The Concepts of Heterogeneous Catalysis

What is catalysis?

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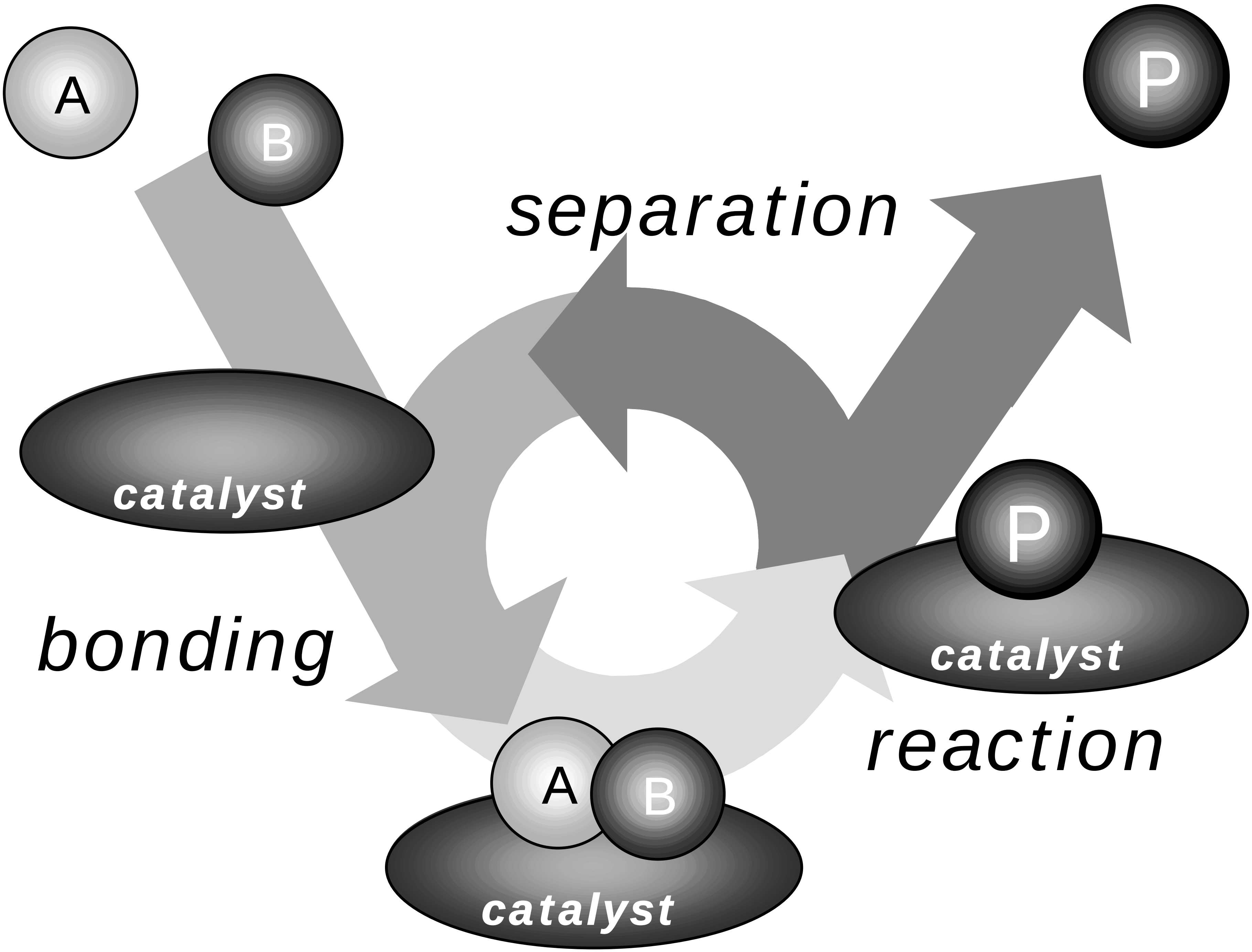
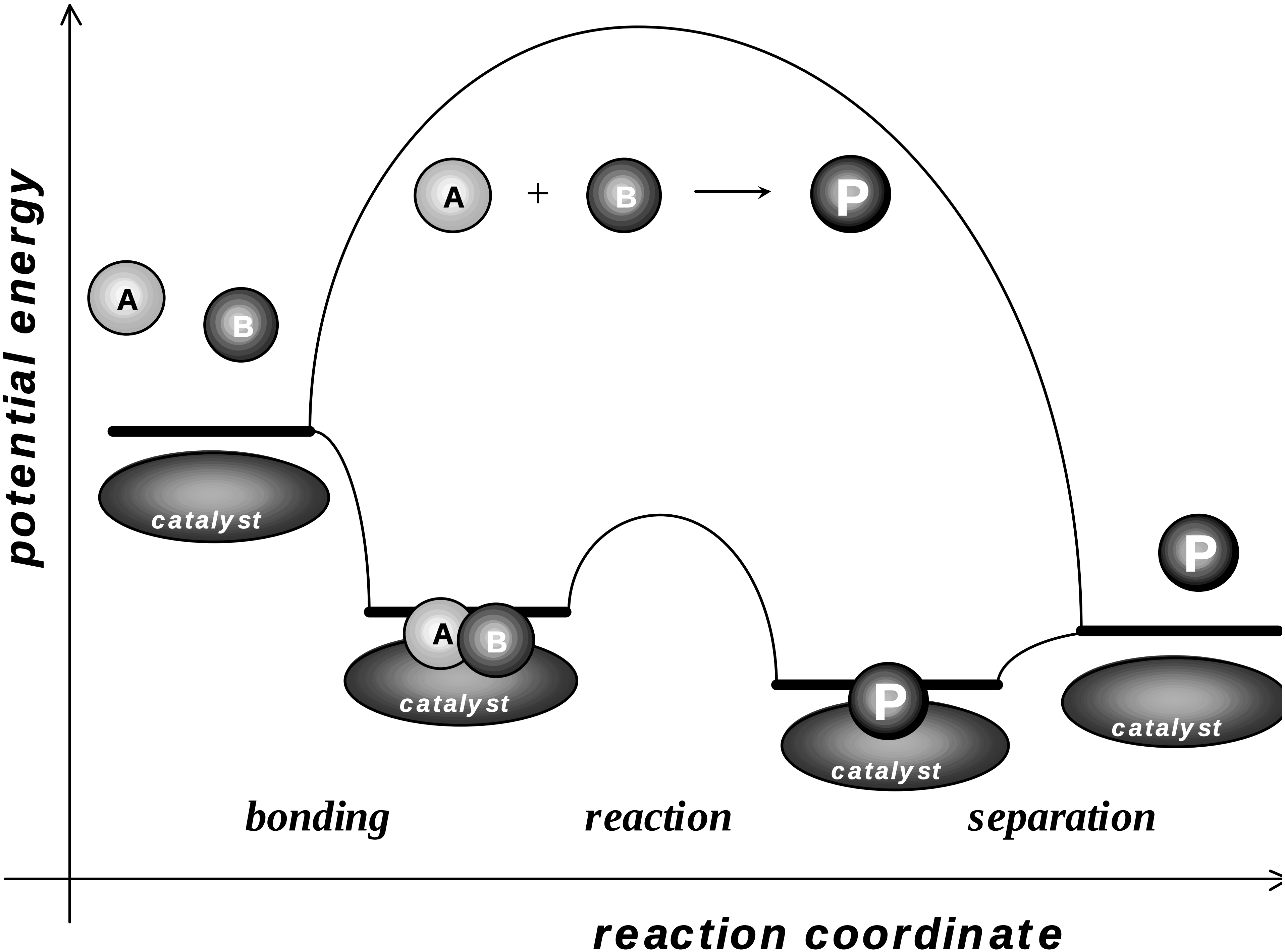
What is catalysis

- The potential energy picture
- The kinetic picture
- The chemical bonding picture


A
B
P
separation
catalyst
P
catalyst
bonding
A
B
catalyst
reaction


potential energy
A
B
catalyst
A + B → P
A
B
catalyst
P
catalyst
P
catalyst
bonding
reaction
separation
reaction coordinate

What is catalysis

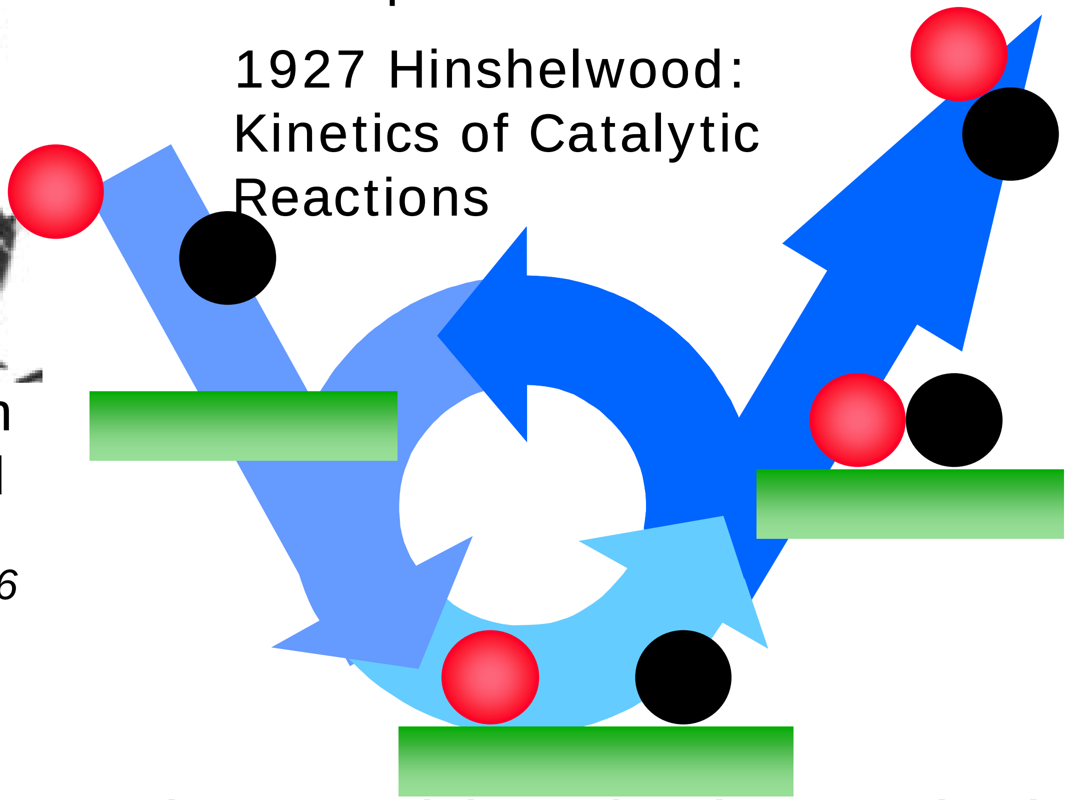
- The potential energy picture
- The kinetic picture
- The chemical bonding picture

Langmuir - Hinshelwood Kinetics

Cyril Norman Hinshelwood
1897 - 1967
Nobel Prize 1956

1915 Langmuir:
Adsorption Isotherm

1927 Hinshelwood:
Kinetics of Catalytic Reactions



Irving Langmuir
1881 - 1957
Nobel Prize 1932

- Consistent with Sabatier's Principle
- Coverage dependence: Volcano plot
- Temperature dependence: Volcano plot

Reaction Mechanism:

$$A + * \Leftrightarrow A_{ads} \qquad \text{equilibrium; } K_A$$

$$B + * \Leftrightarrow B_{ads} \qquad \text{equilibrium; } K_B$$

$$A_{ads} + B_{ads} \rightarrow AB_{ads} + * \qquad \text{r.d.s; } k$$

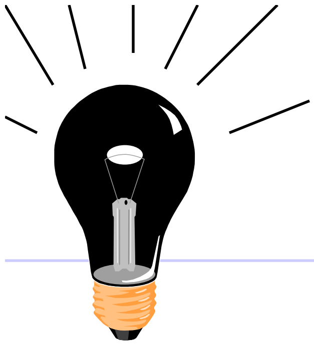
$$AB_{ads} \rightarrow AB + * \qquad \text{fast}$$

Coverages:

$$\theta_A = K_A\, p_A\, \theta_* \qquad \theta_B = K_B\, p_B\, \theta_* \qquad \theta_* = \frac{1}{1 + K_A p_A + K_B p_B}$$

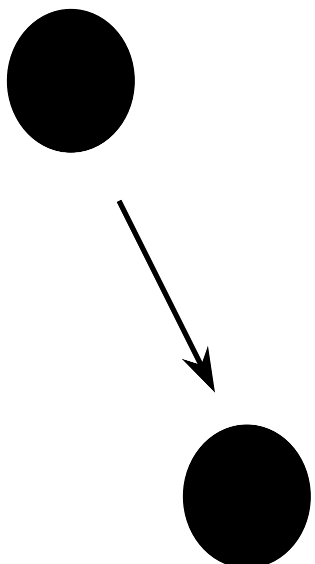
Reaction rate:

$$r = \frac{N_*\ k\ K_A K_B\ \ p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$



Irving Langmuir (1881 - 1957)

