THE HEAT CAPACITY AND SURFACE TENSION OF ETHYLENE IN THE CRITICAL REGION

A Thesis

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by

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CONTRIBUTIONS TO KNOWLEDGE AND SUMMARY

A new type of adiabatic electrical calorimeter has been designed for use at high pressures, by means of which the heat capacities of gases at constant volume can be determined over short temperature ranges with an accuracy of about 0.2%. The arrangements are such that the lags occurring after a change in temperature in the critical region can be followed, and their effect as an error in the heat capacity measurement eliminated.

A very efficient low temperature fractionating unit has been constructed, in order to assure the purity of the material used.

The heat capacity of ethylene has been determined for three fillings near the critical density, and for a fourth filling somewhat removed from this value. These are the first heat measurements made on ethylene in the critical range, and the first measurements made on any material, in which the time lags which occur near the critical temperature are taken into account, and their effect as an error in the heat capacity measurement eliminated.

For three of the fillings, the existence of a hysteresis in the heat capacity has been demonstrated.

The occurrence of a maximum and a minimum in the heat capacity curve has been shown experimentally, and explained theoretically.

The existence of molecular interaction in which is bound appreciable amounts of energy is indicated in both liquid and vapor below the critical temperature, and above this temperature as well.

Time lags in the heat capacity have been observed and systematized for the first time, and these were successfully correlated with a lag in the liquid, (and probably vapor) density. It has been shown that this type of lag is indipendent of the shape of the container.

The surface tension of ethylene has been determined up to a temperature .06° below the critical, which is a higher corresponding temperature than any at which measurements have been hitherto made on any substance. For the first time it has been shown quite definitely that a surface energy persists when the meniscus vanishes.

The disappearance and reappearance of the meniscus has been shown to be a reversible phenomenon to within .02° in the case of ethane and ethylene.

A theory (the dispersion theory) has been developed, in terms of which all the hysteresis effects which have been observed in the critical region are explained. On the basis of this theory, and using experimental results presented in the thesis, it has been possible to calculate the sizes of the dispersed bubbles and droplets.

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GENERAL INTRODUCTION

INTRODUCTION.

Within the last few years great strides have been made towards the solution of the problem presented by the critical phenomena. It is believed that our knowledge of the subject has now advanced sufficiently, to warrant adoption of the logical rather than the historical approach. Consequently it has been decided in this thesis to dispose of the historical side of the question in a single section. Then the various aspects of critical phenomena investigation and theory will be treated in an orderly fashion, without reference to the chronological sequence in which the ideas were developed.

History of the study of critical phenomena: The disappearance of the meniscus was first observed by Cagniard de la Tour in 1822 (72). The researches of Andrews (1,2) served to put the phenomenon on a quantitative basis. Andrews could measure the density of the phases to within a degree or two of the temperature of meniscus disappearance. It was natural to believe that at this temperature the density of the two phases had become equal. Consequently Andrews extrapolated his results to show the densities equal at the critical temperature, and obtained the familiar rather flat headed parabola to represent the density-temperature curve. When van der Waals proposed his simple, semi-empirical equation of state, which qualitatively showed the same behavior as Andrews' curves , and still represented very well the behavior away from the critical region, the theory had already received the foundation on which it rests today.

In 1880 the first dissenting voice was raised. Ramsay (55,56) described experiments which tended to show that the liquid state existed above the temperature of meniscus disappearance. (Hereafter this temperature will be referred to as the critical temperature). However his experimental arrangements were poor, and his conclusions loosely drawn. His paper was severely criticised on this ground by Hannay (27).

Between 1881 and 1900 Cailletet (10,11), Batelli (3), Gallizine (24) and Wesendock (80) carried on experimental work which led them to postulate in common, that the temperature of meniscus disappearance does not mark the point at which the densities of the phases become equal. Their work was criticized by Ramsay (57), Young (83) and Gouy (25) on the various grounds of impurities, poor temperature control, and gravity effect. The conclusions of the first set of investigators and in part the objections of the other group, rested largely on experimental evidence obtained by visual observation of the critical phenomena in sealed glass tubes.

In the next fifteen years, four investigators carried out experiments in which the density of material in a closed glass tube was measured by placing in it glass floats of various known densities. These were Hein (30), de Heen (29), Kammerlingh Onnes and Fabius (49), and Teichner (71). Their results were concordant in most respects. In particular it appeared that a density difference did exist above the critical temperature, but the first three found that with time this density difference disappeared. From this data, Teichner (working with Traube) de Heen, and Hein concluded that the van der Waals — Andrews conception of the critical state did not hold, while Onnes and Fabius took the opposite view.

Traube and de Heen were the first to advance theories to explain the observed deviation from the classical ideas. According to de Heen liquid molecules are more complex than vapor molecules. At the critical temperature it becomes possible for the two types to diffuse into each other, so that a region appears between the two phases in which partial diffusion has occurred, and no meniscus is seen. After a sufficiently long time diffusion is complete, and the phase density difference also disappears. Traube's theory is similar, with the substitution of liquidons for the liquid complexes of de Heen, and gasons for the vapor of de Heen. Traube's idea is drawn from the observation that van der Waals' b is greater for gases than for liquids. Hence the two types of molecules are distinguished by their relative volumes. Traube has published papers advancing this and similar views at intervals from 1902 - 1935 (73). Most recently (74) Traube has endorsed the newer ideas advanced by Maass and coworkers.

Much of the evidence which had been drawn for the existence of the two phases above the critical temperature was based on observation of the critical opalescence. In 1906 - 1908, Smoluchouski (67) advanced a theory explaining the opalescence as being due to the scattering of light by statistical fluctuations in the density of the medium. This was later put to test with considerable success by Keesom (34).

Interest in this branch of research slackened somewhat after 1914, and it was not until 1926 that new experimental work began to appear. Starting at this date, Bennewitz and coworkers published a series of papers on the thermal properties of materials in the critical range (4,5,6). Schroer undertook to measure viscosity and solubility, and to trace the liquid vapor envelope more accurately than before (62 - 66). Callendar was interested in water from the point of view of the power engineer. He observed the persistence of the density difference above the critical temperature of water, and determined some of its properties through the critical range (13).

About 1931, certain observations in this laboratory on the rate of the reaction between propylene and hydrogen chloride in the critical range lead to the institution of a series of researches, which are still being continued. Reaction rates, adsorption, surface tension, dielectric constants, heat capacity and pressure — volume — temperature relationships have been studied. Most recently, opalescence, viscosity and solubility in the critical range have been included on the program.

In 1937 - 1938, a series of articles appeared by Mayer and co-workers (37,38,39) in which a mathematical treatment, based on very general grounds, predicts the result that the temperature at which the surface tension becomes zero, is below the highest temperature at which the pressure-volume coefficient has a zero value. The conclusions drawn by the authors have been very helpful in interpreting the data recently obtained in this laboratory.

The works mentioned are those which have had the greatest influence on this subject. The results of these and other investigators will be referred to in the development which follows.

<u>Molecular interaction in the critical range</u>: Various authors have designated such molecular interaction as association. It is found convenient to use the word association in discussing the effects of interactions on the macroscopic properties of the system. In this treatment, however, use of the word is not meant to carry any a priori notion regarding the

nature of molecular interactions. Thus whether we decide later that these are molecular aggregates with continued existence, or evanescent interactions, or orientation effects, the word association can be used for the time being. The nature of the molecular groupings is best considered only when all the available evidence has been reviewed.

A plot of the pressure-volume isothermals for any fluid in the critical region yields the general picture first shown by Andrews (1,2) to hold for CO_2. Above the critical temperature, the isothermals show a marked inflection in the neighborhood of the critical volume. As the temperature increases the inflection is less marked, and finally a point is reached where the curvature shows no appreciable minimum anywhere. Thus in a temperature interval which for CO_2 extends about 10°-15° above the critical, there is a particular volume region in which the change of pressure with volume is less than in neighboring volume regions. Because of the proximity of this region to the point at which liquid last exists, it is natural to seek the cause of the inflection in the association of molecules. As this region is approached from a greater volume, association occurs decreasing the number of molecules effectively available for kinetic collision, and thus giving rise to a lower pressure-volume coefficient than might otherwise be expected.

The measurement and calculation of energy relationships have proved to be a fruitful source of information in this section of the subject.

Heat capacities in the critical region have been measured by a number of workers. De Heen was the first to discover that if the heat capacity of a pure liquid and its vapor in a closed container be measured through the critical temperature, the value obtained below this temperature is much higher than the value obtained above (85).

This observation was put on a more quantitative basis by Teichner, who measured the heat content of ether from room temperature to temperatures greater than the critical (71). It appeared that the heat capacity rises steadily to reach a maximum value just below the critical temperature, then drops sharply to a curve showing decreasing heat capacity with temperature increasing above the critical. Teichner's data are inaccurate, and the temperature intervals too large to permit of drawing the curve with certainty in the critical region.

The heat capacity at constant volume of CO_2 for two different mass volume ratios was measured through the critical region by Bennewitz and Spittleberger in 1926 (5). These workers found a heat capacity temperature curve with the general characteristics described for that of Teichner. From the point of view of our present considerations, the important fact is that above the critical temperature, C_v continues to decrease, and does not level out even 15° above the temperature at which the system becomes homogeneous.

An exactly similar result was later obtained by Eucken and Hauck, for the heat capacity measured under similar conditions, of the systems air and argon (20).

These results have since been duplicated and extended by the writer for the system ethylene. It will appear from the discussion that that the decrease in heat capacity is due to molecular association, gradually decreasing as the temperature is raised from the critical.

The form of the specific heat curve can also be arrived at by calculation if sufficiently accurate p—V—T data are available. Such data has recently been obtained by Michels, Blaisse, and Michels for CO_2 (43). In this way it is possible to compute the variation of C_v

not only with temperature, but also with volume. The C_v – T curve obtained above the critical temperature is similar to that already described. Along an isothermal, the specific heat shows in every case a maximum at the critical volume. The highest of these maxima occurs at the critical temperature. Below this temperature, of course, where liquid and vapor are dealt with, there is a break in the curve at those volumes which cannot be experimentally realized. Outside of this liquid – vapor region, the heat capacity shows an increase as the volume moves towards the saturation line, with the temperature constant.

Michels, Bijl and Michels show that on the critical isothermal, the second pressure temperature coefficient is zero only at the critical volume (44). This is a fact previously known. Now it has been pointed out by Clark and Katz (18) that since

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

then on the critical isothermal, C_v must show a maximum at the critical volume.

The Joule effect as a measure of the internal energy has been measured for CO_2 by Bennewitz and Andreewa (4), and calculated by Michels, Bijl and Michels, also for CO_2. It appears that for the critical and higher isothermals, the deviations from linearity of the internal energy plotted against the volume are greatest near the critical volume. This is indeed a consequence of the C_v data quoted above.

Bennewitz and Andreewa also worked with A, N_2, O_2, and CH_4 and found that the internal energies on the critical isothermal of these gases were the same, when plotted against the reduced volume, up to densities twice the critical. Since these gases have respectively zero, 2, 2 and three rotational degrees of freedom, they concluded that the rotation of these molecules was not effected even at the highest density reached.

Heat capacities at constant pressure are also recorded in the literature. These data are not as susceptible to interpretation in terms of energy effect as are the heat capacity data at constant volume. This is because in the constant pressure case, the external work done in expansion is measured, in addition to the change in internal energy. Such data will be referred to in other parts of the work.

Perhaps the most direct evidence for the existence of association in the critical range is to be found in the X-ray diffraction data of Noll (48), Spangler (68), and Benz and Stewart (7). The "Cybotactic groups" postulated by Stewart to exist in liquids have been found to persist above the critical temperature. Experimentally, the existence of the groups is shown by the occurrence of a maximum in the plot of the amount against the angle of scattering. This effect was shown to exist for ether and isopentane at temperatures more than 6° above the critical, at densities near the critical density.

These authors also show results indicating that along an isochore, the association is independent of the temperature. This conclusion is however contrary to those drawn from specific heat data. The answer to the contradiction is easily found: All of Stewart and coworkers' isotherms are far removed from the critical volume. One of the isopentane isochores is on a volume of 10% greater than the critical and a closer examination of the results shows that in this case the maximum is greatest for the temperature nearest the critical. It seems probable that the two types of evidence would correlate if X-ray diffraction data were obtained on a critical isochore.

Adsorption of propylene on alumina has been measured in the critical range by Morris and Maass (45), and by Edwards and Maass (17). Here the data is not to be as readily interpreted, but it appears that under conditions where the variation of density with temperature would not contribute to the result, that the adsorption rises to a maximum above the critical temperature, and begins to fall on a regular adsorption isotherm only several degrees above the critical temperature. This effect is probably due to a decreased tendency for adsorption from an associated gas, compared with the gas at the same volume in a non-associated condition.

Several investigators have measured conductivity in various systems through the critical temperature (22,23,78). Neglecting the last reference on the basis of poor technique, it is found that the conductivity of a system decreases in a regular fashion through the critical, and becomes asymptotic to a line parallel to the temperature axis only considerably above the critical temperature. Above the critical temperature, then, the state of affairs is that in a single homogeneous phase at constant volume, the conductivity decreases through a range of increasing temperature. Again the results are best explained in terms of decreasing solvent association in this range.

The dielectric constant too shows a curve steadily decreasing through the critical temperature, and levelling out only several degrees above the critical (22). The interval between the critical temperature and the point at which the curves become horizontal is for ether 14°C., for H_2S, 6°C, and for Cl_2, about 5°C. A change in the dielectric constant of a single phase system can be due only to one cause: A changing degree of molecular association.

Tyrer has measured the solubility of inorganic salts in methyl and ethyl alcohols (86). Plotting the solubility against temperature, in the region above the critical, he found for an isochore of density 0.1 the solubility remained constant when the temperature increased. On an isochore of density 0.5, the solubility decreased with increasing temperature. Since the decreasing association is to be found only near the critical volume, it appears that these results are best explained in such terms.

In the same way the observed results of Holder and Maass (32) on the velocity of the reaction between HCl and propylene in the critical region can be explained. Probably the most significant result of these authors is summarized in the following statement: At densities in the critical range, the reaction velocity — temperature curve on an isochore shows a minimum near the critical temperature. At higher densities the temperature coefficient of reaction is never negative, and this is probably true at lower densities as well. It appears then that structural association decreases much more rapidly very near to the critical temperature than elsewhere. Consequently the temperature effect is more than compensated for in this region, resulting in an overall decrease in reaction velocity. Thus a minimum appears in the curve.

Deviations from van der Waals' and other equations of state have often been attributed to association. Callendar (12,13) has included in his theory "coaggregation terms" to allow for this effect. Attempts have been made to calculate the degree of association. For instance, Walker (79) has on the basis of empirical gas laws, and kinetic considerations, found degrees of association into double molecules, varying between 1 and 1.5. For CO_2 he calculates 1.012. On the other hand, Bennewitz and Andreewa (4) have derived this quantity from experimental data on Joule effect, and find 1.07. It seems that such calculations are not to be given great weight.

For the energy involved in the association of CO_2, Bennewitz and

Andreewa calculate 9000 calories per mol. This is the right order of magnitude for an intermolecular energy.

None of the data quoted has as yet helped to throw any light on the nature of the association. Do the associated groups merely represent fluctuations in the density, or are they definite aggregations of two or more molecules? If they are the latter, do they have more than a transitory existence?

An indication of the answer is afforded by the time lags encountered when certain changes are made in the temperature and volume of systems in the critical region. These lags will be treated in a separate section. The results would lead one to believe that these aggregates have more than a temporary existence.

There is without doubt a correlation between the polarization of molecules and the association in the critical range. Especially in the case of dipoles consideration of the time lags would probably bring in the question of orientation in the molecular complexes. It has been suggested by Maass and co-workers that all the phenomena, and particularly the time lags, point towards the existence of molecular orientation.

Persistence of the phases above the critical temperature:

In this section evidence will be discussed which points towards the persistence of a phase density difference above the temperature at which the meniscus has disappeared.

This density difference has been measured experimentally. The earliest researches of this kind involved the use of glass floats of known density. A number of these floats were placed inside of a glass bomb, filled with the material to be tested and the temperature observed at which the floats occupied various levels in the bomb.

In this way, Teichner (71) working with very pure CCL_4, and under conditions favorable for good temperature control, found density differences in CCl_4 which persisted until a temperature 4^o above the critical had been attained. Work of a similar nature was carried out by Hein (30) on CCl_4, SO_2, and CO_2. The difference in density between the phases was 21% for CCl_4, 13% for CO_2. Onnes and Fabius (49) obtained similar results for CO_2. De Heen apparently carried out similar experiments, but his publications have not been available here for comparison. Hein, and Onnes and Fabius, reported that the density difference was not stable, and vanished after several hours. In the light of data to be presented it will appear that this lack of stability was probably due to poor temperature control.

Most recently the measurement of the density difference has been accomplished by means of the McBain—Bakr quartz spring balance, measuring the bouyant effect on an attached float. In this way Tapp, Steacie and Maass (70) and Winkler and Maass (90) have examined the systems methyl ether and propylene. Their apparatus provided for measurement of the density at various heights in the containing vessel, and made possible also gentle stirring of the contents of the bomb. Their results show the persistence of the two phases, with a sharp break in density at the point where the meniscus had disappeared. The possibility of lack of equilibrium due to slowness of diffusion was answered by the observation of unchanged density on stirring. Their results for different fillings agree sufficiently well, except for a single case in which no density difference was observed (70). The cause of this discrepancy still remains a mystery; under the same conditions, Winkler and Maass obtained a result in accord with the persistence first noted. These last authors could reproduce results quantitatively.

Maass and Geddes (35) have used the quartz spring balance float method to investigate the density of the system ethylene in the critical region. Results were obtained in conformity with those of Tapp, Steacie and Maass.

McIntosh and Maass (41) and McIntosh, Dacey and Maass (42) have continued this phase of the work, also on ethylene. These investigators have succeeded in perfecting the experimental technique so that for the greater part their results are reproducible with quantitative agreement.

Examination of the literature for contradictory results has not been fruitful. No report has ever been made of a direct measurement of the phase density just above the critical temperature in which these were found to be equal (excepting the one anomalous result of Tapp, Steacie, and Maass).

It has been pointed out that if it were true that the densities of the two phases become equal at the critical temperature, the critical phenomena could be observed in a tube filled at only one mass-volume ratio, namely the one corresponding to the critical density. (It is interesting to note no *mathematical* figure can ever be obtained *experimentally*. Hence on the classical point of view, the disappearance of the meniscus away from the top or bottom of the tube could never be observed experimentally!) It is the experience of those who have worked in the field of critical phenomena, that the disappearance of the meniscus can be observed over a range of densities. A number of investigators have reported the ranges over which they observed the meniscus could still be seen away from the ends of the containing vessel when the critical temperature had been reached.

Substance	Range	Reference
Carbon dioxide	0.44 - 0.47	Kuenen (87)
	0.29 - 0.64	de Heen (88)
	0.34 - 0.59	Hein (30)
Ether	0.22 - 0.29	Gallizine (24)
	0.23 - 0.29	Schroer (63)
	0.25 - 0.43	Andant (89)
	0.3 - 0.4	Travers and Usher (75)
Water	0.28 - 0.39	Schroer (62)
	0.26 - 0.44	Callender (13)
SO_2	0.3 - 0.4	Travers and Usher (75)
	20% range	Centnerszwer (15)
NH_3	0.3 - 0.37	Centnerszwer (15)
CH_3Cl	0.3 - 0.4	Travers and Usher (75)

Good agreement is not to be expected for the following reasons: Some of the results are not limits of the ranges, but merely observed ranges; doubtless too some of the earlier investigators used impure materials; finally as we shall see, different values are obtained depending on whether the experimental vessel is shaken or not, and the results can even be affected by the rate of heating.

The range of densities has been observed by Naldrett, Mason and Maass (47), who subjected the ethylene they used to violent stirring. Results obtained without stirring are less consistent, and lie outside of the range obtained with stirring.

A number of investigators have concluded that the phases persist above the critical temperature simply by visual observation. The phase boundary above the critical temperature has been observed by Callendar, who says: "With improved apparatus, and on a larger scale, using very pure water free from air, it was observed that the densities of liquid and vapor did not become equal at 374°C when the meniscus vanished, but that a visible difference in density persisted beyond this point up to 380°C under favorable conditions". By filling quartz tubes with different amounts of water, Callendar was actually able to trace the density of the liquid phase to temperatures six degrees above the critical. Schroer (62) reports seeing ripples on moving a horizontal capillary containing water above the critical temperature.

Bradley, Brown, and Hale produced fog in carbon dioxide near the critical temperature by rapid periodic expansions and contractions (9). They found that this phenomenon occurred both above and below the critical temperature. They reasoned that the fog was due to the formation of liquid droplets by cooling in the expansion process. In this way they were led to the conclusion that liquid and vapor coexisted to a temperature 7° above the critical.

A number of investigators have made the observation, that if a material containing a colored solute is heated through the critical temperature, the color will persist in the space previously occupied by liquid, even though the meniscus has disappeared. The claim that these observations indicate the persistence of the two phases has been criticized on the basis of lack of equilibrium. The systems which have been investigated are sulphur in ammonia (23), alizarine in alcohol (54), iodine in carbon dioxide (10,77), and potassium dichromate in water (8).

The conclusion that the phases exist above the critical temperature was arrived at also by Wesendock (80), who observed opalescence phenomena which occurred on shaking carbon dioxide above its critical temperature.

Hagenbach has determined the conductivity of iodides in sulphur dioxide for both phases, through the critical temperature (26). Eversheim has carried out similar measurements for inorganic salts in ammonia (22). They found that the conductivities had not become the same for the two phases far above the critical temperature.

Eversheim found that the dielectric constant of liquid ammonia also showed a difference when measured at the top or bottom of a tube, indicating thus the presence of the phases above the critical temperature. In the case of liquid ammonia these values become equal only 17° above the critical temperature. Marsden and Maass have carried out measurements on propylene and methyl ether (36). Their results for the dielectric constant — temperature curve of the phases at saturation resemble in appearance the density temperature curve of Tapp, Steacie and Maass (70), the liquid dielectric constant curve being however above the vapor curve. The phase dielectric constant difference is traced 5°- 7° above the critical temperature.

McIntosh and Maass (41) have found that for a region of volume variation of 7%, the pressure of the system ethylene is constant, at a temperature 0.3° above the critical. The constancy of pressure over a range of volumes on an isothermal indicates the presence of two phases for all volumes in this range. More recently McIntosh, Dacey and Maass (42) have traced the pressure—volume—temperature curves in the critical region. It appears from their results that the liquid phase exists at least 0.4° above the critical temperature.

On the other hand, Maass and Geddes have not found $dp/dv = 0$ for any volume of ethylene at 9.80° C (35). This and other disparities seem to indicate that Maass and Geddes had a small percentage of air or other impurity in their ethylene. One other set of measurements has been made with extreme accuracy in this region, those of Michels, Blaisse and Michels for CO_2(43). These investigators found no zero slope for the pressure —volume isothermals above the critical temperature. However, their work is open to criticism on the grounds that a slope appears also in their liquid vapor isothermals below the critical temperature, amounting to an increase of .01- .02 atm. in the transition vap.- liq. The deviation of their curves from the horizontal above the critical temperature is of the same order of magnitude. The presence of an impurity (probably air) is to be suspected.

Mayer and co-workers have developed a statistical mechanical treatment for condensing systems. It is a consequence of their theory when applied to the critical region, that the temperature for which the surface tension becomes zero is below the highest temperature for which dp/dV is zero. Thus a two phase system would persist at a temperature above that at which the meniscus had disappeared. This is in accord with the experimental results. As their discussion forms a very important part of the foundation for the conclusions to be drawn later, it will be described in a separate section.

