

Adsorption Calorimetry

Lecture Series:

Modern Methods in Heterogeneous Catalysis

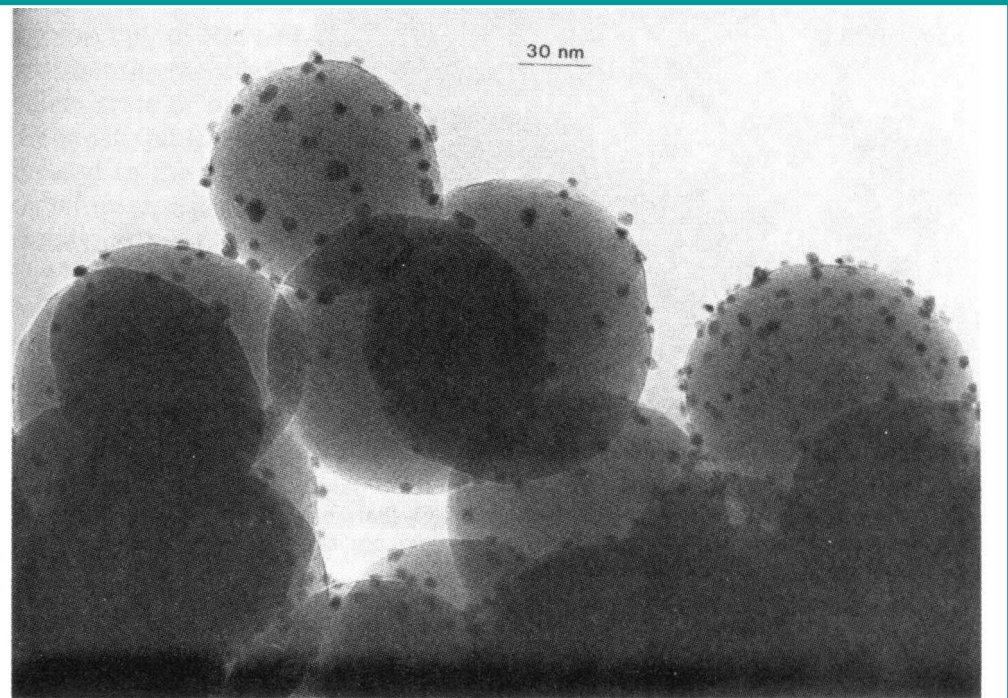
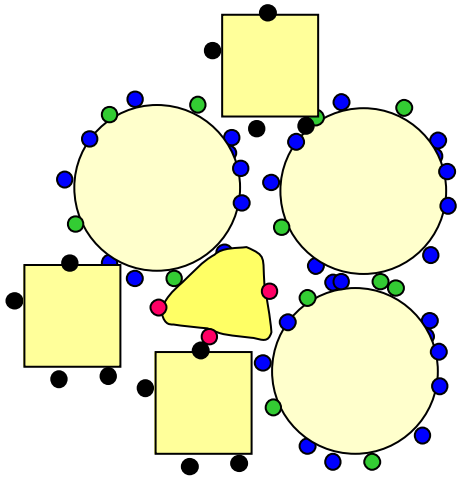
F.C. Jentoft

December 9, 2005

Outline

1. Motivation
2. Heat of adsorption
3. Volumetric System
 - Calibration of volume
 - Measurement of adsorbed amount
4. Calorimeter
 - Calibration of calorimeter
 - Measurement of heat signal
5. Calorimeters in surface science

Motivation: Surface (Active) Sites



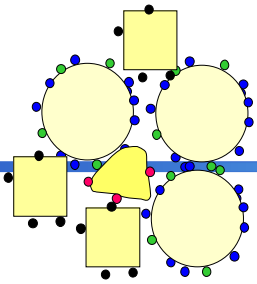
Transmission electron microscopic image of Rh/SiO₂

Questions:

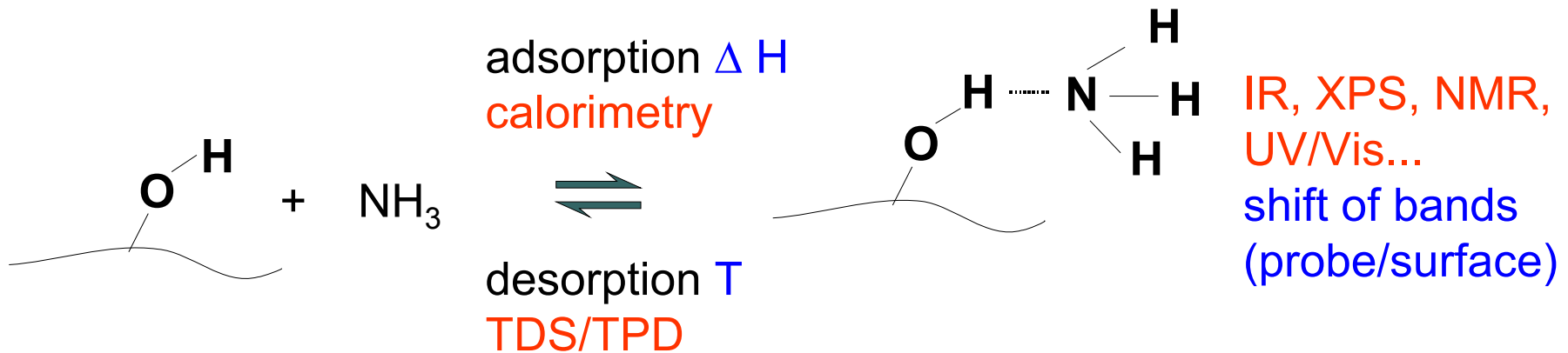
Type?

Number / density?

„Strength“ (interaction with a certain molecule)?



Probing Sites by Chemisorption



Different methods deliver different information

- ❖ isotherms: number of sites
- ❖ spectroscopies: type, strength (but not number unless extinction coefficient known)
- ❖ calorimetry, TDS: number and strength (but not type)

Physisorption and Chemisorption (I)

	Physisorption	Chemisorption
Type of interaction and heat of adsorption (negative enthalpy of adsorption)	van der Waals forces 10 – 20 kJ/mol noble gases, CH ₄ , N ₂ Dipole-dipole 20 – 50 kJ/mol water on oxides	chemical bonding, electron transfer 80 – 500 kJ/mol CO on metals dissociative adsorption (O ₂ , H ₂ on Pt, H ₂ O on oxides)
Reversibility	reversible	reversible or irreversible
Speed	fast	can be slow (e.g. activated adsorption)
Coverage	multilayers possible	monolayer only

Physisorption and Chemisorption (II)

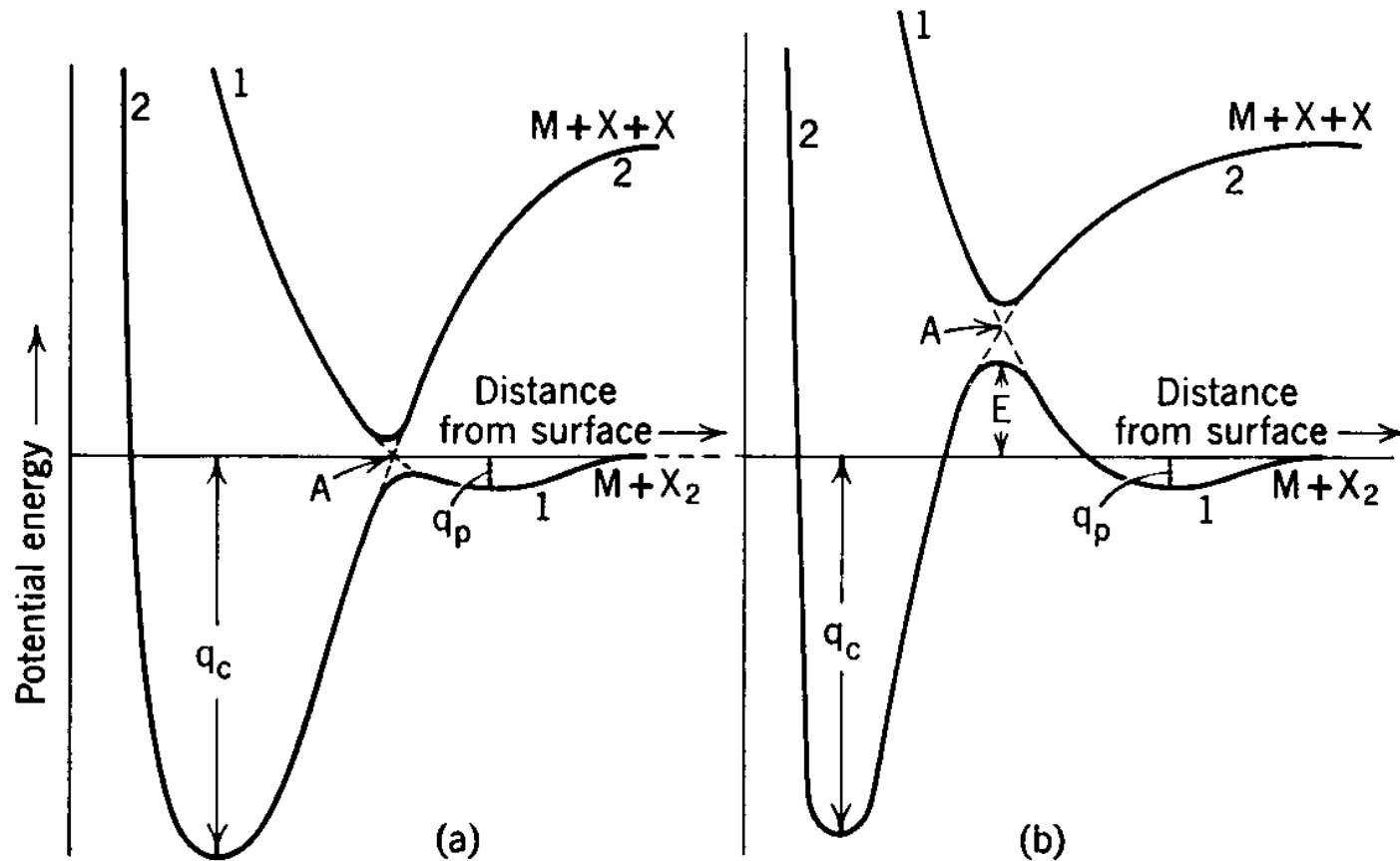


Fig. XIV-3. Potential energy curves for physical adsorption and chemisorption (from Ref. 7).

Determination of Heats of Adsorption

Via isotherms or isobars

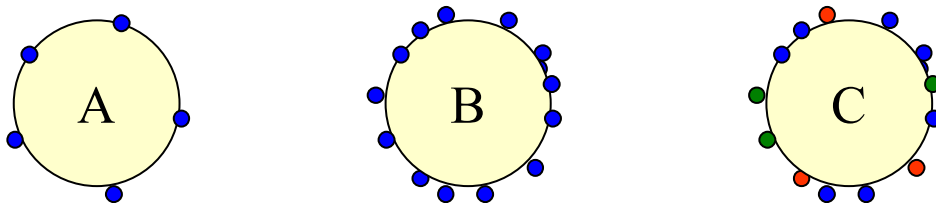
- ❖ Clausius-Clapeyron equation, isosteric heats of adsorption (see class “Adsorption” by W. Ranke)
- ❖ requires adsorption equilibrium (reversibility)

Via TDS

- ❖ activation energy for desorption corresponds to heat of adsorption
- ❖ only if adsorption is non-activated!!!

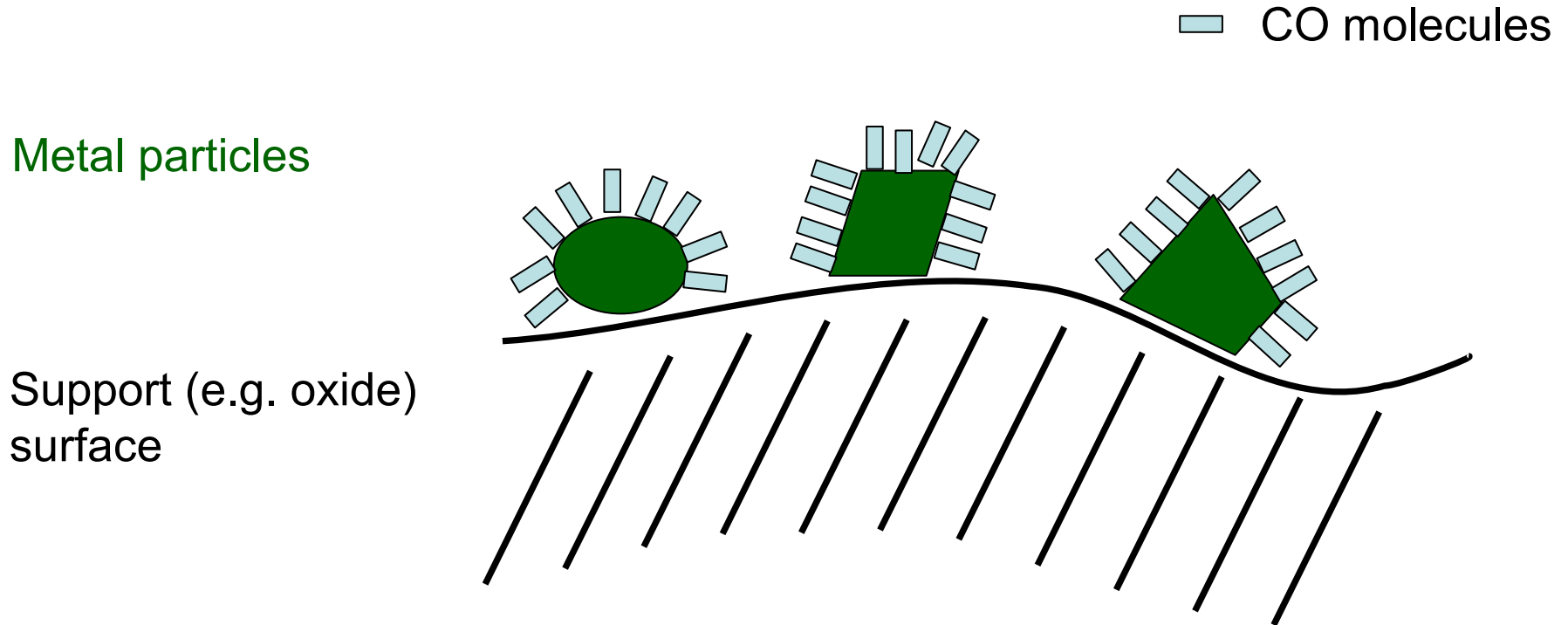
Via calorimetry

Specific Adsorption (Chemisorption)



