Lecture 9

Solid surface:
Adsorption and Catalysis

In this lecture:

- We will consider case of adsorption of small uncharged molecules to the solid-gas interface
- Adsorption is described by adsorption function

$$\Gamma = f(P,T)$$

number of adsorbed moles
per unit area

- Will discuss derivation of adsorption isotherm equations for two models

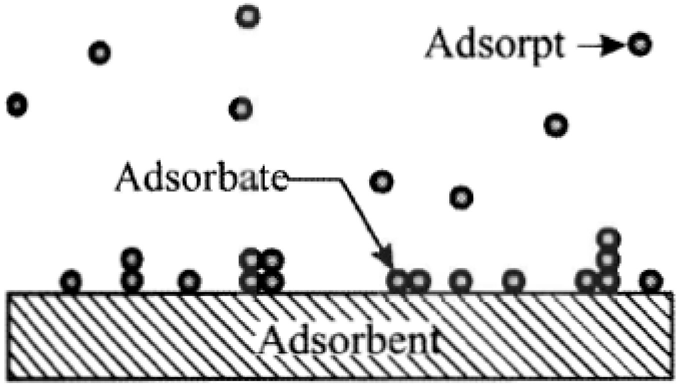
Adsorption

$$\Delta G = \Delta H - T\Delta S$$

ΔG_{ads} should be **negative** (spontaneous process)

ΔS_{ads} is **negative** (reduced freedom)

- ΔH should be negative for adsorption processes (driven by enthalpy)
- Adsorption processes are important for:
  - heterogeneous catalysis (first step of catalysis)
  - characterization of porous materials



Physical and Chemical Adsorption

- **physical adsorption (physisorption):**
  - involves only molecular interaction forces,
  - no chemical bonds formed, $-\Delta_{ads}H < 20$ kJ/mol
  - similar to condensation,
  - easily reversible (e.g. when lowering the pressure)
  - many layers can be formed
  - adsorbate is mobile (free to diffuse and rotate)
  - low temperatures and high pressures close to liquefaction
- **chemical adsorption** (chemisorption)
  - involves formation of chemical bonds, $-\Delta_{ads}H > 80$ kJ/mol
  - involves specific chemistry on the surface
  - adsorbed atoms are localized, often specific binding sites
  - difficult to reverse (breaking chemical bonds is required)
  - only monolayers can be formed (however further physisorpt layers can be formed on top)
  - high temperatures, wide range of pressures

The adsorption time and accommodation coefficient

- Adsorption time – the time the adsorbate spends on the surface
  - elastic case: no interaction between the gas molecule and the surface

From the kinetic theory of gas: $\tau = \frac{2\Delta x}{\bar{v}_x} = \frac{2\Delta x}{\sqrt{kT/m}}$ as $\frac{mv^2}{2} = \frac{3}{2}kT \text{ and } \bar{v}_x^{\,2} = \bar{v}^2/3$

for N_2 at 25ºC: $\Delta x = 1\text{Å}, v_x \approx 300\text{m/s}: \ \tau \approx 7\cdot 10^{-13}\text{s}$

  - inelastic case: attractive force is present

From Arrhenius law: $$\tau = \tau_0 \exp(Q/kT)$$

surface bond vibration 10^{-13} – 10^{-12} s

The adsorption time and accommodation coefficient

- Accommodation coefficient
  measures the extent of energy exchange between the molecule and the surface:

$$\alpha = \frac{T_3 - T_1}{T_2 - T_1}$$

where T_1 – temperature of the molecules before impact, T_2 – surface temperature, T_3 - temperature of the molecules after impact

  - in elastic collision $T_3 \sim T_1$ and $\alpha \sim 0$
  - if resides for long time on the surface $T_3 \sim T_2$ and $\alpha \sim 1$

Adsorption isotherms

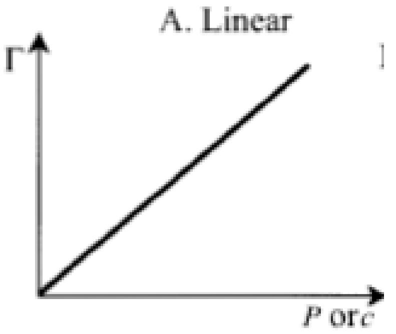
- Adsorption isotherm – a graph showing dependence of the adsorbed amount vs the vapour pressure (or concentration)
- Amount adsorbed:
  - surface access (recall Gibbs convention) $\Gamma = \frac{N^\sigma}{A} \quad \frac{mol}{m^2}$
  - for porous materials: mass per gram adsorbent, specific surface area Σ needs to be known to compare with isotherms

Classification of adsorption isotherms

- Linear adsorption:

Henry equation $\Gamma = K_H P$

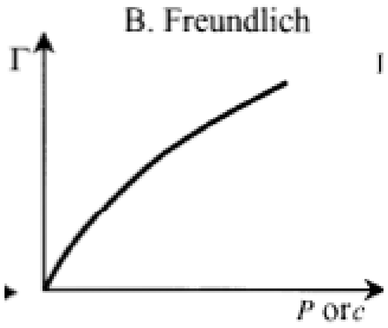
Limiting equation for low Γ


A. Linear

- Freundlich adsorption isotherm:

Freundlich equation $\Gamma = K_F P^q$ q<1

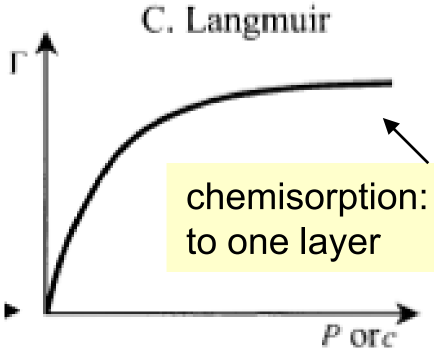
adsorption on a heterogeneous surface or repulsion between the adsorbate molecules


B. Freundlich

- Langmuir adsorption isotherm:

Langmuir equation $$\theta = \frac{\Gamma}{\Gamma_{mon}} = \frac{K_L P}{1 + K_L P}$$

common for adsorption from liquid solution, rarely observed for gases

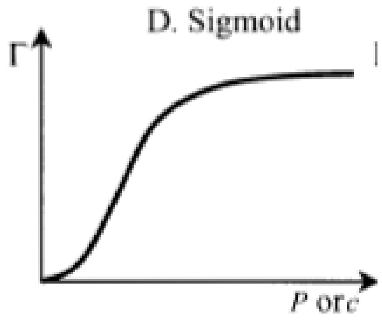

C. Langmuir

chemisorption: limited to one layer

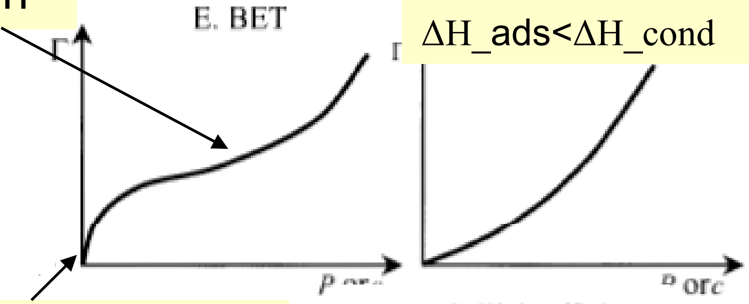
Classification of adsorption isotherms

- Sigmoidal isotherm:

  indicates cooperative effects i.e.molecule binds better when interacts with neighbours;
  flat and homogeneous adsorbent is required



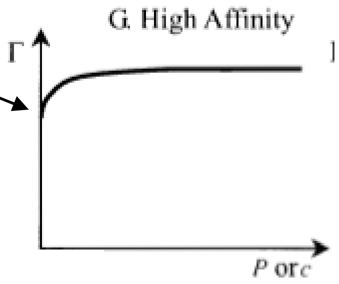
- BET (Brunauer, Emmet, Teller) isotherms:



a monolayer formation

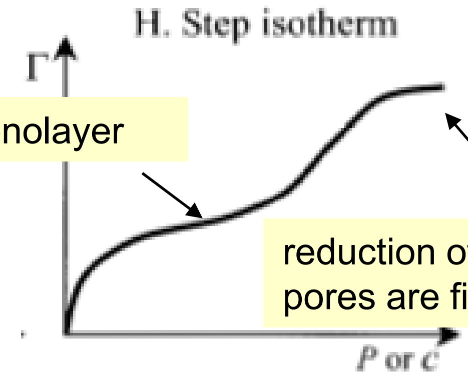
ΔH_ads<ΔH_cond

- High affinity:
  - common for polymer or protein adsorption
  - qualitatively similar to Langmuir



high affinity between gas and solid

- Step isotherm
  - common for porous materials



monolayer

reduction of surface area after pores are filled

Thermodynamics of adsorption

- Integral molar energy of adsorption:
  - difference between the energy of the molecule adsorbed and in the gas phase (per mole)

$$\Delta_{ad}U_m^{\text{int}} = U_m^{\sigma} - U_m^{g}$$

- Integral molar enthalpy and entropy of adsorption

$$\Delta_{ad}H_m^{\text{int}} = H_m^{\sigma} - H_m^{g} \qquad \Delta_{ad}S_m^{\text{int}} = S_m^{\sigma} - S_m^{g}$$

- Difference between internal energy and enthalpy is usually small, indeed for the case of ideal gas:

$$\Delta_{ad}U_m^{\text{int}} = \Delta_{ad}H_m^{\text{int}} - RT \longleftarrow \text{2.4 kJ/mol at 25ºC}$$

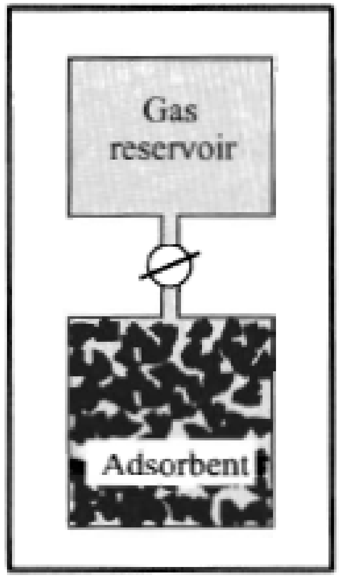
Thermodynamics of adsorption

- Constant volume heat:

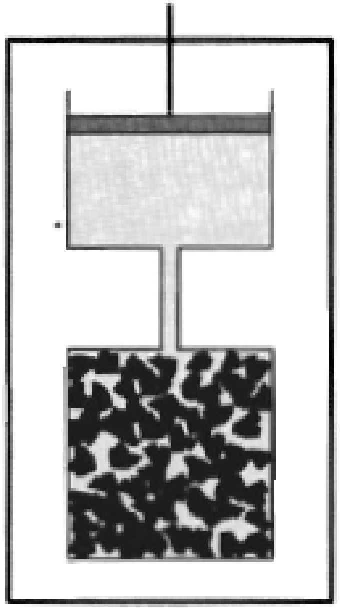
$$Q = -\Delta_{ad} U_m^{\text{int}} \cdot N^{\sigma}$$

- Constant pressure heat:

$$Q = -\Delta_{ad} H_m^{\text{int}} \cdot N^{\sigma}$$



Constant volume



Constant pressure

$$dH = TdS + VdP \xrightarrow{P = const} \Delta_{ad} S_m^{\text{int}} = \frac{\Delta_{ad} H_m^{\text{int}}}{T}$$

Differential quantities

- Differential molar energy of adsorption is defined as

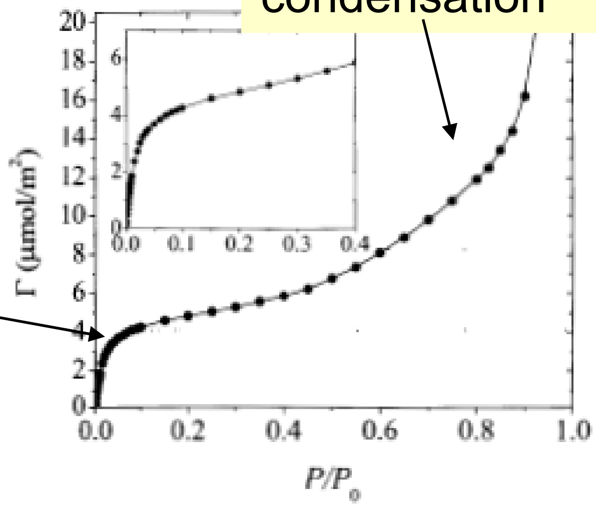
$$\Delta_{ad}U_m^{dif} = \left.\frac{\partial U^{\sigma}}{\partial N^{\sigma}}\right|_{T,A} - U_m^{g}$$

