CH 209 – Basic Organic Chemistry

Reaction mechanisms: Reaction coordinate diagrams, Kinetic vs thermodynamic control

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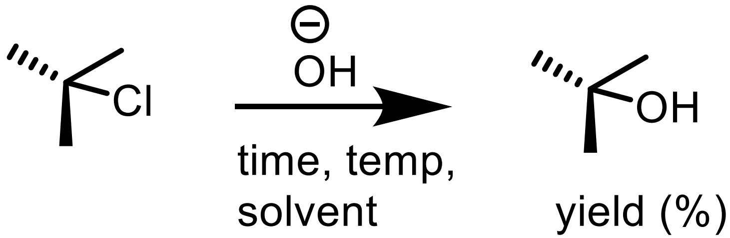
Representing reactions

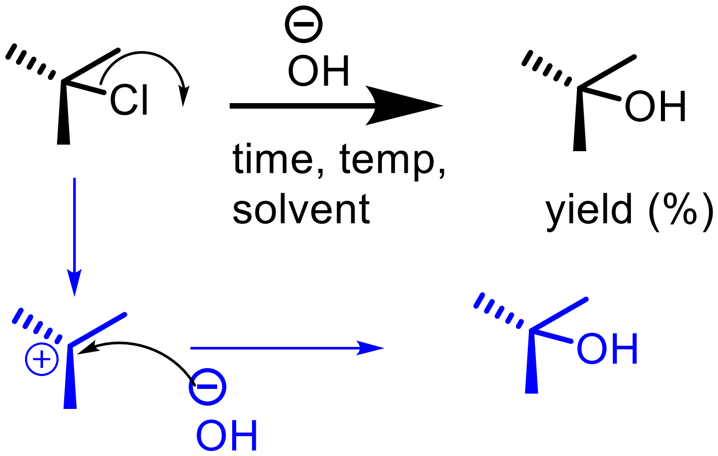


- a chloride being replaced by an OH and now your nucleophile here is OH^-.
- Substitution reaction (S_N1)

1) What information do you get when you look at this?

2) What information do you not get?

Representing reactions



- a chloride being replaced by an OH and now your nucleophile here is OH^-.
- Substitution reaction S_N1

1. What information do you get when you look at this?

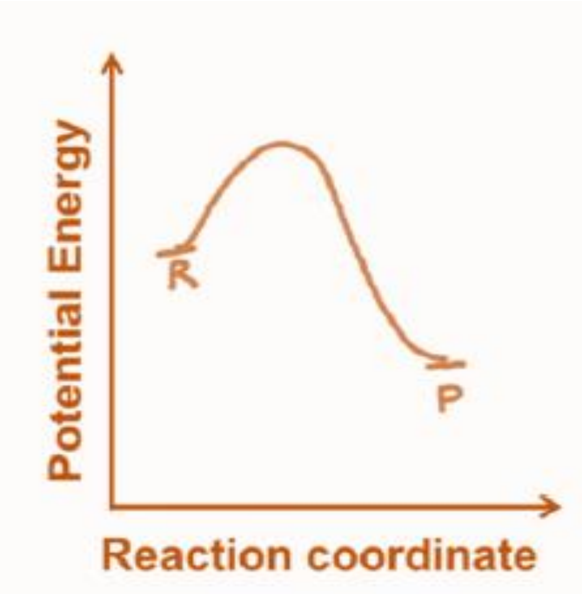
- The reactants
- The reaction conditions
- Can be deduced – the reaction mechanism

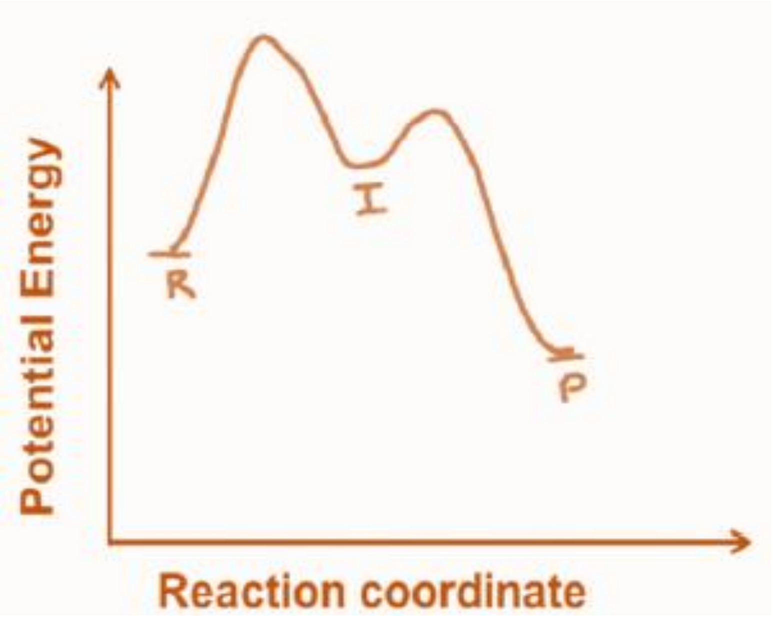
2. What information do you not get?

- Stability of reagents and steps involved
- Energetics of the reaction

Let us look at the stability of the reactions and steps involved!

Understanding reaction coordinate diagram

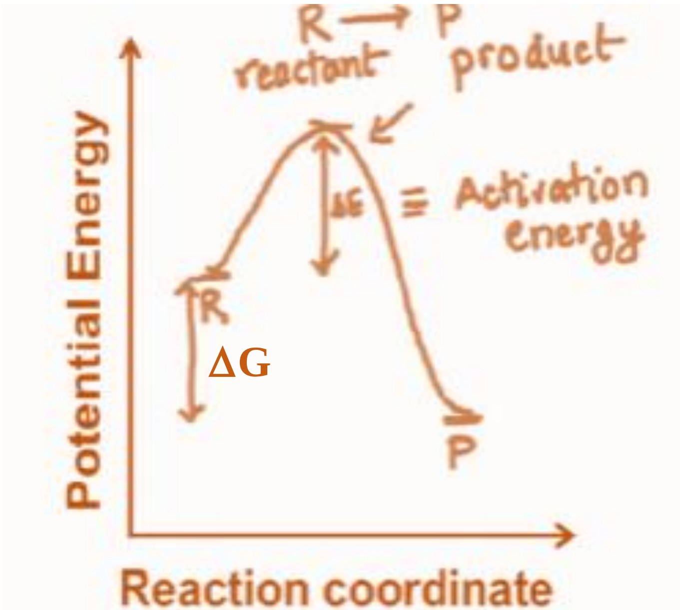


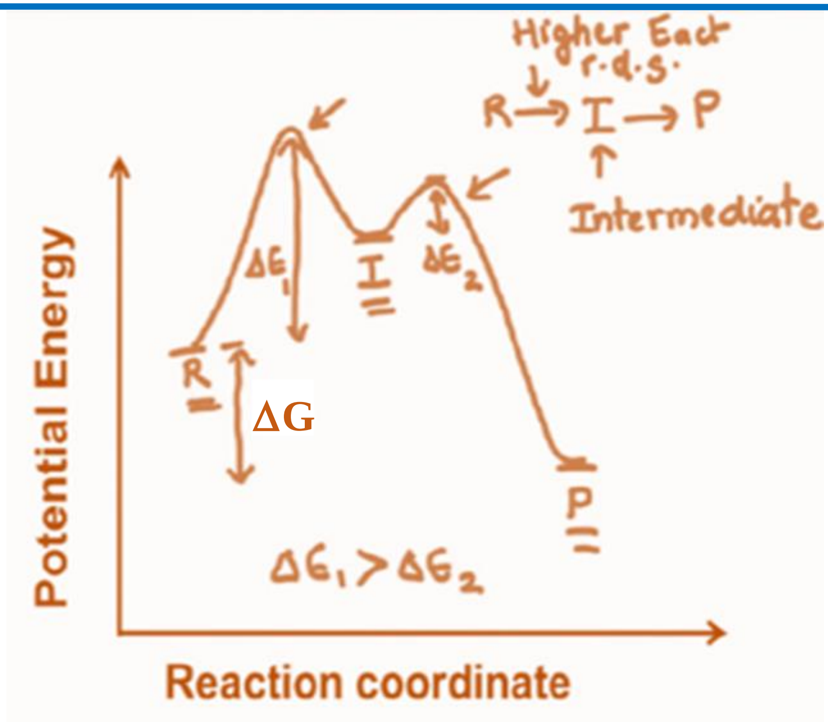


When you look at a diagram like this what exactly does it represent?

