# Adsorption and Catalysis

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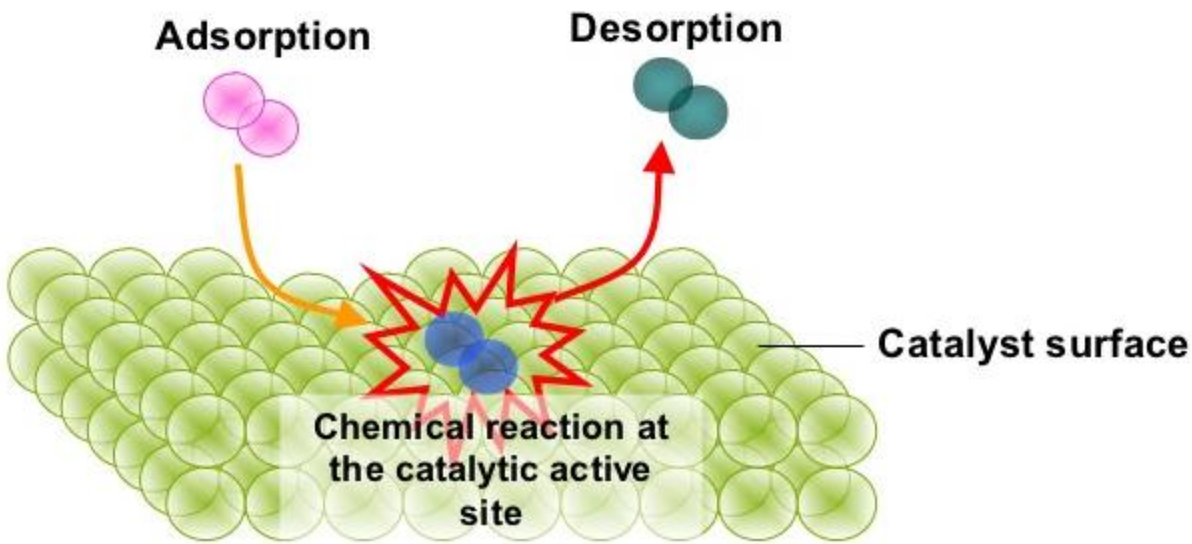
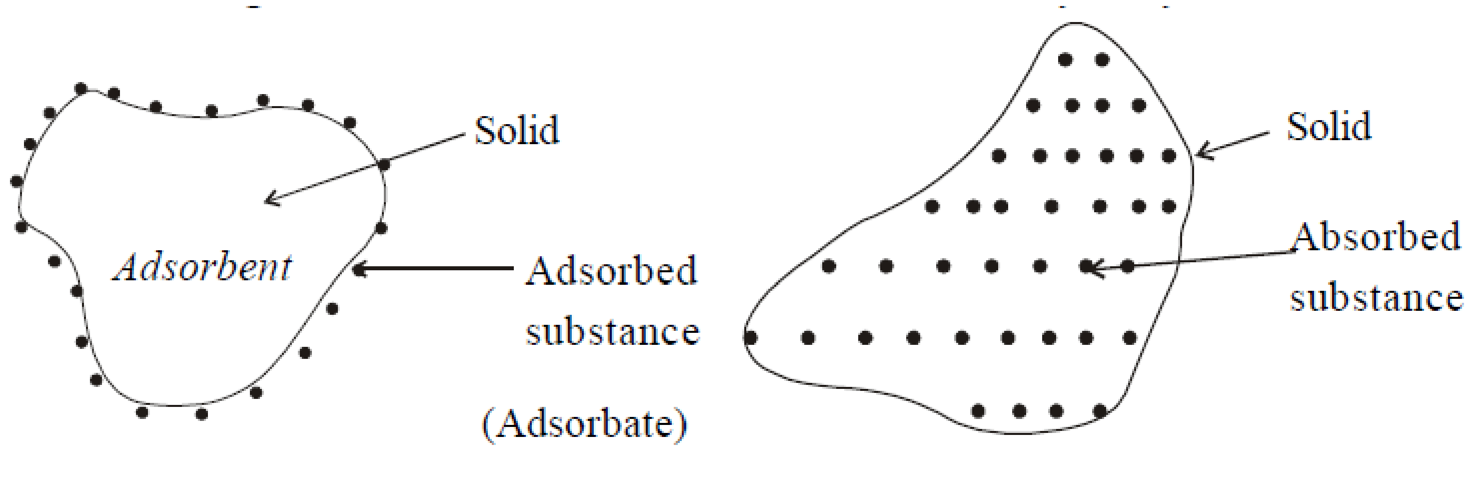

