DEPARTMENT OF CHEMICAL ENGINEERING

COURSE NOTES

CHEE310

PHYSICAL CHEMISTRY FOR ENGINEERS

Adsorption

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INSTRUCTOR:

Sasha Omanovic

ADSORPTION

Adsorption – very important in (electro)catalysis, wastewater treatment, separation of proteins, biomaterials, etc.

Gas-solid systems are usually considered in textbooks, which is due to simplicity. However, liquid-solid systems are very frequent and important in various fields.

Definitions:

- *Adsorbent* (substrate) – material on which a molecule is adsorbed
- *Adsorbate* – a molecule (substance) that adsorbs on the adsorbent

Notice: a**d**sorption ≠ a**b**sorption

Classification/types of adsorption:

- *Physical adsorption (physisorption)* – the molecule is held to the substrate by relatively weak intermolecular van der Waals forces
    - Not specific – a number of molecules could be adsorbed on any solid provided the temperature is low enough
- *Chemical adsorption (chemisorption)* – a chemical reaction occurs at the solid's surface, and the molecule is held to the surface by relatively strong chemical bonds
    - Highly specific – *e.g.* N_2 is chemisorbed at room temperature on Fe, W, Ca and Ti, but not on Ni, Ag, Cu, or Pb.
    - The molecule can form a molecular bond with the substrate both without and with dissociation - *non-dissociative* and *dissociative* adsorption.

The criterion used to distinguish between physi- and chemi-sorption is not sharp. The enthalpy of adsorption is usually used as a criterion, but *it applies usually only to gas/solid* systems:

- Physisorption - $-4 > \Delta H_{ads} > -40$ kJ/mol $\rightarrow$ similar to enthalpy of condensation
- Chemisorption - $-40 > \Delta H_{ads} > -800$ kJ/mol $\rightarrow$ similar to enthalpy of bond formation (which is actually the case in chemisorption)

For any process to be spontaneous, $\Delta G < 0$. Hence, since adsorption is a spontaneous process in a specific temperature range, $\Delta G_{ads} < 0$.

We know that : $$\Delta G_{ads} = \Delta H_{ads} - T\,\Delta S_{ads}$$

Lets consider a simple molecule, AB, that adsorbs on a surface from a gas phase:

- If AB does not dissociate one can expect ΔS_{ads} to be negative, since AB is going from a disordered gas phase onto the solid surface on which it is ordered. Consequently, in order for ΔG_{ads} to be negative, ΔH_{ads} has to be negative
- Now, assuming AB dissociates, ΔS_{ads} could be positive if A and B are mobile on the surface (e.g. H_2 on glass). Also, in adsorption from an aqueous solution (e.g. proteins) ΔS_{ads} could be positive due to an increase in entropy of water molecules pre-adsorbed on the surface and subsequently displaced by protein, or due to a loss of water bound to protein.

In *chemisorption* we can expect only one monolayer of the adsorbate to be formed, since no chemical bond could be formed between the 2nd layer and the substrate. However, we can have a situation in which the 1st layer is chemisorbed and the 2nd layer (or several multilayers) is physiosorbed.

In *physisorption* a multilayer structure is possible since no chemical bonds are formed – the interaction between the 1st physiosorbed layer and the 2nd layer is controlled by intermolecular interactions.

ΔH_{ads} for the 1st layer is 'regular' enthalpy of physisorption, while ΔH_{ads} of the 2nd, 3rd, 4th, ….. layers is equal to the enthalpy of condensation of the adsorbate.

If we consider adsorption of a molecule from a gas phase, the formation of the 2nd, 3rd,… layers is possible usually only at temperatures close to the boiling point of the gas. The reason is that at higher temperatures molecules have high kinetic energy that does not allow them to 'calm down' on the surface, *i.e.* to form a 'fixed' (adsorbed) molecular layer.

Examples of chemisorption:

- Hydrogen adsorption (dissociative): $H_2 + 2S \rightarrow 2S\text{-}H_{ads}$
    - This is a very important reaction with applications in hydrogen production, fuel cells, hydrogenation of hydrocarbons, *etc.*
- Carbon monoxide adsorption (non-dissociative): $CO + nS \rightarrow S_n\text{-}CO_{ads}$ (n = 1 or 2)
    - This is also a very important process, but in a negative sense → it causes poisoning of a catalyst's surface. The adsorption bond is very strong and it is hard to remove CO form the surface. The process is very common in low-temperature fuel cells or any low-temperature catalytic process that involves hydrocarbons. At high temperatures it is not a problem to 'de-poison' the surface, and if oxygen is present the kinetics of CO oxidation to CO_2 is very fast at high temperatures, and CO even serves as fuel.

