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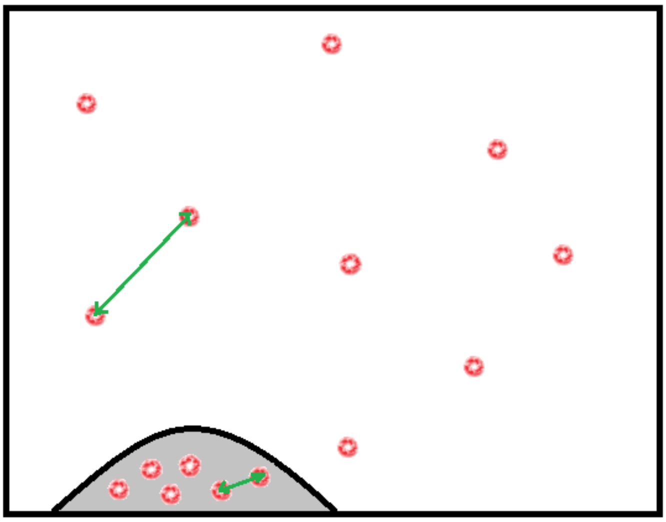
New measurement methods for calculating and modelling adsorption.

Two new measurement methods based on derived relationships between gas concentration and adsorption make it possible to calculate a material’s adsorption ability and capacity. A model for adsorption capacity with respect to adsorption ability, gas concentration, pressure, and temperature can also be developed using the derived relationships.



Summary

New relationships related to adsorption have been developed, providing increased understanding of the underlying processes in adsorption and desorption. Based on the seemingly trivial assumption that adsorption capacity is proportional to how much denser the adsorbed gas is within the adsorption material compared to the surrounding gas, equilibrium relationships have been formulated that describe adsorption and desorption when gas concentration or pressure changes. Measurements indicate that the assumption and the relationships hold for gases with weak adsorption. How well they apply to gases with strong adsorption requires further investigation.

The term *“adsorption ability”* in this report does **not** mean adsorption capacity. Here, *“adsorption ability”* is a new concept that expresses the ratio between gas density in the adsorption material and gas density in the surrounding gas. Adsorption capacity is calculated using the measured adsorption ability. In the capacity calculation (in mg/g), adsorption ability is one of several parameters; the others are pressure, temperature, gas molecular weight, gas concentration, and the density of the adsorption material. (The relationships can also be used to calculate dynamic processes, but that is not covered in this report.)

The relationships enable two new measurement methods for characterizing material properties in ways that have not been possible until now.

The adsorption ability of an adsorbent can be calculated by measuring the amount of gas adsorbed or desorbed after injecting a small volume of gas (see Measurement Method 1) or after changing the pressure (see Measurement Method 2).

One application of the first measurement method (Method 1) is to determine gas concentrations in the adsorption material and in the surrounding gas. Both gas concentrations and adsorption ability can be determined with Method 1. The second measurement method (Method 2) is reversible and therefore does not alter the sample, meaning that multiple samples are not needed to observe how adsorption ability changes as a function of time, pressure, or temperature.

Keywords: adsorption, desorption, adsorption material, concentration equilibrium, gas, relationship, measurement method, atomic spacing

Short summary

Derived adsorption theory enables two new methods to measure adsorption and calculate the adsorption capacity for adsorbents. Derived adsorption models can be used to calculate the adsorption and desorption of the adsorbent with respect to gas concentration, pressure and temperature.

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Introduction

The total amount of nitrogen gas adsorbed in Cemviron Carbon’s Nuclearcarb 203C as a function of gas concentration has been calculated in Figure 1.1 using equation (5), after the adsorption ability was measured with Measurement Method 1.

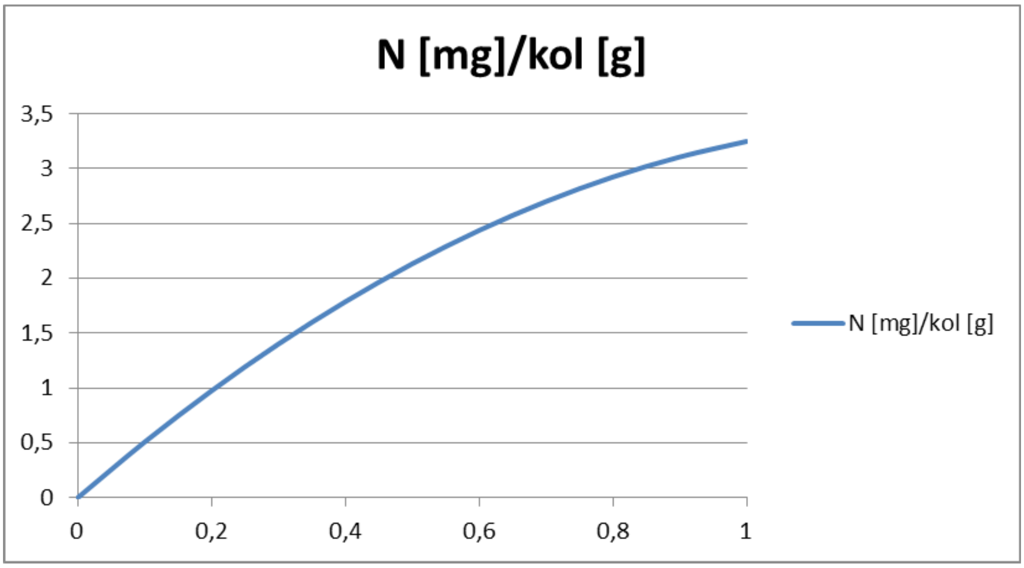

Figure 1.1. Adsorption capacity (qe) as a function of nitrogen gas concentration, where 0.4 on the x-axis corresponds to 40% nitrogen and 60% helium (at 30°C, 1 atm).

