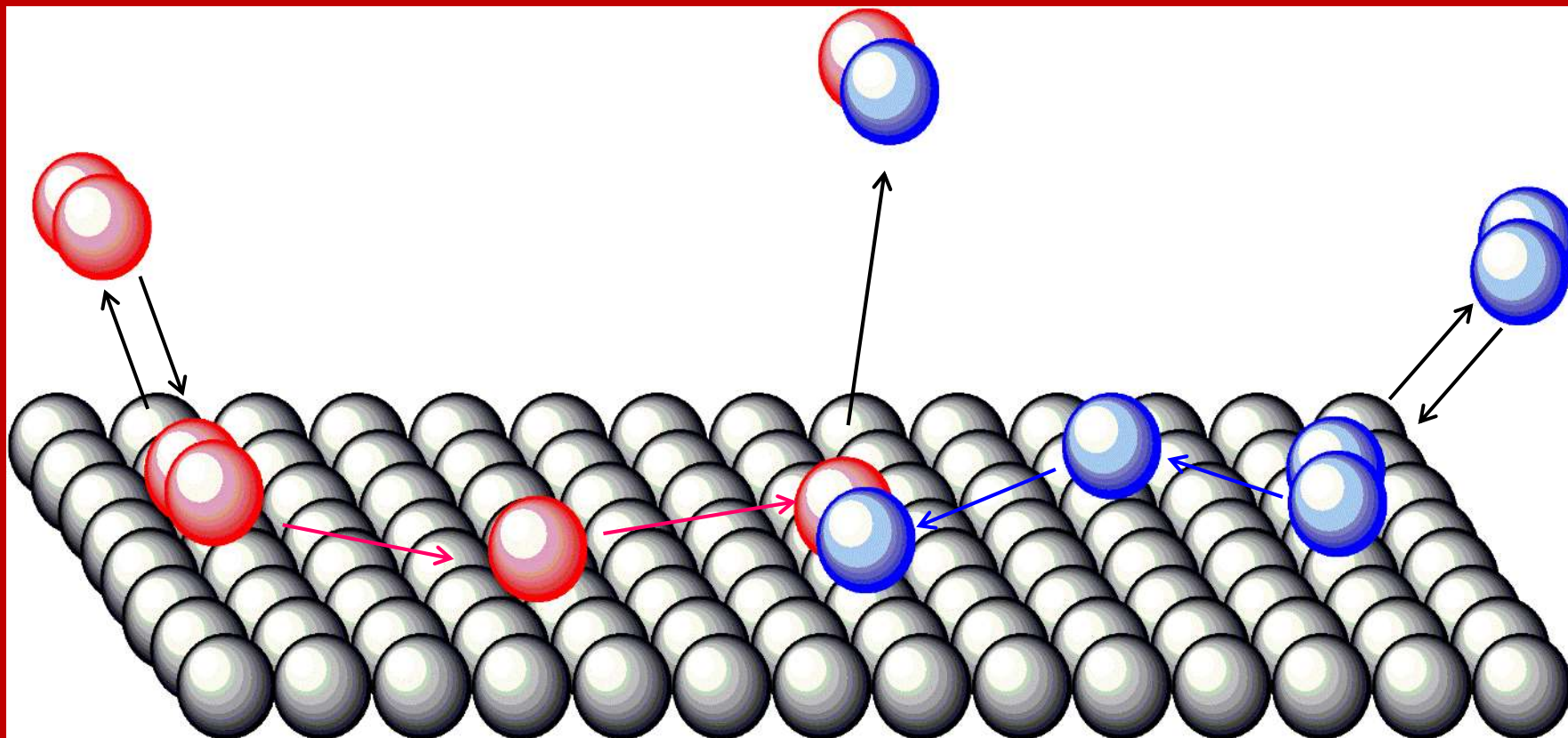


Catalysis

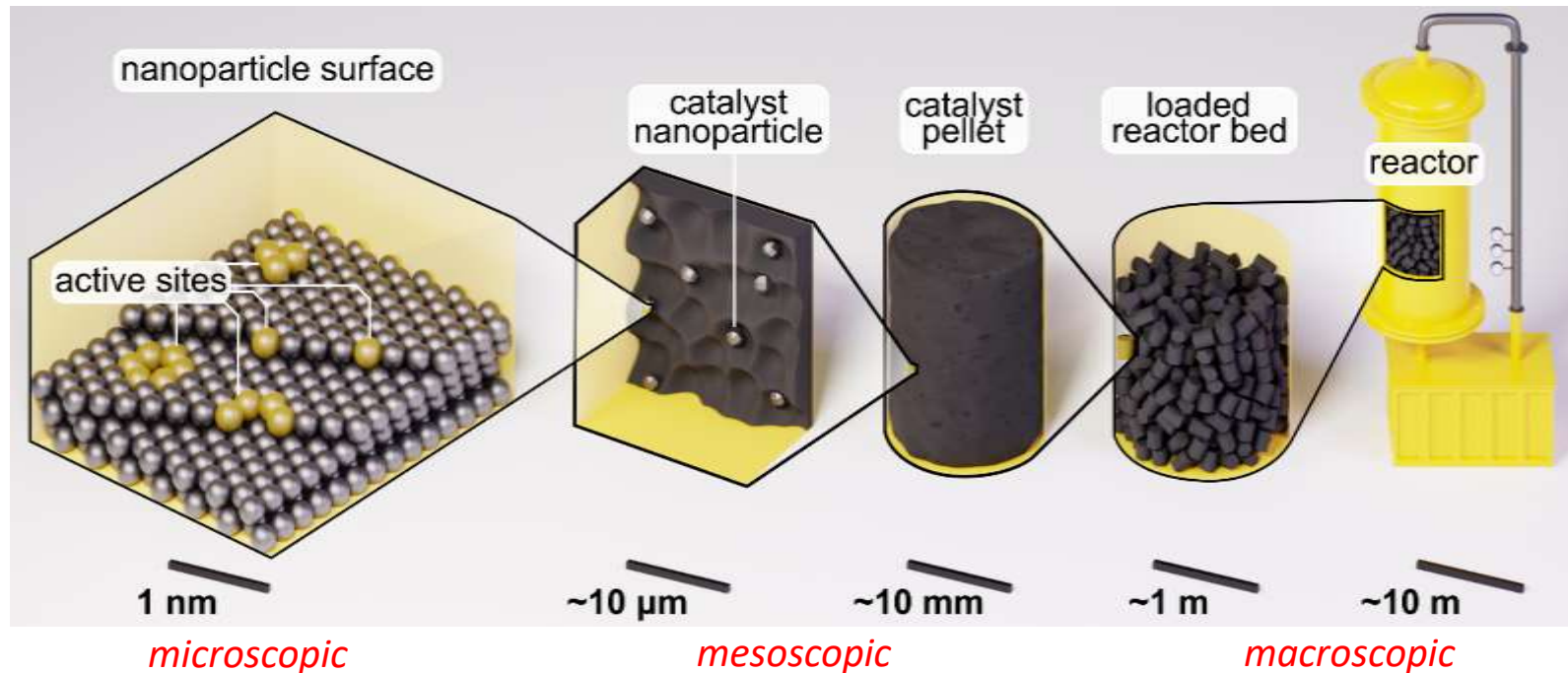
Heterogeneous Catalysis



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Heterogeneous catalysis

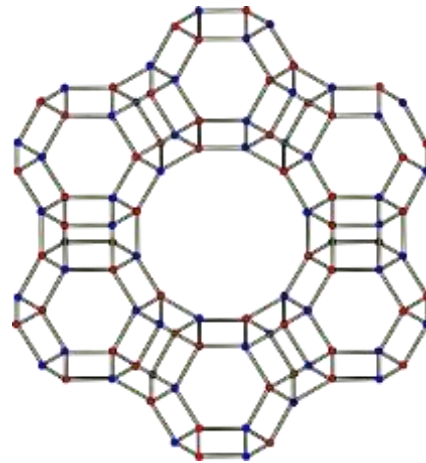
Catalysis in which the catalyst is in a different aggregation state than reactants and products



- Allows easy separation of reactants/products from catalyst, and re-use of the catalyst
- Omnipresent in chemical industry
- Catalyst generally in solid state and often dispersed on a solid (inert, porous) support; reactants often gases
- Catalyst generally in the form of nanoparticles: (i) increased surface area; (ii) different properties than bulk