Adsorption isotherms

We are interested to describe the dependence between the equilibrium concentration of a molecule on the surface and in the bulk phase (gas or liquid) - it is the amount of the adsorbate on the surface versus its either partial pressure in the bulk gas phase (solid/gas interface) or concentration in the bulk solution phase (solid/liquid interface).

For this purpose we use *adsorption isotherms*.

If you have 20 marbles you want to arrange on a table of 1×1 m^2 you can do that without any problems. With 100 marbles you occupy more of the table space, and with 1000 marbles you maybe occupy the whole table area, and if you had 2000, 3000,…. marbles you could still put only 1000 of them on the table surface – you achieve some 'saturation' (monolayer) value of marbles on the surface. The same is with molecules (marbles) that adsorb on a solid surface (table). Hence, you can guess that for a monolayer-type adsorption, the isotherm looks like the one in Figure 1 – a saturation surface coverage (plateau) is achieved at higher bulk concentrations (or pressures). This is so-called ***Type I*** isotherm, and is typical for chemisorption and for a monolayer-physisorption.

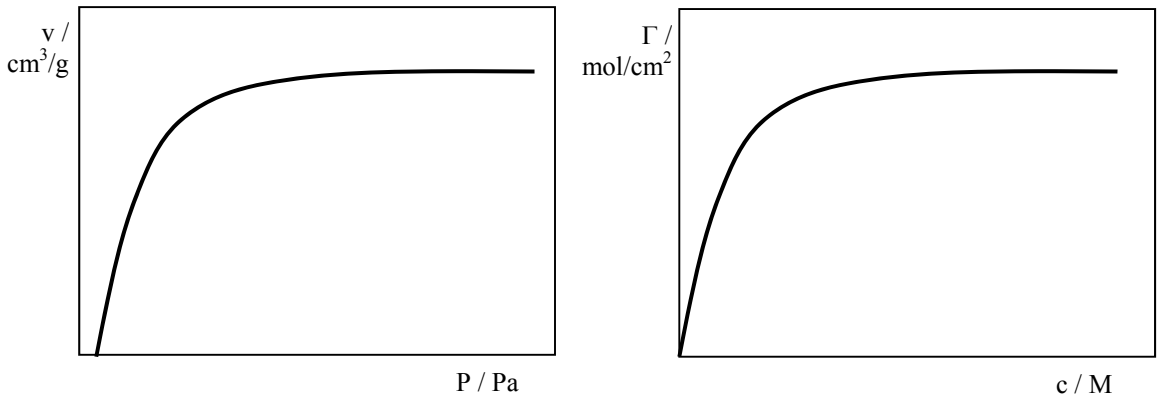

Figure 1 – Type I adsorption isotherms

In case of physisorption, it is possible to see a constant rise in surface concentration, as in Figure 2. This is so-called ***Type II*** isotherm.

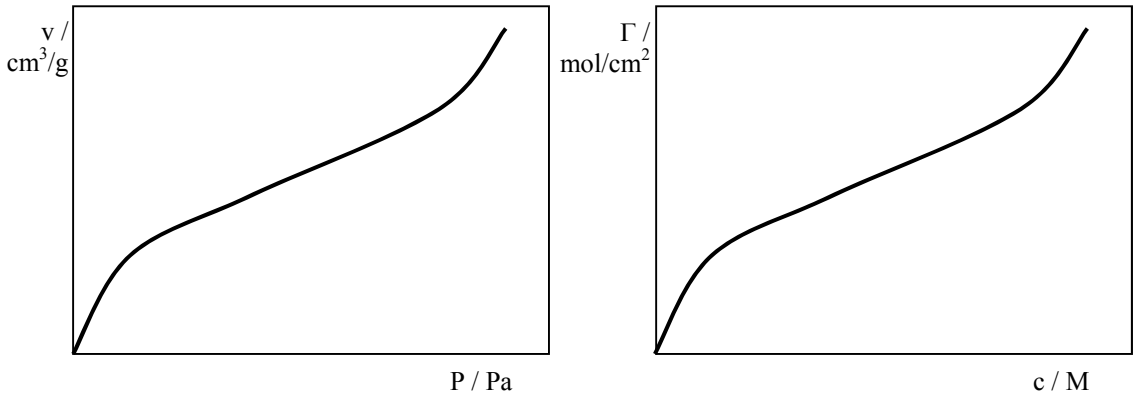

Figure 2 – Type II adsorption isotherms

In the above figures the surface concentration is expressed in terms of volume of gas per gram of surface, or as mols of adsorbate per unit area of the surface (adsorbent). Sometimes the latter is also expressed as mols of adsorbate per gram of adsorbent.

