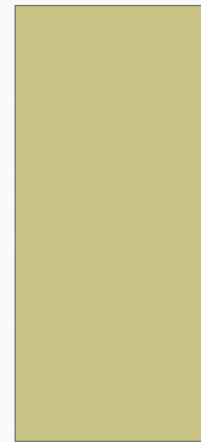


# PROCESSES AT SOLID SURFACES

– HETEROGENEOUS REACTIONS



# OVERVIEW:

## I. Surface

- a) concept, nature;
- b) formation, growth, size;
- c) composition, structure. Measuring methods.

## II. Adsorption

- a) characteristics: physisorption and chemisorption
- b) extent of adsorption: Langmuir isotherm

## III. Catalytic activity of surfaces

- a) heterogeneous catalysis
- b) adsorption and catalysis. Langmuir-Hinshelwood and Eley-Rideal mechanisms.

# I. SURFACE

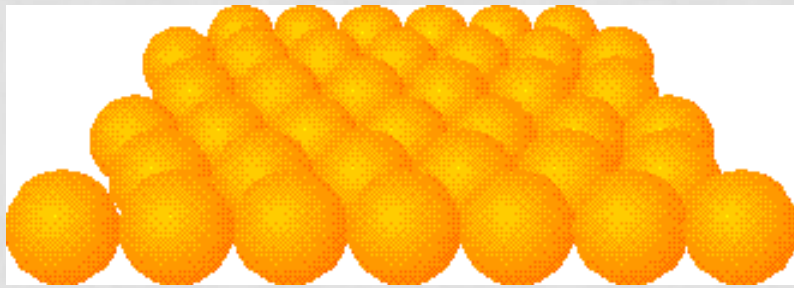
## a) the concept of surface, its nature

- Macroscopic experience – geometric size is unrealistic (e.g for chalk)
- Defined in an atomic-molecular dimension
- Usually, the surface of crystals is examined

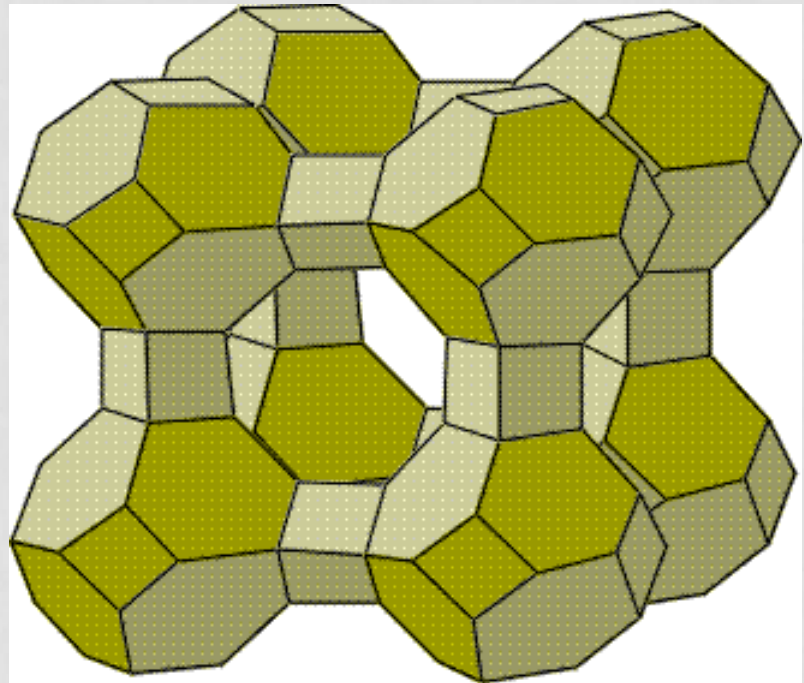
# I. SURFACE

## a) the concept of surface, its nature

- The position of the atoms is varies a lot:



on a flat crystal surface:  
like a tray of oranges

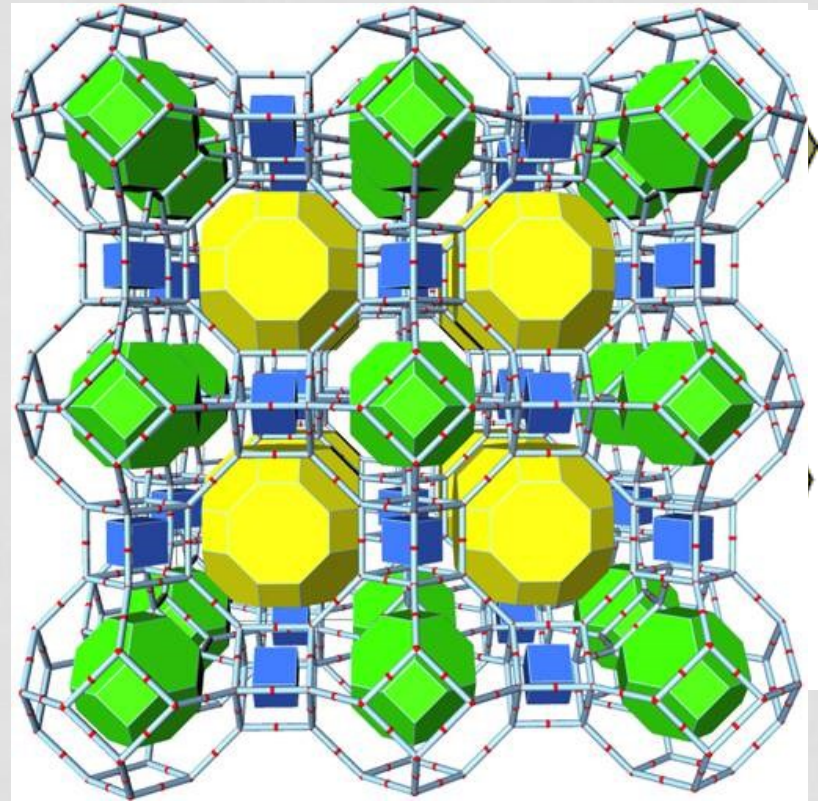


in a zeolite type material

# I. SURFACE

## a) the concept of surface, its nature

- The position of the atoms is varies a lot:
- typical zeolite structure:
  - **truncated octahedra**,
  - **small cubic cages** and
  - **large central cage**.
- This structure results in a huge specific surface.



# I. SURFACE

## b) formation and growth of the surface

- The surface is formed from the crystal nuclei which has a size of only some atoms (molecules). It can grow from a melt, a solution or a gas.
- Forms (can be grown) a:
  - **perfect single crystal**,
  - but general (and even more important) are the **real crystals** with defects (often **polycrystalline** materials).
    - It can be made by grinding (breaking the crystal).

# I. SURFACE

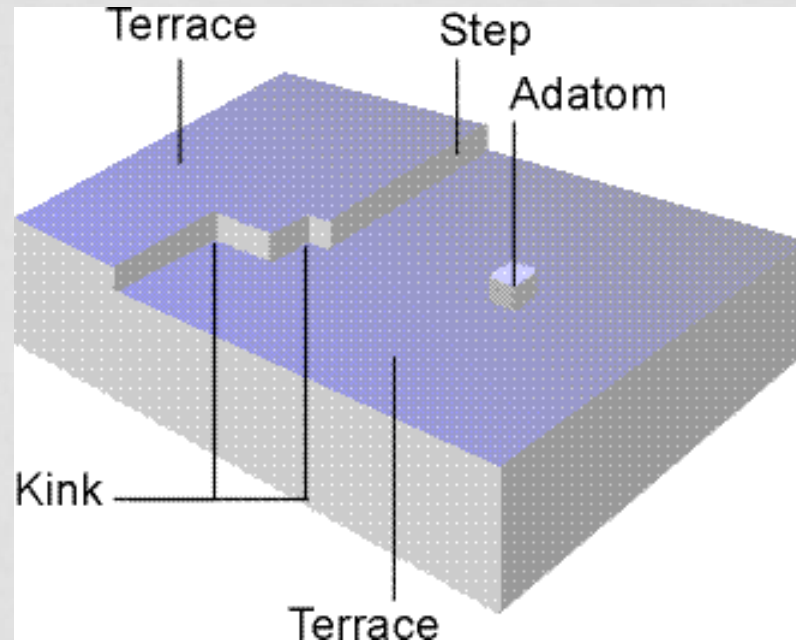
## b) formation and growth of the surface