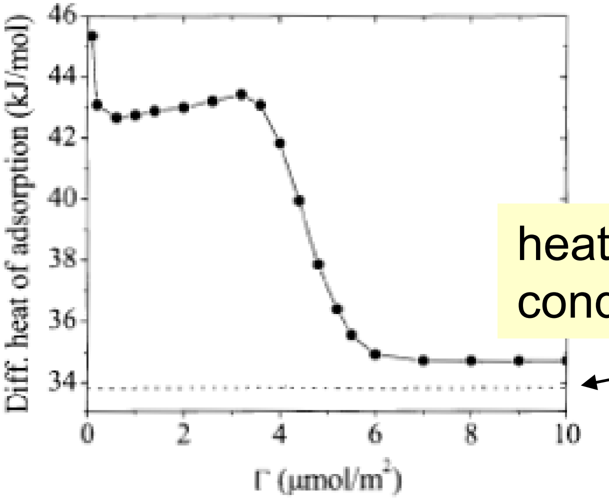
energy of gas doesn't change significantly

- Example: adsorption of benzene on graphitized carbon black

multilayer condensation

monolayer is formed





heat of condensation

Isotherm equations

- at very low pressures can be approximated as a straight line: Henry’s law region
- isotherm equation should describe the shape of the isotherm
- isotherm equation should produce enthalpy of adsorption matching the one deduced by calorimetry

Langmuir adsorption equation

- Langmuir equation (1918) is based on a **chemisorption** model: adsorption is limited to a **single monolayer**

gas pressure

number of molecules adsorbed

$$\frac{n^{\sigma}}{n_m^{\sigma}} = \frac{\alpha p}{1 + \alpha p}$$

number of molecules in a complete monolayer

linearized form

$$\frac{p}{n^{\sigma}} = \frac{1}{\alpha n_m^{\sigma}} + \frac{p}{n_m^{\sigma}}$$

Langmuir adsorption equation

Model:

- dynamic equilibrium between gas and adsorbed phase
- surface contains fixed number of binding sites S,
- molecules can only attach to a vacant binding site

$$\text{rate of adsorption} = \mathrm{k}_{ad} P S_0$$

$$\text{rate of desorption} = k_{de} S_1$$

$$\text{in equilibrium: } k_{de} S_1 = \mathrm{k}_{ad} P S_0 = \mathrm{k}_{ad} P (S - S_1)$$

$$\frac{S_1}{S} = \frac{\mathrm{k}_{ad} P}{\mathrm{k}_{de} + \mathrm{k}_{ad} P}$$

Langmuir equation $\Theta = \dfrac{K_L P}{1 + K_L P}$

Langmuir adsorption equation

- Meaning of adsorption/desorption constants
  - adsorption:
    in case of 100% sticking to the surface equal to the flux towards the surface

$$J=\frac{\sigma_A P}{\sqrt{2\pi m k_B T}};\ \ k_{ad}=\frac{\sigma_A}{\sqrt{2\pi m k_B T}}$$

  - desorption:
    can be expressed in terms of adsorption time

$$k_{de}=\frac{1}{\tau_0}\exp\left(-\frac{Q}{k_B T}\right)$$

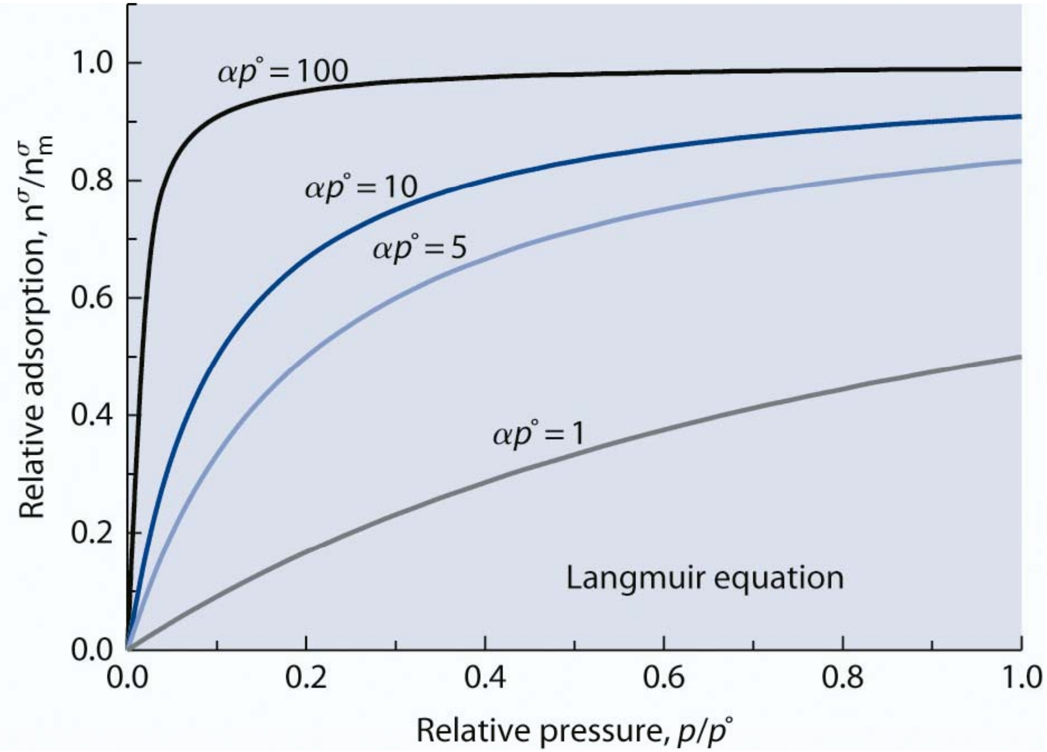
$$K_L=\frac{k_{ad}}{k_{de}}=\frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}}\exp\left(\frac{Q}{k_B T}\right)$$

Upper limit as 100% sticking probablity is assumed

Assumptions of the Langmuir equation

- The enthalpy of desorption E_1 is constant and independent on coverage: uniformity of the surface, no interaction between adsorbed molecules
- Molecules are immobilized on the surface and cannot move around
- Each site can only accommodate one molecule
- Molecules are adsorbed without dissociation

Application of the Langmuir equation



$$\frac{n^\sigma}{n_m^\sigma} = \frac{\alpha p}{1+\alpha p},$$

where $\alpha = K_L$

- Increasing K_L(i.e. Q) leads to steeper adsorption at lower relative pressures

Limitations:

- Applies to only one type of isotherms
- usually lead to inconsistencies like large variations of n_a and E_1 with temperature and adsorbate.
- applicable only to monolayer adsorption while multilayer adsorption is more common in nature

Langmuir constant and Gibbs free energy

- Let’s consider adsorption as a chemical reaction
- Langmuir constant and Gibbs free energy can be linked via the equilibrium constant:

$$K_{ad} = \frac{S_0 P}{S_1} \qquad \Delta_{ad} G_m^0 = -RT \ln K_{ad}$$

$$K_{ad} = \frac{S_0 P}{S_1} = \frac{\left(S - S_1\right) P}{S_1}; \quad S_1 = \frac{SP}{K_{ad} + P}$$