On the basis of what appears to be a semi-empirical "thermodynamic" equation of state, Jacyna shows that a "critical region" should exist rather than a critical point. On the boundaries of this region, dp/dV=0. The extent of the region is calculated to be $.08^\circ$ and .04 atm. for helium. The temperature range for CCl_4 is 2°- 4°, for SO_2, 0.7- 2.4°

for CO_2, 0.43°. The significance of the "region" is not clear.

Callendar worked out a semi-empirical equation to represent the thermodynamic properties of steam up to pressures of about 1000 lbs./sq. inch. When he tried to extend these equations to the critical point, it appeared that no fit could be obtained. He then determined the following properties of water in the critical region (12, 13):

The specific heat at constant pressure.

The absolute total heats.

Variation of the total heat with pressure at constant temperature.

The envelope of the liquid — vapor curve.

We have already referred to his measurement of the liquid densities above the critical temperature. In his new conception of the critical state, the liquid and vapor densities approach each other slowly rather than precipitously, near the critical temperature. His equation obtained at lower densities now fitted this new data.

Bennewitz and Andreewa have arrived at the conclusion that liquid and vapor coexist at the critical temperature, reasoning from their experimental values for the Joule effect (4). They found that the internal energy has a negative value at the classical critical point. They show that from a kinetic point of view, the internal energy should be zero at this temperature. To explain the discrepancy, they postulate a range over which groups of molecules have a transitory existence (causing opalescence) so that liquid and vapor coexist in this region. Their conclusions appear to be in the right direction.

The experimental detection of the density difference has been attributed to the effect of gravity. Because dp/dV becomes small gravitation effects can cause a marked variation of density with height. In a separate section evidence will be put forward which shows that these observed differences are not due to gravity.

Still another criticism that has been made is that the observed effects are due to impurities. This too will be discussed later.

We shall see that results indicating the persistance of the phases can be obtained only when the temperature control is good. Fluctuations in temperature with time, and temperature gradients in the medium, must be absent.

Assuming that the criticisms can be answered, it appears that the persistence of the phases above the critical temperature has been established. The interval above the critical temperature, in which the phase difference appears, seems to lie between 2°- 8°, for the materials which have been investigated to date.

The section on association was placed before the discussion of phase persistence. However, the existence of the phase difference was kept in mind, and the arguments used to prove the existence of association apply to that region where the medium is completely homogeneous, even in the light of the persistence hypothesis.

The nature of the phase boundary: Traube, and a number of others, have sought to explain the observation that no meniscus is to be seen in spite of the phase density difference, in the following manner: At the critical temperature, liquid and vapor molecules become soluble in each other, and diffusion occurs through the phase boundary. The boundary becomes diffuse, and is finally not to be seen at all.

Ostwald has advanced a qualitative theory to explain the opalescence effects observed when the meniscus disappears. (It should be noted that the Einstein-Smoluchowski theory has been shown to apply only at temperatures somewhat removed from the critical temperature). The description is made in terms of colloidal phenomena. Bubbles of vapor of colloidal dimensions form in the liquid and remain in suspension, similarly liquid droplets are carried into the vapor region and remain suspended. The intermediate regions are colloids with properties lying between these two extremes. Some such theory is needed to supplement the Einstein-Smoluchowski hypothesis.

The idea has been advanced that as the critical temperature is approached, the drop in density through the liquid—vapor interface occurs through a greater and greater distance, and finally the meniscus becomes sufficiently diffuse to become invisible.

In the theory of Mayer, the surface tension has disappeared while the phase density difference still persists. The theory does not, however, help us to make conclusions about the nature of the interface between the phases.

On the whole, this part of the subject appears to be in a very undecided state. A theory of the interface may possibly be correlated with the result of Winkler and Maass (90) on the variation of the density in going from the liquid phase to the vapor, above the critical temperature. The density is constant with height for each of the phases, except within a few cms. of the point at which the meniscus had disappeared. The variation of density between the phases occurred over a range of 5 – 12 cms. Although the authors have not pointed it out, examination of a set of curves setting forth this data, shows that the variation occurs over the greatest distance in that case in which the stirring was longest continued (although the density of each of the phases away from this region remained unchanged by six hours stirring).

Hysteresis Effects: A number of the macroscopic properties of systems in the critical range appear to be a function of the history of the system. The results obtained when these properties are measured under varying conditions of previous treatment have been classified as hysteresis effects. These will be presented here as a group.

Tapp, Steacie and Maass (70) found that when methyl ether is heated above the critical temperature, a density difference persists through a range of several degrees. Now if the medium be cooled, no density difference reappears until a temperature below the critical has been reached. In other words, there is a range of temperature just above the critical, in which the medium can apparently have different densities, depending on whether the system has been brought up from below, or brought down from above, the critical temperature. Winkler and Maass (90) have also noticed this hysteresis.

A plot of the density against the temperature yields a hysteresis area. Maass and Geddes (35) and McIntosh and Maass (41) have shown that for a system with a given mass-volume ratio, any point in this area can be realized experimentally, simply by a choice of the proper thermal treatment previous to measurement. An isochore of McIntosh and Maass is reproduced elsewhere in this thesis.

The densities appear to be equilibrium values in the sense that no appreciable change occurs even after standing for hours. Tapp, Steacie and Maass found too that gentle stirring did not alter the density values.

This phenomenon had been previously reported by Teichner, who found that on cooling CCl_4, his floats did not show any density difference in the system, until the critical temperature was reached. A density difference was observed when the temperature rose through the same interval.

It deserves special attention that the hysteresis found for an isochore by Maass and co-workers extends below the critical temperature as well. In the case of ethylene and methyl ether, the interval below the critical temperature in which hysteresis effects are appreciable, is about 1°.

Hysteresis in the density also appears with volume and pressure changes. Maass and Geddes describe the following experiment to illustrate the effect of over all volume change on the liquid density below the critical temperature. If ethylene (critical temperature = 9.50°C) is brought up to 9.25°C from some temperature below 8.50°C, and the density and meniscus level noted, then a decrease in the volume occupied by the system was found not only to raise the level of the meniscus but also to increase the density of the liquid phase. Such a result is anomalous for an orthodox two phase system. On subsequent re-expansion to the original volume, the original liquid density was reestablished. In the reverse process, an expansion and subsequent recompression left the liquid phase with a lower density.

If the temperature of a system be raised above 9.50°C, the difference in density between the phases is altered by a slight compression or expansion, and destroyed altogether if the compression or expansion is sufficiently large. Moreover, the density difference cannot be restored by reversal of the volume change. The only means by which the density difference above the critical temperature can be observed experimentally, is to bring the system up from a temperature below the critical.

Again the densities of the liquid and vapor both above and for one degree below the critical temperature, appear to be a function of the mass-volume ratio for the bomb (41, 90). The surprising observation has been made that liquid densities can be obtained for one mass-volume ratio which are less than vapor densities for the same system at a greater mass-volume ratio.

A number of investigators have reported that the phase level at the time of meniscus reappearance is different from the level at which the meniscus disappeared (e.g.90).. McIntosh, Dacey and Maass have also observed that the liquid level is not reproducible, even after approximately the same heat treatment. It appears that the phase levels are functions of such minor factors as the rate of heating or cooling. Another effect has been observed in tubes filled with an amount of material less than the critical density. If the proper mass-volume ratio is chosen, then it is found that if the bomb is heated up slowly the liquid will persist, while if the heating is rapid, the liquid may disappear before the critical temperature is reached (Traube, 49). Gallizine has also noticed that for other mass-volume ratios the liquid level depends upon the rate of heating (24).

In certain regions, the phase densities are affected by violent shaking. Teichner (71) observed that no density difference persists above the critical temperature, if the medium is sufficiently stirred. Naldrett, Mason and Maass (47) have traced the envelope of the liquid-vapor saturation curve for ethylene. They found different densities with and without shaking of the experimental bombs. The values found without shaking were not as consistent as the others. Winkler and Maass, however, found that gentler stirring does not alter the densities.

There is a hysteresis too in the temperature at which the meniscus disappears and reappears. Hein has reported a 0.12° difference for CO_2 (30). Schroer found a 0.1°- 0.2° difference for water (62). Tapp reported for propylene a difference of 0.5° (70). Maass and Geddes found for ethylene 0.16°, but this figure has been set by McIntosh, Dacey and Maass at 0.3°. The writer has observed for ethane a difference of 0.20° C.

Teichner found that the meniscus in CCl_4 disappeared at a lower temperature with stirring than without. Naldrett, Mason and Maass have made this observation for ethylene, and find that under these conditions of vigorous stirring, the temperature of reappearance becomes equal to the temperature of disappearance. Ramsay set up convection currents in ether just below its critical temperature, and found that the meniscus had disappeared after the establishment of temperature equilibrium (57).

In his examination of salt conductivities through the critical temperature, Eversheim (22) noticed that the conductivity was altered by shaking if the material were above the critical temperature.

Clark has found a hysteresis in viscosity measurements (17). Above the critical temperature,the viscosity with rising temperature differs from the values obtained with falling temperature. Violent stirring tends to remove the hysteresis and to bring the viscosity in both directions near to the curve obtained for falling temperature and no stirring.

It thus appears that many of the properties of systems in the critical region can be altered by varying the thermal history, or the volume history, or by shaking. It may well be noted in this connection that the properties observed are all macroscopic properties of the system.

Temperature Fluctuations and Gradients: Parts of the subject matter under this heading will be seen to be pertinent to the discussion of hysteresis effects as well.

Tapp, Steacie and Maass investigated the effect of a temperature gradient along the length of a bomb in the critical region. They found that if the top of the bomb were kept 0.1° or less colder than the bottom, the difference in phase density above the critical temperature could be removed; in fact the upper part of the tube could in this way be made to show a density greater than the lower part. Moreover, if this gradient was maintained for a sufficiently long time, the density difference did not reappear when the temperature gradient was removed. A reverse temperature gradient, with the bottom colder than the top, served to accentuate the density difference. These results were confirmed by Winkler and Maass (90).

McIntosh and Maass (41) and Winkler and Maass (90) have carried out an experiment in which a temperature gradient was set up by cooling the top of a bomb containing ethylene just above the critical temperature. The density difference was destroyed. Conversely, McIntosh, Dacey and Maass (42) have tried heating the top of a bomb containing ethylene just above its critical temperature, in which the density difference had been previously removed by a suitable temperature treatment. The difference in density was restored.

Maass and Geddes found that if the system were brought up to some point just above the critical temperature, so that a density difference persists, then the amount of the difference can be successively reduced by alternatly heating and cooling the system through a small temperature interval. The values of the density after each cycle then seem to form an infinite sequence having as its limit the mean density of the system.

These authors have pointed out that violent stirring would have the effect of compressing and expanding the medium locally. In this way the difference in density would tend to be destroyed. Many of the previously observed results can be explained in the light of this hypothesis.

Time lags: Geddes and Maass were the first to observe quantitatively the time lags which are encountered in experimental work in the critical region. A time lag is the term applied to the observation that in many cases when a small change is made in one or more of the variables of state, the system has not come to equilibrium in a period very much longer than that required to establish temperature equilibrium.

It was noticed that when the temperature was changed through a standard interval on an isobar, the time lags were greater on cooling than on heating. The lags were greatest when the change was to the critical temperature.

A second type of effect was noticed when the density was increased through standard intervals by lowering the temperature. It was found that the greatest lags occurred for changes to the critical density even when these changes are made greater to other final densities, and these final densities are greater than the critical value.

McIntosh and Maass have observed a small lag in the assumption of density in certain regions, when the temperature is changed on an isochore. The period of this lag is less than twenty minutes. Winkler and Maass found a 40 to 50 minute lag under the same conditions, working with propylene and methyl ether.

It should be noticed that time lags occur also above the critical temperature, and outside of the region of liquid — vapor coexistence as defined on the persistence theory.

It appears then that time lags are an important property of materials in the critical range. A complete theory of the critical phenomena must not omit consideration of these effects.

The utility of specific heat measurements in the critical region:

The specific heat at constant pressure is defined as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left[\frac{d(U+pV)}{dT}\right]_p$$

On the basis of the Andrews - van der Waals conception of the critical phenomena, C_p should be infinite at the critical point, for

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial v}{\partial T}\right)_p$$

and on the basis of the classical theory, at $T = Tc$ and $p = pc$,

$$\left(\frac{\partial p}{\partial T}\right)_{V_c} = \text{constant.}$$

$$\left(\frac{\partial V}{\partial T}\right)_{pc} = \infty .$$

C_v is always positive,

hence $C_p = \infty$.

According to the persistence theory, however, at T_c there is still a difference in density between the phases, and consequently the Clausius-Clapeyron equation can be used to obtain the heat of vaporization,

$$L = T\frac{dp}{dT}(v_2-v_1)$$

Let us assume now that we have a calorimeter designed to make measurements of the specific heat at constant pressure, and in this way have obtained data for the critical region. Then if the persistence theory held, and the results were calculated on the basis of the classical theory, we should find a region above the critical temperature throughout which C_p was infinite. If the classical theory held, Cp would tend to infinity as only a single point, the critical, was approached.

In the former case it would become necessary to accept the persistence theory, and to postulate a co-existence region above the critical temperature, with a heat of vaporization in this region, calculable from the observed results.

Callendar (13) has carried out such measurements for water. At the critical temperature, he finds L = 72.4 Cal./g., and this latent heat does not vanish until a temperature of 6.5° above the critical has been reached. Previously, latent heat measurements had always been extrapolated to zero at the critical temperature, with the last result several degrees below this temperature.

Now let us consider the state of affairs on the borders of the co-existence region. Returning to the pressure —volume isothermal plot, at temperatures lower than and removed from the critical,

$$\frac{dp}{dV} \neq 0$$

at the borders of the liquid vapor envelope. There is therefore a discontinuity in the curvature of the isotherms as they pass into the liq.-vap. co-existence region. McIntosh, Dacey and Maass (42) have however drawn the isotherms with a continuous slope at and above the critical temperature. Also, Harrison and Mayer have postulated this to be true, on the basis of surface tension considerations (40).

Since

$$\left(\frac{dV}{dT}\right)_p = - \frac{\left(\frac{dp}{dT}\right)_V}{\left(\frac{dp}{dV}\right)_T}$$

and

$$\left(\frac{dp}{dT}\right)_V \text{ is always finite,}$$

we should have $\left(\frac{dV}{dT}\right)_p = \infty$ and consequently,

$$C_p = \infty$$

on the borders of the co-existence curve above the critical temperature. In this case the isotherms on an H — p diagram should pass through the co-existence region with continuous curvature. Callendar's diagram for steam does not conform to this requirement. Whether this indicates that the original postulate regarding the form of the p—V isotherms is in error, or whether Callendar's results are in error, cannot be decided with certainty. Unfortunately, Callendar has not published detailed experimental results, to which reference would have to be made to decide this point.

In dealing with the specific heat at constant volume, we are less dependent on the p - V - T data for the system. Since

$$Cv = \left(\frac{dU}{dT}\right)_V ,$$

the determination of Cv gives a measure of the internal energy of the system.

The heat capacity of the simpler gases at low pressures has been thoroughly investigated from both the experimental and theoretical point of view. This subject may be considered to be in a satisfactory state. An excellent review of this field is to be found in Fowler's "Statistical Mechanics," Chap. III.

The effect of increasing the pressure at which the constant volume measurements are made is given by,

$$C_{v_{V=V'}} = C_{v_{V=\infty}} + \int_{\infty}^{V'} T\left(\frac{d^2p}{dT^2}\right) dV$$

On the basis of this equation it should be easy to calculate C_v, provided that the second pressure- temperature coefficient is known over the whole volume range. Extremely accurate p-V-T data is required in order to make this possible; for example, see Michels, Bijl, and Michels(44).

We have seen already how useful C_v data can be in the interpretation of association data. No previous measurements have been made in the critical region in which the existence of the hysteresis reported by Maass and coworkers has been kept in mind. The purposes of the heat capacity investigation were:

(a) To trace the specific heat curve with a greater accuracy than hitherto obtained, and with very pure material.

(b) To investigate possible thermal effects connected with the hysteresis in this region.

(c) To investigate time lags.

THE ORIGINAL CALORIMETER

THE ORIGINAL CALORIMETER.

Requirements: To operate in the critical range the calorimeter had to be capable of withstanding the high pressures encountered. It must yield accurate results when operated over small temperature ranges. Temperature changes should be slow, in order that the material should be as nearly as possible at equilibrium during heating. Finally the apparatus must be capable of detecting and eliminating the effects of time lags occurring after a change in temperature. No apparatus has been described for use in this region which satisfies the last requirement.

Construction: Since the heating rate was to be low, it was essential that heat losses, such as occur in ordinary calorimetric work. be eliminated. The ethylene container was fitted with an electric heater, arranged so that the energy input could be accurately measured. The outer vessel was placed in a water bath whose temperature could be accurately measured and controlled. Heat losses could now be eliminated by keeping the outer container at exactly the same temperature as the inner one.

The Container: The container, illustrated in figure 1, was constructed from drawn steel tubing, with .09" walls. The ends were welded in as shown. The volume was about 47cc. A piece of wire solder slightly smaller than the tube C was placed at E. The end of the tube C was connected to the filling apparatus. After evacuation the bomb was cooled in liquid air, and the requisite amount of ethylene distilled in. Then the tube was heated at B, in order to melt the solder, which flowed down into the previously tinned gooseneck D. Then the tube could be pinched off at A. The bomb was filled with an amount of ethylene calculated to be 10.66 grams. After more than a year, it was weighed and emptied, and the weight of ethylene was 10.653 g. It follows that the seal made in this way was pressure and vacuum tight.

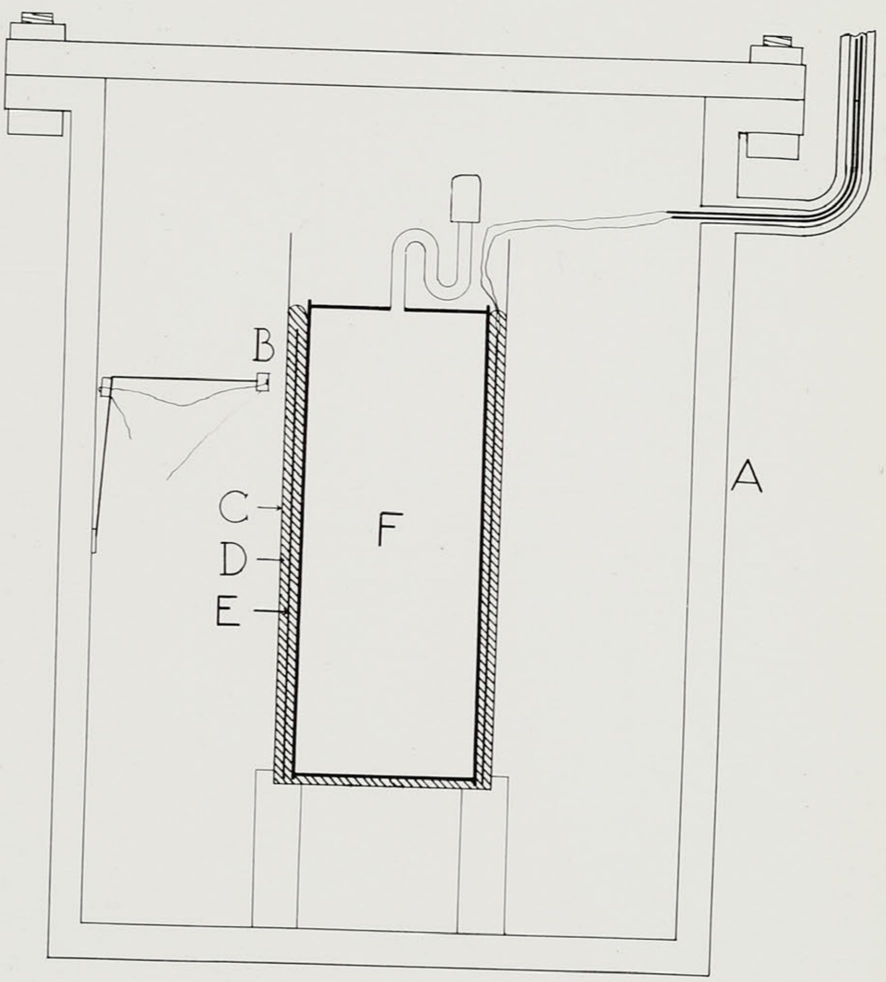

Figure 1.

The original calorimeter.

The inner bath: This is illustrated in the cross section of figure 2. The electrical heating element consists of no. 34 copper wire wound on a thin steel cylinder E, to give a resistance of about 13 ohms. The cylinder was perforated for better heat conduction. It was fitted around the bomb as shown at F. The whole was then placed in a thin steel cylindrical container C, which was finally filled with mercury, D. The purpose of the mercury was to equalize the temperature on the surface of C during heating, so that the inner and outer parts of the calorimeter should have the same temperature everywhere on their surfaces during operation.

The thermocouples, and the inner electrical connections: The inner bath was supported on three bakelite posts cut to knife edges. The wires carrying current to the heating element were led off through a pair of tubes, one of which is shown in figure 2. The optimum size of wire with view to both heat conduction and heat generated was No.26 copper wire. The outer container A is of $\frac{1}{4}$" welded steel, vacuum tight. The copper - constantan thermocouples, constructed of fine flat strip wire, were mounted on supports such as shown at B. Twelve pairs of junctions were mounted so that one set were supported about 1/8" away from the inner bath, and symmetrically placed about it. These were blackened to receive heat by radiation. The other set were separated from the inner wall of the outer container by a thin sheet of mica. The connections to the galvanometer were led outside through a third tube. A fourth inlet was provided for evacuation.

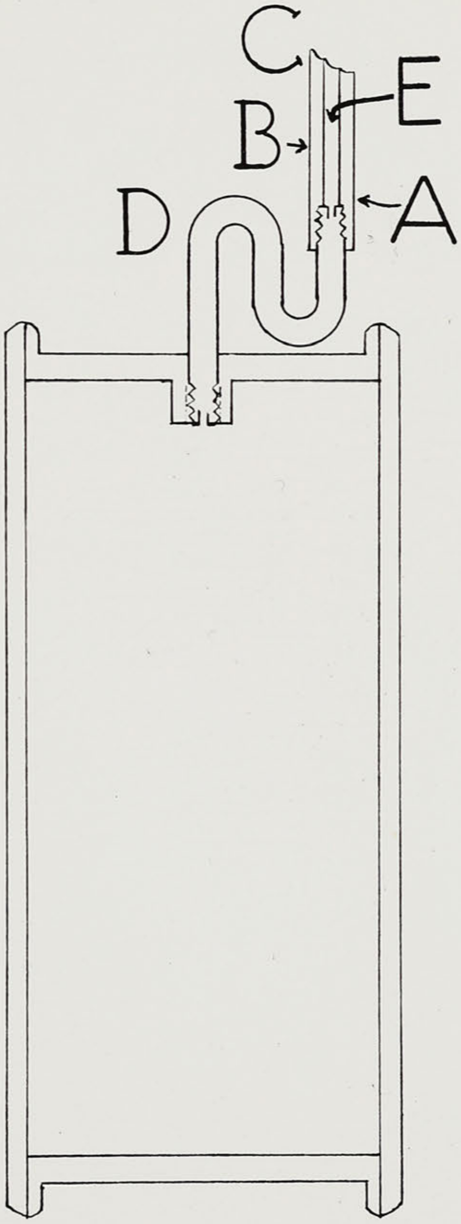

Figure 2.

