Observations on Boiling Carbon Tetrachloride from Surfaces

ROBERT L. NICKELSON,[1] and GEORGE W. PRECKSHOT
University of Minnesota, Minneapolis, Minn.

A GREAT DEAL of research on the boiling of fluids has been done, but still there are no accurate methods for predicting pool boiling coefficients for a given situation. Different metallic surfaces, given the same pretreatment (*5*), in contact with boiling water in the presence of various naturally present organic impurities and dissolved gases, gave different fluxes for the same temperature excess. The same result was experienced with various polished surfaces and organic fluids (*2*). Flux curves were shifted to higher temperature excesses (*3*) for a metallic surface polished with finer emery grit. The size of the roughness as well as its character (*8*) is important in determining the flux from surface-liquid pairs. The presence of dissolved gases in the liquid increased the flux for a given temperature excess (*10*) at a particular surface. This effect is discussed in greater detail (*4*) in connection with bubble formation and growth. Additives to liquids and solids change the surface energy relationships and influence the boiling situation tremendously. Very few attempts have been made to assess the individual effects on nucleate pool boiling of the pure surface itself (*7, 15*); dissolved gases; surface roughness, its magnitude and character; and additives.

The present work has been undertaken with the view of eliminating the effect of adsorbed or dissolved gases on nonboiling natural convection and on pool-boiling nucleate heat transfer. Attempts have been made to hold surface roughness, as measured by a Profileometer, constant in order to gain some insight on the effects of the chemical nature of the surface. The results reported herein are for carbon tetrachloride boiling from solid copper, silver, and gold, or coated copper wires at system pressures of 0.5, 1, and 1.5 atm.

MECHANISMS

Sources of nuclei for steady production of bubbles during nucleate boiling. Submicroscopic bubbles of vapor or inert gases, in metastable equilbrium with the liquid may act as nuclei. As a first approximation the radius is given by the Thomson relation:

$$P - P_\infty = \frac{2\sigma}{r} = \frac{2\sigma\cos[\theta \pm \phi/2]}{d_1} \tag{1}$$

where the minus refers to Figure 1,*a*, and the plus sign refers to Figure 1,*b*.

In a well-degassed but normally superheated liquid, there are too few embryos arising at surfaces per second per milliliter, large enough to serve as nuclei.

Rupture of the liquid-metal interface at points of low adhesion is another possible source of nuclei. With the usual metals, free of greases and other films, this source is not adequate to supply the flux requirements.

Solid particles suspended in the liquid could probably initiate boiling if they were unwetted by the liquid. During nucleate boiling, sources are at the solid surfaces, and will probably not be sufficient to maintain the flux, particularly when the fluid is carefully purified.

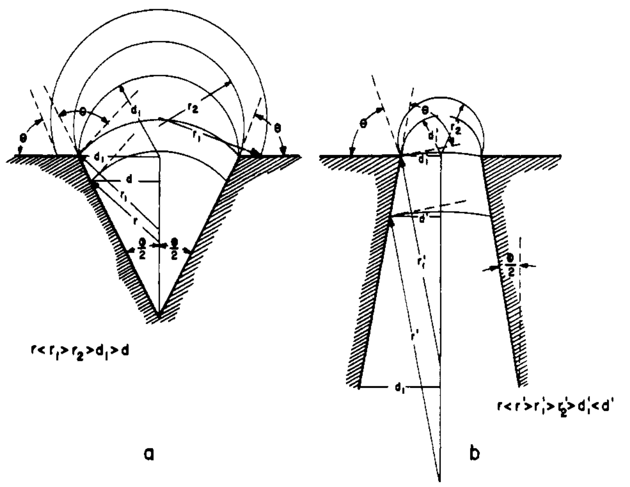


Figure 1. Diagram of cavities

Ions formed by radiation or by strong electric fields serve as nuclei (*6*). Under normal circumstances there are not enough formed by naturally occurring radiation at surfaces to account for the flux.

The fracture of liquid-solid bonds for the production of vapor-solid, vapor-liquid, and vapor-liquid-solid interfaces occurs at high superheats—many times higher than those prevailing under nucleate boiling conditions. The energy required to produce this fracture at perfectly smooth surfaces is very large indeed (*1*), much larger than that corresponding to the high superheats observed for nucleation from and at normal heat transfer surfaces. It is therefore necessary to consider reasonable conditions which assist this process. One may consider then models of idealized regular conical cavities as in Figure 1,*a* and *b*.

