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Contribution to the study of neon-nitrogen mixtures at low temperatures

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Abstract. Theoretical studies show that neon can influence the phase diagram of nitrogen, lowering its triple-point temperature. The use of a neon-nitrogen mixture that could remain liquid at temperatures below the triple-point of nitrogen (63.15 K) could solve some problems in the temperature range from 44 to 54 K, where no pure cryogenic liquids exist at all. This work consists of a preliminary study of mixtures of neon and nitrogen at low temperatures, in order to assess whether a liquid neon-nitrogen mixture below 63.15 K can be obtained. Indications that there may be a process of neon dilution in solid and liquid nitrogen are shown, as well as evidence of changes in the phase diagram of nitrogen due to the introduction of neon, in comparison to a model that supposes no interaction between the two substances. Evidences of a change in the nitrogen triple-point temperature from 63.15 to 62.5 K are presented and discussed.

1. Introduction

In cryogenics, there is a constant search for new and better methods of achieving and maintaining low temperatures. For example, obtaining a stable cryogenic liquid in the temperature range from 40 to 80 K would be of great interest for use in high-temperature superconductors, Joule-Thomson cryocoolers and in phase-change thermal energy storage units [1].

An advantage of having a cryogenic liquid bath as opposed to mechanical cryocoolers is its natural temperature stability: for example, with a pure substance, as long as the saturation pressure is kept constant, so will the temperature. Additionally, the lack of moving parts also makes liquid baths suitable where vibrations are undesirable, or when mechanical wear should be avoided. However, for each cryogenic liquid there is a temperature range one can work in; the pressure can only be adjusted within the limits of the fluid's liquid-vapor saturation curve. Figure 1 shows that there is no cryogenic fluid in the range 45–53 K. This range can be extended to 45–63 K, because even though oxygen and fluorine exist in that range, the vapor pressure is negligible, rendering them unsuitable for practical applications: a fluid with a saturation pressure similar to that of atmospheric conditions would be preferable [2].

It is then important to investigate mixtures of pure fluids as a solution for this gap in cryogenic fluids. Some studies [2, 4] show the potential of a mixture composed of neon and nitrogen; some authors [4, 5] have obtained experimental data with neon-nitrogen mixtures and even with a ternary mixture of neon, nitrogen and helium. REFPROP [3] calculations show that a nitrogen-rich mixture could exist in the liquid state at temperatures around 58 K. However, there is no known experimental data for temperatures below the triple point of nitrogen. This work aims



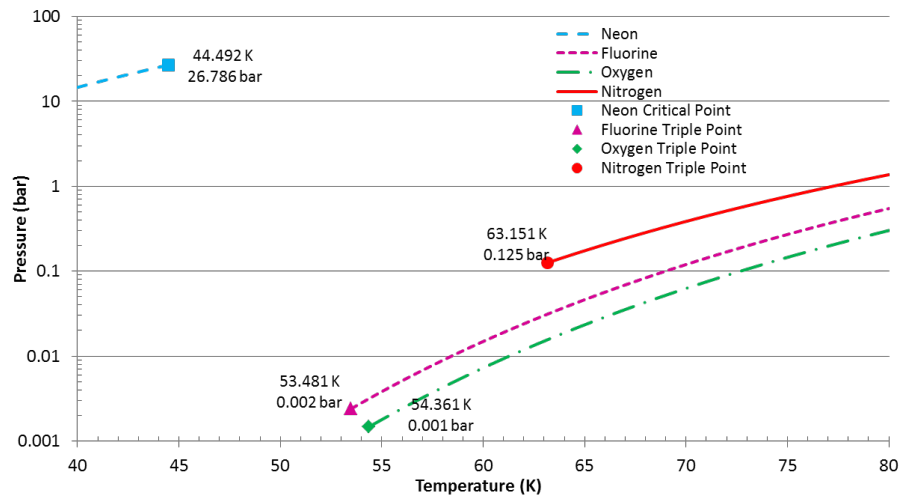


Figure 1. Liquid-vapor coexistence curves of some substances in the temperature range 40–80 K. The nonexistence of a suitable fluid between the critical point of neon (■) and the triple point of nitrogen (●) is visible. Data from REFPROP [3].

to investigate the effects of neon on the triple point of nitrogen, and to assess whether a liquid neon-nitrogen mixture below 63.15 K can be achieved.

