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"Green" use of fluorocarbons in Cherenkov detectors and silicon tracker cooling systems: challenges and opportunities

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Saturated fluorocarbons (SFCs: chemical form $\boldsymbol{C_nF_{(2n+2)}}$) are chosen for their optical properties as Cherenkov radiators, with C_4F_{10} and CF_4 used in the COMPASS and LHCb Ring Imaging Cherenkov detectors at CERN. Their non-conductivity, non-flammability and radiation resistance also make them ideal coolants, with C_6F_{14} liquid used in all LHC experiments, and C_3F_8 used as an evaporative coolant in the ATLAS silicon tracker. While SFCs have high Global Warming Potentials (GWP typically > 5000*CO_2), fluoro-ketones (FKs: of chemical form $\boldsymbol{C_nF_{2n}O}$) can offer similar performance at very low, or zero-GWP.

This paper considers use of heavy SFC and FK vapours in Cherenkov detectors. The blending of high-order (C > 4) SFC or FK vapours with a light carrier gas is explored to replicate the refractivities of CF_4 and C_4F_{10}, to reduce or eliminate the GWP "load" (in equivalent tonnes of CO_2) in large Cherenkov radiator volumes. Subject to optical testing, 3M NOVEC® 5110 ($C_5F_{10}O$) - blended with N_2 and controlled in real time using sound velocity gas mixture analysis - could replace C_4F_{10} and CF_4 in RICH detectors. New, non-cyclic isomers of C_4F_8O could directly replace C_4F_{10} and - blended with N_2 - also replace CF_4.

Noting the impending EU restrictions on fluorinated compounds, and (2025) withdrawal of 3M Corp. from the PFAS (Per- and poly-fluoroalkyl substances) market, radiator GWP load reduction through use of legacy stocks of C_5F_{12} & C_4F_{10} - blended with N_2 to replicate the respective refractivities of C_4F_{10} & CF_4 - is also considered.

The radiation tolerance and thermal performance of 3M NOVEC® 649 ($C_6F_{12}O$) liquid was sufficiently promising for to be considered to replace C_6F_{14} in liquid cooling applications at CERN. Although not industrialized over the full $C_nF_{2n}O$ range, lighter (C < 4) fluoro-ketone molecules - for example C_2F_4O isomers, with similar thermodynamics to C_2F_6, and subject to toxicity, materials compatibility and low-GWP verifications - might allow lower operating temperatures than possible with evaporative C_3F_8 or CO_2 for the cooling of future silicon trackers operating in high luminosity environments.

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1. Introduction

Saturated fluorocarbons (SFCs: of chemical structure $C_nF_{(2n+2)}$) are chosen for their optical properties as Ring Imaging Cherenkov detector radiators. At CERN LHCb RICH-2 uses a 100 m^3 CF_4 radiator, while COMPASS and LHCb RICH-1 respectively use 100 m^3 & 4 m^3 of C_4F_{10}.

SFCs are non-toxic, non-ozone-depleting, radiation resistant, non-conductive and non-flammable, making them ideal coolants for electronics and semiconductor trackers. However their high Global Warming Potentials (GWPs 5000-9000*CO_2) contributed 37% to CERN's CO_2 and CO_2-equivalent direct emissions in 2022 [1], for an SFC loss of around 10 tonnes. Partly through reduced SFC use and losses, improved monitoring and closed-circulation [2], CERN aims by the end of 2025 to reduce its CO_2 equivalent emissions to 72% of 2018 levels.

Figure 1a illustrates the molecular shapes of common SFCs, along with their 20-year GWPs and (low) inhalation toxicity ratings ([H335] under the GHS classification scheme [3]). Below are shown their same carbon-order fluoro-ketone (FK) analogues, based on non-cyclic, spurred oxygen $C_nF_{2n}O$ molecular topology.