It is difficult to say precisely how vapor arises at the bottom of the cavity, 1,*a*. If as Figure 1,*a*, indicates, the radius of curvature approaches zero, residual impurities not removed by present techniques may produce low adhesion tension areas at the apexes of the cavities, and nucleation might easily so arise. A second reasonable possibility is that superheats approaching those at which spontaneous nucleation occurs are reached locally at the apexes of the cavities. That liquids possess finite spontaneous nucleation superheats has been demonstrated (*13*).

Once nucleation has occurred (Figure 1,*a*) the cavity becomes armed very rapidly, because r increases as the vapor interface rises toward the cavity mouth. This situation occurs spontaneously until the vapor-liquid interface reaches the cavity lip. Then the radius of curvature must pass through a minimum for the bubble to be produced at this site. This can occur when the superheat has reached a sufficiently high value to produce the pressure excess $P_x = P - P_\infty$ given by Equation 1 for $r = d_1$. Thus many cavities remain armed, awaiting the appropriate superheat.

The conical cavity pictured in Figure 1,*b*, cannot remain armed in the usual sense. If concave interfacial curvatures

---

[1] Present address, Montana State College, Bozeman, Mont.

are excluded, such a cavity can never remain armed; on the contrary, it can be quenched most readily. However, a combination of the two geometries with 1,*a* below 1,*b* can exist in the armed state. This situation is not shown but is easily visualized. A stable armed state will exist with the interface at d_1 and higher superheats will drive the interface to d_1', whereupon further superheating will be required for the production of a bubble at this site.

Thus steady-state nucleate boiling can continue only after nucleation has occurred within a surface defect. During this stage very high superheats indeed may be required, and often in highly localized areas. So far as is now known, cavities, pits, or surface depressions of small size are required to maintain a steady nucleate boiling flux from a surface. The locally nucleated region is believed to be spread by overspillage of vapor film or by vapor diffusion until the major portion, if not all, of the surface is armed with vapor-filled cavities. The mechanism of this diffusion is not proved, but it might take place along the interfacial planes or through the bulk as in intra- and intergranular diffusion in solid systems. Surface migration or diffusion is much more rapid than bulk diffusion, and perhaps this is the way the majority of the vapor proceeds to arm cavities.

The second stage of this process involves the growth of vapor bubbles from these sites and an increase in the number of sites. How this growth is controlled is not fully understood yet, but obviously, smaller and smaller cavities come into action as the temperature difference is increased. If the surfaces and liquids are kept carefully clean, the quenching of the smaller cavities occurs as the temperature difference decreases. Under such clean conditions, there is no hysteresis in the flux-temperature excess curves. The hystereses observed by many experimentalists can be due to lack of cleanliness or to reactions between the liquid and the surface.

APPARATUS AND PROCEDURE

Experimental heat transfer measurements were made from solid as well as coated surfaces of copper, solid silver, and gold wires to pool boiling carbon tetrachloride at 0.5, 1, and 1.5 atm. The essential features of the experimental equipment are shown schematically in Figure 2. The heat transfer surfaces were 18-gage solid copper, 20-gage solid copper, silver, and gold wires, and 18-gage copper wires vapor coated with copper, silver, or gold. These 12-inch wires were mounted horizontally in the boiler, and heated electrically by a 3 k.w., 6-volt direct current rectifier. To eliminate temperature gradient effects near the ends of the wires (*11*) only the central 6-inch section was used as a test section. The wires were thoroughly annealed, and the resistance of the test section was measured at various temperatures so that the wire could be used as a resistance thermometer. The resistance measurements were made with a Kelvin bridge circuit (*9*).

The boiler was 4 inches in diameter and about 15 inches long. Electrical connections were made through Kovar-glass seals. One-half-inch-diameter copper bus rods were silver-plated to reduce corrosion both inside and outside the boiler. Access tubes permitted the assembly and disassembly of wires in the boiler. Two condensers (Figure 2) maintained the proper flow of condensate and assisted in the coarse control of pressure. The fine control of pressure was achieved with a manometer-controlled bare wire immersion heater in the pressure control bulb. The control was such that only the shape of the mercury meniscus changed, with the pressure variation estimated at < 0.1 mm. of mercury.

The balance of the equipment consisted of a liquid degasser, and mercury diffusion and mechanical vacuum pumps. These were connected to produce vacuums of the order of 10^{-5} mm. of mercury. Glass seals and break-outs permitted the easy closing and opening of certain portions of the system. The major portion of the system was enclosed in bake-out boxes for the removal of absorbed gases and volatile films.

