




5. DYNAMICS OF SURFACE PROCESSES

The kinetics of the adsorption occurring on planar surface was already addressed when we derived the Langmuir equation. The physical picture beyond this model is simplified not only from equilibrium but also kinetic aspect. It neglects, e.g., the energetic heterogeneity of the surface sites, the lateral interaction between the already adsorbed molecules and the mobility of the molecules along the surface. The most plausible reason of the latter is that the concentration difference between the occupied and unoccupied places results in a concentration gradient which may lead to surface diffusion. For example, in Figure 5.1. kT represents the kinetic energy of the free gas molecule (at 293 K the corresponding value is about 2.5 kJ/mol). If this energy is enough to overcome the potential hills between the potential minima (the necessary activation energy E^{act}) the molecule can move along the surface (non-localized adsorption). In practice high adsorption energy does not necessarily mean insurmountable activation energy for surface mobility, as the gap between high energy surfaces can be below kT (see the case of heterogeneous surface in Fig. 5.1.). In Table 5.1. the calculated heat of adsorption of argon are compared on various sites of the surface of nonpolar graphite and polar KCl. From these data we can conclude that the surface of the graphite is energetically more homogeneous and the interactions with argon are stronger (the heat evolving is higher) than in the case of KCl surface sites. At the same time, the energetic difference between the surface sites is much smaller than in the case of KCl.

Table 5.1. Heat of adsorption (Q) of argon at various sites of graphite and KCl surfaces at the same temperature.

	Q , J/mol		Q , J/mol
grafit		KCl	
	7320	Cl—●—Cl	6660
	7160	● K	6070
	7160	● Cl	5320
		Cl—●—K	5480

*The black dot shows the position of the Ar

The diffusion constant D_s varies with the surface coverage Θ in a complex way (Figure 5.1.[14]). As sites with high adsorption energy are occupied first, that implicitly means that in real systems the activation energy of the diffusion and the heat of adsorption are not independent from each other. The activation energy necessary for surface mobility is approximately 10-80 % of the heat of adsorption (which can be extracted from the temperature dependence of the surface diffusion coefficient). In case of non-localised adsorption at low Θ the molecules travel on the surface as a two-dimensional gas. The diffusivity increases with the coverage as the activation energy of the diffusion decreases. The function exhibits a maximum at $\Theta = 1$. At higher occupation the lateral interaction between the adsorbed molecules cannot be neglected anymore, which may result in condensation at lower temperature (in case of porous systems it also depends on the pore size), therefore the diffusion coefficient falls back to the value belonging to liquid phase.

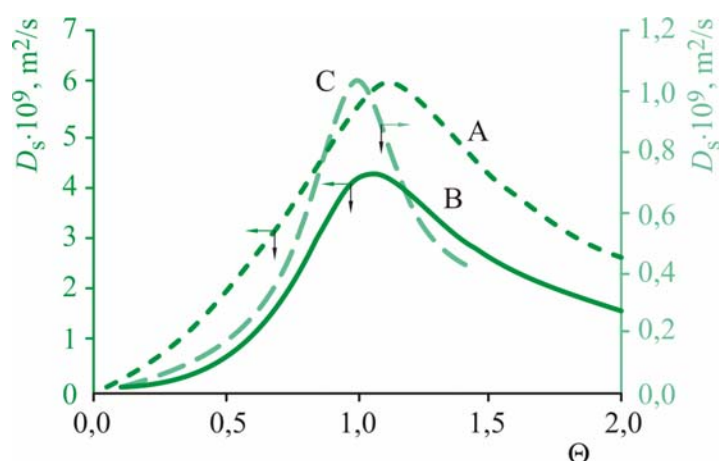


Figure 5.1. The diffusion coefficient is influenced by the surface properties of the coverage. A: argon on silica surface at 89 K; B: argon on silica surface at 77 K; C: N_2 on amorphous carbon surface (Spheron) at 77 K.

