A protocol for accurately calibrating thermocouples at cryogenic temperatures

A S Purandare, S Vanapalli*

Applied Thermal Sciences laboratory, Faculty of Science and Technology, University of Twente, Post Bus 217, 7500 AE Enschede, The Netherlands

Email: s.vanapalli@utwente.nl

Abstract. To study the quenching characteristics of materials in a cryogenic liquid bath transient temperature measurements of high accuracy are necessary. Thermocouple is an ideal tool for this application because of its low self-heat capacity. However, they require calibration before usage that require multiple fixed-point temperatures. The common fixed-point temperatures are the water-ice melting temperature, the dry ice sublimation temperature, and the boiling temperature of liquid nitrogen. It is important to note that there are uncertainties associated with dry ice sublimation and liquid nitrogen boiling temperature inherent to the heat and mass transport phenomenon at their phase-changing interface or inside the bulk medium. The dry ice temperature is influenced by the mass transport phenomenon occurring at the interface between the dry ice and the ambient surrounding it. In a typical lab environment, dry ice temperature is significantly lower than the commonly quoted sublimation temperature of -78.5 °C at 1.013 bar. In the case of liquid nitrogen stored in a cryostat, temperature gradients develop in the liquid bath. This paper describes a protocol for calibrating thermocouples by accurately defining and using fixed-point temperatures of dry ice in a saturated environment and a liquid nitrogen slush.

1. Introduction

Thermocouples are affordable temperature sensors with a low self-heat capacity and quick response time, which makes them well-suited for investigating the cooling behaviour of materials in cryogenic liquids and performing fast and precise transient measurements [1] [2] [3]. They can be obtained in pre-made from manufacturers or constructed easily using bulk thermocouple wire, making them suitable for various scientific and laboratory purposes. To ensure precise temperature measurements, it is essential to calibrate newly acquired thermocouples or recalibrate existing ones. One common method of thermocouple calibration involves determining the electromotive force (EMF) values at various fixed points with known temperatures. To establish this relationship within the low temperature range of 0 °C to -196 °C, the three commonly used fixed point temperatures are the ice-water slush (0 °C), the normal sublimation temperature of dry ice (-78.5 °C), and the normal boiling temperature of liquid nitrogen (-196 °C).

This paper aims to raise awareness regarding the uncertainties associated with the fixed-point temperatures of dry ice sublimation and liquid nitrogen boiling. These uncertainties arise from the inherent heat and mass transport phenomena occurring at the phase-changing interface and within the bulk medium. Specifically, deviations from the commonly quoted value of dry ice sublimation temperature in a typical laboratory setting and the presence of thermal stratification within a pool of liquid nitrogen is discussed. A simple modification for calibrating thermocouples using dry ice involves accurately measuring the CO_2 concentration and ambient pressure during the sublimation process. For more reliable thermocouple calibration using nitrogen, the use of nitrogen slush instead of liquid nitrogen is recommended. In addition to the considerations regarding the fixed-point temperatures, it is essential to familiarize oneself with proper thermocouple installation practices, calculations, and knowledge of cold-junction compensation techniques. It is important to note that these topics are not covered in this paper, but detailed information can be found in various literature sources such as [4] [5].

2. Dry ice sublimation temperature

Solid carbon dioxide, commonly referred to as dry ice, is a readily available commercial product extensively utilized in industrial and laboratory settings. The triple point pressure of carbon dioxide (CO_2) exceeds the normal atmospheric pressure, resulting in the existence of only the solid and gaseous states under normal ambient conditions. The solid state of CO_2 undergoes sublimation, transitioning directly to a gaseous state, at a temperature of approximately -78.5 °C, as illustrated in the Pressure-Temperature diagram shown in Figure 1. This normal sublimation temperature of dry ice often serves as a calibration or checkpoint for thermocouples. It is crucial to note that the thermodynamic variables presented in the phase diagram hold true under equilibrium conditions. For example, the sublimation temperature of -78.5 °C corresponds to the equilibrium between dry ice and pure CO_2 vapor at 1 atmospheric pressure. However, this equilibrium condition is seldom met in the laboratory environment where thermocouples are calibrated. Consequently, a concentration gradient of CO_2 exists in the vicinity of the sublimating interface of dry ice. This concentration gradient drives the diffusive transport of CO_2 vapor from the dry ice towards the ambient environment, which has a lower concentration of CO_2. As a result, dry ice experiences sublimative cooling, leading to a significant reduction in the sublimation temperature compared to the commonly quoted value of -78.5 °C. This reduction continues until it reaches a thermodynamic wet-bulb temperature that corresponds to the steady state concentration and pressure of CO_2 in the far-field environment.

