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Chemistry 12

Reaction Kinetics III

Name:
Date:
Block:

1. **Catalysts**
2. **Mechanisms**

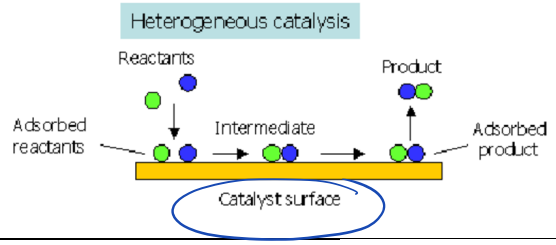
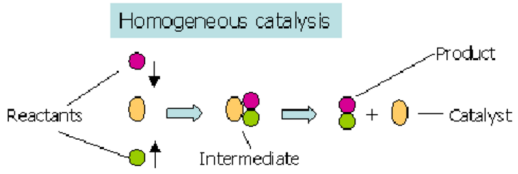
Catalysts

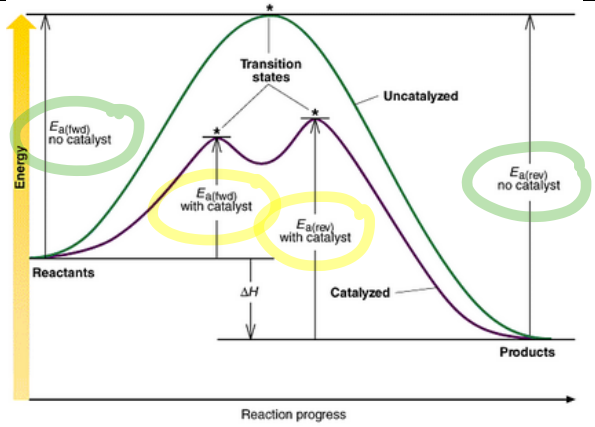
Catalysts provide an alternate reaction pathway in which a different, lower-energy activated complex can form.

- Catalysts must be consumed in one step of a reaction mechanism and regenerated in a later step.

reactant product

There are two types of catalysts:

Heterogeneous	Homogeneous
• The catalyst is in a different phase from the reactants. • Typical example: solid catalyst with reactants as either liquids or gases	• The catalyst is in the same phase as the reactants.
	



It is known that compounds called ***chlorofluorocarbons*** (C.F.C.s) (eg. $CFCl_3$) will break up in the presence of ultraviolet radiation, such as found in the upper atmosphere, forming single chlorine atoms:

$$CFCl_3 \rightarrow CFCl_2 + Cl$$

The Cl atoms then react with Ozone (O_3) as outlined in the following mechanism.

Step 1: $Cl + O_3 \rightarrow ClO + O_2$

Step 2: $ClO + O \rightarrow Cl + O_2$

Overall: $O_3 + O \rightarrow 2O_2$

↳ Multi-step

Cl = Catalyst

ClO = Intermediate

Mechanisms

A reaction mechanism is a series of steps that may be added together to give an overall chemical reaction.

- Cannot be determined by just looking at overall reaction.
- Deduced through much study and research (up to years)
- **You will not be asked to come up with mechanism from scratch.**
- Some mechanisms are known, however, many are yet to be discovered.

Step 1: A + B → C + D

Step 2: D + E → B + F

Overall: A + E → C + F

Intermediate: D

Catalyst: B

Each step is called an elementary step.

Intermediate:

- A species that is produced in one step and then reacted in a later step.
- Cancelled out and not included in the overall reaction

appears as a product 1st, then as a reactant

Catalyst:

- A species that is reacted in one step and then produced in a later step.
- Cancelled out and not included in the overall reaction

vice versa

Overall Reaction:

- Comprised of the species that are not cancelled out

Example: *(known mechanism)*

$4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

Unlikely to occur in one step because it requires 5 molecules to find each other with favourable geometry and sufficient energy.

Mechanism: *(determined from lots of research)*

Step 1: $HBr + O_2 \rightarrow HOOBr$ (slow)

Step 2: $HBr + HOOBr \rightarrow 2\ HOBr$ (fast)

Step 3: $2\ HOBr + 2\ HBr \rightarrow 2\ H_2O + 2\ Br_2$ (moderate)

Overall: $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

Intermediates: HOOBr, 2 HOBr

Catalyst: (none)

Rate determining step (RDS) - the slowest step in the mechanism.

