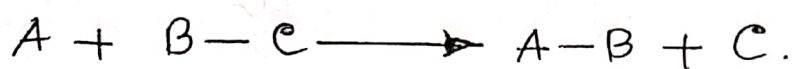


Thermodynamics, Energy Diagram and Kinetics of Organic Reaction

①

class-1

Let us assume following reaction



Is this rxn is possible or not ?



How can we determine ?

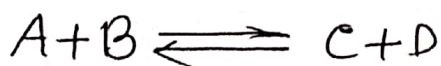


Two factors \longrightarrow 1) Thermodynamic
2) Kinetic

Thermodynamics \longrightarrow This factor will tell us whether the rxn is feasible or not ?

Kinetics \longrightarrow If the rxn is possible, then this factor will tell us the rate of the reaction.

Thermodynamic interpretation of a rxn :-



K_{eq} = Equilibrium constant

$$K_{eq} = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{[C] \cdot [D]}{[A] \cdot [B]} \quad \text{at a fixed temp.}$$

If products are more stable than reactants, $K_{eq} > 1$, if reactants are more stable than products $K_{eq} < 1$. i.e reverse rxn is favoured.

2nd SEM

$$\Delta G^\circ = G^\circ_{\text{Products}} - G^\circ_{\text{Reactants}}$$

$G^\circ_{\text{Products}}$ = standard free energy of Product

$G^\circ_{\text{Reactants}}$ = " " " " " reactant

Again,
$$\Delta G^\circ = -RT \ln K_{eq}$$

$$= -2.303 RT \log K_{eq}$$
 (R = molar Gas const.)

So, if $K_{eq} = +ve$, $\Delta G^\circ = -ve$ \rightarrow rxn is feasible.

Enthalpy and Entropy :-

we know,
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(at a fixed temperature T).

- if $\Delta H^\circ = +ve \rightarrow$ Endothermic rxn
- $\Delta H^\circ = -ve \rightarrow$ Exothermic "

For an exothermic rxn ($\Delta H^\circ = -ve$) ΔG° is always $-ve$ at all temperature if ΔS° is positive, i.e. no. of species increases on going from reactant to Product

so, ΔG° will be negative if numerical value of $(T\Delta S^\circ)$ exceed than ΔH° ,
But when ΔS° is $-ve$, then ΔG° will be $-ve$ only when $(T\Delta S^\circ)$ is numerically less than ΔH° (numerical value)

But what about for endothermic rxn??

$\Delta H^\circ = +ve$

Rxn will not be feasible if $\Delta S^\circ = -ve$ because,

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $= +ve - T(-ve)$

$= +ve \implies$ Non spontaneous.

But, if ΔS° is +ve, and numerical value of $(T \times \Delta S^\circ)$ exceeds ΔH° then

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $= +ve - ve = -ve \implies$ spontaneous
(Greater value)

(Feasible).

Kinetics interpretation of a rxn:

$k = A e^{-E_a/RT}$
(small k)
↑

Arrhenius equation

$E_a =$ activation energy of a rxn.
 $A =$ Arrhenius constant

more the value of E_a , less is the value of k , slower is the rate of the rxn.

less is the value of E_a , more is the value of k , more is the rate of rxn.

E_a can be determined by carrying out the rxn at two different temperatures
 $k_1 = A e^{E_a/RT_1} \implies \ln k_1 = \ln A - E_a/RT_1$
 $k_2 = A e^{E_a/RT_2} \implies \ln k_2 = \ln A - E_a/RT_2$
} $\implies \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$