Surface diffusion is also called Volmer diffusion¹. The mechanism is influenced by the properties of the surface and the adsorbate and – particularly for complicated molecules – it is not fully clarified yet.

Within the pores the motion of the free (non-adsorbed) molecules depends on the ratio of the free pathway of the gas molecules λ and the pore width d . In narrow pores (even in

¹ Max Volmer (3 May 1885 – 3 June 1965) was a German physical chemist discovered the migration of adsorbed molecules, known as Volmer diffusion. He made important contributions in electrochemistry.

mezopores) $\frac{\lambda}{d} \gg 1$, therefore the gas molecules continuously collide to the wall and move by bouncing from wall to wall. This mechanism is called Knudsen-diffusion² (Figure 5.2). If $\frac{\lambda}{d} \ll 1$, i.e., the free path is less than the pore width, molecular or Fickian diffusion³ occurs (Figure 5.3). The diffusion coefficients of the three mechanisms are compared in Table 5.2.

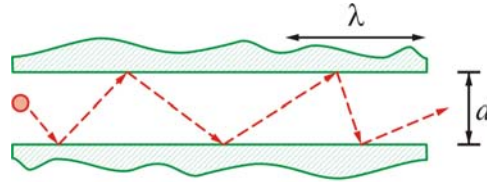


Figure 5.2. In the mesopores ($\frac{\lambda}{d} \gg 1$) the gas molecules typically move by Knudsen mechanism

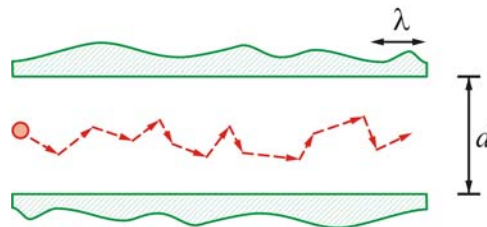


Figure 5.3. Fick diffusion of gas molecules occurs in the wide pores where $\frac{\lambda}{d} \gg 1$.

Table 5.2. Diffusion coefficient of gas molecules moving by various mechanisms in porous systems (293 K, 10^5 Pa).

Type of diffusion	D , m ² /s
Volmer	$\leq 10^{-7}$
Knudsen	10^{-6}
Fick	$10^{-5} - 10^{-4}$

² Martin Hans Christian *Knudsen* (1871-1949) was a Danish physicist renowned for his work on kinetic molecular theory.

³ Adolf Eugen Fick (1829–1901) was a German-born physician and physiologist. He introduced Fick's law of diffusion in 1855.

The role of surface diffusion is of fundamental importance in catalytic processes. Knudsen and Fickian diffusions determine how fast equilibrium is established in sorption processes.

5.1. The rate of surface reactions

The sticking probability s of the gas molecules colliding into the surface can be characterized by the ratio of the sorbed and bombarding molecules, respectively. In practice the ratio of the rate of adsorption v_a and the number of collisions on a unit surface area z is used:

$$s = \frac{v_a}{N} \quad (108)$$

N can be calculated from the kinetic theory of gases (Eq. 30). Each m^2 of a crystalline metal surface consists about 10^{18} - 10^{19} surface atoms. Presuming a 10^{-4} Pa pressure $4 \cdot 10^{18}$ collisions occur in every second, i.e., on average, each atom participates in one collision. Based on the adsorption kinetics discussed at the derivation of the Langmuir model it is expected that the sticking probability s linearly decreases as the surface coverage increases

$$s = s_0(1 - \Theta) \quad (109)$$

The value of the sticking probability on the pure surface s_0 is determined by the potential function of the system, i.e., it depends both on the surface properties (including the landing position of the gas molecule on the crystal plane) and the chemical properties of the gas phase (Table 5.3.).

Table 5.3. s_0 sticking probability of gases on pure surfaces at ambient temperature.