Diagram of the container, showing method of sealing.

<u>The outer bath:</u> The outer vessel was placed in a large water bath. It was important that this bath should be capable of extremely precise temperature control. It was fitted with three stirrers, which provided efficient circulation of the bath fluid. The heating and cooling was accomplished by additions of water at a temperature a few degrees different from that of the bath. A smaller lag results this way, compared with electrical heating. Flow diverters were provided, so that steady flow conditions could be attained, before additions of hotter or colder water were made. In this way the bath temperature could be hand controlled over periods of several minutes to ± .0001°, and over periods of several hours to ±.001° C.

Temperature was measured by means of a Beckmann thermometer. A 0°– 50° thermometer was provided to indicate the absolute Beckmann settings to ± .01° C.

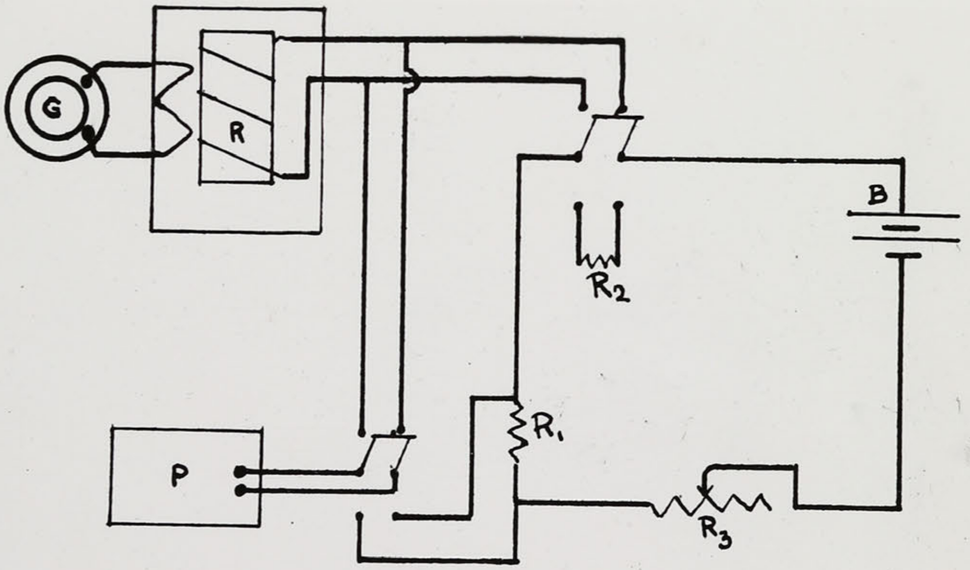

Figure 3. The Electrical Connections.

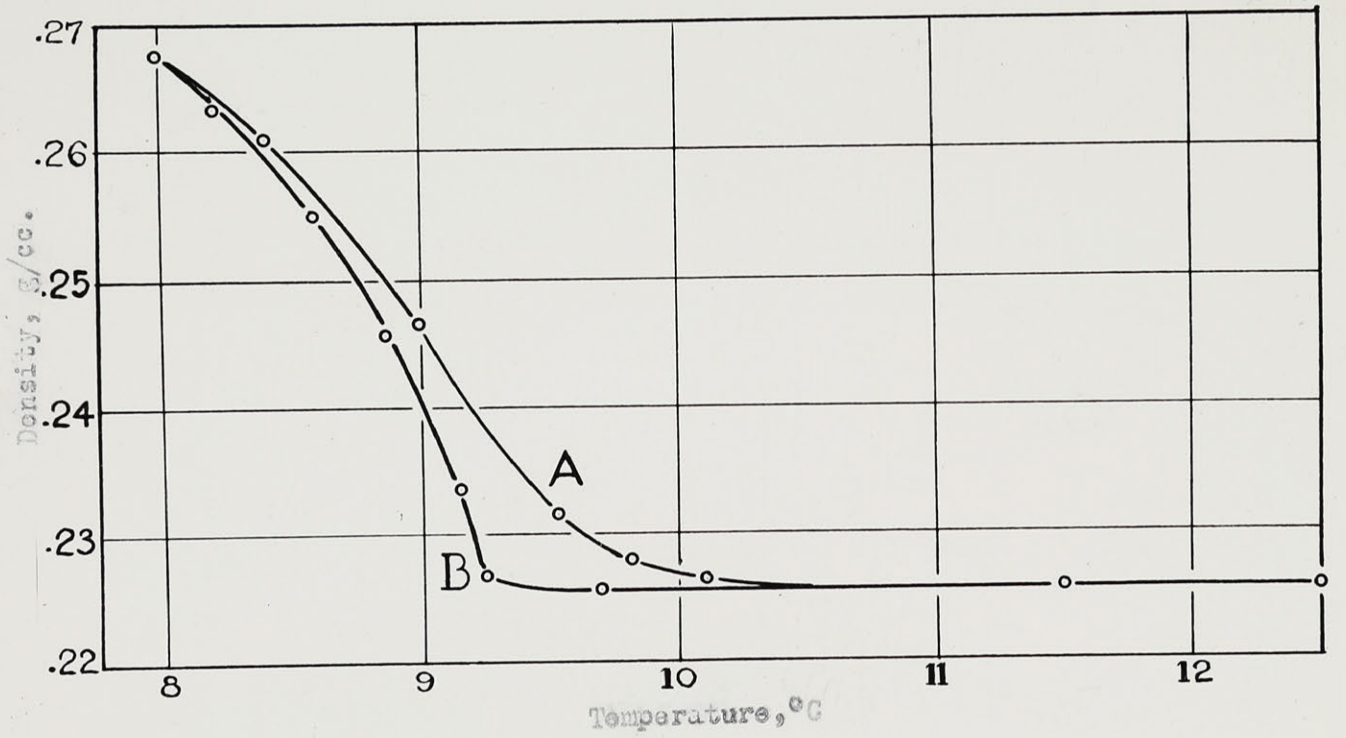

Figure 4. McIntosh and Maass isochore.

The electrical connections: These are illustrated in figure 3. R is the bomb heater. It is connected in series with R_1, a standard resistance of 19.856 ohms, with R_3, a variable resistance and the 4 volt storage battery B. R_2 could be switched in as an alternative to R_1 and its purpose was to assure steady voltage conditions by closing the circuit through R_2 for several minutes before a run was started. The potentiometer P was connected in so that the voltages across R and R_1 could be separately measured. The thermels were placed in series with a very sensitive galvanometer, as shown in figure 3. This galvanometer was chosen to have a small period. Thus the lag in indication occurring after a change has been made in the outer bath temperature was reduced to a minimum. The lag was actually only about five seconds.

The operating characteristics: In operation the voltages across R and R were respectively about 1 and 1.4 volts. This gave a rate of heating of about 1.5 degrees per hour. The voltages did not usually change by more than one part per thousand during the course of a half hour run. With potential readings taken at five minute intervals, the mean of the voltages was accurate to one part in ten thousand.

The thermel galvanometer showed a deflection of one cm. for a difference in temperature between the inner and outer baths of .001°C. A measure of the heat losses is given by the rate of warming of the inner container when the outer bath was at a standard higher temperature. This rate was 1° per hour per degree temperature difference. Thus if the difference in temperature during a one hour run averaged .001° (taking cognizance of the sign of the difference in averaging), the heat loss represented a temperature change of .001°. Since a one degree run took less than an hour to complete, this would represent an error of one part per thousand. In a number of runs the average temperature difference was determined by keeping a log of the instantaneous galvanometer deflections, and was found to be less than .0002°, corresponding to an .02% error. Heating time was measured by means of a chronometer, by means of which the time for a one degree run, about 1500 seconds, could be measured with an accuracy of about .02%.

The power input is given by

$$\frac{EE_1 t}{4.182\ R_1} \text{ calories.}$$

where

E = potential drop across R,

E_1 = potential drop across R_1,

R_1 = resistance of R_1 = 19.856 ohms,

t = heating time, in seconds.

The possible error in the measurement of power input for a one degree run is estimated as the sum of .02% for heat losses, .02% for measurement of time, and .01% in the determination of E and E_1, or .05% altogether.

<u>Calibration of the instruments</u>: The potentiometer was calibrated against a standard Leeds and Northrup Type K instrument, and found to have no error as great as .01%. The standard cell was calibrated against the extremely accurate standards maintained by the Physics Department of this University. The resistance R_1 was measured on a Mueller bridge and is absolutely accurate to better than .01%.

Calibration of the thermometers: The Beckmann thermometer was calibrated very painstakingly against a platinum resistance thermometer. The length of the scale was covered at 0.2° intervals, and at even closer intervals when the calibration changed rapidly. This was repeated several times. However different calibrations over a one degree range could not be repeated to better than .001°. Over the 5° range, disagreements were found as great as .003°. It is believed that these observations represent the ultimate accuracy of the Beckmann thermometer in determining temperature intervals, about 0.1%.

For all phases of the work, and particularly for the time lags and runs over small temperature intervals, it was desirable to read the thermometer to better than the one thousandth degree usually considered the limit of accuracy. In this work, moreover, due to the danger of explosion, the observer was placed several feet from the apparatus. This difficulty was solved by disposing a lens in front of the thermometer, which could be slid up and down. Then a telescope was trained on the lens. Then with strong, glareless lighting, the thermometer could be read to a hundredth of a division, or .0001°. An examination of one of the logarithmic plots for the time lags, shows that single readings all fall within .001° of a straight line, whereas most of them are within .0002°. It is believed that temperature could be read at the beginning and end of a run to better than ± .0003°. The accuracy in the measurement of temperature is estimated at 0.1%, for runs over an interval greater than 0.5°.

Stem corrections were reduced to a minimum by so disposing the bath and lighting, that the thermometer was immersed to the bottom of the scale. The residual corrections were estimated by means of two auxiliary thermometers along the length of the stem, applying the corrections listed by the U.S Bureau of Standards.

Under the circumstances the thermometer could not be tapped before reading to prevent sticking of the mercury column. The equivalent effect was, however obtained by affixing an electrical buzzer to the Beckmann. The 0°-50° thermometer was also calibrated against the platinum resistance thermometer, so that the absolute temperatures are good to ± .01° C.

When extremely accurate comparison of heat capacities at different temperatures was desired, the Beckmann was reset to operate over the same temperature readings in all cases. Then setting corrections were applied as listed by the U.S. Bureau of Standards.

We have estimated the possible error in power measurement as .05% for a one degree run, and the corresponding quantity in temperature determination as 0.1%, making a total of 0.15%. Actually, with but a single exception, no run made over a one degree range disagreed with the finally accepted mean by more than 0.1%. Runs over a 0.14° range showed a maximum deviation from the mean of only 0.4%. Since the ethylene represents only one fifth of the heat capacity of the system, these errors should be multiplied by five, in order to obtain figures applying to the heat capacity of the ethylene itself.

The regulator: In certain regions it is necessary to thermostat the bath temperature for periods of sixteen hours prior to a run. For this purpose a toluene-mercury spiral thermoregular was constructed of 9mm. pyrex tubing. When this was operated in conjunction with a sensitive relay and a 125 watt "lagless" heater, the temperature was kept constant to $.001^\circ$ for long periods of time.

Technique in making a run: In the course of a run, the initial temperature of the bomb is determined by reading the outside temperature with no deflection in the galvanometer. The heating coil is then turned on, the exact time being noted. Adiabatic conditions are maintained by raising the bath temperature simultaneously with that of the bomb, the reading of the thermel galvanometer being kept at zero. E.m.f. readings across both the heater and the standard resistance are noted at regular intervals, and the time when heating is stopped is recorded. Then, adiabatic conditions still being maintained, time is allowed for temperature equilibrium to be established in the bomb assembly, and the final temperature determined in the same way as the first. The rate of heating is about 1.5 per hour. The heat capacity is then calculated from the average value of the two e.m.f's, the heating time, and the temperature interval.

RESULTS.

The isochore of Maass and coworkers: In order to cast a reasonable light on the results, it is necessary to consider the experimental results which are obtained when the densities of the phases are measured in a system containing liquid and vapor in a closed vessel. In figure 4, the curve representing the relation between the density and temperature is shown, as reported by McIntosh and Maass(40). Similar results have been obtained by others(35, 41, 70). As the ethylene temperature is increased, the liquid density decreases regularly through the critical temperature(curve A), and a density

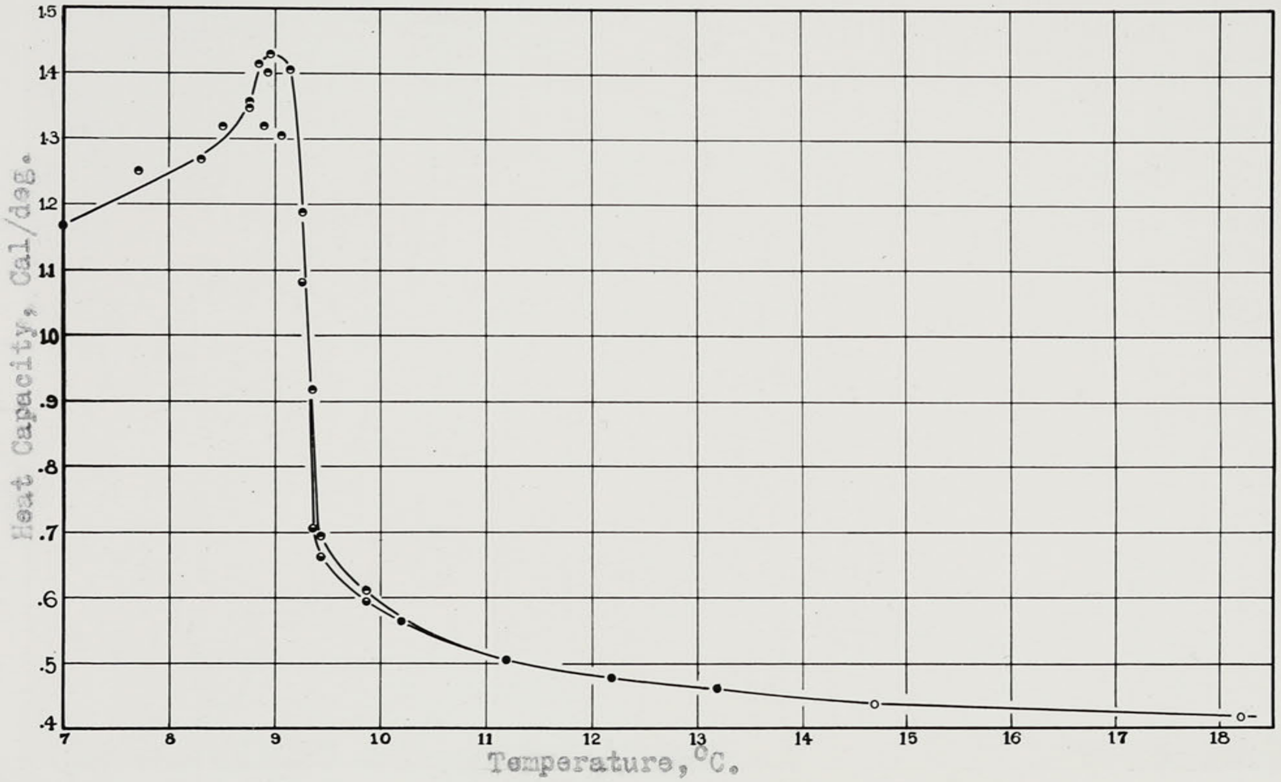

Figure 5. Heat capacity of ethylene, 7° to 18°. ◓ ,Temperature brought up from 8° before run started. ◒ ,Temperature brought down from 15° before run started. Average density = 0.2255.

difference persists until a temperature about 1.5° above the critical has been reached. If the system is cooled from 12.5° no density difference reappears until a temperature of 9.34° is reached. (See curve B). It was desired to ascertain experimentally, whether any difference in heat capacity could be found, which corresponds to this density hysteresis. In discussing the state of the system, we shall for the time being say that the system is homogeneous, if if only one phase is macroscopically evident.

Heat capacity measurements: Values for the heat capacity of the system are given for the range 6.5° to 27° C. With the exception of the first three results in section B of Table I, the measurements in the range 6.5° to 9.5°C were made with two phases coexisting. The heat capacity of the system changes very rapidly in this region: consequently it was necessary to make runs over very small temperature intervals. Furthermore in the neighborhood of 8.5° to 9.5°C long periods were required for the establishment of equilibrium. Both these factors reduce the accuracy of the results obtained in this region compared with those in other temperature ranges.

Density determinations have demonstrated that near the critical temperature the specific volume is dependent on the thermal history of the system. By analogy the heat capacity might also be a function of the previous heat treatment. This has been tested and found to be true. In Table II, the columns headed "Homogeneous" contain the results of those measurements made by bringing the temperature of the system down from at least 5° above the

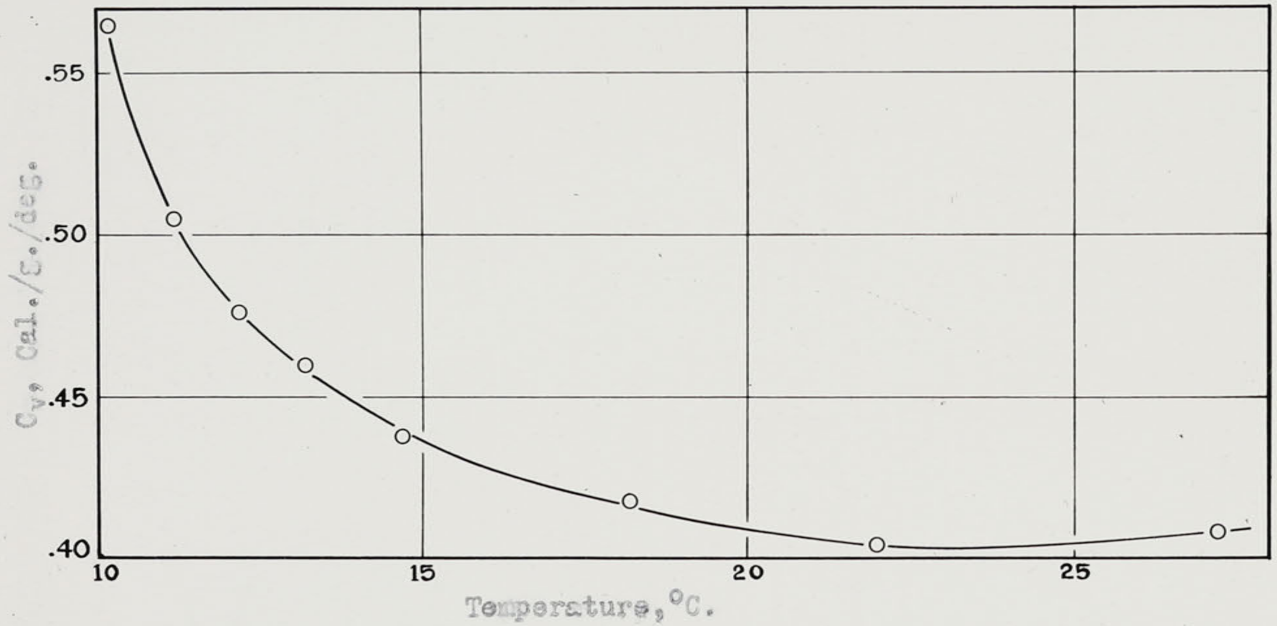

Figure 6. C_v, ethylene. 10° to 27°C. Density = 0.2255.

TABLE I.

Heat Capacity at Constant Volume of the System Ethylene Below the Critical Temperature. Average Density = 0.2255

A. Initial temperature approached from below 8°C.				B. Initial temperature approached from above 15°C.	
Range,°C.	Av. heat capacity cal./°C./gm.	Range, C.	Av. heat capacity cal/°C/gm.	Range,°C.	Av. heat capacity cal./°C./gm.
9.39 - 9.59	0.622	8.75 - 8.96	1.418	9.38 - 9.54	0.633
9.36 - 9.50	0.694	8.66 - 8.86	1.349	9.37 - 9.57	0.647
9.26 - 9.46	0.918	8.66 - 8.86	1.359	9.36 - 9.50	0.663
9.17 - 9.37	1.184	8.41 - 8.61	1.320	9.29 - 9.52	0.651
9.06 - 9.25	1.405	8.21 - 8.41	1.269	9.26 - 9.48	0.705
8.96 - 9.16	1.305	8.03 - 8.21	1.255	9.16 - 9.36	1.082
8.86 - 9.06	1.430	7.47 - 7.96	1.251		
8.806-9.075	1.402	6.49 - 7.47	1.169		
8.80 - 8.99	1.320				

critical temperature. Similarly the heading "Heterogeneous" means that the bomb temperature was brought up from at least 1.5° below the critical temperature before the run was made. Although time lags do not directly affect these results, it may be noted that for the heterogeneous type of run starting at 9.36°C. it is necessary to maintain the temperature constant for at least 14 to 16 hours before a run is started, in order to be certain that equilibrium had been established.

The maximum difference in heat capacity, depending on thermal history, is seen to be 4.5% in the range 9.36° to 9.50° and 2.6% in the range 9.36° to 10.36°.

Table III shows heat capacities of the system at temperatures higher than 13.7°C., where the material is always homogeneous. The

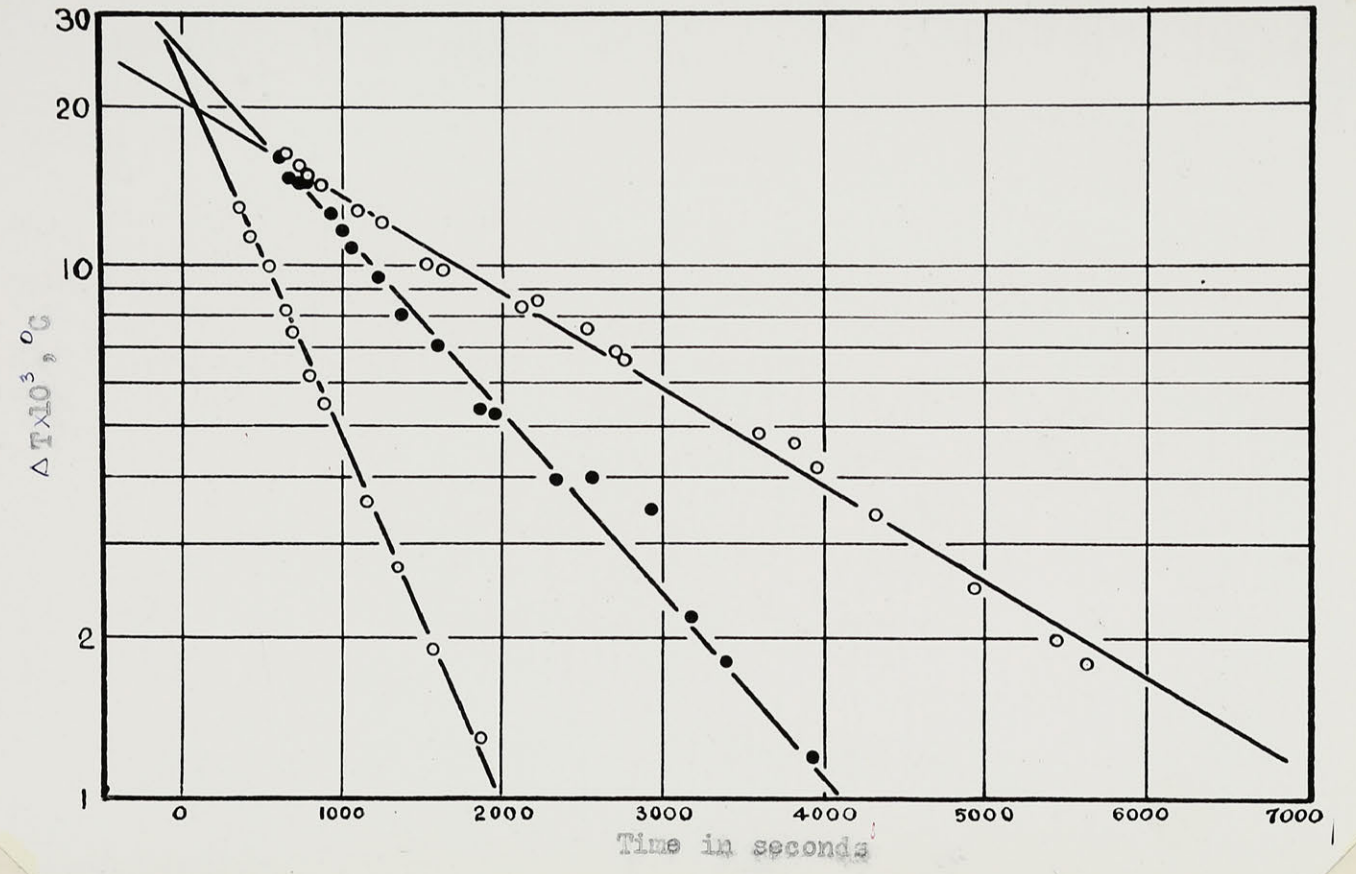

Figure 7. Sample Time Lags. Black circles correspond to Table IV.

