Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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WORD OF MOLECULES

(Molekulák világa)

Reactivity

(Reaktivitás)

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Reactivity

Effects of structure on reactivity can be divided into two types.

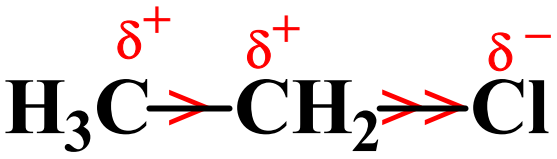
1. electronic effects/*electrical effects*

Inductive effect

Field effect

Mesomeric or resonance effect

Inductive and field effect



difference in electronegativity dipole ⇨

C-Cl bond causes polarization of the C-C bond ⇨
inductive effect: is spreading along the bonds, its value is the largest for the neighboring atoms.

Field effect is similar in its character, but it operates through **space**.

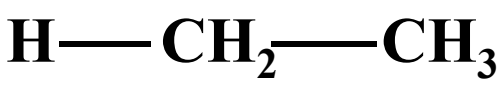
This latter is more important; field effect usually includes the inductive effect too.
Substituents can be classified as electron-withdrawing and electron-donating groups relative to hydrogen.
Abbreviation of inductive effect: -I or +I

Reference: the respective C-H bond

+I: $O^- > COO^- > CR_3 > CHR_2 > CH_2R > CH_3$

- I: $R_3N^+ > NO_2 > SO_2R > CN > COOH > F > Cl > Br > I > OR > COR > OH > C{\equiv}CR > Ar > CH{=}CR_2$

e.g.,



Resonance (mesomeric) effect

Distribution of electrons (the place of electrons) is different, than it would be if there were no resonance.

The mesomeric effect operates only if the group is directly connected to an unsaturated system.

A group with non-bonding electron pair is directly bound to an unsaturated system (but: alkyl group) exerts

+*M effect*: the electrons are relocated from the group to the unsaturated system.

A group having a multiple-bonded electronegative atom directly connected to an unsaturated system exerts

-*M effect*: the electrons are taken from the unsaturated system into the group

2. Steric effect

- Steric hindrance
- Steric acceleration

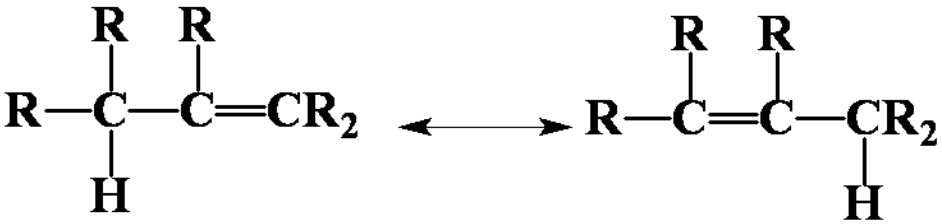
Groups having +M or -M effect

+M effect		-M effect	
$O^{\ominus}$	SR	NO_2	CHO
$S^{\ominus}$	SH	CN	COR
NR_2	Br	COOH	SO_2OR
NHR	I	COOR	NO
NH_2	Cl	$CONH_2$	Ar
NHCOR	F	CONHR	
OR	R	$CONR_2$	
OH	Ar		
OCOR			

Hyperconjugation

‘σ conjugation‘

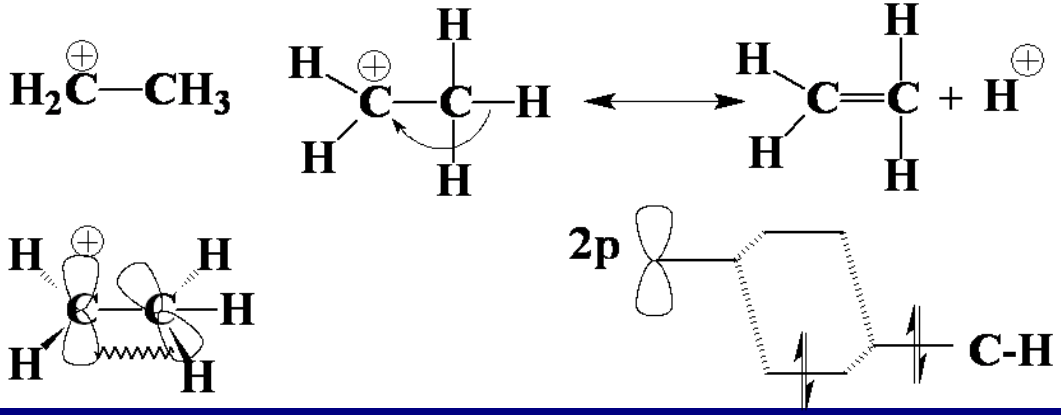
- A carbon atom with at least one hydrogen atom is attached to an unsaturated system, electrons in the C-H bond are closer to C-atom, if there were no hyperconjugation.



