

Effect of Superatmospheric Pressures on Nucleate Boiling of Organic Liquids

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Superatmospheric pressures greatly reduce the temperature differences in nucleate boiling of organic liquids. Since nucleate boiling is characterized by bubble formation at the heating surface, it seems logical to investigate the pressure difference that causes bubble formation. It has been found that for organic liquids the difference in vapor pressure corresponding to the temperature difference behaves in a regular manner with pressure but does not vary greatly. This regular behavior permits prediction of temperature differences at higher pressures with a knowledge of only vapor-pressure and boiling data at one pressure. New boiling data have been obtained in the investigation.

Of all the variables known to influence nucleate boiling, the one single variable which exerts the most marked effect is pressure. This fact was perhaps first pointed out by Cichelli and Bonilla in 1945 (7). As an example of the pronounced effect, these investigators showed that raising the pressure on benzene from atmospheric up to 645 lb./sq. in. abs. decreased the temperature difference from 63° to 3°F. at a heat flux of 50,000 B.t.u./(hr.)(sq. ft.). Despite this large effect, pressure has not been recognized as a significant independent variable in itself. Instead the effect of pressure has been thought of in terms of its effect on other liquid or vapor properties which were changed by an increase in pressure.

The most prominent characteristic of nucleate boiling is that once a certain temperature is exceeded, a large increase in the number of bubbles is brought about by only a slight increase in the surface temperature. This behavior at once suggests that a certain temperature is necessary to allow bubble growth; however, the logical criterion for bubble growth is the difference in pressure between the vapor pressure of the liquid at the temperature of the surface and the pressure of the system.

One might well expect that at different system pressures roughly the same pressure difference would be necessary for the bubbles to form rapidly. However, the temperature difference corresponding to a particular difference in vapor pressure is a very sensitive function of the pressure and the vapor pressure-temperature equilibrium. Thus, just as the pressure determines the boiling temperature it also determines the temperature difference necessary to give a particular difference in vapor pressure.

Assuming that for bubble growth at different pressures it is necessary to exceed the same pressure difference between the vapor pressure of the liquid at the heating surface and the pressure of

the system, then, by picturing the increasing slope of the vapor-pressure curve, one can see how the temperature difference for bubble growth decreases rapidly with increasing pressure.

Perhaps the reason that pressure has not been considered a primary variable in boiling is that the first studies and correlations were made either close to or entirely at atmospheric pressure (2, 5, 9, 10, 13, 14, 15, 19). Jakob's 1935 correlation based on data at atmospheric pressure failed to show the improved heat transfer at higher pressures; therefore in 1938 he modified it. Later, when dimensionless correlations were proposed to include the effect of pressure, this effect was included either superficially or only insofar as it affected the physical properties which had been used to correlate boiling data.

It has been universal practice to use dimensional analysis to arrive at nucleate-boiling correlations; however, dimensional analysis, as it has been used, usually requires that the data at constant pressure fit an equation of the type $q/A = \text{constant} (\Delta T)^n$. To evaluate n , one plots the data on a $\log q/A$ vs. $\log \Delta T$ plot. Plotting the data in this way does not show clearly the sudden way the heat flux rises as the temperature difference becomes large enough to support nucleate boiling.

Two other related experimental facts bear out this idea that a certain pressure difference is necessary to support nucleate boiling. One is that in subcooled boiling it is the temperature of saturated vapor and not the bulk temperature of the liquid which correlates the data. The other is a special case of the first. With mercury, where the density is high, there is an appreciable effect of small liquid heads above the heating surface when the pressure is near atmospheric (4). Measurements show that the temperature of the mercury above the heating surface is uniform and close to the equilibrium temperature corresponding to the pressure over the mercury.

An examination of the published data

lends support to the idea that the pressure difference remained relatively the same for the same liquid at different pressures. It is apparent that more data are required. One important fact that is apparent is that water is an exception. The decrease in the temperature difference with pressure is not so great for water as it is for organic liquids. That water should not behave as an organic liquid in this respect is to be expected in view of its other unique behavior. Its maximum heat flux is three to five times as great as for organic liquids; its temperature differences in nucleate boiling at atmospheric pressure are about half the normal temperature differences of organic liquids; its physical properties, such as thermal conductivity, surface tension, specific heat, and critical pressure, are outside the ranges of those of organic liquids.

DESCRIPTION OF EQUIPMENT

The apparatus consisted principally of a stainless steel pressure vessel containing the boiling surface. A general view of the apparatus is shown in Figure 1; details appear in Figures 2, 3, and 4.

The boiling surface was the outside surface of a type-304 stainless steel tube. The outside diameter of the tube was 0.0643 in. and the wall thickness 0.0082 in. The tube was suspended in the pressure vessel by two electrodes, which also supplied the electrical current with which the tube was heated. A thermocouple was located inside the tube midway between the supporting electrodes.

A three-phase full-wave rectifier supplied direct current to heat the tube. The rectifier was supplied from a variable-voltage transformer, which furnished the means of varying the heat generated in the tube. The vessel was insulated with Fiberglas, which was placed between the vessel and its angle-iron support structure. Additional insulation was placed on top of the vessel.

The pressure was controlled by two external heaters, which supplied heat to the vessel, one being a high-power heater and the other a low-power.

The thermocouples used were 30 gauge copper-constantan made from one lot of

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wire. Sauereisen cement was used to insulate the junctions electrically from the tube wall. Lengths of the 0.065-in. O.D. tubing were used to contain all thermocouple junctions. One end was silver-soldered shut and the thermocouple was threaded into the tube from the other end. A diagram of the thermocouple circuit is shown in Figure 5.

The outside diameter of the boiling tube, which was measured to 0.0001 in., was found to be uniform to within 0.0002 in. The length of the boiling section was measured to 0.0005 in. with a caliper and a 2- to 3-in. micrometer. The wall thickness was calculated as 0.0082 in. by weighing measured lengths of tubing. A number of samples were mounted in plastic and polished so that the cross section might be examined. Examination of the cross section with a projection microscope at approximately 100 diameters magnification revealed variations in the tube wall of only 2%.

EXPERIMENTAL METHODS AND PROCEDURES

The liquids used were acetone, benzene, ethanol, and Freon 113 (1, 1, 2-trichlorotrifluoroethane). Each liquid represented a different family of compounds.

In preparation for a run the vessel was disassembled, cleaned with the liquid to be boiled, and dried. The boiling tube was polished in as reproducible a manner as possible, crocus cloth being brought back and forth along the length of tube.

The vessel was purged of air by allowing vapor to escape during the heating period preceding the actual test. In the heating process the high-powered heater caused violent boiling in the vessel, which was allowed to subside before the tube current was turned on. The tube current was gradually increased. Before a heat flux of 25,000 B.t.u./(hr.)(sq. ft.) was exceeded, it was ascertained that boiling had begun, so that there was no possibility of film boiling occurring. If the boiling initiated during the heating period was allowed to die away completely, as much as thirty minutes was sometimes required before the tube began to boil. Although the boiling began at some one point, it quickly spread along the tube.

Initial Atmospheric Runs

The heat flux was raised to 50,000 to 60,000 B.t.u./(hr.)(sq. ft.) except in the case of Freon 113, where it was limited to 30,000. These heat fluxes were chosen to give high values of the heat flux but still avoid the complication of film boiling. Preliminary readings were taken, and after half an hour or longer, a complete set of data at atmospheric pressure and various heat fluxes was taken.

A set of data at constant pressure consisted of readings at ten or more values of the heat flux. Half of these were taken as the heat flux was decreased and half as it was increased. At each heat flux readings were taken of the tube current, the tube thermocouple voltage, the vapor and liquid thermocouple voltages, and the pressure. The boiling was observed visually. Then the Powerstat was turned to give a new value of the heat flux. About 2 min. was required to take the readings at each heat flux. Either before or after the run the voltage across the tube, the shunt voltage, and the tube current were measured.

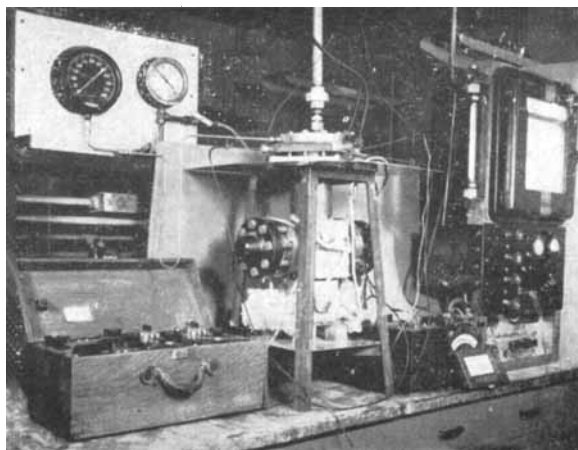


Fig. 1. General view of the apparatus.