TABLE II

HEAT CAPACITY OF ETHYLENE AT CONSTANT VOLUME
Average density = 0.2255

Temp. range, °C.	Heat capacity, bomb assembly, cal./°C.		Mean for bomb assembly		Absolute heat capacity, cal./°C./gm.		Difference cal./°C./gm.
	Homogeneous	Heterogeneous	Homogeneous	Heterogeneous	Homogeneous	Heterogeneous	Heterogeneous minus homogeneous
9.36 - 9.50	40.72 40.99 40.69 40.90 41.05	41.36 41.07 41.35 41.07	40.87	41.20	0.663	0.694	.031
9.36 -10.36	40.18_5 40.18_8 40.11_9	40.29_0 40.37_7 40.26_3 40.37_5	40.15_1	40.32_6	0.594	0.609_5	$.015_5$
9.7 -10.7	39.88_8 39.79_3 39.86_6	39.85_4 39.97_7 39.87_6 39.83_4	39.85_3	39.87_9	0.563	0.565_5	$.002_5$
10.7 -11.7	39.29_4 39.22_3 39.29_7	39.31_9 39.24_7 39.30_8	39.27_1	39.29_1	0.504	0.505_5	$.001_5$
11.7- 12.7	39.04_5 39.08_2 38.98_4	38.95_3 39.08_8 38.98_5	39.03_7	39.00_9	0.478	0.475_5	$-.002_5$
12.7 -13.7	38.88_8 38.91_6 38.89_3	38.84_5 38.91_4 38.87_3	38.89_9	38.87_3	0.461_5	0.459	$-.002_5$
9.7 -13.7	39.26_3* 39.25_9	39.26_5* 39.21_4					

* Mean of 1° runs.

results of Tables I and II are plotted in Fig. 5, and those of Table III, showing a minimum in the curve, in Fig. 6.

TABLE III

SPECIFIC HEAT OF ETHYLENE AT CONSTANT VOLUME AT TEMPERATURES GREATER THAN 13.7°C.

Range, ° C.	12.7°- 16.7°	15.7°- 20.7°	21.0°- 23.0°	26.2°- 28.2°
Heat capacity of bomb assembly, cal./°C	38.70	38.61	38.51,38.57	38.72, 38.60
Mean C_v, cal./°C./gm.	0.438	0.417	0.404	0.408

Time lags: Outside of the range 8° to 9.5°C., temperature equilibrium after heating had been stopped was generally established in 10 min. Sometimes, however, the time required for equilibrium was much longer than this. It was considered to be of some interest to take the value of the changing temperature at intervals, until an asymptotic final value had been reached. These are included and systematized among the results under the heading "time lags".

McIntosh and Maass have reported that a small lag, not greater than twenty minutes, occurs in the assumption of equilibrium density, when a temperature change is made in certain regions on an isochore. Tapp, Steacie and Maass, and Winkler and Maass, have reported somewhat greater lags, of about forty to fifty minutes, in propylene and methyl ether under the same conditions (70, 90).

It was found that if ethylene were heated from 8.96° to 9.16°C, for instance, that heat was absorbed by the system for about 1½ hours after heating had stopped, so that a cooling effect results. If the bomb is heated from 8° to 9.5°C in say a half hour, the temperature continues to fall for more than eight hours after heating has been stopped.

In the calorimetric measurements described here a very large number of observations were recorded in establishing the time lag curves. However, a great simplification in presentation of data is possible, for the curves obtained on plotting temperature against time have the form of first order reaction plots. If the difference between the temperature at time t and the final asymptotic temperature is denoted by ΔT,

$$\frac{d(\Delta T)}{dt} = -k\,\Delta T$$

or in the integrated form,

$$\log_{10}\frac{\Delta T_0}{\Delta T} = kt ,$$

where ΔT_0 is the value of ΔT at zero time.

TABLE IV

TIME LAG

Material heated from 8.96°to 9.16°C. in 560 sec. Zero time counted from instant at which heating is stopped. $\Delta T_0 = 31\times10^{-3}$ °C. $k = 3.4\times10^{-4}$ sec.$^{-1}$

Time, sec.	Temp., Beckmann	$\Delta T\times10^3$ °C	Time, sec.	Temp., Beckmann	$\Delta T\times10^3$ °C
610	1.3015	16.1	2560	1.2884	4.0
670	1.3002	14.8	2920	1.2879	3.5
720	1.2988	14.4	3190	1.2866	2.2
780	1.2988	14.4	3400	1.2862	1.8
940	1.2970	12.6	3760	1.2866	2.2
1000	1.2962	11.8	3940	1.2856	1.2
1060	1.2953	10.9	4480	1.2850	0.6
1210	1.2939	9.5	4680	1.2848	0.4
1370	1.2925	8.1	5340	1.2845	0.1
1600	1.2915	7.1	5860	1.2840	-0.4
1870	1.2898	5.4	6600	1.2845	0.1
1960	1.2897	5.3	7540	1.2843	-0.1
2320	1.2884	4.0	8440	1.2847	0.3

Thus, for each of the time lag curves a straight line is obtained when log ΔT is plotted against the time. A sample of the data recorded in establishing one of these time lags is given in Table IV, and the results are plotted with those of two other runs in Fig. 7. The slope of these lines is read as the value of k, the rate constant. The intercept on the zero time axis also has a meaning, since it represents the value of ΔT at zero time, and therefore corresponds to the total temperature drop. These are the ΔT_0 values; when multiplied by the total heat capacity of the bomb assembly they give the total amount of heat absorbed by the ethylene during the lag. For purposes of calculation, zero time is taken as half way through the heating interval. The k and ΔT_0 values are listed in Table V and plotted against the temperatures in Figs. 8 and 9.

TABLE V

Range		Temp. interval, °C.	Time of heating, sec.	$\Delta T_0 \times 10^3$, °C.	$\Delta T_0 \times 10^3$, correct for a 0.2° interval	$k \times 10^4$ sec.$^{-1}$ $t_{1/2} = \frac{\log 2}{k}$
Initial temp. °C	Final temp. °C					
8.660	8.858	0.1981	560	38.5	39.0	7.27
8.664	8.855	0.1904	510	38.5	40.5	7.20
8.800	8.989	0.1892	505	31.5	33.5	5.36
8.746	8.856	0.2071	570	34.0	33.0	4.30
8.858	9.058	0.2005	555	30.0	30.0	3.81
8.957	9.163	0.2052	560	32.0	31.0	3.40
9.059	9.253	0.1942	525	28.5	29.5	2.68
*9.163	9.363	0.1977	520	16.5	16.5	2.06
9.170	9.367	0.1981	510	24.2	24.5	1.88
9.253	9.356	0.1030	260	13.0	13.0	1.51
*9.260	9.461	0.2011	535	10.7	10.5	1.99
9.312	9.512	0.2000	400	3	3	2.4
9.16	9.834	0.67	180	70		8.3
9.16	9.622	0.46	165	35		4.2
*9.26	9.48	0.22	500	0		
*9.29	9.52	0.23	500	0		
*9.37	9.57	0.2	500	0		
9.36	9.50	0.16	400	0		
9.38	9.7	0.32	600	0		
9.39	9.59	0.2	500	0		

* Initial temperature approached from above 15°C. All others approached from below 8°C.

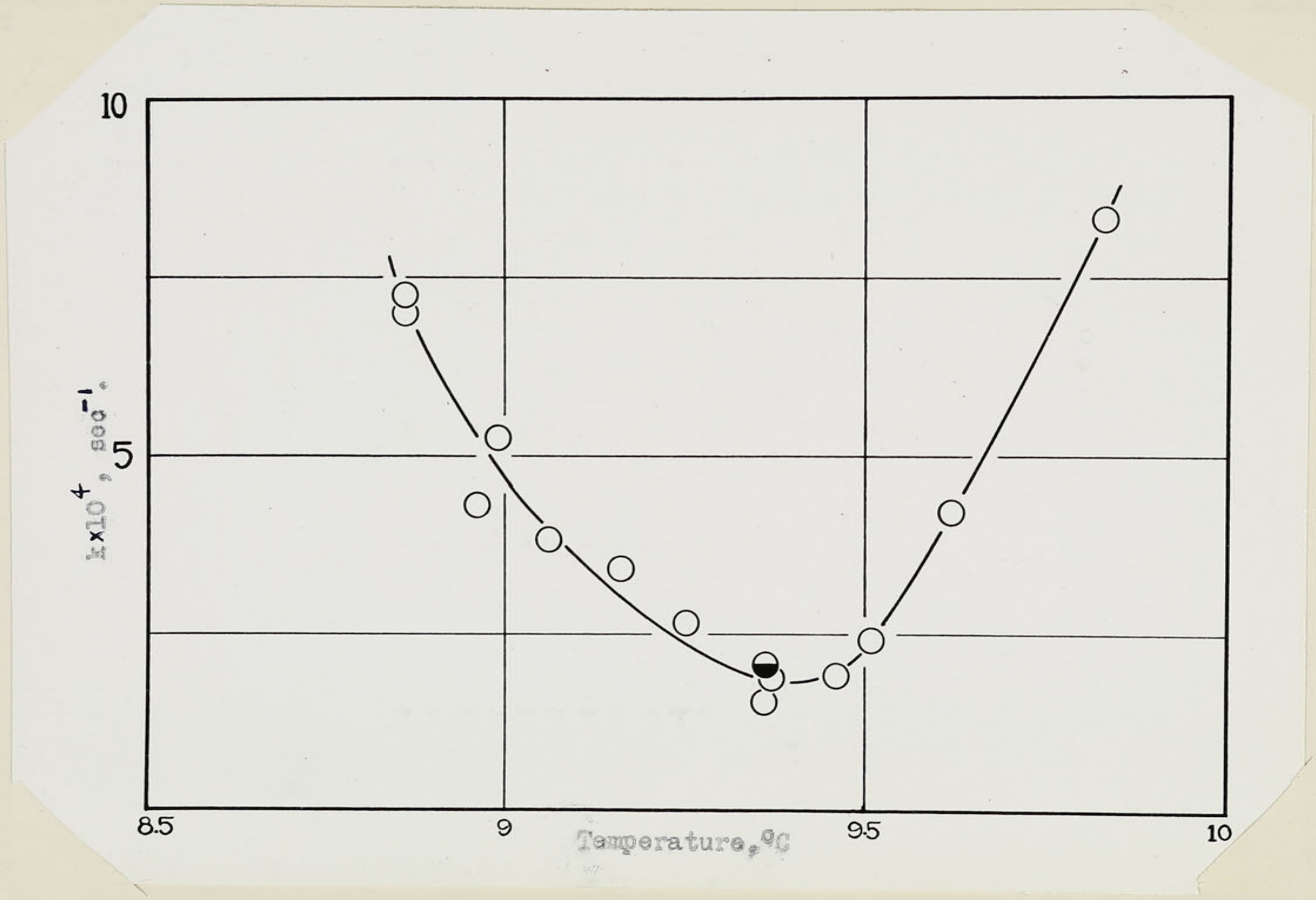

Fig 8. Rate Constants for Time Lags. ○, temperature brought up from below 8°C. ◓, temperature brought down from above 14°C.

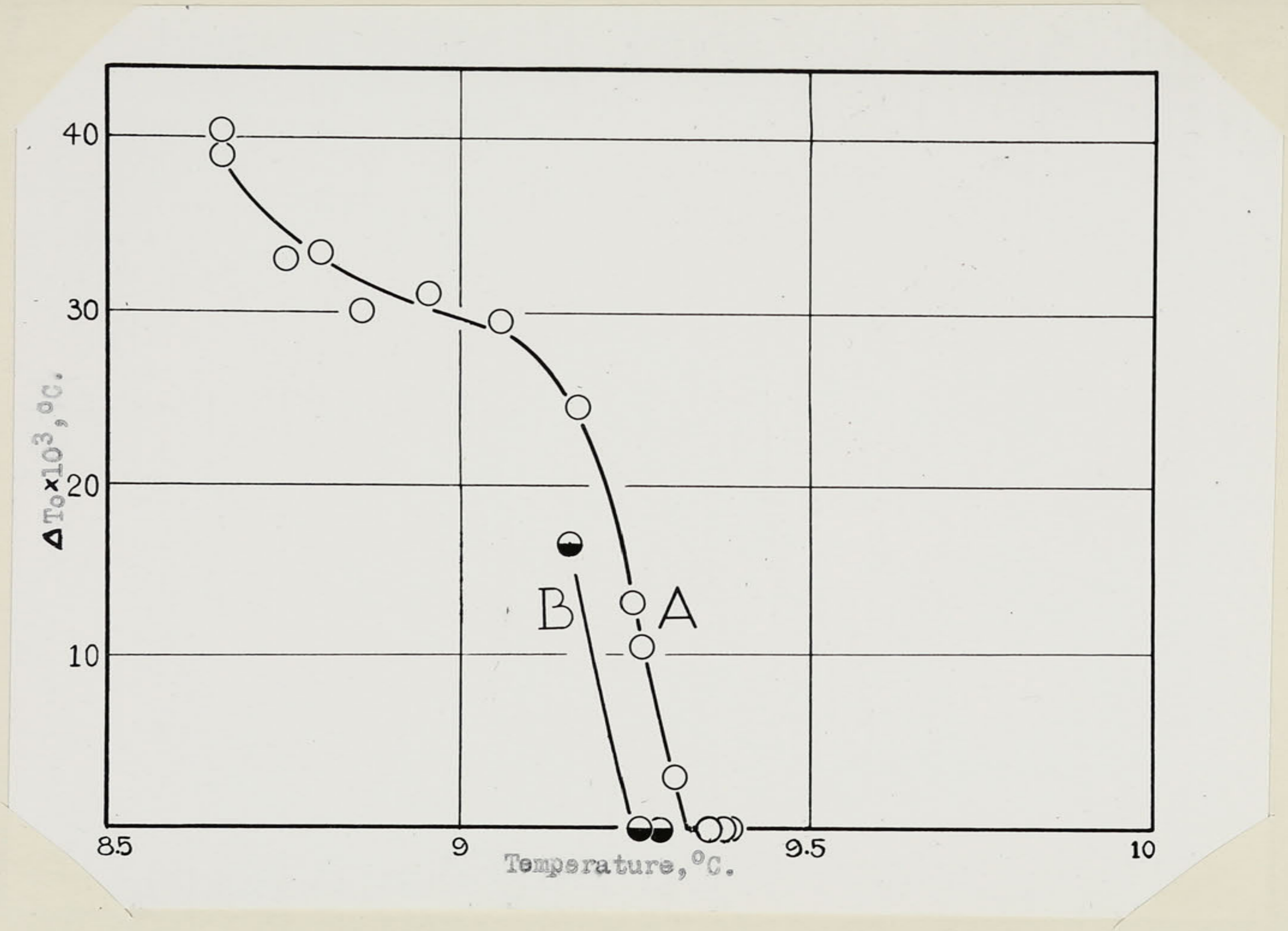

Figure 9. ΔT_0 for time lags. ◒, temperature brought down from above 14°C. ○, temperature brought up from below 8°C.

PURIFICATION OF THE ETHYLENE

PURIFICATION OF THE ETHYLENE.

The original method:

The starting material was tank ethylene supplied by the Ohio Chemical Company for purposes of anaesthesia, of at least 99.7% purity. Further purification was effected by three distillations at a few centimeters pressure, discarding generous first and last fractions. Finally the ethylene was distilled into the bomb, which was then sealed as previously described.

The new low temperature fractionation unit:

It was desired to set up some purification system, in which an absolute check on the material used could be made. For this purpose an adaptation was made of the analytical stills described by Podbelniak (91). The distilling bulb A has a capacity of about 100 cc. (figure 10). It was furnished at the connection to the column with an inner sealed "dripper" B. The column C is 3.6 mms. in diameter, and 100 cms. long. For scrubbing, a spiral of nichrome wire is placed inside of it. The cooling head D has inlets allowing liquid air to be added in direct contact with still head, or to be stored in a chamber for indirect cooling. For measuring and storing gas, a number of calibrated volumes are provided: three 500 cc. flasks, two 5 liter flasks, and one 50 liter flask, all being capable of accurate temperature control. The capillary manometer F served for control during a distillation, and G was used to measure the amount of gas collected.

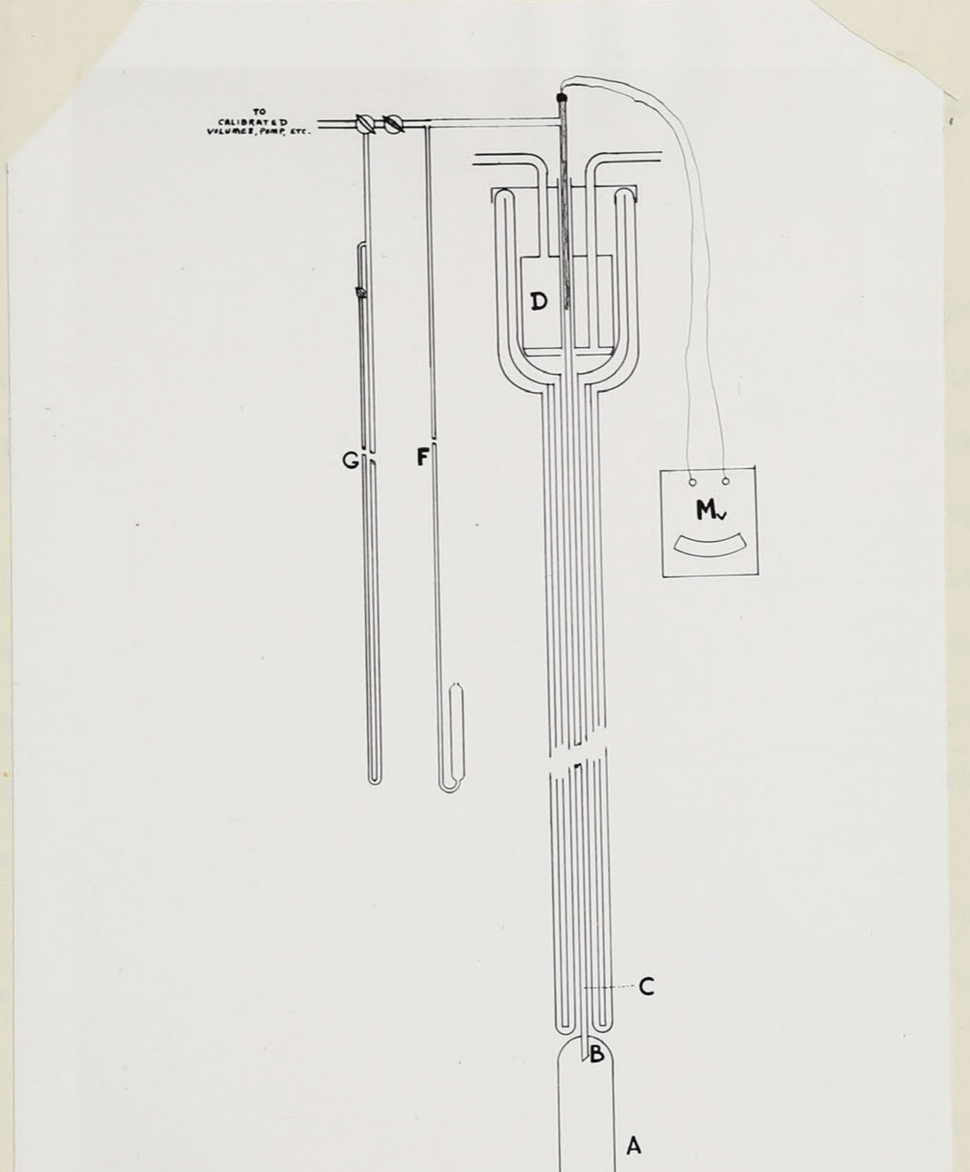

Figure 10. The Low Temperature Fractionating Unit.

Temperatures are determined by means of a copper-constantan thermocouple. For reading the voltage conveniently, a voltmeter with a 5 mv. range was obtained. At -100°C the sensitivity of the couple is about .02 mv./°C; the instrument could be read to .005 mv., or about one quarter of a degree.

The modifications made in adapting the original Podbelniak apparatus were the following:

A larger distilling bulb was used.

Ethylene in particular freezes at liquid air temperature, and the apparatus had to be arranged and operated so that the solid material should not form in small tubes, which would be broken.

Without the drip arrangement, the liquid refluxing down the column flows down the comparatively hot sides of the distilling bulb, and is vaporized before joining the body of liquid. With the arrangement provided, the drops fell directly into the body of liquid. This furthermore made it easy to control the distilling operation, as the amount of reflux could be readily observed.

The column was enclosed in the vacuum jacket E. In the jacket was placed a double aluminum radiation shield, with small holes for viewing the column.

With this apparatus, extremely sharp cuts are obtained between fractions. The voltmeter needle is observed to swing suddenly across the scale, the whole change being complete in 5 to 10 seconds. Since the distillation rate is normally about 15 grams per hour, it is seen that only a very small fraction of the material coming over represents a mixture of two components.

It is probable that using 99.7% material to start, and leaving 10% first and last fractions, the amount of material coming over which is not ethylene, is negligible for any practical purpose. It was in this way that the samples of ethylene used in the work to be described next were prepared.

The still has been used for the preparation of pure ethane, propylene, and methyl ether, and has been satisfactory for these purposes.

THE NEW CALORIMETER

THE NEW CALORIMETER.

Scope of the improvements:

The original calorimeter had functioned satisfactorily, but had the following defects. First, the ratio of the heat capacity of the ethylene to that of the container was very unfavorable. Second, in order to refill the bomb, the whole set-up had to be taken down, and then put together again. Furthermore, the U tube-solder type of seal, though satisfactory once obtained, was hard to realize experimentally.

These objections were removed in successive modifications of the apparatus. The second set-up utilized a new type of bomb which reduced the heat capacity from the previous value by a factor of more than two, and at the same time increased the volume by a factor of more than three. The third experimental arrangement combined this improvement with the means of filling and emptying the bomb at will, without the necessity of taking down the apparatus. Since the third arrangement includes the second, only the third need be described in detail, under the heading of the new calorimeter.

