

Until a correlation which accounts for the effects of surface character upon P.N.B.F. is available, Equation (12) or Equation (5) can be used with equal confidence over the entire liquid range for $P_r > 0.95$ for the cryogenic liquids on solids of high thermal conductivity in the earth's gravitational field. Adjustment of the numerical constant will be needed for other geometries, or for other orientations of a flat surface.

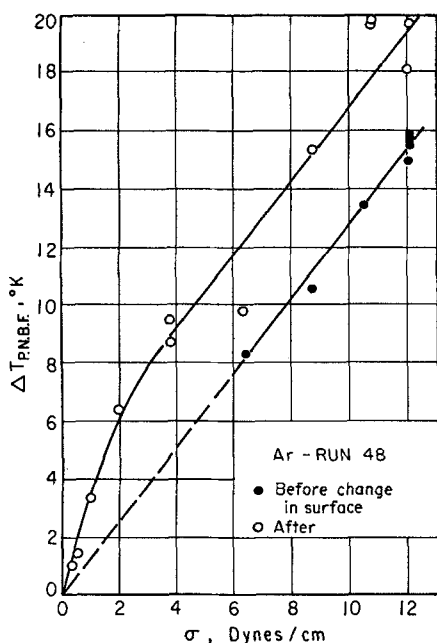


Fig. 5. ΔT at P.N.B.F. vs. vapor-liquid surface tension for argon.

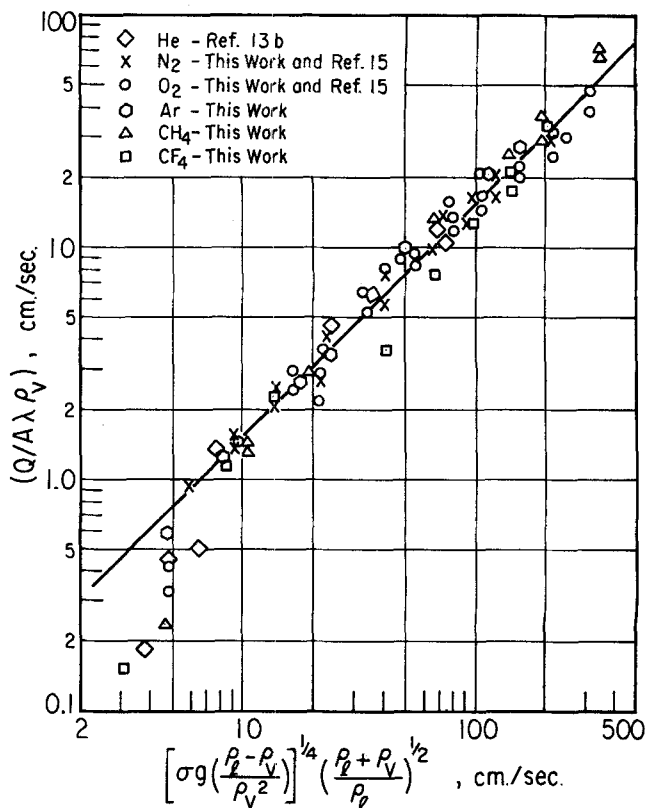


Fig. 6. Collected P.N.B.F. data for cryogenic liquids on horizontal flat platinum compared with Equations (6/9).

ACKNOWLEDGMENT

We are indebted to John C. Lyon for computational assistance.

III. Nucleate Boiling Data and Peak Nucleate Boiling Fluxes for Nitrogen-Oxygen Mixtures

Nucleate boiling curves and peak nucleate boiling fluxes (P.N.B.F.'s) have been measured for oxygen-nitrogen mixtures of 3.25, 8.35, and 68.5 mole % oxygen and for carbon dioxide free air on a flat horizontal platinum surface from 1 atm. to $P_r \sim 0.95$.

The nucleate boiling correlations of Kutateladze and of Borishanskiy-Minchenko, which were successful for the pure components, fail for the mixtures at elevated pressures. Of the correlations tested, that of McNelly is most nearly successful for both pure components and for their mixtures at all pressures.

