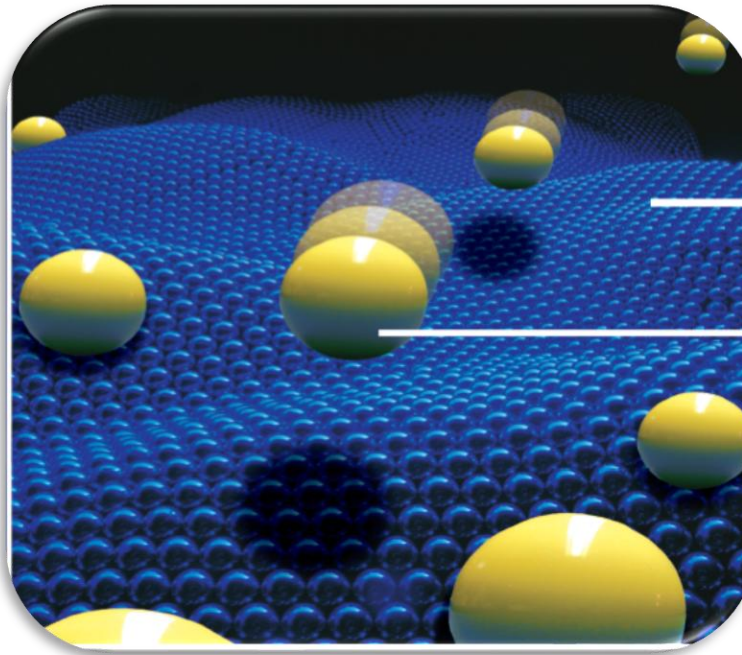


Surface phenomena at the micro and nano scale

Master's Degree in Materials Science



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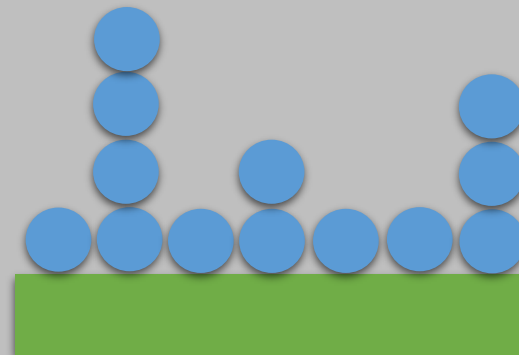
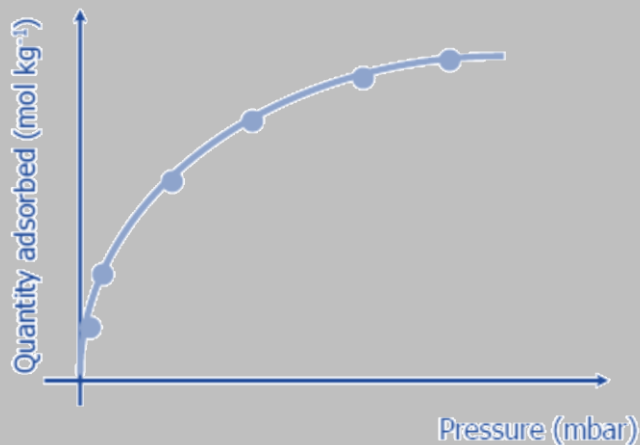
Quantitative Expression of Adsorption: Surface Excess Amount



Adsorption: how can I represent it?



Determination of the Surface Excess Amount



Physical Adsorption on a Planar Surface

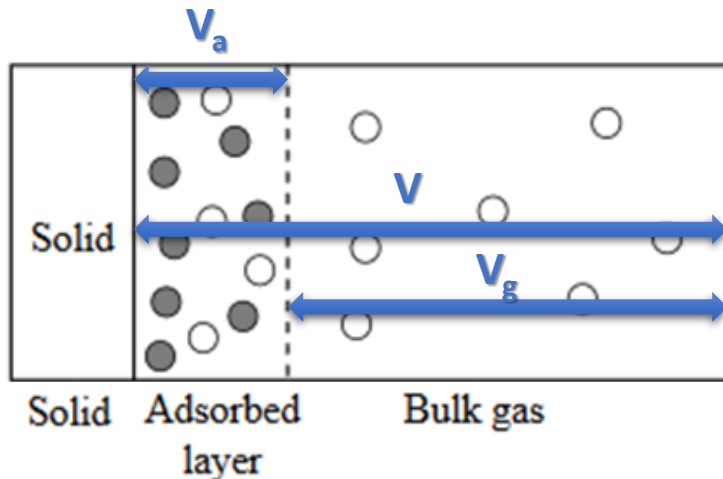
At low T...