- This step determines the **overall rate** for the whole reaction.
- Since each step occurs sequentially, the only way to speed up an overall reaction is to speed up the RDS (eg. by increasing the concentration of a reactant in the RDS)

Practice 1:
Determine the overall reaction, intermediates and catalysts for the following mechanism:

Step 1: $A + 2X \rightarrow AX_2$

Step 2: $AX_2 + B \rightarrow AB + X_2$

Step 3: $AB + A \rightarrow A_2 + B$

Overall: $2A + 2X \rightarrow A_2 + X_2$

Intermediates: AX_2, AB Catalysts: B

Practice 2:
Determine the 3rd step, intermediates and catalysts of the following mechanism:

Step 1: $A^{4+} + C^{2+} \rightarrow C^{3+} + A^{3+}$

Step 2: $A^{4+} + C^{3+} \rightarrow C^{4+} + A^{3+}$

Step 3: $B^{+} + C^{4+} \rightarrow C^{2+} + B^{3+}$

Overall: $2A^{4+} + B^{+} \rightarrow 2A^{3+} + B^{3+}$

Intermediates: C^{3+} C^{4+} Catalysts: C^{2+}

Practice 3:
Determine the 2nd step, intermediates and catalysts of the following mechanism:

Step 1: $Cl_2 \rightarrow Cl + Cl$

Step 2: $CHCl_3 + Cl \rightarrow CCl_3 + HCl$

Step 3: $Cl + CCl_3 \rightarrow CCl_4$

Overall: $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$

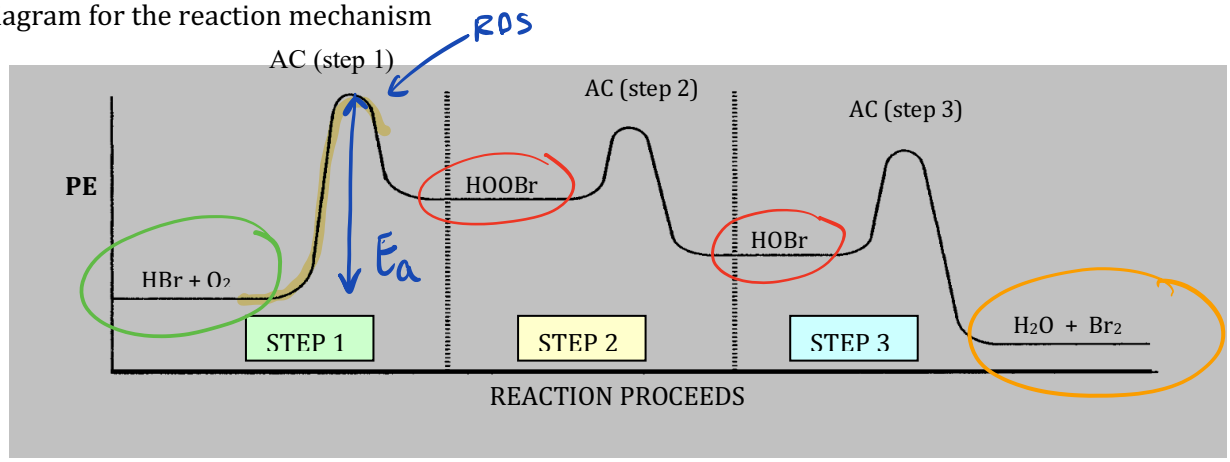
Intermediates: Cl CCl_3 Catalysts: (none)

Returning back to...

$4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$ RDS

Step 1: $HBr + O_2 \rightarrow HOOBr$ (slow)
Step 2: $HBr + HOOBr \rightarrow 2\ HOBr$ (fast)
Step 3: $2\ HOBr + 2\ HBr \rightarrow 2\ H_2O + 2\ Br_2$ (moderate)

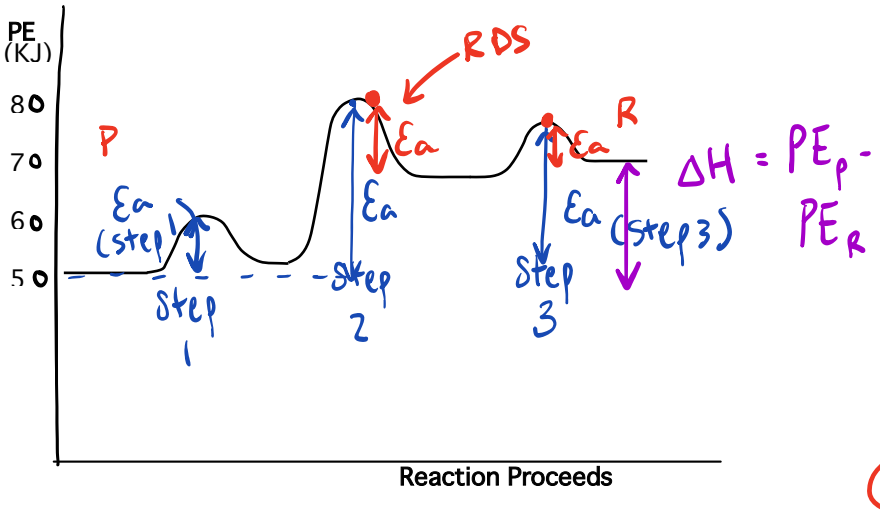
PE diagram for the reaction mechanism



Notes:

- Each "bump" is a step.
- The **higher** the bump, (greater Ea) the slower the step.
- The **highest** bump (from the reactants level) is for the RDS.
- **AC's** at top of bumps, **intermediates** in middle "valleys", **products** in the final "valley".
- The Ea for the forward **overall reaction** is vertical distance from reactants to **top** of **highest bump**.

