

Lecture Note #4 (Spring, 2019)

Chemisorption, Physisorption, & Dynamics

Reading: Kolasinski, ch.3

Type of interactions

Physisorption vs. Chemisorption

Physisorption (physical adsorption)

- Van der Waals interaction
- Small adsorption energy: ≤ 20 kJ/mole
- Similar to condensation
- Multilayer adsorption possible
- No charge transfer
- Substrate non-specific

Chemisorption (chemical adsorption)

- Chemical bonding (covalent bonding)
- Large adsorption energy: ≥ 200 kJ/mole
- Charge transfer : work function change
- Limited to a monolayer
- Substrate specific
- Gas specific

Synoptic table 25.1* Maximum observed enthalpies of physisorption

| Adsorbate | $\Delta_{\text{ad}}H^{\ominus}/(\text{kJ mol}^{-1})$ |
|------------------|--|
| CH ₄ | -21 |
| H ₂ | -10.4 |
| H ₂ O | -59 |
| N ₂ | -21 |

Synoptic table 25.2* Enthalpies of chemisorption, $\Delta_{\text{ad}}H^{\ominus}/(\text{kJ mol}^{-1})$

| Adsorbate | Adsorbent (substrate) | | |
|-----------------|-----------------------|------|------|
| | Cr | Fe | Ni |
| CH ₄ | -427 | -285 | -243 |
| CO | | -192 | |
| H ₂ | -188 | -134 | |
| NH ₃ | | -188 | -155 |

Table 3.1 *A comparison between chemisorption and physisorption*

| Chemisorption | Physisorption |
|---|---|
| electron exchange | polarization |
| chemical bond formation | van der Waals attractions |
| strong | weak |
| ≥ 1 eV (100 kJ mol^{-1}) | ≤ 0.3 eV (30 kJ mol^{-1}), stable only at cryogenic temperatures |
| highly corrugated potential | less strongly directional |
| analogies with co-ordination chemistry | |

Cryogenic temperatures: liquid He (4K), liquid N₂ (77K)

- Adsorption, especially chemisorption \rightarrow surface free energy $\downarrow \rightarrow$ surface tension, $\gamma \downarrow$
- Chemisorption \rightarrow usually exothermic process $\rightarrow \Delta S < 0$ (gas in 2D), $\Delta G < 0$ (constant T & P, free energy \downarrow , spontaneous) $\rightarrow \Delta G = \Delta H - T\Delta S \rightarrow \Delta H < 0$ (exothermic)
- Temperature $\downarrow \rightarrow$ Adsorption \uparrow
- exception: dissociate adsorbates & high translational mobility on the surface ($\Delta S > 0$). Repulsion between adsorbates by coverage $\uparrow \rightarrow$ less exothermic

e.g., H_2 on glass: endothermic, $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{glass})$, $\Delta S > 0 \rightarrow \Delta H > 0$

Terminology

- Adsorption site density

$$N_s = \# \text{ of sites /cm}^2 \sim 10^{15} /\text{cm}^2$$

- Coverage

$$\text{fractional coverage } \theta = N_s / N$$

$$\text{saturation coverage : } \theta_s = 1$$

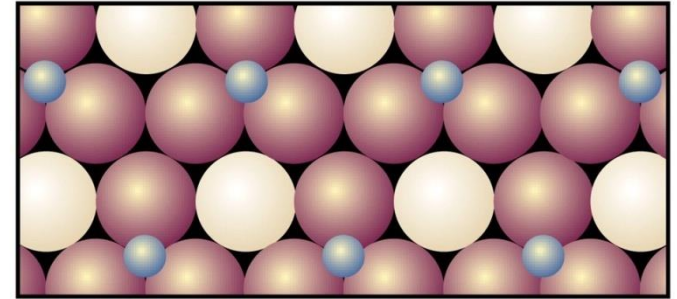
- Wall collision rate Z_w

$$Z_w = \# \text{ molecules striking a surface /cm}^2 \cdot \text{s}$$

$$Z_w = P / (2\pi mkT)^{1/2} \sim 10^{15} \text{ molecules /cm}^2 \cdot \text{s}$$

$$\text{@ } 10^{-6} \text{ Torr and } 298 \text{ K}$$

$$1 \text{ L (Langmuir)} = 10^{-6} \text{ Torr} \cdot \text{s of gas exposure.}$$

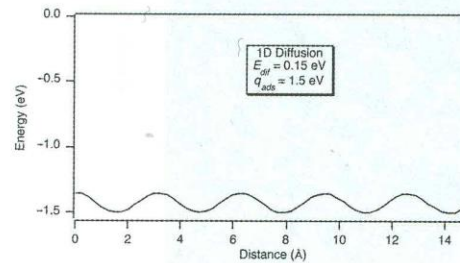


- Monolayer completion time $\sim 1\text{sec @ } 10^{-6} \text{ Torr}$

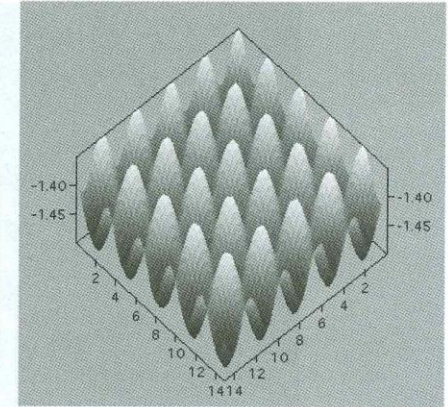
Binding sites and diffusion

Surface sites are separated by energetic barriers \rightarrow diffusion barrier

Potential energy surface (1-D and 2-D)



(a)



(b)

Figure 3.1 The interaction potential of an adsorbate is corrugated as can be seen in these (a) 1D and (b) 2D representations of energy versus position on ideal defect-free surfaces.

Step-up diffusion (E_s)

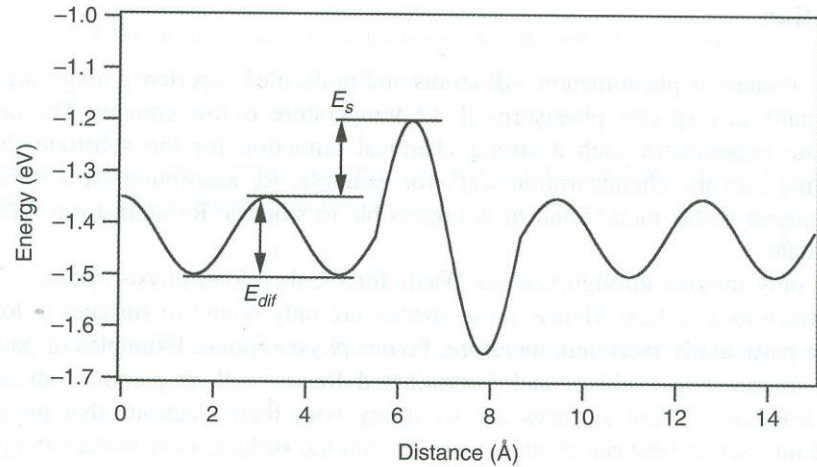


Figure 3.3 A step changes the diffusion activation energy, E_{dif} [one-dimensional (1D) diffusion]. Step-up diffusion is often negligible because of the increased barrier; note also the increased binding strength at the bottom of the step – a feature that is often observed. E_s , Ehrlich-Schwobell barrier.