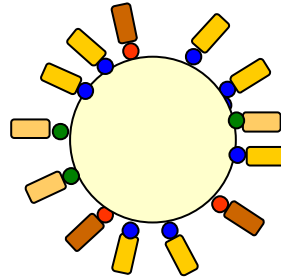
- ❖ Physisorption (e.g. N_2) yields geometric surface area
 $A \approx B \approx C$
- ❖ Specific adsorption / chemisorption gives information about a particular type of site which depends on the type of probe used
A, B can be distinguished,
B and C may be distinguished


Metal Surface Sites



- ❖ specific adsorption of probe on only one type of site (e.g. on metal and not on support): depends on strength of interaction of probe with metal/support sites, conditions (T, p) can be optimized

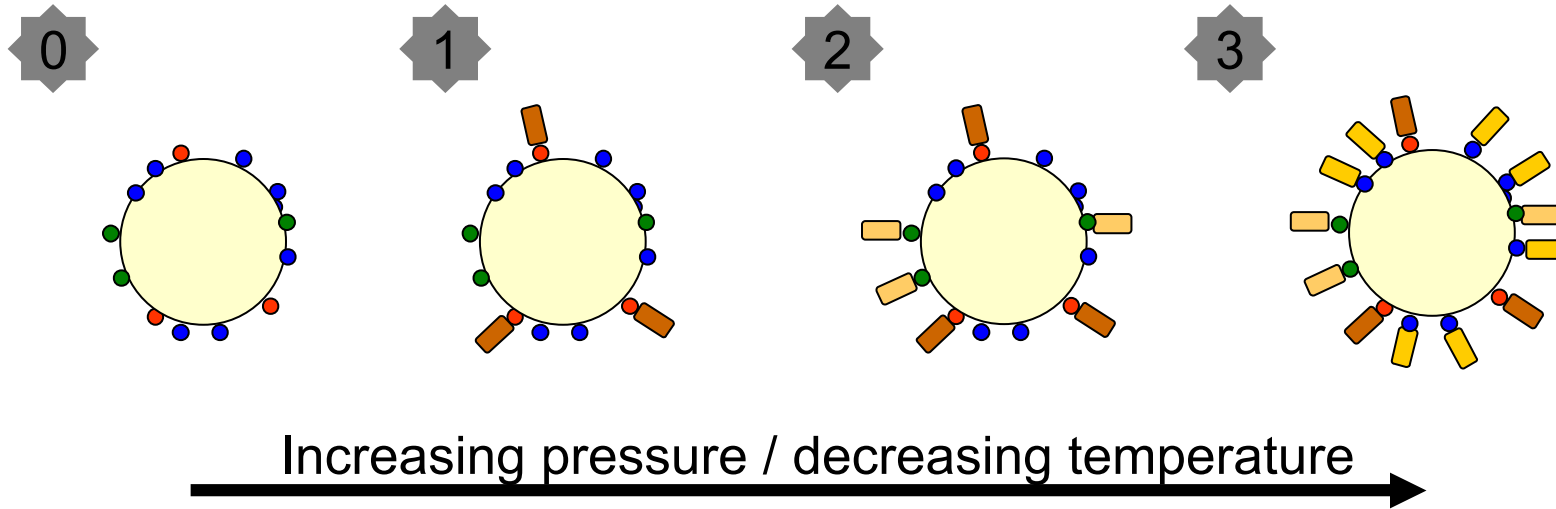
Integral Heat of Adsorption



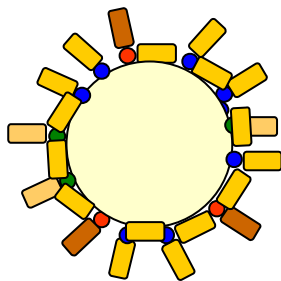
- ❖ A probe () may chemisorb on different sites under production of different heats of adsorption
- ❖ If all sites are covered at once, the evolved heat will be an integral heat
- ❖ if the number of adsorbed molecules is known, an average / mean heat of adsorption can be calculated

Differential Heats of Adsorption

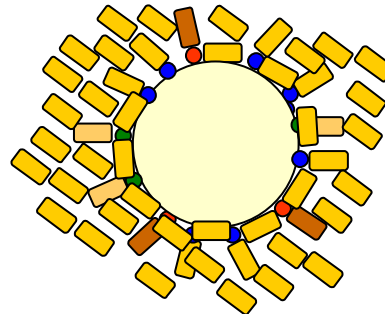
❖ Sites can be covered step by step



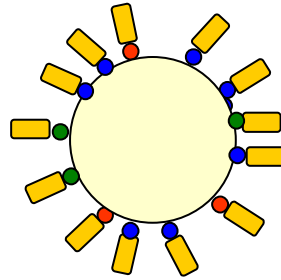
Physisorption



Condensation



Differential Heats of Adsorption



$$q_{diff} = (\delta Q_{int} / \delta n)_{T,A}$$

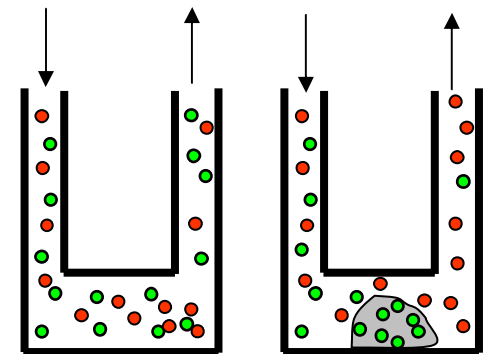
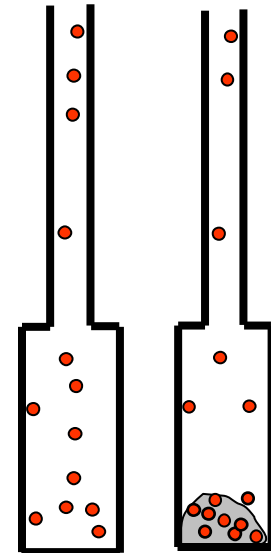
- ❖ Differential heats of adsorption as a function of coverage can be determined
- ❖ A general concept: example dissolution
“first”, “last” heat of dissolution = differential heats

Adsorption Calorimetry Experiment

- ❖ The sorptive must be introduced stepwise, i.e. at constant temperature, the pressure is increased slowly
- ❖ For each adsorption step, the adsorbed amount must be determined (isotherm)
- ❖ For each adsorption step, the evolved heat must be determined
- ❖ The differential heat can then be determined by division of evolved heat through number of molecules adsorbed in a particular step

Measurement of the Adsorbed Amount

- ❖ adsorption via dosing of N_2 into vacuum: pressure decrease upon adsorption (volumetric-barometric)
- ❖ adsorption via dosing in flow, vary N_2 partial pressure by variation of flow composition N_2/He : thermal conductivity measurement of effluent gas
- ❖ adsorption via dosing into vacuum or in flow: weight increase (gravimetric)
- ❖ spectroscopic methods (if extinction coefficient for transition of adsorbed species known)
- ❖ via the evolved heat (if heat of adsorption known and constant)



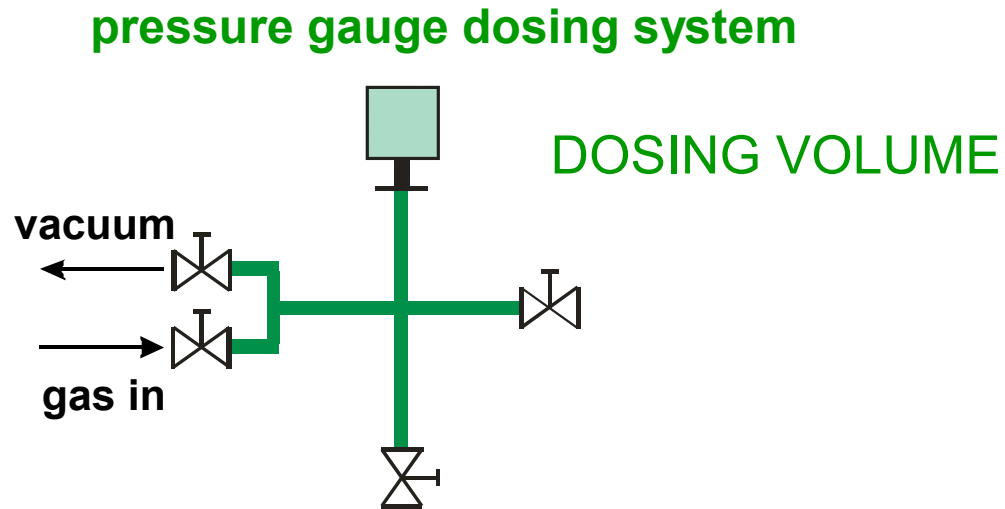
Pressure Decrease Method

- ❖ A known number of molecules of the sorptive is introduced into the sample cell
- ❖ The sorptive is distributed into three partitions: gas phase, wall adsorption, sample adsorption
- ❖ the equilibrium pressure with sample is compared to the equilibrium pressure without sample at equal number of sorptive molecules in the cell
- ❖ from the pressure difference the number of adsorbed molecules can be calculated

Dosing a Known Amount of Gas

- ❖ A known number of molecules of the sorptive is introduced into the sample cell
- ❖ If we know the volume, temperature and pressure, we can calculate the number of gas molecules
- ❖ Need V , T , p

The Dosing Volume

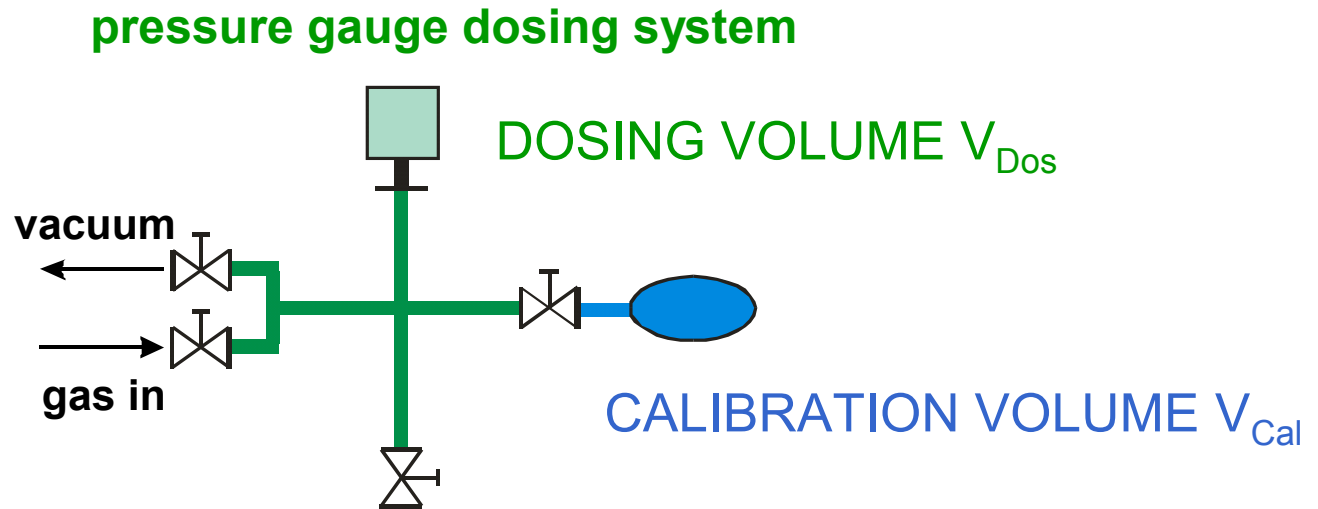


- ❖ p , T can be easily measured
- ❖ V needs to be determined

Volume Calibration

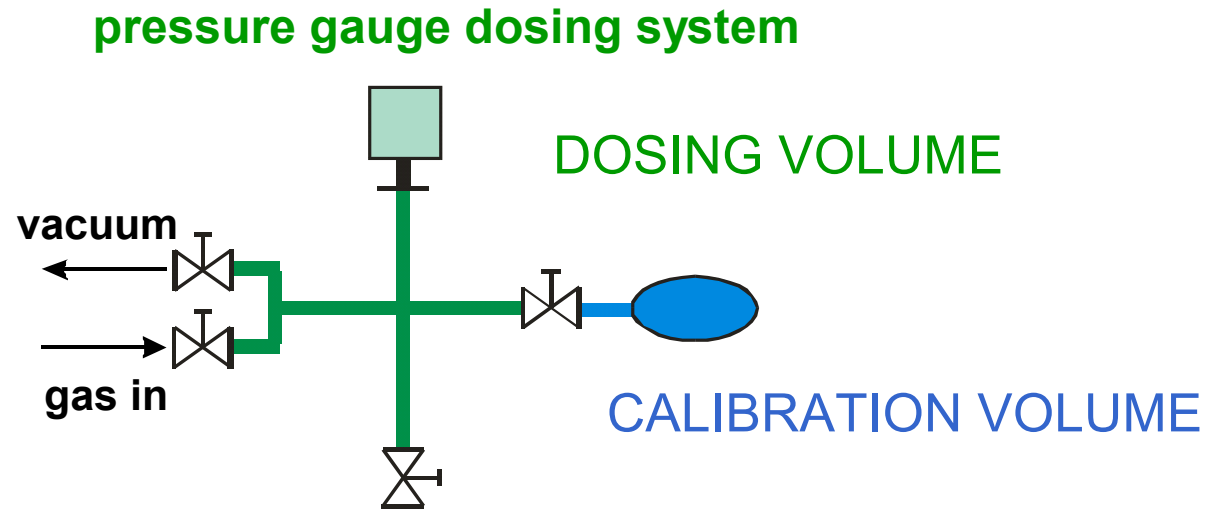
- ❖ A volume can be measured by determining the amount of liquid that it can take up
 - a) gravimetrically: weight / density of liquid
 - b) volumetrically: add liquid from a burette
- ❖ An unknown volume of any shape can then be determined through expansion from gas (an ideal gas that does not stick much to the walls) from one volume to the other and pressure measurement before and after the equilibration

Calibrating the Dosing Volume



- ❖ fill V_{Cal} and V_{Dos} , same pressure
- ❖ close valve between V_{Cal} and V_{Dos}
- ❖ set pressure in V_{dos} to p_{Dos}
- ❖ open valve, equilibrate

