Free Energy :

→ for a reaction, rx. is said to be in equilibrium, when conc. of reactants & products do not change.
Equilibria are described by K. (Eq. Constant).

→

$$A \rightleftharpoons B \quad K = \frac{[B]}{[A]}$$

$$\Delta G = -RT \ln K$$
$$= -2.303\, RT \log K \quad (\text{in Kcal/mol})$$

ΔG° = (free energy of products) − (free energy of reactants)

R = 1.986 cal/deg·mol
T = Temp., in degrees K

$$\Delta G^\circ = -1.36 \log K \quad (\text{at room temp.})$$

ΔG = −ve (indicates favourable rx, going to completion & release of energy.

★ Large value of K indicates a larger favorable free energy change.

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

(ΔG° free energy of products − free energy of reactants) = (ΔH° enthalpy of products − enth of reactants) − (ΔS° entropy of products − entropy of reactants)

ΔH = Heat of Rx. at constant P

ΔH° = (Sum of strengths of bonds broken) − (Sum of strengths of bonds formed)

(weaker bonds broken & stronger bonds formed)

For exothermic Rx, ΔH° = −ve ΔG = −ve

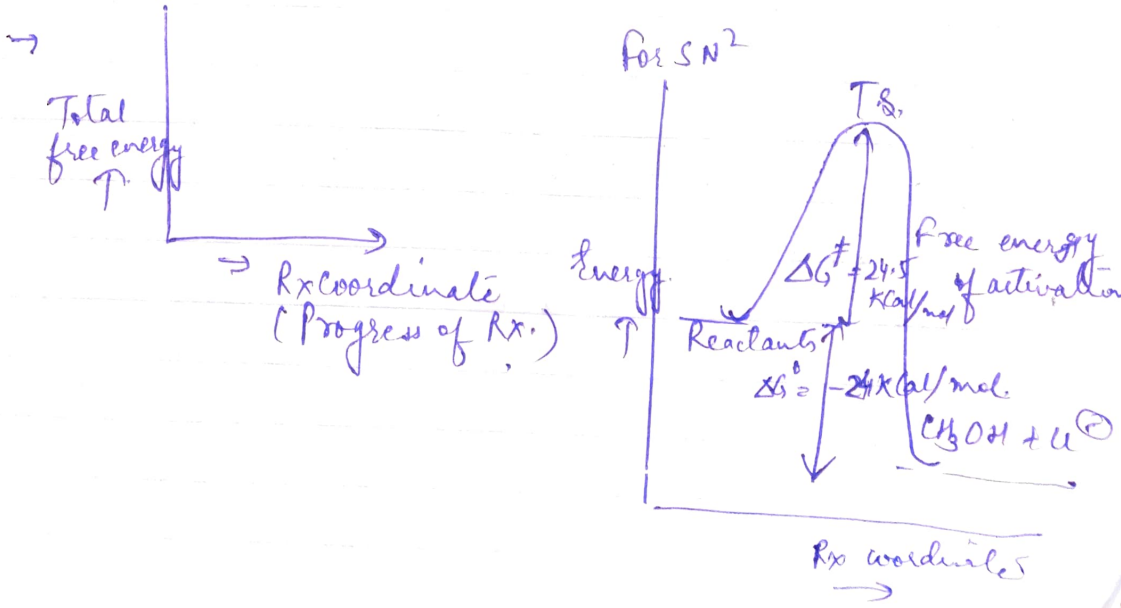
For endothermic Rx, ΔH° = +ve ΔG = +ve

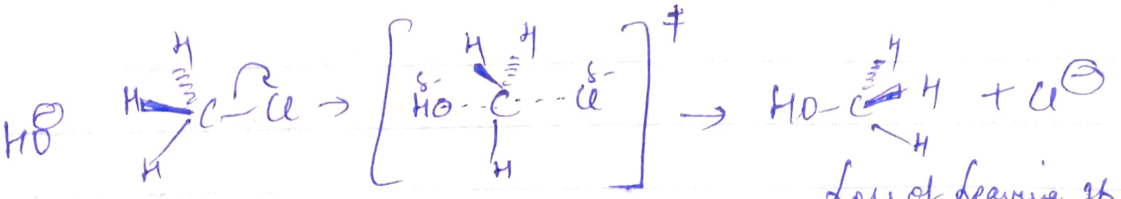
ΔS° → Measure of changes of order of a system or freedom of motion of a system.

