A45-A Adsorption von Methylbutan an Holzkohle

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Theoretical Basics

Adsorption

There are two different types of adsorption; physisorption and chemisorption. If the molecules get attached to the surface because of Van-der-Waals forces, it's called physisorption. This process is reversible and there can be more layers of molecules on the surface. If the molecules get attached to the surfaces because of covalent bonding, it's called chemisorption. This process can be irreversible and there can be only one layer on the surface.

Langmuir-Isotherm

The Langmuir-Isotherm is only valid for small pressures.

Additional the following five assumptions have to be true:

1. Only one layer on the surface
2. Adsorptionenergy is equal for each molecul and place on the surface
3. No interaction between the molecules
4. The molecules don't move on the surface
5. the gas is ideal

The equation for the Langmuir isotherm is:

$$\Theta = \frac{n_a}{n_{mono}} = \frac{K_a \cdot p}{K_a (p+1)}$$

n_a: amount of adsorbet substance
Θ: solidity
p: pressure
n_{mono}: amount of substance adsorbed by a full surface
$K_a = \frac{1}{2}$: Equilibrium-Constant

BET-Isotherm

At high pressure or low temprature the Langmuir-Isotherm fails. There will be more layers on the surface. This not considered by the Langmuir-Isotherm.

The BET-Isotherm describes this:

$$\frac{p}{n_a(p_0-p)} = \frac{1}{C \cdot n_{mono}} + \frac{(C-1)p}{n_{mono} \cdot C \cdot p_0}$$

p_0: vapor pressure
C: Energy-Parameter $C = \exp\left[\frac{a_{ads}H - a_{liquid}H}{RT}\right]$

Aims and Execution

We want to find the parameters for our two equations: n_{max}, C, k_a, a

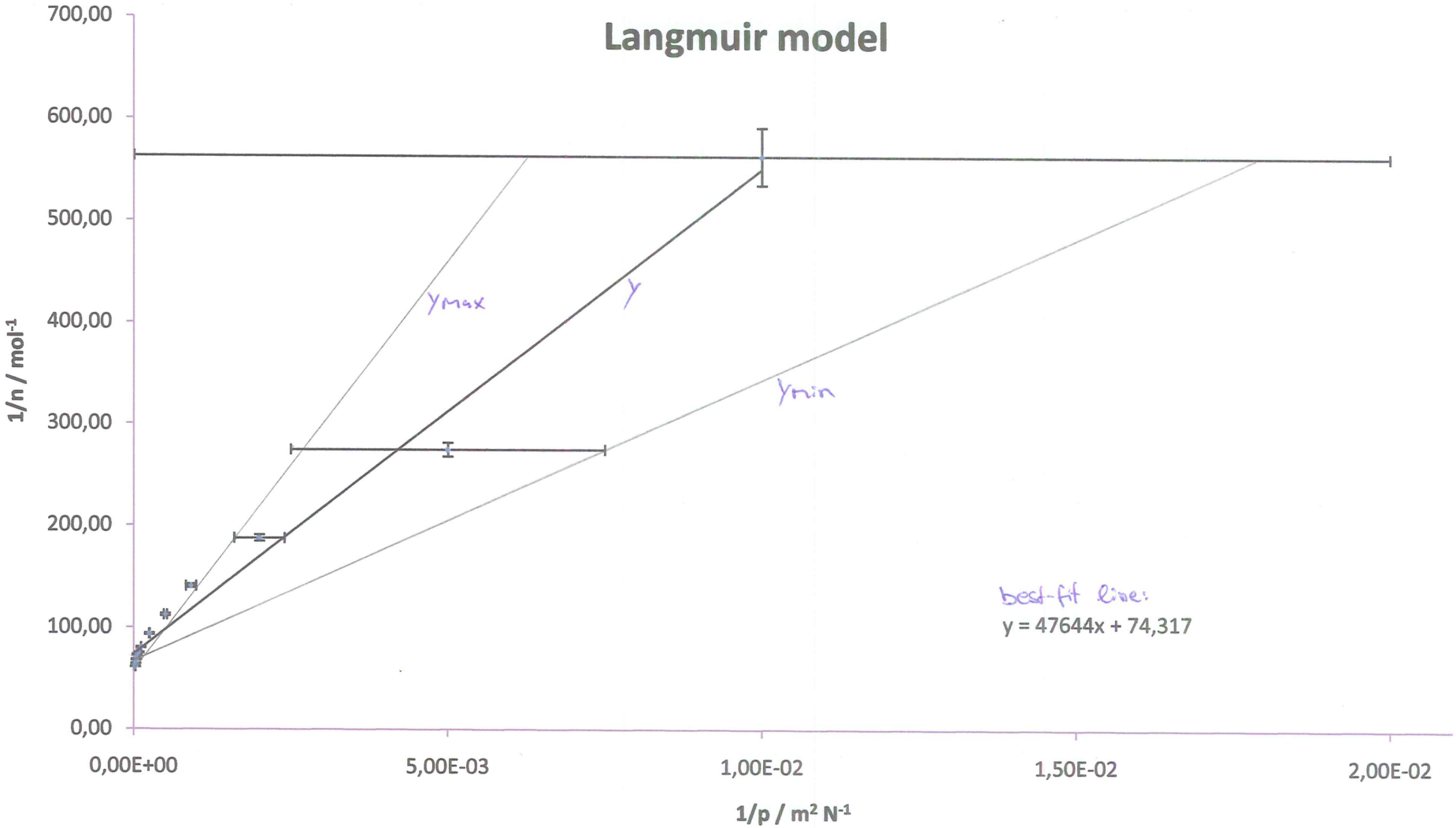
For that we evacuate our system (see description) and fill it step by step with methyl-Ln. So we know the amount of it in the system. We measure the pressure. ~~and~~ Now we close shielded and can get our searched parameters out of the graph. The not measured but needed variables are given due our system buildup. For example g can be ~~manu~~ looked up for 0°C and 25°C.

