SURFACE SCIENCE

"Adsorption on Surfaces"
Readings

1. Zangwill, Ch. 8 - Physisorption
   Ch. 9 - Chemisorption
   Ch. 14 - Kinetics and Dynamics

2. Attard and Barnes, pp. 1-17, 27-34, 71-75

3. G. A. Somorjai, "Introduction to Surface Chemistry and Catalysis", (Wiley 1994)
   Ch. 3.8, Thermodynamics of Monolayers
   Ch. 4, Dynamics at Surfaces
   4.3.4, ff: Surface Diffusion
   Ch. 6, The Surface Chemical Bond

4. R. I. Masel, "Principles of Adsorption and Reaction on Solid Surfaces", (Wiley, 1996)
   Ch. 3, Binding of Molecules to Surfaces
   Ch. 4, Adsorption Isotherms
   Ch. 5, Kinetics of Adsorption

5. B. Hammer and J. K. Norskov, "Theory of Adsorption and Surface Reactions", in R. M. Lambert and G. Pacchioni, eds., "Chemisorption and Reactivity on Supported Clusters and Thin Films", NATO ASI Series E: Applied Sciences Vol. 331 (Kluwer Academic Pub. Dordrecht 1997) p. 285-352.

6. Woodruff and Delchar, Ch. 5, p. 356 ff., Desorption Spectroscopies

7. M. R. Albert and J. T. Yates, Jr., "The Surface Scientist's Guide to Organometallic Chemistry" (American Chemical Society, Washington, DC, 1987).

Adsorption of Atoms and Molecules

Physisorption

Chemisorption

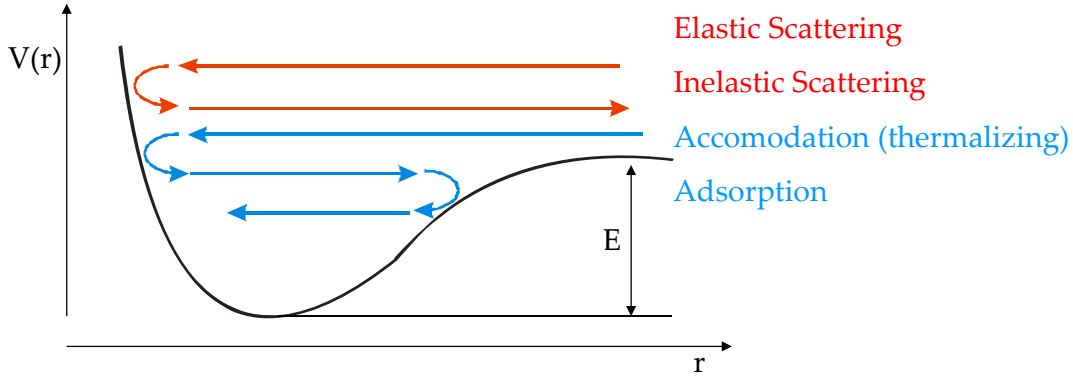
Surface Bonding

Kinetics of Adsorption/Diffusion/Desorption

(Scattering Dynamics)

Outcomes of Collision Process

Rebound (elastically or inelastically)



Adsorption
- Physisorption
- Chemisorption
- Surface Reaction
- Desorption

True elastic scattering is a purely quantum mechanical phenomenon

H_2, HD, He

Physisorption of Atoms and Molecules

Weak bonding, Van der Waals Interaction

Binding Energy ~ Bulk (adsorbate) vaporization energy

Physisorption will occur for any gas-solid system for a suitable range of T, P.

Multilayers can form

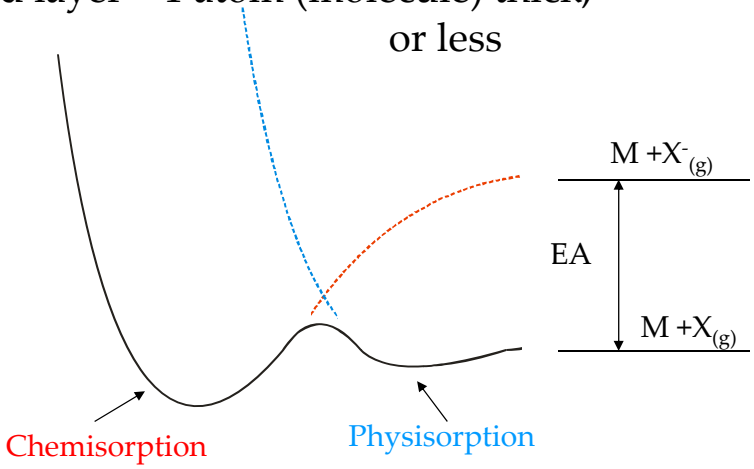
Typical E ~ 1 to 40 kJ mol^{-1}

Chemisorption of Atoms and Molecules

Chemisorption associated with charge transfer (see example below)

Binding Energy E ~ 50 to 400 kJ mol^{-1}

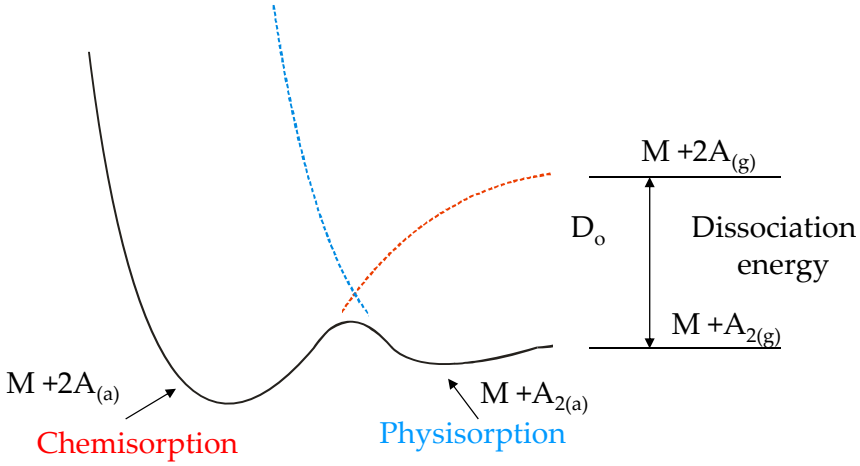
Chemisorbed layer ~ 1 atom (molecule) thick, or less



