29 the data previously tabulated has been expressed graphically, both for the inverted U-tube and for the straight tube. The similarity in behavior of the contents in each will at once be evident.


Time.—Level. Isotherms
for U Tube inverted
125.8°
126°
126.2°
126.2°
125.8°
4.20
3.70
3.25
3.25
2.35
Meniscus Level in centimetres
Time (minutes)
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8
9


Time — Level Isotherms
for Straight Tube
125.2°C
125.6°C
126.2°C
126.7°C
127.1°C
125.2°C
125.6°C
126.2°C
126.7°C
127.1°C
← 3.30 cms.
← 3.10 cms
← 2.90 cms.
← 2.60 cms.
2.70 cms
2.55 cms
2.35 cms
← Liquid Level in cms. →
← Time in Minutes →
3.7
3.6
3.5
3.25
3
2.75
2.5
2.25
2
1.75
5
10



T1
T2
T3
T4
Tc
P
pc
p'
C
X
Y
V'
Vc
V''
V

DISCUSSION

The viscosity at the critical temperature makes it necessary to have a very efficient stirring arrangement and also to have the same temperature along the whole tube. In spite of that the meniscus may vanish at points other than the middle of the tube with amounts of liquid several per cent different from the right amount. (Ref. #5). The following attempts have been made at an explanation. (Ref. #6).

The influence of gravity is great near the critical point as the compressibility must be very high there.

$\frac{dp}{dv} = 0, \quad \frac{d_2p}{dv^2} = 0, \quad K = \frac{1}{v}, \quad \frac{dv}{dp} =$ so at different heights in the tube the density may vary rather much.

The critical temperature is observed by the disappearance of the meniscus between the liquid and vapor phases. Hence both liquid and vapor must be present when this temperature is reached. A brief discussion will indicate that theoretically only one condition of rates of amount of substance to volume of container makes this possible and that then at the critical temperature the volume of vapor and of liquid must be the same.

The diagram illustrates the pressure-volume isotherms representing the experimental pressure-volume relationships at various temperatures for a given mass of a pure compound. $T_1$, $T_2$, $T_3$ etc. are curves representing the bahavior of the system at temperatures below the critical temperature. The point of inflection "C" corresponds to the critical condition and $p_c$ and $v_c$ are the critical pressure and volume respectively.

Now if we consider a certain definite amount of liquid, say 1 gram, in every case then v becomes the volume in which the liquid is enclosed and consequently $V_c$ is the volume of the container at the critical temperature. According to the diagram, $V_c$ can have only one value to correctly fulfill the critical conditions. Suppose we consider a value $V^1$ which corresponds to a large proportion of liquid relative to the available space. If we raise the temperature which is equivalent to proceeding vertically from $V^1$, the point X is reached which corresponds to a tube entirely filled with liquid, before the critical temperature has been attained. On the other hand if a point $V''$ be chosen on the other side of $V_c$, as the temperature is raised a point Y is finally reached which corresponds to a tube filled only with the gaseous phase. Obviously, then only when a volume $V_c$ is chosen to contain the 1 gram of material do we get the correct critical conditions. This means that the relative proportion of material to available space is of vital significance in making possible the observation of the critical temperature. This condition is fulfilled when the weight of material is equal to the total available space multiplied by the critical density, i.e. $W = {}_c V$.

When this correct proportion of material is used a definite ratio also exists between the relative volumes of gas and liquid just at the critical temperature. This is shown by the following derivation of a general case.

Suppose:

$W$ = weight of material

$V$ = volume of tube

$V_g$ = volume of gas $\Delta_g$ = density of gas

$V_l$ = volume of liquid and $\Delta_l$ = density of liquid

$\Delta_c$ = density of contents at critical temperature.