Description of the new Bomb.

A sphere has the least ratio of mass to volume for a given pressure - volume factor of safety. The spherical bomb B (figure 11) was constructed of brass, with 1/32 inch walls, and was $2\frac{5}{8}$ inches in diameter. The fabrication process consisted of spinning two halves, which were then silver soldered together. The bomb weighed about 114 grams. It was uniformly wound over its whole surface with 5400 cms. of no. 26 enamelled copper wire, which had a resistance of about 19 ohms, and increased the weight of the assembly to 135 grams.

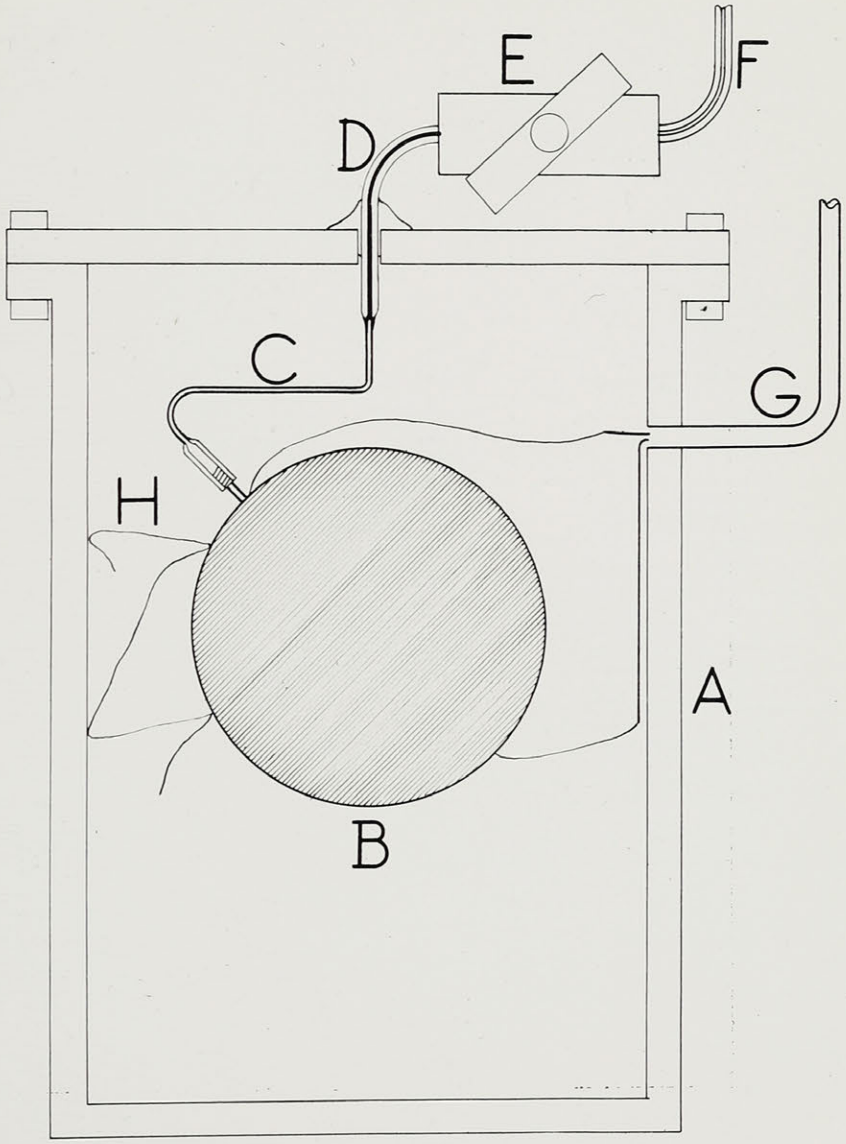

Figure 11. Diagram of the new calorimeter.

In the case of the second set-up, the bomb was fitted with a brass U tube, into which solder was melted for sealing.

For the third apparatus, the bomb was connected to a platinum-iridium tube C, which was about 0.8 mms. inside diameter, 1.2 mms. outside, and about 20 cms. long. This was connected through the copper capillary tubing D to the high pressure valve E (supplied by the American Instrument Company). The volume of tubing and dead space in the valve represents only about 1/1000 th of the volume of the bomb, and was neglected in making calculations. The heat losses due to this tube were calculated to be less than 2% of the total heat losses.

From spherical symmetry considerations, and the uniformity with which the bomb surface is covered by the heating element, it appears that the temperature of the surface of the bomb should be the same everywhere during heating. The maintenance of adiabatic conditions was possible , by keeping zero deflection in the galvanometer connected in series with the thermocouples H.

<u>Contact versus "radiation" thermocouples</u>:

Previously one set of thermocouple junctions had been mounted near to, but not touching, the bomb assembly. This was done on the supposition that heat losses would be cut down by avoiding direct wire connections from the inside to the outside container. The supported ends were supposed to take up the temperature of the bomb assembly surface by radiation.

A calculation from the known coefficient of heat conduction, and dimensions, of the thermocouple wire, showed that the amount of heat conducted was negligible compared with conduction by air.

Furthermore it is easily shown that radiation thermels do not conduct any less heat than do the others. Suppose for example that a .001° gradient exists. Eight contact thermels (new set-up) gave a galvanometer deflection of 1 cm. Twelve radiation thermels (original set-up) showed the same sensitivity. Hence the difference in temperature between the hot and cold ends of the last is $(8/12)\times.001^{\circ}$C. The thermels were of similar construction so that the heat conducted by each wire pair connection was the same in each case. Hence in the contact case, the heat conducted is

$$Q_1 = 8k\times.001 = .008k ,$$

and in the radiation case,

$$Q_2 = 12k\times.001\times\frac{8}{12} = .008k = Q_1,$$

so that they are the same.

There is in fact some disadvantage in this respect in the use of radiation thermels. In practice a heavy support is necessary to hold up the free end in this case. In the other case the junction can be lightly sprung against the bomb surface. Thus there is an overall higher heat conduction for radiation than for contact thermocouples.

The design adopted in the new apparatus was therefore of the contact type. Eight pairs of junction were mounted in an arrangement which could be set up as a unit inside the container A (figure 11). The mount (not illustrated) was constructed of four short and four tall brass posts, alternately and symmetrically placed on the periphery of a disc whose diameter was just slightly smaller than the inner diameter of A. The outer

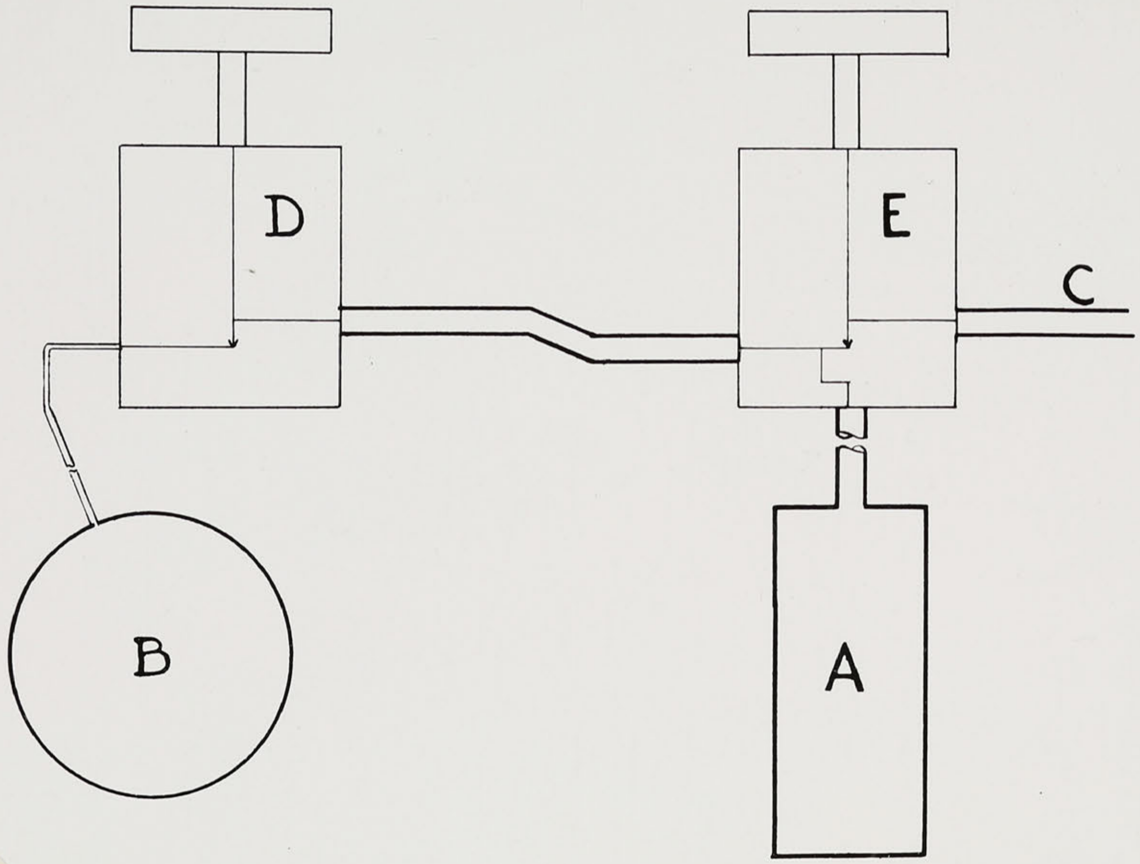

Figure 12. The filling apparatus.

junctions of the eight couples were fastened between two thin sheets of mica on the outer edge of the posts. The inner junctions were cemented to the ends of thin celluloid strips, sprung from the brass posts to rest on the bomb when in position. The assembly was placed in A, and the posts wedged to make the outer junctions bear firmly against the side of A. The upper four celluloid strips were next forced back by inserting an annular ring of greater diameter than the bomb. Then the bomb was inserted so as to rest on the ends of the bottom four strips, Finally the annular ring was withdrawn, allowing the top four junctions to fall into place.

The filling apparatus:

Filling of the calorimeter bomb without removal is accomplished by means of an auxiliary bomb and valve as shown in figure 12. The tube C leads to the purification apparatus and a fifty liter calibrated volume. The apparatus is first evacuated, then with the valve D closed, E is opened, and a known amount of ethylene distilled into A by surrounding it with liquid air. Then E is closed, D is opened, B is cooled to 0°C, A is warmed to 25°C, and most of the ethylene thus transferred to B. Finally D is closed, E opened, and the amount of residual gas is determined.

Characteristics of the new calorimeter:

The apparatus was found to work best when the container A was filled with air at 1 mm. pressure. The amount of heat conducted under these conditions was about 50% greater than in the first set-up. This may be ascribed to the increased size of the bomb, as the distance between the walls of the bomb and the outer container was decreased.

The heat conducted is, however, a minor term in the total experimental error. It was expected that the accuracy in determining over all heat capacity would be about 0.15%. In a typical run, the heat capacity of the assembly was 30 calories, while that of the bomb was 13 calories. The possible error is therefore .045 calories, or about 0.25% in the heat capacity of the ethylene.

Results Obtained with the New Calorimeter.

Presentation:

The results presented here are listed under the main headings, second filling and third filling. The second filling refers to results obtained with the first modification of the original calorimeter, while the third filling represents values obtained with the second modification. Results obtained with another filling outside of the critical range are also given, in a final section.

Second filling:

The bomb was so filled that the average density was the same as that used in the previous work, namely 0.2255.

Three sets of data were experimentally determined.

(1) Dependence of heat capacity of ethylene on thermal history. The maximum difference, due to extreme variation of the thermal history, of the

heat capacity of the whole system between 9.36° and 10.36° was found to be 3.1%. The separate results are listed in Table VI. The value previously found for this same quantity was 2.6%. It was, however, thought that there might be an error as great as ±1% in this quantity. The new value is probably good to ±0.3%, so that the existence of the thermal history effect is placed outside of the limits of experimental error.

TABLE VI.

DEPENDENCE OF THE HEAT CAPACITY OF ETHYLENE ON THE THERMAL HISTORY.
9.36° TO 10.36° C. AVERAGE DENSITY, 0.2255

Type of system	C_v, cal./°C./gm.	Mean C_v, cal./°C./gm.
Heterogeneous (brought to initial temp. from below 8°C.)	0.6040 0.6040 0.6017	0.6032
Homogeneous (brought to initial temp. from above 13°C.)	0.5846 0.5818 0.5866	0.5843

In the range 9.36° - 10.36° the two fillings give as absolute values of the heat capacity of the heterogeneous system, 0.609 and 0.603, again in good agreement.

(2) Heat capacities below the critical temperature (Table VII). In this case the absolute agreement with the previous results is not as good. However, the position of the maximum in the heat capacity curve at 9.0° is verified, and the same sharp drop between 9.2° and 9.4° is noted. The results are listed in Table VII.

(3) Time lag results: These appear in Table VIII. Owing to the

TABLE VII

HEAT CAPACITY OF THE SYSTEM ETHYLENE BELOW THE CRITICAL TEMPERATURE AVERAGE DENSITY 0.2255

Range, °C.	8.72 - 8.84	8.84 - 9.01	9.01 - 9.21	9.21 - 9.35
Average heat capacity, cal./°C./gm.	1.483	1.529	1.524	0.993

great change in the ratio of the heat capacity of ethylene to the heat capacity of the container, comparison of these results with those previously obtained is difficult. However at least approximate agreement can be demonstrated. At 8.84°C, k for the first bomb is 6.1×10^{-4} sec.$^{-1}$; for the second it is 5.1×10^{-4} sec.$^{-1}$. Similarly the results for the heat absorbed after heating through the interval 9.01° to 9.21°C. are respectively 0.14 and 0.23 cal. per gm., corresponding to the widely different values for ΔT_0 of .029° and .120°C.

TABLE VIII

UNIMOLECULAR RATES, AND ΔT_0 VALUES, FOR TIME LAGS

Range, °C.	Temperature interval, °C.	Time of heating, sec.	$\Delta T_0 \times 10^3$, C.	$\Delta T_0 \times 10^3$, corrected to a 0.2° range	k, sec.$^{-1} \times 10^4$
8.72 - 8.84	0.122	550	82	134	5.1
8.84 - 9.01	0.172	800	109	127	3.55
9.01 - 9.21	0.196	910	118	120	1.75
9.21 - 9.35	0.142	475	41.5	58	1.9

In this same region, no time lags were observed on cooling through an interval.

Third filling: The average density in this case was 0.2069. For the sake of simplicity the results will be presented mainly by analogy with previous work.

Table IX contains results for the heat capacity of ethylene below the critical temperature, and corresponds to Table I.

TABLE IX

HEAT CAPACITY AT CONSTANT VOLUME OF THE SYSTEM ETHYLENE BELOW THE CRITICAL TEMPERATURE.
Average Density = 0.2069.

A. Initial temperature approached from below 8°C.				B. Initial temperature approached from above 15°C.	
Range °C	Av. Ht. Cap. cal./°C./gm.	Range °C	Av. Ht. Cap. cal./°C./gm.	Range °C	Av. Ht. Cap. cal./°C./gm.
8.10 - 8.49	1.471	9.20 - 9.38	0.978	9.33 - 9.55	0.5964
8.37 - 8.80	1.523	9.38 - 9.58	0.567	9.12 - 9.36	1.108
8.76 - 9.25	1.436	8.44 - 8.64	1.520		
9.15 - 9.52	0.6439	8.72 - 8.94	1.637		
8.63 - 8.85	1.435	8.93 - 9.11	1.442		
8.85 - 9.03	1.441	8.66 - 8.84	1.597		
9.03 - 9.20	1.366	8.84 - 9.03	1.626		

The hysteresis in heat capacity is shown in Table X. It may be compared with Tables II and VII.

TABLE X

DEPENDENCE OF THE HEAT CAPACITY OF ETHYLENE ON THE THERMAL HISTORY.
9.41° - 10.41°. Average Density = 0.2069

Type of system	Av. Heat Cap. cal./°C./gm.	Av. Heat Cap. cal./°C./gm.
Heterogeneous (brought up to initial temperature from below 8°C)	0.5463 0.5491 0.5514	0.5489
Homogeneous (brought to initial temperature from above 13°C)	0.5453 0.5460	0.5456

The difference caused by thermal history variation is seen to be .033 calories, or 0.6%.

Results used for plotting the remainder of the heat capacity curve are listed in Table XI. The curve is shown in figure 13.

TABLE XI

HEAT CAPACITY OF ETHYLENE FROM 9.5° TO 25°C. DENSITY = 0.2069

Range, °C	C_v cal./°C./g.	Range, °C	C_v cal./°C./g.
9.41 - 9.62	0.5932	10.06 - 10.42	0.5376
9.44 - 9.61	0.5826	10.13 - 10.41	0.5306
9.53 - 9.74	0.5836	10.05 - 11.01	0.5220
9.48 - 9.70	0.5770	10.10 - 10.28	0.5520
9.53 - 9.74	0.5664	10.28 - 10.50	0.5294
9.55 - 9.75	0.5386	10.40 - 10.67	0.5180
9.61 - 9.82	0.5689	10.50 - 10.87	0.5348
9.62 - 9.86	0.5613	10.89 - 11.86	0.4920
9.62 - 10.10	0.5536	11.01 - 12.00	0.4910
9.74 - 10.07	0.5547	11.73 - 12.73	0.4824
9.74 - 9.94	0.5657	13.93 - 14.92	0.4470
9.82 - 10.06	0.5804	14.04 - 15.08	0.4475
9.76 - 10.89	0.5340	17.54 - 18.52	0.4215
9.86 - 10.10	0.5405	17.73 - 18.69	0.4215
9.93 - 10.13	0.5514	22.56 - 23.61	0.4036
		25.99 - 26.99	0.3969

The time lag results for this filling could be classified in the same manner as before, each temperature having a characteristic unimolecular rate constant, and a ΔT_0 value corresponding to the total temperature drop in the lag. These results appear in Table XII.

The variation of the k values with temperature is much smaller than before (filling density = 0.2255) and the absolute values are also less. The accuracy in this case is not sufficient to permit the

TABLE XII.

RATE CONSTANTS AND ΔT_0 VALUES, AVERAGE DENSITY 0.2069.

Range, °C	$\Delta T_0 \times 10^3$, °C.	$k \times 10^{+4}$, sec^{-1}
8.07 - 8.45	187	2.46
8.31 - 8.74	158	1.41
8.69 - 9.18	208	1.86
8.40 - 8.61	99	1.75
8.60 - 8.81	98	1.54
8.67 - 8.89	112	1.03
8.72 - 8.96	99	1.33
8.81 - 8.98	98	1.72
8.89 - 9.07	82	1.18
8.90 - 9.09	120	0.91
8.98 - 9.18	109	1.71
9.07 - 9.31	82	1.10
9.18 - 9.33	57	2.7

construction of a definite plot of the results, which might be expected to resemble figure 8. The analogue of figure 9, in which ΔT_0 is plotted against the temperature, cannot be obtained for the same reason. These appear to be only about $\frac{3}{4}$ of the magnitude of the ΔT_0's for the second filling.

Filling at density 0.116:

The density here is far removed from the critical. The results shown in Table XIII, nevertheless show a definite trend, decreasing as the temperature is raised from the critical. The absolute values are somewhat lower than those obtained with higher densities, as is to be expected.

TABLE XIII.

C_v, ethylene. Density = 0.116.

Temperature °C	8.6	9.6	15.6	19.8
C_v, Cal./°C./g.	0.378	0.375	0.368	0.360

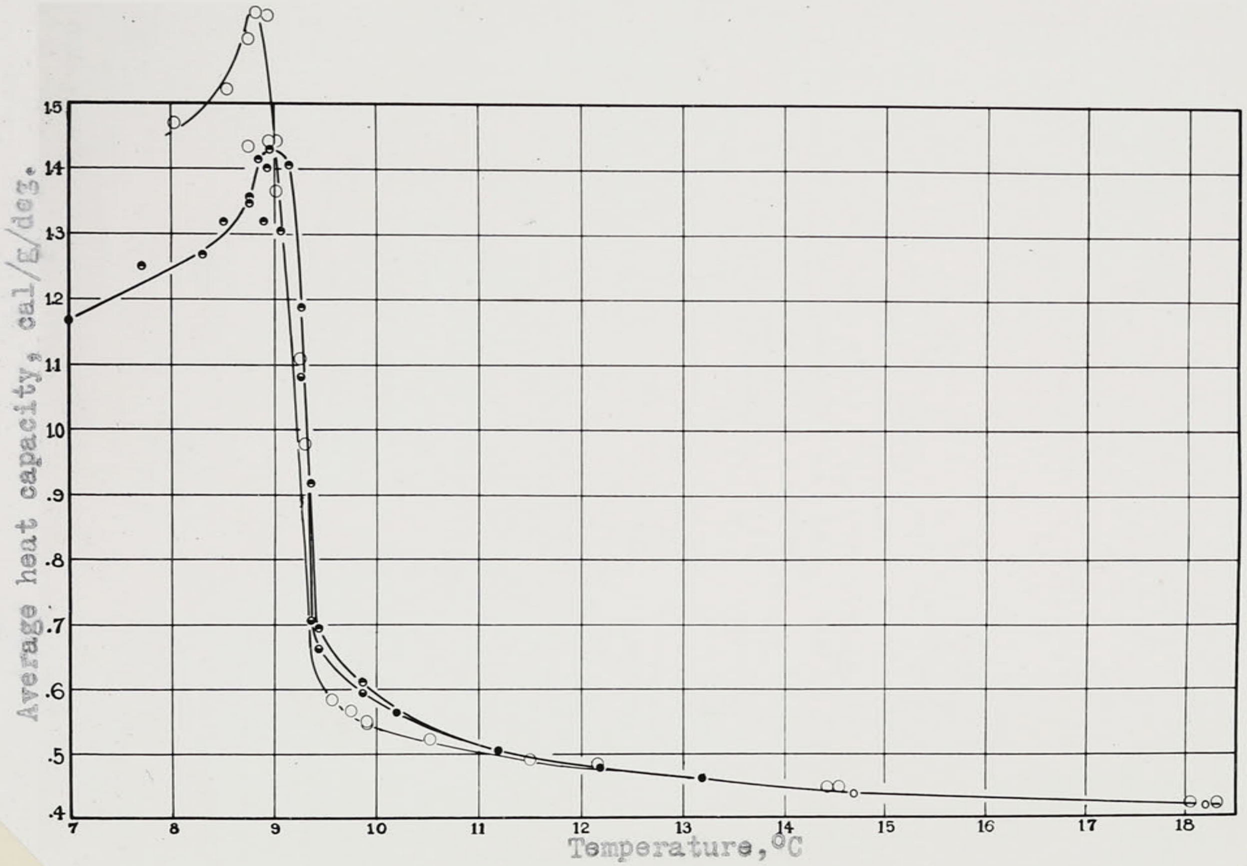

Figure 13. Heat capacity of ethylene. Small circles, density 0.2255. Large circles, density 0.2069. Hysteresis in filling at density 0.2069 too small to be shown graphically.

DISCUSSION OF THE HEAT CAPACITY RESULTS.

DISCUSSION OF THE HEAT CAPACITY RESULTS

The two phase region:

The volumes and weights of the phases can be calculated if the volume-temperature curve is known. This data has been supplied with sufficient accuracy for a qualitative discussion by McIntosh, Dacey and Maass (42).

In the case of the denser filling ($v = 4.435$ cc/g) the mass of the liquid phase decreases as the temperature is raised up to 9.05°C. Above this temperature the amount of liquid increases until the whole bomb is filled with liquid at about 9.9°C. Similarly, in the case of the less dense filling ($v = 4.832$) it is found that the mass of liquid is always decreasing and the last trace vanishes between 9.6° and 9.7°C.