- worked at General Electrics
- oxygen adsorption on tungsten filaments of light bulbs
- 1932: Nobel Prize in Chemistry
- Langmuir Adsorption Isotherm:



$$\theta_A = \frac{K_A\,[A]}{1 + K_A\,[A]}$$

Rate of reaction, Activation energy, Order of reaction:

$$r = \frac{N_* \; k \; K_A K_B \; p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

$$E_a^{app} = -R \frac{\partial \ln r}{\partial (1/T)} = RT^2 \frac{\partial \ln r}{\partial T}$$

$$= E_a^{rds} + (1 - 2\theta_A)\, \Delta H_A + (1 - 2\theta_B)\, \Delta H_B$$

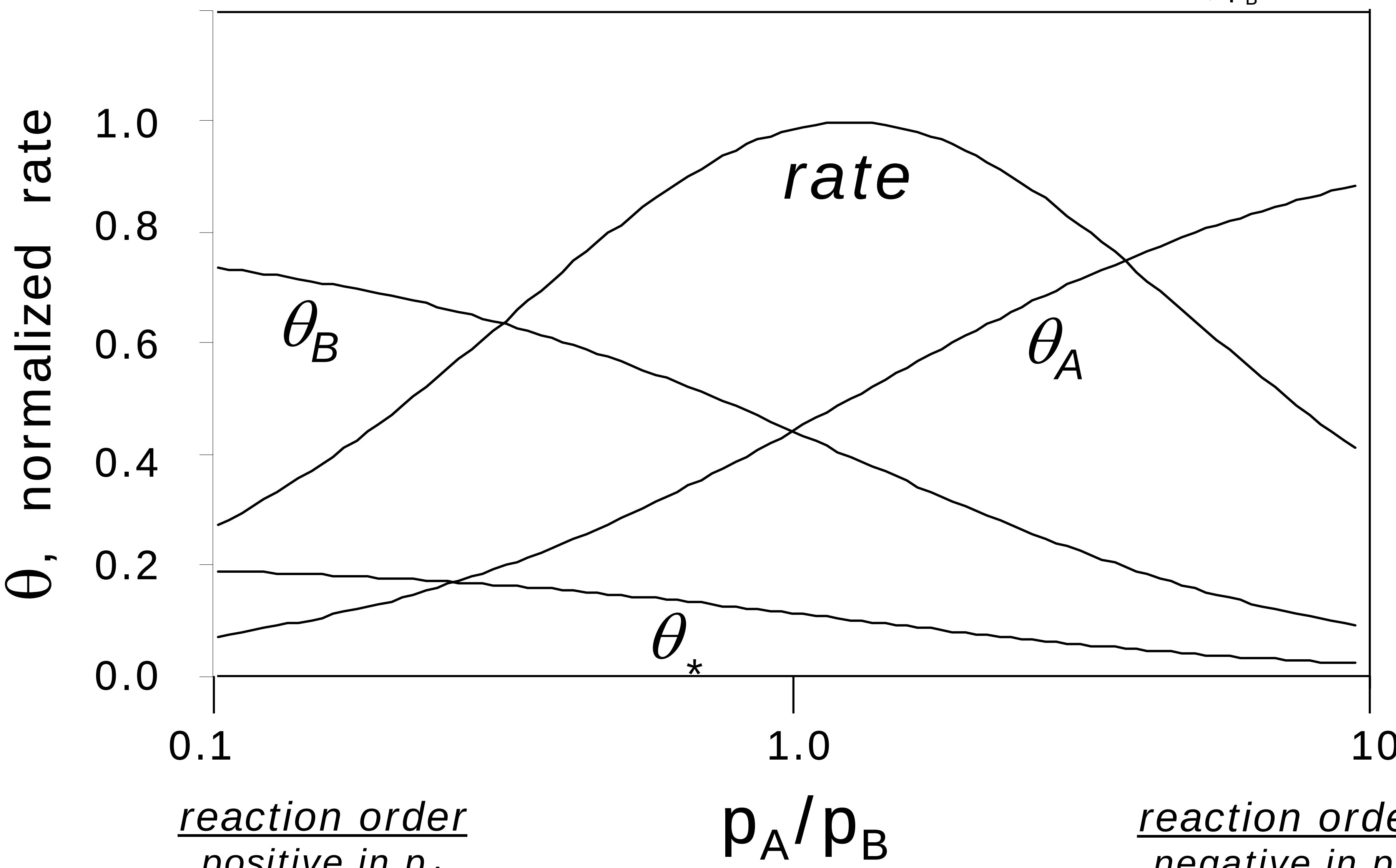
$$n_A = \frac{\partial \ln r}{\partial \ln p_A} = p_A \frac{\partial \ln r}{\partial p_A} = 1 - 2\theta_A$$

Rate of a Catalytic Reaction: **Pressure Dependence**

$E_{ads}(A) = E_{ads}(B) = 125$ kJ/mol

$s(B) = s(A)$; $E_{act} = 50$ kJ/mol

$T = 600$ K; p_B is fixed

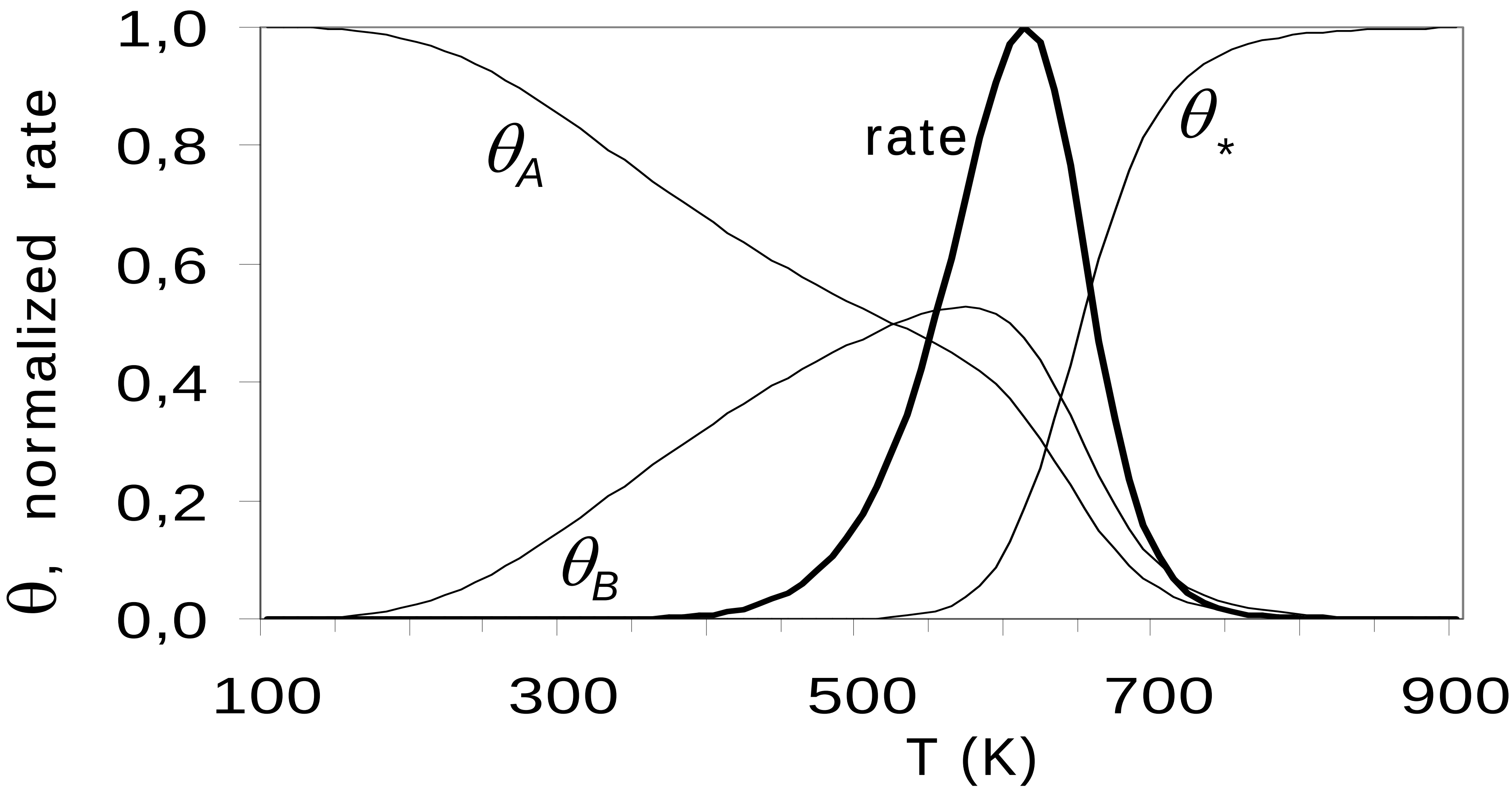


reaction order
positive in p_A
negative in p_B

reaction order
negative in p_A
positive in p_B

Rate of a Catalytic Reaction:
Temperature Dependence

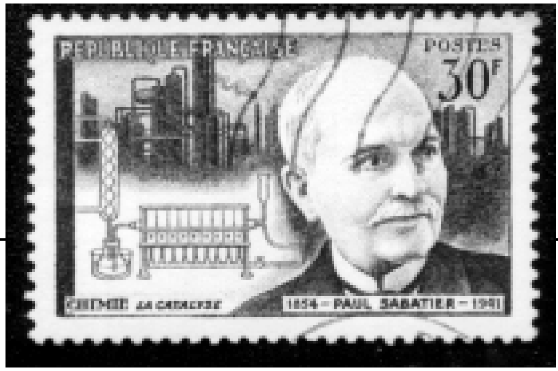
E_{ads} (A) = 135 kJ/mol
E_{ads} (B) = 125 kJ/mol
s(B) p_B = 10 s(A) p_A
E_{act} = 50 kJ/mol

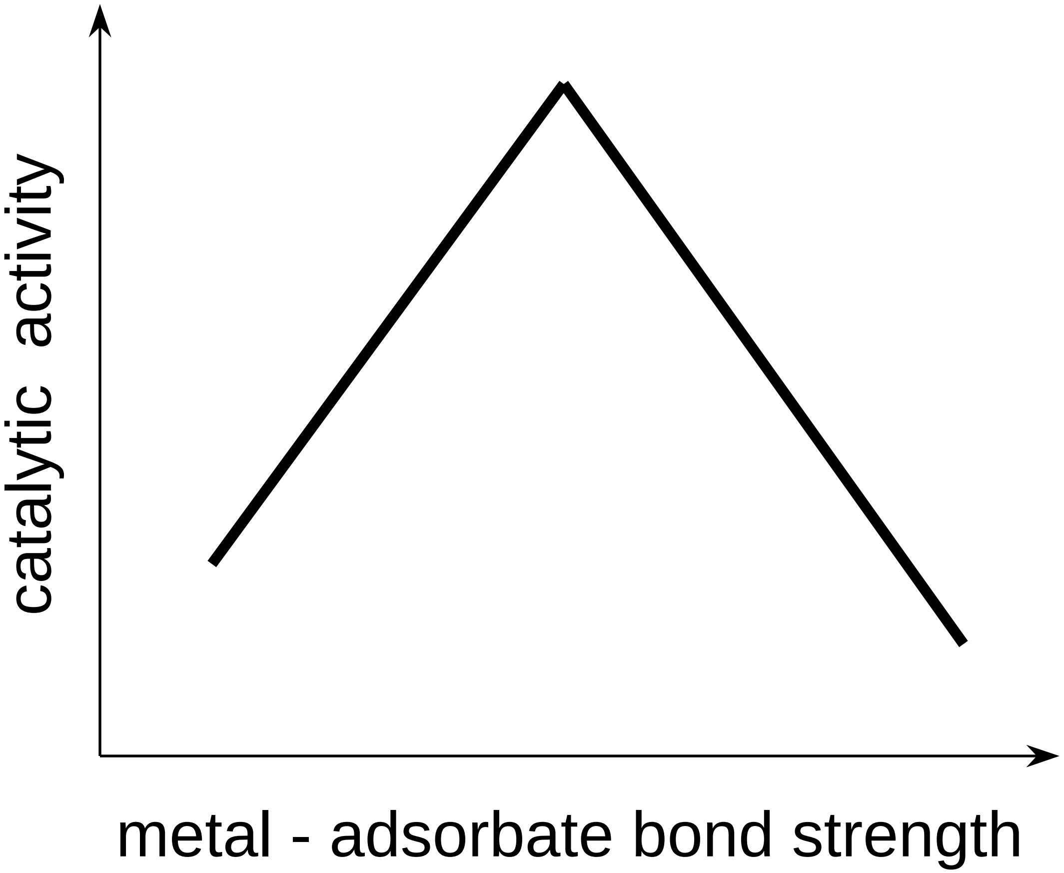


<u>reaction order</u>
negative in p_A
positive in p_B

<u>reaction order</u>
positive in p_A and p_B

The Sabatier Effect





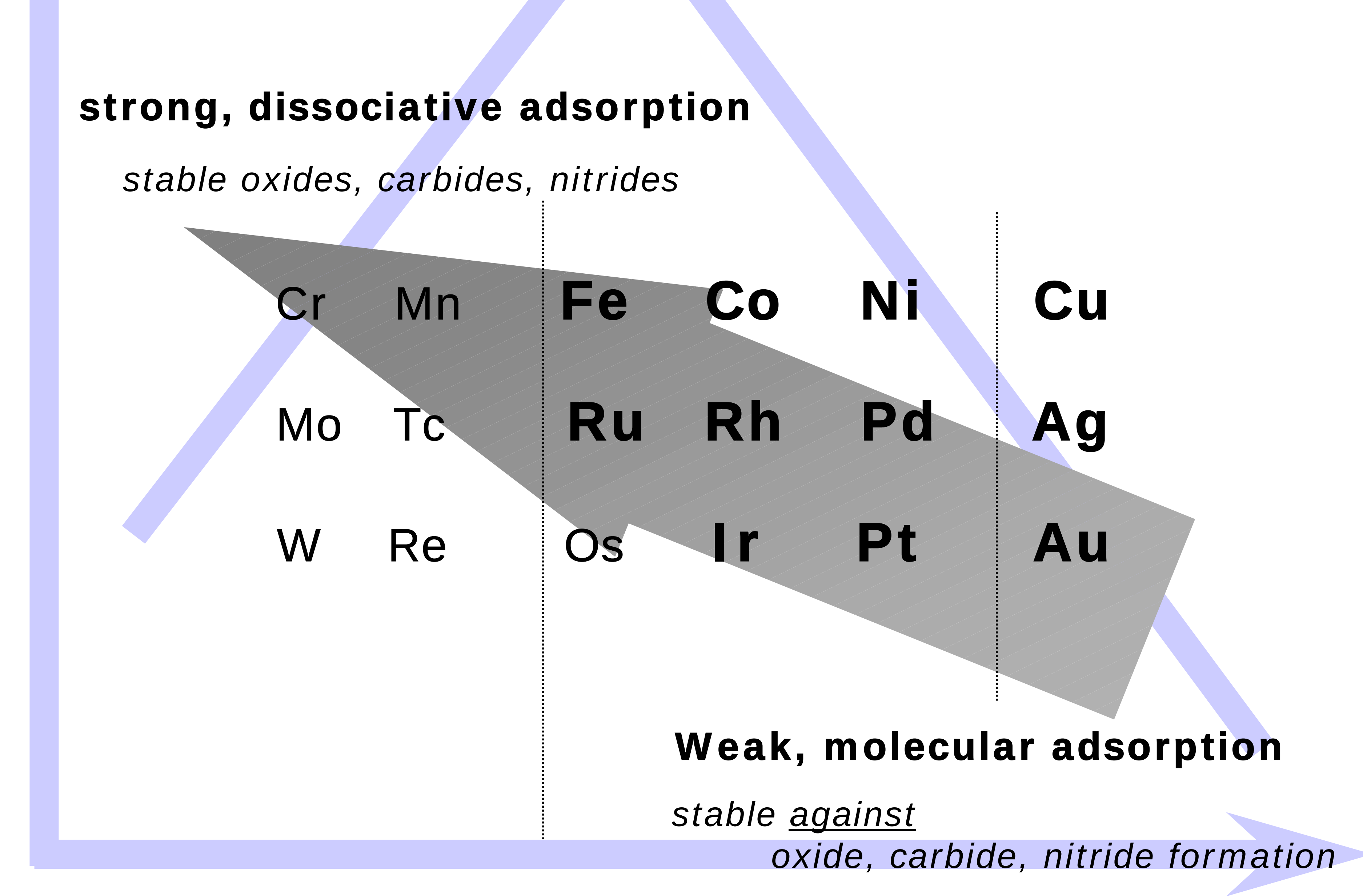
optimum interaction

catalyst - adsorbate:

- *not too strong*
- *not too weak*

optimum coverage

Catalysis by Metals: Trends in Reactivity



What is catalysis

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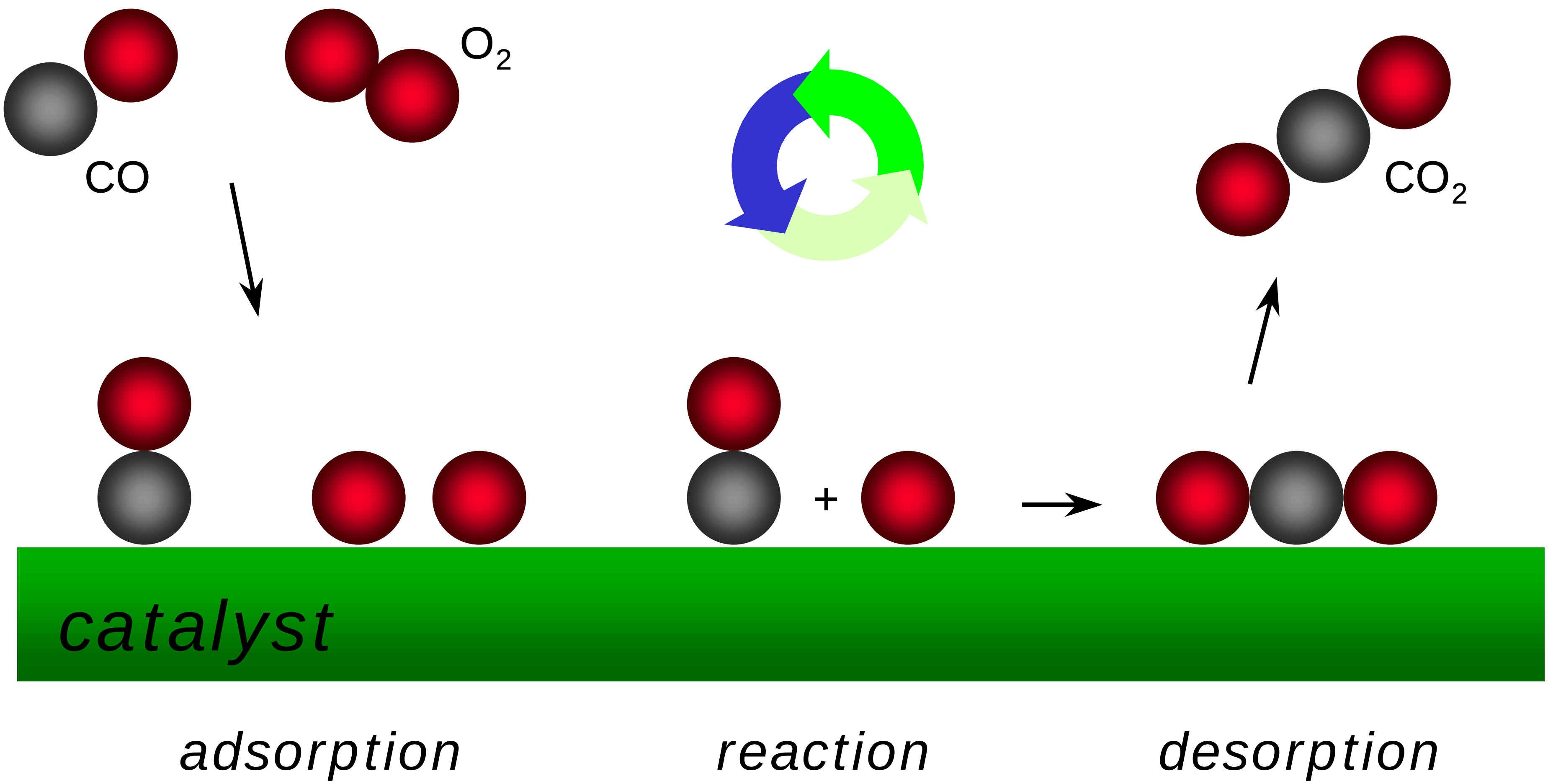
Example: CO Oxidation



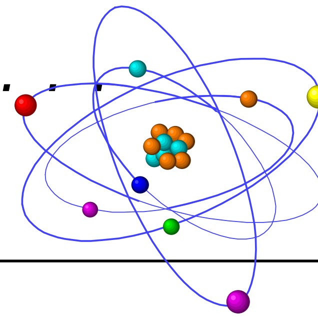
What is the most essential thing that the catalyst does ?

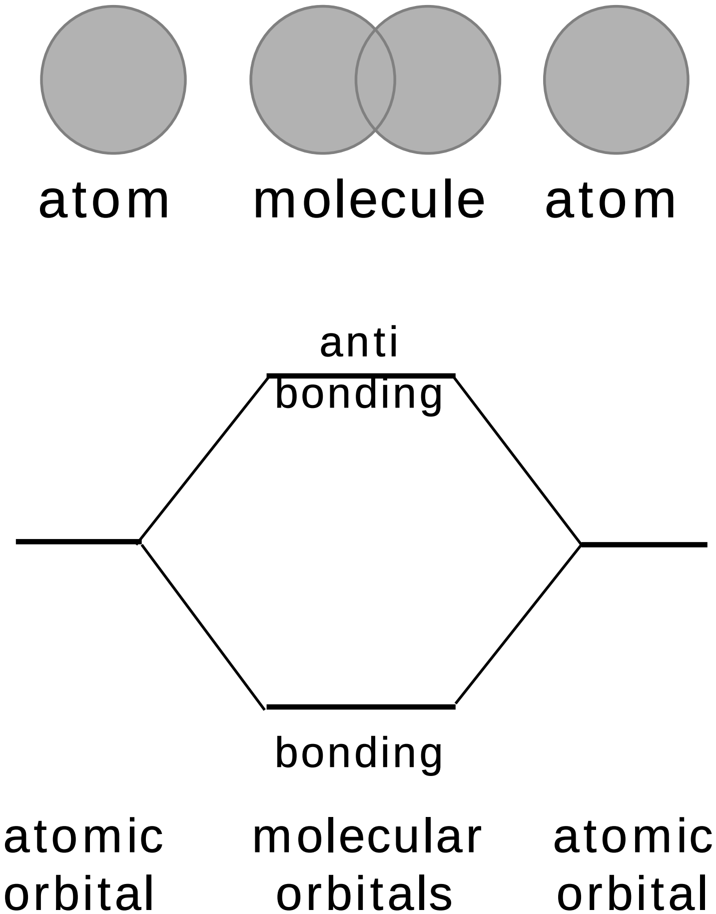
a catalyst breaks bonds.........

......and lets other bonds form

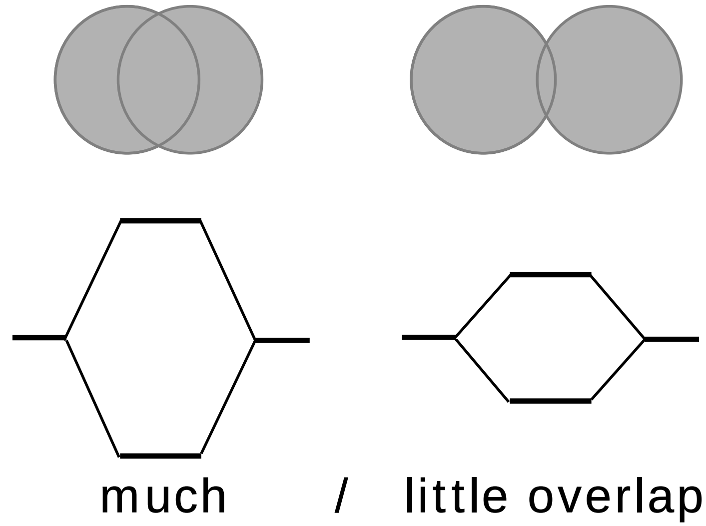
The minimum you need to know about . . . . . .

Molecular Orbitals

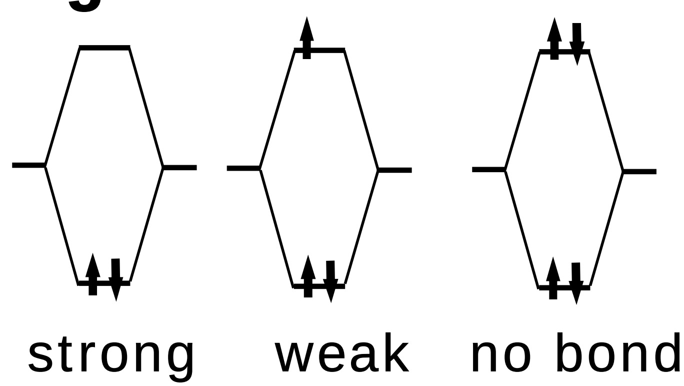




Overlap:

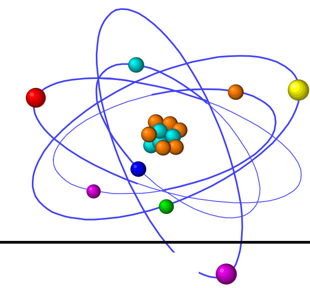


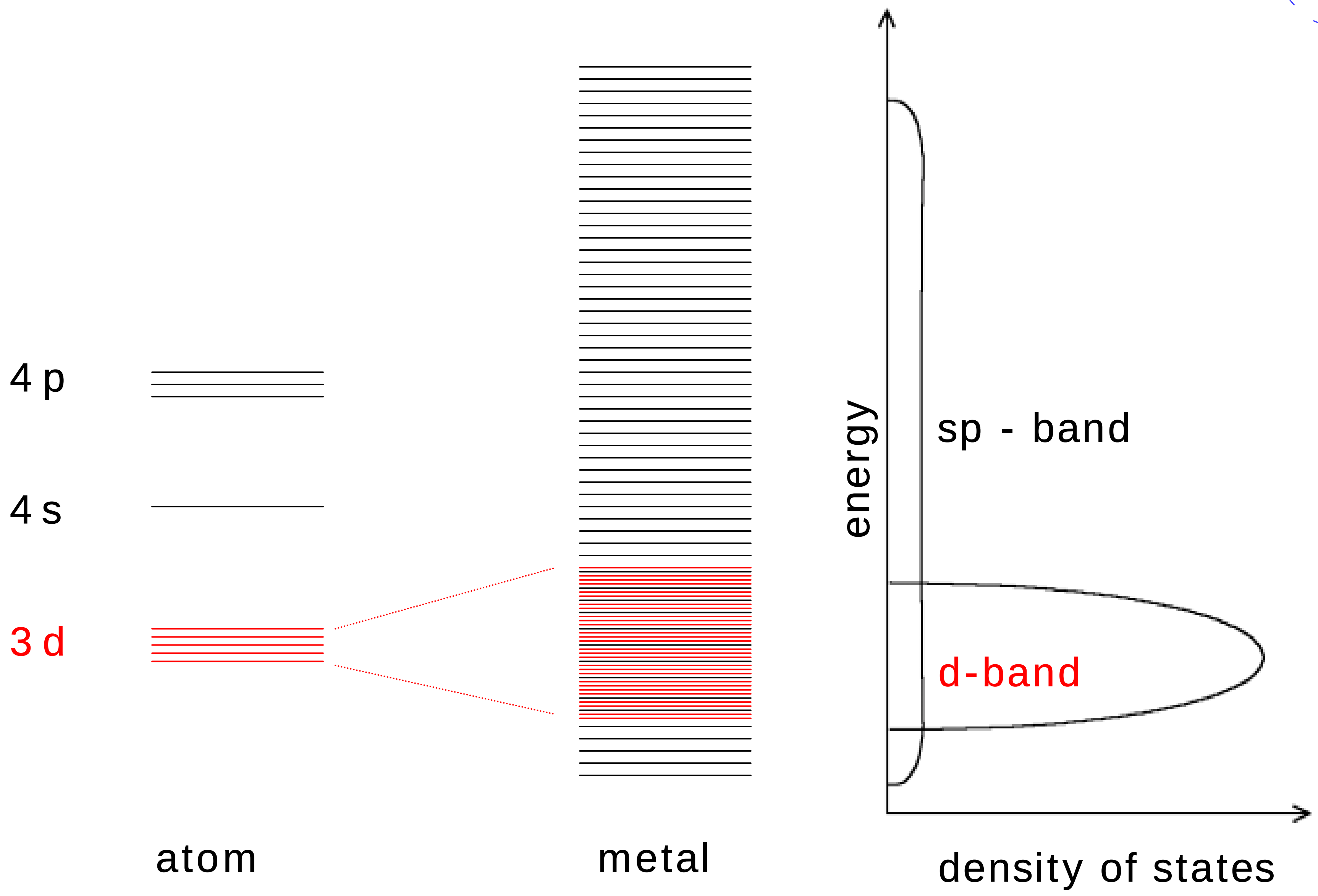
Filling:



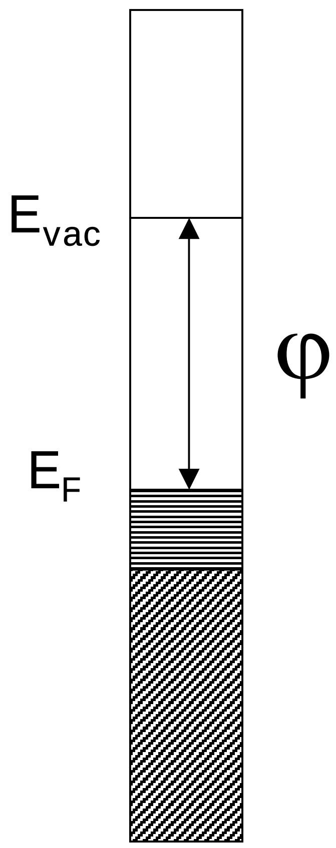
and about . . . . .

