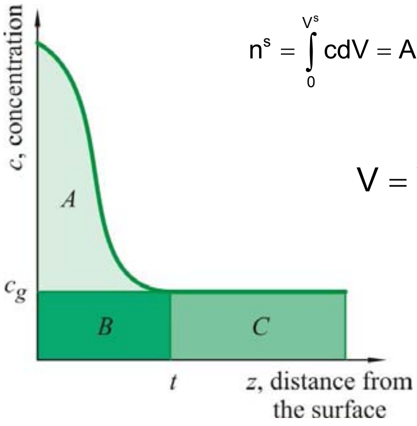
## Quantitative description of the adsorption

$$A_s = \frac{\text{surface area}}{\text{mass of solid}}$$



$V^s = A_s t$

$$n^s = \int_0^{V^s} c\,dV = A_s \int_0^t c\,dz \qquad n = A_s \int_0^t c\,dz + c^g V^g$$

$n^s = n - c^g V^g$ **adsorbed amount**

$$V = V_{solid,0} + V^{g,0} = V_{solid} + V^s + V^g$$

$V^{g,0} = V^g + V^s$

$n^\sigma = n - c^g V^{g,0}$ **adsorbed excess**

$n^\sigma = n - c^g V^g - c^g V^s$

$n^s = n^\sigma + c^g V^s$

$n^s \approx n^\sigma$ **if $c^g$ is low**

$V^s << V^g$

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## Thermodynamic state functions

$$U^\sigma = U - U_g - U_{szil}$$

$$H^\sigma = H - H_g - H_{szil}$$

$$S^\sigma = S - S_g - S_{szil}$$

$$F^\sigma = F - F_g - F_{szil}$$

F = U-TS

## Thermodynamic condition of the adsorption equilibrium

Adsorption: $dn^\sigma > 0$ $\qquad n^\sigma = n - n^g$

$$\left(\frac{\partial F}{\partial n^\sigma}\right)_{T,V,A_s,n} = 0 \qquad F^\sigma = F - F^g - F^s$$

$$\left(\frac{\partial F}{\partial n^\sigma}\right)_{T,V,A_s,n} = \left(\frac{\partial F^\sigma}{\partial n^\sigma}\right)_{T,A_s} + \left(\frac{\partial F^g}{\partial n^\sigma}\right)_{T,V} + \left(\frac{\partial F^s}{\partial n^\sigma}\right)_{T,A_s} = 0$$

0 (physisorption)

In a closed system: $dn = dn^\sigma + dn^g = 0$

$$\left(\frac{\partial F^\sigma}{\partial n^\sigma}\right)_{T,A_s} = -\left(\frac{\partial F^g}{\partial n^\sigma}\right)_{T,V} = +\left(\frac{\partial F^g}{\partial n^g}\right)_{T,V}$$

$$\mu^\sigma = \mu^g$$

Chemical potential

## Physisorption vs Chemisorption

| PHYSISORPTION | CHEMISORPTION |
|---|---|
| WEAK, LONG RANGE BONDING<br>Van der Waals interactions | STRONG, SHORT RANGE BONDING<br>Primary chemical bond involved. |
| NOT SURFACE SPECIFIC<br>Physisorption takes place between all molecules on any surface providing the temperature is low enough. | SURFACE SPECIFIC<br>E.g. Chemisorption of hydrogen takes place on transition metals but not on gold or mercury. |
| $\Delta H_{ads}$ = 5 ….. 50 kJ mol-1 | $\Delta H_{ads}$ = 50 ….. 500 kJ mol$^{-1}$ |
| Non activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage. | Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption. |
| No surface reactions. | Surface reactions may take place:- Dissociation, reconstruction, catalysis. |
| MULTILAYER ADSORPTION | MONOLAYER ADSORPTION |

Electron transfer

# Adsorption at S/G interfaces

Always occurs when a solid surface is exposed to a gas phase

**Separation techniques**

**Environmental processes**

**Protection of the environment**

**Gas separation and purification**

**Analytical chemistry**

**Materials science**

**Characterisation of solid surfaces**

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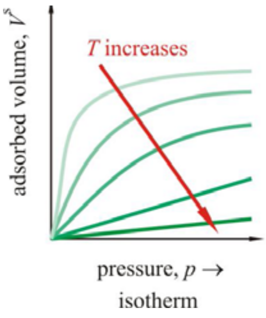
## Quantitative description of S/G adsorption



**Adsorption occures on the whole accessible surface**

Most often measured:

$$m^s, n^s, V^s_{(p,T)} = f(p)_T \qquad n^s = f(p)_T$$

# Steps for Measurement

1. Sample Preparation

2. Data Collection (Adsorption Analysis)

3. Interpretation

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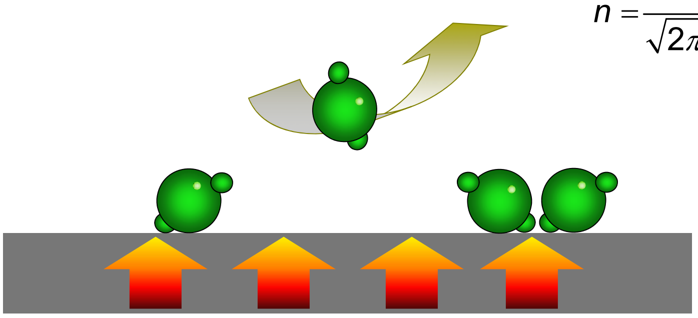
## 1. Sample preparation

$$n = \frac{p}{\sqrt{2\pi mkT}}$$



Ambient air, 25 °C

$10^{15}$ surface atom/cm$^2$

→ ~ $10^8$ collision/s

$3\times10^{23}$ collision/cm$^2$s

- removal of surface moisture, pollution
- vacuum
- temperature – heat resistancy of the materials
- sample size