What is the physical significance of the Y-axis and the X-axis?

Understanding reaction coordinate diagram

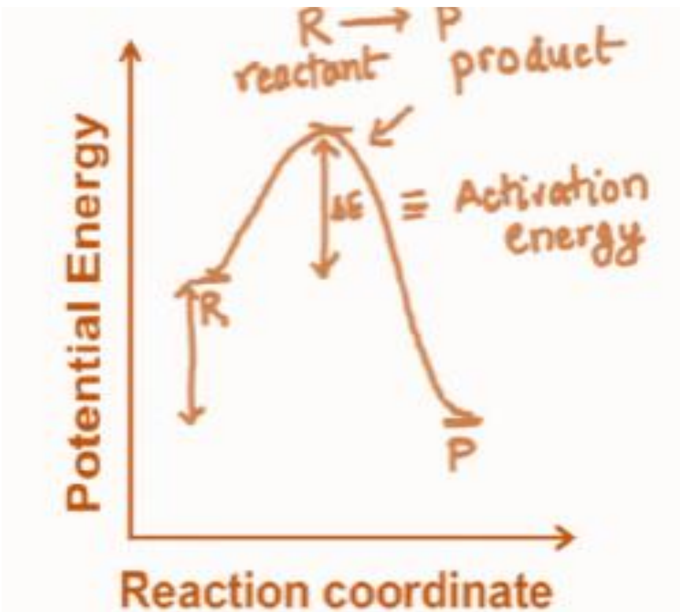


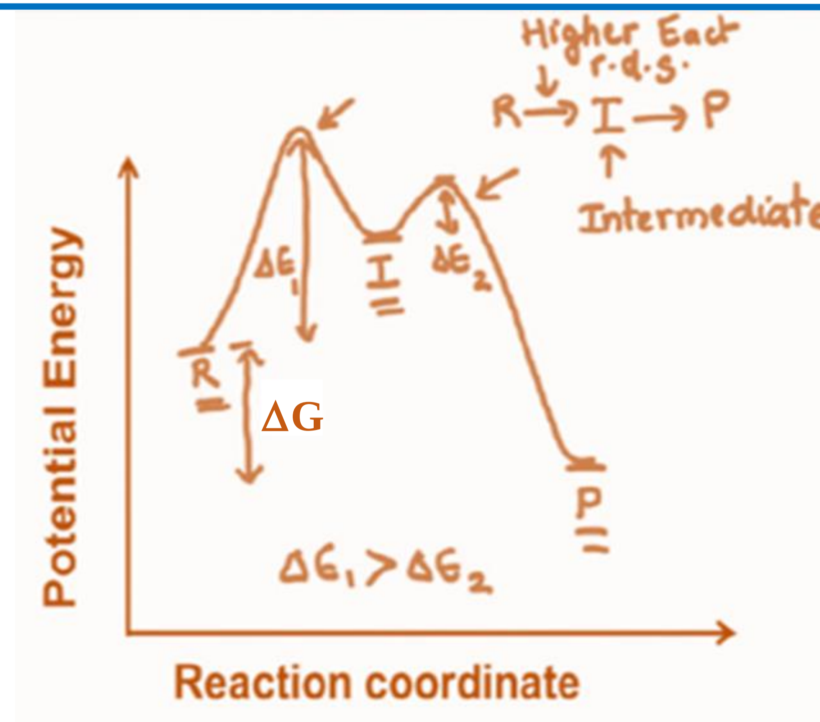


R is going to **P**!
R – reactant, **P** – product
One Hill
Activation energy

R going to **I**, going to **P**!
I is intermediate
R – reactant, **P** – product
2 Hills, one valley
$\Delta E1>\Delta E2$
Step involving higher activation energy:
Rate determining step (RDS)

Understanding reaction coordinate diagram

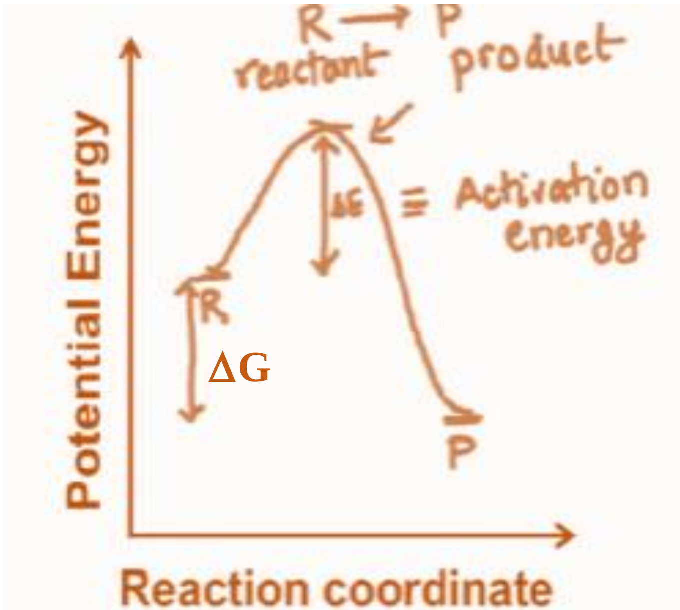


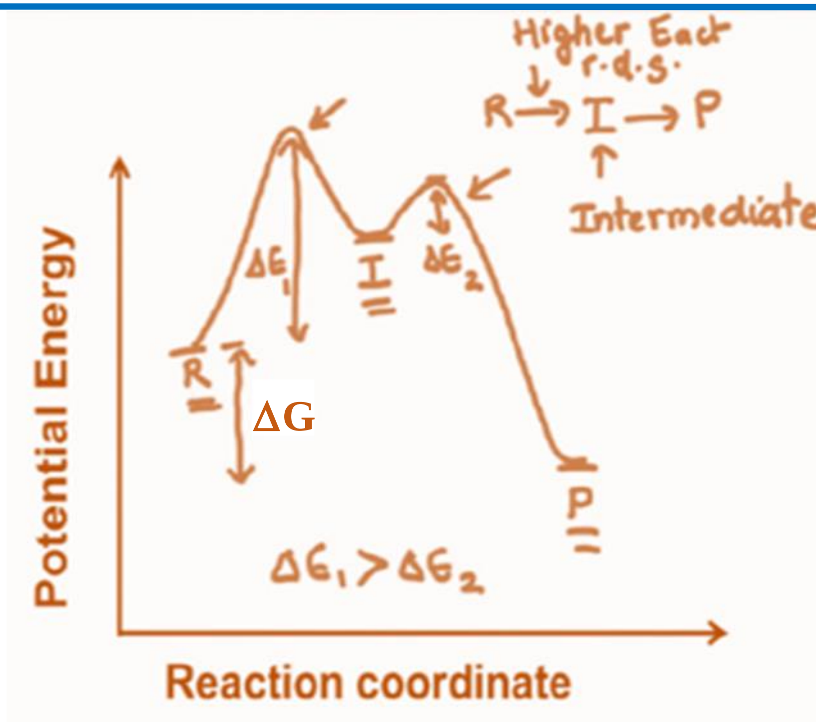


- These simple diagrams would give us about the energy of reactant, product
- Information about what all intermediates are present and the relative energy of the intermediate with respect to reactant as well as the product.

