BET surface area ... argon and krypton would be better, they are spherical atoms... no idea how to place that N₂-molecule to reach the 0.162 nm²...

Why do we measure surfaces and pores with argon and krypton gas adsorption much more often in future?

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Introduction

he fundamentally reviewed IUPAC report »Physisorption of gasses, with special reference to the evaluation of surface area and pore size distribution« was published in 2015 and is an up-to-date compendium for the characterization of porous materials using gas sorption /1/. Besides an extended isotherm classification, this updated release includes numerous recommendations for the measurement and interpretation of isotherm data. "New recommendations" that have been the basis of applying our measurement methods since many years. A fact that becomes obvious in this central topic: the characterization of micropores using physisorption of argon at a temperature of 87 K (boiling temperature of argon). We have identified this advantage more than 20 years ago and realized the 87 K temperature by use of liquid argon for a long time. Recently we connected our instruments with a so-called CryoSync option, which has been specified from the producer with 82 - 100 K temperature range originally, but has been changed up to 115 K in the meantime on the basis of our recommendation. Our further research shows, that we can also reach the 120 K and that is a very interesting temperature, the boiling point of the krypton noble gas. This article describes these additional research options with a critical discussion of the nitrogen results as traditional basis not only for pore but also for surface determination.

The advantages of argon isotherms at 87 K in micropore analysis

For the sake of completeness, the main advantages of argon adsorption at 87 K compared to N₂ isotherm measurements at 77 K are as follows:

- Unlike nitrogen, argon has no quadrupole moment which is the reason that no specific interaction between adsorptive and polar or ionic surface areas is to be expected.
- Accordingly, argon isotherms produce much more reliable texture data regardless of the solid surface's chemical properties.
- Compared to nitrogen sorption at 77 K, argon adsorption analysis at 87 K is considerably less time-consuming, because the filling of similar pores can occur much more readily at much higher relative pressures (see Fig. 1).



Figure 1 Ar-87 K and N₂-77 K isotherms in zeolite 13 X

The inventive idea was to make these advantages available to studies that have no liquid argon available. Because of the availability of technical solutions for liquid argon compensation, such ways of thermostates are explicitly mentioned in the current IUPAC report. The following section explains additional measurement possibilities arising from the use of CryoSync, as the temperature range is not limited to 87 K. When filled with liquid nitrogen, a temperature range between 82 - 120 K was possible to realize for our studies.

Determination of BET surface areas with alternative adsorptives and the question for correct area occupation of adsorbate molecules

The determination of specific surface areas A_s is almost exclusively done with BET evaluation of nitrogen isotherms at 77 K. In general, it determines the number of adsorbate molecules forming a monolayer n_M on the solid surface which is then multiplied by the average area occupation a_m of the adsorbate molecules:

$$A_S = a_m n_M N_A$$
 Eq. 1

A value for the area occupation a_m can be calculated using the molar mass M and the density of the liquefied adsorptive pL at the corresponding measuring temperature:

$$a_m = 1,091 \left(\frac{M}{\rho_L N_A}\right)^{2/3}$$
 Eq. 2

In case of nitrogen at 77 K, the area occupation is $a_m(N_2) = 0.162 \text{ nm}^2$.

There are very pragmatic reasons for the fact that nitrogen has become the adsorptive for the determination of specific surface areas. This is mainly attributable to the cost-efficient availability of this chemical material as high-purity inert gas on the one hand and in liquid state for the cooling of specimen, which was obviously the only choice in the 1930s and 1940s. Knowing that noble gases have more favorable adsorption properties because of their spherical symmetry, scientists soon started using alternative gasses such as argon, krypton and xenon as adsorptives for the determination of specific surface areas. However, in most cases and due to lacking alternatives, a measurement temperature of 77 K was used. For all of the above-mentioned noble gasses, this temperature is below the triple point temperature. Accordingly, these substances re-sublimate with increasing pressure, which puts into question the unequivocal calculation of the area occupation of atoms adsorbed at the solid surface. The area occupation calculation of equation 2 requires the exact knowledge of the liquid density at the selected measurement temperature.