- Key concept: **dislocation** (deviation from perfect).
- It is so important that it is often induced artificially (e.g. a perfect AgBr crystal is not photo-sensitive).
- The difference between the flat layers, the edge, and the peak is obvious: the environment of the atoms / ions is different, resulting in a different potential energy.
- Types of defects (often mixed):
  - geometric and chemical defects,
- which can be located
  - on the surface or inside the bulk crystal.

# I. SURFACE

## b) formation and growth of the surface

- Geometric defects: on the surface or inside the crystal bulk
- Some types of surface geometry defects:
  - (terrace – not a defect!)
  - step
  - kink
  - peak
  - adatom





# I. SURFACE

## c) composition and structure of the surface

- The fresh surface of the solid material is "immediately" covered by gas molecules – by fast collisions.
- This can be calculated from the kinetic theory of gases:

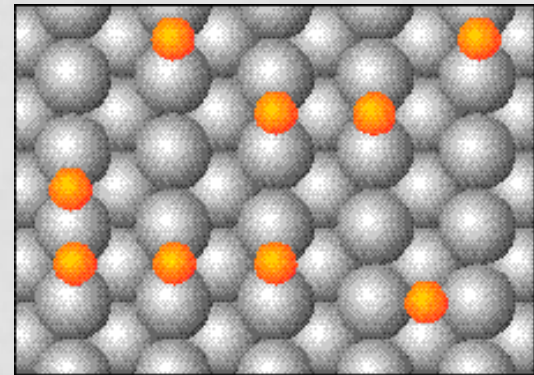
$$Z_W = \sqrt{\frac{p}{2\pi m k_B T}}$$

- In air ( $M \sim 29$  g/mol, 1 atm, 25 °C):  $Z_W = 3 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$ .
- Since there are  $10^{19}$  atom/m<sup>2</sup>, each surface lattice atoms has  $10^8$  collisions/s,
- that is, the fresh crystal lattice surface is practically immediately covered by the gas molecules (they are adsorbed on the surface).

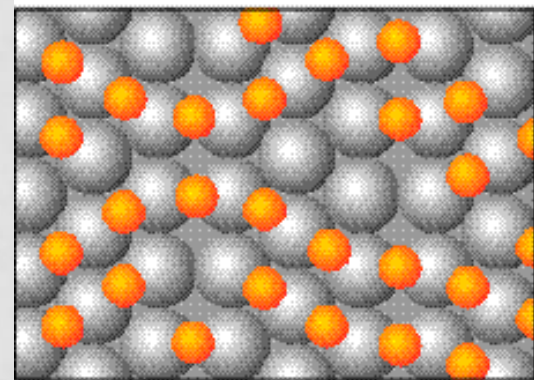
## II. ADSORPTION

### a) characteristics

- **A**dsorption is a quantitative surplus on the surface and at the same time – by some kind of interaction – causes a "quality" (structural, energetic) change.
- CO adsorbed on (111) platinum surface:
  - a) at low coverage, the original lattice structure remains
  - b) at higher coverage, a metastable metal lattice develops



(a)



(b)

*[A**b**sorption is enrichment (surplus) in another phase, not on the surface.]*

## II. ADSORPTION

### a) characteristics

- Definitions of adsorption:
  - adsorbent: the adsorbing solid (with large surface)
  - adsorbate: the substrate that adsorbs on the surface
- Desorption: a process opposite to adsorption; the removal of the adsorbate from the surface (adsorbent).
- Quantitative characteristics or extent of adsorption is the **fractional coverage**:

$$\Theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

- $\Theta$  changes during the adsorption process and reaches a state of equilibrium, a value depending on the conditions (substances,  $p$ ,  $T$ ).