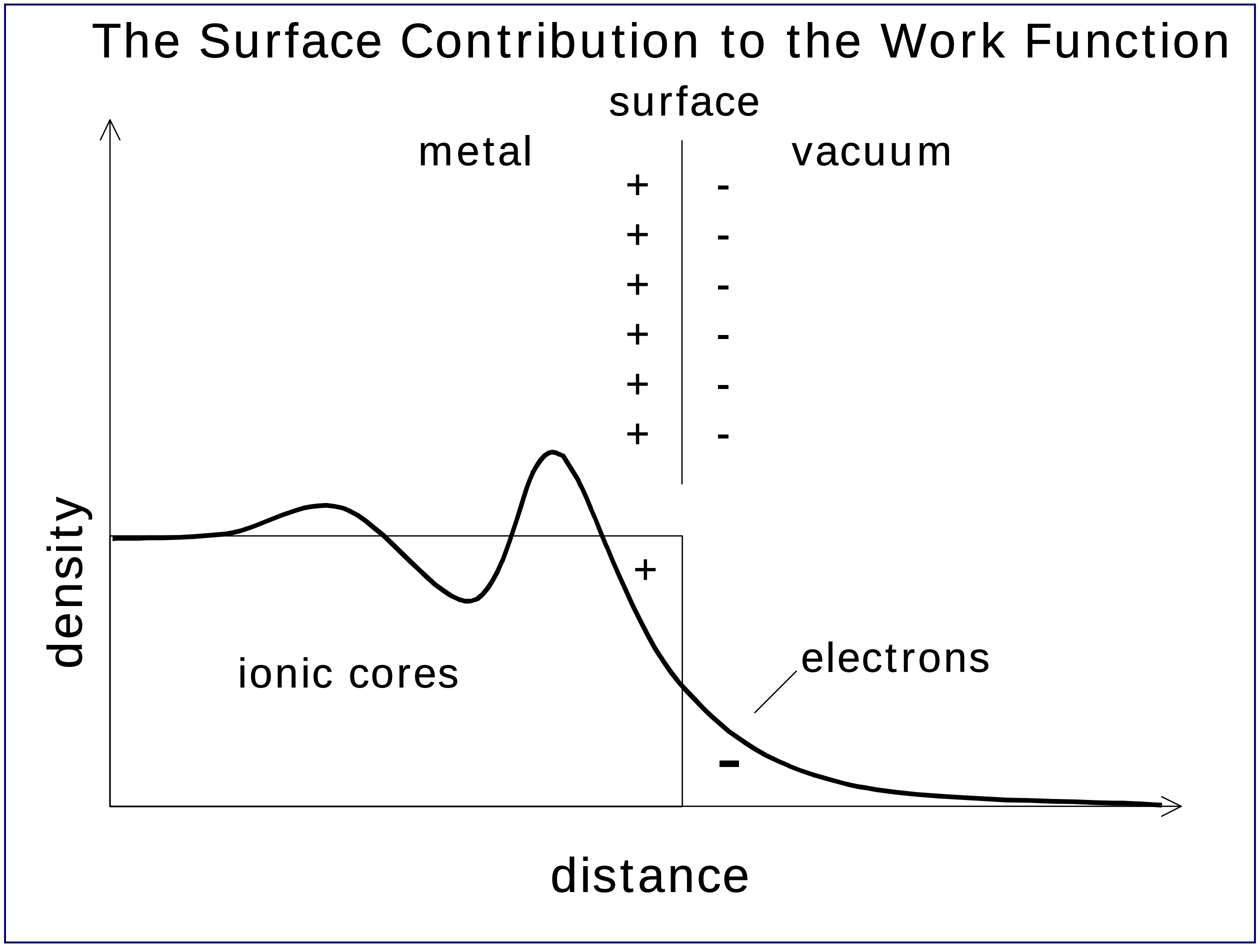
Bonding in Metals





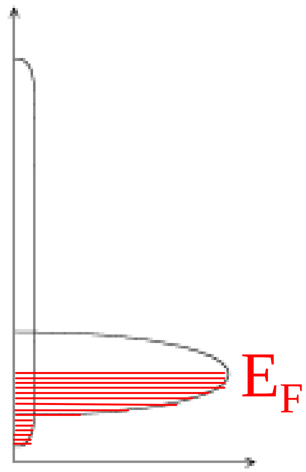
Work Function: Ionization Potential of a Metal



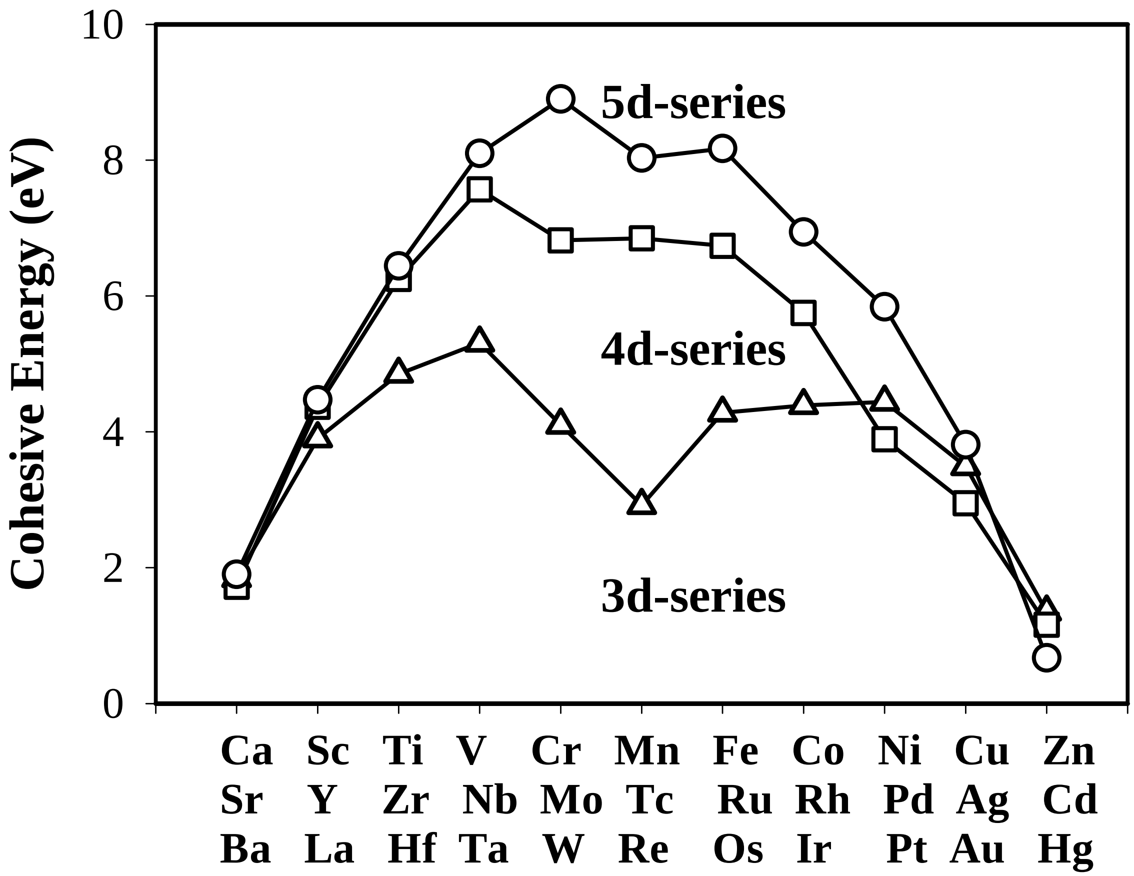


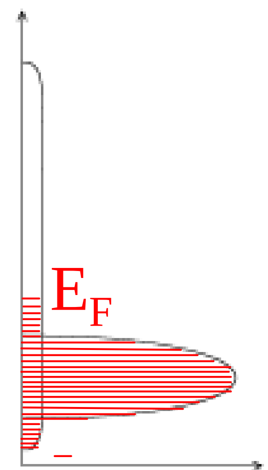
φ : energy barrier for electrons leaving the surface