Calibrating the Dosing Volume



❖ Initial situation:

$$nRT = p_{Cal} V_{Cal} + p_{Dos} V_{Dos}$$

❖ After opening valve:

$$nRT = p_{fin} (V_{Cal} + V_{Dos})$$

❖ n , T are constant

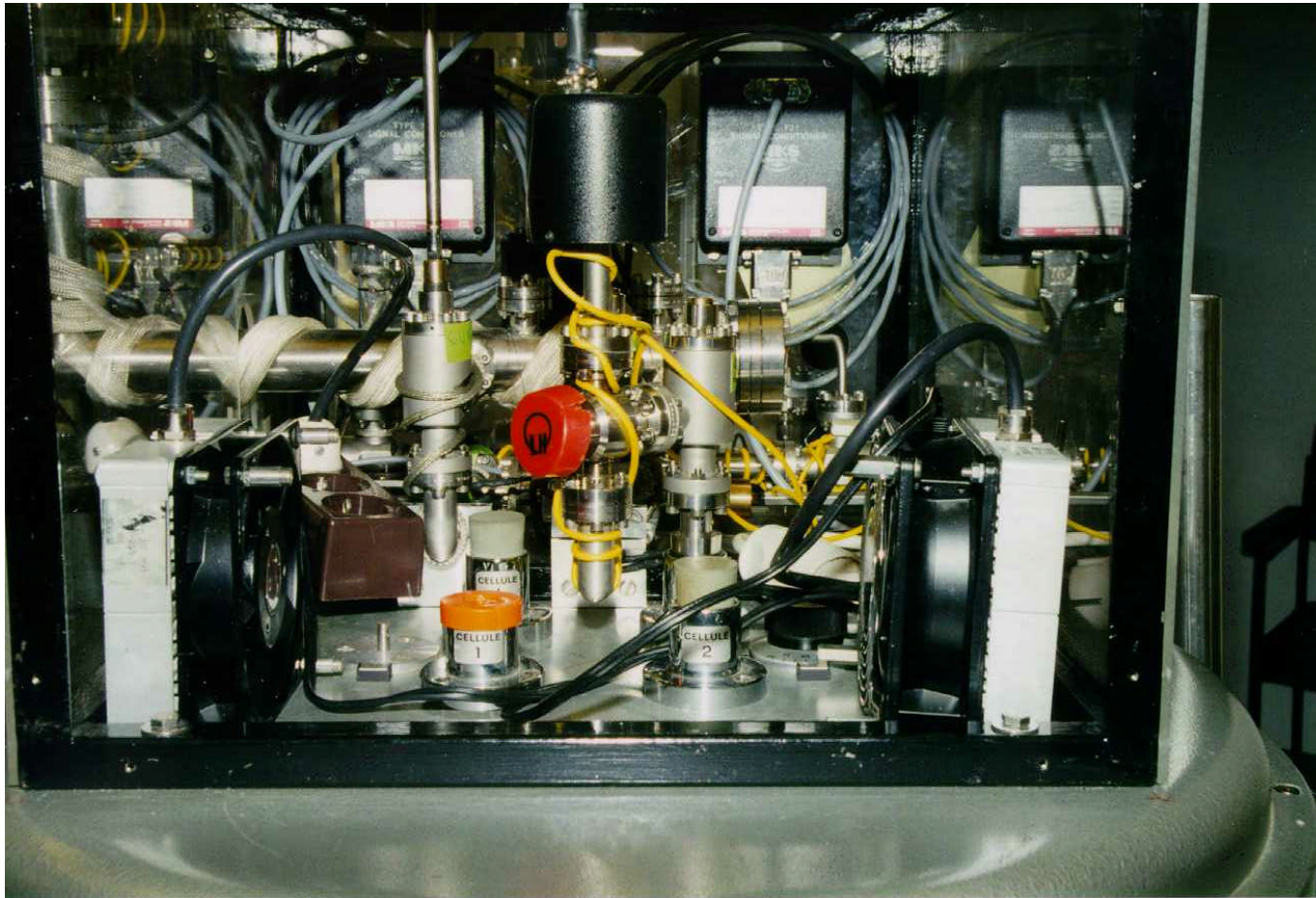
$$V_{Dos} = \frac{p_{Cal} - p_{fin}}{p_{fin} - p_{Dos}} V_{Cal}$$

Example Data

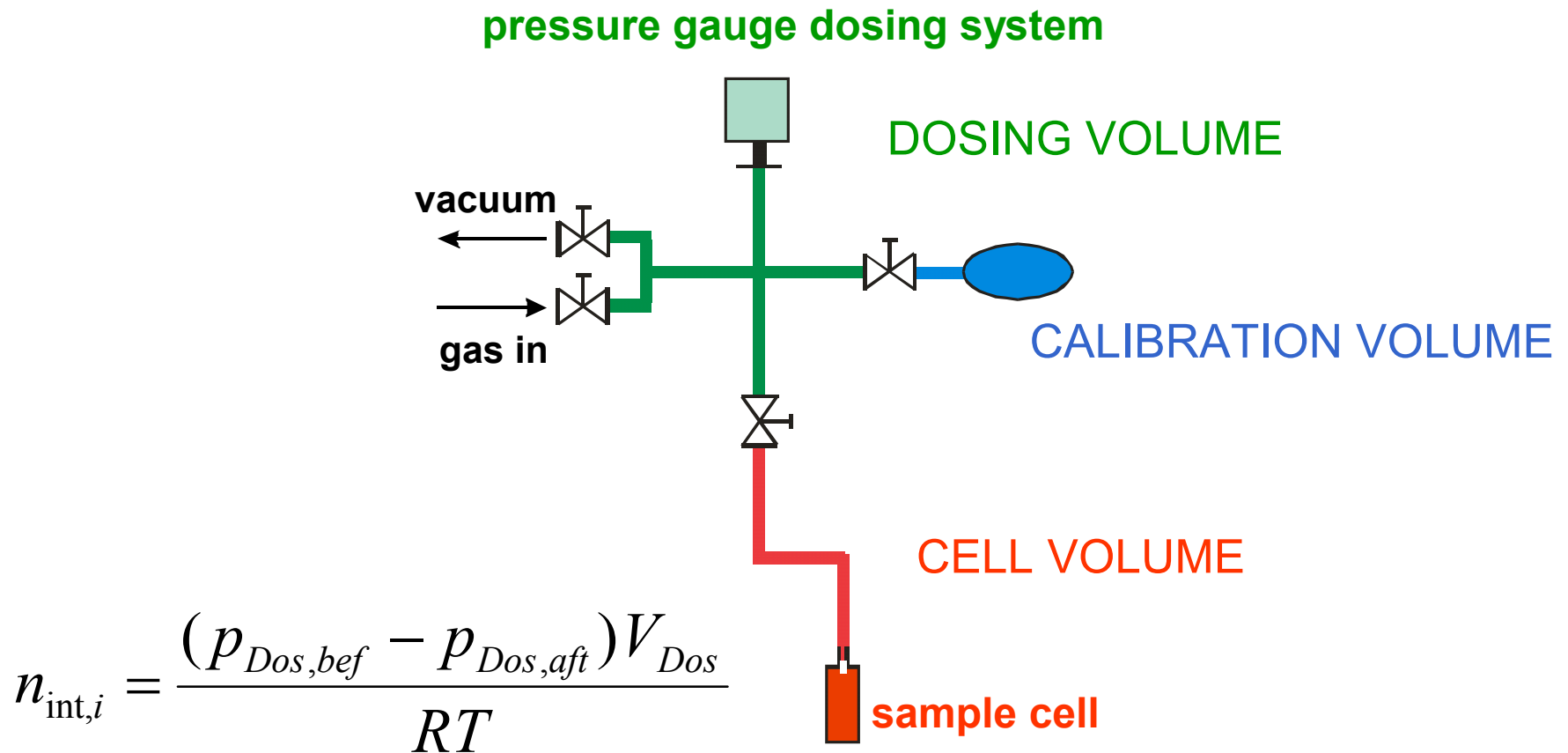
Nr	p_{Cal} [mbar]	p_{Dos} [mbar]	p_{fin} [mbar]	V(Dos) [ml]
	before	before	after equilibration	
1	5,314	9,467	8,683	137
2	8,683	7,648	7,843	137
3	7,638	6,341	6,585	137
4	6,585	4,768	5,111	137
5	5,111	4,712	4,787	137
6	4,786	3,197	3,496	137
7	3,469	2,701	2,846	136

- ❖ It is important that the entire system is at the same constant temperature!

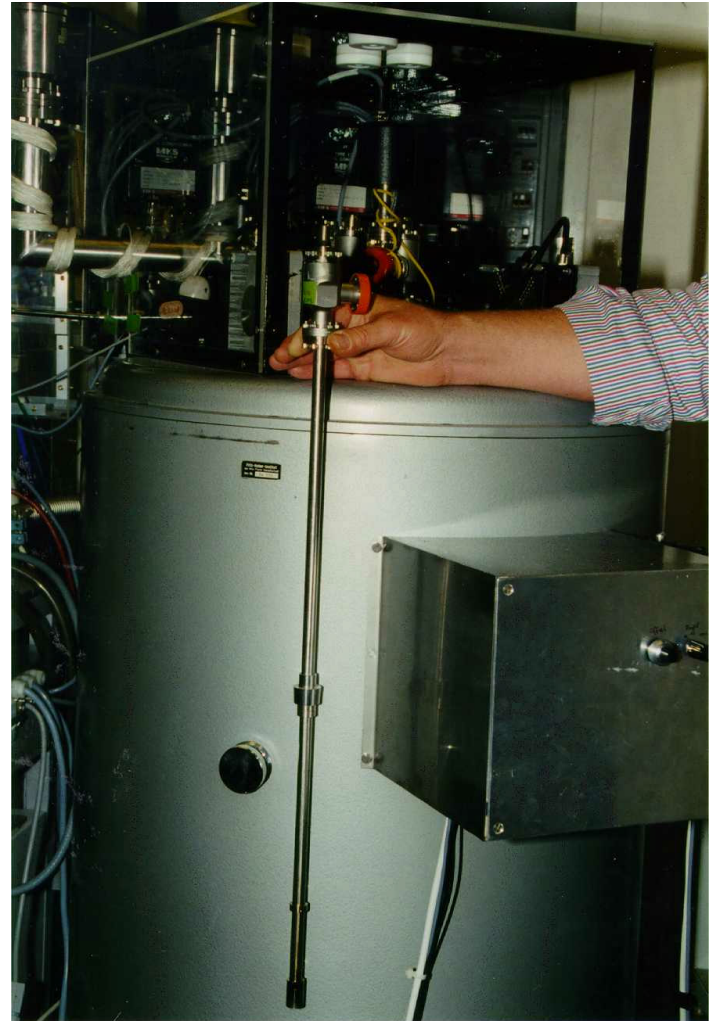
Calibration and Dosing System



Determining the Dosed Amount



The Cell



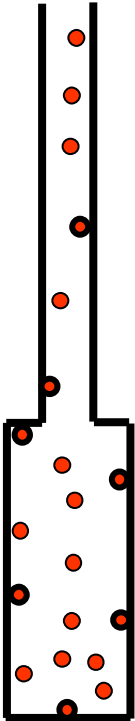
Total Number of Molecules in Sample Cell

- ❖ Total number of molecules accumulated in cell

$$n_{SC,tot,i} = \sum_i n_{int,i} = n_{SC,tot,i-1} + n_{int,i}$$

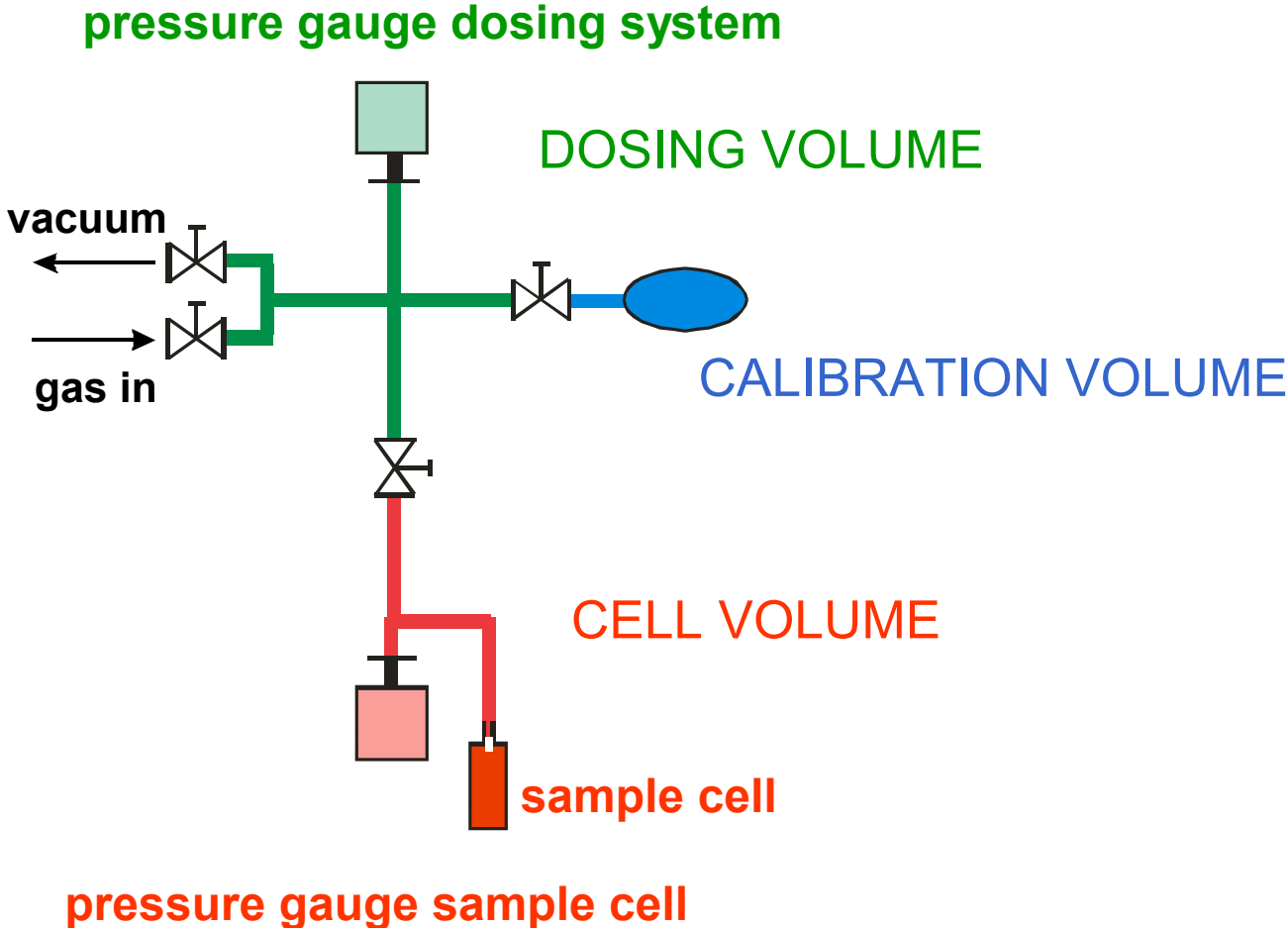
- ❖ i.e. the sum of
 - the number of molecules already in the cell
 - the number of molecules introduced in the i^{th} step