## II. ADSORPTION

### a) characteristics

Adsorption is characterized by the nature and strength of the surface bonding. Based on this, there are:

#### physisorption

- small  $\Delta_{\text{ad}}H^\theta$  [kJ/mol]  $< 0$
- long range
- multilayer
- non-specific
- no change in molecular structure
- mobile molecules
- van der Waals interaction

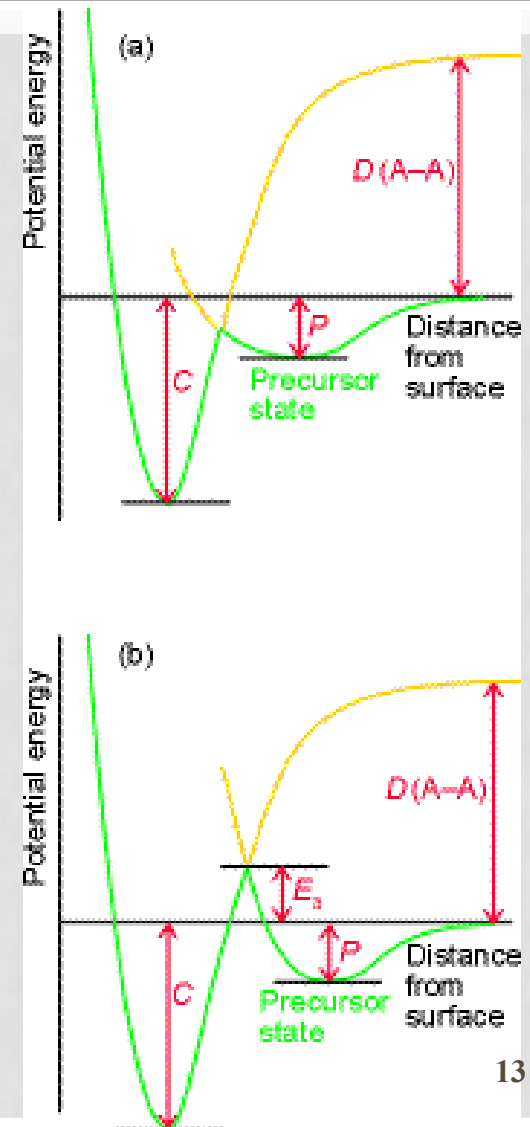
#### chemisorption

- large  $\Delta_{\text{ad}}H^\theta \ll 0$
- short range
- monolayer
- specific
- change in molecular structure
- localized (bonded) molecules
- chemical [covalent] bond

# II. ADSORPTION

## a) characteristics

- Schematic representation of the two types of adsorption (the figures refer to a similar phenomenon, but also reflect the essence of physisorption and chemisorption).
- **Physisorption** ( $P$ ) means greater distance from the surface and less bond energy,
- the adsorbate, which is closer to the surface and more strongly bound to it, is characteristic of **chemisorption** ( $C$ ).



## II. ADSORPTION

### b) extent of adsorption

- Reversible equilibrium process (reverse direction: desorption): a dynamic equilibrium between the gas phase adsorbent and the adsorbate.
- The extent of equilibrium (extent of adsorption) depends on:
  - the chemical identity of the surface and the gas,
  - the pressure  $p$  and
  - the temperature  $T$ .
- Equilibrium description: Adsorption isotherm (how  $\theta$  changes with pressure at constant temperature)
- **Langmuir-**, **BET-**, **Temkin-**, **Freudlich isotherms**

## II. ADSORPTION

### b) extent of adsorption

- The dynamic equilibrium is created by the adsorption ( $k_a$ ) and desorption ( $k_d$ ) processes:



- Rate of adsorption ( $\propto$  uncovered surface):

$$\frac{d\Theta}{dt} = k_a p [N(1 - \Theta)] \quad [N = \text{total number of sites}]$$