Strength of metals:
Filling of bands



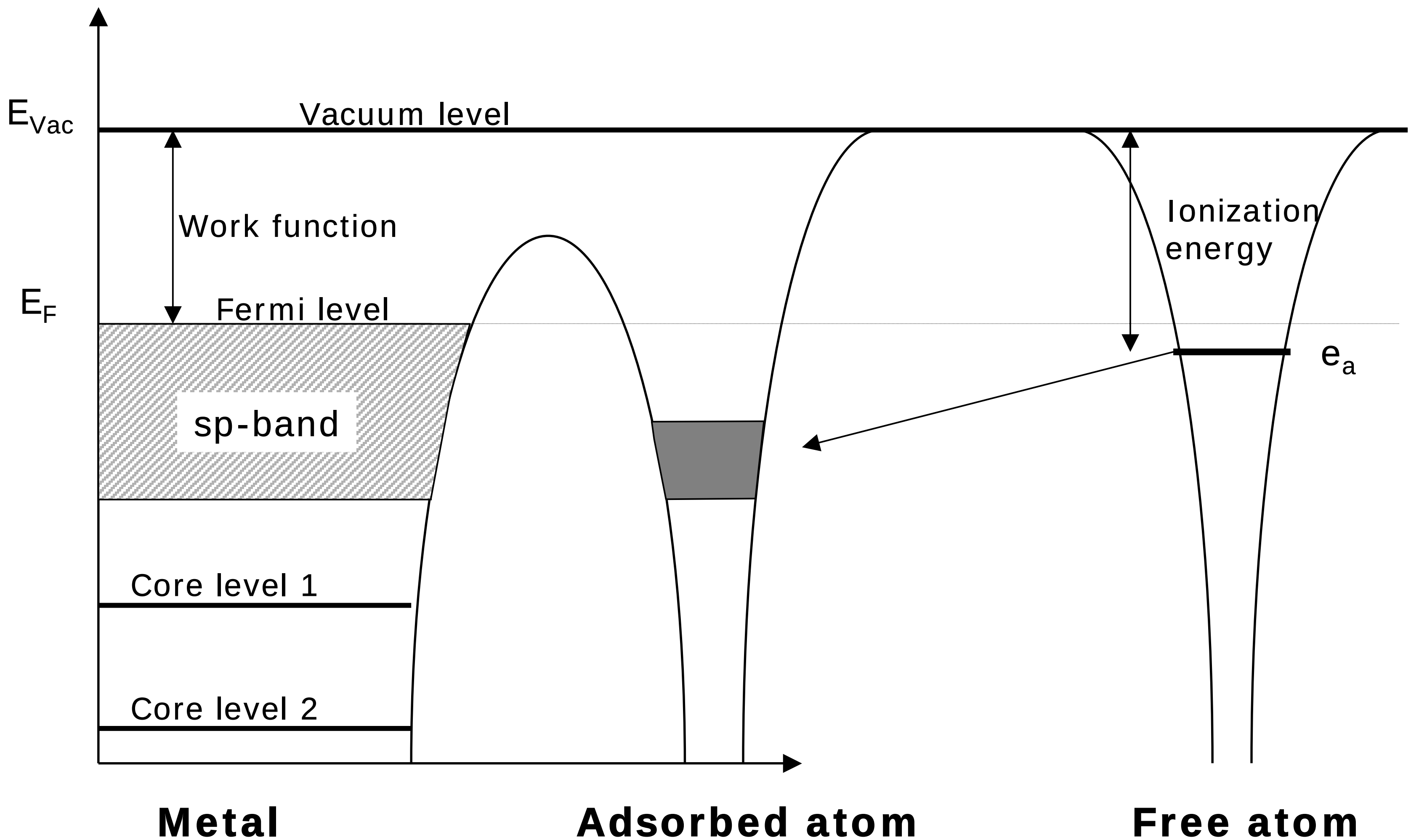
—E_F





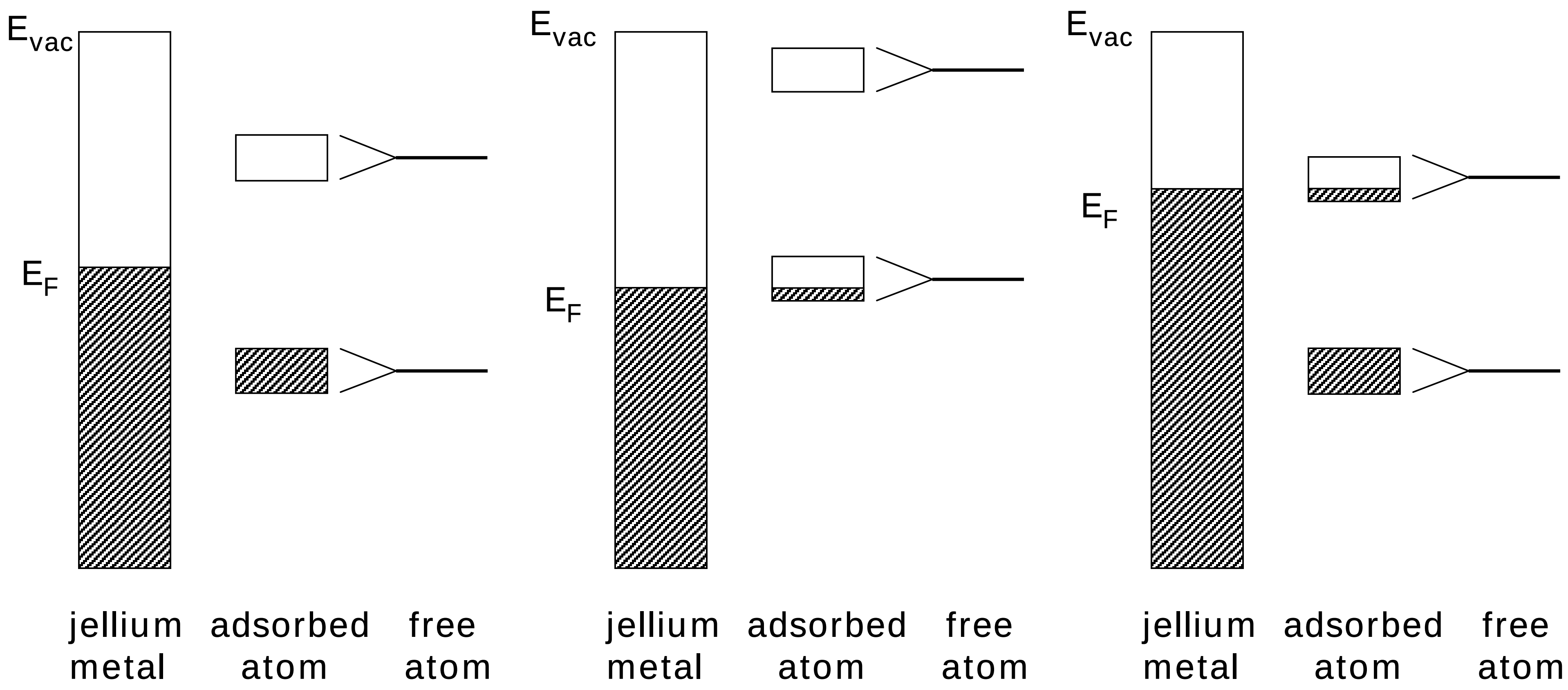
Atomic Adsorption in the 'Resonant Level Model'

(the simplest description)

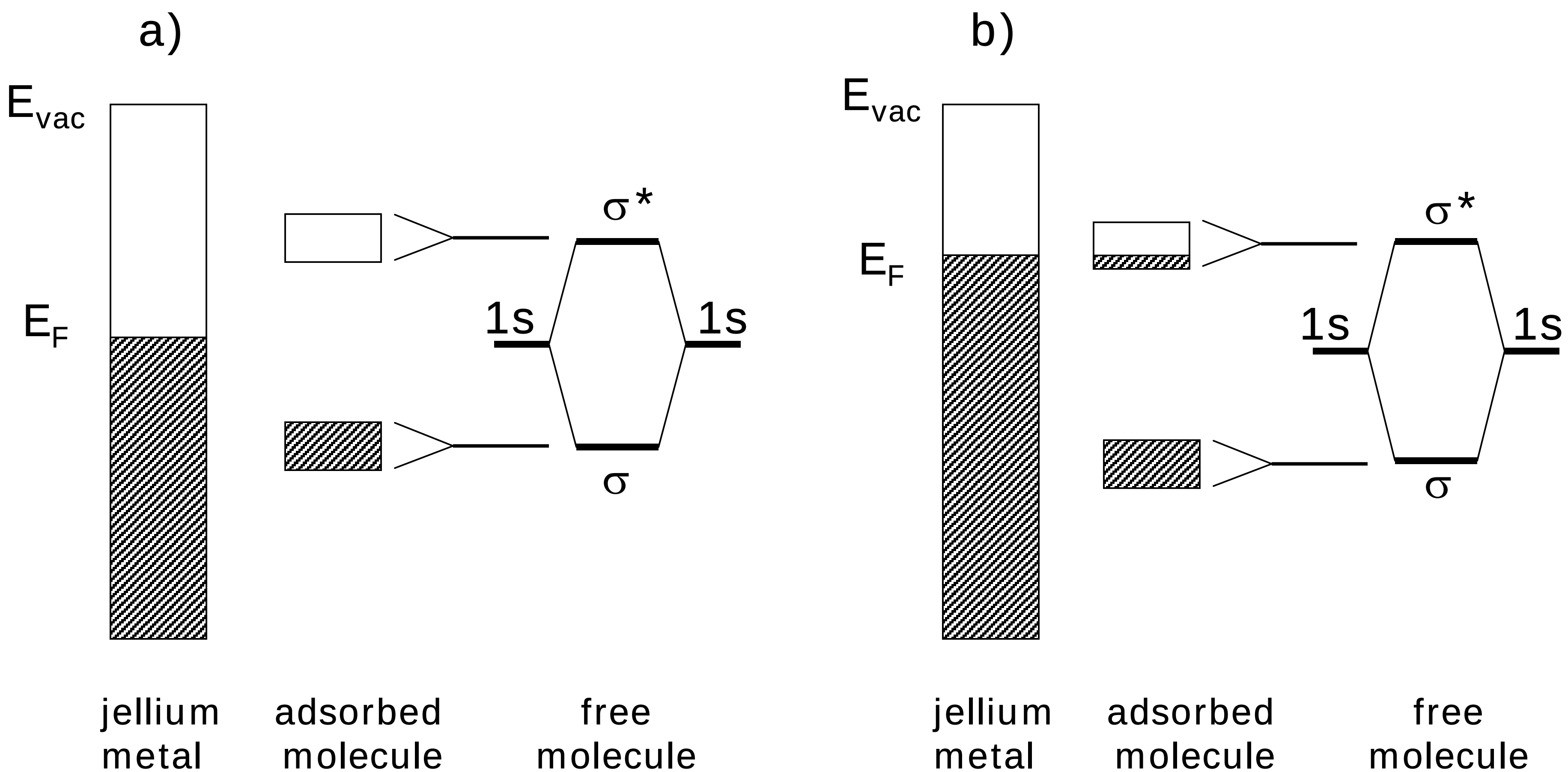


Jellium has no d-band
(e.g. Al)

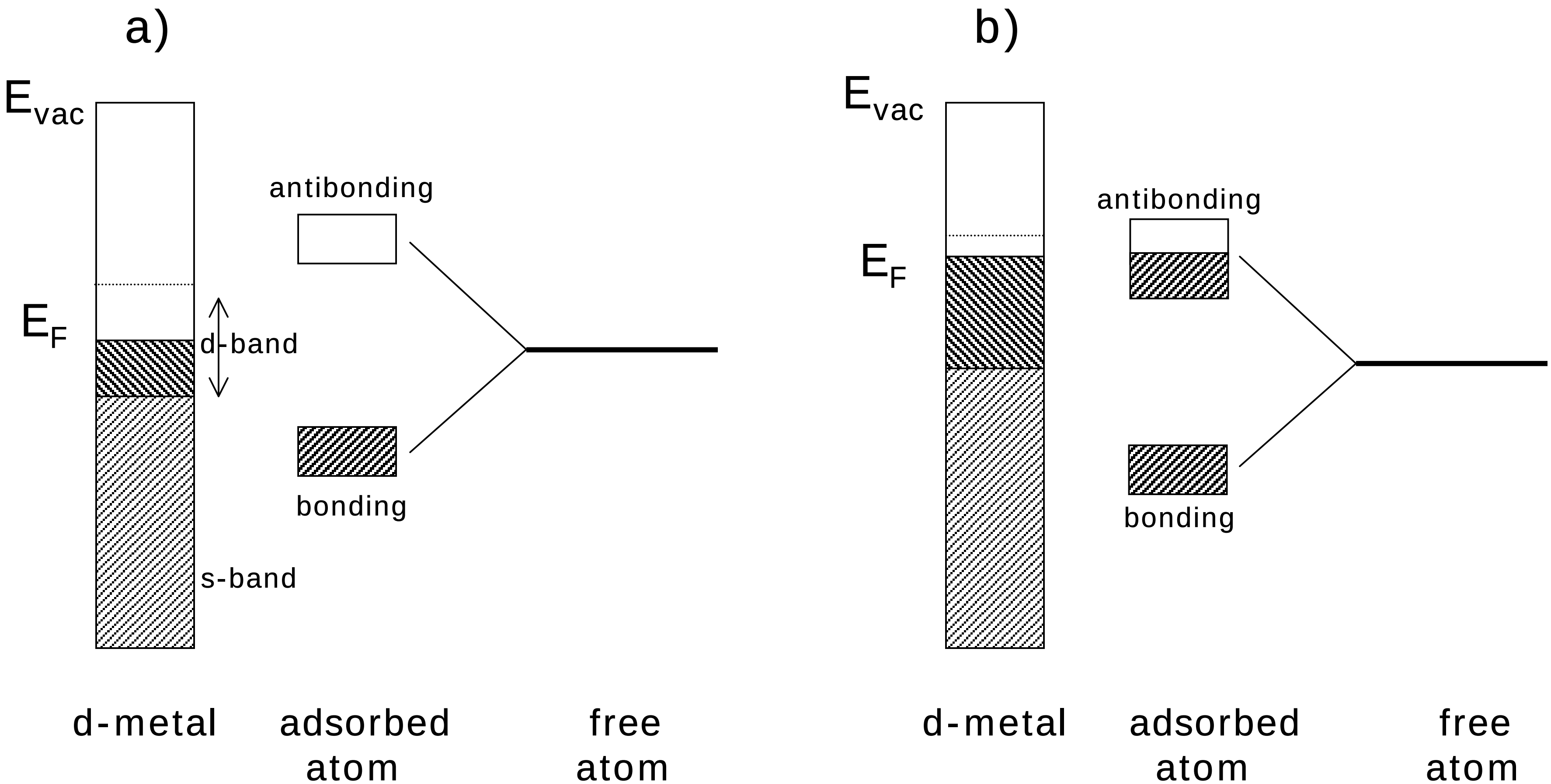
Atom on free-electron metals (no d-band):



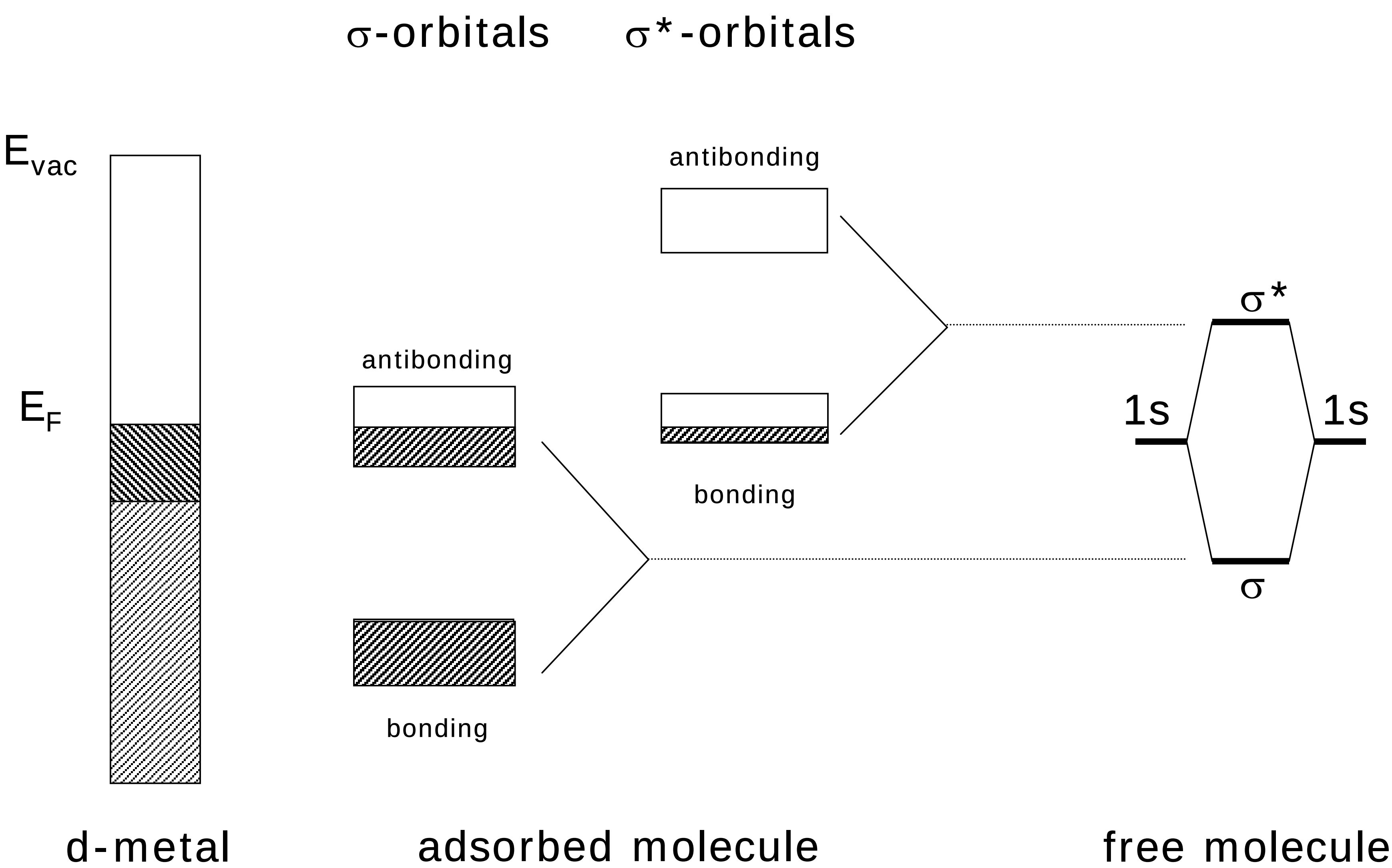
Molecules on free-electron metals (no d-band):



