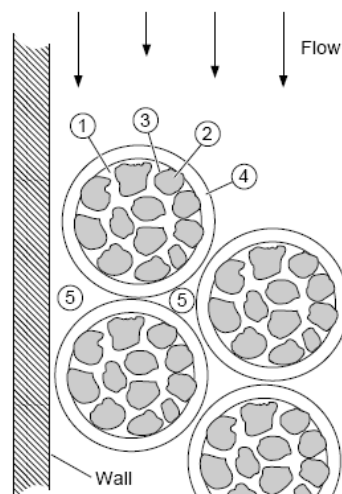


## Dynamics of surface processes

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1

## Transport mechanisms in porous materials

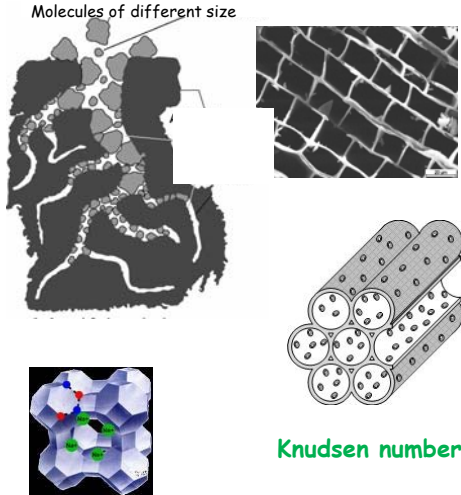


- 1 diffusion in pores
- 2 solid diffusion
- 3 reaction/adsorption at phase boundary
- 4 free transport on the surface
- 5 mixing in the fluid phase

2

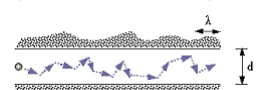
### Mobility within the pores

Molecules of different size



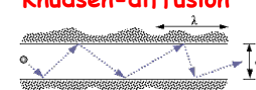
**Knudsen number:**  
 $Kn = \lambda/d$

**Molecular (Fick) diffusion (Brownian motion)**



$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

**Knudsen-diffusion**




$Kn \ll 1$  viscous flow  
 $Kn \gg 1$  Knudsen flow

3

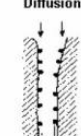
transport type	pore diameter (nm)
viscous flow	> 20
molecular diffusion	> 10
Knudsen diffusion	2-100
micropore (configurational) diffusion	< 1.5

**Activated diffusion (Volmer)**

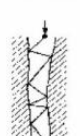
**Solid Diffusion**




**Surface (Volmer) Diffusion**



**Knudsen Diffusion**



**Free (Molecular) Diffusion**



$Q_2 \uparrow \uparrow \text{CH}_4$ 
 $\lambda$ 
 $10^5$  [ÅE]

Porewidth

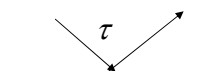
$D: < 10^{-5}$ 
 $< 10^{-3}$ 
 $\sim 10^{-2}$ 
 $0.1 - 1$  [ $\frac{cm^2}{sec}$ ]
 $20^\circ C$

Diffusion	$D, m^2/s$
Fick	$10^{-5} - 10^{-4}$
Knudsen	$10^{-6}$
Volmer	$10^{-7}$

4

## Interactions with the surface

- Difference in the binding energies of the different sites
- Occupied and unoccupied sites  $\rightarrow \Delta c \rightarrow$  diffusion



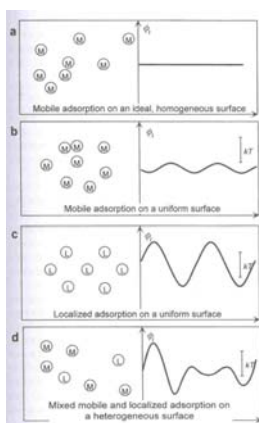
random  
vibration energy  $> E_{ads}$

$$D = D_0 e^{-\frac{E_{diff}}{RT}}$$

Affecting parameters?