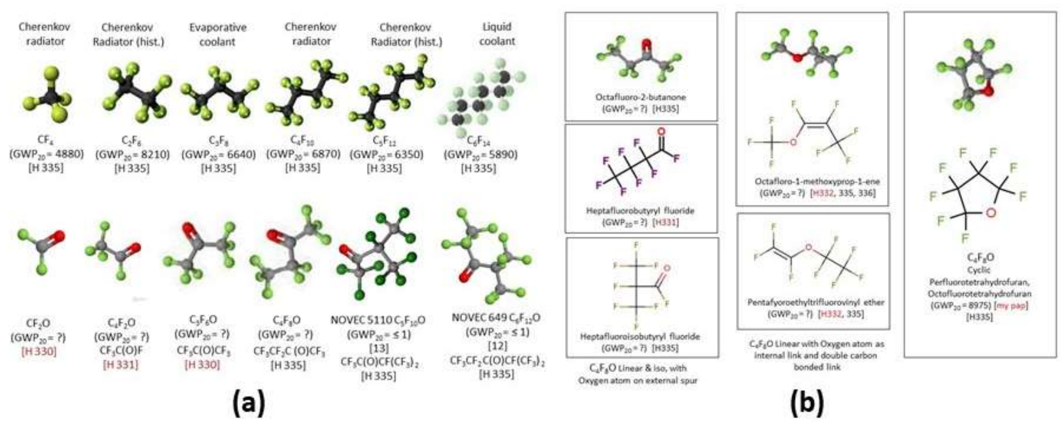

Figure 1a: ***upper row***: molecular shapes of SFCs, including Cherenkov gas radiators and coolants
lower row: shapes of non-cyclic $C_nF_{2n}O$ FK analogues.
20-year GWPs and GHS hazard ratings [3] shown where known or listed.
Figure 1b: Shape examples of cyclic, non-cyclic & non-cyclic, double carbon-bonded C_4F_8O FK isomers.

Among the FKs octofluoro-tetrahydrofuran (cyclic-C_4F_8O: CAS no. 773-14-8) was studied as a potential Cherenkov gas radiator [4]. Despite offering similar optical performance to C_4F_{10} its robust closed molecular ring geometry (fig. 1b - *right*), - incorporating the oxygen atom as an internal link - offered no improvement in GWP.

The 3M NOVEC® range currently includes two non-cyclic (spurred oxygen) $C_nF_{2n}O$ molecular forms [5]. NOVEC649 (Perfluoro-2-methyl-3-pentanone, CAS no. 756-13-8: $C_2F_5C(O)CF(CF_3)_2$) and NOVEC5110 (Perfluoro-2-methyl-3-butanone, CAS no. 756-12-7: $CF_3C(O)CF(CF_3)_2$). As with the SFCs, these fluids are non-flammable, non-toxic, non-conductive and non oxone-depleting, but with GWPs of ≤ 1. They are of interest at CERN. The radiation tolerance of NOVEC 649 was tested and looked encouraging [6] for liquid cooling in high radiation zones near the LHC beams. It currently cools multi-anode PMTs in LHCb RICH application [7], but unresolved concerns remain on possible acid formation in the presence of water, and materials compatibility [7].

By analogy with NOVEC 649 & 5110 an attractive candidate Cherenkov radiator gas might be the non-cyclic C_4F_8O isomer Octafluoro-2-butanone (CAS no. 337-20-2: $CF_3CF_2C(O)CF_3$). Several C_4F_8O FK isomers are shown in fig. 1b. It is likely that geometries with the oxygen atom on a spur of the molecule will have low GWPs, as in the case of NOVEC5110. Isomers having the oxygen atom at the end of the molecule tend to have higher inhalation toxicity, exemplified by GHS hazard ratings H330 and H331 [3]. As the order ***n*** of the $C_nF_{2n}O$ molecule decreases fewer isomers and oxygen atom placements are available: toxicity ratings are greater at the 'light' end of the carbon 'spectrum'.

While optical and radiation resistance performance might motivate a "special case" argument for continued SFC use at CERN, legislation and external market forces will limit future availability. In 2023 the European Chemical Agency (ECHA) published a list of more than 10 000 per- and poly-fluoroalkyl substances (PFAS) to be investigated for future restriction [8]. The EU aims to reduce, by 2025, the use of fluorinated chemicals to 25% of 2015 levels, partly through application of dynamically-varying levies [2]. An outcome might be the disappearance of most SFCs and some FKs, conversely perhaps with the industrialisation of new low-GWP alternatives. Future industrialization of safe $C_nF_{2n}O$ substitutes for SFCs will probably be dominated by the needs of semiconductor manufacture, vapour phase reflux soldering and cooling in the electronics industry.

