Organic Chemistry Concepts LOKT.09.051

Organic reactions

What can we observe?

Change of molecular structure!

In some cases visual effects can be observed:

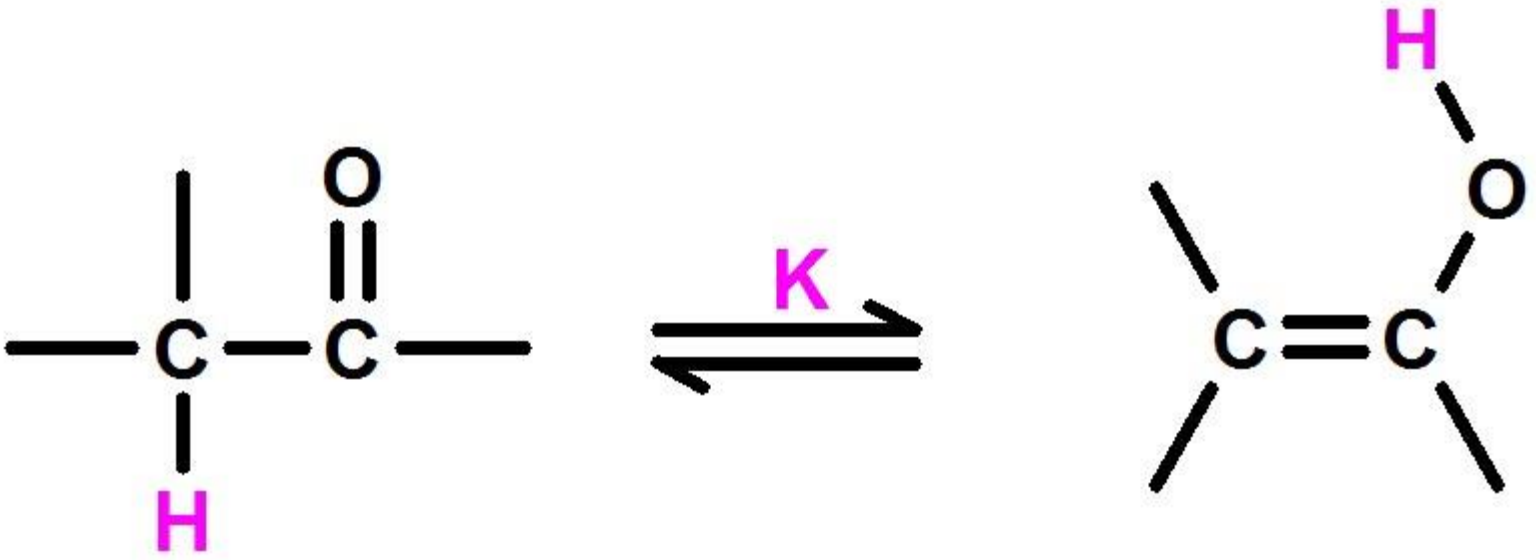
- Flashes
- Gase release, smell etc
- Precipitation

But this is not essential

What is important to know?

- **Which bonds are breaking and which bonds are formed?**
- **In which order they are breaking and forming?**
- **What is the energy balance of this process?**
- **How fast these changes take place?**