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## Mobility on surface (surface diffusion)



Non-localized diffusion  $E^{act} \leq RT$

E.g.:  $H_2$  on metal surface (generally as H)




Localized adsorption  $E^{act} > RT$

Activated diffusion

Low activation energy between high adsorption energy sites

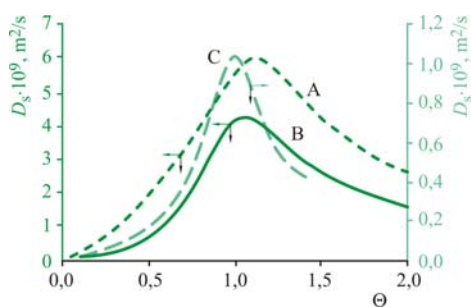
$$E_{ads} = E^{act} \text{ seldom} \quad \text{typically } E^{act} = 0.1 \div 0.8 E_{ads}$$

6

	$E_{ads}$ J/mol
Ar/graphite	
	7315
	7145
	7145
Ar/KCl	
Cl —•— Cl	6646
K	6061
Cl	5308
Cl —•— K	5476

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## Further factors influencing surface mobility



A: argon/silica 89 K  
 B: argon/silica 77 K  
 C: N<sub>2</sub>/amorphous carbon 77 K

Properties of the chemicals  
 Temperature  
 Coverage

Low  $q$   $\theta$ : random walk for time  $\tau$  ideig, 2D gas

$\theta$  increases  $\rightarrow$  liquid like properties

$\sim$ Activation energy follows the adsorption energy

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## CHEMISORPTION

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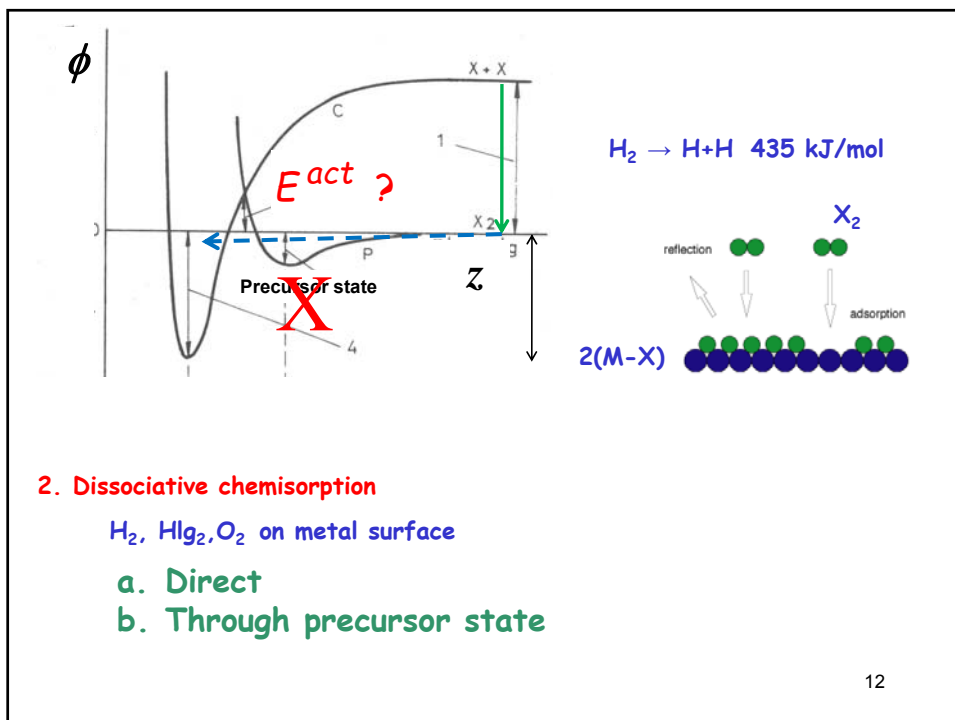
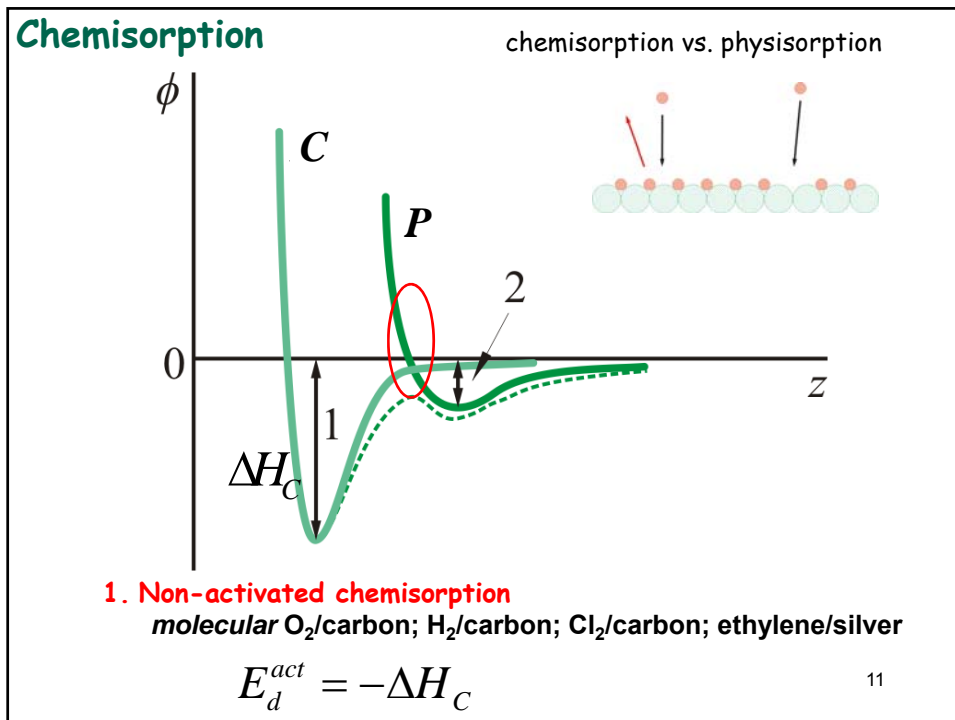
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### Physisorption vs Chemisorption

