

# PEAK NUCLEATE-BOILING HEAT FLUXES AND NUCLEATE-BOILING HEAT-TRANSFER COEFFICIENTS FOR LIQUID N<sub>2</sub>, LIQUID O<sub>2</sub> AND THEIR MIXTURES IN POOL BOILING AT ATMOSPHERIC PRESSURE

DAVID N. LYON

Low Temperature Laboratory, Departments of Chemistry and Chemical Engineering,  
University of California, Berkeley, California

(Received 15 September 1963 and in revised form 14 February 1964)

**Abstract**—Pool boiling heat-transfer coefficients and peak nucleate-boiling fluxes for N<sub>2</sub>, O<sub>2</sub> and their mixtures have been measured on a number of cylinders of gold, copper and several chemical films in a variety of surface textures or roughness. Nucleate-boiling coefficients have been found to be dependent upon cylinder orientation, as well as upon the surface character. Heat-transfer coefficients for a mixture were in all cases lower than for either pure component. Peak nucleate-boiling fluxes were found to be reproducible for any surface of constant character, and to depend upon cylinder orientation and chemical nature of the surface, but to be independent of surface roughness.

## INTRODUCTION

THIS PAPER represents data collected in this laboratory over a period of several years for nucleate-boiling heat transfer to liquid nitrogen, liquid oxygen and their mixtures together with observations on the effect of the chemical nature and the physical condition of the surface upon such heat transfer and upon the corresponding peak nucleate-boiling fluxes.

Since the low-boiling gases commonly referred to as "cryogenic" liquids are all stable with respect to chemical decomposition at temperatures at which they experience nucleate boiling, and since there will be no measurable chemical reaction between these substances and almost any solid surface at their boiling temperatures, these liquids are eminently suitable for studies in boiling where one wishes to maintain a surface of given chemical and physical characteristics over a long period of time. The heat-transfer coefficients themselves for these liquids are valuable in the design of cryogenic apparatus in addition to any value they possess for such light as they may shed on the fundamentals of the boiling heat-transfer process.

## PREVIOUS WORK

In previous work with liquid "air", N<sub>2</sub> and

O<sub>2</sub> in "pool" boiling, the power input often was insufficient to include the maximum or peak nucleate-boiling heat flux (pnbf) and frequently the heat flux for a given temperature difference varied by more than a factor of ten, indicating some major unrecognized variation in surface character.

Giauque *et al.* [1] reported values for nucleate- and film-boiling heat-transfer coefficients between a 2½ in o.d. × 5 in vertical copper cylinder (with hemispherical bottom) and liquid ethane, methane, oxygen and 50% oxygen-50% nitrogen at approximately 1 atm. Power was inadequate to permit direct measurement of the pnbfs. Coefficients in the metastable region were obtained from the heat capacity of the test apparatus, the temperature differences between the apparatus and the bulk liquid and the corresponding rates of cooling of the apparatus through the metastable region.

Haselden and Peters [2] measured nucleate-boiling coefficients at 1 atm between liquid oxygen and liquid nitrogen and copper cylinders ranging from ⅜ in o.d. to ⅝ in o.d. in both horizontal and vertical orientation. They give no values of the pnbfs. They emphasize the "ageing" of copper surfaces recently etched with aqueous HCl in boiling heat transfer in liquid oxygen.

Haselden and Prosad [3] report values of heat-transfer coefficients for liquid oxygen and liquid nitrogen boiling inside vertical tubes so that liquid convection is greatly enhanced over that pertaining in pool boiling.

Weil and Lacaze [4] reported values for nucleate- and film-boiling coefficients between liquid nitrogen at 740 mm Hg pressure and copper wires ranging from 0.1 mm to 1.5 mm o.d. They report nucleate-boiling coefficients and pnbfs between liquid nitrogen and copper (0.1 mm o.d.), platinum (0.2 mm o.d.), and lead (0.4 mm o.d.) wires at pressures ranging from 0.21 to 25 atm.

Fritz and Johnston [5] report overall heat-transfer coefficients between double enamel insulated copper magnet wire and liquid nitrogen boiling at 1 atm. No correction was applied for the thermal resistance of the enamel, and the surface effective in heat transfer was not well defined.

Mulford and Nigon [6] report values of 5.95 and 6.00 W/cm<sup>2</sup> for the pnbf between liquid nitrogen at 590 mm Hg pressure and a 12 mm o.d. horizontal copper cylinder, with corresponding temperature differences of 3.0 and 4.0 degK.

Ruzicka [7] reports nucleate- and stable film-boiling coefficients between copper tubing (10 to 20 mm o.d.) and copper and platinum wires (0.051 to 0.295 mm o.d.) wound into helical coils and liquid nitrogen presumably boiling at one atmosphere. He obtained coefficients in the metastable boiling region from the cooling rate of a warm copper tube.

Roubeau [8] gives curves of  $q/A$  vs  $\Delta T$  up to the pnbf for liquid N<sub>2</sub> boiling on a horizontal copper surface at pressures ranging from 1.35 atm to 25 atm. Unspecified partial pressures of helium in the vapor space were used to control heat transfer to the 77°K condenser, and thus the boiling temperature of the nitrogen.

Flynn *et al.* [9] duplicated the geometry of Haselden [2] and reported nucleate-and film-boiling coefficients for a  $\frac{5}{8}$  in o.d.  $\times$  2 in horizontal copper cylinder in nitrogen at approximately 1 atm. They include coefficients in the metastable region and a value of 5.8 W/cm<sup>2</sup> for the pnbf.

Most values of the pnbf reported at 1 atm

by previous workers were considerably lower than those predicted by the curve of Bonilla and Cichelli [10] which purports to correlate pnbf and the reduced pressure of boiling liquids.

That the physical character of the surface is critically important in determining nucleate-boiling heat-transfer coefficients is well known [11, 12, 13]; whether the nature of the surface affects the value of the peak nucleate-boiling flux is less well established, although the observations of Bonilla and Cichelli [10] and others with liquids which decompose and foul the heat-transfer surface indicate that there is a dependence. Since the beginning of the measurements reported in this paper, Class *et al.* [14] have reported an increase of approximately 50 per cent in the pnbf for liquid hydrogen on a silicone grease surface compared to a clean Karma alloy metal surface.

The relatively successful correlations of Kutateladze [15] and of Zuber and Tribus [16] for pnbf predict the value for any specific liquid to be independent of the surface from which the heat is derived.

#### EXPERIMENTAL APPARATUS AND PROCEDURE

In this work, cylindrical copper test pieces were provided with concentric electrical resistance heaters, and with copper-constantan thermocouples located in the body of the test piece a known radial distance from the metal-boiling liquid interface in solder filled wells. Measurements were made with copper surfaces, with various of the copper cylinders electroplated with gold, and with thin films of various chemical materials on the surface of the test cylinder.

Test Block I was obtained by modifying the experimental test block of Giauque *et al.* [1] subsequent to some preliminary measurements, and is shown in Fig. 1. All measurements were made with the axis of this cylinder vertical. Copper-constantan thermocouples were located in a single  $\frac{3}{16}$  in diameter well filled with Wood's metal and centered  $\frac{1}{8}$  in (radially) inside the cylinder surface. Two 600 W tinned Calrod heating elements were wound into a tight double helix which fit the 1.75 in diameter well of the block. Tinned copper shot and 60% Sn-40% Pb solder filled the free space in the well to

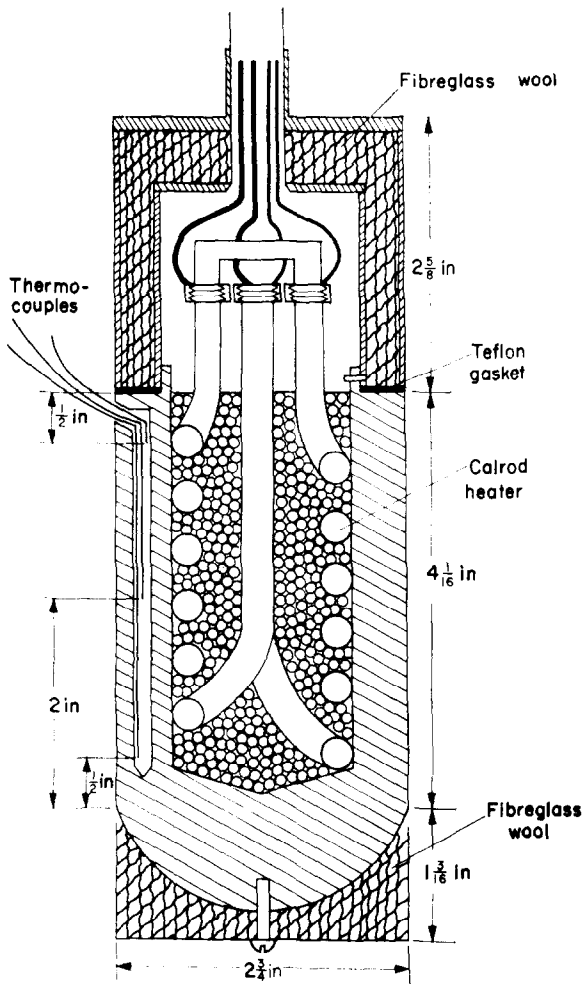


FIG. 1. Test Block 1.

ensure uniform thermal contact. Monel metal caps connected to the block through low thermal conductance paths minimized heat loss from the ends of the cylinder.

Test Blocks 3, 4, 5 and 6 (Fig. 2) were similar to No. 1 except that the copper-constantan thermocouples were located in individual wells drilled in the copper cylinders which surrounded and were soldered to commercial (Watlow Mfg. Co. "Firerod") cartridge electric heating elements. Thermocouple junctions were located a known distance inside the metal-liquid surface at the middle and  $\frac{1}{2}$  in from each end of the cylinder. End caps of low thermal

H.M.—3U

conductivity material (initially laminated phenolic resin which was replaced with glass fiber filled Teflon for use with  $O_2$ ) minimized heat loss from the ends of the cylinders.

