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Role of Calorimetry in the study of Adsorption and Adsorbents

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Role of Calorimetry in the study of Adsorption and Adsorbents

A/ Introduction to calorimetry and calorimeters

B/ Experimental procedures of adsorption and immersion, derivation of thermodynamic quantities

C/ Applications of gas adsorption calorimetry

D/ Applications of immersion calorimetry

A/ Introduction to calorimetry and calorimeters

1/ Definition, objective, strength and difficulties of calorimetry

2/ General presentation and classification of calorimeters

3/ Selection of those suited for gas adsorption calorimetry and immersion calorimetry

1/ Definition, objective, strength and difficulties of calorimetry

- « Calorimeter » : term coined in 1789 by Lavoisier to designate an equipment able to measure heat
- The objective is to better understand a phenomenon (like adsorption) after the measurement of the heat exchanged
- This requires assessing the changes of a state function (*U*, *H*, *S*)
- One should then fully control the initial state (synthesis, sampling, outgassing, *P*, *T*…) and the final state (amount adsorbed, *P*, *T*…)
- One should also fully control the calorimetric experiment proper, to be able to derive a state function (isothermicity, reversibility)

A/ Introduction to calorimetry and calorimeters

1/ Definition, objective, strength and difficulties of calorimetry

2/ General presentation and classification of calorimeters

3/ Selection of those suited for gas adsorption calorimetry and immersion calorimetry

2/ General presentation and classification of calorimeters

a) A good clarification is requested

- «More than 100 different types of calorimeters invented, in 200 years, to « catch » the heat

- More than 10 different classifications were proposed

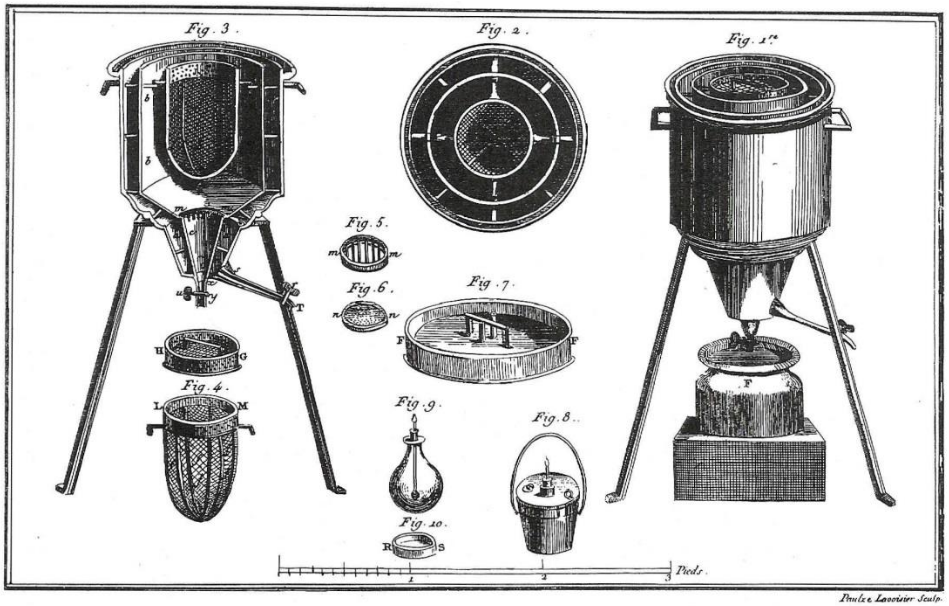
- This makes that the student – but usually also the teacher – has much difficulties to have a clear view about calorimetry

1st example of confusion:
so many calorimeters and so many names !

« reaction », « isothermal », « ice », « drop », « temperature jump », « solution », « liquid flow », « heat flow », « stop flow », « adiabatic », « ordinary », « AC », « laser flash », « battery »

« flame », « combustion », « cone », « conduction », « deformation », « thermopile », « bomb », « pneumatic », « mixing », « biocalorimeter », « photocalorimeter », « surface calorimeter » etc...

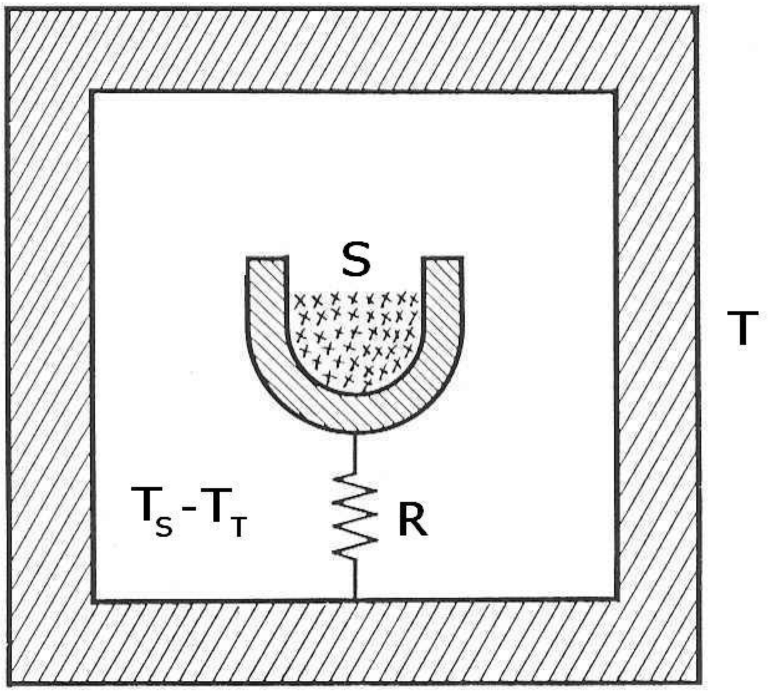
2nd example of confusion: even a single calorimeter is described in many different ways, *sometimes inconsistent with each other*



For instance, Laplace and Lavoisier 's ice calorimeter is classified as:

- **Phase change**
- **Isothermal**
- **Conduction**
- **Compensation**
- **Adiabatic**

b) A simple classification is requested, which starts with the **schematic representation of a calorimeter**



- ⌘ S : system made up of the sample and its container or vessel (with which it is in good thermal contact)
- ⌘ T : surrounding thermostat (characterized by its temperature T_T)
- ⌘ R : thermal resistance through which the heat exchanges between S and T occur
- ⌘ T_S - T_T : temperature difference between S and T

Extreme modes of operation of calorimeters after the heat exchange

⌘ Adiabatic mode (αδιαβατοζ, adiabatos, «which cannot be crossed»)

No heat exchange between the system and the thermostat

⌘ Diathermal mode(διαα, dia, « through », and θερμοσ, thermos, « hot »)

The whole energy involved by the system transformation is exchanged with the thermostat

Classification of real calorimeters: 2 groups, 4 categories

Adiabatic calorimeters	1/« active » 2/« passive »
Diathermal calorimeters	1/ « active » 2/ « passive »

Classification of real calorimeters: 2 groups and 4 categories

A/ **Adiabatic** calorimeters

1/ « active » : heat exchange minimized by servo-controlling **the thermostat T after the sample T** (« true » adiabatic)

2/ « passive » : heat exchange simply minimized by thermal insulation between sample and thermostat (« quasi » adiabatic or isoperibolic: Berthelot, Thomsen, « water calorimeter »)

B/ **Diathermal** calorimeters

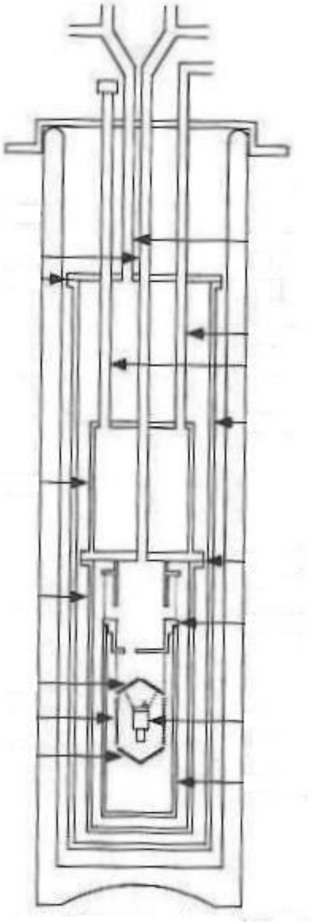
3/ « passive » : heat exchange favoured by simple thermal conduction (ex ;Tian-Calvet heat flowmeters, phase-change)

4/ « active » : heat exchange replaced by an *in-situ* power compensation which mimics a good thermal conduction (ex:heat flowmeter with Peltier compensation)

Applying this classification with special attention to the calorimeters used for adsorption or immersion studies

1/ « Active » adiabatic calorimeters

(« true » adiabatic) *(continued)*

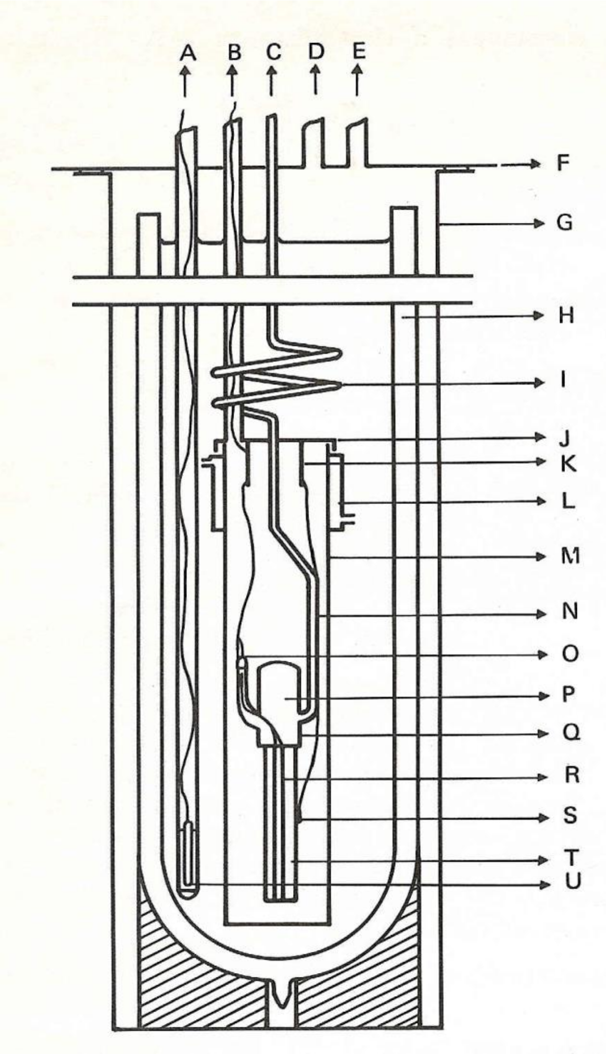


- Heat exchange minimized by servo-controlling the thermostat temperature after the sample temperature

Typical examples

Low temperature calorimeters, with multiple shields in vacuum (Westrum, Suga, Grönvold, Gmelin…)

G.L.Kington and P.S.Smith, in 1964, set up a low-temperature, **active adiabatic** adsorption calorimeter, with vacuum insulation and automatic cancellation of ΔT.



Issues:

- Adsorptive introduced through thin capillary « C » (needed to lower heat leaks), which impedes correct outgassing and controlled starting state
- Non isothermal, by principle
- Heavy to handle: sample in center of several air-tight containers

2/ « Passive » adiabatic calorimeters

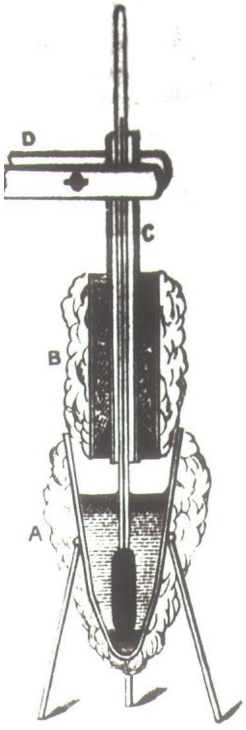
(« quasi-adiabatic », « isoperibol »)

- Heat exchange is minimized by thermal insulation
- dQ exp = dQ stored + dQ exchanged (corrective term for heat losses)
- No mutual dependence between T_S and T_T (no coupling)

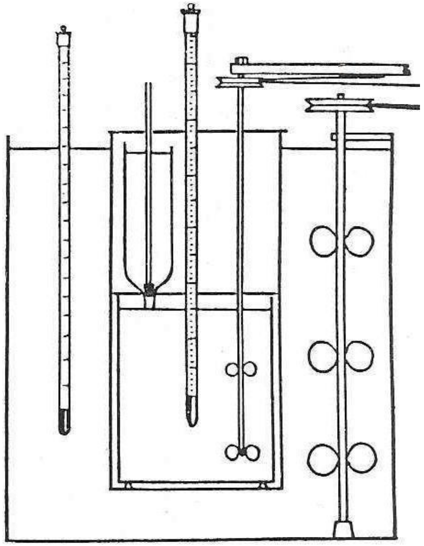
Typical examples:

« Water » calorimeters:

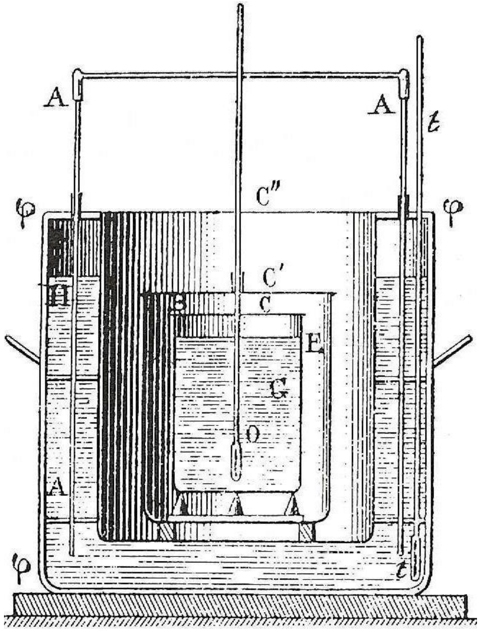
Pouillet (immersion)
Zettlemoyer (immersion)
Thomsen (reaction)
Berthelot (bomb)



Pouillet 1822



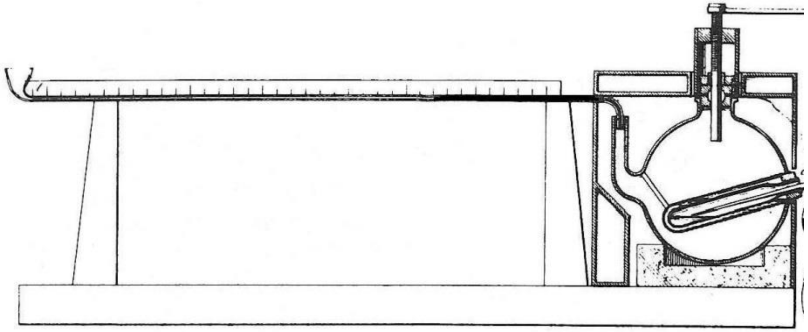
Thomsen,1869



Berthelot,1870

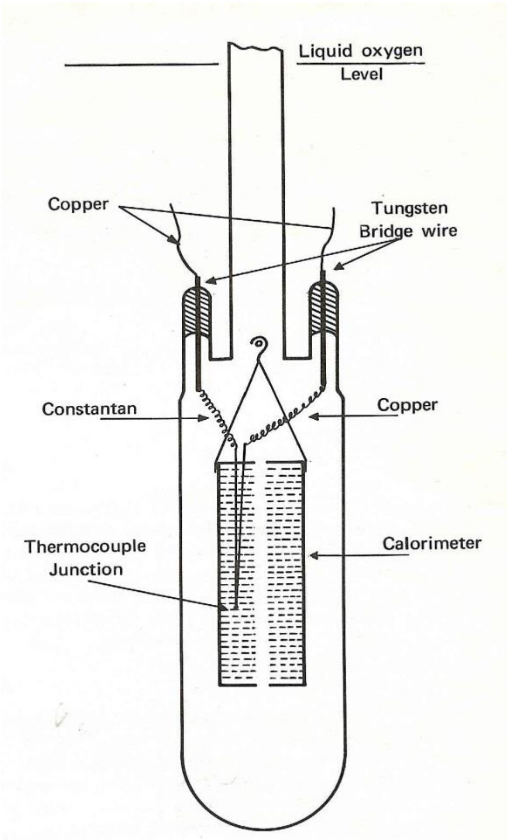
- ***Pierre-Antoine Favre*** *made use of 2 quasi-adiabatic calorimeters: one with a mercury thermometer whose bulb (with 10kg mercury!) was the calorimeter proper, the other a standard « water calorimeter » insulated with swan feathers.*