The experimental procedure was carefully arranged to prepare clean surfaces and bring them in contact with pure, gas-free carbon tetrachloride. The wires annealed at 850° F. and calibrated over the range of 170° to 270° F. to detect temperature changes at ±0.05° F. These were cleaned and

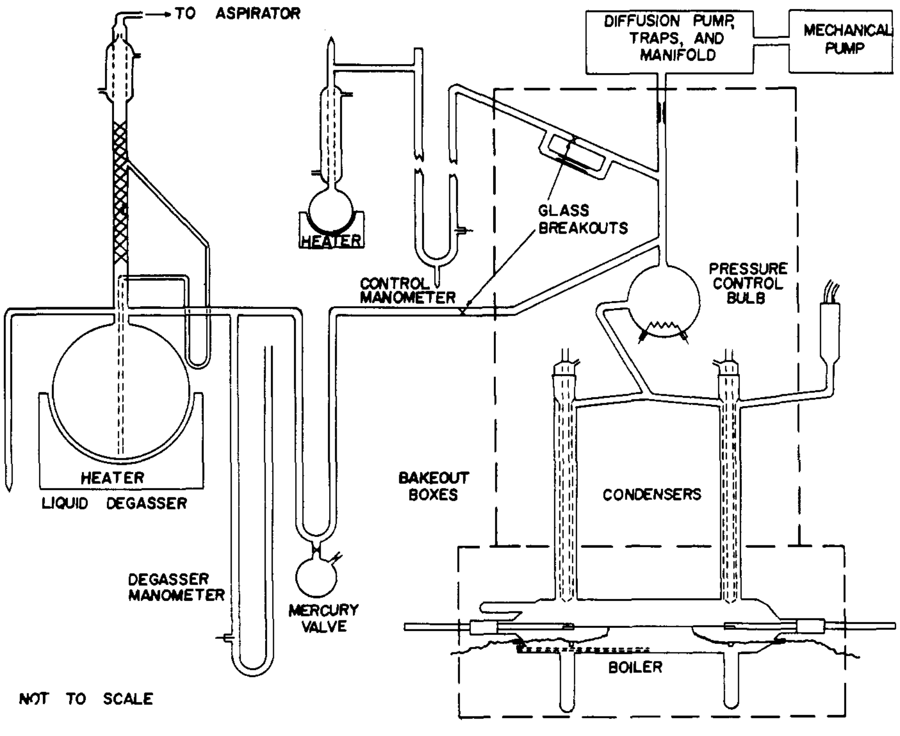


Figure 2. Sketch of apparatus

inserted in the boiler which was degassed for 4 hours at 850° F. and 10^{-6} mm. of mercury. The system was cooled to 400° F., and the surfaces were reduced in a hydrogen atmosphere before being re-evacuated and again degassed at 850° F. While this was taking place, the Eastman spectroscopic grade carbon tetrachloride was fractionated to remove absorbed gases and impurities. The device shown in Figure 2 was provided with a side arm vapor injector to eliminate bumping at 200 mm. of mercury, particularly as the liquid became purer. The overhead gases and a little carbon tetrachloride were taken off through a critical flow orifice to prevent back-diffusion of gases. Degassing was carried out for more than 24 hours.

The liquid degasser pressure was raised to 800 to 850 mm. of mercury prior to the introduction of carbon tetrachloride into the highly evacuated boiler. Then sufficient carbon tetrachloride for the heat transfer measurements was distilled into the boiler at pressures of 300 to 800 mm. of mercury. The pressure was controlled by adjusting the bake-out box temperatures, the condenser water flow rates, and the settings on the pressure-regulating device.

All solid test wires were given the same pretreatment. Grease was removed with acetone and other surface materials were removed with a 1-minute etch in a 25 volume % aqueous solution of nitric acid. The potential leads were 30-gage copper wires silver-soldered electrically to the test wire in an inert atmosphere. Care was taken that only a small fillet of zinc-free silver-solder formed at the junction and that neither wire was physically deformed. The copper and silver wires were oxygen-free. Other details are given elsewhere (*9*).

The surface roughnesses of wires were measured by a Brush Surfanalyzer and were found to be 2 to 4.5, 4 to 6, and 5 to 8 root mean square microinches for 18- and 20-gage copper and 20-gage silver and gold wires, respectively. These measurements were made longitidinally; the circumferential roughness was several orders of magnitude larger, indicating the presence of draw marks. Pretreated 18-gage copper wires were vapor-coated in a modified Distillation Products Vapor-Coater unit described in some detail earlier (*12*).