Reactive Chemisorption of Molecules

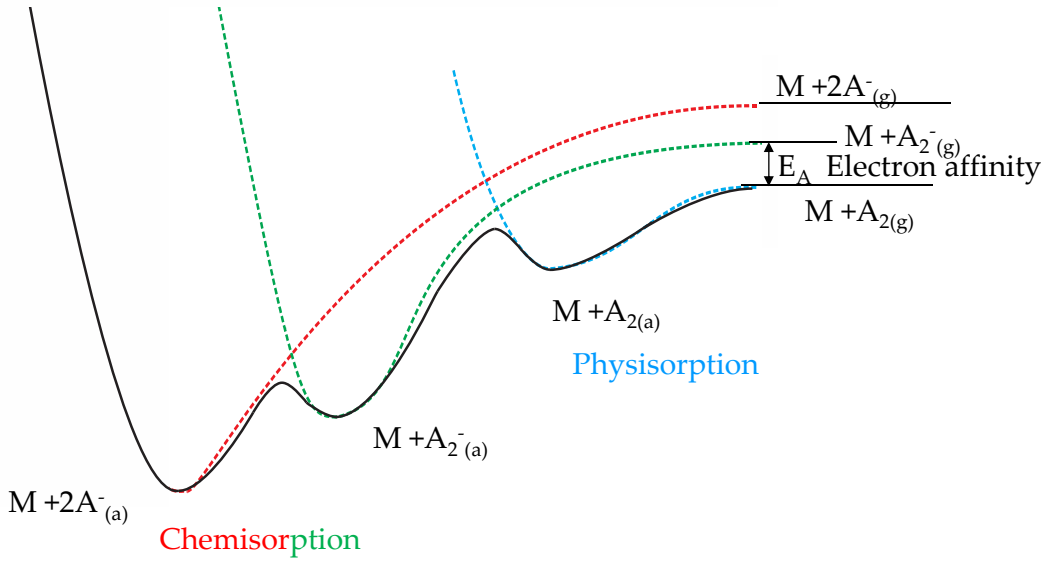
Chemisorption possibly associated with molecular decomposition

E.g. Dissociative adsorption
(charge transfer will occur also!)



Oxygen on Pt(111)

Chemisorbed molecular species too



Other Reactive Processes

Catalysis ($A_2 + B_{2(ads)} \rightarrow 2AB$)

Substrate reaction (Oxidation etc.)

Desorption (+"Chemistry with a sledge hammer"!)

Xe

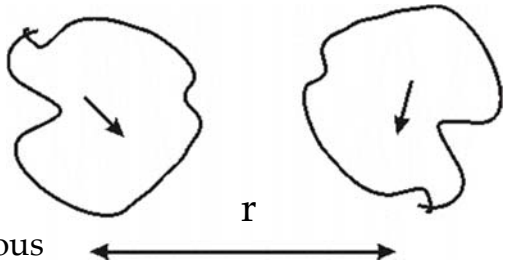
$M + B_{2(a)} \rightarrow M + B_{2(g)}$

Xe

$M + B_{2(a)} \rightarrow M + 2B_{(a)}$

Physisorption arises from dispersion forces

Consider non reacting species



Instantaneous fluctuations in charge distribution interact with instantaneous dipole moments (also multipole moments) in neighboring species.

Consequence: attractive interaction of the form

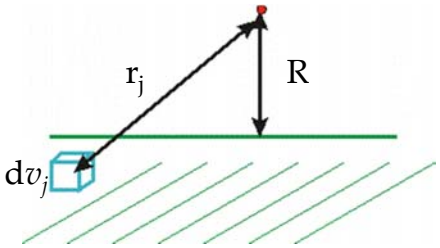
$$E = - C / r^6$$

where $C = f(I_i, \alpha_i, \mu_i)$ I = ionization potential, α polarizability, μ = dipole moment.

Dispersion forces above a surface

The 6-12 Lennard-Jones potential is commonly used to describe both Van der Waals and overlap repulsive interaction potentials

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



For pairwise interactions with all surface species:

$$E = \sum_j E_j \qquad E = \int_{V_{substrate}} \left(Dr^{-12} - Cr^{-6}\right) N dv$$

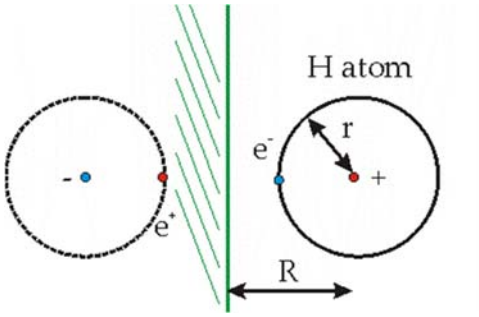
Substrate atoms/unit volume

$$\Rightarrow \quad E \propto \left[\frac{C_1}{R^9} - \frac{C_2}{R^3}\right]$$

Works best for insulating substrates

Electrostatic interaction(s) give rise to attractive forces above metallic faces also