- Rate of desorption ( $\propto$  covered surface):

$$\frac{d\Theta}{dt} = -k_d [N\Theta]$$

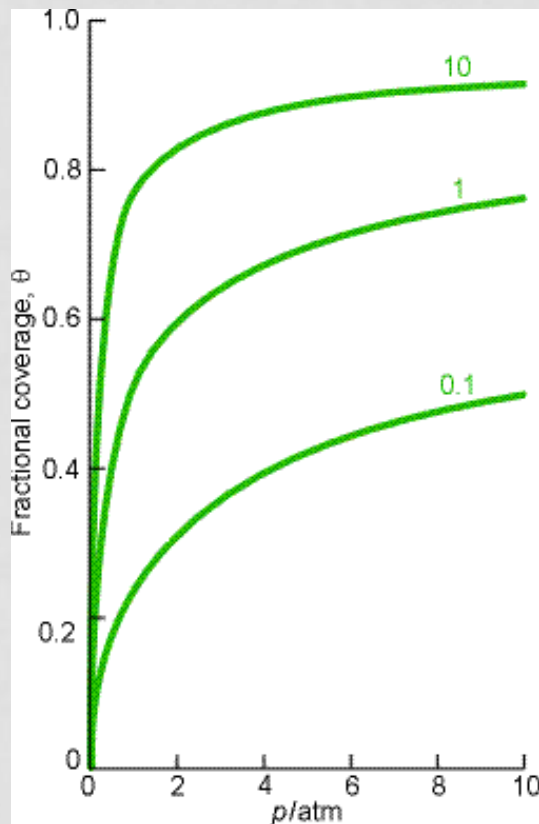
- In equilibrium, the two rates are equal, so:

$$\Theta = \frac{Kp}{1 + Kp}, \text{ where } K = \frac{k_a}{k_d}$$

# II. ADSORPTION

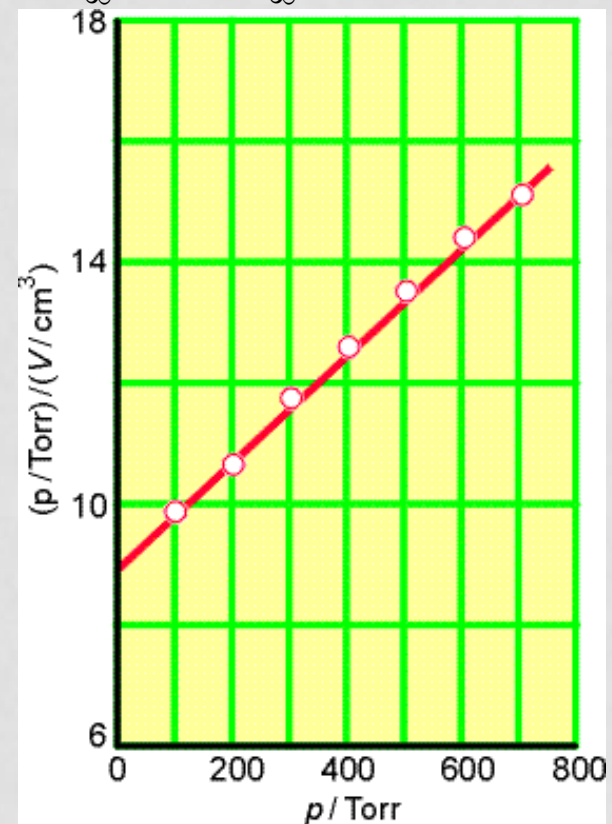
## b) extent of adsorption

- The **Langmuir isotherm** for different  $K$  values:



- Linearization:**

$$\frac{p}{V} = \frac{p}{V_{\infty}} + \frac{1}{KV_{\infty}}, \text{ where } \Theta = \frac{V}{V_{\infty}}$$



