How isothermal is an isotherm

Characterization of
particles · powders · pores

Introduction

Nitrogen adsorption at the boiling point of liquid nitrogen, N_2@77K, has become the established method for quality control. However, scientific surface and pore investigations are increasingly being performed with different adsorptives at higher temperatures, such as Ar@87K, CO_2@195K or CO_2@273K. One question for every measurement is the accuracy of the used measuring temperature. As example in technical articles, the specification of the experimental temperature with 77.35 K as the boiling temperature of liquid nitrogen suggests an unrealistic accuracy of two decimals if a standard liquid nitrogen dewar is applied. In scientific articles, however, the adsorption temperature of N_2 measurements is often given as 77 K, 77.3 K, 77.4 K, 77.5 K or 78 K. Few users are aware that their reported temperature could very likely vary by as much as 0.5 K because of the dependence of the boiling temperature both from the purity of the liquid nitrogen, but mainly from the ambient pressure. Not only must the temperature dependence of the saturation vapor pressure be evaluated for very accurate results, but also the exact measuring temperature and its constancy must be known over the complete measuring time. So far, this is the state of the art for relating thermostats with temperature accuracies of 0.01 K close to room temperature and should be aimed at for other temperature ranges as well. The new developed cryoTune 77 option offers an easy-to-handle technical solution for such significant temperature stability improvement for accurate sorption studies.

The inaccurate temperature of liquid nitrogen

The boiling temperature of a pure liquid, such as water or liquid nitrogen, depends on the ambient pressure. Due to that, the saturation pressure p_0 must be measured in parallel with the actual standard N_2@77 K measurement. This would not be necessary in case of a constant measuring temperature. The literature boiling temperature of liquid nitrogen of 77.35 K is only right in case of standard ambient pressure of 101.325 kPa, which is rarely present. Frankly, a published temperature of 77.35 K for such measurements pretends an accuracy that is not true. Fig. 1 shows ambient air pressures in different locations in 2022, and only the ambient pressure fluctuations for our own laboratory in Leipzig/Germany in 2022 cause temperature swing in a pure liquid nitrogen bath between 77.15 and 77.58 K. In other words: if different worldwide laboratories measured the same sample on one day, they measure at different temperatures. Additionally, the measuring temperatures change, e.g., during a 2-days micropore-mesopore measurement in one single lab because of the ambient pressure changes. So we can conclude that a conventional N_2@77K isotherm is rather not strictly isothermal, but that effect can be compensated for N_2@77K with parallel measurements or calculations of the p_0-value from the real temperature in the coolant.