*Mercury **dilatation** calorimeter (Favre, 1846)*



- He was the first to measure **heats of adsorption of gases** (SO_2, NH_3, HCl, NO, CO_2) **on solids** (charcoals) between 1854 and 1871 (« wetting of solids by gases »)
- 1st Professor of Chemistry of the Faculty of Sciences of Marseilles

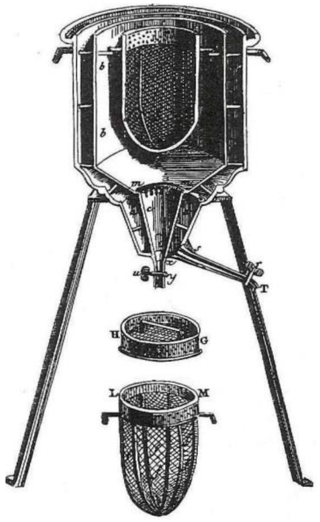
- **Ralph Beebe** devised, around 1950, a quasi-adiabatic, low-temperature, adsorption calorimeter immersed into liquid oxygen or nitrogen



- Insulation is provided by gaseous adsorptive surrounding the sample cell

- Issue: insulation varies when adsorptive pressure increases and experiment is non-isothermal

3/ « Passive » diathermal calorimeters (« thermal conduction ») with phase change

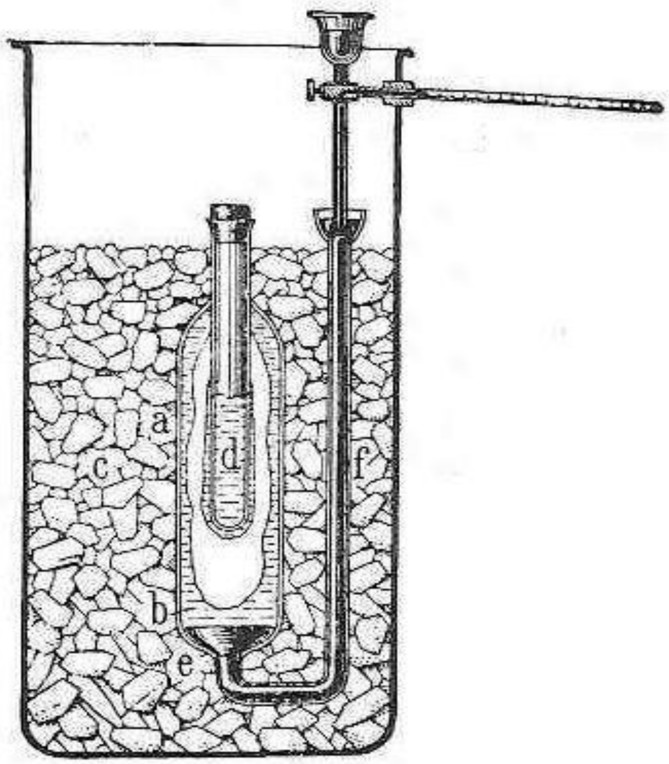


Lavoisier 1783

- Good heat exchange thanks to thermal conduction
- Sample temperature passively follows that of the thermostat
- dQ stored ≤≤ dQ exchanged so that dQ exp ≈ dQ exchanged

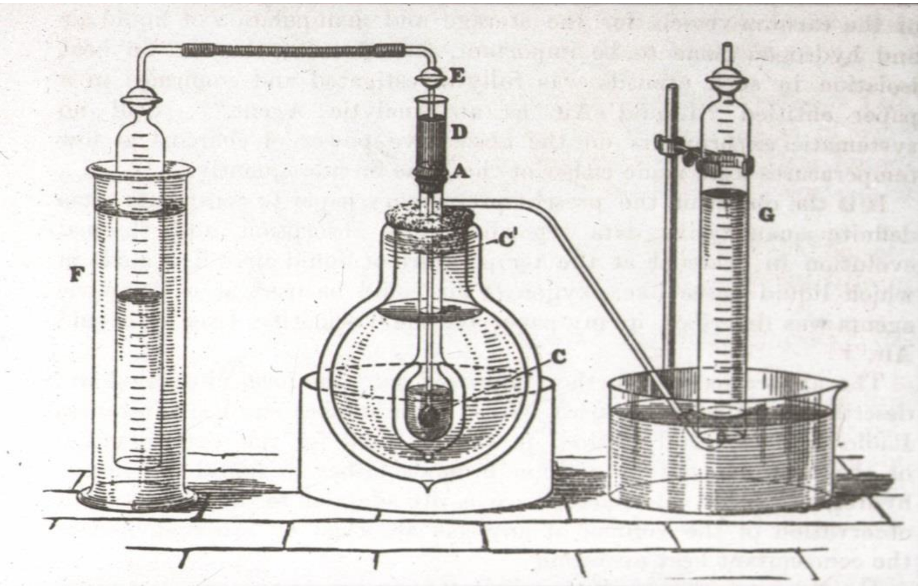
- dQ exchanged measured by help of a **phase change**
- Typical: Lavoisier ice calorimeter, 1783)

- **Robert Wilhelm Bunsen** devised an **ice calorimeter** later used (until 1975) for adsorption studies because it was **isothermal** and **sensitive**.
- ***Converted measurement of heat into measurement of length*** *(contraction on ice melting followed by mercury in capillary)*



- Improved by use of **diphenyl-ether (melts at 27°C** and expands on melting, hence more regular displacement of mercury index
- Issue: **limited autonomy** and most « **temperamental** » (after J.Gregg),

- **James Dewar** devised, in 1905, a smart, adsorption calorimeter in liquid air : left buret measures consumption of adsorptive, right buret measures production of air by vapourization (type: passive diathermal with phase-change)

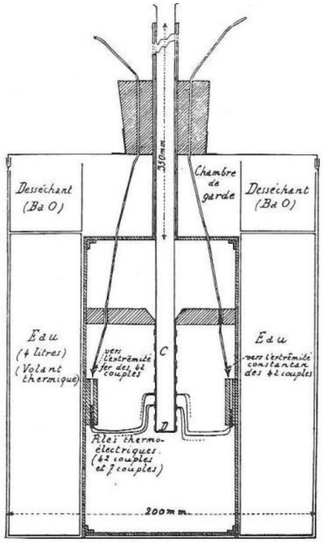


- Later improved by replacing liquid air by liquid nitrogen

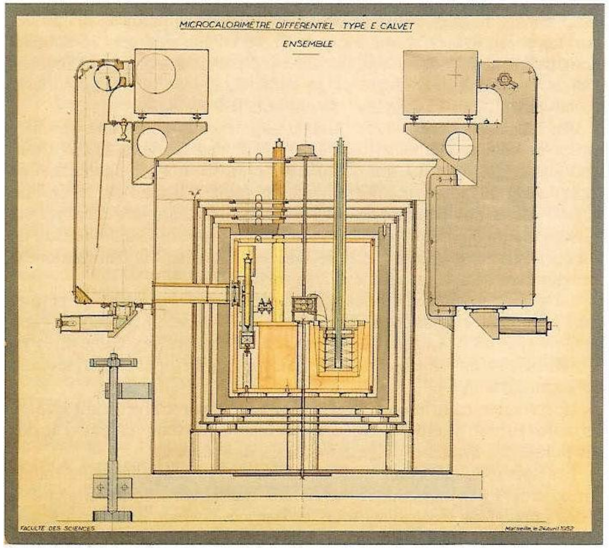
- Issue: **limited autonomy** and poor stability, since most sensitive to fluctuations of atmospheric pressure

4/ « Passive » diathermal calorimeters (« thermal conduction ») with heat flowmeter

- Good heat exchange thanks to thermal conduction
- Sample temperature passively follows that of the thermostat
- dQ stored ≤≤ dQ exchanged so that dQ exp ≈ dQ exchanged
- dQ exchanged measured by **heat flowmeter** (Tian-Calvet,1923-1948, Wadsö, 1968,)



Tian 1923



Tian-Calvet 1950

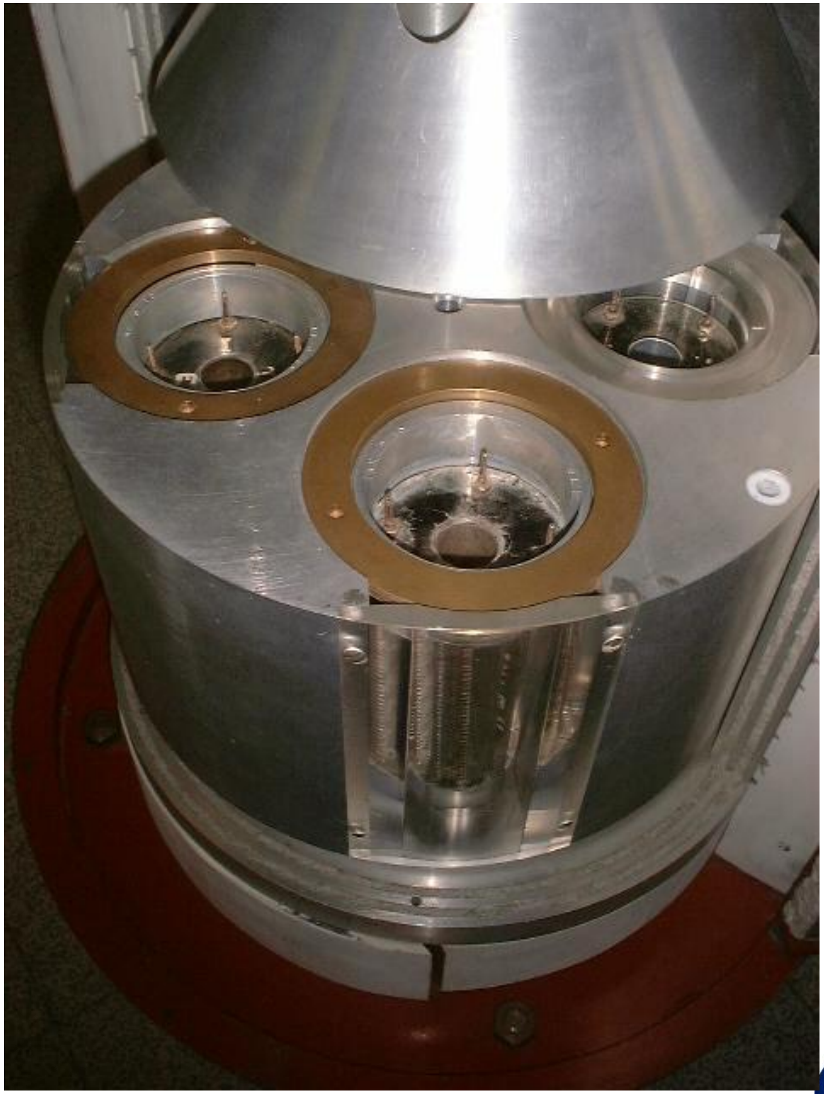
Albert Tian (1880 - 1972)

- Professor of Chemistry at the Faculty of Sciences of Marseille (1921-1950)
- **Invented the heat-flux microcalorimeter:** isothermal, with a thermopile of 42 + 7 thermocouples and with Joule or Peltier power compensation
- **Invented the multi-shielded thermostat** (stable within 10^{-6} K) used by A.F.H.Ward, under his guidance, in 1930 (adsorption calorimetry of H_2 on copper)
- Launched a school of microcalorimetry…

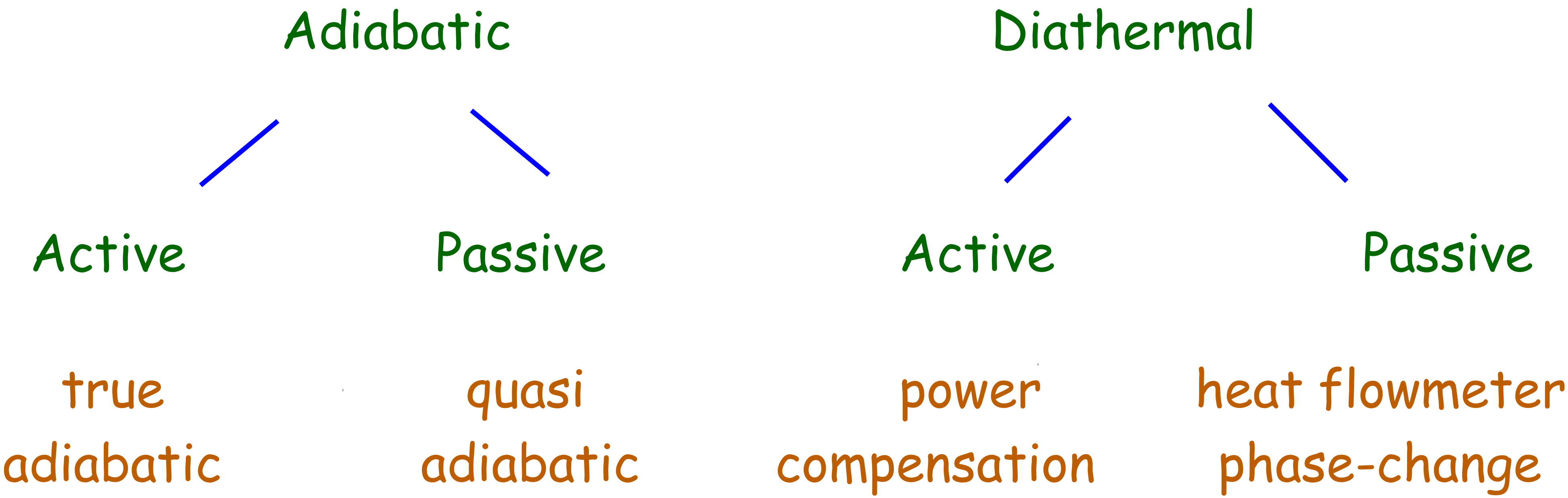
Edouard Calvet (Marseille,1895-1966)

- A.Tian 's student, and then successor
- Introduced, in 1947, the **differential mounting**
- Made the Tian-Calvet microcalorimeter an extremely versatile piece of equipment
- Had a special Institute built by the CNRS, in 1959, for the development of microcalorimetry

The Tian-Calvet microcalorimeter



Finally, for a simple introduction to calorimetry, the following scheme may be enough:



Adiabatic

Active

true adiabatic

Passive

quasi adiabatic

Diathermal

Active

power compensation

Passive

heat flowmeter

phase-change

A/ Introduction to calorimetry and calorimeters

1/ Definition, objective, strength and difficulties of calorimetry

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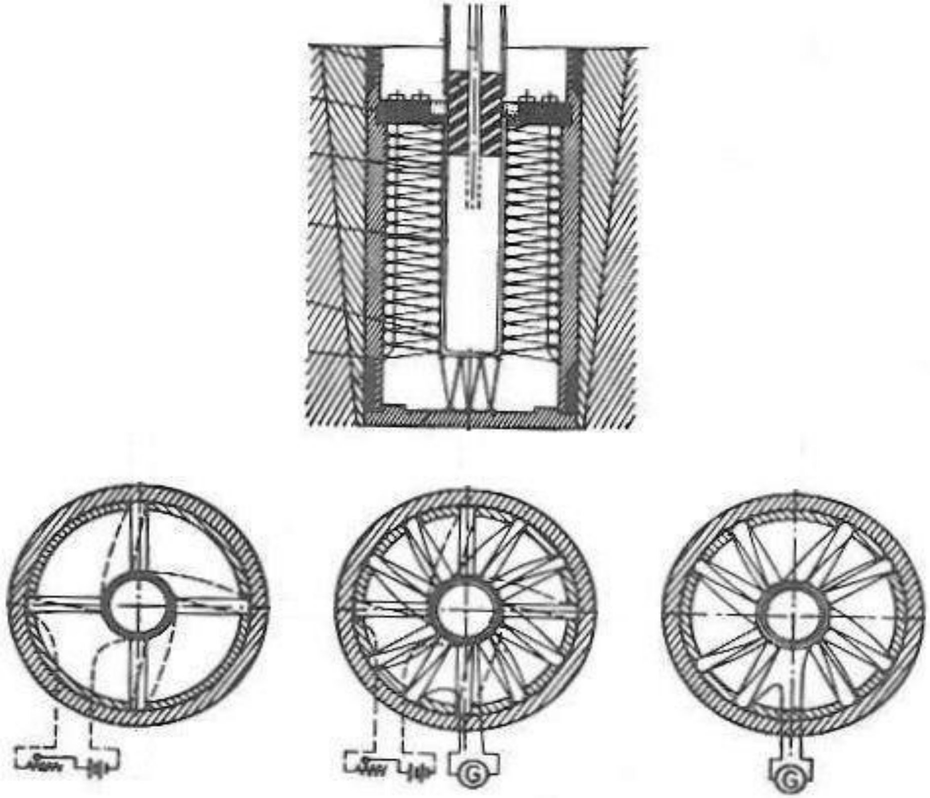
3/ Selection of the calorimeters most suited for:
a) adsorption calorimetry