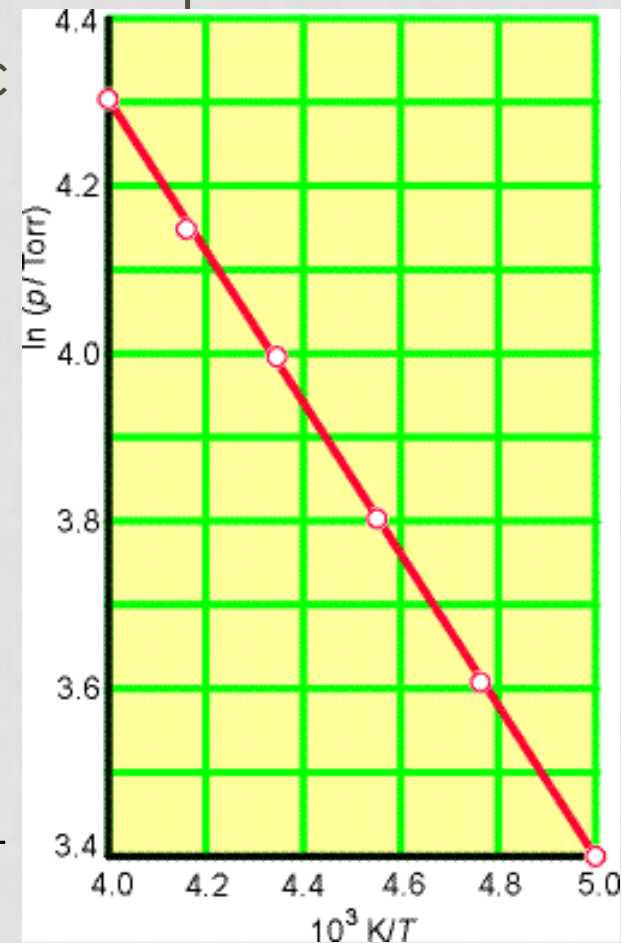


## II. ADSORPTION

### b) extent of adsorption

- Temperature dependence of the equilibrium:
  - Adsorption is usually an exothermic process, so its extent decreases with increasing  $T$ .
  - As it is an equilibrium process, the van't Hoff equation gives the temperature dependence of  $K$  using the  $\Delta_{ad}H^\theta$  **isosteric enthalpy of adsorption** (i.e. standard enthalpy of adsorption at a fixed surface coverage):

$$\left( \frac{\partial \ln K}{\partial T} \right)_\theta = \frac{\Delta_{ad}H^\theta}{RT^2} \quad \text{and} \quad \left( \frac{\partial \ln p}{\partial (1/T)} \right) = -\frac{\Delta_{ad}H^\theta}{R}$$



# III. CATALYTIC ACTIVITY OF SURFACES

- Examples of activation energies of catalyzed reactions:

Reaction	Catalyst	$E_a$ (kJ/mol)
$2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$	-	184
	Au	105
	Pt	59
$2 \text{NO}_2 \rightarrow \text{N}_2 + 2 \text{O}_2$	-	245
	Au	121
	Pt	134
$2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$	-	350
	W	162

# III. CATALYTIC ACTIVITY OF SURFACES

- The **mechanism**: the reaction obviously happens on the solid surface (contact catalysis). Two cases:
  - both reactants adsorb on the surface, the reaction takes place, then the product(s) leave the surface,
  - only one of the reactants is adsorbed and the other reacts with this, then the product(s) leave.
- Meanwhile, the structure of the solid surface is often transformed – at least temporarily.
- A general theory used for heterogeneous catalysis is not yet known, many approaches are known instead. These can be (very) good, accurate for a given case, but not generalizable for all cases.

# III. CATALYTIC ACTIVITY OF SURFACES

- **Langmuir–Hinshelwood mechanism:**

- both reactants (A and B) are chemisorbed
- stoichiometry:  $A + B \rightarrow P$
- kinetics  $v = k \Theta_A \Theta_B$
- If the Langmuir isotherm is valid (often):

$$\Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad \Theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

- It gives the mathematical form of the rate equation – which can be experimentally determined and then compared with the assumed one:

$$v = k \cdot \Theta_A \cdot \Theta_B = \frac{k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

# III. CATALYTIC ACTIVITY OF SURFACES

- **Eley–Rideal mechanism:**

- a reaction between an adsorbed (A) and a gas-phase molecule (B) :
- stoichiometry:  $A + B \rightarrow P$
- kinetics:  $v = k \Theta_A p_B$
- If the Langmuir isotherm is valid for A (often):

$$v = k \cdot \Theta_A \cdot p_B = k \frac{K_A p_A}{1 + K_A p_A} p_B$$

- The Langmuir–Hinshelwood mechanism is much more common, but there are also examples of the Eley–Rideal mechanism (e.g.  $H_2(\text{gas}) + D_2(\text{ad})$ ).