photocatalytic reaction

- photoabsorption to yield photoexcited electron ($e^-$) and positive hole ($h^+$)
- reaction of SURFACE-ADSORBED compounds with $e^-$ and $h^+$.
- In other words,

only adsorbed compounds can be reacted.
adsorption isotherm

interaction of compounds with surfaces
• van der Waals force: physical adsorption
• chemical bond: chemisorption

concentration (pressure) dependence of adsorbed amount:

isotherm
Answer the names of these isotherms.

A. Henry
B. Langmuir
C. Brunauer–Emmett–Teller
D. Freundlich
List up the three assumptions for Langmuir adsorption isotherm.
three assumptions for derivation of Langmuir eq.

- All the adsorption sites are same in quality, i.e., strength of capturing an adsorbate is constant

- Only one adsorbate is adsorbed by one site.

- There is no interaction between sites, i.e., adsorption not influenced by adsorption of neighboring sites
Q: Langmuir isotherm to show amount of ads.

Same rate of adsorption and desorption at equilibrium

rate of adsorption: \( r_a = k_a[v]C \)
rate of desorption: \( r_d = k_d[o] \)

\[
k_a[v]C = k_d[o]
\]

\[
KC \frac{[v]}{([v]+[o])} = \frac{[o]}{([v]+[o])}
\]

\[
KC (1 - \theta) = \theta
\]

(amount of adsorption) = [o] = s\theta

(amount of adsorption) = \( sKC/(1 + KC) \)

vacant site: [v], occupied site: [o], concentration at equilibrium: C, rate constants: \( k_a \) and \( k_d \), adsorption equilibrium constant: \( K = k_a/k_d \), saturation limit of adsorption: \( s \)
adsorption equilibrium:

same rates of adsorption and desorption

Adsorption rate depends on (1) concentration in bulk and (2) number (density) of vacant sites ($V$).

Desorption rate depends on number (density) of occupied sites ($O$).
Q How does Langmuirian equation show the characteristics of surface phenomenon?

A + B ⇌ A-B
Q: Who are BET?

\[ \nu = \frac{\nu_m c x}{(1 - x)(1 - x + c x)} \]

- \( \nu_m \): saturation amount of first layer of adsorption
- \( c \): a constant
- \( x \): relative pressure (0-1)
Brunauer–Emmett–Teller isotherm

\[ v = \frac{v_m c x}{(1 - x)(1 - x + c x)} \]

- \( v_m \): saturation amount of first layer of adsorption
- \( c \): a constant
- \( x \): relative pressure (0-1)

A kind of "agglomeration"

\[ \frac{x}{v (1 - x)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} x \]

A Dewar flask with liquid nitrogen

Dewar flask with liquid nitrogen

Get the 1-layer saturated adsorption amount of nitrogen's adsorption area (0.162 nm²) and the surface area (m²) to calculate the surface area (m² g⁻¹) and set it as the bulk volume.
Q: How is relative pressure, \( x \), measured?

\[
v = \frac{\nu_m c x}{(1 - x)(1 - x + cx)}
\]

\( \nu_m \): saturation amount of first layer of adsorption
\( c \): a constant
\( x \): relative pressure (0-1)

\( x \): pressure of nitrogen measured under the same CONDITIONS = saturated vapor pressure of nitrogen

The condition: boiling point of nitrogen at the temperature of liquid nitrogen in a Dewar bottle, and the vapor pressure is the same at atmospheric pressure around an instrument. Therefore, atmospheric pressure has to be measured.
Q If a compound adsorbed on a photocatalyst surface in Langmuirian fashion is oxidized (or reduced) by the positive hole (or photoexcited electron) in the photoirradiated photocatalyst, what is a rate expression for the reaction?
rate \( (r) \) of reaction for

\[ A \rightarrow B \]

is expressed using \( k \) (rate constant) and concentrations of \( A \) ([A]), as

\[ r = k [A] \]
Why the rate is proportional to concentration?