Now we have fair understanding of Y-axis and let us look at X-axis

Understanding reaction coordinate diagram





What do you think the reaction co-ordinate actually means?

What does it signify?

What property of the reaction are you talking about when you talk about reaction coordinate?

Understanding reaction coordinates

- Reactions involve formation and breaking of a bond
- Bond stretching, compression
- Vibrational modes with “N” number of atoms

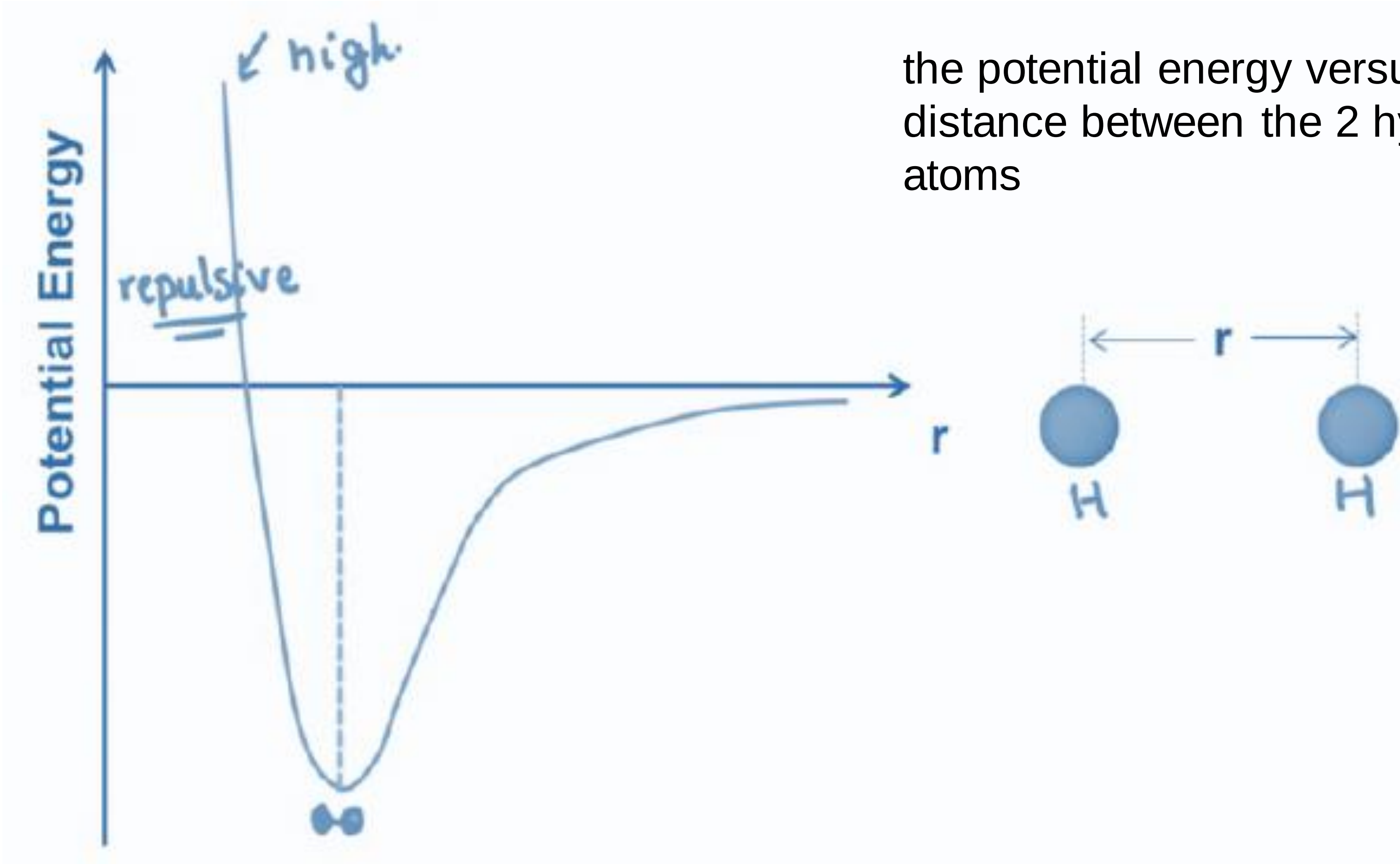
Linear molecule: 3N-5 (translational and rotational)
Non-linear molecules: 3N-6 (translational and rotational)

Let us consider the simplest molecule, hydrogen

How many vibrational modes in hydrogen (H_2)?

2 atoms, linear, one vibrational mode

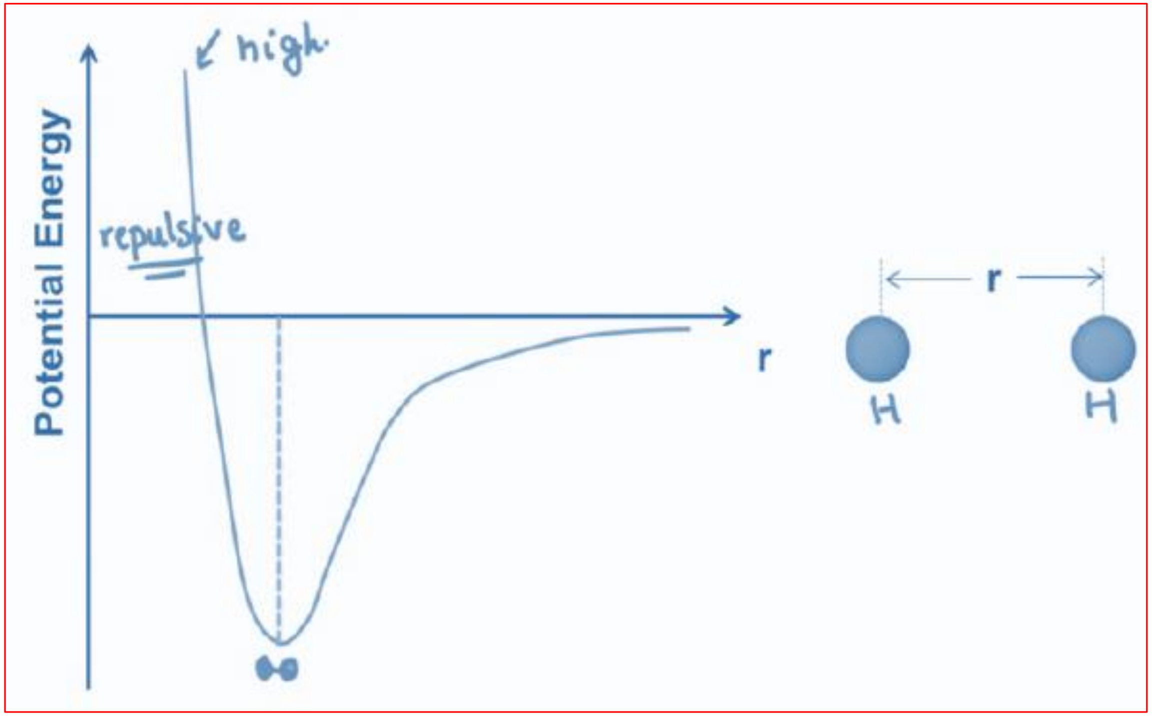
Representing hydrogen

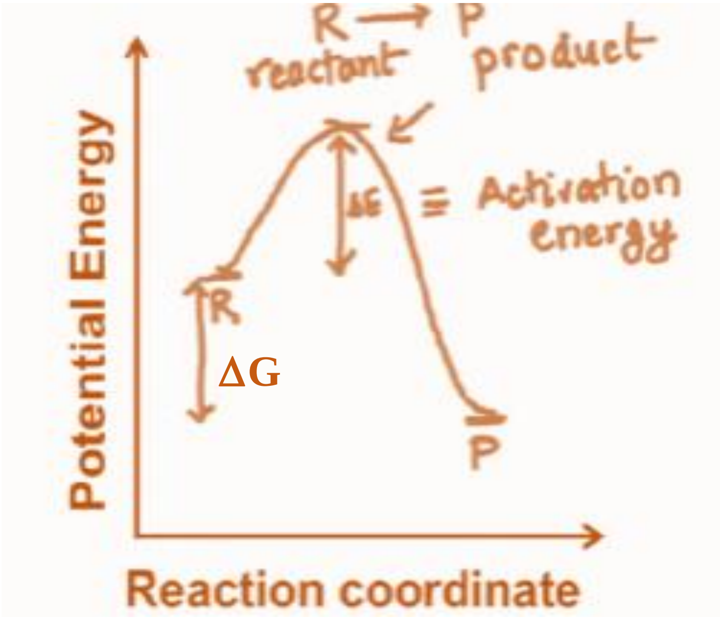


the potential energy versus the distance between the 2 hydrogen atoms

- When the distance is very small, so you have these 2 atoms very close to each other, highly repulsive forces
- At an optimal distance, constructive overlap of the hydrogen atomic orbitals would give hydrogen molecule; refers to lowest energy