2. GWP reduction in Cherenkov gas radiators: motivation and methodology

A Cherenkov radiator of volume $V(m^3)$ containing gases of densities ρ_i (kgm^{-3}), molar concentrations w_i and individual Global Warming Potentials GWP_i can be considered to have a GWP environmental "load" (and release potential) L (in tonnes CO_2 equivalent) given by:

$$L = \frac{V}{1000} \sum_i \omega_i . p_i \, . GWP_i \tag{1}$$

The refractivity of the radiator gas mixture, $(n\text{-}1)_{rad}$, can be calculated according to:

$$(n-1)_{rad} \quad = \sum_i \omega_i (n-1)_i \tag{2}$$

The GWP load, L, can be reduced by blending a heavier vapour, x, of refractivity $(n\text{-}1)_x$ at low molar concentration, ω_x, with a light gas, y, *of* refractivity $(n\text{-}1)_y$ to replicate the refractivity ($(n\text{-}1)_{ztarget}$) of a lighter SFC, z, being replaced:

$$w_x = \frac{((n-1)_{ztarget} - (n-1)_y)}{((n-1)_x - (n-1)_y)} \tag{3}$$

Ideally the heavier component would be a zero-GWP FK, but the use of legacy stocks of C_4F_{10} and C_5F_{12} could also result in significant GWP load reductions, particularly in the large COMPASS and LHCb RICH-2 radiators.

A Cherenkov radiator often contains small molar concentrations of light contaminant gases including CO_2 and O_2, whose concentrations can be respectively monitored by Non-Dispersive Infra-Red (NDIR) sensors and electrochemical cells. For a group of up to j_{max} contaminant gases of individual molar concentrations w_j and refractivities $(n\text{-}1)_j$ eq. (3) can be recast as:

$$w_x = \frac{(n-1)_{ztarget} - (n-1)_y - \sum_{j=1}^{jmax} w_j[(n-1)_j - (n-1)_y]}{(n-1)_x - (n-1)_y} \tag{4}$$

while eq. (2) becomes:

$$(n-1)_{z(target)} = w_x[(n-1)_x - (n-1)_y] + (n-1)_y + \sum_{j=1}^{jmax} w_j[(n-1)_j - (n-1)_y] \tag{5}$$

Figure 2 illustrates the GWP load in $100m^3$ radiator volumes at operating pressure of 10^5 hPa (1 bar_{abs}) as the refractivity of **(a)** CF_4 ($(n\text{-}1)_z$=488.10^{-6}, L_{100m^3}=1737 t) and **(b)** C_4F_{10} ($(n\text{-}1)_z$ =1450.10^{-6}, L_{100m^3} = 6849 t) are respectively replicated by blends of a heavier SFC or FK gas in a light zero-GWP carrier (for example N_2 : $(n\text{-}1)_y$ = 310.10^{-6})). A load reduction of 44.9% (1737➔957t) is seen using C_5F_{12} ($(n\text{-}1)_z$=1750.10^{-6}) at 13% molar concentration, and 35.6% (1737➔1119t) with C_4F_{10} ($(n\text{-}1)_z$=1450.10^{-6}) at 16.3%. Reductions using C_2F_6 and C_3F_8 would be less, due to the higher molar concentrations required, with none in the case of C_2F_6 due to its higher GWP. Load reductions through the replacement of CF_4 with around 14% of NOVEC5110 $C_5F_{10}O$ FK would be total, as also for a suitable non-cyclic C_4F_8O isomer blended at around 18%. Here unknown FK refractivities have been assumed the same as the corresponding SFCs; a probable overestimate since they are lighter by 22 units of molecular weight. Their required concentrations can thus be expected to be slightly higher. For 'completeness', hypothetical blend concentrations are also shown for several lower-order FKs, including C_3F_6O and C_2F_4O, although these would probably be toxicologically unsuitable (fig. 1a). Substitutions with xenon and krypton are also shown. For Kr the required molar concentration exceeds 100%, implying a radiator running at an overpressure to achieve the required refractivity.