ΔS° = +ve (products have more freedom of motion than reactants), contributing to favourable (−ve) value of ΔG°.

Reaction Profile Diagrams

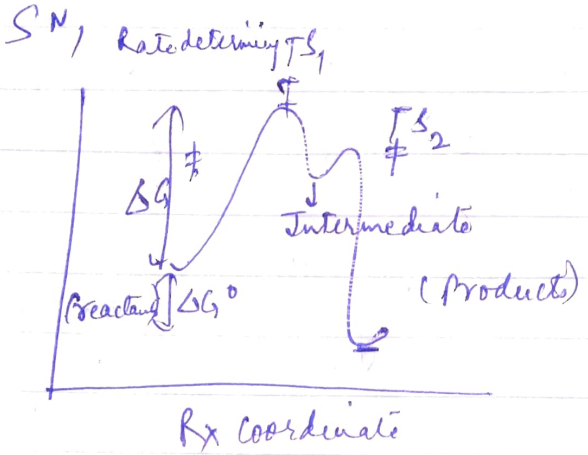
→ Course of a Rx is represented thru an energy profile diagram.

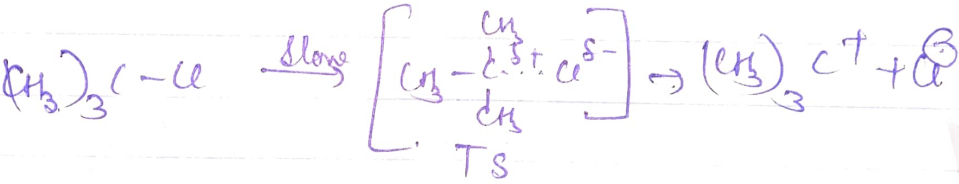




Backside attack of $Nu^{\ominus}$ | SN^2 T.S. | Loss of leaving gp

SN^2 Mech.





* T.S has a definite geometry & charge distribution, & has no finite existence. The system at this point is c/a activated complex.

* In P.E. diagrams, highest energy step of a multi step rx is the "bottle neck" & it determines the overall rate.
The step involving formation of highest energy T.S → Rate determining step.

T.S.:- not a normal covalent mol. (or ion) as some bonds partially broken & formed.

→ State of highest P.E. acquired by reactant during transformation.

→ possesses a definite geometry & charge distribution

→ highly unstable due to high energy.

→ may be 1/2.

→ No. of T.S. in a multistep Rx is always = to no. of steps.

→ Properties are often studied, as assuming it resembling to a real mol. closely).

Intermediate:-

→ normal covalent molecules (or ions) possessing a definite geometry & can be isolated.

→ Even when they are too unstable to be isolated, their properties can be studied directly by methods such as spectroscopy or alternatively, can be trapped in substances, if they react rapidly.

→ Stable.

→ generally one.

→ No. of intermediates = always one less than no. of steps.

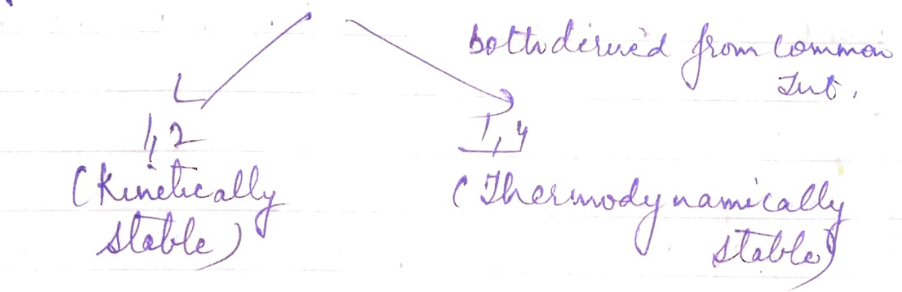
Thermodynamic & Kinetic Control :-

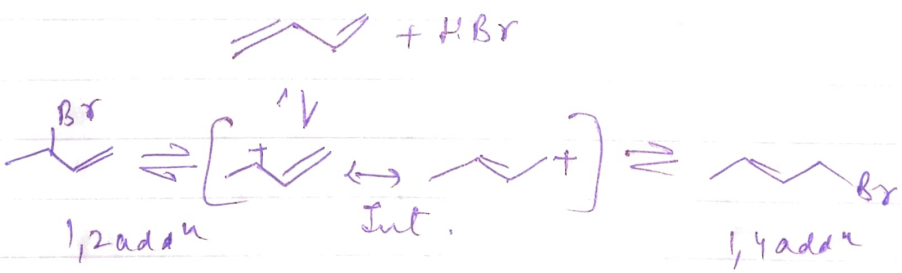
→ In Reversible Rxn conditions, Ratio of possible products is determined by relative stability of each product, measured by ΔG_i°