A C-H σ bond is overlapping with a C-C π bond

•At carbocations:

A C-H bond is overlapping with a p orbital



R—Br + EtOH

R	Relative rate
CH_3	17.6
CH_3CH_2	1
$CH_3CH_2CH_2$	0.28
$(CH_3)_2CHCH_2$	0.030
$(CH_3)_3CCH_2$	4.2×10^{-6}

Steric hindrance

Energy profile of reactions

E - r

G - r

$\Delta G^{\#}$

Kinetic controll

Thermodinamic controll

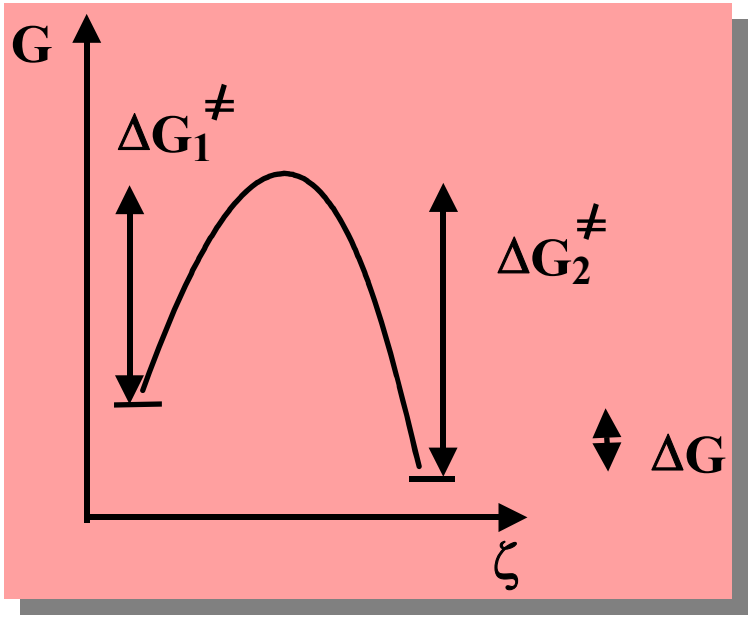
Thermodynamic requirements

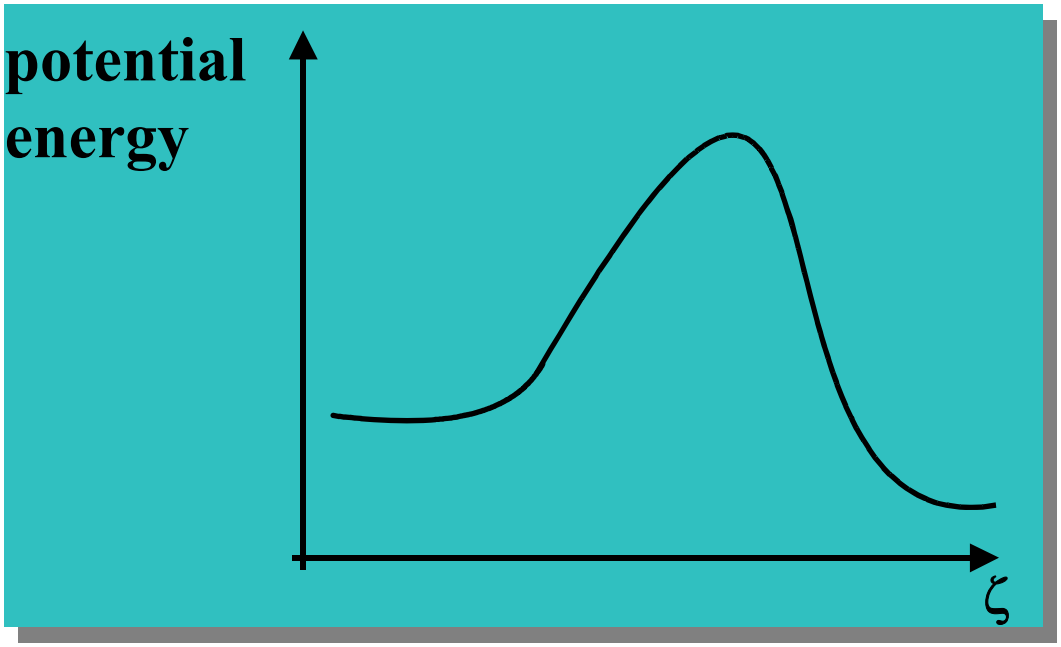
$\Delta G = \Delta H - T\Delta S$

spontaneous: ΔG is negative
not spontaneous: by adding energy

ΔH ≈ difference of bond energies between the products and the reactants and the difference of the solvation energy