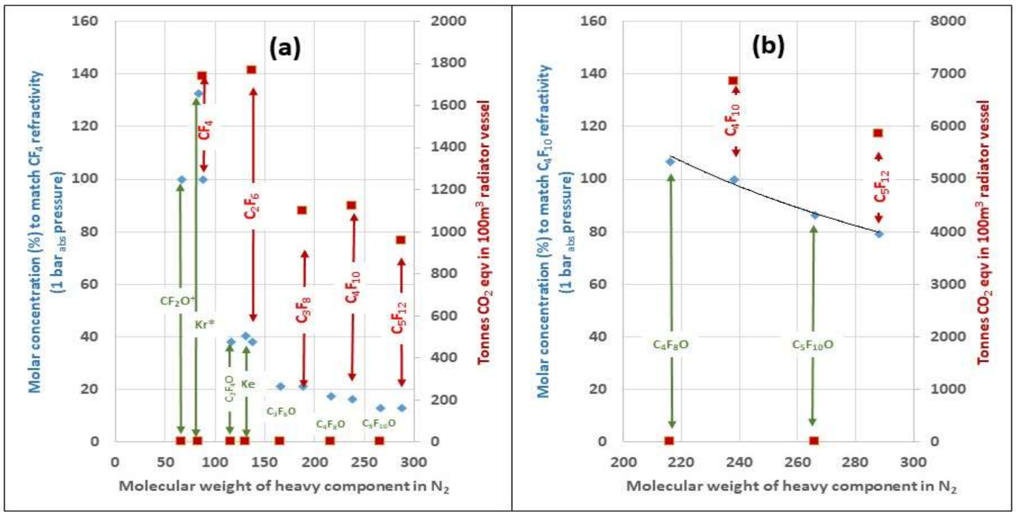

Figure 2a: GWP load variation in a 100m³ radiator at 10^5 hPa with refractivity of CF_4 replicated by blends of a heavier molecular weight vapour in a nitrogen carrier.
Figure 2b*:* refractivity of C_4F_{10} replicated by blends of a heavier m.w. vapour in a nitrogen carrier.
Note: currently unmeasured FK refractivities taken as equal to the refractivity of same order SFC: see text.

For C_4F_{10} replacement there is clearly less room to manoeuvre; the only practical high-order alternatives being C_5F_{12} or NOVEC5110. (Substitution with C_4F_8O would probably require a slight overpressure due to its lower density.) A reduction in GWP load of 14.5% can be expected with C_5F_{12} at 79% concentration (6849➔5857 t). The GWP load reduction with NOVEC5110 at around 85% molar concentration is total, of course. Since the boiling points of C_5F_{12} and NOVEC5110 at atmospheric pressure are respectively 30 and 27 ˚C it may be necessary to warm the outer surface of the Cherenkov radiator vessel above this temperature if high concentrations of these vapours are used. Since the refractivities of non-cyclic FKs are currently unknown, figs 2a & 2b are only an indicator of what may be achievable, but might stimulate optical measurements in these fluids.

3.Blending and the blend monitoring approach

While continuous optical measurement of refractive index in dynamically changing gas mixtures can be very demanding, sound velocity monitoring provides simple, reliable and continuous real-time mixture information. Indeed the speed of sound in a Cerenkov gas radiator is a monitor of its speed of light, and with it the thresholds in GeV for particle species $e^{\pm}$, $\mu^{\pm}$, $p^{\pm}$, $K^{\pm}$, $p^{\pm}$. An ultrasonic ("sonar") technique was first used for controlling the real-time blending of C_5F_{12} with N_2 in a 87%/13% ratio for the SLD CRID at the SLAC linear collider, and has also been since used for more than 10 years to monitor C_3F_8 coolant leaks from the ATLAS silicon tracker [9].

Sound velocity, $\boldsymbol{v_s}$, is continuously monitored to determine the concentrations, $\boldsymbol{w_{i=1,2}}$, of a pair of gases of primary interest (in ATLAS: C_3F_8 into N_2-purged environmental volumes) in the presence of known concentrations of other contaminant gases [9]:

$$v_s = \sqrt{\frac{\frac{\sum_i \omega_i C_{P_i}}{\sum_i \omega_i C_{V_i}} \cdot R \cdot T}{\sum_i \omega_i M_i}} \tag{6}$$

where $\boldsymbol{M_i}$, $\boldsymbol{C_{Pi}}$ and $\boldsymbol{C_{Vi}}$ are the molecular weights and specific heats at constant pressure and volume for all the gases in the blend, $\boldsymbol{R}$ is the molar gas constant (8.3145 J·mol⁻¹·K⁻¹), and $\boldsymbol{T}$ is the absolute temperature (K). The

ATLAS sonar SFC leak monitoring system and algorithm are sensitive to changes in C_3F_8 concentration of 10^{-5} in N_2 on top of varying known concentrations of CO_2, typically in the range 0-20000 ppm [9].