At low temperatures (around the boiling temperature of the adsorptive) a monolayer of molecules is formed at pressures far below the saturation pressure (p_0) of the adsorptive and a multilayer of increasing thickness and liquid like density builds up on strongly adsorbing substrates as p_0 is approached.

In this low-temperature region, the adsorption can be analyzed in terms of a two-phase model, in which an adsorbed phase coexists with the bulk adsorptive phase:

$$n = n_a + n_g$$

$$V = V_a + V_g$$



n = total amount of gas is given by the amount adsorbed and the amount remaining in the gas phase.

V = the overall macroscopic volume accessible to the gas molecules

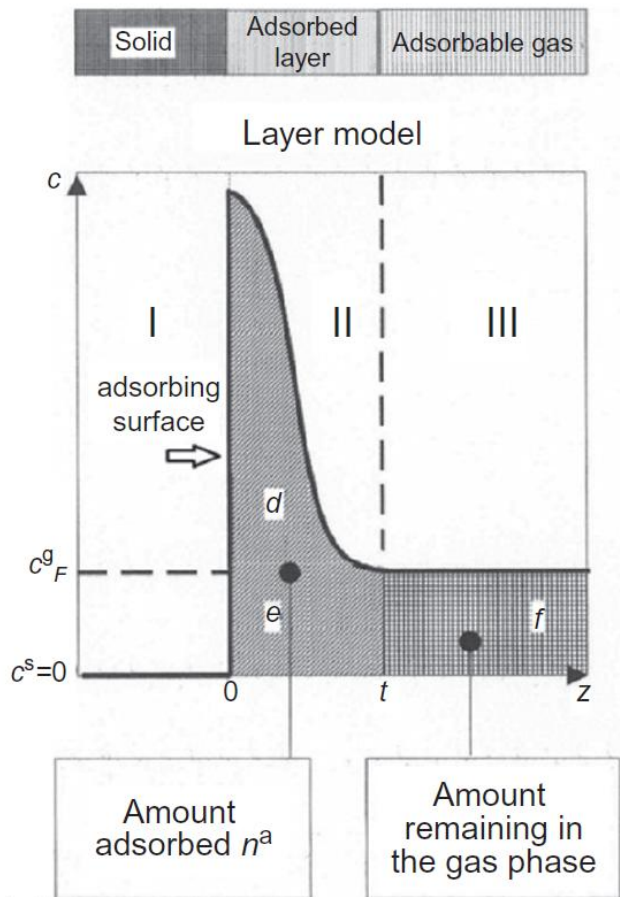
n_a and V_a = amount and volume of the adsorbed phase

n_g and V_g = amount and volume of the gas phase(adsorptive)

Physical Adsorption on a Planar Surface

Concentration of the adsorbable component decreases progressively with increased distance (z) from the adsorbent surface; at a distance equal to the thickness t of the adsorbed layer, this concentration reaches the constant value c^g of the gas phase.

Gas Concentration Profile



Zone I

- Occupied only by the adsorbent.
- $c_s = 0$ (c_s - adsorptive concentration in the solid).