Understanding reaction coordinates

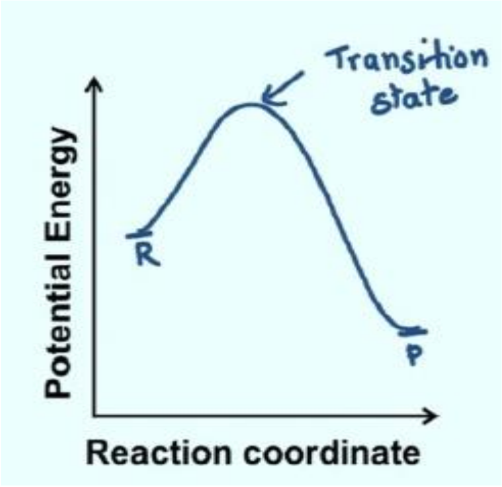


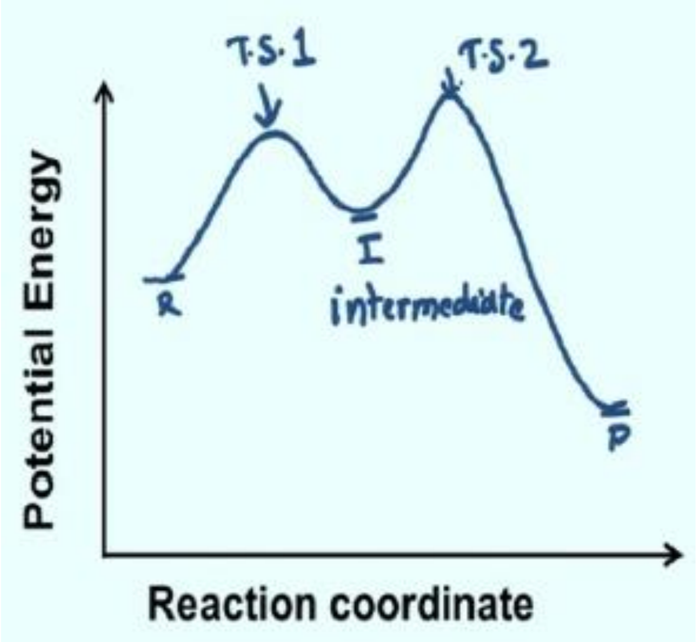


When you look at the hydrogen potential energy diagram do you see a correlation to reaction coordinate diagram?

- The X-axis of reaction coordinate diagram essentially gives an idea about the bonding changes that take place or the changes in the geometry of the molecule as the reaction takes place.
- It has nothing to do with time, all it signifies is the change in the bonding or geometry

Intermediates and Transition states





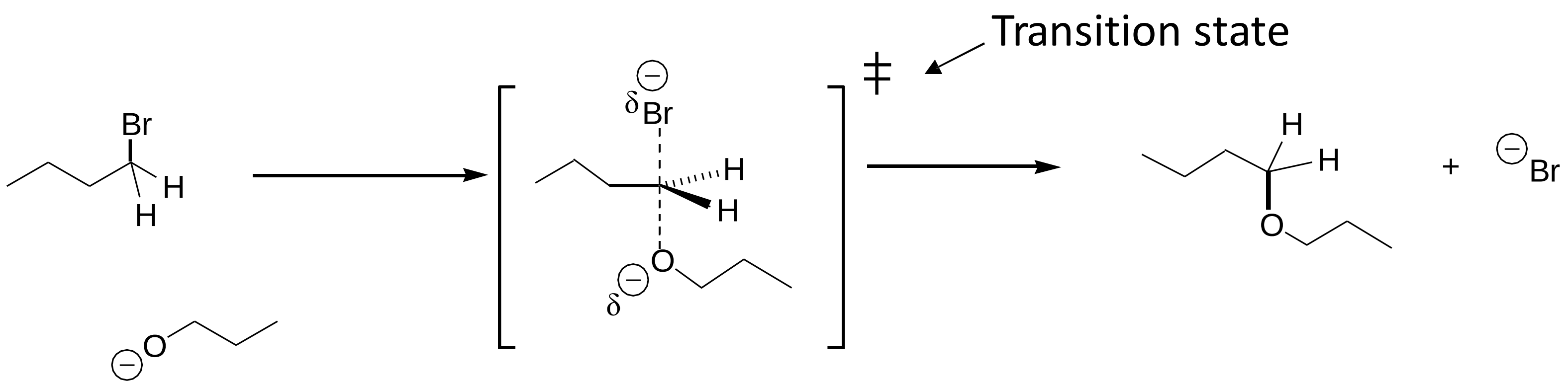
One transition state

Two hills – two transition states
One intermediate

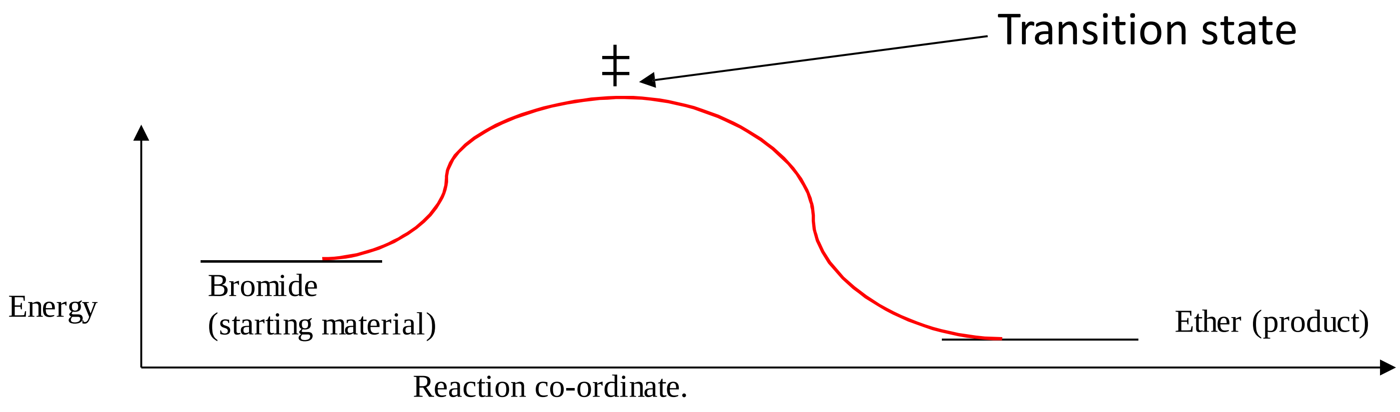
What information do you get?