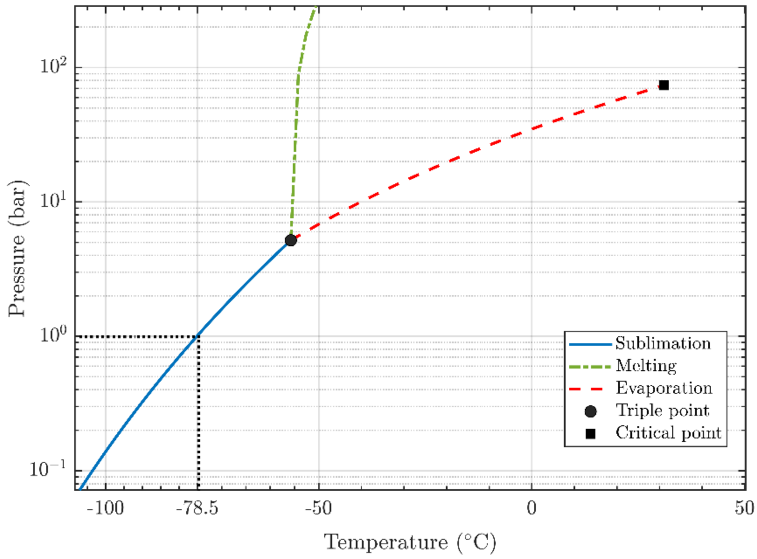

Figure 1. Pressure-Temperature diagram of carbon dioxide. The dashed lines indicate 1.013 bar pressure on y-axis and corresponding sublimation temperature of approximately -78.5 °C.

A schematic diagram, as depicted in Figure 2, displays the sublimation temperature of crushed dry ice under different experimental conditions. The temperature is measured using a pre-calibrated and accurate temperature diode sensor. When the dry ice is enclosed in a container and covered with a lid (not leak tight) the sublimation temperature remains at approximately -78.5 °C or 194.6 K because the dry ice is surrounded by its own vapor. However, upon exposure to the normal laboratory ambient by removing the lid of the container, the temperature of the dry ice begins to decrease and settles in our experiment to -88.5 °C or 184.76 K. Notably, a significantly lower temperature is observed when the CO_2 vapor is actively flushed away from the interface of the dry ice by a fan. In our experiment a temperature of -96.8 °C or 176.4 K is measured.

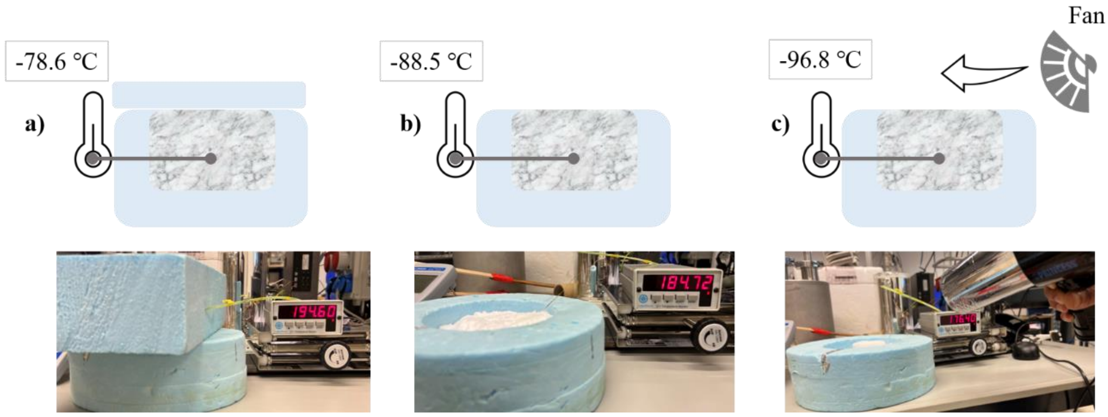

Figure 2. Measurement of the dry ice sublimation temperature under various conditions; a) a closed environment with tiny vents to overcome pressure built-up, b) an open lab environment, c) Flushed with a blower.