E.g. H above a perfect conductor substrate a



$$V(R) = -\frac{1}{8}\frac{e^2 r^2}{R^3}$$

Compare E_{LJ} α $1/R^3$

Physisorption energy (of Xe) on a metal face

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

Long + short range interactions

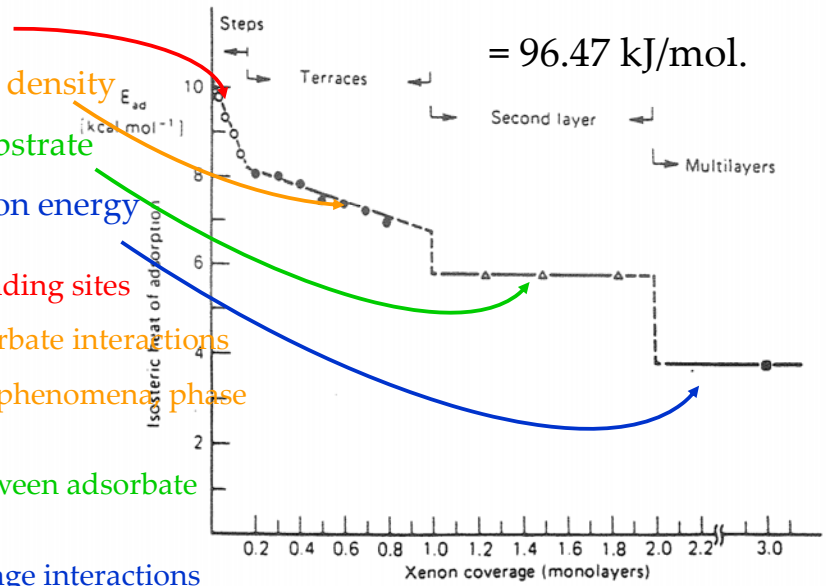
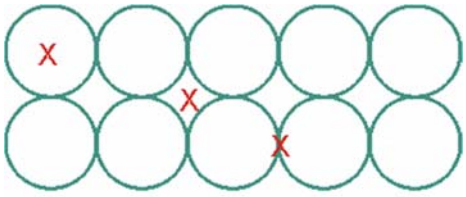


Figure 6.29. Heat of xenon adsorption on the stepped palladium 8(100) × (110) surface as a function of coverage [45].

Chemisorption: the chemical bond

Chemisorption is site specific



Sequential filling of binding sites

Binding energies depend on crystal face

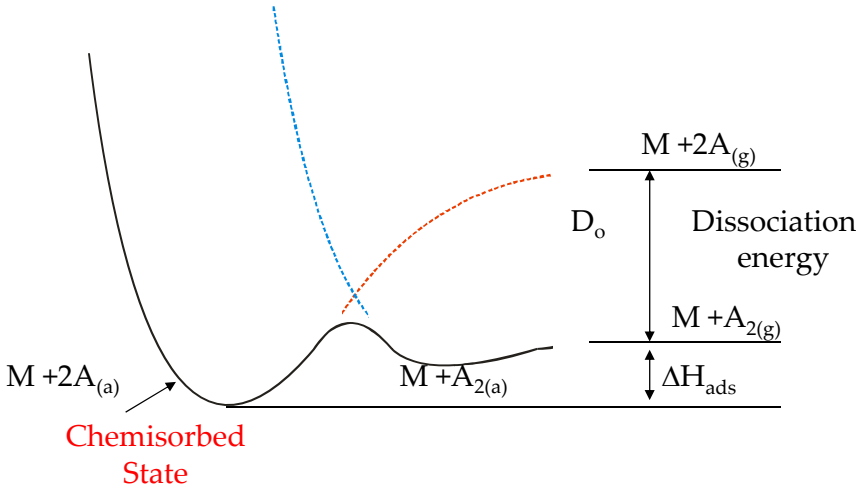
Steps, defects affect adsorption energies

2-D alloyed layers, compound layers can exist when no such bulk phase is known

Adsorption chemistry on extended surface is often very analogous to inorganic/cluster chemistry

Heats of Chemisorption

E.g. again dissociative adsorption



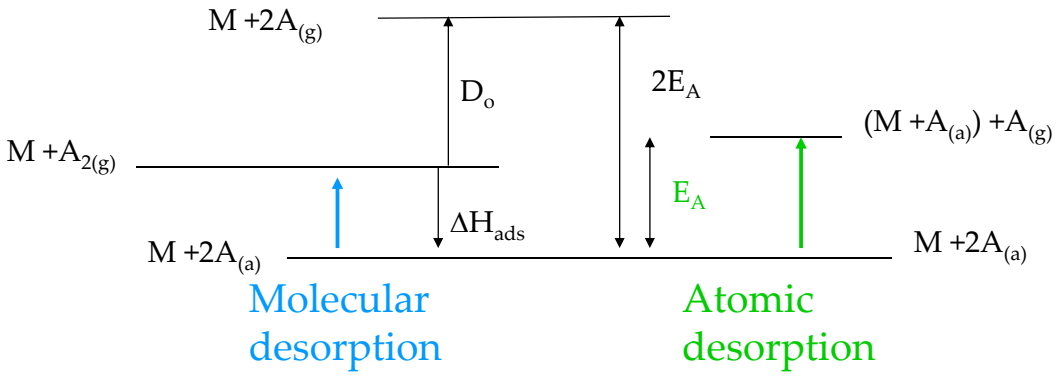
Predictions from Heats of Adsorption

Given dissociative adsorption,

is molecular or atomic desorption preferred?

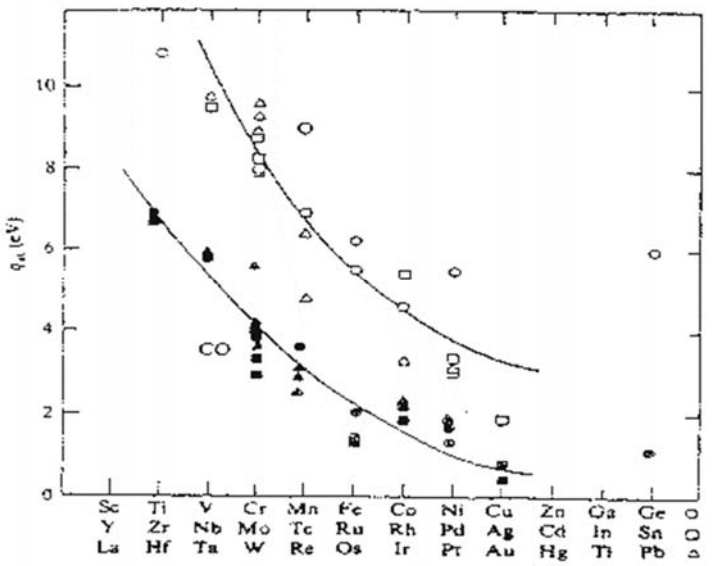
Is $|\Delta H_{ads}| < E_A$ or $|\Delta H_{ads}| > E_A$?

