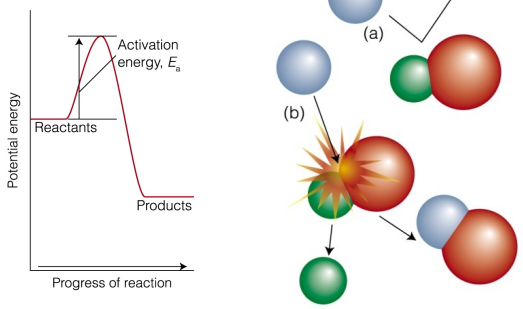
Teorija sudara



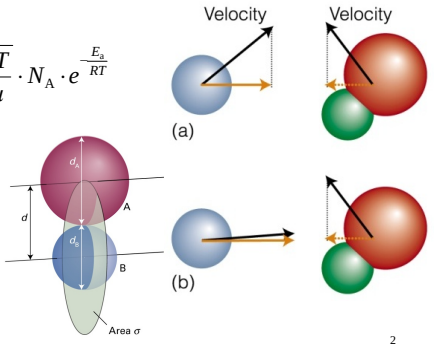
1

Teorija sudara

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

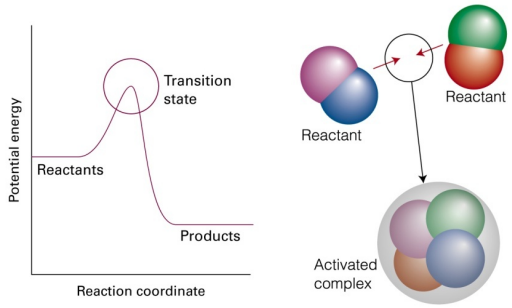
$$k = P\sigma\sqrt{\frac{8kT}{\pi\mu}} \cdot N_A \cdot e^{-\frac{E_a}{RT}}$$

P je sterički faktor, σ je sudarni presjek μ je reducirana masa reaktanata.



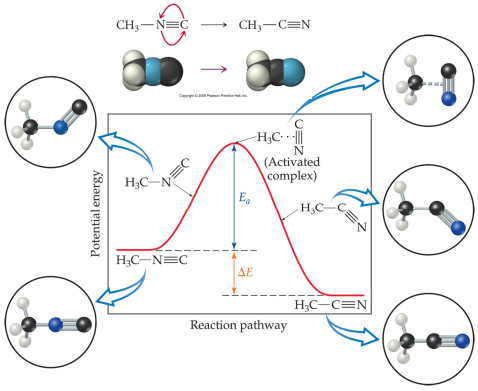
2

Teorija prijelaznog stanja



3

Teorija prijelaznog stanja



4

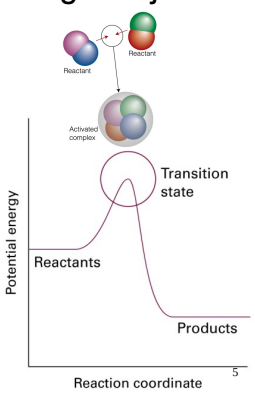
Teorija prijelaznog stanja

$$A + B \rightleftharpoons C^{\ddagger}$$

$$K^{\ddagger} = \frac{c_C^{\ddagger} \cdot c^{\ominus}}{c_A \cdot c_B}$$

Eyringova jednadžba, κ je transmisijski koeficijent:

$$k = \kappa \cdot \frac{k_B T}{h} \cdot K^{\ddagger}$$



5

Eyringova jednadžba

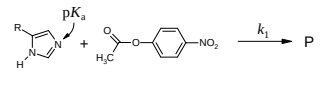
Iskazana pomoću termodinamičkih aktivacijskih parametara.

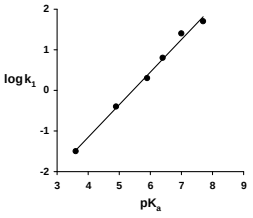
$$k = \frac{k_B T}{h} \cdot e^{-\frac{\Delta^{\ddagger}H - T \cdot \Delta^{\ddagger}S}{RT}}$$

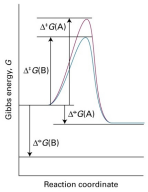
$$k = \frac{k_B T}{h} \cdot e^{\frac{\Delta^{\ddagger}S}{R}} \cdot e^{-\frac{\Delta^{\ddagger}H}{RT}}$$