- Active adiabatic calorimeters :
  - OK to measure heat capacity of adsorption system vs T, to study phase changes
  - But for *one composition* of the system (closed system)
  - Problems of outgassing
- Passive adiabatic calorimeters (Favre, Beebe)
  - Non isothermal: experiment ends at higher T, desorption
- Passive diathermal with phase change (Bunsen, Dewar)
  - Limited autonomy and choice of T, delicate to operate
- Passive diathermal with heat flowmeter
  - Open systems, large choice of T, high stability and sensitivity (when differential)

3/ Selection of the calorimeters most suited for:
b) immersion calorimetry

- Active adiabatic calorimeters :
  - Complicated set-up for immersion calorimetry-Never used
- Passive adiabatic calorimeters (Zettlemoyer)
  - Simple experiment. Most used in the past. Limited sensitivity
- Passive diathermal with phase change (Chessick, liquid nitrogen)
  - Delicate to operate, inaccurate
- Passive diathermal with heat flowmeter (Tian-Calvet)
  - Combines easy operation and high sensitivity. The most used to-day

Features of the Tian-Calvet thermopile



400 to 2000 thermocouples :

- Integrate **whole heat flow**
- Convert heat-flow into voltage
- Provide high sensitivity
- Also provide high isothermicity
- When metallic, used between 77 to 1300 K

Whith differential arrangement*, Tian-Calvet thermopile suited for open system, with tubes, and compensates for heat leaks:* ***well suited for adsorption studies***

B/ Experimental procedures and derivation of thermodynamic quantities

1/ Gas adsorption calorimetry

2/ Immersion calorimetry

1/ Gas adsorption calorimetry

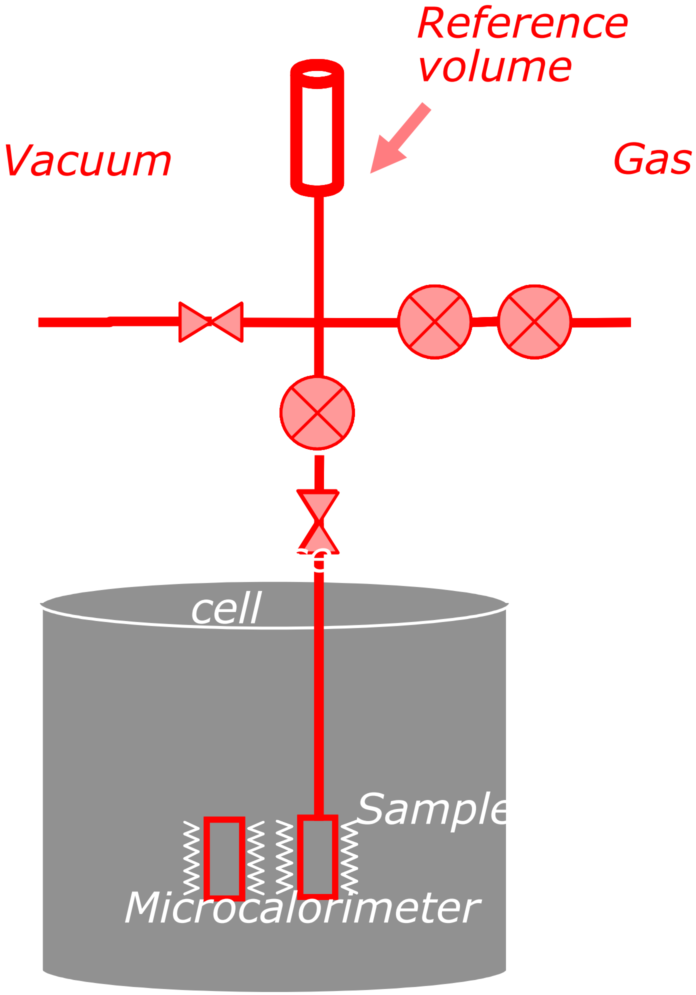
Experimental procedures

- ⌘ Basic procedure: step by step introduction of the adsorptive
- ⌘ High resolution procedure
- ⌘ « Calorimetric weighing » procedure

Assessment of thermodynamic functions

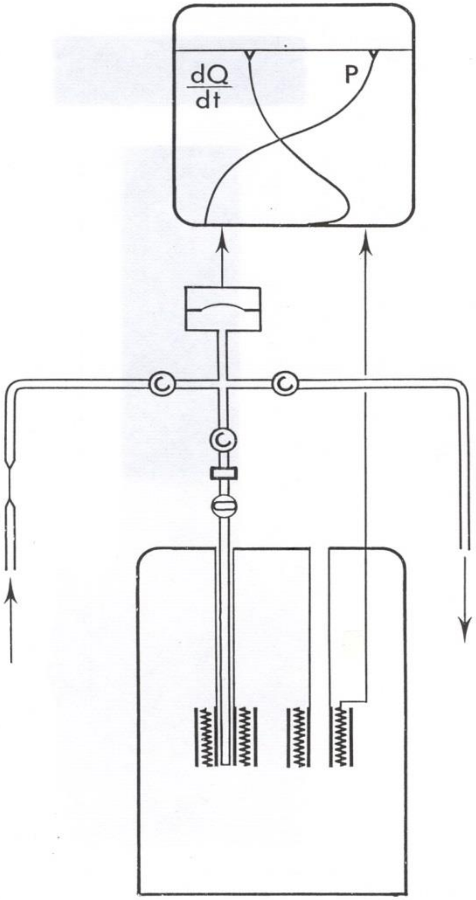
- ⌘ Simplified and accurate reporting of adsorption experiment: the Gibbs representation of surface excess quantities
- ⌘ Without calorimeter: the isosteric method
- ⌘ With the step-by-step procedure (open system, external work, reversibility requested for correct calculation and measurement)
- ⌘ With the high-resolution, quasi-equilibrium procedure

The basic, point-by-point procedure for gas adsorption calorimetry

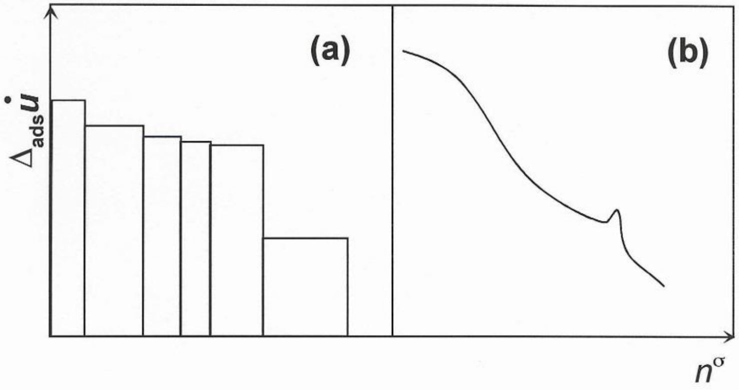


- *Necessarily associates calorimetry with either adsorption manometry (usual) or adsorption gravimetry*
- *Adsorptive must be introduced:*
  - *slowly*
  - *at same T as calorimeter*

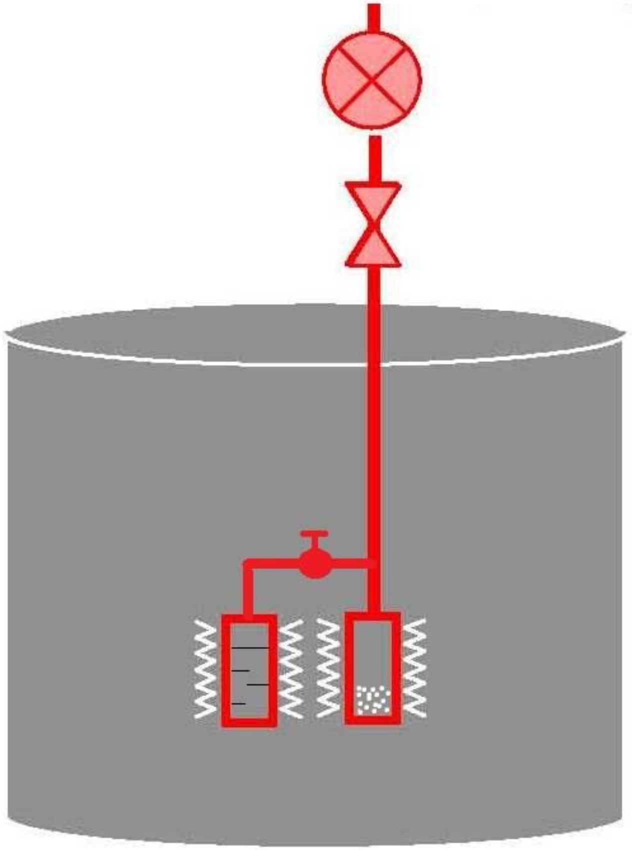
The high-resolution procedure for gas adsorption calorimetry, with slow and continuous introduction of the adsorptive



- A special device (sonic nozzle or gas-low controller) allows slow and continuous introduction of adsorptive, at constant rate (ca 1 cm3 STP/h)
- Allows direct recording of heat flow vs amount of adsorptive introduced
- Detects minute changes in mobility of adsorbate
- Conveniently used up to 1 bar



The procedure of adsorption calorimetry with Calvet's « calorimetric weighing »



- No need of external adsorption manometry or gravimetry
- Associates 2 calorimeters in same thermostat
- One to measure heat produced by adsorption
- Another one to measure heat absorbed by liquid vaporizing towards adsorbent
- Issue: spurious condensation, opening of valve produces noise in recording
- Water condensation can be avoided by lowering p° by salt

1/ Gas adsorption calorimetry

Experimental procedures

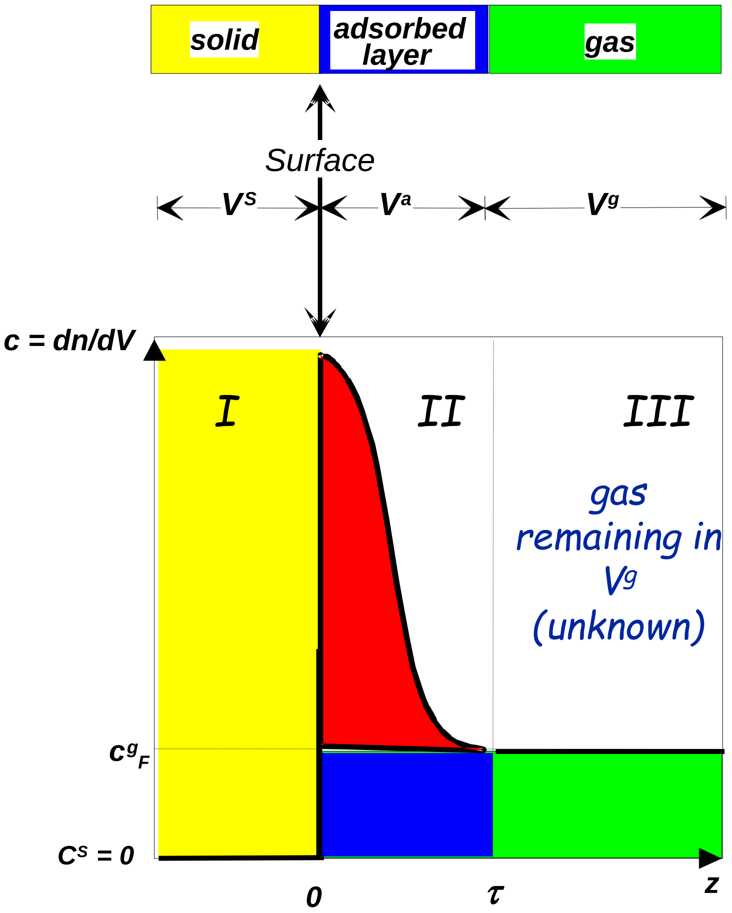
- ⌘ Basic procedure: step by step introduction of the adsorptive
- ⌘ High resolution procedure
- ⌘ « Calorimetric weighing » procedure

Assessment of thermodynamic functions

- ⌘ Simplified and accurate reporting of adsorption experiment: the Gibbs representation of surface excess quantities
- ⌘ Without calorimeter: the isosteric method
- ⌘ With the step-by-step procedure (open system, external work, reversibility requested for correct calculation and measurement)
- ⌘ With the high-resolution, quasi-equilibrium procedure

Two representations of adsorption equilibrium

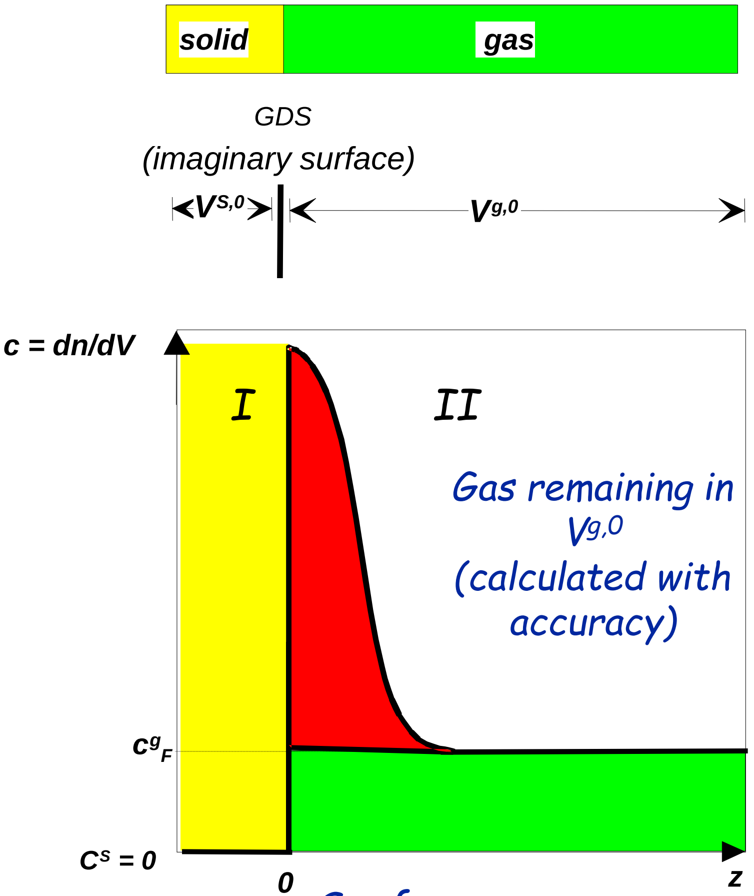
Interfacial layer model



Adsorbed amount n^a

$$n^a = A\int_0^\tau c.dz$$

Gibbs representation



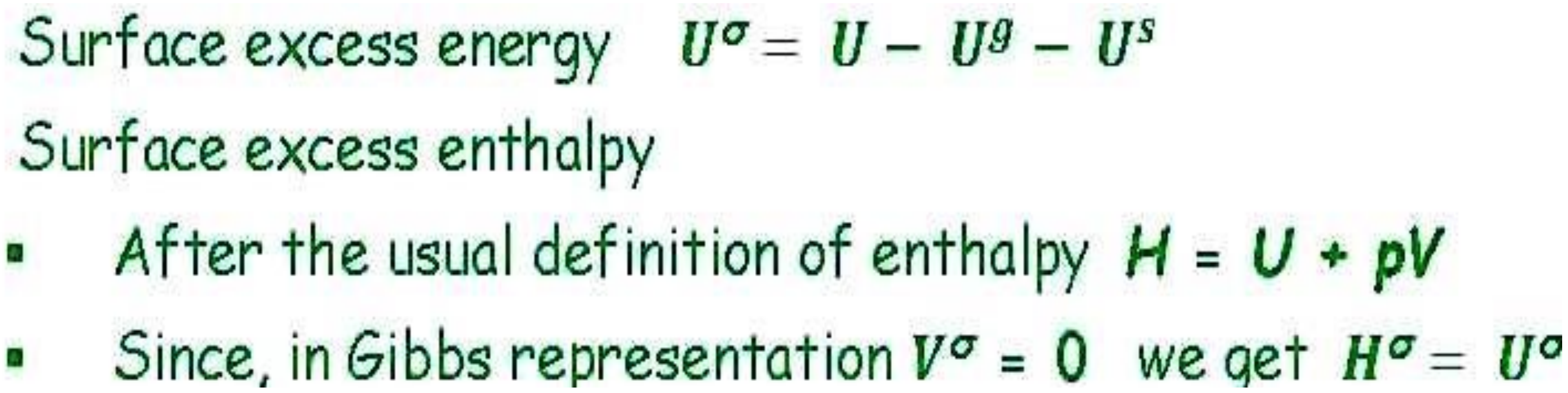
Surface excess amount n^σ
(supposed on the GDS)

$$n^\sigma = n_I^g - n_F^g$$

$$n^a = n^\sigma + c^g.V^a$$

Thermodynamics of adsorption in Gibbs representation

Surface excess quantities (i.e. for a state)