RESULTS AND DISCUSSION

Natural Convection. The nonboiling natural convection data for both 18- and 20-gage wires are shown in Figure 3. These data deviate less than 2% from the approximate natural convection correlations. The maximum error in heat flux is estimated at 1.3%, and the maximum estimated error in the measurement of temperature excess is ±0.8° F. Considering these estimates the agreement is excellent, and this in effect proves the reliability of the method of measurement. These natural convection data were used in the calculation of the nucleate pool boiling contributions per active nucleus.

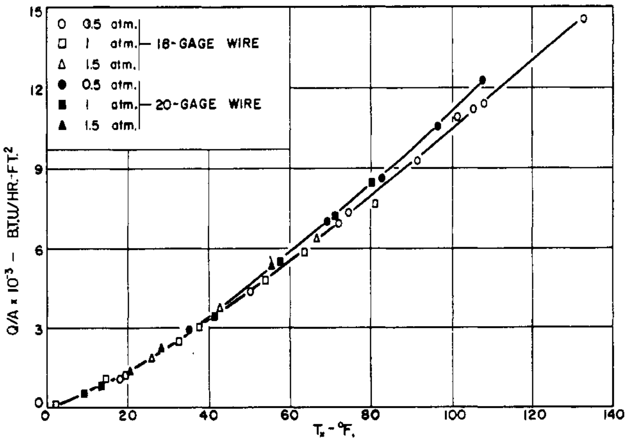


Figure 3. Natural convection heat tranfer data

There is about a 6% increase in flux from the 20-gage wire over that from the 18-gage wire at the same temperature. This is in agreement with that of the correlations. There is no effect of pressure because the Grashof-Prandtl product is essentially temperature independent for carbon tetrachloride. Neither the surface roughness nor the chemical nature affects the heat transfer in nonboiling natural convection.

Nucleate Boiling. Great effort was required to prepare the surfaces and liquid, so the nucleate pool boiling heat transfer data were obtained only to about 50% of the estimated burn-out flux which at 1 atm. was 70,000 B.t.u. per hour per square foot. A representative run for an 18-gage copper wire is shown in Figure 4. Several important observations can be made here. Boiling heat flux curves shifted with boiling time toward higher temperature excesses, and this shift was accompanied by a slight tarnishing of the surfaces. No shift was noticed when there were long periods without boiling. The tarnishing was probably due to a chemical reaction of the metal with the liquid or its trace impurities. There was no shift with gold wires, only a slight shift with silver wires, and a very definite shift with copper wires. Another indication that a chemical reaction was taking place was that the shift was accelerated at higher temperatures. The tarnishing could affect the boiling heat transfer properties in any or all of several ways. The products resulting from the tarnishing reaction could change the size of the cavities from which bubbles arose, or could affect the solid-liquid contact angle, or could add a thin but relatively nonconducting film on the surface.

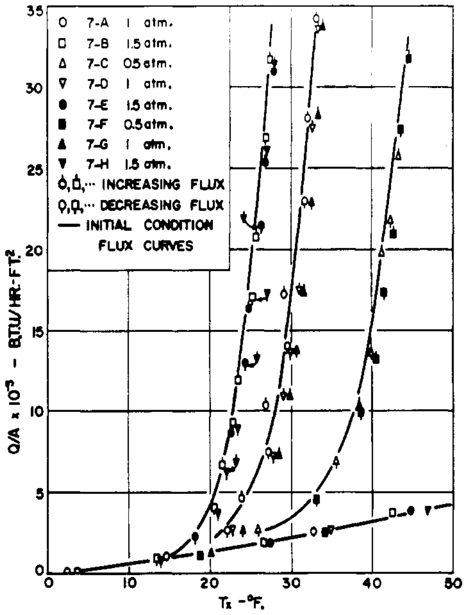


Figure 4. Typical nucleate boiling flux curves for 18-gage copper wires

To have data representing a known initial surface, the boiling results were extrapolated to zero boiling time by measuring the shift of values of T_x as a function of boiling time and extrapolating the values to zero boiling time. This approach seems reasonable. The boiling periods for the parts of run 7 in Figure 4 ranged from 0.7 to 1.3 hours while the cumulative boiling time for runs 7A to 7H ranged from 1.1 to 7.5 hours. The initial-condition flux curves are shown as solid lines and the points represent actual data for the three pressures when shift took place after a finite boiling time. In subsequent comparisons of pure surface materials, only initial-condition flux curves were considered.