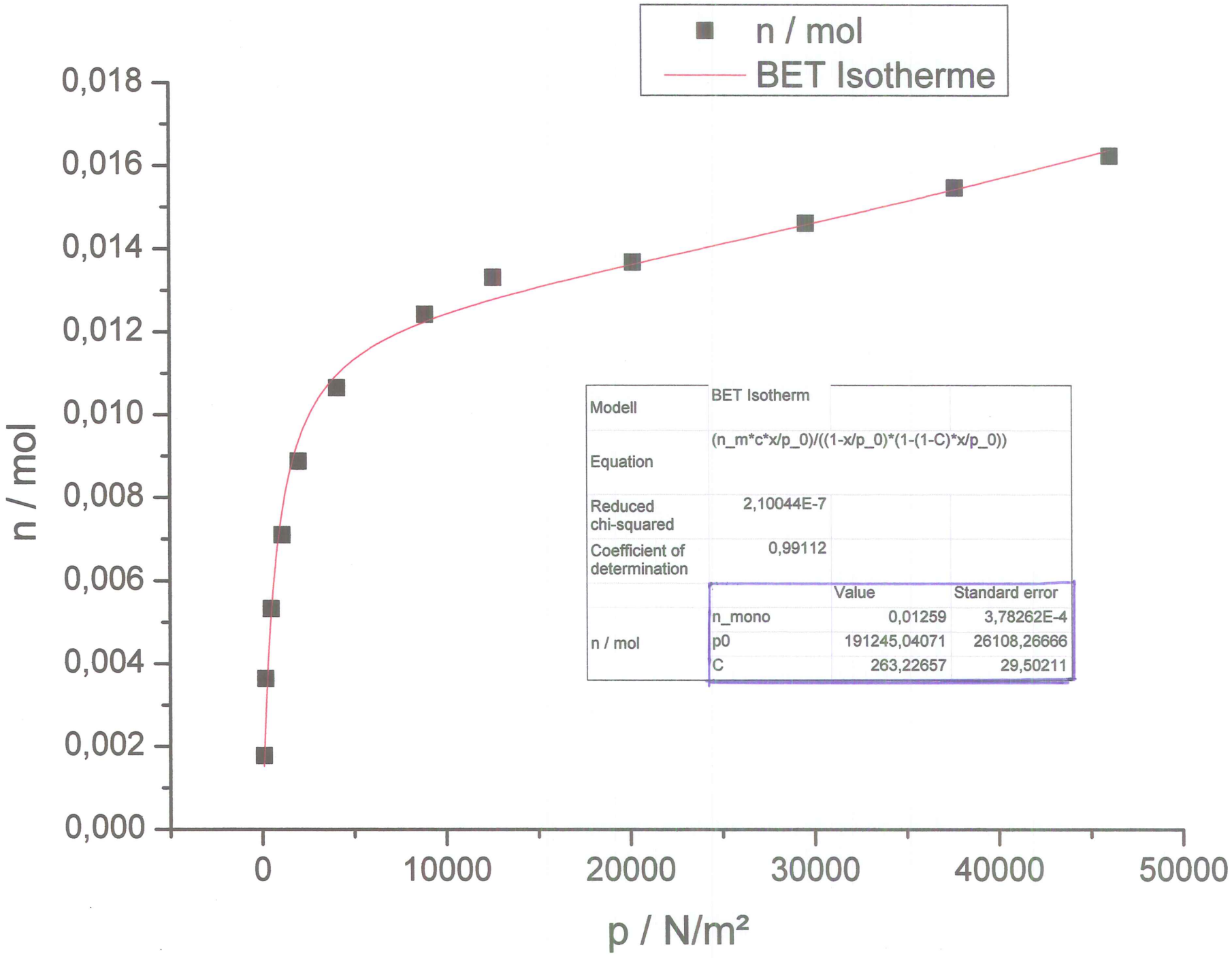
Adsorption of methylbutane on charcoal

V / ml	p / mbar	p / N m^{-2}	T / °C	m / g	Δm / g	n / mol	Δn / mol	1/n / mol^{-1}	Δ1/n / mol^{-1}	1/p / m^2 N^{-1}	Δ1/p / m^2 N^{-1}
0,20	1	100	0	0,128	0,0064	0,00178	8,88E-05	563,14	28,16	1,00E-02	1,00E-02
0,41	2	200	0	0,263	0,0064	0,00364	8,88E-05	274,70	6,70	5,00E-03	2,50E-03
0,60	5	500	0	0,384	0,0064	0,00533	8,88E-05	187,71	3,13	2,00E-03	4,00E-04
0,80	11	1100	0	0,512	0,0064	0,00710	8,88E-05	140,79	1,76	9,09E-04	8,26E-05
1,00	20	2000	0	0,641	0,0064	0,00888	8,88E-05	112,63	1,13	5,00E-04	2,50E-05
1,20	41	4100	0	0,769	0,0064	0,01065	8,88E-05	93,86	0,78	2,44E-04	5,95E-06
1,40	89	8900	0	0,897	0,0064	0,01243	8,88E-05	80,45	0,57	1,12E-04	1,26E-06
1,50	126	12600	0	0,961	0,0064	0,01332	8,88E-05	75,09	0,50	7,94E-05	6,30E-07
1,60	202	20200	23,7	0,988	0,0062	0,01369	8,55E-05	73,06	0,46	4,95E-05	2,45E-07
1,71	296	29600	23,7	1,055	0,0062	0,01463	8,55E-05	68,36	0,40	3,38E-05	1,14E-07
1,81	377	37700	23,7	1,117	0,0062	0,01548	8,55E-05	64,59	0,36	2,65E-05	7,04E-08
1,90	461	46100	23,7	1,173	0,0062	0,01625	8,55E-05	61,53	0,32	2,17E-05	4,71E-08

ρ(Methylbutane, 0°C) / g ml^{-1}	0,6406
ρ(Methylbutane, 23,7°C) / g ml^{-1}	0,6172
M(Methylbutane) / g mol^{-1}	72,15

Δp / mbar	1
Δp / N m^{-2}	100
ΔV / ml	0,01


Langmuir model
700,00