Given the following Potential Energy Diagram for a reaction mechanism:



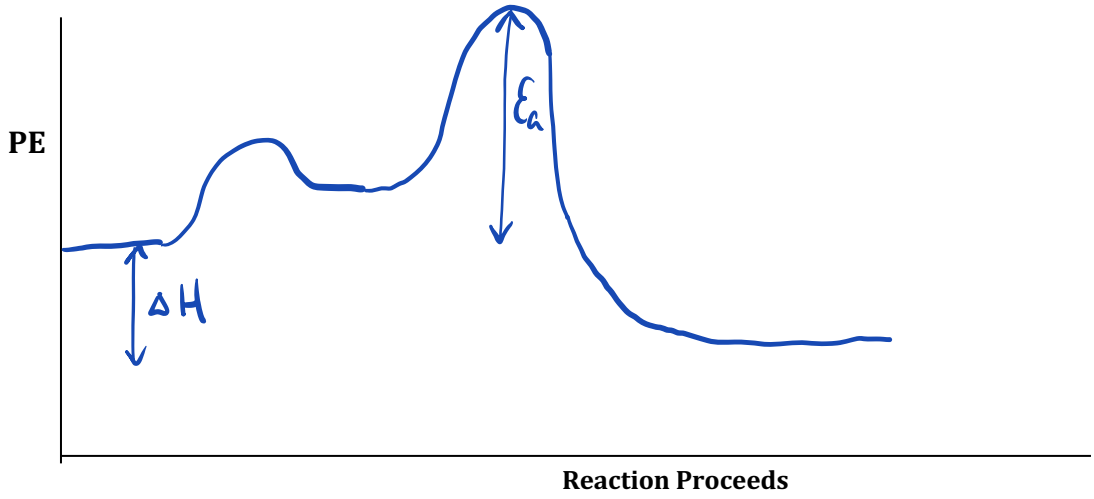
1. This mechanism has 3 steps. Number each step.
2. Ea for overall reaction = 30 kJ
3. Step 2 is the RDS
4. Step 1 is the fastest step.
5. The overall reaction is endo thermic.
6. ΔH = 20 kJ
7. ΔH for **reverse** rx. = -20 kJ
8. Ea (reverse rx.) = 10 kJ
9. RDS for **reverse** reaction is step 2

small bump

big bump

Draw a **Potential Energy Diagram** for a **reaction mechanism** with **2 steps**.

- The first step is **fast** and the second step is **slow**.
- The first step is **endothermic** and the second step is **exothermic.**
- The overall reaction is **exothermic**.
- With **labeled arrows** show the **overall Activation Energy (E_a)** and the **ΔH** for the **forward** reaction.



1. In the following reaction mechanisms, identify:
   i. The catalyst
   ii. The reaction intermediates
   iii. The overall reaction

a) 2 NO → ~~N_2O_2~~
~~N_2O_2~~ + H_2 → ~~N_2O~~ + H_2O
~~N_2O~~ + H_2 → N_2 + H_2O

i. (none) ii. N_2O_2, N_2O iii. $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

b) A + B → ~~C~~
~~C~~ + ~~D~~ → ~~E~~ + F
~~E~~ + B → ~~D~~ + F

i. D ii. C, E iii. $A + 2B \rightarrow 2F$

2. "All catalyzed reaction mechanisms have more than one step." Why must this statement be true?

A catalyst must be consumed in one step and regenerated in another

3. Suppose a catalyzed reaction is occurring in a reaction container. If the catalyst were removed what would happen to the rate of reaction? Explain your answer.

Your reaction would slow down.

4. Consider the following reaction mechanism:
   X + Y → Z (very fast)
   Z + Y → P (slow)
   P + Y → Q (very fast)
   Suppose there were a catalyst that would work on step 1 and another catalyst that would work on step 2. Which catalyst would be ineffective in increasing the overall reaction? Why?

   The catalyst in step 1 would be ineffective
   ↳ In order to ↑ the overall rxn rate, we must speed up the RDS.

5. Consider the following reaction:

   $$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

   The rate law is found through experiments to be rate = $k[NO]^2$.

   A valid mechanism is consistent with the overall equation and the experimentally-determined rate law. Which of the following proposed mechanisms is consistent with the reaction data? Explain your answer.

   Mechanism 1:

(1)	$NO + O_2 \rightarrow NO_2 + O$	slow
(2)	$NO + O \rightarrow NO_2$	fast

   Mechanism 2:

(1)	$NO + O_2 \rightarrow NO_3$	fast
(2)	$NO_3 + NO \rightarrow 2\ NO_2$	slow

   Mechanism 3:

(1)	$2\ NO \rightarrow N_2O_2$	slow
(2)	$N_2O_2 + O_2 \rightarrow 2\ NO_2$	fast

Complete Reaction Mechanisms Worksheet

Hebden Workbook
Pg. 28 #46, 53
Pg. 34 #56, 57, 59, 60, 61