ChemE 2200 – Chemical Kinetics Lecture 16

Today: The Kinetics of Heterogeneous Catalysis, cont'd

Adsorption Isotherms

Rate Equations

"*What adsorption properties must be balanced for an effective catalyst*?"

Recap: The Basic Mechanism of Heterogeneous Catalysis

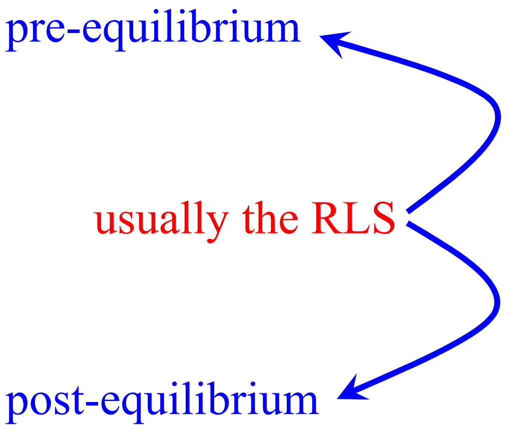
$$A \xrightarrow{M} P$$

The Langmuir-Hinshelwood Mechanism of Elementary Reactions:

$$A + M \underset{k_{\text{des, A}}}{\overset{k_{\text{ads, A}}}{\rightleftarrows}} M\text{-}A$$ adsorption

$$M\text{-}A \overset{k_{\text{surface}}}{\rightarrow} M\text{-}P$$ surface reaction

$$M\text{-}P \underset{k_{\text{ads, P}}}{\overset{k_{\text{des, P}}}{\rightleftarrows}} P + M$$ desorption


pre-equilibrium

usually the RLS

post-equilibrium

The Thermodynamics of Adsorption

$$A + M \underset{k_{\text{des, A}}}{\overset{k_{\text{ads, A}}}{\rightleftarrows}} M\text{-}A$$

Often in equilibrium.
Almost always exothermic.

$\Delta\overline{H}_{\text{ads}}$ depends on adsorbate, surface, ~~and coverage.~~ will ignore in ChemE 2200

Two Categories of Adsorption:

Physical Adsorption (aka physisorption)

Weak M-A bond: $-\Delta\overline{H}_{\text{ads}}$ is 0 to 25 kJ/mol.

Examples: saturated hydrocarbons: CH_4, CH_3CH_3

Chemical Adsorption (aka chemisorption)

Strong M-A bond: $-\Delta\overline{H}_{\text{ads}}$ is 40 kJ/mol and higher

Examples: dissociative adsorption: $H_2 + 2M \rightleftarrows 2M\text{-}H$

polar compounds: CO, NO, H_2O

The Thermodynamics of Adsorption, cont'd

For the catalyzed reaction $A + B \xrightarrow{M} P$ the surface reaction is

$$M\text{-}A + M\text{-}B \rightarrow M + M\text{-}P$$

Both A and B must be adsorbed on M.

Truncated Solids: Heats of Adsorption

poor catalysts: adsorbed H_2 excludes adsorbed N_2

		$-\Delta\bar{H}_{ads}$, kJ/mol			
reaction	adsorbate	Fe	Ni	Rh	Pt
$N_2 + 3H_2 \rightarrow 2NH_3$	H_2	142	155	117	107
	N_2	168	< 20	< 20	< 20
$2CO + O_2 \rightarrow 2CO_2$	O_2	570	500	503	294
	CO	192	176	193	201

good catalyst: comparable adsorption

poor catalysts: adsorbed O_2 excludes adsorbed CO

good catalyst: comparable adsorption

Comparable adsorption is necessary, but not sufficient.

The Thermodynamics of Adsorption, cont'd

For the catalyzed reaction $A + B \xrightarrow{M} P$ the surface reaction is

$$\text{M-A} + \text{M-B} \rightarrow \text{M} + \text{M-P}$$

Both A and B must be adsorbed on M.

Adsorption of both reactants is ***essential***
to the Langmuir-Hinshelwood Mechanism.

An alternative reaction,

$$\text{M-A} + \text{B(gas)} \rightarrow \text{M-P}$$

is unlikely and rare.

Ballistic impact from the gas phase
is the Eley-Rideal Mechanism.