## Pure solid surface

$$n = \frac{p}{\sqrt{2\pi mkT}}$$

Ambient pressure, 25 °C  $3\times10^{23}$ collision/cm$^2$s

$10^{15}$ surface atom/cm$^2$

→ ~ $10^{8}$ collision/s

~ $10^{-8}$ ambient  $4\times10^{14}$ cm$^{-2}$s$^{-1}$

1 collision within 3 s

~ $10^{-12}$ ambient  $10^{11}$ cm$^{-2}$s$^{-1}$

~ $10^{-14}$ ambient  $10^{9}$ cm$^{-2}$s$^{-1}$

1 collision within $10^{3}$-$10^{5}$ s

The vacuum as medium

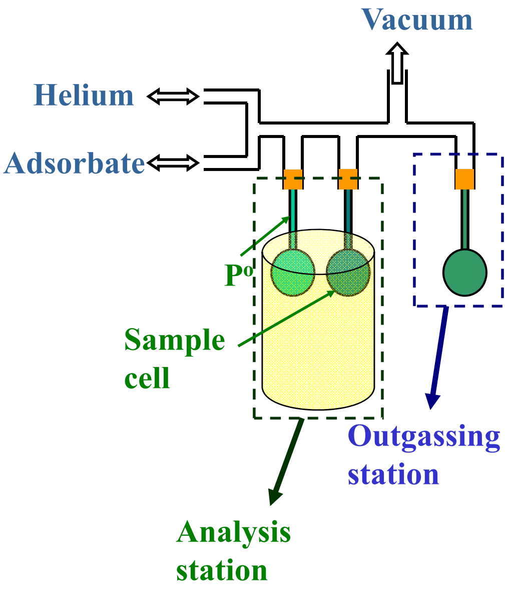
$10^{-4}$ Pa  1 collision/ ~ 1 m free path

## 2. Data collection methods

### static methods: – VOLUMETRIC

### – gravimetric

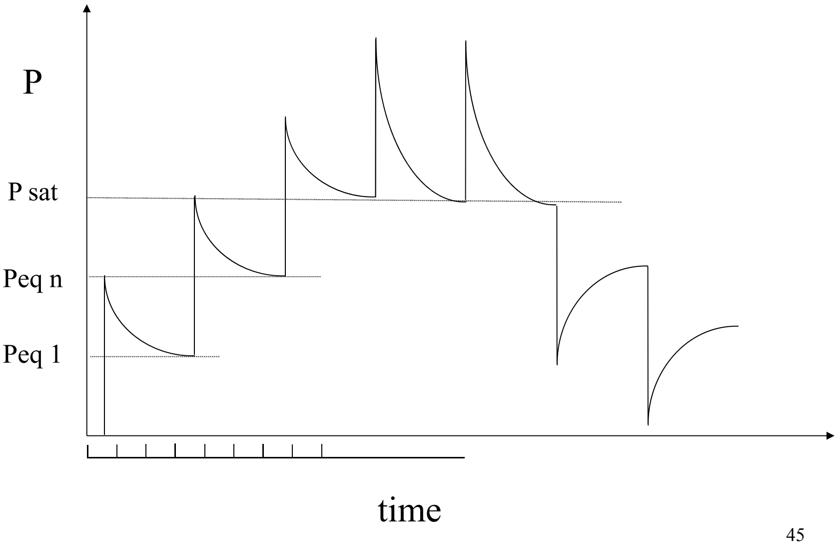
Automatic commercial instruments



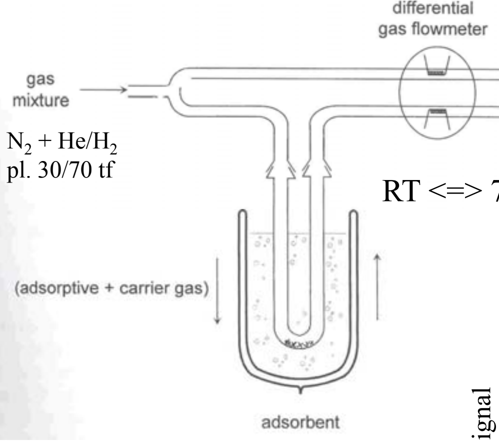
- Surface contamination is removed by application of:
    - Temperature
    - Flowing gas (helium or nitrogen)
    - Vacuum
- Backfill can be done using helium or adsorbate gas.
- According to IUPAC standards, porous materials should be outgassed for **at least 16 hours**.

Mass of the sample

## Criteria of equilibrium pressure



# Dynamic method



$N_2$ + He/$H_2$
pl. 30/70 tf

RT <=> 77 K

1- Calibration peak
2- transfer to liquid $N_2$
3- Adsorption peak
4- transfer to water
5- desorption peak