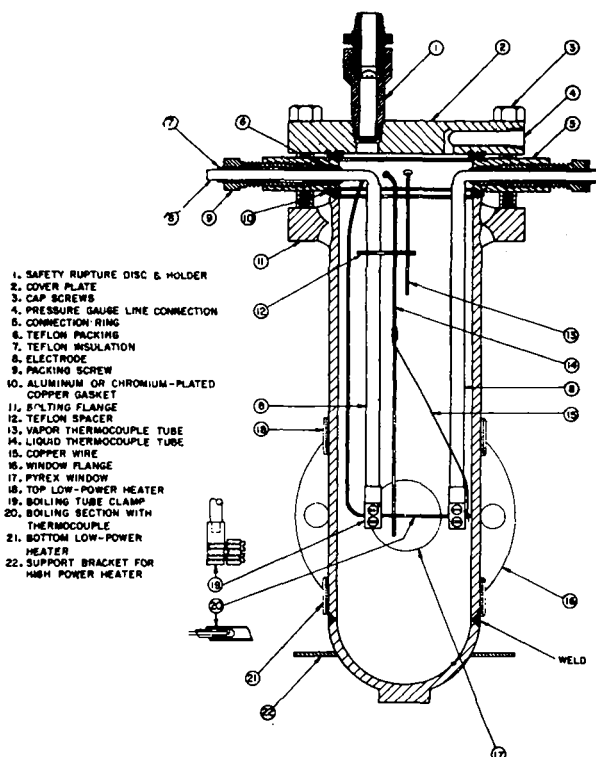


Fig. 2. Sectional view of the pressure vessel.

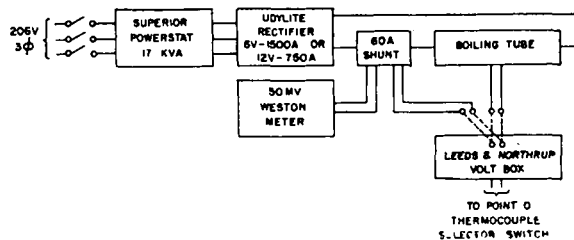


Fig. 3. Boiling-tube power supply.

If the liquid thermocouple voltage indicated a change, the current through the low-power heater was altered accordingly. When an adjustment was made, the new value of either the voltage or current was recorded, and thus the liquid temperature was maintained constant to within 2°F. and usually within 1°F.

Removing the insulation from around the vessel made it possible to dissipate all the heat generated in the boiling tube even when boiling Freon 113 at 117°F. At 450°F. with all the insulation in place it was necessary to add about 400 watts to maintain the temperature.

The lowest value of the heat flux at which readings were taken was usually 8,000 to 12,000 B.t.u./(hr.)(sq. ft.). At this heat flux the tube was still boiling, and at the lower pressures it was possible to count the number of bubble columns. In no case was the heat flux lowered to such a value that boiling ceased during a set of measurements at constant pressure.

Normally the tube was allowed to boil overnight and the atmospheric run repeated before measurements were taken at higher pressures.

Pressure Runs

The pressures to be run were selected on the basis of giving approximately equal reductions in the value of the difference between the surface and the liquid-saturation temperatures. From preliminary measurements the pressures were chosen as 15, 25, 40, 65, 115, 265, and 515 lb./sq. in. abs. For benzene and Freon 113 the two highest pressures were chosen as 216 and 365 lb./sq. in. abs. This was done for Freon 113 so as to not exceed the 495 lb./sq. in. critical pressure and for benzene so as to not exceed the 482°F. limitation of the Teflon packing used.

A complete set of pressures was run at one time to give as consistent data as possible. Consecutively higher pressures were used because it was easier to heat than to cool the vessel.

The high-power heater was used to increase the pressure. Between 15 and 30 min. was required to increase the pressure one step. The tube current was turned off during the heating because of the violent boiling caused by the high-power heater. After the heater was turned off, the boiling was allowed to subside before the tube current was turned on.

When the tube current was turned on, it was increased in steps to approximately the same maximum value as at atmospheric pressure. Preliminary readings were taken while the low-power heaters were being adjusted to give the desired liquid temperature. The tube was allowed to boil 15 to 20 min. while this was being done, before a run was made.

The liquid level was not maintained constant for various pressures but was allowed to increase as the density decreased. The level at the highest pressure was calculated to be 3 to 4 in. higher than at atmospheric pressure for the various liquids. Preliminary data indicated that changes in level at atmospheric pressure showed no significant effect on the boiling.

Final Atmospheric Run

When the run at the highest pressure was completed, all heat to the vessel was

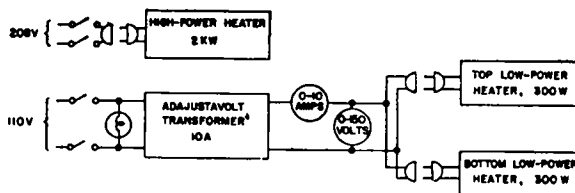


Fig. 4. Heater power supplies.

turned off and the vessel was allowed to cool. A day or so later the vessel was heated and another run was made at atmospheric pressure. In most instances air had leaked back into the vessel, probably because of differential contraction on cooling. It was necessary to purge the vessel again. During the pressure runs some vapor generally escaped through unnoticeable leaks, but never was the amount greater than 400 ml. This always left the tube submerged at least 1 in. in liquid.

After the atmospheric run the vessel was allowed to cool. The cover plate and the connector ring were removed, the liquid level was measured, and the appearance of the tube was noted.

Ripple Voltages

The root mean square ripple voltage across the boiling tube was measured and found to be 5.5% of the dc voltage. The ripple voltage, therefore, accounted for only 0.3% of the power dissipated by the direct current. It was neglected in computing the heat flux.

Boiling Tubes

One boiling tube was used to obtain the data on ethanol, benzene, and acetone and another to obtain the data on Freon 113. Two tubes were ruined in attempts to boil Freon 113 at too high heat fluxes. In film boiling the tube acquired a dark adherent coating which could not be removed by polishing with crocus cloth.

Treatment of the Data

The heat flux was computed from the measurements of the outside diameter of the tube, the length of the boiling section, the resistance of the boiling section, the calibration of the shunt millivolt meter

with its leads, and the reading of the shunt millivolt meter.

The temperature drop across the tube wall was calculated with the following assumptions:

1. Heat generation is uniform in the wall of the tube.
2. The cross section of the tube is uniform.
3. The temperature of the outside surface of the tube is constant.
4. There is no heat flow to the interior of the tube.

The resulting relationship is

$$T_i - T_o = \frac{q/A_o}{2k} r_o \left[1 - \frac{\ln(r_o/r_i)^2}{(r_o/r_i)^2 - 1} \right] \quad (1)$$

where T = temperature, r = radius, q/A_o = heat flux, and k = thermal conductivity. The subscripts i and o refer to the inside and outside of the tube wall. The thermal conductivity of stainless steel varies only 5%/100°F. according to Kreith and Summerfield (16). The thermal conductivity was taken at 212°F., and the temperature drop across the tube wall became

$$T_i - T_o = 3.78 \times 10^{-5} q/A_o \quad (2)$$

Experimental Accuracy

The temperatures are probably accurate to 0.2°F. and the heat flux is accurate to about 2.6% at 50,000 B.t.u./(hr.)(sq. ft.) and 5% at 10,000. The accuracy of the calculated temperature drop across the tube wall is probably better than 15%.

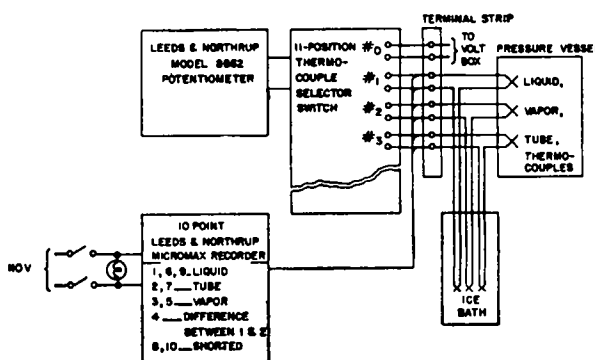


Fig. 5. Thermocouple circuit.

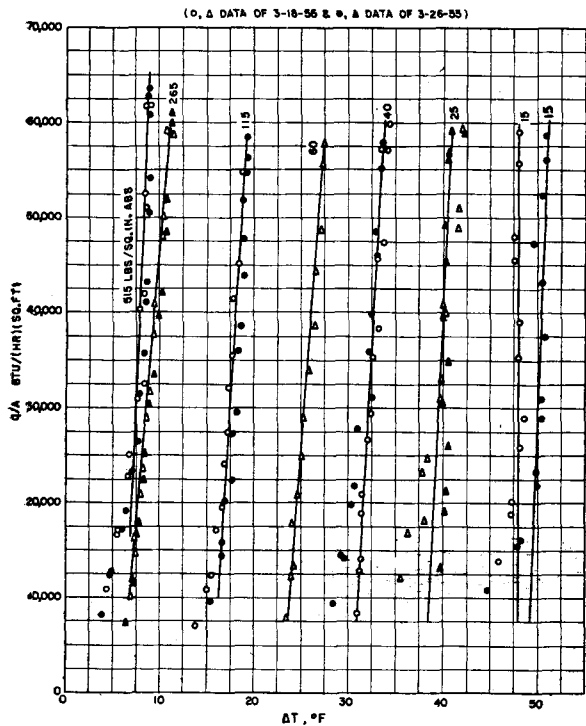


Fig. 6. Superatmospheric boiling data for acetone.