Surface excess energy $U^{\sigma} = U - U^{g} - U^{s}$

Surface excess enthalpy

- After the usual definition of enthalpy $H = U + pV$
- Since, in Gibbs representation $V^{\sigma} = 0$ we get $H^{\sigma} = U^{\sigma}$

Thermodynamics of adsorption in Gibbs representation *(continued)*

Adsorption quantities (i.e. not for a state, for a change)

- Integral energy of adsorption (from 0 to n^σ)

$$\Delta_{ads}U = n^\sigma(\bar{u}^\sigma - u^g)$$

- Integral molar energy of adsorption (from 0 to n^σ)

$$\Delta_{ads}\bar{u} = \Delta_{ads}U \,/\, n^\sigma = \bar{u}^\sigma - u^g$$

- Differential (derivative) energy of adsorption

$$\Delta_{ads}\dot{u} = \frac{dU}{dn^\sigma} = \dot{u}^\sigma - u^g$$

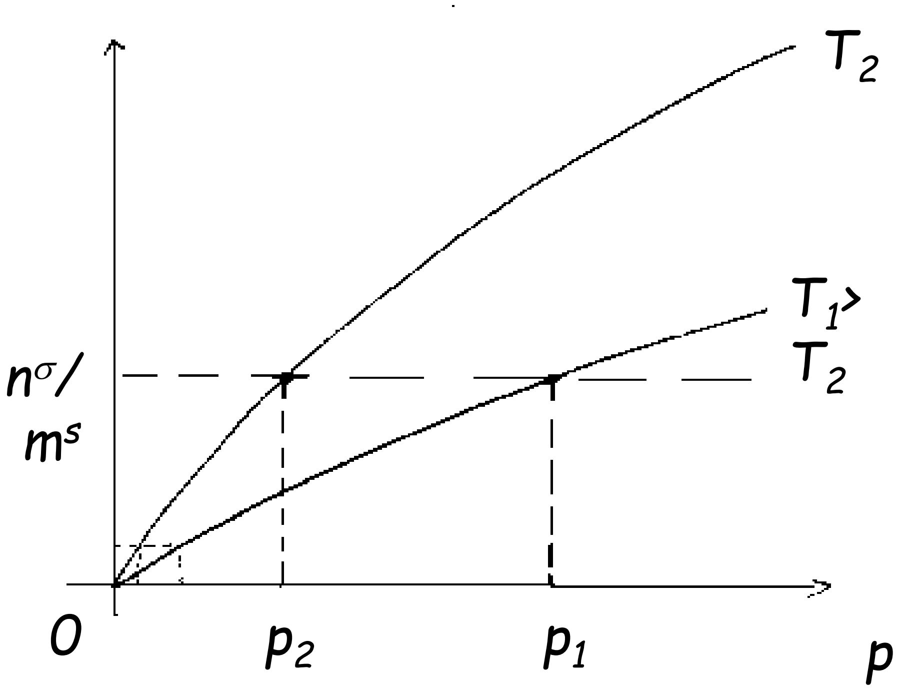
- Differential (derivative) enthalpy of adsorption

$$\Delta_{ads}\dot{h} = \frac{dH}{dn^\sigma} = \dot{u}^\sigma - h^g = \dot{u}^\sigma - u^g - RT$$

- Isosteric enthalpy (heat) $q_{st} = -\Delta_{ads}\dot{h}$

The isosteric method

« Isosteric » i.e. for same « volume » adsorbed



$$Q_{st} = R\,T_1T_2/(T_2 - T_1)\ \ln\,(p_2/p_1)$$

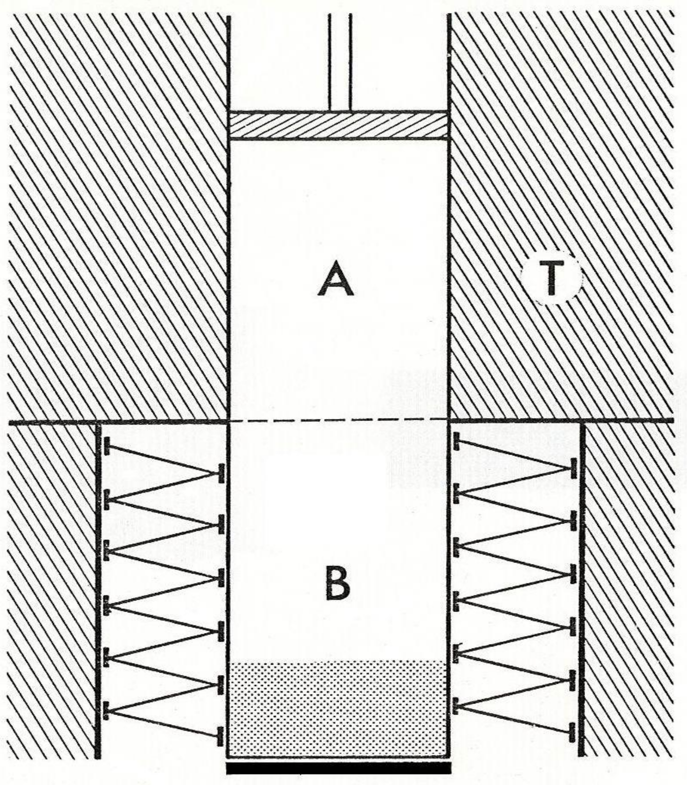
$$\Delta_{ads}\dot{h} = -R\,T_1T_2/(T_2 - T_1)\ \ln\,(p_2/p_1)$$

One can easily replace the term « isosteric heat » by the more explicit term « isosteric enthalpy » .

This makes easier the connection and comparison with enthalpies obtained by calorimetry

Open system: point by point gas adsorption calorimetry

To reach an adsorption enthalpy, how can we take into account the fact that the system is open?



(Rouquerol and Everett,1985)

- Imagine all adsorptive in a cylinder, partly in calorimeter
- Assume reversible compression by slowly depressing the piston
- Calculate the heat of compression evenly dissipated to the surroundings at constant *T*
- Take into account that calorimetric cell B only dissipates part of the total heat of compression

Open system: point by point gas adsorption calorimetry

Interest of « isothermal » calorimetry :

→ T of the adsorption system remains constant

Association with adsorption manometry :

→ The adsorption system is an open system

Calculation of compression work due to gas entrance

(possible check by blank experiment) :

Gas should be introduced slowly enough to ensure reversibility, so that: $dW = V_c\, dp$

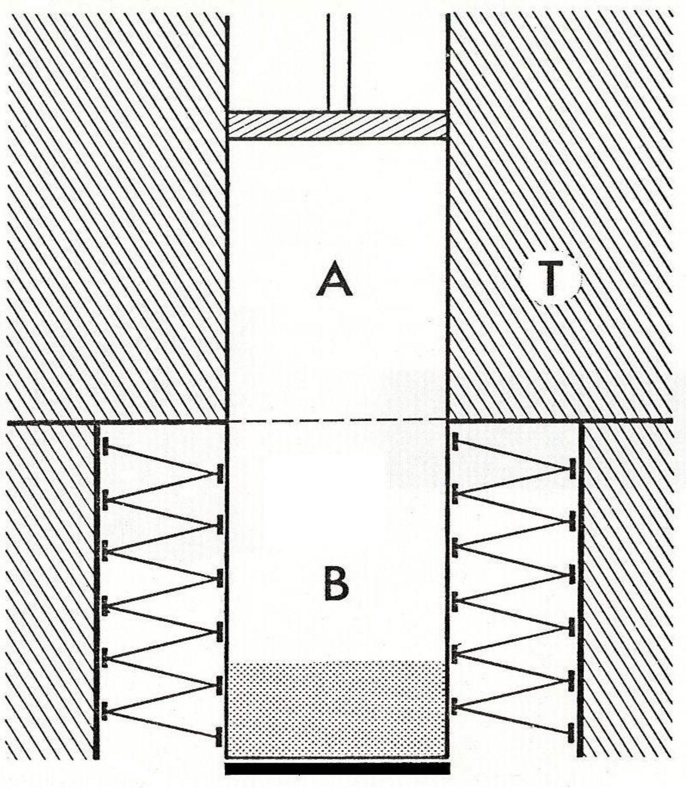
For open system, 1st principle of thermodynamics tells :

- ○ $dU = dW_{T,V} + dQ_{T,V} + u^g\,(dn^g + dn^\sigma)$
- ○ $dW = V_c dp + RT\, dn^\sigma$

$$\frac{dQ}{dn^\sigma} + V_C \frac{dp}{dn^\sigma} = \left[\frac{dU}{dn^\sigma} - u^g\, RT\right] = \Delta_{ads}\dot{h}_{T,\Gamma}$$

Open system: point by point gas adsorption calorimetry

Conditions to satisfactorily assess an enthalpy of adsorption :



(Rouquerol and Everett,1985)

- Well-defined starting state (careful outgassing)
- Consider operation in open system
- Introduce adsorptive reversibly
- Calculate heat of compression
- End with differential enthalpy of adsorption (and not with « heat », which depends on calorimeter and procedure)

1/ Immersion calorimetry

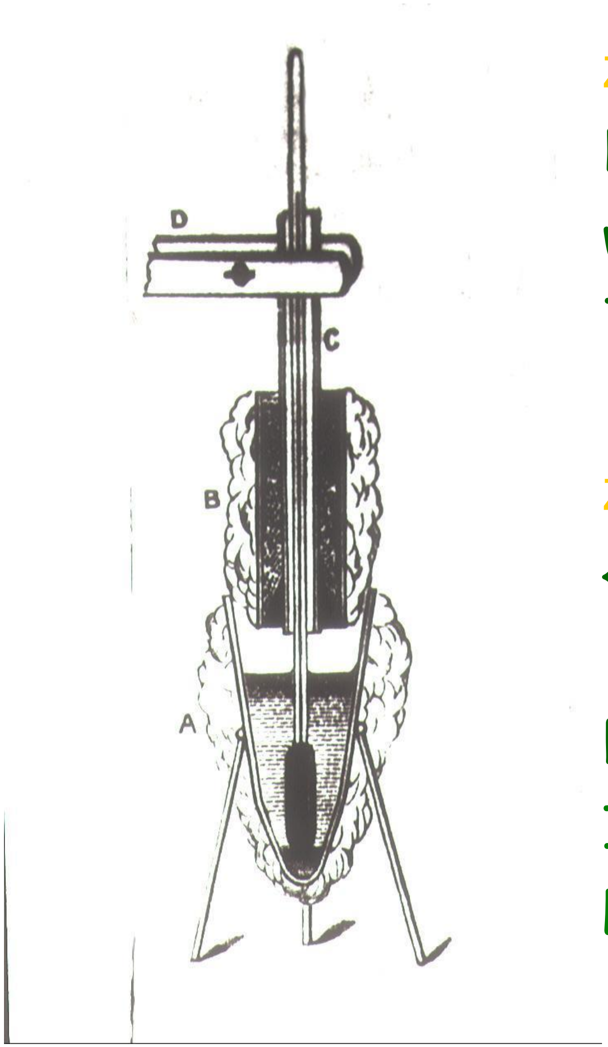
Experimental procedures

- First experiment: Pouillet: dry adsorbent falls into water
- Up to 1975: glass bulb broken (up to 2 J!)
- Then many trials to lower this irreproducible effect
- Still to-day, glass bulb, with brittle end, the safest. Limits extension of immersion calorimetry
- Finally, recommended procedure

Assessment of thermodynamic functions

- Need of well-defined starting and final states (hence glass bulb!)
- Needs corrections; achieves good reproducibility
- The enthalpy of immersion can be compared with the enthalpy of adsorption

Various forms of Immersion Calorimetry



z Claude Pouillet 's experiment (1822)

Dry sand flows from black cylinder down to water enclosed in glass vessel, wool-insulated

Thermometer reads increase of *ca* 2 K. (±30%)

z A.C.Zettlemoyer (1950-1970) made use of a «water » or « isoperibol » calorimeter

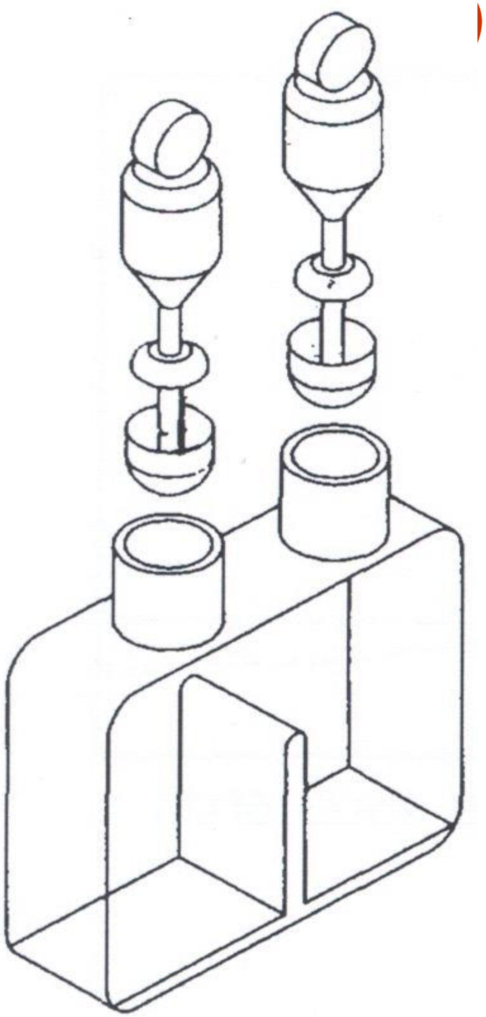
with glass spherical bulb to

be broken

Interest of glass bulb: well-defined starting state

Limitation: heat of breakage up to 1 J (±5-10%)

Various forms of Immersion Calorimetry



z J.Rouquerol and J.Van der Deelen (1971) and C.Moreno-Pirajan *et al.*(1996) made use of a **revolving cell** with partial separation (cf drawing)
Interest: most easy to use
Limitation: starting sample in the presence of vapour

z J.Rouquerol and S.Partyka (1974) separated liquid and solid by thin **metal foil** with O-ring, to be pierced by a lancet
Interest: easy to use, no glass blowing
Limitation: not as tight as a glass bulb

z Finally, J.Rouquerol and S.Partyka (1975) proposed procedure which successfully:
- lowers value of corrective terms
- reaches enthalpy change, not only heat (±1-2%)

1/ Immersion calorimetry

Experimental procedures

- First experiment: Pouillet: dry adsorbent falls into water
- Up to 1975: glass bulb broken (up to 2 J!)
- Then many trials to lower this irreproducible effect
- Still to-day, glass bulb, with brittle end, the safest. Limits extension of immersion calorimetry
- Finally, recommended procedure