Empty Cell: The Wall Adsorption



- ❖ Molecules are in the gas phase but also adsorbed on the wall surface
- ❖ Only the gas phase molecules contribute to the measured pressure
- ❖ The number of molecules adsorbed on the walls depends on the pressure

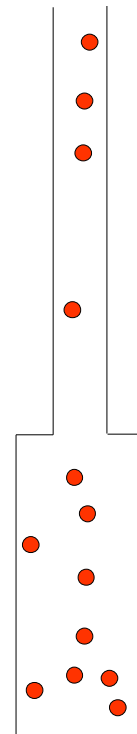
Volumetric-Barometric System



Wall Adsorption Blank Measurement

- ❖ Measure the pressure in the cell as a function of the total number of molecules introduced into the cell
- ❖ Without wall adsorption and without sample, the relation between pressure and number of molecules in the sample cell would be given by the ideal gas law

$$P_{SC,i} = \frac{n_{SC,tot,i}RT}{V_{SC}}$$



Wall Adsorption Blank Measurement

- ❖ **With wall adsorption and with or without a sample**, the relation between number of molecules in the gas phase + on the walls and the pressure can be written as a polynomial expression

$$n_{SC,w+g,i} = a(p_{SC,i}) - b(p_{SC,i})^2 + c(p_{SC,i})^3 - d(p_{SC,i})^4 \dots$$

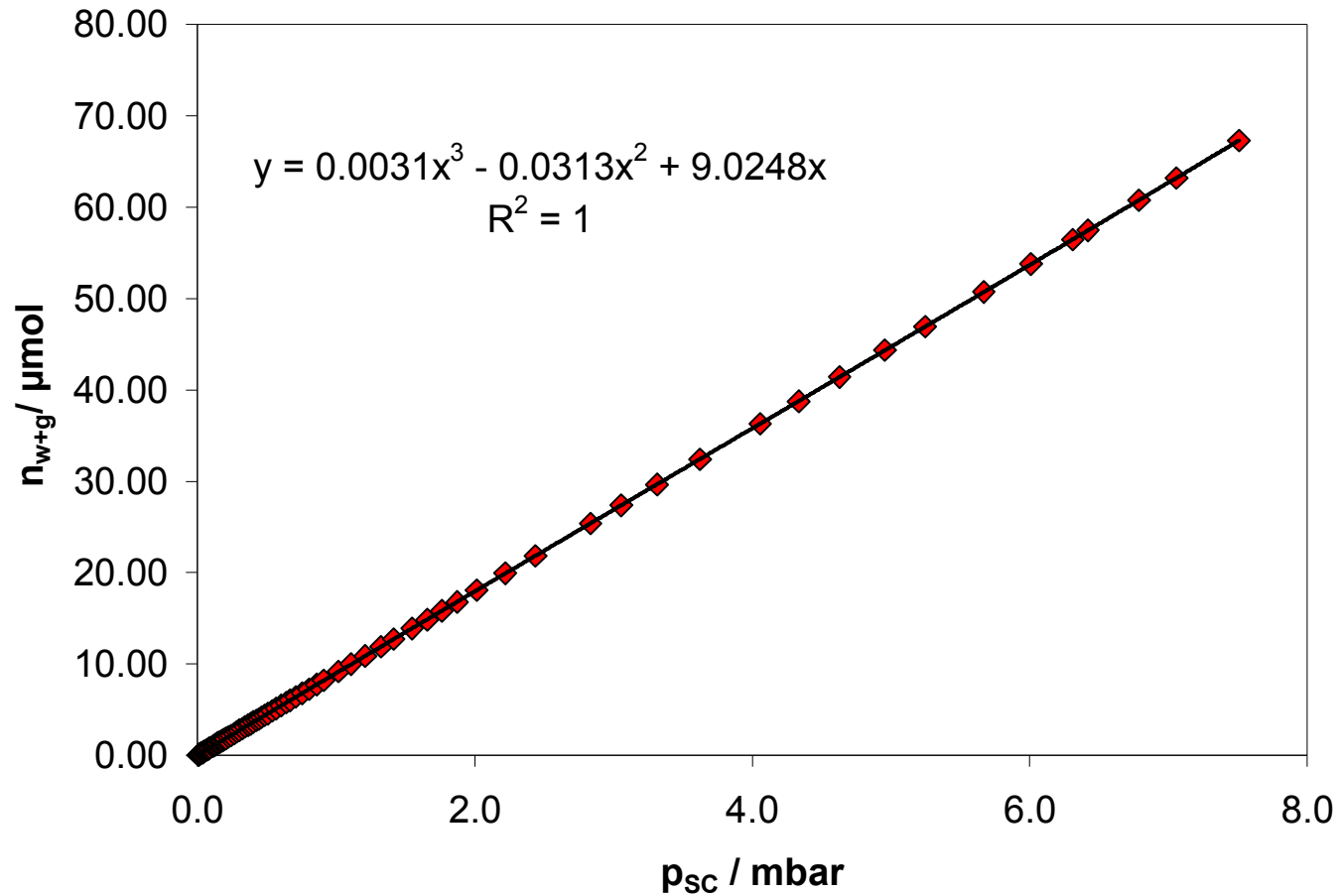
- ❖ **Without a sample**, the coefficients can be determined

$$n_{SC,w+g,i} = n_{SC,tot,i}$$

Example Blank Measurement

Nr	$p_{\text{Dos,be}}/\text{mbar}$	$p_{\text{Dos,af}}/\text{mbar}$	$p_{\text{Sc,i}}/\text{mbar}$	$n_{\text{nt,i}}/\mu\text{mol}$	$n_{\text{Sct,i}}/\mu\text{mol}$
1	9,682	9,674	0,007	0,04	0,04
2	9,653	9,641	0,026	0,06	0,10
3	9,607	9,591	0,054	0,08	0,18
4	9,562	9,544	0,081	0,09	0,27
5	9,499	9,481	0,117	0,09	0,36
6	9,442	9,428	0,147	0,07	0,43
7	9,392	9,371	0,181	0,11	0,54
9	9,230	9,195	0,283	0,18	0,72
10	9,128	9,091	0,344	0,19	0,91
11	9,024	8,988	0,403	0,19	1,10
13	8,814	8,758	0,537	0,29	1,39
14	8,644	8,582	0,640	0,32	1,71
15	8,466	8,386	0,755	0,42	2,13
16	8,209	8,122	0,909	0,45	2,58
17	7,783	7,612	1,208	0,90	3,48
19	6,672	6,487	1,870	0,97	3,45
20	5,893	5,526	2,436	1,93	5,38
21	4,477	4,041	3,314	2,30	7,68
22	9,146	8,409	4,056	3,88	11,56

Correction for Wall Adsorption



- ❖ The adsorption of isobutane on the walls is insignificant

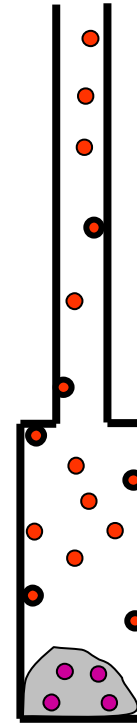
Calculation of Adsorbed Amount

- ❖ Total number of molecules in sample cell after the i^{th} step

$$n_{SC,tot,i} = n_{ads,tot,i} + n_{SC,w+g,i}$$

- ❖ Total number of molecules in sample cell after the $(i+1)^{\text{th}}$ step

$$n_{SC,tot,i+1} = n_{ads,tot,i} + n_{ads,i+1} + n_{SC,w+g,i+1}$$



- ❖ The difference in number of molecules between i^{th} and $(i+1)^{\text{th}}$ step is the number of molecules introduced in the $(i+1)^{\text{th}}$ step

Calculation of Adsorbed Amount

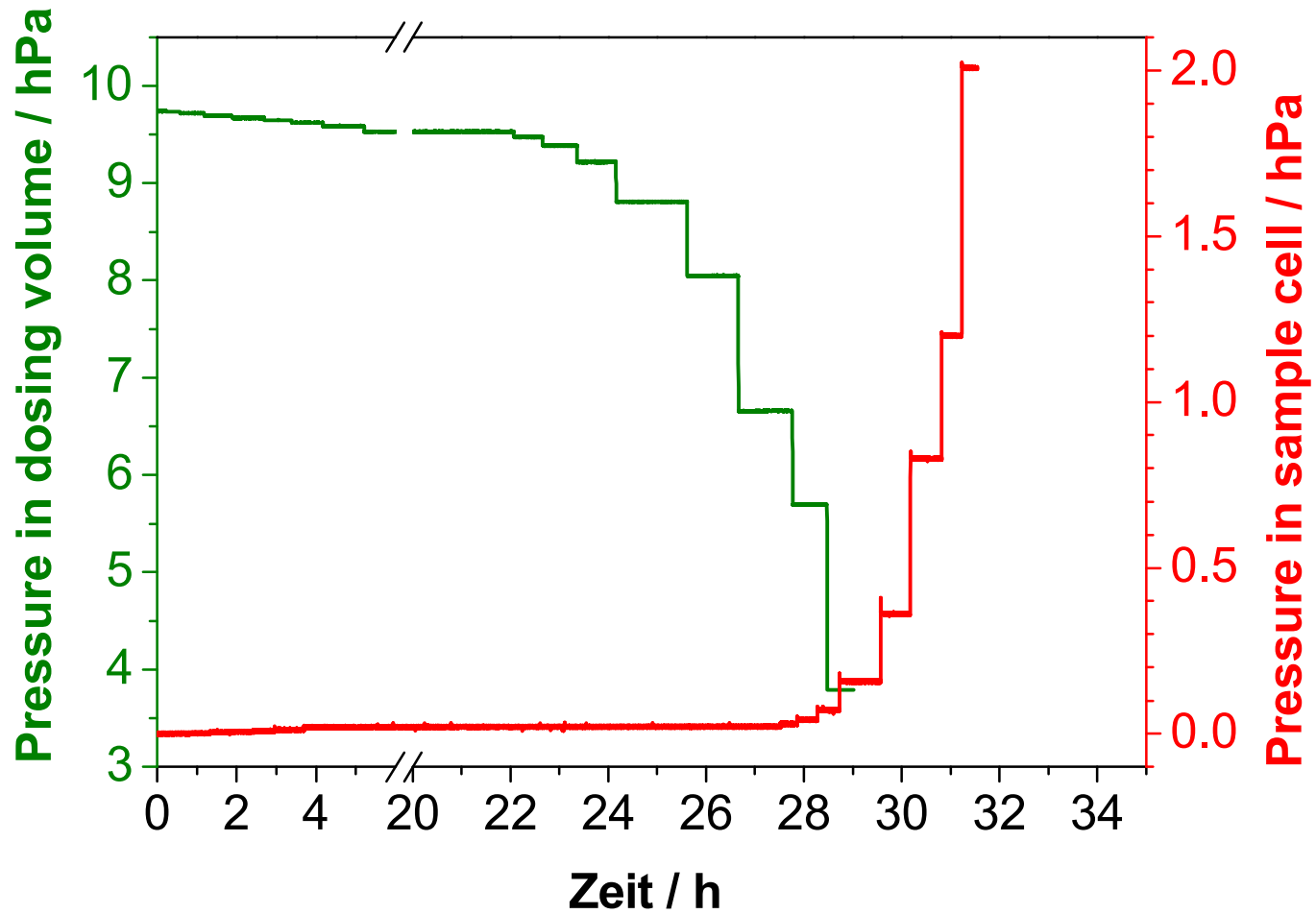
- ❖ the number of molecules adsorbed in the $(i+1)^{\text{th}}$ step is then

$$n_{ads,i+1} = n_{int,i+1} + n_{SC,w+g,i} - n_{SC,w+g,i+1}$$

- ❖ the total number of molecules adsorbed after $(i+1)$ steps is

$$n_{ads,tot,i+1} = n_{ads,tot,i} + n_{ads,i+1}$$

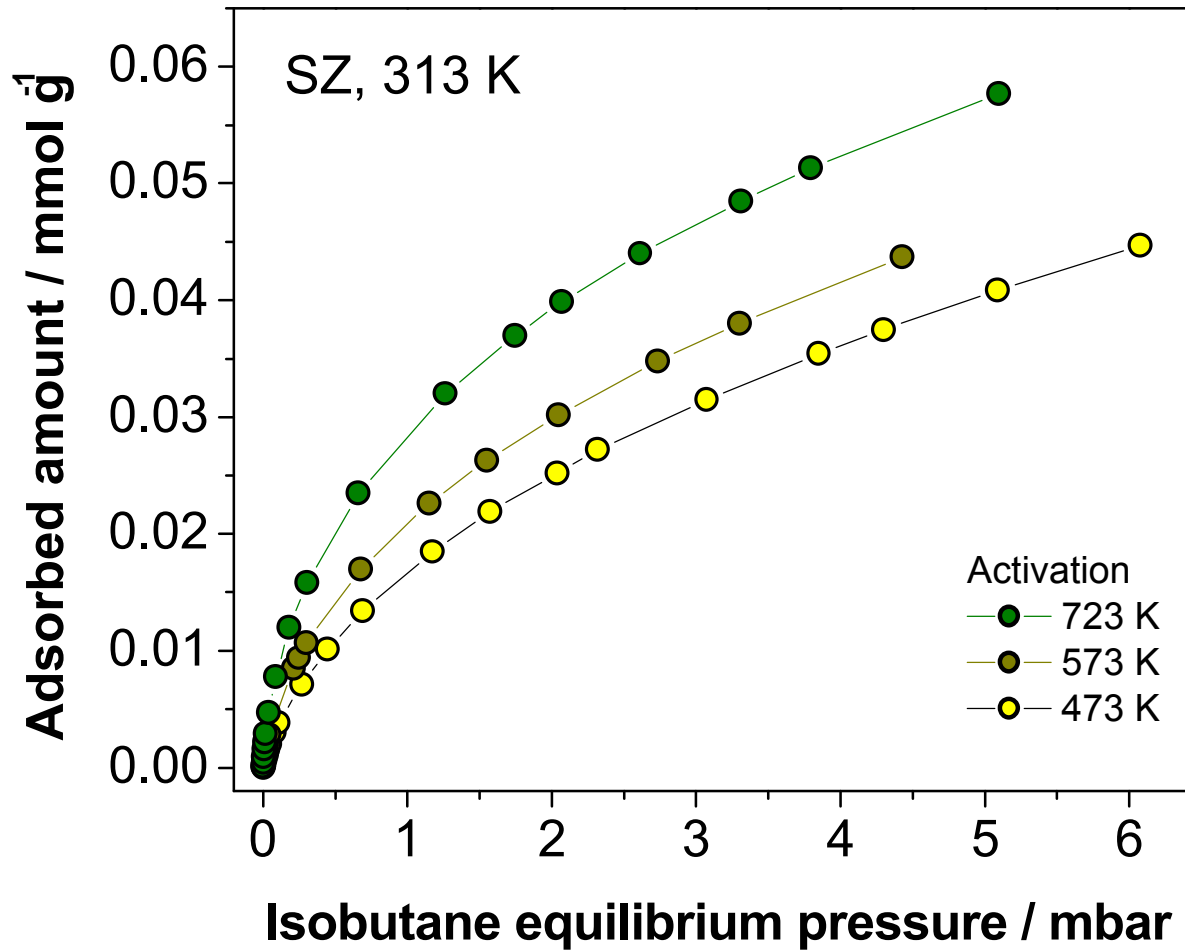
Raw Data Pressure



Multiple Adsorption Steps, Generation of Isotherm

- ❖ The total number of molecules in the cell is determined by addition of the amounts introduced in each single step
- ❖ The isotherm is created by plotting the adsorbed amount vs. the equilibrium pressure