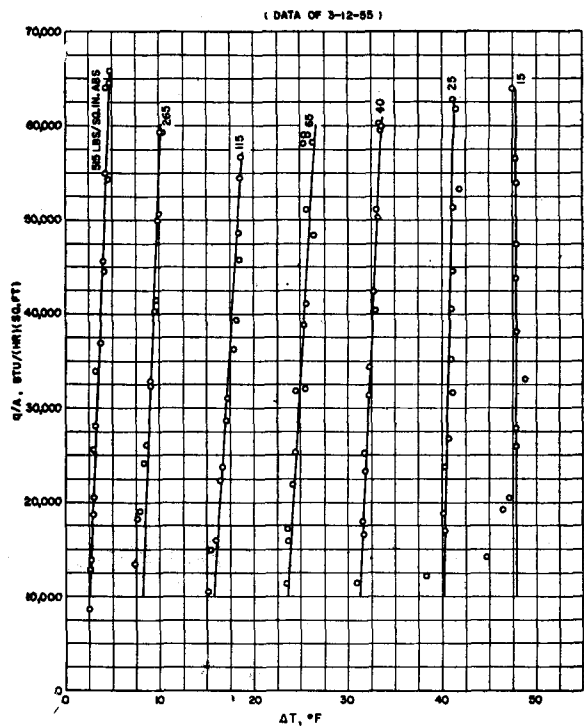


Fig. 8. Superatmospheric boiling data for ethanol.

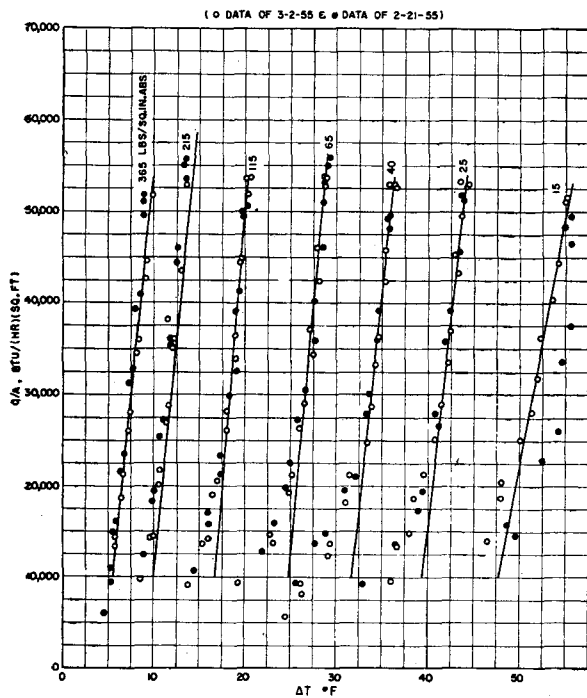


Fig. 7. Superatmospheric boiling data for benzene.

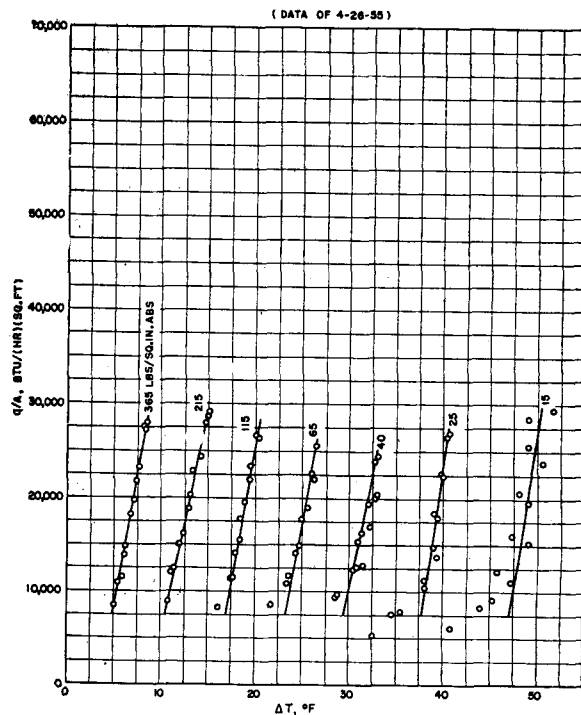


Fig. 9. Superatmospheric boiling data for Freon 113.

RESULTS

Plots of Data

Plots of heat flux vs. temperature difference at various pressures for acetone, benzene, ethanol, and Freon 113 are given in Figures 6, 7, 8, and 9. The results are given in Table 1.* Plots for atmospheric pressure are given separately in Figures 10 and 16 to show the shifts in the curves before, during, and after a sequence of superatmospheric pressure runs. In all the plots the temperature difference is the difference between the vapor-thermocouple temperature and the boiling-tube thermocouple temperature, with the difference corrected for temperature drop across the tube. The vapor temperature was used because it is believed to be a better measure of the liquid-saturation temperature. In no instance did the liquid- and vapor-thermocouple temperatures differ by more than 2°F. and usually by less.

The data were taken with both increasing and decreasing heat fluxes. Since the readings were not different except in a very few cases, the two sets of readings are not distinguished on the plots.

Two independent series of pressure runs were made with acetone. The agreement is good although a 7°F. difference exists between two of the atmospheric runs. Both series were preceded by boiling overnight. The temperature difference increased in one case and decreased in the other after the pressure runs.

Two series of pressure runs were also made with benzene. The liquid was the same but the surface was polished between runs. The atmospheric temperature difference decreased about 7° before the pressure run in the second set. Both series showed a 5°F. difference in the temperature difference between just before and after the pressure runs.

For ethanol at atmospheric pressure the temperature difference increased 3° overnight before the pressure run and then decreased the same amount after the run.

Freon 113 gave experimental difficulties. It film-boiled twice, once at 42,000 B.t.u./(hr.)(sq. ft.) and once at 60,000. Subsequently the heat flux was limited to about 30,000 but the bubbles were smaller than usual, the temperature differences low, and the surface was quickly fouled. This may have been due to small particles dispersed in the liquid. The first three samples taken from the shipping cylinder were cloudy. Finally, the vessel was given an especially good cleaning, all copper was replated with chromium, and clear liquid was charged in. The clear liquid was then boiled, and although it still gave a low temperature

difference, it gave a normal boiling appearance. A pressure run was made and on reboiling at atmospheric pressure the temperature difference had increased 13°. Then another pressure run was made and a subsequent atmospheric test showed the temperature difference to be unchanged. Tube-temperature fluctuations at atmospheric pressures were larger for Freon 113 than for other liquids.

Figures 11, 12, 13, and 14 compare the data of this investigation with those of Cichelli and Bonilla (7) for benzene and ethanol. Figure 14 also shows the data of Perry (21) for ethanol. For the data of Cichelli and Bonilla the steeper slopes do not occur until somewhat higher heat fluxes. Although the exact values of the two sets of data differ slightly, as would be expected, both sets of data show the same effect of pressure.

Figure 15 compares the data of Perry for acetone at atmospheric pressure with those of this investigation. Figure 16 compares the atmospheric results of Corty (8) for Freon 113 with those of this investigation. Corty boiled Freon 113 on both a highly polished copper surface and a highly polished nickel-plated surface but offered no explanation of the shift to lower temperature differences on subsequent days for the data from the nickel surface.

Surface-temperature Fluctuations

With nucleate boiling at atmospheric pressure the tube thermocouple did not show a constant temperature, as it did at higher pressures. The fluctuations were rapid and changed in less than a second at times. A plot of the thermocouple voltage against time made with a recorder showed random behavior, the fluctuations being more prominent at lower heat fluxes in the nucleate boiling region. Similar fluctuations have been reported in the literature (6).

With the tube in purely convective heat transfer the temperature varied over much larger values but more slowly. This was interpreted to mean that the tube temperature was a function of the circulation in the vessel and that the tube was acting like a hot-wire anemometer.

Tests were made to determine whether the temperature difference in nucleate boiling was also a function of circulation. Varying the heat input into the vessel, which would give more violent agitation, did not affect the nucleate-boiling temperature difference. This is in agreement with an observation by Addoms (1) and by Robinson and Katz (22).