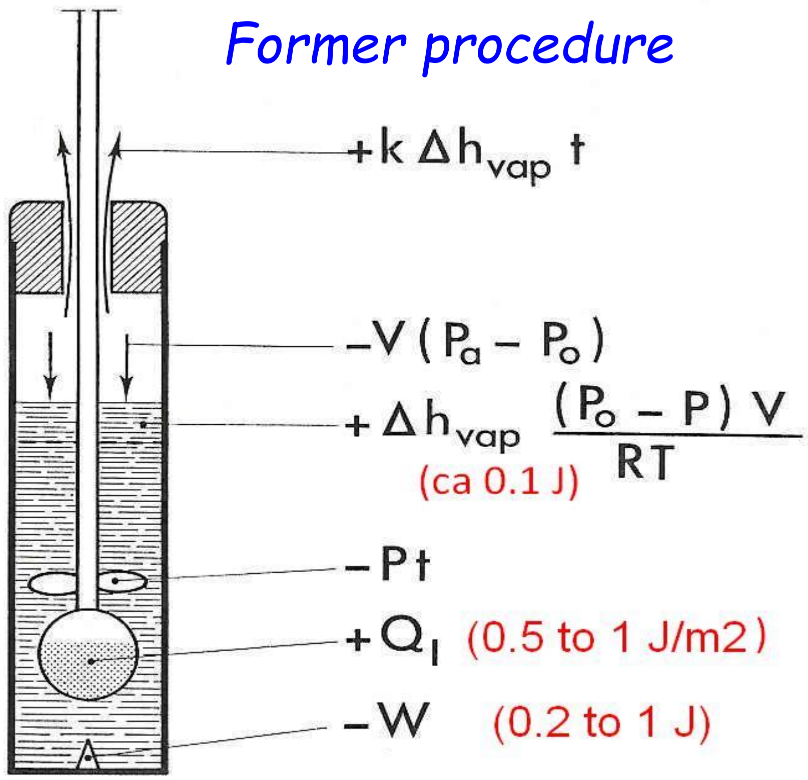
Assessment of thermodynamic functions

- Need of well-defined starting and final states (hence glass bulb!)
- Needs corrections; achieves good reproducibility
- The enthalpy of immersion can be compared with the enthalpy of adsorption

Multiple origins of heat effect in immersion experiment

$Q_{measured} = \Delta_{imm}U$ immersion energy (0.5 to 1 J.m^{-2})

Former procedure



- W_b ampoule breaking (0.2 to 1J, if spherical bulb)
- work of atmospheric pressure on depression of liquid level, when filling void volume of bulb
- energy of vaporization (around 0.1 J)

Conlusion: need to reduce and control corrective terms in order to only assess meaningful $\Delta_{imm}U$

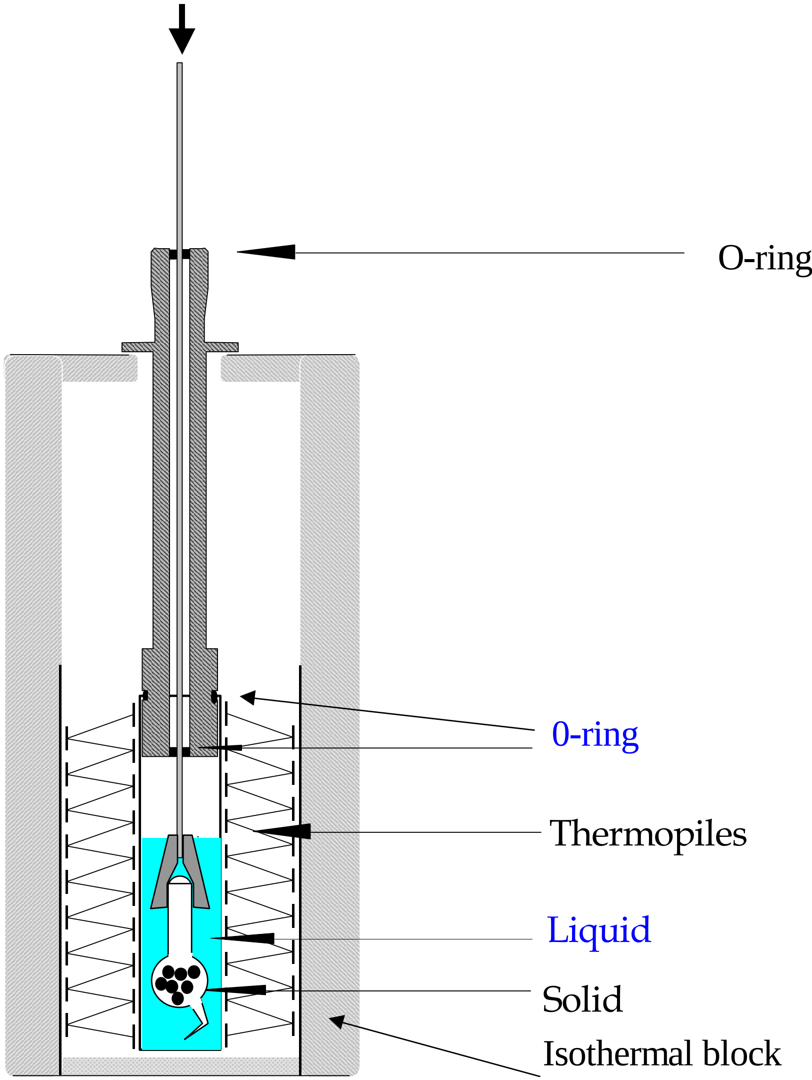
Strict procedures to assess state function in immersion calorimetry (Rouquerol and Partyka,1975)

Makes use of:

- *Tian-Calvet differential microcalorimeter (passive diathermal)*
- *Sealed bulb (keeps sample outgassed)*
- *Fragile brittle end (reduces heat to 5-10 mJ)*
- *Tight system (O-ring) to prevent evaporation and avoid work of atmospheric pressure*
- *O-ring out of calorimeter to avoid heat of friction to be measured*

Requests:

- *Glass-blowing to make the bulb*
- *Careful sample outgassing (by Controlled Rate Thermal Analysis when possible)*
- *Sealing*
- *Evaluate all corrections to assess a ΔimmH*



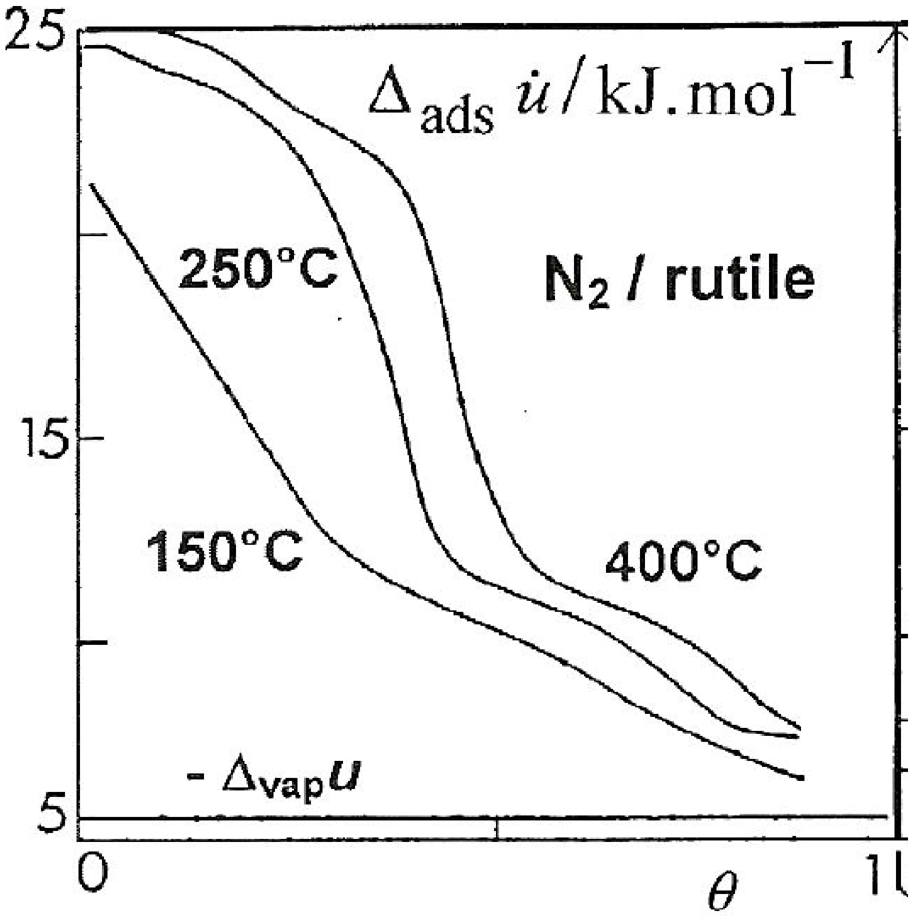
C/ Three applications of gas adsorption calorimetry

1/ Evaluation of the validity of the BET model

2/ Detection of mobility or phase changes

3/ Study of deformation of adsorbents

BET assumes $\Delta_{ads}H$ constant during completion of monolayer

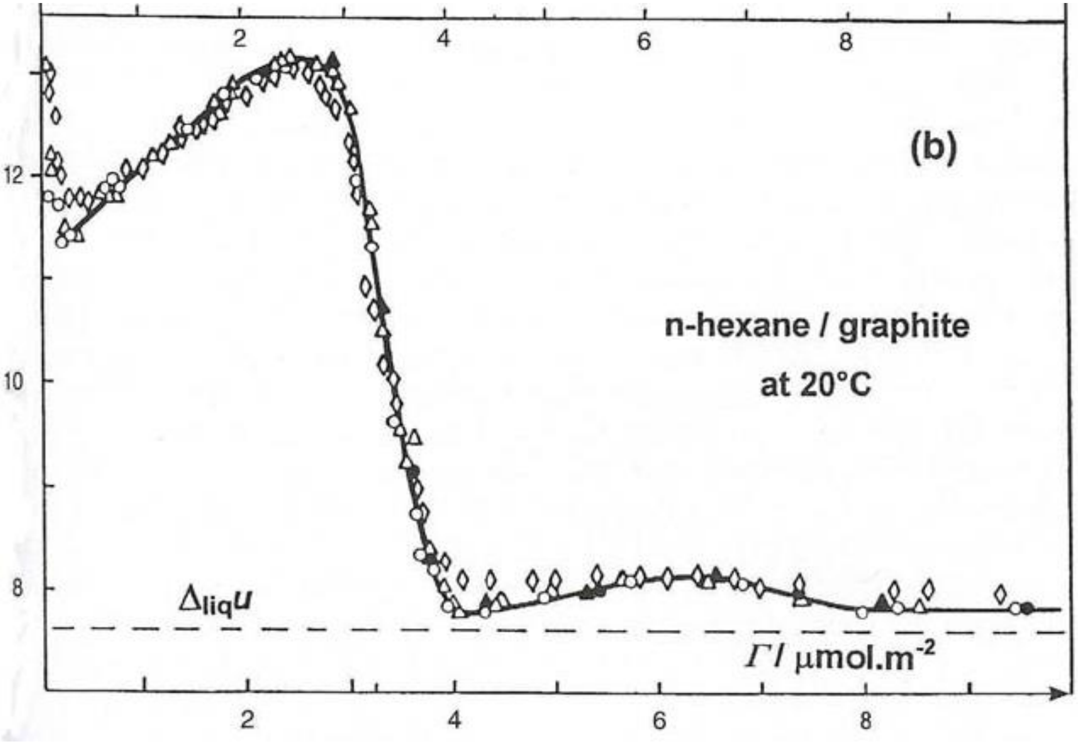


Direct calorimetric measurements show that, even in the absence of microporosity, ΔadsU varies much, even with argon, as soon as « active sites » are on the surface (here, hydroxyls and Ti^{+++}cations)

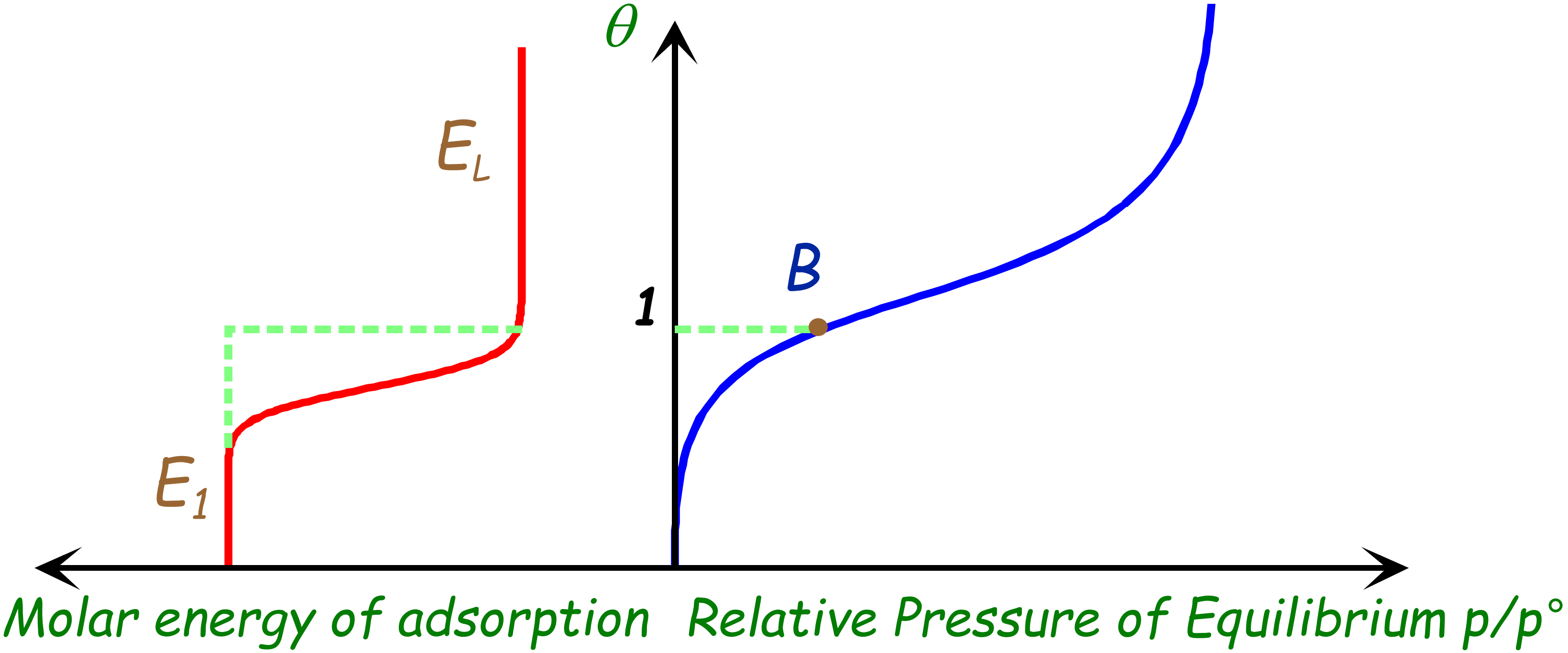
BET assumes no "lateral interactions" during formation of 1st layer

Calorimetry clearly shows increased interaction between N-hexane molecules during formation of monolayer

(A.A.Isirikian and A.V.Kiselev,1962)



BET assumes multilayer starts before monolayer is completed (correct)