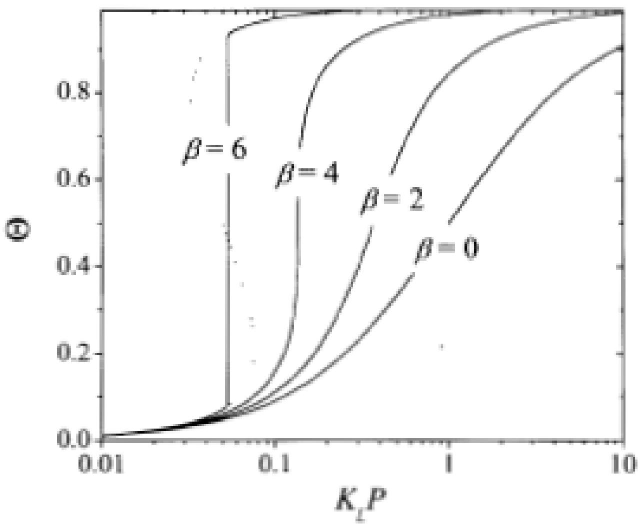
$$\theta = \frac{S_1}{S} = \frac{P}{K_{ad} + P}; \quad K_{ad} = \exp\left(-\frac{\Delta_{ad} G_m^0}{RT}\right)$$

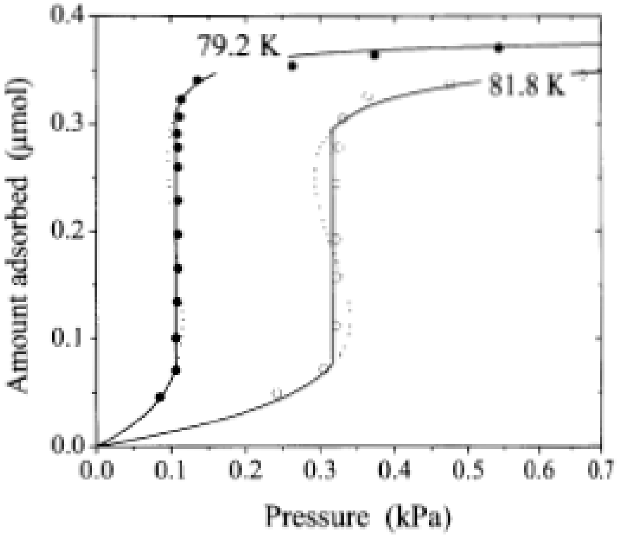
Langmuir adsorption with lateral interaction

- if every binding site has ***n*** neighbors, the average number of neighbors is ***nθ***:

$$K_L' = K_L^0 \cdot \exp\left(\frac{Q + nE_p\theta}{RT}\right) = K_L \cdot \exp\left(\overbrace{\frac{nE_p\theta}{RT}}^{\beta}\right)$$

- causes steep increase of adsorption in the intermediate range
- called Frumkin-Fowler-Guggenheim isotherm
- if >4, negative slope is observed, corresponding to two phase equilibrium on the surface





adsorption of krypton on graphite fitted with β=4.5

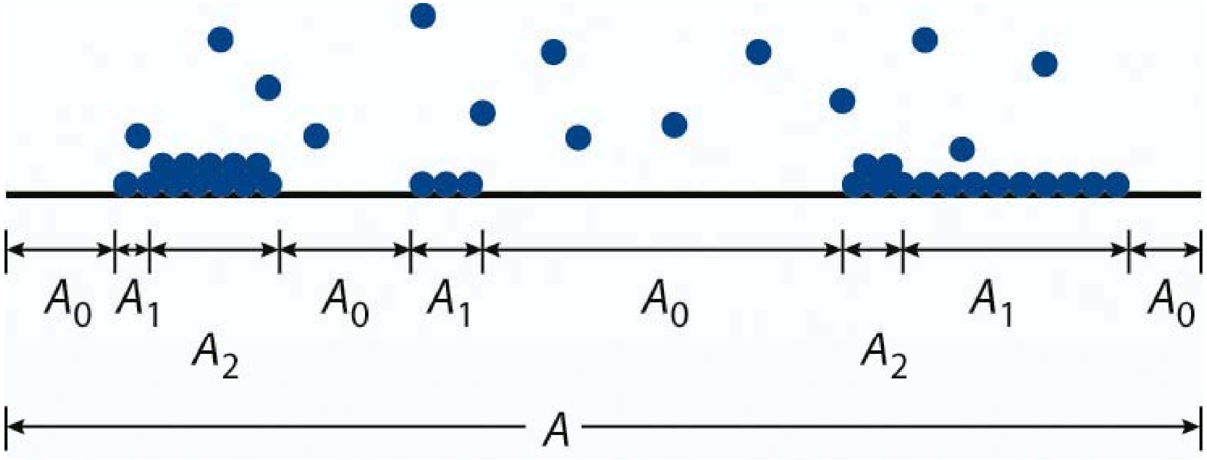
The BET equation

- BET equation (1938): the extension of Langmuir isotherm proposed by Brunauer, Emmet and Teller to include **multilayer** adsorption

$$\frac{n^{\sigma}}{n_m{}^{\sigma}} = \frac{Zp}{(p^0 - p)\left\{1 + (Z-1)\left(p/p^0\right)\right\}},$$

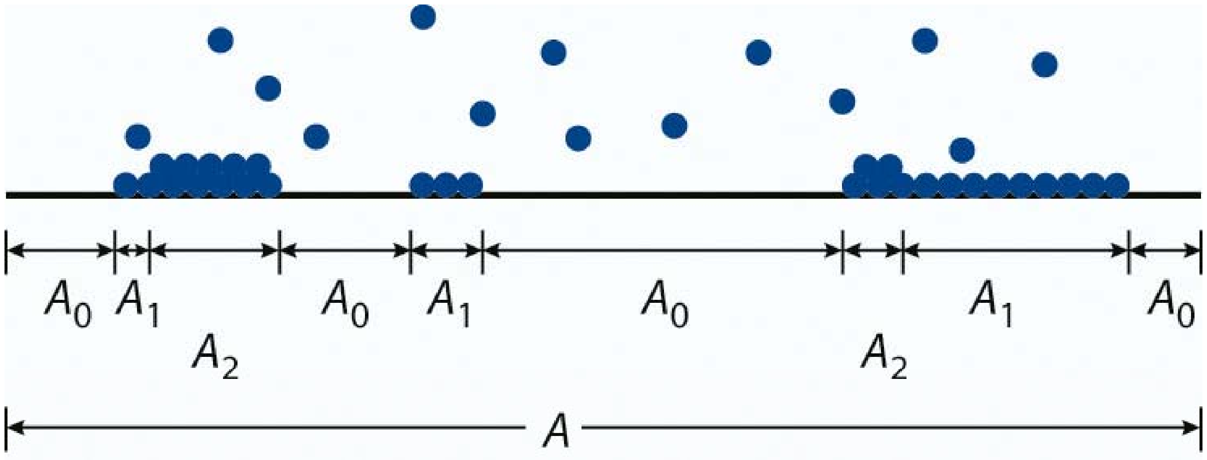
$$\text{where } Z \approx \exp\left\{\left(E_1 - E_v\right)/RT\right\}$$

The BET equation



- Model:
  - – no limit to the number of layers adsorbed
  - – the Langmuir equation applies to each layer
  - – adsorption and desorption only occurs at exposed surfaces
  - – at equilibrium, the distribution of adsorbant between different layers is constant.