When the tube-thermocouple voltage was measured, an average value was taken and the violence of the fluctuations noted. The actual temperature fluctuation of the surface would be greater than that indicated by the thermocouple for other than the slowest fluctuations.

At pressures above atmospheric no

fluctuations were noted. Because of the fluctuations at low pressures, no data were taken at pressures below atmospheric. Because of the more violent fluctuations at low heat fluxes, data were not taken in the convection or transitional regions.

Visual Observations

The effect of pressure was to make the bubbles rising from the tube smaller until at the highest pressures the bubbles appeared like a fog rising above the tube. At pressures up to 50 to 100 lb./sq. in. gauge a heat flux of 5,000 to 10,000 B.t.u./(hr.)(sq. ft.) gave 10 to 30 bubble columns along the 2-in. length of tube. At higher pressures the bubbles were too small to count in individual columns. The number of columns at the same heat flux increased with pressure.

At low heat fluxes and low pressures bubbles originated almost entirely at the top of the tube. With higher heat fluxes bubbles appeared at the bottom of the tube, and at the highest heat fluxes bubbles almost completely covered the surface of the tube. At the highest heat fluxes bubbles coalesced above the tube to form large volumes of vapor. When film boiling was encountered, the vapor surrounded the tube, and large volumes of vapor would break off and rise to the surface.

When Freon 113 first boiled, the number of vapor columns rising from the tube was far greater and the bubbles were smaller than for the other liquids. As mentioned previously, later runs showed the normal behavior.

The appearance of the surface after a series of pressure runs varied. In every case the surface still had a shine but was colored brown or tan of various intensities. The discoloration was not even and showed numerous pockmarks or small dark rings.

DISCUSSION OF RESULTS

Boiling Curves

In the plots of heat flux vs. the difference between the surface and the saturated-liquid temperatures, the most striking feature is the steepness of the curve in the nucleate-boiling region. Furthermore, the curve appears to be quite linear in this region. The effect of higher pressures is to displace the steep portion of the curve in a parallel manner toward lower temperature differences.

To examine this effect further, the available data were plotted and lines were drawn through the data at the higher heat fluxes so as to represent the data as well as possible. The reciprocal slopes of these lines were computed and are tabulated in Table 2.*

The reciprocal slopes were examined rather than the slopes because it is less

*Tabular material has been deposited as document 5497 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$3.75 for photoprints or \$2.00 for 35-mm. microfilm.

*See footnote in column 1.

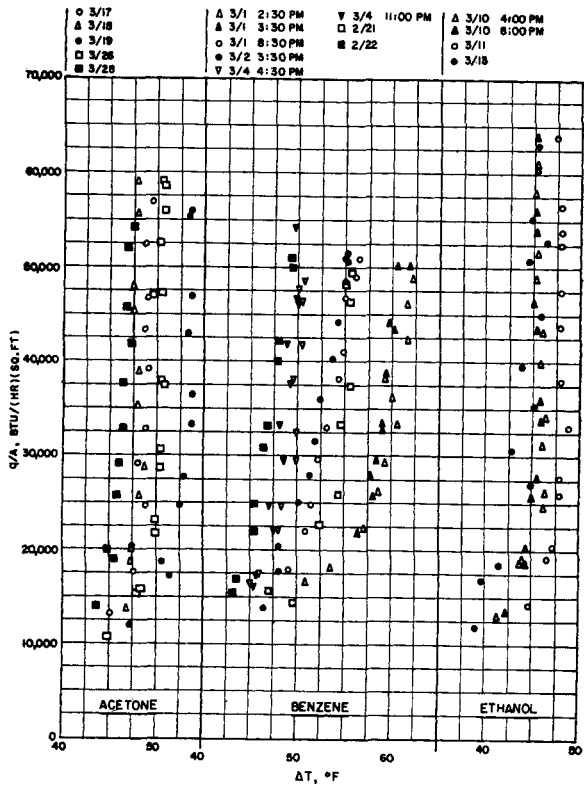


Fig. 10. Atmospheric boiling data for acetone, benzene, and ethanol.

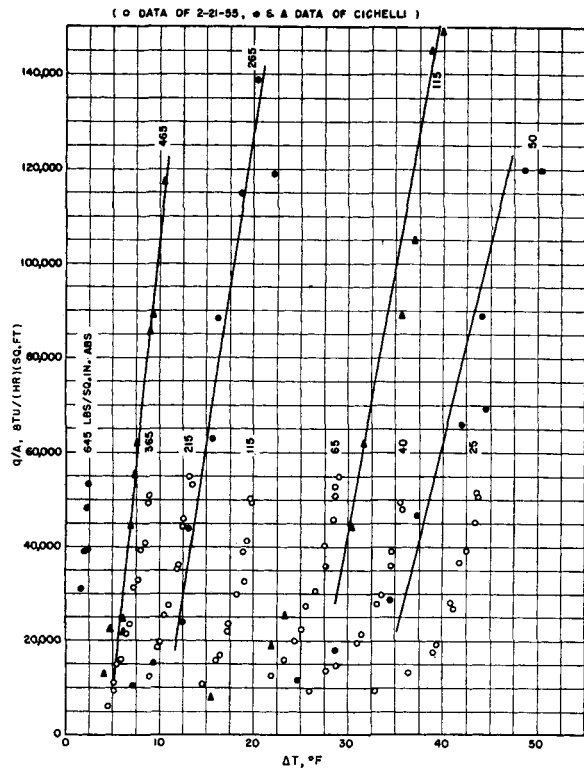


Fig. 11. Superatmospheric boiling data for benzene compared with data of Cichelli and Bonilla (7).

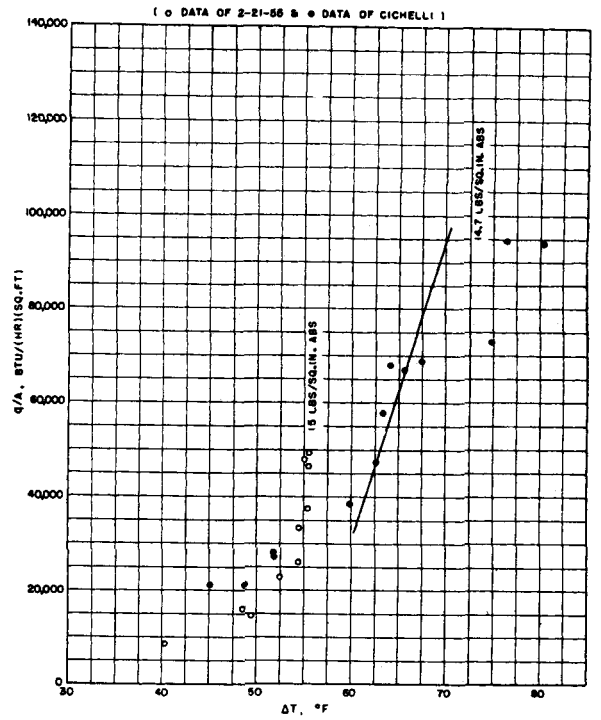


Fig. 12. Atmospheric boiling data for benzene compared with data of Cichelli and Bonilla (7).

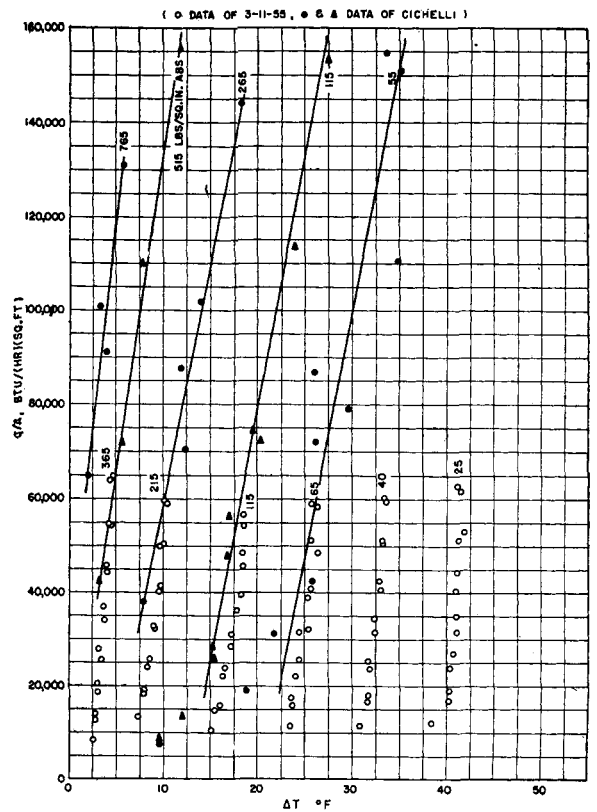


Fig. 13. Superatmospheric boiling data for ethanol compared with data of Cichelli and Bonilla (7).

misleading to consider the heat flux as the independent variable, the nucleate boiling region covering only a small range of temperature differences while the range of heat fluxes is not so limited. The reciprocal slopes are conveniently treated in terms of the increase in the temperature per 100,000 B.t.u./(hr.)(sq. ft.).

