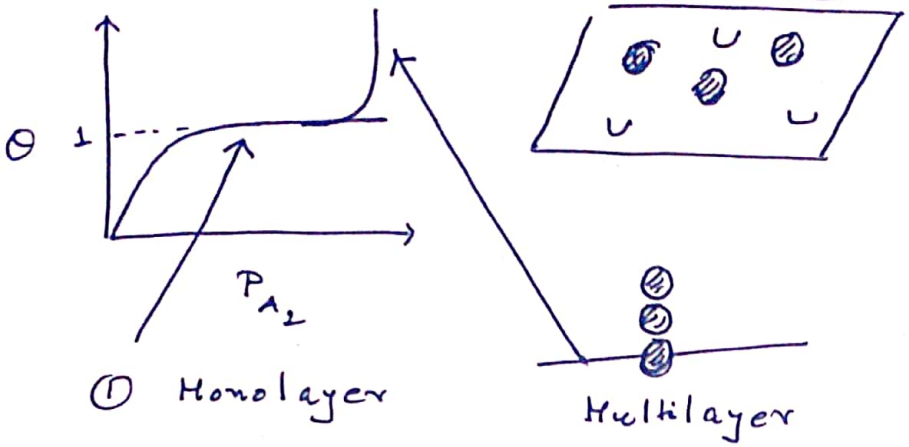
Langmuir adsorption isotherm:



① Monolayer

Multilayer

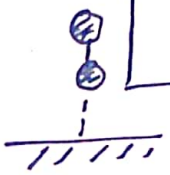
Mechanism

↓

* Irvine Langmuir — surface science
* Cyril Hinshelwood
* Nikolai Semenov

radical reactions

NLs (~1940 ?)

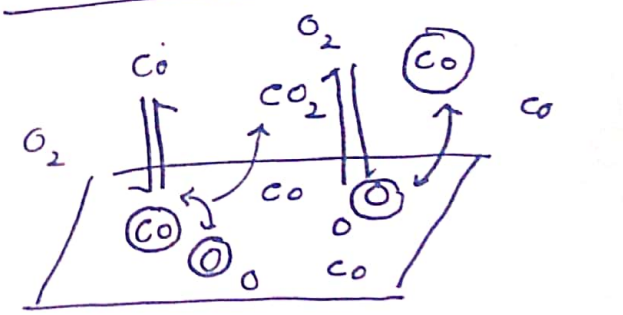


$$A_2 + S \rightleftharpoons A_2 \cdots S$$

$$A_2 + 2S \rightleftharpoons 2\,A\text{--}S$$

$$2CO + O_2 \xrightarrow{S} 2CO_2$$

?



Mechanism :

$$O_2\,(g) \rightleftharpoons 2\,O\,(ads)$$

$$CO\,(g) \rightleftharpoons CO\,(ads)$$

#1 $CO\,(ads) + O\,(ads) \longrightarrow CO_2\,(g)$

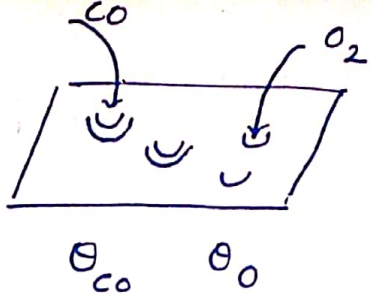
#2 $CO\,(g) + O\,(ads) \longrightarrow CO_2\,(g)$

Langmuir – Hinshelwood

Eley – Rideal

Rate = ?

#eley rideal mechanism



$$O_2 + 2S \rightleftharpoons 2O-S$$

$$k_{a_{O_2}} \times [O_2] \times (1-\theta_{CO}-\theta_O)^2 \sigma_0^2 = k_{d_{O_2}} \times \theta_O^2 \times \sigma_0^2$$

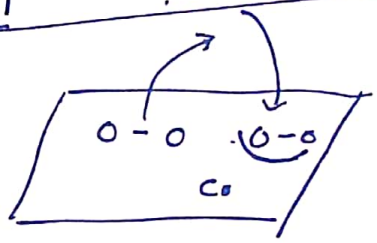
$$(1-\theta_{CO}-\theta_O)^2 = \frac{1}{k_{O_2}[O_2]}\,\theta_O^2$$

$$\boxed{1-\theta_{CO}-\theta_O = \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O} \quad \text{—— (1)}$$

$$CO + S \rightleftharpoons CO-S$$

$$k_{a_{CO}} \times [CO] \times (1-\theta_{CO}-\theta_O) = k_{d_{CO}} \times \theta_{CO} \times \sigma_0$$

$$\boxed{1-\theta_{CO}-\theta_O = \frac{1}{k_{CO}[CO]}\,\theta_{CO}} \quad \text{—— (2)}$$