This phenomenon has been systematically investigated in our recent study, which focuses on the heat and mass transport at the interface between a dry ice sphere and a controlled ambient environment in terms of pressure and CO_2 concentration [6]. For this purpose, the dry ice sphere is suspended on a thin E-type thermocouple wire (calibrated) within a cross-shaped KF vacuum flange. The ambient surrounding the dry ice sphere is well-controlled by flushing the flange with a gaseous mixture of N2 and CO2, with a known concentration and pressure, as schematically shown in Figure 3 b).

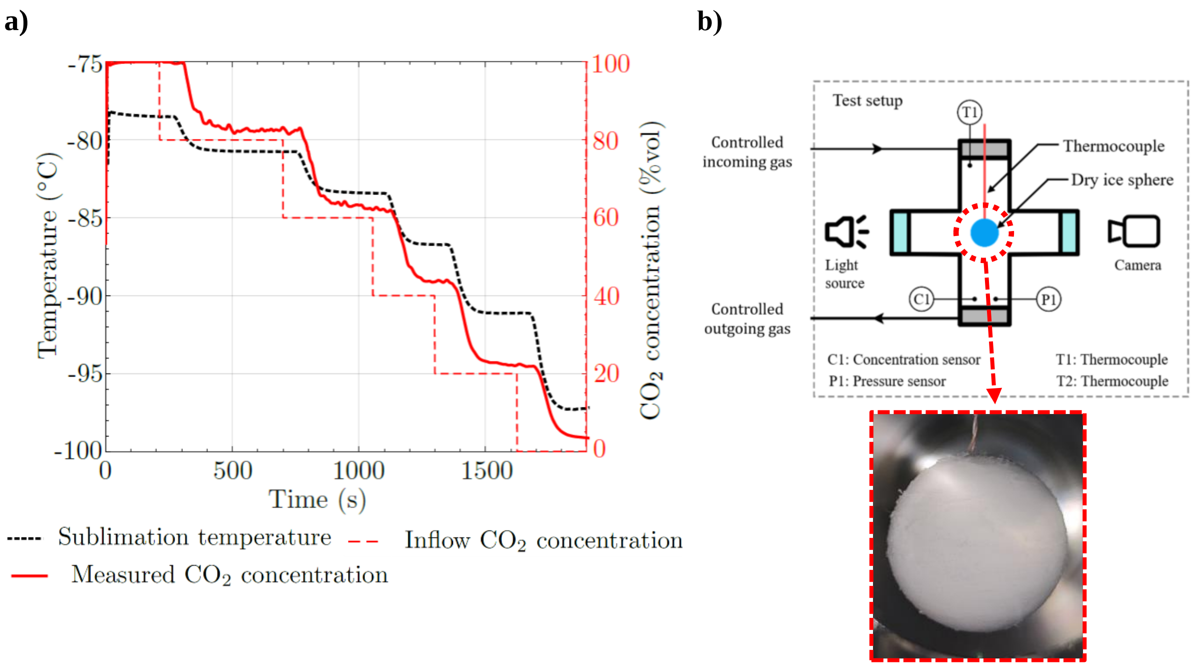

Figure 3. a) Measured values of the sublimation temperature of dry ice for different far-field CO_2 concentrations evaluated from the systematic experiments carried out in [6]. b) The schematic of the test section of the experimental setup used to produce the results shown in a).

Further information on the experimental setup, as well as extensive experimental and theoretical results, can be found in [6]. Figure 3 a) presents the only relevant result for this paper, displaying the measured values of the sublimation temperature of a suspended dry ice sphere in an environment with one atmospheric pressure and varying CO_2 concentrations. As anticipated, the sublimation temperature measures approximately -78.5 °C at 100 % volume CO_2 concentration. However, as the concentration is gradually reduced in 20 % volume increments, the sublimation temperature also decreases and reaches a wet bulb temperature corresponding to the specific concentration level. The lowest sublimation temperature at one atmospheric pressure, with an approximate 0 % volume CO_2 concentration in the ambient, was measured to be -97.3 °C. Therefore, precise measurement of the pressure and CO_2 concentration of the ambient surrounding dry ice is crucial, and precautions must be taken when calibrating thermocouples using the fixed-point temperature of dry ice, as previously noted by R.B. Scott [4].

