

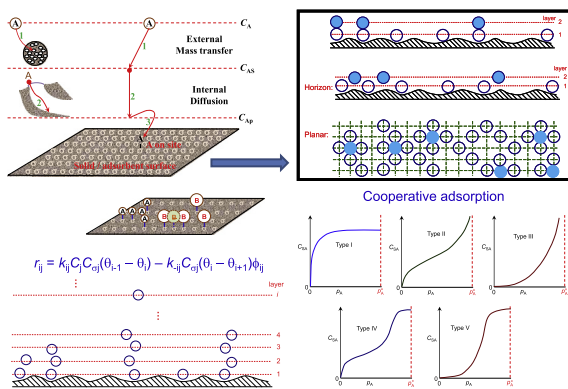
# Cooperative adsorption on solid surfaces



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Adsorptions are commonly of monolayer coverage of adsorbate molecules on adsorbent sites, in particular for chemisorptions, where Langmuir adsorption isotherm equation and kinetics are adequate. The Langmuir adsorption is termed ideal adsorption as the surface active centers are uniformly distributed, the molecules are of point-sizes and the interactions between adsorbate molecules and the adsorbent are uniform. However, there are more cases where Langmuir adsorption isotherm and/or kinetics are inadequate in describing the adsorption behavior. Apparent multilayer adsorption has been shown to be descriptive of both physisorptions and chemisorptions as a means of idealization to nonideal adsorptions. The deviation of adsorption isotherm and/or kinetics from (ideal) Langmuir adsorption is due to cooperative adsorption, or interactions between adsorbates or between adsorbate and adsorbent caused deviation from “uniform” interactions. The multi-layer or apparent multilayer behavior of adsorption is an excellent model to describe cooperative adsorption. Adsorption kinetics and isotherms have been derived for adsorptions without differentiating the different types of adsorptions. The simplistic approach can explain majority of the adsorption isotherms and kinetic behaviors.

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## 1. Introduction

Adsorption is the phenomenon of solute(s) in a bulk fluid phase attaching onto an interface or surface. Adsorption can be classified as gas adsorption and liquid adsorption based on the initial state of

solute(s). The solute participating in the adsorption process is also called adsorbate and the material that provides the surface is called the adsorbent. The adsorbed molecules are restricted on the interface and thus lost their mobility akin to fluid. While adsorption can occur on liquid–liquid interfaces, adsorption is commonly known to occur on solid surfaces. Adsorption on solid surfaces is widely applied in separation, clarification and purification of matter. In [1] a mathematical model was derived based on

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multilayer approximation for adsorption of single species, which was extended to multiple species competitive adsorption in [2].

To illustrate the adsorption process for quantitative description, Fig. 1 exemplifies the steps in adsorption [3]. Adsorbate molecule  $A$  in the bulk fluid phase diffuses (through the solvent or mixture) to the external surfaces of the solid matrices (1), next diffuses through the internal pores of the solid matrix, reaching the “active center”  $\sigma$  on the solid material (2), becoming attached or “fixed” on the solid material (3). The action of a free adsorbate molecule  $A$  in the fluid phase becomes “fixed” on the solid surface is known as adsorption. The kinetics of adsorption is thus controlled by both mass transport (of adsorbate to the active center) and the “attachment” (adsorption).

Clearly, steps (1) and (2) are mass transfer steps. This implies that mass transfer can be important in adsorption processes. The rates (or volumetric fluxes) of mass transfer are given by

$$N_{AE} = k_c(C_A - C_{AS}) \quad (1)$$

$$N_{AI} = k_p(C_{AS} - C_{Ap}) \quad (2)$$

where  $N_A$ 's are volumetric based transfer flux (or rate) of species  $A$  from the bulk fluid phase (with a concentration of  $C_A$ ) to the solid external surface (where concentration  $A$  in the fluid phase is  $C_{AS}$ ) and to the “end” of the internal pore (where the concentration of  $A$  in the fluid phase is  $C_{Ap}$ ), at which the molecule is fixed or adsorbed on the surface.

The pore permeation or transfer is through a net-work of internal pores of the solid matrix. The pores are of distributed length/depth, and diameter. Thus, pore permeability or internal mass transfer rate constant  $k_p$  can appear to be a function of time due to the adsorption occurring first on sites where adsorbate is accessed first. In [1], the pore mass transfer or permeation coefficient is given by

$$k_p = k_{p0} \frac{C_{A0} - C_{Ae}}{C_{A0} - C_A} \quad (3)$$

where  $k_{p0}$  is constant and  $C_{Ae}$  is the concentration of species  $A$  in the fluid phase at the adsorption equilibrium or infinite residence time. One can show that Eq. (3) is consistent with the Weber–Morris model (of intraparticle diffusion limited adsorption) and the exact solution of adsorption to an isolated sphere with negligible external mass transfer by [4] at short-times.

