CH15 The Effect of Temperature & Catalyst on Reaction Rate

15.1 Activation Energy and Arrhenius Equation

Check point 15-1

Determine the activation energy of the reaction

A + B ➔ C

Using the data provided only

Temperature (K)	Rate Constant (mol dm^{-3})
350	0.096
400	0.400

Gas constant R = 8.314 JK^{-1} mol^{-1}

Solution:

$$\ln\frac{k_1}{k_2} = -\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{0.096}{0.400} = -\frac{Ea}{8.314}\left(\frac{1}{350} - \frac{1}{400}\right)$$

$-1.4271 = -4.2957 \times 10^{-5} Ea$

Ea = $\underline{33.2217 kJ\ mol^{-1}}$

15.3 Energy Profile

How does the following reaction carry out?

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + Br^- + H^+$$

Hydrolysis of 2-bromo-2-methylpropane is a multi-stage Reaction

Stage 1

(slow)

Stage 2

(fast)

Reaction energy profile

Note:

Slow step ➔ ⇧ Ea

Fast step ➔ ⇩ Ea

c.f.

Activated complex	Intermediate
1. It is very stable. 2. It CANNOT be isolated. 3. Its structured is usually unknown.	1. It is meta-stable. 2. It may be isolated 3. Its structure may be deduced.

Reaction mechanism **反應機理**

Chemical reactions usually take place in series of elementary steps. The series of elementary steps for the *conversion* of reactants to products is called a reaction mechanism.

Rate determining step (**RDS**) **速度控制步驟**

Consider a multi-step Rx

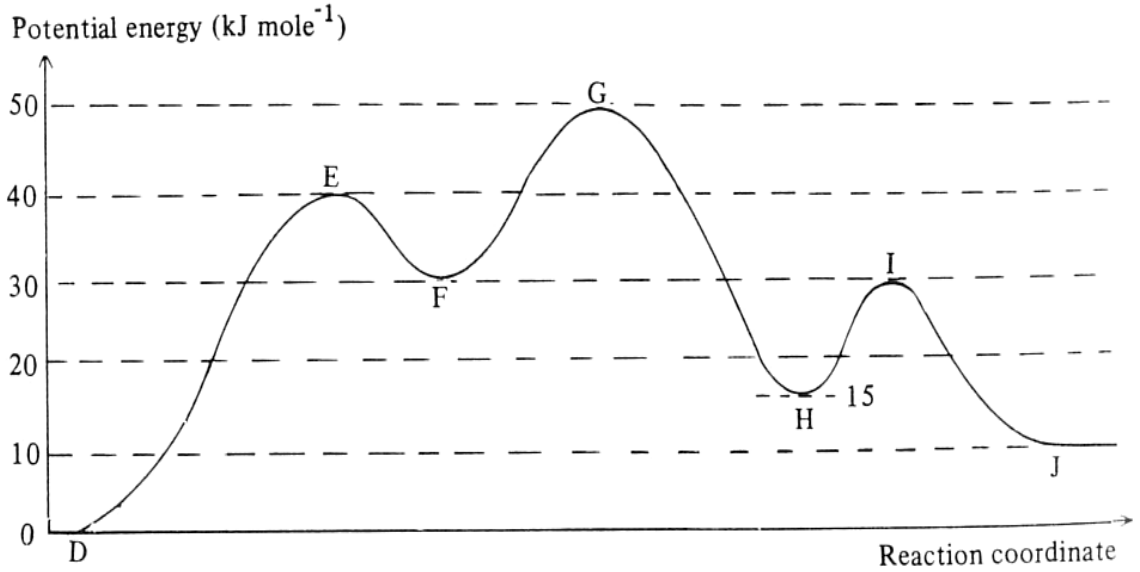
Step 1 $A \rightarrow I_1$ (slow)

Step 2 $I_1 \rightarrow I_2$ (fast)

Step 3 $I_2 \rightarrow B$ (fast)

Which step is the **rate determining step** of the overall reaction?

Check-Point



Questions

1. What are represented by point F and G?
2. What is ΔH of the reaction D ➔ J?
3. Which is the fastest step of the reaction? Why?
4. Which is the rate determining step of the reaction D ➔ J? Why?

(1978 HKCU)

Answers

1. F is intermediate.

   G is an activated complex or a transition state

2. P.E of J – P.E. of D

   = 10 – 0

   = 10 kJ mol^{-1}

3. The fastest step H ➔ J.

   Because the activation energy is the lowest.

4. The rate determining step is D ➔ F.

   Because the activation energy is the highest.