3. Liquid nitrogen

Commercial liquid nitrogen is another widely available substance utilized in laboratory settings for the calibration of thermocouples at low temperature. This calibration process typically involves immersing the thermocouples in a bath of liquid nitrogen contained within an open cryostat or an LN_2 comparator, which is a closed cryostat with a copper block designed to hold the thermocouples [7]. The normal boiling point temperature of liquid nitrogen, approximately -196°C, serves as a fixed-point temperature for the calibration of thermocouples. However, it is important to consider two factors that can introduce errors in thermocouple calibrations: thermal stratification and oxygen condensation and dissolution within the liquid nitrogen.

Thermal stratification refers to the vertical variation in temperature that commonly occurs in cryogenic liquids with low thermal diffusivity when stored in cryostats in the absence of agitation or stirring. In such cases, the warmer liquid accumulates at the top of the liquid column, while the colder liquid settles at the bottom as schematically shown in Figure 4 a). Heat from the surrounding environment enters the cryogenic liquid through the cryostat walls, causing the temperature of the fluid near the walls to increase. This leads to a decrease in density, causing the fluid to rise and move towards the liquid-vapor interface. As a result, a warmer layer forms at the top, gradually increasing in thickness and resulting in a higher temperature at the interface compared to the bulk temperature [8] [9]. In their experimental work, Kang et al. [8] demonstrate that the degree of stratification depends on the thermal aspect ratio, which represents the ratio of heat ingress from the sides of the cryogenic tank to the total heat ingress. They also show that the degree of stratification, indicating the temperature difference between the surface and bottom of the cryogenic fluid, is a function of the fluid level within a given cryogenic tank. In their case, the degree of stratification ranged from 1 to 3 when the cryogenic tank is initially 80 % full. Such phenomenon can introduce errors during thermocouple calibration in a bath of liquid nitrogen since the temperature of the liquid is not uniformly fixed at -196 °C and varies within the bulk. Another potential source of error during thermocouple calibration with liquid nitrogen is the enrichment of oxygen. When a cryostat is exposed to air, the oxygen present in the air condenses due to its higher boiling point compared to that of liquid nitrogen. Since liquid oxygen is miscible in liquid nitrogen, the concentration of oxygen within the cryostat containing liquid nitrogen increases over time. This alteration in composition causes the boiling temperature of the mixture to deviate from that of pure liquid nitrogen, resulting in calibration errors.

To further elaborate the uncertainties associated with thermocouple calibration using the fixed point of liquid nitrogen's normal boiling temperature, a preliminary experimental investigation was conducted. This investigation focused on examining the density gradients present within the liquid nitrogen bath and the vapor above the liquid-vapor interface using Schlieren imaging technique. Figure 4 b) presents a Schlieren image depicting the liquid nitrogen passively boiling within a glass cryostat. The bright and dark regions observed in the Schlieren image, visible in the enlarged region of Figure 4 b), represent density gradients that may arise due to temperature or concentration variations. In the case of the liquid nitrogen pool, the density gradients are likely attributed to a combination of temperature gradients caused by natural convection resulting from heat transfer from the surroundings and concentration gradients due to oxygen enrichment. Consequently, these gradients can lead to deviations from an isothermal state within the liquid pool. Additionally, a thermal stratification is observed in the gas phase above the liquid nitrogen pool, as evident by the diminishing intensity in the vertical direction seen in Figure 4 c). This region is preceded by a dark region near the liquid-vapor interface, indicating a potentially isothermal zone of the vapor near the interface. To conclude whether the thermal stratification in the vapor phase may also contribute to alterations in the temperature of the liquid pool, further quantitative and systematic investigations are necessary to fully understand these effects. Nonetheless, the qualitative results presented in Figure 4 highlight the uncertainties associated with using the fixed point of liquid nitrogen's normal boiling temperature for thermocouple calibration.

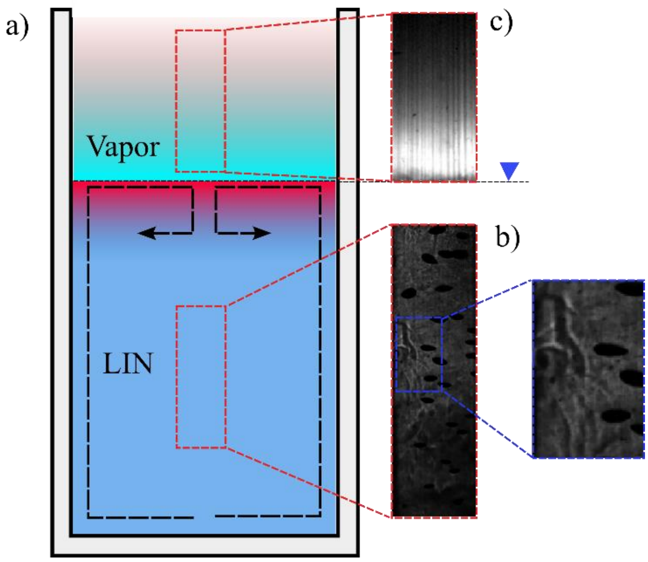

Figure 4. a) Schematic of the thermal stratification in a pool of liquid nitrogen and in the vapor above the pool; b) Schlieren image depicting density gradients inside a pool of liquid nitrogen; c) Schlieren image depicting density gradients in vapor above the pool.