For Type I isotherm it is also convenient to express the surface concentration as *surface coverage* (a fraction of the surface covered by the adsorbate), θ:

$$\theta = \frac{v}{v_{mono}} = \frac{\Gamma}{\Gamma_{mono}}$$

However, in the above expression you have to be careful – the assumption is that the molecule does not change its orientation on the surface. Lets take fibrinogen, a serum rod-like protein with a length-to-width ratio of ca. 7, as an example. At low concentrations in the bulk solution the protein can lay side-on on the surface and in that configuration achieve some Γ_{mono}. However, with a further increase in bulk concentration the protein can tilt on the surface and finally achieve a monolayer converge but with an end-on orientation. Hence, you can see that we had two monolayer points. Sometimes you see this as a regular Type I isotherm, sometimes as a double-step Type I isotherm (Figure 3), but only in a Γ vs. c presentation – the θ vs. c presentation gives almost a regular Type I response since after

reaching the monolayer level in the first orientation, the surface remains completely covered by the layer.

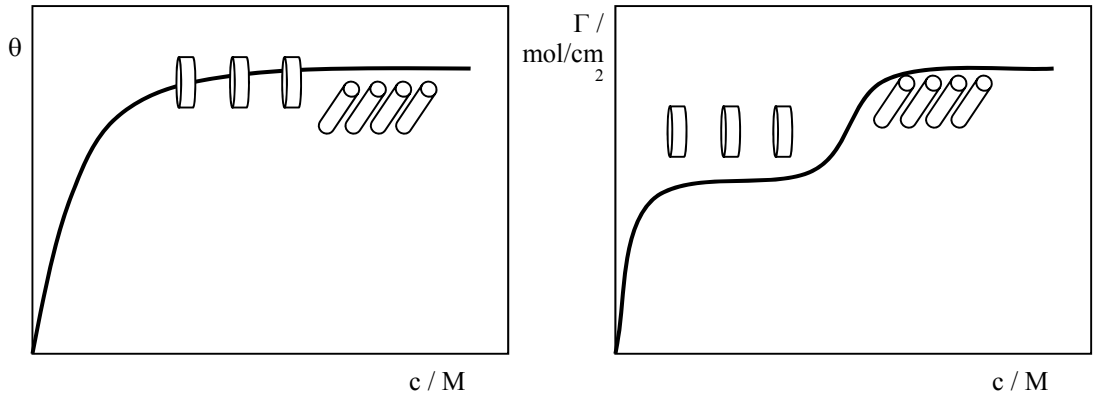

Figure 3 – Type I adsorption isotherm for a case of adsorption with a change in orientation.

It would be interesting now to mathematically describe Type I isotherm, however bearing in mind that certain quantities involved in the description should have their physical meaning.

Lets make some assumptions:

1. the solid has a uniform surface (perfectly flat surface) – all surface sites are equivalent,
2. adsorbed molecules don't' interact with one another on the surface, *i.e.* the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites, and
3. only a monolayer can be formed.

Kinetic approach:

Lets define the kinetics of adsorption of A from a gas phase on a solid surface S in terms of coverage at constant temperature:

$$A + S \leftrightarrow S\text{-}A_{ads}$$

$$\frac{d\theta}{dt} = k_a P N (1-\theta)$$

where k_a is the adsorption constant [$atm^{-1}\ s^{-1}$], N is the total number of surface sites available for adsorption, while $(1-\theta)$ is then the fraction of the surface free of the adsorbate, and P is the partial pressure of the adsorbate [atm]

It is obvious that the rate of change of surface coverage due to adsorption is proportional to the partial pressure of the adsorbate (or concentration in the bulk solution for a gas/liquid system) and the number of surface vacant sites.

Similarly, the rate of desorption is proportional to the number of adsorbed molecules:

$$\frac{d\theta}{dt} = -k_d N \theta$$

where k_d is the desorption constant [s^{-1}].