Adsorption
Desorption
Catalyst surface
Chemical reaction at the catalytic active site




(a) (b)

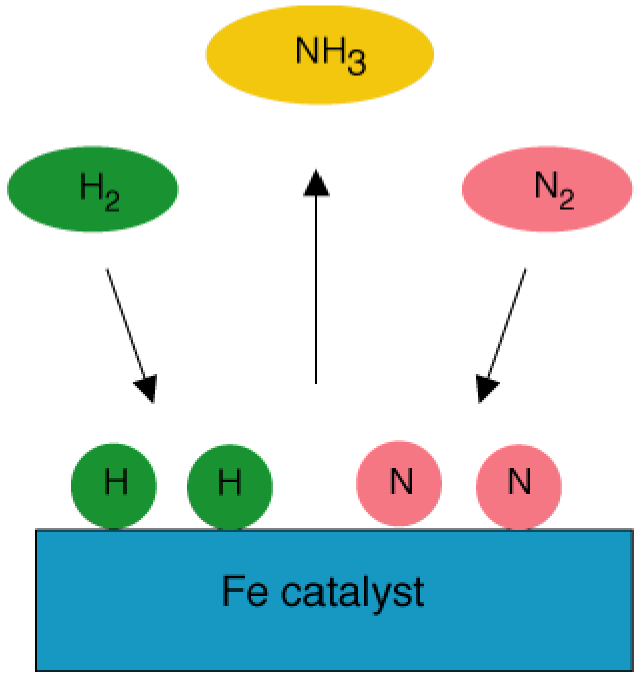
Different solids would adsorb different amounts of the same gas even under similar conditions.

Substances like charcoal and silica gel are excellent adsorbents. Why?

The substances that are porous in nature and have rough surfaces are better adsorbents.

| | **Physisorption** | **Chemisorption** |
|---|---|---|
| *force* | van de Waal | chemcal bond |
| *number of adsorbed layers* | multi | only one layer |
| *adsorption heat* | low (10-40 kJ/mol) | high ( > 40 kJ/mol) |
| *selectivity* | low | high |
| *temperature to occur* | low | high |

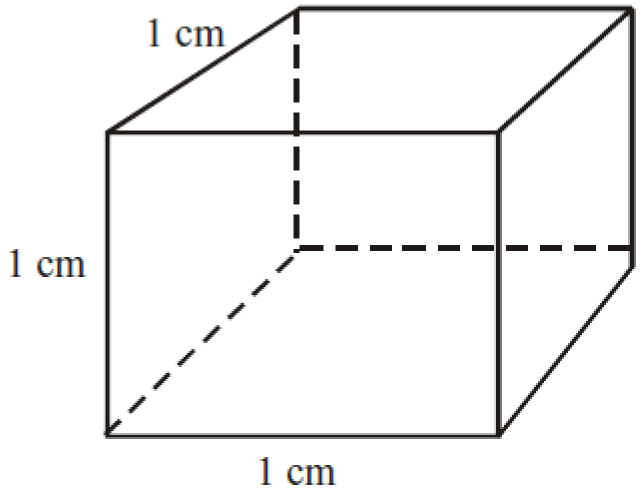
## Factors that affect adsorption



**1.Surface area of the solid**

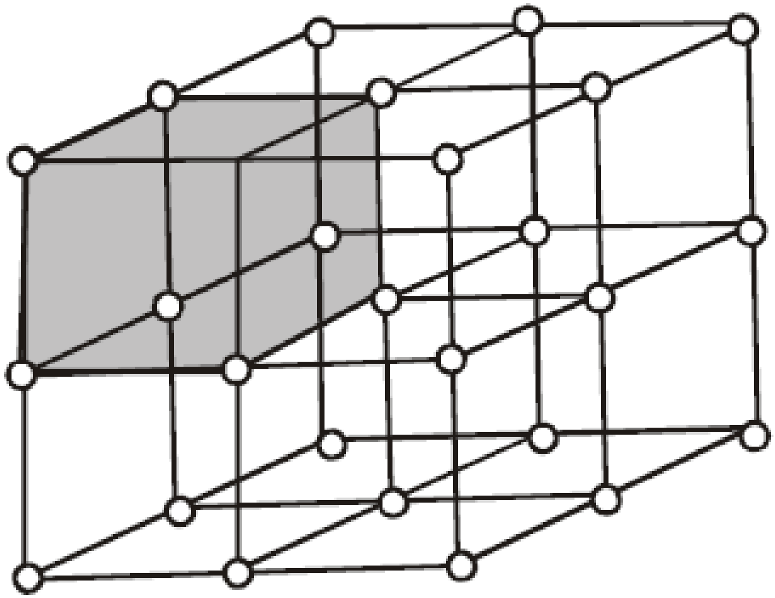
Higher the surface area, more is the surface available for adsorption and greater is the adsorption.