Surface	Gas	s_0
transient metal	CO	0,1-1
silver	O ₂	0,0001
rhenium	N ₂	<0,01

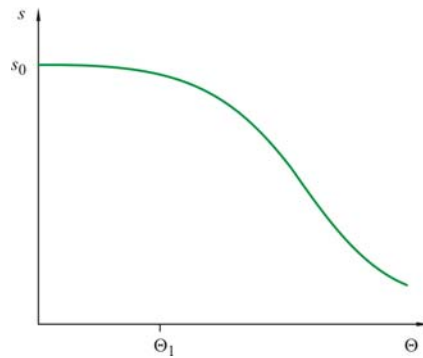


Figure 5.4. *The influence of the surface coverage on the sticking probability at constant temperature.*

The shape of the experimentally determined $s = f(\Theta)$ function very often deviates from the linear expectations (Figure 5.4.). At low coverage (up to ca 50 %) s might be even independent from Θ , as the gas molecules can easily find a free site for landing, at higher coverage however it might take some time.

5.2. Chemisorption

When a chemical bond forms between the adsorbent and the adsorbate the process is called chemisorption. Such process occurs during heterogeneous catalytic processes or in most cases during hydrogen storage.

Earlier (Table 2.1) we already concluded the most characteristic differences between physi- and chemisorption. It was noted however, that the distinction based on the interaction energies is not always straightforward. In case of narrow pores, e.g., the heat developing during the sorption process is comparable, i.e., the strength of the interactions is very similar to the strength of chemical bonds.

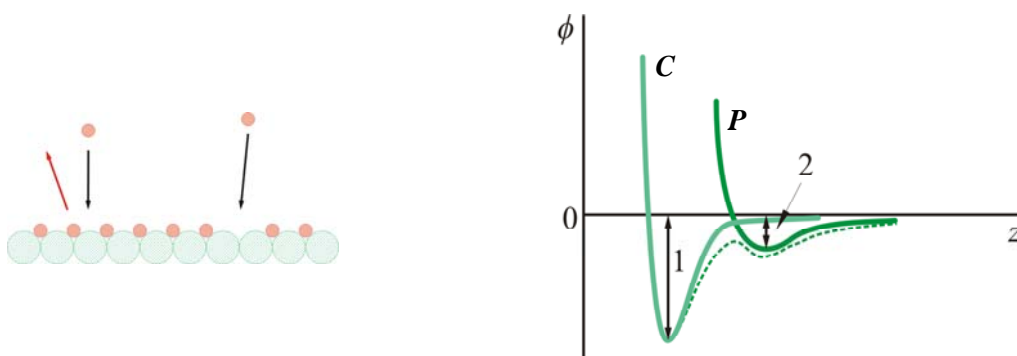


Figure 5.5. *Potential curve of physi- and chemisorption.*

In Figure 5.5. the potential curves of physi- (P) and chemisorption (C) processes are compared. As in most of the cases the chemisorption is preceded by physisorption (precursor state), the real potential curve can be given as the total of the two curves (dotted line in Figure 5.5.). The chemisorption process itself starts at the crossover of the two curves and can be characterized by the potential minimum “1”. This exothermic energy is the enthalpy change ΔH_C of the chemisorption process. Based on the shape of the potential curve in Figure 5.5., there is no activation energy, i.e., $E_a^{act} = 0$. This is a *non-activated chemisorption* process, which occurs when *molecular* gases (oxygen, hydrogen, chlorine) contact a pure carbon surface or ethylene gas interacts with metallic silver. According to the irreversible nature of chemisorption, the desorption process require an activation energy E_d^{act} identical to the heat of chemisorption, i.e., $E_d^{act} = -\Delta H_C$

In most of the cases chemisorption is accompanied with the dissociation of the adsorptive molecule: *dissociative chemisorption* process. A possible situation of the two potential curves is illustrated in Figure 5.6. Arrow “3” symbolizes the dissociation enthalpy ΔH_{diss} of molecule A_2 . For the $H_2 \rightarrow 2H$ dissociation it requires about. 435 kJ/mol.

