Lecture 6

Thermodynamics and Kinetics for Adsorption, Diffusion and Desorption

Physisorption

Chemisorption

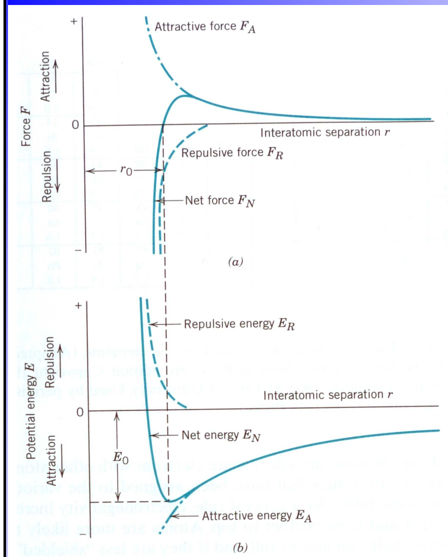
Surface Bonding

Kinetics of Adsorption/Diffusion/Desorption

References:

1) Zangwill, Chapter 8, 9, 14
2) Attard and Barnes, p.1-17, 27-34, 71-75
3) Woodruff & Delchar, Chapter 5, p.356
4) Kolasinski, Chapter 3 and 4
5) Somorjai, Chapter 3.8, 4, 5

Force and Energy Diagram



$$F_{net} = F_{attactive} + F_{repulvise}$$

$$F_{ATTR} = -\frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_o a^2}$$

$$F_{REP} = -\frac{nb}{a^{n+1}}$$

n and b are constants; $n = 7-9$

$$F_{NET} = 0 = -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a^2} = \frac{bn}{a^{n+1}}$$

$$n = 9; \quad -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a^2} = \frac{9b}{a^{10}};$$

$$b = -\frac{Z_1 Z_2 e^2 a^8}{4\pi\varepsilon_o \times 9} = -\frac{1}{36}\frac{Z_1 Z_2 e^2 a^8}{\pi\varepsilon_o}$$

6.1 Basics of Collision Process

(a) Elastic Scattering

(b) Inelastic Scattering

Adsorb
(c) Chemisorption
(d) Physisorption
Surface diffusion
Surface Reaction
Desorption

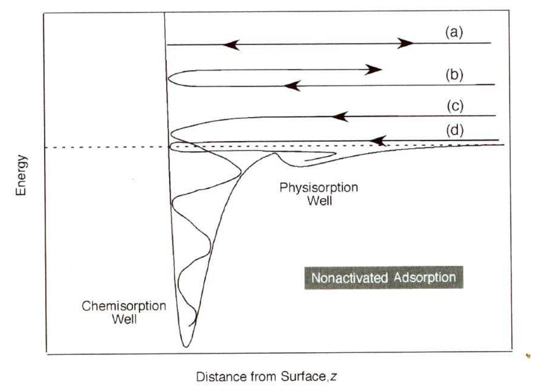
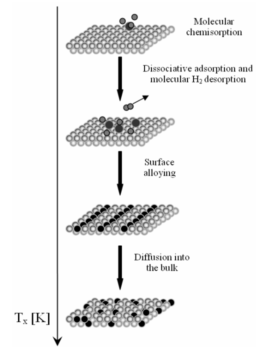


Figure 3.14 *A one-dimensional representation of nonactivated adsorption: (a) elastic scattering trajectory; (b) direct inelastic scattering trajectory; (c) sticking event (chemisorption); (d) sticking event (physisorption).* **Cf. Kolasinski**



Physisorption vs Chemisorption

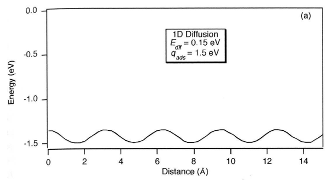
Chemisorption	Physisorption
Electron exchange Chemical bond formation Strong > 1eV (100 kJ mol $^{-1}$) Highly corrugated potential Analogies with coordination chemistry Second phase can form for suitable T and P	Polarization Van der Waals attractions Weak < 0.3 eV (30kJ mol $^{-1}$) Stable only at cryogenic temperatures (N_2 77K, He 4K) Less strongly directional Multilayers can form