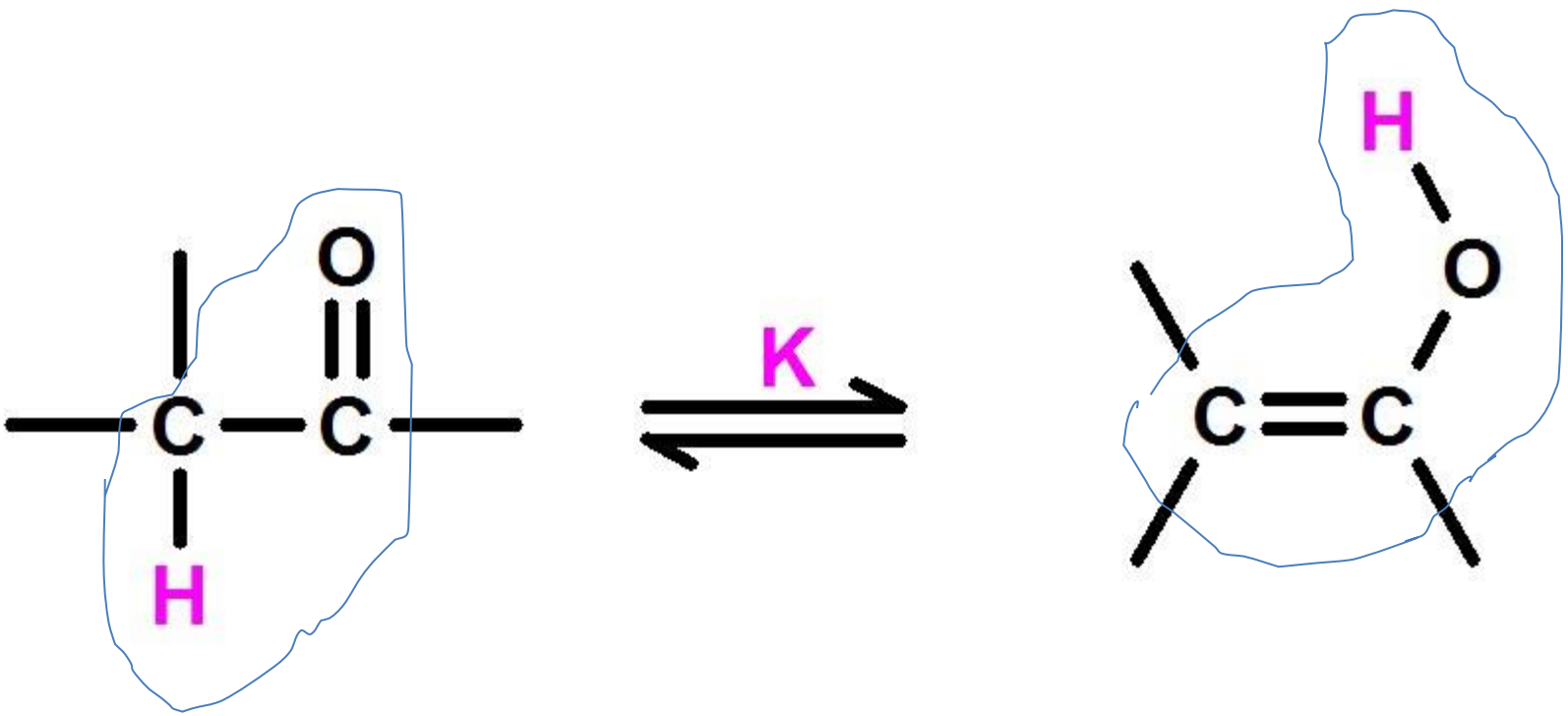
Direction of chemical changes



Ketone

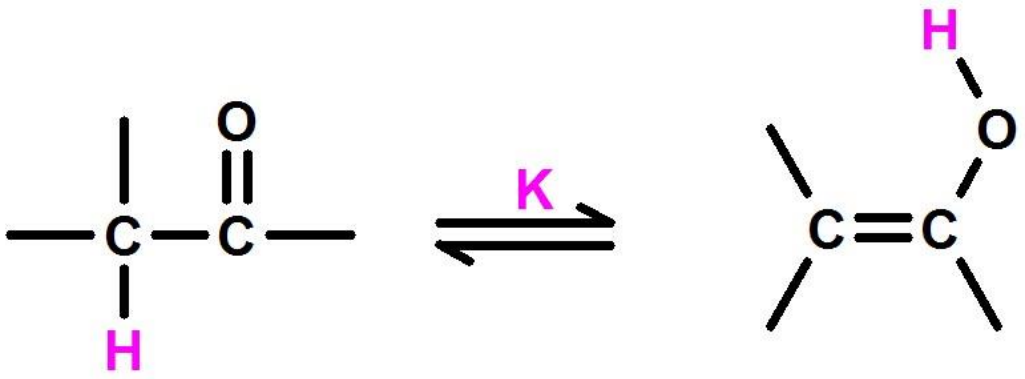
Enole

Direction of chemical changes

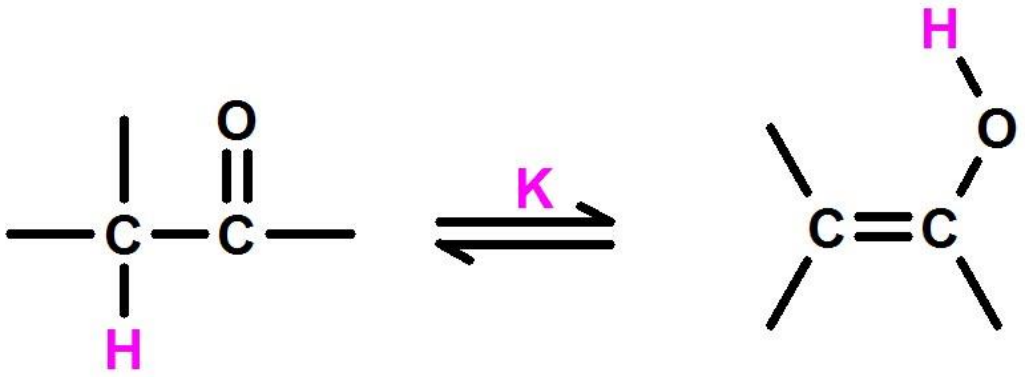


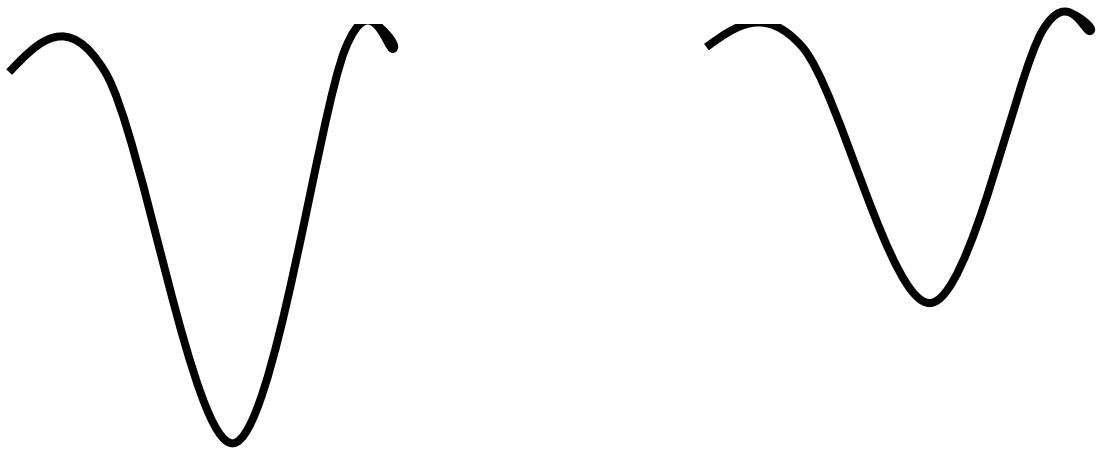
Ketone

Enole

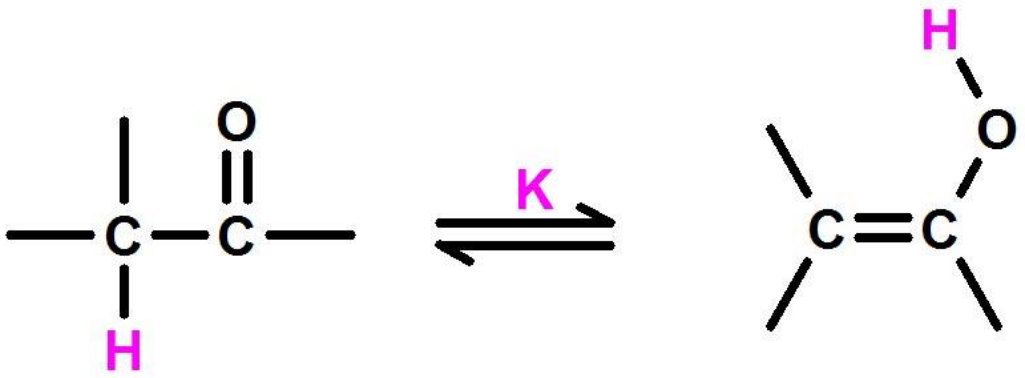


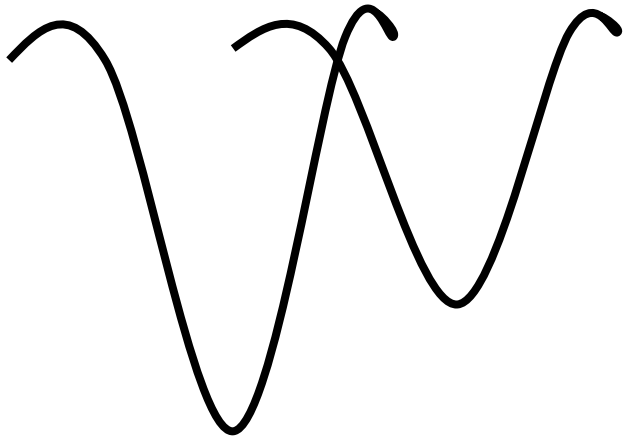
C-H	96 kcal/mol	C=C	146 kcal/mol
C-C	83 kcal/mol	C-O	85 kcal/mol
C=O	173 kcal/mol	O-H	110 kcal/mol
	----------		----------
	352 kcal/mol		341 kcal/mol