$Ni\text{-}H_2$ or $W\text{-}O_2$

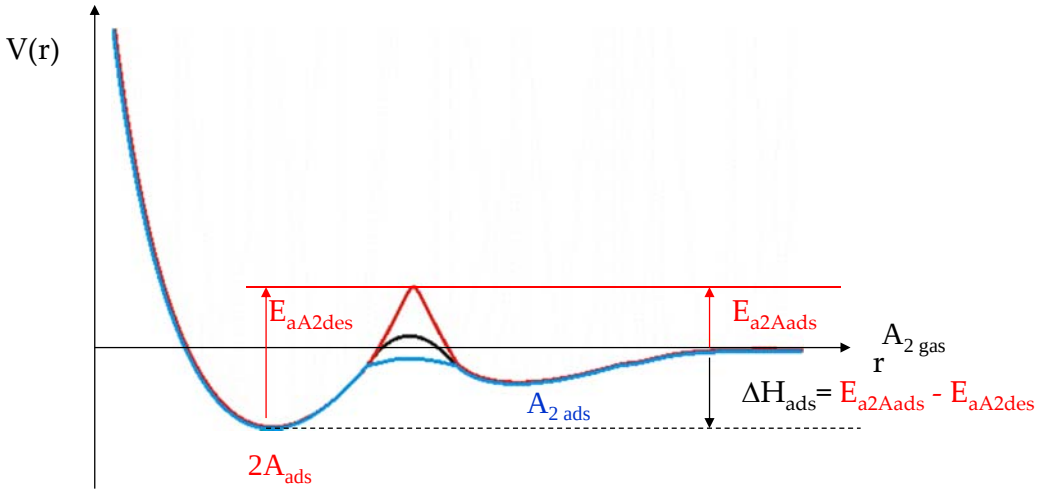


Trends in Heats of Adsorption

Fig. 9.4. Heat of adsorption of CO and O on polycrystalline metal surfaces (Toyoshima & Somorjai, 1979).

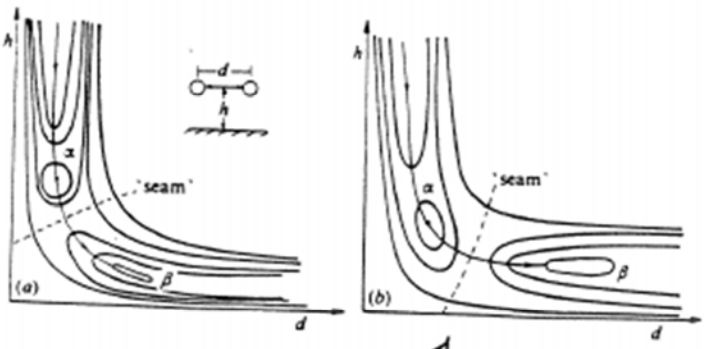


Activated dissociative adsorption



Routes for Activated dissociative adsorption

Fig. 14.12. Schematic two-dimensional potential energy diagrams for dissociative chemisorption. Both situations exhibit a physisorbed state (α) and a chemisorbed state (β). The barrier to adsorption can occur in the (*a*) entrance channel or the (*b*) exit channel (Ertl, 1982).



cf. Zangwill, p. 374

increased translational energy promotes dissociation
$H_2/Cu\ (100)$
?

increased vibrational energy promotes dissociation
$CH_4/Pt\ (111)$

Charge transfer on adsorption:

Electropositive adsorbate

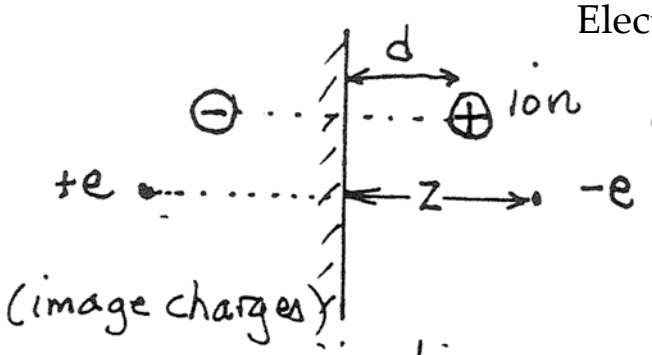


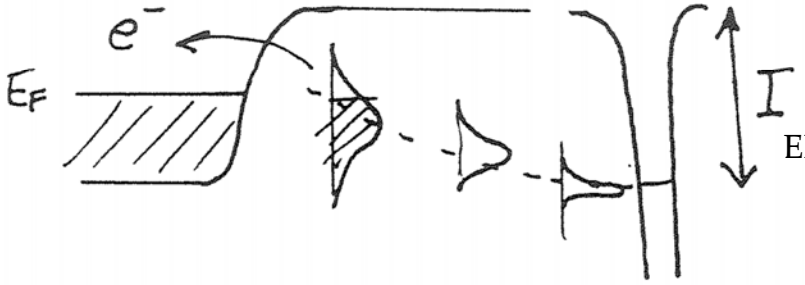
Image force acting on outgoing electron at distance z is

$$F = -\frac{e^2}{4z^2} + \frac{e^2}{(d+z)^2}$$

attractive ↖ repulsive

ionization energy is decreased by

$$W = \int_d^\infty F\,dz = e^2/4d = -V_{im}$$



Electron transfer to surface

e.g. alkali metals

Charge transfer on adsorption:

Electronegative adsorbate

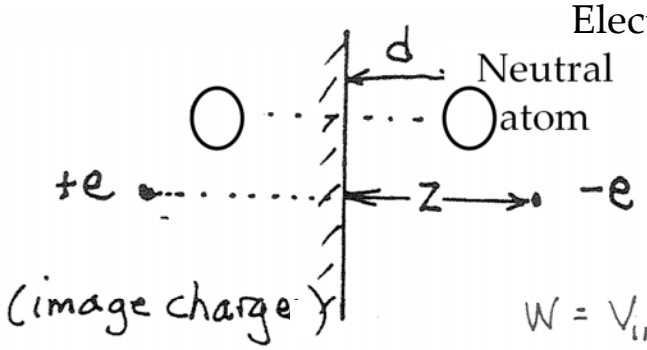


Image force acting on outgoing electron at distance z is

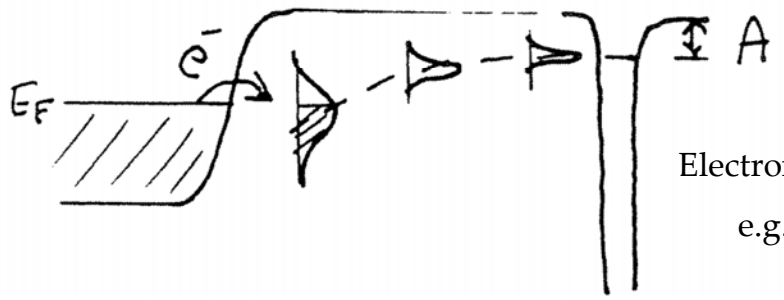
$$F = -\frac{e^2}{4z^2}$$

attractive

$W = V_{im}$

effective affinity level $A_{eff} = A + V_{im}$

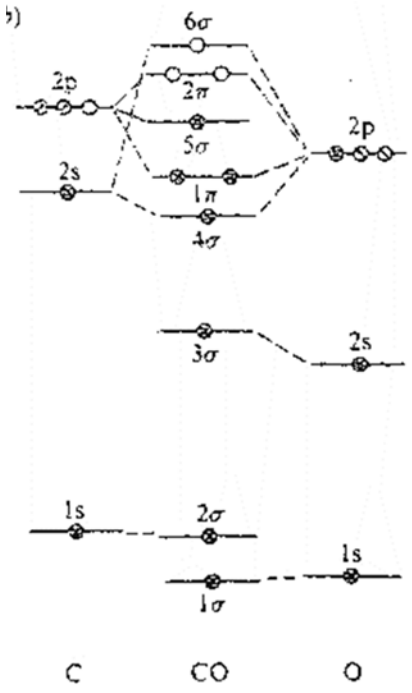
⇒ A level shifts down

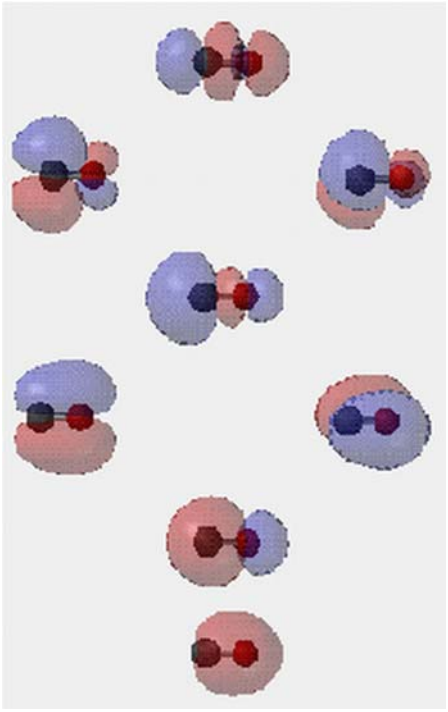


Electron transfer to adsorbate

e.g. adsorbed O, Cl, F

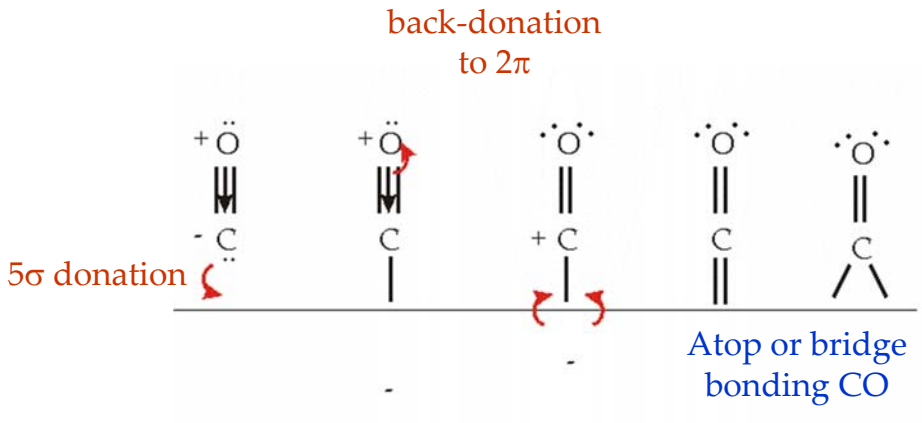
Isolated CO





C O

CO-Surface bonding

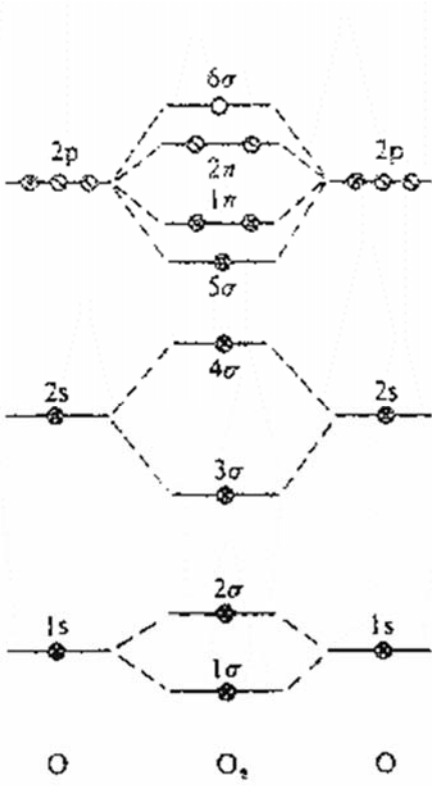


Blyholder model

Isolated O_2 molecules

O_2-Surface interaction leads to dissociative adsorption!