At equilibrium the rate of adsorption is the same as the rate of desorption, and by equating the above two equations and solving for θ we get:

$$\theta = \frac{BP}{1+BP}$$

where $B = k_a / k_d$ [atm^{-1}] is the *adsorption affinity constant* and is temperature dependant.

For adsorption of A from a liquid phase, we obtain:

$$\theta = \frac{Bc}{1+Bc}$$

where c is the concentration of adsorbate A [mol dm^{-3} = M], and $B = k_a / k_d$ [M^{-1}] is again the adsorption affinity constant.

This is so-called ***Langmuir isotherm***. However, note that the isotherm is based on a number of assumptions made by Langmuir (and listed above), and thus is not always suitable for real applications. However, the isotherm is found to work reasonably well for many cases of chemisorption.

Thermodynamic approach:

Again taking the previously outlined assumptions, we can say that the thermodynamic equilibrium will be established if the chemical potential of the adsorbate in the bulk phase (A) is equal to the chemical potential of the adsorbate on the surface (SA):

$$\mu_A = \mu_{SA}$$

We know that the chemical potential of the adsorbate in the bulk gas (or solution) is:

$$\mu_A = \mu_A^o + RT \ln \frac{P}{P^o}$$

where μ_A^o is the standard chemical potential of the adsorbate, P is the partial pressure of the adsorbate [atm], and P^o is the standard pressure [1atm].

or in the bulk liquid:

$$\mu_A = \mu_A^o + RT \ln \frac{c_A}{c_{solvent}}$$

where c_A is the concentration of the adsorbate [M], and $c_{solvent}$ is the concentration of the solvent (*e.g.* for water it is 55.5 M).

Similarly, the chemical potential of the adsorbate on the surface is:

$$\mu_{SA} = \mu_{SA}^o + RT \ln \frac{\theta}{1-\theta}$$

Taking into account that at equilibrium $\mu_A = \mu_{SA}$, we can further write:

$$\frac{\theta}{1-\theta} = \frac{P}{P^o} \exp\left[-\frac{\mu_{SA}^o - \mu_A^o}{RT} \right]$$

You learned with Prof. Cooper that the difference in chemical potentials of a species could be equated to a difference in Gibbs energy. Hence:

$$\Delta G^o_{ads} = \mu^o_{SA} - \mu^o_A$$

$$\frac{\theta}{1-\theta} = \frac{P}{P^o}\exp\left[-\frac{\Delta G^o_{ads}}{RT}\right]$$

We can do some substitution:

$$B = \frac{1}{P^o}\exp\left[-\frac{\Delta G^o_{ads}}{RT}\right]$$

or for the liquid/solid system:

$$B = \frac{1}{c_{solvent}}\exp\left[-\frac{\Delta G^o_{ads}}{RT}\right]$$

where $c_{solvent}$ is the concentration of the solvent (for water it is 55.5 mol/dm^3). This 'correction' factor is needed due to the energy required to de-solvate (dehydrate) solvated adsorbate molecules. In addition, in the derivation of the Langmuir isotherm, the chemical potential equation is:

Finally, we can write:

$$\theta = \frac{BP}{1+BP}$$

which is again the ***Langmuir isotherm***.

For the adsorption of *A* from the solution phase we can write that:

$$\theta = \frac{Bc}{1+Bc}$$

Further, instead of using surface coverage, we can use *surface concentration*, Γ, and knowing that $\theta = \Gamma / \Gamma_{mono}$ we can write:

$$\Gamma = \frac{\Gamma_{mono} Bc}{1+Bc}$$

Figure 4 shows a set of Langmuir isotherms at various *B* values.

Note that the adsorption affinity constant *B* is related to the Gibbs energy of adsorption and temperature. Therefore, by fitting experimental data using the Langmuir isotherm one can easily calculate a value of Gibbs energy of adsorption at various temperature and then to calculate both the enthalpy and entropy of adsorption knowing that:

$$\Delta G_{ads} = \Delta H_{ads} - T\,\Delta S_{ads}$$

Then by comparing ΔH_{ads} and $T\,\Delta S_{ads}$ it is possible to conclude which of the two quantities controls the adsorption, *i.e.* which one represents the driving force for adsorption.