The reciprocal slopes were gathered from the data of Corty (8), Cichelli and Bonilla (7), Perry (21), Kaulakis and Sherman (15, 2), and this investigation. However, only the reciprocal slopes from Cichelli and Bonilla and this investigation apply to superatmospheric pressures.

The reciprocal slopes do not show a consistent decrease with pressure. Although some sets show a slight decrease, in no case is the decrease so great as the temperature difference; other sets remain relatively constant, and still others show a random variation. The large variability of the reciprocal slopes for the atmos-

range of values is from 5 to 20. An average value is about 10.

It should be kept in mind that the slopes in Table 2 calculated from the data of Cichelli and Bonilla are based on very few points and are thus subject to error. Table 2 gives the range of heat fluxes over which the data fall near the straight lines drawn through the data. If this range was limited by the range of the data, that fact is noted by an asterisk. The linearity of the steep portion of the curve extends above the range investigated here and appears from the data of Kaulakis and Sherman (15, 2), Perry (21), and Cichelli and Bonilla (7) to extend to almost the maximum heat flux.

The shifts with pressure of the heat-flux vs. temperature-difference curves will again be considered. Since a principal characteristic of the nucleate-boiling region is the necessity of slightly exceeding a certain temperature, it is not

ing to the temperature differences at a constant heat flux of 50,000 B.t.u./(hr.)(sq. ft.), or 25,000 in the case of Freon 113. The results are tabulated in Table 3. This pressure difference for each set of data varies by no more than a factor of 2, and the temperature difference varies by a factor of 8 to 10.

There appear to be two independent effects. One is the constant slope of the lines and the other their displacement. To separate the two effects it seems logical to extrapolate the lines to zero heat flux and to use the intercept as a measure of the displacement of the lines. The vapor-pressure difference calculated from this extrapolated temperature difference should be a better measure of the pressure difference to permit bubble growth than that evaluated at $q/A = 50,000$. Extrapolating to zero heat flux is the more feasible of several possible methods of attempting to separate variables (heat flux and pressure). One disadvantage is the departure of the data from a linear behavior at low heat fluxes. The extrapolation *does not imply* that the data should fall on the extrapolated line since at low heat fluxes convective heat transfer becomes predominant. Another more logical possibility might be to stop the extrapolation (or interpolation) just above the transition from nucleate boiling to convection. However, this transition is gradual and a transition region exists. No clear-cut definition exists which separates the nucleate-boiling region from the transition region. It is not logical to define nucleate boiling simply as the appearance of bubbles, since with very few bubbles heat transfer is still largely by convection. The pressure differences calculated from these temperature differences are shown in Table 3 and are plotted in Figure 17 against log pressure. In addition, the pressure difference divided by its average value in the relatively constant region for the respective liquid is plotted against log pressure in Figure 18. The pressure difference was normalized by dividing by an average value to take advantage of the decreased variance of an average, compared with a single, value.

This last plot brings all the data to a common curve except for one point at the highest pressure for acetone. An examination of the highest pressure ΔT vs. q/A curve for acetone reveals abnormal behavior, but the reason for this behavior is not known. The behavior of the pressure difference is to increase about 20% with an increase in pressure from atmospheric to about 100 lb./sq. in. Above this pressure the pressure difference decreases apparently toward zero at the critical pressure. Detailed analysis of the behavior of the pressure differences at pressures of 365 lb./sq. in. and above is complicated by the decrease in accuracy of the data and of the extrapolation to

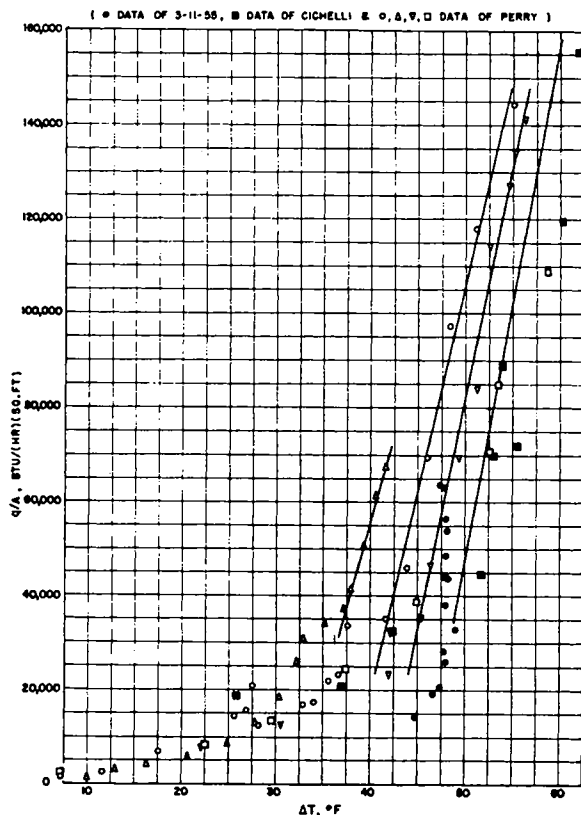


Fig. 14. Atmospheric boiling data for ethanol compared with data of Cichelli and Bonilla (7) and of Perry (21).

pheric data of this investigation is due to the fluctuations of the tube temperature.

The data of Kaulakis and Sherman and of Perry show exceptionally high values, as high as 40°F./100,000 B.t.u./(hr.)(sq. ft.), for the reciprocal slopes. However, Perry's own data show more values of 10 to 18 for the same liquids. If these extremely high values, as well as the zero values from this investigation, are excluded as not representative, the

difficult to reason that this temperature is required to permit the bubble growth and evolution associated with nucleate boiling. The most appropriate driving force for bubble growth is a pressure difference. More particularly, the pressure difference would be the difference in pressure between the vapor pressure of liquid at the temperature of the surface and the pressure of the system. For the data obtained in this investigation this difference was calculated correspond-

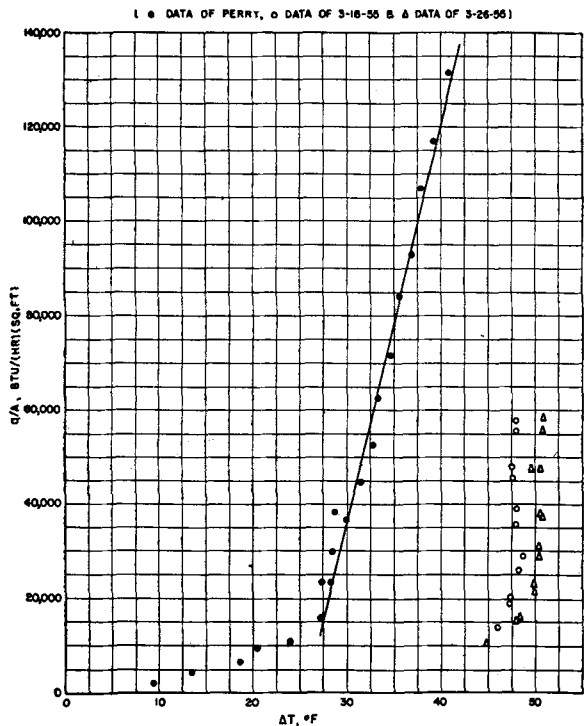


Fig. 15. Atmospheric boiling data for acetone compared with data of Perry (21).

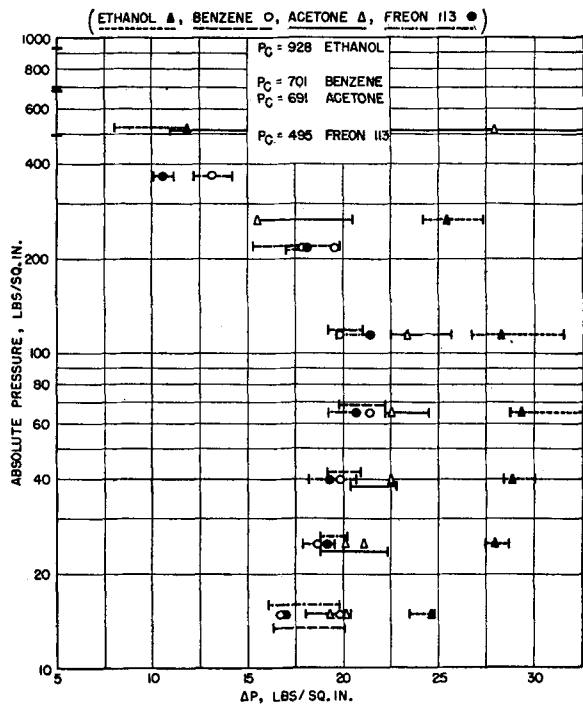


Fig. 17. The difference between the pressure and the vapor pressure of the liquid evaluated at extremely extrapolated values of the surface temperature at zero heat flux, the difference being plotted vs. pressure.