The Adsorption Isotherm



Calorimetry

- ❖ Calor (Latin): heat, warmth
- ❖ Metron (Greek): measure



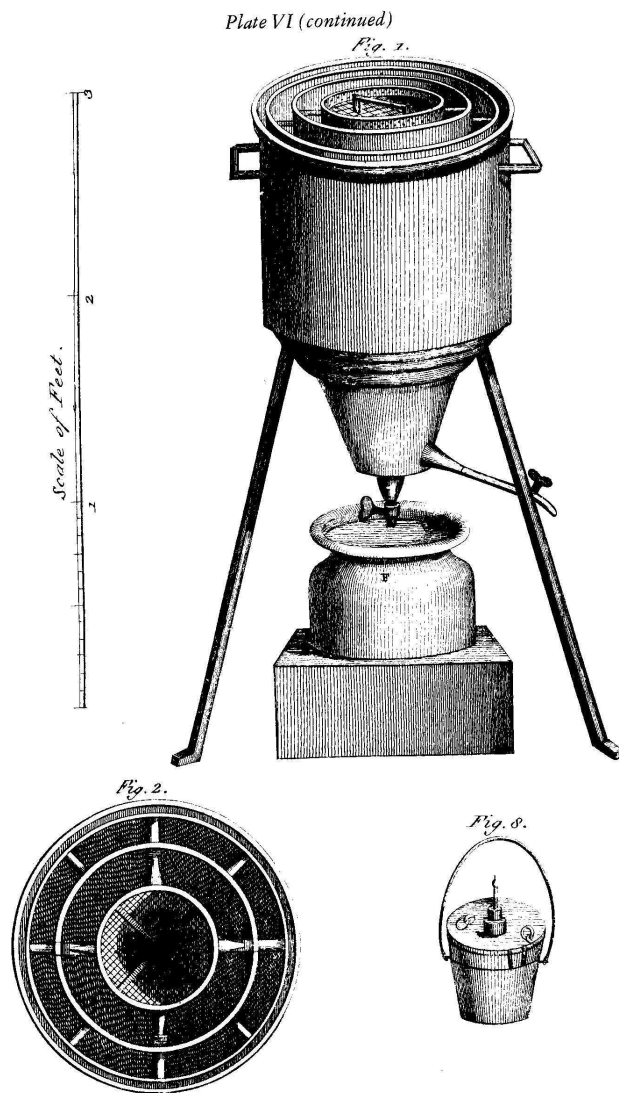
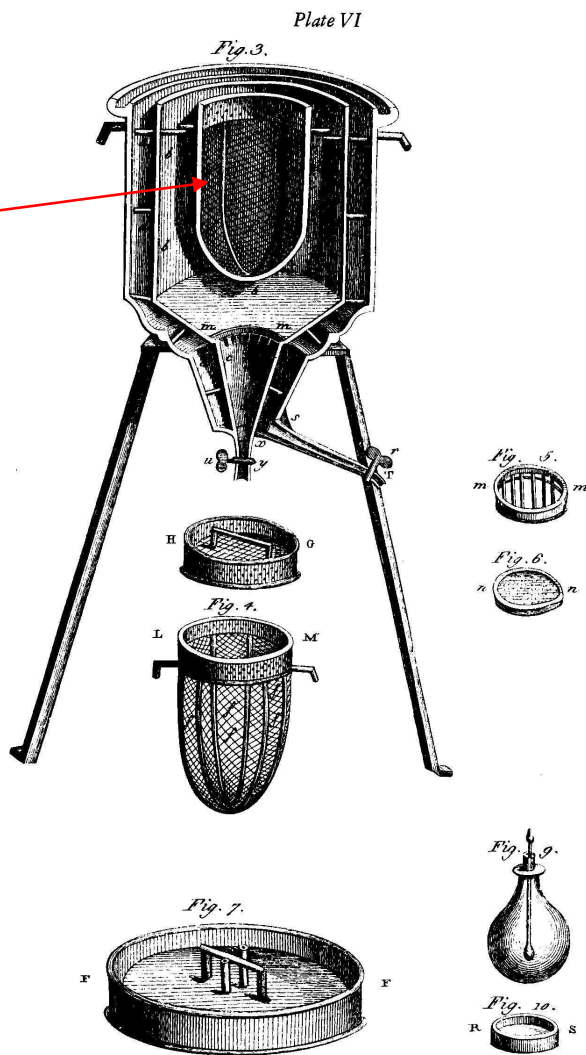
Johan C. Wilcke (1732-1796)

Antoine L. Lavoisier (1743-1794)
and Marie P. Lavoisier

Ice Calorimeter

Lavoisier

Cu-sheet



Specific Heat Capacity

Gmelin 1817

Specifische Wärme einiger Körper, die des Wassers zu 1,000 gesetzt.

Luft	—	—	0,2669	Delaroché und Berard.
Wasserstoffgas	—	—	3,2936	
Deerzeugendes Gas	—	—	0,4207	
Kohlenoxyd Gas	—	—	0,2884	
Stickgas	—	—	0,2754	
Drybirtes Stickgas	—	—	0,2369	
Sauerstoffgas	—	—	0,2361	
Kohlensaures Gas	—	—	0,2210	
Wasserdampf	—	—	0,8470	
Wasser	—	—	1,000	
Eis	—	—	0,900	Kirw.
Liquides Ammoniak von 0,948 spec. Gewicht	—	—	1,030	
Arterielles Blut	—	—	1,030	Crawf.
Venoses Blut	—	—	0,893	
Salpetersäure von 1,360 sp. Gew.	—	—	0,63	Dalton.
— von 1,200 sp. Gew.	—	—	0,76	
Salzsäure von 1,153 sp. Gew.	—	—	0,60	
Schwefelsäure von 1,844 sp. Gew.	—	—	0,35	
Weingeist von 0,817 sp. Gew.	—	—	0,70	
Schwefeläther von 0,760 sp. Gew.	—	—	0,66	
Wallrathöl von 0,87 sp. Gew.	—	—	0,52	
Terpenthinöl	—	—	0,472	Kirwan.
Quecksilber	—	—	0,031	Lap. u. Lapl. u. Kirwan.
Kalk	—	—	0,30	Dalton.
Kalkhydrat	—	—	0,28	Sadolin.
Kohlensaurer Kalk	—	—	0,27	Dalton.
Holzkohle	—	—	0,2631	Crawf.
Schwefel	—	—	0,199	Kirwan.
Eisen	—	—	0,1264	Mittel zw.
Kupfer	—	—	0,1121	Wilke und
Zink	—	—	0,0981	Crawf.
Silber	—	—	0,082	Wilke.
Zinn	—	—	0,0704	Lap. u. Lap.
Antimon	—	—	0,0645	Crawf.
Gold	—	—	0,050	Wilke.
Blei	—	—	0,042	
Bismuth	—	—	0,042	

CRC-Handbuch 1987

Mercury (Quecksilber)	0.033
Sulfur (Schwefel)	0.175
Iron (Eisen)	0.106
Copper (Kupfer)	0.092
Zinc (Zink)	0.093
Silver (Silber)	0.057
Tin (Zinn)	0.052
Antimony (Antimon)	0.049
Gold (Gold)	0.031
Lead (Blei)	0.038
Bismuth (Wismut)	0.029

(cal*g⁻¹*K⁻¹)

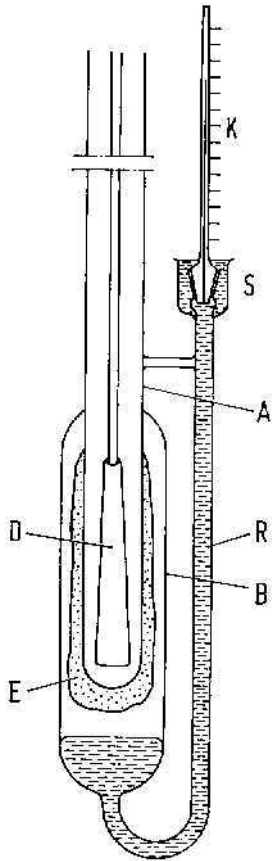


Bild 5.23. Eiskalorimeter. Nach Vallée

Ice calorimeter
Bunsen 1870, Vallée 1962

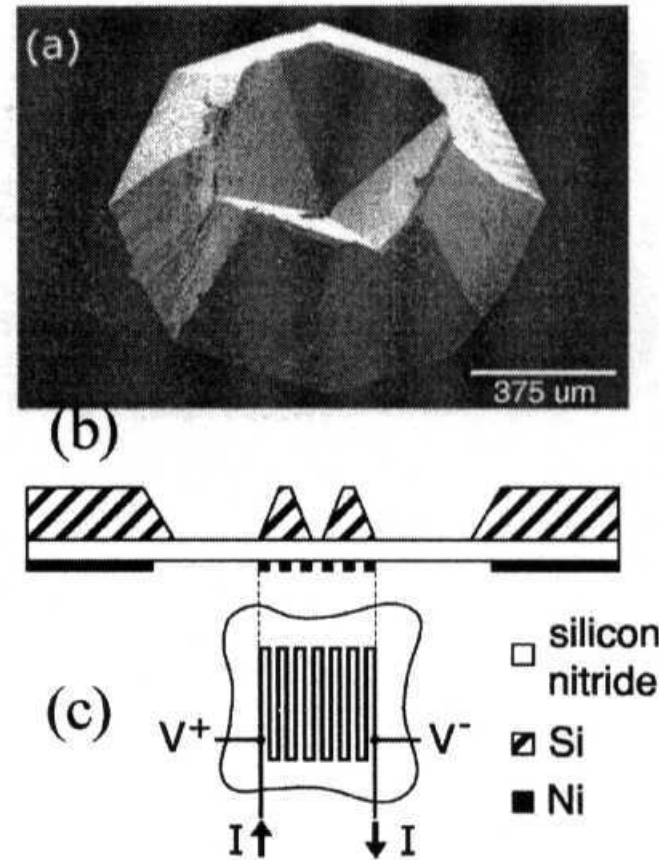
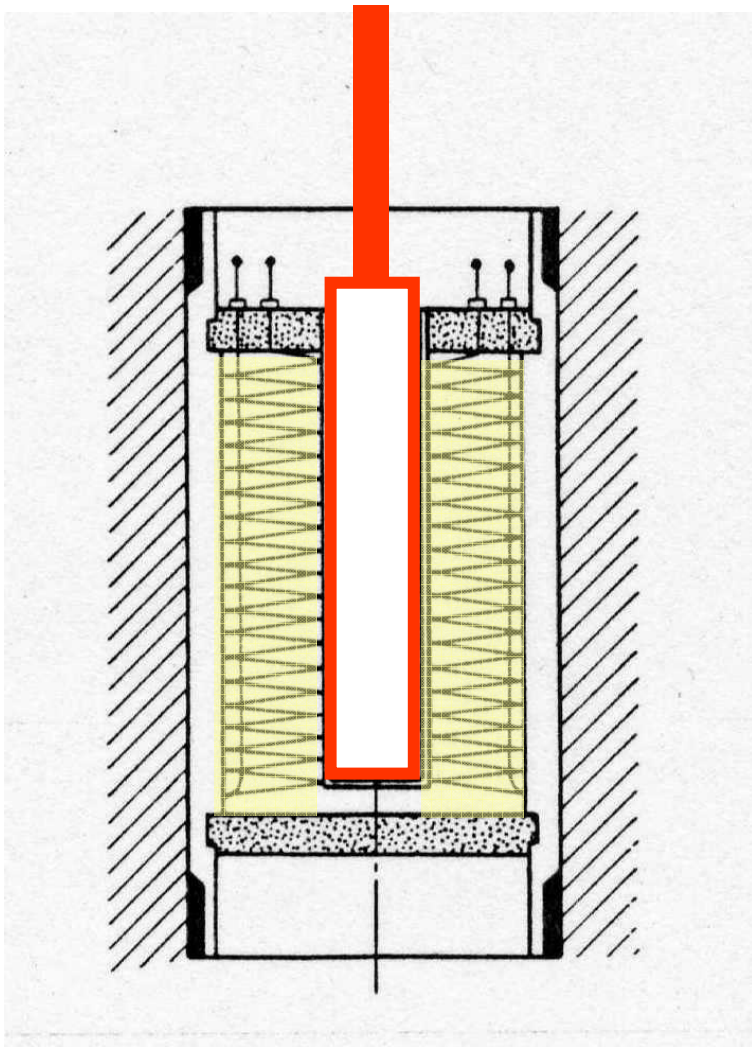


FIG. 1. Electron micrograph of the silicon box (a), a cut-away schematic of the calorimeter (b), and a top view of the heater (c). Relative dimensions in (b) and (c) have been exaggerated for clarity.