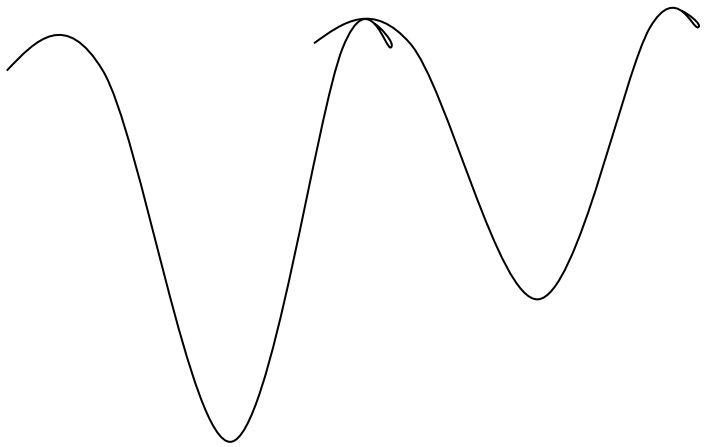


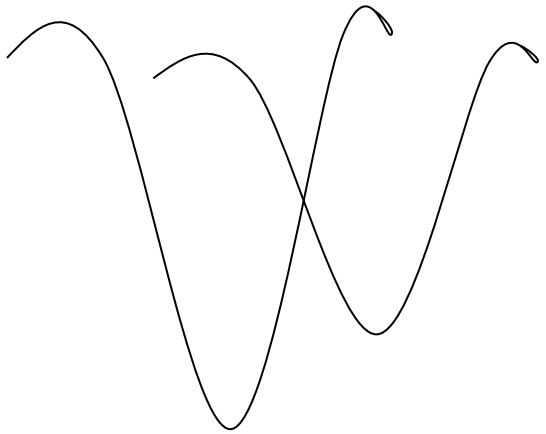
$\Delta H = -352$ kcal/mol $\Delta H = -341$ kcal/mol





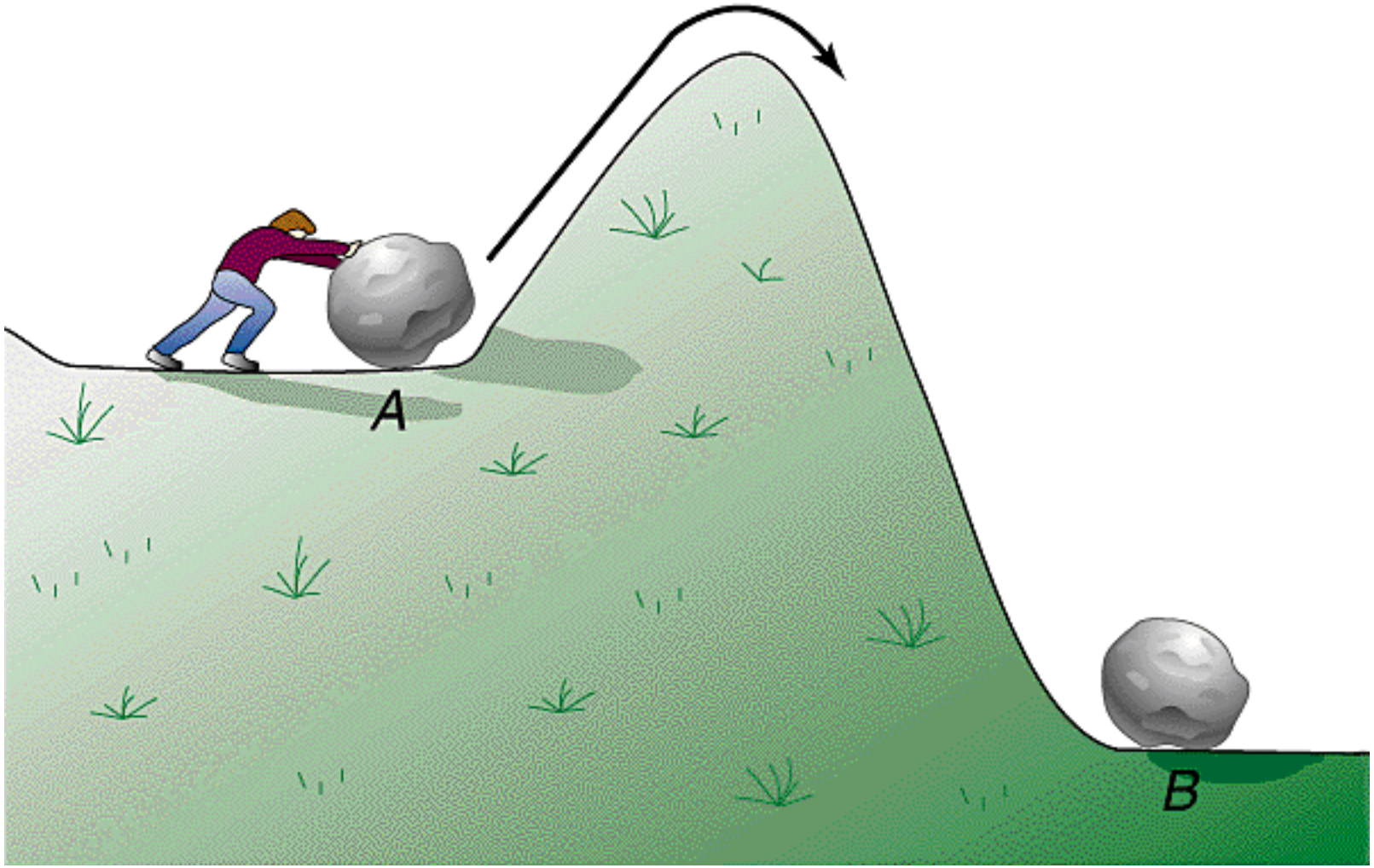
$\Delta H = -352$ kcal/mol $\Delta H = -341$ kcal/mol





