

# Pool Boiling of Cryogenic Nitrogen, Oxygen, and Their Mixtures

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Pool boiling of cryogenic nitrogen and oxygen is important, as both substances represent more than 99 % of all particles in the atmosphere. Boiling of cryogenics is commonly utilized in gas processing, air separation, cooling, or superconducting systems. The so-called chilldown is a characteristic process when handling cryogenics, which occurs when a surface at ambient temperature gets into contact with a cold cryogenic liquid. The chilldown is accompanied by transient film boiling. Investigating critical heat fluxes and film boiling of cryogenics is thus more important compared with non-cryogenic liquids. This contribution deals with heat transfer during pool boiling of cryogenic nitrogen, oxygen, and nitrogen–oxygen mixtures. Knowledge of heat transfer coefficients and of critical heat fluxes is crucial for qualified design of cryogenic apparatuses and for improved handling of cryogenics. In this contribution, pool boiling performance of pure nitrogen, oxygen, and their mixtures is investigated and suitable predictive correlations for the heat transfer coefficient and critical heat flux are analyzed. It was found that variations of thermophysical properties with composition are quite weak and sufficiently linear for nitrogen–oxygen mixtures. The pure-fluid correlation of McNelly is shown to be suitable for HTC estimation during boiling of pure nitrogen and oxygen. The mixture correlation of Thome was found to be suitable for nitrogen–oxygen mixtures.

## 1. Introduction

Pool boiling is a process which offers intense heat transfer at relatively small driving temperature differences. In other words, it is characterized by high heat transfer coefficients (HTCs) defined by the Newton's cooling law

$$\alpha = \frac{q}{(T_w - T_{\text{sat}})} \quad (1)$$

where  $T_w$  is the temperature of the heating surface and  $T_{\text{sat}}$  is the saturation temperature of the boiling liquid. The nucleate boiling regime offers the highest HTCs with respect to other boiling regimes. The maximum heat flux which can be reached during nucleate boiling is called the critical heat flux (CHF). When the heat flux  $q$  is greater than the CHF, transition from nucleate boiling to film boiling occurs which results in a strong decrease of the HTC. The rapid increase of the surface temperature during the transition can melt or damage the heating surface. HTC and CHF are the most important parameters which characterize the boiling performance. Knowledge of HTC and CHF is necessary for efficient design and operation of industrial apparatuses.

### 1.1 Cryogenic oxygen and nitrogen

Cryogenic liquids (cryogenics) are liquefied gases at temperature below  $-153$  °C. Pool boiling of cryogenics is important due to its employment for direct cooling of electronic devices, servers, or reactors by submerging them into liquid pools. Cryogenics are very often used for direct cooling of devices by boiling. For example, nitrogen is used for direct cooling to reach the so-called high-temperature superconductivity. Nitrogen is the most often used cryogen due to its inertness and abundance in Earth's atmosphere.

Large scale production of highly pure nitrogen and oxygen ( $\geq 10^2$  tons of oxygen per day with purity of the produced oxygen  $\geq 99.5$  %) is typically done by cryogenic distillation of air (Rao and Muller, 2007). Air is a mixture of mostly nitrogen (molar or volumetric concentration of 78.1 %) and oxygen (20.9 %) which together represent more than 99 % of all the molecules in the atmosphere (Lutgens and Tarbuck, 2016). Although boiling

of nitrogen is, by far, the most often studied in the literature, reliable pool boiling data for oxygen and nitrogen–oxygen mixtures are required for efficient distillation of nitrogen and oxygen from air.

Pure oxygen (or oxygen-enriched air) is often employed in various processes, such as metallurgy, glass industry, or gasification (Fu et al., 2014). Oxyfuel combustion is able to significantly reduce fuel and energy consumption, lower toxic NO<sub>x</sub> emissions, and enable more efficient carbon capturing (Soundararajan et al., 2014). It was also reported that oxyfuel combustion prevents synthesis of unwanted hydrocarbons during gasification of municipal solid waste, which, in future, might become a more environmentally friendly successor of the now-used waste incineration (Rao and Muller, 2007).