Like a termolecular elementary reaction,

$$\text{A(gas)} + \text{B(gas)} + \text{C(gas)} \rightarrow \text{P}$$

reaction by ballistic impact is possible

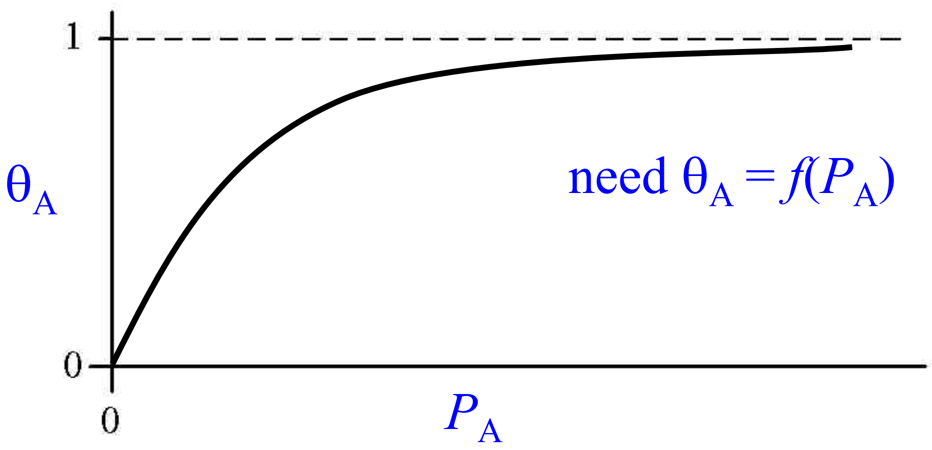
but ***improbable***

relative to the reaction of two adsorbed reactants.

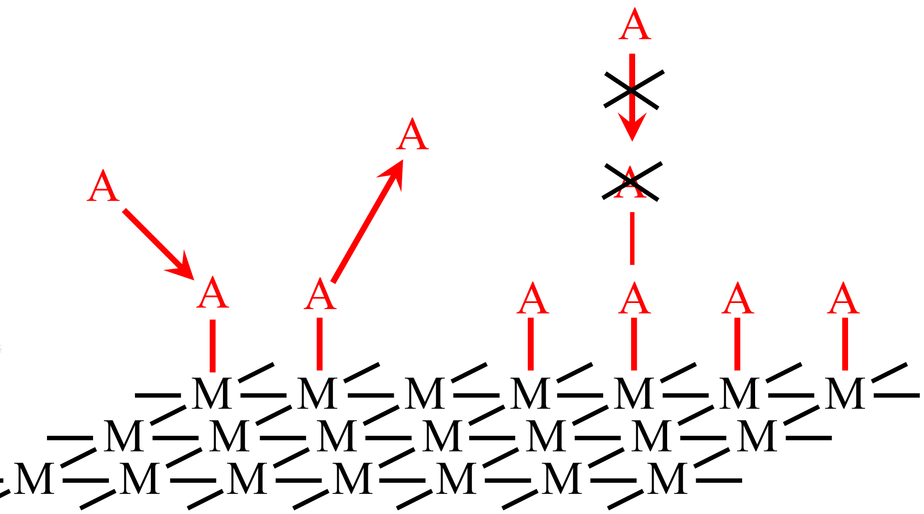
The Thermodynamics of Adsorption - Adsorption Isotherms

constant T

$$\text{Fractional Coverage of A} \equiv \theta_A = \frac{\text{adsorption sites occupied by A}}{\text{total adsorption sites}}$$



need $\theta_A = f(P_A)$



Langmuir Isotherm.

Assumes $\Delta \overline{H}_{ads}$ is independent of surface coverage.

Assumes only a single layer of adsorbed A.

excellent model for P_A < vapor pressure of A.

$$A + M \underset{k_{des,A}}{\overset{k_{ads,A}}{\rightleftarrows}} M\text{-}A$$

At equilibrium: $k_{ads,A}[A][M] = k_{des,A}[M\text{-}A]$

need [M] = …, [M-A] = …

The Thermodynamics of Adsorption - Adsorption Isotherms

$$\mathrm{A} + \mathrm{M} \underset{k_{\mathrm{des,\,A}}}{\overset{k_{\mathrm{ads,\,A}}}{\rightleftarrows}} \mathrm{M\text{-}A}$$