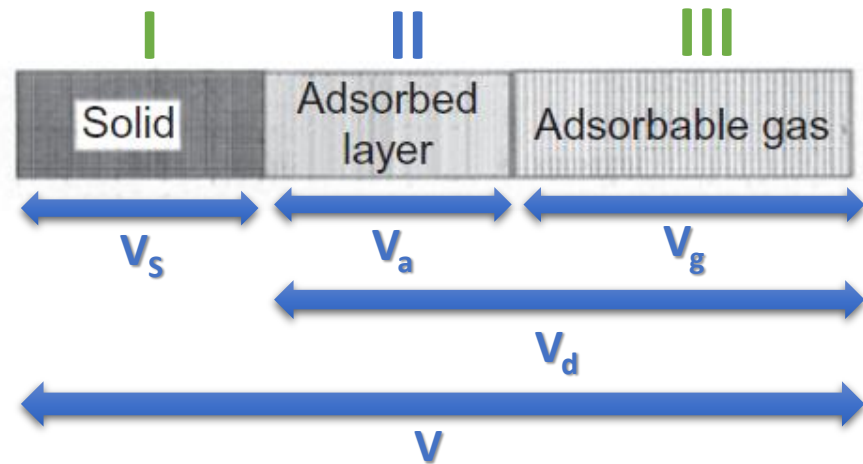
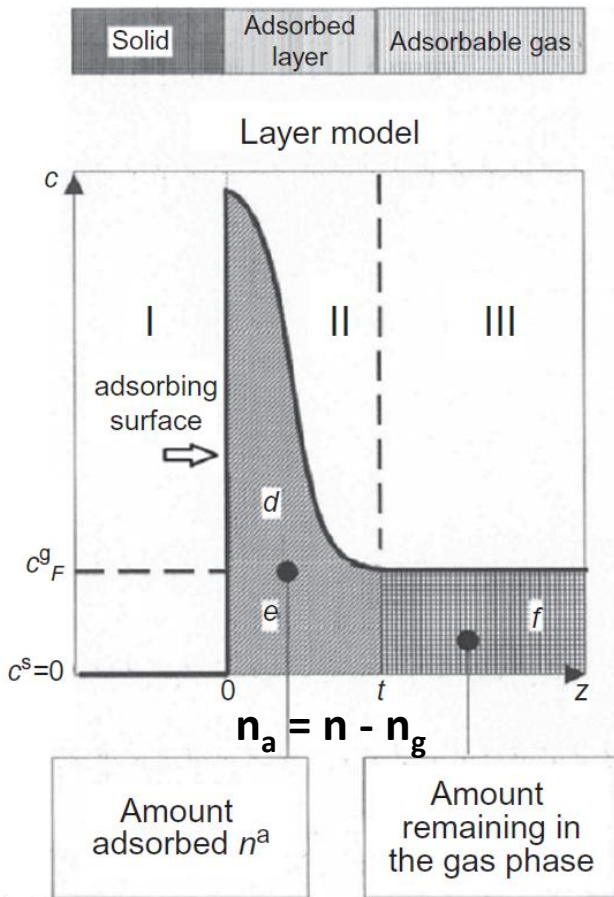
Zone II

- The “**adsorbed layer**”, within the limits $z = 0$ and $z = t$
- $c > c_g$ (the local concentration is higher than the concentration of the gas in zone III and is dependent on z).

Zone III

- The adsorptive is at sufficient distance from the solid surface to have a **uniform concentration**.
- For $z > t$, c_g is **constant** (c_g - adsorptive concentration in the bulk gas).

Physical Adsorption on a Planar Surface



- The **void volume V_s** is the volume of the solid which is impenetrable for the adsorptive gas. It is typically measured by helium pycnometry.
- The **dead volume V_d** is the difference between the total system volume ($V = V_s + V_a + V_g$) and the void volume: $V_d = V - V_s$

The amount of adsorbed gas n_a is equivalent to area (d+e)

The exact evaluation of n_a requires a knowledge of the variation of the local concentration, c , with respect to z (not easy to achieve).

Physical Adsorption on a Planar Surface

At high T...

The model of an adsorbed phase becomes progressively unrealistic:

- The tendency of molecules to accumulate near the surface of the adsorbent becomes less pronounced.
- Due to the weaker physisorption at elevated temperatures, higher pressures have to be applied in order to reach significant surface coverage.

The density of the bulk gas phase is no longer negligible compared to the density near the surface and a clear separation between adsorbed phase and bulk gas phase is not possible!

The definition of the adsorbed amount, becomes problematic and other concepts have to be applied...