Strong ionic bonding of $O^{\delta-}$ with surface



Adsorbate Induced Work function changes on adsorption/charge transfer

Work function change

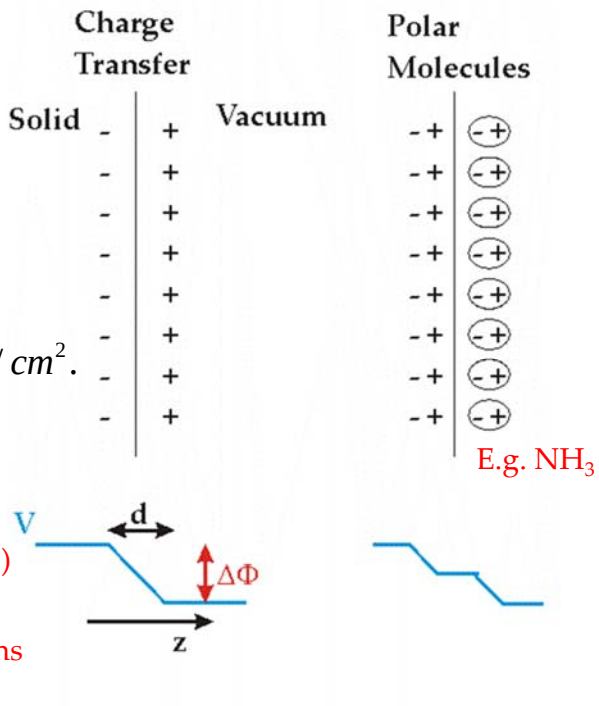
given by Helmholtz equation

$$\Delta\Phi = \frac{\sigma d}{\varepsilon_o}$$

$$\Delta\Phi = -3.76\,x10^{-15}\ \mu\ N$$

$\Delta\Phi$ *in* V, μ *in Debye*, N *in atoms* $/ cm^2$.

$3.3\,x10^{-30}$ *Cm / Debye.*



Electronegative adsorbates (O,Cl,F,H,..) cause work functions to increase.
Electropositive adsorbates (Li,Na,K,Ba…) cause work functions to decrease

Physisorbates also decrease work functions (usually)

Dipole depolarization

E.g. Adsorbed alkali, Cs

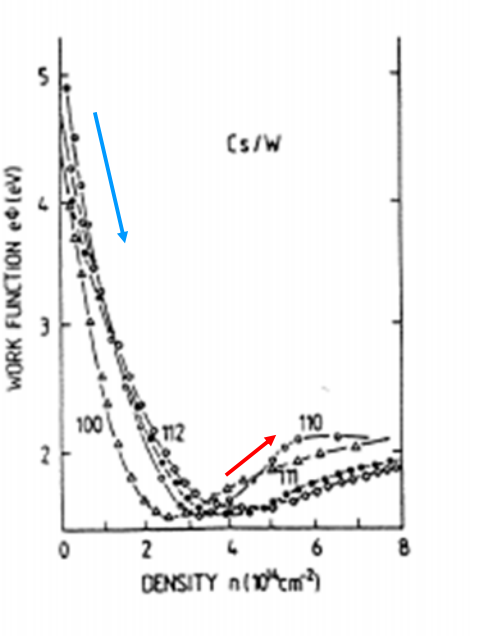
ΔΦ initially –ve.

Dipoles of like polarization cause depolarization.

Topping's Model

$$\Delta\Phi = -\frac{\mu N}{\varepsilon_o\left(1+\frac{9\alpha}{4\pi}N^{\frac{3}{2}}\right)}$$

α = polarizability



Kinetics: Probabilities for adsorption, sticking coefficients.

Sticking probability

$$S = \frac{rate\ of\ adsorption}{rate\ of\ collision} = \frac{dN}{dE}$$

dN: Adsorbate density/m²

dE: Exposure/m²

$$S = \frac{R_a}{p/(2\pi mkT)^{\frac{1}{2}}}$$

$$S = f(\theta)\, s^*\, k_a$$

$$R_a = \frac{p}{\sqrt{2\pi mkT}} f(\theta)\, s^*\, k_a$$

k_a: Rate constant for adsorption

$\frac{p}{\sqrt{2\pi mkT}}$: Collision rate, atoms/m² at P,T

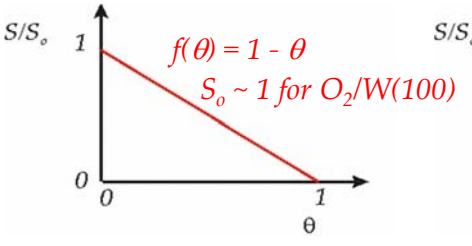
s^*: Condensation coefficient on an empty site

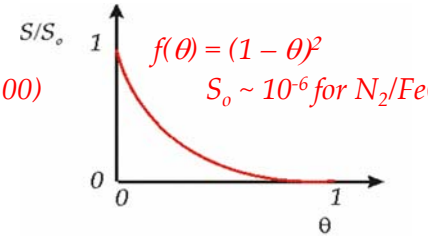
$f(\theta)$: Fraction of available sites

No adsorption if incident molecule/atom hits occupied site(s).

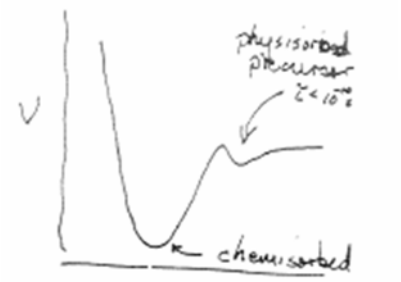
$$S(\theta)/S(\theta=0) = S(\theta)/S_o = f(\theta)$$

Compare non-dissociative and dissociative adsorption

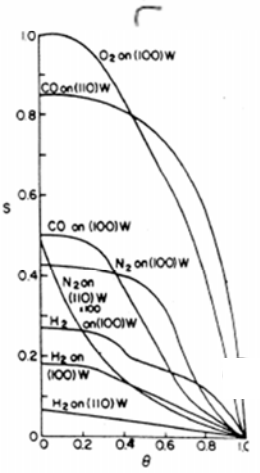




Precursors in sticking coefficients



Assume: adsorption occurs into precursor state, above occupied or empty site.



gas ⇌ precursor → chemisorbed state (chemisorption; desorb; migration)