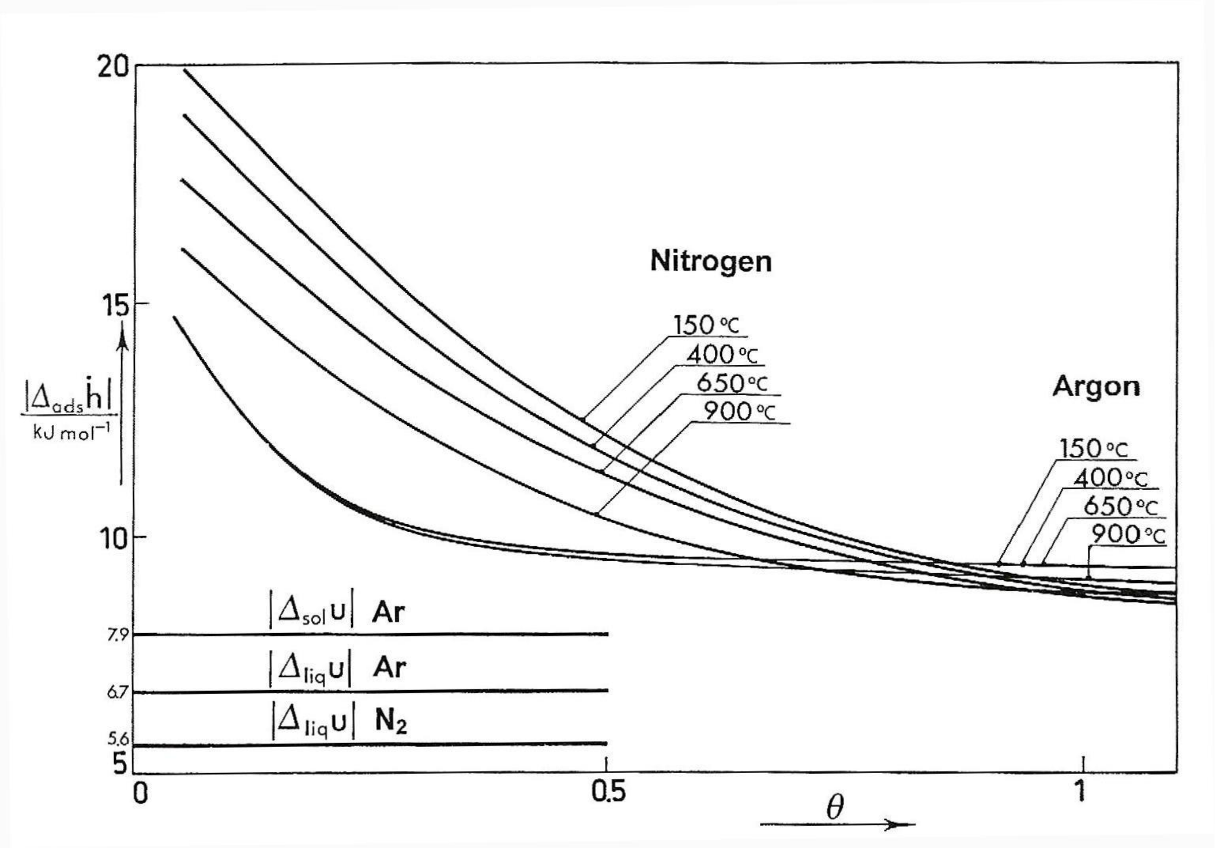


E_1 = Molar energy of adsorption for the first adsorbate layer

E_l = Molar energy of liquefaction of the adsorptive at the temperature of adsorption

BET assumes N_2 molecule takes any orientation in the monolayer

Calorimetric study of N_2 interaction with hydroxyls on silica surface



- ➢*For Ar, no effect of concentration of OH groups*
- ➢*For N_2 , $\Delta_{ads}H$ increases by 3kJ from bare to fully hydroxylated surface*
- ➢*Enough to explain orientation of N2 molecule on surface*

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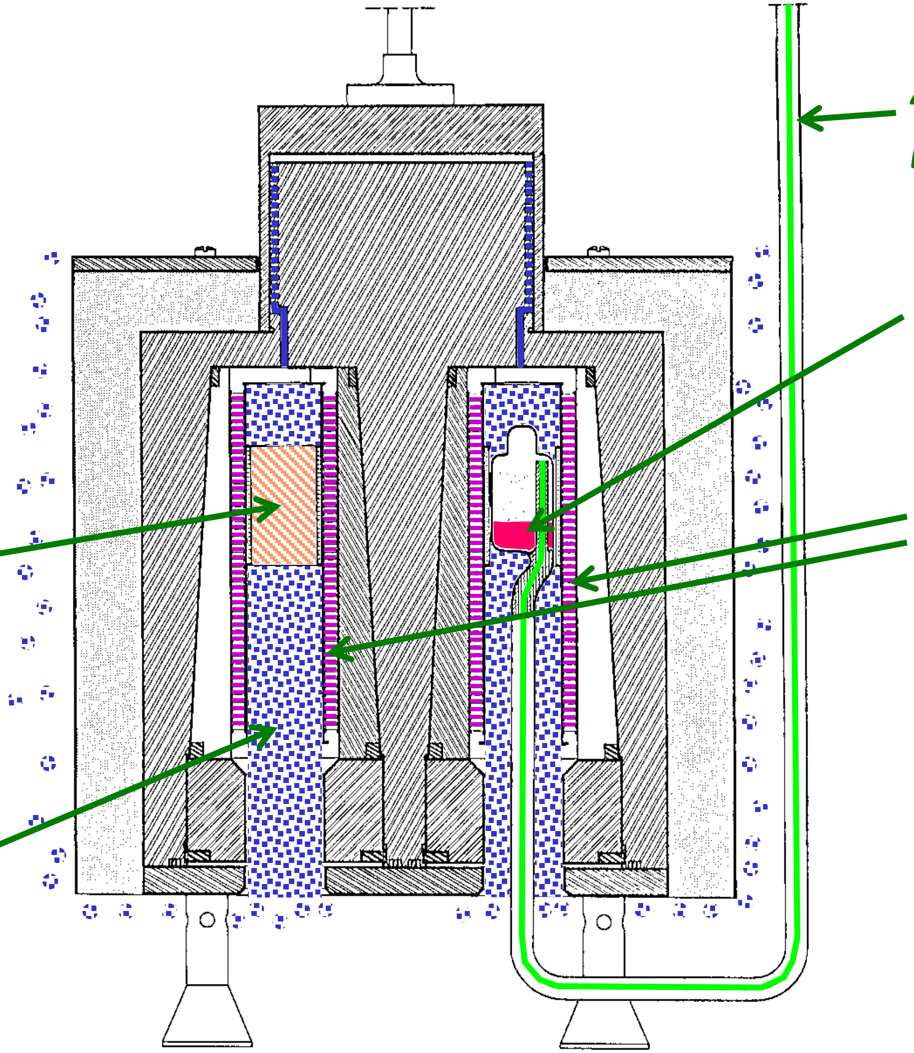
Adsorption calorimetry at liquid N_2 or Ar temperature



Adsorbable gas inlet

Adsorbing sample

Thermopiles connected in opposite (2 x 1000 thermo-couples)

Resistor for Joule effect

Slight over pressure of helium

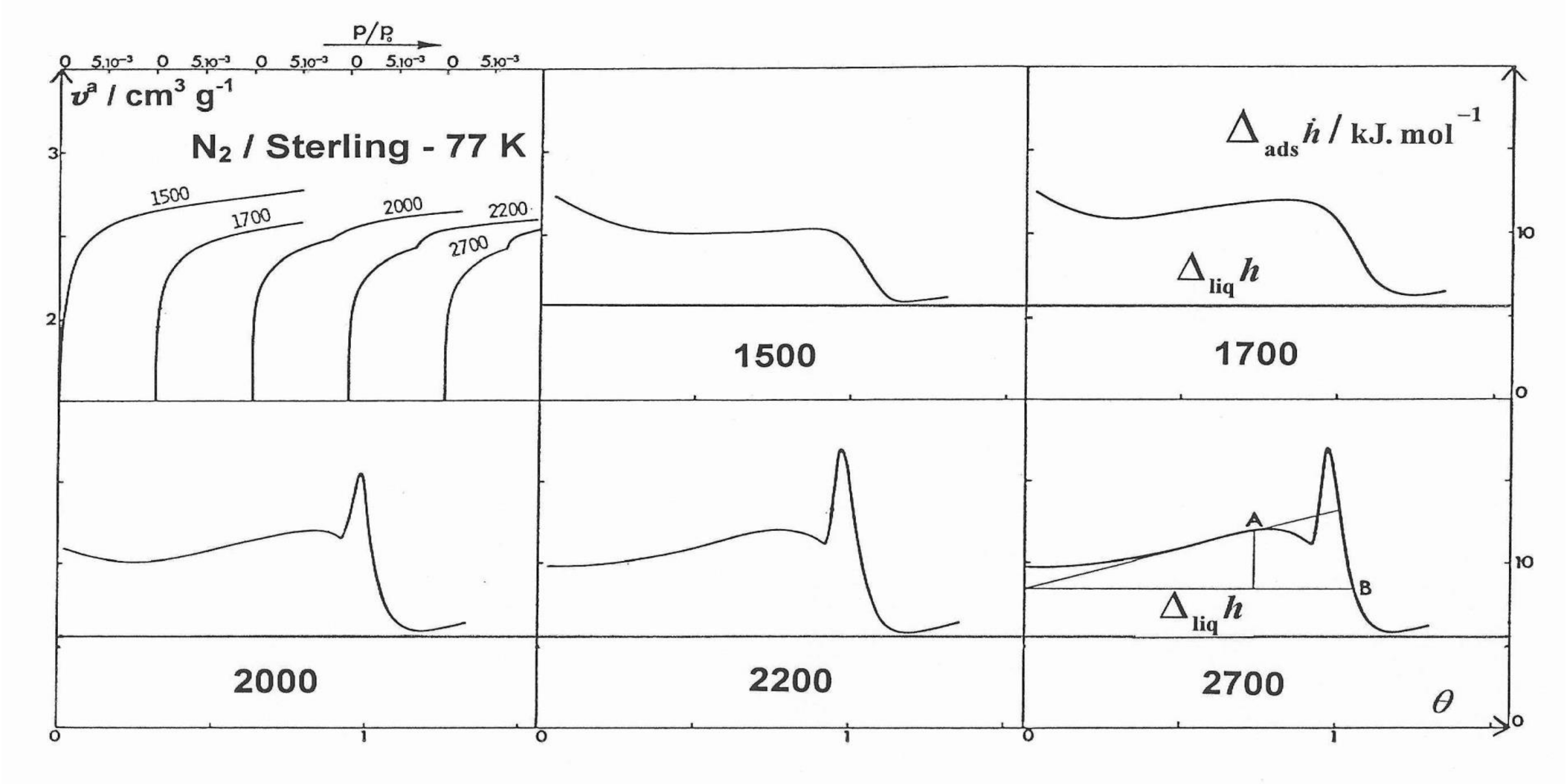
The Gas AdsorptionCalorimeter in its Liquid Cryostat

Completely immersed in either

liquid nitrogen or liquid argon

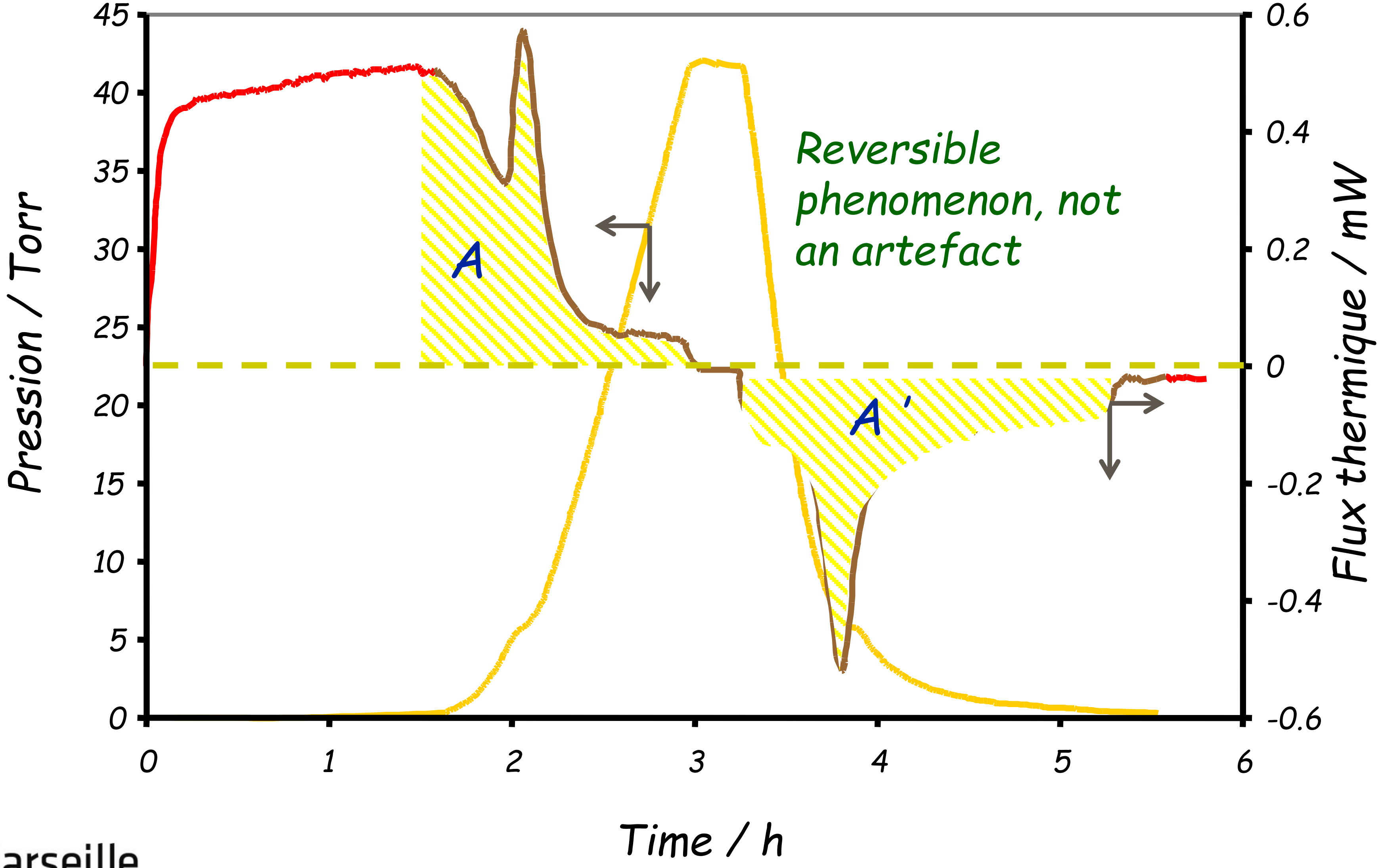
Helium gas (flow rate 1 ml.mn^{1}) carefully cooled in « aluminum tower » (3 m cooling path).

Adsorption calorimetry of N_2 on carbon black at 77 K : as graphitization T increases, exothermic peak (and substep) more and more visible at completion of monolayer



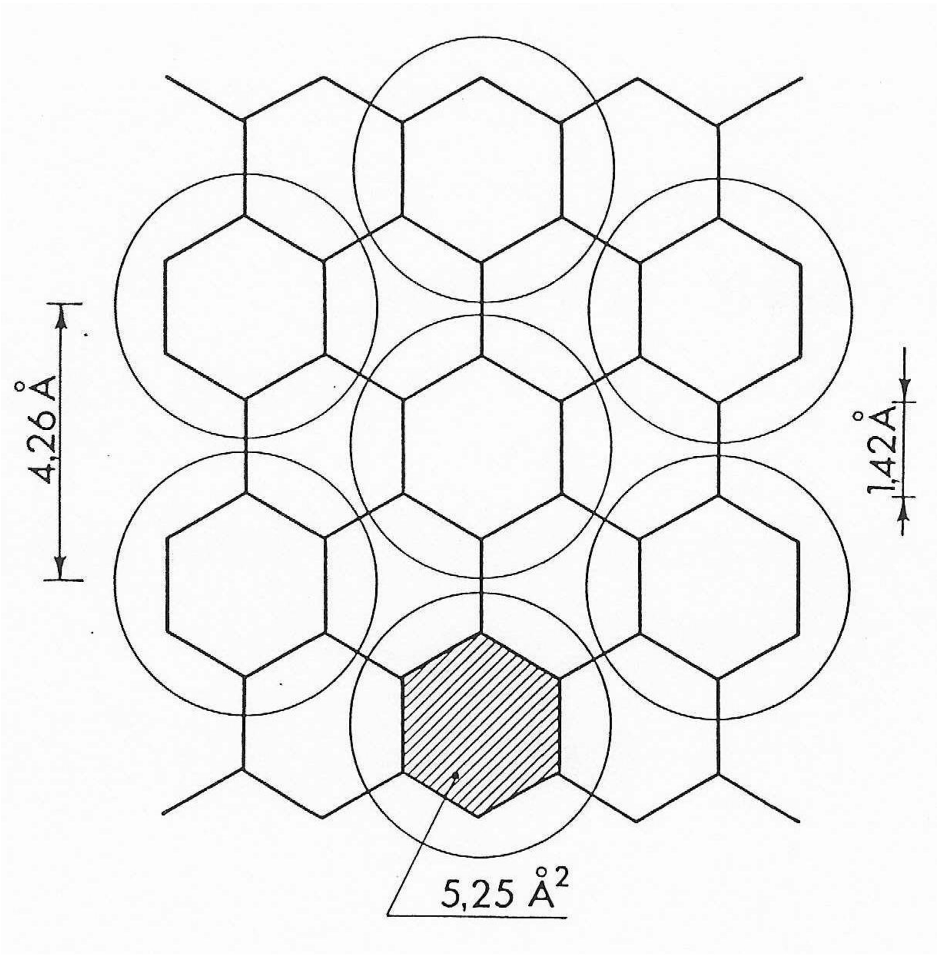
- Is it an artefact due to quasi-equilibrium procedure ?