Of course, it was bound to happen: the BET surface areas determined with noble gasses considerably deviated from the values gathered with nitrogen, although the deviations were mostly explained with the undefined condition of the adsorbate phase below the triple point. In addition, there was disagreement about which saturated vapor pressure is to be used for the calculation of BET surface areas in this case: the saturated vapor pressure of the re-sublimated gas or of the subcooled liquid. To overcome these differences in the surfaces, area occupation for noble gasses was postulated there and then, which reproduced the values obtained with nitrogen using equation 1. Depending

Table 1 Area occupation of N₂, Ar and Kr at 77 K (from [2])

adsorbed argon atoms were calculated even
with one and the same measurement tem-
perature and the same surface conditions,
depending on whether the calculation of
the BET surface area refers to the saturated
vapor pressure of the subcooled liquid or
the solid argon (see table 2).
Table 1 compiles the area accupation of

on the chemical properties of the evaluated

surface, different values were constructed

[2,3,4]. The argon example furthermore indi-

cates that different are occupation values for

Table 1 compiles the area occupation of nitrogen, argon and krypton at a temperature of 77 K resulting from the calculation based on equation 2 (from [2]). In case of argon and krypton, calculation was based on the density of liquids subcooled to 77 K. The standard area occupation is indicated for comparison purposes. It becomes obvious that the calculated area occupation of argon and nitrogen has prevailed. In contrast, there is a considerable difference between the calculated and the commonly used area occupation requirement for krypton; a deviation caused by the alignment with the surface obtained with nitrogen, and which does not have a scientific basis. Table 2 is even clearer about this issue. It

	Area occupation [nm ²]			
Adsorptive	Calculated with eq. 2 from liquid density	Commonly used value		
N ₂	0.162	0.162		
Ar	0.138	0.138		
Kr	0.152	0.202		

 Table 2
 Area occupation of an argon atom [nm²] at 77 K (from [4])

Calculated with graphitized carbon black using p _o (subcooled liquid)	Calculated with oxides using p _o (liq.) (subcooled liquid)	Calculated with oxides using p _o (solid) (solid material)
13.8	16.3	18.2
14.3	17.7	18.5
13.7	16.1	17.9
15.1	16.7	18.2
13.7	16.6	18.1
14.3	15.3	17.9
12.9	16.6	17.4
13.0	17.6	17.8
Average value: 13.85 ± 0.7	Average value: 16.65 ± 0.6	Average value: 18.0 ± 0.3

summarizes 3 different average area occupations for argon at 77 K obtained for surfaces determined with nitrogen and subsequent averaging. In this context, it is beyond comprehension why specifically argon atoms should require 20 – 30 % more area than in non-polar carbon surfaces, while the dumbbell-shaped nitrogen molecule with its additional quadrupole moment is allocated universal area. An arrangement that can only be explained with lacking technical alternatives back at that time.

From a scientific perspective, the questions remain why the use of different adsorptives usually leads to different BET surface areas of solid material and which adsorptive is the most suitable one for coming closest to the actual geometrical surface. As these questions are still not fully answered, there is still a lot of uncertainty about the BET method, and especially among critical users of it.

It seems questionable to us that deviating results of other adsorptives compared to N_2 77 K BET calculations can be aligned simply by altering the area occupation. Recent studies clearly confirm the doubts expressed quite some time ago already [3]. The fact that the N_2 molecule is indeed a somewhat special and certainly not the ideal case, as it does not occur as atom (spherical symmetry) and as it has an interfering quadrupole moment. Time may have come to turn the scientific discussion upside down, as from scientific perspective, our following postulate seems to be worth a more profound research:

All texture-determinating sorption measurements based on molecule area occupation, in which the direct interaction between adsorptive atoms and solid surface play a significant role, should be carried out as noble gas adsorption at the noble gases boiling temperature, or it should at least be verified with such measurement.

Of course, this area occupation a_m is unable to consider the various positions of a nitrogen molecule in a solid surface area - the contrary is the case. Based on the BET calculations from noble gas isotherms, we critically evaluate the question whether the BET surface area determined with nitrogen is scientifically plausible.

Figure 2 Hg intrusion curves of macroporous alumina N5





Adsorptive	T [K]	Area occupation calculated from	Area occupation [nm ²]	AS (BET) [m²/g]
N ₂	77	p _o (liquid) 0.162 nm ²		5.42
Kr 77 adjusted to a _m (N ₂)		0.202 nm ²	5.01	
Ar	77	adjusted to $a_m(N_2)$ with p_0 (liquid)	0.166 nm ²	5.22
Ar	77	adjusted to a _m (N ₂) with p _O (solid)	0.180 nm ²	5.24

Determination of the specific surface area of a macroporous alumina with selected adsorptives

Using the example of macroporous alumina (N5), BET surface areas determined for different adsorptives and measurement temperatures are to be compared. The specimen is a granulate with a grain diameter between 1 and 2 mm. The BET surface area (N₂ at 77 K) is approx. 5 m²/g. The cumulative pore distribution determined with mercury intrusion is shown in Fig. 2 from which a total pore volume of about 0.28 cm³/g can be read. The pore size distribution reaches from approx. 0.1 to almost 10 µm. This implies a distinctive macroporous material with a negligible share of larger mesopores; the presence of micropores can even be completely excluded. Therefore, this material is perfectly suitable for our purposes, as multilayer adsorption at the solid surface area is the only sorption mechanism suitable and meeting the requirements for the correct implementation of the BET method.