If an adsorption material is enclosed in a container (without external influence), the concentration of adsorbed gas reaches equilibrium with the gas concentration, provided that the gas is loosely adsorbed onto the material. The equilibrium point is determined by the material’s adsorption ability at that gas concentration.

Adsorption ability describes how much denser the adsorbed gas is in the carbon compared to the surrounding gas (at a given gas concentration, etc.). In this report, adsorption ability is denoted by **S**. For an idealized adsorption material, adsorption ability **S** is equal to the concentration of adsorbed gas **KB** divided by the concentration of non-adsorbed gas **KO**, according to **S = KB / KO**.

Here, concentrations are given in volume fractions (not, as usual, in mg/L). For example, if 10 mL of gas is adsorbed onto 1 mL of carbon and the gas concentration **KO** is 0.1 mL/mL, then **S = KB / KO = (10/1) / (0.1) = 100**.

Adsorption ability depends on the type of gas being adsorbed.

The adsorption of nitrogen in Cemviron Carbon’s Nuclearcarb 203C exhibits different **S** values depending on the gas concentration; see Figure 1.2 on the next page.

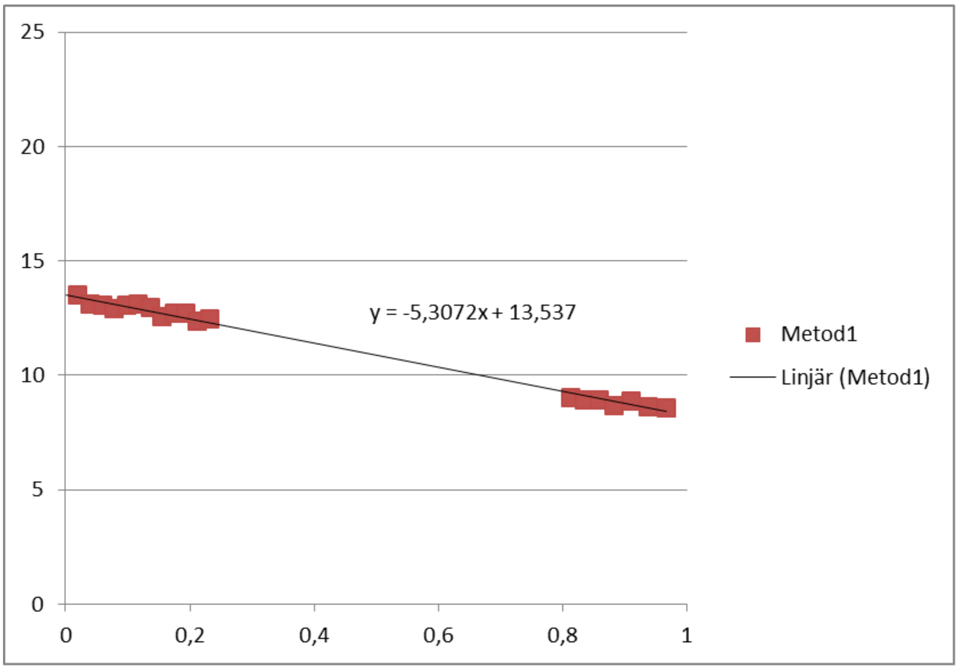

Figure 1.2 Measured values of adsorption ability **S** at different nitrogen concentrations. The calculation of adsorption capacity **qe** (in Figure 1.1) is based on these measurements.

In this case, the adsorption ability **S(KO)** appears to have a linear dependence on **KO**; according to Figure 1.2, **S(KO) = -5.31·KO + 13.5**.
How **S** is measured is described in Sections 2 and 3.

Adsorption capacity depends on pressure and temperature, and adsorption ability also has a pressure and temperature dependence, but this has not been investigated in this report.

If the gas concentration surrounding the adsorption material changes, adsorption or desorption occurs until the balance between the adsorbed concentration and the gas concentration is restored. This equilibrium can be described by **KB = S·KO** for an ideal adsorption material, i.e., the concentration of adsorbed gas **KB** is in balance with the concentration of non-adsorbed gas **KO**. This equilibrium applies to both adsorption and desorption. In the derived relationships, desorption is treated as adsorption with a negative value.

Using the derived relationships, the adsorption ability of a material can be calculated either by injecting a known amount of gas (Measurement Method 1) or by changing the pressure (Measurement Method 2). Measurement Method 2 shows that adsorption is not actually about maintaining equilibrium between two concentrations, but between two atomic spacings: the atomic spacing in the gas and that in the carbon.

Note in Figures 1.1 and 1.2 the difference between adsorption capacity and adsorption ability. How adsorption capacity depends on adsorption ability, pressure, and temperature is described in Section 5.

Measurement method 1

This measurement method for determining **S**, unlike Measurement Method 2, cannot be performed without changing the gas concentration. However, this method has the significant advantage that only a small amount of gas is needed to determine the adsorption ability for that gas.