The BET equation



at equilibrium

$A_0 = const$ $$a_1 p A_0 = b_1 A_1 \exp(-E_1 / RT)$$

$A_1 = const$ $$a_2 p A_1 + b_1 A_1 \exp(-E_1 / RT) = $$
$$= a_1 p A_0 + b_2 A_2 \exp(-E_2 / RT)$$
$$a_2 p A_0 = b_2 A_2 \exp(-E_2 / RT)$$

Generally: $$a_i p A_{i-1} = b_i A_i \exp(-E_i / RT)$$
$$A_i = \left\{ \left(a_i / b_i \right) p \exp(-E_i / RT) \right\} A_{i-1}$$

The BET equation

$$A_i = \left\{\left(a_i / b_i\right) p \exp(-E_i / RT)\right\} A_{i-1}$$

$$A = \sum_{i=0} A_i \qquad n^{\sigma} = \frac{n_m{}^{\sigma}}{A} \sum_{i=1} iA_i \quad \Rightarrow \quad \frac{n^{\sigma}}{n_m{}^{\sigma}} = \frac{\sum_{i=1} iA_i}{\sum_{i=0} A_i}$$

- assumptions:

$$E_1 = E_2 = ... = E_v$$

$$b_2 / a_2 = b_3 / a_3 = ... = C$$

- definitions:

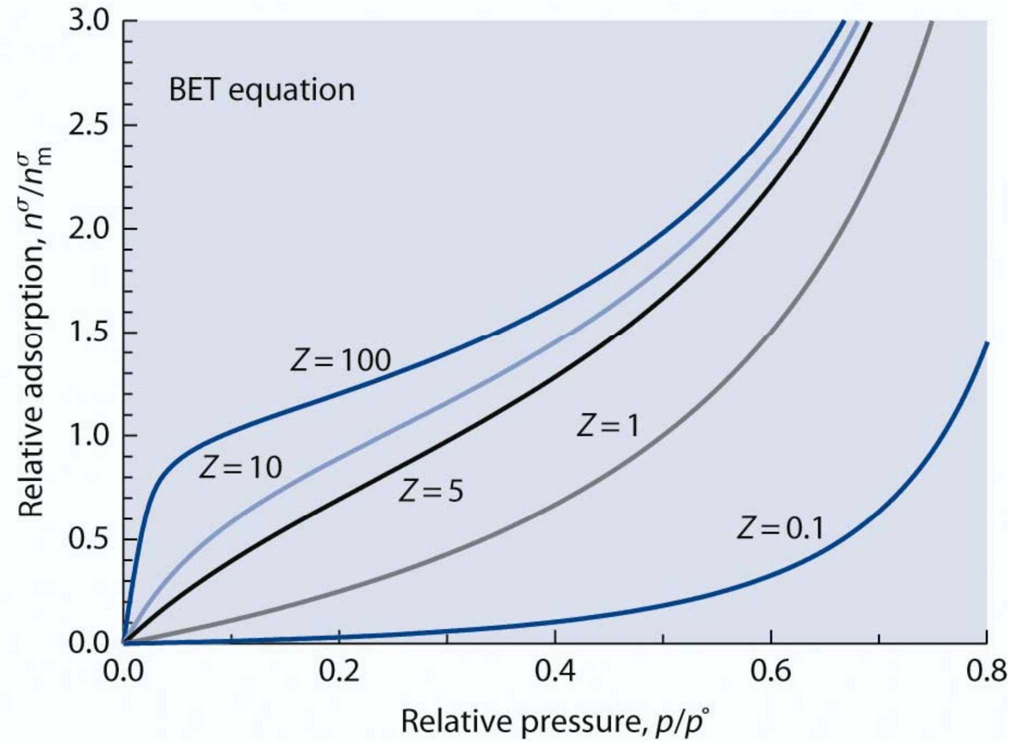
$$Y = (a_1 / b_1) p \exp(E_1 / RT)$$

$$X = (1/C) p \exp(E_v / RT)$$

$$Z = Y / X$$

$$A_i = ZX^i A_0 \quad \text{and} \quad \frac{n^{\sigma}}{n_m{}^{\sigma}} = \frac{ZX}{(1-X)(1-X+ZX)}$$

Application of the BET equation



$$\frac{n^\sigma}{n_m{}^\sigma} = \frac{Zp}{(p^0 - p)\left\{1 + (Z-1)\left(p/p^0\right)\right\}},$$

$$\text{where } Z \approx \exp\left\{\left(E_1 - E_v\right)/RT\right\}$$

- the BET equation can describe type “E” and “F” isotherms (low Z)

Limitation of the BET equation:

- unrealistic picture of the adsorbed film: “battered metropolis”
- full enthalpy released irrespective of the number of neighbors

Adsorption on heterogeneous surfaces

- Heterogeneous surfaces have a distribution of binding energies ***f(Q)***

$$\theta(P) = \int_0^\infty \theta^H(Q,P)\cdot f(Q)\,dQ$$

- this could lead to the Freundlich isotherm assuming exponentially decaying distribution of adsorption energies and Langmuir behavior for θ^H:

$$\theta = \left(\frac{P}{P_0}\right)^{kT/Q^*}, \text{ if } \; f(Q) \propto \exp\left(-Q/Q^*\right)$$

Potential theory of Polanyi

- Let's assume that the molecules condense on the surface due to presence of a potential (e.g. van der Waals)

$$d\mu = -S_m dT + V_m dP + dU_m$$

- due to equilibrium the integral taken between any two points (e.g. x and ∞) is 0:

$$-U_m(x) = \int_P^{P_x} V_m dP \underset{\nwarrow}{=} RT \ln \frac{P_x}{P}$$

for an ideal gas

- at some distance x from the surface an equilibrium vapor pressure P_0 is reached, that the distance up to which we have condensation