Adsorbed Amount as Surface Excess*

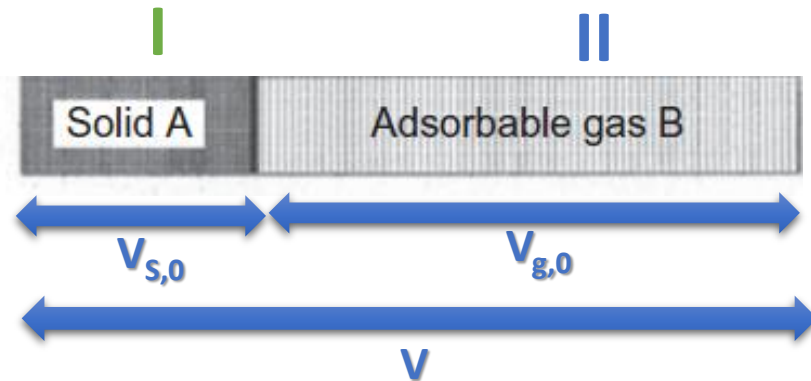
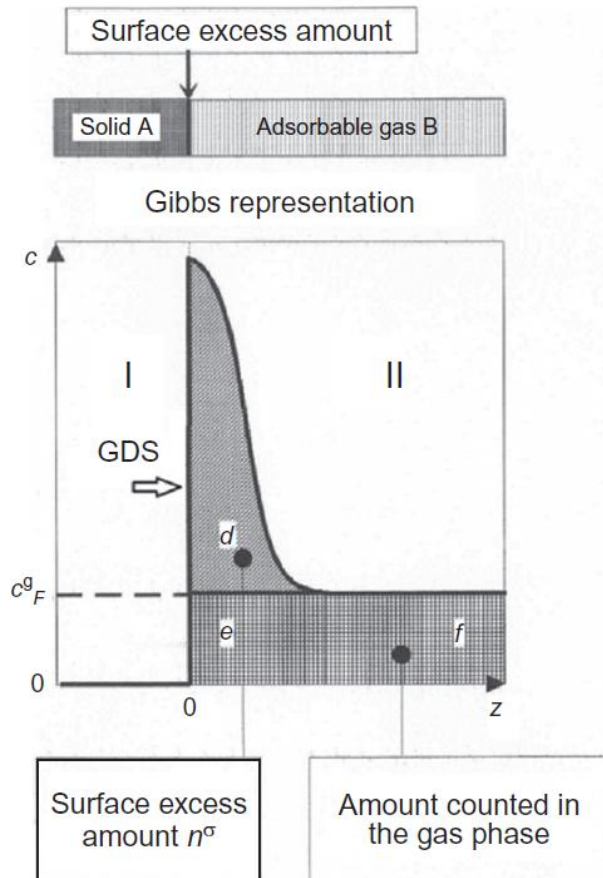
* Quantity actually measured by using volumetric or gravimetric techniques



Gibbs Dividing Surface (GDS)

Quantitative Expression of Adsorption

Gibbs compared the real system with a reference system made of two zones, divided by an imaginary surface (the GDS) placed parallel and close to the adsorbent surface. The reference system occupies the same total volume V of the real system. In the Gibbs model, the chemical components of the bulk phases (solid and adsorptive) remain unchanged except when approaching the dividing surface.



Zone I

- Occupied only by the adsorbent ($V_{s,0}$).
- $c^s = 0$ (c^s - adsorptive concentration in the solid).

Zone II

- The concentration of the adsorptive remains constant in the volume $V_{g,0}$ up to the GDS.

Surface excess amount (n_{ex})

$$n_{ex} \text{ (area d)} = n \text{ (areas d+e+f)} - n_{g,0} \text{ (areas e+f)}$$

Surface Excess Amount

Surface excess is the difference between the total amount n of the adsorptive in volume V and the amount which would be present in the volume $V_{g,0}$ of the reference system if the concentration c_g of the adsorptive would be constant and equal to that of the bulk gas up to the GDS.

The surface excess is the amount of adsorptive present in the adsorbed layer in excess of the bulk gas density.

For p up to 1 bar



$$n_a \approx n_{ex}$$

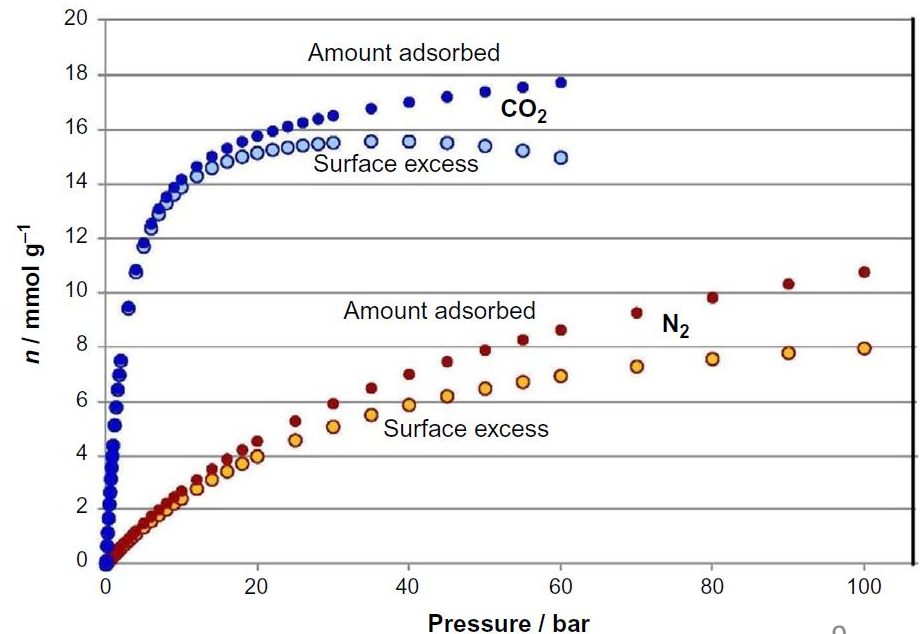
For p above 1 bar



$$n_a \neq n_{ex}$$

Concentration of the adsorptive in the gas phase is no longer negligible as compared to its concentration in the adsorbed phase.