ΔS ≈ difference of orderness between the products and the reactants

Trend: low enthalpy
high (positive) enthropy





ζ = reaction coordinate (e.g., combination of two inner coordinate)

potential energy :
energy belonging to a given arrangement of the accompanied atoms or ions

Pressure units and conversion factors*

pascal, Pa	1 Pa = 1 N m^{-2}
bar	1 bar = 10^5 Pa
atmosphere, atm	1 atm = **101.325** kPa = **1.013 25** bar
torr, Torr†	**760** Torr = 1 atm
	1 Torr = 133.32 Pa

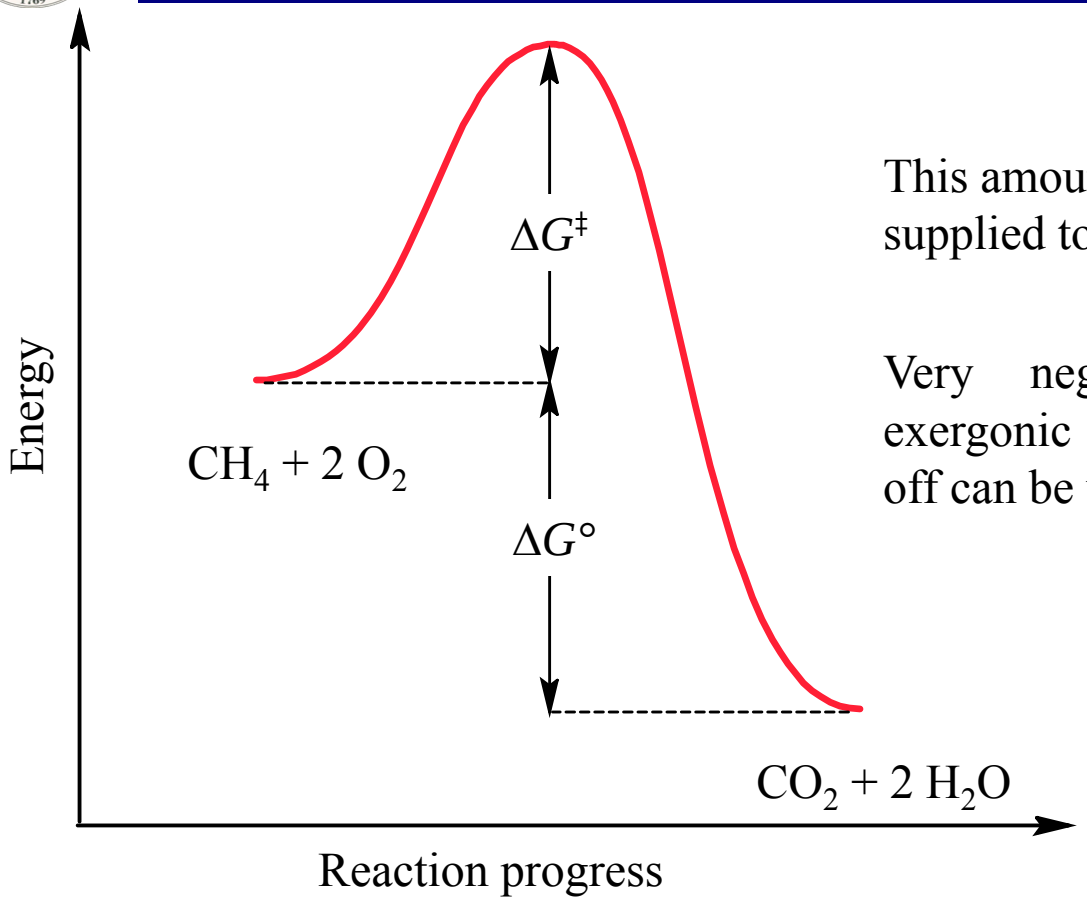
*Values in bold are exact.
†The name of the unit is torr; its symbol is Torr.