The test blocks were mounted on stainless-steel tubes through which the potential and current leads for the heater were carried. The test block was suspended (Fig. 3) by this tube from a metal cap which covered and sealed the 5.3 in. i.d.  $\times$  34 in deep Pyrex Dewar to which the experimental liquid was added at the rate required to maintain a constant "level". Test Blocks 3, 4, 5 and 6, could be raised into the vapor space above the liquid in order to warm them to any desired extent without exposing them to atmospheric contamination, or could be lifted entirely out of the apparatus to coat or treat the heat-transfer surface without disturbing the thermocouples or other electrical leads.

Bulk liquid temperature was measured by a copper-constantan thermocouple, mounted at the average elevation of the heated surface but approximately one centimeter distant in the liquid. The surface temperature was obtained by subtracting from the thermocouple temperature the calculated temperature drop for uniform heat flow in a copper cylinder of radial thickness equal to the separation between the thermocouple junction and the surface. The thermal conductivity for copper was taken as 4.5 W/cm degK from Powell *et al.* [17]. These corrected temperatures were averaged and the indicated bath temperature was subtracted to obtain  $\Delta T$  for calculation of  $h$ .

The emf's of the thermocouples were measured with Leeds and Northrup White double potentiometers using galvanometers, or d.c. amplifiers and strip chart recorders, with 1  $\mu$ V or better sensitivity for null detection.

The thermocouples were calibrated at the boiling points of pure  $N_2$  and pure  $O_2$  and the sublimation point for  $CO_2$ . Using these calibration points, curves for the deviation of the observed thermocouple emf's from smoothed values derived from the table of Giauque *et al.* [18] were drawn and used to obtain a temperature from an observed thermocouple reading. Over the calibration interval this procedure has been found to give an accuracy

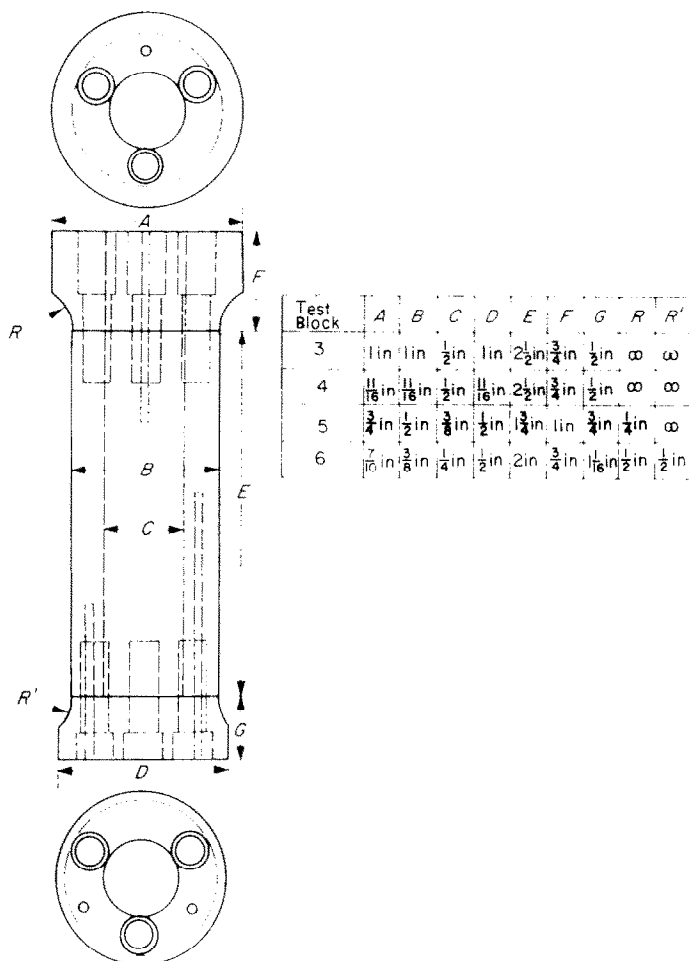


FIG. 2. Schematic arrangement of Test Blocks 3, 4, 5 and 6.

of better than  $\pm 0.2$  degK, and since the temperature at a given flux frequently varied by a degree or more at the different junction locations, the uncertainty in thermocouple calibration contributes little to the uncertainty in the heat-transfer coefficients,  $h$ .

Power for the heaters was obtained from the laboratory 250 V d.c. generator for the preliminary measurements with Test Block 1, and from 3-phase bridge rectifiers fed from variable auto transformers for all other measurements. The current was derived from the potential drop across calibrated shunts read with calibrated Weston Model 45 millivolt meters. The potential drop across the heater element

itself was read directly with Weston Model 45 voltmeters.

The experimental liquids were liquid  $N_2$  (99.97%) and liquid  $O_2$  (>99.5%) (or suitable mixtures of the two) obtained directly from the air fractionating column operated by the Low Temperature Laboratory. The liquid nitrogen is very pure with respect to high boiling materials; as is discussed later, the liquid  $O_2$  contains small amounts ( $\sim 10$  ppm) of organic materials. Except for preliminary measurements with Test Block 1, the liquids were passed through a silica gel bed at 77°K or 90°K to remove any high boiling solutes. This adsorbent bed was followed by a sintered metal filter to remove any

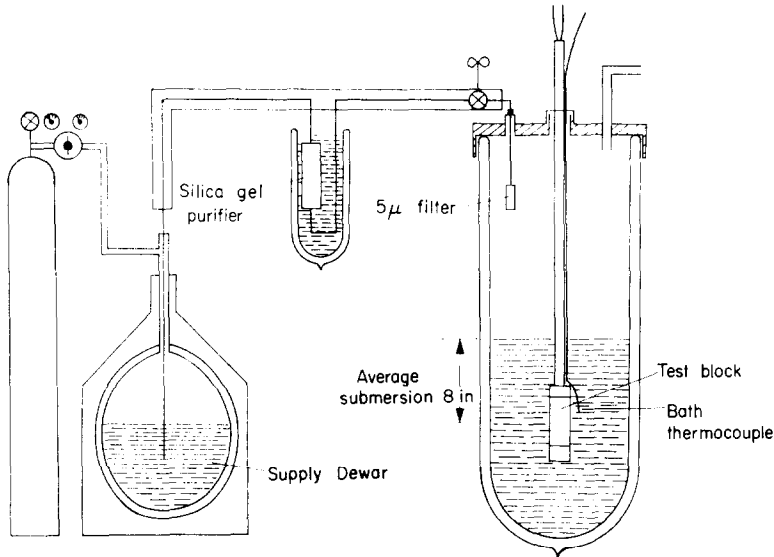


FIG. 3. Schematic arrangement of experimental apparatus.

suspended solids larger than a few microns in size.

For mixtures, the liquid *added* to the container at steady state was the same composition as the vapor leaving, so it was necessary to allow an initial heating period to bring the liquid in the boiling pool to that composition in equilibrium with vapor corresponding to the make-up liquid. The temperature of the boiling liquid was monitored and heating continued until a steady state was achieved before measurements were recorded.

#### *Preliminary measurements*

Preliminary measurements made in July 1953 in collaboration with W. F. Giauque using Test Block 1 with a copper surface suspended in an open Dewar indicated a slight dependence of the heat-transfer coefficient for pure  $N_2$  upon the depth of liquid above the test block and confirmed for  $N_2$  the existence of the two branches of the  $h$  vs  $\Delta T$  curve at very low heat fluxes observed by Giauque *et al.* [1] for air,  $O_2$ ,  $CH_4$  and  $C_2H_6$  and by Corty and Foust [12] for pentane, etc. Values for  $h$  for a given temperature difference, when measured in descending from a high heat-flux, fell well above those on the lower branch of the curve obtained

as the heat flux was gradually increased from zero. The upper branch of the curve was characterized visually by nucleation sites remaining active to much lower power levels, when reducing the flux, than at which they spontaneously become active when increasing the flux from zero.

These preliminary measurements also demonstrated a drift (increase) in the values of  $h$  for liquid  $O_2$  and  $O_2$  rich mixtures as evaporation continued at a given power setting. Although it was not recognized at the time, this drift was almost certainly due to the continuing deposition of minute amounts of solids on the heat-transfer surface.

The preliminary measurements indicated a high degree of reproducibility for liquid  $N_2$  during any given immersion, but a poor reproducibility when the test unit was cycled between low and room temperature without pains being taken to protect the copper surface of the block from atmospheric "corrosion".

Figure 4 shows data for  $h$  vs  $\Delta T$  obtained in liquid  $N_2$  with Test Block 1 with copper surfaces of varying surface finishes produced mechanically by treating the surface with machinist's abrasive cloth. (In all of these measurements the available heater power was

insufficient to determine the peak flux.) Curve 1 was obtained after the surface had been cleaned with No. 240 abrasive cloth. No pains were taken at this time to produce an especially uniform

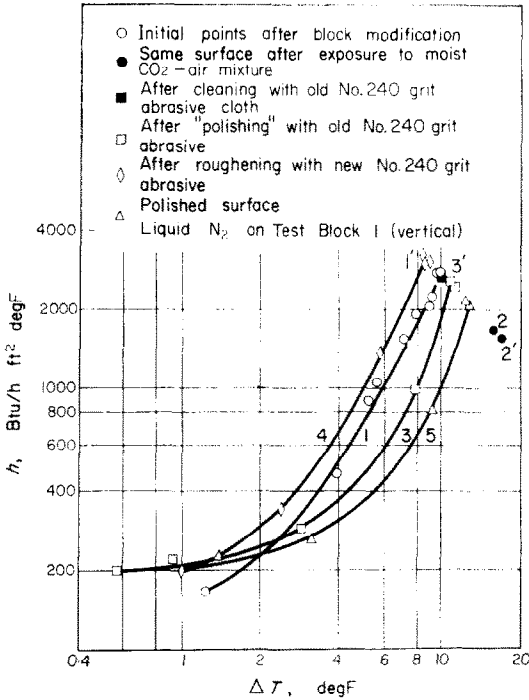


FIG. 4. Variation of liquid N<sub>2</sub> heat-transfer coefficients with mechanical treatment of copper surface of Test Block 1.

surface, but only to "clean" it from all discolorations resulting from the handling and heating operations used to install the bottom insulating cap. The points at the higher fluxes were quite reproducible: two measurements at 26 000 Btu/h ( $\Delta T = 9.6$  degF,  $h = 2720$  Btu/h ft<sup>2</sup> degF) taken 1½ h apart agreed to within 1 per cent.