Although nitrogen is often viewed as a byproduct of oxygen production, selling nitrogen of a high purity might be advantageous and profitable. Due to its excellent inertness, pure nitrogen is used as a preservative in food, beverage, or pharmaceutical industries. It can be utilized for manufacturing of electronics, especially in semiconductor industry. Cryogenic nitrogen is also used for liquefaction of natural gas, which might become more important in the future, when difficult-to-access deposits are extracted.

## 1.2 Motivation of this work

This contribution aims to analyze models based on thorough literature review, which enable to calculate HTC and CHF values during pool boiling of pure nitrogen, pure oxygen, and nitrogen–oxygen mixtures. The literature was investigated to identify the heat transfer correlations suitable for estimation of boiling performance. HTC and CHF values calculated with these models are presented and compared in this work.

## 2. Thermophysical properties of nitrogen–oxygen mixtures

Table 1 lists the most important thermophysical properties of nitrogen–oxygen mixtures (including pure nitrogen and oxygen) which are required to calculate HTC and CHF using the correlations published in the literature.

*Table 1: The thermophysical properties of nitrogen–oxygen mixtures. All listed properties were evaluated using REFPROP (Lemmon, 2018), except for  $\Delta h_{LG}$  which was evaluated using VMG Thermo (2018).*

$x_{N_2}$ (–)	$y_{N_2}$ (–)	$T_b$ (°C)	$T_d$ (°C)	$\rho_L$ (kg m <sup>-3</sup> )	$\rho_G$ (kg m <sup>-3</sup> )	$\Delta h_{LG}$ (kJ kg <sup>-1</sup> )	$c_{pL}$ (J kg <sup>-1</sup> K <sup>-1</sup> )	$\mu_L$ (mPa s)	$\lambda_L$ (W m <sup>-1</sup> K <sup>-1</sup> )	$\sigma$ (mN m <sup>-1</sup> )
0.00	0.00	–183.0	–183.0	1141	4.47	211.7	1699	0.195	0.151	13.2
0.10	0.32	–185.6	–183.7	1109	4.43	212.8	1726	0.199	0.153	12.6
0.20	0.51	–187.7	–184.6	1075	4.42	213.4	1755	0.199	0.154	12.0
0.30	0.64	–189.3	–185.5	1039	4.44	213.5	1786	0.198	0.155	11.4
0.40	0.73	–190.6	–186.5	1004	4.46	213.2	1818	0.195	0.154	10.9
0.50	0.80	–191.7	–187.5	970	4.48	212.4	1852	0.191	0.154	10.4
0.60	0.86	–192.7	–188.7	935	4.50	211.0	1887	0.186	0.153	9.9
0.70	0.90	–193.6	–190.1	902	4.53	209.1	1923	0.181	0.151	9.6
0.80	0.94	–194.4	–191.6	869	4.56	206.5	1961	0.174	0.149	9.3
0.90	0.97	–195.1	–193.5	837	4.58	203.0	2000	0.168	0.147	9.1
1.00	1.00	–195.8	–195.8	806	4.61	198.2	2042	0.161	0.145	8.9

In nitrogen–oxygen mixtures, nitrogen is the more volatile component. However, the difference between saturation temperatures of both pure components of about 12.8 °C is not high. The so-called boiling range

$$\Delta T_{db} = T_d - T_b \quad (2)$$

where  $T_d$  and  $T_b$  is the dew-point temperature and bubble-point temperature, respectively, remains relatively low with respect to common non-cryogenic mixtures (the highest  $\Delta T_{db}$  of only about 4.2 °C corresponds to  $x_{N_2} = 0.50$ ). Figure 1 shows the variation of Property ratio ( $\gamma / \gamma_{O_2}$ ), where  $\gamma$  is a certain property, with respect to the molar composition  $x_{N_2}$ . It is obvious that the variation of all plotted properties with changing composition is quite weak and might be linearly approximated. The surface tension  $\sigma$  and liquid phase density  $\rho_L$  exhibit the strongest dependence on  $x_{N_2}$ , but their maximum variations are only around 30 %. For counterexample, the variations of vapor phase density  $\rho_G$  and liquid phase viscosity  $\mu_L$  in ethanol–water mixtures are very non-linear and higher than 300 % and 150 %, respectively (Fujita and Tsutsui, 2002).