The surface area depends upon the particle size of the substance



(a)

A cube of each side equal to 1cm has six faces.
Each of them is a square with surface area of $1cm^2$.
Thus, the total surface area of this cube is $6\ cm^2$



(b)

Here, each side is divided into two equal halves, ½ cm long, and the cube is divided into two equal halves, ½ cm long, and the cube is cut along the lines indicated in the Fig (b).
The cube is now divided into 8 smaller
cubes with each side 0.5 cm long

Surface area of each small cube - (6 x 0.5 x0.5) = 1.5 $cm^2$
Total surface area of all the 8 smaller cubes = 12 $cm^2$ which is double the surface area of the original cube.
If it is subdivided into smaller cubes, each of side equal to 1 x $10^{-6}$ cm the surface area will increase to 6 x $10^6$ $cm^2$ or 600 $m^2$.
Imagine the effect on adsorption!

## 2. The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas.

The gases which are more easily liquefied  are more readily adsorbed than others.

For example, under similar conditions, the amount of $SO_2$ or $NH_3$ adsorbed by charcoal is much more than that of $H_2$ or $O_2$ gases.

It is because the intermolecular forces are stronger in more easily liquefiable gases.
Hence they get adsorbed more strongly.

## 3. Temperature

The extent of adsorption decreases with rise in temperature.

For example, under one atmosphere pressure, one gram of charcoal adsorbs about 10 cm$^3$ of $N_2$ gas at 272 K.

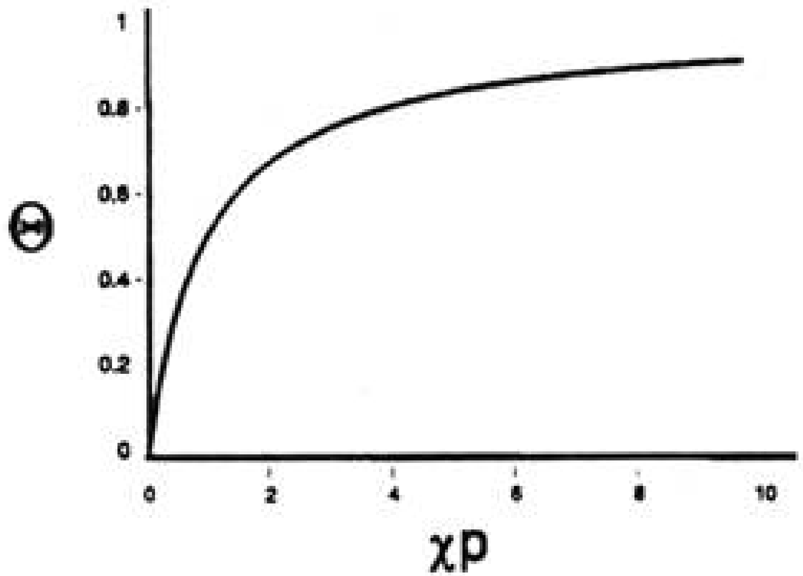
The same surface adsorbs 20 cm$^3$ at 248 K and 45 cm$^3$ at 195 K.

$$\underset{\text{adsorbate}}{\text{gas}} + \underset{\text{adsorbent}}{\text{solid}} \rightleftharpoons \text{gas adsorbed on the solid} + \textit{heat}$$