Flux curves for increasing flux are identical with those for decreasing flux, Figure 4. This is attributed to the clean surfaces and liquid used and has not been reported earlier. This result prevails even where shift has occurred, if there is no long boiling time between the experiments for increasing and decreasing flux measurements.

The variation of the boiling heat flux curves from one metal to another is shown in Figure 5. It is somewhat difficult to ascertain whether this effect is due to surface roughness differences, character of the roughness, or the chemical nature of the surface. The surface roughnesses of copper, silver, and gold wires were measured as 2 to 4.5, 4 to 6, and 5 to 8 root mean square microinches, respectively. However, in Figure 6 the heat flux curves were practically identical for a solid copper wire and one vapor-coated with copper. Their roughnesses were 2.5 to 4 and 5 to 7 root mean square microinches, respectively. The differences in order of the slopes of the flux curves in Figure 5 indicate that the effect is other than simple roughness. It is believed therefore that differences in the character of the roughness exist or that there is a strong effect of the chemical nature among the three wires shown in Figure 5. This is still to be established with certainty.

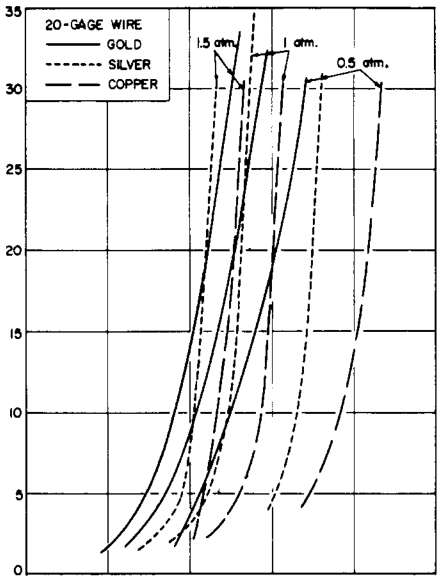


Figure 5. Nucleate boiling flux curves various metallic wires

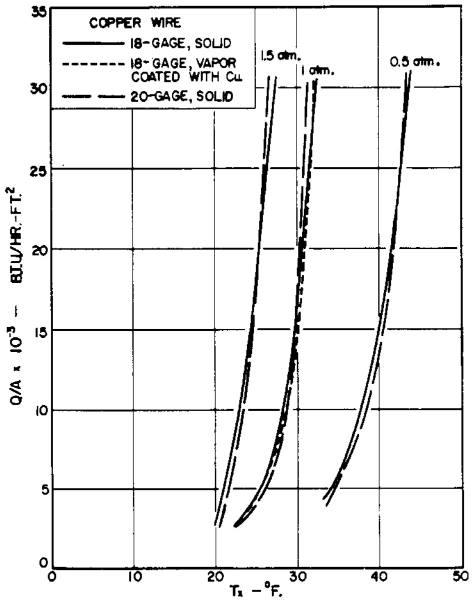


Figure 6. Effect of diameter on nucleate boiling flux

Copper wires vapor-coated with silver and gold were unstable under the conditions of the experiments, and no useful conclusions regarding the relative effects of roughness and chemical nature could be drawn from them. The heat flux curves from these coated wires were shifted to lower temperature excesses; but these were much smaller in magnitude than those shown in Figure 5. These heat flux results could be interpreted to be due to a greater surface roughness or surface area because the slopes of the flux curves are the same, and the coatings were visibly deteriorated. No further attempts were made to improve the quality of the vapor-coating to assess the effect of chemical nature.

The effect of diameter on nucleate boiling has been explored before. The results of this work indicate that there is little difference in nucleate boiling flux curves for 18- and 20-gage copper wires. These results, shown in Figure 6, are well within the errors in the measurement of temperature excess.

Nucleation was not studied as such, but the following incidental observations were made. Superheats up to the highest value of 140.3° F. were observed at 0.5 atm. and these observations could be repeated within a few minutes of one another. When nucleation took place, the greater portion of the wire was covered with a vapor film momentarily, thus arming all cavities which were later effective in nucleate boiling. At the higher pressures, somewhat lower superheats were observed before boiling took place. All these were equivalent to a pressure excess of approximately 3 atm. This requires a nucleus with a radius of 6×10^{-6} inch, which is an order of magnitude smaller than that for the active sites under nucleate boiling conditions. These observations show clearly that extraneous sources of nuclei such as gases and dust particles had been removed successfully. Apparently, there is no liquid-metal fracture as the flux is increased during nucleate boiling, but additional armed cavities make their contribution to the flux.