Thermodynamic aspect:
reaction energy

Kinetic aspect: activation energy



A ⇌ **B**

Reaction types

- **Substitution**

A-B + C-D → A-C + B-D

- **Addition**

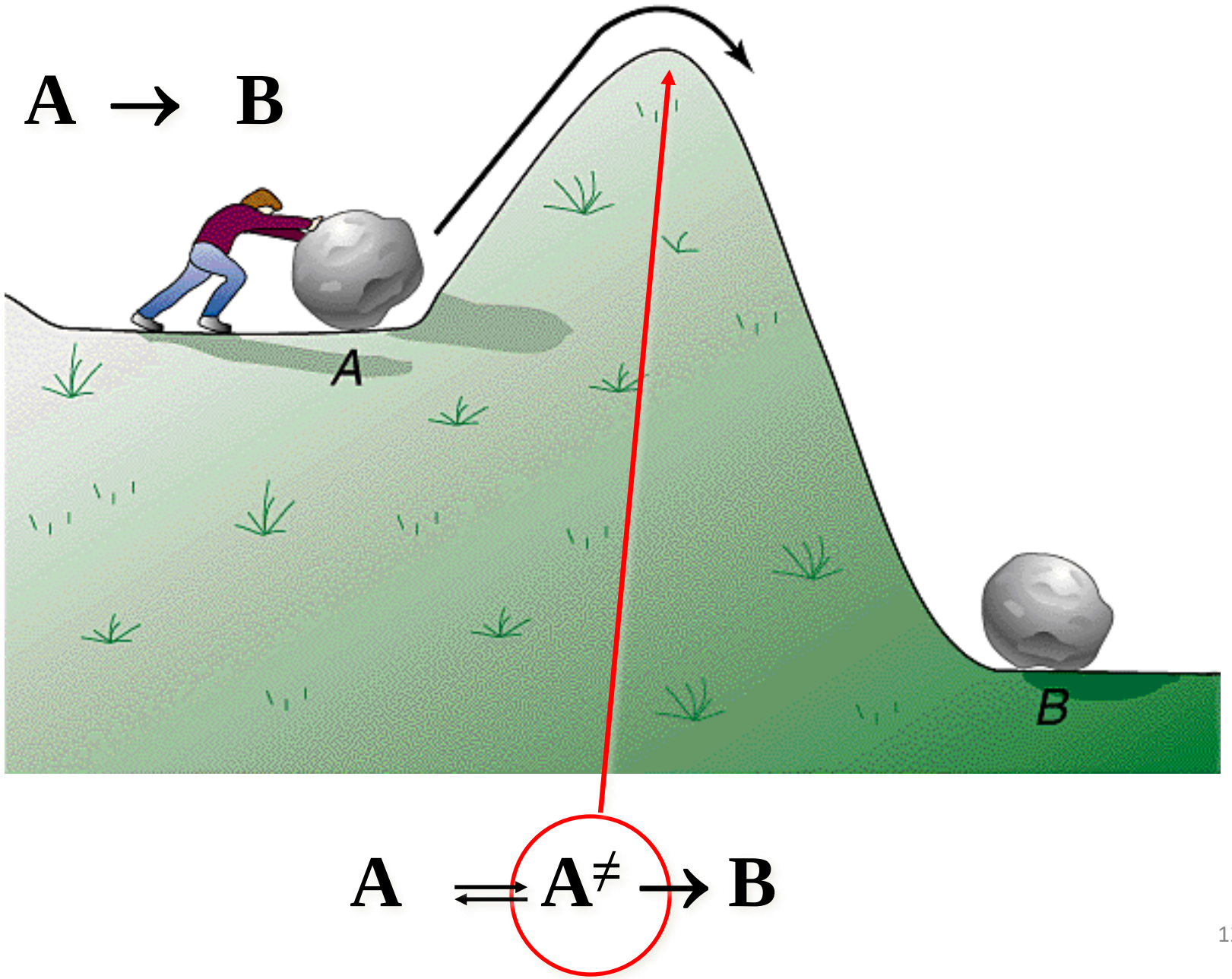
A + B → A-B

- **Elimination**

A-B → A + B

- **Rearrangement**

A → B

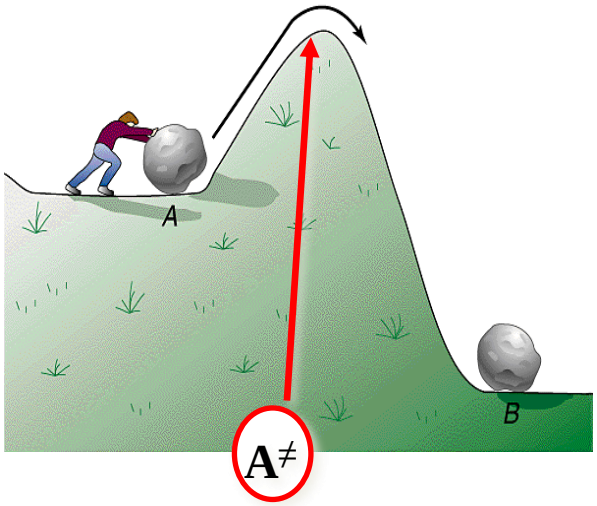

A → B
A
B
A ⇌ A≠ → B

Transition state (TS)

Reaction:

$$A \rightarrow B$$

Hypothesis: there is a transition state between A and B



$$A \overset{K}{\underset{}{\rightleftarrows}} A^{\neq} \rightarrow B$$

$$k = 6\ 10^{12}\ 1/s$$

$$A \xrightarrow{k} B$$

$$v = k\,[A]$$

$$A \rightleftharpoons A^{\neq} \xrightarrow{k^{\neq}} B$$

$$v = k^{\neq} K^{\neq} [A]$$

$$v = k^{\neq} [A^{\neq}]$$

$$K^{\neq} = \frac{[A^{\neq}]}{[A]}$$

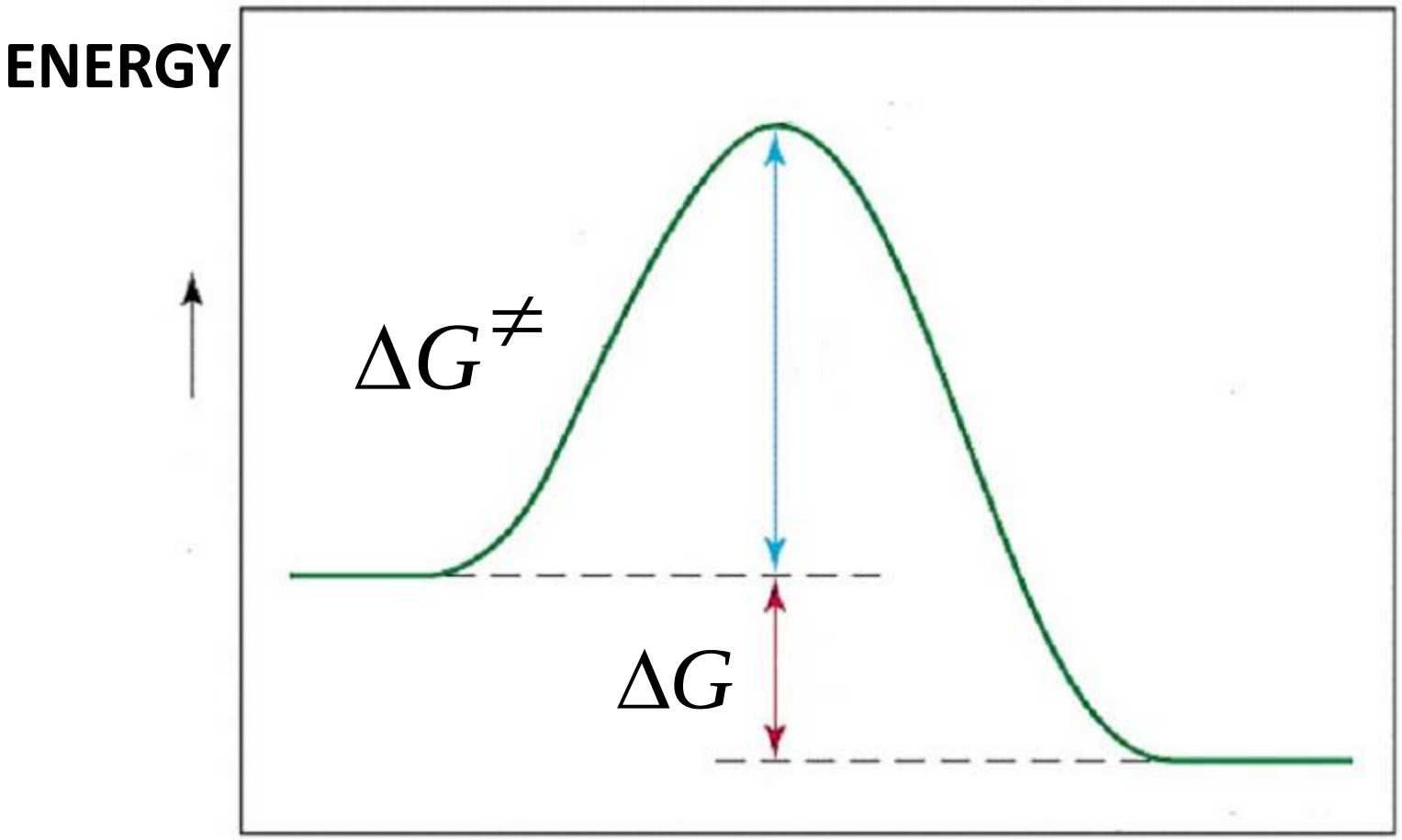
$$\Delta G^{\neq} = -RT \ln K^{\neq}$$

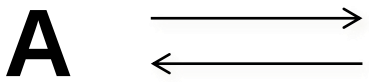
$$A \overset{K^{\neq}}{\rightleftharpoons} A^{\neq} \overset{k^{\neq}}{\rightarrow} B$$