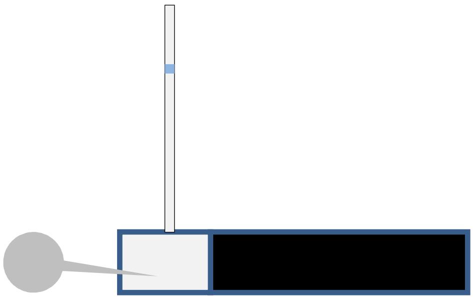

Figure 2.1 A test tube is partially filled with an adsorption material. A volume meter is illustrated by the upper tube in the figure, where a movable water drop serves as a volume indicator. Gas is injected into the test tube through a septum.

When a gas with a higher concentration than that of the gas in the test tube is injected, adsorption occurs. The amount of gas that is not adsorbed is measured by the syringe by drawing out enough gas to return the volume to its original level. The difference between the injected volume and the withdrawn volume represents the adsorbed amount. In practice, a differential pressure meter connected to a reference tube should be used to eliminate the effects of temperature and atmospheric pressure variations.

The concentration of adsorbed gas **KB** is measured in volume of adsorbed gas per volume of adsorption material **Vcms**. If the volume is porous, the pores are not included in this volume; **Vcms** should represent the net volume.
The concentration of non-adsorbed gas **KO** is measured as the volume of non-adsorbed gas per total gas volume **Vgas**.
The value of **S** depends on the selected gas and the adsorption material. Note that **S** is dimensionless.

If the gas in the test tube is a mixture, e.g., xenon and helium with a known xenon concentration, **S** for xenon can be calculated after injecting xenon at a different concentration.

Definitions:

- **Vads** = Volume of adsorbed gas (e.g., nitrogen)
- **VI** = Injected volume (e.g., nitrogen)
- **Vgas** = Total gas volume in the test tube (e.g., helium + nitrogen)
- **Vcms** = Net volume of adsorption material in the test tube

What happens when gas is injected into the test tube?
The volume in the test tube, including the measurement tube, initially changes from **Vgas** to **Vgas + VI**, but adjusts to **Vgas + VI − Vads** once equilibrium is

restored. Here, **Vads** is the amount that needs to be adsorbed (or desorbed if adsorption is negative) for static equilibrium according to **$KB = S \cdot KO$** to be achieved.

The amount of the injected gas in the gas mixture in the test tube initially changes from $(KO\,Vgas)$ *to* $(KO\,Vgas + KI\,VI)$ *when the gas is injected, but then changes to* $(KO\,Vgas + KI \ast VI - Vads)$ once concentration equilibrium is restored (through adsorption or desorption). Pressure and temperature can be kept constant.
If $KB = S \ast KO$, then after injection:

$$KB + Vads/Vcms = S \ast (KO\,Vgas + KI\,VI - Vads)/(Vgas + VI - Vads)$$

$$S\,KO + Vads/Vcms = S \ast (KO\,Vgas + KI \ast VI - Vads)/(Vgas + VI - Vads)$$

$$Vads/Vcms = S \ast (KO \ast (-VI + Vads) + KI \ast VI - Vads)/(Vgas + VI - Vads)$$

$$Vads/Vcms = S \ast ((KI-KO) \ast VI + (KO-1) \ast Vads)/(Vgas + VI - Vads)$$

Solving for S gives:

$$S = ((Vgas + VI - Vads)/Vcms) \ast Vads / (VI \ast (KI-KO) + Vads \ast (KO-1)) \quad (1)$$

Vads is negative for desorption and positive for adsorption.
By injecting two different concentrations (e.g., 0% and 100%), it is possible to determine both the gas concentration KO and S.

After an injection, the new gas concentration can be calculated as:

$$KOny = (KO\,Vgas + KI\,VI - Vads)/(Vgas + VI - Vads)$$

Two practical special cases:

Pure adsorption – Measurement Method 1a:
If the adsorption material is in 100% helium and xenon is injected:

Vads = Adsorbed volume of injected gas

$$S = ((Vgas + VI - Vads)/Vcms) \ast Vads / (VI - Vads)$$

Pure desorption – Measurement Method 1d:
If the adsorption material is in 100% xenon and helium is injected:

Vdes = Desorbed volume due to injected helium

$$S = ((Vgas + VI + Vdes)/Vcms) \ast Vdes / VI$$

3 Measurement method 2

This measurement method for determining **S** is simple and is based on how much gas desorbs or adsorbs during a pressure change. The measurement can be repeated without altering the gas concentration. This method provides much better accuracy at high gas concentrations than at low gas concentrations.

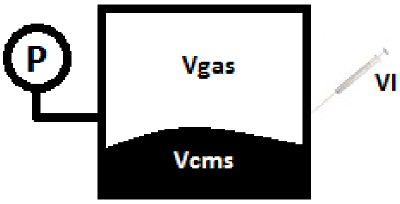

Figure 3.1 If a volume **VI** is withdrawn and then pushed back into a vessel with a known volume **Vgas** and known net volume **Vcms**, then **Vads**, **Vdes**, and **S** can be calculated.

What pressure change results from a volume change?