2. Pressure cell for mixture experiments

A special, multipurpose cell was built, enabling the detection of temperature changes induced by liquid drop into the evaporator and of temperature plateaus that occur during a triple-point transition, and the measurement of $P(T)$ saturation curves. To “force” the dilution of neon in liquid nitrogen, the cell was built to withstand pressures up to 25 bars. Figure 2 illustrates one of the working modes of this cryogenic cell.

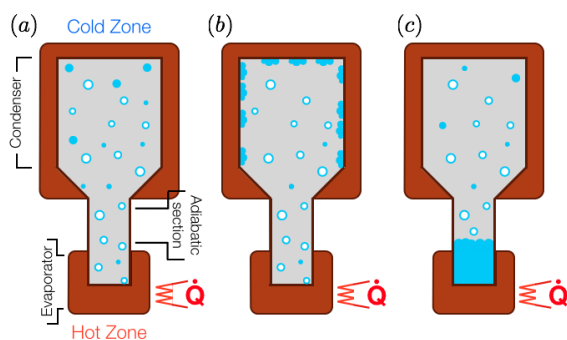


Figure 2. One of the operation modes of the cell: (a) at the beginning of operation, there is only gas inside the cell; (b) liquid starts to condense in the colder part (condenser), in equilibrium with its vapor; (c) enough liquid condenses so that it can drain through the adiabatic section down to the evaporator.

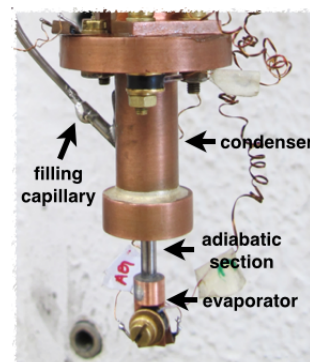


Figure 3. Multipurpose cryogenic cell mounted in the cryocooler via a gas-gap heat switch (not shown). Thermometers, resistive heaters and filling capillary are highlighted.

It is composed of a condenser ($\approx 2.5 \text{ cm}^3$) and a much smaller evaporator ($\approx 28 \text{ mm}^3$).

Both the condenser and evaporator are zones with a good thermal homogeneity, made out of copper; the two are separated by a thin-walled stainless steel tube (wall thickness 250 μm) which allows for a reasonable thermal decoupling between the condenser and the evaporator. A low-temperature cell of this type seems to be a solution for the study of neon-nitrogen mixtures for various reasons: the evaporator can be made small and with a low thermal inertia, making it possible to detect if small amounts of liquid fall into it: assuming that the solid phase remains stuck to the condenser walls, an abrupt decrease in the evaporator's temperature would indicate that liquid had been formed. Figure 2 illustrates the steps of such an experiment. The cell was coupled to a two-stage Gifford-McMahon cryocooler via a gas-gap heat switch that was extensively characterized in our laboratory [6], although the heat switch was kept in its ON state at all times. Figure 3 illustrates the cell as well as thermometer and heater placement. We used Cernox thermometers, which were calibrated against a silicon diode thermometer, using its standard curve (± 0.4 K).

The filling capillary was connected to a room-temperature manifold for gas management and pressure measurements. This allows us to have an additional temperature reading inside the cell: through pressure measurements (± 5 mbar), one can deduce the temperature of the liquid-vapor (or solid-vapor) interface along the saturation line of a pure fluid. Pressure measurements will also inform on how the saturation curve of nitrogen is modified (or not) if neon is diluted into its condensed phases.

3. Liquid drop as an indicator of phase change

Some preliminary tests with pure nitrogen were carried out to study the thermodynamic behavior of the cell and whether liquid drop could be observed in the evaporator (Figure 2). One such test is depicted in Figure 4, where the system was filled with 3 bars of nitrogen at room temperature, making up ≈ 35 mm³ of liquid (or solid) at the triple-point temperature (63.15 K).