Following the measurements on N<sub>2</sub> of curve 1, the apparatus was used to make similar measurements (extending over three days) with O<sub>2</sub> and N<sub>2</sub>-O<sub>2</sub> mixtures during which the unit occasionally was warmed to room temperature. The surrounding Dewar was then filled with powdered CO<sub>2</sub> for thermocouple calibration. The apparatus stood in the moist CO<sub>2</sub>-rich

atmosphere remaining after evaporation of the CO<sub>2</sub> for approximately two days. It was wiped with a clean dry cloth and heated to 50°C in air for 10-15 min to dry before immersing in liquid N<sub>2</sub> and remeasuring the coefficient at 26 000 Btu/h ft<sup>2</sup>. Points labelled 2 and 2' were obtained on succeeding days with continuous submersion in liquid N<sub>2</sub>. The values of  $h$  were less than 60 per cent of the original results of curve 1 although there was no evidence of gross change in the surface. It was slightly stained from reaction between copper and the moist CO<sub>2</sub>-air atmosphere.

The surface stains were removed with No. 240 grit abrasive cloth and point 3' obtained. Additional polishing with *used* No. 240 grit cloth produced a surface giving curve 3. (Typical values of surface finish obtained in this way range from 10 to 15  $\mu$ in, rms.) Treatment to leave the surface as rough as obtainable with new No. 240 grit cloth gave the results of curve 4. (Typical surface finishes measured after such preparation range from 25 to 30  $\mu$ in, rms.) Measurements of  $h$  at 27 000 Btu/h ft<sup>2</sup>, separated by 18 h of continuous immersion, agreed to within 3.5 per cent, well within the accuracy of measurement of the average surface temperature.

The surface was then carefully polished and was finally burnished with a clean, dry cotton buffing wheel. (Typical finishes for surfaces so prepared ranged from 2-4  $\mu$ in.) This surface yielded the results of curve 5. It was kept submerged in liquid N<sub>2</sub> for 96 h. At the end of that period, the coefficient at 27 000 Btu/h ft<sup>2</sup> agreed with the initial value to within 3 per cent. During the next 48 h, the unit was quickly warmed to room temperature on three occasions under conditions so as to minimize condensation of moisture on the surface, and then recooled in liquid N<sub>2</sub>. At the end of this period, the heat-transfer coefficient at 26 000 Btu/h ft<sup>2</sup> was 14 per cent higher than the initial value for the freshly polished block.

To minimize changes in surface character due to chemical corrosion from exposure to the laboratory atmosphere, Test Block 1 was plated with ~0.0006 in gold and carefully polished. A power supply capable of exceeding the peak flux requirement for the unit was assembled. Measured heat-transfer coefficients and

peak flux values in "unpurified" liquid O<sub>2</sub> at 1 atm increased steadily as the experiment continued and as the cumulative amount of oxygen vaporized increased as is shown in Table 1. The critical temperature difference for the second peak flux determination (11.6 degF at 59 700 Btu/ft<sup>2</sup>) was but 68 per cent of the initial temperature difference which had been measured for a flux of only 38 per cent of the peak flux.

At the time of the measurements for the last entry in Table 1, it was noticed that the surface was covered with a very thin white powdery coat (estimated to aggregate 100–200 mg) of material which was almost certainly organic in character. The experiment was immediately terminated and the remaining liquid O<sub>2</sub> was removed from the Dewar. The test block was slowly heated and the melting temperature of the surface deposit was noted to be in the range of 145–155°K which is consistent with the known presence of various 3, 4 and 5 carbon aldehydes in trace amounts in the air feed to the

distilling column in which the liquid oxygen is produced.

The aforementioned silica gel adsorbent vessel was installed in the liquid supply line as shown in Fig. 3 to strip these dissolved impurities from the liquid O<sub>2</sub> fed into the Dewar. To establish unequivocally that the *steady state* peak nucleate boiling flux is truly dependent upon the chemical nature of the heated solid surface, the smaller Test Blocks 3, 4, 5 and 6 were assembled so as to reduce the quantity of liquid vaporized.

#### NUCLEATE-BOILING HEAT-TRANSFER COEFFICIENTS

Measurements were made to indicate the extent of the effect of geometrical orientation, of surface roughness and chemical identity, and of liquid phase composition upon nucleate-boiling heat-transfer coefficients.

Care was taken to prevent uncontrolled variables (chemical reaction or "corrosion" at the surface, deposition of foreign material at the

Table 1. Variation of peak nucleate flux and heat-transfer coefficient in "impure" liquid O<sub>2</sub> with amount of O<sub>2</sub> vaporized. Test Block 1 (polished gold surface) at 1 atm

Cumulative heating time (min)	Cumulative liquid O <sub>2</sub> vaporized (l)	( $Q/A$ ) (Btu/h ft <sup>2</sup> )	$\Delta T$ (°F)	Btu/h ft <sup>2</sup> degF
5	0.7	20 900	17.1	1230
11	3.8	28 700	16.2	1770
18	8.1	37 600	16.4	2300
24	13	41 600	16.4	2550
41	19	46 000	16.9	2730
50	34	45 800	14.8	3100
Let unit stand unheated in liquid O <sub>2</sub> for ~20 h				
58	43	59 200	14.6	4060
60	45	peak < 61 400	14.3	4300
69	50	28 900	13.1	2200
74	55	peak ≥ 59 700	11.6	5160
76	57	peak < 60 900	~12.0	5070
77	58	peak ≥ 60 400	12.7	4980
80	61	peak ≥ 61 400	12.2	5030
83	65	peak < 62 300	12.3	5050
89	72	peak ≥ 63 600	12.15	5240
93	76	peak ≥ 63 600	11.7	5440
95	78	peak ≥ 66 100	(11.5)*	(5750)*
99	82	peak ≥ 67 300	(10.8)*	(6230)*
103	88	peak ≥ 72 500	11.65	6220

\* Based upon single thermocouple reading.

surface or a change in composition of the test liquid) from obscuring the effect of the variable under test.

#### Surface preparation

Each metal surface was carefully cleaned with reagent grade benzene and hexane following the polishing (or abrasion) to remove all traces of oil and wax. Immediately prior to each set of measurements, the surface was repeatedly washed with 95% ethyl alcohol, and then heated to  $\sim 70^\circ\text{C}$  and allowed to cool in the laboratory air.

With the exceptions discussed for the peak flux measurements, the test blocks were heated to  $\sim 70^\circ\text{C}$  after coating with a given chemical and the excess was allowed to drain to the bottom of the cylinder where it was removed by touching any accumulation with filter paper so as to leave as uniform a film as possible. Thickness of the organic films was estimated by measuring the weight increase for polished copper test pieces of accurately known surface area when coated by procedures essentially identical to those followed with the test blocks. For phenylacetonitrile it was not possible to obtain a film sufficiently stable to permit its measurement (in agreement with the instance of its agglomeration on the test block upon warming). For technical grade tri-2 ethylhexylphosphate films of heights ranging from  $1\frac{3}{4}$  in to 3 in, the average thickness was  $4 \times 10^{-4}$  cm.

#### Effect of cylinder orientation upon heat-transfer coefficients

Test Block 2 (not illustrated) was mounted so that its orientation could be changed from horizontal to vertical while submerged, and could be rotated about its axis while in the horizontal position. Unfortunately, pnbf data obtained with it were grossly discordant with those from all other units ( $\sim 50$  per cent low). Dismantling revealed that an intermediate copper sleeve, which carried the thermocouples in its design, had not bonded uniformly in soldering to the outer copper sheath which was in contact with the boiling liquid. All data for this unit were discarded and Test Block 5 with gold surface was mounted on its support tube by means of two  $45^\circ$  tubing elbows. By rotation at the joint between elbows, the orientation of the cylinder

axis could be changed from horizontal to vertical. This required warming the unit to room temperature and removing it from the Dewar. For the gold surfaces, reproducibility is such that differences between the two sets of data safely can be ascribed to orientation effects rather than changes in chemical character of the surface between measurements. Figure 5 gives the data

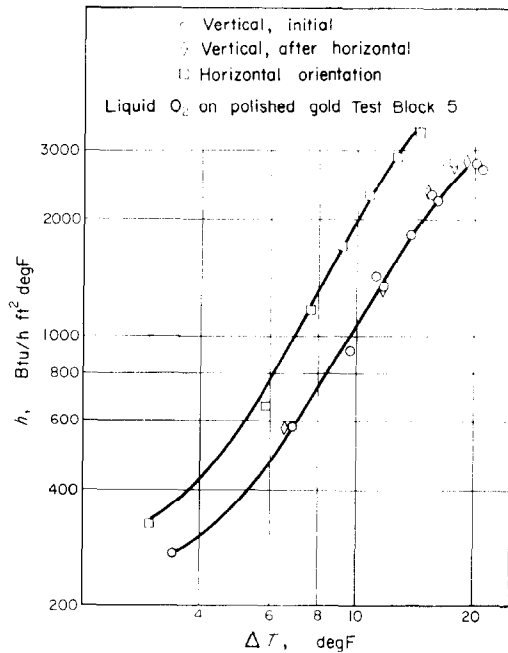


FIG. 5(a). Liquid  $\text{O}_2$  heat-transfer coefficients on 0.5 in. o.d. gold cylinder in vertical and horizontal orientation.

for  $h$  vs  $\Delta T$  for a polished gold surface ( $1\text{--}4$   $\mu\text{in}$  rms profilometer reading) for liquid  $\text{N}_2$  and liquid  $\text{O}_2$  in vertical and horizontal orientations.