If nothing is adsorbed when the volume is increased by **VI**, the pressure **P1** is:
$P0*Vgas = P1*Vgas + P1*VI$

If the volume **Vdes** is desorbed when the volume **VI** is withdrawn, then:
$P0*Vgas + P2*Vdes = P2*Vgas + P2VI$

Rearranged:
$$Vdes = (P2*Vgas + P2*VI - P0*Vgas) / P2 \qquad (2.1)$$

If the volume **VI** is pushed back in and the volume **Vads** is adsorbed, then:
$P2*Vgas + P2*VI = P0*Vgas + P2*Vads$

Rearranged:
$$Vads = (P2*Vgas + P2*VI - P0*Vgas) / P2 \qquad (2.2)$$

Adsorption and desorption are thus equal in magnitude. This is reasonable because the processes are reversible. Therefore, the relationships for adsorption and desorption are the same.

In a single process, negative adsorption corresponds to desorption.
For the process describing desorption, it may therefore be appropriate to write:
$$Vads = - (P2*Vgas + P2*VI - P0*Vgas) / P2 \qquad (2.3)$$

When the pressure changes, desorption is significant even at 100% gas concentration. This shows that desorption depends on the changed atomic spacing rather than the gas concentration, since the gas concentration remains unchanged. In fact, desorption is greatest at 100% gas concentration.
Here, atomic spacing is assumed to be proportional to volume at constant temperature and gas amount. What happens to the atomic-spacing equilibrium if the volume changes from Vgas to Vgas + VI?

The gas volume in the test tube becomes Vgas + VI and does not change once atomic-spacing equilibrium is restored.
Since desorption has occurred, the concentration of adsorbed gas decreases from SKO to $SKO + \mathrm{Vads}P2 / \mathrm{Vcms}P0$.
The volume Vcms does not change at different pressures; instead, a quantity of gas is desorbed from the volume, so the concentration change is calculated as $\mathrm{Vads}P2 / \mathrm{Vcms}P0$ rather than Vads / Vcms. (Note that Vads is negative during desorption.)

Thus, if KB = S*KO and the adsorption material is in a gas (adsorbate) with concentration KO, then (at pressure P2):

$$SKO + (\mathrm{Vads}*P2)/(\mathrm{Vcms}*P0) = S * (KO*\mathrm{Vgas} - \mathrm{Vads}) / (\mathrm{Vgas} + VI)$$

Solving for S:

$$S = (-\mathrm{Vads}*P2 / (\mathrm{Vcms} * P0)) * (\mathrm{Vgas} + VI) / (KO*VI + \mathrm{Vads}) \quad (3)$$

Here, Vads (at pressure P2) is calculated from the measured pressure change:

$$\mathrm{Vads} = (P0 / P2) * \mathrm{Vgas} - \mathrm{Vgas} - VI$$

Note: Measurements have not been made at different pressures to verify equation (3), so it is very uncertain whether the pressure dependence in (3) is correct. The relationship (3) for Measurement Method 2 is not as straightforward as relationship (1) for Measurement Method 1.

Measurement Method 1 is conducted at pressure P0 and Measurement Method 2 at pressure P2, so when comparing results from the methods, differences in pressure should be taken into account as they can lead to different outcomes.

4 Measurement result.

The adsorption material used is Cemviron Carbon's Nuclearcarb 203C. The measurements below were performed for different nitrogen concentrations in helium, using both measurement methods simultaneously to determine **S** with both methods for the same sample and at the same gas concentration and temperature. In fact, four different measurement approaches were used: adsorption by injecting a high concentration, desorption by injecting a low concentration, desorption by a pressure decrease, and adsorption by a pressure increase.

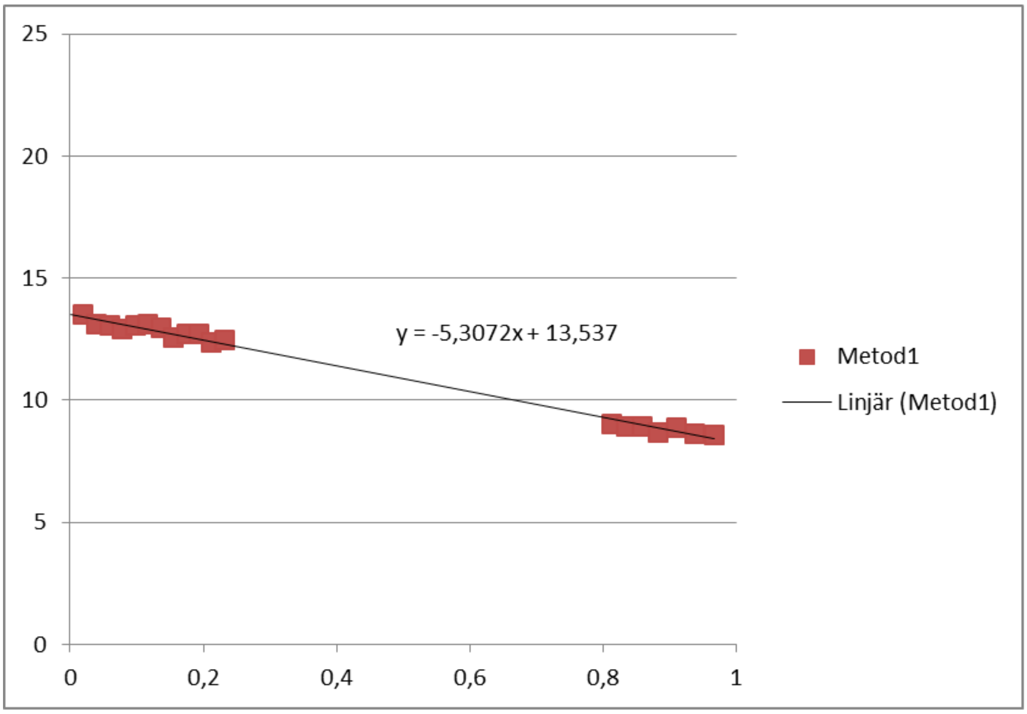

***Figure 4.1** Results using Measurement Method 1. Measured **S** values as a function of nitrogen concentration, where 0 to 1 corresponds to 0 to 100% nitrogen concentration. From the diagram, **S = 13 − 5·KO**.*