Single-stage Reaction

A—B + C ➔ A + B—C

A—B + C ➔ [A···B···C] ➔ A + B—C

transition state

e.g.
Substitution of 1-bromobutane and H_2O

Multi-stage Reaction

Stage 1	D—E	➔	Intermediate	(slow)
+) Stage 2	Intermediate + F	➔	D—F + E	(fast)
Overall	**D—E + F**	➔	**D—F + E**	

Which stage is slower? Why?

Stage 1. Because ⇧Ea ➔ ⇩Rx rate

e.g.

Hydrolysis of 2-bromo-2-methylproprane.

Check-Point

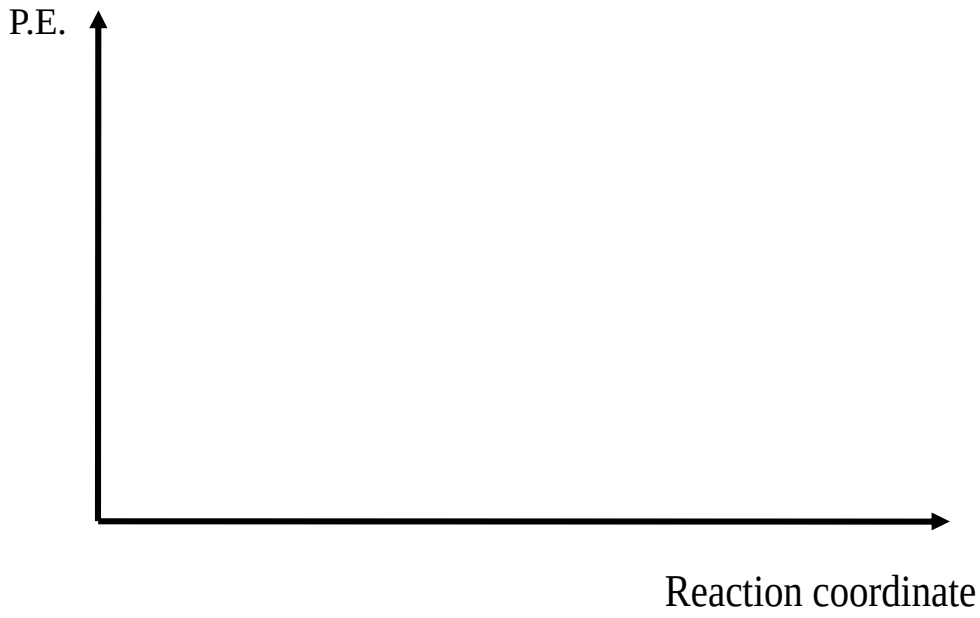
$2A + B_2 \rightarrow 2AB \qquad \Delta H = +ve$

It proceeds in 2 steps

Step 1: $A + B_2 \rightarrow I$ (slow)

Step 2: $I + A \rightarrow 2AB$ (fast)

Q1. Sketch an energy profile



15.4 Catalysts

What is a catalyst?

- A catalyst is a substance that can **change the rate of a reaction** but remains **chemically unchanged** at the end of the reaction.
- A catalyst works by providing an **alternative pathway for the reaction**.

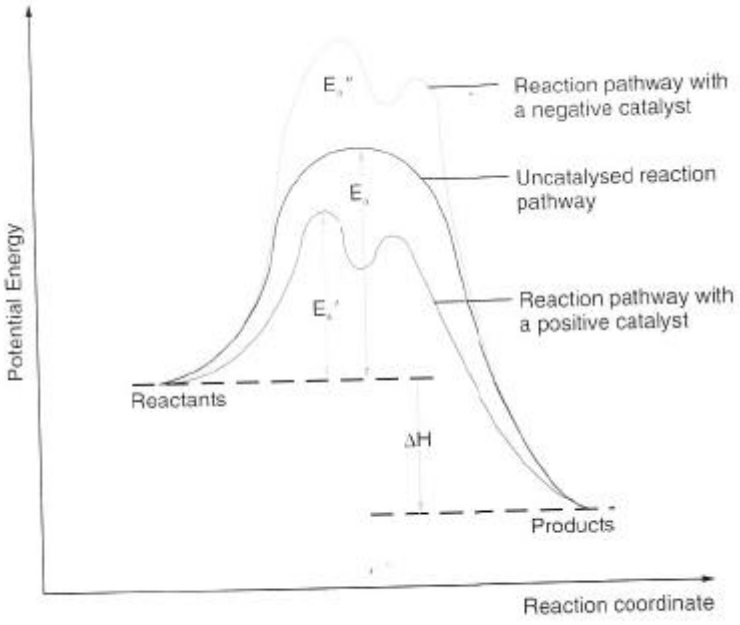


Fig.15-15 *Energy profiles of catalysed and uncatalysed reaction pathways*

Positive catalysts ➔ ⇧reaction rate

Negative catalysts ➔ ⇩reaction rate

What are the characteristics of catalysis?