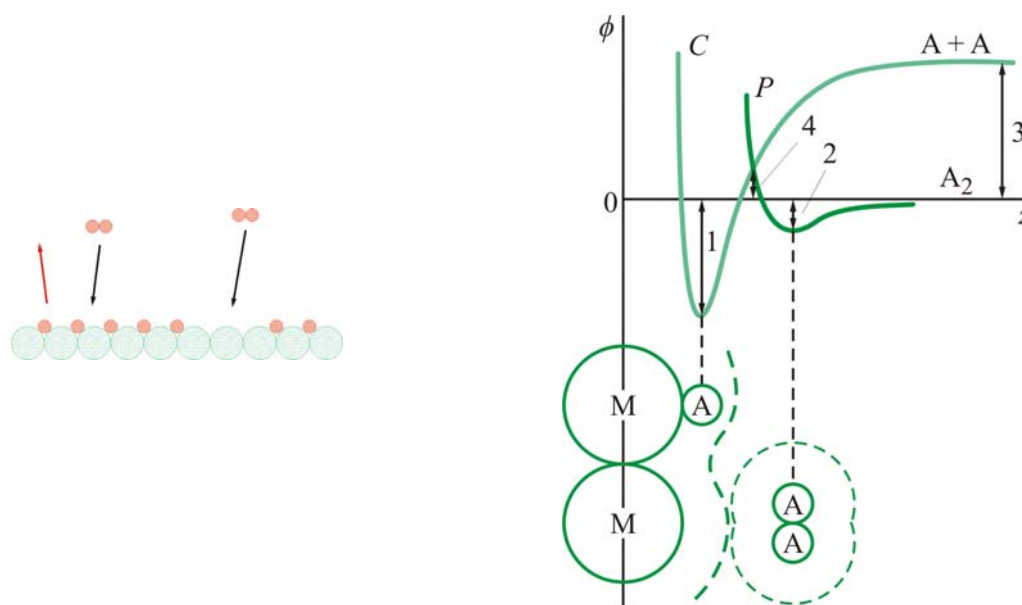


Figure 5.6. Potential curve of physisorption and dissociative .

The relative position of the C and P curves define whether the chemisorption requires activation energy. If the situation is similar to the one shown in Figure 5.6., i.e., the crossover

falls into the positive potential region, the process requires an activation energy of E_a^{act} (arrow “4”): *activated dissociative chemisorption*. For example, the activated dissociative chemisorption of H₂ on copper surface requires an activation energy of 20-40 kJ/mol. Similar process occurs when hydrogen chemisorbs on iron, cobalt or ZnO surfaces. The activation energy of the desorption $E_d^{act} = -\Delta H_C + E_a^{act}$.

If the crossover point is in the negative potential range, *non-activated dissociative chemisorption* happens. In these cases the process has no activation energy, i.e., the process is fast. Therefore, neither the activation energy nor the rate of the process is enough to distinguish physi- from chemisorption.

In surface chemical reaction the time spent on the surface by the adsorbate, the residence time is crucial. Either physi- or chemisorbed molecules require activation energy for their desorption which determines the rate constant of the process

$$k_d = A e^{-\frac{E_d^{act}}{RT}} \quad (110)$$

where E_d^{act} is the activation energy of the desorption. As it was pointed out earlier (Eq. 36), the desorption is a first order process, therefore its half-life is

$$t_{1/2} = \frac{\ln 2}{k_d} = \frac{\ln 2}{A} e^{\frac{E_d^{act}}{RT}} = \tau_0 e^{\frac{E_d^{act}}{RT}}. \quad (111)$$

The $\frac{\ln 2}{A} = \tau_0$ residence time is also influenced by the surface coverage.