	$\Delta H_f°$/kcal mol^{-1}	$S°$/cal mol^{-1} K^{-1}
C_2H_5OH	–66,55	38,4
CH_3COOH	–116,2	38
$CH_3COOC_2H_5$	–110,7	62
H_2O	–68,32	16,9

$\Delta H°$= +3,5 kcal mol^{-1} = +14,6 kJ mol^{-1}

$\Delta S°$= +2,5 cal mol^{-1} K^{-1} = +10,5 J mol^{-1} K^{-1}

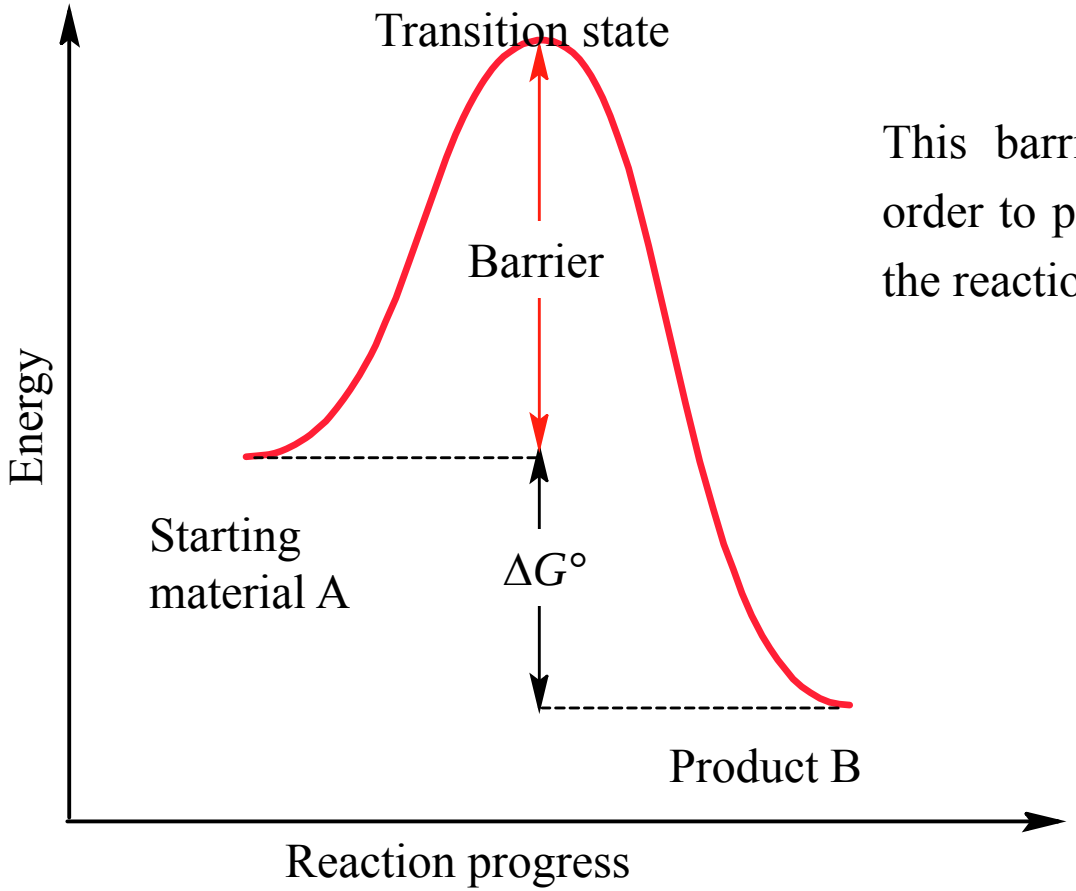
$\Delta G°$= +2,8 kcal mol^{-1} = +11,7 kJ mol^{-1} (T = 298 K)



This amount of energy must be supplied to start the reaction

Very negative for this highly exergonic reaction; the energy given off can be used to supply $\Delta G^{\ddagger}$!

An exergonic reaction can provide the energy necessary to pass over an activation barrier. Once such a reaction is started, it continues until one reactant is used up.



This barrier must be surmounted in order to produce product, even though the reaction A ⟶ B is exergonic.

Rates of reactions are not determined by the $\Delta G°$ between starting material and product, but by the height of the barrier separating starting material and product. Some very unstable materials are protected by high barriers, and thus can be isolated.