600,00
500,00
400,00
300,00
200,00
100,00
0,00
1/n / mol-1
0,00E+00
5,00E-03
1,00E-02
1,50E-02
2,00E-02
1/p / m2 N-1
ymax
y
ymin
best-fit line:
y = 47644x + 74,317


n / mol
BET Isotherme
0,018
0,016
0,014
0,012
0,010
0,008
0,006
0,004
0,002
0,000
n / mol
0
10000
20000
30000
40000
50000
p / N/m²
Modell
BET Isotherm
Equation
(n_m*c*x/p_0)/((1-x/p_0)*(1-(1-C)*x/p_0))
Reduced chi-squared
2,10044E-7
Coefficient of determination
0,99112
n / mol
Value
Standard error
n_mono
0,01259
3,78262E-4
p0
191245,04071
26108,26666
C
263,22657
29,50211

Interpretation and analysis of the measured data

1)

The measured volumes and pressures can be found in the table. The errors of the other data has been calculated the following way:

- $m = \rho \cdot V \Rightarrow \Delta m = \left|\frac{\partial m}{\partial V}\right| \Delta V = \rho \cdot \Delta V$
- $n = \frac{m}{M} \Rightarrow \Delta n = \left|\frac{\partial n}{\partial m}\right| \Delta m = \frac{\Delta M}{M}$
- $\frac{1}{n} \Rightarrow \Delta \frac{1}{n} = \left|\frac{\partial \frac{1}{n}}{\partial n}\right| \Delta n = \frac{\Delta n}{n^2}$
- $\frac{1}{\rho} \Rightarrow \Delta \frac{1}{\rho} = \left|\frac{\partial \frac{1}{\rho}}{\partial \rho}\right| \Delta \rho = \frac{\Delta \rho}{\rho^2}$

We used $\Delta p = 1$ mbar and $\Delta V = 0{,}01$ ml.