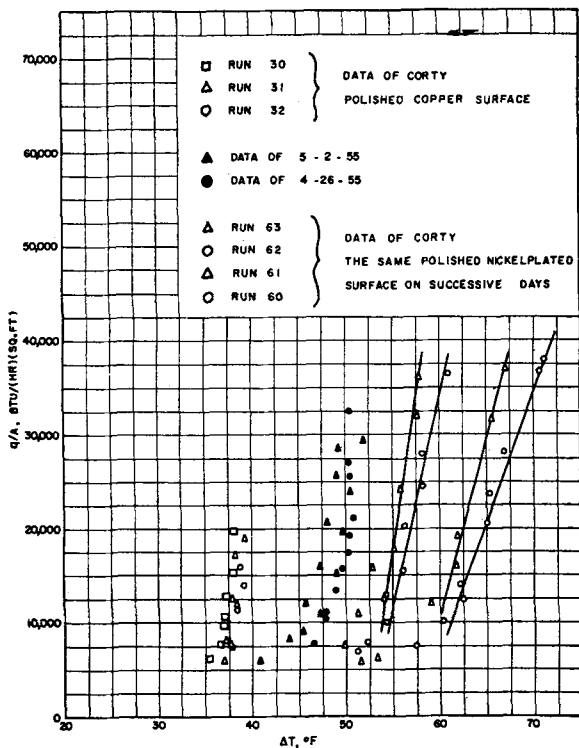


Fig. 16. Atmospheric boiling data for Freon 113 compared with data of Corty (8).

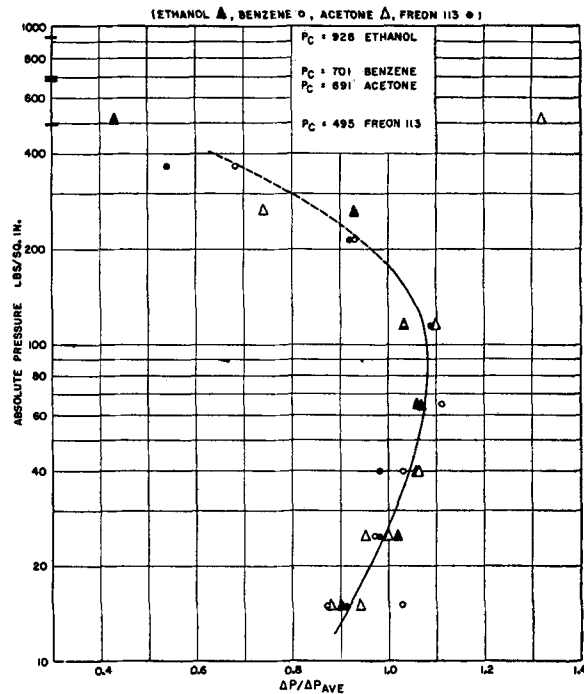


Fig. 18. Values at various pressures of the normalized difference between the pressure and the vapor pressure of the liquid at the surface temperature extrapolated to zero heat flux.

zero heat flux. At these pressures the temperature differences are less than 7.5°F.

Because the common curve of $\Delta P/\Delta P_{0.0}$ vs. log pressure represents data from four distinctly different organic liquids, it should apply for a wide range of other organic liquids. With the use of the curve, the vapor pressure of the liquid, the average slope of the boiling curve, and one nucleate-boiling temperature difference, the nucleate-boiling curve at any pressure between atmospheric and about two thirds of the critical can be predicted. As an example of this prediction the nucleate boiling data for *n*-pentane were predicted and compared with the data of Cichelli and Bonilla (7). The comparison is shown in Figure 19. The prediction, which agrees with the data to within about 2°F., was made on the basis of $\Delta T = 50^\circ$ at $q/A = 50,000$ for nucleate boiling at 22 lb./sq. in. abs.

The nucleate-boiling curves for an organic liquid can be estimated without any boiling data for the liquid. A value of 50°F. estimates to within 50% the value of the temperature difference at a heat flux of 50,000 B.t.u./(hr.)(sq. ft.) for atmospheric boiling of various organic liquids. This is seen by examining Table 4, which lists data from the literature. With this value of 50°F. the superatmospheric behavior can be predicted.

Theory

A theory has been proposed by Corty (8) and others (11) to account for the phenomenon encountered in nucleate boiling. It is reasoned that as a bubble leaves a surface it leaves behind a much smaller bubble with a radius of the order of magnitude of 10 μ in. The size of the bubble left behind is the all-important factor. It is its size that determines what specific temperature the surface temperature must exceed to maintain nucleate boiling. Perhaps several small bubbles are left behind by the departing bubble. According to capillary theory the excess pressure inside a spherical bubble is

$$\Delta P = \frac{2\sigma}{r} \quad (3)$$

This pressure difference must be exceeded to cause growth of the bubble.

An important fact which supports this theory is that the surface temperature can exceed the temperature usually giving nucleate boiling for a time without the occurrence of boiling. This commonly occurs with increasing heat flux before boiling has started. Then some portion of the surface starts to boil and the boiling quickly spreads across the surface. Such behavior was observed in this investigation and by others (3, 8).

Still further support for the theory is the way in which bubbles rise from particular points on the surface. The behavior is as if a departing bubble left

TABLE 2. VALUES OF RECIPROCAL SLOPES AND TEMPERATURE DIFFERENCES

Temperature, °F.	Pressure, lb./sq. in. abs.	$\frac{d(\Delta T)}{d(q/A)} 10^5$	$\Delta T, ^\circ\text{F.}$ $q/A = 50,000$	Range of heat flux $(q/A)(10^{-3})$
Acetone (3/19/55)				
418	515	3.8	8.4	15 to 60*
345	265	7.0	10.4	15 to 60*
270	115	6.0	18.7	15 to 60*
236	65	7.7	27.0	15 to 60*
191	40	5.4	33.9	15 to 60*
162	25	0	41.6	15 to 60*
134	15	0	47.6	15 to 60*
	15	2.2†		
Acetone (3/26/55)				
418	515	3.2	8.8	15 to 60*
345	265	7.2	10.7	15 to 60*
270	115	3.4	19.0	15 to 60*
191	40	6.1	32.8	15 to 60*
162	25	4.7	40.5	15 to 60*
134	15	1.7	50.2	15 to 60*
	15	3.8†		
Benzene (2/21/55 and 3/2/55)				
460	365	10	9.2	25 to 50*
397	215	10	13.2	25 to 50*
331	115	8.4	20.0	25 to 50*
280	65	9.0	28.5	25 to 50*
242	40	10.4	35.8	25 to 50*
209	25	10.4	43.7	25 to 50*
177	15	15.6	55.3	25 to 50*
	15	19.8	5.4	
	15	18.8	7.6	
	15	14.6	0	
Benzene: Cichelli and Bonilla (7)				
538	645	—	2.2	30* to 50*
491	465	5.2	7.1	20 to 120*
418	265	7.5	14.0	20 to 140*
331	115	9.0	30.5	40 to 150*
256	50	12.0	38.5	40 to 120*
177	14.7	15.8	63.0	40 to 70*
Ethanol				
409	515	4.0	4.3	10 to 60*
350	265	4.0	9.9	20 to 60*
286	115	6.4	18.6	10 to 60*
250	65	6.0	25.8	10 to 60*
223	40	5.0	33.2	15 to 60*
199	25	2.5	41.6	20 to 60*
175	15	0	46.5	20 to 60*
		7.5†		
Ethanol: Cichelli and Bonilla (7)				
449	765	5.7	—	70* to 130*
409	515	7.5	3.9	45* to 150*
350	265	9.9	9.0	40* to 140*
286	115	9.3	17.2	25 to 200*
239	55	9.6	25.2	30 to 150*
173	14.7	9.3	50.2	45 to 150*
Freon 113				
			$q/A = 25,000$	
376	365	17.0	8.0	10 to 30*
318	215	20.8	14.2	10 to 30*
259	115	17.0	19.9	10 to 30*
213	65	17.8	25.4	10 to 25*
179	40	20.0	33.0	10 to 25*
148	25	14.0	40.3	10 to 25*
119	15	15.4	50.0	10 to 30*
		0†		

*Upper or lower limit of the data (see text).
†Repeat runs where results were not reproducible.