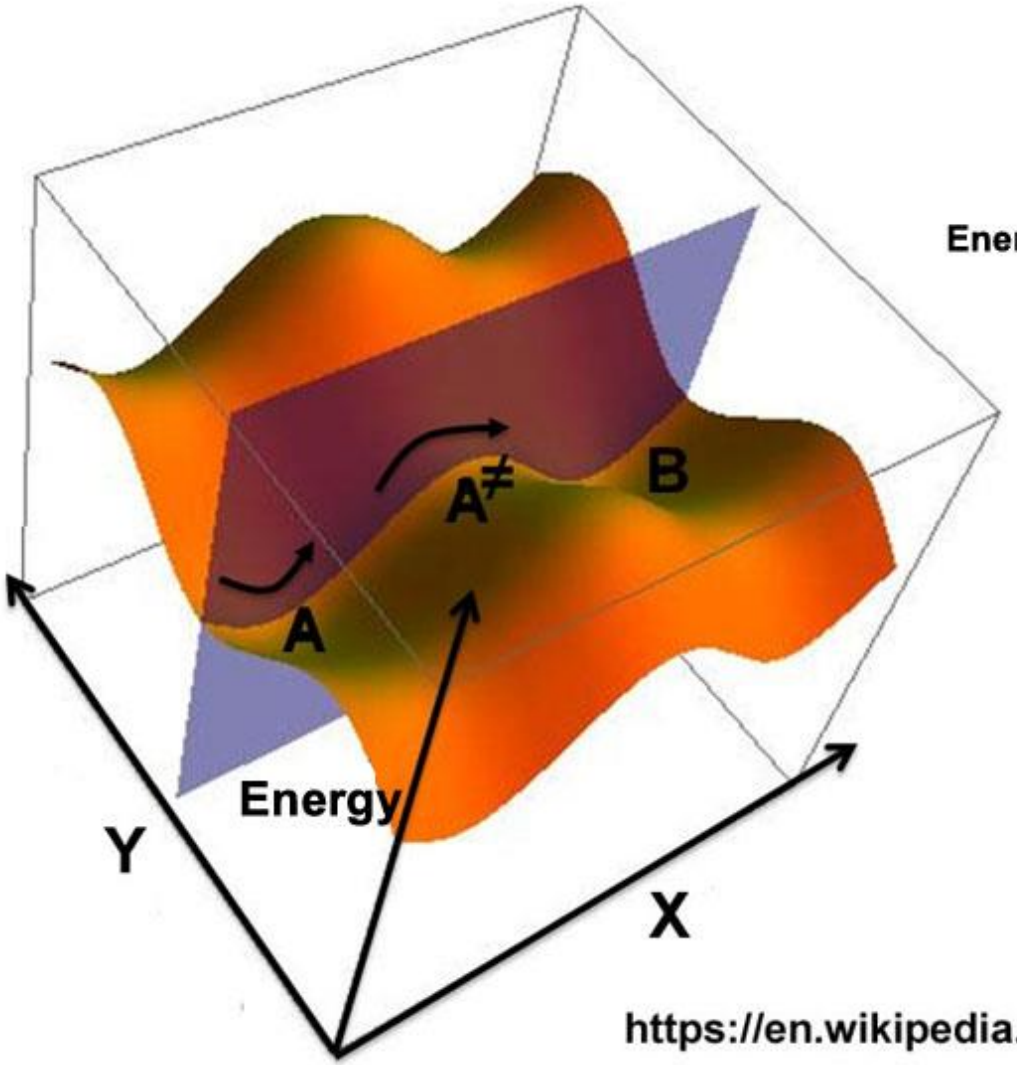
$$k = k^{\neq} K^{\neq}$$

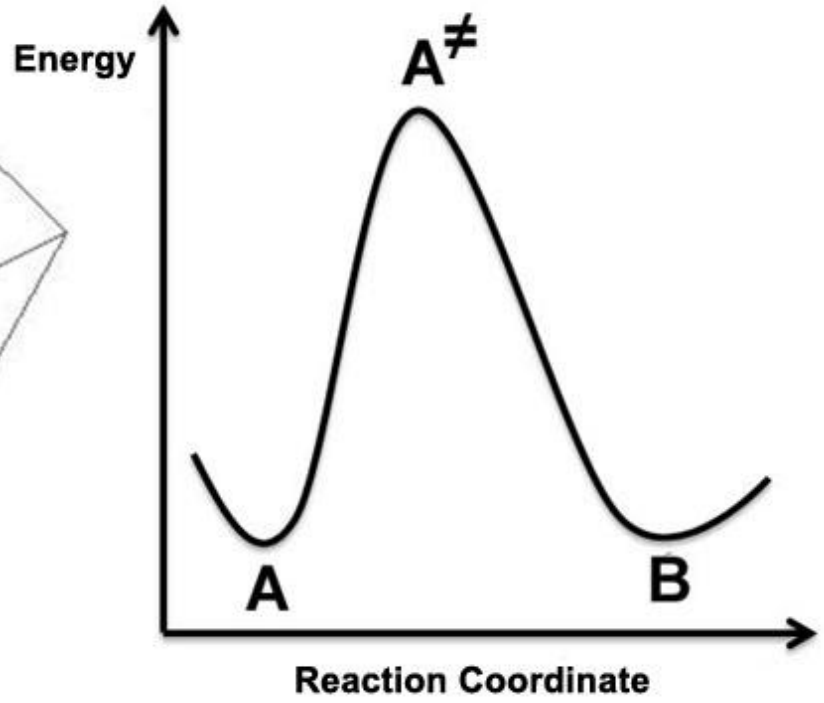
$$\mathbf{\ln k = \ln k^{\neq} + \ln K^{\neq}}$$

$$\Delta G^{\neq} = RT \ln k^{\neq} - RT \ln k = const - RT \ln k$$

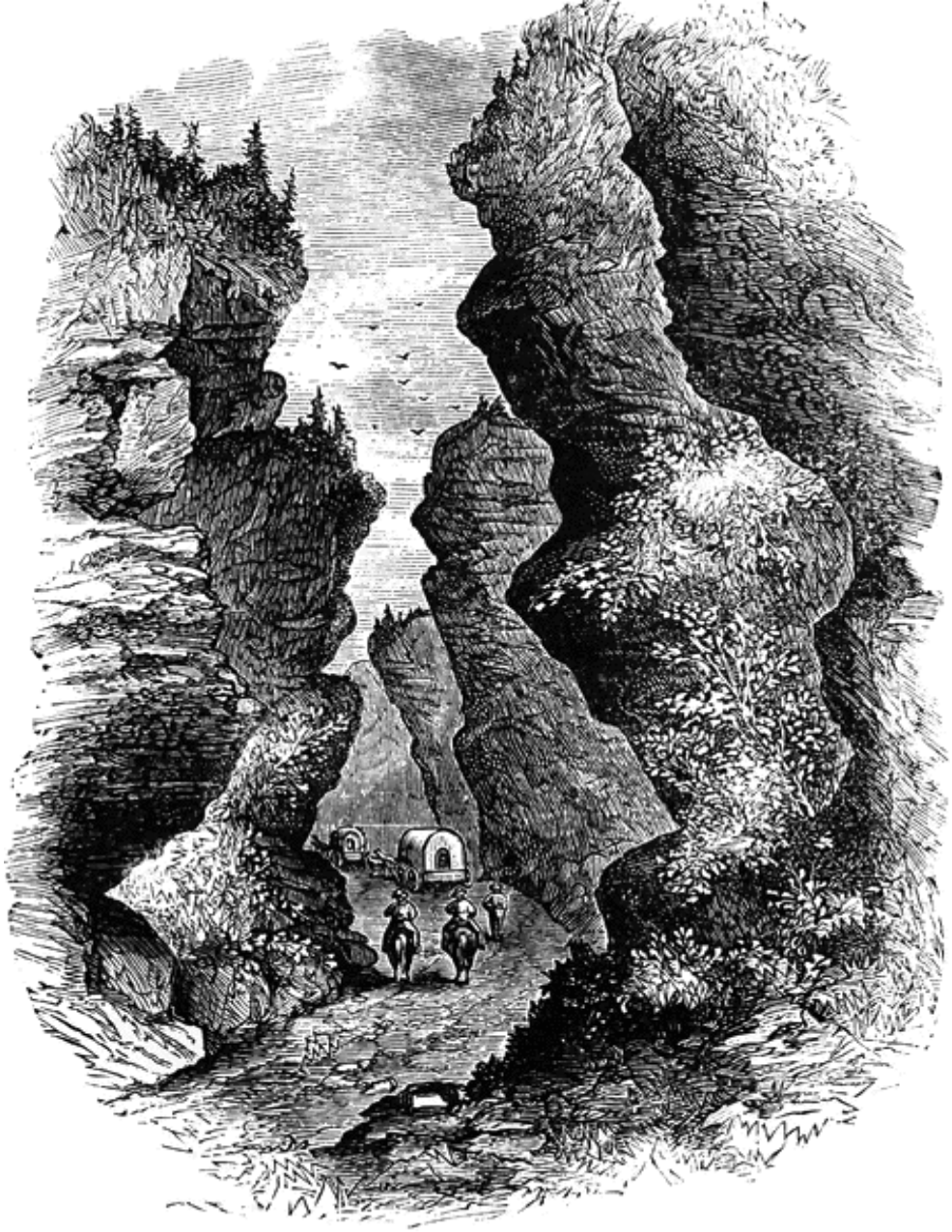

ENERGY
$\Delta G^{\neq}$
ΔG
Reaction Coordinate







https://en.wikipedia.org/wiki/Energy_profile_(chemistry)

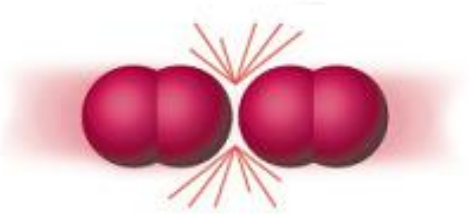


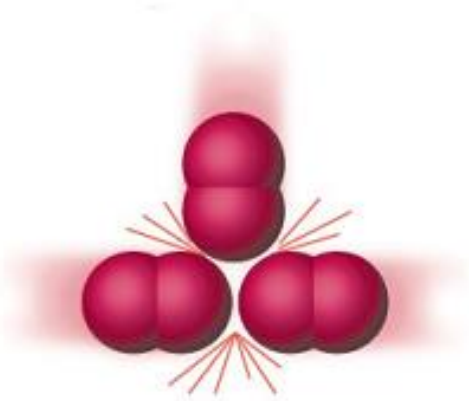
http://etc.usf.edu/clipart/30600/30634/mountain_30634.htm

Elementary reactions

Molecularity

A → Products	Mono	$v = k[A]$
2A → Products	Bi	$v = k[A]^2$
A + B → Products	Bi	$v = k[A][B]$
2A + B → Products	Ter	$v = k[A]^2[B]$