In the first case, as the temperature is raised, heat is evolved by condensation of vapor above 9.05°. In the other, heat is always absorbed by the evaporation of liquid.

The specific heat of the condensed phase per gram at saturation (h_1) is always positive and may be very large if the coefficient (dv_1/dT) is large (v_1 is the specific volume of the liquid phase). The specific heat per gram at saturation of the vapor phase (h_2) can be and is negative near the critical temperature. Moreover, h_1 and h_2 are very much larger in absolute value than the specific heats of the phases at constant volume, C_{v_1} and C_{v_2}.

In considering the form of the curve, all these factors must be taken into account. C_{v_1} and C_{v_2} probably lie between 0.4 and 0.6 cal/g/deg. The values of the latent heat, the rate of change of liquid mass with temperature, h_1, and h_2 are all large near the critical temperature, and some of the terms cancel each other in a complicated manner in the computation. Hence a qualitative discussion of the form of the curve, using as a basis, the order of magnitude of the contributing terms is not possible. We shall see, however, that the maximum may correspond to the existence of an inflection point in the volume-temperature curve near this temperature.

The specific heat at constant volume of the phases can be calculated on the basis of the following equations:

$$\begin{aligned} h_1 &= C_{v_1} + T(dp/dT)_{v_1}(dv_1/dT)_{h} = C_{v_1} + J_1 \\ h_2 &= C_{v_2} + T(dp/dT)_{v_2}(dv_2/dT)_{h} = C_{v_2} + J_2 \end{aligned} \qquad (1)$$

where h_1 = specific heat of the condensed phase along the saturation curve,

h_2 = specific heat of the vapor phase along the saturation curve,

v_1, v_2 are the specific volumes of the liquid and vapor respectively.

$$H = m_1h_1 + m_2h_2 + \ell\,(dm_2/dT) \qquad (2)$$

where

H = observed heat capacity,

$$m_1 = \frac{\text{mass liquid phase}}{\text{total mass material}} = 1 - m_2$$

$$m_2 = \frac{\text{mass vapor phase}}{\text{total mass material}} = 1 - m_1$$

ℓ = latent heat of vaporization

$$= T(dp/dT)\,(v_2 - v_1).$$

Combining these relationships, we find

$$m_1C_{v_1} + m_2C_{v_2} = H - (m_1J_1 + m_2J_2 + \ell\,(dm_2/dT)).$$

If measurements are available of H for two different average densities, it becomes possible to solve the resulting simultaneous equations for C_{v_1} and C_{v_2}.

The same results can be arrived at in still another manner, from a single set of determinations of H, using the equation

$$h_2 - h_1 = d\ell/dT - \ell/T,$$

which when combined with (2) enables h_1 and h_2 to be calculated separately, and then C_{v_1} and C_{v_2}, using (1).

The available p - V - T data are those of McIntosh, Dacey and Maass (42). Their V - T curve is shown in figure 14, marked ABB'BA. The critical temperature reported by these investigators is 9.5°C. A smooth parabola-like curve, drawn according to the classical theory, has also been constructed tangent to the ordinate at 9.5°; this is AA'A.

In order to make calculations on the basis of these results, it was found necessary to fit these curves with mathematical equations. In view of their extremely complex nature, this would have been a very arduous task, had ordinary methods of curve fitting been used. The fit was accomplished by drawing segments of circles to match small portions of the curve, drawn so that the slope was continuous everywhere. Thus in figure 14, the curve AA'A was fitted by means of the three equations:

9° - 9.5° $\quad (v_1 - 4.56)^2 + (T - 8.78)^2 = 0.72^2$,

9° - 9.37° $\quad (v_2 - 4.35)^2 + (T - 8.41)^2 = 1.16^2$,

9.37°-9.50° $\quad (v_2 - 4.60)^2 + (T - 8.78)^2 = 0.72^2$.

For an equation of the form

$$(v - v_0)^2 + (T - T_0)^2 = c^2$$

we find

$$\frac{dv_1}{dT} = \left|\frac{T - T_0}{v - v_0}\right| \qquad \frac{dv_2}{dT} = -\left|\frac{T - T_0}{v - v_0}\right|$$

Since $m_1+m_2 = 1$ and $m_1v_1 + m_2v_2 = V$, where

$$V = \frac{\text{volume of bomb}}{\text{total mass of material}}$$

we should find

$$m_1 = -\frac{V-v_2}{v_2-v_1} \qquad \text{and} \qquad m_2 = 1 - m_1$$

The superscripts "'" and "''" refer respectively to the results for V = 4.435 and V = 4.832 cc/g. The values of $(dp/dT)_{v_1}$ and $(dp/dT)_{v_2}$ are obtained from the results of McIntosh, Dacey and Maass, and are probably good to 5% at 9°C and 1% at 9.8°C.

The quantity dm_2/dT is obtained by differentiating the expression for m_2 in terms of the specific volumes. The calculations made on the basis of the classical curves are shown in Table XIV.

Now the values of C_{v_2} may be estimated to be about 0.4 – 0.5 while those of C_{v_1} probably lie between 0.5 and 0.6. It follows then that the quantity of $m_1C_{v_1} + m_2C_{v_2}$ should fall between 0.4 and 0.6. It is seen that on the basis of the classical curve negative specific heats appear (Table XIV and figure 14). It may be concluded, therefore, that the classical curve cannot represent the true density temperature relationship.

This conclusion is open to criticism on the ground that if $(dp/dT)_{v_1}$ were in error to the extent of being 10% too great, and $(dp/dT)_{v_2}$ were 5% too small, the specific heats calculated would be of the correct order of magnitude. In order to check on this point, a calculation was made, using the equation of corresponding states, and the data of Michels, Blaisse and Michels for CO_2 (43). The results indicated that $(dp/dT)_{v_1}$ chosen was if

TABLE XIV

Calculation of $m_1C_{v_1} + m_2C_{v_2}$ Classical Curve.

Temperature, °C	9	9.1	9.2	9.3	9.4	9.45
v_2, cc/g.	5.353	5.286	5.201	5.094	4.957	4.854
v_1, cc/g.	3.880	3.913	3.973	4.060	4.187	4.290
m_1', g.	0.623	0.620	0.625	0.637	0.678	0.742
m_1'', g.	0.3535	0.3305	0.3007	0.2533	0.1620	.0373
$(dp/dT)_{v_1}$, atm/deg	1.42	1.39	1.35	1.30	1.23	1.18
$(dp/dT)_{v_2}$, atm/deg	0.85	0.88	0.90	0.94	0.99	1.02
J_1, cal/g/deg	3.15	4.71	6.63	9.26	14.02	20.05
$-J_2$, cal/g/deg	3.42	4.44	5.72	7.70	13.07	18.51
$-dm_2'/dT$, g/deg	-.0143	.0196	.0791	0.1674	0.662	2.050
dm_2''/dT, g/deg	0.181	0.240	0.351	0.631	1.741	4.371
ℓ, cal/g.	10.80	10.07	9.00	7.58	5.65	4.14
$m_1'J_1 + m_2'J_2 + \ell \frac{dm_2'}{dT}$	0.83	1.03	1.29	1.83	1.55	1.81
$m_1''J_1 + m_2''J_2 + \ell \frac{dm_2''}{dT}$	0.85	1.00	1.15	1.39	1.16	0.95
$m_1'C_{v_1} + m_2'C_{v_2}$	0.60	0.39	.06	-1.04	-0.80	-1.15
$m_1''C_{v_1} + m_2''C_{v_2}$	0.60	0.26	-0.12	-0.40	-0.53	-0.35

anything too small, and that $(dp/dT)_{v_2}$ was if anything too large. Hence the classical V - T curve may be eliminated as a possibility on the basis of specific heat data.

Recently (see section on surface tension) new experimental data has been obtained which makes it seem probable that the true critical

TABLE XV

Calculation of $m_1C_{v_1} + m_2C_{v_2}$, curve of McIntosh, Dacey and Maass.

Temperature,° C	9.4	9.5	9.6	9.7	9.8	9.85
v_2, cc/g.	4.976	4.912	4.877	4.825	4.734	4.662
v_1, cc/g.	4.187	4.300	4.344	4.363	4.385	4.416
m_1', g.	0.686	0.779	0.828	0.844	0.857	0.923
m_1'', g.	0.1825	0.131	.0845			
$(dp/dT)_{v_1}$, atm/deg	1.24	1.17	1.13	1.10	1.08	1.07
$(dp/dT)_{v_2}$, atm/deg	0.99	1.03	1.05	1.06	1.07	1.07
J_1, cal/g/deg	14.13	5.45	1.84	1.42	2.54	6.44
$-J_2$, cal/g/deg	5.97	3.04	2.77	4.90	8.60	12.50
$-dm_2'/dT$, g/deg	1.090	0.710	0.254	0.117	0.362	2.76
dm_2''/dt, g/deg	0.525	0.468	0.616			
ℓ, cal/g.	5.78	4.48	3.90	3.385	2.56	1.802
$m_1'J_1 + m_2'J_2 + \ell\frac{dm_2'}{dT}$	1.53	0.39	.03	.04	.02	.01
$m_1''J_1 + m_2''J_2 + \ell\frac{dm_2''}{dT}$	0.73	0.17	.01			
$m_1'C_{v_1} + m_2'C_{v_2}$	-0.78	0.28	0.62	0.59	0.60	0.60
$m_1''C_{v_1} + m_2''C_{v_2}$	-0.10	0.43	0.59			

temperature of ethylene is 9.2° instead of 9.5°. It is evident from the trend of the results, that if a parabola were drawn, which is tangent to the ordinate at 9.2° the resulting calculated C_{v_1} and C_{v_2} would be negative and even greater in absolute value.

Under the circumstances it did not seem worthwhile to calculate separately the quantities C_{v_1} and C_{v_2}.

It was considered to be of interest next to carry out a similar calculation for the curve of M. D. and Maass ABB'BA in figure 14. This curve is represented by equations of the form:

$$(v - v_0)^2 + (T - T_0)^2 = a^2$$

where v_0, T_0, and a take on the following values:

	Range, °C.	v_0	T_0	a
v_1	9- 9.41	4.56	8.78	0.72
	9.41- 9.635	4.05	9.67	0.30
	9.635- 9.795	5.21	9.54	0.865
	9.795- 9.90	4.53	9.75	0.15
v_2	9-9.35	4.35	8.41	1.16
	9.35- 9.55	5.26	9.65	0.38
	9.55- 9.887	4.41	9.42	0.50
	9.887- 9.90	4.53	9.75	0.15

The calculation is summarized in Table XV, and the resulting curves appear in figure 14. Negative specific heats still appear between 9.2° and 9.5°, but outside of this region the results are satisfactory as regards order of magnitude.

The very large H values appear (figure 13) in the neighborhood of 9° and these values are satisfactorily corrected when the curve of figure 14 is used. On the basis of this consideration one would say that the absolute values of dv_1/dT and dv_2/dT should be greatest near 9°, i.e. there should be an inflection point in the volume-temperature curve at this temperature. Such a curve cannot, however, be reconciled with the manner in which McIntosh, Dacey and Maass have drawn their curve above 9.5°. A compromise was effected by drawing an inflection point near 9.3°C. This revised curve of McIntosh, Dacey and Maass is represented in figure 14 by ACB'CA. Since a new set of calculations was to be embarked upon here, it was considered worthwhile to produce the curves C on the basis of the same equations and see what the results were in the case of the curves ACC' and C'CA. The constants v_0, T_0 and a for these curves are:

	Range,°C.	v_0	T_0	a
v_1	8.9- 9.31	4.56	8.78	0.72
	9.31- 9.90	3.01	10.30	1.47
v_2	8.9- 9.24	4.35	8.41	1.16
	9.24- 9.9	6.56	10.61	1.90

The calculations are shown in Table XVI, and the resulting curves plotted in figure 14. It appears that an improvement in the $(m_1C_{v_1}+ m_2C_{v_2})$ values results on the basis of this assumption. Nevertheless, unreasonable values of the specific heat are still found. Both the curves BB'B and CC' give reasonable values for the specific heats

TABLE XVI

Calculation of $m_1C_{v_1} + m_2C_{v_2}$, revised curve of McIntosh, Dacey and Maass.

Temperature, °C	9.3	9.4	9.5	9.6	9.7	9.8	9.85
v_2, cc/g	5.104	5.020	4.948	4.884	4.825	4.774	4.731
v_1, cc/g	4.060	4.157	4.231	4.295	4.350	4.386	4.422
m'_1, g.	0.640	0.678	0.716	0.762	0.821	0.874	0.958
m'', g.	0.2603	0.218	0.162	0.0883			
$(dp/dT)_{v_1}$, atm/deg	1.30	1.24	1.17	1.13	1.10	1.08	1.07
$(dp/dT)_{v_2}$, atm/deg	0.94	0.99	1.03	1.05	1.06	1.07	1.07
J_1, cal/g/deg	9226	6.67	5.45	4.22	3.37	2.66	2.08
$-J_2$, cal/g/deg	5.80	5.33	4.86	4.34	3.82	3.32	2.85
$-dm'_2/dT$, g/deg	0.328	0.324	0.383	0.474	0.577	0.671	0.827
dm''_2/dT, g/deg	0.378	0.514	0.655	0.807			
ℓ, cal/g.	7.65	6.32	5.25	4.31	3.48	2.84	2.265
$m'_1J_1 + m'_2J_2 + \ell\frac{dm'_2}{dT}$	1.33	0.75	0.37	0.20	.08	-.01	0
$m''_1J_1 + m''_2J_2 + \ell\frac{dm''_2}{dT}$	1.01	0.52	0.22	0.12			
$m'_1C_{v_1} + m'_2C_{v_2}$	-0.23	0	0.30	0.45	0.55	0.63	0.61
$m''_1C_{v_1} + m''_2C_{v_2}$	-0.22	0.11	0.38	0.46			

at constant volume at 9.8° - 9.9° and it is not possible to choose between the two curves on this criterion.

It seems possible that if more accurate p - V - T data were obtained, the results would show an inflection point in the V- T curve near 9.0°.

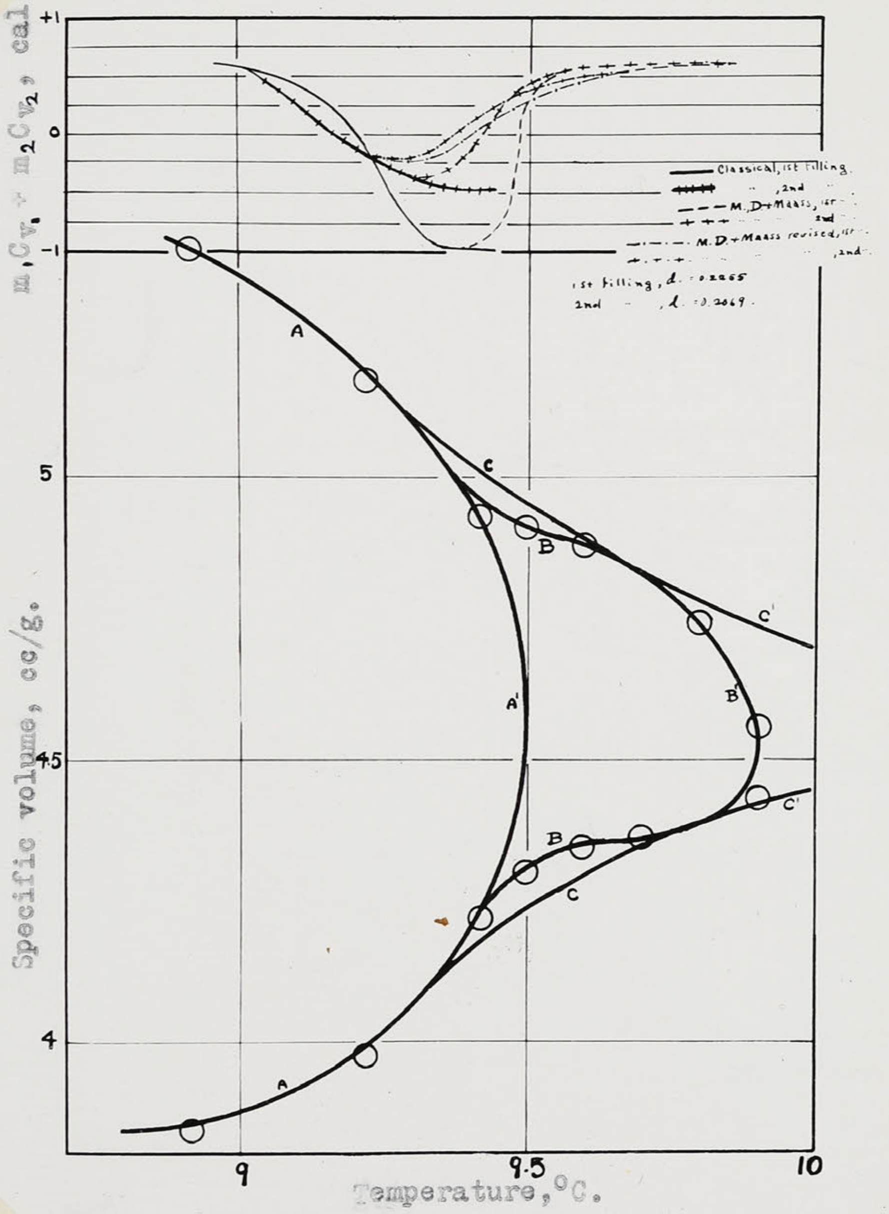

Figure 14. Volume - temperature curves and derived heat capacities at constant volume.

This discussion may be summarized as follows: The classical volume - temperature curve is rejected on the basis of the specific heat calculations. McIntosh, Dacey and Maass' curve fits above 9.5°C, but seems to be in error below this temperature.

Bennewitz and Spittleberger have measured the heat capacity at constant volume of the system CO_2 through the critical range (5). These authors have carried out calculations along the same lines as indicated here. They also have found negative specific heats at constant volume on the basis of the accepted p - V - T data for CO_2. Their results are however open to severe criticism on the grounds that the apparatus they used requires an extrapolation of the final temperature to compensate for heat losses. Now it has been shown that the heat absorbed in the time lags encountered with ethylene may amount to 50% or more of the observed heat capacity. Consequently the results of Bennewitz and Spittleberger may be low by amounts of this order just below the critical temperature.

For this reason, calculations based on their results do not carry much weight. Nevertheless, it was considered to be of interest to recalculate their results on the basis of an arbitrarily drawn V - T curve, resembling the curve for ethylene. On this basis, C_{v_2} was positive and reasonably valued everywhere, and C_{v_1} was negative in only a small region just below T_c. This represents a tremendous improvement over the values of C_{v_1} and C_{v_2} of Bennewitz and Spittleberger, whose values dip to -0.6 calories in some regions.

Similarly the data of Eucken and Hauck (20) are in error in this region, if similar lags occur for air and argon. It is possible too, that lags occur also when C_p is measured. In this case the results obtained by Callendar (13) for water would also be affected.

The dispersion theory:

A theory whose elements have been suggested by a number of authors, and in particular by Harrison and Mayer (40), has been adapted to afford an explanation of the experimental results obtained in the critical region.

On the basis of this theory, near the critical temperature, the phases are capable of forming a dispersion in one another which possesses a stability analagous to that of a colloidal sol. In this region the surface tension is low, or zero, and the difference between the densities of the two phases is very small. These factors would tend to endow such a dispersion with considerable stability.

From this point of view a small body of liquid suspended in the vapor does not settle due to Brownian movement of the whole, with perhaps the question of electrical surface charges entering also. The surface tension being low or zero, the vapor pressure of such small bodies is not appreciably greater, or not at all greater, than that of a larger body of the liquid phase.

Later we shall see in detail how this theory can be developed and applied to render consistent the available experimental data. For the moment we may confine ourselves to a discussion of the hysteresis in the density, and then see what light this casts on the analagous hysteresis in the heat capacity.

It will be sufficient for our present purposes to consider only the region above the critical temperature. Referring now to figure 4, showing the isochore of McIntosh and Maass, it is seen that the phase density difference persists as the temperature is raised through the critical. On cooling no density difference reappears in the region above 9.34°. According to the dispersion theory, the state of affairs here is that liquid actually condenses out, but remains dispersed in the vapor (or conversely vapor forms and is suspended in the liquid), so that no macroscopic difference in density appears. Hence there is an apparent hysteresis in the density.

The Hysteresis in the heat capacity:

We have seen that on the basis of the dispersion theory, the only difference between the systems we have referred to in Tables II, VI and X as heterogeneous and homogeneous, is that the latter represents a state in which one phase is uniformly dispersed in the other. Nevertheless, we deal in both cases with systems containing the same amounts of condensed and vapor phase.

The difference between these two types of system lies solely in the amount of the surface common to the liquid and vapor. In order to assign the observed hysteresis to energy inherent in this surface, we must admit of the existence of a surface energy in this region. In the discussion of the surface energy, it will not only be shown that this is a plausible concept, but the amount of the energy will be calculated as well.

Since the dispersed (homogeneous) system has a higher energy than the heterogeneous system, a smaller amount of energy will be required to bring the former up to the same truly homogeneous state a degree or so above the critical temperature. Hence a smaller observed heat capacity.

The volume - temperature data of McIntosh, Dacey and Maass, illustrated in figure 14, was obtained by measuring the pressure on isothermals, and determining the volume region over which the pressure was constant. These then represent within their experimental accuracy the true liquid and vapor volumes, as contrasted with the macroscopically measured volumes. According to these data, at density 0.2255, the bomb is filled with liquid at about 9.85°- 9.9°C. Examining Table II, we see that the hysteresis is finite and measurable when runs are started at 9.36°. Those determinations made starting at 9.7° show no appreciable hysteresis. At 9.36° the system contains masses of liquid and vapor in the ratio 0.65 to 0.35. At 9.7° the ratio is 0.85 to 0.15. The area represented by $\int_{9.36}^{9.9}(4.435 - v_1)dT$ is seven times greater than the area $\int_{9.7}^{9.9}(4.435 - v_1)dT$. Hence it is not at all surprising that the hysteresis should be found only for those measurements starting at the lower temperature.

The hysteresis shown in Table X for the lower density 0.2069 is smaller, about 0.6%. This we should also expect, for the last trace of the liquid phase disappears in this case at 9.65°- 9.7°. As a rough basis of comparison, we might take the ratio of the area $\int_{9.36}^{9.9}(4.435 - v_1)dT$ to the area $\int_{9.41}^{9.7}(v_2 - 4.832)dT$. This ratio is about 3:1. The ratio of the hysteresis energies is 5:1.

Later it will be shown that it is possible to arrive at an estimate of the surface energy, and this data will be combined with the value of the hysteresis energy to obtain a value for the order of magnitude of the volume of the dispersed groups.

On the basis of the orientation theory, which has been tentatively advanced to explain some of the observed phenomena, the hysteresis in heat capacity is due to a decreased "dynamic structure" in the homogeneous system compared with the other under the same conditions. Such an explanation must postulate a frozen equilibrium to explain the observed density difference. It must regard the equality of the pressures of the heterogeneous and homogeneous systems as purely coincidental. Finally the constancy of pressure in the homogeneous system over a range of volumes on an isothermal, is in the light of the phase rule possible only if two phases are present.

In view of these objections, and considering the ease and comparative elegance with which the results can be correlated on the basis of the dispersion theory, it seems probable that explanation of the hysteresis effects does not lie in an orientation theory. Later, however, we shall have to turn to such a theory in order to deal with time lags.