At equilibrium: $k_{\mathrm{ads,\,A}}[\mathrm{A}][\mathrm{M}] = k_{\mathrm{des,\,A}}[\mathrm{M\text{-}A}]$ need [M] = …, [M-A] = …

total concentration of adsorption sites $\equiv [\mathrm{M}]_0 = [\mathrm{M}] + [\mathrm{M\text{-}A}]$

substitute

from the definition of θ_A: $$\theta_A = \frac{[\mathrm{M\text{-}A}]}{[\mathrm{M}]_0} \Rightarrow [\mathrm{M\text{-}A}] = \theta_A[\mathrm{M}]_0$$

$$\theta_A = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{M}]_0} \Rightarrow [\mathrm{M}] = (1-\theta_A)[\mathrm{M}]_0$$

$$k_{\mathrm{ads,\,A}}[\mathrm{A}](1-\theta_A)\cancel{[\mathrm{M}]_0} = k_{\mathrm{des,\,A}}\theta_A\cancel{[\mathrm{M}]_0}$$

Define $K_A \equiv \dfrac{k_{\mathrm{ads,\,A}}}{k_{\mathrm{des,\,A}}}$ $\Rightarrow$ $K_A[\mathrm{A}](1-\theta_A) = \theta_A$ $\Rightarrow$ $\boxed{\theta_A = \dfrac{K_A[\mathrm{A}]}{1+K_A[\mathrm{A}]}}$

Convert [A] to P_A: $[\mathrm{A}] = \dfrac{n_A}{V} = \dfrac{P_A}{RT}$ $\Rightarrow$ $\boxed{\theta_A = \dfrac{\dfrac{K_A}{RT}P_A}{1+\dfrac{K_A}{RT}P_A}}$

[A] is awkward for reactor design.

The Thermodynamics of Adsorption - Adsorption Isotherms

Using the Langmuir Isotherm in Rate Equations.

Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

A Langmuir-Hinshelwood Mechanism of Elementary Reactions:

$$A + M \underset{k_{des,A}}{\overset{k_{ads,A}}{\rightleftarrows}} M\text{-}A \qquad \text{adsorption}$$

$$M\text{-}A \xrightarrow{k_{surface}} M\text{-}P \qquad \text{surface reaction}$$

$$M\text{-}P \underset{k_{ads,P}}{\overset{k_{des,P}}{\rightleftarrows}} M + P \qquad \text{desorption}$$

Need expressions for [M-A] and [M-P] to derive the rate equation.

Assume Langmuir Isotherms for the adsorption/desorption of A and P.

This assumption allows one to write –

$$k_{ads,\,A}[M][A] = k_{des,\,A}[M\text{-}A] \quad \text{and} \quad k_{ads,\,P}[M][P] = k_{des,\,P}[M\text{-}P]$$

This assumption yields two useful expressions:

$$\boxed{[M\text{-}A] = K_{ads,\,A}[M][A]} \quad \text{and} \quad \boxed{[M\text{-}P] = K_{ads,\,P}[M][P]}$$

Rate Equations for Heterogeneously-Catalyzed Reactions

Recall our goal for Chemical Kinetics:

Given the Overall Reaction and Rate Equation,
devise a Mechanism of Elementary Reactions.

Recall our Strategy:

Gain experience by starting with
a Mechanism of Elementary Reactions
and deriving the Rate Equation.

Heterogeneous Catalysis: Case Study 1

metal catalyst

Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

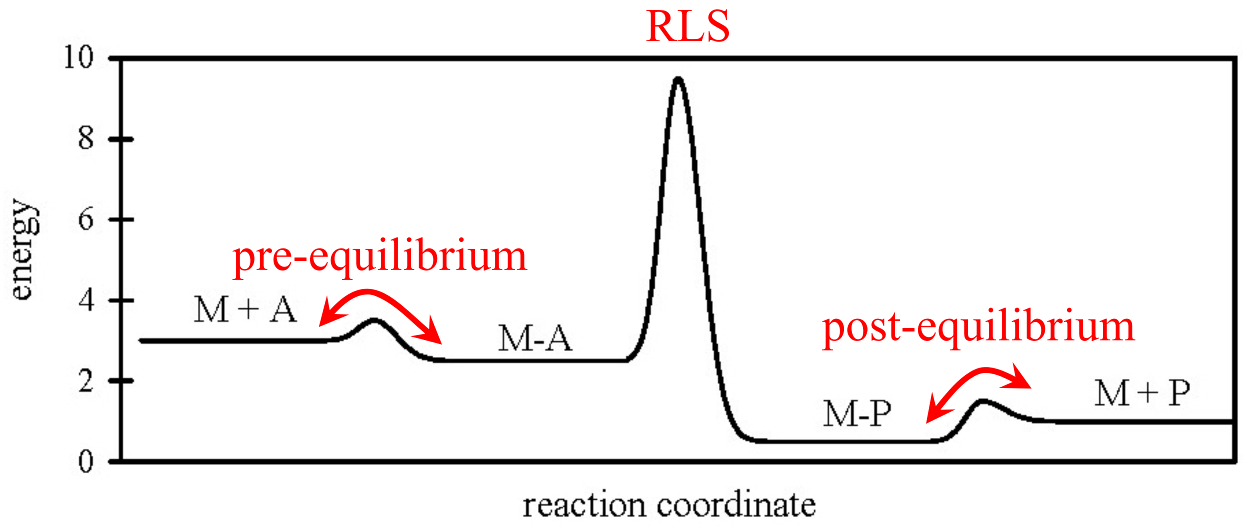
A Langmuir-Hinshelwood Mechanism of Elementary Reactions:

$$A + M \underset{k_{des,A}}{\overset{k_{ads,A}}{\rightleftarrows}} M\text{-}A$$ adsorption

$$M\text{-}A \xrightarrow{k_{surface}} M\text{-}P$$ surface reaction

$$M\text{-}P \underset{k_{ads,P}}{\overset{k_{des,P}}{\rightleftarrows}} M + P$$ desorption

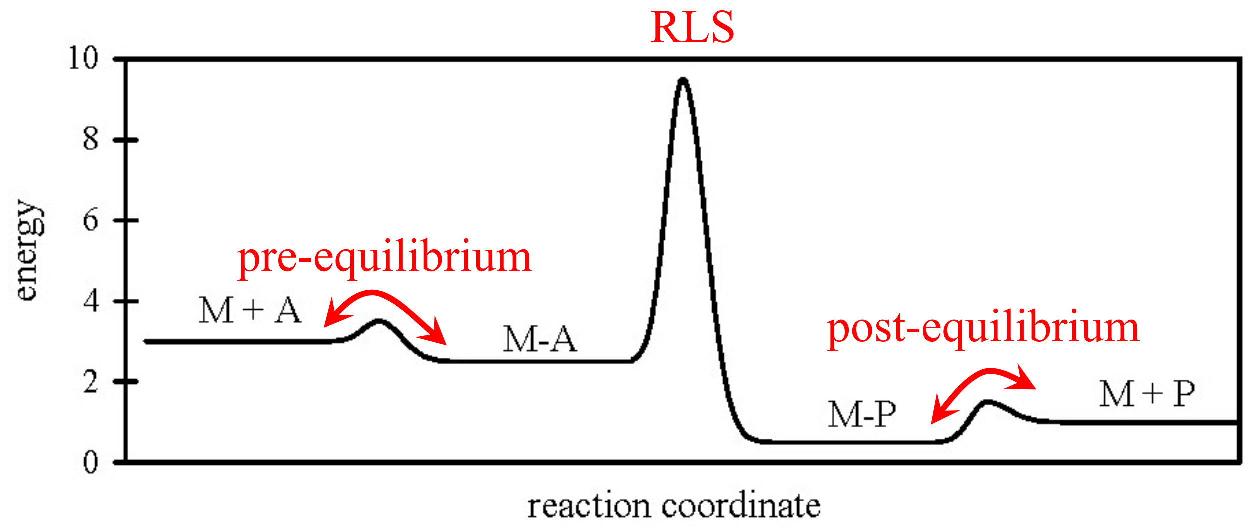
Example 1.



Heterogeneous Catalysis: Case Study 1 - Example 1

Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

Example 1.



Because the surface reaction is the RLS: $\frac{d[P]}{dt} = k_s[M\text{-}A]$

$$[M\text{-}A] = \theta_A[M]_0 = \boxed{\frac{[M\text{-}A]}{[M] + [M\text{-}A] + [M\text{-}P]}}[M]_0 = \frac{K_{ads,A}[A]\cancel{[M]}}{\cancel{[M]} + K_{ads,A}[A]\cancel{[M]} + K_{ads,P}[P]\cancel{[M]}}[M]_0$$

Assume Langmuir Isotherms for A and P.