5.3. Heterogeneous catalysis

In homogeneous catalytic processes all the participants are in the same physical state. That is the case in enzyme catalysed processes. In heterogeneous catalysis the reactants and the catalyst are in different physical phases, e.g., in solid and fluid or in two immiscible liquid phases. In the most important heterogeneous catalytic reaction the catalyst is in solid phase

and the reactants are either liquids or gases. Table 5.4. lists a couple of well-known heterogeneous catalytic processes of high industrial importance.

Table 5.4. *Industrial scale heterogeneous catalytic processes.*

Process	Reactants	Catalyst	Product(s)
ammonia-synthesis (Haber-Bosch)	N_2+H_2	Al_2O_3 supported iron oxides	NH_3
ethylene-oxide synthesis	$C_2H_4+O_2$	Al_2O_3 supported silver	C_2H_4O
desulphurization of mineral oil	H_2+R_2S	Al_2O_3 supported Mo-Co	$RH + H_2S$
polymerization of olefins (Ziegler-Natta)	propylene	$MgCl_2$ supported $TiCl_3$	polypropylene

An additional process is catalytic cracking in petroleum chemistry to produce fuel. In vehicles also heterogeneous (solid) catalysts are used in order to promote the perfect oxidation of the fuel and thus suppress the emission of CO and NO_x. Enantiomer selective synthesis can be performed with the application of chiral heterogeneous catalysts.

5.3.1. Mechanism of heterogeneous catalysis

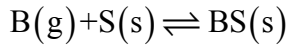
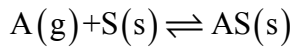
1. Langmuir- Hinshelwood mechanism

It was developed by two British physico-chemists.

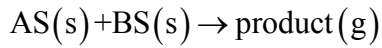


Figure 5.7. *The Langmuir-Hinshelwood mechanism.* (see slides)

Reactants A and B *adsorb independently* on the surface of the S catalyst.



Then they start to *diffuse on the surface*, the chemical reaction occurs when they meet during their migration on the surface. Finally, the product desorbs from the surface:



It is made of the following steps:

- i) adsorption of the reactants
- ii) surface diffusion
- iii) reaction on the surface
- iv) desorption of the product(s)

The rate of the reaction

$$v = k\Theta_A\Theta_B \quad (112)$$

and

$$\Theta_A + \Theta_B + \Theta_{free} = 1 \quad (113)$$

where Θ is the coverage of the species A and B as labelled in the subscript and the ratio of the free, unoccupied sites, k is the reaction rate constant. Based on the Langmuir equation for competitive systems

$$n_i^s = n_{m,i}^s \frac{K_i p_{i,e}}{1 + \sum K_i p_{i,e}} \quad \text{or} \quad \Theta_i = \frac{K_i p_{i,e}}{1 + \sum K_i p_{i,e}} \quad (113b)$$

for reactants A and B

$$\Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad (114)$$

and

$$\Theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (115)$$

K is the equilibrium constant of the adsorption of the corresponding component, p is its partial pressure. Therefore, the rate of the reaction

$$v = \frac{kK_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (116)$$

As both k and K depends on the temperature, the T dependence of the rate is quite complex. It is also not straightforward to determine the reaction order. Below a few extreme cases are discussed.

Both reactants A and B adsorb weakly

Then both $K_A p_A$ and $K_B p_B$ are $\ll 1$, therefore

$$v \approx kK_A p_A K_B p_B \quad (117)$$

i.e., the reactions are of first order for both components.

One of the components adsorbs weakly

If this is the component B, then $K_B p_B \ll 1$, i.e.,

$$v \approx \frac{kK_A p_A K_B p_B}{(1 + K_A p_A)^2}, \quad (118)$$

the reaction is of first order for component B. If the concentration (partial pressure) of A is low, it will be of first order for component A as well. If the relative pressure of A is high,

$$v \approx \frac{kK_B p_B}{K_A p_A} \quad (119)$$

i.e., the reaction order of A is -1. It means that its increasing concentration slows down the reaction, it behaves as an inhibitor.