If a linear S(KO) can be expected, then a single measurement at 0% KO and a single measurement at 100% KO are sufficient to determine, using equation (5), the amount of gas that binds to one gram of carbon from 0 to 100% KO.

Unfortunately, the measurement results cannot be regarded as a "definitive reference," especially with regard to Measurement Method 2. Figures 4.2 and 4.3 show how the results for Measurement Method 2 are affected if more than one gas is desorbed. At low gas concentrations, measurement Method 2 produces large measurement errors.

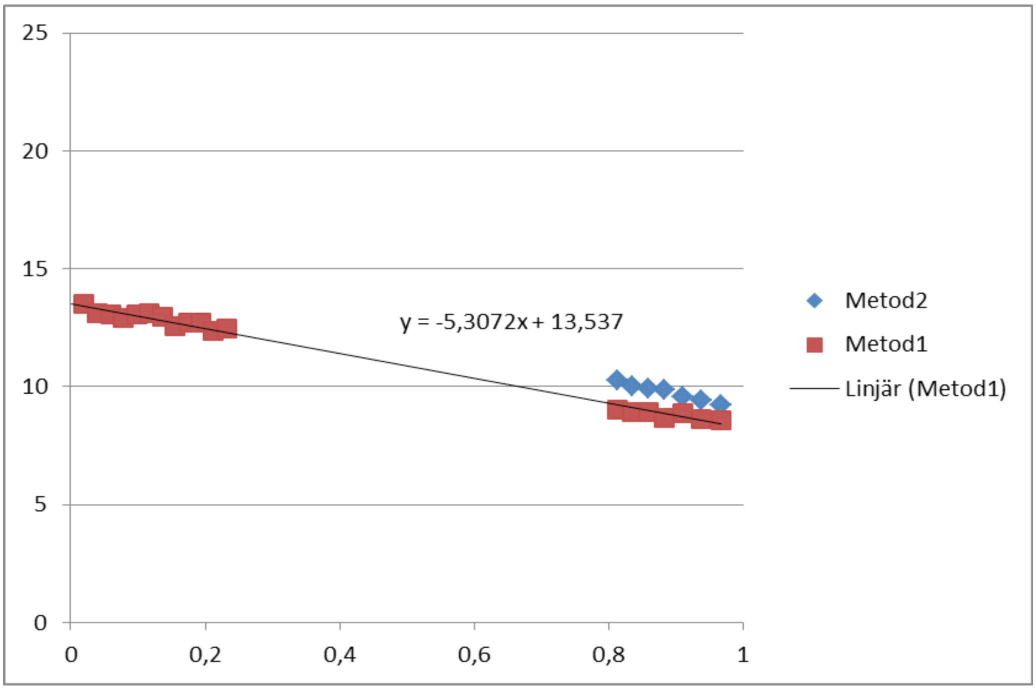

Figure 4.2 If no correction is made for helium also desorbing when Measurement Method 2 is used, these deviant **S** values are obtained between Measurement Methods 1 and 2. The measurement results for Method 2 at low nitrogen concentrations fall outside the diagram.