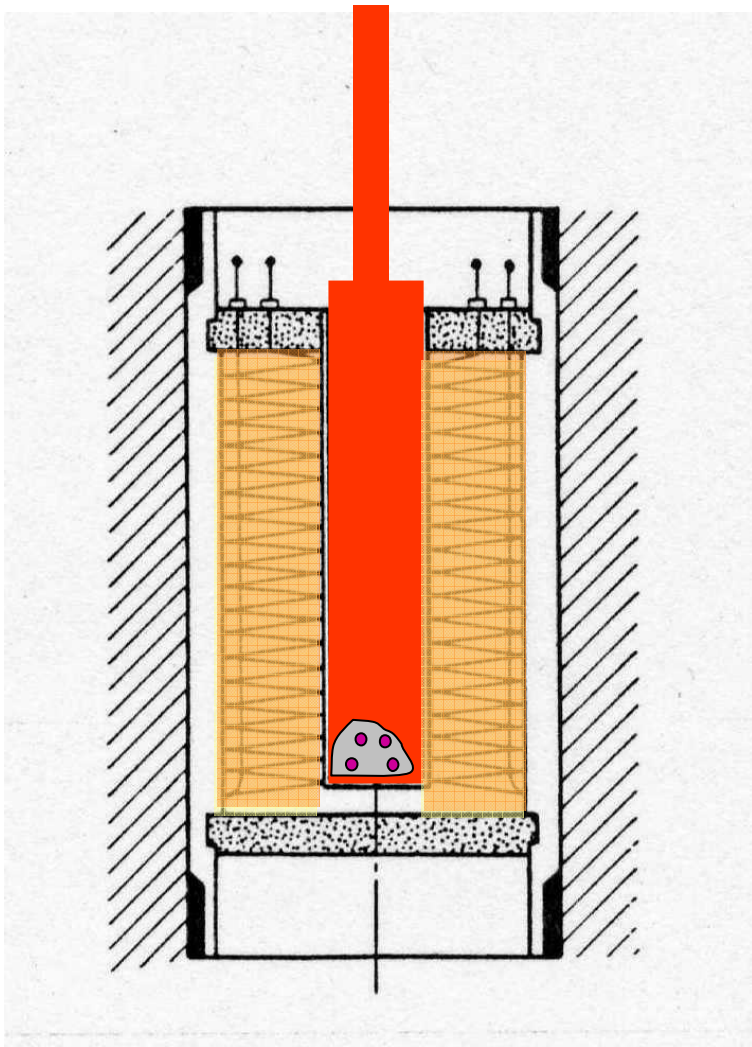
„Nano“ calorimeter
Olson et al. 2000

The Calorimetric Element



- ❖ The sample cell is placed into a calorimeter element
- ❖ The cell is surrounded by a thermopile made of more than 400 thermocouples in series
- ❖ Thermopile has 2 functions: transfers heat
generates signal

Heat and Heat Flow



❖ The heat produced by the reaction is consumed by two processes

1. Increase of the temperature of the sample cell
2. Once there is a temperature gradient between cell and surrounding block, heat flow through the thermopile

Power

- ❖ The power P [W] necessary to heat the cell by $d\theta$ is proportional to the heat capacity C [J/K] of the cell

$$P = C \frac{d\theta}{dt}$$

- ❖ The heat flow Φ [power] is proportional to the temperature gradient $\Delta\theta$ between cell and block and to the thermal conductance G [W/K] (thermischer Leitwert)

$$\Phi = G (\theta_{cell} - \theta_{block}) = G \Delta\theta$$

Power Balance and Signal

- ❖ Total thermal power of cell

$$P_{total} = C \frac{d\theta}{dt} + G \Delta\theta$$

- ❖ The electrical signal is proportional to the temperature difference

$$U = g \Delta\theta$$

- ❖ The relation between power and electrical signal is then

$$P_{total} = \frac{C}{g} \frac{dU}{dt} + \frac{G}{g} U$$

The Tian Equation

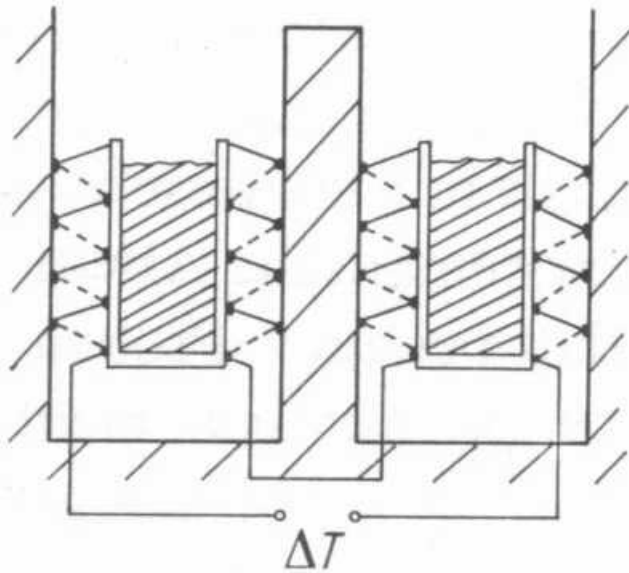
- ❖ G [W/K] is constant and if C [J/K] can be considered constant, then C/G is a constant with units of time

$$\tau = \frac{C}{G}$$

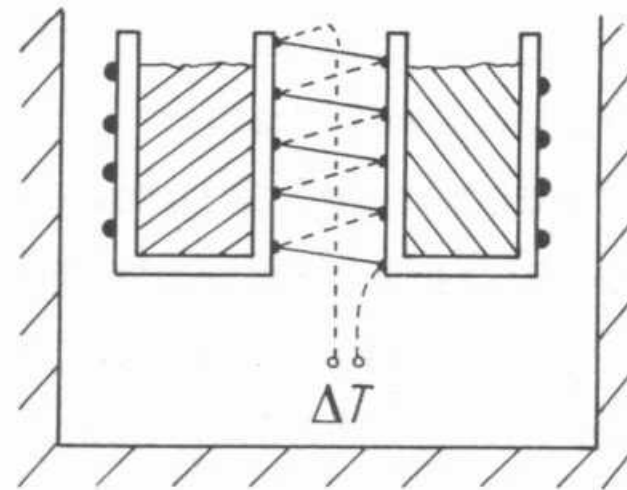
- ❖ The Tian equation shows that the power is not proportional to the temperature difference, the power is delayed with respect to the signal U produced by the cell

$$P_{total} = \frac{G}{g} \left(U + \tau \frac{dU}{dt} \right)$$

Reference Cell

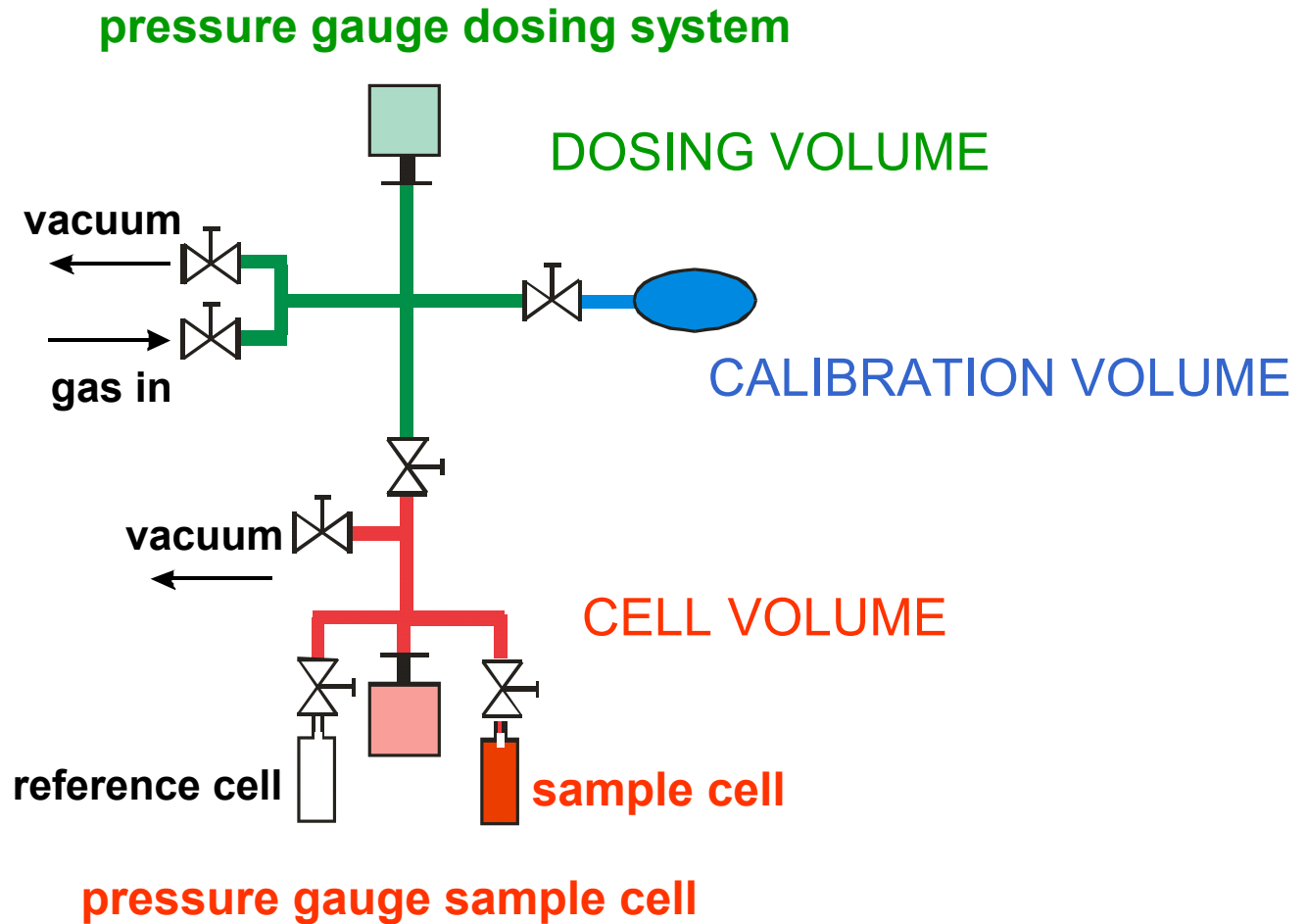


Setup according to
Tian and Calvet

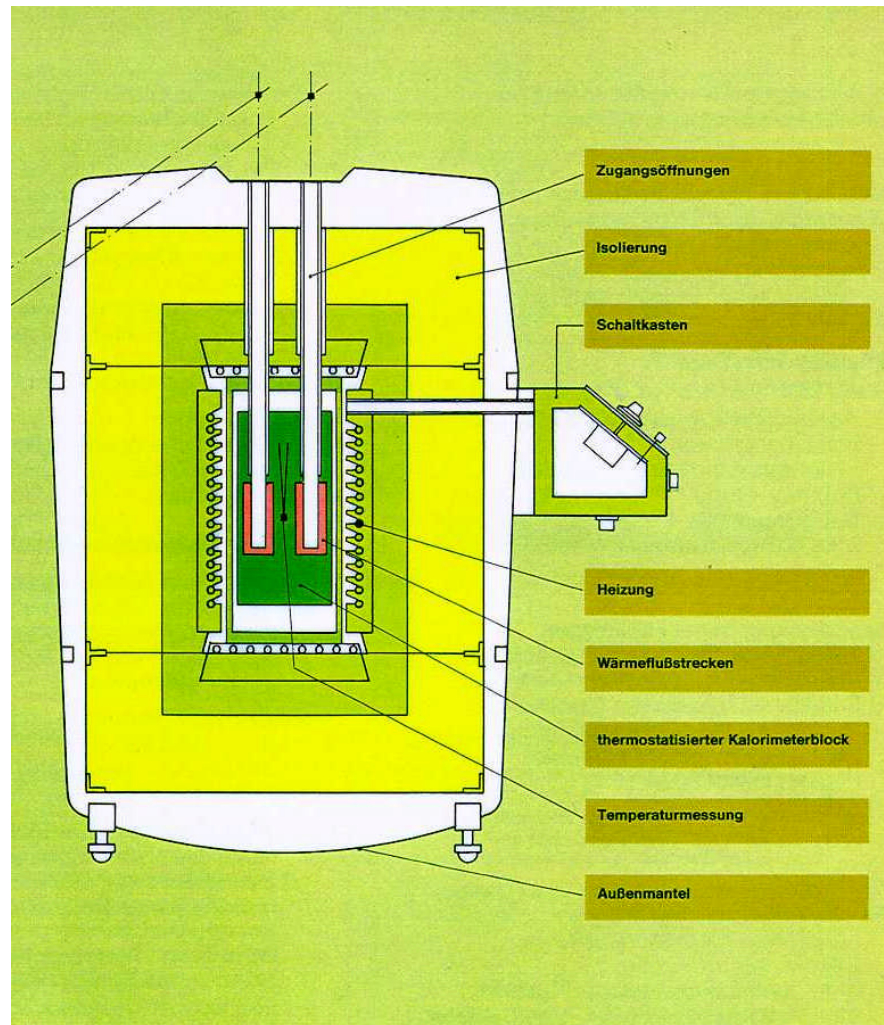


Setup according to
Petit

Complete System

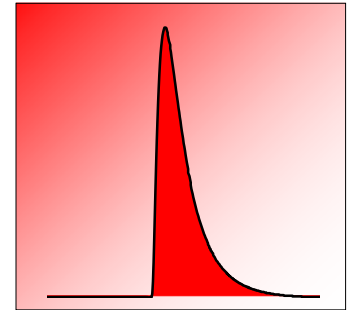


The Calorimeter



Calculation of Evolved Heat

- ❖ If heat is released in the cell for a limited period of time, e.g. through adsorption, then a signal with an exponential decrease is obtained for U
- ❖ The integral under the curve is proportional to the evolved heat