instead, jump to this

$$[M\text{-}A] = \frac{K_{ads,A}[A]}{1 + K_{ads,A}[A] + K_{ads,P}[P]}[M]_0$$

$$\frac{d[P]}{dt} = k_s[M\text{-}A] = \boxed{\frac{k_s K_{ads,A}[A]}{1 + \underline{K_{ads,A}[A]} + \underline{K_{ads,P}[P]}}[M]_0}$$

unoccupied M sites

M-A sites

M-P sites

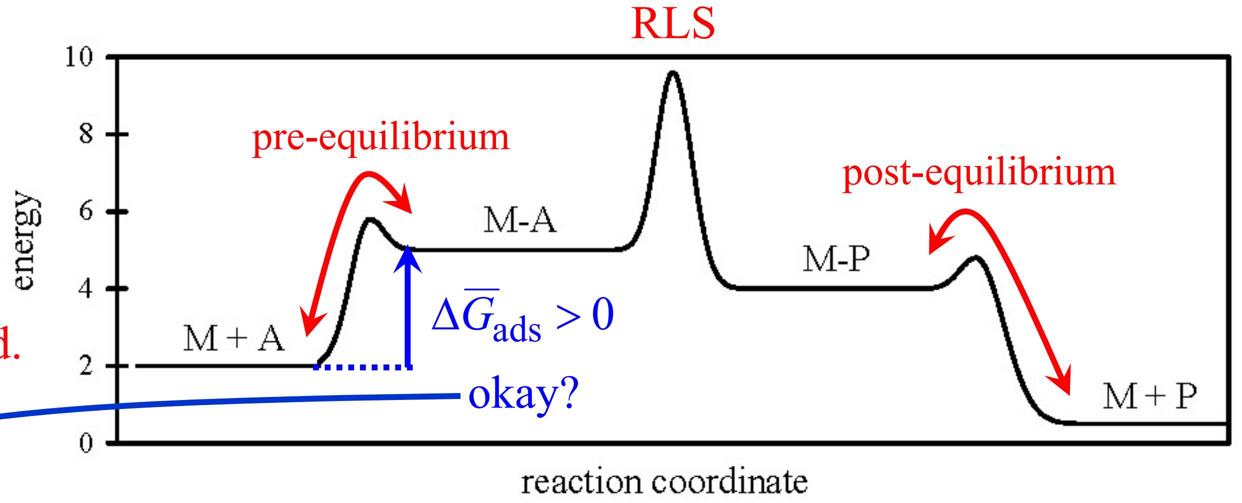
Heterogeneous Catalysis: Case Study 1 - Example 2

Overall Reaction: $\mathrm{A_{(gas)}} \xrightarrow{\mathrm{M}} \mathrm{P_{(gas)}}$

Example 2.

A and P are weakly adsorbed.

surface sites are mostly unoccupied.



assume
Langmuir isotherms

$$[\mathrm{M}] \gg [\mathrm{M\text{-}A}], [\mathrm{M\text{-}P}] \quad \Rightarrow \quad 1 \gg K_{\mathrm{ads,A}}, K_{\mathrm{ads,\,P}}$$

$$\frac{d[\mathrm{P}]}{dt} = \underset{\text{RLS}}{\underline{k_{\mathrm{s}}[\mathrm{M\text{-}A}]}} = \frac{k_{\mathrm{s}} K_{\mathrm{ads,A}}[\mathrm{A}]}{1 + \cancelto{0}{K_{\mathrm{ads,A}}[\mathrm{A}]} + \cancelto{0}{K_{\mathrm{ads,P}}[\mathrm{P}]}}[\mathrm{M}]_0 \approx \boxed{k_{\mathrm{s}} K_{\mathrm{ads,A}}[\mathrm{A}][\mathrm{M}]_0}$$

clue in rate equation:
denominator = 1

although $\Delta\bar{H}_{\mathrm{ads}} < 0$ (exothermic),

may have $\Delta\bar{G}_{\mathrm{ads}} > 0$ because

$\Delta\bar{G}_{\mathrm{ads}} = \Delta\bar{H}_{\mathrm{ads}} - T\Delta\bar{S}_{\mathrm{ads}}$