- The number of steps/intermediates in a reaction
- The relative energy of R, I, TS, P
- The position of TS with respect to R and P

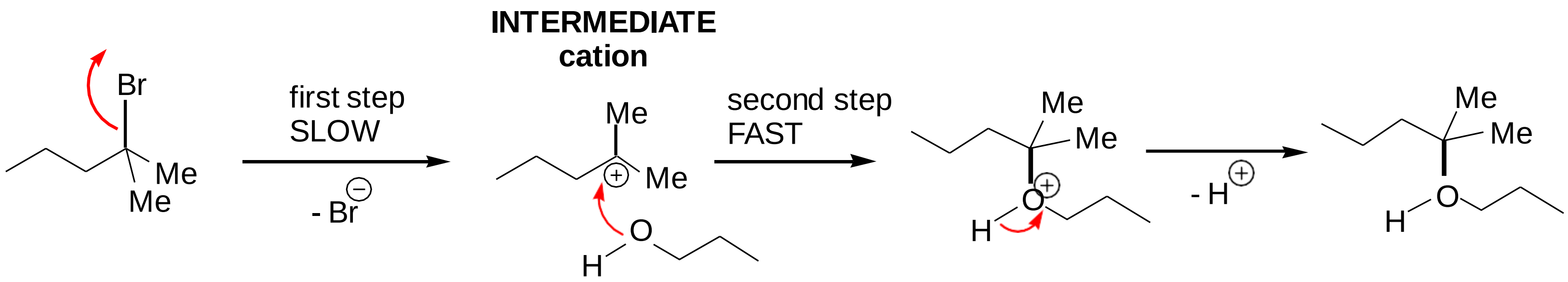
Example of a single step reaction



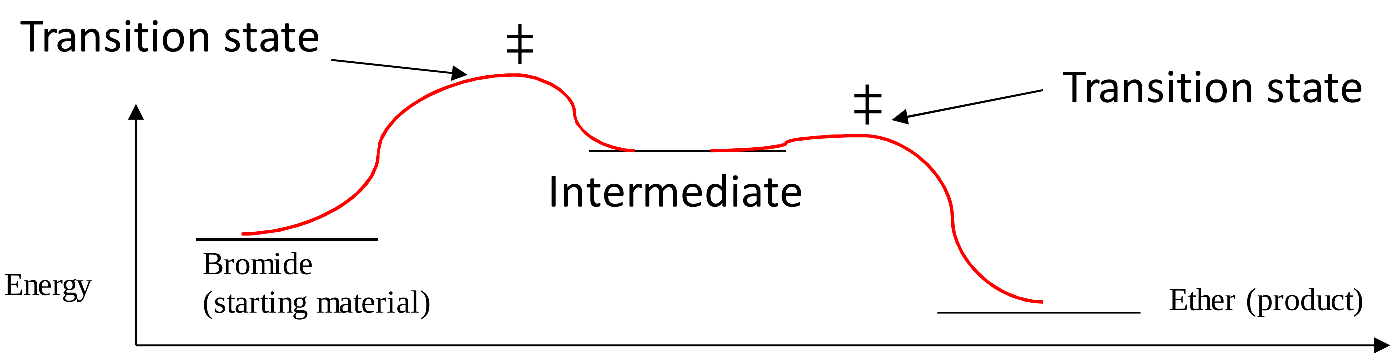
Potential energy of the product is less than reactant



Example of a two-step reaction

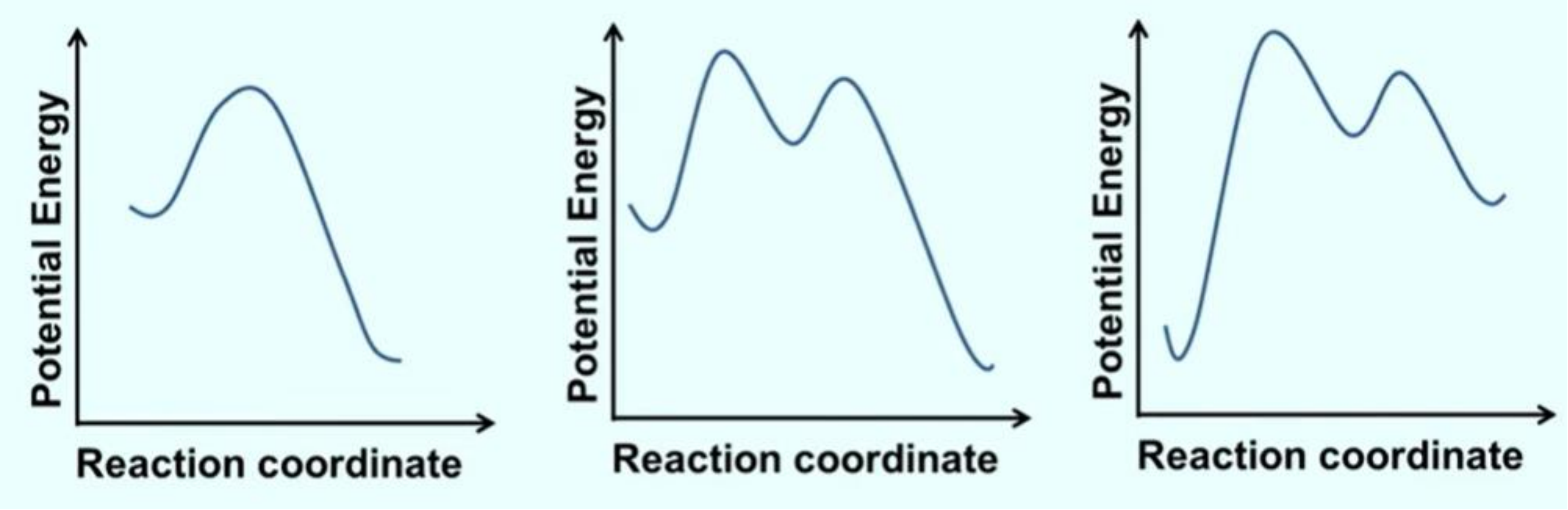


- Potential energy of the product is less than reactant



Examples of reaction coordinate diagrams

Draw each of these diagrams on your note book.
Label the reactant as R, product as P, transition state as TS, intermediate as I.
Identify the rate determining step.



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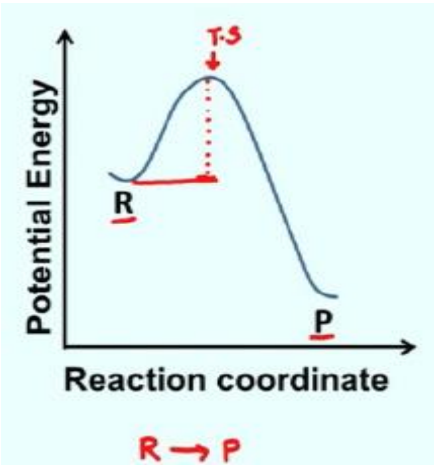
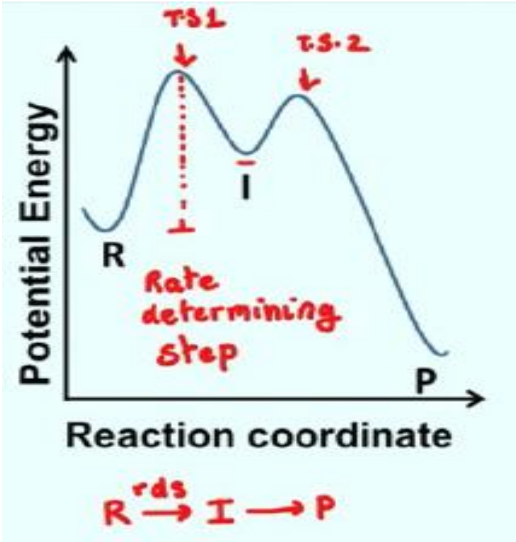
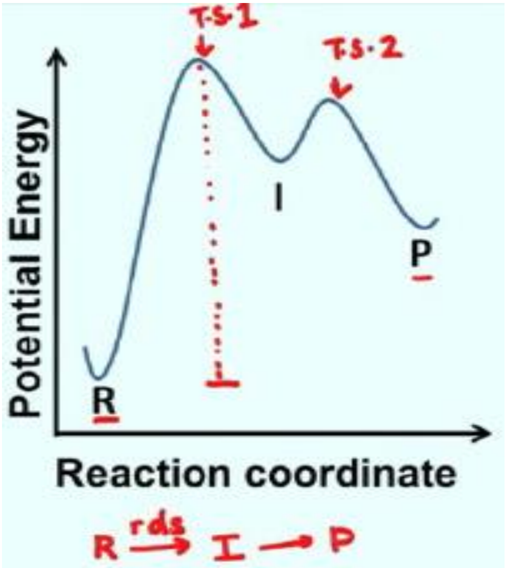