- the isotherm with vdWaals potential

$$\Gamma = \frac{x_f}{V_m} = \frac{1}{V_m}\sqrt[3]{\frac{C}{RT\ln\left(P_0/P\right)}} - \frac{D_0}{V_m}$$

Measurement of gas adsorption

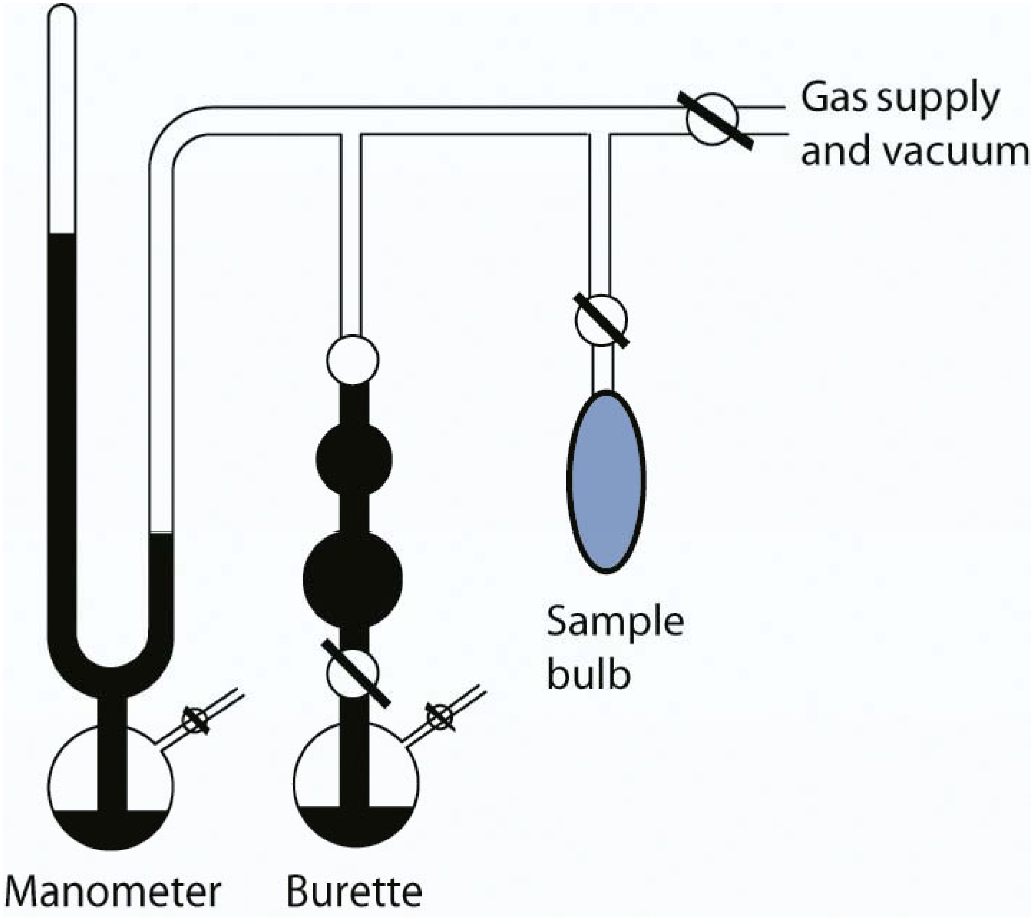
- **volumetric methods:**
  change in the gas volume is measured over a range of pressures

- **gravimetric methods:**
  change in a sample mass is measured (e.g. by a microbalance)

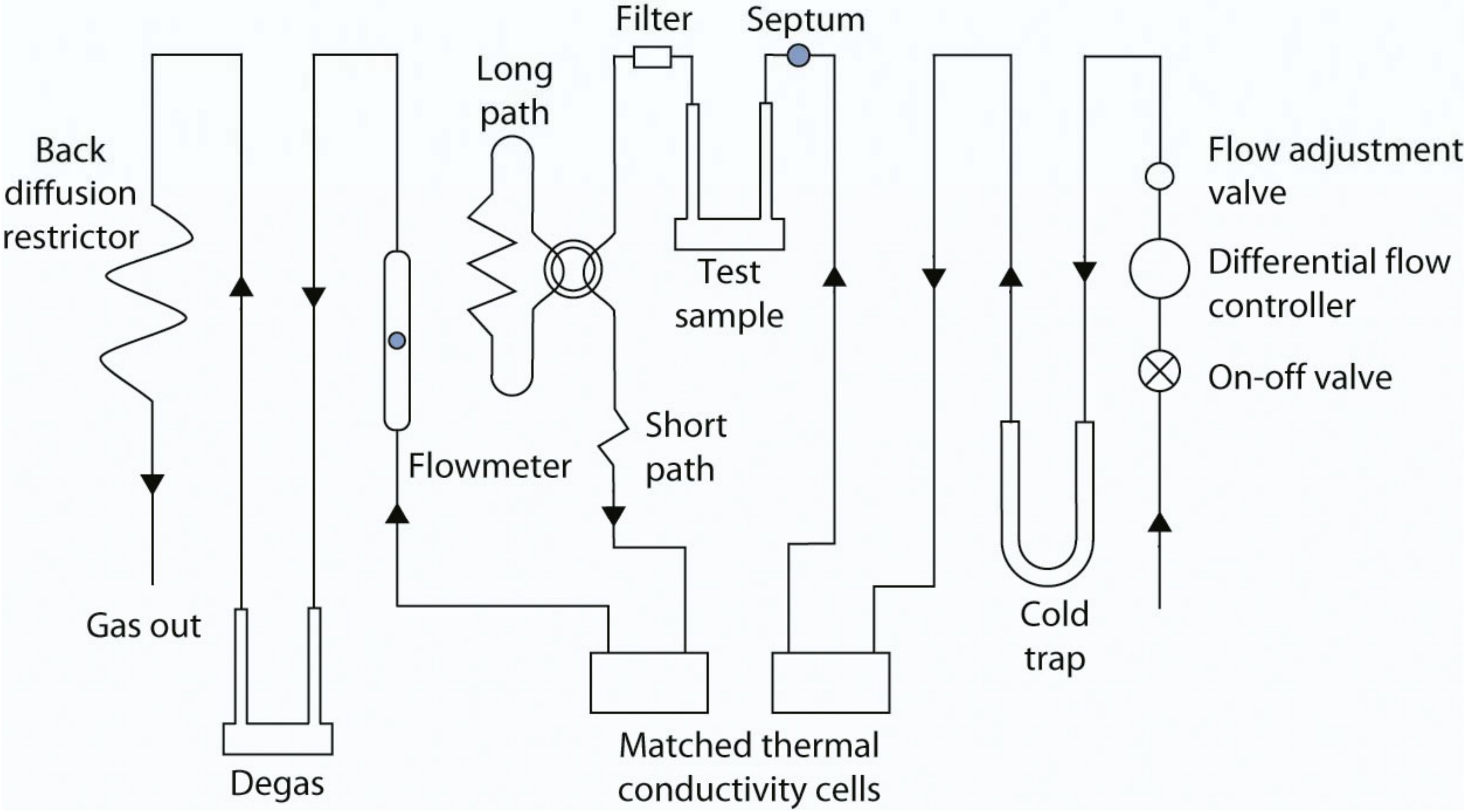
- **flow methods:**
  changes in a gas concentration are measured

