

Lecture

Chem484/673

Kinetic Derivation

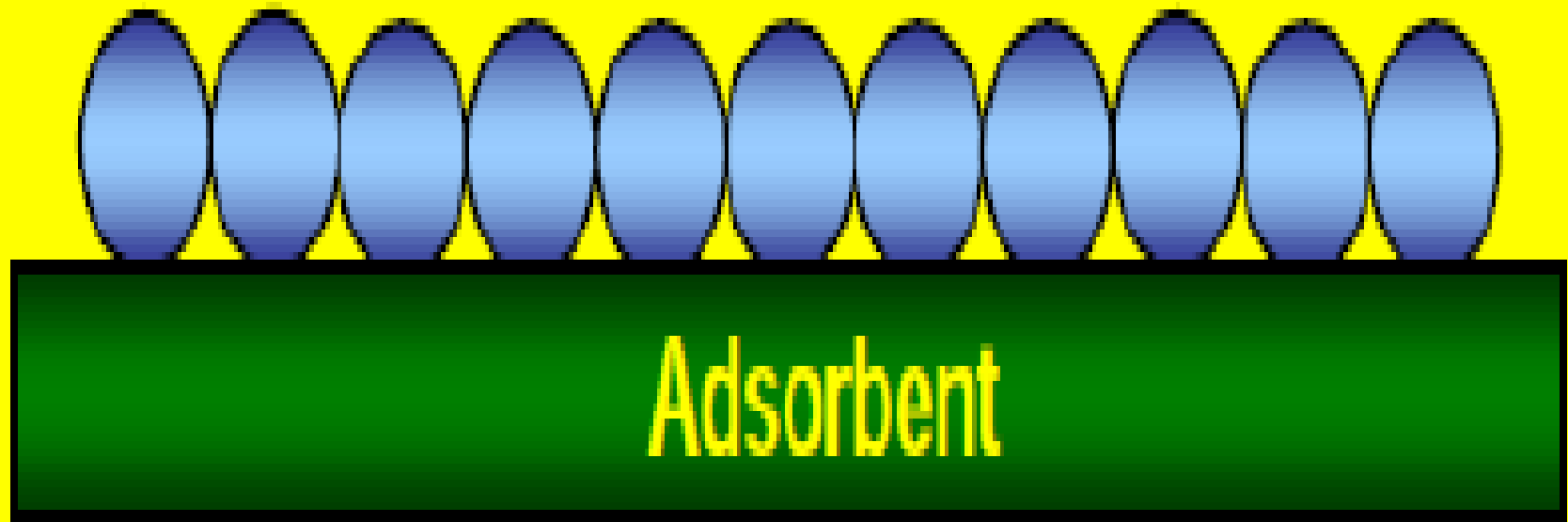


Fig. 1.9. Monolayer model of Langmuir adsorption.

Instead of the surface concentration c^s or the total adsorbed amount a the fractional coverage of a surface defined by the quantity θ (**the surface coverage**) is often used.

surface coverage θ

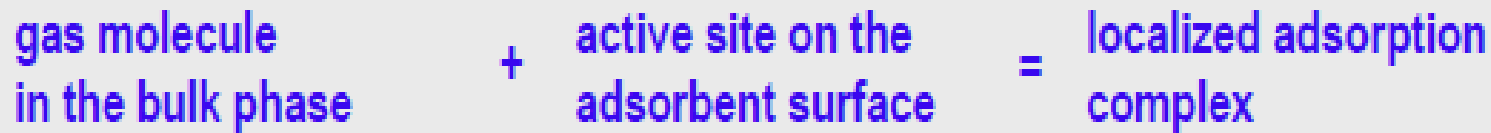
The number of adsorbed molecules on a surface divided by the number of molecules in a filled monolayer on that surface:

$$\theta = \frac{\text{number of occupied adsorption sites}}{\text{total number of possible sites}}$$

$$\theta = \frac{c^s}{c_m^s} = \frac{a}{a_m} = \frac{a^s}{a_m^s} \quad (12)$$

where , c_m^s , a_m and a_m^s are the quantities corresponding to the complete coverage of the adsorbent surface by the filled monolayer of the adsorbate.

The adsorption equilibrium at $p, T = \text{const}$ is expressed as follows:



The isotherm was formulated on the basis of a dynamic equilibrium between the adsorbed phase and the gas or vapour phase.

Kinetic derivation

Equilibrium represents a state in which the rate of adsorption of molecules onto the surface is exactly counterbalanced by the rate of desorption of molecules back into the gas phase, i.e. when the rate of adsorption equals the rate of desorption, **dynamic equilibrium** occurs.

The rate of adsorption depends on:

1. the change of surface coverage due to adsorption which is proportional to the pressure p ,
2. the collision probability with a free active site:

$$1 - \frac{a^s}{a_m^s}$$

where a^s is the concentration of **the occupied active sites** on the surface, i.e. the surface concentration of the adsorbate, a_m^s is the surface concentration at the monolayer coverage of the adsorbate.

3. the activation energy of an adsorption $\exp(-E/RT)$

The rate of desorption depends on:

1. fractional coverage of the surface $\frac{a^s}{a_m^s}$
2. the activation energy of a desorption $\exp(-E'/RT)$

At equilibrium the adsorption rate certainly equals the desorption rate:

$$p \left(1 - \frac{a^s}{a_m^s} \right) \exp \left(-\frac{E}{RT} \right) = k' \left(\frac{a^s}{a_m^s} \right) \exp \left(-\frac{E'}{RT} \right) \quad (1)$$

where k' is the proportional coefficient.

Hence

$$p = k' \exp \left(\frac{\Delta H_{\text{ads}}}{RT} \right) \frac{\frac{a^s}{a_m^s}}{1 - \frac{a^s}{a_m^s}} \quad (2)$$

where $\Delta H_{\text{ads}} = E - E'$ is the heat of adsorption (-).