Examples of heterogeneous catalysis

Catalytic cracking of petroleum



*Zeolite catalyst
(aluminum silicate)*

Catalysts in cars

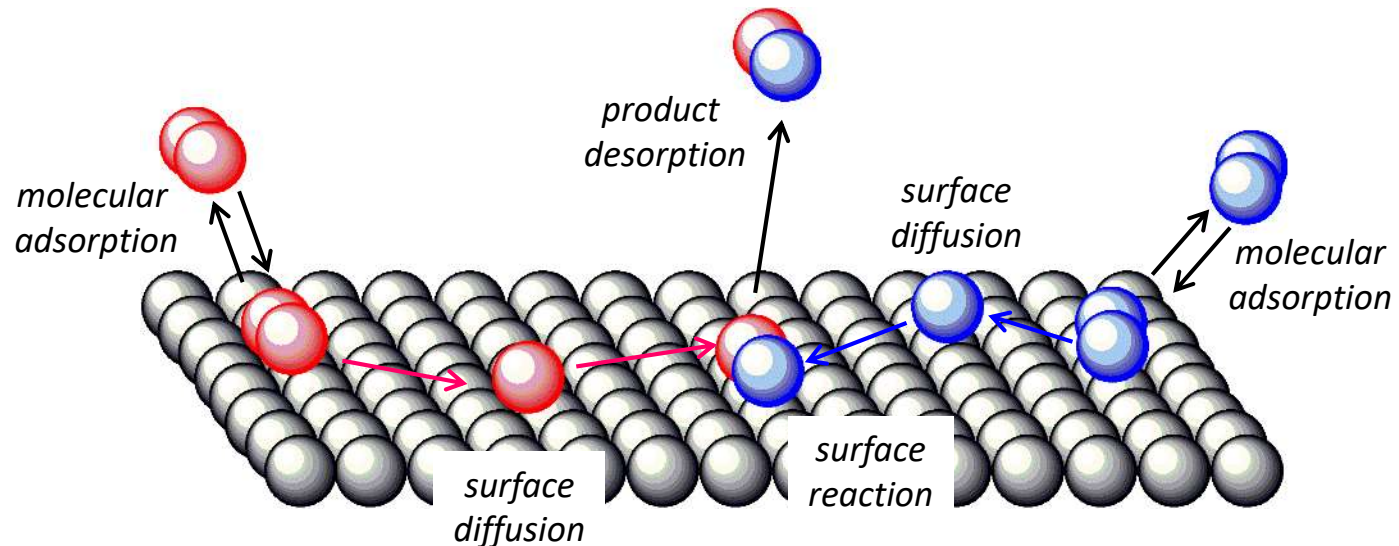
1. $2 \text{CO}(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{CO}_2(\text{g})$
2. $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$
3. $4 \text{C}_x\text{H}_y(\text{g}) + (4x + y) \text{O}_2(\text{g}) \rightarrow 2y \text{H}_2\text{O}(\text{g}) + 4x \text{CO}_2(\text{g})$



*Pd as oxidation catalyst
Rh as reduction catalyst
Also Pt, Fe, Mn, Ce catalysts*

Catalytic cycle heterogeneous catalysis

1. Transport of the reactant(s) to the active site
2. Adsorption of the reactant(s)
3. Surface reaction between adsorbed intermediates and product(s)
4. Desorption of the product(s)
5. Transport of product(s) away from the active site



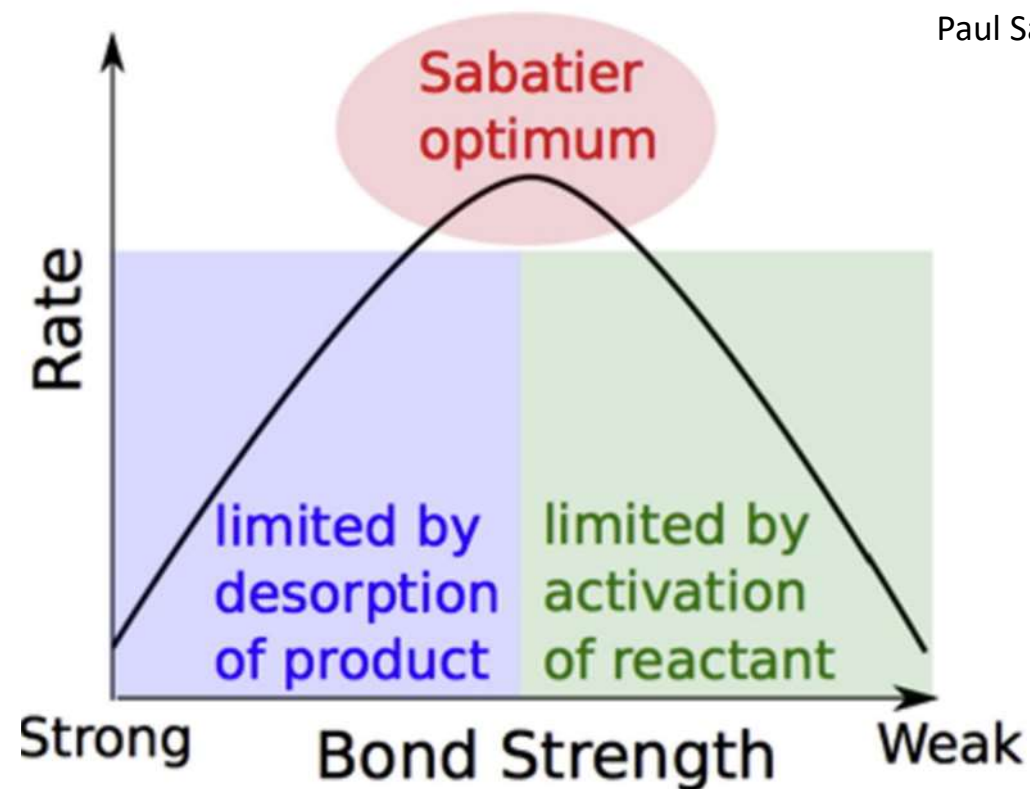
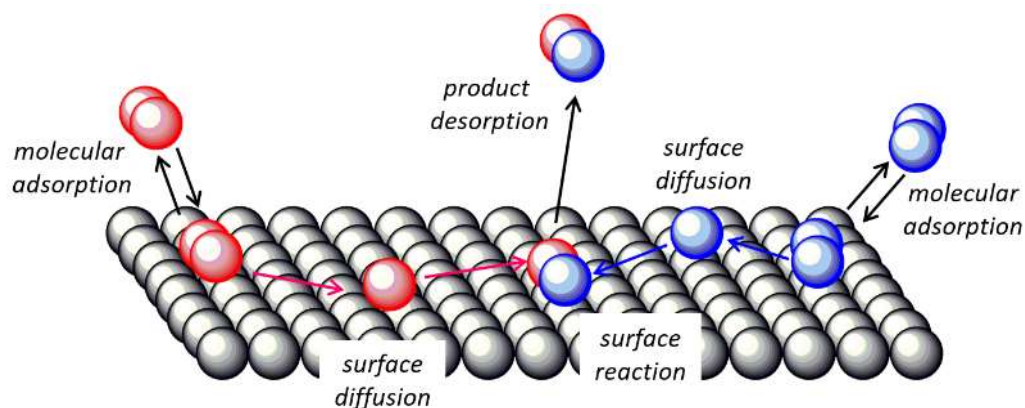
Sabatier principle

“Interactions between catalyst and substrate should not be too weak or strong”

- Too weak: substrate does not adsorb long enough to react
- Too strong: - substrate not mobile enough to diffuse and react with another substrate
- product may not desorb from the catalyst surface