The **activated complex** is the assembly of atoms (charged or neutral) which corresponds to the maximum in the potential energy profile (or the saddle point on the potential energy surface) describing the transformation of reactant(s) into product(s) in a single step reaction with the vibrations and rotations appropriate to the reaction conditions (temperature, pressure, solvent, etc.).

A **transition state** is a hypothetical thermodynamic state corresponding to the maximum in the reaction profile of a single reaction step.

A **transition structure** is the hypothetical motionless assembly or arrangement of atoms which corresponds to the maximum in the potential energy profile (or the saddle point on the potential energy surface) describing the transformation of reactant(s) into product(s) in a single reaction step. This term is usually applied to structures which are the outcome of theoretical chemical calculations and corresponds to an arrangement of atoms without vibrational or rotational motion.

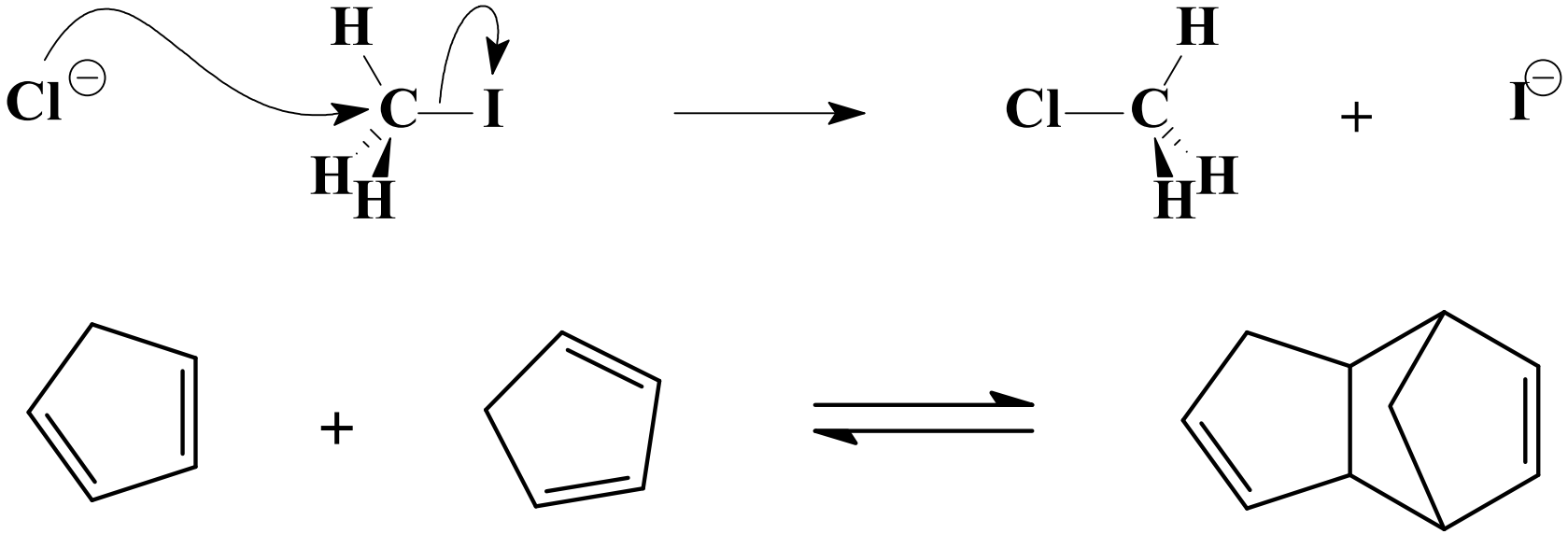
An **elementary reaction** is a single step in a more complex kinetic scheme, i.e. a chemical reaction in which there are no intermediates and occurs through a single transition state.