The Chang-Snyder form of the Kutateladze correlation for the P.N.B.F. is successful for mixtures up to $P_r = 0.75$, beyond which it overpredicts the P.N.B.F. No anomalies in P.N.B.F. at 1 atm. similar to those reported for binary aqueous systems were observed.

The dramatic differences between the boiling heat transfer properties of pure fluids and of their mixtures are well known. Van Wijk et al. (68) found pronounced maxima, and occasionally double maxima, in the peak nucleate boiling flux (P.N.B.F.) vs. composition curves for the water-alcohol and water-ketone systems. Less than 0.1% of 1-octanol in water enhanced the P.N.B.F. \sim twofold. Westwater and co-workers (30, 31) found that as little as 10^{-4} mole % of certain solutes produced dramatic shifts in the boiling curves and P.N.B.F.'s of isopropanol.

Sterling and Tichacek (69) and Huber and Hoehne (70) found that the nucleate boiling heat transfer coefficient h was lower for intermediate compositions than the coefficient for either pure fluid for a wide variety of binary organic systems.

We are unaware of the existence of boiling data for cryogenic mixtures other than the 1 atm results of Giaque et al. (29) for 50% oxygen in nitrogen and the 1 atm. data (6) for the complete composition range of oxygen in

nitrogen on vertical gold plated cylinders. In both studies, the curve of h vs. ΔT for a mixture was in all cases lower than those for pure components.

The nucleate boiling correlations listed and tested in Part I appear only partially successful in predicting the behavior of mixtures. We present here data for 3.25, 8.35, 20.96, and 68.5 mole % oxygen in nitrogen over the pressure range from 1 atm. to $P_r > 0.9$ for the various mixtures and compare the data with the correlations found in Parts I and II to be most successful in predicting the behavior of the pure components.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus and procedure have been described in Part I.

All mixtures except the 20.96 mole % oxygen and the 3.16 mole % oxygen compositions were prepared by combining 99.97% liquid nitrogen and $99.6 \pm 0.1\%$ liquid oxygen (the remainder argon). The argon content was inferred from the known argon/oxygen ratio and from the oxygen content indicated by the Pauling meter. The 20.96% oxygen sample was obtained by condensing pure, dry, carbon dioxide free air. That sample therefore contained 0.93 mole % argon. The 3.16% oxygen-96.1% nitrogen-0.7% argon sample was obtained by condensing purified argon in the cryostat at the end of the tests with the 3.25% oxygen sample.

THERMOPHYSICAL PROPERTY ESTIMATION

Data for the various thermophysical properties of the oxygen-nitrogen mixtures are extremely scarce. T_c and P_c were taken to be those temperatures and pressures at which the composition of the vapor and liquid phases became identical as determined by the Pauling oxygen analyzer and thus correspond to the plain points. These results (1) for the P_c and T_c are virtually linear with composition, in agreement with the mixture data of Kuenen et al. (71, 72).

Various forms of the law of corresponding states as listed in Table 1 were used to interpolate or estimate the property data from the pure component data and the few existing data for mixtures.

Except for k , the pure component and mixture property data, when correlated as indicated, lie on a single curve to within the $\pm 5\%$ scatter in the measurements.

We know of no experimental data for k for liquid mixtures of oxygen and nitrogen other than the obviously erroneous measurements of Hammann (78). The literature data for k of both pure liquid oxygen and nitrogen fall on a single curve when plotted vs. (ρ_l/ρ_c) . We assumed that this same curve pertains for mixtures of the two components. This assumption requires the thermal conductivity of saturated liquid to be the same at the critical point for all compositions. Ziebland and Burton's data (22) indicate that k for nitrogen, oxygen and argon are equal at $T_r = 1.0$ to within the uncertainty in extrapolating measured values to T_c and P_c .

The liquid viscosity data of Rudenko (28) for oxygen, nitrogen, and air were cross plotted to interpolate viscosities for other compositions.

The surface tension data of Blagoi and Rudenko (76) for oxygen-nitrogen mixtures are adequately represented over their limited range of measured temperatures by the Ferguson (77) relationship

$$\sigma/\sigma_o = (1 - T_r)^{11/9} \quad (1)$$

as are the pure component data over the full liquid range.