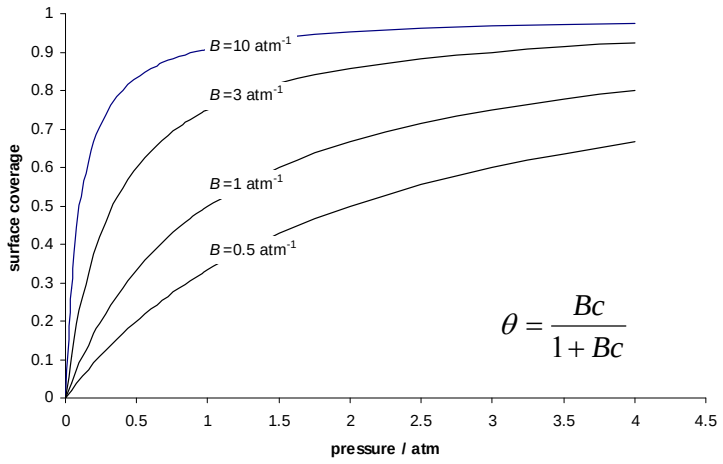

Figure 4 – Langmuir isotherms of fractional surface coverage versus gas pressure for several values of the adsorption affinity constant.

Consequences:

- at low bulk partial pressures of A (or low solution concentrations) the product BP (or Bc) $\rightarrow 0$ and then we can write:

$$\theta \approx BP$$

  which means that the coverage increases linearly with concentration (or concentration)

- at high bulk partial pressures of A (or high solution concentration) $\theta \rightarrow 1$, or $\Gamma \rightarrow \Gamma_{mono}$.

In order to test whether a given set of adsorption data can be described by the Langmuir isotherm the most convenient way is to linearize the isotherm:

$$\frac{c}{\Gamma} = \frac{1}{B\Gamma_{mono}} + \frac{c}{\Gamma_{mono}}$$

and if a plot of c/Γ versus c gives a straight line then the system obeys the Langmuir isotherm, and from the slope of the line Γ_{mono} is calculated and from the intercept of the line B is calculated, and then ΔG_{ads}.

Alternatively, we can also write that:

$$\frac{\theta}{1-\theta} = Bc$$

and if the dependence of $\theta/(1-\theta)$ versus c is linear, the Langmuir isotherm describes the adsorption. From the slope of the dependence B can be calculated and then ΔG_{ads}.

Also, we can further modify the isotherm and write:

$$\frac{c}{\theta} = \frac{1}{B} + c$$

and if the dependence is linear from B is obtained from the intercept.

In the previous considerations only one type of molecule was adsorbed. However, if we have two different molecules (A and B) that adsorb on the same surface, then we can write:

$$\theta_A = \frac{B_A P_A}{1 + B_A P_A + B_B P_B} \qquad \text{or} \qquad \frac{\Gamma}{\Gamma_{mono}} = \frac{B_A P_A + B_B P_B}{1 + B_A P_A + B_B P_B}$$

where θ_A is the fraction of adsorption sites occupied by A molecules.\

On the other hand if we have a dissociative-type of adsorption:

$$A_2 + 2S \leftrightarrow 2S\text{-}A_{ads}$$

then we can write:

$$\frac{d\theta}{dt} = k_a P\left[N(1-\theta)\right]^2$$

Similarly, the rate of desorption is proportional to the number of adsorbed molecules:

$$\frac{d\theta}{dt} = -k_d\left(N\theta\right)^2$$

At equilibrium the rate of adsorption is the same as the rate of desorption, and by equating the above two equations and solving for θ we get:

$$\theta = \frac{B^{1/2}P^{1/2}}{1 + B^{1/2}P^{1/2}}$$

As already mentioned, the four assumption made by Langmuir are not very often valid in real cases, and a number of other isotherms have been proposed. One of them is the empirical ***Freundlich isotherm*:**

$$\Gamma = B' P^a \quad \text{or} \quad \Gamma = B' c^a$$

where B' and a are the Freundlich adsorption constants (with $0 < a < 1$).

The experimental data is usually verified by:

$$\log(\Gamma) = \log(B') + a\log(c)$$

which should give a straight line when $\log(\Gamma)$ versus $\log(c)$ is plotted if the Freundlich isotherm is valid.

The Freundlich isotherm can be derived by modifying the Langmuir assumptions to allow for several kinds of adsorption sites on the surface, each kind having a different heat of adsorption.

The Freundlich isotherm is not valid at high pressures, but is frequently more accurate than the Langmuir isotherm at low pressures.

The Freundlich equation is often applied to adsorption of solutes from liquid solutions onto solids.