Reaction kinetic mechanism

$$2A + B \rightarrow E + F$$

Steps

$$A + B \rightarrow C$$

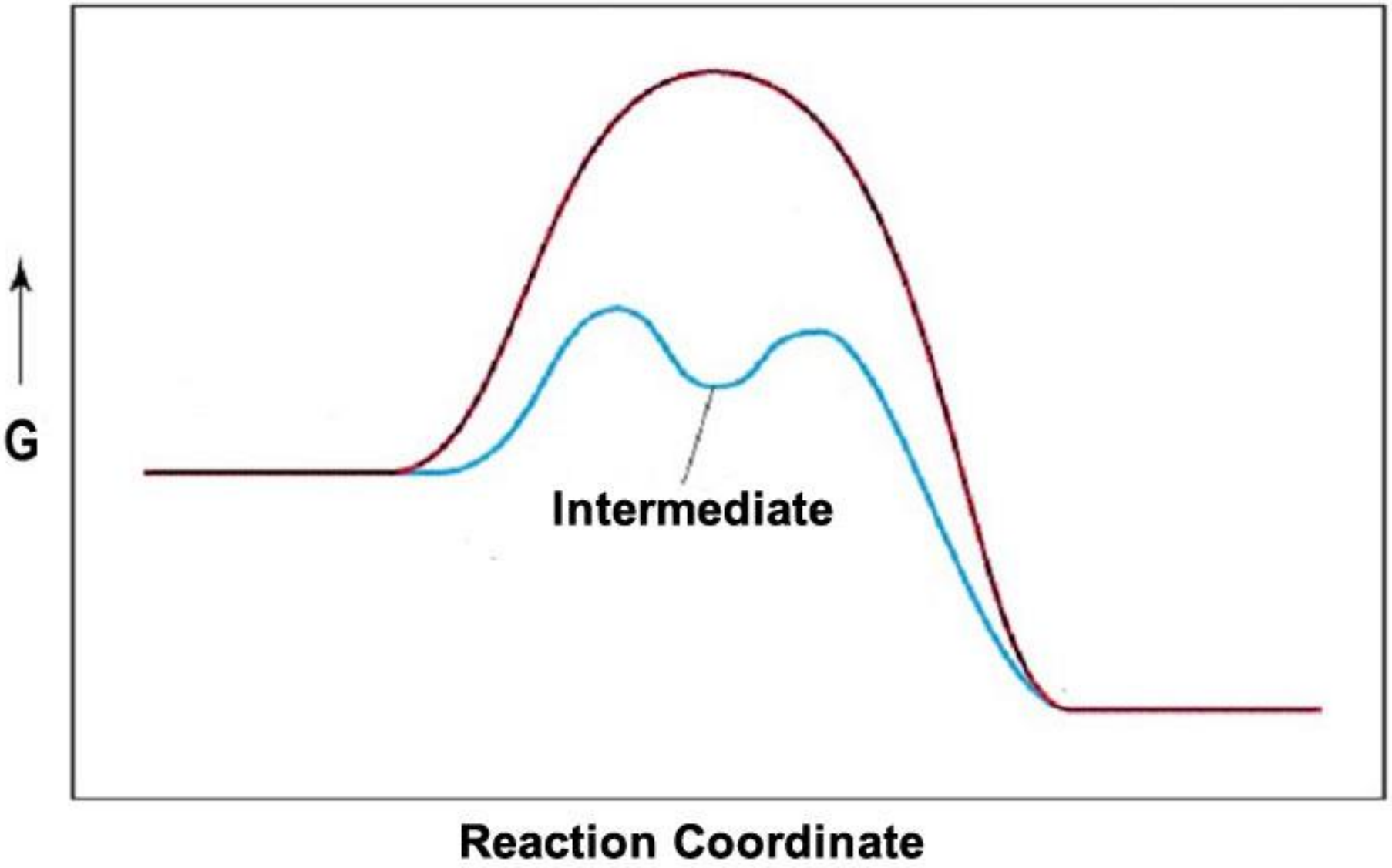
$$C + A \rightarrow D$$

$$D \rightarrow E + F$$

$$A + B + \cancel{C} + A + \cancel{D} \rightarrow \cancel{C} + \cancel{D} + E + F$$

$$2A + B \rightarrow E + F$$

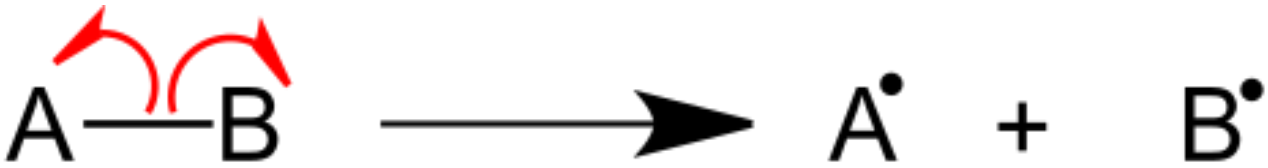
C and D are intermediates


G
Intermediate
Reaction Coordinate

The key questions in organic chemistry

Intermediates and their structure
Transition states and their structure
Rate of elementary step (fast vs slow)