Cryogenic liquids have an excellent wettability to most of the surfaces (even Teflon is wetted by cryogenics) which is a consequence of their low surface tension. Pool boiling of cryogenics is comparable with non-cryogenic wettable refrigerants, such as Freons (Bier and R uthlein, 1988). Due to their high wettability, boiling of cryogenics is often characterized by delayed initiation, significant temperature overshoot at the onset of nucleate boiling, and significant boiling hysteresis (HTC is higher when heat flux is decreased relative to HTC measured at

increasing heat flux). The relatively low Prandtl numbers of cryogenes are in the range from 1 to 10. Cryogenes are easily contaminated. The presence of contaminants was reported to decrease the HTC (Marto et al., 1968).

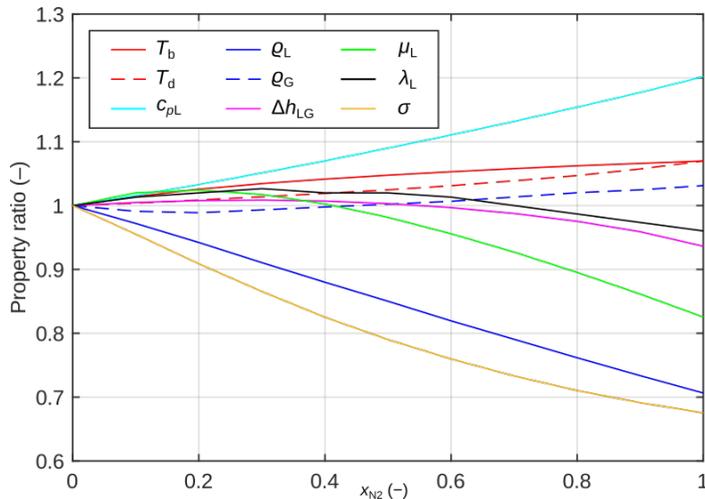


Figure 1: The ratio of various properties listed in Table 1 evaluated for all nitrogen molar fractions  $x_{N_2}$ .

### 3. HTC and CHF during pool boiling of pure nitrogen and oxygen

The correlations recommended in the literature for cryogenes were investigated. Correlations of Rohsenow (1952), Kutateladze and Borishanski (1966), Borishanski and Minchenko (1963), Labuntsov (2000), and McNelly (1953), which were all reported to be suitable for either pure nitrogen or pure oxygen, are shown in Figure 2 for pure nitrogen and in Figure 3 for pure oxygen. CHF correlations of Kutateladze (1951), Chang and Snyder (1960), and Zuber and Tribus (1958), verified in the literature for the investigated cryogenes, are also included. The average curves plotted in Figures 2 and 3 were obtained from the plotted HTC and CHF correlations. Mean standard deviations between the average and the plotted correlations are 20.2 % and 20.9 % for nitrogen and oxygen, respectively. It can be seen that the average HTC curves are very close to the predictions of the McNelly correlation. Mean relative errors between the average HTC curve and McNelly correlation are 1.6 % and 1.7 % for nitrogen and oxygen, respectively. CHFs of  $177 \text{ kW m}^{-2}$  for nitrogen and  $225 \text{ kW m}^{-2}$  for oxygen were obtained by averaging the CHF correlations. The intersection between the average HTC and CHF curves corresponds to the superheats of  $9.7 \text{ }^\circ\text{C}$  and  $12.1 \text{ }^\circ\text{C}$  for nitrogen and oxygen, respectively. The predicted CHF values for both nitrogen and oxygen are listed in Table 2 together with the corresponding HTCs and superheats. The calculated values in Table 2 generally agree with the literature.