Measurement of gas adsorption

- volumetric methods:
  change in the gas volume is measured over a range of pressures
  - Helium is usually used for calibration:
  - Nitrogen – as an adsorbate
  - surface area can be calculated as volume adsorbed divided by the area of N_2 molecule 0.162 nm^2.



Measurement of gas adsorption

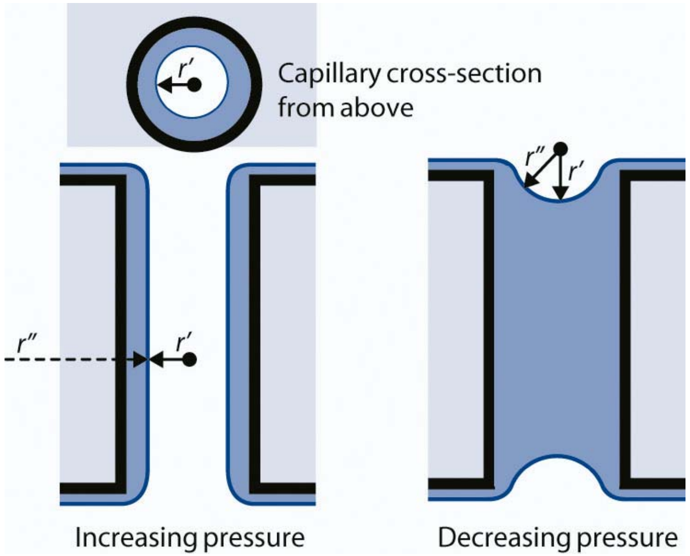


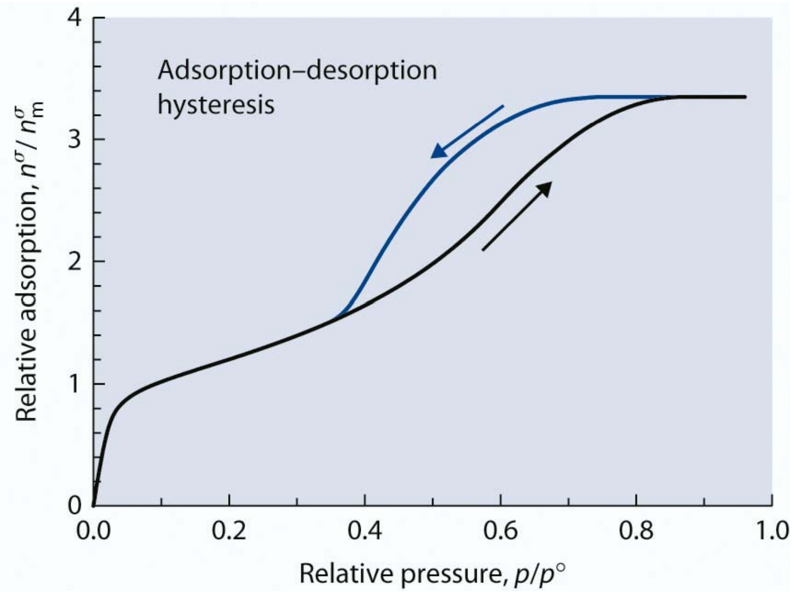
- flow methods:
  - adsorbant gas (e.g. N_2) is diluted in diluent gas (e.g. He).
  - changes in a gas concentration are measured used thermal conductivity

Capillary condensation

- If the surface is curved the vapour pressure will be different than p^0: Kelvin equation.

$$\ln\left(\frac{p^c}{p^\infty}\right) = \left(\frac{\gamma \bar{V}^L}{RT}\right)\left(\frac{1}{r'} + \frac{1}{r''}\right)$$

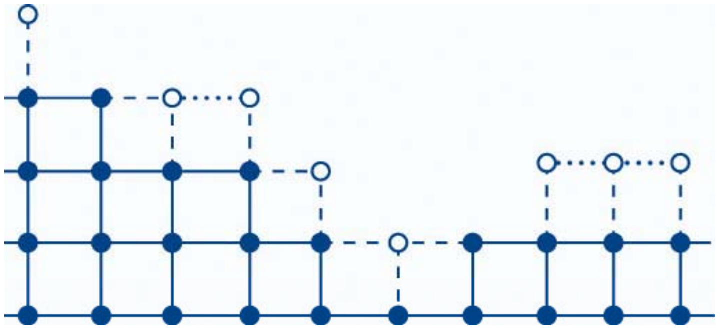




$$\left(\frac{1}{r'} + \frac{1}{\infty}\right) = \frac{1}{r'}$$

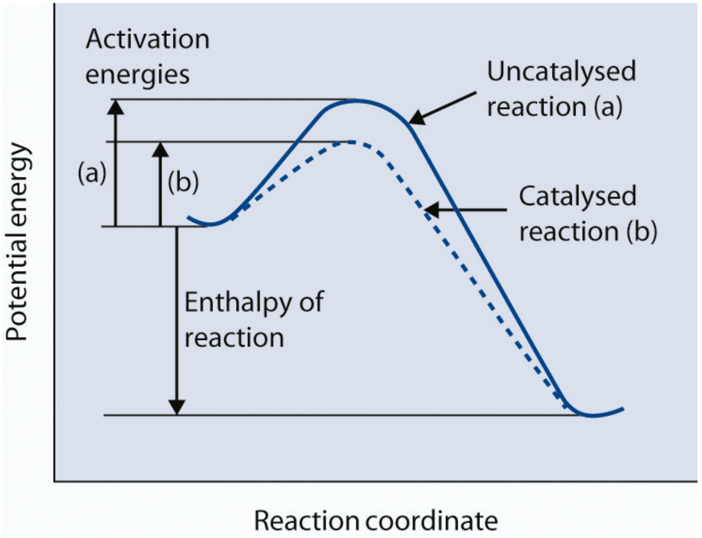
$$\left(\frac{1}{r'} + \frac{1}{r'}\right) = \frac{2}{r'}$$