When using the adapted area occupation for krypton (tab. 1) and argon (tab. 2) for our alumina, following BET surface areas (see table 3) are the result of using the adsorptives at 77 K.

The results are impressive proof of the fact that rather similar surface areas can be caluclated for different adsorptives, if you adhere to certain conventions and use the "adapted" area occupations of noble gasses. If you remember the origin of the "adapted" area occupations, matching values are no surprise, while the deviations occurring with different oxides become clear when reviewing the values of columns 2 and 3 of table 2.

The results for alumina N5 differ substantially, if the area occupation calculated from the liquid densities is used for the BET surface area calculations.

These results are summarized in table 4. Further, this table includes results from argon and krypton isotherms which could be measured at their boiling temperatures (87 and 120 K). Thus, concerns resulting from the questionable nature of the adsorbate phase below the triple point temperature

Figure 3 Krypton sorption at 120 K in macroporous alumina N5



 Table 4
 BET surface areas of alumina N5 with area occupation of adsorbate molecules calculated from liquid densities

Adsorptive	T [K]	Calculated area occupation [nm ²]	BET surface area [m ² /g]
Krypton	77	0.152	3.84
Krypton	120	0.163	3.70
Argon p _o (liquid)	77	0.138	4.35
Argon p _o (solid)	77	0.138	4.03
Argon	87	0.143	4.11
Nitrogen	77	0.162	5.42

can be removed. You have read correctly: with the temperature range of 82 – 120 K we can easily measure krypton isotherms at their boiling temperature of 120 K (see Fig. 3). Beside argon at 87 K, another noble gas turns out to be suitable for carrying out isotherm measurements at its boiling temperature, such a rare isotherm is shown in Fig. 3.

If using the area occupation calculated with equation 2 from liquid density, the BET surface area value determined from nitrogen now deviates considerably. If - regardless of minor deviations - the surface area values based on spherical adsorptives argon and krypton are rather similar at about 4 m²/g, the calculation with nitrogen produces a substantially higher value of more than 5 m²/g – a considerable deviation by more than 25 %.

This result lets us assume that the nitrogen molecules adsorbed in the first molecule layer can be oriented in close arrangement at a polar surface and that nitrogen molecules are oriented rather in upright position at the solid surface, and closer then at random orientation in liquid nitrogen. In this case, it would only be consequent for the evaluation of oxidic surface areas to use a modified, reduced area occupation for nitrogen.

Summary

- The BET surface area quotient of argon and nitrogen used from Tab. 4 leads to an area occupation of nitrogen at alumina of 0.123 nm². This value nicely corresponds to the outcome of other studies [2] and suggest a reduction of the nitrogen area occupation to 0.13 nm².
- 2. The possibility of measuring krypton isotherms at 120 K opens innovative approaches for questioning considerably larger N₂ BET surface areas of oxidic materials.
- 3. Further investigations seem necessary to evaluate the relatively small difference in material parameters, e.g. between krypton measurements of 77 K and 120 K. In unporous, macroporous and mesoporous materials, the corresponding specific surface area generally have a fixed value, i.e. one adsorptive should produce the same specific surface are even with different measuring temperatures. Such options as the CryoSync now offers a quite simple

approach for measuring an entire isotherm family and interpreting the results for BET surface area, adsorbate density and area occupation between 87 K (p_0 of krypton approx. 12 Torr) and 120 K (p_0 of krypton approx. 760 Torr).

- 4. Our LabSPA (Lab for Scientific Particle Analysis) has such options available to run simple measurements of following adsorptives at their corresponding boiling temperatures:
- Argon at 87 K
- Krypton at 120 K
- Methane at 112 K
- Nitrogen at 77 K
- Oxygen at 90 K

Argon and krypton are atomic adsorptives (noble gasses) without permanent electrical dipole or quadrupole moments. Due to its tetrahedon-shaped molecule, methane is also of interest as symmetrical adsorptive molecule without permanent electrical dipole or quadrupole moment [5]. Some of our further measurement programs will evaluate which deviations occur between the nitrogen to the argon and krypton BET-results in various organometallic (MOFs) and other meso and microporous pore structures.

We gladly keep you updated on further adsorptive application results. If you are interested in such temperature option as the CryoSync, please contact us directly. Such option is to use not only to use with the adsorption instruments of 3P INSTRUMENTS but with other gas adsorption instruments too, and we can help to find the right procedure.

The topic of the use of different adsorptives will be in the focus of our 3P European workshop 2019, which will be held in English on May 15, 2019, in the nice city Leipzig/ Germany – in combination with the Symposium on Dynamic Sorption Methods at the same place on May 14, 2019. Please contact us for more information or use the link to **www.dynamicsorption.com** for further information and the form to register you early enough.

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