We assumed that Equation (1) would hold over the full range for all mixtures. Values of σ_o were interpolated from a plot of liquid composition vs. σ_o values derived from Blagoi's measurements.

TABLE 1. CORRESPONDING STATES CORRELATIONS USED FOR ESTIMATING THERMOPHYSICAL PROPERTY DATA FOR OXYGEN-NITROGEN MIXTURES

Property	Functional relationship used	Source and data used to establish function
P	$P_r = \Phi_1(T_r)$	O ₂ , N ₂ (3, 12), air (12)
ρ_l, ρ_v	$\rho/\rho_c = \Phi_2(T_r)$	O ₂ , N ₂ (11, 12), air (12, 71), 50%, 75% O ₂ (72)
λ	$\lambda\rho_c/P_c = \Phi_3(T_r)$	O ₂ , N ₂ (16), air (73, 74), 50%, 75% O ₂ (73)
C_l	$C_l\rho_c T_c/P_c = \Phi_4(T_r)$	O ₂ , N ₂ (16), air (75)
k	$k = \Phi(\rho_l/\rho_c)$	O ₂ , N ₂ (22, 23)

EXPERIMENTAL RESULTS

The mixture data were taken in a continuous sequence of runs without exposing the test surface to the atmosphere. Nitrogen check runs to test consistency of surface properties were interspersed as indicated in Table 2.

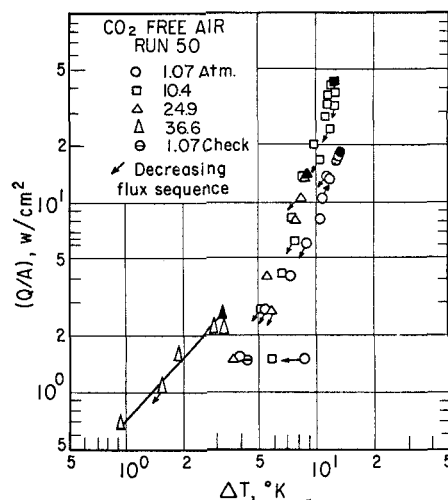


Fig. 1. Nucleate boiling curves for carbon dioxide free air on flat horizontal platinum.

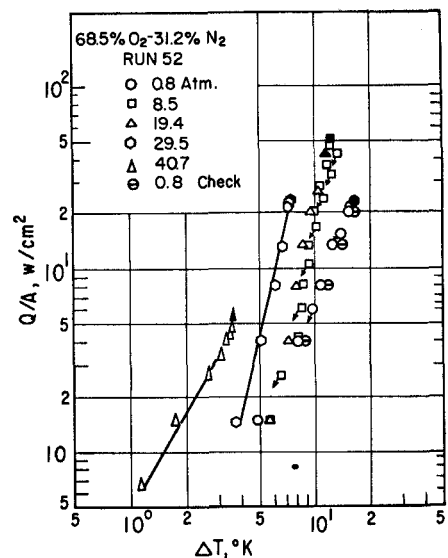


Fig. 2. Nucleate boiling curves for 68.5% oxygen-31.2% nitrogen on flat horizontal platinum.

TABLE 2. COMPOSITIONS AND SEQUENCE OF MEASUREMENTS FOR OXYGEN-NITROGEN MIXTURES

Run No.	%O ₂	%N ₂	%Ar
49	—	99.97	—
50	20.96	78.11	0.93
51	—	99.97	—
52	68.5	31.2	0.3
53	—	99.97	—
54	8.35	91.5	0.1
55	3.25	96.55	0.2
56	3.16	96.14	0.7
57	—	99.97	—

The values for h in nitrogen at 3.5 atm. increased by ~ 50% between Runs 49 and 51 but remained constant thereafter to $\pm 10\%$. The initial low pressure isobar for each mixture was repeated at the end of the run. Only for 68.5% oxygen did the check fail to duplicate the initial results (~ 10% shift in h).

Experimental results for Q/A vs. ΔT for the mixtures are shown in Figures 1, 2, 3, and 4. [They are tabulated in Appendix B of Kosky (1).] The data for the final check run with nitrogen are included in Figure 4.