Active Nuclei Counts. Some of the earlier work had indicated that boiling was taking place from preferred sites. The early consideration in the present work suggested that the number of bubble sites would be an important consideration in obtaining useful criteria for nucleate boiling. The number of bubble sites could be counted when the fluxes were low, up to about 10% of the maximum flux, where they numbered 180 sites per square inch of area. These data are presented in Figure 7 for new surfaces or for surfaces for

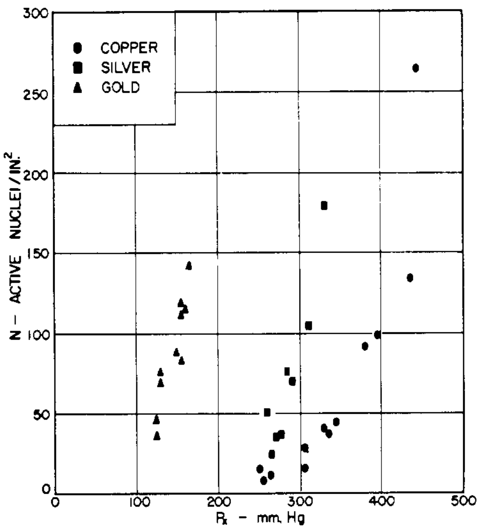


Figure 7. Nucleus population at various P_x

which the boiling flux curves did not shift. The abscissa is pressure excess, which is related to the cavity radius by Equation 1. The data for 0.5, 1, and 1.5 atm. are plotted for the 20-gage copper, silver, and gold wires, and there are some data for 18-gage copper wires. Referring to Equation 1, it is seen that P_x depends on σ, θ, d_1, and $\phi/2$. For the pressures concerned, σ and θ do not vary greatly. The scatter in Figure 7 then is probably due to a distribution of cavity half angles, $\phi/2$. As a first approximation then for this work, it is assumed that a narrow distribution of $\phi/2$ exists. Thus if P_x is only a function of d_1, the data for each metal are represented by a single curve. It is doubtful that this simplification can be made for a pressure range wider than given here.

An attempt was made to evaluate the contribution of each active nucleus (bubble site) to the over-all heat transfer, using the heat transfer data and the active nucleus counts. To obtain the nucleate boiling heat flux contribution per active nucleus, the normal natural convection heat flux corresponding to the temperature excess was subtracted from the total heat flux. This was then divided by the number of active nuclei. This procedure removed the large error at low nuclei center counts, where most of the heat is transferred by nonboiling natural convection. When the number of active nuclei becomes large, the subtraction of the natural convection heat flux has little effect on the heat transferred per active nucleus.

Whether or not the growth rates of bubbles are affected by surface tension and contact angles, they will be affected by the distance of one bubble column or active nucleus from another. One would then expect that the nucleate heat transfer per active nucleus will be a function of the active nucleus population.

In order that a variety of "surfaces" could be used, boiling data which showed a shift towards higher temperature excesses were used as well as those for fresh surfaces and those which showed no shift. Both the 18- and 20-gage wire data are considered together, and these are plotted in Figures 8 to 10 for the three system pressures. Here the nucleate heat transfer per active nucleus is plotted *vs.* the number of active nuclei per square inch for various values of P_x. These limited data do indicate the influence of nucleus population, the nucleate heat flux per active nucleus at constant P_x decreasing with nucleus population. This corresponds to varying surfaces with the same liquid. The data indicate a hyperbolic curve of the form:

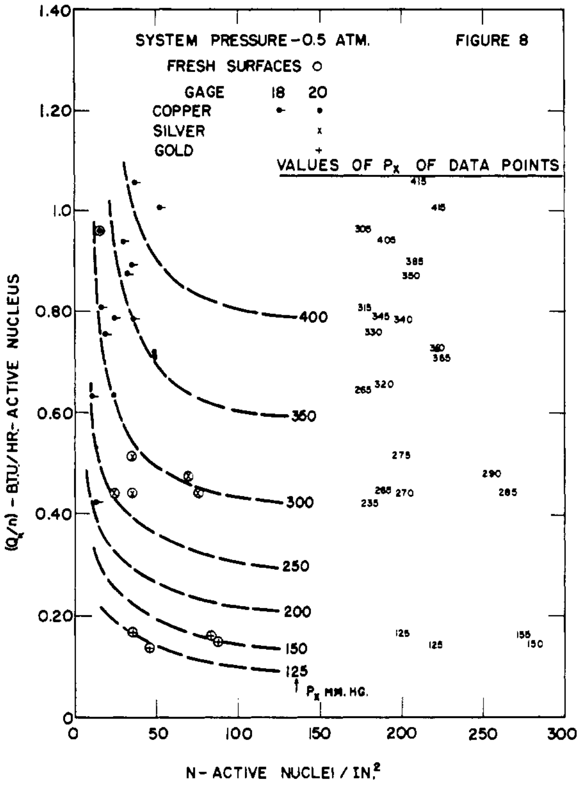
$$[(Q_n/n) - f(P_x, P)]N = p(P_x, P) \qquad (2)$$