It is worth to note that the Langmuir and Frequndlich isotherms apply to Type I isotherms only, and cannot be applied for a multilayer adsorption. However, in 1938, Brunauer, Emmett and Teller

modified Langmuir's assumptions to give an isotherm for multilayer physical adsorption (Type II). The final equation (***BET isotherm***) is:

$$\frac{\mathrm{v}}{\mathrm{v}_{mono}} = \frac{\Gamma}{\Gamma_{mono}} = \frac{n}{n_{mono}} = \frac{kz}{(1-z)\left[1-(1-k)z\right]} \qquad \text{where } z = P/P^*$$

where v is the volume of the adsorbate per mass of adsorbent [cm^3/g], n is the number of mols of adsorbate per mass of adsorbent [mol/g] and Γ has been defined previously, k is a constant at fixed T, and P^* is the vapor pressure of the adsorbate at the temperature of the experiment.

For $P \geq P^*$ the gas condenses to a liquid.

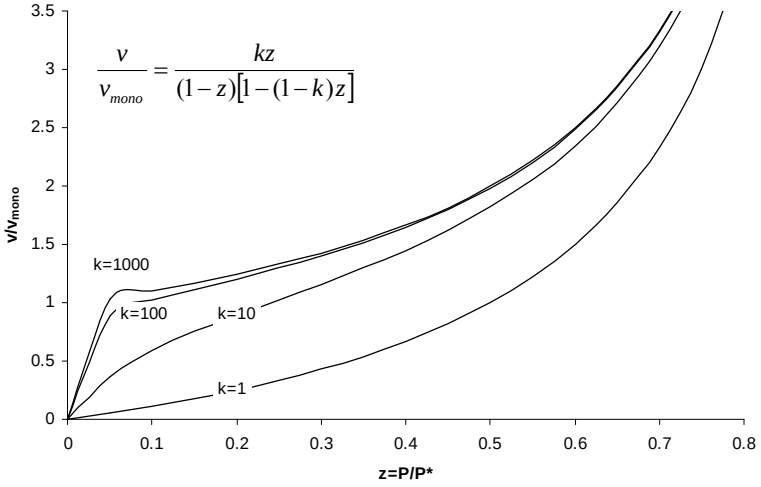

Figure 5 – BET isotherms for different values of k. Note that the v/v_{mono} rises indefinitely because the adsorbate may condense on the covered substrate surface.

If we linearize the isotherm we get:

$$\frac{P}{\mathrm{v}(P^*-P)} = \frac{1}{\mathrm{v}_{\mathrm{mono}}k} + \frac{k-1}{\mathrm{v}_{\mathrm{mono}}k}\frac{P}{P^*}$$

and the constants k and v_{mono} (or n_{mono} or Γ_{mono}) can be obtained from the slope and intercept of a plot of:

$$P/\mathrm{v}\,(P^*\text{-}P) \text{ versus } P/P^*$$

The information on v_{mono} is very important since it could be used to measure the surface area of porous (high-surface-area) surfaces (of course, the surface area occupied by unit molecule has to be known). Usually N_2 is used and then we can say that the surface area of the substrate per its weight is:

$$\overline{A} = \frac{N_A n_{mono}\sigma}{m}$$

where N_A is the Avogadro number, σ is the surface area occupied by N_2 (15.8 A^2) and m is the mass of the sample

This isotherm is commonly used for this purpose in industry and research labs (we also have an instrument for these measurements in Prof. Berk's lab).

The BET isotherm fits many Type II isotherms well, especially at moderate pressures or coverages between 0.8 and 2 and fails at low and high coverages.

Catalytic activity of surfaces

As you know, without the use of catalysts various production processes would not exist today. The purpose of catalysts is to increase the reaction rate, without disturbing the final equilibrium. Catalysis is divided in *heterogeneous* and *homogeneous* (and there is also enzymatic catalysis, which you covered with Prof. Leclerc).

Since we are discussing adsorption in this chapter, we are thus interested in the *heterogeneous* catalysis. As the word *heterogeneous* implies there are two phases involved in the reaction, and we are now interested in the solid/gas and solid/liquid systems.

An advantage of heterogeneous catalysis over homogeneous is that the separation step is much simpler. However, since one of the reaction steps involves adsorption onto a solid surface, you can guess that one of the disadvantages of heterogeneous catalysis is due to the limitation related to the surface area available for the reaction.