Figure 3 illustrates sound velocity monitoring of Cherenkov thresholds for particle species. In **(a)** legacy C_4F_{10} is considered to replace CF_4 in the context of the LHCb RICH-2 radiator, while in **(b)** C_5F_{12} replaces C_4F_{10} for COMPASS and LHCb RICH-2. Sound velocity in C_5F_{12} and C_4F_{10} is based on extensive thermodynamic data: corresponding required concentrations for $C_5F_{10}O$ and C_4F_8O will be slightly higher due to their lower densities.

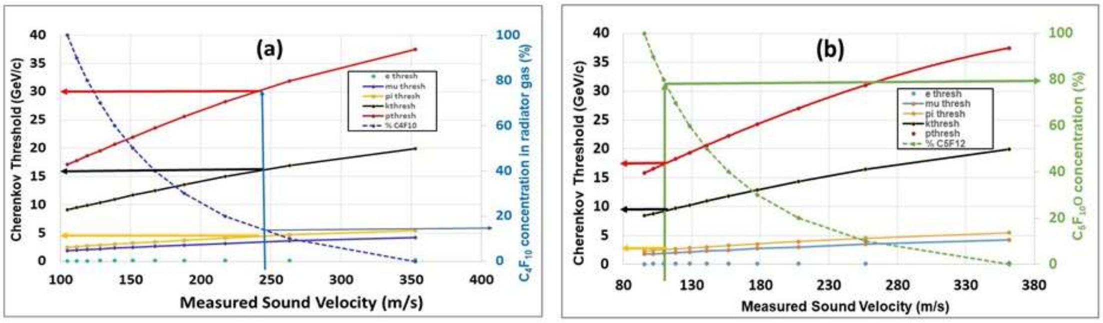

Figure 3: (a) sound velocity monitoring of Cerenkov thresholds: 16 % legacy C_4F_{10} (in N_2) replacing CF_4 **(b)** with 79 % legacy C_5F_{12} (in N_2) replacing C_4F_{10}.

4. GWP reduction in the cooling of silicon trackers

Currently C_6F_{14} is used extensively at CERN as a liquid coolant, including for part of the CMS silicon tracker, while C_3F_8 evaporatively cools part of the ATLAS silicon tracker. Both fluids are to be replaced by evaporative CO_2 cooling in the upgraded CMS and ATLAS trackers, planned for High Luminosity LHC operation (2029-41). CO_2 evaporative cooling has been successfully applied in the upgraded LHCb VELO silicon tracker, evaporating within (200 x 120) µm micro-channels etched into 500 µm thick silicon heat sink plates onto which pixel detector modules are bonded. The heat conduction path to the evaporant is very short, with few material interfaces, giving excellent thermal figures of merit (***TFM***) in the range 1.5-3.5 K cm^2 W^{-1} [10], where:

$$TFM = \frac{(T_{(Si\ module)} - T_{Coolant})}{(\text{Si module power}/cm^2)} \tag{7}$$

The upgraded CMS and ATLAS silicon trackers will use a 'tube & block' construction method with metallic cooling tubes and blocks attaching the silicon modules. Thermal paths are longer, with more material interfaces and correspondingly inferior TFMs, in the range 24 - 40 K.cm^2.W^{-1} [11]. Concern has been raised that CO_2 may be unable to maintain silicon modules cold enough for adequate protection against leakage current-induced thermal runaway throughout the full HL-LHC program. It is planned to replace the ATLAS ITk inner pixel layers part way through. This temperature limitation is related to the high CO_2 triple point at -56 ˚C and the known loss