Concentration of the adsorptive in the gas phase is much lower (i.e. negligible) than that of the adsorbed phase.



Surface Excess Amount

The surface excess is the quantity measured by volumetric or gravimetric techniques.

- Data are presented as a **specific excess amount** expressed in respect of the mass:

$$n^* = \frac{n_{\text{ex}}}{m_s}$$

where m_s is the adsorbent mass.

- It is also common to present the excess adsorption as a weight percent:

$$n^*(\text{wt}\%) = \left(\frac{m_{\text{ex}}}{m_s} \right) \times 100$$

where m_{ex} is the surface excess mass.

Adsorption: how can I represent it?

The adsorbed amount (**as surface excess**) of a specific gas-solid system can be expressed as:

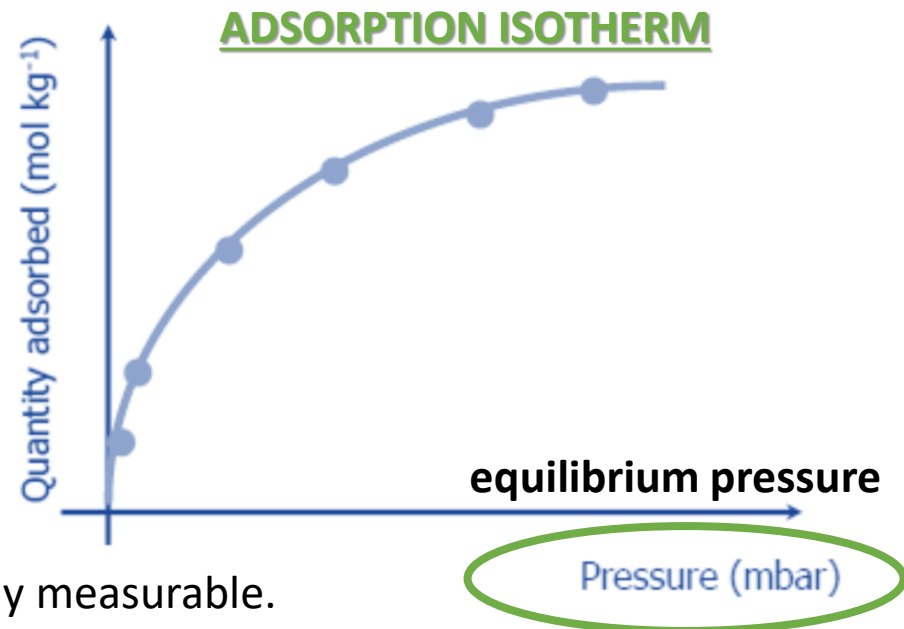
- **Moles of adsorbed gas (n_a)** per unit mass of the adsorbing solid (mmol/g or mol/kg)
- **Volume of adsorbed gas (V_a) in STP** conditions per unit mass of the adsorbing solid (cm³/g)

The adsorbed amount (n_a) is dependent on the equilibrium pressure (p_{eq}), the temperature (T) and the nature of the gas–solid system.

$$n_a = f(p, T, \text{gas}, \text{solid})$$

Graphically we can represent it as:

- **ISOTHERM** $\rightarrow n_a = f(p)_T$
- **ISOBAR** $\rightarrow n_a = f(T)_p$
- **ISOSTERE** $\rightarrow p = f(T)_{n_a}$



Isotherms are the adsorption curves more easily measurable.

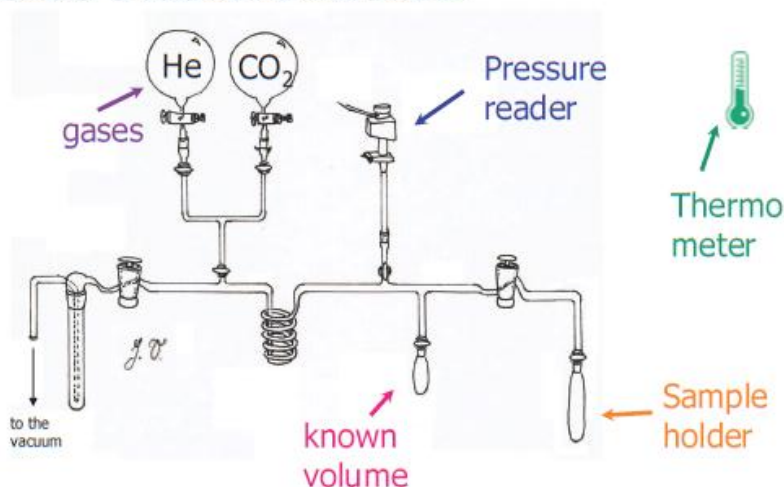
Determination of the Surface Excess Amount

The **surface excess amount can be measured directly** and plotted against the equilibrium pressure (or the relative pressure p/p_0 , where p_0 is the saturation pressure) to build an **adsorption isotherm**.