The density of methylbutene has been calculated with this formula:

$$\rho(T) = \frac{0{,}6406}{1 + 1{,}527 \cdot 10^{-3} \cdot T + 3{,}11 \cdot 10^{-6} \cdot T^2}$$ T: Temperature

We used the Langmuir model and plotted $\frac{1}{n}$ vs. $\frac{1}{\rho}$ to get the value of n_{mono}.

y_{min} and y_{max} define the error ranges:

$y_{min} = 27636\,x + 67{,}43$

$y_{max} = 80747\,x + 58{,}52$

$\Rightarrow$ gradient error = 32503 ; y-axis error = 15,80

$\Rightarrow y = (47644 \pm 32503)x + (74{,}32 \pm 15{,}80)$

The y-axis intersection represents $\frac{1}{n_{mono}}$.

$\hookrightarrow n_{mono} = (0{,}01346 \pm 0{,}00286)$ mol ✓

The gradient m represents $\frac{a}{n_{mono}}$:

↳ $m = \frac{a}{n_{mono}} \Rightarrow a = m \cdot n_{mono} = 641{,}29 \frac{N}{m^2} \pm 573{,}80 \frac{N}{m^2}$

$= (6{,}413 \pm 5{,}738)$ bar → mbar

$a = \frac{1}{k_a} \Rightarrow k_a = \frac{1}{a} = (0{,}001559 \pm 0{,}001395) \frac{m^2}{N}$

$k_a = 0{,}156 \frac{1}{mbar}$

2.) Determination of the specific surface of charcoal

$A = n_{mono} \cdot N_A \cdot \sigma \quad ; \quad \sigma = \left(\frac{V(\ell)}{N_A}\right)^{2/3} \quad ; \quad V(\ell) = \frac{M}{\rho}$

$= n_{mono} \cdot N_A \cdot \left(\frac{V(\ell)}{N_A}\right)^{2/3} = n_{mono} \cdot N_A \left(\frac{\frac{M}{\rho}}{\sqrt[3]{N_A}}\right)^{3/2}$

$\Rightarrow A = 0{,}01346 \text{ mol} \cdot 6{,}022 \cdot 10^{23} \frac{1}{mol} \cdot \left(\frac{72{,}15 \frac{g}{mol}}{0{,}61 \frac{g}{cm^3} \cdot 6{,}022 \cdot 10^{23} \frac{1}{mol}}\right)^{3/2 \cdot 2/3}$

$= (2{,}192 \cdot 10^{-11} \pm 4{,}66 \cdot 10^{-12})\ cm^2$

error discussion

- As the first pressure we measured was only 1 mbar and our error for the pressure is 1 mbar too, this value has a huge error and so does every other value, that depends on this one ($n_{mono} \rightarrow a \rightarrow k_a$, etc)
- The 10 minute waiting time between the messurments might not be long enough for the equilibrium to establish.
- Cleaning of the charcoal could be insufficient.
- The glas might also adsorbate some methylbutane.

Additional questions

1] The van-der-Waals forces are responsible for the physisorption. These forces are induced dipol-forces. The movement of the electrons in the orbitals creates a momentary electric charge which induces another momentary dipol in the adjected molecule/atom.

2] 

Depending on the distance to the surface the attractive or repulsiv forces are stronger.
The difference between the two adsorptions are the distance to the surface.

Physisorption: - particles keep their chemical identity
- orbitals don't overlap
- no chemical bond
- distance relativley big

Chemisorption: - orbitals overlap due to chemical bonding
- small distance

3] With the Van't-Hoff-equation it's possible to calculate the adsorption enthalpy

$$\left(\frac{d\ln K}{dT}\right)_\Theta = \frac{\Delta H^\ominus}{RT^2} \quad \text{or} \quad \ln K = -\frac{\Delta H^\ominus}{RT} \quad (*)$$

With the Langmuir model you can calculate K for different temp. You get K(T)
The adsorption enthalpy is the part of the gradiat of the graph from (*).

45A

Methylbutan in ml	Druck in mbar	Temperatur in °C
0,2	1	23,7
0,41	2	23,8
0,6	5	23,8
0,8	11	23,8
1,0	20	23,9
1,2	41	23,9
1,4	89	24,0
1,5	126	24,2
1,6	202	23,7
1,71	296	23,7
1,81	377	23,7
1,9	461	23,7

~0°C

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