Diffusion for strongly interacting atoms (metal on metal)

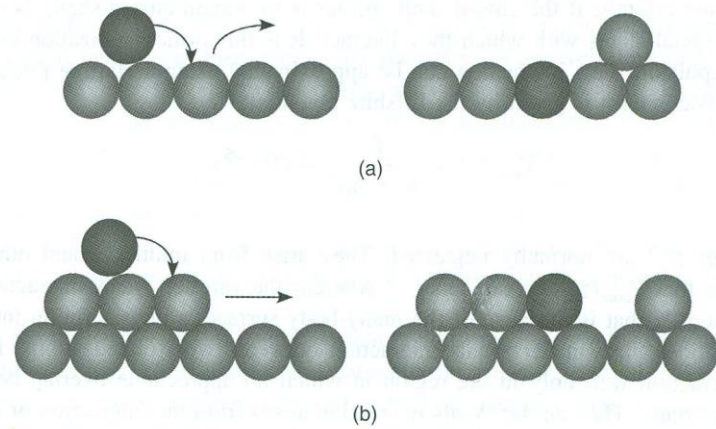


Figure 3.4 The exchange mechanism of diffusion. Mass transport occurs via the replacement of one atom with another. This can happen either (a) on a terrace or (b) at a step

Non-dissociative chemisorption

Theoretical treatment of chemisorption

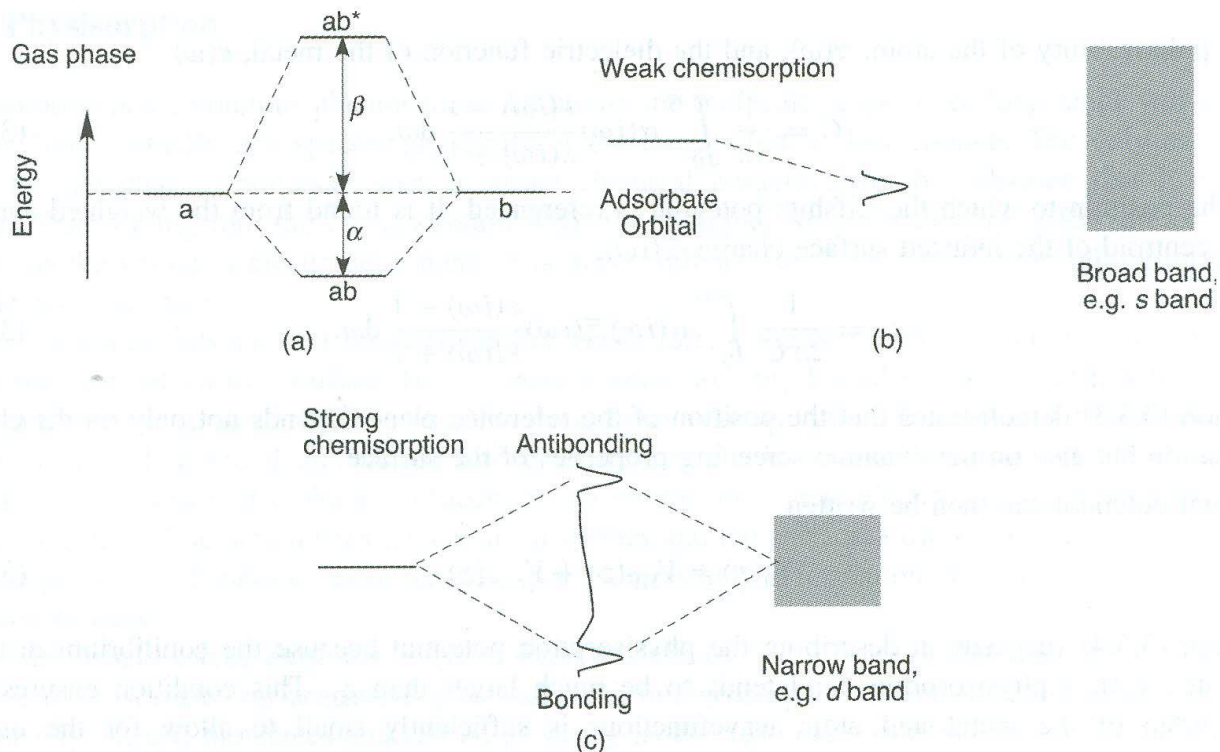


Figure 3.5 Orbital interactions. (a) Gas phase. (b) Weak chemisorption. (c) Strong chemisorption. a , b , atomic orbitals; ab , ab^* , bonding and antibonding molecular orbitals; α , β energy shifts of molecular orbitals with respect to the mean energy of a and b .

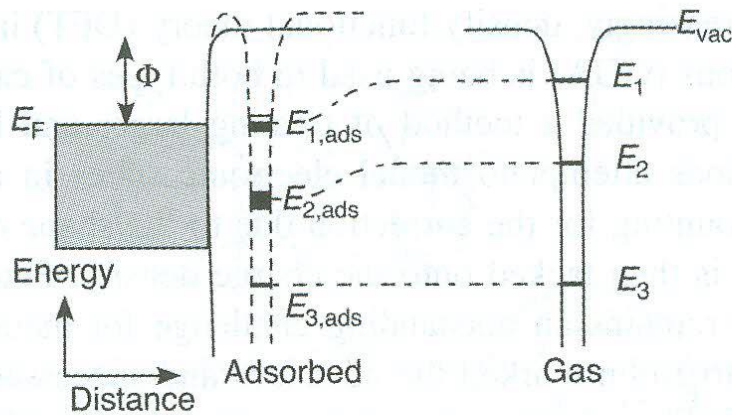


Figure 3.6 Diagram of broadening and shifting of adsorbate levels as they approach a surface. E_F , Fermi energy; E_{vac} , vacuum energy; Φ work function of the surface material; E_1, E_2, E_3 , energies of molecular orbitals 1, 2 and 3, respectively, of the molecule far from the surface; $E_{1,ads}, E_{2,ads}, E_{3,ads}$, energies of molecular orbitals 1, 2 and 3, respectively, of the adsorbed molecule; shaded area, occupied band (e.g. valence band).