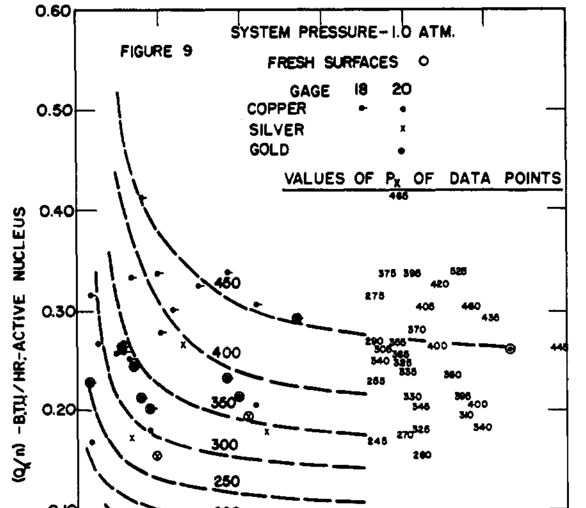
For $P_x = 445$ and $P = 1$ atm. the relation is:

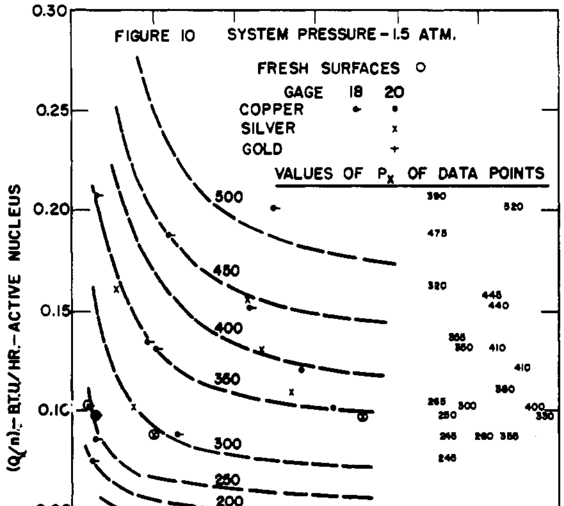
$$[(Q_n/n) - 0.235]N = 6.69 \qquad (3)$$

Equation 3 indicates that for a variety of surfaces with carbon tetrachloride at 1 atm., the nucleate boiling flux is proportional to the active nuclei or bubble sites. Not enough data of this kind were collected to determine con-

Figures 8, 9, 10. Nucleate boiling heat flux







stants for other P_x and P, and the above are presented only in an illustrative way.

The values of the nucleate contribution per active nucleus for a given pure metallic surface tend to group themselves together for a definite system pressure over a range of values of N. This suggests that (Q_n/n) is an important characteristic of pure metal surfaces and depends only on the system pressure. This is shown in Figure 11, which is a plot of (Q_n/n) for all pure surfaces for all three pressures. Considering the difficulties involved, the scatter of the (Q_n/n) values about a mean value for each of the pure metals at each of the pressures is not too serious. From this, one draws the conclusion that for pure surfaces and carbon tetrachloride at 1-atm. pressure, the nucleate boiling flux is proportional to the number of bubble sites.

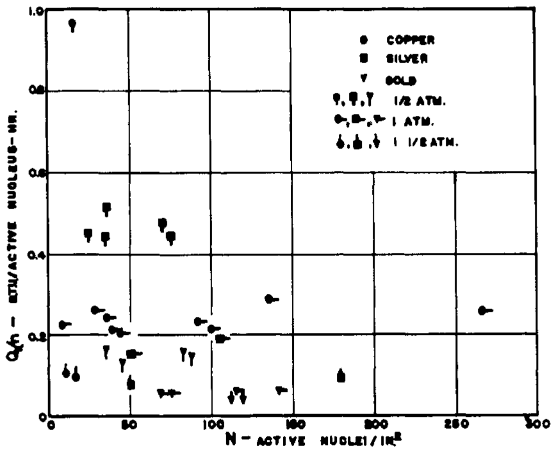


Figure 11. Nucleate flux contribution parameter for varying nucleus population

For a given pure metallic surface, at a specific system pressure, the nucleate contribution is essentially independent of pressure excess. Apparently the decrease in the nucleate contribution per active nucleus with N is counteracted by the effects of increasing pressure excess (also temperature excess). This above conclusion agrees with that of earlier investigators (*4*). The results in Figure 11 demonstrate the increase in nucleate contribution per active nucleus with decreasing pressure.