#### Effect of surface roughness and character upon nucleate-boiling heat-transfer coefficients

Figure 6 combines the data for polished ( $1\text{--}4$   $\mu\text{in}$ , rms) and rough gold surfaces ( $25\text{--}30$   $\mu\text{in}$  from No. 240 grit cloth) for Test Block 3 in liquid  $\text{N}_2$  and in liquid  $\text{O}_2$  in the vertical orientation.

With some of the chemical films it was possible to obtain differing surface roughnesses or mechanical textures by varying the rate of cooling. Very low cooling usually produced a surface



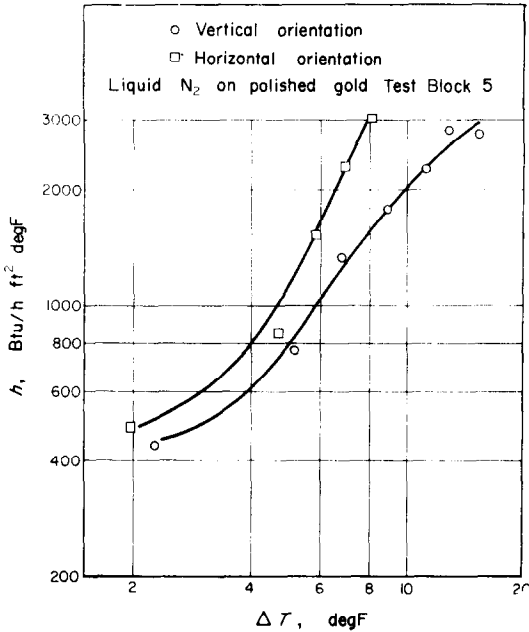


FIG. 5(b). Liquid N<sub>2</sub> heat-transfer coefficients on 0.5 in o.d. gold cylinder in horizontal and vertical orientation.

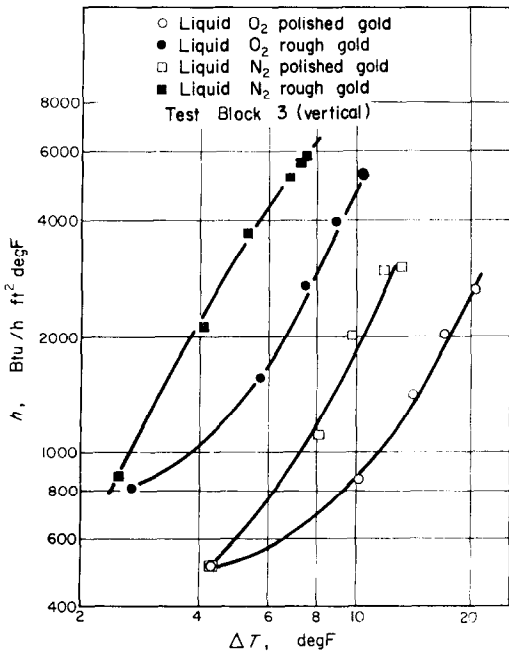


FIG. 6. N<sub>2</sub> and O<sub>2</sub> heat-transfer coefficients on mirror polished and rough vertical gold cylinders.

composed of many crystals or at least a highly crazed surface; plunging a warm film covered test block directly into liquid N<sub>2</sub> or O<sub>2</sub> could produce a glassy surface with varying (small) numbers of surface cracks and fractures. This affords a means of demonstrating the effect of surface texture where there can be no question of introducing foreign materials (other than possibly inclusions of vapor of the test liquid) in the course of altering the surface texture. Unfortunately, it is difficult to get a quantitative measure of the surface texture or roughness. Figure 7 shows data for liquid oxygen on Test

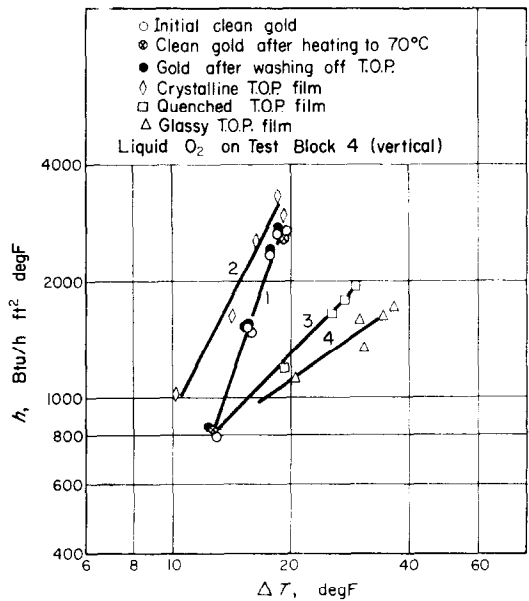


FIG. 7. Liquid oxygen heat-transfer coefficients vs ΔT for vertical gold and triethylphosphate cylinders.

Block 4 (vertical) for a clean polished gold surface, and with that gold surface covered with a film of technical grade tri-2 ethylhexylphosphate (triethylphosphate). The degree of reproducibility for a "clean" polished gold surface can be judged from curve 1 which includes data points for the initial measurements, points obtained after lifting the test block out of the Dewar, warming it to 70°C and allowing it to cool in the laboratory atmosphere before re-submerging in liquid O<sub>2</sub>, and points obtained

after washing the surface free of trioctylphosphate following the intervening measurements with the coated surface. Curve 2 is for a highly crystalline ("frosty" appearing) coat of trioctylphosphate obtained by cooling the coated block in the vapor above the liquid bath over a period of ~20 min. Upon completion of curve 2, the test block was raised into the vapor just above the liquid  $O_2$ , warmed above the melting point of the film and then quickly lowered into the liquid to quench the film. The resultant film was glassy except for some crazing or "frostiness" over the bottom quarter and gave the data of curve 3. The melting and quenching was repeated to give an almost perfectly glassy coat which yielded the data of curve 4. All curves were carried to the critical or pnbf.

Figure 8 is corresponding data for the same test block for "clean" and trioctylphosphate coated surfaces in liquid  $N_2$ . Again curve 1 illustrates the reproducibility of the "clean" gold data, curve 2 is for a crystalline coating, and curves 3 and 4 are for quenched glassy films. All measurements were extended to include the pnbf.

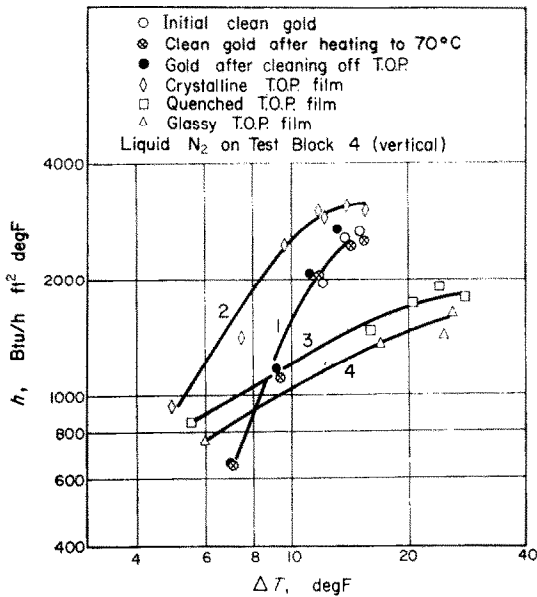


FIG. 8. Liquid  $N_2$  heat-transfer coefficients on vertical cylinders of gold and trioctylphosphate.

Figure 9 (Test Block 3, vertical in liquid  $N_2$ ) illustrates the reproducibility of data for a given surface. The lower curve represents initial "clean" gold. The upper curve represents data for a crystalline phenylacetonitrile coat. Two

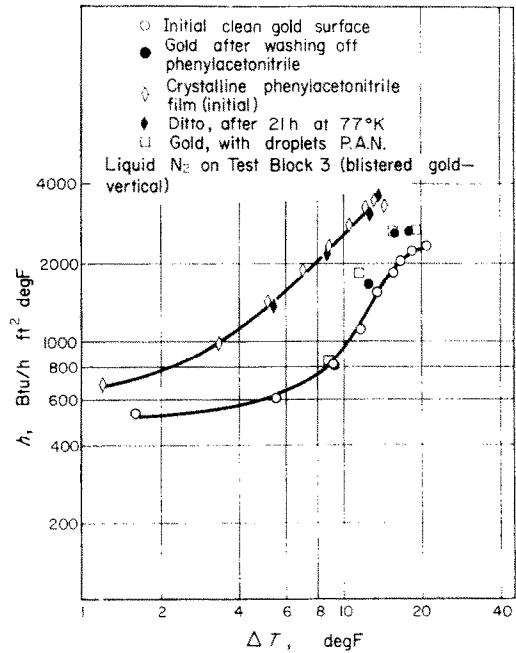


FIG. 9. Liquid  $N_2$  heat-transfer coefficients on vertical gold and phenylacetonitrile cylinders.

sets of data are included between which the film had been kept at liquid nitrogen temperatures for 21 h. Upon lifting into the vapor and melting (in the hopes of obtaining a glassy coat) the film ruptured and agglomerated into a few small droplets scattered over the surface. The data for this heterogeneous surface (including pnbf) were essentially those of the "clean" gold surface obtained on washing the phenylacetonitrile film off with ethyl alcohol. (In this case, the initial performance was not recovered after washing off the chemical film. However, prior to these sets of measurements, this test block had been accidentally overheated to above  $300^\circ C$ . This produced some slight blistering of the gold plate and the cleaning for this blistered surface may have been inadequate. Both the nucleate-boiling characteristics and the pnbf for the

gold surface after overheating were definitely different from the initial values. The data in Fig. 9 are *not* representative of a polished gold surface, but the curve for the phenylacetonitrile film illustrates the reproducibility of a specific surface.)