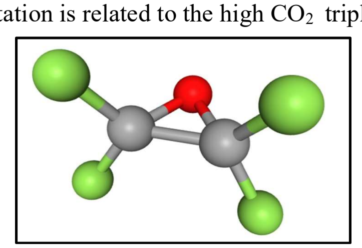

Figure 4: Tetrafluorooxirane C_2F_4O: a speculative evaporative coolant?

in CO_2 system performance below -40 ˚C [12]. Maintaining a sufficient safety margin or 'thermal headroom' below the expected onset temperature of thermal runaway is more demanding as silicon modules accumulate high radiation doses during the HL-LHC profile. These concerns have led to the exploration of alternative cooling approaches, including the use of krypton evaporative cooling in a complex transcritical thermodynamic cycle [12]. Fluids with better adapted thermodynamics incude xenon and C_2F_6[1]. The high GWP of C_2F_6 (fig. 1a) is problematic. By analogy with the similar thermophysical characteristics of C_6F_{14} and $C_6F_{12}O$ [6], a C_2F_4O isomer might be worth consideration. While the Trifluoroacetyl fluoride isomer (fig. 1a) has undesirable toxity, Tetrafluorooxirane (CAS no. 694-17-7: fig. 4) - though a closed ring topology - might be worth investigation through GWP, toxicology, radiation resistance and material compatibility studies.

5. Conclusion

This paper has considered use of high GWP $C_nF_{(2n+2)}$ SFC and $C_nF_{2n}O$ FK fluids as Cherenkov radiator media and detector coolants in high radiation environments. Ultrasonic blending of high-order (C > 4) SFC or FK vapours with light carrier gas could replicate the refractive index of CF_4 and C_4F_{10}, while reducing or eliminating their GWP "load" (tonnes CO_2 eqv.) in large Cherenkov radiators. In addition to ongoing studies with $C_6F_{12}O$, consideration should also be given to study non-cyclic forms of C_4F_8O and perhaps also the TFO C_2F_4O isomer, which might offer advantages over C_3F_8 and CO_2 as an evaporative coolant for silicon tracking detectors.

References

[1] CERN Environment Report 2017–2018 https://doi.org/10.25325/CERN-Environment-2020-001

[2] B. Rigoletti, *Overview of CERN strategies for the reduction of greenhouse gas emissions from particle detectors* (these proceedings)

[3] *Globally Harmonized System (GHS) for material hazard classification* https://unece.org/sites/default/files/2023-07/GHS%20Rev10e.pdf

[4] G. Hallewell, *The "green" use of fluorocarbons in Cherenkov detectors and silicon tracker cooling systems: challenges and opportunities in an unfolding era of alternatives,* Eur. Phys. J. Plus (2023) 138: 1141 https://doi.org/10.1140/epjp/s13360-023-04703-w

[5] 3M NOVEC® 649; https://multimedia.3m.com/mws/media/569865O/3m-novec-engineered-fluid-649.pdf, 3M NOVEC® 5110; https://multimedia.3m.com/mws/media/1132123O/3m-novec-5110-insulating-gas.pdf

[6] CERN Technical Note 1751219 2017-334 rev 1: NOVEC Fluids Qualification Report: 22/12/2017

[7] S. Jacobsen, *Environmentally friendly fluids for detector cooling in LHCb* (these proceedings)

[8] ECHA/NR/23/04; https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal & Candidate list of substances of high concern; https://echa.europa.eu/candidate-list-table

[9] G. Hallewell et al; *Applications and Perspectives of Ultrasonic Multi-Gas Analysis with Simultaneous Flowmetry.* MDPI Instruments (2021) 5(1), 6;

[10] O. de Aguiar Francisco et al, *Microchannel cooling for the LHCb VELO Upgrade I,* Nucl. Instr. Meth A. 1039 (2022) 166874 https://www.sciencedirect.com/science/article/pii/S0168900222003394

[11] D. Alvarez et al: *Thermo-Mechanical Performance of the Local Supports for the ATLAS ITk Pixel Outer Barrel*; Forum on Tracking Detector Mechanics 2023, Tuebingen Germany May 31-June 2 2023

[12] L. Contiero et al; *Cold Krypton system for the Phase III Upgrade of the LHC:* **ibid**

[1] Critical temperature & pressure for C_2F_6: 19.8 ˚C & 30.4 bar_{abs}: for Xe: 16.6 ˚C & 58.4 bar_{abs}