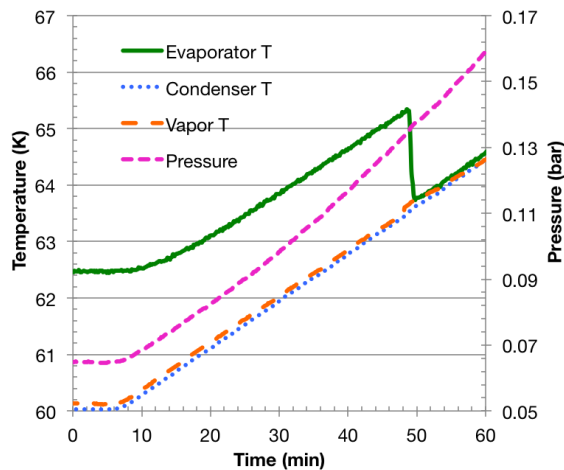


Figure 4. Liquid drop in the evaporator from the solid phase in the condenser for pure nitrogen. Filling pressure is 3 bars (condensed volume ≈ 35 mm³).

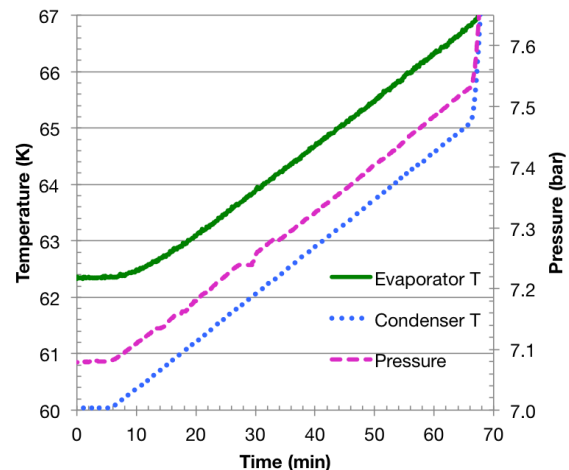


Figure 5. Absence of liquid drop in the evaporator from the solid phase in the condenser for a 17% nitrogen, 83% neon mixture. Nitrogen partial pressure is 3 bars.

At $t = 0$ min, after a rapid cooling that leads to $T_{\text{condenser}} < T_{\text{evaporator}}$, all of the nitrogen has been condensed into its solid phase in the condenser (confirmed by the fact that T_{vapor} is in agreement with $T_{\text{condenser}}$), and the evaporator is being kept hot (5 mW applied directly onto it) so that $T_{\text{evaporator}} > T_{\text{condenser}}$, forcing the condensation to occur in the condenser. At $t = 7$ min

the whole cell is heated slowly in a controlled ramp, while the evaporator maintains its thermal gradient due to the extra heating.

At $t = 49$ min the condenser passes the triple point of nitrogen (measured 63.30 K, 125 mbars): the solid melts, coating the condenser walls. The 150 mK discrepancy to the reference value (63.15 K [3]) was consistently observed, and is in agreement with the calibration uncertainty of the thermometers described in section 2. At $t = 50$ min the liquid drops into the evaporator, as indicated by the sudden drop in temperature. This experiment shows that our cell is suitable to detect liquid droplets falling into the evaporator, and that the solid phase that is formed in the condenser remains stuck to its walls. However, this method for detecting liquid drop is not suitable for tiny liquid amounts, as when the solid-to-liquid phase change occurs the resulting liquid coats the condenser walls in the form of multiple droplets that, not percolating, do not fall into the evaporator.

After assessing that liquid drop could be detected in a well-known case (pure nitrogen) and in the previously described conditions, we performed a similar experiment with a neon-nitrogen mixture. The mixture contained the same quantity of nitrogen (partial pressure of ≈ 3 bars), but 14 bars of neon gas were added, making up a 17% nitrogen, 83 % neon mixture. Figure 5 shows the results obtained with this mixture, in an experiment equivalent to that shown in Figure 4.

Because pressure cannot be converted unambiguously into temperature for neon-nitrogen mixtures as was the case for a pure substance, pressure measurements were only used to assess where the solid-liquid-vapor coexistence takes place: similar behavior of this curve to either the condenser or the evaporator one will give that information.

At the beginning of the heating ramp we observe that the pressure follows the behavior of the condenser temperature, meaning that this is where the condensed phase is at $t = 0$ min. There is no registered liquid drop in the evaporator even as the triple point temperature of nitrogen is reached. Though there are no definite answers to this phenomenon yet, it might be explained if a smaller amount of nitrogen is condensed due to the presence of neon, rendering the resulting liquid amount unable to drop through percolation to the evaporator. These preliminary results alone do not yet allow for a full and clear understanding of the mechanisms at play. Let us note that a small pressure dip can be observed at $t = 30$ min, without any signs of temperature change: an explanation for this small anomaly seems premature in the light of our current understanding of these phenomena.