Figure 10 illustrates the sensitivity of performance in liquid N<sub>2</sub> for a copper surface (Test

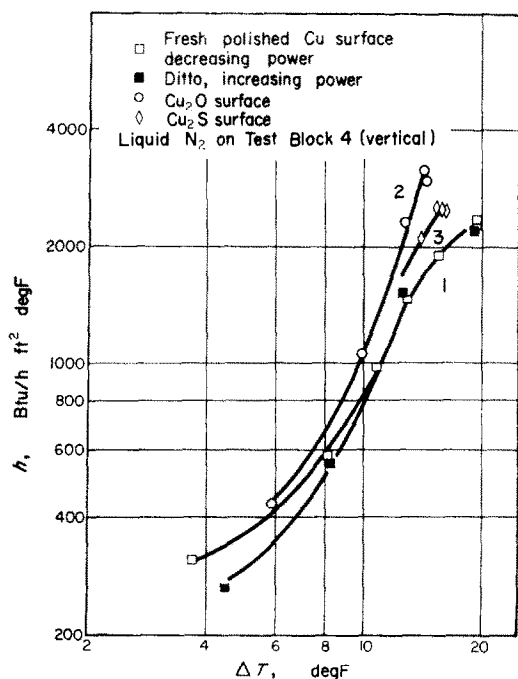


FIG. 10. Liquid N<sub>2</sub> heat-transfer coefficients on vertical copper cylinders of various chemical identities.

Block 4) to chemical corrosion and “hysteresis” at low flux. Curve 1 is initial data for the freshly polished surface with a characteristic pale reddish copper color. Data points taken in order of decreasing power, and on increasing power from zero show the effect at low flux of persistent nucleation. Curve 2 is for the same surface after it had been used in pure O<sub>2</sub> during which the surface acquired a deep rich red color suggestive of a molecular coat of Cu<sub>2</sub>O. Curve 3 was obtained after treating the surface with a solution of ammonium polysulfide to form a coat of Cu<sub>2</sub>S, washing repeatedly with distilled H<sub>2</sub>O and finally with

95% alcohol and heating to 70°C to dry in the standard fashion.

*Effect of liquid phase composition on nucleate-boiling heat-transfer coefficients*

By changing the composition of the test liquid being added to the Dewar, it was possible to obtain heat-transfer characteristics for a given surface in various oxygen–nitrogen mixtures without exposing it to the atmosphere and the hazards of changing its chemical or physical identity. The sequence of measurements in all cases started with pure nitrogen, followed by successively richer oxygen mixtures up to “pure” oxygen. In most cases, the measurements in pure nitrogen were then repeated.

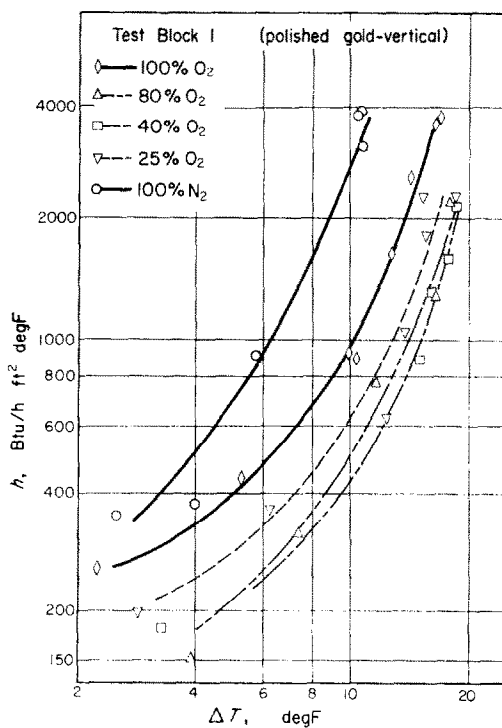


FIG. 11. Heat-transfer coefficients for N<sub>2</sub>, O<sub>2</sub> and various N<sub>2</sub>–O<sub>2</sub> mixtures on vertical gold cylinder.

Figure 11 gives data for pure N<sub>2</sub>, O<sub>2</sub> and approximately 25 ± 5 mol % O<sub>2</sub>, 40 ± 5 mol % O<sub>2</sub>, and 80 ± 5 mol % O<sub>2</sub> on a polished gold surface on Test Block 1 in vertical orientation. (The variation in liquid composition arises

from the difficulty in quickly matching flow rates of feed liquid to the large variations in heater power as one traverses the curve.) Measurements made with Test Blocks 4 and 5 with vertical polished copper surfaces, indicate that the absolute values for the curves for a given composition may differ markedly for various surfaces, but the relative position for various compositions on a given surface is the same as that shown in Fig. 11. Separate curves have been drawn for the 40% and 80% compositions in Fig. 11, but the measurements on copper surfaces indicated that the coefficients for any liquid composition between 35 and 80 mol % O<sub>2</sub> could be represented by a single curve to within the scatter of the data.

In all cases, the curve for any mixture lay below that for either pure component, rather than intermediate between the pure component curves. This is in agreement with the observations of Sterling and Tichacek [19] on liquid mixtures boiling at higher temperatures.

#### PEAK NUCLEATE-BOILING FLUXES

Measurements were made to ascertain the effect of surface roughness, of cylinder orientation and of the chemical nature of the surface upon pnbf.

Peak flux determinations were made as part of all complete flux vs  $\Delta T$  curves. In addition, separate determinations of pnbf alone were made for various surface coatings and conditions for which complete curves were not run.

Measurements were made for all test blocks by slowly increasing the power (stepwise) until a transition to film boiling occurred, indicated by abrupt decreases of 100  $\mu V$  or more in the thermocouple readings. As soon as possible after the transition to film boiling occurred, power was turned off and the unit allowed to recool to bath temperature before reestablishing a heat flux and repeating the sequence. (For Test Block 1, a series of determinations of pnbf using the rate of cooling of the block and its known heat capacity were made prior to the assembly of a power supply adequate to exceed the peak flux requirements.)

Values of pnbf were accepted to be those which could be maintained for at least 60 s without

the onset of film boiling. Experience indicated that if a given flux could be maintained for 60 s, it could usually be maintained indefinitely. Entries in Tables 1 and 4 marked with the < inequality represent tests where the block sustained the indicated flux temporarily but went into film boiling in less than 60 s.

Upon completion of measurements with a test block coated with a chemical film, the unit was lifted from the Dewar, the coating washed off with suitable solvents and the surface treated in the standard preparatory routine and the values for the "clean" surface remeasured and compared with those obtained prior to coating the surface. For those cases in which a polished copper surface was exposed to H<sub>2</sub>S fumes or treated with ammonium polysulfide to create a Cu<sub>2</sub>S surface, no attempt was made to reproduce the original surface and heat-transfer results since the formation of Cu<sub>2</sub>S is so irreversible that it would have required drastic chemical treatment and mechanical repolishing to have approximated the original surface.

Drift in the peak flux values measured with the "purified" oxygen was less than for "raw" oxygen. However, the heat-transfer coefficients and pnbf for oxygen are so sensitive to the presence of organic compounds on the surface that reliable values could not be obtained in liquid which had experienced a several fold concentration by continued boiling. It is felt that peak flux values given here for oxygen on "clean" metals probably are high and represent upper limits for this reason.

#### *Effect of cylinder orientation upon peak nucleate-boiling flux*

Test Block 5 was used with polished gold and with roughened gold (fresh No. 240 grit abrasive to give 25–30  $\mu in$ , rms, surface finish) to check the effect of horizontal as contrasted to vertical orientation of the cylinder axis upon the pnbf for pure nitrogen and pure oxygen. For a given fluid, measurements in the vertical orientation were followed by horizontal orientation measurements. The vertical orientation measurements were then repeated. Only the standard surface preparation intervened between measurements in the various orientations. The results are given in Table 2.

Table 2. Peak nucleate-boiling fluxes for N<sub>2</sub> and O<sub>2</sub> on Test Block 5 (gold surfaces) for vertical and horizontal orientation

Fluid	Run no.	Peak nucleate-boiling flux (Btu/h ft <sup>2</sup> )	
		Vertical	Horizontal
Polished gold:			
Nitrogen	V-7, 8	43 100 ± 700 (8)	36 500 ± 400 (3)
Nitrogen	V-9	40 700 ± 1000 (2)	33 800 ± 400 (2)
Oxygen	V-11	56 400 ± 700 (6)	48 500 ± 1200 (5)
Rough gold:			
Oxygen	V-13	53 500 ± 600 (3)	48 800 (2)
Nitrogen	V-14	40 600 ± 800 (6)	37 400 ± 500 (4)

The "uncertainties" given in Table 2 are simply the average deviations of the upper and lower flux limits (between which the pnbflay) from their arithmetical average for the number of determinations made (given in parentheses). For runs V-7 and V-8 (made on the same day) the *difference* between vertical and horizontal orientation agrees well with the *difference* between the two orientations for run V-9 on the succeeding day, despite the fact that both values were some 7-8 per cent lower in the latter run. The data suggest, but are probably insufficient to justify, the conclusion that the difference between horizontal and vertical orientation is actually smaller for the rough surface than for the polished surface. There is no doubt, however, that the pnbfl for a 0.5 in. o.d. cylinder of length/diameter ratio of 3.5 is definitely greater

in the vertical than the horizontal orientation.