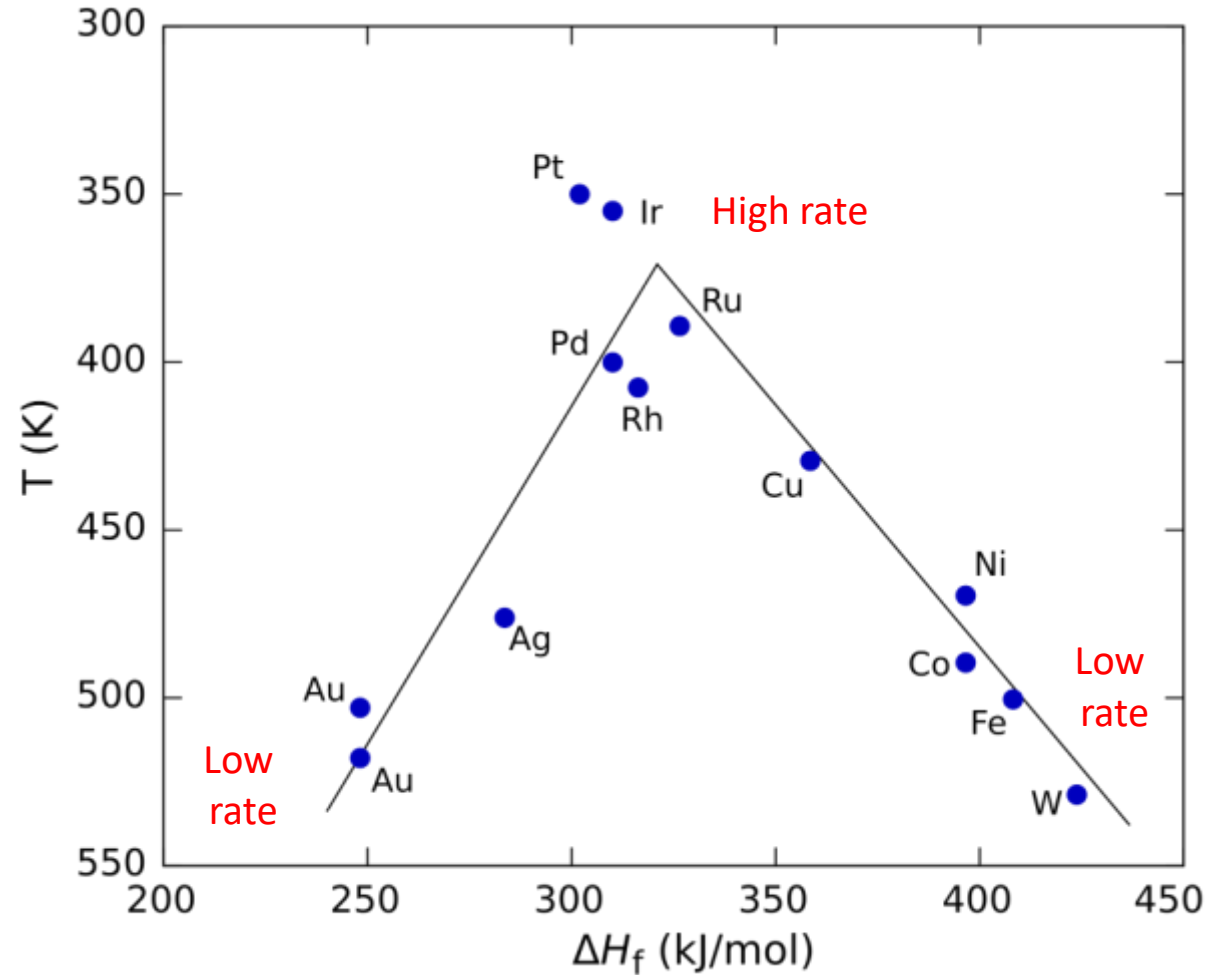


Paul Sabatier



Sabatier principle

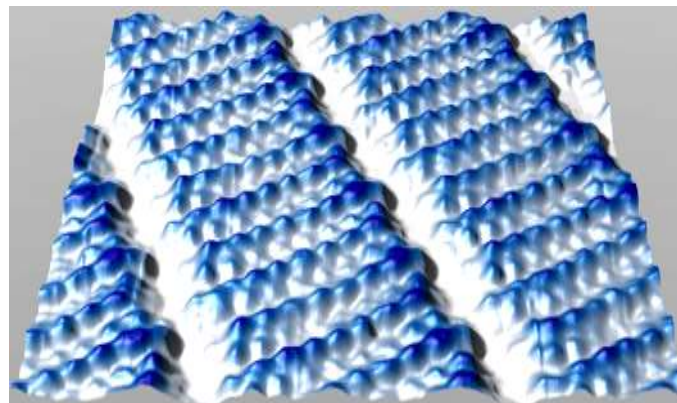
Example: decomposition formic acid on metal surfaces ($\text{HCOOH} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{H}_2$)



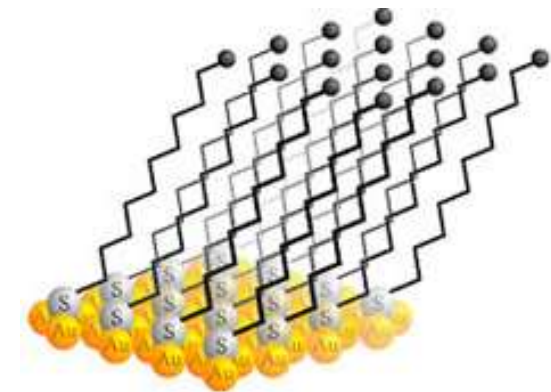
Adsorption on a surface

Two classes: physisorption and chemisorption

	Physisorption	Chemisorption
Interaction strength	$\Delta H_{\text{ads}} < 30 \text{ kJ/mol}$	$\Delta H_{\text{ads}} 30\text{-}500 \text{ kJ/mol}$
Interaction type	Dipole-dipole, Van der Waals	Chemical bonds
Site preference	Relatively unspecific, monolayers & multilayers	Specific, monolayers
Examples	H_2 , N_2 , alkane derivatives	C, H, O and N atoms, CO, O_2 , OH, SH



STM image of stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) molecules physisorbed to graphite

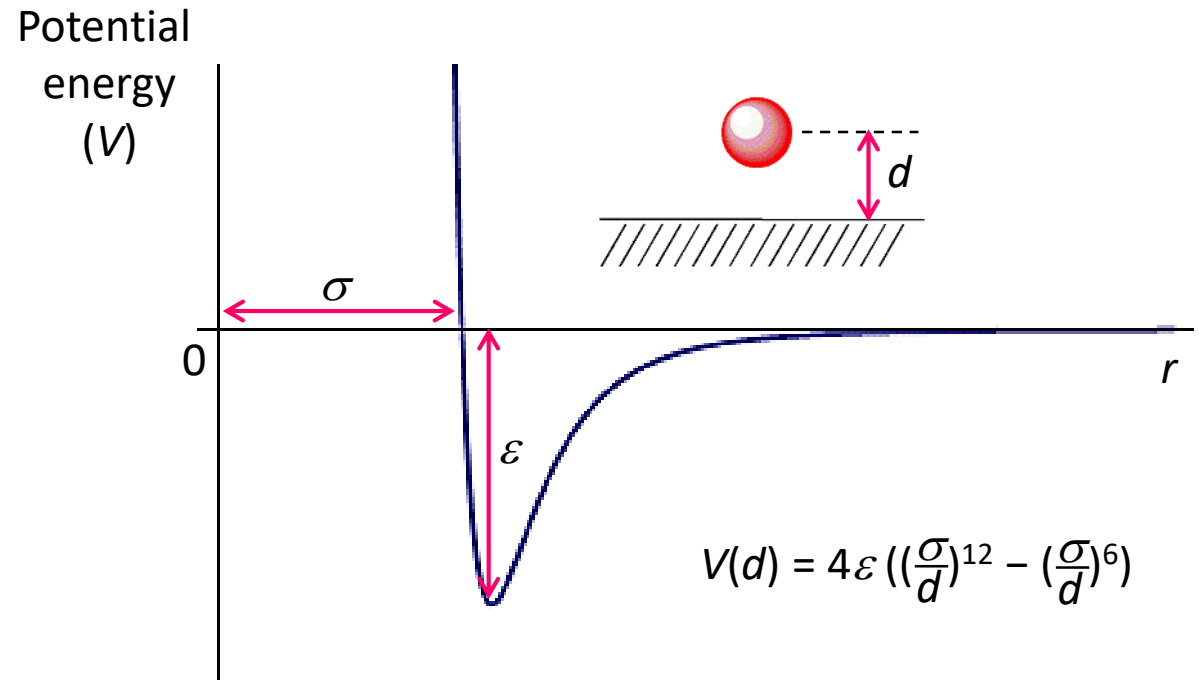


Undecane thiol ($\text{C}_{11}\text{H}_{23}\text{SH}$) molecules chemisorbed to gold

Adsorption: often **entropically** unfavorable, but **enthalpically** favorable (both ΔS and $\Delta H < 0$)