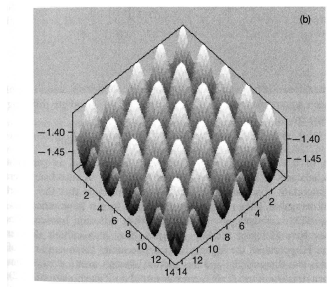
O/Fe, Al, Si
H/Pd
NH3/Cu

H_2/ Fe, Au
H_2O/Au
NH_x/Cu

6.2 Binding Sites and Diffusion

The binding energy of an adsobate depends on its position on the surface, or on the **binding site**





- sites separated by energetic barriers
- can be thought of diffusion barriers

Effects of T on diffusion:

Diffusion rate in a system will increase with temperature:

$$D = D_o \times e^{-\frac{E_A}{RT}}$$

D – diffusivity, m^2/s
D_0- proportionality constant, m^2/s, independent of T
E_A – activation energy for diffusing species, J/mol
R – molar gas constant; R = 8.314 J mol-1 K-1

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Fick's first law of diffusion

$$J = -D\frac{dC}{dx}$$

For steady-state diffusion condition (**no change in the system with time**), the net flow of atoms is equal to the diffusivity D times the diffusion gradient dC/dx

$$J\left(\frac{atoms}{m^2 s}\right) = -D\left(\frac{m^2}{s}\right)\frac{dC}{dx}\left(\frac{atoms}{m^3}\times\frac{1}{m}\right)$$

'-' sign: flux direction is from the higher to the lower concentration; i.e. it is the opposite to the concentration gradient

Diffusivity D depends on:

1. Diffusion mechanism
2. Temperature of diffusion
3. Type of crystal structure (bcc >
4. Crystal imperfections
5. Concentration of diffusing species

Solute	Solvent (host structure)	Diffusivity (m^2/s) 500°C (930°F)	1000°C (1830°F)
1. Carbon	FCC iron	(5×10^{-15})*	3×10^{-11}
2. Carbon	BCC iron	10^{-12}	(2×10^{-9})
3. Iron	FCC iron	(2×10^{-23})	2×10^{-16}
4. Iron	BCC iron	10^{-20}	(3×10^{-14})
5. Nickel	FCC iron	10^{-23}	2×10^{-16}
6. Manganese	FCC iron	(3×10^{-24})	10^{-16}
7. Zinc	Copper	4×10^{-18}	5×10^{-13}
8. Copper	Aluminum	4×10^{-14}	10^{-10} M†
9. Copper	Copper	10^{-18}	2×10^{-13}
10. Silver	Silver (crystal)	10^{-17}	10^{-12} M
11. Silver	Silver (grain boundary)	10^{-11}	
12. Carbon	HCP titanium	3×10^{-16}	(2×10^{-11})

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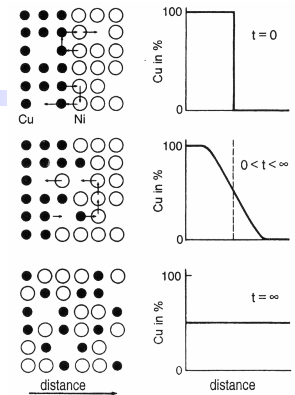
Non-Steady-State Diffusion

In practice the **concentration** of solute atoms at any point in the material changes **with time** – **non-steady-state diffusion**

For non-steady-state condition, diffusion coefficient, D - NOT dependent on time:



Change in concentration in 2 semi-infinite rods of Cu and Ni caused by diffusion, From G. Gottstein "Physical Foundations of Material Science"

Second Fick's law of diffusion: $\frac{dC_x}{dt} = \frac{d}{dx}\left(D\frac{dC_x}{dx}\right)$

If $D \neq D(x)$, in 1D case: $\frac{dC_x}{dt} = D\frac{\partial^2 C}{\partial x^2}$

The rate of compositional change is equal to the diffusivity times the rate of the change of the concentration gradient

In 3D case: $\frac{dC_x}{dt} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)$

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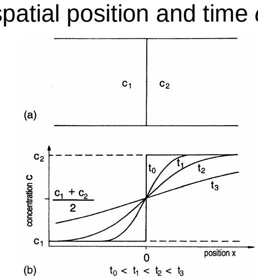
Non-Steady-State Diffusion (continued)

With specific initial or boundary conditions this partial differential eqns can be solved to give the concentration as function of spatial position and time *c(x, y, z, t)*

Let us consider two rods with different concentrations c_1 and c_2 which are joined at x=0 and both are so long that mathematically they can be considered as infinitely long



The concentration profile at t = 0 is discontinuous at x = 0:

$x < 0$, $c = c_1$; $x < 0$, $c = c_2$

We can obtain solution of: $\frac{dC_x}{dt} = D\frac{\partial^2 C}{\partial x^2}$

$$c(x,t) - c_1 = \frac{c_2 - c_1}{\sqrt{\pi}} \int_{-\infty}^{\frac{x}{2\sqrt{Dt}}} e^{-\xi^2} d\xi = \frac{c_2 - c_1}{2}\left(1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

where $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\xi^2} d\xi$, is known as the error function

$$z = \frac{x}{2\sqrt{Dt}}$$

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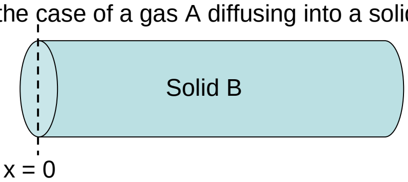
Gas diffusion into a solid

Let us consider the case of a gas A diffusing into a solid B



$$\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_S – surf. C of element in gas diffusing into the surface

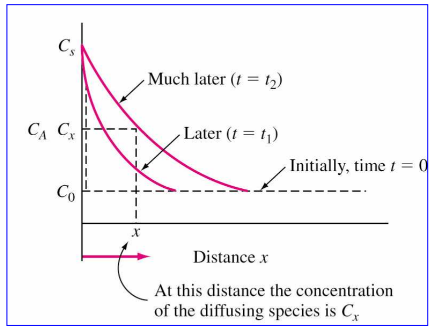
C_o – initial uniform concentration of element in solid

x - distance from surface

D – diffusivity of diffusing solute element

t – time

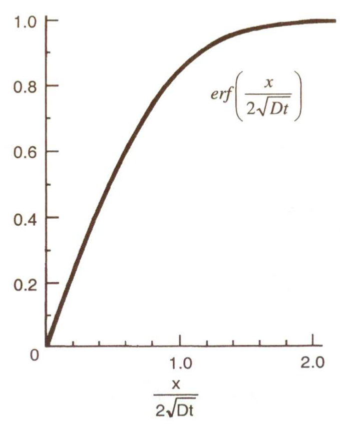
erf – mathematical function called **error function**



Error function

Curve of the error function *erf (z)* for

$$z = \frac{x}{2\sqrt{Dt}}$$



z	erf *z*	*z*	erf *z*	*z*	erf *z*	*z*	erf *z*
0	0	0.40	0.4284	0.85	0.7707	1.6	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.7	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.8	0.9891
0.10	0.1125	0.55	0.5633	1.0	0.8427	1.9	0.9928
0.15	0.1680	0.60	0.6039	1.1	0.8802	2.0	0.9953
0.20	0.2227	0.65	0.6420	1.2	0.9103	2.2	0.9981
0.25	0.2763	0.70	0.6778	1.3	0.9340	2.4	0.9993
0.30	0.3286	0.75	0.7112	1.4	0.9523	2.6	0.9998
0.35	0.3794	0.80	0.7421	1.5	0.9661	2.8	0.9999

Atomistics of Solid State Diffusion

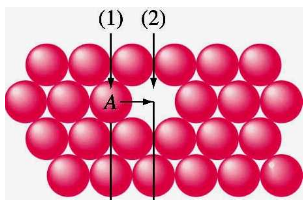
- Diffusion mechanisms:

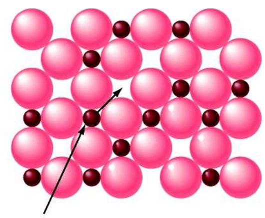
1. **Vacancy** (substitutional) diffusion – migration of atom in a lattice assisted by the presence of vacancies

Ex.: self diffusion of Cu atoms in Cu crystal

2. **Interstitial** diffusion – movement of atoms from one interstitial site to another neighboring interstitial site without permanent displacement any of the atoms in the matrix crystal lattice

Ex.: C diffusion in BCC iron





Interstitial atom diffusing into interstitial vacancy

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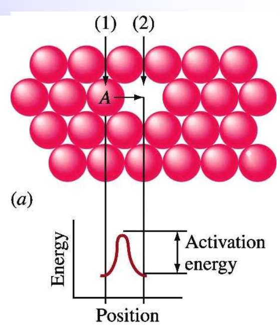
Vacancy (Substitutional) Diffusion Mechanism

Substitutional (in homogeneous system - self-diffusion, in heterogeneous system – solid state solutions)

- Vacancies are always present at any T
- As T increases ⇒ # of vacancies increases ⇒ diffusion rate increases
- Move atom A (from (1) to (2)) = move vacancy from (2) to (1)..?