→ Composition of Eq. mix. does not depend on how fast ($\Delta G^\ddagger$) each product is formed in Rx. This is c/a Thermodynamic or Equilibrium Control

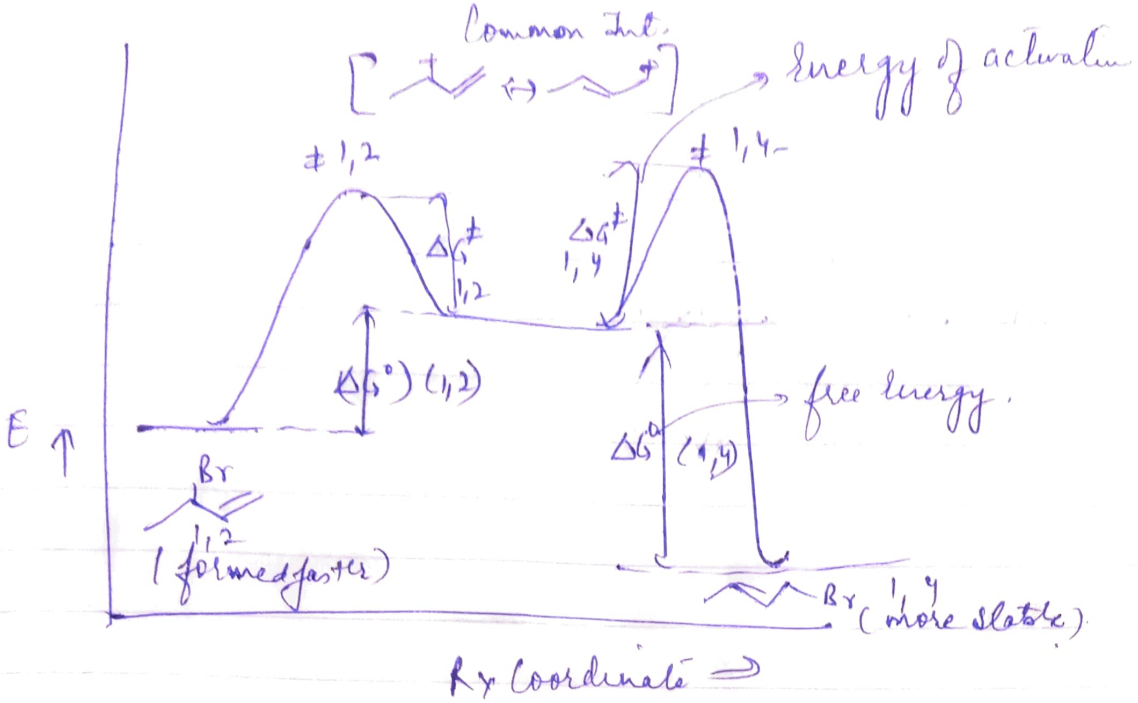
* When quantity of each possible product is determined by how fast each product is formed & is not a function of relative stability ΔG° of each product. → This is c/a Kinetic Control.

Eq. HBr addn to 1,3-Butadiene





At −80°	80%	20%
At +40°	20%	80%



→ 1,4 → predominates at higher temp (40°c), where equilibrium is more rapidly attained, even though, formed more slowly than 1,2 add^n product.

→ 1,2 → predominates at low temp (−80°c), where equilibrium is not attained very rapidly.

→ At lower temp., the rates at ∈ two Rx occur, dictate ∈ product is preferred. Rx that occurs fastest produces preferred product (1,2 add^n)
This is Kinetic control.

→ At higher temp., energies associated ∈ products dictate ∈ is preferred.. More stable product is preferred. This is thermodynamically controlled.

ΔG° for 1,4 > 1,2 ⇒ 1,4 → more stable (thermodynamic control)

$\Delta G^\ddagger$ for 1,2 < 1,4 ⇒ 1,2 → (Kinetic control)

* → However, it must be rembered that if conditions of Rx do not permit interconversion, then Kinetically controlled product will invariably predominate.