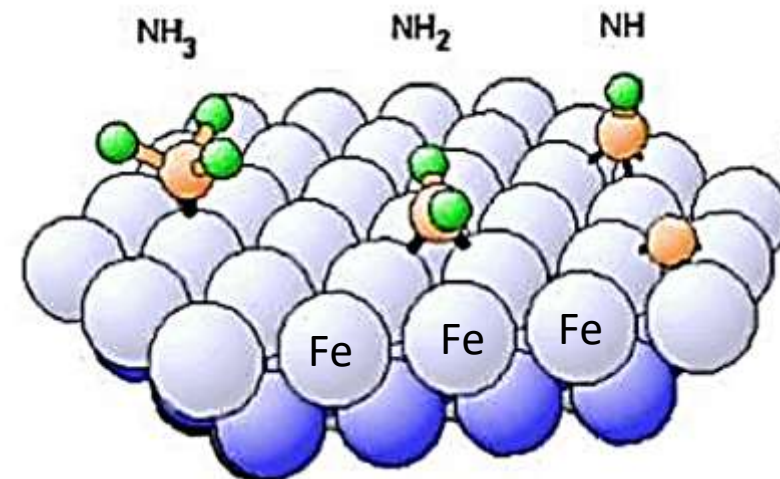
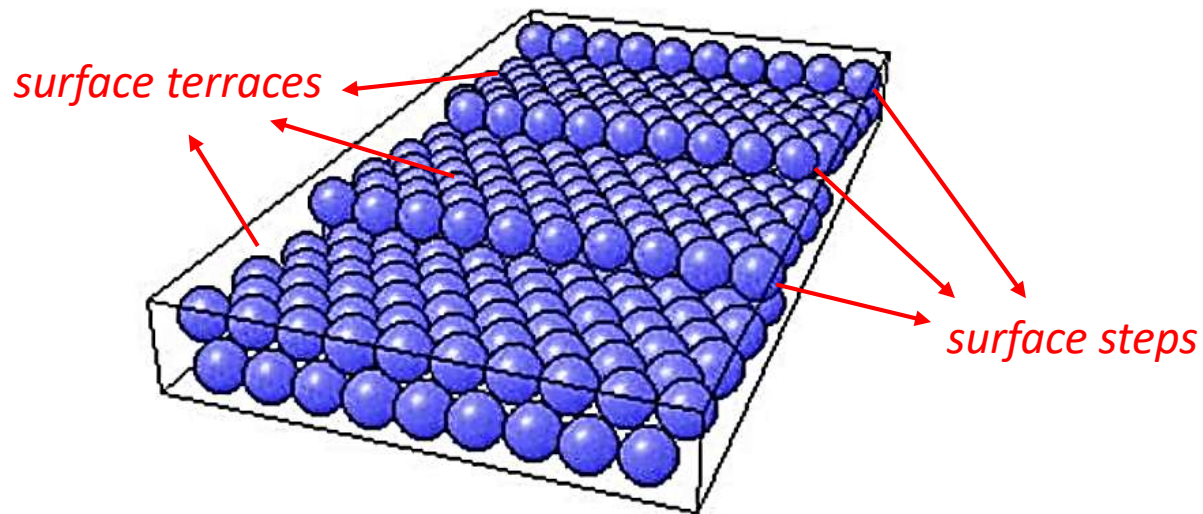
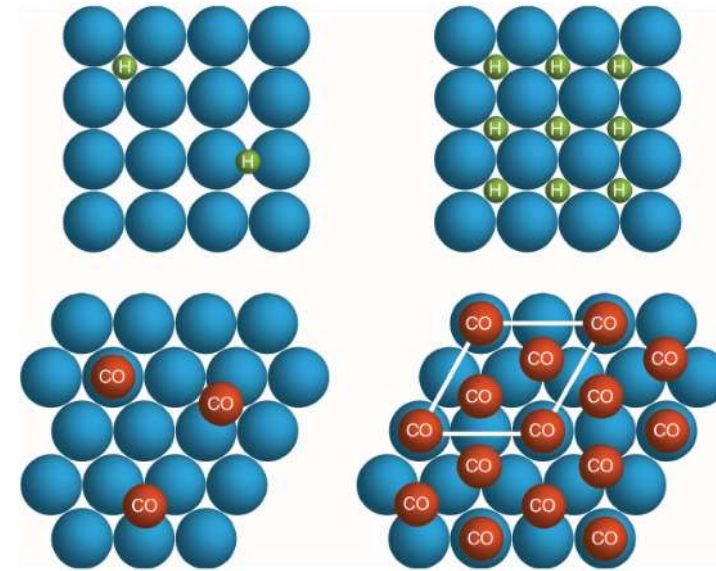
Physisorption on a surface

- Balance between short-range electronic repulsion and long-range Van der Waals attractions
- Surface-molecule ('vertical') and also molecule-molecule ('lateral') interactions
- Generally observed for rare gases and stable molecules (H_2 , N_2 , alkanes)



Chemisorption on a surface

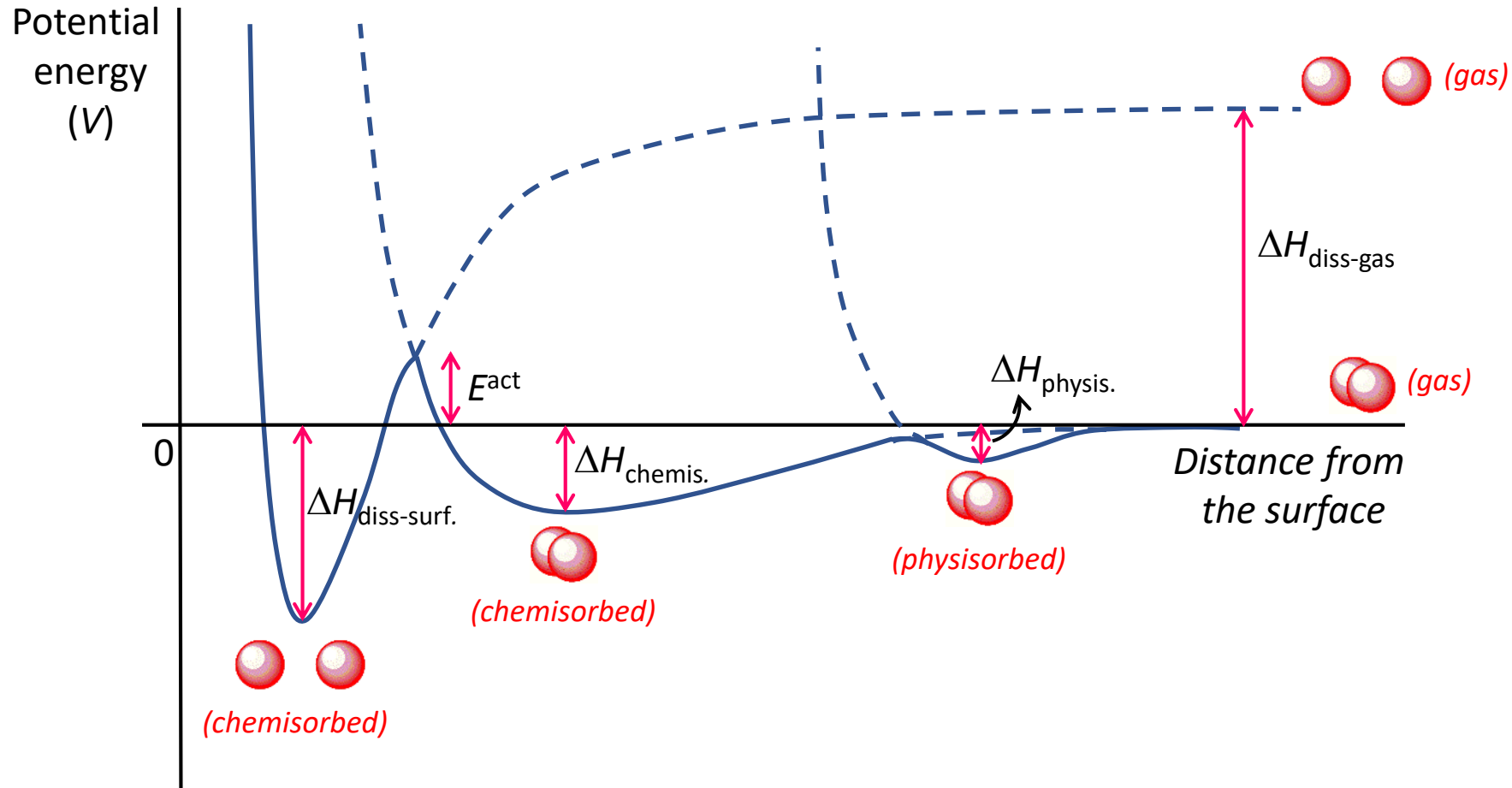
- Chemical bonds are formed between surface and molecules or atoms
- Binding of atoms or molecules at specific surface sites
- Different surface adsorption sites may lead to different catalytic reactivity