Metal	Melting point (°C)	Crystal structure	Temperature range studied (°C)	Activation energy kJ/mol	Activation energy kcal/mol
Zinc	419	HCP	240–418	91.6	21.9
Aluminum	660	FCC	400–610	165	39.5
Copper	1083	FCC	700–990	196	46.9
Nickel	1452	FCC	900–1200	293	70.1
α iron	1530	BCC	808–884	240	57.5
Molybdenum	2600	BCC	2155–2540	460	110

higher T_{melt} ⇒ stronger bonding between atoms ⇒ high activation energy to move V

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Ehrlich-Schwoebel Barrier, E_S

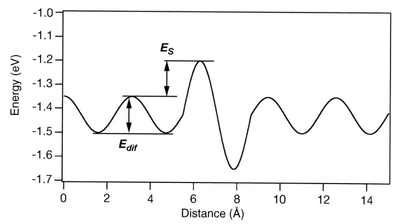


Figure 3.3 A step changes the diffusion activation energy, E_{dif} [one-dimensional (1D) diffusion]. Step-up diffusion is often negligible because of the increased barrier; note also the increased binding strength at the bottom of the step – a feature that is often observed. E_s, Ehrlich-Schwoebel barrier.

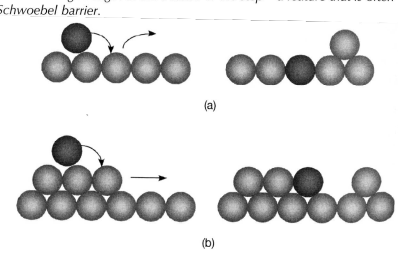
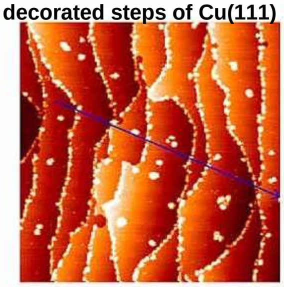


Figure 3.4 The exchange mechanism of diffusion. Mass transport occurs via the repl of one atom with another. This can happen either (a) on a terrace or (b) at a step.

Exchange mechanism of diffusion

(important for metal-on-metal growth)

STM image of chromium decorated steps of Cu(111)



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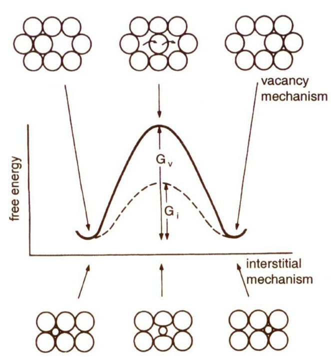
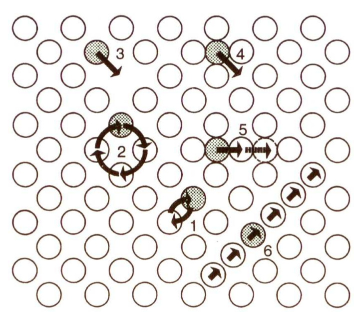
Possible mechanisms of self-diffusion and their activation energy

1. Neighboring atoms exchange sites
2. Ring mechanism
3. Vacancy mechanism
4. Direct interstitial mechanism
5. Indirect interstitial mechanism





	Migration	Formation	Total
1	8 eV	-	8 eV
3	1 eV	1 eV	2 eV
4	0.6 eV	3.4 eV	4 eV
6	0.2 eV	3.4 eV	3.6 eV

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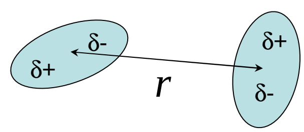
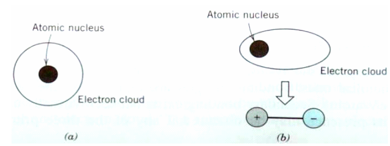
6.3 Physisoption

Physisorption arises from **dispersion forces**



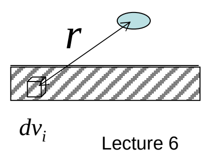


Instantaneous fluctuations in charge distribution interact with instanteneous dipole moments in neighboring species

$$E_{ATTR} = -\frac{C}{r^6}; \quad \text{where } C = f(a_i, \mu_i)$$

The **6-12 Lennard-Jones potential** is commonly used to describe both Van der Waals and steeply rising repulsive interaction potential

$$E \cong 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



$$E \cong \int_{V_{substrate}} \left[\left(\frac{D}{r}\right)^{12} - \left(\frac{C}{r}\right)^{6}\right] N dv$$