Step (3) exemplifies the approaching of adsorbate molecule ( $A$ ) to the active center in the solid material. Each active center  $\sigma$  can attract and attach one adsorbate molecule. The reverse or desorption occurs in the reverse order.

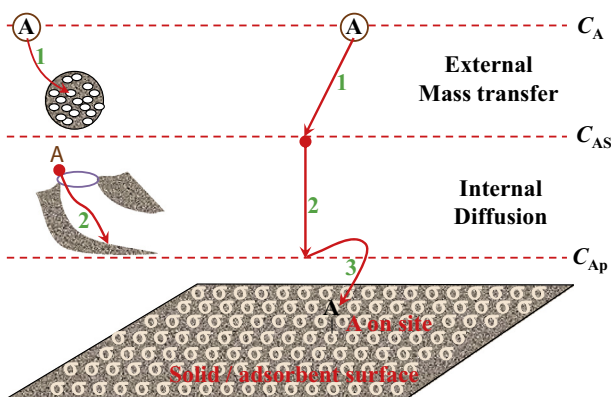


Fig. 1. Typical steps of adsorption involving one species ( $A$ ) in the bulk fluid phase and one active site ( $\sigma$ ) group in the solid material.

It becomes clear that the last step, step (3), is the key step intrinsic to adsorption. Often, when we speak of adsorption kinetics, we mean the kinetics of step (3). It is most convenient to consider the adsorption as chemical reaction or surface reaction. That is,



As Eq. (4) indicates, the adsorption is reversible. The reverse of adsorption is desorption. It is the nature of reversibility that made adsorption an effective separation technique for liquids and gases.

The Gibbs free energy for the adsorption process is given by

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where  $\Delta H$  is the enthalpy change due to adsorption of the molecule on the solid surface or heat of adsorption,  $\Delta S$  is the entropy change from the bulk phase (more random) to the adsorbed phase (more orderly),  $T$  is the temperature, and  $\Delta G$  is the Gibbs free energy change due to adsorption. For the adsorption to occur,  $\Delta G < 0$ , therefore,  $\Delta H = \Delta G + T\Delta S < 0$  or the adsorption is exothermic. This condition holds because  $\Delta S < 0$  for the adsorption process if the adsorption does not involve the breaking apart of the adsorbate molecule, as opposes to that in dissociative adsorption. The decrease in entropy is because of the change from a disorderly state (in fluid phase) to an orderly state (“fixed” on the interface). For dissociative adsorption, the heat of adsorption can be endothermic as the entropy change is positive when a molecule is breaking into two parts.

The kinetics of adsorption follows naturally with the collision theory. Consider the rate at which adsorbate  $A$  molecules in a homogeneous gas (or liquid) phase will strike a solid surface, the collision frequency is given by

$$Z_{ct}(A, \text{surface}) = N_{AV} C_A \sqrt{\frac{RT}{2\pi M_A}} \quad (6)$$

which for gas adsorption is equivalent to

$$Z_{ct}(A, \text{surface}) = \frac{N_{AV} P_A}{\sqrt{2\pi M_A RT}} \quad (7)$$

Only after the adsorbate molecule strikes the surface, it could produce adsorption. The rate of adsorption is thus a fraction of the collision frequency. Therefore, adsorption rate can be considered either in concentrations for liquid and gas adsorptions or in partial pressures for gas adsorption.

Based on Eq. (6), the adsorption as represented by Eq. (4) can be regarded as elementary reaction. The net rate of this adsorption is given by

$$r = k_{ad} C_A C_{\sigma v} - k_{des} C_{\sigma A} \quad (8)$$

or

$$r = k_A C_A \theta C_{\sigma} - k_{-A} \theta_A C_{\sigma} \quad (9)$$

where  $k_{ad} = k_A$  is the adsorption rate constant,  $C_A$  is the concentration of the adsorbate in the bulk fluid phase (near the adsorbent surface, which should be  $C_{Ap}$  in Fig. 1),  $C_{\sigma v}$  is the surface concentration of vacant active centers,  $C_{\sigma A}$  is the surface concentration of the active centers that are occupied by the adsorbate molecule  $A$ ,  $\theta$  is the fraction of the vacant active centers,  $C_{\sigma}$  is the surface concentration of the total possible available positions or sites or active centers where  $A$  can be adsorbed,  $\theta_A$  is the fraction of the total possible available positions that are occupied by  $A$ . Clearly,

$$\theta = \frac{C_{\sigma v}}{C_{\sigma}} \quad (10)$$

$$\theta_A = \frac{C_{\sigma A}}{C_{\sigma}} \quad (11)$$

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