As a molecule approaches a surface, its electronic states interact with the electronic states of the metal
 → this broadens the MOs and it also lowers the energy of the MOs
 → the reason why MOs experience a shift and broadening is that they interact with the electron of the substrate

Blyholder model of CO chemisorption on a metal

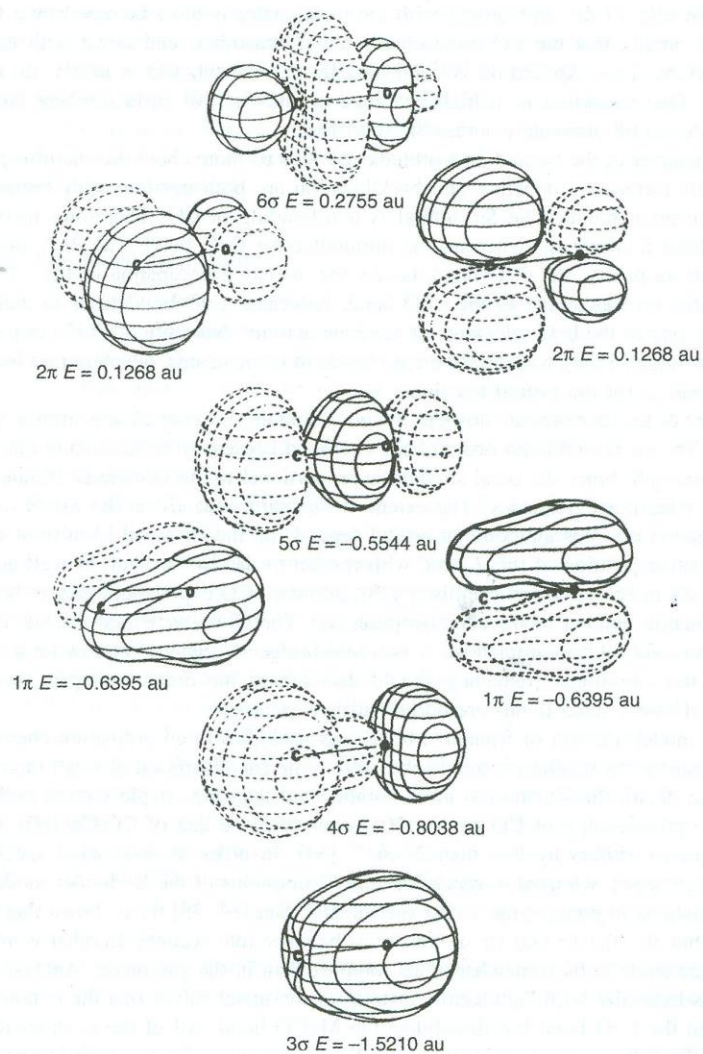
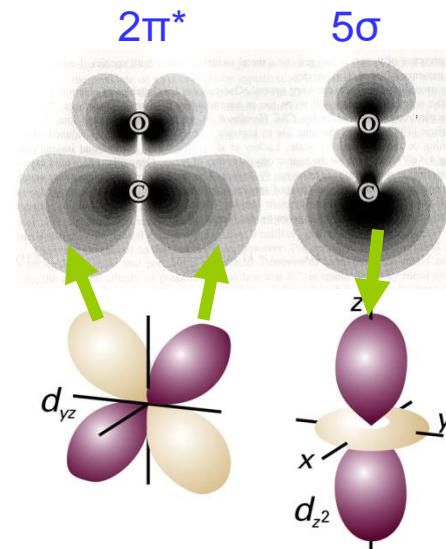


Figure 3.7 The molecular orbitals of gas-phase CO. The wavefunction changes sign in going from the regions enclosed by solid lines to those enclosed by dashed lines. Energies, E , are given in atomic units (1 atomic unit = 27.21 eV). Orbitals with negative energies are occupied in the ground state of the neutral molecule. Reproduced from W. L. Jorgensen, L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York. © (1973) with permission from Academic Press.

- Charge transfer : work function change
 - e⁻ donation + backdonation
 - Orbital symmetry
-
- Transition & noble metal : d-band metal
-
- Heat of adsorption: bond strength
 - Dissociation
 - Activated adsorption



Molecular oxygen chemisorption

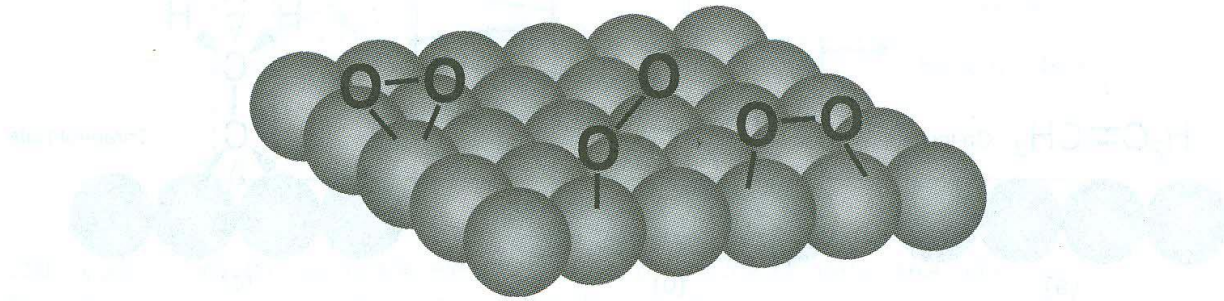


Figure 3.8 $O_2/Pd(111)$ adsorbate structure. The labelling of the three states (ω_1 , ω_2 and ω_3) correlates with the loss peaks observed in the electron energy loss spectrum as shown in Fig. 2.30.

The binding of ethene

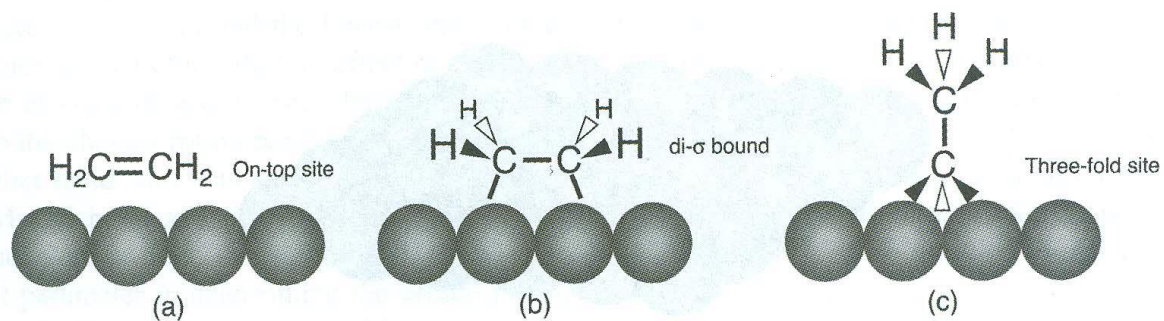


Figure 3.9 The binding of ethene at a metal surface. (a) The weakly chemisorbed π -bonded C_2H_4 . (b) The σ -bonded chemisorbed state. (c) Ethylidyne.

