

PROCESSES AT SOLID SURFACES

- HETEROGENEOUS REACTIONS

HETEROGENEOUS REACTIONS

- (So far, we were talking about homogeneous reactions in g and l phases.)
- Heterogeneous reactions occur at the surface between two phases.
- The change can be physical or chemical,
- may involve nucleation or may be nucleation-free,
- may be catalytic or non-catalytic.
- Combinations: *s-l*, *s-g*, *s-s*, *l-l* (here are just examples, details will be discussed in colloid chemistry):
 - melting, physical dissolution, adsorption (clarification)
 - leaching, surface treatment (oxidation, phosphating)
 - electrode reactions (later)
 - corrosion
 - precipitation, crystallization, etc.

SURFACE PHENOMENA - APPLICATION EXAMPLES

- Heterogeneous (contact) catalysis (gas/solid) is very important in the chemical industry (> 90%) [kinetics]
- Methods of separation techniques [equilibrium]:
 - chromatography (column, paper, thin layer, gas, liquid: many versions),
 - ion exchangers (natural [zeolites, etc.] and artificial resins),
 - *carbo medicinalis*, soil tillage and wastewater treatment - lots of applications.
 - Electrolysis, galvanic cells.

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: equilibrium adsorption isotherms: Langmuir, BET and other equations
 - c) rate: kinetics of adsorption, desorption, and surface diffusion
- 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 (NaCl versus chalk)
- today: defined in an atomic-molecular dimension
- the surface of crystals is examined and used (amorphous materials can also be studied)
- crystals consist of atoms, ions or molecules: atomic, ionic, molecular lattices
- crystals are composed of unit cells, based on which there are 7 crystal systems.
- the geometric structure of the surface, the distances of the atoms, etc. are important.

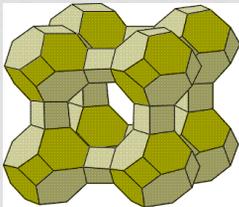
I. SURFACE

a) the concept of surface, its nature

- The position of the atoms is varies a lot:



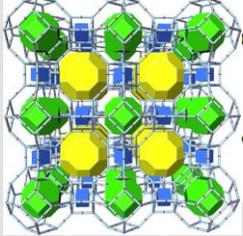
on a flat crystal surface:
like a tray of oranges



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.



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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).
- [About the determination of the surface area, see later.]

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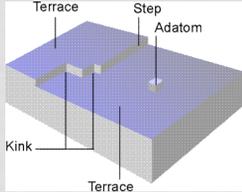
I. SURFACE
b) formation and growth of the surface

- 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.

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I. SURFACE
b) formation and growth of the surface

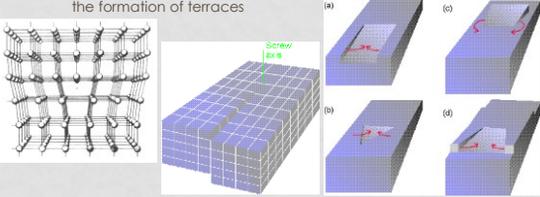
- Geometric defects: on the surface or inside the crystal bulk
- Some types of surface geometry defects:
 - (terrace – not a defect!)
 - step
 - kink
 - peak
 - adatom



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I. SURFACE
b) formation and growth of the surface

- Internal (geometric) dislocations:
 - edge dislocation
 - screw dislocation around a **screw axis**
 - counter-rotating screw dislocations on the same surface lead to the formation of terraces



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I. SURFACE
b) formation and growth of the surface

- Chemical defects: some deviation in composition
 - simple hole = point defect = **vacancy**: an atom/ion is missing from the lattice position
 - interstitial** is an atom/ion that occupies a place outside the normal lattice position (results in lattice distortion around the defect)
- e.g. for photoemulsions: precipitating Ag⁺ with a lot of Br and traces of I⁻
- e.g. semiconductors are made with artificial impurities: they are diffused, infiltrated, etc. into the lattice (solid state physics)

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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:

$$Z_w = \sqrt{\frac{p}{2\pi mk_B T}}$$

- 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/m², 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).

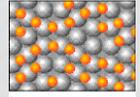
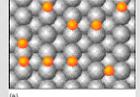
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II. ADSORPTION

a) characteristics

- Adsorption 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



[Adsorption is enrichment (surplus) in another phase, not on the surface.]