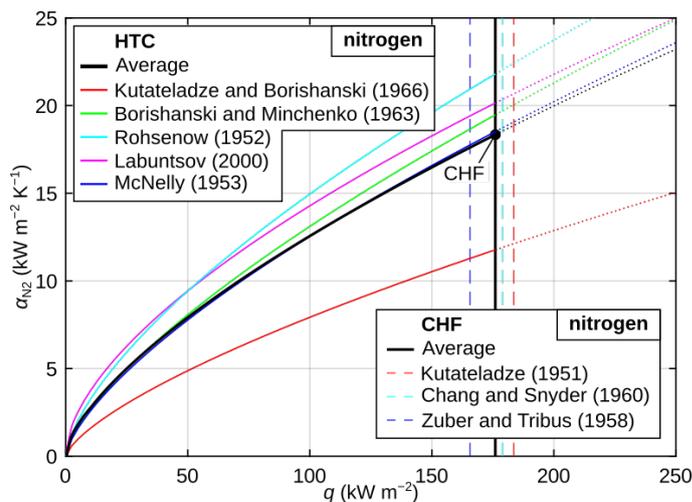


Figure 2: The comparison of the CHF and HTC during nucleate boiling of pure liquid nitrogen predicted with suitable correlations from the literature.

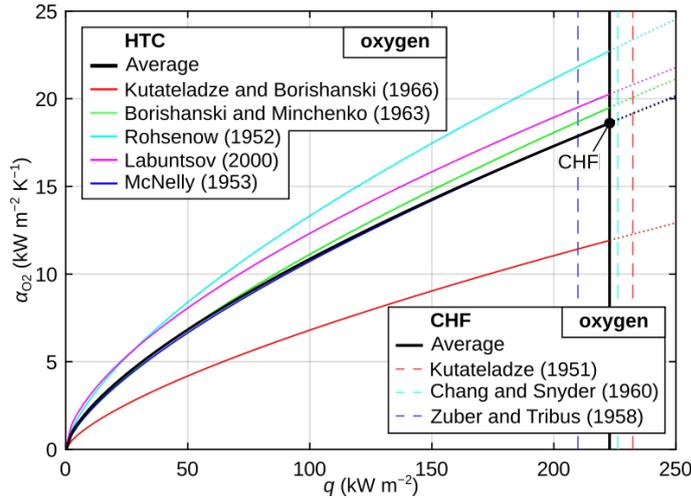


Figure 3: The comparison of the CHF and HTCs during nucleate boiling of pure liquid oxygen predicted with suitable correlations from the literature.

Table 2: The CHF together with the corresponding superheats and HTCs during boiling of nitrogen and oxygen.

Cryogen	CHF (kW m <sup>-2</sup> )	Superheat (K)	HTC (kW m <sup>-2</sup> K <sup>-1</sup> )
Nitrogen	176.0	9.6	18.3
Oxygen	222.8	12.0	18.6

#### 4. HTC and CHF during pool boiling of nitrogen–oxygen mixtures

HTCs during pool boiling of nitrogen–oxygen mixtures were calculated using the correlation of Thome (1983) which was originally developed for nitrogen–argon mixtures. According to the correlation,  $\alpha = \alpha_{id} / (1 + F)$ , where the correction factor ( $F = \Delta T_{db} / \Delta T_{id}$ ) is the ratio between the boiling range  $\Delta T_{db}$ , defined in Eq(2), and the so-called ideal superheat ( $\Delta T_{id} = q / \alpha_{id}$ ). Thome recommends to estimate the so-called ideal HTC  $\alpha_{id}$  using the harmonic mean

$$\alpha_{id} = \left( \frac{x_{N_2}}{\alpha_{N_2}} + \frac{1 - x_{N_2}}{\alpha_{O_2}} \right)^{-1} \quad (3)$$

across the HTC values for pure components ( $\alpha_{N_2}$ ,  $\alpha_{O_2}$ ). The molar fractions of nitrogen ( $x_{N_2}$ ) and oxygen ( $1 - x_{N_2}$ ) are used as weight coefficients in Eq(3). It was shown in Figures 2 and 3 that, for pure oxygen and nitrogen, the average of HTC correlations corresponded very well to the dimensionless correlation of McNelly (1953)

$$\frac{\alpha L_{ch}}{\lambda_L} = 0.225 \left( \frac{c_{pL} \mu_L}{\lambda_L} \right)^{0.69} \left( \frac{q L_{ch}}{\Delta h_{LG} \mu_L} \right)^{0.69} \left( \frac{p L_{ch}}{\sigma} \right)^{0.31} \left( \frac{q_L}{q_G} - 1 \right)^{0.33} \quad (4)$$