Dissociative chemisorption: H_2 on a simple metal

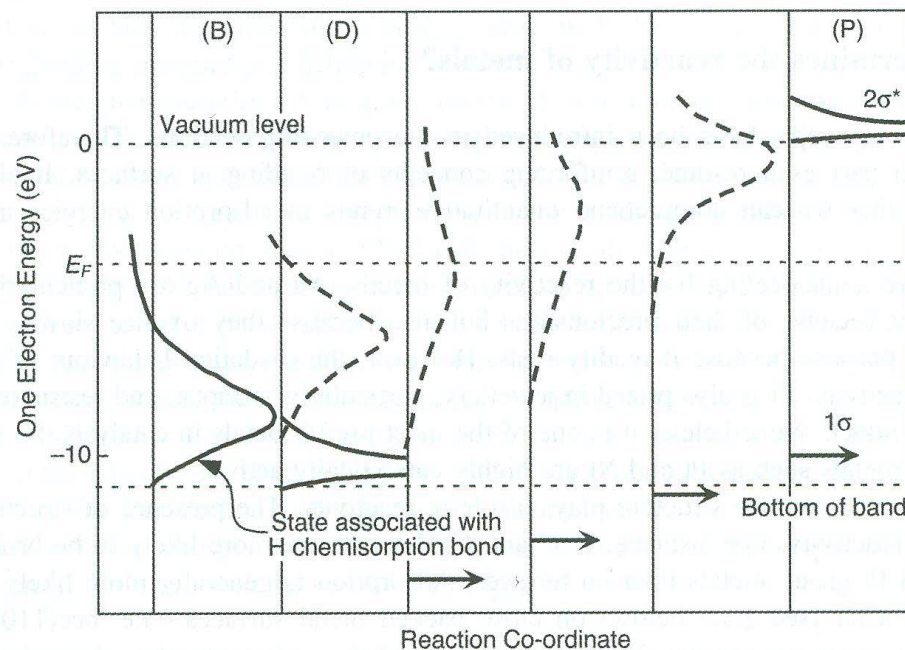
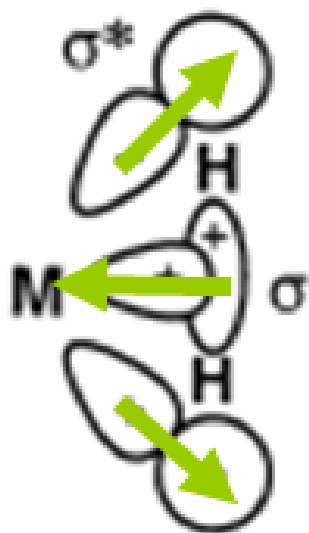
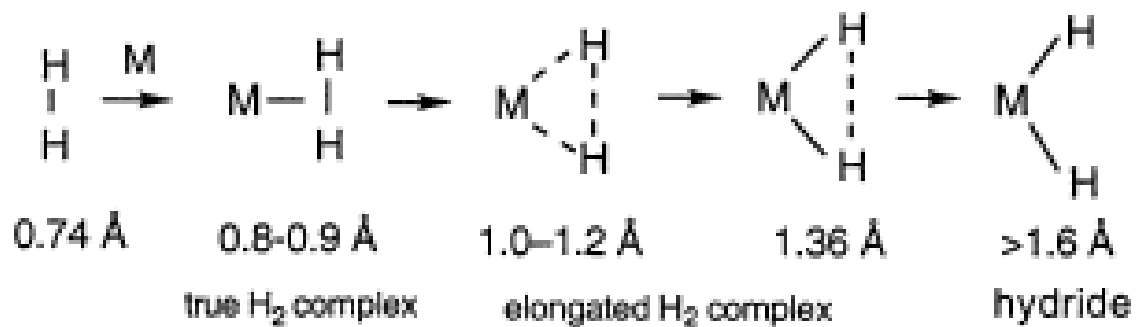


Figure 3.10 Calculated changes in the electronic structure of the orbitals associated with H_2 as the molecule approaches a Mg surface. Moving to the left in the diagram represents motion toward the surface. Reproduced from J. K. Nørskov, A. Houmøller, P. K. Johansson, B. I. Lundqvist, *Phys. Rev. Lett.*, 46, 257. © 1981, with permission from the American Physical Society.



Kubas interaction



What determines the reactivity of metals?

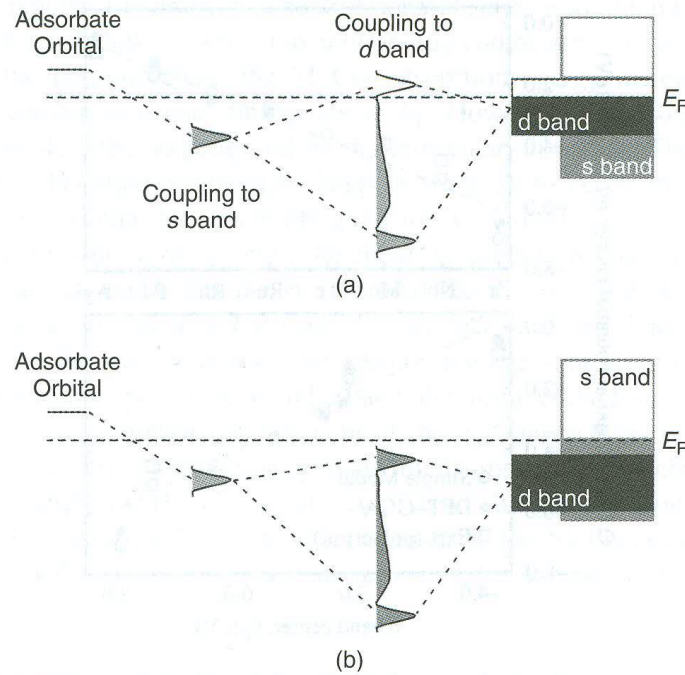


Figure 3.11 The two-step conceptualization of chemisorption bond formation on transition metal surfaces. (a) Early transition metal. (b) Coinage metal.