Application of the first law of thermodynamics shows that there must be another hysteresis loop of equal area at a temperature just below the appearance of the one discussed, in which the order of the curves is reversed. The second law is not violated, because it is not possible to realize one of these loops, without going through the other.

The heat capacity above the critical temperature:

In the bomb filled at density 0.2255, the bomb is completely filled with liquid at a temperature of 9.9°. In the other case, at density 0.2069, the bomb fills with vapor at 9.7°. Above 9.9° we are concerned in both cases with a single homogeneous phase. Nevertheless, the heat capacity continues to decrease rapidly with increasing temperature. The heat capacity at 9.9° has a high value, being 0.60 cal/g/deg at density 0.2255, and 0.55 cal/g/deg at density 0.2069.

In the case of the filling at density 0.116, the heat capacity is lower, being 0.376 at 9.9°. A composite of the results of Eucken and Parts (21) and Heuse (31) shows that at 9.9° the specific heat at constant volume, calculated to density zero, is 0.280 cal./g.

If then a plot were made of the heat capacity against the density, we see that C_v would increase as the critical density is approached, on the isothermal at 9.9°. Now it is a known property of the critical volume that at this density only, $d^2p/dT^2 = 0$. Applying the thermodynamic relationship

$$\left(\frac{dC_v}{dv}\right)_T = T\left(\frac{d^2p}{dT^2}\right)_v$$

it is seen that C_v must pass through a maximum at the critical volume. Hence it follows that since the density 0.2255 is already greater than the critical, measurements made at higher densities will result in lower measured specific heat values. The same considerations will hold for isothermals taken at somewhat higher temperatures.

Michels, Bijl and Michels have calculated the specific heat of carbon dioxide on the basis of their p - V - T measurements, and obtain a set of curves consistent with the description set forth here (44).

Along an isochore the heat capacity continues to decrease until a temperature about 15° above the critical is reached. Above this temperature a slight rise is shown. At low pressures the specific heat increases on account of the increasing availability of the intramolecular vibrations as modes of adsorbing energy. (See Eucken and Parts (21) or Fowler's Statistical Mechanics, Chap.III). There is no reason to believe that this process is greatly affected by the increased density. The rate of increase of the specific heat at 10° is about 10^{-3} cal/g/deg^2. At higher densities there is another factor tending to decrease the heat capacity as the temperature is raised from the critical. When the rate due to this factor becomes equal in absolute value to the other increasing rate, the curve passes through a minimum, and the specific heat rises at all higher temperatures.

Even at density 0.116 the heat capacity shows a diminishing trend up to about 20° C.

The difference between the heat capacities at the two higher densities becomes smaller, and is less than the experimental error at about 12.5°C.

We come next to enquire into the cause of the diminishing heat capacity on an isochore in this region. The mean intermolecular distance here is about 6 Å , center to center, and it is improbable that the vibrational specific heat is affected more than slightly at these densities. Bennewitz and Andrewa have concluded that for a number of substances the rotational specific heats are also unaltered at these and even higher densities. The validity of these conclusions is, however, open to doubt, even though there is no positive evidence to the contrary. A specific heat of 0.6 calories per gram represents a heat capacity at constant volume of 8.5 R per mol. Subtracting the contribution of the vibrational specific heat there is left at 9.9° a heat capacity of roughly 7 R. Allowing R for rotation and 3/2 R for translational energy, there would be left 9/2 R . Finally we could even postulate a crystalline lattice with 3 N vibrational modes and still be left with 3/2 R !

It is clear that the observed heat capacity cannot be interpreted in terms of a changing number of modes available for energy storage, for it seems impossible to find enough such modes to accommodate the experimental value. It becomes necessary to postulate some sort of dissociation process, in which heat is absorbed. As the temperature is raised, dissociation occurs and heat is absorbed.*

Since ethylene is perfectly stable under these conditions, the transition occurring is not an intramolecular one. We are led to ask next, what is the nature of the dissociating assembly?

In the bomb filled at density 0.2255, the whole container becomes full of liquid just below 9.9°. At constant volume, as the temperature is raised from 9.9°, an important change occurs. We must

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* See for analogy, the heat capacity curve of sulphur in Lewis and Randall, "Thermodynamics" p. 79, and the curves for NH_4Cl and NH_4NO_3, Fowler's "Statistical Mechanics," second edition p. 814.

conclude that there was in the liquid phase below 9.9° some sort of molecular interaction, in which appreciable amounts of energy are bound, and which decreases very rapidly in amount as the temperature is raised above the critical.

Considering now the bomb filled at density 0.2069, the container is filled with vapor at 9.7°. In this case too the heat capacity is too high to be accounted for except on the basis of a dissociation process. We must conclude then that the molecular interaction exists also in the vapor just below the critical temperature. It is however less in degree than in the liquid state, for the heat absorbed in the deassociation process is less.

Most of the dissociation occurs very near to the critical temperature, and as the temperature is raised, this factor becomes less and less important. For this reason the two curves will be asymptotic to each other, provided that the absolute density difference is not too great, as is the case here.

In order to arrive at an idea of the order of magnitude of the energies involved in this process the curve for density 0.2255 has been used to evaluate the integral $\int_{9.9}^{23}(C_v - 0.405)dT$. The result is about 0.6 calories per gram, or 16 calories per mol. Hence the energy is small when averaged over all the molecules. On the other hand if the energy results from the association of only a relatively small number of molecular groups the individual energies might be considerably higher.

Molecular coupling energies due to mutual polarization may amount to several thousand calories per mol. It is due to thermal agitation that such molecular complexes tend not to form in gases. On the other hand we might think of liquids as consisting wholly of such complexes, and at sufficiently low temperatures at least the whole body of liquid may be considered to be a single complex of this kind, each molecule being connected directly or indirectly to every other one (see Mayer 38, 39, 40).

As the temperature of the liquid is raised, the volume increases due to the greater thermal agitation, and the number of such bonds is less. Thus deassociation must contribute to the specific heat of a liquid but this contribution may be very small away from the critical temperature.

Due to the lack of sufficiently accurate p - V - T data, it has not been possible to calculate specific heats at constant volume of the phases below T_c. It is probable, however, that these show curves rising to a maximum at, or somewhat below, T_c. The critical temperature, then, has this property, that near it the rate of decrease of molecular interaction is greatest.

From an examination of the heat capacity data above the critical temperature, it appears that here also the process of deassociation continues.

The next step would be an extension to densities above and below the critical value, and farther removed from it than those heretofore considered. We have already ventured to predict the general nature of the results which might be expected in this region. These predictions are, however, hardly sufficiently certain to warrant a discussion of their significance.

Regarding the nature of the molecular interaction, the first tendency is to postulate the existence of pairs, or more complex groups, of molecules. On this basis, suppose we consider that every collision with a molecule having an energy greater than 6000 calories per mol is effective in decomposing such a complex. Then the average life of these groups is of the order of magnitude 10^{-9} seconds.

If the molecular interaction took this form, it is clear that those properties dependent upon the association would come to a state of equilibrium after a change in volume or temperature, practically as soon as temperature equilibrium was established. It has been established experimentally that this is not the case. Time lags of hours duration occur in homogeneous systems, when certain changes of this kind are made (35).

Consequently we must seek another way of picturing the molecular interaction. We might postulate a tendency of material in this volume and temperature range to assume a quasi-crystalline state, in which all the molecules tend towards some definite orientation, with this tendency counteracted by thermal agitation. A somewhat similar assumption has been made for liquids by Eyring, in his theory of holes in liquids. Such a state of equilibrium might be reached only a considerable time after a change in temperature or volume has been made. We should then postulate that the average distance between molecules, which corresponds to the critical volume, is the most favorable for the appearance of molecular orientation.

A theory of this kind is only pure conjecture, and may seem extremely unlikely from some points of view. Nevertheless, it does afford an explanation of the time lags, and from this point of view is better than any other yet proposed.

The time lags:

The energy changes involved in these lags are considerable. In certain regions the energy absorbed in a lag may amount to more than 50% of the heat capacity itself. For this reason it seemed probable that corresponding lags should be observed in other physical properties, and particularly in the density.

A lag in the liquid density after a change in temperature on an isochore has indeed been reported in this region (70, 90, 42), but for ethylene the time involved is a matter of twenty minutes or so at most when the density is measured by the float method. Apparently if the two lags do correspond the method of heat capacity measurement is much more sensitive than the other.

Changes in the liquid density can be followed more accurately by observing the meniscus level in a long bomb mostly filled with liquid. By this method lags were observed in the meniscus level extending over several hours. This work will be discussed in a separate section, and it will be shown why the heat capacity lags may be considered to tie in with the liquid density lag.

Considering for the moment that the two are correlated, the following deductions can be made:

(1) That there is a fundamental change in the nature of the liquid phase, which takes place at 9.3°, since no time lags are observed for runs starting above this temperature. This is near to the temperature of meniscus disappearance, 9.2°C.

(2) That equilibrium is reached most slowly at 9.3°, and the rate is greater both above and below this temperature.

(3) Comparing the results for the two fillings near the critical density, it is seen that below the critical temperature, the rate constant for the one containing the most liquid is highest. This is to be expected, for the liquid is changing from a more complex to a simpler state. In the case of the vapor the change as the temperature is raised is towards a more complex state. Hence the rate in the latter case will be lower. Near the critical temperature the two rates become about the same, as the phases become more nearly alike.

SURFACE TENSION OF ETHYLENE NEAR THE CRITICAL TEMPERATURE.

SURFACE TENSION OF ETHYLENE NEAR THE CRITICAL TEMPERATURE.

Introduction:

It is a consequence of the Andrews-van der Waals theory, that the surface tension becomes zero at the critical temperature. Moreover, the quantity $T(d\lambda/dT)$, where λ is the surface tension, must also be zero, for this quantity represents a "latent heat of surface formation" and is part of the total surface energy. This means that if the theory holds, the surface tension must approach zero asymptotically near the critical temperature.

On the basis of the persistence of the phases, it is not necessarily true that either of these conditions should be fulfilled by the surface tension. Hence a choice between the two theories could be made on this criterion.

The literature on the subject is not extensive. Winkler and Maass have carried out investigations nearer to the critical temperature than any other authors (93). In Ramsay and Shields' famous paper on the molecular weights of liquids, values are listed for a number of liquids up to a temperature a few degrees from the critical (58). Katz and Saltman have contributed some results in this field (92). These investigations have extrapolated the surface tension curve to zero at the critical temperature, but their curves have a finite slope at this temperature. Examining their results it appears that this is the most natural thing to do, but it is by no means certain that the extrapolation is justified. The curve might still be drawn with zero slope at $T = T_c$, as suggested by the dashed curve in figure 16.

These results extend at best to a temperature 1.5° below the critical. It was considered possible that results could be obtained even closer to the critical temperature with a sufficient degree of accuracy to settle the questions which have been raised. Moreover, although the properties in the critical range of the system ethylene have been the subject of a thorough investigation in this laboratory, its surface tension has never been determined.

Experimental:

The capillary rise method was used. The bomb, shown in figure 15, was 6.5 mm. inside diameter, and about 10 cms. long. The capillary had a diameter of 1.092×10^{-3} cms. This part of the apparatus was conveniently obtained from a Beckmann thermometer of which the bulb had been broken. Meniscus heights were measured by means of a cathetometer to about .025 mm. Corrections for the volume of the meniscus were neglected; such corrections would have been meaningless, for in such a small capillary it was not possible to distinguish the outlines of the meniscus. The curvature of the meniscus in the containing bomb is not serious, as near the critical temperature the distance from the wall at which the surface is no longer affected by capillarity becomes small.

Temperatures were determined by a calibrated thermometer graduated in tenths of a degree. A Beckmann was provided for accurate temperature control. The well stirred water bath was fitted with two plate glass windows placed opposite each other. Through one of these diffuse light was allowed to fall on the bomb, which was separated from the light source by more than a foot of water. (High values are obtained if the light is not well shielded by an infra-red absorbing layer. This factor was checked by observing the height immediately after the light was turned on. No change occurred even at the point taken closest to the critical temperature). The bath temperature was automatically controlled by a thermoregulator to better than .01°. By hand, control to .001° was readily possible. Very near to the critical temperature this fine control is necessary.

The bomb was filled at a density of 0.23 and sealed off under vacuum. The ethylene used had been purified in the low temperature fractionation outfit previously described.

The first run was made over a period of twenty-four hours, with twenty hours taken to cover the range 8° - 9.03°. It was found that after the temperature was raised through a 0.1° interval in the neighborhood of 9° C, the meniscus continued to rise for several hours after the change had been made. The value of the capillary rise did not change appreciably during this time, but it was considered safer to wait until there was no further change in density with time, as indicated by the meniscus coming to rest. Succeeding runs also took long periods of time to complete. The points at 9.10° and 9.16° were taken after the temperature had been brought up from 8.7° over a period of twenty hours.

Near the critical temperature the value of the capillary rise becomes small, and in order to maintain the relative accuracy, ten readings were taken of each rise. The worst agreement was shown by the set: 8.74°C, 0.525, 0.575, 0.525, 0.55, 0.50, 0.525, 0.475, 0.525, 0.500, 0.475 mm; mean = 0.52. The best set was: 9.10°C, 0.175, 0.175, 0.175, 0.175, 0.175, 0.150, 0.175, 0.200, 0.200, 0.200 mm; mean = 0.18.

Figure 15. Surface tension apparatus.

Calculation of the Results:

In order to use this method for the determination of the surface tension, it is necessary to know the densities of the coexisting phases. This data was derived from a combination of the results of Naldrett, Mason and Maass (47), and McIntosh and Maass (41).

It is assumed everywhere that the angle of contact is zero. A careful observation of the appearance of the meniscus showed that even at 9.15°, the liquid curved upwards near the walls of the containing vessel. The assumption therefore appears to be a credible one. If the angle of contact is not zero, then the surface tension calculated would be even higher as the critical temperature is approached. Winkler and Maass have compared surface tensions determined by the ring pull and by the capillary rise method between 111.5° and 120° for methyl ether (T_c= 126.9°C). Fitting the results at 111.5° to agree, they are still found to be concordant at 120°. Hence, if the angle of contact is not zero, at least the temperature coefficient of the angle is zero in this range. If the last state of affairs held, only the slope of the curve would be altered.

The formula used to calculate the surface tension was

$$\lambda = \frac{rgh}{2}(d_{\ell} - d_{v})$$

where r = radius of the capillary

h = capillary rise in cms.

g = acceleration due to gravity

d_{ℓ}, d_{v} are the liquid and vapor densities

Lord Rayleigh (94) has deduced the more accurate formula

$$\lambda = \frac{rgh}{2}(d_{\ell} - d_{v})\left[1 + \frac{r}{3h} - 0\left(\frac{r}{10h}\right)^{2}\right]$$

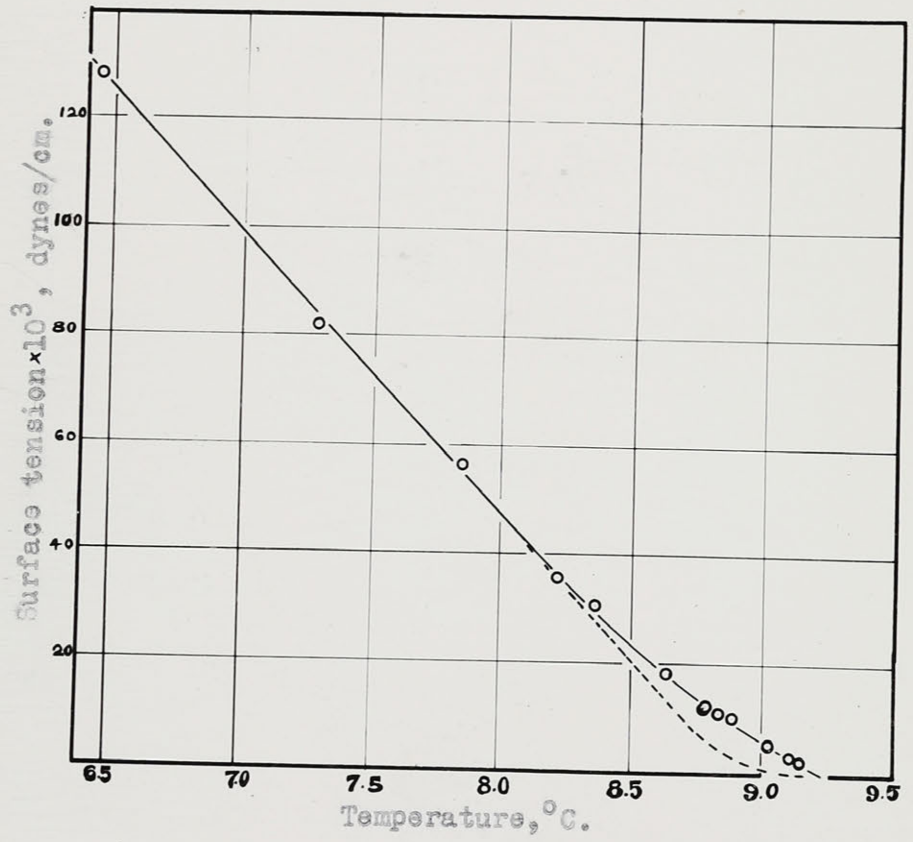

Figure 16. Surface tension of ethylene.

The lowest value of h encountered was 0.2 mm. The resulting error is 2×10^{-4} dynes per cm, and may be neglected.

The data and calculated values are listed in Table XVII, and the results are shown graphically in figure 16.

TABLE XVII

SURFACE TENSION OF ETHYLENE.

Run No.	Temperature, °C	Capillary rise, mm.	$(d_l - d_v)$ g/cc	$\lambda \times 10^3$, dynes/cm
1	6.45	3.50	0.137	128
	7.29	2.45	0.124	81.3
	7.85	1.85	0.112	55.5
	8.345	1.17	.097	30.4
	8.64	0.80	.084	18.0
	8.84	0.57	.074	11.3
	9.03	0.34	.062	5.65
2	8.22	1.29	0.101	34.9
	8.79	0.61	.076	12.4
	8.89	0.52	.071	9.9
3	8.97	0.45	.066	7.95
	9.11	0.21	.054	3.0
	9.15	0.18	.051	2.4

The Critical Temperature of Ethylene:

The critical temperature has been defined in this thesis as the temperature of meniscus disappearance. Its value has been reported by Maass and Geddes and others in this laboratory to be 9.50° for ethylene. Naldrett, Mason and Maass (47) found, however, that when the ethylene was violently shaken, the meniscus disappeared at 9.20°, which was now the temperature of reappearance as well. McIntosh, Dacey and Maass (42) report 9.20° for the temperature of reappearance without shaking. Mason and Maass (95) found the maximum opalescence occurs at 9.20°, whether the temperature is raised or lowered towards this value.

The question arises, does the case without shaking constitute a true hysteresis, or is it true, that if sufficient time were allowed to elapse, the meniscus would disappear at 9.20°? It was particularly important to settle this question in order to place on a firm foundation the interpretation of the surface tension results.

In the course of the first run the bomb was heated from 8°to 9.15° over a period of twenty hours, and kept for five hours at this temperature. The meniscus was still sharp and easily visible, and showed curvature near the sides of the vessel. When now the temperature was raised to 9.25°, all trace of the presence of a discontinuity had vanished in ten minutes.

In a second experiment, the apparatus was thermostated for six hours at 9.15°, at the end of which time the meniscus was still sharply defined. At 9.16°, the line of demarcation between the phases was still clear and sharp. At 9.18° the appearance had not changed. At 9.195° the meniscus became a band which kept broadening out and became fainter and fainter with time.

At the end of run No. 3, the bomb had been brought from 8.7° to 9.15° over a period of twenty hours. When the temperature was raised slowly from 9.15°, the meniscus was observed to suddenly become a band at about 9.215° and to disappear completely two or three hundredths of a degree above the temperature.

In these experiments the bomb was suspended in such a way that it suffered no mechanical vibration whatsoever, so that this result cannot be due to the same cause as the "shaking temperature" of Naldrett, Mason and Maass.

Correlating these results with those mentioned before, it appears that the critical temperature of ethylene can be fixed at 9.21° ± .02°. On this basis the rather more pleasing result is obtained, that the disappearance and reappearance of the meniscus is a reversible phenomenon.

It must not be supposed, however, that there is to be found in these results a contradiction of the density persistence previously reported. Indeed, support for the persistence is forthcoming, for the meniscus here vanished away from the end of the tube, which proves that the densities were not equal.

Discussion of the surface tension results:

Winkler and Maass extended their observation to 1.6 ° below the critical temperature of propylene and their lowest surface tension value is .05 dynes/cm. Referring to figure 16, it is seen that from a surface tension of this value, an extrapolation to the critical temperature is an extremely dangerous business. The curve could be drawn with finite slope at the critical temperature; on the other hand the dashed curve, showing zero slope at $T = T_c$ would be equally possible.

As drawn, the curve for ethylene extrapolates to zero surface tension at 9.22° C. We have settled the critical temperature as being 9.21°± .02°, so it appears that the surface tension is zero at the critical temperature. The extrapolation extends over only .07°, but in view of the rapid changes which (on the classical theory) take place near this temperature, even this might be criticized.

It is, however, quite certain that the curve cannot possibly be drawn so as to have a value of $\lambda = 0$ at 9.21° and also to have zero slope at this temperature. From this point of view. we must conclude that $d\lambda/dT$ is finite at $T = T_c$, which is a direct contradiction of the classical theory.

This conclusion might conceivably be criticized on the ground that since the density data used does not conform to the classical theory, the surface tension data derived therefrom can hardly be expected to conform. There is, however, very little doubt regarding the form of the density curve just below 9.2°C, as it has been verified by Naldrett, Mason and Maass (47) using a method which entails violent stirring, as well as by McIntosh, Dacey and Maass (42) and previous investigators (35, 41) using a float method.

The curve could be drawn in only one other fashion near the point of meniscus disappearance. This alternative would have the surface tension finite at $T = T_c$, with $d\lambda/dT$ either equal to zero or finite. This would again constitute a contradiction of classical theory. It would moreover not be the natural way in which to extrapolate the results, nor does it seem likely from other considerations that the curve has this form.

We must reject a form of the curve in which it slopes over sharply just above 9.15°, and then tends to zero asymptotically at 9.21° C. This would involve a large increase in the surface energy just below the critical temperature, after which it would rapidly go to zero, all in a .06° range.

For the curve as drawn, the latent heat of surface formation at $T = T_c$ is $T(d\lambda/dT) = -43.5$ ergs/cm^2, and since λ is zero at this temperature, the total surface energy is

$$\lambda - T(d\lambda/dT) = 43.5 \text{ ergs/cm}^2.$$

It may be mentioned that there arises at this point, a fundamental contradiction in the theory of Andrews-van der Waals. The surface tension and surface energy must certainly be functions of the densities of the liquid and vapor phases. Now just below T_c the rate of change of these densities with temperature is very high (on classical theory). Hence the liquid and vapor densities change very rapidly, but the surface tension is asked to show a rate of change with temperature tending to zero! That is, the variation of the surface tension must be supposed to be least when the variation of the densities is greatest. These two conditions are not compatible.

In discussing Callendar's (13) results on steam, Porter (96) has proposed that it might be possible to obtain an equation for the surface tension of the form:

$$\lambda = f\left(\frac{\rho_2}{s_2} - \frac{\rho_1}{s_1}\right)$$

where ρ_1, ρ_2, are the densities of the phases.
S_1, S_2, are the average distances apart of the molecules.