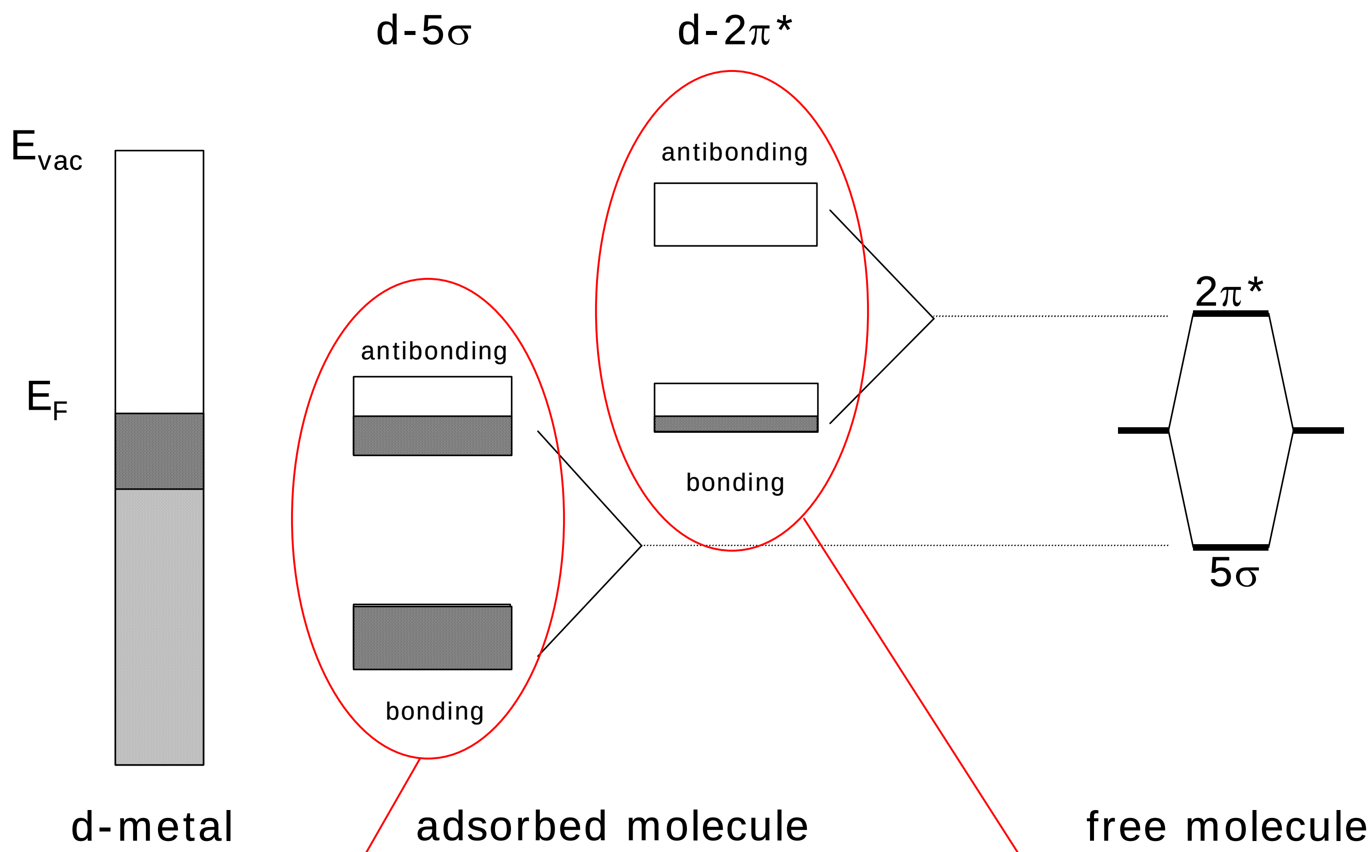
Atom on d-metal:



Molecular Adsorption on a d-metal



CO adsorption on a d-metal

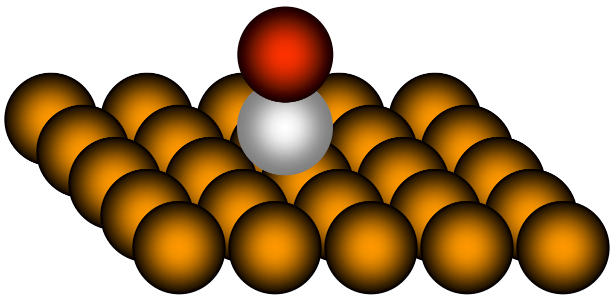


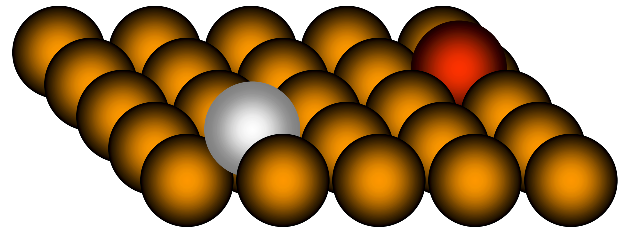
"relieved repulsion"
favors on-top adsorption
often called "donation"

"back donation"
binds molecule to surface
weakens internal CO bond!
favors multiple coordination

This picture is the key to understanding catalysis in terms of orbital theory

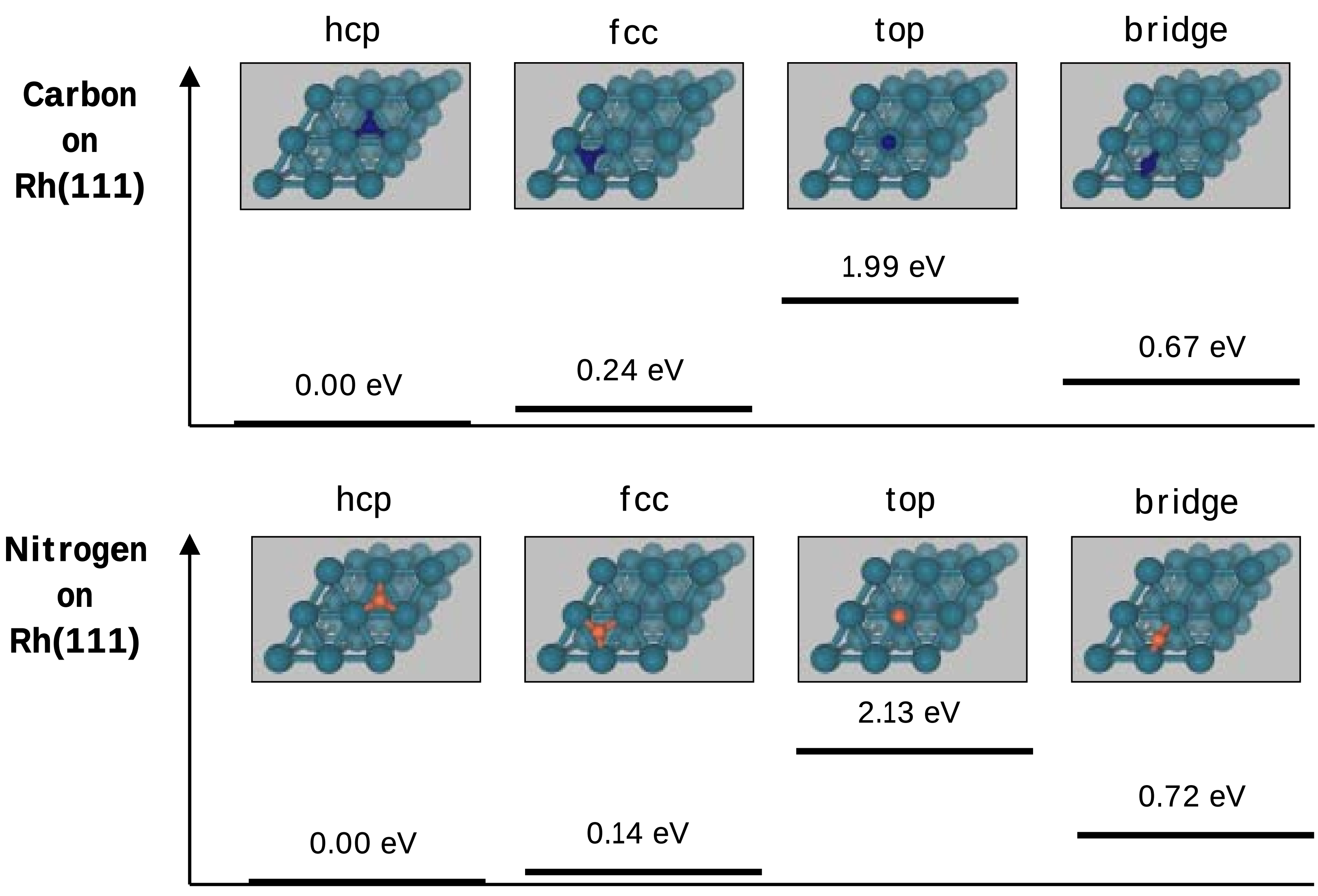
a catalyst breaks bonds.........





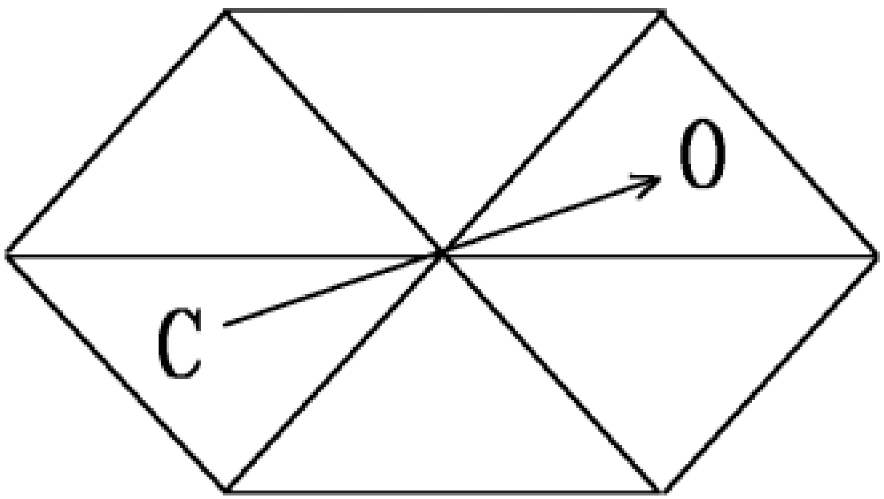
How?

Atoms prefer high coordination sites

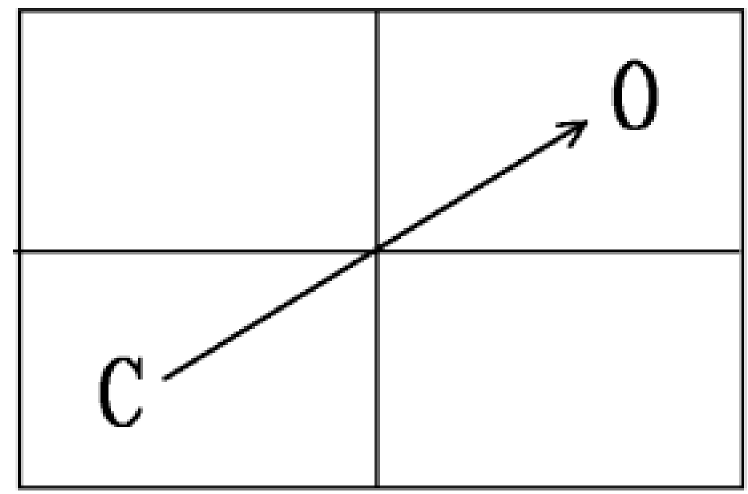


Paco Ample, Dani Curulla, Josep Ricart, Hans Niemantsverdriet, 2002

Dissociation:



(111)



(100)