- Single step



- Two step
- Higher activation energy to reach TS1 and I; that is the slow step and rate determining step
- First step is RDS
- The barrier for transition state 2 is lesser



- Two step
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Examples of reaction coordinate diagrams

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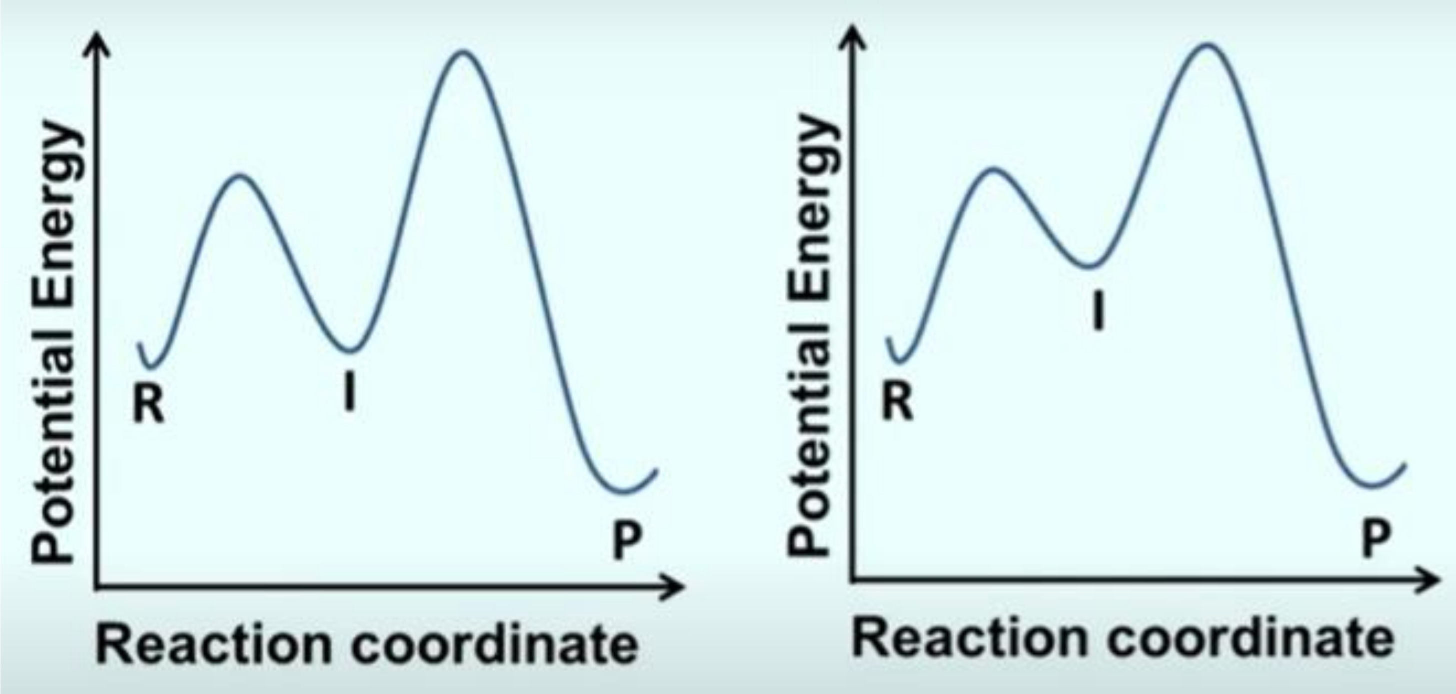
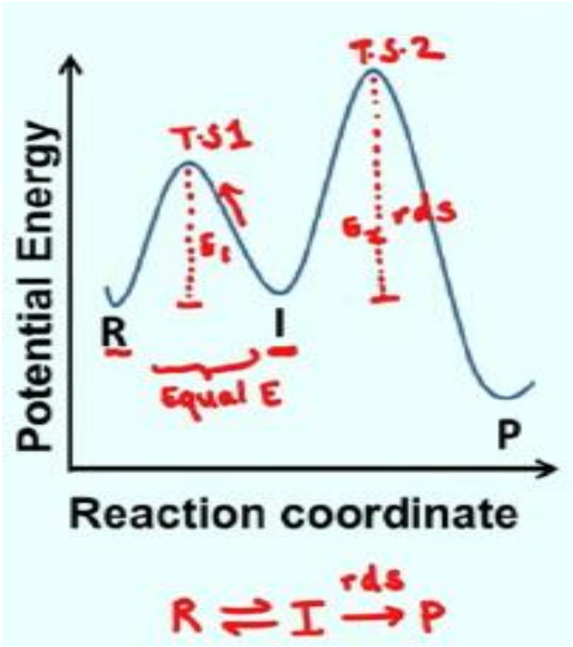
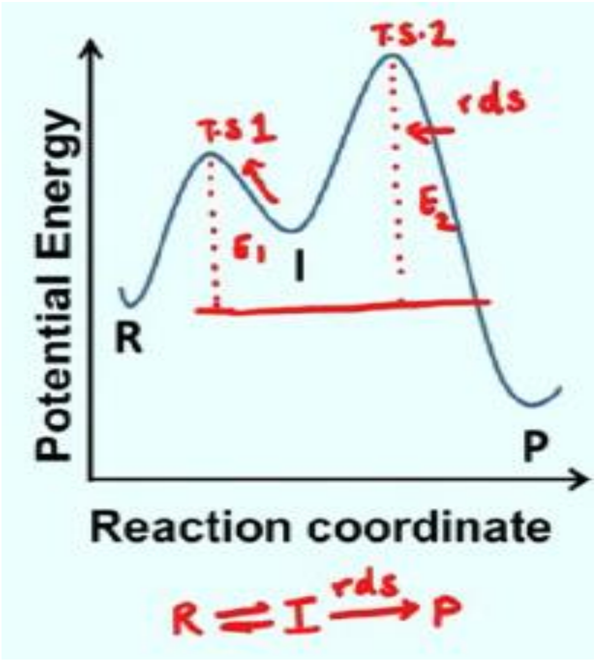
Identify the rate determining step



Examples of reaction coordinate diagrams





- Energy barrier for **TS2** is higher
- Second step is **RDS**
- Energy barrier for **I** to go back to the **R** is lesser than the barrier for it to go to the product
- Equilibrium between the **R** and the **I**
- Energy levels of **R** and **I** are equal

- **I** is at a higher energy or more reactive than **R**.
- The barrier to go from the **I** to **TS1** is less than the barrier to go from **R** to the **TS1**.
- Energy barrier for **TS2** is higher
- Chance of an equilibrium
- Second step is **RDS**

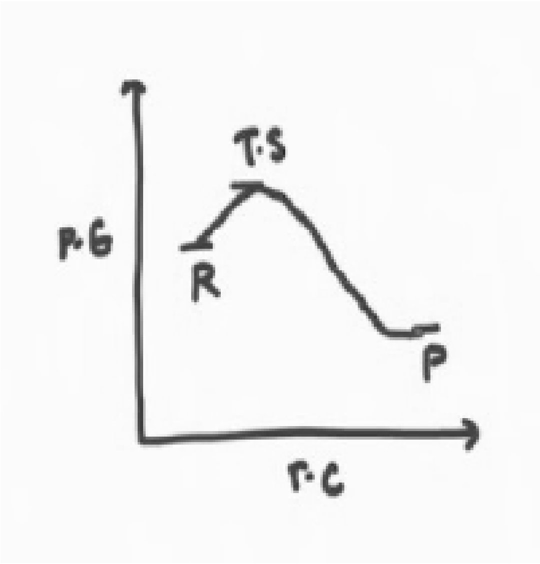
Hammond's postulate

- The activated complex most resembles the adjacent reactant, intermediate or product that it is closest in energy to, as long as the energy difference between the transition state and the adjacent structure is not too large