## 4. Pressure of the gas

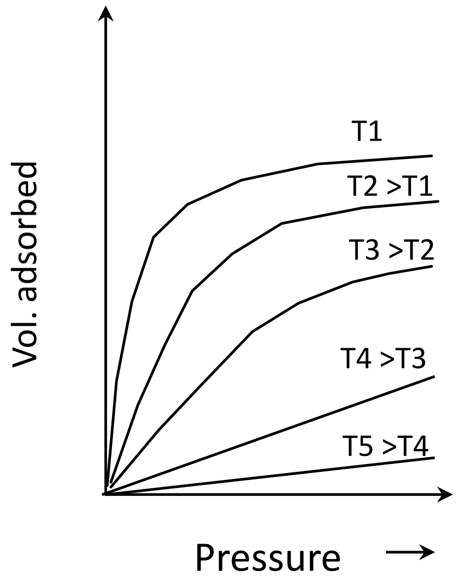
At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate)

# What is this plot ?

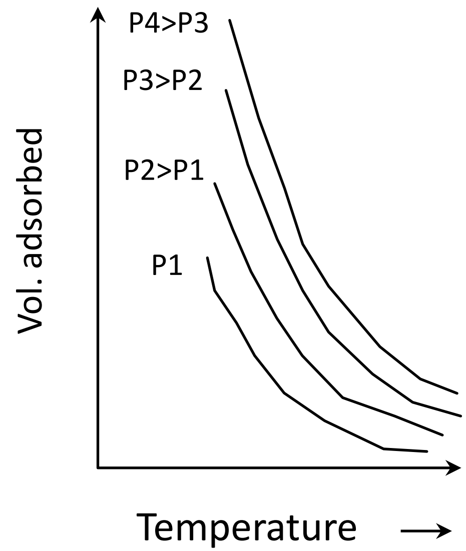


# Adsorption Isoterms

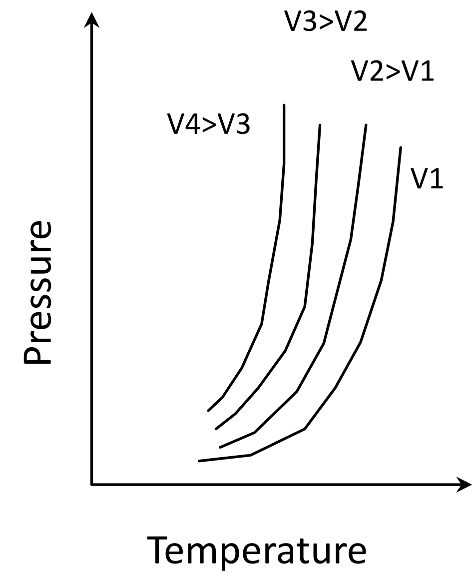
| NAME | ISOTHERM EQUATION | APPLICABILITY |
|---|---|---|
| Langmuir | $q = \frac{q_m k_1 . C}{1 + k_1 C}$ | Chemisorption and physical adsorption |
| Freundlich | $q = K_F C^{1/n}$ | Chemisorption and physical adsorption at low coverages |
| Temkin | $q_e = \frac{RT}{b} \ln(A_T C_e)$ | Chemisorption |




**Adsorption Isotherm**

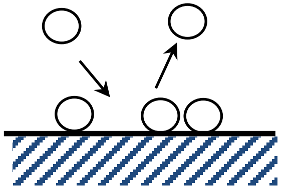



**Adsorption Isobar**




**Adsorption Isostere**

**Langmuir Adsorption Isotherm**



A dynamic equilibrium exists between adsorption and desorption.

The layer of the adsorbed gas is only one molecule thick -unimolecular.

surface uniform ($\Delta H_{ads}$ does not vary with coverage) .

No interaction between adsorbed molecules and adsorbed molecules are immobile.

$$A\,(g) \Leftrightarrow A\,(ads) \longrightarrow B$$

Decomposition occurs uniformly across the surface.