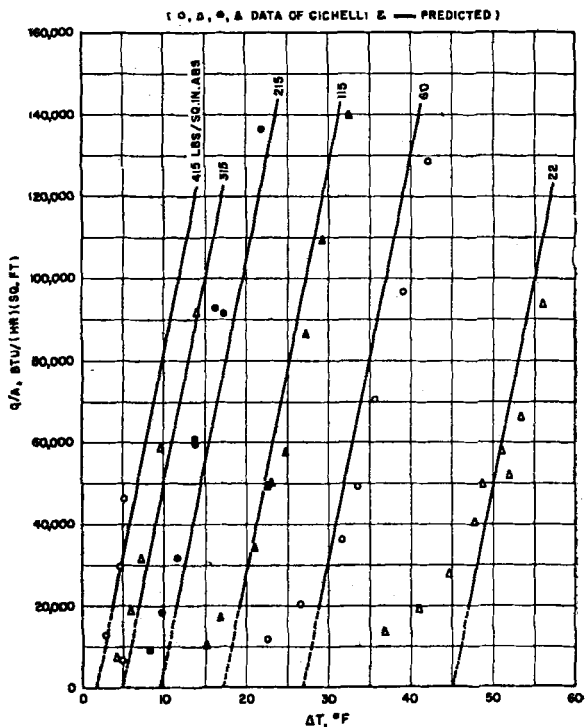


Fig. 19. Comparison of the predicted superatmospheric boiling data for *n*-pentane with data of Cichelli and Bonilla (7).

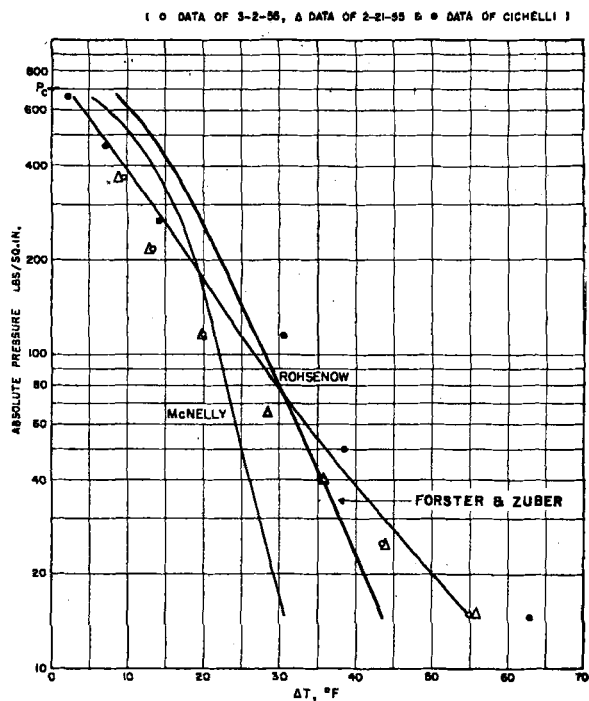


Fig. 21. Superatmospheric temperature differences at $q/A = 50,000$ B.t.u./(hr.)(sq. ft.) for benzene compared with Rohsenow's (23), Forster and Zuber's (12), and McNelly's (17) predictions.

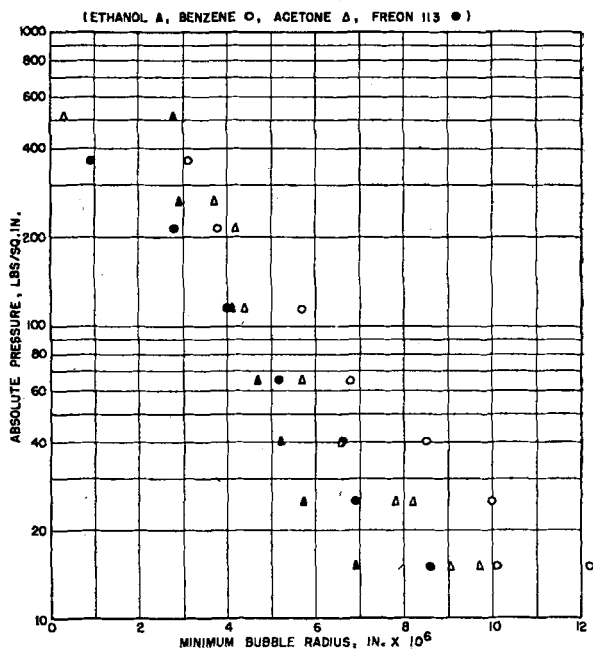


Fig. 20. Minimum radii of bubbles that are able to grow under the pressure differences shown in Figure 17.

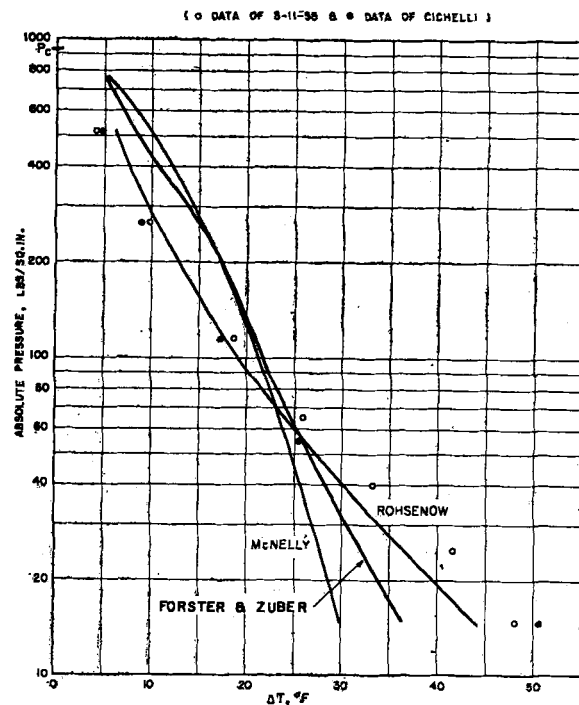


Fig. 22. Superatmospheric temperature differences at $q/A = 50,000$ B.t.u./(hr.)(sq. ft.) for ethanol compared with Rohsenow's (23), Forster and Zuber's (12), and McNelly's (17) predictions.

behind a smaller bubble from which the next departing bubble could grow.

A spherical bubble being assumed, the equilibrium radii corresponding to the pressure differences shown in Figure 17 were calculated. These are shown in Figure 20. At atmospheric pressure the radii range from 7 to 12 μ m. This is the same variation that Corty obtained (*n*-pentane, 13.5 μ m.; diethyl ether, 7.5; Freon 113, 6.9 and 5.0).

A decrease in radius with pressure is shown for all four liquids. At the highest pressure the radii for acetone and Freon 113 are much smaller than those for benzene and ethanol. This may not be significant because accuracy of the data is poor at high pressures. The radii always decrease with increasing pressure. The pressure difference from which these radii were calculated first increased with pressure from atmospheric to 100 lb./sq. in. and then decreased with further increase in pressure.

Bubble Size

The bubbles from the boiling surface were much smaller at higher pressures, particularly at pressures over 200 lb./sq. in.

Recent work of Van Wijk, Vos, and Van Stralen (25) showed that for binary mixtures certain compositions gave much smaller bubble sizes than others. They also found that the compositions which gave the smallest bubbles also gave the highest burn-out heat fluxes. Data of Cichelli show that the burn-out heat flux increases with pressure up to close to the critical temperature but then decreases. These observations seem to give a clue to the better understanding of burn-out heat flux.

Recent Correlations

Two correlations have been proposed recently which claim to predict the effect of pressure on nucleate boiling. Rohsenow (23) published the following correlation in 1952:

$$\frac{h}{k_L} \sqrt{\frac{g_c \sigma}{g(\rho_L - \rho_V)}} = \frac{1}{C_{s,f}} \quad (4)$$

$$\left[\frac{q/A}{\mu_L \lambda} \sqrt{\frac{g_c \sigma}{g(\rho_L - \rho_V)}} \right]^{0.667} \left[\frac{C_{L\mu_L}}{k_L} \right]^{-0.7}$$

McNelly (17) published an equation in 1953:

$$\frac{hD}{k_L} = 0.225 \left[\frac{Dq/A}{\lambda \mu_L} \right]^{0.69} \left[\frac{PD}{\sigma} \right]^{0.31} \left[\frac{\rho_L}{\rho_V} - 1 \right]^{0.33} \left[\frac{C_{L\mu_L}}{k_L} \right]^{0.69} \quad (5)$$

In these two equations h is the heat transfer coefficient, k the thermal conductivity, D a length which is arbitrary since it cancels out, g_c the version factor in Newton's law of $\tau = g$ the acceleration of gravity, σ the surface