Two main methods:

- **Adsorption micro-gravimetry:** this method is based on the measurement of the adsorbent mass and of its variation upon gas adsorption (Δm) by means of a vacuum microbalance.
- **Gas adsorption volumetry:** this method is based on the measurement of the gas pressure in a calibrated, constant volume, at a known temperature.

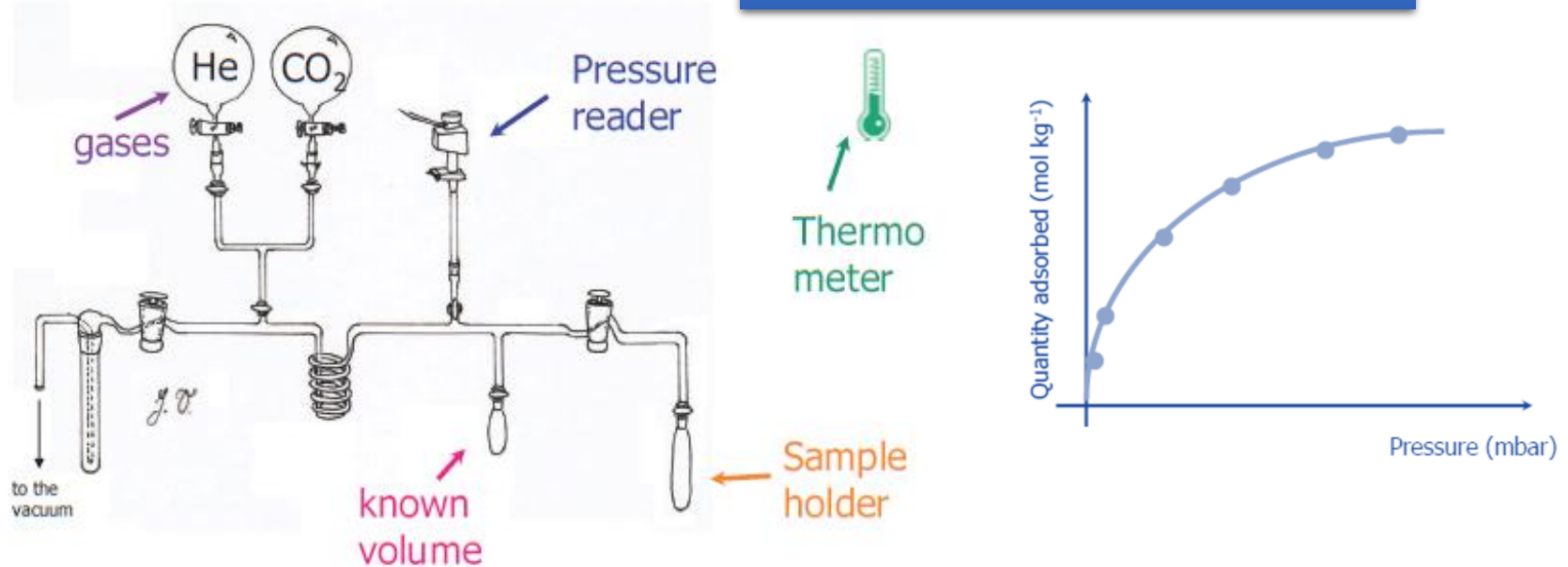
A scheme of a volumetric instrument:



- ❖ A discontinuous (or point-by-point) experimental procedure.
- ❖ Adsorption measured up to the atmospheric pressure (1 bar)

Gas Adsorption Volumetry Apparatus

A scheme of a volumetric instrument:

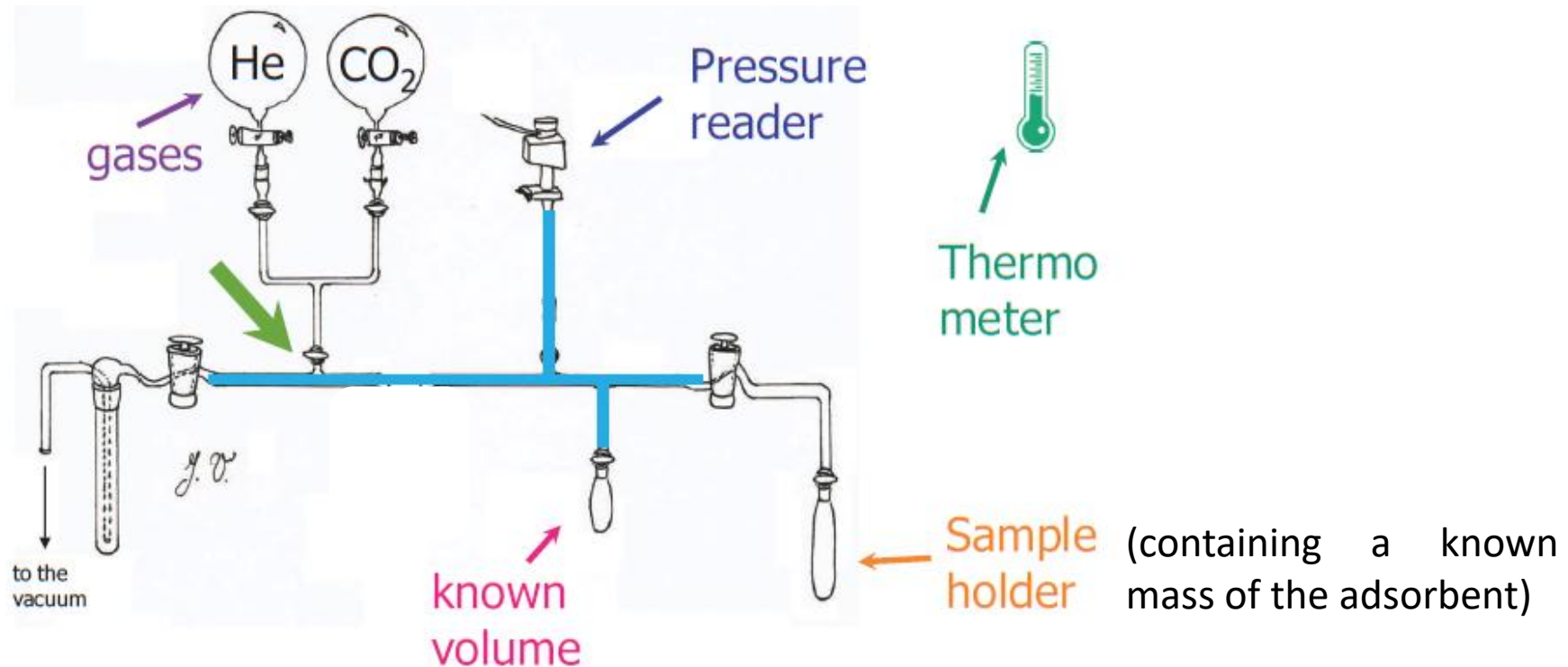


A pressure of gas p_1 is dosed on the sample. When equilibrium is reached (no more variation in the pressure reading) the final pressure p_2 is recorded.

Because all the volumes inside the instrument are known, $(p_1 - p_2)$ is translated to moles of adsorbed gas using a gas law.

- ❖ **The sample is activated** (atmospheric adsorbates are removed from the surface by applying vacuum and heat).
- ❖ **Sample mass is measured.**