Chemisorption on a surface

Chemisorption on a surface can enhance chemical reactivity

Example: dissociation of a diatomic molecule



Adsorption isotherms

Interaction between a gas and a surface

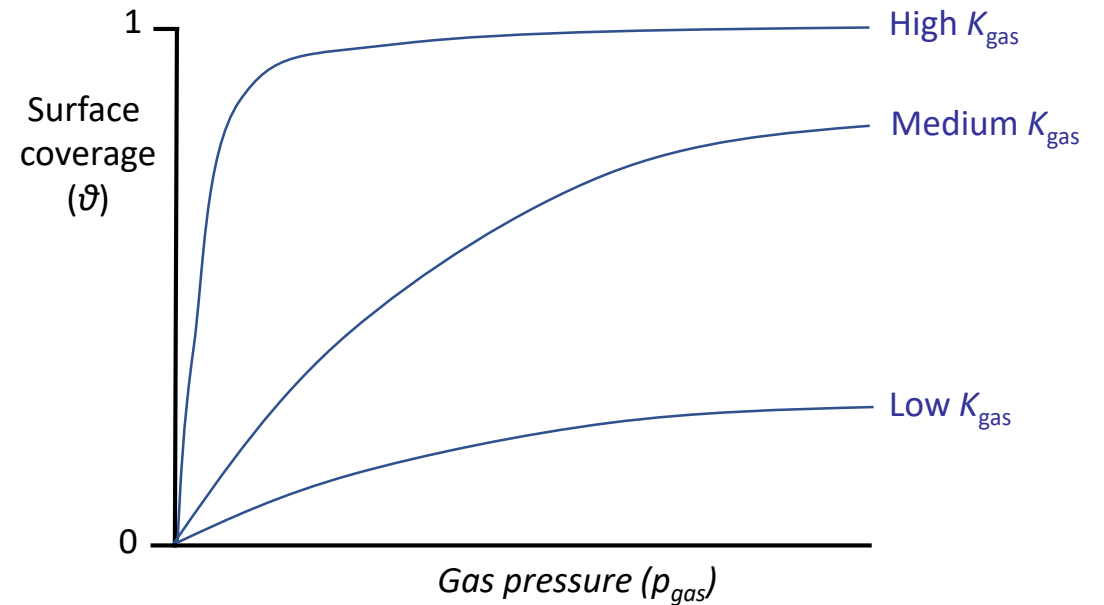


- Surface coverage (θ) of a gas is related to its pressure (p_{gas}) in a system and the adsorption constant K_{gas}

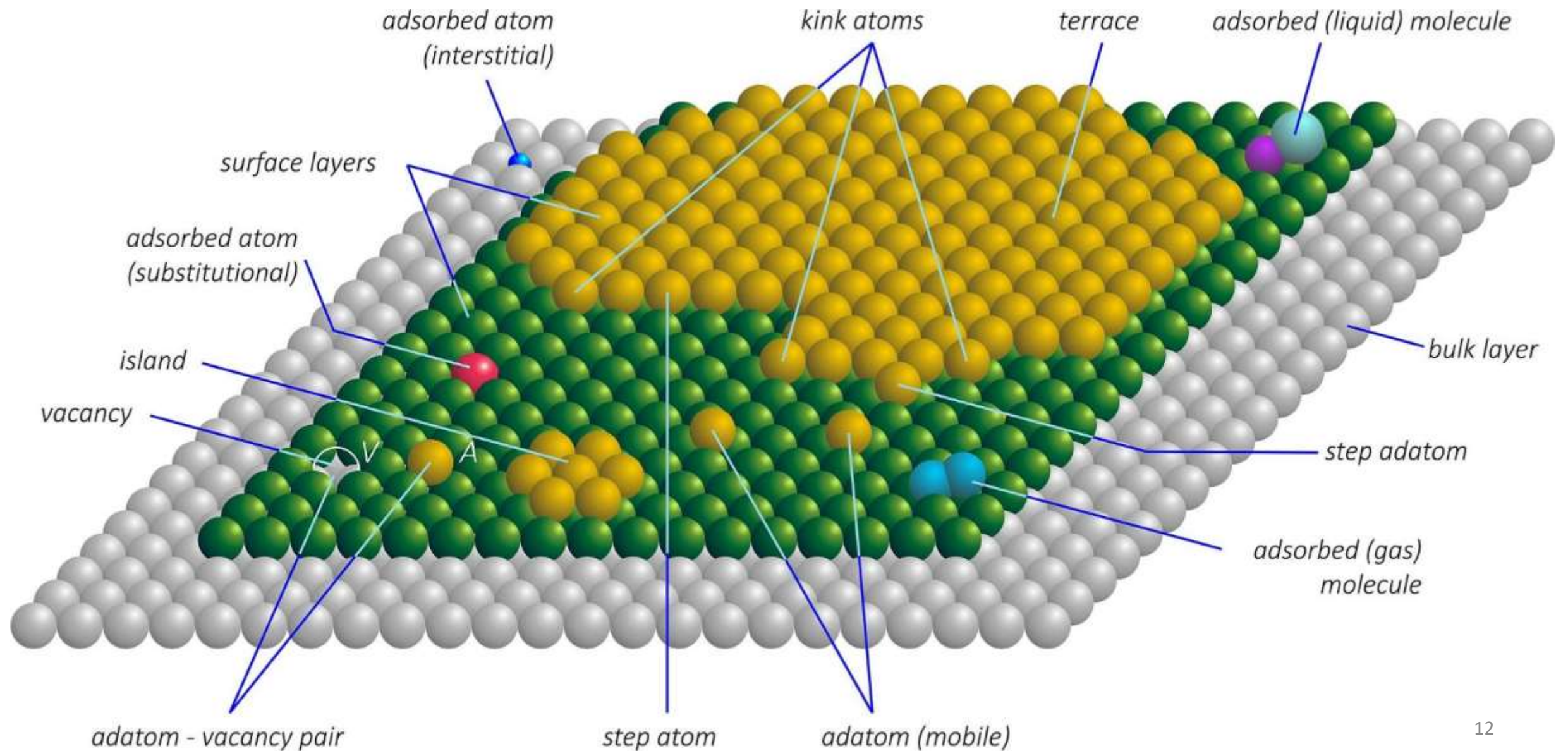
$$\theta_{\text{gas}} = \frac{K_{\text{gas}} p_{\text{gas}}}{1 + K_{\text{gas}} p_{\text{gas}}}$$

Langmuir adsorption isotherm

- K_{gas} depends on T , p , type of surface-site, type of gas
- Adsorption isotherms ignore differences between surface sites and dependence of K_{gas} on lateral interactions between gas molecules on the surface



What metallic surfaces often *really* look like



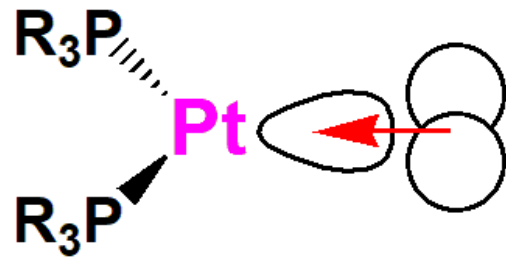
From homogeneous to heterogeneous catalysis

Example: **oxidative addition** reaction of dihydrogen to a Pt(0) complex

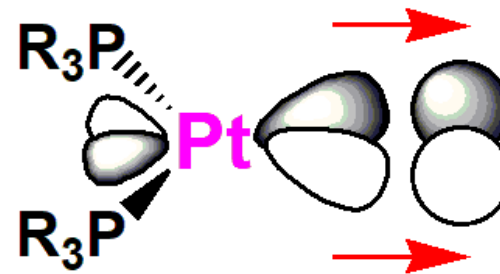


- Formal oxidation state from Pt(0) to Pt(II)
- Hydrogen atoms formally added as hydrides

Mechanism:

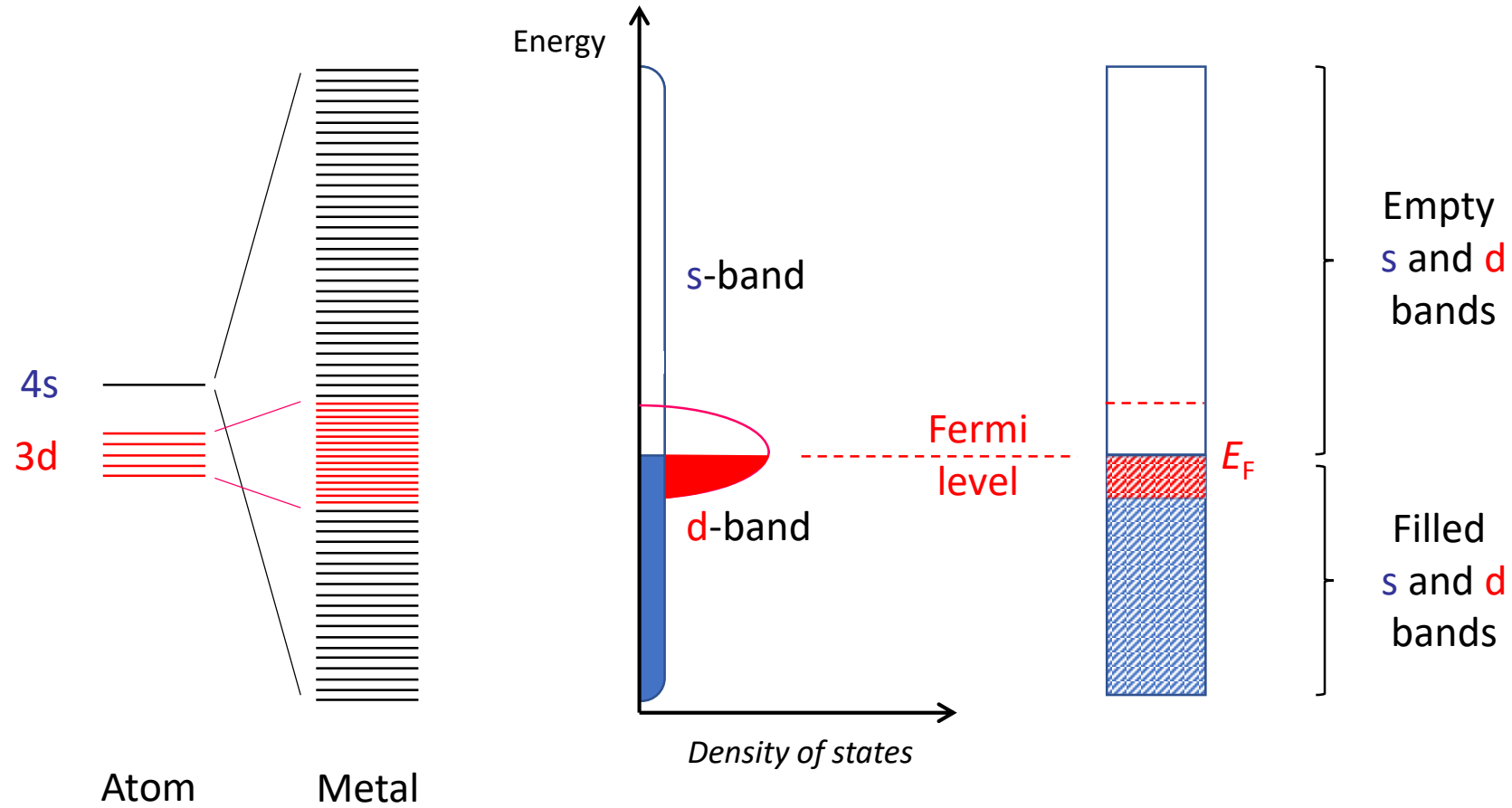


σ -donation of electron density from filled σ orbital of H_2 into an empty metal orbital



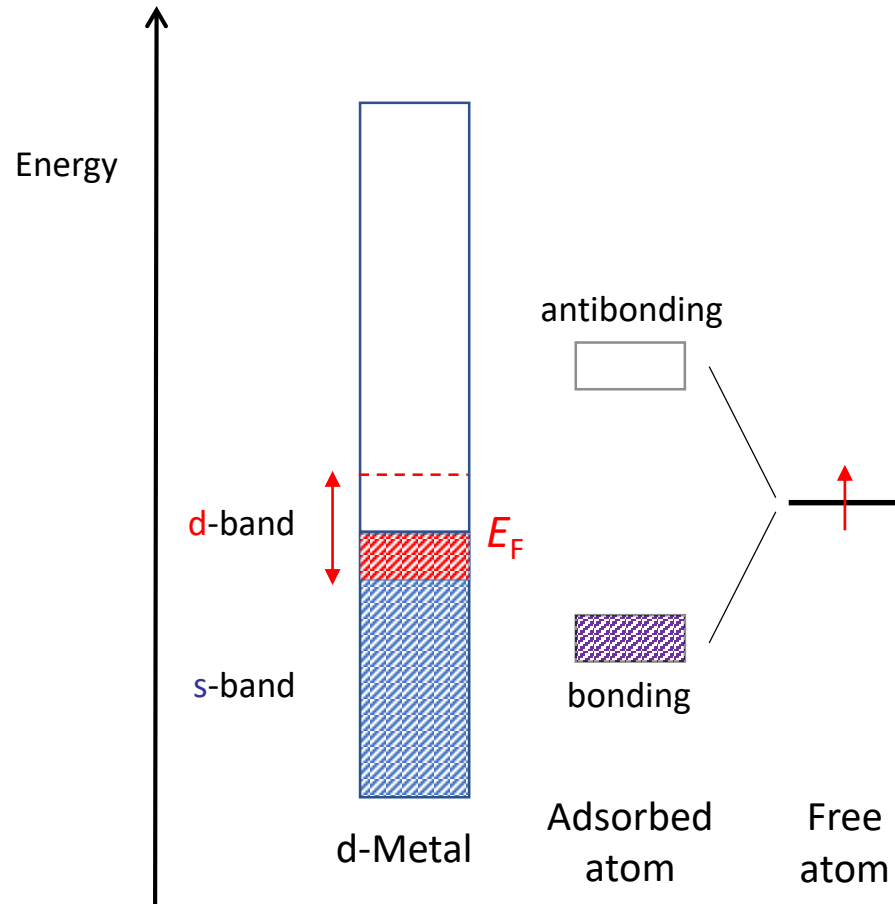
π -back donation of electron density from filled metal orbital into empty σ^* orbital of H_2

Chemisorption and chemical bonding



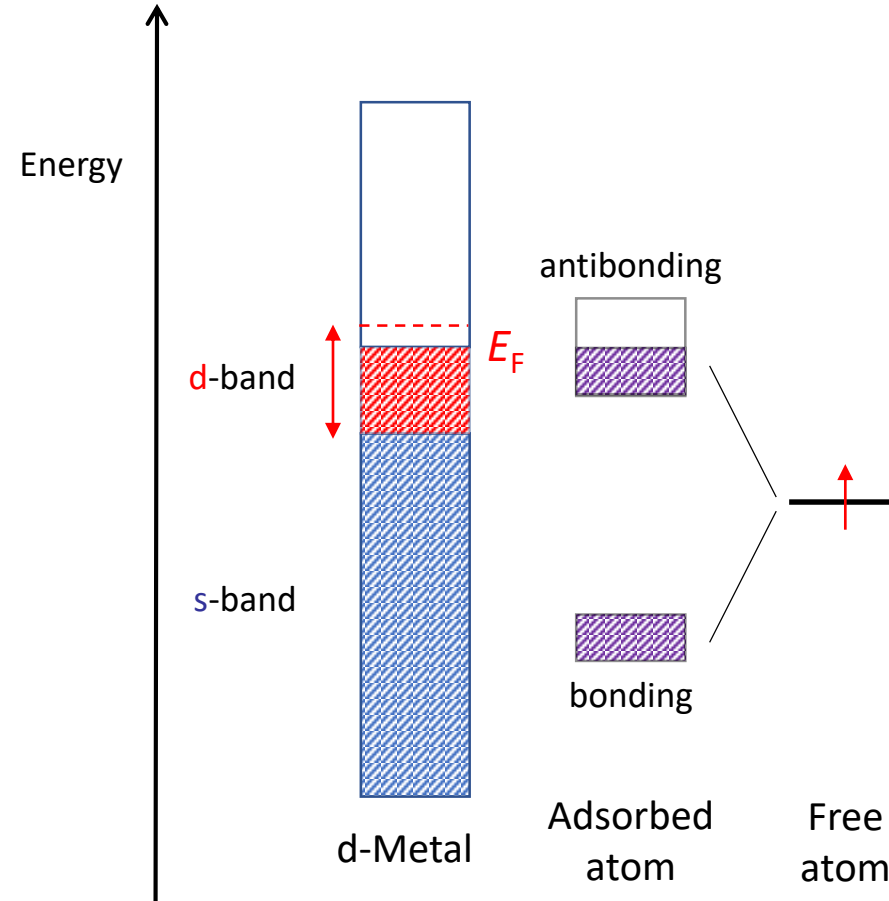
Chemisorption and chemical bonding of an atom