and $\Delta\bar{S}_{\mathrm{ads}} < 0$

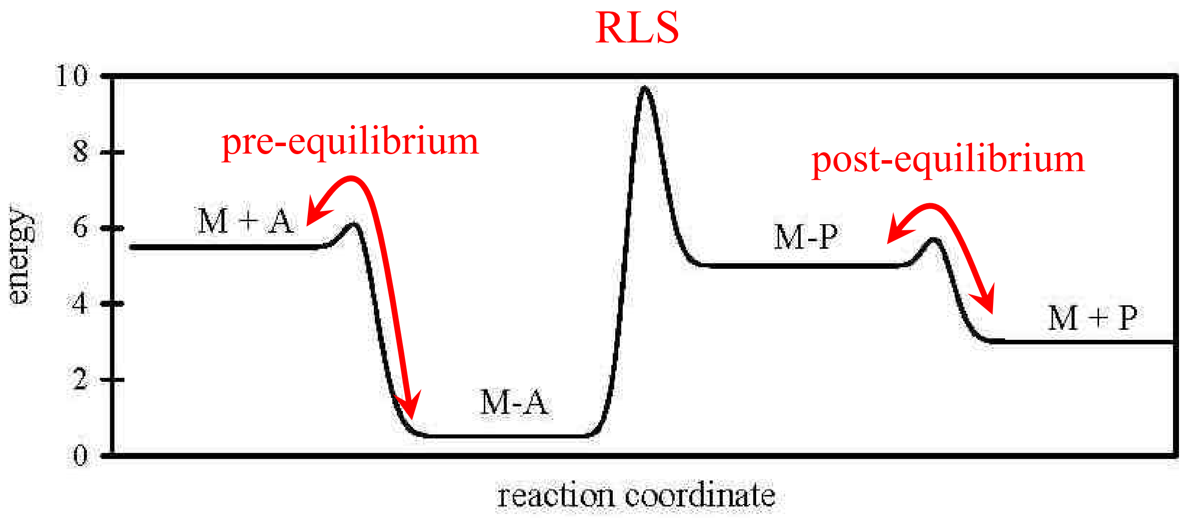
Heterogeneous Catalysis: Case Study 1 - Example 3

Case Study 1. Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

Example 3.

A is strongly adsorbed.
P is weakly adsorbed.

surface sites are
mostly occupied by A.



assume
Langmuir isotherms

$$[M\text{-}A] \gg [M], [M\text{-}P] \quad \Rightarrow \quad K_{ads,A} \gg 1, K_{ads,P}$$

Clues in rate equation:
1. denominator = 1
2. No [A] term.

$$\frac{d[P]}{dt} = \underbrace{k_s[M\text{-}A]}_{\text{RLS}} = \frac{k_s K_{ads,A}\cancel{[A]}}{\cancelto{0}{1} + K_{ads,A}\cancel{[A]} + \cancelto{0}{K_{ads,P}[P]}}[M]_0 \approx \boxed{k_s[M]_0}$$

Rate is independent of [A]! How can this be?

The RLS is proportional to [M-A]. Increasing [A] does not increase [M-A] because the surface is saturated with adsorbed A.

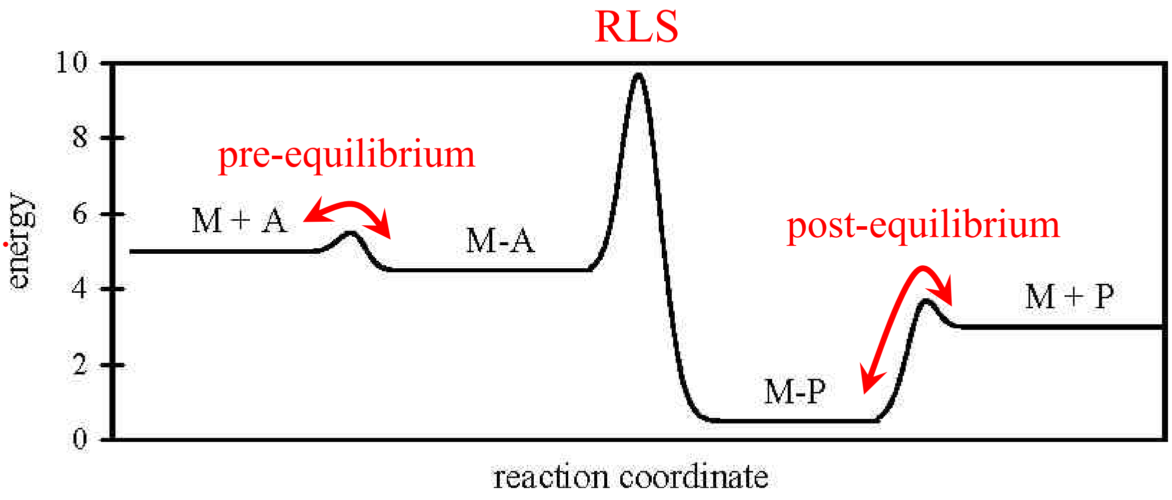
Heterogeneous Catalysis: Case Study 1 - Example 4

Case Study 1. Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

Example 4.