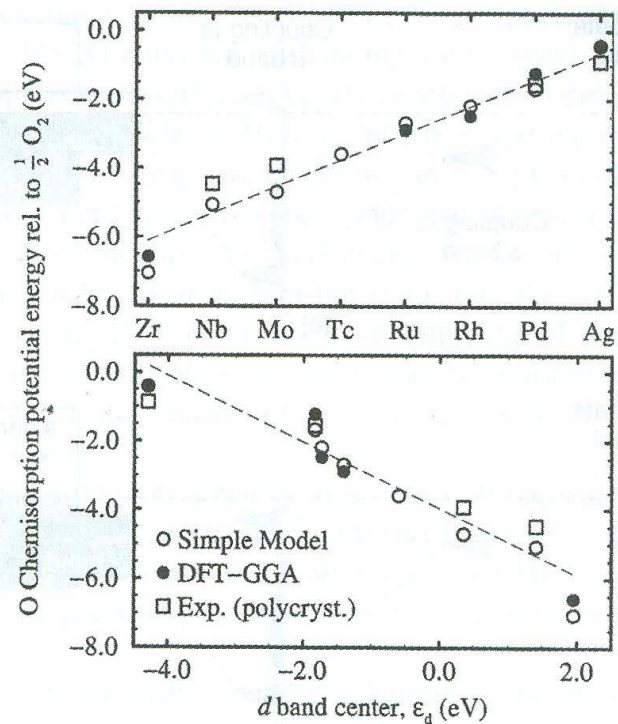


Figure 3.12 The interaction strength of chemisorbed O and how it varies across a row of transition metals. In the upper panel, the good agreement between experimental and theoretical results is shown. In the lower panel, the linear relationship between interaction strength and the d band centre is demonstrated. Source of data for experimental results: I. Toyoshima, G. A. Somorjai, *Catal. Rev – Sci. Eng.*, 19 (1979) 105. Reprinted from B. Hammer and J. K. Nørskov, *Theoretical surface science and catalysis – Calculations and concepts*, *Adv. Catal.*, Vol. 45 (Eds B. C. Gates, H. Knözinger), Academic Press, Boston, p. 71. © 2000 with permission from Academic Press.

Atoms and molecules incident on a surface

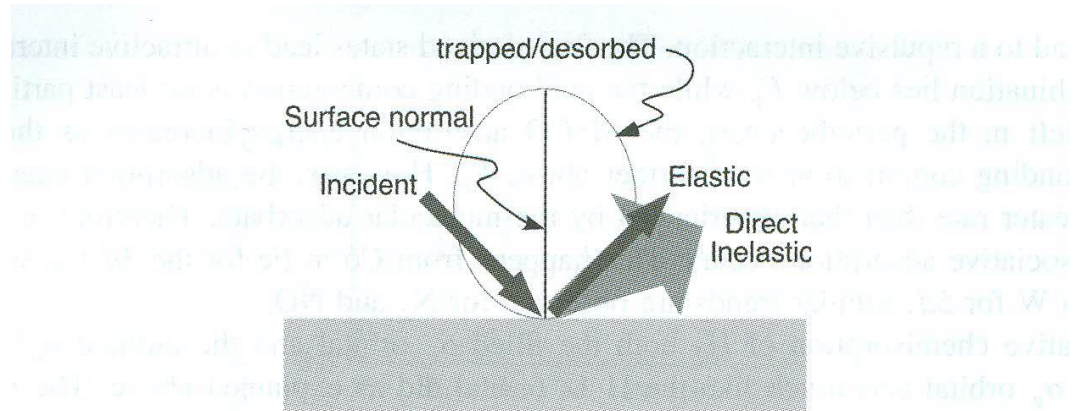


Figure 3.13 Scattering channels for a molecule incident upon a surface.

Adsorption dynamics

- The outcome of the gas-surface collisions;
 - 1) **Trapping**: becoming a bound state after the 1st collision
 - 2) Direct reflection to the gas phase
- The **trapping probability** is determined by the amount of the **energy transfer** to the surface.
- Energy transfer occurs via **multiphonon** excitations.

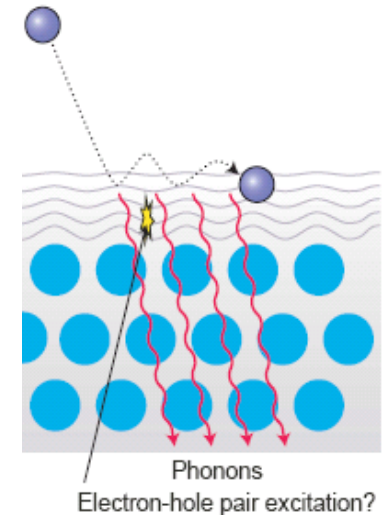
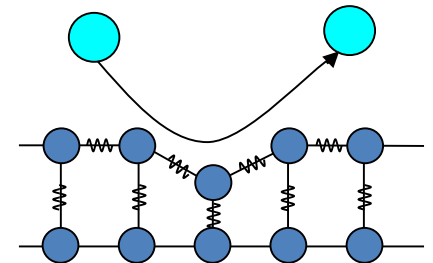
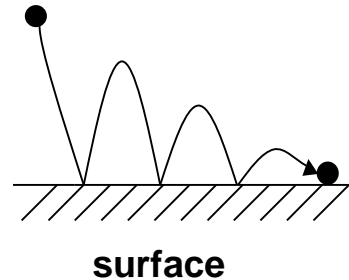
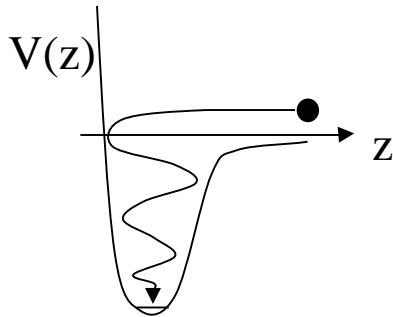


TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K

| Gas | Surface | $S(0)$ | Gas | Surface | $S(0)$ |
|----------------|---------|-------------|-----------------|-------------|----------------------|
| H ₂ | Ni(100) | 0.06 | N ₂ | W(320) | 0.7 |
| H ₂ | Ni(111) | 0.02 | N ₂ | W(110) | $< 3 \times 10^{-3}$ |
| H ₂ | Pt(110) | 0.2 | Ga | GaAs(100)-B | 1.0 |
| H ₂ | Si(100) | $< 10^{-4}$ | As ₄ | GaAs(100)-B | $< 10^{-3}$ |
| CO | Pt(111) | 0.67 | As ₄ | GaAs(100)-A | 0.5 |