A significant tendency to superheat markedly prior to nucleation is characteristic of the mixtures and is illustrated by the initial points at low pressures.

The richer oxygen mixtures showed slender inverted hysteresis loops when the test surface temperatures reached and exceeded 120°K., similar to the much more pronounced hysteresis for oxygen and argon (Part I).

The differences in behavior of the richer oxygen mixtures and the pure components are seen most graphically in a comparison of Figures 1 and 2 with Figures 4 and 7 of Part I. For the mixtures there is roughly a fourfold change in the ΔT at the P.N.B.F. in going from 1 atm. to the immediate vicinity of the critical point, while for the pure components there is roughly a seventyfold change in the P.N.B.F. ΔT 's. The slope of Q/A vs. ΔT for the pure components increases markedly as the critical pressure is approached, while for the richer mixtures there is little, if any, increase in slope with pressure.

From Figure 4, differences between the dilute oxygen mixtures and pure nitrogen are still marked as the pressure increases.

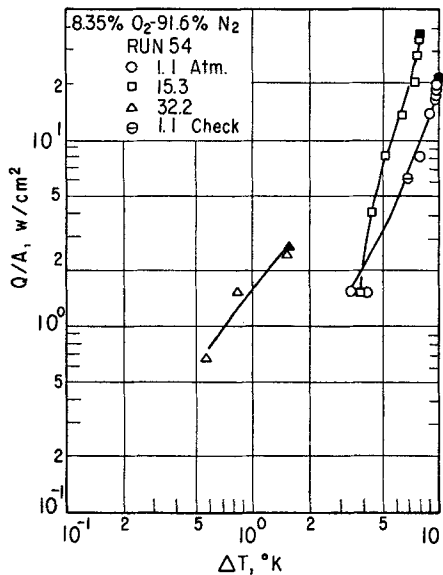


Fig. 3. Nucleate boiling curves for 8.35% oxygen-91.6% nitrogen on flat horizontal platinum.

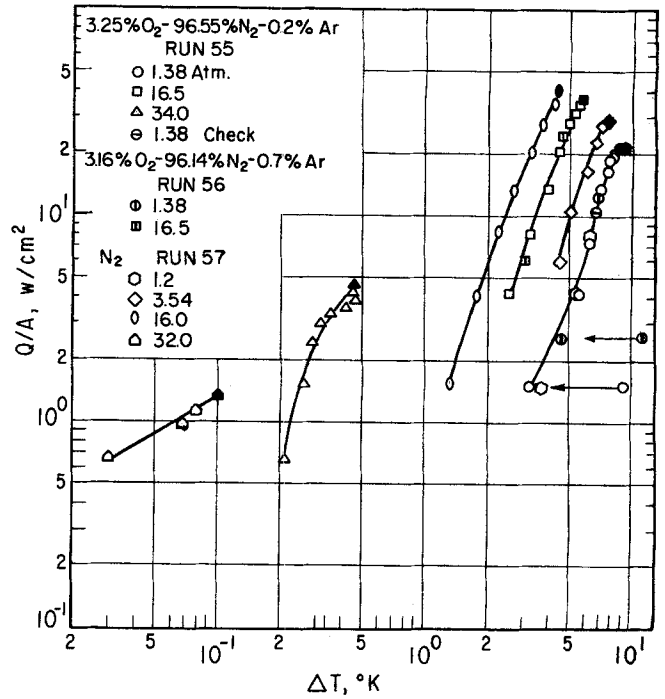


Fig. 4. Nucleate boiling curves for 3.25% oxygen-96.7% nitrogen, 3.16% oxygen-96.1% nitrogen, and pure nitrogen on flat horizontal platinum.