A is weakly adsorbed.
P is strongly adsorbed.

surface sites are
mostly occupied by P.



assume
Langmuir isotherms

clue in rate equation:
denominator contains
only a [P] term.

$$[M\text{-}P] \gg [M], [M\text{-}A] \quad \Rightarrow \quad K_{ads,P} \gg 1, K_{ads,A}$$

$$\frac{d[P]}{dt} = \underset{\text{RLS}}{\underline{k_s[M\text{-}A]}} = \frac{k_s K_{ads,A}[A]}{\cancelto{0}{1} + \cancelto{0}{K_{ads,A}[A]} + K_{ads,P}[P]}[M]_0 \approx \boxed{\frac{k_s K_{ads,A}}{K_{ads,P}}\frac{[A]}{[P]}[M]_0}$$

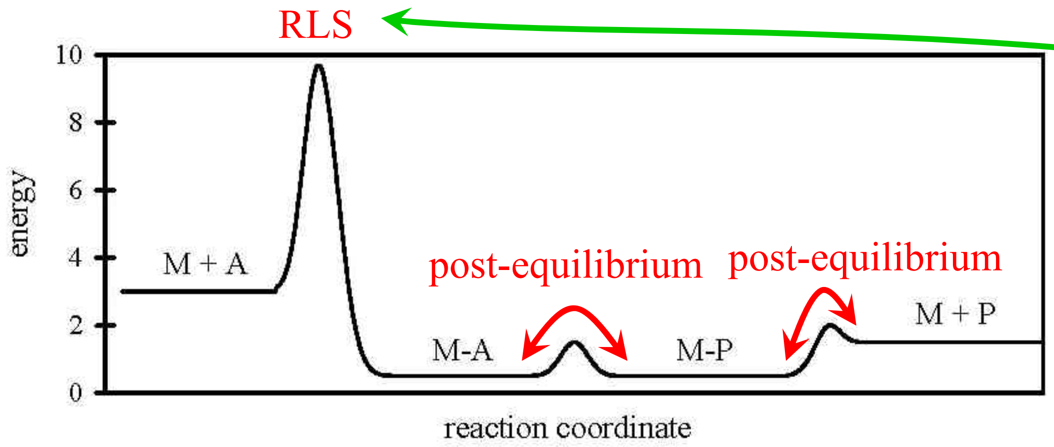
The product P in an *irreversible* reaction hinders the reaction! How can this be?

P monopolizes the surface sites, which reduces [M-A].

Heterogeneous Catalysis: Case Study 1 - Example 5

Case Study 1. Overall Reaction: $A_{(gas)} \xrightarrow{M} P_{(gas)}$

Example 5.



by definition

$$\text{RLS:}\ \frac{d[P]}{dt} = k_{ads,A}[A][M] \qquad [M] = \theta_{empty}[M]_0 = \boxed{\frac{[M]}{[M] + [M\text{-}A] + [M\text{-}P]}}[M]_0$$

Assume Langmuir Isotherm for P. $[M\text{-}P] = \boxed{K_{ads,P}[P][M]}$

Assume post-equilibrium for surface reaction: $k_s[M\text{-}A] = k_{-s}\boxed{[M\text{-}P]} = k_{-s}K_{ads,P}[P][M]$

$$[M] = \frac{\cancel{[M]}}{\cancel{[M]} + \frac{k_{-s}}{k_s}K_{ads,P}[P]\cancel{[M]} + K_{ads,P}[P]\cancel{[M]}}[M]_0 = \frac{1}{1 + K_{ads,P}\left(1 + \frac{k_{-s}}{k_s}\right)[P]}[M]_0$$

$$\frac{d[P]}{dt} = \underset{\text{RLS}}{\underline{k_{ads,A}[A][M]}}\ \boxed{= \frac{k_{ads,A}[A]}{1 + K_{ads,P}\left(1 + \frac{k_{-s}}{k_s}\right)[P]}[M]_0}$$

clues in rate equation: denominator contains ‘unoccupied sites” term ***and*** [P] term.