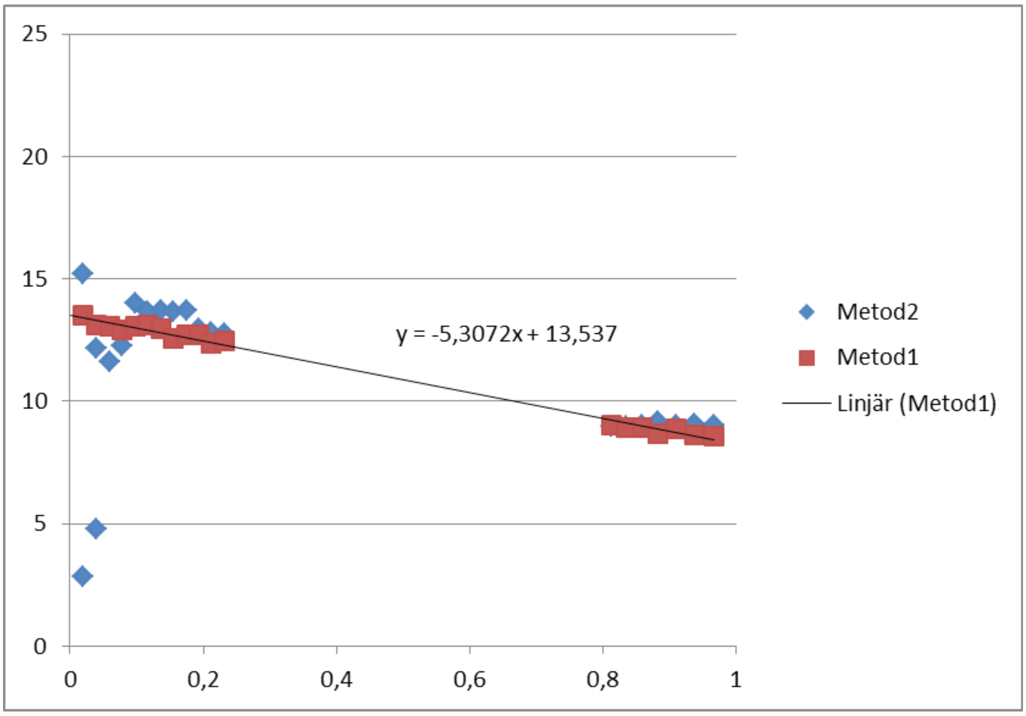

Figure 4.3 After correction for helium desorption. At KO = 0, only helium is adsorbed to the carbon, while at KO = 1 there is no helium at all. Therefore, it is reasonable to correct by removing 100% of the measured desorption at KO = 0 and 0% of the measured desorption at KO = 1. Here, Measurement Method 2 has been linearly corrected for 100% of the desorption at KO = 0 and 0% of the desorption at KO = 1.

Measurement Method 2 produces large measurement errors at low nitrogen concentrations because helium also desorbs from the carbon while the nitrogen concentration is very low. Therefore, these measurements are completely incorrect in Figure 4.2. After correcting for helium desorption, however, the measurement values improve significantly. Measurement accuracy at low nitrogen concentrations is much better with Measurement Method 1. Thus, the two methods complement each other.

Measurement Method 1 is also effective at high nitrogen concentrations, but in that case, Measurement Method 2 is practical to use. Using both methods simultaneously has the advantage that the gas concentration can also be determined. Moreover, incorrect input data or measurement values can often be identified. For example, if the gas volume is measured incorrectly, the results from the two methods will not match.

The spread in measured values is partly due to the difficulty of reading the syringe volume. A 2% reading error on the syringe can result in an 8% error in **S** with Measurement Method 1. In Measurement Method 2, the syringe volume is only read near its maximum, and a 1% reading error can give a 2% error in **S**. However, measurement accuracy with Method 2 becomes very poor at low concentrations.

Measurement Methods 1 and 2 should be used to determine **S** for individual gases, not for mixtures. **S** values for mixtures can instead be calculated as a concentration-weighted average based on the **S** values for each individual gas.

Example of Excel Calculations

Adsorption material: Cemviron Carbon’s Nuclearcarb 203C

- Weight = 8 [g]
- Bd = Bulk density = 1700 [mm³/g]
- NBd = Net/Bulk density = 0.43 (density ratio compressed/porous)
- Vcms = Weight * Bd * NBd = 8 * 1700 * 0.43 = 5848 [mm³]
- Test tube volume = 34,000 [mm³]
- Vgas = Test tube volume − Vcms = 34,000 − 5,848 = 28,152 [mm³]

Measurement Method 1

- Injected gas = Helium
- Test tube gas = 83% nitrogen + 17% helium
- KO’ = KO before injection = 0.83
- KI = 0 (i.e., 0% nitrogen, 100% helium)
- Psyringe = 1.01 [atm], pressure in the syringe before injection
- P0 = Psyringe + 0.00306 [mm³]
- VI = 1000*(Psyringe/(Psyringe+P0)) = 996 [mm³], injected volume at pressure P0
- Withdrawn = 2,068 [mm³]
- Vads = VI − Withdrawn = −1,071 [mm³]
- KO = (KO’*Vgas* + *KI*VI − Vads)/(Vgas + VI − Vads) = 0.81
- S = −((Vgas + VI − Vads)/Vcms) * Vads / (VI*(KI − KO) + Vads*(KO − 1)) = 9.04

Measurement Method 2

- Test tube gas = 81% nitrogen + 19% helium
- KO = 0.81
- VI = 2,000 [mm³], volume increase via syringe
- Patm = 1.01 [atm], ambient pressure
- P0 = Patm + 0.00306 [mm³], pressure in test tube before volume increase
- P2 = Patm − 0.0285 [mm³], pressure in test tube after volume increase
- HeVdes = 260 [mm³], measured desorption at KO = 0 using Method 2
- Vads = (P0*Vgas* − *P2*Vgas − P2*VI)/P2* + *HeVdes*(1 − KO) = −1,044 [mm³]
- S = −(Vads*P2/(Vcms*P0)) * (Vgas + VI)/(KO*VI + Vads) = 8.95

See Section 5 for the calculation of the adsorbed amount based on the adsorption capacity **S**.

5 Adsorptions capacity

Total bound volume VB is obtained from $KB = S*KO$
i.e.
$VB = S(KO)*KO*Vcms$
This applies under the assumption that the adsorbed gas is not bound so strongly that it remains attached even when the adsorption capacity decreases. The total amount adsorbed in units of [mol] depends on volume, pressure, and temperature according to $n=p*VB/(R*T)$

molar mass	14	g/mol	
weight	8	g	
Bd	1700	mm3/g	
NBd	0,43	Net density / Bulk density	
Vcms	0,000005848	m3	Net volume
p	100000	Pa	
R	8,314	J/mol*K	
T	303	K	
S	13-5*KO	(dimensionless)	

(4)
Total amount adsorbed [mol] = $p*S(KO)*KO*Vcms/(R*T)$

The adsorbable gas amount given as grams of gas per gram of carbon is obtained by multiplying by the molar mass and dividing by the amount of carbon.
(5)
Gas [g] / Carbon [g] = $\text{molar mass} * KO*S(KO)*p*Vcms/(R*T*\text{weight})$

For nitrogen, S(KO) has been measured up to S(KO)=13-5*KO at 30°C, 1 atm, for the tested adsorption material Cemviron 203C. The molar mass can be replaced by molar volume (22414 [mL/mol] at 0°C, 1 atm) if you want the bound amount in units of mL.