In the majority cases of heterogeneous catalysis the adsorption is actually *chemisorption*.

A reactant can dissociate spontaneously on the catalyst's surface, which thus lowers the reaction activation energy. Then, the adsorbed intermediate can react with another reactant that's diffusing towards the reaction site (catalyst's surface) from the bulk gas/solution which then either reacts with the adsorbed intermediate directly, or first gets adsorbed and reacts with the neighboring adsorbed intermediate:

Overall reaction: $A + B \rightarrow P$

Mechanism I - Eley-Rideal	Mechanism II – Langmuir-Hinshelwood
$A + S \leftrightarrow S\text{-}A_{ads}$	$A + S \leftrightarrow S\text{-}A_{ads}$
$S\text{-}A_{ads} + B \rightarrow P$	$B + S \leftrightarrow S\text{-}B_{ads}$
	$S\text{-}A_{ads} + S\text{-}B_{ads} \rightarrow P + 2S$

Let's derive kinetic expressions for both mechanisms assuming the adsorption obeys the Langmuir adsorption law:

Mechanism I (Eley-Rideal mechanism): The kinetic equation for this mechanism is:

$$\frac{dc_P}{dt} = k_2 c_B \theta_A$$

and taking into account that Step 1 can be described using the Langmuir isotherm:

$$\theta_A = \frac{Bc_A}{1 + Bc_A}$$

we can write:

$$\frac{dc_P}{dt} = k_2 \frac{Bc_A}{1 + Bc_A} c_B$$

Now, assuming that concentration of B does not change, i.e. B is in large excess, the relation reduces to:

$$\frac{dc_P}{dt} = k' \frac{Bc_A}{1 + Bc_A}$$

Note that $k' = k_2 c_B$

Consequences:

- At low *A* concentrations the rate becomes:

$$\frac{dc_P}{dt} = k' B c_A$$

and the reaction is of first order with respect to A.

- At high *A* concentrations the rate becomes:

$$\frac{dc_P}{dt} = k'$$

and the reaction is of zeroth order with respect to A, since the coverage of the surface with A is one.

Many heterogeneous reactions are first-order, which indicates that the *rds* is the adsorption process.

However, if concentration of B changes, then we have to write:

$$\frac{dc_P}{dt} = k_2 \frac{Bc_A}{1 + Bc_A} c_B$$

Consequences:

- At high *A* concentrations the surface is completely covered by A, and the rate becomes:

$$\frac{dc_P}{dt} = k_2 c_B$$

and the reaction is of first order with respect to B and zeroth with respect to A. In this case the *rds* is the collision of B with the adsorbed A.

- At low *A* concentrations the rate becomes:

$$\frac{dc_P}{dt} = k_2 B c_A c_B$$

and the extent of surface coverage is rate-determining.

Mechanism II (Langmuir-Hinshelwood mechanism): Assuming both A and B follows the Langmuir adsorption, the kinetic equation for this mechanism is:

$$\frac{dc_P}{dt} = k\theta_A\theta_B$$

$$\frac{dc_P}{dt} = k\frac{B_A c_A B_B c_B}{\left(1 + B_A c_A + B_B c_B\right)^2}$$

In low temperature fuel-cells that run either on reformed hydrogen or direct methanol adsorption of CO on the catalyst surface represents the major problem which decreases the power density of the cell. That's one of the reasons we still cannot see fuel-cell-powered cars on streets. The reaction is:

$$Pt + CO \rightarrow Pt\text{-}CO_{ads}$$

The Pt-CO bond is extremely strong and it is not quite easy to remove CO from the catalyst's surface. In order to remove CO it has to be oxidized to CO_2, which then goes into the atmosphere. In order to oxidize CO we need oxygen, and this oxygen comes from water present in the fuel cell. Namely, oxygen from water gets adsorbed on the free Pt catalyst site, in the neighborhood of the adsorbed CO:

$$Pt + H_2O \rightarrow Pt\text{-}O_{ads} + 2H^+ + 2e^-$$

Then the two neighboring molecules react together:

$$Pt\text{-}O_{ads} + Pt\text{-}CO_{ads} \rightarrow 2Pt + CO_2$$

You can see that this reactions follows Mechanism II, *i.e.* the Langmuir-Hinhselwood mechanism.

Almost all thermal surface-catalyzed reactions are thought to take place by the LH mechanism, but a number of reactions with an ER mechanism have also been identified from molecular beam investigations.