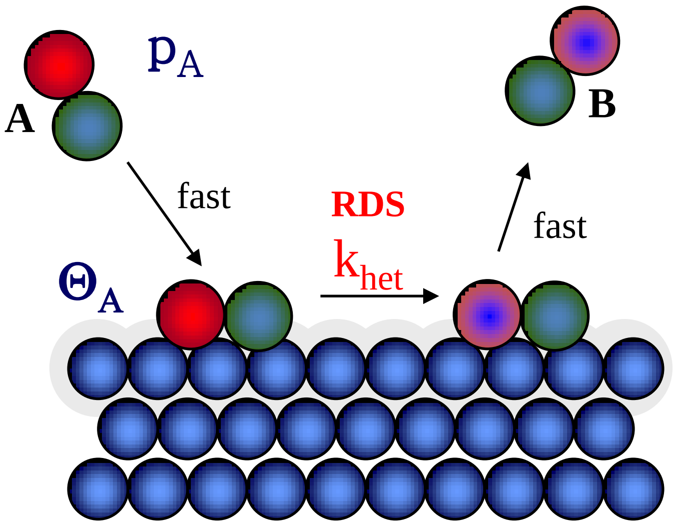
Products are weakly bound and rapidly desorbed.

The rate determining step (rds) is the surface reaction step.

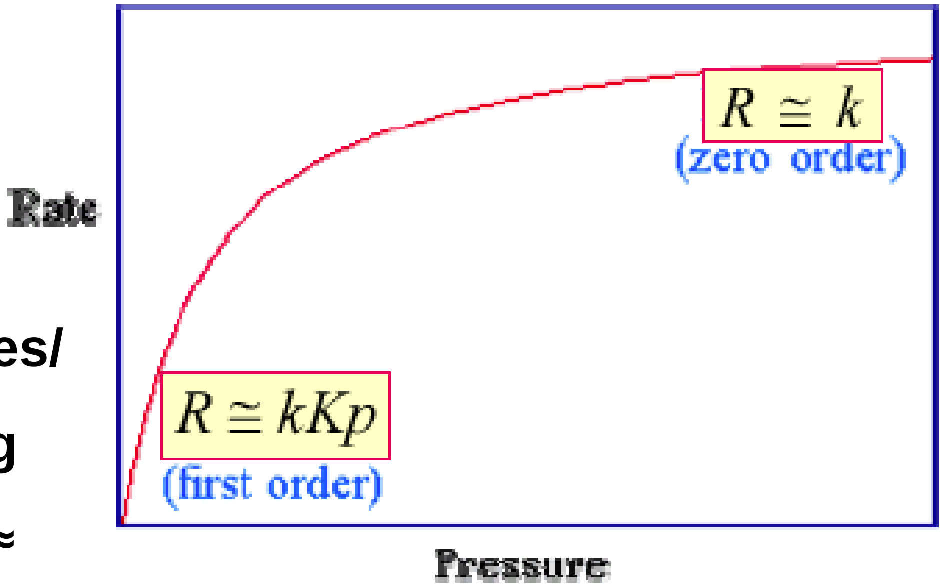
**Rate = k $\theta_A$**

For Langmuir adsorption

$$\text{Rate} = \frac{k\text{K}p}{1+\text{K}p}$$



## Two limiting cases




**Low pressures/**

**Weak binding**

K*p*<<1 ;Rate ≈ *k*K*p*

Rate linearly dependent on gas pressure

First order reaction

Surface coverage very low

**High pressures/**

**Strong binding**

K*p*>>1; RateA ≈ *k*

Rate independent of gas pressure

Zero order reaction

Surface coverage =1

# Langmuir- Hinshelwood model for bimolecular reaction

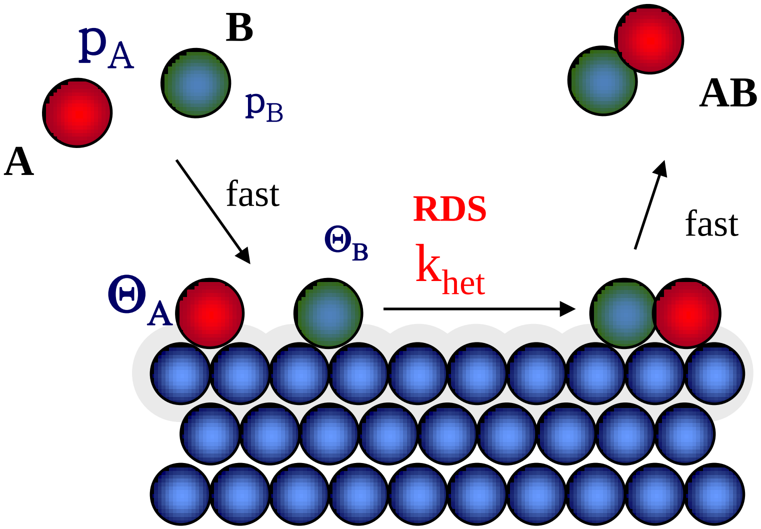
$$\mathrm{A\,(g)} \Leftrightarrow \mathrm{A\,(ads)}$$