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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**: $\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$
- θ changes during the adsorption process and reaches a state of equilibrium, a value depending on the conditions (substances, p , T). $\theta = V/V_{\text{max}}$ (V_{max} for 1 layer)
- Rate of adsorption: change of θ in time.

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II. ADSORPTION

a) characteristics

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

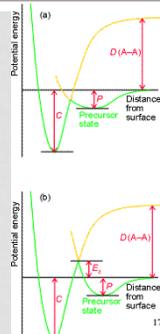
- | physisorption | chemisorption |
|--|---------------------------------------|
| • small $\Delta_{\text{ad}}H^0$ [kJ/mol] < 0 | • large $\Delta_{\text{ad}}H^0 \ll 0$ |
| • long range | • short range |
| • multilayer | • monolayer |
| • non-specific | • specific |
| • no change in molecular structure | • change in molecular structure |
| • mobile molecules | • localized (bonded) molecules |
| • van der Waals interaction | • 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)**.



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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 θ changes with pressure at constant temperature)
- Langmuir-, BET-, Temkin-, Freundlich isotherms**
- Irreversible adsorption: the equilibrium is shifted right!

II. ADSORPTION

b) extent of adsorption

- Dependence of equilibrium on gas pressure.
- Derivation of the **Langmuir adsorption isotherm**: (This applies to monolayer chemisorption - multilayer physisorption is described by the BET isotherm.)
- It is based on four assumptions:
 - adsorption is a reversible equilibrium process,
 - it cannot proceed beyond monolayer coverage,
 - all sites of the surface are equivalent,
 - The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites (i.e. there are no interactions between the adsorbed molecules).
- These assumptions are often valid entirely, but sometimes only partially.

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II. ADSORPTION

b) extent of adsorption

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

$$A(g) + M(s, \text{surface}) \rightleftharpoons AM(s, \text{surface})$$
- 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:

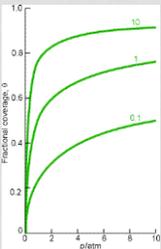
$$\theta = \frac{Kp}{1+Kp} \quad \text{where } K = \frac{k_a}{k_d}$$

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II. ADSORPTION

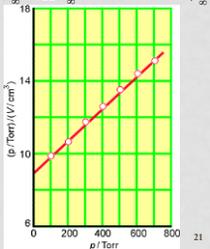
b) extent of adsorption

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



- **Linearization:**

$$\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$$
 where $\theta = \frac{V}{V_\infty}$



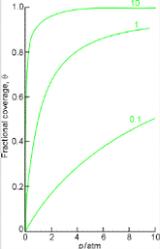
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II. ADSORPTION

b) extent of adsorption

- Adsorption may also be accompanied by the dissociation of the molecule [$X_2 \rightleftharpoons 2X$]. The **Langmuir isotherm** now is:
 - adsorption: $\frac{d\theta}{dt} = k_a p [N(1-\theta)]^2$
 - desorption: $\frac{d\theta}{dt} = -k_d [N\theta]^2$
 - In equilibrium, these are equal

$$\theta = \frac{\sqrt{Kp}}{1 + \sqrt{Kp}}$$
 - In this case, the coverage is less dependent on the pressure!



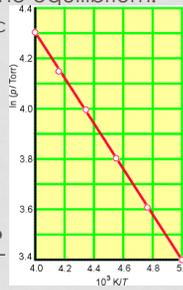
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II. ADSORPTION

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):

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



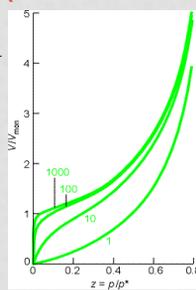
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II. ADSORPTION

b) extent of adsorption

- For multilayer physisorption, the **BET (Brunnauer-Emmett-Teller) isotherm** can be used:

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)[1-(1-c)z]}$$
 where $z = \frac{p}{p^*}$
 - p^* : the vapour pressure above a layer of adsorbate that is more than one molecule thick
 - V : volume of gas adsorbed
 - V_{mon} : volume of gas corresponding to monolayer coverage
 - c : constant
- BET instruments are widely used in industry to determine the surface areas of solids.