Two types of precursors: above empty or filled site

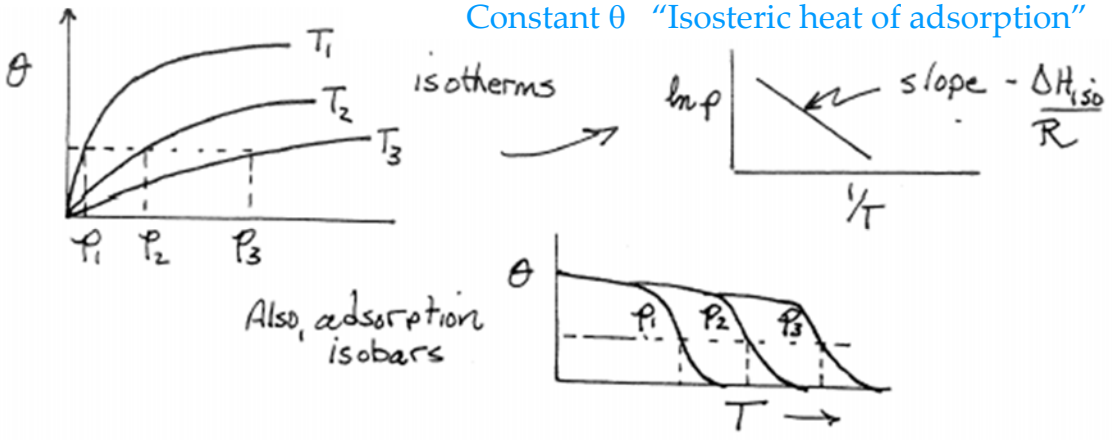
empty site (1) (intrinsic) → filled site (2) (extrinsic)

FIG. 19. Plot of sticking coefficient versus fractional coverage on several single crystal planes at 300 K. The shape of the curves (plateau region) in many cases is more significant than the absolute value of *S*.

Kinetics: Adsorption Isotherms.

- Adsorption isotherms are measures of equilibrium (steady state) between gas pressure *P* and coverage θ
- Useful for determining ΔH_{ads}, surface coverage, mechanistic information, and phase equilibria in 2-D systems. $\frac{\partial(\ln P)}{\partial T} = \frac{\Delta H_{ads}}{RT^2} \quad \Rightarrow p = p_o \exp\left(-\frac{\Delta H_{ads}}{RT}\right)$
- Assumed, at equilibria $R_d = R_a$; desorption and adsorption rates are balanced.

Constant θ "Isosteric heat of adsorption"



Kinetics of Desorption

Used $R_d = k_d f'(\theta) = k_d \theta^2$

More generally $f'(\theta) = \theta^n$

Equally $R_d(t) = -\frac{dN}{dt} = \nu_n N^n \exp\left(-\frac{E}{RT}\right)$ [1]

for n^{th} order desorption kinetics

n = 1 anticipated for desorption of atoms, undissociated molecules

n = 2 recombinative desorption, e.g. Cl_2, C_2N_2 (NCCN)

n = 0 free sublimation with no change in surface area,

2-D phase equilibria

Info from isosteric heat of adsorption, isothermal desorption, or TPD (temperature programmed desorption)

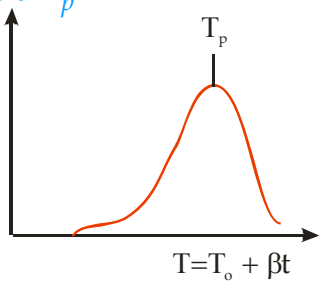
TPD (Temperature Programmed Desorption)

Conventionally a linear heating rate

$$T = T_o + \beta t$$

Substitution in [1] and setting $\frac{d}{dt}\left(\frac{dN}{dt}\right) = 0$ at T_p

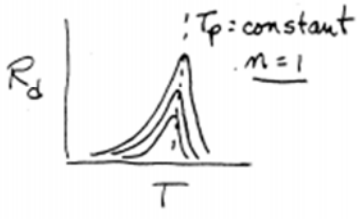
P^*

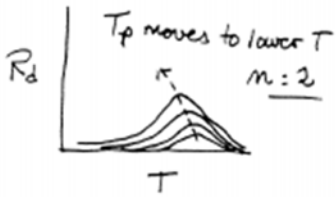


[2] $$\frac{E}{RT_p^2} = \left(\frac{\nu_1}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right) \qquad n = 1$$

[3] $$\frac{E}{RT_p^2} = N_o\left(\frac{\nu_2}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right) \qquad n = 2$$

Eq. [2] shows that T_p independent of coverage N for 1st order des.;
Eq. [3] indicates that T_p varies with N_0 for second order





Also note $N(t) = \int_0^t R_d(t)\,dt$

not integral over T unless $T = T_0 + \beta t$, linear with t !

First order desorption of Cl/W(100)

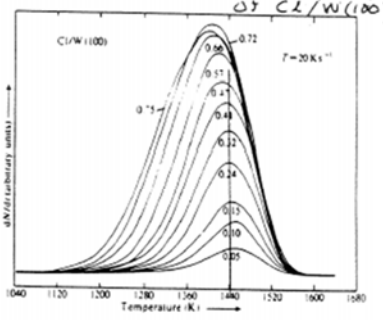
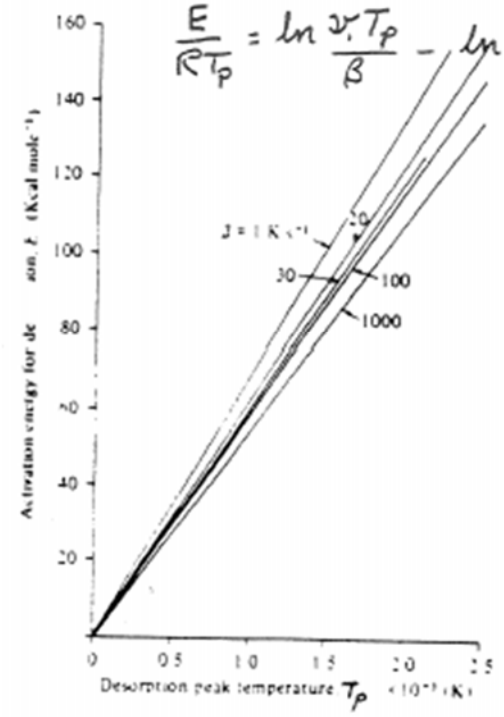


Fig. 3.12. Desorption of chlorine atoms from tungsten (100). The mass spectrometer was in line of sight from the sample. The curves show the essentially temperature-independent maximum characteristic of first order desorption, eqn (3.14). The curves yield a coverage-independent energy of desorption of 82 kcal mol^{-1}. (From Kramer and Bauer 1981.)