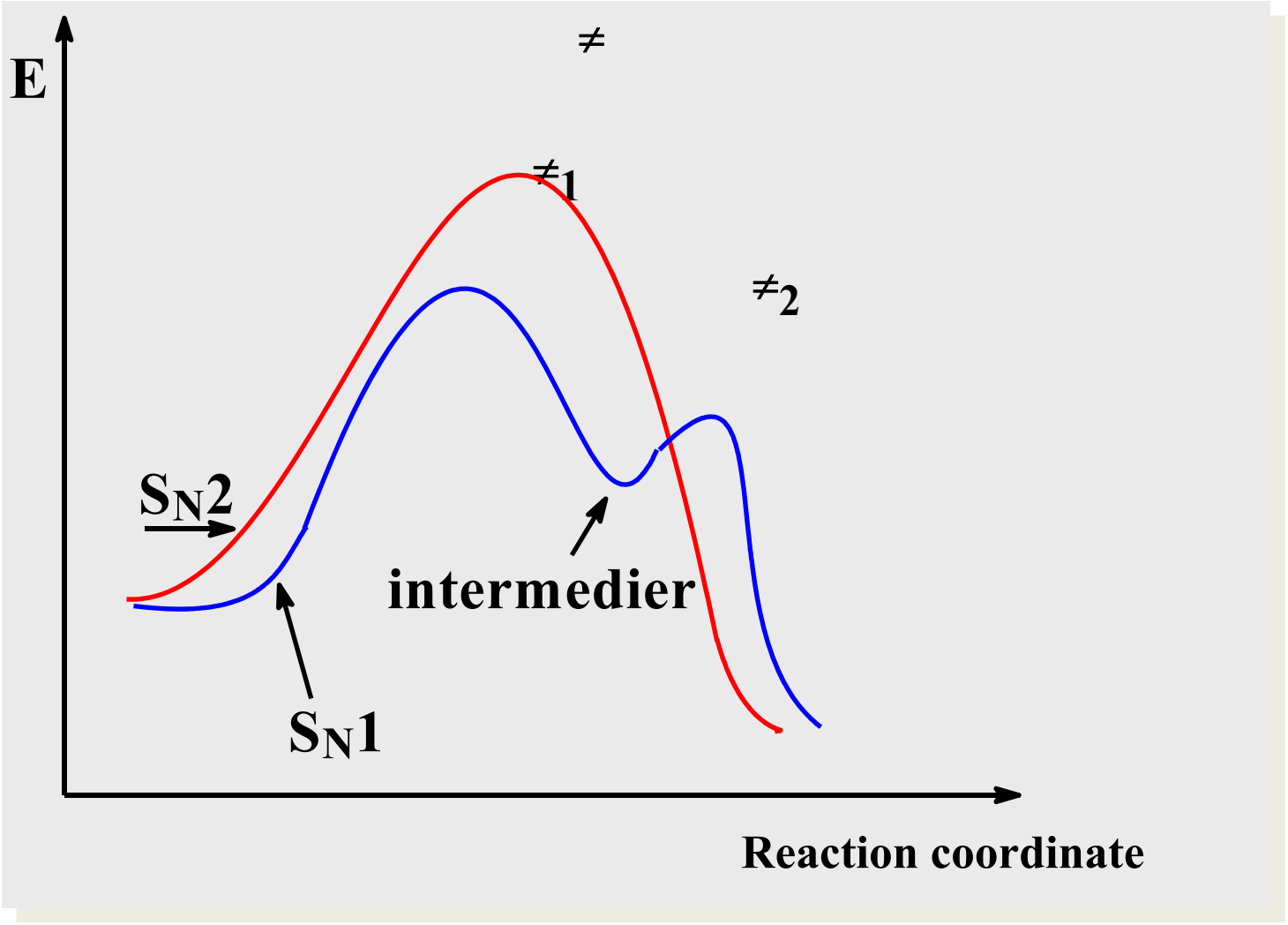
Concerted is the term applied to two or more changes occurring in a single step reaction, e.g. the bond forming and bond breaking in an S_N2 mechanism. These changes may be synchronous or asynchronous.

Synchronous is the term applied to two or more changes occurring at exactly the same time in a single step reaction; such changes are necessarily concerted.

Molecularity

The molecularity of an elementary reaction is the number of molecules (or ions) involved in the formation of one activated complex.




E
≠
≠1
≠2
SN2
intermedier
SN1
Reaction coordinate

$$aA + bB \rightleftharpoons cC + dD$$

$$[C]^c\,[D]^d = K[A]^a\,[B]^b$$

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$$\Delta G^\circ = -RT\ln K$$

$$\Delta G^\circ = -2.3RT\log K$$

The relationship between $\Delta G°$ and K at 25 °C

ΔG° (kcal/mol)	K	More Stable Comp (%)
– 0.1	1.2	54.5
– 0.5	2.4	69.7
– 1	5.4	84.4
– 2	29.3	96.7
– 5	4631	99.98
– 10	2.1×10^7	99.999996