Under all conditions:

$$(V - V_g)\Delta_1 + V_g \Delta_g = W$$

$$V_g = \frac{W - V\Delta_1}{\Delta_g - \Delta_1}$$

As T approaches $T_c$ then $\Delta_c$ approaches $\frac{\Delta_g + \Delta_1}{2}$

and $W \doteq \Delta_c V$

Substituting these special conditions in the general equation we get:

$$V_g = \frac{\Delta_c V - V\Delta_1}{\Delta_g - \Delta_1}$$

$$= \frac{\left(\frac{\Delta_g + \Delta_1}{2}\right)V - V\Delta_1}{\Delta_g - \Delta_1}$$

$$= \frac{V}{2}\left(\frac{V_g - \Delta_1}{V_g - \Delta_1}\right)$$

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

This means that the meniscus would disappear at the centre of a uniform tube providing that the correct volume $V_c$ had been chosen to contain it.

CONCLUSION

Just what conclusions to draw from the mass of observations that have been tabulated is a matter of some difficulty. It has been definitely shown that the observations of others with regard to the critical phenomenon taking place within a wide range of average density is correct.

A number of explanations have been advanced with regard to the fact that the critical temperature can be observed in a tube filled with more or with less than the amount of material required to give the critical density at the critical temperature.

The first of these may be called the "experimental conditions" explanation, the second the discontinuity of state and the third the effect of gravity.

It has been suggested that due to the high viscosity existing in the medium at the critical temperature the true temperature, pressure density equilibrium is not established and that the disappearance of the meniscus can be observed because of the lag in the establishment of equilibrium throughout the tube. Since great care was taken in the experiments described to vary the temperature very gradually and to use large quantities of materials in relatively wide tubes the explanation does not seem adequate. It was unfortunately not possible to obtain floats just at the critical temperature but the one which was used closest to the critical temperature (4 or 5 degrees away) acted instantaneously in its change in position over the smallest temperature interval which the thermometer would show, indicating that here at least a steady state was established instantaneously.

The discontinuity of state hypothesis is a qualified one due to J. Traube and his collaberators. He supposes that in the liquid state the molecular aggregation is different to that in the gaseous state consisting of so called "fluidons" in the liquids and "gasons" in the vapor, the difference not corresponding to ordinary association such as exists in what are known as associated liquids but in the combination of "gasons" to form a "fluidon" which consists of far more loosely held molecules than ordinarily is considered to be the case in normal association or polymerization. The assumption is then made that after the disappearance of the meniscus the "fluidons" can still persist indefinitely thus giving a discontinuity in density at and above the critical temperature.

The gravity hypothesis also calls for a variation in density throughout the tube after the critical temperature has been reached. It has been observed that the isothermal just above the critical temperature has an inflection so that $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv^2}$ is also $= 0$ which means that the compressibility approaches infinity, consequently the mere weight of the fluid in the tube due to gravity causes a variation of density throughout and only at the level where the meniscus disappears does the density correspond to that at the critical temperature.

The results obtained are not adequate to substantiate or reject the last two hypothesis. Traube's aggregation hypothesis does not appeal to the writer in view of the necessity of stipulating a new type of aggregation other than association of molecules. It may however, be possible to make use of a modified form of this hypothesis by substituting a sudden change in regional orientation in the neighborhood of the critical temperature.

Neither Traube's hypothesis nor the gravity one gives any explanation of the phenomenon which as far as the writer knows was observed for the first time, namely the difference in level always noted between the disappearing and reappearing meniscus.

It has been planned to make density measurements in various parts of a long tube by means of quartz spirals placed at intervals along its length, each one attached to a float whose density is always greater than that of the medium. The extension of the spiral and the volume of the float gives a means of determining the density at any time during a critical temperature determination. By quantitative measurements it will then be possible to answer first of all the question as to the extent and position in the tube, of any density variation just below and just above the critical temperature.

**SUMMARY**

The behavior of methyl ether liquid in equilibrium with its own vapor has been investigated in the temperature region on both sides of the critical temperature. In every trial a definite difference was obtained between the volume of liquid in equilibrium with its vapor at any specified temperature near the critical temperature depending upon the direction of approach to this temperature. Furthermore the temperature and position at which the meniscus vanished as well as the position of cloud formation depended upon the relative amount of liquid present as compared to the available space within the tube.

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