Metal with few d-electrons



- Antibonding orbital above Fermi level and bonding orbital below: **strong binding**
- Examples: C on Cr, O on Fe

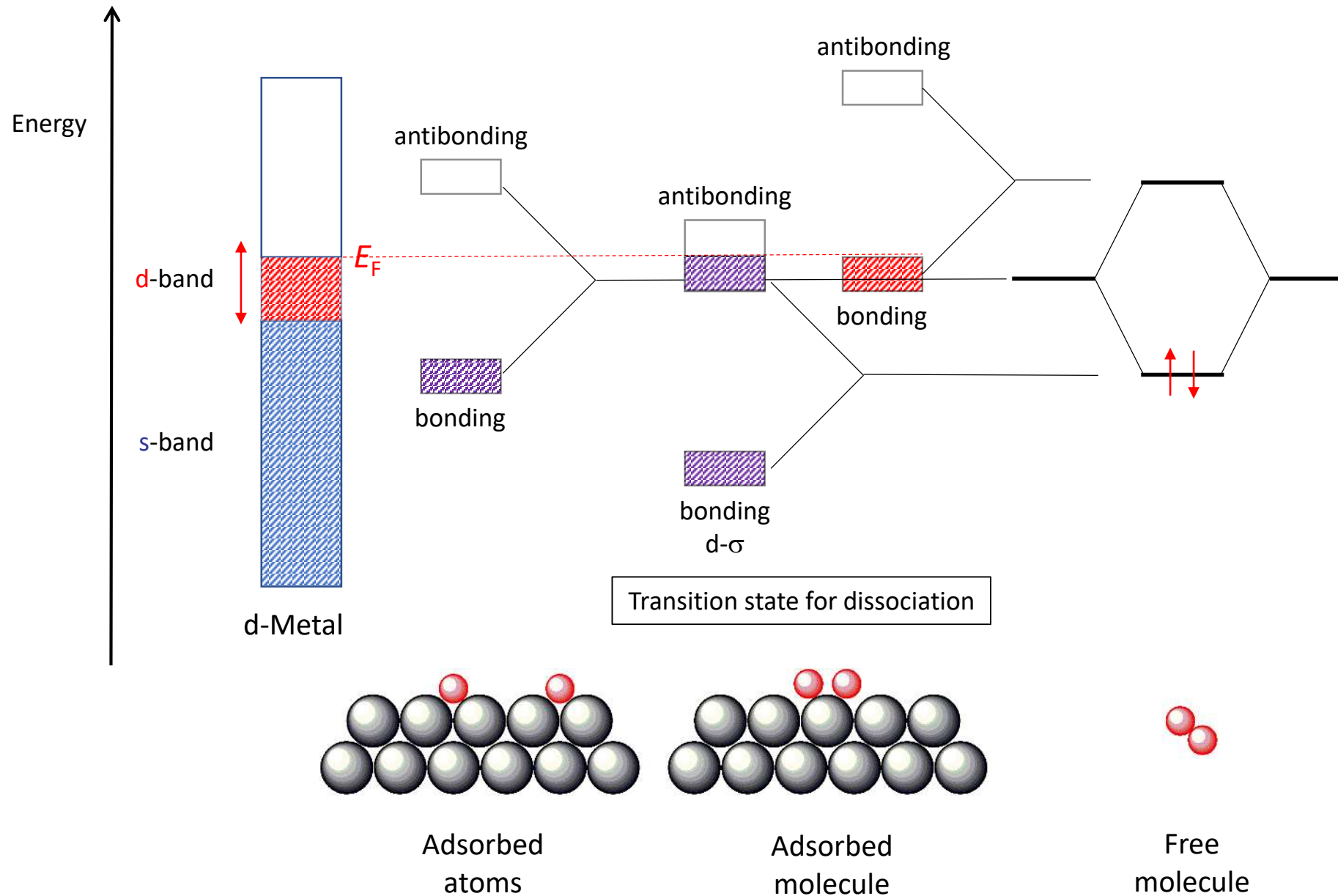
Metal with many d-electrons



- Antibonding orbital partly below Fermi level and bonding orbital below: **moderate binding**
- Examples: C on Pt, O on Rh, H on Ru