#### *Effect of surface texture upon peak nucleate-boiling flux*

PNBF values for Test Block 3 with polished, and with rough gold (20-30 μin, rms) were measured in addition to those with Test Block 5. For these mechanically roughened surfaces there is a possibility of incorporating foreign material into the surface in the roughening process. The results are summarized in Table 3. Peak flux values for N<sub>2</sub> and O<sub>2</sub> were measured on the vertical trioctylphosphate (T.O.P.) surfaces represented in Figs. 7 and 8, where the only variable contaminant would be vapor of the test fluid. Those results are summarized in Table 4.

The average difference in pnbfl (polished minus rough) for N<sub>2</sub> from Table 3 (-400 ±

Table 3. Peak nucleate-boiling fluxes for N<sub>2</sub> and O<sub>2</sub> on polished and rough gold surfaces

Fluid	Surface	Peak nucleate-boiling flux (Btu/h ft <sup>2</sup> )	
		Polished	Rough
N <sub>2</sub>	Test Block 5, Vertical	42 600 ± 900 (10)	40 600 ± 800 (6)
N <sub>2</sub>	Test Block 5, Horizontal	35 300 ± 1300 (5)	37 400 ± 500 (4)
N <sub>2</sub>	Test Block 3, Vertical	41 400 ± 800 (5)	42 500 ± 900 (8)
O <sub>2</sub>	Test Block 5, Vertical	56 400 ± 700 (6)	54 200 ± 1200 (4)
O <sub>2</sub>	Test Block 5, Horizontal	48 500 ± 1200 (5)	48 800 (2)
O <sub>2</sub>	Test Block 3, Vertical	55 800 ± 900 (5)	57 400 ± 1100 (6)

Table 4. Peak nucleate-boiling fluxes for N<sub>2</sub> and O<sub>2</sub> on vertical trioctylphosphate surfaces of various roughnesses

Fluid	Surface	Peak nucleate-boiling flux (Btu/h ft <sup>2</sup> )
O <sub>2</sub>	Crystalline T.O.P. (Curve 2, Fig. 7)	> 63 300 < 64 500
	Quenched T.O.P. (Curve 3, Fig. 7)	> 63 400 < 65 300
O <sub>2</sub>	Glassy T.O.P. (Curve 4, Fig. 7)	> 63 400 < 64 200
N <sub>2</sub>	Crystalline T.O.P. (Curve 2, Fig. 8)	> 47 500 < 48 400
	Quenched T.O.P. (Curve 3, Fig. 8)	> 48 900 < 50 300
N <sub>2</sub>	Glassy T.O.P. (Curve 4, Fig. 8)	> 47 400 < 48 700

1600 a.d.) and for O<sub>2</sub> (+100 ± 1700 a.d.) indicates that any roughness effect is less than 5 per cent, and is probably zero. The data of Table 4 indicate unequivocally that there is no dependence of pnbf for N<sub>2</sub> or O<sub>2</sub> upon the mechanical texture of vertical trioctylphosphate surfaces. These conclusions are in agreement

with the results of Berenson [13] for mechanically roughened surfaces.

*Variation of peak nucleate-boiling flux with chemical nature of heated surface*

Tables 5 and 6 summarize the peak nucleate boiling flux results for the various blocks with the different surfaces tested. In arriving at the average values for gold for Test Blocks 3 and 5, both polished and rough data have been included. For other metal surfaces, the figures are for mirror polished conditions. No data for overheated Test Block 3 (blistered gold) are included in that average. For Test Blocks 3, 4 and 5, the averages for the metal surfaces include determinations made on several different occasions (runs), separated by cycling to room temperature, tests with other liquids and surfaces, etc. The spread in those results is correspondingly greater, for (with the exceptions noted previously for oxygen, and below for ethyl alcohol surfaces) the spread in successive pnbf determinations was much smaller than the spread between values made on different occasions.

Although the barometer was read on each occasion, no corrections have been applied since all barometric pressures (corrected) fell within

Table 5. Peak nucleate-boiling fluxes for liquid nitrogen on various vertical cylindrical surfaces at 1 atm

Surface	Peak nucleate-boiling flux (10 <sup>8</sup> Btu/h ft <sup>2</sup> )			
	Test Block 1	Test Block 3	Test Block 4	Test Block 5
Gold	40.6 ± 0.5 (6)	40.5 ± 0.4 (9)	40.6 ± 1.4 (6)	41.0 ± 1.7 (22)
Copper	45.1 ± 0.5 (4) <sup>1</sup>	45.7 ± 0.7 (6)	44.6 ± 0.9 (5)	42.4 ± 1.0 (5)
Cu <sub>2</sub> S		{ 49.1 <sup>2</sup> 45.0 <sup>3</sup>	39.8 <sup>4</sup>	45.7 ± 0.3 <sup>5</sup>
Phenylacetoneitrile		51.5 ± 0.5 (9)		48.9 ± 0.8 (3)
Ethyl alcohol (95 %) <sup>7</sup>		51.9 ± 2.5 (3)		47.6 ± 0.6 (7)
Trioctylphosphate			47.8 ± 0.9 (5)	49.6 ± 0.6 (5)
KEL-F Oil No. 3				46.8 ± 0.4 (2)
Fluorochemical N-43 <sup>6</sup>				49.8 ± 0.5 (3)
White mineral oil (Tech. Grade)				40.2 ± 0.4 (5)
H <sub>3</sub> PO <sub>4</sub> (85 %) <sup>7</sup>				39.9 ± 0.3 (2)
H <sub>2</sub> SO <sub>4</sub> (96 %) <sup>7</sup>				

1. Obtained from quenching curves; 2. Initial value; surface not washed with ethyl alcohol; 3. After above surface stood in liquid N<sub>2</sub> 8 h; 4. Standard surface preparation; 5. Surface not washed with ethyl alcohol; 6. Minnesota Mining and Mfg. Co.; 7. Concentration at time of application.

Table 6. Peak nucleate-boiling fluxes for liquid oxygen on various vertical cylindrical surfaces at 1 atm

Surface	Peak nucleate-boiling flux ( $10^3$ Btu/h ft <sup>2</sup> )				
	Test Block 1	Test Block 3	Test Block 4	Test Block 5	Test Block 6
Gold	58.5 ± 1.0 (6)	56.7 ± 1.3 (10)	53.3 ± 0.6 (4)	55.6 ± 1.3 (18)	
Copper	56.7 ± 3.5 (6) <sup>1</sup>		59.6 ± 1.1 (3)	57.9 ± 0.5 (4)	55.0 ± 1.3 (2)
Cu <sub>2</sub> S				58.7	
Ethyl alcohol (95%) <sup>3</sup>		43.9 <sup>2</sup> 49.2		62.3 <sup>3</sup> 69.5	
Trioctylphosphate					
KEL-F Oil No. 3			64.1 ± 0.6 (4)	62.8 ± 1.0 (7)	68.1 ± 0.5 (4)
White mineral oil				64.4 ± 0.6 (4)	
H <sub>3</sub> PO <sub>4</sub> (85%) <sup>3</sup>				60.9 ± 0.8 (3)	
H <sub>2</sub> SO <sub>4</sub> (96%) <sup>3</sup>				51.3 ± 0.7 (6)	
				50.0 ± 0.6 (2)	

1. Obtained from quenching curves; 2. Value increased with each determination. See text; 3. Concentration at time of application.

the range of  $753 \pm 3$  mm and corrections to the pnbfs would be small compared to the scatter.

The composition of hygroscopic chemicals (ethyl alcohol, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>) given is the nominal composition of the liquid applied to the surface. Since the surface was in contact with the laboratory air for some little time before inserting into the Dewar, moisture may have been adsorbed from the air to change the actual composition.

For the relatively volatile materials (ethyl alcohol and Fluorochemical N-43) it was not possible to heat the surface to 70°C. For ethyl alcohol, it was necessary to cool a test block to -40° to -60°C, lift it from the Dewar momentarily and apply ethyl alcohol in order to obtain a macroscopic coat. If not pre-cooled, the alcohol evaporated from the surface as it cooled through the film boiling region. Nothing can be said about the thickness of such a film. A film of phenylacetonitrile was obtained on but one occasion, and that agglomerated when it was reheated above the melting point. Films of H<sub>2</sub>SO<sub>4</sub> also were metastable and tended to agglomerate upon rewarming. Attempts to obtain a suitable film of water were unsuccessful even when using detergents to reduce surface tensions because of the volatility of the water as well as the wetting problem.

Except for the ethyl alcohol surfaces, the agreement is quite good for the same surface where it was tested on more than one block. In

the case of liquid nitrogen, it appears that there is a definite difference between the pnbfs on copper surfaces and on electroplated gold as prepared in these samples. In the case of oxygen, the scatter between the various test blocks is such as to obscure any such difference that may exist. It is felt that some of the scatter in the oxygen results stems from the difficulty of maintaining an oxygen liquid bath of adequate purity in open loop operation.

The measurements with ethyl alcohol films were undertaken to establish whether the "clean" metal surface values are representative of the metal surface or whether they are determined by adsorbed ethyl alcohol left on the surface by the preparatory treatment. The results obtained indicate that there is a significant difference between such "clean" metal values and those for a macroscopic film of ethyl alcohol.