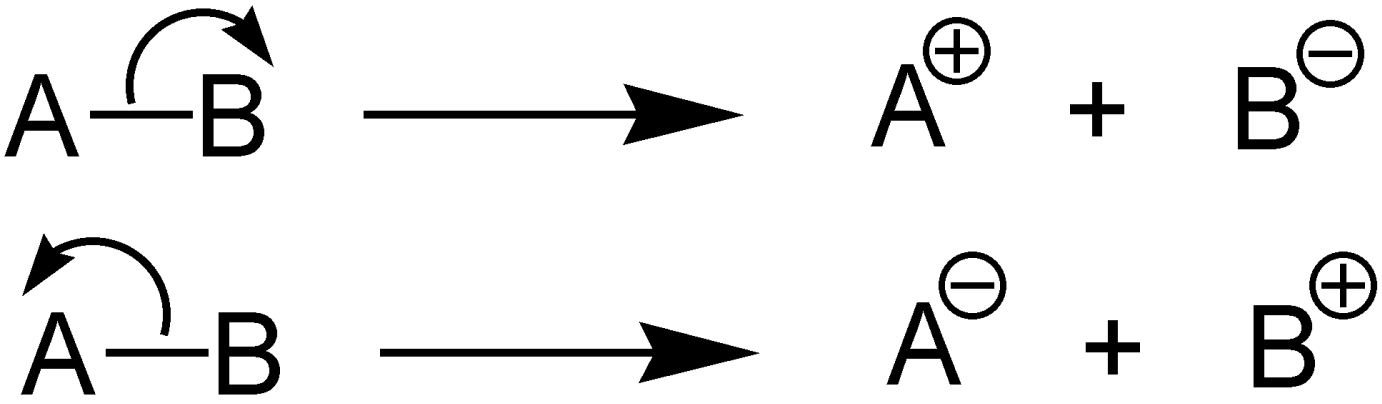
Radical formation



https://commons.wikimedia.org/w/index.php?curid=11940651

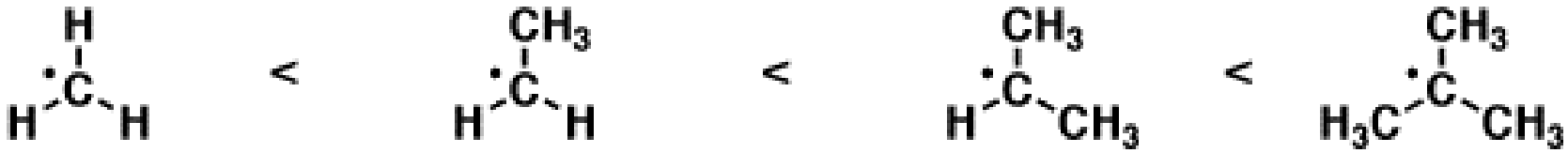
Molecular mechanisms

Bond heterolysis



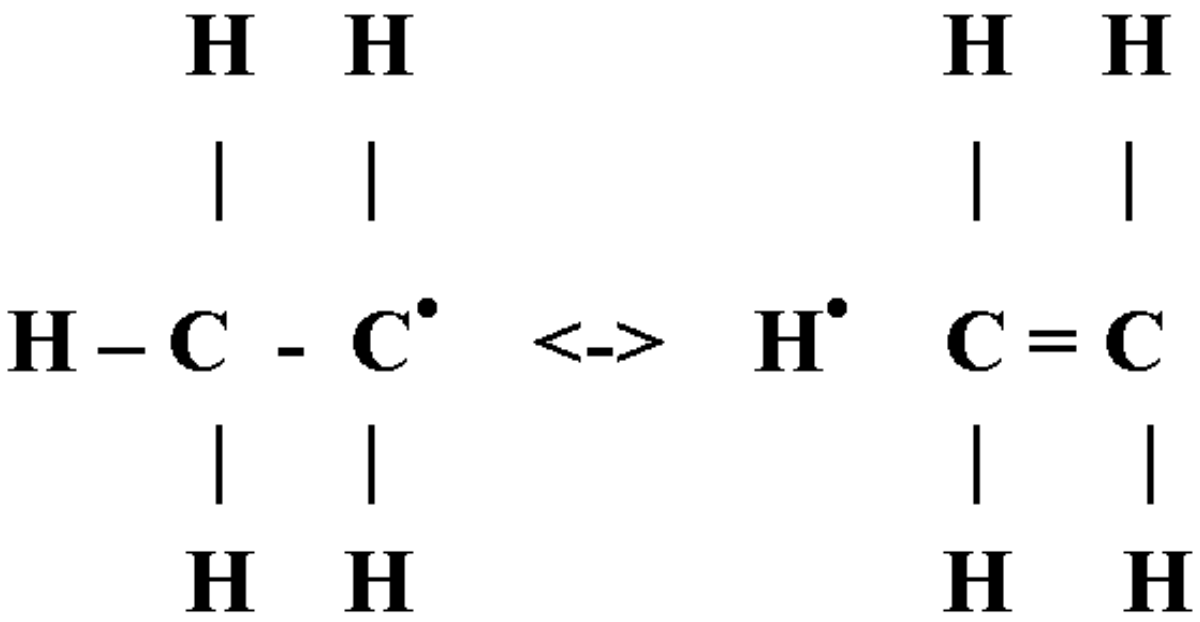
https://commons.wikimedia.org/w/index.php?curid=11940651

Radical stability increases in the order methyl < primary < secondary < tertiary

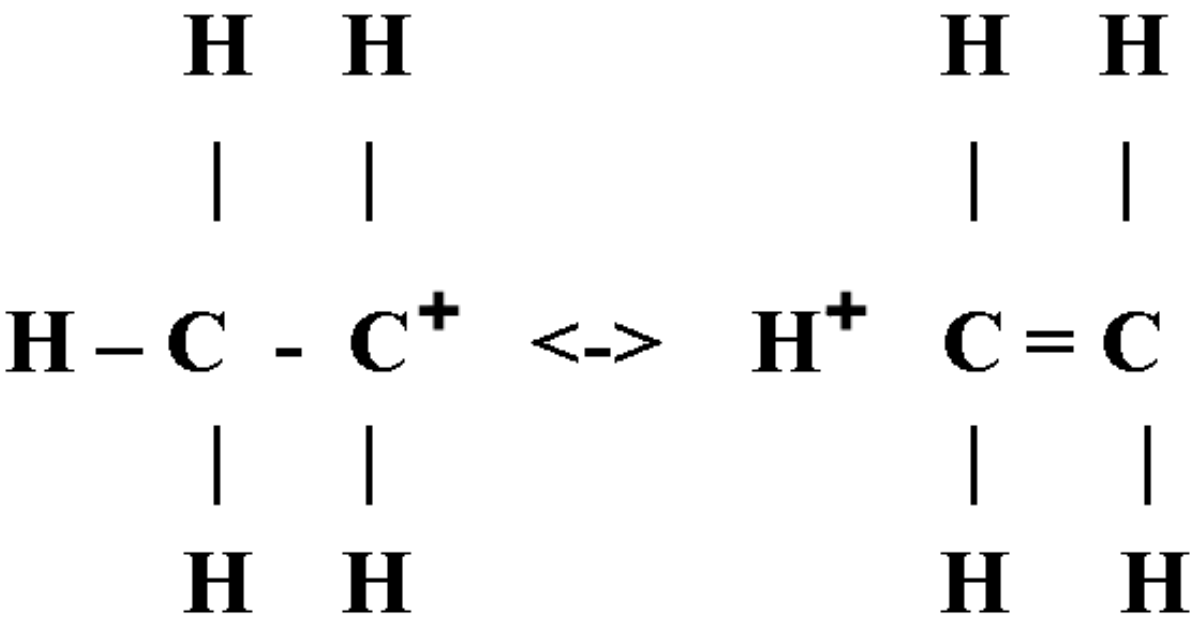


Methyl radical < **Primary radical** < **Secondary radical** < **Tertiary radical**

Least stable — **Most stable**



Hyperconjugation



Hyperconjugation

Redistribution of electrons stabilizes molecules

HOMEWORK

CHAPTER 5

ROOS, G, ROOS, C, ORGANIC CHEMISTRY CONCEPTS, ACADEMIC PRESS 2015,