1. The amount of catalyst needed

   Theoretically, a **small** amount of catalyst is enough as it is NOT used up.
2. Specificity

   One catalyst is often specific to a certain Rx.
3. Promoters

   ➔ +ve catalysts
4. Inhibitor

   ➔ -ve catalysts
5. Poisoning

   The efficiency of a catalyst may be ⇩ by impurities.
6. Autocatalysis

   One of the products formed in the reaction catalyses the reaction

   e.g.

   $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq)$

   ➔ $\underline{2Mn^{2+}}(aq) + 5O_2(g) + 8H_2O(l)$

Classification of catalysts

1. Homogeneous catalysis

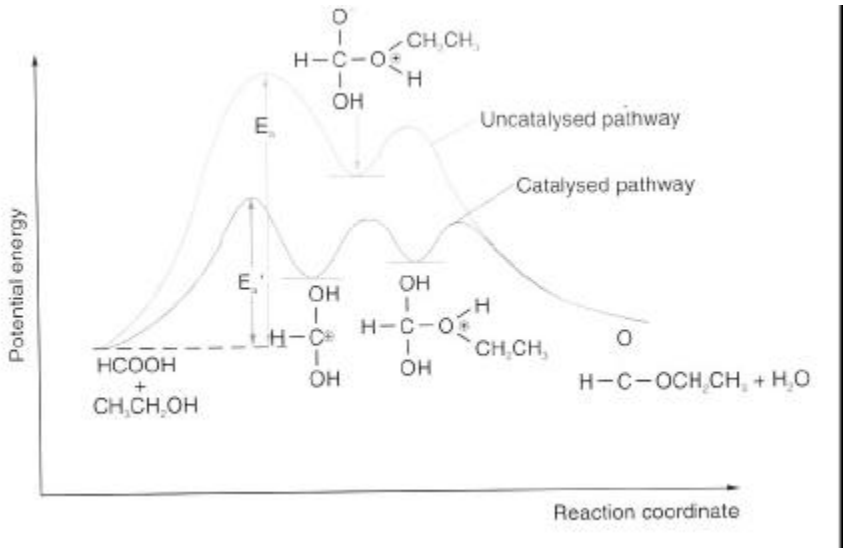
Catalyst and reactants are in the **same phase**, e.g. both are in liquid phase

■ Intermediate formation

e.g Esterification of CHOOH and CH_3OH

Uncatalysed:

Catalysed:

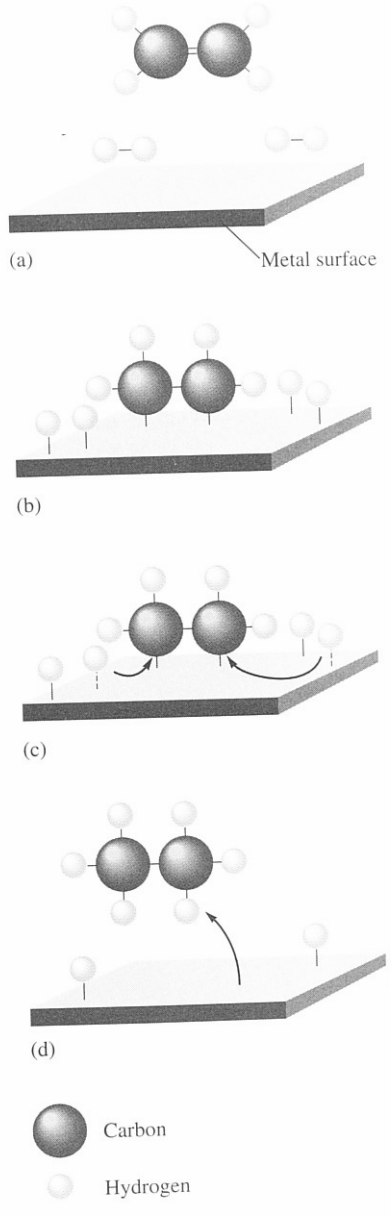


2. Heterogeneous catalysts

Catalyst and reactants are in **different phases**, e.g. reactants in liquid phase, catalyst in solid phase.

- The reactants are adsorbed on the surface of the catalysts,
- Where bonds are broken and new bonds are formed.
- The products are then desorbed from the surface.

e.g Hydrogenation of alkene



Many biological processes are catalysed by protein called enzyme. However, enzyme-catalysed reactions do not obey the Arrhenius equation. WHY?