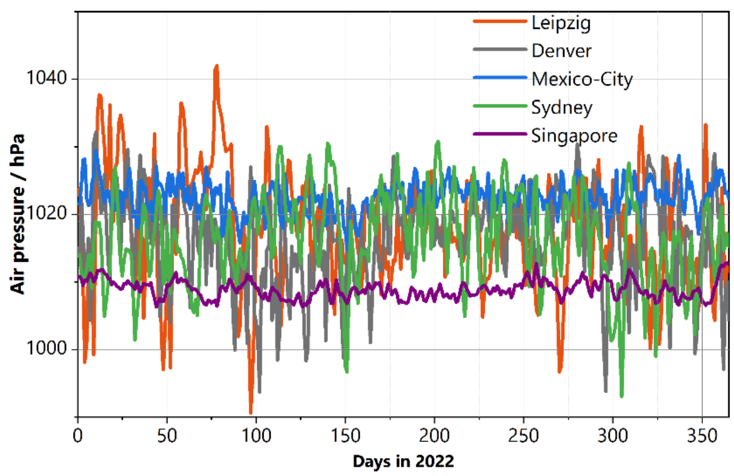

Figure 1 Ambient air pressures in different spots in 2022

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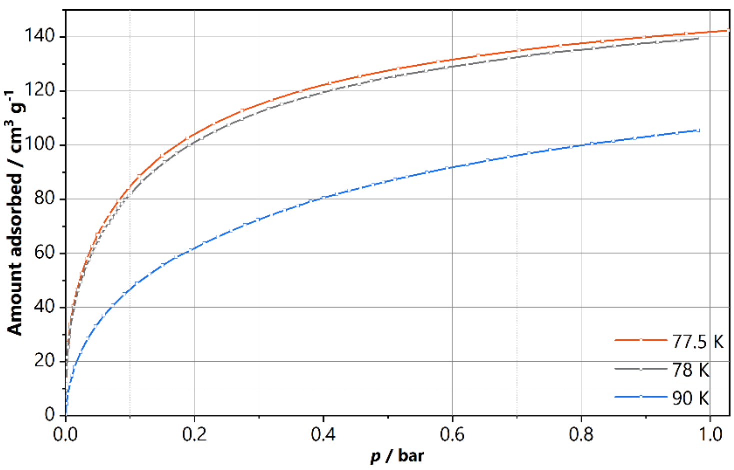
Temperature dependent differences in sorption results

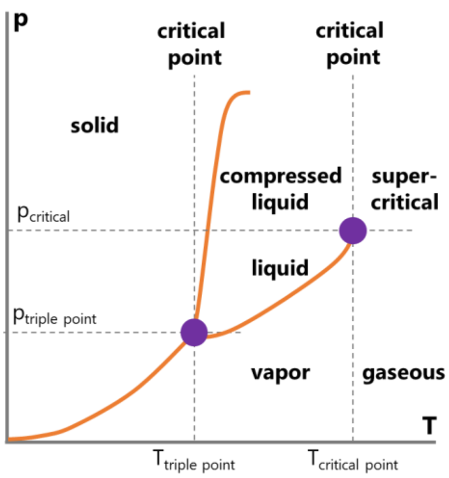
Accurate control of the adsorption temperature is particularly important when the vapor pressure of the corresponding adsorptive cannot be measured. In the following, we will give two examples where the actual p_0 cannot be measured, namely Kr@77K and H_2@77K.

Hydrogen is known to be supercritical above 34 K, which is why no p_0 exists or can be measured. This means that any ambient pressure and/or temperature fluctuations of the liquid nitrogen between individual measurements cannot be controlled and, if necessary, compensated for. It is therefore important to be able to control the temperature reproducibly. The influence of a temperature difference of 0.5 K on the measurement can be seen in Fig. 2. Here, H_2 adsorption was performed on Zeolite 5A at 77.50 K and 78.00 K by use of a cryoTune 77 option (remark: we give the two temperature decimals for the cases of constant temperatures better than 0.01 K). The uptake difference is only 2.5 $cm^3\ g^{-1}$ or 2 % respectively, in this specific case. This may seem negligible at first, but this is a random and especially avoidable error, which makes a comparison between different materials measured in different labs with a standard liquid nitrogen coolant difficult.



In addition, we also collected an isotherm at 90 K, also shown in Fig. 2. By increasing the adsorption temperature by 12 K, the total uptake is reduced by 35 $cm^3\ g^{-1}$ with respect to the measurement at 78 K. This further highlights the great impact of the adsorption temperature on the adsorption behavior of porous materials.

Figure 2 *Accurate H_2 sorption measurements at 77.50 K, 78.00 K and 90 K on Zeolite 5A.*



Another example is Kr@77K. Such a measurement is performed when the sensitivity of a "normal" N_2@77K measurement is not sufficient to perform a complete material characterization. If a measurement is conducted with krypton around 77 K, the measurement will be well below the triple point of the gas. This means that physically there is no longer a transition between the vapor and the liquid phase, but that the vapor becomes solid directly by resublimation as the pressure increases (Fig. 3). If a measurement is carried out with krypton in liquid nitrogen, only the vapor pressure of krypton ice can be determined. However, the ISO 9277 norm recommends a p_0-value of the so-called undercooled krypton liquid phase at 77.35 K of p_0 = 0.35 kPa (2.63 Torr). But this phase is only present inside the pores, and therefore, a p_0 measurement is not possible.