An alternative and reliable method for calibrating thermocouples at low temperatures involves using a fixed-point temperature of liquid nitrogen slush (63.2 K). To create the slush, the initially saturated liquid nitrogen within a cryostat, at a temperature of 77.3 K and 1 atmospheric pressure (Point 1 in Figure 5), is subjected to vacuum pumping. As the pumping progresses, the pressure above the liquid nitrogen interface decreases, leading to a reduction in the liquid temperature. Eventually, the triple point temperature and pressure of nitrogen are reached (red line in Figure 5), and solid nitrogen begins to form. The pumping continues until a sufficient fraction of solid nitrogen is formed within the slush, effectively surrounding the thermocouples. Finally, the pressure above the cryostat is restored to atmospheric pressure and the thermocouples are calibrated at fixed point temperature of nitrogen slush (region 2 in Figure 5).

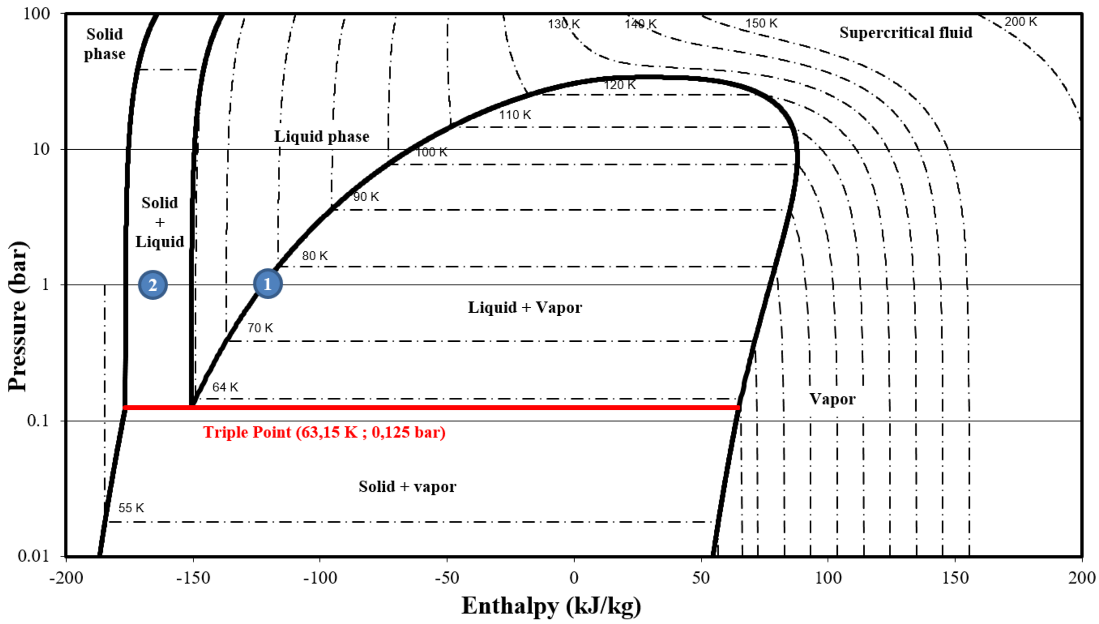

Figure 5. Pressure-enthalpy diagram of Nitrogen. State 1 and 2 represents saturated liquid nitrogen and slush at 1.013 bar pressure, respectively.

4. Calibration protocol

A calibration protocol of thermocouples used in our lab is described in this section. The calibration process involves using three fixed point temperatures: ice water slush, dry ice, and nitrogen slush. While the creation of the latter two fixed point sources has been described in the previous section, the preparation of ice water slush is relatively straightforward. It involves cooling de-ionized water until a mixture of approximately 90% ice and 10% water is obtained. Once the three fixed point sources are ready, the thermocouples to be calibrated are individually placed in one of the fixed-point sources, and the corresponding voltages are measured. Modern data acquisition systems have pre-loaded sensitivity data for various types of thermocouples. We recommend the data acquisition card to be housed within an insulating box to maintain the junction at uniform temperature.