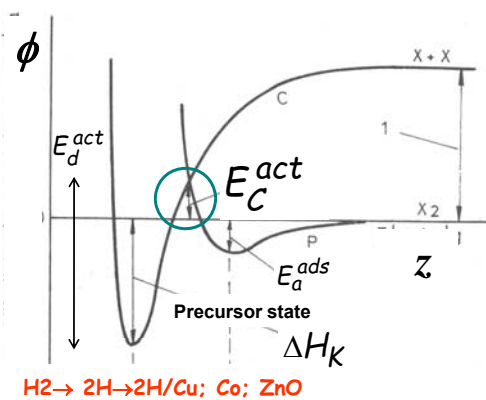
PHYSISORPTION	CHEMISORPTION
WEAK, LONG RANGE BONDING Van der Waals interactions	STRONG, SHORT RANGE BONDING Chemical bonding involved.
NOT SURFACE SPECIFIC Physisorption takes place between all molecules on any surface providing the temperature is low enough.	SURFACE SPECIFIC E.g. Chemisorption of hydrogen takes place on transition metals but not on gold or mercury.
$\Delta H_{\text{ads}} = 5 \dots 50 \text{ kJ mol}^{-1}$	$\Delta H_{\text{ads}} = 50 \dots 500 \text{ kJ mol}^{-1}$
Non activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage.	Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.
No surface reactions.	Surface reactions may take place: Dissociation, reconstruction, catalysis.
MULTILAYER ADSORPTION	MONOLAYER ADSORPTION

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Electron transfer



## b) Through a precursor state



↓  
20-40 kJ/mol

$$E_d^{act} = -\Delta H_C + E_C^{act}$$

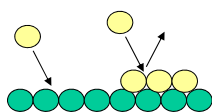
chemi vs physi: rate is not necessarily helps to decide

$$k = A e^{-\frac{E^{act}}{RT}}$$

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## Rate of the surface reactions

number of collisions:  $z$



$$z = \frac{p}{\sqrt{2\pi mkT}}$$

$10^{18} - 10^{19}$  surface atom/ $m^2$

Ambient pressure, 25 °C

$3 \times 10^{27}$  collisions/ $m^2s$

on a single surface site  $\rightarrow \sim 10^8$  collisions/s

$10^{-6}$  torr

$4 \times 10^{18} m^{-2}s^{-1}$

1 collision/s

$V_{ads} = \text{frequency of collisions} \times \text{sticking probability}$

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### Rate of desorption (1st order)

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

Residence time

$$E_d^{act}, \text{kJ/mol} \quad \tau_0 = \frac{\ln 2}{A}, \text{s}$$

0.4	$6 \cdot 10^{-14}$	
4.0	$2.7 \cdot 10^{-13}$	typical
40	$1.6 \cdot 10^{-6}$	
60	$9 \cdot 10^{-3}$	
80	50	
100	$3 \cdot 10^5$	
120	$2 \cdot 10^9$	

$\tau_0 = f(\Theta)$     ~ covered site  
                          ~ lateral interaction with the neighbour<sup>15</sup>