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

Non-activated adsorption

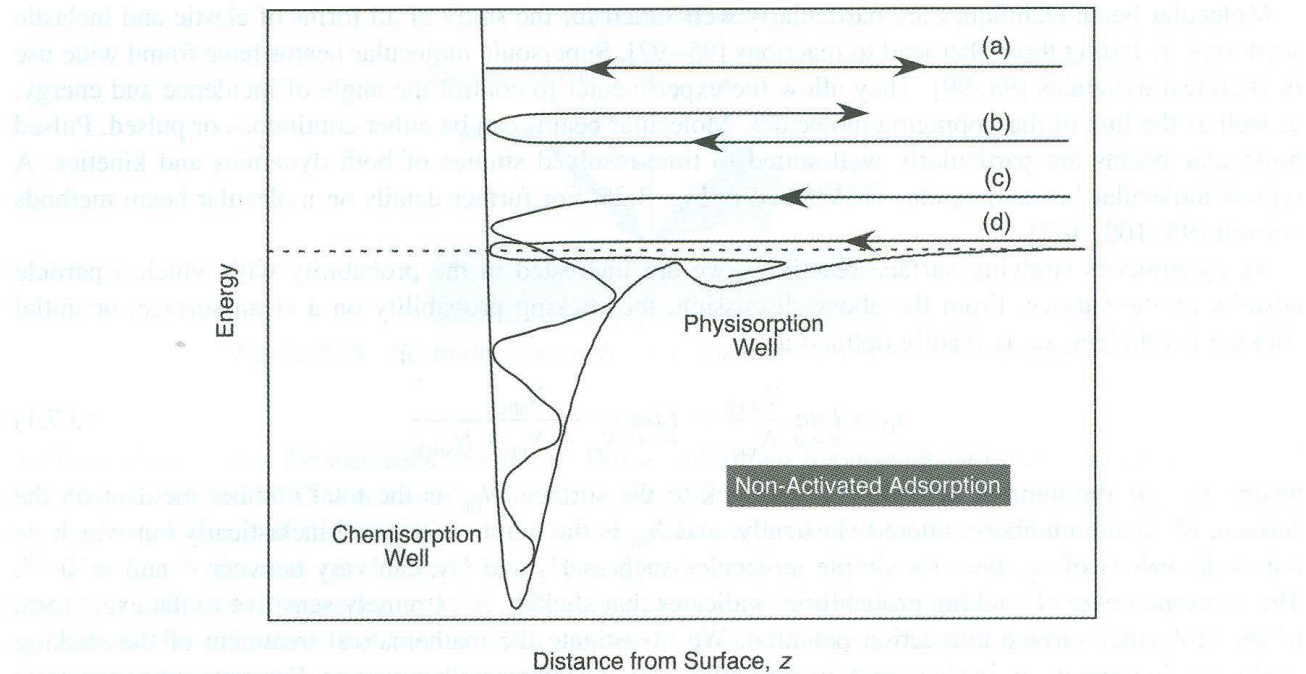


Figure 3.14 A one-dimensional representation of non-activated adsorption: (a) elastic scattering trajectory; (b) direct inelastic scattering trajectory; (c) sticking event (chemisorption); (d) sticking event (physisorption).

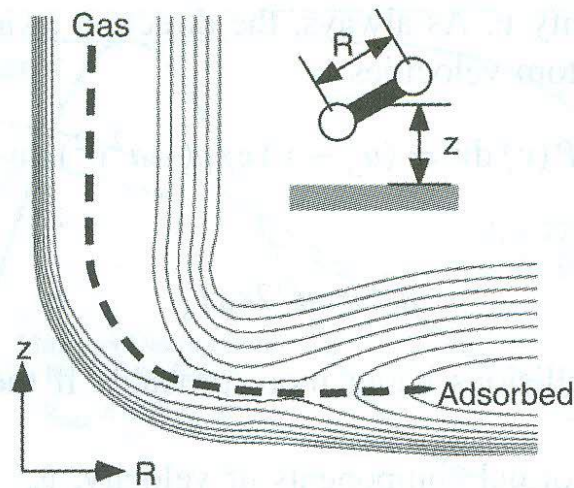


Figure 3.15 2D PES for non-activated dissociative adsorption. z is the distance from the molecular centre of mass to the surface. R is the internuclear distance between the atoms of the molecule.

Hard cube model for non-activated adsorption

Activated adsorption

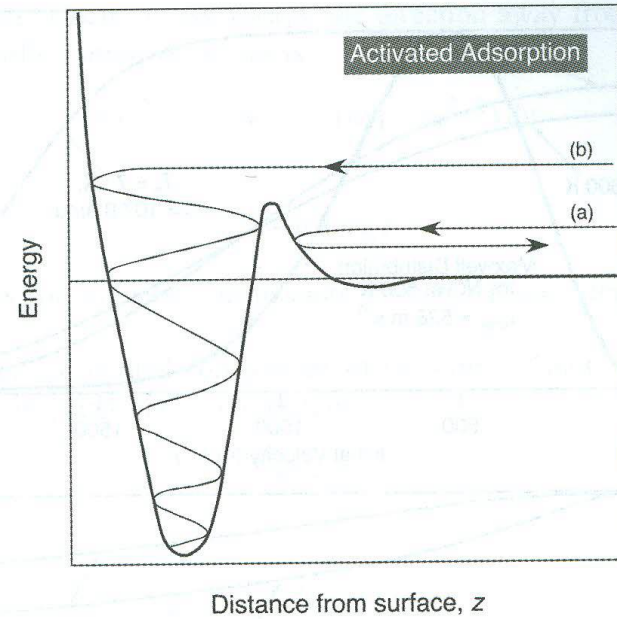
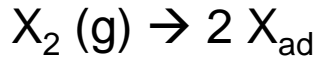
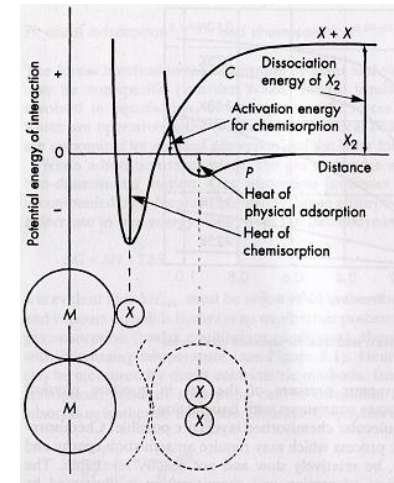
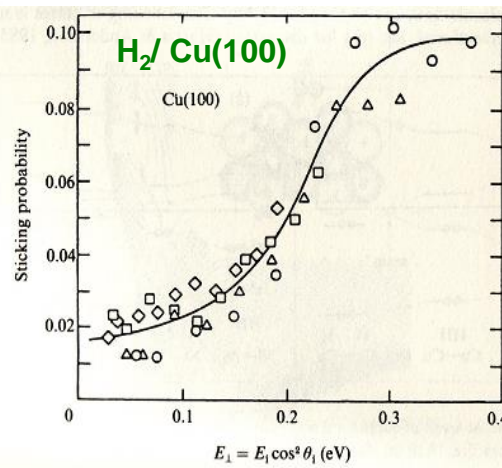
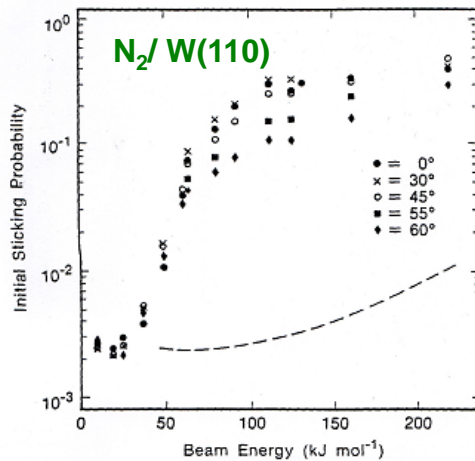
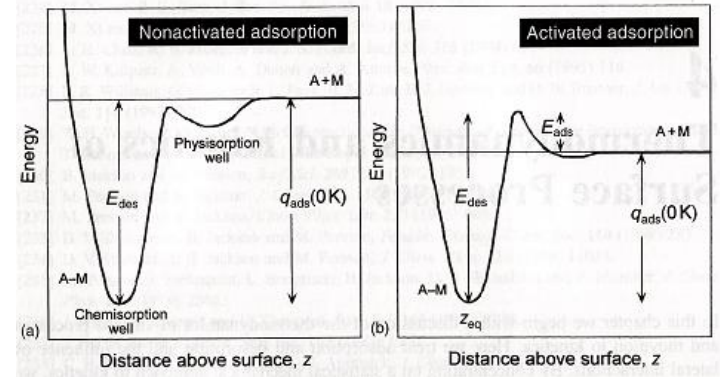