Due to the agreement,  $\alpha_{N_2}$  and  $\alpha_{O_2}$  in Eq(3) were predicted using the McNelly correlation (4). In the McNelly correlation, HTC  $\alpha$  does not depend on the characteristic length  $L_{ch}$ , since  $L_{ch}$  might be omitted from both sides of Eq(4).

Besides, it was also tested whether the ideal HTCs  $\alpha_{id}$  calculated for nitrogen–oxygen mixtures with the pure-fluid correlation of McNelly could be used instead of Eq(3). Although using correlation (4) instead of (3) requires knowledge of various thermophysical properties, which were adopted from Table 1, the advantage of this approach lies in the fact that one does not require the HTCs of both pure components ( $\alpha_{N_2}$  and  $\alpha_{O_2}$ ), which might be laborious to obtain.

Figure 4 shows the HTCs calculated for nitrogen–oxygen mixtures at various molar fractions  $x_{N_2}$ . The HTCs are the highest for pure nitrogen and pure oxygen. All the HTCs obtained for nitrogen–oxygen mixtures are lower which is common and typical for binary mixtures. Figure 4 also shows that differences in results of the Thome correlation are negligible when  $\alpha_{id}$  is calculated either with interpolation (3) or with the McNelly correlation (4). CHF of nitrogen–oxygen mixtures were reported to be more predictable than HTCs. Also, correlations for CHF were reported to be more accurate than HTC correlations (Kosky and Lyon, 1968). CHF valid for pure oxygen was reported to quickly decrease to that of pure nitrogen if the nitrogen molar fraction is in the range  $x_{N_2} \geq 0.2$  (Lyon, 1964). Because of this, the CHF plotted in Figure 4 is assumed to be equal to the CHF of pure nitrogen.

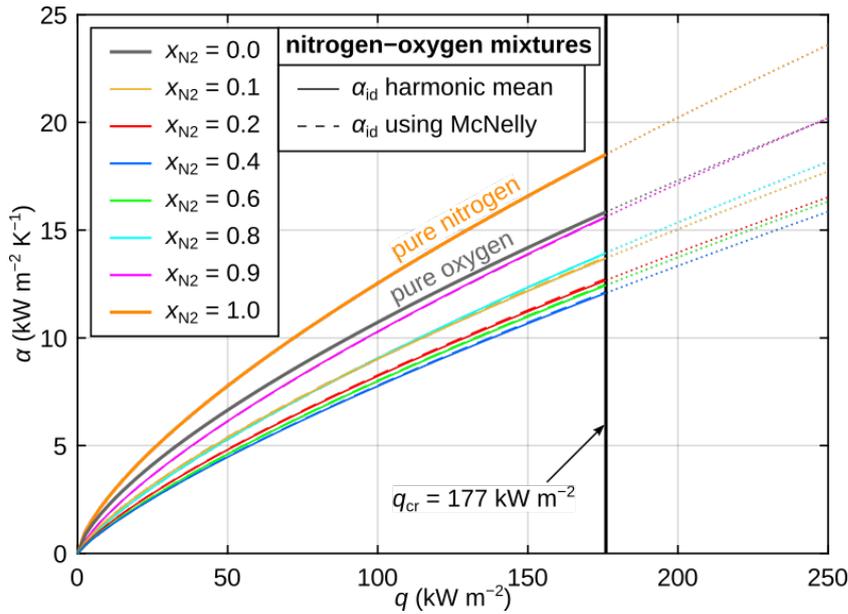


Figure 4: HTC during pool boiling of liquid nitrogen–oxygen mixtures. Results obtained by the interpolation of  $\alpha_{id}$  and by the correlation of McNelly, see Eq(3) and Eq(4), respectively, are indistinguishable.