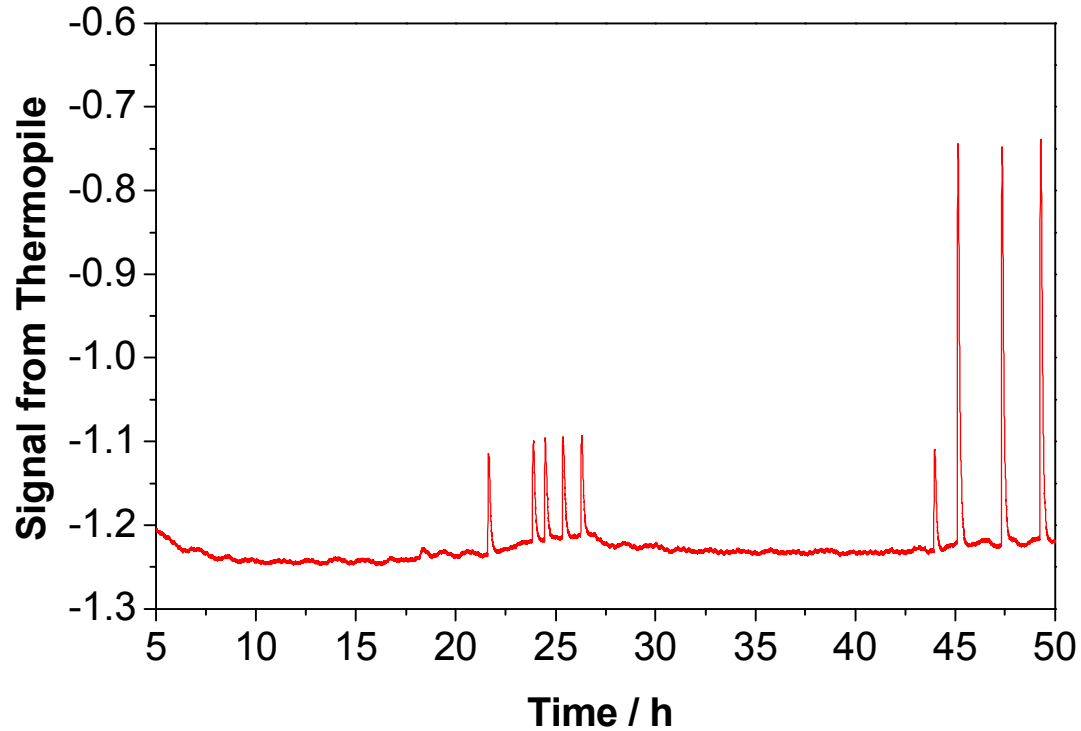
$$Q = \frac{G}{g} \int U dt = f A$$

- ❖ A : area under curve [Vs]
- ❖ f : calibration factor [J/(Vs)]

Calibration Procedure

- ❖ The calorimeter can be calibrated in two different ways, easily achieved by using an Ohm resistance:
 1. Constant power
 2. Produce a certain amount of heat, $Q = U \cdot I \cdot t$
- ❖ Disadvantage of the electrical calibration: heat transfer through wiring!
- ❖ Calibration by chemical reaction

Calibration Data

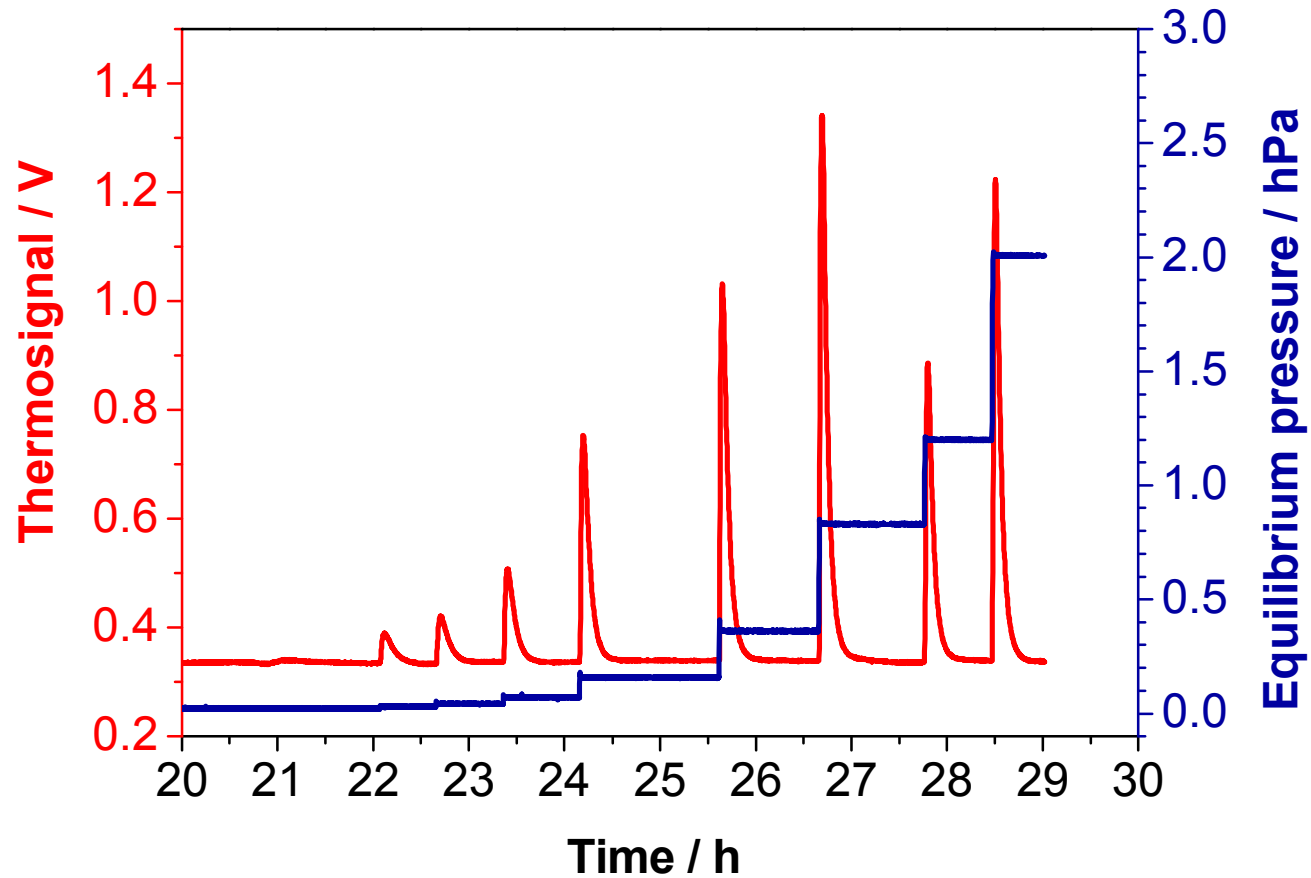


- ❖ The calibration factor is temperature dependent
- ❖ Check for linearity

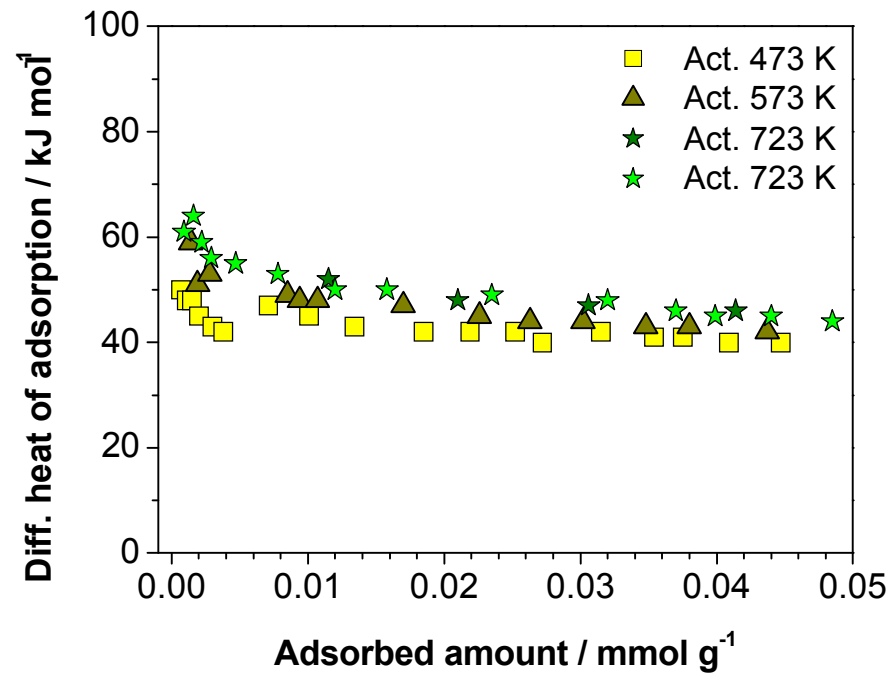
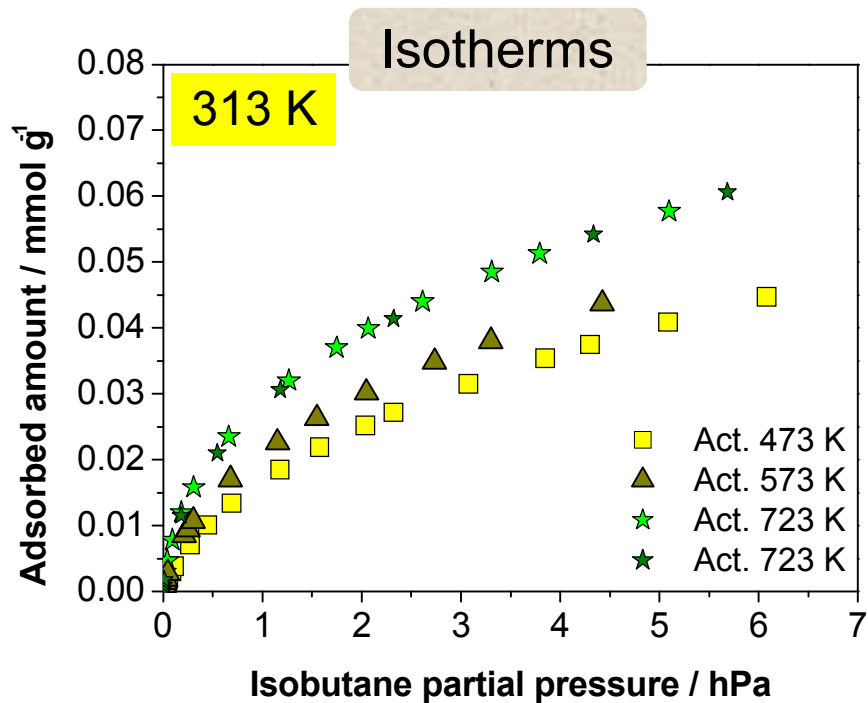
Calibration Data

Nr.	Strom	Spannung	Dauer	eingeführte E	Signalfläche	Umrechnungsfaktor	Mittelwert des Umrechnungsfaktors
	[A]	[V]	[s]	[Ws] = [J]	[Vs]	[Ws / Vs]	[Ws / Vs]
1	0,003	3,049	3	0,03	57,19178	4,79807E-04	
2	0,003	3,049	3	0,03	56,22411	4,88065E-04	
3	0,003	3,049	3	0,03	57,3727	4,78294E-04	
4	0,003	3,049	3	0,03	58,12257	4,72123E-04	
5	0,003	3,049	3	0,03	57,2947	4,78945E-04	für E= 0,03 J 4,83287E-04
6	0,003	3,049	3	0,03	54,61038	5,02487E-04	
7	0,006	6,094	3	0,11	233,31794	4,70140E-04	
8	0,006	6,094	3	0,11	231,50681	4,73818E-04	
9	0,006	6,094	3	0,11	229,02877	4,78944E-04	
10	0,006	6,105	3	0,11	222,57276	4,93726E-04	
11	0,006	6,105	3	0,11	221,47272	4,96178E-04	
12	0,006	6,104	3	0,11	225,52719	4,87179E-04	für E= 0,11 J 4,82957E-04
13	0,006	6,105	3	0,11	228,59869	4,80711E-04	
14	0,01	10,179	10	1,02	2107,62384	4,82961E-04	
15	0,01	10,179	10	1,02	2101,93455	4,84268E-04	für E=1,02 J 4,83861E-04
16	0,01	10,179	10	1,02	2101,55696	4,84355E-04	
						Mittelwert	4,83368E-04

Raw Data: Equilibrium Pressure and Thermosignal



Surface Sites: Effect of Activation



- ❖ with increasing activation temperature, the differential heats of adsorption increase

Ammonia Adsorption on Heteropolyacids

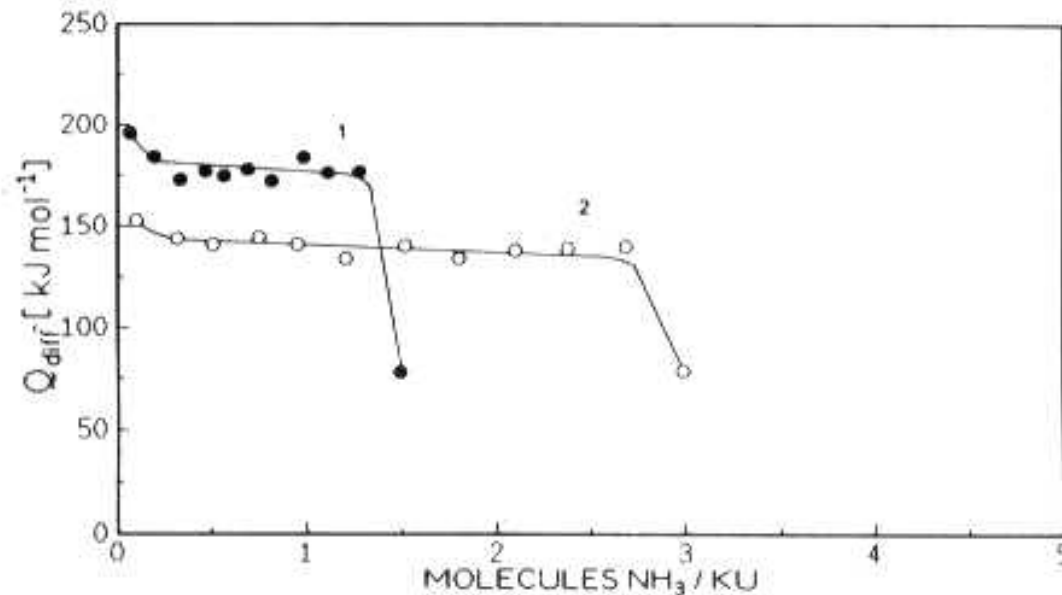
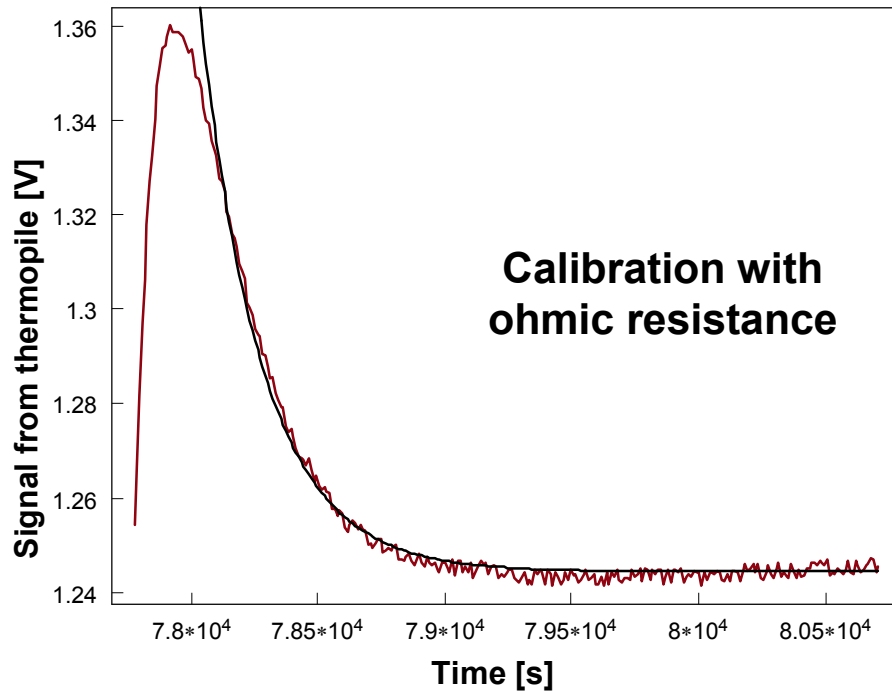


Fig. 2. Differential heats of ammonia sorption on HPW at 323 K. (1) Activation: 423 K/2 h/UHV. (2) Activation: 523 K/1 h/UHV.