ACKNOWLEDGMENT

The authors acknowledge the financial support of the Atomic Energy Commission and the National Science Foundation for the experimental program. Both thank General Mills Inc. and Minneapolis-Honeywell Regulator Co. for assistance in making surface roughness measurements.

NOMENCLATURE

A = surface area, sq. ft.
d, d_1 = radius of surface cavity, ft.
f = nucleate boiling flux contribution per active nucleus at very high nucleus populations, a function of P_x and P, B.t.u. per hr.—active nucleus
N = number of active nuclei per sq. inch.
n = total number of active nuclei in test section surface
P = total system pressure or pressure within vapor bubble of radius of curvature r, mm. Hg.
P_∞ = external pressure on liquid, mm. Hg.
P_x = pressure excess, $P - P_\infty$, mm. Hg.
p = hyperbolic constant, a function of P_x and P
Q = heat flow, B.t.u. per hr.
Q_n = nucleate pool boiling heat flow, B.t.u. per hr.
r = curvature of vapor-liquid interface
T_x = temperature excess, ° F.
σ = surface tension
θ = contact angle
$\phi/2$ = conical cavity half angle

LITERATURE CITED

(1) Bankoff, S.G., "Ebullition from Solid Surfaces in the Absence of Pre-existing Gaseous Phase," 1956 Heat Transfer and Fluid Mechanics Institute, Standford University, Standford, Calif., June 1956.
(2) Bonilla, C.F., Perry, C.W., *A. I. Ch. E. Trans.* **37**, 685-705 (1941).
(3) Corty, C., "Surface Variables in Boiling," Ph.D. thesis, Department of Chemical Engineering, University of Michigan, Ann Arbor, Mich., 1951.
(4) Ellion, M.E., "Study of the Mechanism of Boiling Heat Transfer," Jet Propulsion Lab., California Institute of Technology, Pasadena, Calif. Memo. 20-88, 1954.
(5) Farber, E.A., Scorah, R.L., *Trans. Am. Soc. Mech. Engrs.* **70**, 369-84 (1948).
(6) Glaser, D.A., Rahm, D.C., *Phys. Rev.*, **97**, 474-9 (1955).
(7) Harrison, W.B., Levine, Zelvin, Thomas, F.A., Jr., Woodward, L.A., "Wetting Effects on Boiling Heat Transfer," Engineering Experiment Station, Georgia Institute of Technology, Atlanta, 1955.
(8) Mikhail, N.R., "Studies in Heat Transfer to Boiling Liquids at Low Temperatures," Ph.D. thesis, Imperial College of Science and Tech. University, London, September 1952.
(9) Nickelson, R.L., "Some Effects of Heat Transfer Surfaces Observed in Natural Convection and Nucleate Pool Boiling Heat Transfer," Ph.D. thesis, Dept. Chem. Eng., University of Minnesota, Minneapolis, Minn., 1957.
(10) Pike, F.R., Miller, P.D., Jr., Beatty, K.O., Jr., "Effect of Gas Evaluation on surface Boiling at Wire Coils," Gas Evaluation on Surface Boiling at Wire Coils," A. I. Ch. E. Heat Transfer Symposium, Preprint No. 2, St. Louis, Mo. 1953.
(11) Preckshot, G.W., Gorman, J.W., *Ind. Eng. Chem.* **50**, 837 (1958).
(12) Preckshot, G.W., "Effect of Chemical Nature of Heating Surfaces on the Heat Transfer Coefficients of Pool Boiling Liquids," U.S. At. Energy Comm., A.E.C.U.-3183 (December 1955).
(13) Wakeshima, Hiromu, Takata, Kazuo, *J. Phys. Soc. Japan* **13**, 1398-403 (1958).
(14) Westwater, J.W., Perkins, A.S., *A. I. Ch. E. Journal* **2**, 471-6 (1956).
(15) Westwater, J.W., Clark, H.B., Strenge, P.S., "Active Sites for Nucleate Boiling," A. I. Ch. E. Second National Heat Transfer Conference, Chicago, August 1958.

RECEIVED for review April 13, 1959. Accepted October 1, 1959.