Figure 4 also shows that HTCs obtained for mixtures with  $x_{N_2}$  of 0.2, 0.4, and 0.6 are nearly identical. This was already noticed by Lyon (1964) according to whom, a single boiling curve might be used to represent boiling performance for mixtures in the range of  $x_{N_2}$  from 0.25 to 0.65.

For a quick estimation of HTC, the empirical power-law function

$$\alpha = C q^n \quad (5)$$

is often used. The values of the empirical coefficient  $C$  and exponent  $n$ , both evaluated from the curves in Figure 4, are given in Table 3 for the entire range of  $x_{N_2}$ . To use the values in Table 3, the heat flux  $q$  needs to be in ( $W m^{-2}$ ) and the resulting  $\alpha$  is in ( $W m^{-2} K^{-1}$ ). The values of the exponent  $n$  are comparable with the literature. During pool boiling of various cryogenes,  $n$  was reported to be in the range from 0.66 to 0.78.

Table 3: Values of the empirical coefficient  $C$  and exponent  $n$  of Eq(5) calculated for nitrogen–oxygen mixtures.

Coefficient	$x_{N_2}$ (-)										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$C (W^{1-n} m^{-2-2n} K^{-1})$	3.81	1.76	1.20	0.99	0.91	0.89	0.93	1.07	1.33	2.05	4.45
$n (-)$	0.69	0.74	0.77	0.78	0.79	0.79	0.79	0.78	0.77	0.74	0.69

## 5. Conclusions

Based on the literature review, HTC and CHF models for boiling of nitrogen, oxygen, and nitrogen–oxygen mixtures were investigated. Pool boiling of pure nitrogen is characterized by higher HTC and lower CHF compared with pure oxygen. Nitrogen–oxygen mixtures follow the HTC trends typical for ordinary binary mixtures, i.e., HTC of mixtures is lower than HTCs of both pure components. The McNelly pure-fluid correlation can be used for quite accurate predictions of boiling HTCs for pure nitrogen and oxygen. It can be also employed for calculation of the ideal HTCs during pool boiling of nitrogen–oxygen mixtures. The mixture correlation of Thome was found to give results comparable with the literature and might be applied for estimation of HTC during nucleate boiling of nitrogen–oxygen mixtures.

### Nomenclature

$C$  – empirical coefficient,  $W^{1-n} m^{-2-2n} K^{-1}$   
 $c_{pL}$  – specific thermal capacity,  $J kg^{-1} K^{-1}$   
 $L_{ch}$  – characteristic length, m  
 $n$  – empirical exponent, –  
 $p$  – pressure, Pa

$q$  – heat flux,  $W m^{-2}$   
 $T_b$  – bubble-point temperature,  $^{\circ}C$   
 $T_d$  – dew-point temperature,  $^{\circ}C$   
 $T_{sat}$  – saturation temperature,  $^{\circ}C$   
 $T_w$  – surface temperature,  $^{\circ}C$

$x_{N_2}$  – molar fraction of nitrogen in liquid, –  
 $y_{N_2}$  – molar fraction of nitrogen in vapor, –  
 $\alpha$  – heat transfer coefficient,  $W\ m^{-2}\ K^{-1}$   
 $\alpha_{id}$  – ideal heat transfer coefficient,  $W\ m^{-2}\ K^{-1}$   
 $\Delta h_{LG}$  – latent heat of vaporization,  $J\ kg^{-1}$   
 $\Delta T_{db}$  – boiling range, K

$\lambda_L$  – liquid thermal conductivity,  $W\ m^{-1}\ K^{-1}$   
 $\mu_L$  – liquid dynamic viscosity, Pa s  
 $\rho_G$  – vapor density,  $kg\ m^{-3}$   
 $\rho_L$  – liquid density,  $kg\ m^{-3}$   
 $\sigma$  – surface tension,  $N\ m^{-1}$

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