DISCUSSION

In Part I, the McNelly, the Kutateladze, and the Borishanskiy-Minchenko correlations were found to predict the fluid property dependence of nucleate boiling heat transfer for the pure components reasonably well, subject to variation in the value of the numerical constant K_{sf} . Figure 5 is a Borishanskiy-Minchenko plot for the carbon dioxide free air data, including nitrogen check run data. The correlation's inadequacy is apparent. This is a general conclusion which is true for all mixtures tested and which applies equally to the Kutateladze correlation. The other correlations tested in Part I were no better for mixtures than for pure components. McNelly's correlation (40)

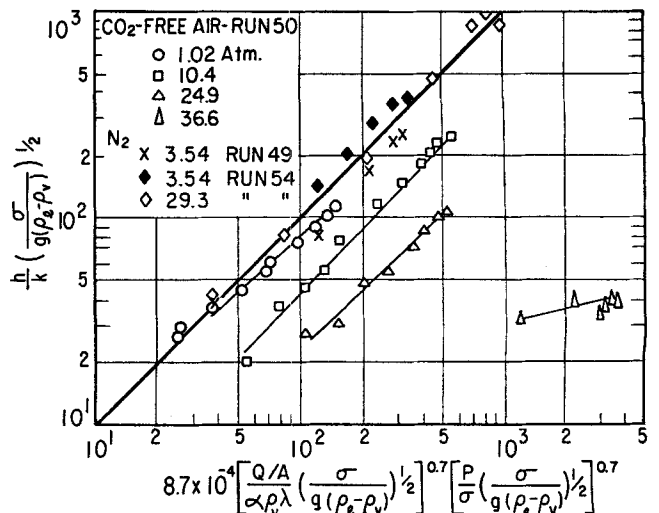


Fig. 5. Borishanskiy-Minchenko correlation plot for dry carbon dioxide free air and nitrogen on flat horizontal platinum.

$$\frac{hD}{k} = 0.225 \left(\frac{DQ/A}{\lambda\mu} \right)^{0.69} \left(\frac{PD}{\sigma} \right)^{0.31} \left(\frac{\rho_l}{\rho_v} - 1 \right)^{0.33} \left(\frac{C\mu}{k} \right)_l^{0.69} \quad (2)$$

was found to be the most successful of those tested. Figure 6 plots all mixture data in accordance with Equation (2).

Various authors (79, 80) have suggested that surface tension induced flows (Marangoni effect) contribute to nucleate boiling heat transfer. We have been unable to correlate the shift in the Borishanskiy-Minchenko curves with pressure with a Marangoni number for the mixtures.

In part II, the Kutateladze correlation for P.N.B.F. as modified by Chang and Snyder

$$\left(\frac{\text{P.N.B.F.}}{\lambda\rho_v} \right) = K \left(\frac{\sigma g(\rho_l - \rho_v)}{\rho_v^2} \right)^{1/4} \left(\frac{\rho_l + \rho_v}{\rho_l} \right)^{1/2} \quad (3)$$

was found to be most successful in representing the P.N.B.F. data for the pure components. In Figure 7, the data have been normalized at 1 atm. to eliminate the effect of changes in surface character. The richer oxygen mixtures deviate significantly from Equation (3) for $P_r > 0.75$, with Equation (3) predicting too large a P.N.B.F. For pure nitrogen and oxygen (Part II), corresponding deviations occurred only for $P_r > 0.9$. We found no anomalies for the mixtures similar to those reported by Van Wijk et al. (68), except for the 3.25% oxygen mixture when the critical pressure is closely approached. Here, the reliability of the measurements is poor for the reasons discussed in Part II because the physical property data are much less certain here even than are those for the pure components. For 3.25% oxygen, $\rho_v/\rho_l = 0.88$ corresponds to a temperature $\sim 0.2^\circ\text{K}$. below T_c . The P.N.B.F. of 4.5 w./sq. cm. there was duplicated to within 2% and appears real, although five times that calculated by Equation (3). This is outside the estimated ($\pm 100\%$) uncertainty due to that in the predicted physical property data.