$$\mathrm{B\,(g)} \Leftrightarrow \mathrm{B\,(ads)}$$

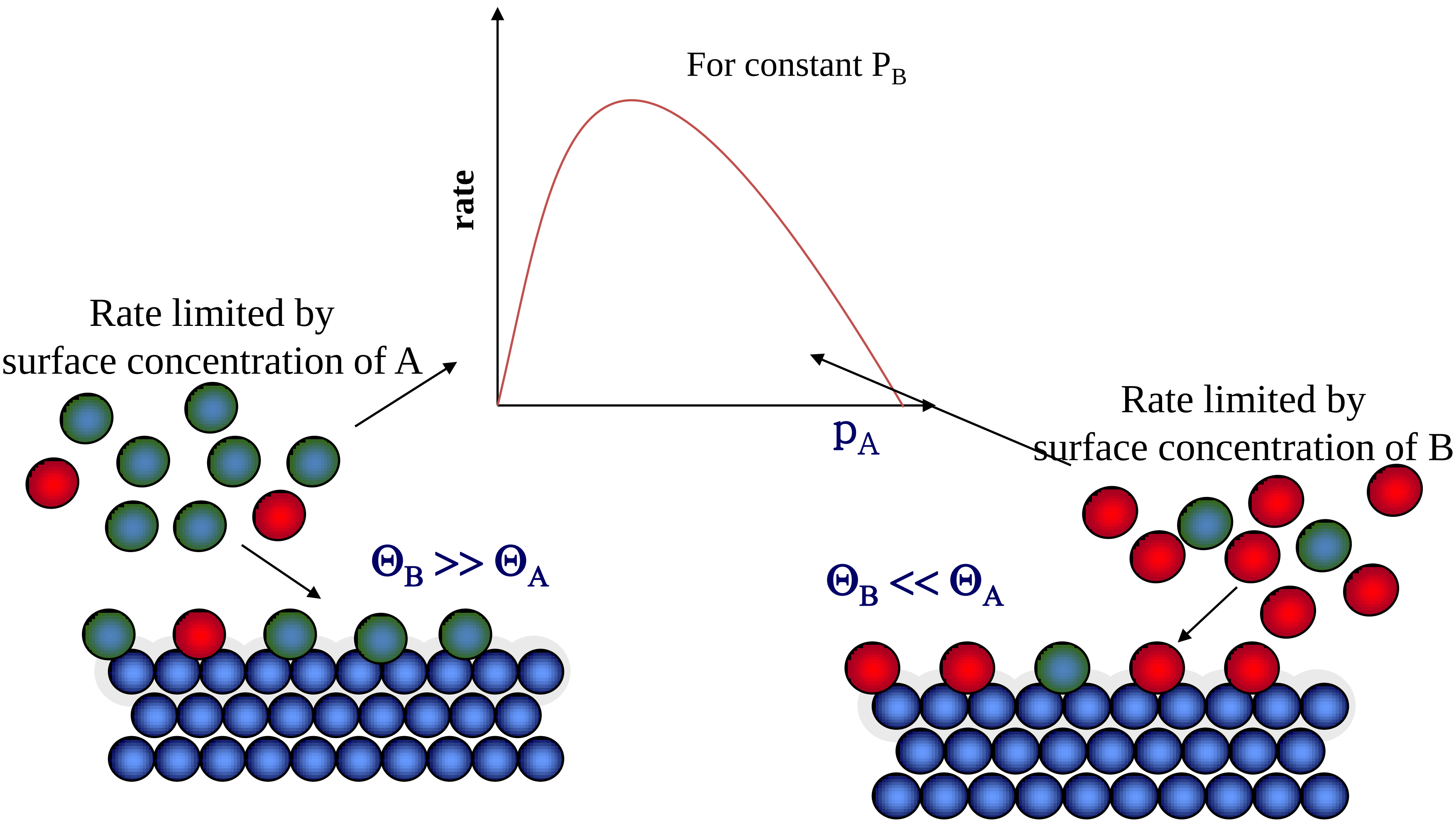
$$\mathrm{A\,(ads)} + \mathrm{B\,(ads)} \xrightarrow{rds} \mathrm{AB\,(ads)} \xrightarrow{\text{fast}} \mathrm{AB\,(g)}$$