Figure 3 *Schematic phase diagram of a substance.*

Additionally, the value of 0.35 kPa is calculated and only valid for exactly 77.35 K. However, if a closer look is taken on Fig. 1, one can see that for example in Leipzig/Germany the air pressure fluctuates around 5 % only within two weeks. With other words also the boiling temperature of liquid nitrogen deviates between 77.15 and 77.58 K.

The influence of air pressure becomes even clearer when an isotherm that has been measured is evaluated fictitiously with different air pressures. For this purpose, the standard material BAM-101 was measured with krypton at a temperature of 78 K (Fig. 4) and the surface area was determined using the BET equation (Tab. 1).

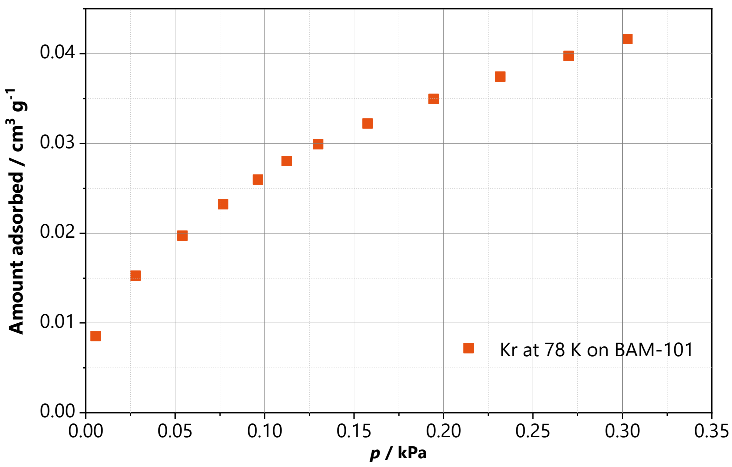


Figure 4 *Krypton isotherm at 78 K on BAM-101.*

Subsequently, based on the air pressures, fictitious p_0 values were used for the evaluation. The results show that solely due to the fluctuation of the air pressure an error of about 5 % occurs in the evaluation of the data. In addition to the vapor pressure, the liquid density and the resulting spatial requirement of each adsorptive are also temperature-dependent. The influence is discussed in more detail in AppNote 2-13. This clearly shows that a control of the temperature, especially for measurements where the vapor pressure cannot be determined experimentally, is essential for a reproducible and reliable measurement. 3P Instruments has therefore extended its cryoTune portfolio to reliably control the measurement environment near the boiling point of liquid nitrogen

Table 1 *Temperature and pressure fluctuations and resulting surface areas of BAM-101*

Air pressure / hPa	T_{LN2} / K	P_0^*, Kr / kPa	SA_{BET} / m² g⁻¹
1042	77.58	0.371	0.173
990.6	77.15	0.335	0.164
1016.7	77.38	0.355	0.169
irrelevant	78	0.4053	0.177

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Technical aspects of the new cryoTune 77

The fourth cryoTune within this series completes the temperature range from 77 K or the boiling point of liquid nitrogen up to 298 K or room temperature (Fig 5). Due to these innovations, almost all adsorptives can be measured with a large temperature constancy (deviation < 0.004 K).