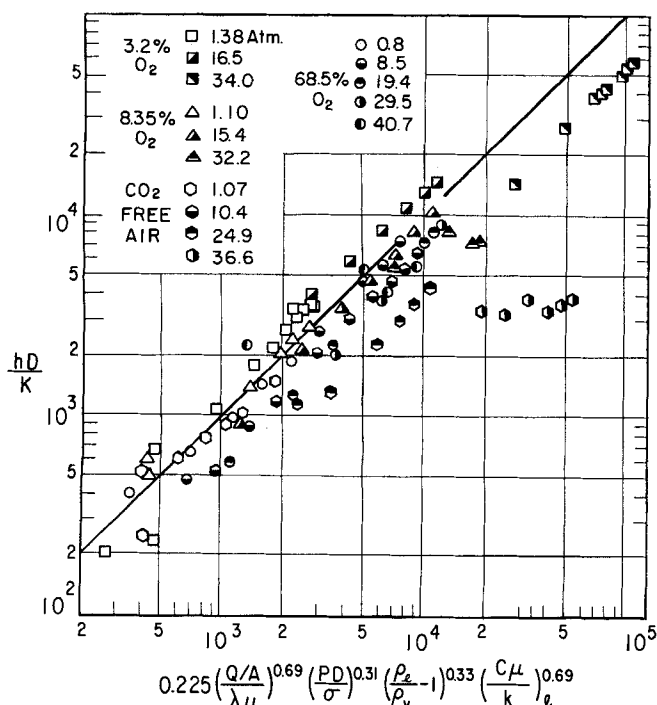


Fig. 6. Composite McNelly correlation plot for oxygen-nitrogen mixture data on flat horizontal platinum.

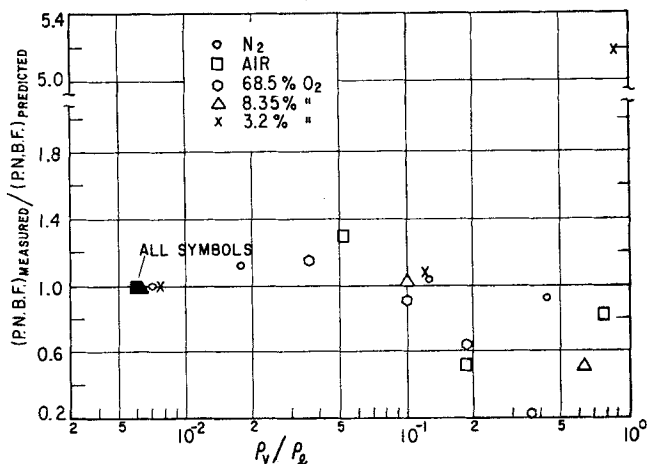


Fig. 7. Ratio of measured to P.N.B.F. Predicted by Equation (7) (Normalized at 1 atm.) for oxygen-nitrogen mixture data on flat horizontal platinum.

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NOTATION

- A = area, sq. cm.
- b = numerical constant
- C = heat capacity, joules/g. $^\circ\text{K}$.
- D = characteristic dimension of heated surface, cm.
- g = earth's gravitational acceleration, cm./sec.²
- h = heat transfer coefficient, w./sq. cm. $^\circ\text{K}$.
- H = enthalpy, joules/g.
- k = thermal conductivity, w./cm. $^\circ\text{K}$.
- K, K_A = proportionality constants
- K_{st} = adjustable parameter in correlations for nucleate boiling heat transfer
- n, n_1, n_2 = numerical exponents
- P = absolute vapor pressure (at bubble point for mixtures), dynes/sq. cm.
- ΔP = difference in saturated vapor pressure of liquid corresponding to a change in liquid temperature of ΔT $^\circ\text{K}$., dynes/sq. cm.
- Q = heat flux, w.
- T = absolute temperature, $^\circ\text{K}$.
- ΔT = temperature difference between test surface and bulk liquid, $^\circ\text{K}$.
- V = specific volume, cc./g.

Greek Letters

- α = thermal diffusivity of liquid phase, sq. cm./sec.
- λ = latent heat of vaporization, joules/g.
- μ = viscosity of liquid phase, g./cm. sec.
- ϕ = empirical function
- ρ = density, g./cc.
- σ = surface tension, dynes/cm.

Subscripts

- av = average value
- c = property at thermodynamic critical or plait point
- l = liquid phase property
- r = property reduced by property value at critical point
- sat = property along liquid/vapor saturation line
- v = vapor phase property

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