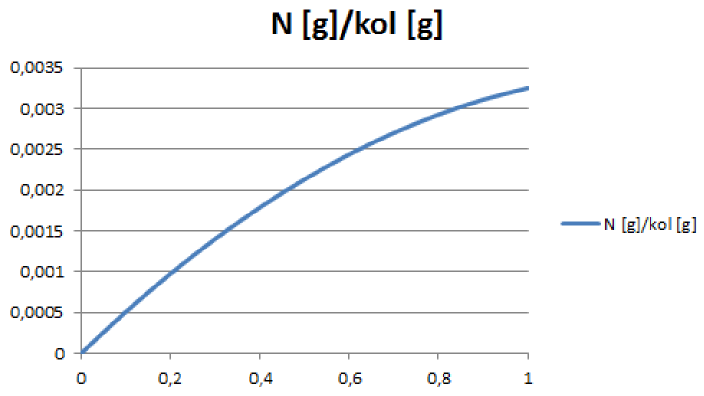

Figure 5.1. Nitrogen adsorbed per gram of carbon as a function of the nitrogen concentration in the gas.

Note that S has been measured for the net volume of carbon.
Net volume Vcms [mm3]= *Vikt *Bd*NBd* =
8*1700*0,43 [mm3]=5848 [mm3].
Where NBd = 0.43 is a measured conversion factor used to convert the bulk density of the carbon to net density. The factor was determined by filling a volume of carbon with water and measuring how much water fit into the pores of the carbon. The measured factor was 0.44, but some air bubbles remained in the carbon. The slightly lower value of 0.43 compensates for this.
Equations (4) and (5) can only be used for different pressures if the pressure dependence of S has been measured. The pressure dependence of S could potentially be measured using measurement method 2, assuming that the pressure dependence in equation (3) is correct. For example, by reducing the pressure between measurements by extracting more and more gas from the sample tube.

If the temperature is constant but the pressure is increased, the number of atoms per unit volume in the gas increases, which means that more atoms must be adsorbed onto the carbon. This results in more gas being adsorbed at higher pressure, even if S decreases with increasing pressure.

A special case for xenon gas and other gases with strong adsorption.
Xenon being adsorbed has different S depending on the gas concentration, see Figure 5.2.

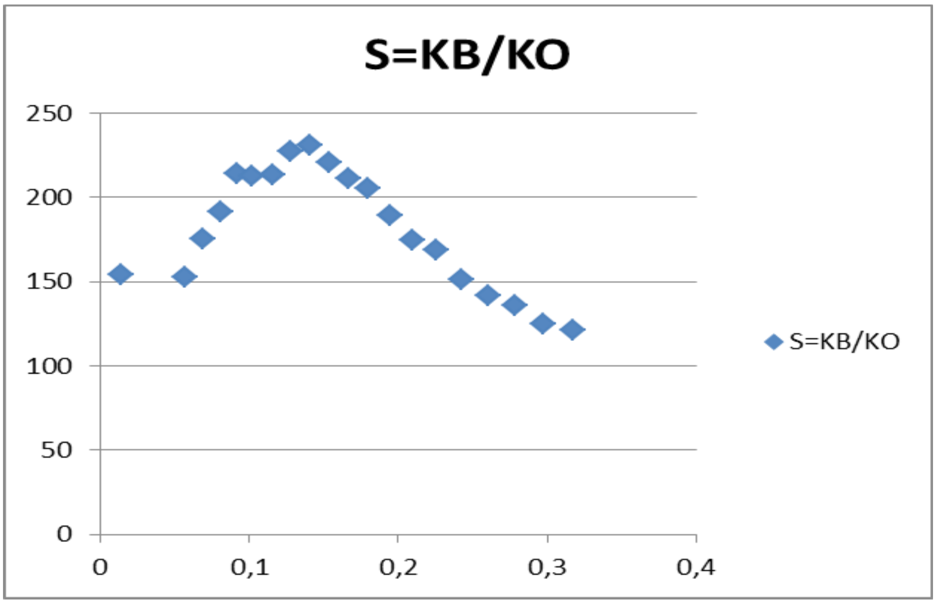

Figure 5.2. The measured adsorption capacity S for xenon as a function of gas concentration, where 0.4 corresponds to 40% xenon and 60% helium (at 30°C, 1 atm).

It is noteworthy that the adsorption capacity at low concentrations increases with increasing concentration. However, this may be due to measurement errors. The measurements also show that adsorbed xenon does not desorb as expected when the adsorption capacity decreases. For xenon, it is therefore not

sufficient to calculate the capacity at a single gas concentration, i.e., at one point. Instead, the contributions from all concentrations between 0 and KO must be summed.
The capacity at a specific gas concentration is then obtained as:
(6)
Gas [g]/Carbon [g] = ***(molar weight * p/(R*T))*∑adsorbed_volume /weight***

The total amount of xenon gas adsorbed in Cemviron Carbons Nuclearcarb 203C as a function of gas concentration has been calculated using (6) and measured with measurement method 1, as shown in Figure 1.1.