N_2 / Graphite at 77 K: exothermic peak on adsorption, endothermic on desorption

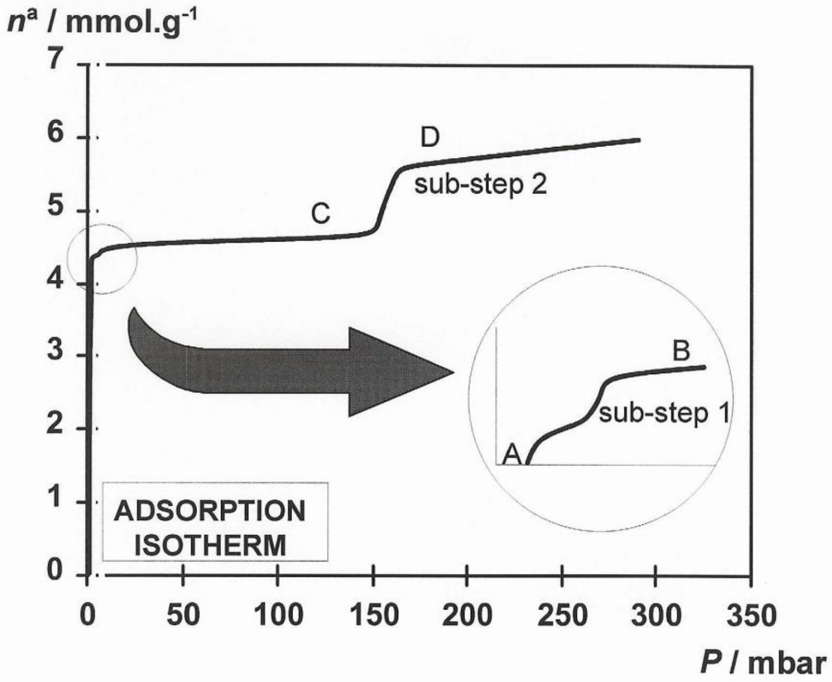


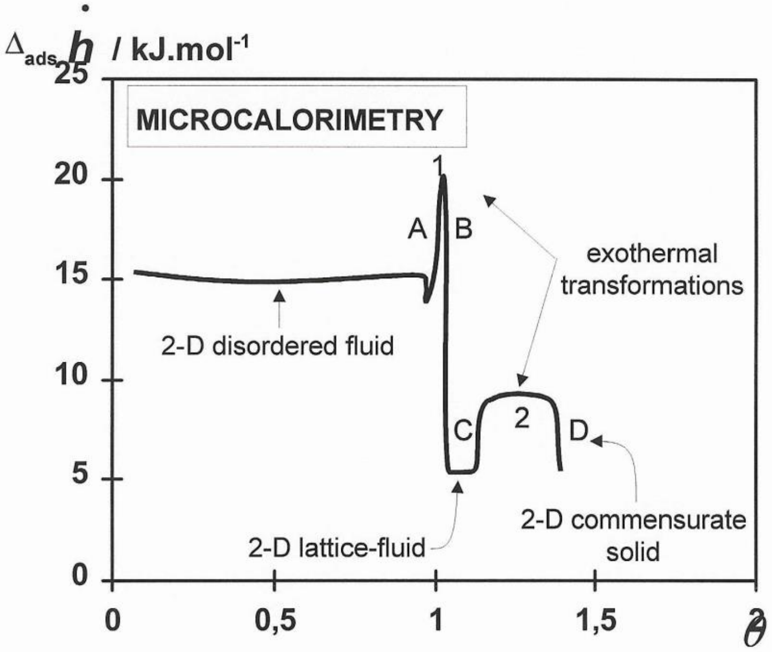
Reversible phenomenon, not an artefact

Explanation of exothermal peak at completion of N_2 monolayer on graphite



- Neutron diffraction shows epitaxial superstructure appearing during occurrence of peak
- Just as if we had sudden freezing of monolayer
- Diffraction parameters correspond to 1 N_2 over 3 graphitic rings *ie* 15.75 A^2
- Hence a precise mode of determination of the surface area of graphite





Nitrogen on Silicalite at 77 K

(P.Llewellyn et al., 1993)

- On adsorption isotherm: 2 substeps
- On curve of differential enthalpy of adsorption: 2 exothermal peaks, for same coverage as substeps
- Neutron diffraction shows peaks correspond to changes in mobility and localisation

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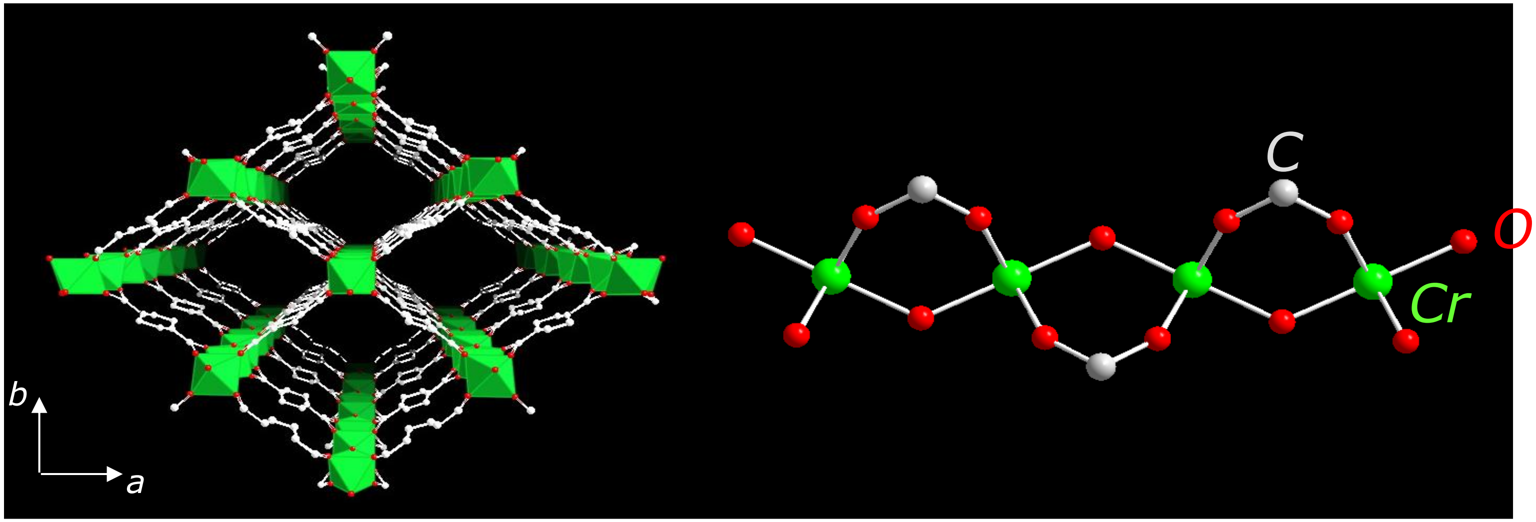
MOF MIL-53 (Cr) : Chromium 1,4-benzenedicarboxylate

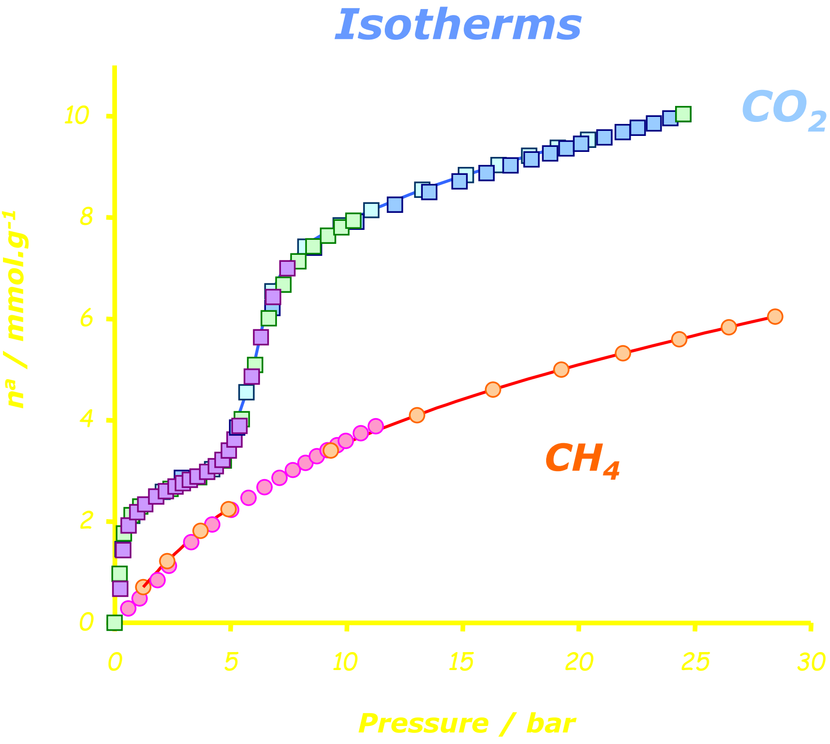
$Cr^{III}(OH)[O_2C–C_6H_4–CO_2]$

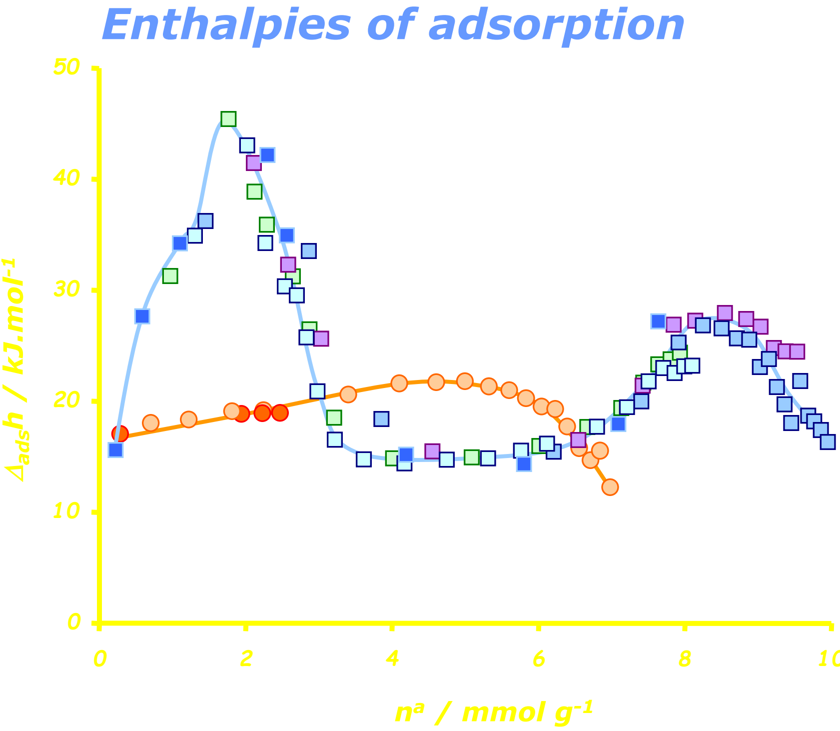


- ✓ Chains of corner-sharing **$CrO_4(OH)_2$** octahedra interconnected by dicarboxylate groups
- ✓ Nanoporous open-framework with empty pores of width ~ 0.8 nm
- ✓ Stable up to 300°C in air

G.Ferey et al., J.Amer.Chem.Soc.,2002

CO_2 vs. CH_4 on (Cr)MIL-53 @ 304K





Explanation: step (isotherm) and peak (enthalpies) correspond to enhanced interaction of CO2 with more compact porous framework. Why ?

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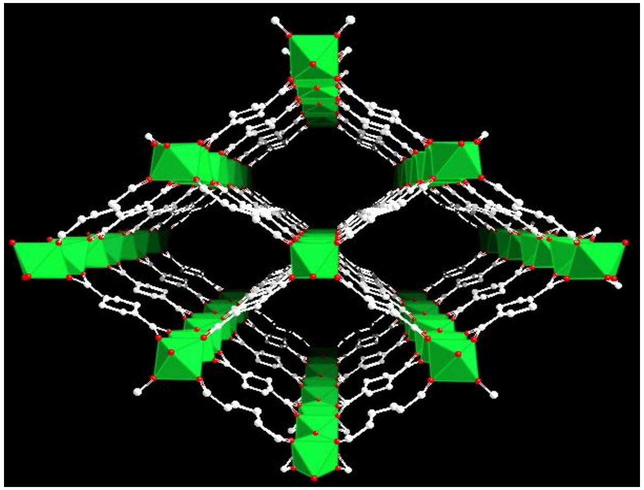
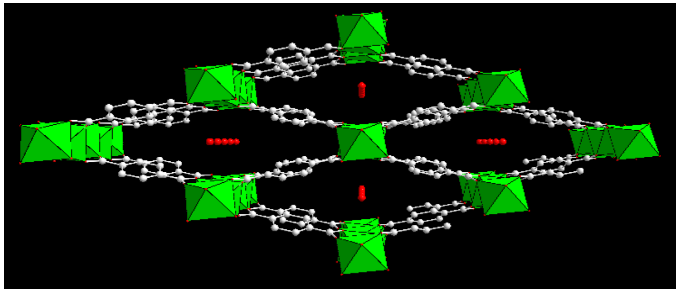
On MIL-53 (Cr), a breathing phenomenon occurs with CO2, like for H2O

Adsorption-desorption process is accompanied by a reversible breathing effect and shrinkage of the pores





Confirmed by synchrotron XRD (structure change) and FTIR (interaction change)

(P.Llewellyn and S.Bourelly,,2008,, submitted to publication)

D/ Three applications of immersion calorimetry

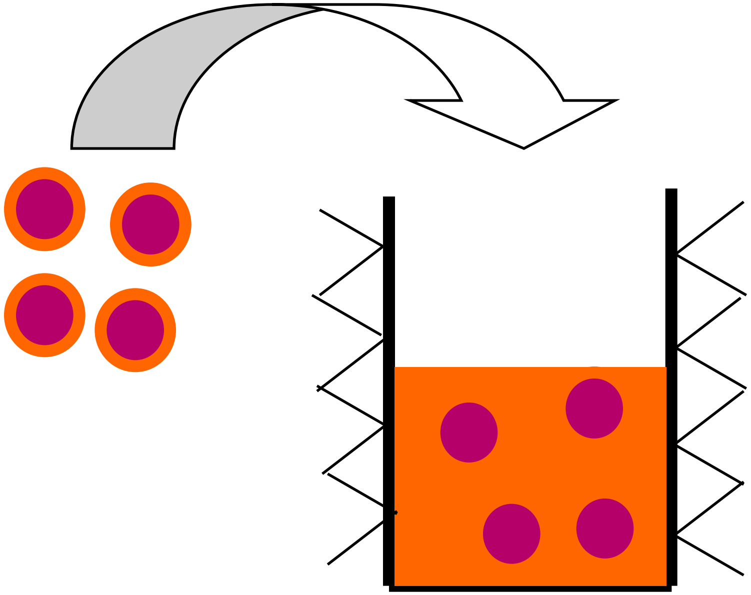
1/ Determination of the non-microporous surface area of adsorbents by the modified Harkins and Jura calorimetric method

2/ The determination of the overall surface area (including microporous) of activated carbons

3/ The "screening" with immersion liquids of different molecular sizes to determine a micropore size distribution or a separation ability

Modified Harkins and Jura 's « absolute » method for the determination of the specific surface area of non-porous powders