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Physisorption energy of Xe on a metal surface

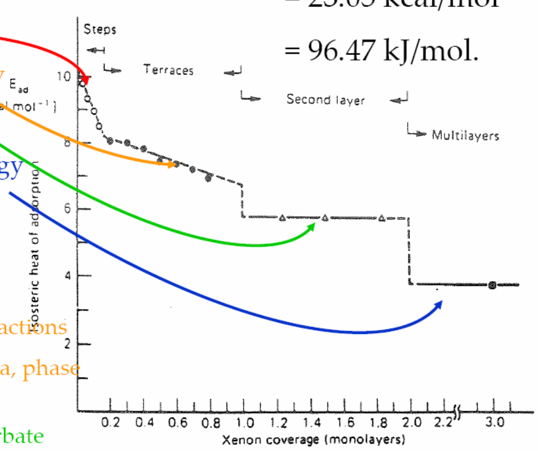
1eV/atom(molecule)

= 23.05 kcal/mol

= 96.47 kJ/mol.

Factors affecting binding energy

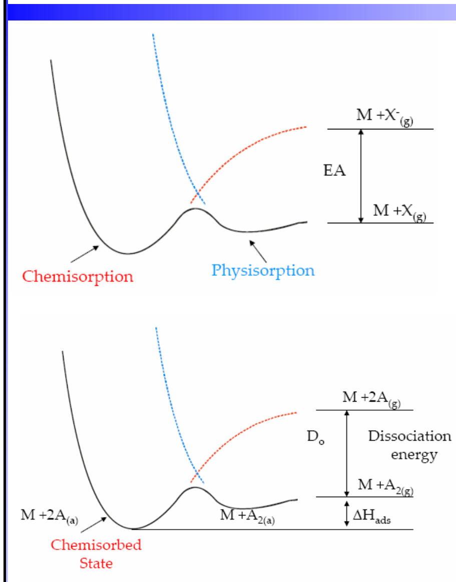
- Roughness
- Local adsorbate density
- Proximity of substrate
- Bulk vaporization energy



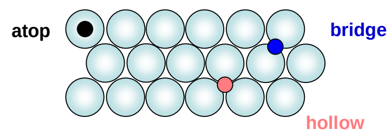
- Geometry in binding sites
- Adsorbate-adsorbate interactions
- Order/disorder phenomena, phase transitions
- Distinction between adsorbate and substrate

Figure 6.29. Heat of xenon adsorption on the stepped palladium 8(100) × (110) surface as a function of coverage [45].

6.4 Nondissociative Chemisorption



- Sequential filling of binding sites



- Binding energies depend on crystal face
- Steps, defects affect adsoprtion energies
- 2D alloyed layers, compound layers can exist when no such bulk phase is known
- Adsorption chemistry is analogous to cluster inorganic chemistry

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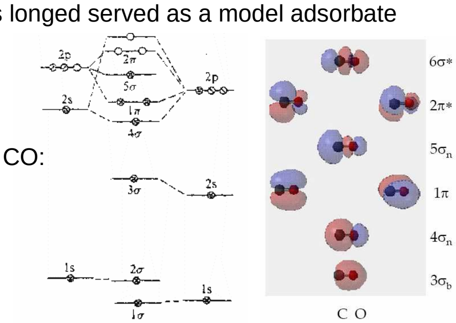
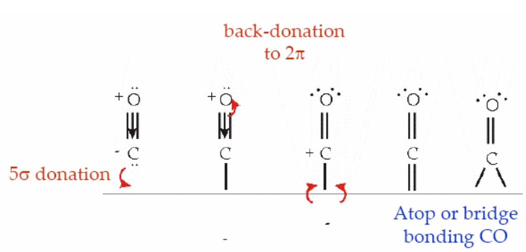
The Blyholder Model of CO Chemisorption

CO has longed served as a model adsorbate

Isolated CO:



- MO of gas-phase CO.
- The wavefunction changes sign in going from the region shown by different color



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Molecular Oxygen Chemisorption

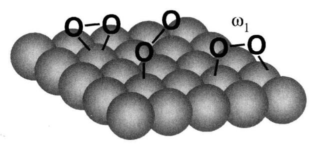
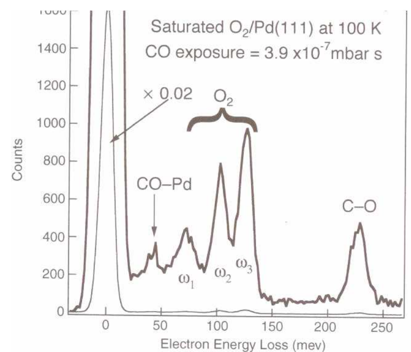