Total # of sites
↓ ↘ occupied
$\theta_{CO} \times \sigma_0$ $\theta_O \times \sigma_0$
$\{1-(\theta_{CO}+\theta_O)\}\sigma_0$

$$\theta_{CO} = 1 - \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O - \theta_O$$

$$1 = \frac{1}{k_{CO}[CO]} + \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O + \theta_O$$

$$\frac{1}{k_{CO}[CO]}\,\theta_{CO} = \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O$$

(2) $\Rightarrow$ $1 - \frac{k_{CO}[CO]}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O - \theta_O = \frac{1}{k_{CO}[CO]}\,\theta_{CO}$

$$= \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}}\,\theta_O$$

$$\theta_O = \left\{ \frac{k_{CO}[CO]}{k_{O_2}^{1/2}[O_2]^{1/2}} + 1 + \frac{1}{k_{O_2}^{1/2}[O_2]^{1/2}} \right\} = 1$$

(2)

$$\theta_0 = \frac{k_{O_2}^{1/2} [O_2]^{1/2}}{1 + k_{CO}[CO] + k_{O_2}^{1/2} [O_2]^{1/2}}$$

$$\theta_{CO} = \frac{k_{CO}[CO]}{1 + k_{CO}[CO] + k_{O_2}^{1/2} [O_2]^{1/2}}$$

Check if correct

LH mechanism

$$CO(ads) + O(ads) \xrightarrow{k_3} CO_2(g)$$

Rate: $v_{LH} = k_3 \times \theta_{CO} \times \theta_0$

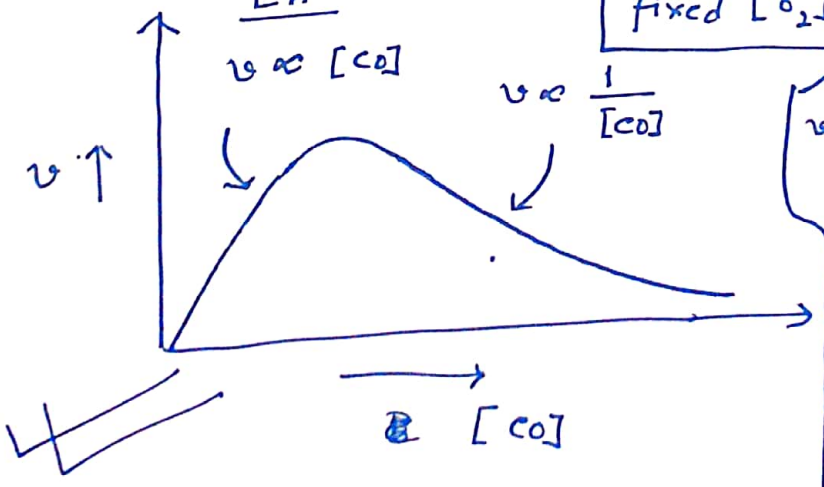
$$= \frac{k_3 K_{O_2}^{1/2} K_{CO} [O_2]^{1/2} [CO]}{\left(1 + K_{CO}[CO] + k_{O_2}^{1/2}[O_2]^{1/2}\right)^2}$$

ER mechanism

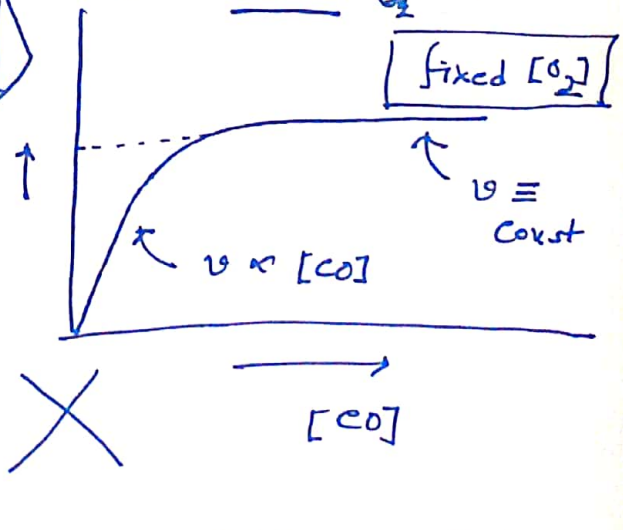
$$CO(g) + O(ads) \xrightarrow{k_3} CO_2(g)$$

$v_{ER} = k_3 \times [CO] \times \theta_0$

$$= \frac{k_3 K_{O_2}^{1/2} [O_2]^{1/2} [CO]}{\left(1 + K_{CO}[CO] k_{O_2}^{1/2}[O_2]^{1/2}\right)}$$