- If the transition state energy very similar to the reactant energy it would resemble the reactant more

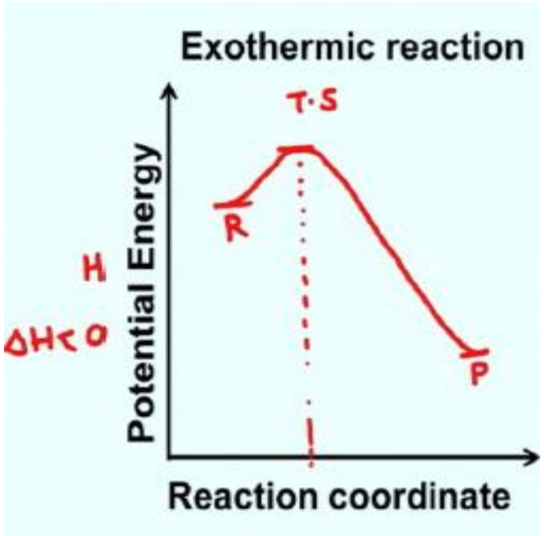
- If the transition state energy very similar to the intermediate energy it would resemble the intermediate more

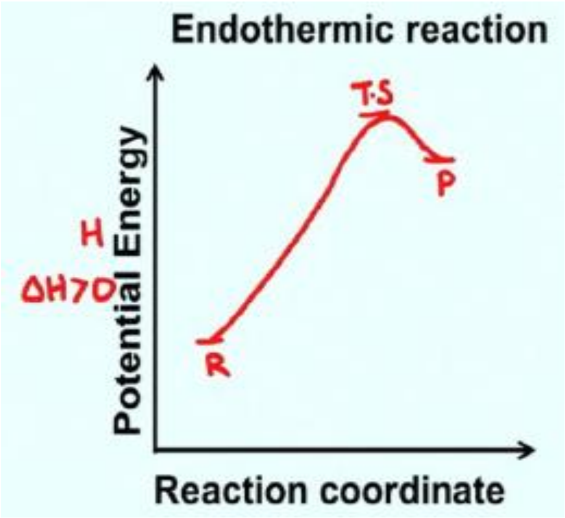
- If the transition state energy very similar to the product energy it would resemble the product more



Hammond's postulate

- Draw exothermic and endothermic reaction coordinate diagrams for a single step reaction R to P





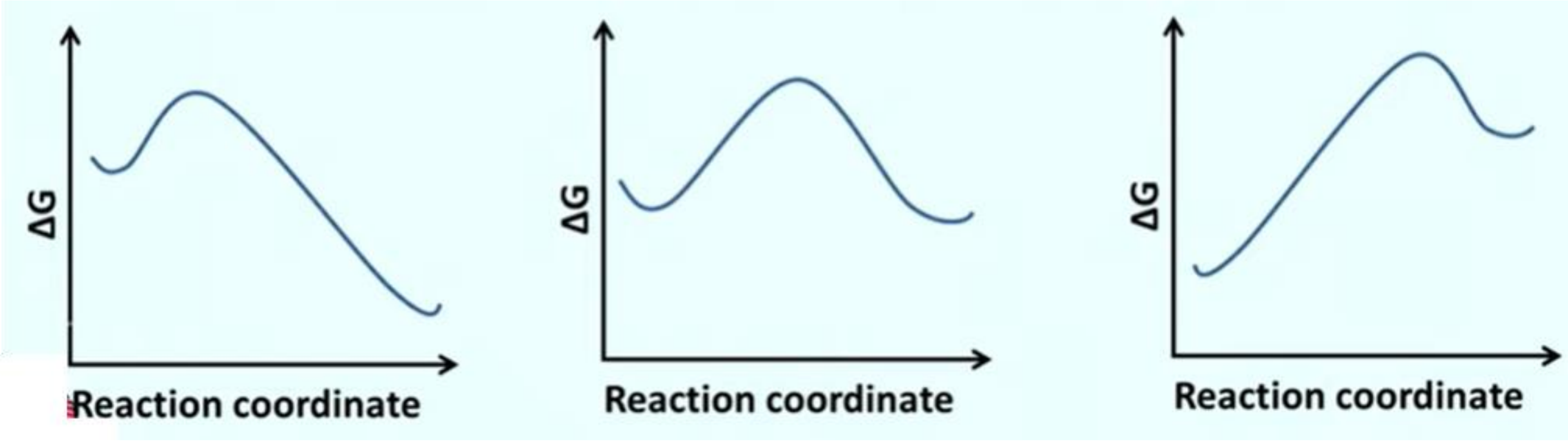
- ΔH is negative
- Liberates heat
- Reactant is at a higher energy as compared to product

- ΔH is positive
- Absorbs heat
- Product is at a higher energy as compared to reactant

What about position of the transition state?

Hammond's postulate

- In highly exothermic steps it will be expected that the transition states will resemble reactants closely and in endothermic steps the products will provide the best models for the transition states



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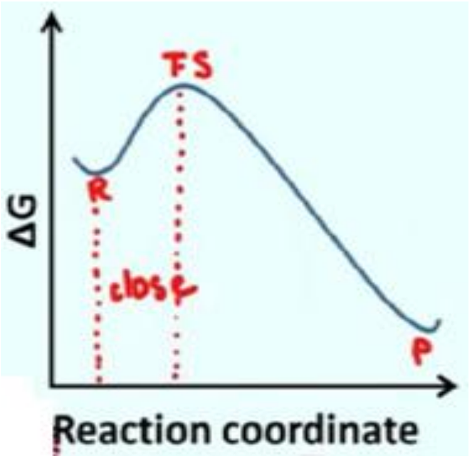
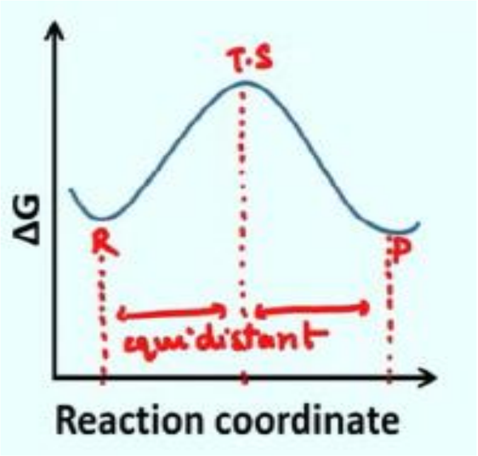
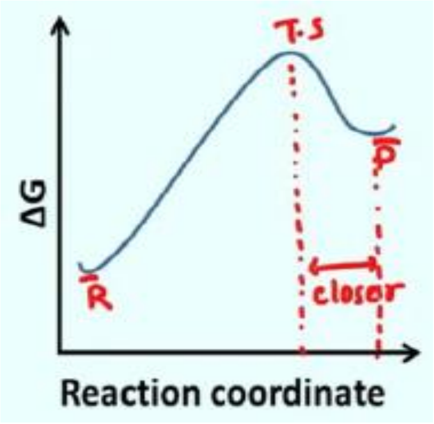






Kinetic versus Thermodynamic Control

$$R \rightarrow \begin{cases} A \\ B \end{cases}$$

If multiple products are possible for a reaction, ratio of products can be dictated by