If we assume that the heat of adsorption does not depend on the surface coverage we can write:

$$k' \exp \frac{\Delta H_{\text{ads}}}{RT} = \frac{1}{k} \quad (3)$$

where k is the constant depending on the temperature.

$$k = \frac{1}{p} \frac{a^s}{a_m^s} \frac{a_m^s}{(a_m^s - a^s)} \Rightarrow k = \frac{a^s}{p(a_m^s - a^s)} \quad (4)$$

From the definition it results that

$$a^s + a_o^s = a_m^s \quad (5)$$

or

$$\theta + \theta_o = 1 \quad (6)$$

where

$$\theta_o = \frac{a_o^s}{a_m^s} \text{ is the fraction of the surface with free active sites} \quad \theta = \frac{a^s}{a_m^s} \Rightarrow a^s = \theta \cdot a_m^s$$

Taking into account the surface coverage we obtain:

$$k = \frac{\theta}{p(1-\theta)} \quad \text{i.e.} \quad \theta = kp(1-\theta) \quad (7)$$

Transforming equation (7) for θ the following relationship is obtained:

$$\theta = \frac{kp}{1+kp} \quad \text{i.e.} \quad \theta = kp(1-\theta) \quad (8)$$

$$a^s = \frac{a_m^s kp}{1+kp} \quad (9)$$

$$a = \frac{a_m kp}{1+kp} \quad (10)$$

Equations (8) (9) and (10), are a different form of **the Langmuir adsorption isotherm** describing adsorption on a homogeneous surface when no interactions take place between the adsorbate molecules, which were derived in a kinetic way.

I case – If adsorption occurs at low pressures $kp \leq 1$ then:

$$\theta \approx kp \quad (11)$$

$$a = a_m kp \quad (12)$$

$$a^s = a_m^s kp \quad (13)$$

Adsorption is proportional to the pressure, so in this pressure range the **Langmuir equation** is transformed to that of **the Henry equation**.

II case – If the pressure of the adsorbing substance is sufficiently high, then $kp \gg 1$, and we can neglect unity in the denominator of equations (11)-(13) yielding:

$$\theta \rightarrow 1, \dots a \rightarrow a_m, \dots a^s \rightarrow a_m^s \quad (14)$$

It follows from the above relations that the amount of adsorbed gas initially increases linearly with the increasing pressure, then gradually decreases, and at appropriately high pressures the adsorption reaches a constant value.

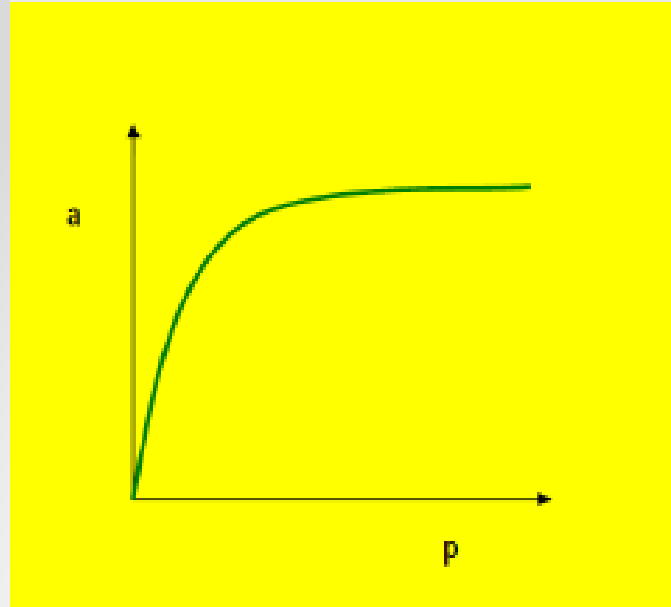


Fig. 1.10. Langmuir adsorption isotherm.

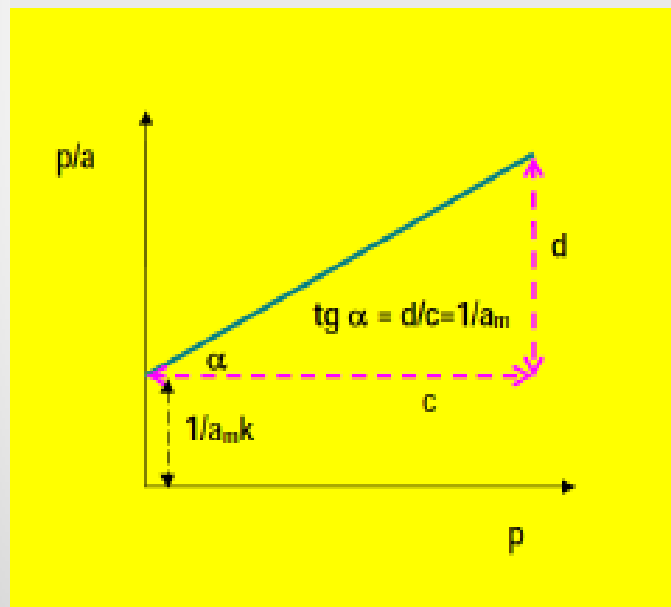


Fig. 1.11. Determination of the constant a_m and k from the linear form of the Langmuir isotherm

The Langmuir adsorption isotherm equation, e.g. equation (10) can be presented in the linear form:

$$a = \frac{a_m K p}{1 + K p} \quad (15)$$

$$a (1 + K p) = a_m K p \quad (16)$$

$$1 + K p = a_m K \frac{p}{a} \quad (17)$$

$$\frac{p}{a} = \frac{1}{a_m} p + \frac{1}{a_m K} \quad (18)$$