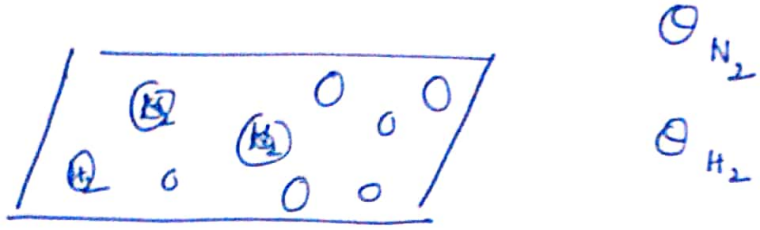


fixed $[O_2]$



Haber process

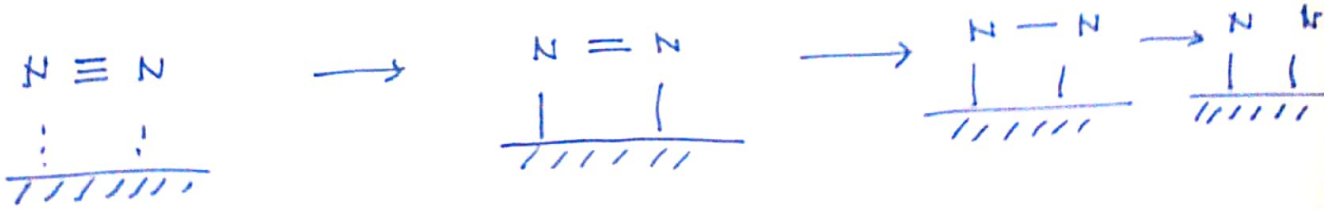
$$N_2 + 3H_2 \overset{Fe\ cat}{\rightleftharpoons} 2NH_3$$



① $N_2 + 2S \rightleftharpoons 2\ N\text{-}S$

② $H_2 + 2S \rightleftharpoons 2\ H\text{-}S$

This is RDS



This is NOT RDS!

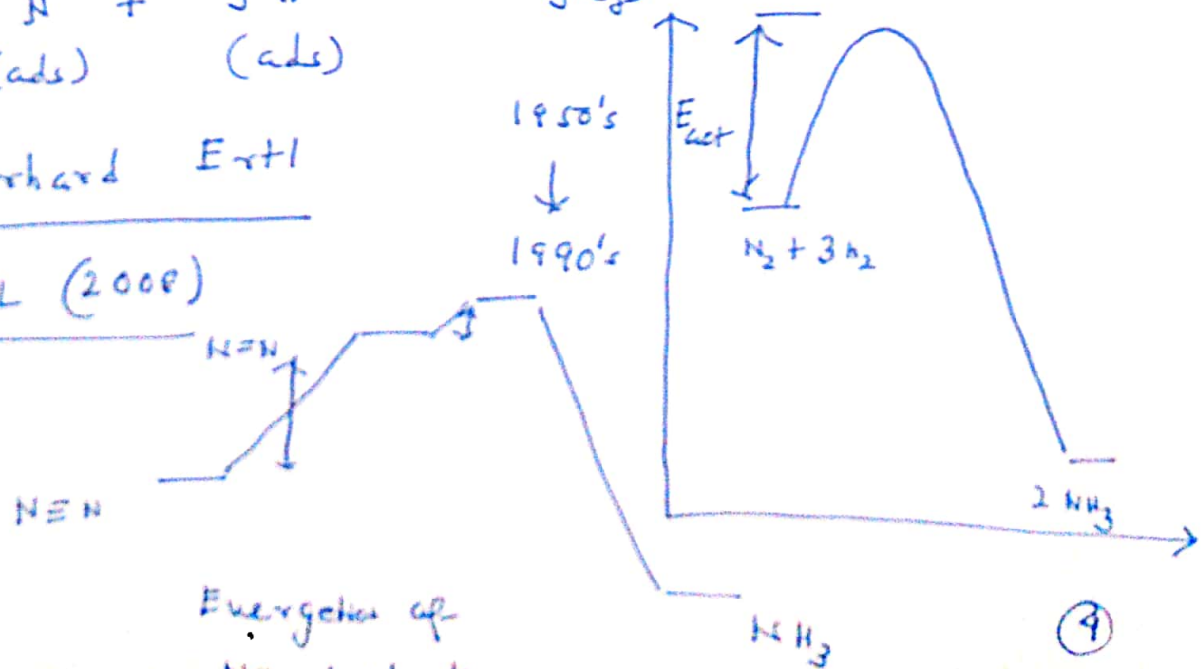
③ $N_{(ads)} + 3H_{(ads)} \longrightarrow NH_3(g)$

Gerhard Ertl

NL (2008)

1950's

1990's



Energetics of NH_3 production

④