The results obtained with the macroscopic ethyl alcohol films are most interesting. In the case of liquid nitrogen there is modest agreement between the values on Test Blocks 3 and 5, and the pnbfs values for either block were moderately reproducible. In the case of liquid oxygen the values obtained with Test Block 3 and Test Block 5 are grossly discordant; one representing an enhancement and one a depression from the clean metal surface values. Moreover, the value of the pnbfs increased with each successive determination of the flux so long as the film was not allowed to melt on the occasions when it went

into film boiling. With Test Block 3 at a power setting approximately 20 per cent below the pnbf value, the surface temperature decreased rapidly with time as boiling progressed much in the same fashion as was observed with impure liquid oxygen (Table 1). In addition, at powers approaching the pnbf the fluctuations of a given thermocouple were very much greater than for other surfaces. For Test Block 5, four successive determinations of the pnbf increased regularly from 62 300 to 69 500 Btu/h ft<sup>2</sup>. The block was lifted from the liquid and heated to just above the melting point of the ethyl alcohol film. It was then quenched and the measurements repeated. The first value again was approximately 62 300 Btu/h ft<sup>2</sup> and in four determinations increased regularly to the vicinity of 69 000. This secular drift was very much smaller, if present at all, for liquid nitrogen on ethyl alcohol. It is felt that it probably represents a continuing change in the character of the ethyl alcohol surface through its solution in the liquid oxygen, and the solution of some oxygen in the solid alcohol film. Since the freezing point of the alcohol would be 156°K or lower, for the  $\Delta T$ 's involved at peak nucleate-boiling flux the solid film is not far from its melting point and solubility effects would be much greater than for any of the other materials investigated.

The values for cuprous sulfide surfaces are likewise discordant and somewhat unreproducible for a given surface. Some of this variation may stem from the fact that Test Blocks 3 and 5, which were exposed to the fumes above a solution of ammonium polysulfide, were not subsequently washed with ethyl alcohol and given the standard preparatory treatment which was given Test Block 4. In addition, the surface

coat of sulfide tends to spall off on long standing or repeated temperature cycling.

In addition to the definite difference for N<sub>2</sub> on copper as compared to gold, both O<sub>2</sub> and N<sub>2</sub> results make it unequivocal that there are differences of as much as 25 per cent in the pnbf for a given liquid on different chemical surfaces. This is consistent with the result of Class *et al.* [14] for liquid hydrogen and of van Stralen [20] who reports pnbf's for water and 86.13 wt % water-methyl ethyl ketone mixtures on horizontal oxidized nichrome V wire ranging from 20 to 120 per cent larger than for the same fluids on platinum wire. Unfortunately, the nichrome wire was 0.05 cm dia. vs 0.02 cm for the platinum so that interface effects can not be readily separated from hydrodynamic effects.

*Variation of peak nucleate-boiling flux with composition for nitrogen-oxygen mixtures*

Table 7 indicates the values for the peak nucleate-boiling flux for various oxygen-nitrogen mixtures as obtained on three test blocks used in those measurements. Although the results are somewhat impaired by variation in liquid composition both in successive determinations and between the various test blocks, it is evident that the peak nucleate boiling flux for mixtures of N<sub>2</sub> and O<sub>2</sub> when compared to the pure fluids exhibit no such anomalies as do the nucleate boiling heat-transfer coefficients for mixtures. This is in contrast to the behavior van Stralen [20] reports for binary mixtures of water and various alcohols or ketones on 0.02 cm dia. horizontal platinum wires. He finds a maximum, or maxima, in pnbf for binary mixtures. The behavior is said to be qualitatively correlated by bubble dynamics considerations.

Table 7. Peak nucleate-boiling fluxes for O<sub>2</sub>-N<sub>2</sub> mixtures on vertical metal cylinders

Test block	Surface	Peak nucleate-boiling flux (10 <sup>3</sup> Btu/h ft <sup>2</sup> )				
		100% N <sub>2</sub>	25 ± 5% O <sub>2</sub>	40 ± 5% O <sub>2</sub>	80 ± 5% O <sub>2</sub>	100% O <sub>2</sub>
No. 1	Pol. Gold	40.5 ± 0.5	38.0 ± 0.5	41.4 ± 0.5	39.6 ± 0.4	60.6 ± 0.7*
No. 4	Pol. Copper	45.2 ± 0.5	49.2 ± 0.5	44.7 ± 0.5	45.1 ± 0.4	60.2 ± 0.5
No. 5	Pol. Copper	44.1 ± 0.7	43.6 ± 2.5	46.0 ± 0.5	46.0 ± 0.5	57.9 ± 0.5

Probably contaminated surface. PNBf dropped to 58.5 ± 1.0 after washing with EtOH etc.



Kutateladze [21] reports that Bobrovich *et al.* found a minimum in pnbfs for water-butanol mixtures on "large" surfaces (plates) in the composition region where wires exhibited a maximum.

### DISCUSSION

In view of the three- to fivefold variation in nucleate-boiling heat-transfer coefficients for a given liquid with surface condition, it is unreasonable to expect agreement with the work of other experimenters to better than this unless the surfaces were identically prepared and installed in identical geometries.

Agreement with the work of Haselden and Peters [2] is quite reasonable, recognizing that their curves extend only to fluxes of about one half the pnbf.

Direct comparison with the work of Roubeau [8] is difficult since his lowest pressure was 1.35 atm. Making reasonable allowances for the effects of pressure, based upon his work and subsequent work in this laboratory [22], the results appear to agree within the above range for heat-transfer coefficients and within 10 per cent for pnbf.

Comparison with the work of Weil and Lacaze [4] and Ruzicka [7] on small wires in a variety of geometries agrees only to order of magnitude for heat-transfer coefficient, but fairly well in terms of pnbf.

Agreement with the work of Flynn *et al.* [9] is poor at best, recognizing that a very limited amount of work was done here with horizontal cylinders (and none of that with copper). His curves agree with those of Haselden at low flux but rapidly fall far below Haselden's as the flux increases, as though there were some unrecognized thermal resistance between the thermocouples and the liquid surface. However, the principal reason for doubting the Flynn work is that the quoted pnbf of 5.8 W (18 300 Btu/h ft<sup>2</sup>) is far below any other reliable figure quoted for N<sub>2</sub> at 760 mm Hg pressure. Both the shape of the  $h$  vs  $\Delta T$  curves and the low pnbf are very similar to results obtained in this work with defective Test Block 2 where contact between the heater and the copper sheath in contact with boiling liquid was found to be nonuniform.

The work of Fritz and Johnston [5] is not

directly comparable with that for clean metal surfaces because of the unknown thermal resistance of the enamel coat on their wire. This resistance becomes quite important at higher fluxes and causes the apparent heat-transfer coefficient to fall below the true. Their results agree reasonably well with the data of Fig. 8 for a quenched T.O.P. film considering the uncertainty in their effective surface.

Because of this uncertain thermal resistance of the chemical films, no attempt has been made here to report critical temperature differences or peak heat-transfer coefficients for coated test blocks. Likewise, caution must be exercised in attributing all differences between the curves for the crystalline and glassy trioctylphosphate surfaces (Figs. 7 and 8) to differences in the density of nucleation sites. The thermal conductivity of such organic materials between 80 and 100°K is unknown but probably the thermal conductivity is higher for the crystalline than for the glassy state.

The average of the thermal conductivities of several inorganic glasses at 80°K is 0.0044 W/cm degK [23] and the thermal conductivity of Teflon at 80°K is 0.0024 W/cm degK. Using the lower thermal conductivity (for Teflon), at a flux of 60 000 Btu/h ft<sup>2</sup> one calculates a temperature drop of 5.3 degF through a  $3.7 \times 10^{-4}$  cm film, and 1.8 degF at 20 000 Btu/h ft<sup>2</sup>. Referring to the curves for quenched and crystallized coatings in Fig. 7 it appears that  $\sim \frac{1}{3}$  of the 18 degF difference at 60 000 Btu/h ft<sup>2</sup> could be explained on the above basis *if k for the crystallized film were very large*. There is no way of knowing whether the interfacial thermal resistances between the metal and the organic film was sufficiently great and sufficiently different in the two cases to account for any major fraction of the observed change in the overall  $\Delta T$ 's. Because of these uncertainties, no positive conclusions can be drawn about differences in value of  $h$  on the various coated surfaces, or on coated as opposed to bare surfaces.

Over the last decade a number of relatively successful correlations for nucleate-boiling heat flux vs temperature difference in terms of the physical properties of the liquid and vapor of the boiling substance have appeared. McNelly [24] and Forster *et al.* [25, 26] correlate with a

function of fluid properties multiplied by a single constant which can be chosen to represent the average of the range which spans the performance of surfaces of different character. The fluxes predicted by these correlations for  $N_2$  and  $O_2$ , using the recommended values of the "constants", fall five- to tenfold below these experimental values, even for polished surfaces, so that it is inconvenient to display them on the graphs presented here. Reasonable agreement can be obtained by re-evaluating the "constant" for each surface-fluid combination as Rohsenow [27] does. The statement is frequently made that pool boiling heat-transfer data are insensitive to geometry of the surface. This work, and the work of Haselden and Peters [2], finds that the heat-transfer coefficient in the nucleate region for a horizontal tube in oxygen is greater than for the same tube in the vertical position, and at equal fluxes the two researches agree approximately as to the difference. Haselden and Peters show no difference between the two orientations in  $N_2$  as was found here but their  $N_2$  curves were extended only to very modest fluxes (7000 Btu/h ft<sup>2</sup>). This orientation effect suggests that the rate-controlling mechanism for nucleate boiling in one fluid may well be different from that for a second fluid, and the insensitivity to geometry is a special rather than a general characteristic of nucleate boiling.

The correlations of Kutateladze [15], Rohsenow and Griffith [28], and Zuber and Tribus [13] for peak nucleate-boiling flux all contain only fluid properties. The Kutateladze and Zuber-Tribus forms are very similar. The correlation of the latter workers is given by

$$\frac{(Q/A)_{\max}}{\rho_v \Delta H_{\text{vap}}} = K \left[ \frac{\sigma g (\rho_l - \rho_v)}{\rho_v^2} \right]^{1/4} \left[ \frac{\rho_l}{\rho_l + \rho_v} \right]^{1/2} \quad (1)$$

where  $(Q/A)_{\max}$  = peak nucleate-boiling flux,  
 $\Delta H_{\text{vap}}$  = heat of vaporization per unit mass,  
 $\rho_v$  = vapor density,  
 $\rho_l$  = liquid density,  
 $\sigma$  = vapor-liquid surface tension,  
 and  
 $g$  = gravitational acceleration.