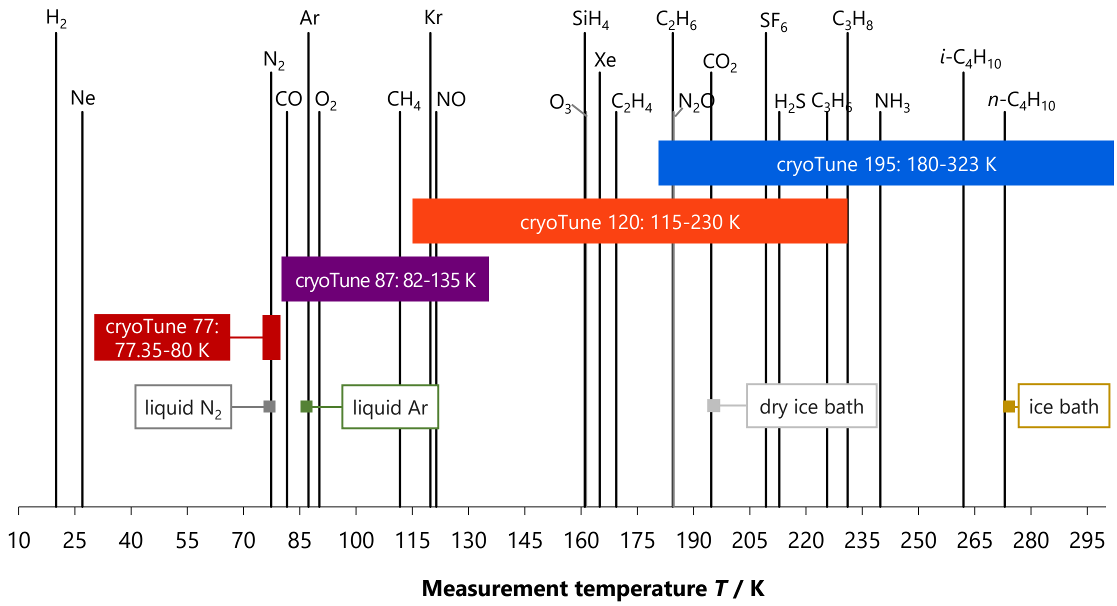
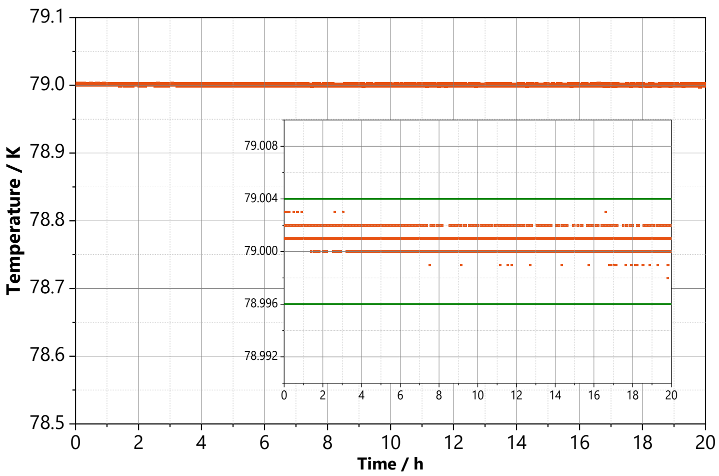


Figure 5 *The cryoTune portfolio of 3P Instruments*

The principle of operation of the cryoTune 77 is analogous to the already known versions cryoTune 87, cryoTune 120 and cryoTune 195.



Only small changes in the structure and design of the cryoTune allow the temperature range of 77.35 K - 80 K to be achieved. Due to these changes and the fact that it operates just above the boiling point of liquid nitrogen, the service is somewhat shorter compared to the other models. However, at 79 K, this is still 20 hours (Fig 7). At lower temperatures such as 78 K or 77.5 K, the service life is correspondingly longer and more than sufficient for the above examples (H_2@78 K and Kr@78K).

Figure 7 *Temperature stability test at 79 K for 20 hours with the cryoTune 77.*

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Conclusion

To optimize the accuracy of scientific sorption measurements, a thermostatic system at constant temperature over the complete measuring time of an isotherm should be used. For exact scientific sorption studies, a measuring system with precise temperature control over the entire measuring time of an isotherm is necessary. In this way, both the measurement temperature and the saturation vapor pressure of the adsorptive are constant over the entire measurement time.

Figure 8 *The cryoTune 77, 87, 120 and 195, available for all modern types of sorption analyzers, here 3 of them in use with the 3P micro 300 sorption analyzer in parallel with different gases at different temperatures.*

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