ADSORPTION ON ACTIVE SITES:

For a reaction to happen on a solid catalyst surface, chemisorption of the reactant molecules on catalyst active sites is necessary.

If A is a reactant molecule and S denotes an active site, then the attachment of reactant molecule on the active site can be easily depicted. A.S is the occupied site.

Total molar concentration of active sites, C_t = Total number of active site/unit mass of catalyst/Avogadro no (mol/g. of catalyst)

$$A + S \Longleftrightarrow A.S, \text{ adsorption of A on S}$$

Total molar concentration of vacant sites, C_v = Total number of vacant site/unit mass of catalyst/Avogadro no (mol/g. catalyst)

Similarly, total molar concentration of occupied sites can be expressed. In the absence of catalyst deactivation, total molar concentration of active sites is assumed to remain constant.
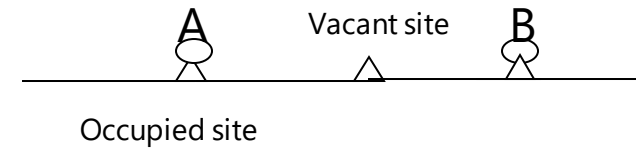
If two species, A and B are adsorbed on the active sites, that can be shown as,

$A + B + 2S \iff A.S + B.S$,
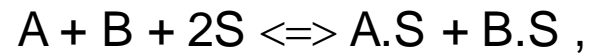
Where, S is vacant active site and A.S and B.S are occupied sites.

Total concentration of sites is,

$C_t = C_v + C_{A.S} + C_{B.S}$, this is called site balance.

A   Vacant site   B

Occupied site

Conceptual model of adsorption of two species on active sites

P_i = Partial pressure of species i in gas phase, atm

$C_{i.s}$ = Surface concentration of sites occupied by species i, gmol/g. catalyst

ADSORPTION ISOTHERM:

If we consider adsorption of a non-reacting gas on the surface of a catalyst, the adsorption data are reported in the form of adsorption isotherm

Adsorption Isotherm: The adsorption curve formed by the data of the amount of gas adsorbed on a solid surface at different pressures but at single temperature.
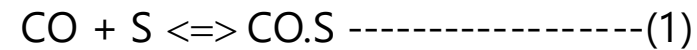
Steps in Adsorption:

Adsorption models are postulated to define the experimental data.

If the experimental data fit well into a proposed model, the model can be said to reasonably describe what is occurring physically in a real system.
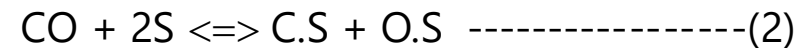
Two models are proposed for adsorption:

➢ Molecular or non-dissociative adsorption

$$CO + S \iff CO.S$$ -----------------(1)

Here the carbon dioxide molecule adsorbs on the active site as a molecule

➢ Dissociative adsorption

$$CO + 2S \iff C.S + O.S$$ ----------------(2)

Here, the carbon dioxide molecule is dissociated and carbon and oxygen atoms adsorb on two different active sites.

MOLECULAR ADSORPTION

Molecular adsorption is   CO + S <=> CO.S

The adsorption is considered as elementary step.

➢ Rate of attachment (forward step) is proportional to :

1. No. of collisions of the molecules make per sec. [No. of collisions per sec is proportional to the partial pressure of carbon dioxide (P_{CO})]

2. Concentration of the vacant sites of the catalyst (C_v)

∴ Rate of attachment α P_{CO} and C_v

Rate of attachment = k_A $P_{CO}C_v$, (k_A is the adsorption rate constant)

Rate of detachment of the molecule is proportional to concentration of the sites occupied by carbon dioxide ($C_{CO.S}$)

$\therefore$ Rate of detachment α $C_{CO.S,}$ rate of detachment = $k_{-A}C_{CO.S}$, k_{-A} is desorption rate constant

$\therefore$ Overall rate of adsorption $r_{AD} = k_A P_{CO} C_v - k_{-A} C_{CO.S}$