4. Changes in the solid-liquid-vapor coexistence temperature

In order for a triple-point transition to be observable by thermal measurements in similar conditions to those described in the previous section, the phase change needs to occur in the evaporator of the cell: if the phase change occurs in the condenser, its relatively large thermal mass and the fact that it is coupled to the cold finger of the cryocooler will render the transformation virtually undetectable. To overcome this, the experiments described in this section were prepared so that the condensed phase forms and remains in the evaporator.

Figure 6 shows the triple-point transition for pure nitrogen in the cell, for a filling pressure of 1.5 bars at room temperature, corresponding to a condensed volume of $\approx 15 \text{ mm}^3$ at the triple-point temperature. The cold finger temperature was slowly ramping up, keeping the evaporator temperature lower than the condenser's at all times. Between $t \approx 3$ min and $t \approx 6$ min, both pressure and evaporator temperature show a plateau: the change from the solid to the liquid phase at constant pressure and temperature is characteristic of a triple point for a pure substance. Due to the aforementioned deviations in thermometer calibration, the temperature at which the phase change occurs was measured to be 63.30 K, same triple-point temperature of Figure 4, 150 mK above the nominal temperature for pure nitrogen. Pressure measurements, however, indicate the expected 125 mbars; both temperature and pressure measurements were

shown to be reproducible. With this experiment we conclude that it is possible to observe a triple-point transition in the evaporator for condensed volumes as small as 15 mm^3 .

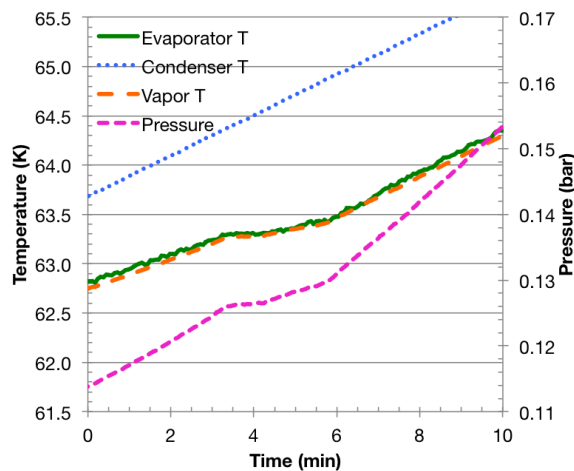


Figure 6. Triple-point transition of pure nitrogen, filling pressure of 1.5 bars.

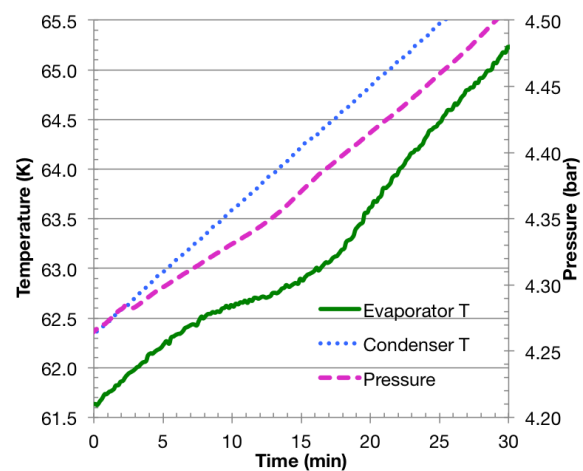


Figure 7. Triple point transition for a 33% neon, 67% nitrogen mixture, filling pressure of 16.5 bars and positive temperature slope. The phase change at a temperature below 63.15 K is visible.

A similar experiment was carried out with a mixture containing 33% neon, 67% nitrogen with a nitrogen partial filling pressure of 11 bars at room temperature. As in the experiment with pure nitrogen, the temperature of the cold finger is slowly ramped up; results are depicted in Figure 7. An anomaly in the evaporator temperature (also observable in the pressure), reminiscent of a plateau, clearly starts at 62.5 K. Considering the previously mentioned calibration deviation, this anomaly would start at around 62.35 K, 0.8 K below the nominal triple-point temperature for pure nitrogen.