Chemisorption



- can be described to some extent by Langmuir equation
- defects on the surface cause various enthalpy at various sites: as adsorption proceeds the enthalpy will decrease
- usually occurs via physisorption and involves diffusion on the surface

Heterogeneous catalysis



Catalyst:

- increases rate of a chemical reaction
- doesn’t take in the overall chemical reaction
- is unchanged chemically at the end of the reaction, the amount of catalyst stays the same as well
- required in a relatively small quantity
- doesn’t affect the position of equilibrium but reduces the barrier

Mechanism of heterogeneous catalysis

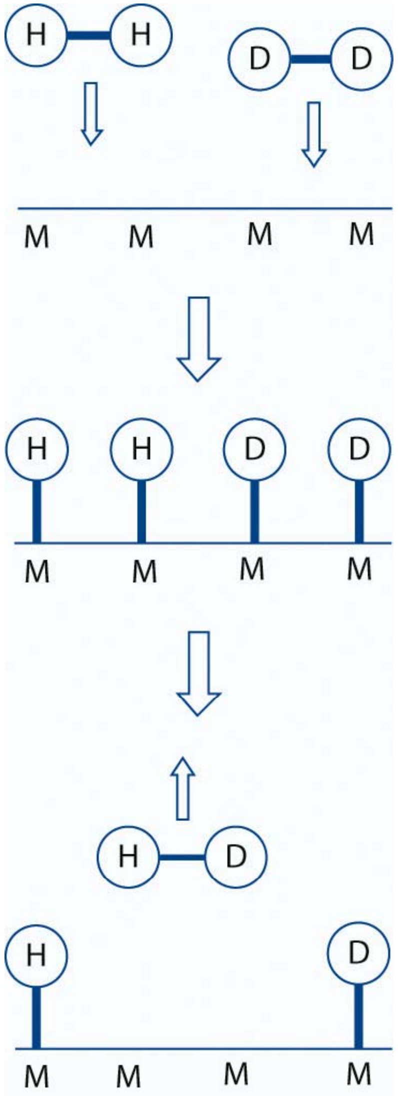
Steps of the catalytic reaction:

- diffusion of reactants to the surface
- adsorption of the reactants
- reaction within the adsorbed layer
- desorption of the products
- diffusion of the products away from the surface

- Adsorption of the reactants:
  - always involves a chemisorption, although physisorption might occur as well: catalysts are active at high temperature, many catalysts are highly specific, IR spectroscopy shows change in the spectrum of adsorbed components
  - **active sites**: positions where strength of the chemisorption bond is optimal for the reaction

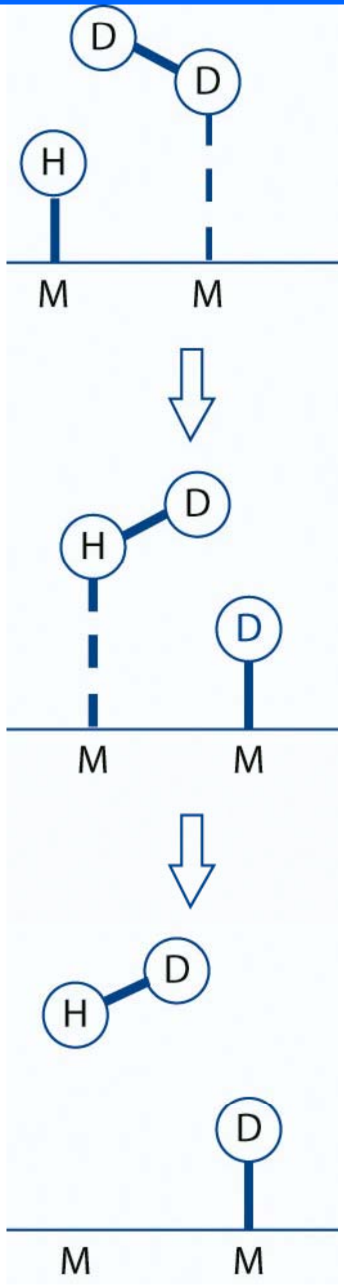
Mechanism of heterogeneous catalysis

- Langmuir-Hinshelwood mechanism: reaction takes place between two adjacent chemisorbed atoms or radicals



Mechanism of heterogeneous catalysis

- The Rideal-Eley mechanism
  - no net breakage of chemical bonds: as one forms another is broken



Kinetics of reaction in the adsorbed layer

- Unimolecular reaction

$$v = -\frac{dp_A}{dt} = k\theta_A = \frac{k\alpha_A p_A}{1+\alpha_A p_A}$$

first order if $\alpha_A p_A \ll 1$

zero order if $\alpha_A p_A \gg 1$

Kinetics of reaction in the adsorbed layer

- Bimolecular reaction

$$v = k\theta_A\theta_B$$

$$\theta_A = \frac{\alpha_A p_A}{1+\alpha_A p_A+\alpha_B p_B} \quad and \quad \theta_B = \frac{\alpha_B p_B}{1+\alpha_A p_A+\alpha_B p_B}$$

$$v = k\frac{\alpha_A p_A \alpha_B p_B}{\left(1+\alpha_A p_A+\alpha_B p_B\right)^2}$$

Limiting cases:

if one of the gases (B) is not chemisorbed: $v = k\frac{\alpha_A p_A p_B}{\left(1+\alpha_A p_A\right)}$

if A is adsorbed strongly and B weakly: $v = k\frac{\alpha_B p_B}{\alpha_A p_A}$

Summary

- adsorption: physisorption and chemisorption
- 8 major types of adsorption isotherms shapes
- equations:
  - Langmuir: monolayer,
  - BET: multilayer
- capillary condensation on porous surfaces: hysteresis
- methods for measuring gas adsorption: volumetric, flow and gravimetric methods
- heterogeneous catalysis: Langmuir-Hinshelwood and Rideal-Eley mechanism

Problems

- **End of chapter problems: 9.2, 9.5, 9.6**
- **Additional problem:** The data in the table are for the adsorption of nitrogen on a 10 mg sample of mica at 90 K. Show that the data fit the Langmuir isotherm and evaluate the constants in the expression. Given that the cross-sectional area of a nitrogen molecule is 0.162 nm^2, calculate the specific surface area of the mica.

p/Pa	**V^{σ}/mm^3 (at STP)**
0.293	12.0
0.506	17.0
0.973	23.9
1.773	28.2
3.479	33.0

where V^{σ} is the volume of gas adsorbed at standard temperature (273.15 K) and pressure (101.32 kPa).