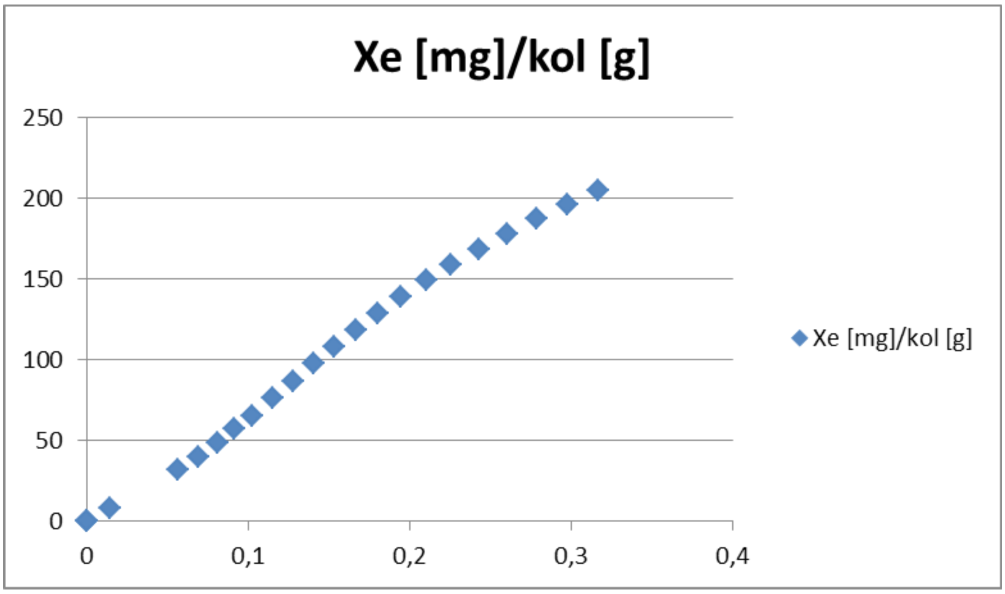

Figure 5.3. Adsorption capacity (qe) as a function of xenon gas concentration, where 0.4 on the x-axis corresponds to 40% xenon and 60% helium (at 30°C, 1 atm).
Note that the simpler relation (5) applies only to a gas that binds weakly, e.g., nitrogen. Xenon binds strongly, so (6) must be used for xenon.

Once S(KO) for a gas has been determined, it should also be possible to calculate the capacity using:

Gas [g] / Carbon [g] = *(molar weight* p*Vcms/(R*T*weight))* ∫S(KO)*dKO*
This relation for calculating the capacity has not been verified.
A different result is obtained if the adsorption capacity is calculated using (5). This gives the incorrect adsorption capacity shown in Figure 5.4. It demonstrates that adsorbed xenon does not desorb to the expected extent when the adsorption potential decreases.

Therefore, the capacity for xenon should not be calculated using (5).

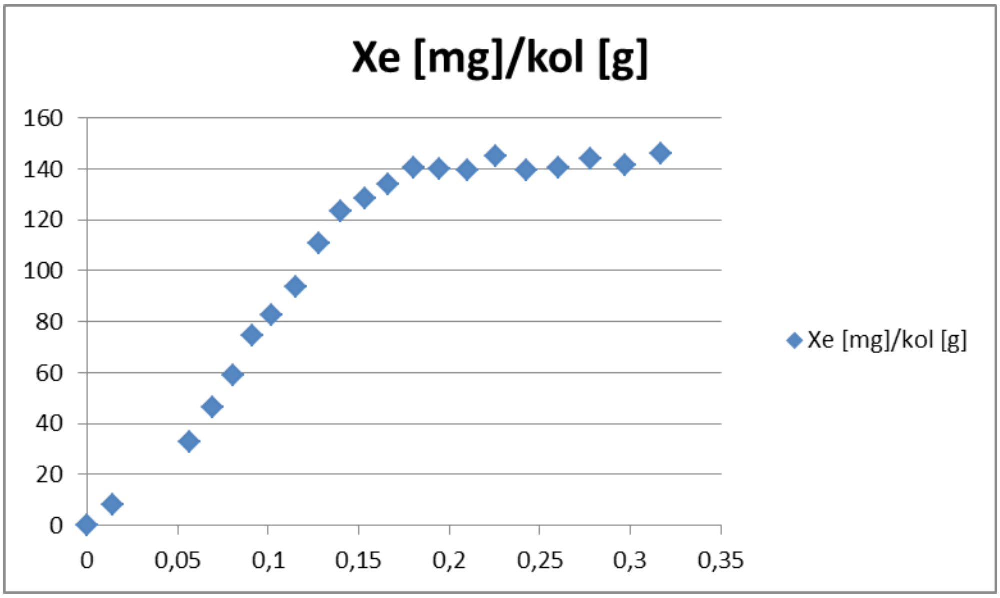

Figure 5.4. If the capacity for xenon is calculated using (5), this incorrect result is obtained.

The capacity for xenon should be calculated using (6). Figure 5.1 shows the correct result.

How the measurement methods and calculation models are affected by strong adsorption requires further investigation.

6 References

K.Y. Foo, B.H. Hameed. Insights into the modeling of adsoption isotherm systems.