TABLE 3. VALUES OF THE PRESSURE AND TEMPERATURE DIFFERENCES

Pressure, lb./sq. in. abs.	$q/A = 50,000$				Extrapolated to $q/A = 0$		
	ΔT , °F.	ΔP , lb./sq. in.	ΔT , °F.	ΔP , lb./sq. in.	ΔT , °F.	ΔP , lb./sq. in.	$\frac{\Delta P}{\Delta P_{atm}}$
Acetone	3/18/55		3/26/55				
515	8.4	37.5	8.8	39.5	6.3	28	1.32
265	10.4	28.6	10.7	29.4	5.8	15.5	.74
115	18.7	28.5	19.0	29.0	15.5	23.3	1.10
65	27.0	27.0			23	22.5	1.06
40	33.9	25.5	32.8	24.5	30.5	22.5	1.06
25	41.6	23.1	40.5	22.4	39	20.2	.95
					37.5	21.2	1.0
15	47.6	18.6	50.2	20.1	47.5	18.6	.88
					50	19.9	.94
Benzene	2/21/55		3/2/55				
365	8.8	25.6	9.6	27.9	4.5	13.1	.68
215	13.0	26.0	13.3	26.6	9.2	17.8	.93
					10	19.6	
115	19.9	25.5	20.1	25.8	15.7	19.8	1.03
65	28.5	25.1	28.5	25.1	24.3	21.4	1.11
40	35.8	23.4	35.8	23.4	30.7	19.8	1.03
25	43.8	21.2	43.6	21.1	38.5	18.7	.97
15	55.6	20.7	55.0	20.4	46.6	16.7	.87
					53.0	19.8	1.03
Ethanol							
515	4.3	23.3			2.2	11.8	.43
265	9.9	33.2			7.7	25.4	.93
115	18.6	35.3			15.2	28.3	1.03
65	25.8	33.4			23.0	29.3	1.07
40	33.2	31.5			31.0	28.9	1.06
25	41.6	29.6			40.0	28.0	1.02
15	46.2	24.6			48.0	24.6	.90
Freon 113	$q/A = 25,000$						
365	8.0	23.5			3.6	10.6	.54
215	14.2	29.8			8.8	18.1	.92
115	19.9	27.7			15.6	21.4	1.09
65	25.4	24.3			22.0	20.7	1.06
40	33.0	23.4			28.0	19.3	.98
25	40.3	21.6			36.7	19.2	.98
15	49	19.6			45.9	17.9	.91
	50.6	20.6					

tension, ρ the density, q/A the heat flux, μ the viscosity, λ the latent heat of vaporization, C the heat capacity, and P the absolute pressure. $C_{s,f}$ is a constant depending upon both the liquid and the surface. The subscripts L and V refer to the liquid and vapor, respectively.

Forster and Zuber (12, 24) published an equation which they derived to correlate nucleate boiling data and which they tested only at maximum heat flux. Perkins and Westwater (20) compared boiling data predicted from the Forster and Zuber equation with experimental data that they obtained for nucleate boiling of methanol at atmospheric pressure. The Forster and Zuber equation is

$$\left[\frac{C_{L\rho_L} \sqrt{\pi \alpha_L} q/A}{k_L \lambda \rho_V} \right] \left[\frac{2\sigma}{\Delta P} \right]^{1/2} \left[\frac{\rho_L}{g_c \Delta P} \right]^{1/4} = 0.0015 \left[\frac{P_L}{\mu_L} \left(\frac{C_{L\rho_L} \Delta T \pi \alpha_L}{\lambda \rho_V} \right)^2 \right]^{0.62} \left[\frac{C_{L\mu_L}}{k_L} \right]^{0.33} \quad (6)$$

Here ΔT is the temperature difference between the surface and the liquid saturation temperature, α is the thermal

diffusivity, and ΔP is the pressure difference between the equilibrium vapor pressures corresponding to the temperatures in ΔT .

For comparison of these correlations with data obtained here, a plot of the temperature differences at a heat flux of 50,000 B.t.u./(hr.)(sq. ft.) vs. log pressure was prepared. Figure 21 shows the plot for benzene and Figure 22 for ethanol. Also plotted are interpolated values from the data of Cichelli and Bonilla. The physical properties to evaluate the equations were taken from Mesler (18).

Rohsenow's equation shows the best agreement. To use Rohsenow's equation the value of $C_{s,f}$ must be evaluated experimentally. Values of $C_{s,f}$ proposed by Rohsenow to fit the data of Cichelli and Bonilla were used for Figures 21 and 22. These values have a 5.5-fold variation, which he attributes to undeterminable surface factors.

Both Rohsenow's and McNelly's correlations at constant pressure are of the form

$$\Delta T = \text{constant } (q/A)^n \quad (7)$$

where n is 0.333 for Rohsenow's and 0.31 for McNelly's correlation. Accordingly,

the quantity $[d(\Delta T)]/[d(q/A)]$ at constant heat flux varies as ΔT whereas for the data of this investigation the quantity was shown to be almost independent of ΔT .

The predicted value of the reciprocal slope at a heat flux of 50,000 B.t.u./ (hr.) (sq. ft.) decreases from 33.3°F./100,000 B.t.u./ (hr.) (sq. ft.) at $\Delta T = 50^\circ\text{F.}$ to 6.7 at $\Delta T = 10^\circ\text{F.}$

CONCLUSIONS

The results of this investigation substantiate the fact that higher pressures always reduce the difference between the surface and the liquid-saturation temperatures at a constant heat flux in nucleate boiling.

In this study it was determined that the nucleate-boiling data for organic liquids are well represented by straight lines on a *linear* plot of heat flux vs. the temperature difference. This observation is verified by data in the literature as well as by data of this investigation. In the transitional region between the convection and nucleate-boiling regions the temperature differences increase more rapidly with increasing heat fluxes than in the nucleate-boiling region. Also, close to the maximum heat flux the increase is more rapid.

The reciprocal slopes of the lines representing nucleate-boiling data are in the range of from 5° to $20^\circ\text{F./100,000 B.t.u./ (hr.) (sq. ft.)}$. An average value is about 10. They are, at least to a first approximation, independent of pressure.

The effect of pressure is to shift the lines representing nucleate boiling to lower temperature differences. Extrapolating the nucleate-boiling lines to zero heat flux makes it possible to consider separately the effect of pressure and the effect of heat flux on the temperature difference.

The pressure difference between the pressure of the system and the vapor pressure of the liquid at the surface temperature, extrapolated to zero heat flux, behaves in a regular manner. This pressure difference increases about 20% between atmospheric pressure and about 100 lb./sq. in. and then apparently tends to zero at the critical pressure. The behavior, which is not shown by water, is illustrated in Figure 18.

Corty (8), on the basis of a theory which he formulated, suggested that a pressure difference such as is defined here would behave somewhat as it does. His theory supposes that departing vapor bubbles leave behind much smaller bubbles attached to the surface. The temperature of the surface must be high enough so that the vapor pressure is great enough to permit the small attached bubbles to grow.

By taking the reciprocal slopes of the lines representing the nucleate boiling data as $10^\circ\text{F./100,000 B.t.u./ (hr.) (sq. ft.)}$

and by using the aforementioned behavior of the pressure difference, one can predict the temperature differences in nucleate boiling at pressures from atmospheric to about two-thirds the critical pressure. The prediction requires either a knowledge or an assumption of a nucleate-boiling temperature difference at some pressure and heat flux. A value of 50°F. estimates to within 50% the atmospheric nucleate-boiling temperature difference at a heat flux of 50,000 B.t.u./ (hr.) (sq. ft.) for organic liquids. This prediction does not require a knowledge of any of the physical properties except vapor pressure.

Rohsenow's (23) equation adequately predicts the effect of pressure on the nucleate boiling of the organic liquids studied in this investigation, for which physical-property data are available at superatmospheric pressures. McNelly's (17) and Forster and Zuber's (12) equations give poorer predictions particularly in underestimating temperature differences at lower pressures and overestimating temperature differences at higher pressures.

The effect of superatmospheric pressure on the appearance of nucleate boiling is to make bubbles smaller. At 350 to 500 lb./sq. in. the bubbles are almost too small to be seen individually.

Experimental results obtained showed the importance of repeating boiling runs and of being able to take the data over a time period which is short compared with

the time over which random variations are obtained.

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TABLE 4. VALUES OF NUCLEATE-BOILING TEMPERATURE DIFFERENCES AT ATMOSPHERIC PRESSURE

	$q/A = 25,000$ B.t.u./ (hr.) (sq. ft.) $\Delta T, ^\circ\text{F.}$	$q/A = 50,000$ B.t.u./ (hr.) (sq. ft.) $\Delta T, ^\circ\text{F.}$
This investigation		
Acetone		46 to 54
Benzene		49 to 62
Ethanol		44 to 48
Freon 113	48 to 51	
Cichelli and Bonilla (7)		
Benzene		61 to 67
<i>n</i> -Pentane (22 lbs./sq. in.)		49 to 51
<i>n</i> -Heptane		38 to 48
Ethanol		50 to 53
Kaulakis and Sherman (15)		
Water		17 to 19
<i>iso</i> -Butanol		50
<i>iso</i> -Propanol		45
<i>n</i> -Butanol		38
Banchero, Barker and Boll (3)		
Oxygen		23 to 29
Corty (8)		
Freon 113	38 to 66	
<i>n</i> -Pentane	23 to 39	
Ether	36 to 50	
Perry (21)		
Acetone		32
Butanol		46
Ethanol		39 to 49
Water		21 to 25

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