Assuming ν is fixed (known) in TPD

Fig. 5.5. Activation energy of desorption E_a as a function of T_p for a first order reaction and a linear temperature sweep, assuming $\nu = 10^{13}\ s^{-1}$ (Redhead, 1962).



[2] rearranged

Can often ignore the last term

Given T_p , β_p and guess of ν, can get E directly

Better method; vary β.

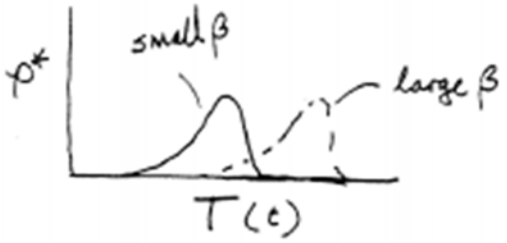
$$\frac{E}{RT_p^2}-\left(\frac{\nu_1}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right)=0 \quad n=1$$

$$D.w.r.t.\ \frac{-1}{T_p}$$

$$\frac{2E}{RT_p}-\left(\frac{\nu_1}{\beta}\right)\frac{E}{R}\exp\left(-\frac{E}{RT_p}\right)=0$$

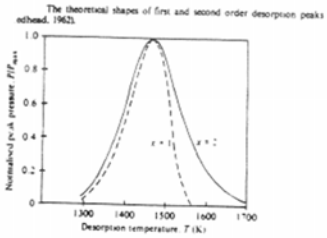
$$\frac{2\beta}{\nu_1 T_p}=\exp\left(-\frac{E}{RT_p}\right)$$

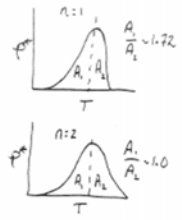
$$\Rightarrow \ln\left(\frac{T_p}{\beta}\right)=C+\frac{E}{R}\frac{1}{T_p}$$



Gradient = E/R.

Ideal first and second order desorption peaks

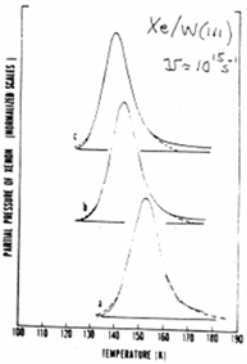




- Many factors can cause broadening of peaks
  - E is a function of θ
    - * interactional effects
    - * unresolved binding states
  - role of precursor
  - experimental artifacts
    - * temperature gradients
    - * finite pumping speed
- when a narrow peak is observed, physics gets interesting!

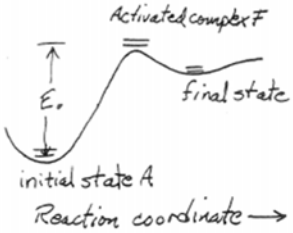
For Xe/W(111), $\nu \sim 10^{15}\,s^{-1}$ ⇒ desorption from immobile layer rather than 2-d gas

For CO/Ru(0001), very large ν's, p. 39



Comparison of theoretical first-order desorption curves for Xe with experiment [Xe physisorbed on W(111)]. Initial fractional coverage of xenon θ_{Xe} = (a) 0.0025, (b) 0.021, (c) 0.134. E_a (kcal mole^{-1}) = (a) 10.23, (b) 9.61, (c) 9.34. $\nu = 10^{15}\,s^{-1}$. Dotted line is for theory, solid for experiment. (From Dresser *et al.*)

Why is ν often taken as 10^{13}? Transition State Theory.



In this theory, the rate constant for the overall reaction is related to the concentration of ‡ and its rate of "falling apart".

Rate constant:

$$k_r = \frac{kT}{h}\frac{q^{\ddagger}}{q_A}e^{-E_o/RT}$$

- $kT/h \sim 6.3\times10^{12}\ s^{-1}$ at 300K
- q's are partition functions for the species

$$q = \sum_i g_i e^{-\varepsilon_i/kT}$$

where g_i is the degeneracy of the quantum state ε_i

$$\varepsilon_i = \varepsilon_{t_i} + \varepsilon_{e_i} + \varepsilon_{r_i} + \varepsilon_{v_i}$$

$$q = q_t q_e q_r q_v$$

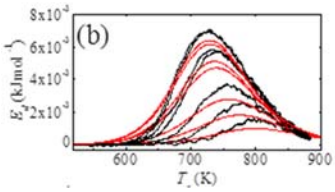
for translation, $q_t = \frac{2\pi m kT}{h^2}A$ ← total area available for translating complex

- Usual assumption for adsorption, desorption

$$q^{\ddagger}/q_A \approx 1$$

$$k_r = \frac{kT}{h}e^{-E_o/RT}$$

Summary of quick TPD analysis methods



Redhead

$$\frac{E}{RT_p^2} = \left(\frac{\nu_1}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right)$$

Vary	measure	use	assume	find
T	T_p	β_p	E_d const., ν; n=1	E_d
T, β	T_p	β_p	E_d const., ν; n=1	E_d , ν/β
T, θ_o	T_p , θ_p		E_d, ν, β const.,	E_d , ν/β
T, θ_o	T_p , I_p, θ_p		ν, β_p const.,	ν, E_d^o, $E_d(\theta)$

$$\frac{E}{RT_p} = \ln\left(\frac{\nu_1 T_p}{\beta_p}\right) - \ln\left(\frac{E}{RT_p}\right)$$

$$\ln\left(\frac{T_p}{\beta}\right) = C + \frac{E}{R}\frac{1}{T_p}$$

Redhead

Ciftlikli, Hinch. Langmuir (2010).

n = 2 recombinative desorption,

C_2N_2 (NCCN)/Cu(001)