Taking into account the reproducibility of our measurements, we consider this lowering of the triple-point temperature as significant and we attribute it to the presence of neon, that exerts its partial pressure over the condensed nitrogen phase and that can also be diluted in the condensed phase itself, effectively preventing solidification. Additionally, whereas we can observe a plateau in both pressure and temperature in the case of pure nitrogen, in the mixture the pressure does not remain constant at the transition (and neither does the temperature). This is expected for a solid-liquid-vapor coexistence scenario in binary mixtures: according to the Gibb's phase rule, for a binary mixture there is one additional degree of freedom where these three phases coexist in equilibrium, meaning that both the pressure and the temperature can vary throughout the phase change.

To confirm that this change in the triple-point temperature was not due to the cell's thermal behavior or hysteresis, the same experiment was performed with the same mixture but with a negative slope ramp in temperature, *i.e.* creating solid from a liquid-vapor mixture; results are shown in Figure 8. The phase transition starts at $\approx 62.6 \text{ K}$, clearly below 63.15 K, with a small plateau in pressure as well as in temperature. Both experiments show similar results for the temperature at which this anomaly occurs, regardless of the direction of the phase change. The slightly different pressure at which this phenomenon occurs could be explained in the framework of the results described in the next section.

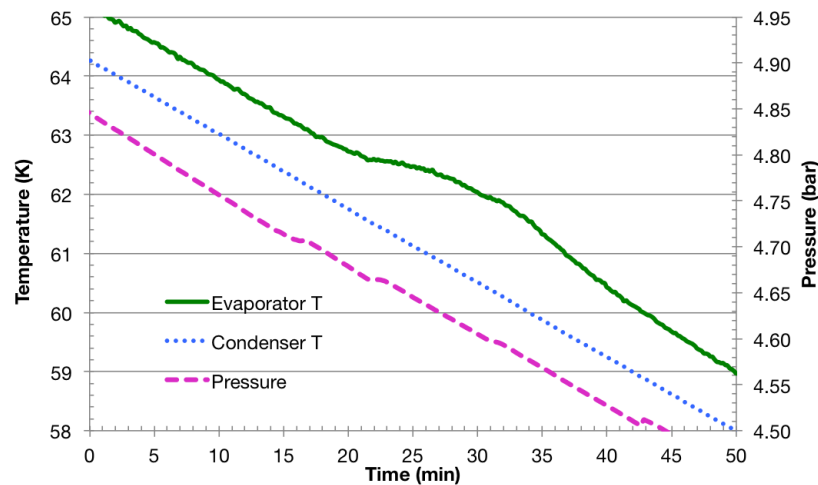


Figure 8. Triple point transition for a 33% neon, 67% nitrogen mixture, filling pressure of 16.5 bars and a negative temperature slope. The phase change at a temperature below 63.15 K is visible.

5. Changes in the phase diagram of a mixture

Figure 9 depicts the pressure-temperature diagram for the 17% nitrogen, 83% neon mixture experiment shown in section 3, compared to a non-interaction model [7]: for this experiment we chose this mixture (richer in neon) so that the effects of neon, if any, on the nitrogen phase diagram would be amplified. The non-interaction model computes the pressure-temperature behavior for a given filling pressure and mixture composition. It assumes that there is no interaction between neon and nitrogen molecules, *i.e.* that neon cannot influence the phase diagram of nitrogen. Because we assume no interaction, the total pressure is the sum of the partial pressures of neon and nitrogen in the system for any given temperature, whatever the existing phases in the cell may be. The existence of an equilibrium curve other than the one predicted by the model may indicate a change in the mixture's phase diagram, effectively showing that neon can influence nitrogen phase changes.

In Figure 9, a good agreement between the model and experimental data is found for the temperature range 300–80 K, where both neon and nitrogen are in the gaseous state, behaving as an ideal gas mixture. The temperature range from 80 down to 30 K, however, differs strongly from the model. Figure 10 depicts a close-up of this area.

This temperature range is where nitrogen starts to exist in a condensed state. Three different equilibrium curves can be observed, as indicated by the arrows. The existence of equilibrium curves different from the one predicted by the model indicates that neon does play a part in influencing the phase diagram of nitrogen, and that the mixture does not behave as an ideal one when there is condensation. The phase diagram was thus changed due to the dilution of neon in the condensed phases of nitrogen.