$\therefore$ Considering $K_A = \frac{k_A}{k_{-A}}$ = Adsorption equilibrium constant,

$\therefore$ $r_{AD} = k_A (P_{CO} C_v - \frac{C_{CO.S}}{K_A})$

CONTD…

Now at equilibrium, rate of attachment= rate of detachment,

$$P_{CO}C_v = \frac{C_{CO.S}}{K_A}, \quad \text{or,} \quad C_{CO.S} = K_A P_{CO} C_v, \quad C_v = \frac{C_{CO.S}}{K_A P_{CO}}$$

Site balance, $\quad C_t = C_v + C_{CO.S}, \quad C_v = C_t - C_{CO.S}, \quad \frac{C_{CO.S}}{K_A P_{CO}} = C_t - C_{CO.S},$

$$C_{CO.S} = K_A P_{CO}(C_t - C_{CO.S}), \quad C_{CO.S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}} \text{---------------------(3)}$$

This is the relation between concentration of occupied sites with the partial pressure of gas, and is called Langmuir adsorption isotherm.

Langmuir Isotherm Fig (a) shows the Langmuir Isotherm curve.
Here, Concentration of adsorbed site = f(CO pressure)
i.e, Amount of CO adsorbed = f(CO pressure)

By linearizing the Eq (3), we get,
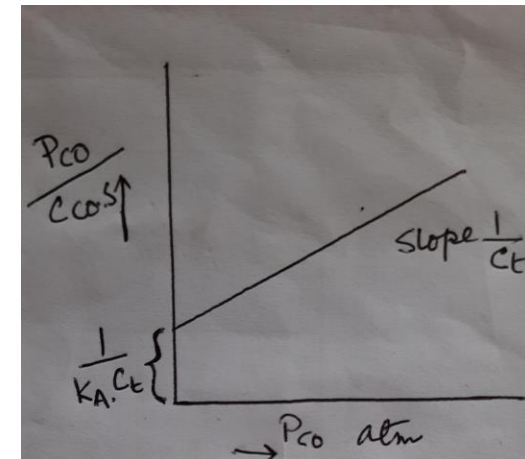
$$\frac{P_{CO}}{C_{CO.S}} = \frac{1}{K_A.C_t} + \frac{P_{CO}}{C_t}$$

Plotting the equation, we get a straight line, as shown in Fig (b), where slope is $\frac{1}{C_t}$ and intercept $\frac{1}{K_A C_t}$.
From these, the adsorption equilibrium constant K_A and total active site concentration C_t can be determined.
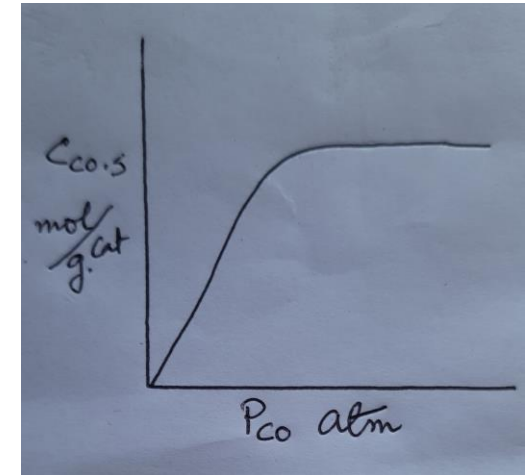
a

b

DISSOCIATIVE ADSORPTION

Dissociative adsorption is   CO + 2S $<=>$ C.S + O.S

Here again, rate of attachment α partial pressure of the gas and square of the vacant sites adjacent to each other

(as for dissociative adsorption, two adjacent vacant sites are necessary for adsorption of two atoms dissociated from a molecule)

$\therefore$ Rate of attachment = $k_A P_{CO} C_v^2$

Rate of detachment α two adjacent occupied sites

Rate of detachment = $k_{-A} C_{C.S} C_{O.S}$

Total rate of adsorption is,

$$r_{AD} = k_A P_{CO} C_v^2 - k_{-A} C_{C.S} C_{O.S}$$

$$= k_A \left(P_{CO} C_v^2 - \frac{C_{C.S} C_{O.S}}{K_A} \right), \quad K_A = \frac{k_A}{k_{-A}} = \text{adsorption equilibrium constant.}$$

For dissociative adsorption, k_{-A} will increase with increase in temperature. So, K_A will decrease with temperature.