Q Interpret the reason why the rate is proportional to concentration?
kinetic energy = temperature (heat)

Translational motion: Average velocity is defined as "temperature"
The higher the temperature, the more the number of particles (molecules) of higher kinetic energy.
activation energy

- Arrhenius equation shows the relation between a rate constant \( (k) \) and activation energy \( (E_a) \) and temperature \( (T) \), as well as a constant \( A \).

Q Show Arrhenius equation.
activation energy

• Arrhenius equation shows the relation between a rate constant \((k)\) and activation energy \((E_a[J \text{ mol}^{-1}])\) and temperature \((T/K)\), using gas constant \(R\) and a constant \(A\).

• Arrhenius equation is

\[
k = A \exp\left(-\frac{E_a}{RT}\right).
\]

• This equation tells that the rate constant is proportional to the proportion of molecules having energy greater than \(E_a\), since the rate is proportional to the number of those molecules. The absolute number (concentration) of those molecules should be a product of \(\exp(-Ea/RT)\) and \([A]\). Therefore, for a reaction from \(A\) to \(B\), the rate \(r\) is

\[
r = [A] \cdot A \exp\left(-\frac{E_a}{RT}\right).
\]
What is "Boltzmann distribution"?

Energy distribution: occupied states
Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

(probability of excited state) =

$$\Delta E \quad \text{energy measured from a standard}$$
$$k \quad \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J K}^{-1}$$
$$T \quad \text{absolute temperature} = 298 \text{ K (ambient temperature)}$$
$$kT \quad [4.11 \times 10^{-21} \text{ J}] \text{ at ambient temperature}$$
$$A \quad 1 \text{ (assumption)}$$
What is "Boltzmann distribution"?

Energy distribution: occupied states
Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

(probability of excited state) = \( A \exp( -\frac{\Delta E}{kT} ) \)

\( \Delta E \)  energy measured from a standard
\( k \)  Boltzmann constant = \( 1.38 \times 10^{-23} \) J K\(^{-1} \)
\( T \)  absolute temperature = 298 K (ambient temperature)
\( kT \)  [ \( 4.11 \times 10^{-21} \) J ] at ambient temperature
\( A \)  1 (assumption)

- if \( \Delta E = 10^{-19} \) J (visible region), the probability is almost 0.
- if \( \Delta E = 10^{-20} \) J (infrared region), the probability is ca. \( 4.5 \times 10^{-5} \)
- if \( \Delta E = 10^{-24} \) J (microwave region), the probability is ca. 0.999
time course of a reaction

• Assuming a first-order kinetics, derive the equation of substrate concentration ([A]_t) as a function of time, using a rate constant \( k \), time \( t \) and initial concentration \([A]_0\).
time course of a reaction

- Assuming a first-order kinetics, derive the equation of substrate concentration ([A]_t) as a function of time, using a rate constant k, time t and initial concentration [A]_0.

\[ r = -\frac{d[A]}{dt} = k[A]_t \]
\[ \frac{1}{[A]_t}d[A] = -k \, dt \]
\[ \ln [A]_t = -kt + C \]

- When time = 0, [A] = [A]_0. Therefore,

\[ C = \ln [A]_0 \]
\[ [A]_t = [A]_0 \exp(-kt) \]
Q Draw a time-course curve for a photocatalytic reaction of A obeying a first-order kinetics.
Q: Draw a time-course curve for a photocatalytic reaction of A obeying a first-order kinetics.
What kind of mechanism of photocatalytic reaction can interpret the experimental results, if a first-order kinetics, like plots below, is observed?
photocatalytic reaction

• photoabsorption to yield photoexcited electron (e\textsuperscript{-}) and positive hole (h\textsuperscript{+})
• reaction of SURFACE-ADSORBED compounds with e\textsuperscript{-} and h\textsuperscript{+}.
• In other words,

only adsorbed compounds can be reacted.

Why first-order kinetics?
comments on this lecture

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大谷文章
某教授
光触媒の応用例について知り、その基本が化学であることを学びました。光と物質のかかわりについてさらに知りたいので本を調べてみます。
絶版になっている「光触媒標準研究法」はどこかで入手可能ですか。