The interpretation of these multiple $P(T)$ curves is far from easy. However: 1) Whereas in the non-interaction model liquefaction starts at 79 K, in our experiment this phase transition starts at ≈ 74 K. This delay in liquefaction seems to indicate that neon effectively modifies the nitrogen liquid-vapor transition; 2) All the $P(T)$ results indicate that for a given temperature, the corresponding pressure is always higher or equal to that calculated by the non-interaction model. Again, this is what the work of other authors predicted [2, 4]; 3) The apparent existence of three and only three equilibrium $P(T)$ curves is puzzling. Progressive distillation of neon and

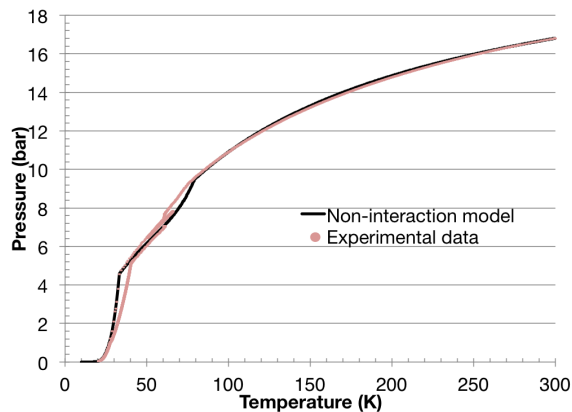


Figure 9. Pressure-temperature diagrams obtained with a 83% neon mixture and a filling pressure of 16.7 bars at room temperature.

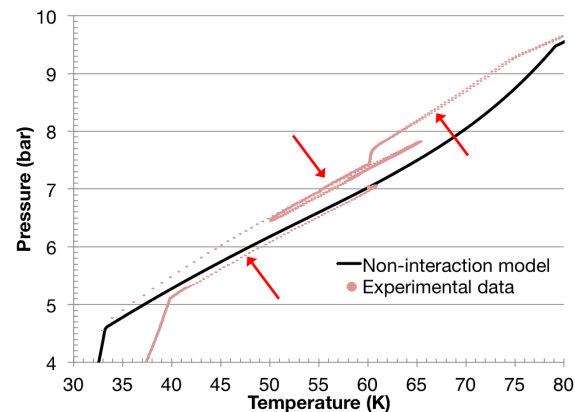


Figure 10. Close-up on the 30–80 K range of the pressure-temperature experimental data for the 83% neon mixture.

nitrogen in the cell and in the room temperature volume could explain this. If this is the case, the actual composition of the mixture inside the cell changes with time, leading to different $P(T)$ curves. As a matter of fact, starting with an 83% neon mixture the “first” liquefaction curve is at a significantly higher pressure than the predicted curve. At $T \approx 60$ K the pressure decreases, leading to a lower $P(T)$ equilibrium curve. In the condensed phases of nitrogen, the dilution of neon can be much smaller than in the gaseous phase, which would lead to an enrichment of the cell volume in nitrogen. Allowing this process to extend further may lead to a significant change in the initial composition inside the cell, and hence to different $P(T)$ results along the experiments. Further experiments, possibly in a modified experimental set-up, are needed to study these effects, as well as the development of a model that accounts for interaction between neon and nitrogen; for now the development of such model was considered premature, as there are many still many variables left to understand.

6. Conclusions

This work aimed to initiate an experimental study on neon-nitrogen mixtures at low temperatures, to investigate whether this type of mixture can be a solution for a working fluid in the 40–80 K range for cryogenic applications. Preliminary experimental data has shown that there is a dilution of neon atoms into the condensed phases of nitrogen, observable by pressure deviations to the phase diagram of the pure fluid. This dilution induces changes in the phase diagram, evidenced by the comparison with a non-interaction model. As far as literature review enabled us to assess, this is the first time that there is experimental data that shows a modification in the phase diagram due to the dilution of neon in the condensed phases of nitrogen in the region where solid nitrogen usually exists. As a matter of fact, we observed the characteristic plateau at the triple point for pure nitrogen and we have shown that, for neon-nitrogen mixtures, this plateau changes into a much smoother anomaly that starts at a temperature 0.8 K lower than it does for the pure fluid. Despite this rather small shift in temperature, these results indicate that it may be possible to have a liquid mixture below the triple point of nitrogen. While the results presented in this paper are not yet fully understood, further work is needed on this subject. As far as experimental work is concerned, it is mandatory to develop a reliable way to detect liquid inside the low temperature cell and distinguish it from the solid phase. It would also be useful to gather the composition of the condensed phase.

Experiments performed in a closed low temperature cell would allow for different and interesting results, as this would avoid progressive distillation phenomena and render the interpretation of the experiments easier.

Acknowledgements

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