Figure 3.17 A Lennard-Jones diagram is a one-dimensional representation of the potential energy. In the case shown here, the one dimension is taken as the distance above the surface. A barrier separating the chemisorption well from the gas phase distinguishes activated adsorption. Also shown in the diagram are the energies of two hypothetical trajectories at (a) low and (b) high kinetic energy. Classically, only high energy trajectories can overcome the adsorption barrier.

Activated adsorption



- Important process in heterogeneous catalysis
- **Very small s_0** due to the presence of an adsorption barrier
- A fast N_2 can overcome the barrier to directly populate the atomic state
- **A large kinetic energy dependence of s_0**



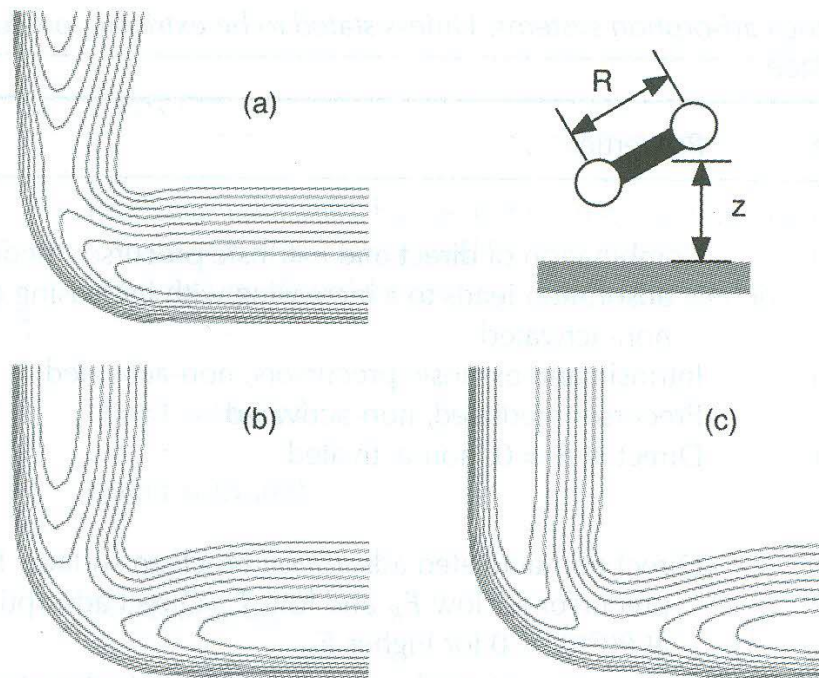


Figure 3.18 Potential energy surfaces (PESs) for activated dissociative adsorption with (a) early, (b) middle and (c) late barriers. z , the distance from the molecular centre of mass to the surface (vertical axis); R , internuclear distance between the atoms of the (diatomic) molecule (horizontal axis). George Darling is thanked for providing these very fine model PESs.

Direct vs. precursor mediated adsorption (Table 3.2)

Competitive adsorption & collision induced processes

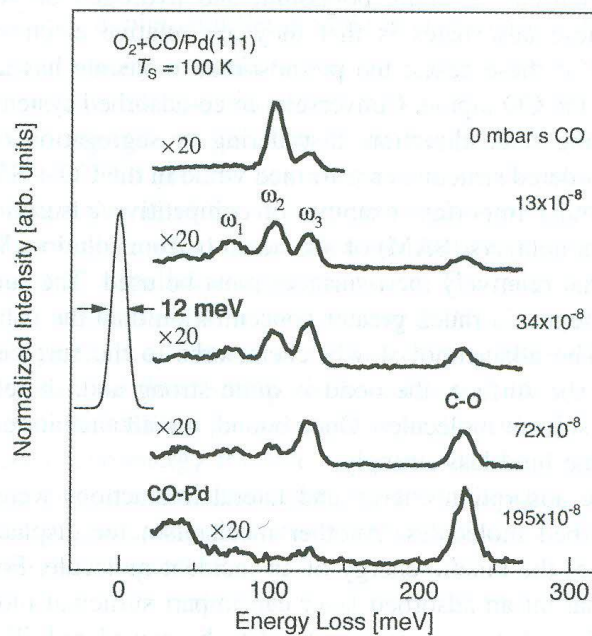


Figure 3.23 Competitive adsorption in the $CO + O_2/Pd(111)$ system is investigated by electron energy loss spectroscopy (EELS). The species associated with species ω_1 , ω_2 and ω_3 are illustrated in Fig. 3.8. arb units, arbitrary units; T_s , surface temperature. Reproduced from K. W. Kolasinski, F. Cemič, A. de Meijere, E. Hasselbrink, Surf. Sci., 334, 19. © 1995, with permission from Elsevier.