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II. ADSORPTION

b) extent of adsorption

- BET isotherm can be **linearized**:

$$\frac{z}{(1-z)V'} = \frac{1}{cV_{mon}} + \frac{(c-1)}{cV_{mon}}z$$

- From V_{mon} , the molecular size (molecular dimension) of the surface can be calculated. Based on such measurements, the surfaces of porous solids is as high as some 10 m²/g (which is approx. 10⁶ times the geometric surface of 1 g solid).

II. ADSORPTION

c) rates of surface processes

- (only the rate of adsorption, desorption and mobility on surfaces – not heterogeneous catalysis jet)
- A key datum is the **sticking probability (s)**:

$$s = \frac{\text{rate of adsorption of particles by the surface}}{\text{rate of collision of particles with the surface}}$$
 - the numerator can be measured by observing the rate of change of pressure,
 - the denominator can be calculated from the kinetic theory of gases.
- Mechanism: the arrival and the collision is followed by diffusion on the surface, and then binding.
- Desorption is a kinetically first-order process that requires activation. Its examination is very important.²⁶

III. CATALYTIC ACTIVITY OF SURFACES

- Heterogeneous catalysis – this is a chemical change *i.e.* reaction!
- Catalysts (as discussed earlier):
 - increase the reaction rate (forward and backward),
 - do not influence the equilibrium,
 - open a new reaction path with lower energy of activation,
 - are not involved in the stoichiometry.
- Heterogeneous catalysis: usually the catalyst is in a phase other than the reactant (s) and product (s).
- Heterogeneous processes can also be described by „normal“ rate equations.
- The study of the molecular mechanism is also important.²⁷

III. CATALYTIC ACTIVITY OF SURFACES

- Examples of activation energies of catalyzed reactions:

Reaction	Catalyst	E _a (kJ/mol)
2 HI → H ₂ + I ₂	-	184
	Au	105
	Pt	59
2NO ₂ → N ₂ + 2O ₂	-	245
	Au	121
	Pt	134
2NH ₃ → N ₂ + 3H 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.²⁹

III. CATALYTIC ACTIVITY OF SURFACES

- Langmuir–Hinshelwood mechanism**:
 - both reactants (A and B) are chemisorbed
- stoichiometry: A + B → 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:

$$v = k \cdot \theta_A \cdot \theta_B = \frac{k K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$
³⁰

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. $H_2(\text{gas}) + D_2(\text{ad})$).

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III. CATALYTIC ACTIVITY OF SURFACES

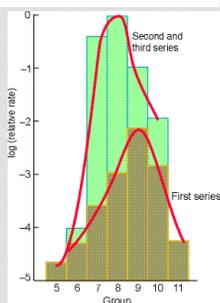
- Inorganic chemistry examples:** contact sulfuric acid synthesis, ammonia synthesis, nitric acid production.
- Examples of heterogeneous catalysis in **organic chemistry:**

Type of catalyst	type of reaction	example
Metals	hydrogenation	
	dehydrogenation	Fe, Ni, Pt, Ag
Semiconductor Oxides and Sulfides	oxidation	NiO, ZnO, MgO
	desulfurization	Bi_2O_3/MoO_3 , MoS_2
Insulating Oxides	dehydration	Al_2O_3 , SiO_2 , MgO
Acids	polymerization	H_3PO_4 , H_2SO_4
	isomerization	SiO_2/Al_2O_3
	cracking	zeolites
	alkylation	

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III. CATALYTIC ACTIVITY OF SURFACES

- The typical **volcano curve** of heterogeneous catalytic activity for the transition metals (*d*-block metals):
- A **volcano curve** of catalytic activity arises because although the reactants must adsorb reasonably strongly, they must not adsorb so strongly that they are immobilized.



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III. CATALYTIC ACTIVITY OF SURFACES

- The practice of heterogeneous (contact) catalysis:
 - Usually supported catalysts are used (many catalysts are very expensive and a high specific surface can be obtained with the porous support),
 - they work in open flow reactors,
 - co-catalysts accelerate the rate even further.
 - The catalysts are occasionally regenerated because of the presence of inhibitors and even catalyst poisons,
 - therefore it is important to pre-purify the reactants.
 - The catalyst often not only accelerates, but also controls (*meta*-substitution instead of *ortho*-; how „far” does C-oxidation go (C-OH, C=O, COOH)).
 - The radical mechanisms are frequent (strong chemisorption causes homolytic bond breaking).

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