A summary of the procedure for various fixed points is shown in ***Figure 6***. Ice cubes from a freezer are mixed with water to form a slush, the fixed-point temperature is 0 °C or 273.1 K. Dry ice can be either procured from a supplier or made from liquid CO_2. Dry ice must be placed in a foam box and closed by a lid but not very tight to allow sublimated CO_2 gas to escape not build pressure in the box. The fixed-point temperature is -78.5 °C or 194.6 K at 1.013 bar. Note that the local pressure varies with location above the sea level, therefore the sublimation temperature corresponding to the lab pressure must be used (see Figure 1). The pressure of a saturated liquid nitrogen is reduced by using a rough vacuum pump to a pressure slightly below 0.125 bar, wait for a while to allow formation of solid nitrogen and depressurise the container to form a slush of nitrogen. The fixed-point temperature is -210.1 °C or 63.2 K. The melting temperature of water-ice and solid nitrogen is less sensitive to local pressure.

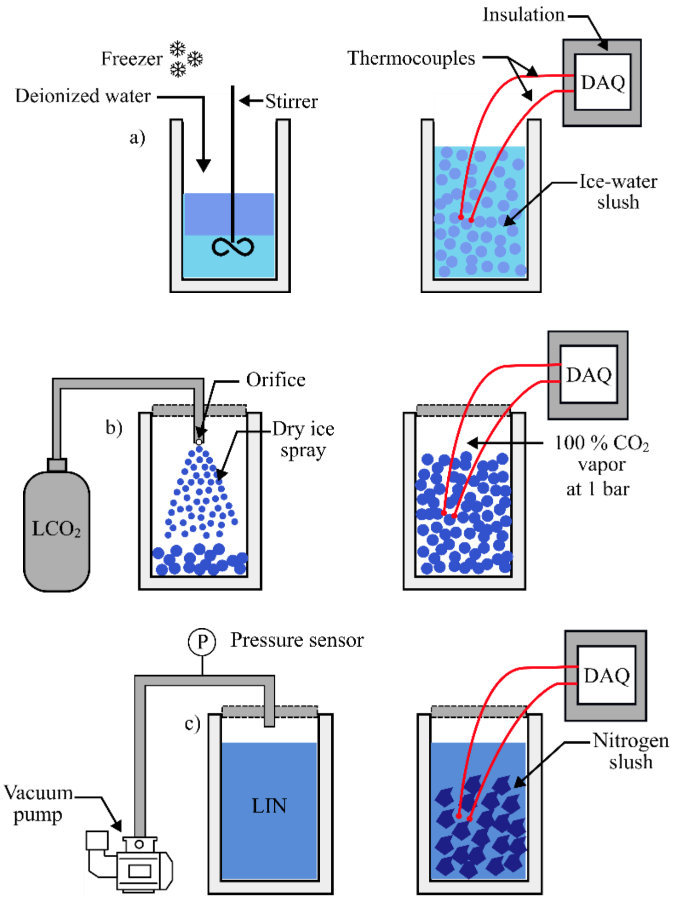

Figure 6. Schematic of the methods to generate three fixed points for thermocouple calibration: a) Ice-water slush melting temperature (273.15 K); b) Dry ice sublimation temperature (194.65 K); c) Nitrogen slush melting temperature (63.2 K)

5. Conclusions

This paper provides a brief overview of the uncertainties associated with the fixed-point temperatures of liquid nitrogen and dry ice, which are commonly used for the calibration of thermocouples. These fixed-point temperatures can exhibit variations due to the inherent heat and mass transport phenomena occurring at the phase-changing interface and within the bulk medium. During the calibration process using the normal sublimation temperature of dry ice, it is crucial to ensure that the environment surrounding the dry ice consists of pure CO2 vapor. On the other hand, when using a bath of liquid nitrogen for calibration, it is susceptible to thermal stratification and oxygen enrichment, which can alter the saturation temperature of the bath. To address this, it is recommended to utilize nitrogen slush as a more reliable option for thermocouple calibration. In addition to the considerations regarding the fixed-point temperatures, implementing good installation practices as outlined in various literature sources is essential for achieving accurate temperature measurements with thermocouples.

6. References

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