It was arrived at by considering the hydrodynamics of the relative flow of the vapor generated

at the heated surface and the liquid flowing to the surface. The peak nucleate-boiling catastrophe is postulated to result from the hydrodynamic instability that results when this relative flow of the two phases exceeds a critical value. Arguing that the formation of vapor jets from a surface is subject to statistical fluctuations, Zuber concludes that the peak nucleate-boiling flux will be reproducible only within the limits corresponding to  $0.157 \geq K \geq 0.12$ . From this correlation one calculates for nitrogen at 77.3°K:

$$63\,500 \geq (Q/A)_{\max} \geq 47\,500 \text{ Btu/h ft}^2$$

and for oxygen at 90.2°K:

$$78\,500 \geq (Q/A)_{\max} \geq 60\,500 \text{ Btu/h ft}^2$$

The uncertainties in the interpretation of heat-transfer coefficients introduced by the thermal resistance of the films do not apply to the values for the steady state peak nucleate-boiling fluxes and the important conclusions that can be drawn from these experiments are that the value of the pnbf for a specific surface is reproducible to within a few per cent and is a function of the chemical identity of the surface rather than its physical character, as demonstrated by values for metal as opposed to organic films, and by the glassy as opposed to the crystalline trioctylphosphate films. These facts make it seem improbable that vapor-liquid hydrodynamic relations govern the peak flux catastrophe for all pool boiling systems.

This work indicates that there are differences of at least as much as 25 per cent for the pnbf of a given liquid on different chemical surfaces of the same geometry. These data do not permit one to decide whether this variation arises from interfacial free energy effects or whether it possibly stems from kinetic effects attributable to the thermal conductivity of the heated surface. In view of the fact that the peak nucleate-boiling flux can be enhanced as by KEL-F Oil No. 3 or depressed as by sulfuric acid, this seems improbable. Since there was no difference between pnbf values for the trioctylphosphate surfaces of glassy as opposed to crystalline character it seems even less probable. The thermal conductivity of the glassy film should be significantly smaller than the crystalline material.

Few data exist for solid-liquid and solid-vapour interfacial free energies in systems with a single component fluid phase, particularly for superheated liquid conditions.

### CONCLUSION

Data for nucleate-boiling heat-transfer coefficients and the peak nucleate-boiling fluxes of  $N_2$ ,  $O_2$  and their mixtures have been presented.

The nucleate-boiling heat-transfer coefficients for  $N_2$  and  $O_2$  on cylinders have been found to be dependent upon the orientation of the cylinder as well as upon the microscopic mechanical character of the surface.

The peak nucleate-boiling fluxes have been shown to be dependent upon surface orientation and upon the chemical nature of the surface, but to be quite insensitive to the microscopic mechanical character of the surface. The peak nucleate-boiling flux for a macroscopic body has been found to be quite reproducible when there was no reason to suspect a change in the identity of the surface or the liquid.

The available correlations for nucleate boiling are qualitatively successful, but obviously incomplete. Further improvement will call for very meticulous control of the identity of the liquid-solid surface in order to evaluate the influence of the various forces and properties that affect the boiling process.

### ACKNOWLEDGEMENTS

The author is indebted to Professor W. F. Giaque for personal assistance in making the preliminary measurements and for continuing encouragement.

### REFERENCES

1. W. F. GIAQUE, J. W. STOUT, R. E. BARIEAU and C. J. EGAN, Report of 1 March 1942, Division B, National Defense Research Committee, Office of Scientific Research and Development, OSRD No. 491, Serial No. 201 (1942).
2. G. G. HASELDEN and J. I. PETERS, *Trans. Inst. Chem. Engrs* **27**, 201 (1949).
3. G. G. HASELDEN and S. PROSAD, *Trans. Inst. Chem. Engrs* **27**, 195 (1949).
4. L. WEIL and A. LACAZE, *C.R. Acad. Sci., Paris* **230**, 186 (1950); *Bull. Int. Inst. Refrig. Annexe* (1955-2) 85-88 (1954).
5. J. J. FRITZ and H. L. JOHNSTON, *Rev. Sci. Instrum.* **21**, 416 (1950).
6. R. N. MULFORD and J. P. NIGON, Los Alamos Scientific Laboratory Report, LA-1416 (unclassified) (1952).
7. J. RUZICKA, Problems of low temperature physics and thermodynamics, *Proc. Meeting of Comm. 1 of Int. Inst. of Refrig.* 1958, p. 323. Pergamon Press, New York (1959).
8. P. ROUBEAU, Comité Energie Atomique France Centre Etudes Nucleaires, Saclay, Rapp't 1877 (49) 1961.
9. T. M. FLYNN, J. W. DRAPER and J. J. ROOS, *Advances in Cryogenic Engineering*, Vol. 7, p. 539. Plenum Press, New York (1962).
10. C. F. BONILLA and M. T. CICHELLI, *Trans. Amer. Inst. Chem. Engrs* **41**, 755 (1945).
11. W. H. MCADAMS, *Heat Transmission*, Chapter 14, 3rd ed. McGraw-Hill, New York (1954).
12. C. CORTY and A. S. FOUST, *Chem. Engng Prog. Symp. Series No. 17*, **51**, 1 (1955).
13. P. BERENSON, Paper No. 18, ASME-AIChE Heat Transfer Conference, Buffalo, New York (1960).
14. C. R. CLASS, J. R. DEHAAN, M. PICCONE and R. B. COST, *Advances in Cryogenic Engineering*, Vol. V, p. 254. Plenum Press, New York (1960).
15. S. S. KUTATELADZE, *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk*, No. 4, 342 (1951).
16. N. ZUBER and M. TRIBUS, *UCLA Report No. 58-5* (1958).
17. R. L. POWELL, W. M. ROGERS and H. M. RODER, *Advances in Cryogenic Engineering*, Vol. II, p. 166. Plenum Press, New York (1956).
18. W. F. GIAUQUE, R. M. BUFFINGTON and W. A. SCHULZE, *J. Amer. Chem. Soc.* **49**, 2343 (1927).
19. C. V. STERNLING and L. J. TICHACEK, *Chem. Engng Sci.* **16**, 297 (1961).
20. S. J. D. VAN STRALEN, *Warmteoverdracht Aan Kokende Binaire Vloeistofmengels*. H. Veenman, Wageningen (1959).
21. S. S. KUTATELADZE, *Int. J. Heat Mass Transfer* **4**, 31 (1961).
22. P. G. KOSKY, M.S. Thesis, University of California, Berkeley (1963).
23. V. J. JOHNSON, *WADD Technical Report 60-56*, p. 3.501, Part II (1960).
24. M. J. McNELLY, *J. Imp. Coll. Chem. Engng Soc.* **7**, 18 (1953).
25. H. K. FORSTER and N. ZUBER, *J. Appl. Phys.* **25**, 474 (1954).
26. H. K. FORSTER and R. GRIEF, Paper No. 58-HT-11, ASME-AIChE Heat Transfer Conference (1958).
27. W. M. ROHSENOW, *Trans. Amer. Soc. Mech. Engrs* **74**, 969 (1952).
28. W. M. ROHSENOW and P. GRIFFITH, *Chem. Engng Prog. Symp. Series No. 18*, **52**, 47 (1956).

**Résumé**—Les coefficients de transport de chaleur dans l'ébullition en piscine et les flux maximaux dans l'ébullition par germes pour  $N_2$ ,  $O_2$  et leurs mélanges ont été mesurés sur un certain nombre de cylindres en or, en cuivre et avec plusieurs pellicules chimiques et une variété de textures de surface ou

de rugosité. On a trouvé que les coefficients d'ébullition par germes dépendent de l'orientation du cylindre, aussi bien que de la caractéristique de la surface. Les coefficients de transport de chaleur pour un mélange étaient dans tous les cas plus faibles que pour chaque constituant pur. On a trouvé que les flux maximaux dans l'ébullition par germes étaient reproductibles pour n'importe quelle surface de caractéristique constante et dépendaient de l'orientation du cylindre et de la nature chimique de la surface, mais étaient indépendants de la rugosité de la surface.

**Zusammenfassung**—Die Wärmeübergangskoeffizienten und der Höchstwärmefluss für Blasensieden bei  $N_2$ ,  $O_2$  und ihren Gemischen in freier Konvektion wurden an einer Reihe von Gold- und Kupferzylindern, sowie einigen chemischen Filmen mit verschiedenster Oberflächenbeschaffenheit gemessen. Die Wärmeübergangskoeffizienten erwiesen sich als abhängig von der Orientierung und den Oberflächeneigenschaften des Zylinders. Die Wärmeübergangskoeffizienten für ein Gemisch waren in jedem Fall geringer als die für eine reine Komponente. Der Höchstwärmefluss für Blasensieden war für gleichartige Oberflächen reproduzierbar und hing von der Orientierung des Zylinders und der chemischen Natur der Oberfläche ab; er war aber unabhängig von der Oberflächenrauigkeit.

**Аннотация**—Измерялись коэффициенты теплообмена и критические тепловые потоки при объемном пузырьковом кипении  $N_2$ ,  $O_2$  и их смеси на ряде цилиндров из золота, меди и на нескольких химических пленках с различной текстурой и шероховатостью поверхности. Было обнаружено, что коэффициенты пузырькового кипения зависят от ориентации цилиндра, а также от характера поверхности. Коэффициенты теплообмена для смеси были во всех случаях ниже чем для любого чистого компонента. Было найдено, что критические тепловые потоки при пузырьковом кипении воспроизводимы для любой поверхности, имеющей постоянную характеристику и зависят от ориентации цилиндра и химической природы поверхности, но не зависят от шероховатости поверхности.