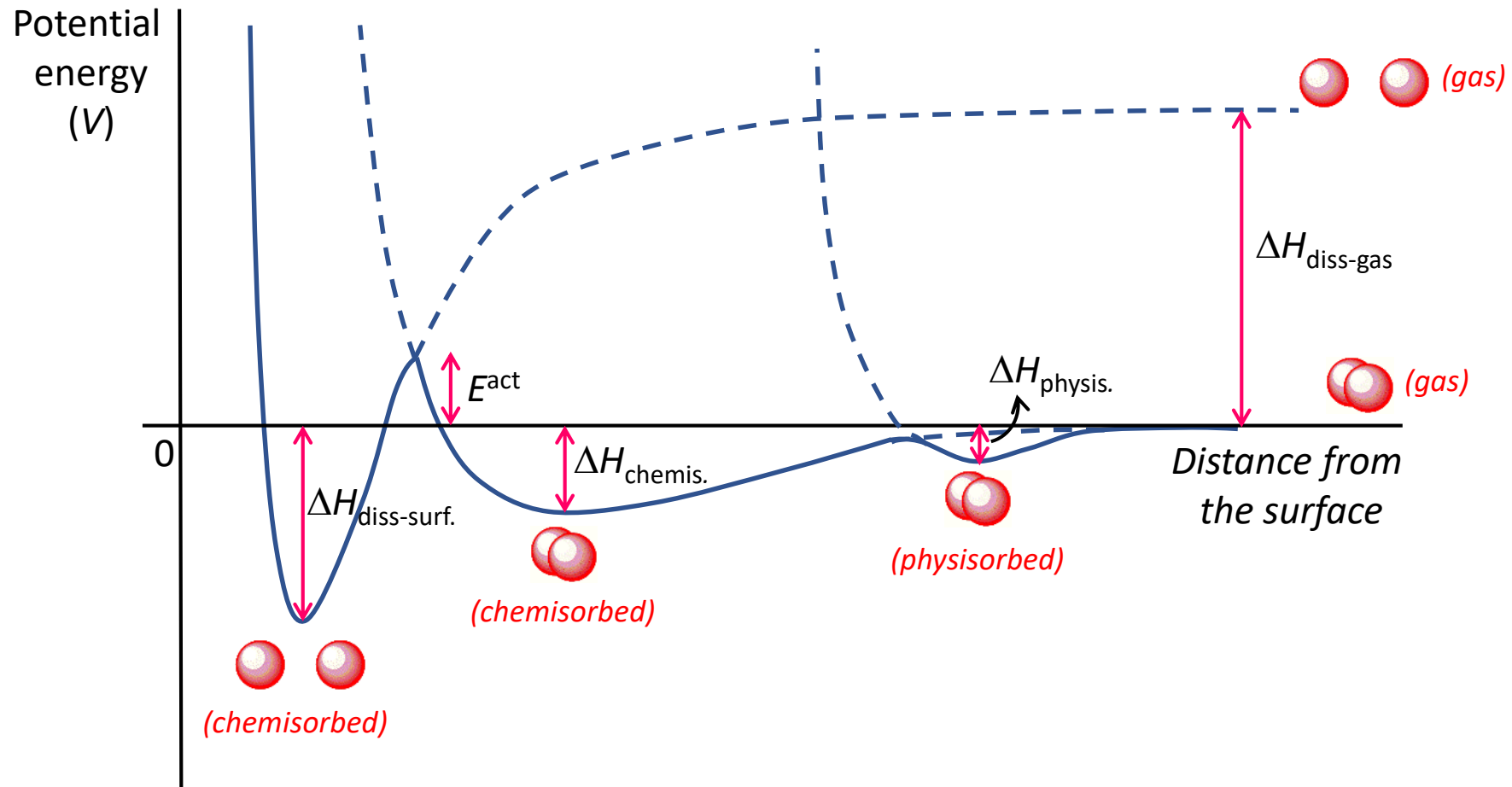
**Good
for
catalysis!**

Chemisorption and chemical bonding of a molecule



Thermodynamics and kinetics

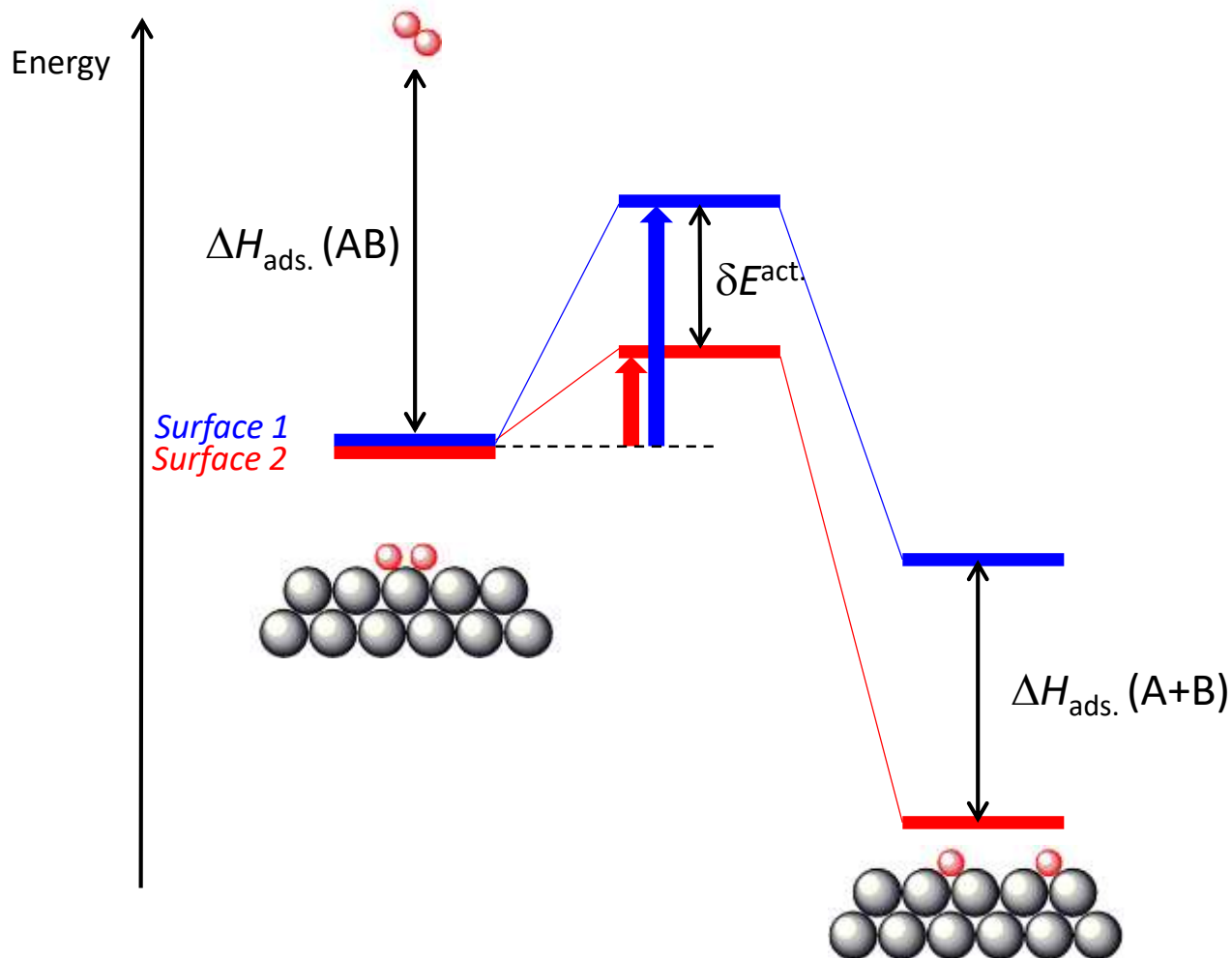
- Thermodynamic driving force of dissociation: metal-atom bonds stronger than atom-atom bonds
- E^{act} should not be larger than $\Delta H_{\text{chemis.}}$.



Thermodynamics and kinetics

Correlation between ΔH and E^{act} of a reaction

Adsorption and dissociation of a molecule AB on two different metal surfaces



Brønsted-Evans-Polanyi (BEP) relation

- E^{act} decreases when atoms become more strongly adsorbed
- Adsorption energy of molecules similar, but of dissociated atoms (very) different

$$\delta E^{\text{act}} = \alpha_{\text{BEP}} \Delta H_{\text{react}}^{\text{A+B-AB}}$$

- α : BEP-parameter, varies between 0 and 1
- When $\alpha = 0$: early TS, hardly dissociated
- When $\alpha = 1$: late TS, nearly dissociated (this is generally observed)

Adsorption strengths

Strong atomic and dissociative adsorption

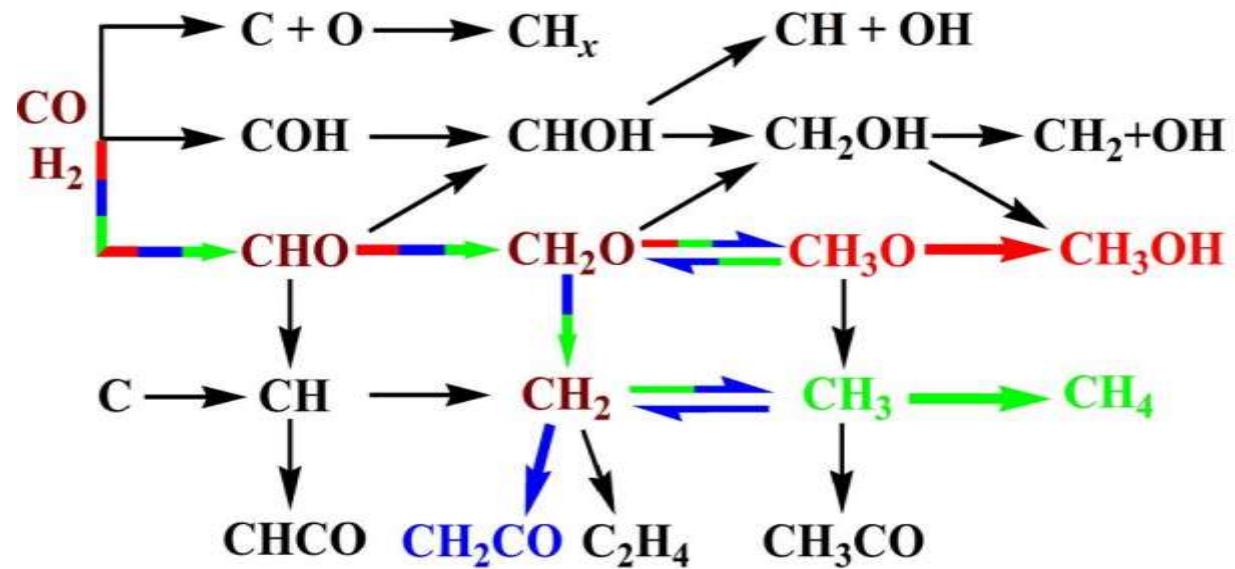
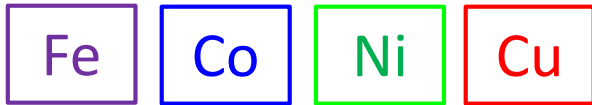
Metal atoms larger
Binding energy of atoms weakens

Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

Filling of d-orbitals
Binding energy of atoms weakens

Moderate atomic and dissociative adsorption

Hydrogenation of CO on Co, Ni and Cu



Favorable pathways on Cu (**red**), Co (**blue**) and Ni (**green**)

- **Cu** does not dissociate CO \rightarrow CH₃OH is formed
- On **Ni**: C and O bind stronger and CO dissociation occurs slowly \rightarrow CH₄ is formed
- On **Co**: C and O bind strongly and CO dissociation occurs fast \rightarrow aldehydes and alkanes are formed
- On **Fe**: iron carbides (Fe_xC_y) form and then longer alkanes are formed (Fischer-Tropsch process)