- Relative energy of transition states – Kinetic control (KC)

$$B \leftarrow R \xrightarrow{E_{act}\ \text{lower}} A$$

Faster

Speed is important

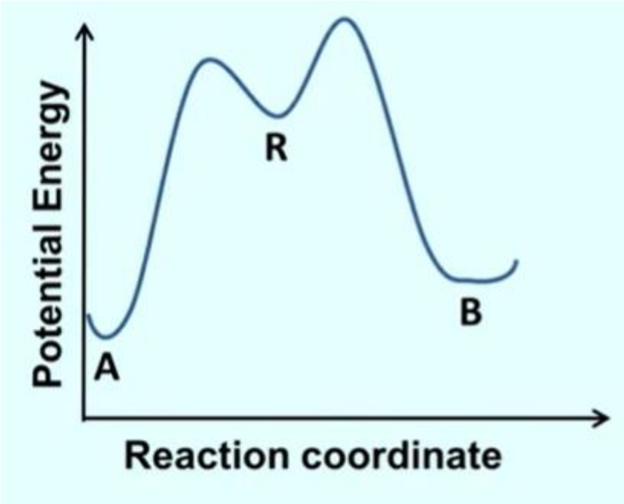
- Relative energy of products – thermodynamic control (TC)

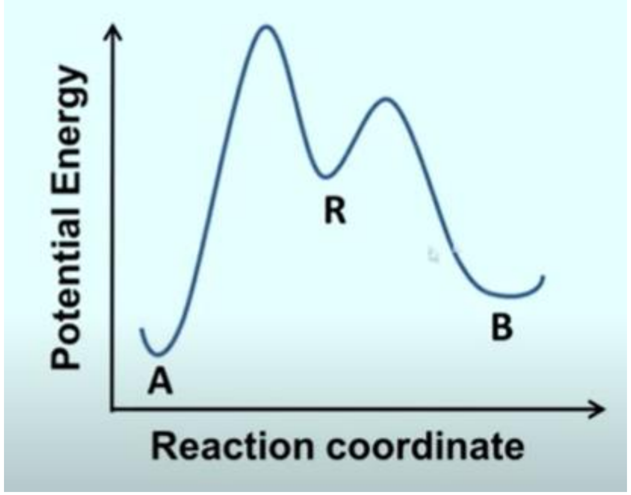
$$B \leftarrow R \rightarrow A$$

More stable

Stability is important

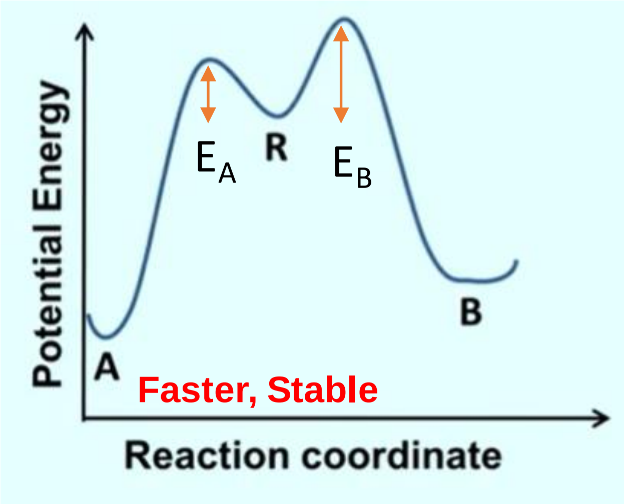
Kinetic versus Thermodynamic Control

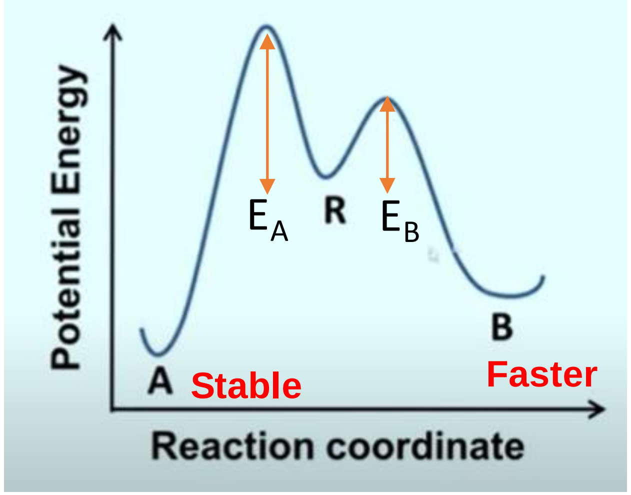




Look at both of these reaction coordinate diagrams and then point out in both of these cases which is the product corresponding to the faster reaction, which is kinetic control and which is the product corresponding to stability, which is thermodynamic control.

Kinetic versus Thermodynamic Control

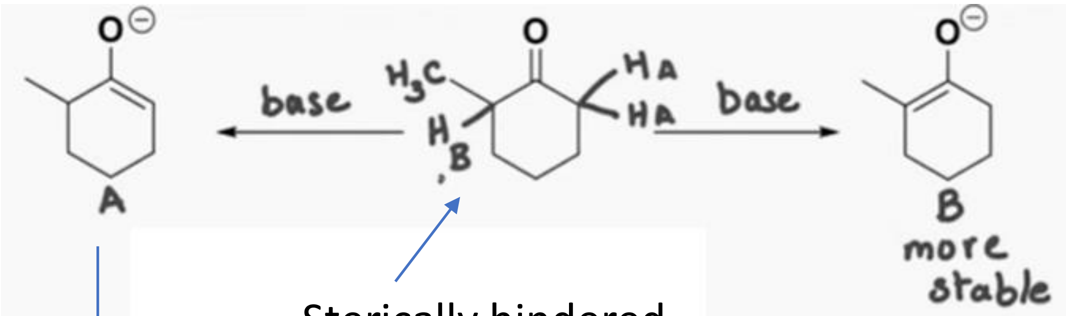




- $E_A < E_B$
- A is more stable than B
- Kinetic control product 'A'
- Thermodynamic product 'A'

- $E_B < E_A$
- A is more stable than B
- Kinetic control product 'B'
- Thermodynamic product 'A'

Classic example: Kinetic versus Thermodynamic Control



Draw reaction coordinate diagram

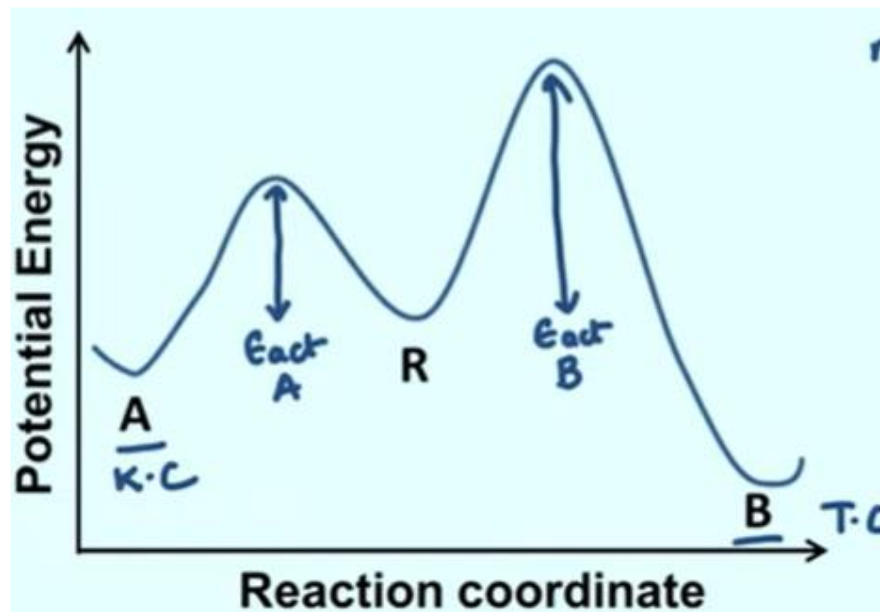
Sterically hindered
High energy

<u>Kinetic control</u>

Bulky base
Low temperature
Strong base

<u>Thermodynamic control</u>

High temperature
Weak base



Specific example