1/ Pre-cover powder with only 2 layers of water

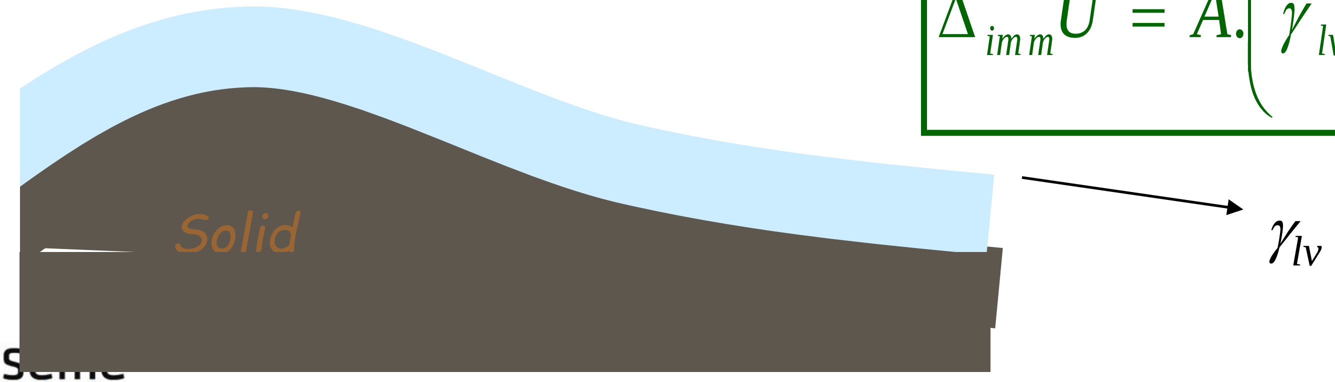


2/ Immerse in water in calorimeter

Disappearance of the water/vapour interface

Liquid film, thick enough to screen high energy sites

$$\Delta_{imm}U = A.\left(\gamma_{lv} - T.\left(\frac{\partial\gamma_{lv}}{\partial T}\right)_A\right)$$



Specific surface area: comparing the modified Harkins and Jura immersion calorimetric method with the BET (N_2)

Powder	Harkins-Jura	BET
Aerosil	**140**	**129**
Alumina	**100**	**81**
Titania	**63**	**57**
Gallium Hydroxide	**21.3**	**21**
Kaolin A	**19.4**	**19.3**
Kaolin B	**19.2**	**12.1**
Quartz	**4.2**	**4.3**
Zinc Oxide	**3.1**	**2.9**
Calcite	**0.8**	**0.6**
Gibbsite	**27**	**24**

Advantages:

- *no assumption about cross section of adsorbed molecule*
- *interesting reference method*

Limitations:

- *requests full wetting of material*
- *time consuming experiment*
- *only assesses « external » area (non-microporous)like the BET*
- *but this limitation is solved by another calorimetric method*

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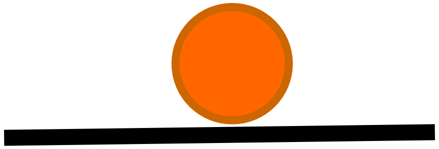
For microporous materials, weakness of BET assumption that area σ covered by a molecule is constant

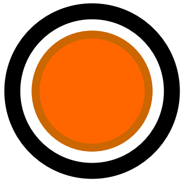
On flat surface, as always assumed by BET



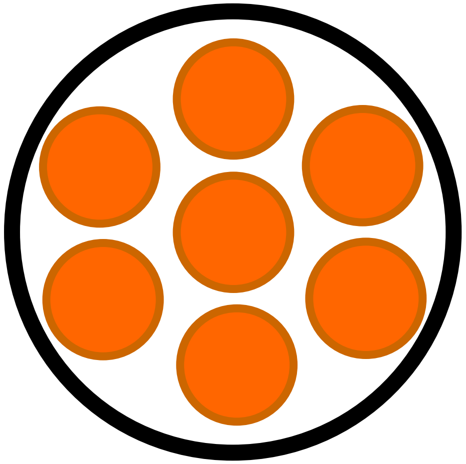
$\sigma = 1$

In cylindrical pores

$\sigma = 4$

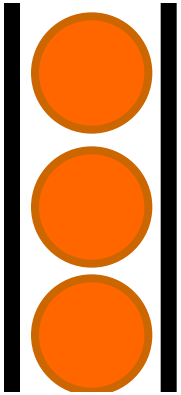


$\sigma = 0{,}85$



In slit-shaped pores

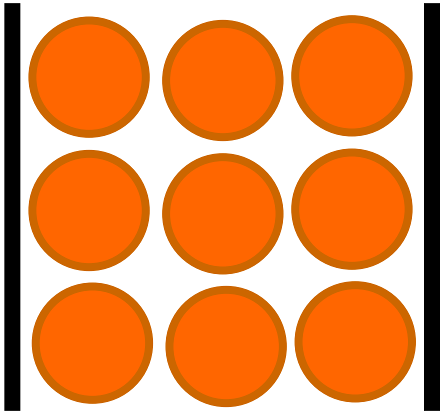
$\sigma = 2$



Ultramicropores

*BET **under**estimates*

$\sigma = 0{,}6$

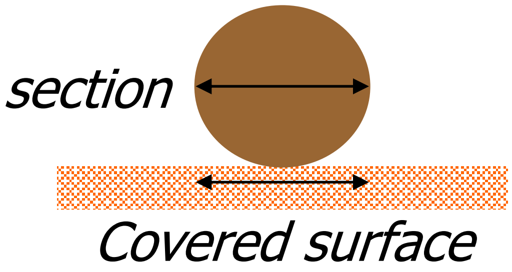


Supermicropores

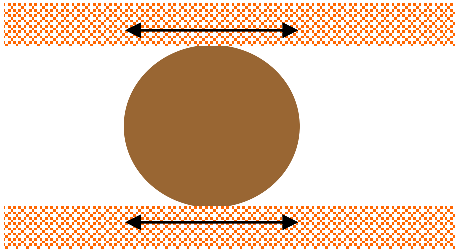
*BET **over**estimates*

σ is the area covered per molecule

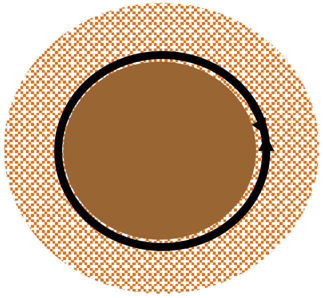
The adsorption potential is proportional to the area covered by one molecule adsorbed



Non porous surface $a_{BET}=a_{real}$
Covered surface = 1 molecular cross section
Interaction energy 1 U°



Slit-shaped micropore: $a_{BET}=a_{real}/2$
Covered surface= 2 molecular cross sections
Interaction energy U=2 U°



Cylindrical micropore : $a_{BET}=a_{real}/4$
Covered surface= 4 molecular cross sections
Interaction energy U=4 U°

(Interaction energies calculated from dispersion forces, Everett and Powl,1976)

For the assessment of the surface area of microporous materials, how calorimetry can help?

- ⌘ Calorimetry is sensitive to the interaction energy
- ⌘ Now, the adsorption potential is proportional to the area covered by one molecule adsorbed
- ⌘ Therefore, the energy of immersion is proportional to the area, even for microporous materials

Hence derivation of surface area a_{imm} accessible by immersion calorimetry in non-polar liquids (non specific interaction, mainly dispersion forces)

$$\mathbf{a_{imm}} = \frac{\Delta_{imm}H(sample)/J\ g^{-1}}{\Delta_{imm}H(ref)/J\ g^{-1}} \cdot a_{BET}(ref)/m^2\ g^{-1}$$

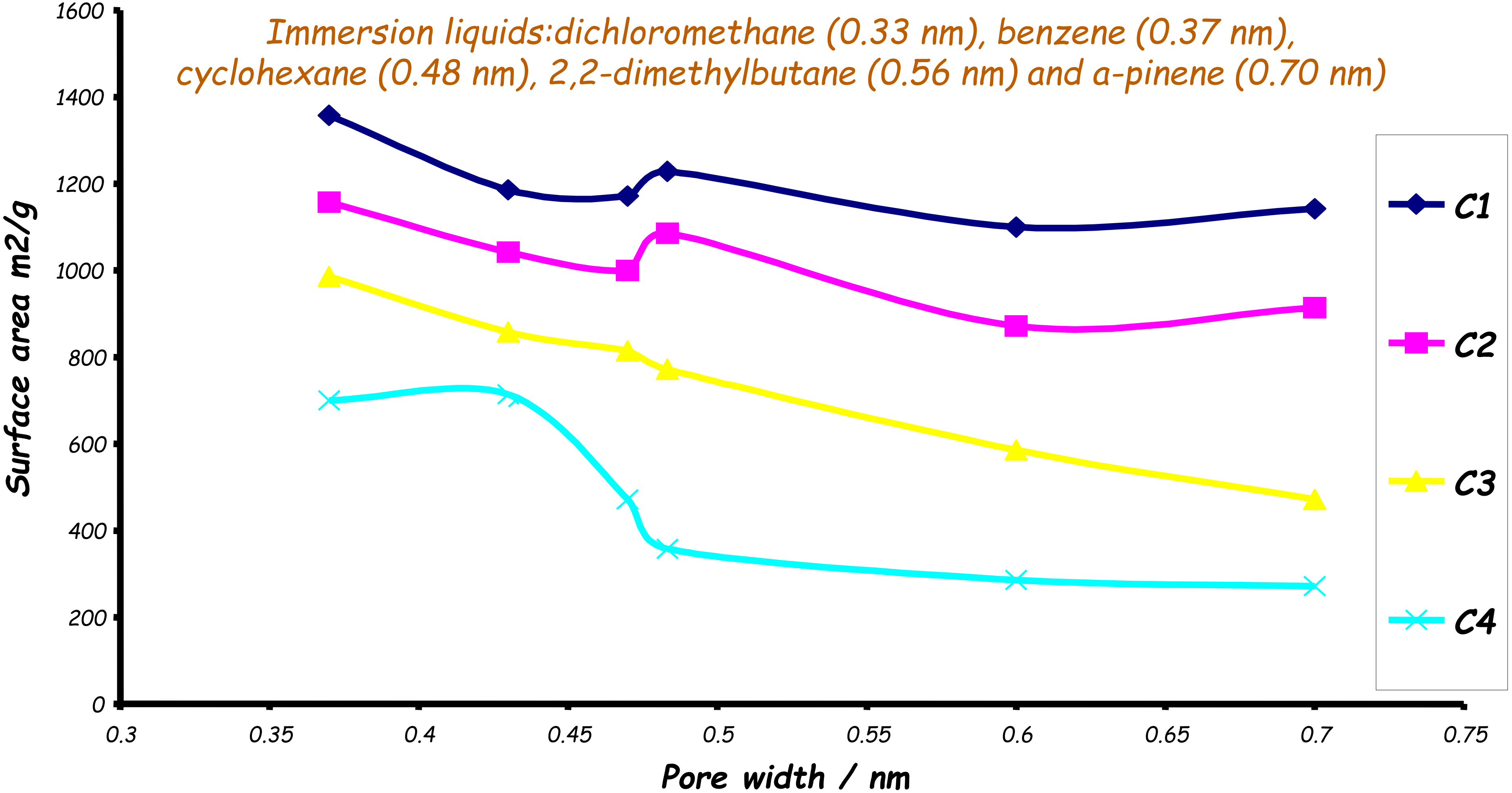
Possible immersion liquids:

Non-polar organics are good candidates. Now, their use is limited those materials they can wet, i.e. essentially carbons

Since the accessibility of micropores depends on size of molecules, screening of micropore size can also be done

Accessible surface area as a function of probe size (= surface area available above a given pore width)

for carbons with increasing activation from C1 to C4
(after Denoyel et al., Langmuir, 1993)



Immersion liquids:dichloromethane (0.33 nm), benzene (0.37 nm), cyclohexane (0.48 nm), 2,2-dimethylbutane (0.56 nm) and a-pinene (0.70 nm)

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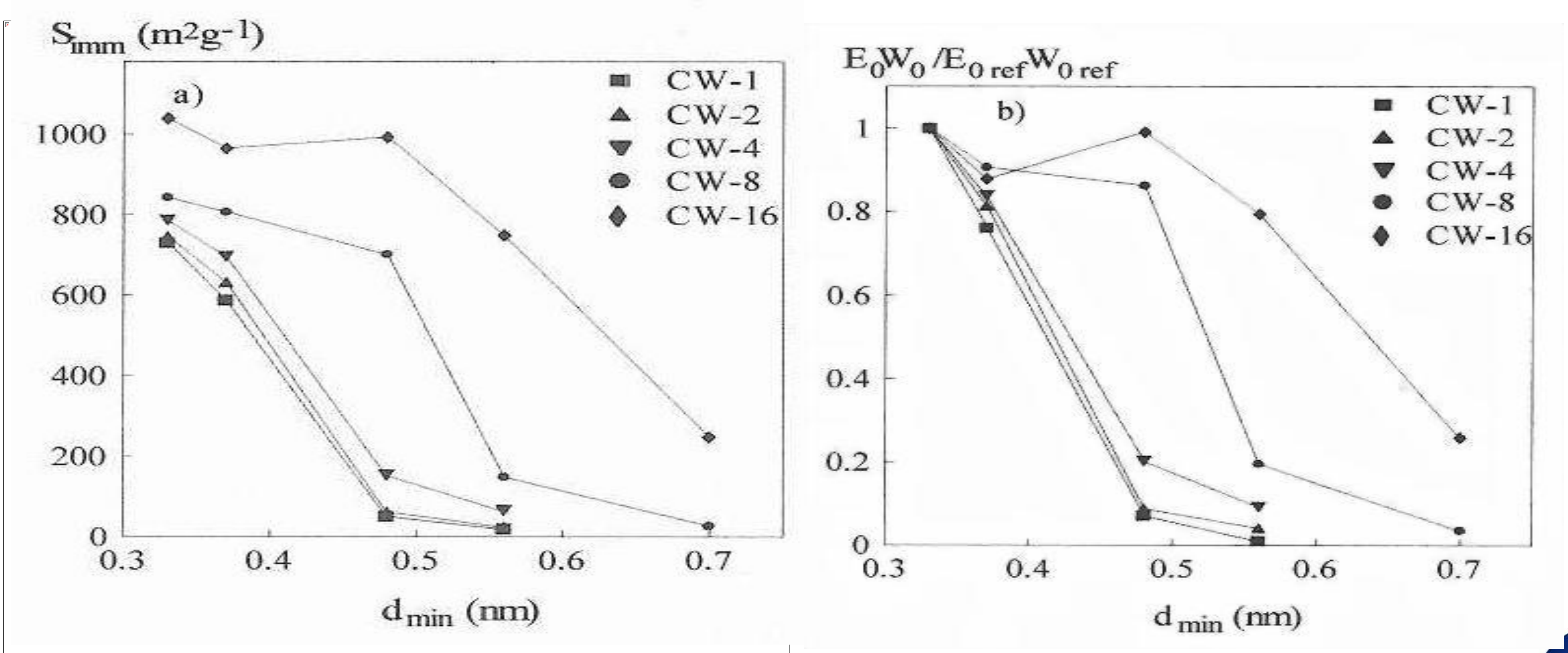
Immersion calorimetry of a series of activated carbons: *area* accessible to molecules of different size (left) and resulting *pore-size distribution* (right)
(after F.Rodriguez Reinoso et al., 2000)

Immersion liquids:dichloromethane (0.33 nm), benzene (0.37 nm), cyclohexane (0.48 nm), 2,2-dimethylbutane (0.56 nm) and α–pinene (0.70 nm)



Conclusions

- Calorimetry is more than 200 years old, adsorption calorimetry started more than 150 years ago, but there is still much to do
- Much work was qualitative (heats). We now must assess energy or enthalpy changes and avoid absolutely the term « heats of adsorption »
- This requires much care in designing, analysing and carrying out the experiment
- Other calorimetric experiments are available for the study of adsorption or adsorbents:
  - Adsorption calorimetry from solutions
  - Thermoporometry to study the freezing of adsorbate in mesopores and derive the pore-size distribution
  - Desorption calorimetry to apply BJH in the macropore range

Marsella: ciudad de 2600 años, donde cresce la calorimetria de adsorcion desde 160 años !