Classification of reaction mechanism

Langmuir-Hinshelwood mechanism

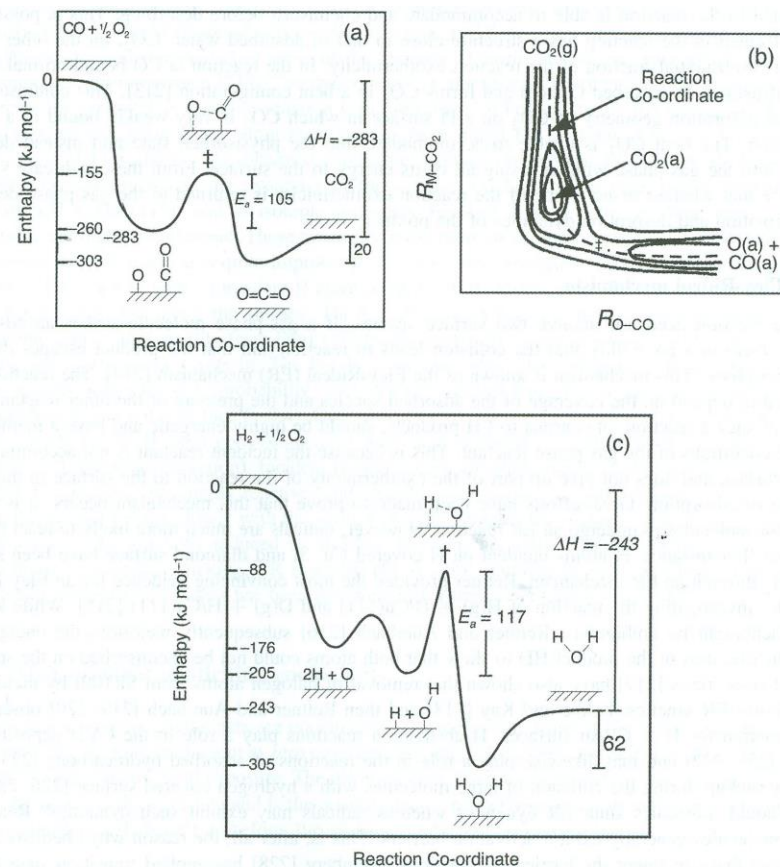
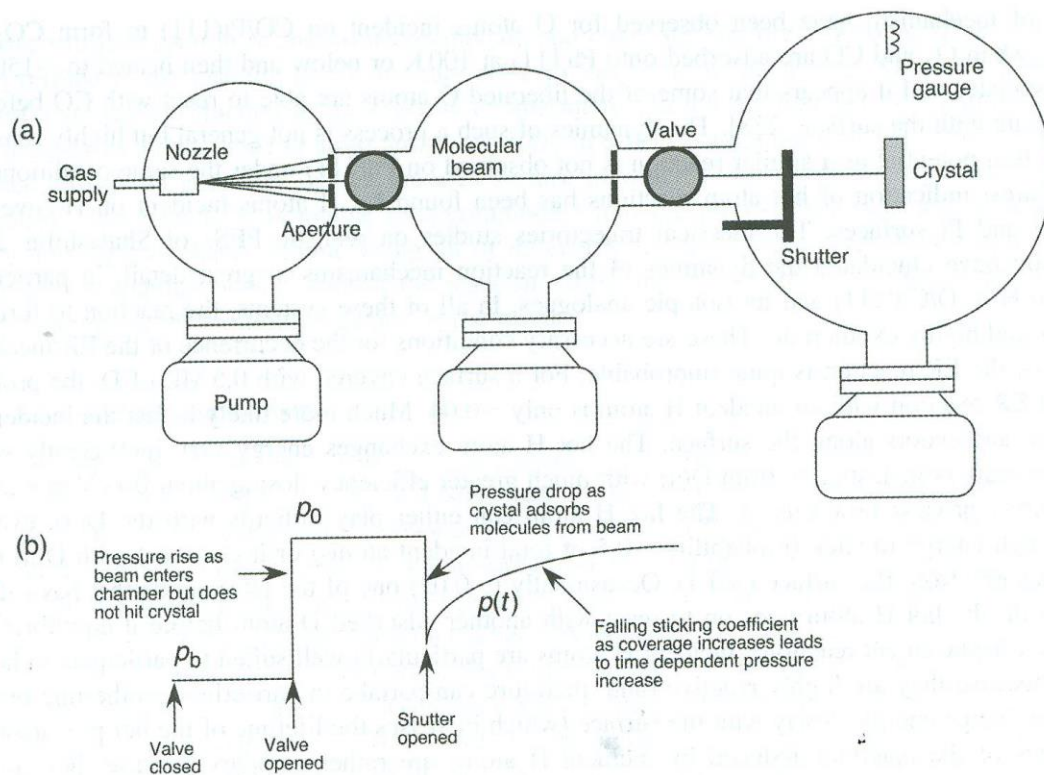


Figure 3.24 The oxidation of CO to form CO₂ and H₂ to form H₂O on Pt(111) follow Langmuir-Hinshelwood mechanisms. The changes in energy along the reaction pathway are as follows. (a) Enthalpy changes associated with CO + O₂ reaction. The transition state † is a stretched and bent CO₂ entity. (b) A two-dimensional potential energy surface of the CO + O₂ reaction, portraying the energetic changes as a function of the CO₂-surface distance [r(M-CO₂)] and the forming OC bond length [r(O-CO)]. (c) Enthalpy changes associated with the H₂ + O₂ reaction. Two intermediates (2H + O, and H + OH) are formed during the reaction. The transition state † reached prior to the formation of H₂O(a) is also bent and stretched; however † resembles H₂O(a) more closely than † resembles CO₂(a). Parts (a) and (b) Reproduced with permission from G. Ertl, Ber. Bunsenges. Phys. Chem. 86 (1982) 425. © 1982 Wiley VCH. Values for (c) taken from M. P. D'Evelyn and R. J. Madix, Surf. Sci. Rep. 3 (1983) 413.

Eley-Rideal mechanism

Hot atom mechanism

Measurement of sticking coefficients



$$s(t) = \frac{p_0 - p(t)}{p_0 - p_b}$$

Figure 3.25 The King and Wells method of sticking coefficient determination: (a) apparatus, (b) pressure curve.

- Sticking probability

$$s = \frac{\text{\# molecules adsorbed}}{\text{\# molecules impinging on a surface}}$$

- Molecular beam method, in which the partial pressure change is monitored with a QMS (quadrupole mass spectroscopy)

TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K (Chemisorption)

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| CO | Pt(111) | 0.67 | As ₄ | GaAs(100)-A | 0.5 |

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

Factors influencing s_0 in chemisorption

- Gas- surface combination
- Efficiency of energy transfer in gas-surface collisions
- Surface orientation of the surface for a given single crystal material
- Presence of an energy barrier for dissociative adsorption: **activated adsorption**