One of the reactants adsorbs very strongly

If component A exhibit an outstandingly strong adsorption $K_A p_A \gg 1$ and $K_A p_A \gg K_B p_B$, therefor

$$v \approx \frac{k K_B p_B}{K_A p_A} \quad (120)$$

The reaction order of B is 1, and of A is -1, i.e., independently of the concentration of A it always behaves as an inhibitor.

Examples for Langmuir-Hinshelwood mechanism are listed in Table 5.5.

Table 5.5. *Examples for Langmuir-Hinshelwood mechanism.*

Reactants	Catalyst	Product(s)
2 CO + O ₂	platinum	2CO ₂
CO + 2H ₂	ZnO	CH ₃ OH
C ₂ H ₄ + H ₂	copper	C ₂ H ₆
N ₂ O + H ₂	platinum	N ₂ + H ₂ O
C ₂ H ₄ + ½ O ₂	palladium	CH ₃ CHO
CO + OH	platinum	CO ₂ + H ⁺ + e ⁻

2. Eley-Rideal mechanism

It was described first by two British scientists, D. D. Eley and E. K. Rideal. In this case only one of the components is attached to the surface, the other component reacts with the already adsorbed partner.

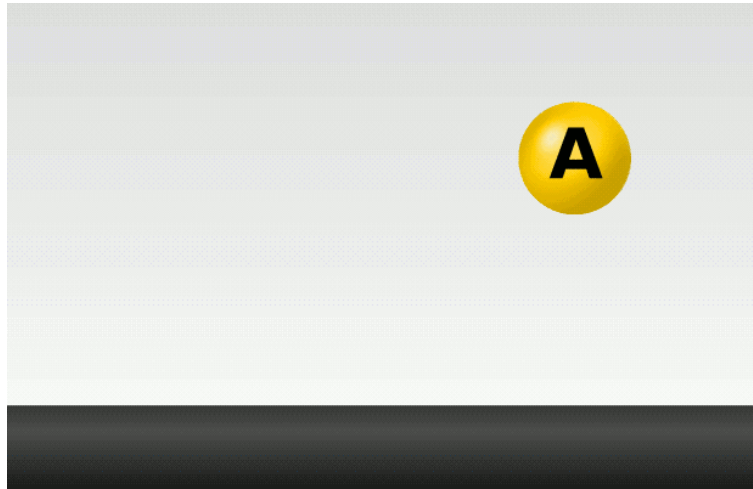
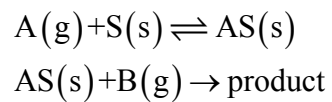


Figure 5.8. *Eley-Rideal mechanism. (see slides)*



The reaction rate is:

$$v = k p_B \Theta_A \quad (121)$$

Using the Langmuir equation to describe the $\Theta = f(p_A)$ function

$$v = \frac{k K_A p_A p_B}{1 + K_A p_A} \quad (122)$$

If the partial pressure of A is low ($K_A p_A \ll 1$) the reaction order of A is 1. If p_A is high

$$v \approx k p_B \quad (123)$$

i.e., the reaction order of A is 0.

Examples for Eley-Rideal mechanism are listed in Table 5.6.

Table 5.6. *Examples for Eley-Rideal mechanism.*

Reactants	Catalyst	Product(s)
$\text{CO}_2 + \text{H}_2(\text{s})$		$\text{H}_2\text{O} + \text{CO}$
$\text{C}_2\text{H}_2 + \text{H}_2(\text{s})$	iron or nickel	C_2H_4
$2 \text{NH}_3 + \frac{1}{2} \text{O}_2(\text{s})$	platinum	$\text{N}_2 + 3 \text{H}_2\text{O}$
$\text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2(\text{s})$		H_2COCH_2

5.4. Suggested references

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