❖ $H_3PW_{12}O_{40} \cdot x H_2O$ reaction with ammonia

Calorimetry: Time Constant



Fit equation:

$$y = y_0 + A \cdot \exp\left(-\frac{x - x_0}{\tau}\right)$$

y – signal from thermopile [V]

x – time [s]

y_0 – y offset, baseline height [V]

A – peak height [V]

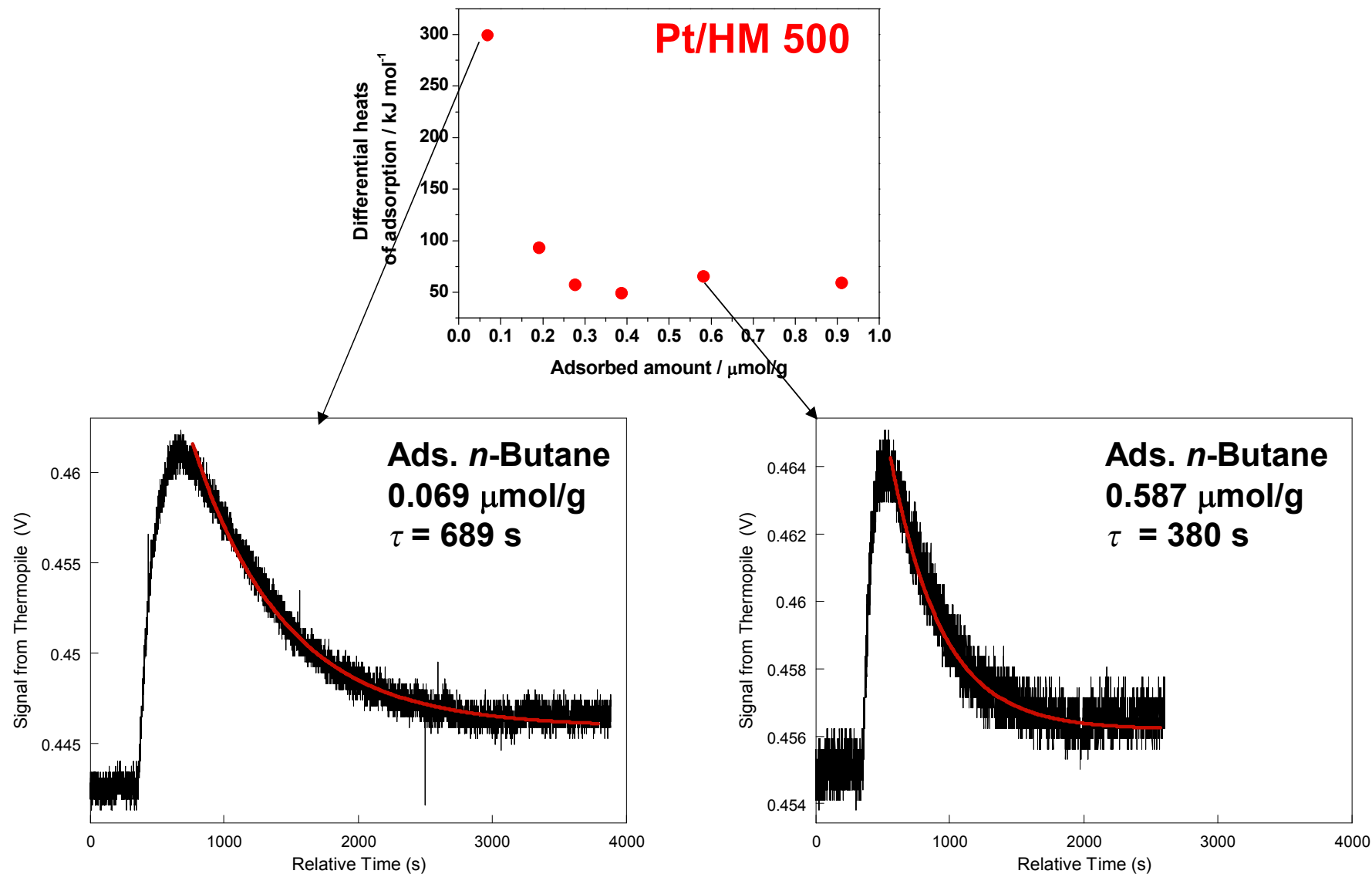
x_0 – peak position on time scale [s]

τ – time constant [s]

- ❖ slower or faster decay of signal indicates endo- or exothermic secondary reactions after adsorption

C. Pluntke, G. Wedler, G. Rau, Surf. Sci. 134 (1983) 145-160

Correlation of Heats and Signal Decay for Interaction of **Pt/HM 500** with *n*-Butane

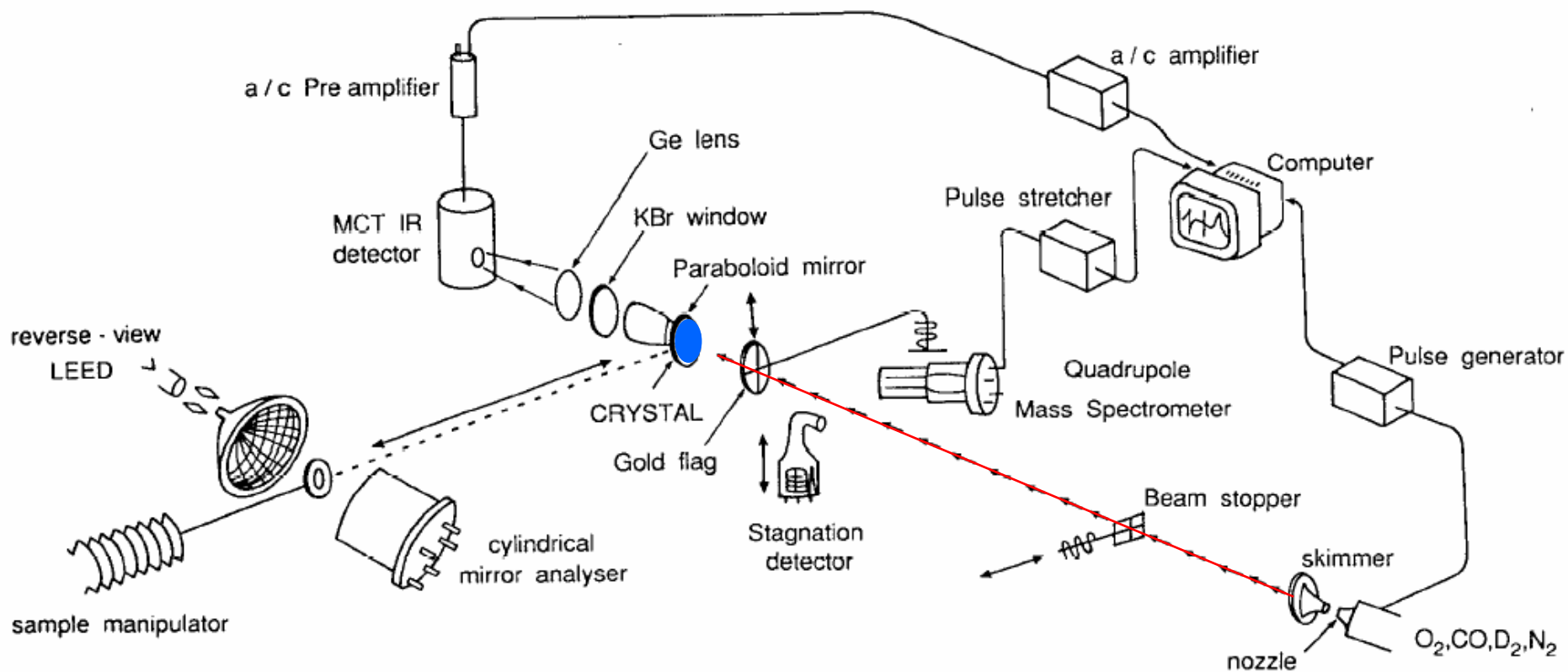


Calorimeters for Single Crystals / Thin Films

System descriptions

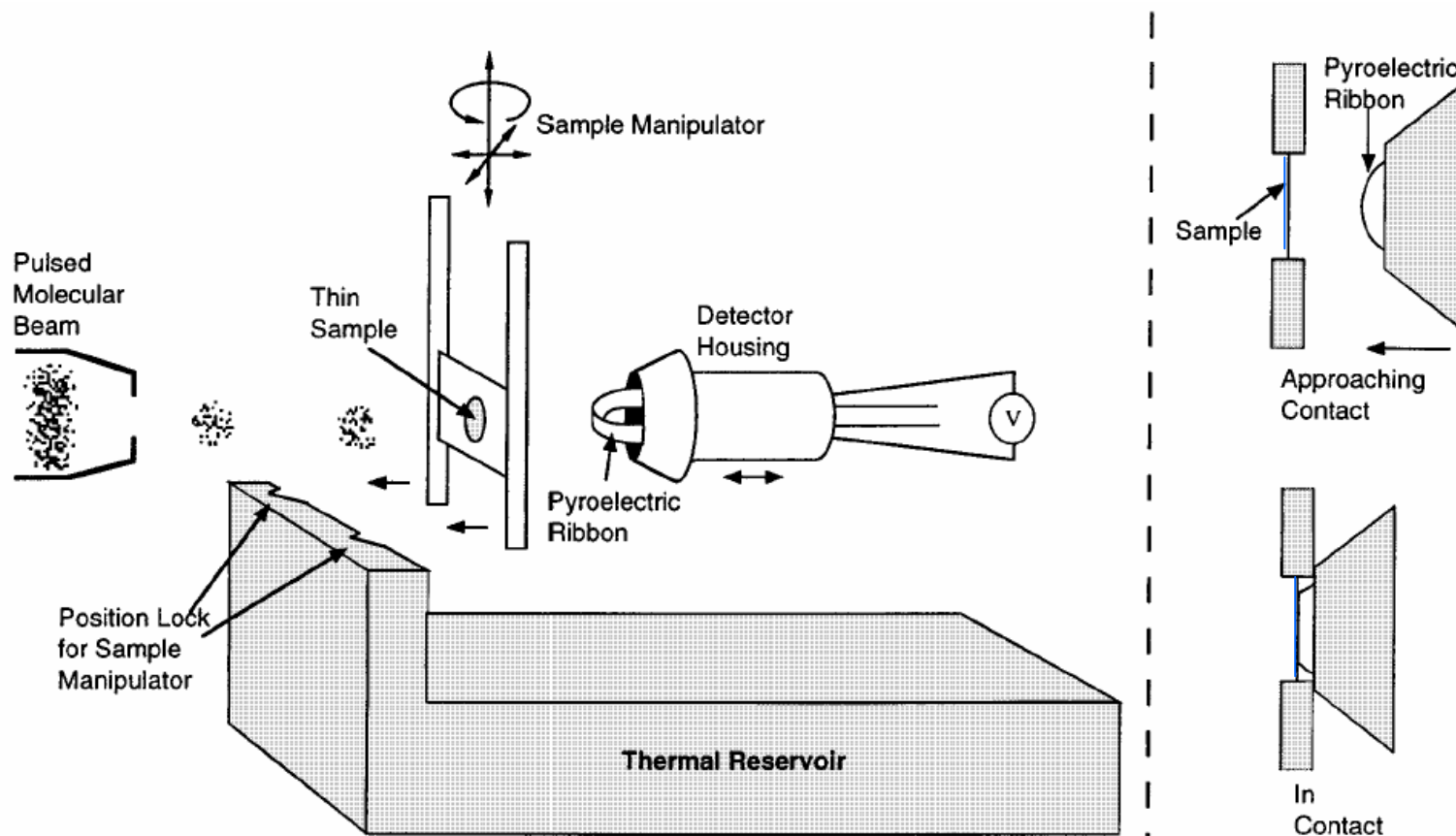
- ❖ O. Beeck, W.A. Cole, A. Wheeler, Disc. Faraday Soc. 8 (1950) 314.
- ❖ D.A. Kyser, R.P. Masel, J. Vac. Sci. Technol. A4 (1986) 1431.
- ❖ G. Wedler, I. Ganzmann, D. Borgmann, Ber. Bunsenges. Phys. Chem. 97 (1993) 293.
- ❖ C.E. Borroni-Bird, D.A. King, Rev. Sci. Instrum. 62 (1991) 2177.
- ❖ J.T. Stuckless, N.A. Frei, C.T. Campbell, Rev. Sci. Instrum. 69 (1998) 2427.
- ❖ H.M. Ajo, H. Ihm, D.E. Moilanen, C.T. Campbell, Rev. Sci. Instrum. 75 (2004) 4471.

Example I



❖ C.E. Borroni-Bird, D.A. King, Rev. Sci. Instrum. 62 (1991) 2177

Example II



- ❖ J.T. Stuckless, N.A. Frei, C.T. Campbell, Rev. Sci. Instrum. 69 (1998) 2427.

Literature

- ❖ A. Auroux “Thermal Methods: Calorimetry, Differential Thermal Analysis, and Thermogravimetry” in “Catalyst characterization: physical techniques for solid materials”, Eds. B. Imelik, J.C. Vedrine, Plenum Pr., New York 1994
FHI 28 I 57
- ❖ E. Calvet, H. Prat, H.A. Skinner “Recent progress in microcalorimetry”, Pergamon Pr., Oxford 1963
FHI 6 Z 17