In the normal case in which the average distances apart of the molecules are inversely proportional to the cube root of the density (no association) λ would equal zero only for $\rho_1 = \rho_2$

If, however, due to association in the liquid, the average effective intermolecular distance were increased, there would exist a pair of values ρ_1 and ρ_2 , $\rho_1 \neq \rho_2$ for which

$$\frac{\rho_2}{s_2} = \frac{\rho_1}{s_1}$$

and the resulting surface tension is zero. Porter concludes by saying "One would anticipate it (the working out of this problem) to be a problem of extraordinary difficulty."

It is probable that some such theory, based on the amount of molecular interaction in the phases, will eventually supply an explanation for the observed phenomenon; namely, the disappearance of the surface tension while the density difference is still finite.

The theory of Mayer predicts that the surface tension shall disappear while the density difference persists (38, 39, 40). The theory is pleasing in the simplicity and fundamental nature of the assumptions made; on the other hand it is difficult to interpret the results in purely kinetic terms such as molecular interaction. The prediction made is well verified in the results of the experimental work just described.

THE CRITICAL TEMPERATURE OF ETHANE

The Critical Temperature of Ethane.

Much of the confusion regarding the determination of the critical temperature has arisen due to the complex and time dependent nature of the phenomena which occur when this temperature is approached. For instance, most descriptions of the critical phenomena describe an opalescent band which appears in the neighborhood of the meniscus just below the temperature of disappearance. In an experiment in which the heating is very slow,however, the band does not appear at all. If heating is rapid, the band appears, but if the bomb is then thermostated for a sufficient length of time, the band will slowly disappear, leaving either a sharp meniscus, or no discontinuity, depending on the temperature.

A number of experiments made on ethane are described here. The ethane was purified in the low temperature still described in a previous section. The bomb was suspended in front of a plate glass window, from a vibration free support. It could be lighted by diffuse transmitted light, coming from a source placed on the opposite side of the bath, or by reflected light from various angles.

In the first set of experiments, the bomb was heated from 30°C to the temperature shown, and held there at the time indicated. The phenomena observed are described opposite the corresponding times and temperatures.

Time	Temperature °C	Observation
8.43	32.02	Meniscus visible.
8.48	32.11	Meniscus surrounded by a dense opalescent band.
8.57	32.15	Meniscus has been replaced by an opalescent band.
9.01	32.18	Opalescent band is wider, about ½ mm.
9.06	32.21	Band is more diffuse and about 1 mm wide.
9.11	32.25	Band more diffuse, but still distinguishable by reflected light. No discontinuity by transmitted light.
9.22	32.33	Band very diffuse and barely distinguishable.
9.26	32.28	Bomb appears uniform everywhere.

On heating several degrees, and then cooling slowly, the meniscus reappears at 32.15°C.

The bomb used had one end ground and polished optically flat. A similar experiment was carried out, with the bomb in a horizontal position, viewing through the end. The same phenomena were observed. The last trace of discontinuity disappeared at 32.38°,and reappearance occurred at 32.15°.

This then is the nature of the hysteresis in the meniscus disappearance and reappearance. On the basis of these results we should have reported a hysteresis of about 0.2°.

In the next set of experiments the bombs were raised to the temperature noted, and kept there for a length of time.

Temperature °C	Time	Observation
32.15	1¼ hrs	Opalescent band disappears on standing leaving clean meniscus.
32.29	1 hr	Band, originally about 0.7 mm wide, becomes more and more diffuse and finally disappears.
32.19	3hrs	Band is originally quite distinct and about 0.4 mm wide. It keeps broadening out and by this time is very difficult to distinguish at all.
32.18	2hrs	Band still fairly distict and about 2 mm wide.
	7hrs	Band 4-7mm wide.
	18 hrs	Existence of band is questionable.

On cooling from 35°, the meniscus does not reappear after 3 hours at 32.18°, but on cooling to 32.16°, it reappears.

It follows that the hysteresis if any is not greater than .02°, and is in fact probably not present at all.

An aside worth noting here is the following comparison: Whereas in the first experiment, bomb vertical, the meniscus moved up about 8 mm between 31.5° and the temperature of disappearance, the amount of the meniscus rise in the experiment carried out in the horizontal bomb was less than a mm. The bomb is about 10 cm long, and 5.5 mm in internal diameter. This experiment constitutes a refutation of the argument that the fact that the meniscus vanishes away from the end of the tube is due to gravity. On the basis of the gravity hypothesis the amount of the meniscus movement in the horizontal tube should have caused it to move up to the top and fill the whole tube with liquid before the meniscus disappears.

THE LAG IN THE MENISCUS LEVEL

The Lag in the Meniscus Level.

In endeavoring to find an explanation for the observed time lags in the heat capacity, a search was made for some physical property with which the lag could be correlated.

McIntosh and Maass have reported a time lag in the density of liquid ethylene on heating in this region, but the duration of the lag is in this case twenty minutes or less.

In the pursuit of the surface tension investigation, the probable answer was found. Lags of several hours duration were observed in the meniscus level after a change in temperature had been made.

The bomb was filled at a density somewhat higher than the critical, and the meniscus height was about 4/5ths up the tube at 9°, so that the changes observed probably correspond roughly to changes in the liquid density.

No lags were observed below 8°C, but on changing the temperature from 7.8° to 8.3° about thirty minutes was required for the establishment of equilibrium, the meniscus showing an upward motion during this time. On changing the temperature from 8.81° to 9.01°, a lag of five hours duration was observed.

There was no appreciable lag on cooling through an interval. This is true of the thermal time lags also.

The meniscus height lags occurred under conditions of constant temperature. The heat capacity lags were, however, observed under adiabatic conditions. In order to complete the analogy, a meniscus level lag was followed, in which the temperature of the bomb was rapidly raised through an interval, and the temperature then smoothly lowered, in such a way as to correspond to the temperature change experimentally observed in a thermal lag. When the logarithm of the difference between the instantaneous level and the asymptotic level was plotted against the temperature, a straight line was obtained. The slope of this line showed a unimolecular rate constant of 2.5×10^{-4} sec^{-1}; the corresponding lag in the heat capacity was 4×10^{-4} sec^{-1}. In a second experiment the results to be compared were 3.8×10^{-4} and 4.3×10^{-4} sec^{-1}. The agreement is sufficiently good to establish the correspondence.

It follows that this lag is indipendent of the shape of the container, for the surface tension bomb was 10 cms long and 6.5 mm inside diameter, while the heat capacity bomb is much larger and spherical. Hence there is no question of time for diffusion through a phase interface.

CALCULATION OF THE DISPERSION CONSTANTS

Calculation of the Dispersion Constants

Theory:

The quantity designated in the section on heat measurements as the hysteresis energy was interpreted to represent the energy resident in the surface of a dispersion, which had been formed by cooling ethylene from 13° to 9.36° C.

The energy resident in the surface per cm^2 has been calculated in the section on surface tension, for the system ethylene at 9.21° C. In consideration of the way in which the density curve goes, it seems safe to assume that the surface energy willstill be of the order of 40 $ergs/cm^2$ at 9.36° C.

On the basis of this assumption the interfacial area in the dispersed phase at 9.36° can be calculated. Then, knowing the specific volumes of the liquid and vapor from the determinations of McIntosh, Dacey and Maass (42), the average radius of a particle of the dispersed phase can be determined.

Calculation:

(1) Density 0.2255.

Total surface energy = .02 cal = 8.4×10^5 ergs/g.

Surface energy = 40 $ergs/cm^2$.

$$\text{Surface area} = \frac{8.4 \times 10^5}{40} = 2.1 \times 10^4 \ cm^2/g.$$

Mass vapor per gram system = 0.34 g.

Mass liquid per gram system = 0.66 g.

It seems best to assume that in this case the vapor is suspended as spherical bubbles in the liquid. Let the average radius = r, and the total number of bubbles = n. Specific volume of vapor = 5.02 cc/g.

$$4/3\pi r^3 n = 0.34 \times 5.02 = 1.7.$$

$$4\pi r^2 n = 2.1 \times 10^4$$

$$r = 2.5 \times 10^{-4} \text{ cm.}$$

(2) Density 0.2069. T = 9.41°C.

Total surface energy = .0035 cal = 1.5×10^5 ergs/g.

$$\text{surface area} = \frac{1.5 \times 10^5}{40} = 4000 \text{ cms.}$$

Mass liquid per gram system = 0.18 g. Specific volume liquid = 4.2 cc/g. If liquid is suspended in vapor, the average droplet diameter r is calculated from

$$4/3\pi r^3 n = 0.18 \times 4.2 = 0.75$$

$$4\pi r^2 n = 4000$$

$$r = 5.5 \times 10^{-4} \text{ cm.}$$

Discussion:

In view of the small density difference, the sizes deduced for the bubbles and droplets seem to be of a reasonable magnitude.

The vapor pressure of small droplets would not be at all higher than that of a larger body of liquid, in the temperature range where the surface tension is zero. Below 9.21° the surface tension has a finite value. For example at 9° the surface tension is .006 dynes per cm, and the increase in pressure due to the surface tension for a droplet of radius 2×10^{-4} cm would be

$$\frac{2 \times .006}{2 \times 10^{-4}} = 60 \text{ dynes/cm}^2 = 6 \times 10^{-5} \text{atm.}$$

The increase in vapor pressure is so low that it seems probable that a suspension, once formed just below T_c, would be stable from an experimental point of view.

If there is a difference in refractive index between the phases, we should expect that the dispersion would show up as an opalescence effect. Except very near to 9.2°C, this does not appear to be the case, because at all other temperatures the amount of opalescence in a dispersed system has been measured by Mason and Maass (95) and found to be the same as in a non-dispersed system at the same temperature. At 9.2°, where the opalescence is a maximum, a difference was indeed found.

GENERAL DISCUSSION

General Discussion

Theory of Mayer and Harrison:

If one assumes that the potential energy of a gas can be expressed as the sum of mutual potential energies of pairs of molecules, it is possible by making certain approximations and using otherwise the general methods of Statistical Mechanics, to derive an equation of state, in which the second virial coefficient appears, calculable in terms of intermolecular constants. Such a calculation is carried out in Fowler's Statistical Mechanics, Chapter 8.

Making the same assumptions, Mayer and Harrison followed through the method more completely, and arrived at an equation predicting the formation of a second(liquid) phase, and the existence of a critical temperature.(38,39,40)

The property of surface tension was then introduced in what appears to be a somewhat arbitrary manner, the chief justification being the final appearance of an energy which is proportional to the 2/3rds power of the volume of a droplet of the liquid phase. It follows in the subsequent development that the surface tension disappears at a characteristic temperature T_m , which is lower than T_c, the latter being defined as the higest temperature for which dp/dv can be zero.

This prediction has been admirably verified by the work of McIntosh, Dacey and Maass (42), combined with the surface tension results reported in this thesis.

Mayer and Harrison then go on to construct a diagram of the pressure - volume - temperature relationships in the critical region. At every temperature below T_c it must be possible for two phases to coexist (provided that the proper average volume is chosen), but in the interval T_m to T_c, due to the absence of the surface tension, the system may be expected to have certain peculiar properties.

Below T_m the existence of a surface tension allows the phenomenon of supersaturation to occur; here too the isothermals show discontinuous curvature on the borders of the liquid - vapor envelope, which permits curves corresponding to supercooling to be drawn. Because above T_m the surface tension vanishes the isothermals are drawn with continuous slope everywhere. McIntosh, Dacey, and Maass have indeed drawn their curve in a somewhat similar manner.

Certain other of their assumptions are based on less firm grounds, and have not been borne out in detail in this laboratory. Based as they are mainly on conjecture, these have not the value of the previous results relating surface tension and volume- temperature curves, and need not be discussed in detail. Fundamentally, the idea expressed is that that on any isothermal between T_m and T_c, any macroscopic volume can be experimentally realized, but within certain boundaries the microscopic densities v_l and v_g are limited to these two values, corresponding to the densities of the condensed and vapor phases. The intermediate macroscopic values which can be obtained correspond to a dispersion of one of these phases in the other. Here are the elements of the dispersion theory, which has already been referred to, and which will be further elaborated in this discussion.

Density gradients due to Gravity:

It has been suggested that the difference in density observed in the experiments of Maass and coworkers, and others, is due to a gravity gradient in the fluid considered. Near the critical volume dp/dv is zero at one point. Hence any pressure gradient, such as that due to gravity, will in the neighborhood of this point cause the appearance of a region through which the density varies rapidly with height.

If there were available an equation of state applying exactly in this region, it would be possible to calculate the magnitude of the density difference resulting under a given set of conditions. When the question to be answered is, what is the exact value of dp/dv near v_c, there is no equation of state to which we can refer, which can be relied upon to give even the correct order of magnitude. For this reason calculations such as those of Gouy (25) and Ruedy (60) are of no value whatsoever.

It becomes necessary to appeal to experiment to settle this point, and conclusive evidence has indeed already been obtained.

Geddes and Maass (35) for instance found on isobars that outside of the region in which the meniscus is visible, the density observed by a quartz spiral - float technique was the same as that calculated from the volume of the bomb. Hence in this case there was no appreciable density gradient.

Winkler and Maass(90) report no variation of density with height away from the region of the meniscus. Although this is convincing evidence, it does not constitute a definite proof, for the p - v curve might be so shaped that the gradient was very large near to the meniscus and inappreciable away from this region.

Most conclusive is the observation that the density difference observed on an isochore does not appear on cooling the system through the same region.(35,41,42,70) On the basis of a gravity effect the density difference should appear on cooling as well.

In the section of this thesis on the critical temperature of ethane, an experiment was described, in which the critical phenomena were observed in the same tube in the horizontal and vertical positions. This too constitutes definite evidence that the observed density difference is not due to gravity.

On the basis of these considerations, it may be stated that gravity has had no appreciable effect in the experiments heretofore performed.

Impurities:

The persistence of the density difference above the critical temperature has been attributed to the presence of impurities in the experimental medium. It is easy to show that this criticism does not rest on a sound basis.

Let us suppose that there are impurities in the system; then we deal with a two component, or n component system. It is just as upsetting to the classical ideas if in this multicomponent case a density difference persists after the meniscus disappears ! Hence to attempt to explain these phenomena by simply using the word "impurities" is not to explain them at all.

It is true, however, that a density difference, once there, can be accentuated by an impurity. This part of the subject can well be discussed in some detail.

In order to calculate the effect of an impurity on the density of the condensed phase, it is necessary to know the relative distribution between the phases, and the pressure-volume coefficient of the liquid material. These data are not available.

It is, however, possible to obtain an idea of the amount of impurity whose effect will be negligible. Supposing the worst possible case, take ethylene with air as impurity, absolutely insoluble in the condensed phase at 9.8°C.

We have already shown that the effect of gravity is negligible. Now a typical experimental tube is one square centimeter in cross section, and 20 cms. long. Filled with material at density about 0.25 it may contain half liquid and half vapor by volume, or 3 grams condensed and 2 grams vapor phase. The pressure on the liquid phase due to the weight of the vapor is 2 g/cm^2 or 2×10^{-3} atm. But this pressure, as we have seen, has a negligible effect. If we had an amount of air in the tube sufficient to exert the same partial pressure, its effect would also be negligible. Assuming all the air is in the vapor, the amount of air permissible is one part in 10^5 of the whole mass of material.

Actually the amount permissible is probably much greater, for the liquid might show an inappreciable (0.1% by the float method) change in density for a pressure greater than 2×10^{-3} atm. Also the distribution between the phases is probably never as unfavorable as assumed in the calculation.

It is probable that most of the ethylene used in this laboratory has satisfied the $1/10^5$ criterion, particularly since the low temperature still has become available.

It might further be argued that the presence of traces of impurities so impedes the attainment of equilibrium, that it would never be reached under ordinary experimental conditions. It is indeed concievable that if a lag occurred due to diffusion through the meniscus, its duration might be prolonged due to the accumulation of impurities in certain regions. On the other hand it is difficult to see how the expansion of a liquid, or a volume change on an isobar in a homogeneous medium, could be appreciably affected by the presence in it of one molecule of foreign material in 10^5. Furthermore, McIntosh and Maass (41) have shown that time lags are reproducible, which would not be the case if they depended on the presence of small traces of impurities. These authors showed too that lags in a system containing air are if anything of shorter duration than in one in which air is absent.

Hysteresis effects and dispersion theory:

Let us first examine what happens when a one component system is heated up towards the critical temperature. Just below T_c, bubbles of vapor which form within the liquid may remain suspended there, and at the same time, droplets of liquid carried into the vapor can remain suspended in that phase. For this reason, in a range extending one degree below the critical temperature, the apparent (macroscopic) density of the liquid is lower than the true density, while the apparent density of the vapor is too high. If the average concentration is such that the mass of the liquid is decreasing, vapor may be formed to some extent by evaporation from the surface, but probably the main process is the formation of bubbles of vapor within the liquid, which under favorable conditions remain suspended. For this reason the apparent density of the liquid is very much lower than than the true or microscopic value. Since the liquid is evaporating the vapor will be relatively free of liquid droplets and will show a value near its true density. On the other hand, if the average volume is such that the liquid is increasing in mass, then vapor originally suspended in the liquid will tend to condense as the temperature is raised, and a higher liquid density is registered. Under these circumstances, the amount of liquid suspended in the vapor will if anything tend to increase, and a comparatively high macroscopic vapor density will result.

In this way, one would explain the results of McIntosh and Maass (41), showing that the density of the phases in ethylene is a function of the average volume, as also the similar results of Winkler and Maass for methyl ether. We see too why different isochores are obtained for every mass - volume ratio. It now becomes clear why different densities are obtained depending on whether heating is rapid or slow; in the latter case more evaporation occurs from the liquid surface, and a higher density is registered, which is nearer to the true value.

As heating is continued above T_c, a point will be reached where the whole system lies outside of the boundaries of the liquid - vapor coexistence region. Here the medium has been converted to either liquid or vapor. Now on cooling (curve B, figure 4) the phases form a homogeneous suspension in each other, and there is no apparent density difference. At or near the critical temperature, with the reappearance of the surface tension, the stability of the suspensoid is no longer sufficiently great, and settling occurs, with the reappearance of the meniscus. The liquid is still left with the maximum amount of vapor suspended in it, and the vapor similarly carries the maximum amount of liquid droplets. Hence the liquid value is lower than the density obtained with rising temperature, and the vapor density is higher. Finally a point is reached a degree or so below T_c, where the liquid density is not appreciably less coming down than it is going up, and the hysteresis loop is closed. In this way the density curves reported by McIntosh and Maass (41) and Maass and Geddes (35) fall in line with the theory.

Gentle stirring such as was used by Winkler and Maass (90) and by Tapp, Steacie and Maass (70) should cause no great change in the density; it seems possible, however, that a dispersion is formed in the neighborhood of the interface only. On the other hand, violent shaking, as described by Naldrett, Mason and Maass (47) would tend to form a dispersion and alter the densities.

If ethylene just below the critical temperature be compressed, there will be a tendency for vapor to change to liquid, and the highest and most nearly true liquid densities should be observed in this manner. Similarly, the lowest and most nearly correct vapor densities would appear after an isothermal increase in system volume. In such terms the effects reported by Maass and Geddes on the results of expansions and contractions just below T_c are fitted into the theory.

Above the critical temperature the macroscopic density of the system is particularly sensitive to isothermal compression and expansion. We should expect that a compression would rapidly increase the apparent density of the vapor to equal that of the liquid, and a expansion would have the same final effect. If the system were taken through the liquid - vapor envelope on an isobar, a macroscopic density difference would never appear at any average volume.

An examination of the investigation of Clark on viscosity (17) shows that the results obtained with falling temperature, and those resulting with violent stirring, fall on the same curve within the experimental error. This is readily explicable on the dispersion theory.

Temperature fluctuations would tend to increase the amount of dispersion in each phase. This conforms with the results of Maass and Geddes (35).

When a temperature gradient is set up in which the top of the bomb is colder than the bottom, the material distills around the tube, and the net effect is that observed with fluctuations in the temperature, as described in the previous paragraph. The final result will be the removal of any apparent density difference.

If in a bomb in which the phases are originally uniformly dispersed, the top is heated, some of the liquid will be converted to vapor, and when uniform temperature is reestablished, a macroscopic density difference will have been restored. This experiment has been carried out by McIntosh, Dacey, and Maass(42).

Form of the Pressure - Volume - Temperature Curves above the Temperature of Meniscus Disappearance:

It has already been remarked that from the point of view of the surface energy, the coefficients dv_1/dT and dv_2/dT (subscripts refer to the liquid and vapor phase respectively) cannot be infinite at the temperature at which the phases become identical. On the persistence theory, the same considerations apply equally well when the form of the liquid vapor envelope is considered. We should draw the liquid vapor envelope so that $|dv_1/dT|$ and $|dv_2/dT|$ pass through a maximum probably near the temperature of meniscus disappearance, and the gradually decrease, tending to a zero value. Here the liquid boundary and vapor boundary would tend to each other with increasing temperature, persisting however to infinite temperatures.

It is well known that the slope dp/dv becomes increasingly greater as the temperature is raised away from the critical, and at first it seems difficult to reconcile this fact with the condition that within the liquid vapor boundary $dp/dv = 0$.

On the basis of the Einstein - Smoluchowski theory, the intensity of the critical opalescence is inversely proportional to dp/dv, and in the case of a liquid or vapor, this means the value of dp/dv on the liquid or vapor border of the envelope. Now Mason and Maass (95) have found for ethylene that the maximum opalescence occurs at 9.2° C. Then the minimum dp/dv outside of the coexistence region occurs at 9.2°, and at higher temperatures the slopes on the boundaries of this region should be drawn with greater and greater values.

If this result is accepted, the curve of McIntosh, Dacey and Maass (42) depicting the p - v isothermals, could be drawn to show liquid and vapor coexisting at temperatures higher than 9.9°, and still be in agreement with their experimental points. Their results would then agree better with the magnitude of the density persistence found by direct measurement on an isochore.

This radical departure from classical ideas is of course still conjecture. If it were really true, an important consequence would be that there is no real continuity of state, for it would be impossible to take a system from the liquid to the vapor state without passing through a coexistence region. Of course at very high temperatures, the extent of the coexistence region, the heat of vaporization, and the surface energy, would become very small.

CONCLUSIONS

Conclusions

The Andrews - van der Waals ideas do not apply in the critical region, insofar as there is a persistence of a phase density difference above the temperature of meniscus disapearance.

The origin of the numerous hysteresis effects which have been observed near the critical temperature (including the hysteresis in the heat capacity) may definitely be ascribed to the phase dispersion which forms in this region.

The existence of molecular interaction in both the liquid and vapor below T_c, and also above this temperature, has been conclusively demonstrated. The exact nature of the interaction is still open to speculation.

The surface tension vanishes before the densities of the phases have become equal. The surface energy is large and finite even when the surface tension is zero.

The type of time lag investigated here has been shown to be indipendent of the form of the containing vessel; i.e. the lag is a unique property of the system.

It is probable that the volume - temperature curve of ethylene shows an inflection point near 9°C, and possibly continuously decreasing slope thereafter. The last statement if true would constitute a contradiction of the theory of the continuity of state.

With the proper light cast on the hysteresis effects, it is to be expected that progress in the field of investigating the changes in molecular interaction in the transition from liquid through the critical region should be facilitated. Here should be found an answer to the question set by the existence of the time lags, and perhaps data of fundamental importance in the problem of liquid structure.

It has been the object in this thesis to present a description of the critical phenomena which is as complete as possible. In attempting to achieve this purpose, it has been necessary to put forward parts of the theory which are based more or less on speculation. It should be realized that some of the ideas set down are merely tentative, pending the completion of further experimental and theoretical work.

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