At equilibrium, $\quad P_{CO} C_v^2 = \frac{C_{C.S} C_{O.S}}{K_A}$

If, $C_{C.S} = C_{O.S}$, then, $P_{CO} C_v^2 K_A = C_{O.S}^2 \quad \therefore C_{O.S} = (P_{CO} K_A)^{1/2} C_v$ ------(4)
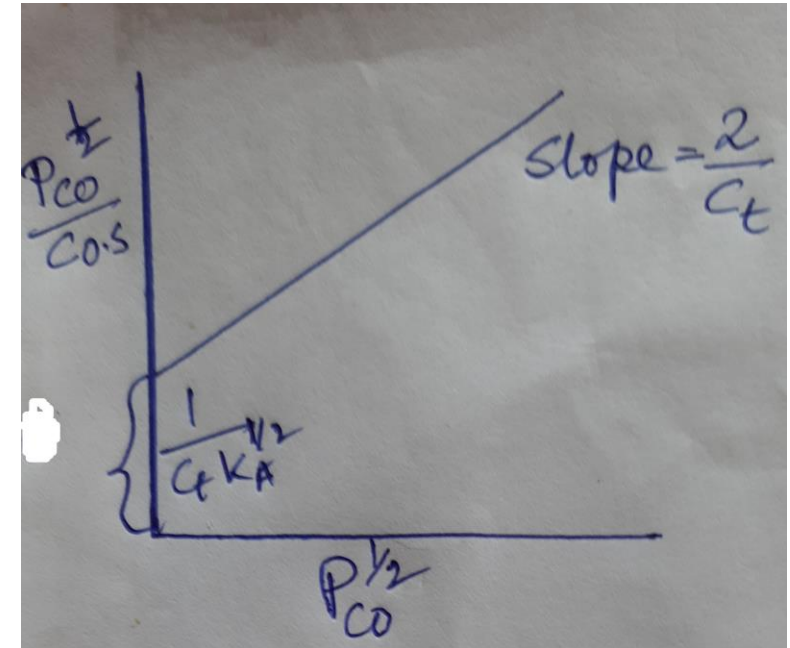
For site balance, $C_t = C_v + C_{C.S} + C_{O.S}$ or, $C_v = C_t - 2C_{O.S}$

Putting the value of C_v in Eq. (4), $C_{O.S} = (P_{CO} K_A)^{1/2} (C_t - 2C_{O.S})$

Solving, $C_{O.S} = \dfrac{C_t (P_{CO}K_A)^{1/2}}{1 + 2(P_{CO}K_A)^{1/2}}$

Linearising, $\dfrac{1}{C_{O.S}} = \dfrac{1}{C_t (P_{CO}K_A)^{1/2}} + \dfrac{2}{C_t}$

Fig (C) shows the plot.

(C)

When more than one molecule is present, say A and B, then adsorption of A in presence of B (B is not adsorbing),

$C_{A.S} = \dfrac{K_A \, P_A \, C_t}{1 + K_A P_A + K_B P_B}$, where, K_A and K_B are the adsorption equilibrium constants of A and B, P_A and P_B are the partial pressures of A and B, $C_{A.S}$ and C_t are the concentrations of occupied sites of A and total sites respectively.

All the time, a uniform surface is assumed in deriving Langmuir Isotherm. That means any active site has the same attraction for an impinging molecule as does any other site.

Isotherms, different from Langmuir type are also derived, considering various assumptions, including non-uniform surface.