**Rate = k $\theta_A$ $\theta_B$**

$$\text{Rate} = \frac{kK_A p_A K_B p_B}{\left(1 + K_A p_A + K_B p_B\right)^2}$$



# How does the rate change with $P_A$ or $P_B$?

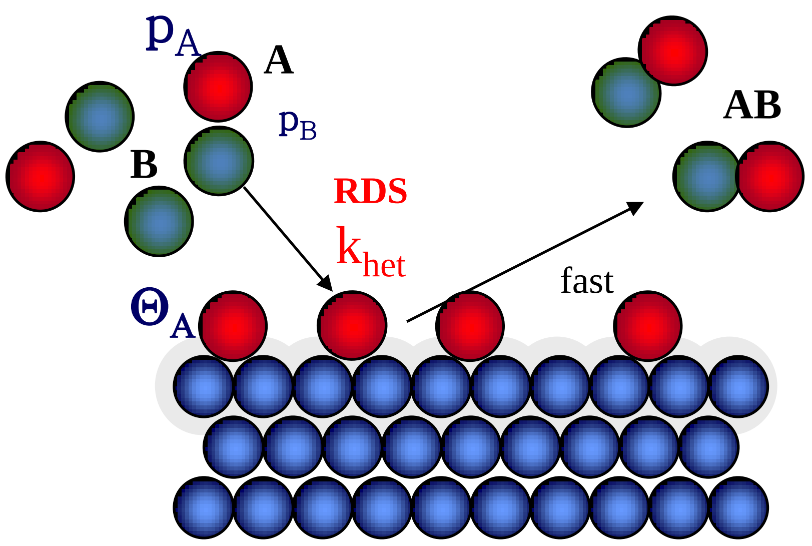


# Eley-Rideal
# Bimolecular surface reactions

An adsorbed molecule may react directly with a gas phase molecule by a collisional mechanism

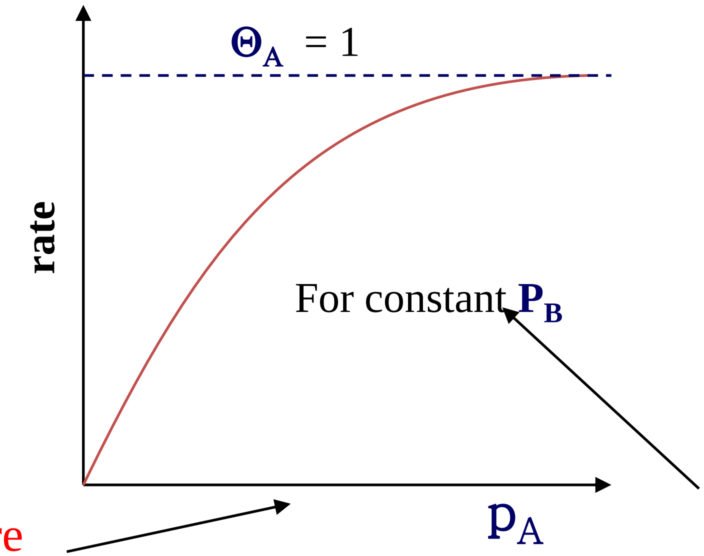
rate = $k\ \boldsymbol{\theta_A}\ \mathbf{p_B}$

$= k\ K_A p_A\ \mathbf{p_B} / (1+K_A p_A)$



# Eley-Rideal
# bimolecular surface reactions

For constant $p_A$, the rate is always first order wrt $\mathbf{p_B}$




Low pressure
Weak binding

High pressure
Strong binding

$K_A p_A << 1$

$K_A p_A >> 1$

rate = $k_{het} K_A \; p_A \; \mathbf{p_B}$ …….. first order in A

rate = $k \; \mathbf{p_B}$ …….. zero order in A

$k_{exp}$

$k_{exp}$

# Diagnosis of mechanism

If we measure the reaction rate as a function of the coverage by A, the rate will initially increase for both mechanisms.

Eley-Rideal- Rate increases until surface is covered by A

Langmuir-Hinshelwood- Rate passes a maximum and ends up at zero, when surface covered by A.

B + S ⬄ B-S

cannot proceed when A blocks all sites.