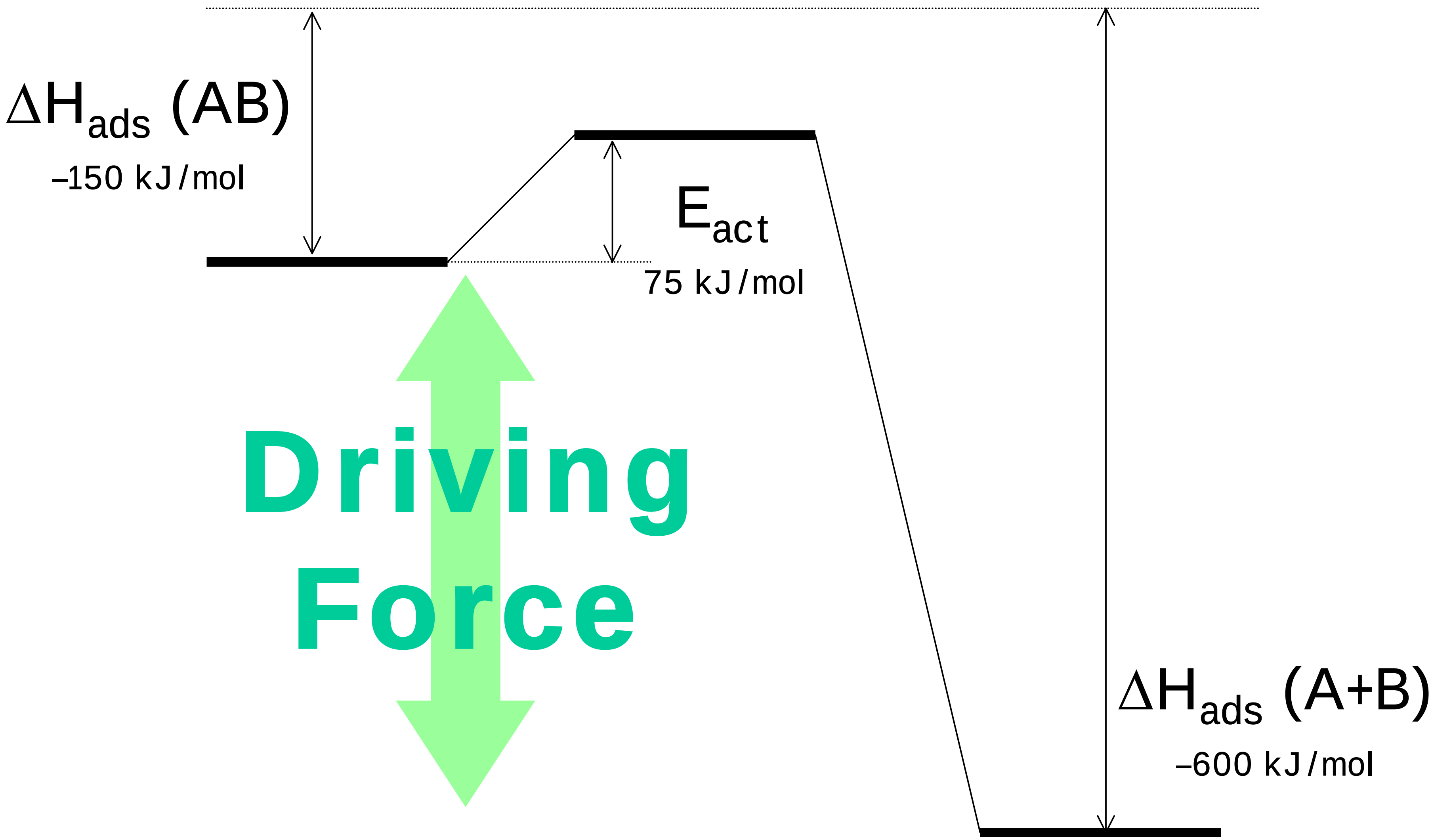
The CO molecule dissociates in the transition state:

optimal overlap between d- and $2\pi^*$-orbitals

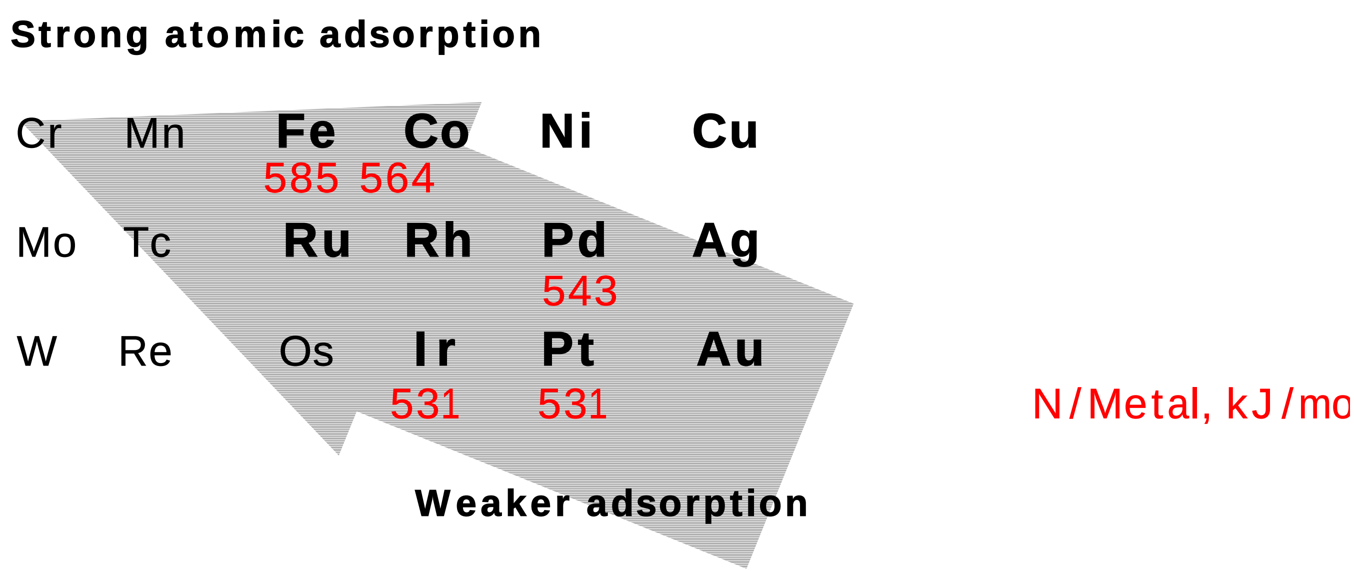
De Koster and Van Santen

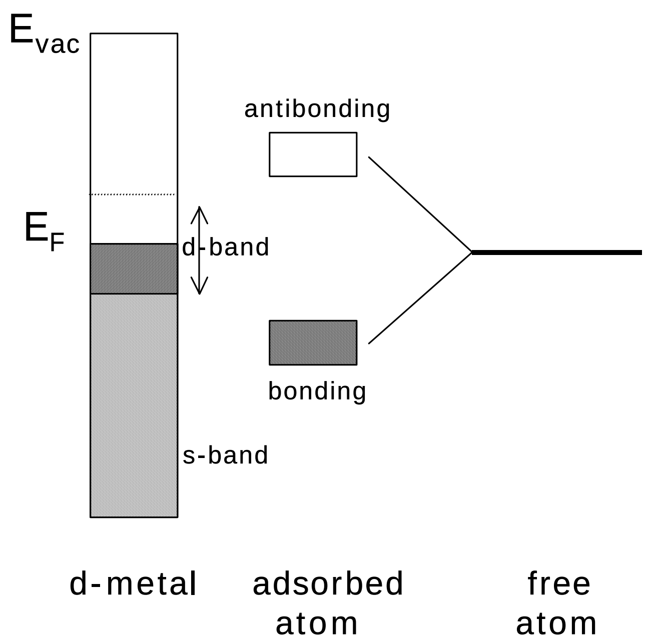
Energetics of Dissociation

on a transition metal such as Fe, Ru

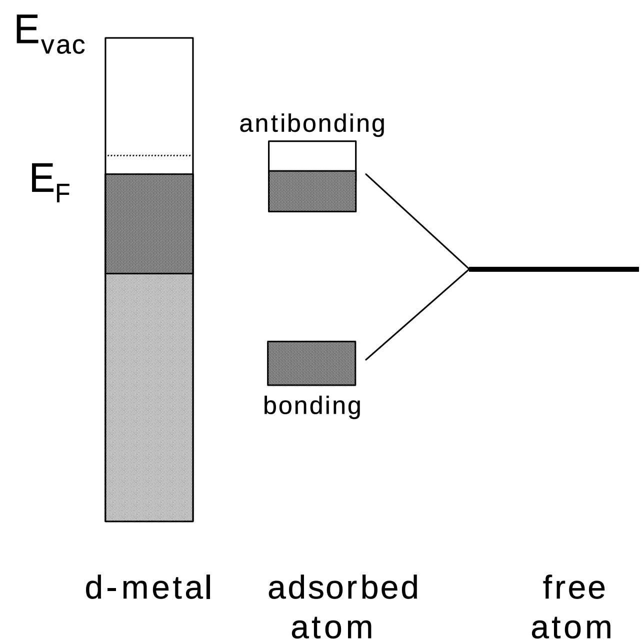


Trends in chemisorption





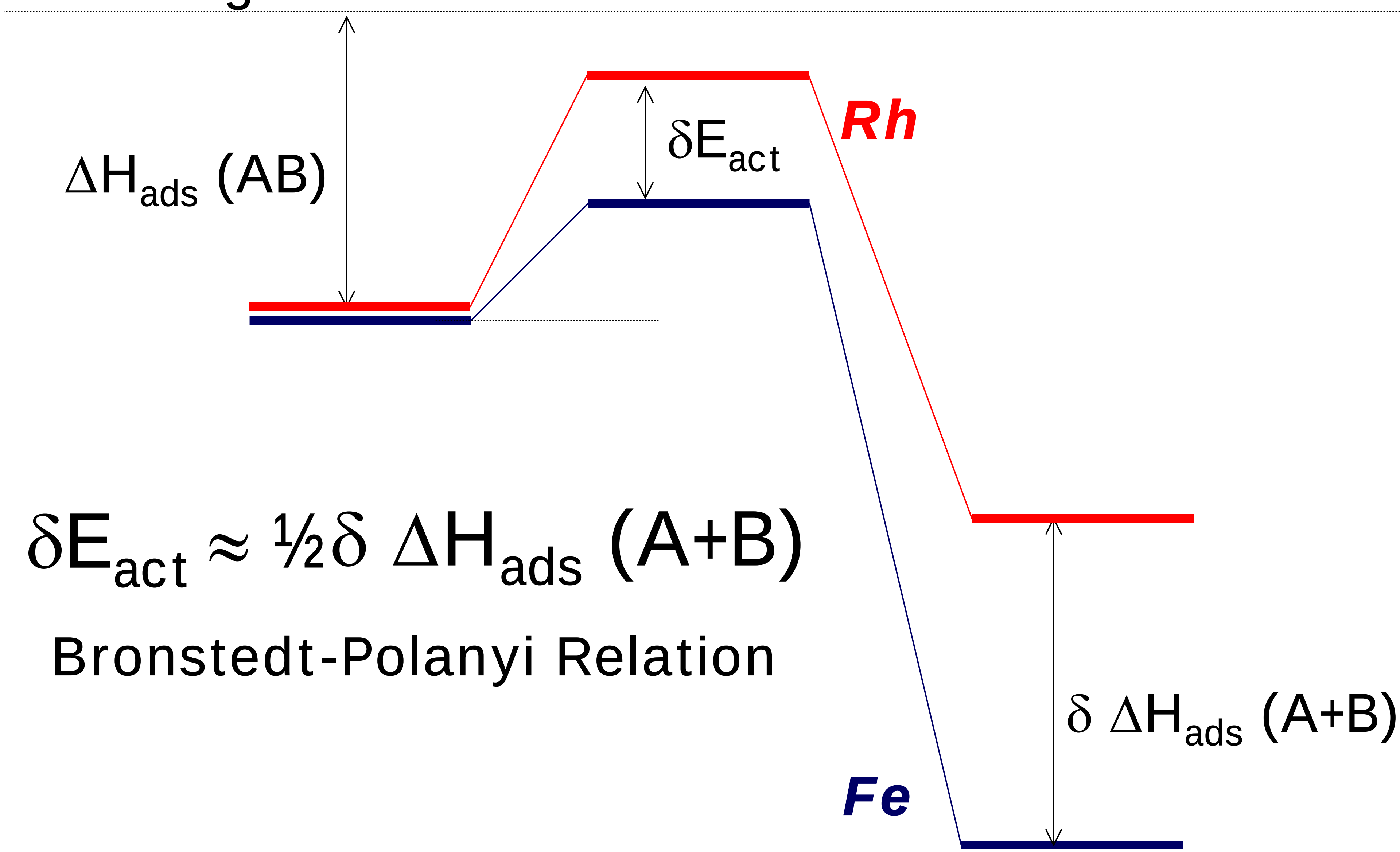
d-band < half filled
strong bond



d-band > half filled
weaker bond

Dissociation on Different Metals

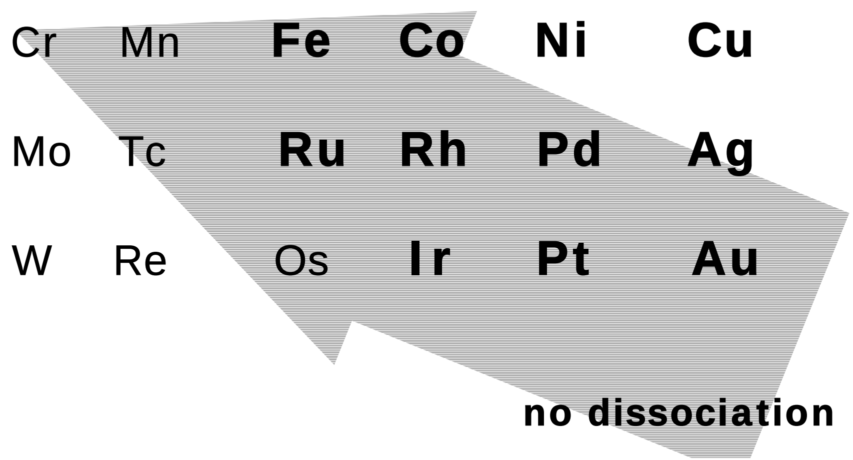
e.g. Rh and Fe



$$\delta E_{act} \approx \tfrac{1}{2}\delta\ \Delta H_{ads}\ (A+B)$$

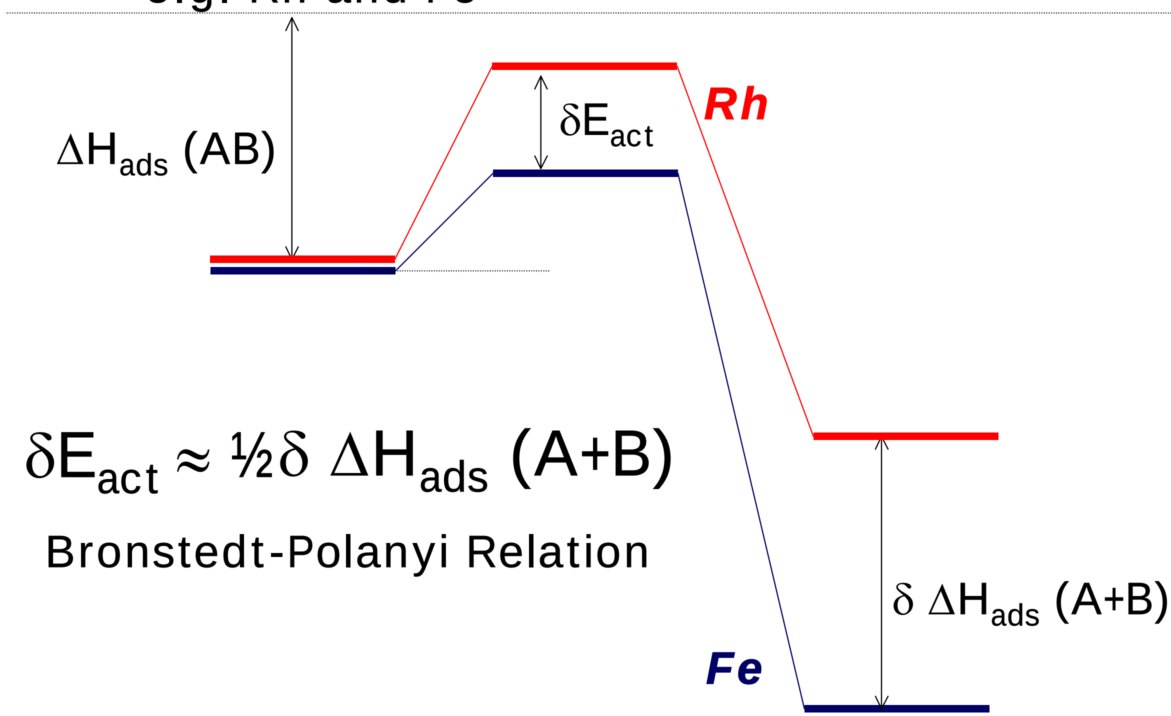
Bronstedt-Polanyi Relation

Trends in chemisorption



Dissociation on Different Metals

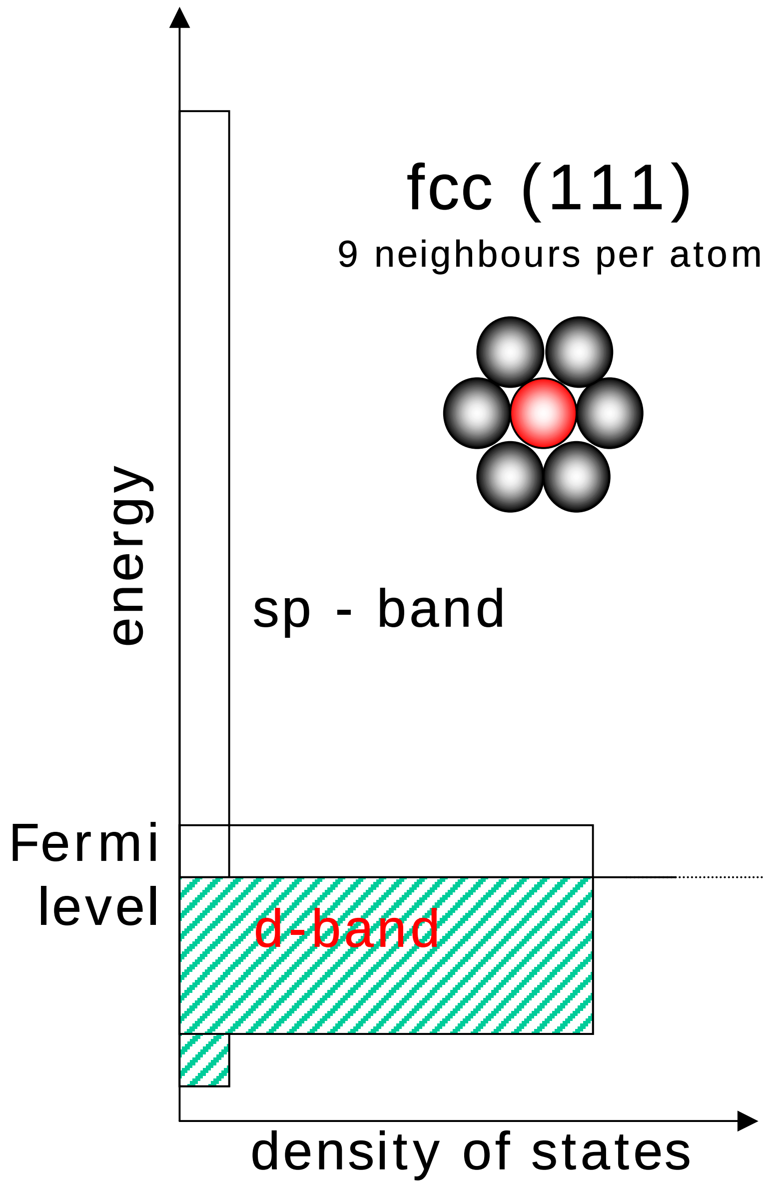
e.g. Rh and Fe

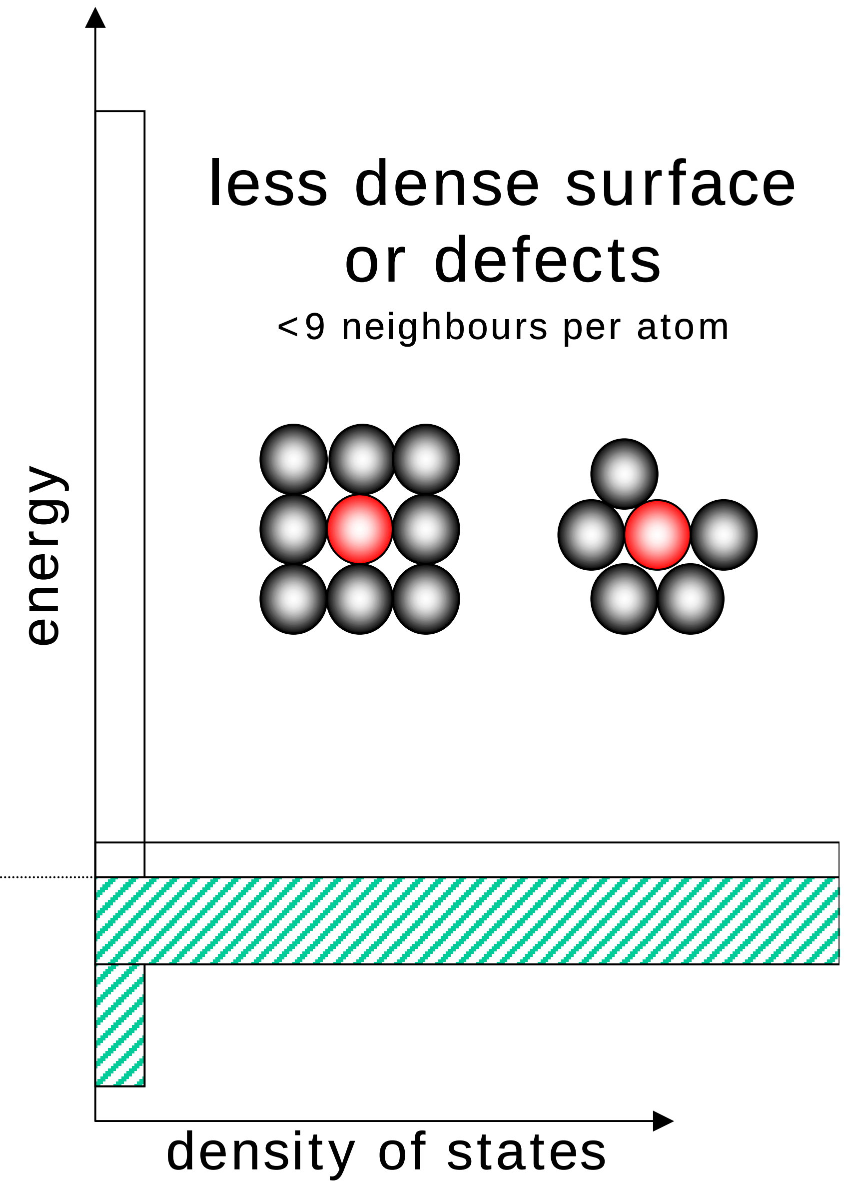


$$\delta E_{act} \approx ½\delta\ \Delta H_{ads}\ (A+B)$$

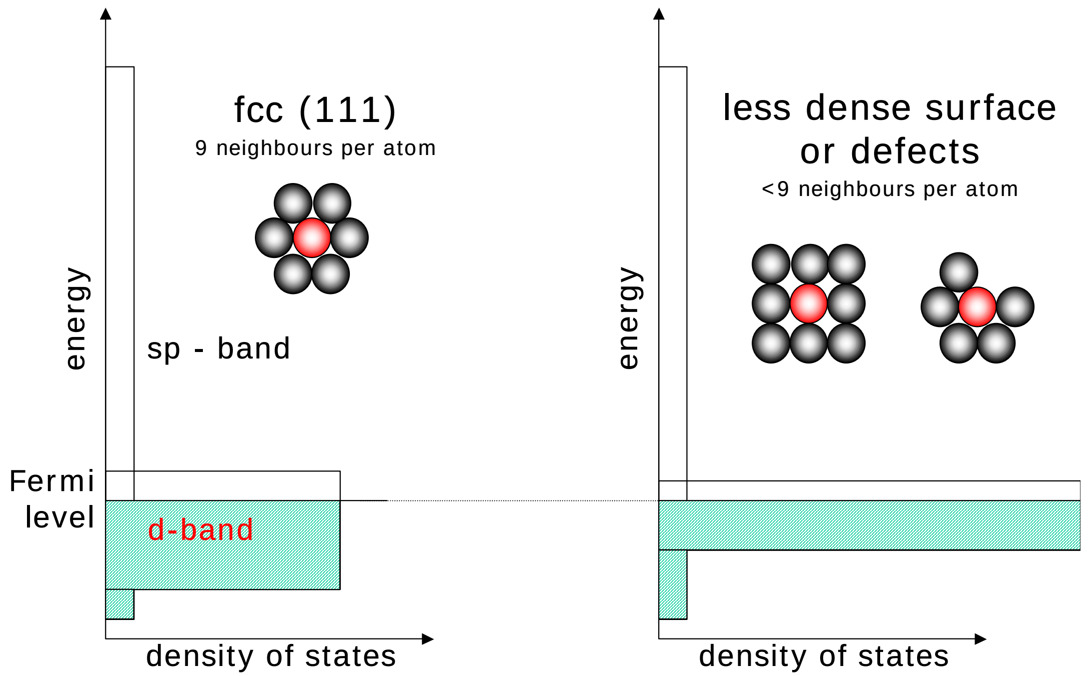
Bronstedt-Polanyi Relation

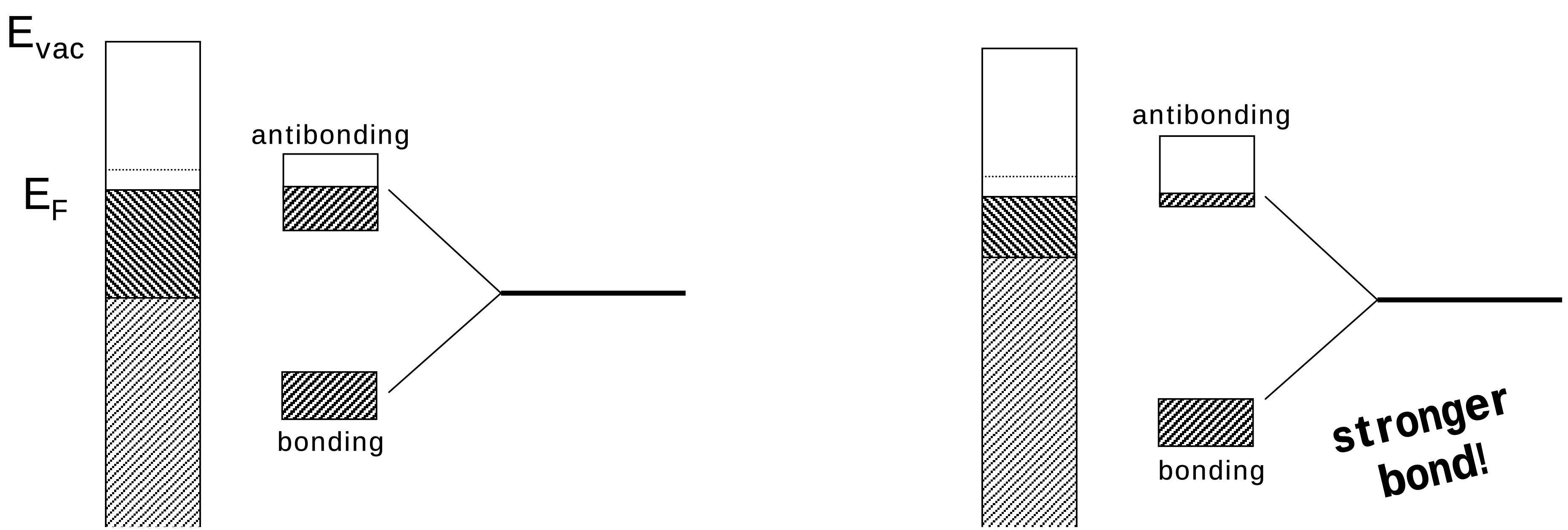
Coordinative unsaturation: higher reactivity





Coordinative unsaturation: higher reactivity





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If you can explain catalysis along these three lines you have a pretty good understanding of what catalysis on metals means.