Gas Adsorption Volumetry Apparatus

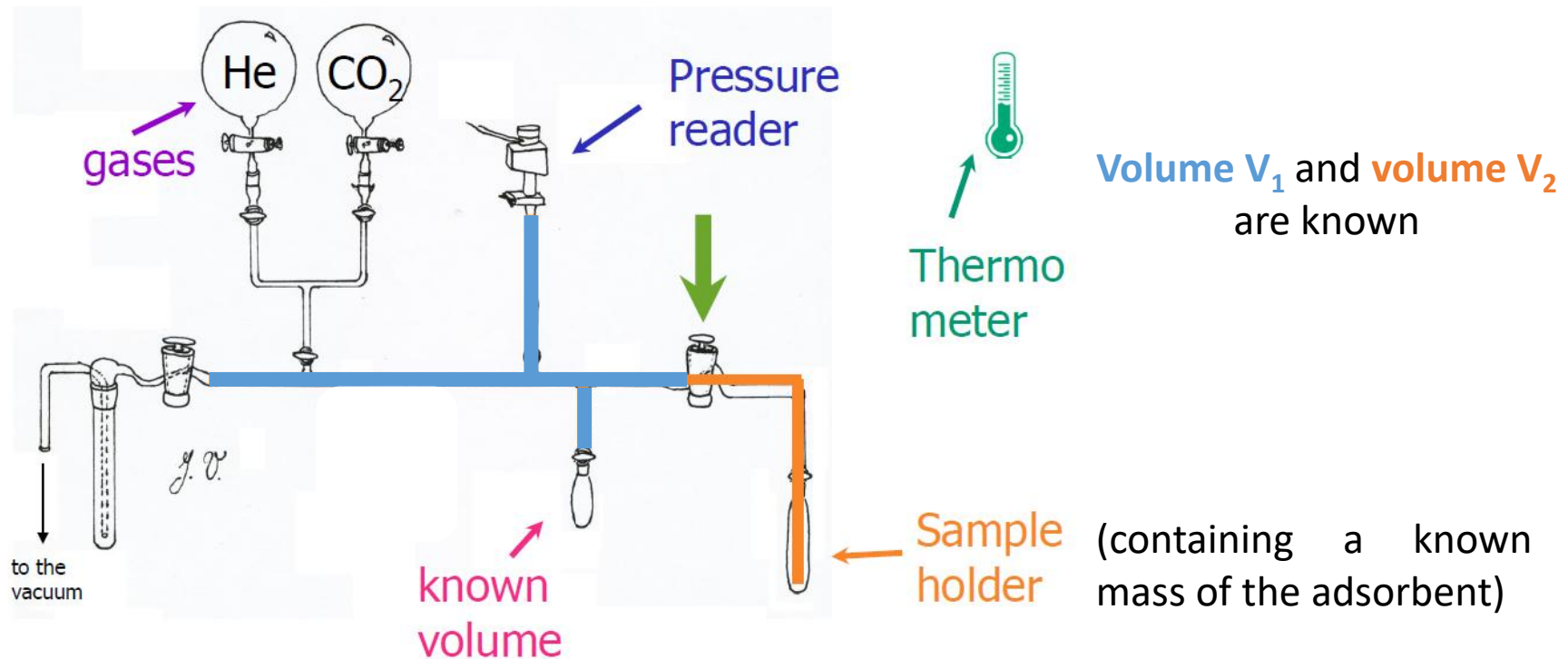


A point-by-point experimental procedure. How do we measure a point?

1. Open the **tap**.
2. Open the balloon (for example CO₂). A pressure p_1 of the gas is dosed in **volume V_1** . Close the balloon.
3. Close the **tap**. Take note of p_1 and the temperature T_1 .

We have a pressure p_1 in the volume V_1

Gas Adsorption Volumetry Apparatus



A point-by-point experimental procedure. How do we measure a point?

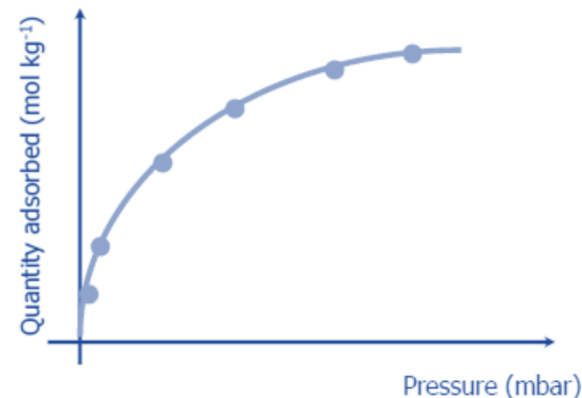
4. Open the **tap** and expand the gas from **volume V_1** to **volume V_2** .
5. Wait until the pressure does not change anymore (equilibrium is reached).
6. Take note of p_2 (**equilibrium pressure**) and temperature T_2 .

We have a pressure p_2 in the volume $V_1 + V_2$

How do we build an isotherm?

By repeating what reported in previous slides (see points from 1 to 6), i.e. sending in contact with the adsorbent incremental doses of the adsorptive and waiting each time for equilibrium.

p_1	T_1	p_2	T_2
5.3	25.3	2.1	25.3
7.2	25.4	4.1	25.4
10.3	25.2	6.3	25.2
20.0	25.6	14.0	25.6



After adsorption equilibrium has been established, the **amount adsorbed for each dose** is calculated from the change in pressure ($p_1 - p_2$) and from the application of the **ideal gas law**:

$$PV = nRT$$

We can apply the ideal gas law if:

- We are working at low pressures.
- We are far from the condensation temperature of the adsorptive gas.

or, alternatively, from a **real gas law** when required by the gas properties in the pressure and temperature range.