Figure 3.8 O_2/Pd(111) adsorbate structure. The labelling of the three states (ω_1, ω_2 and ω_3)



adapted from *Surf.Sci.* 334, 19

- Three distinct vibrational frequencies $\Rightarrow$ three molecular species
- Decreasing frequency $\Rightarrow$

$\Rightarrow$ increasing M-O_2 bonding

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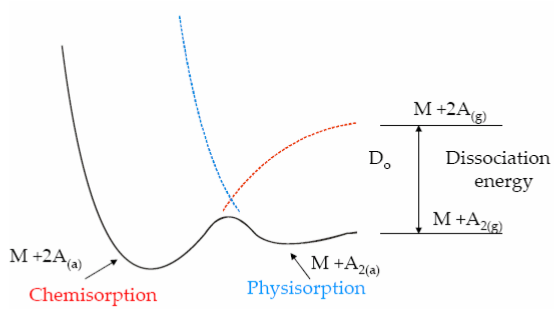
6.5 Reactive (Dissociative) Chemisorption

Chemisorption associated with molecular decomposition



<u>Other Reactive Processes</u>:
Catalysis (A_2+ B_2(ads)$\rightarrow$ 2AB)
Substrate reaction (Oxidation, etc)
Desorption (+"Chemistry with a sledge hammer"!)

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Dissociate Adsorption Examples

O_2 on Al(111)

- At 80K pairs for oxygen adatoms withinteratomic distances 1-3 Al spacing

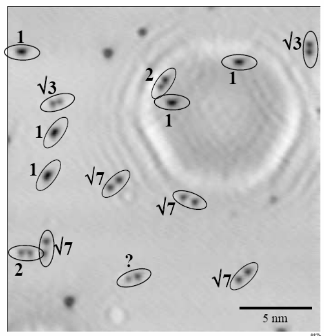
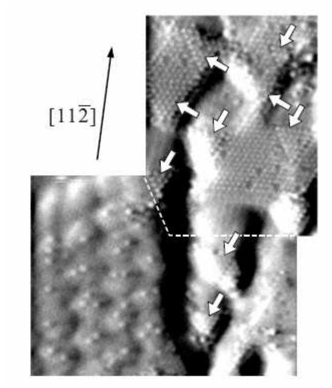


Fig. 2. LT-STM image (20 × 20 nm²; −3 mV, 0.75 nA) obtained at 80 K after adsorption of O_2 at 150 K. Pairs of oxygen atoms are labeled with their O–O distance (in multiples of the Al nearest neighbor spacing a_0). The interference pattern weakly visible is due to a subsurface argon bubble [18] and has been partly suppressed by a high-pass filter applied to the image for background subtraction.

Surf.Sci. 478 (2001) L355-362.

Cl_2 on Si(111)

- At 80K pairs for oxygen adatoms withinteratomic distances 1-3 Al spacing



PRB 68 (2003) 075408

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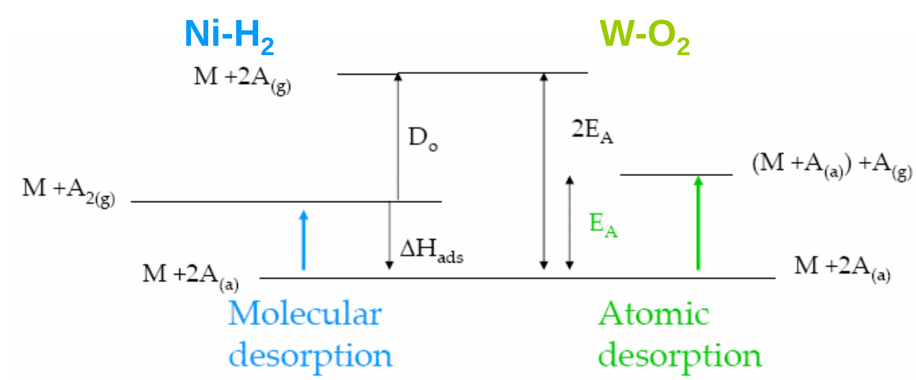
Prediction from Heat of Adsorption

Given dissociative adsorption: is **molecular** or **atomic desorption** preferred?

Is $|\Delta H_{ads}| < E_A$ or $|\Delta H_{ads}| > E_A$



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