6

Linearne korelacije slobodne energije



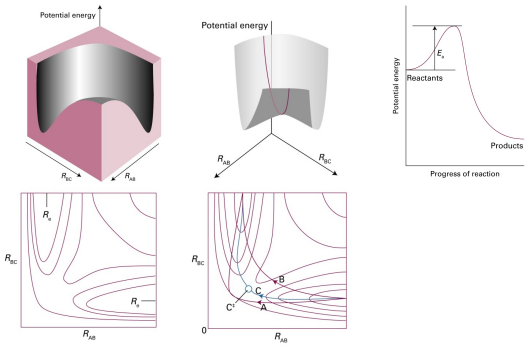




7

Reljef potencijalne energije

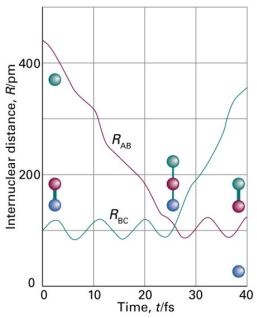
$$A\text{-}B + C \rightleftharpoons A + B\text{-}C$$

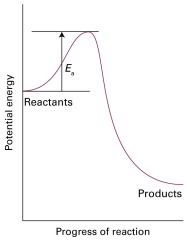


8

Reljef potencijalne energije

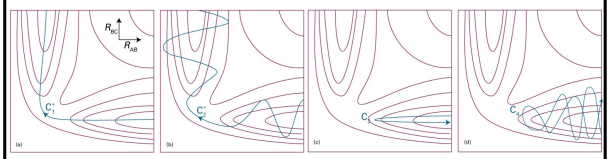
$$A + B\text{-}C \rightleftharpoons A\text{-}B + C$$





9

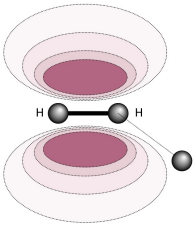
Kinetička i vibracijska energija

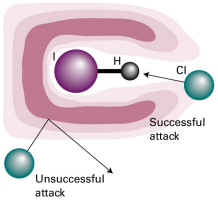


10

Međusobna orijentacija reaktanata

$$H\text{-}H + \mathbf{H} \rightleftharpoons H + H\text{-}\mathbf{H} \qquad I\text{-}H + Cl \rightleftharpoons I + H\text{-}Cl$$





11

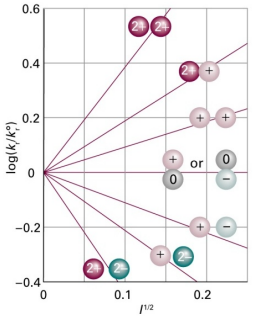
Kinetički solni efekt

$$A^{n\pm} + B^{n\pm} \rightleftharpoons C^{\ddagger\, n\pm}$$

$$\log k = \log k_\circ \cdot 2Az_A z_B \sqrt{I}$$

$$\log\left(\frac{k}{k_\circ}\right) = 2 \cdot A \cdot z_A \cdot z_B \cdot \sqrt{I}$$

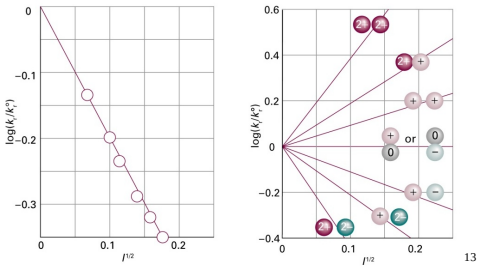
k i $k_\circ$ su konstante brzine reakcije pri ionskoj jakosti 0 i I, A iznosi 0.509 za vodenu otopinu pri 25°C, z_A i z_B su naboji reaktanata.



12

Kinetički solni efekt

$$\log(\frac{k}{k_\circ}) = 2Az_A z_B\sqrt{I}$$



Kinetika prijenosa elektrona

$$D + A \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} D^+ + A^- \qquad \frac{1}{k_{obs}} \approx \frac{1}{k_a}\left(1+\frac{k_a'}{k_{et}}\right)$$

•Kada je $k_{et} >> k_a'$, $k_{obs} \approx k_a$, brzina prijenosa elektrona određena je brzinom difuzije D i A kroz otopinu.

•Kada je $k_{et} << k_a'$, $k_{obs} \approx (k_a/k_a')k_{et}$, brzina prijenosa elektrona određena je energijom aktivacije za prijenos elektrona unutar DA kompleksa.

•Ako su D i A na stalnoj udaljenosti (npr. kod enzima):

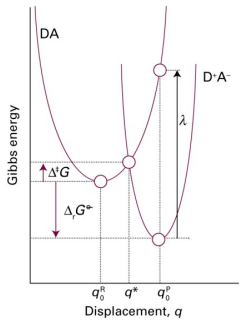
$$k_{et} = \kappa \cdot \frac{k_B T}{h} \cdot e^{\frac{-\Delta^\ddagger G}{RT}}$$

Prijenos elektrona

$$D + A \rightleftharpoons D^+ + A^-$$

$$\Delta^\ddagger G = \frac{(\Delta_r G^\ominus + \lambda)^2}{4\lambda}$$

Marcusova jednadžba za aktivacijsku Gibbsovu energiju kod prijenosa elektrona, λ je reorganizacijska energija.

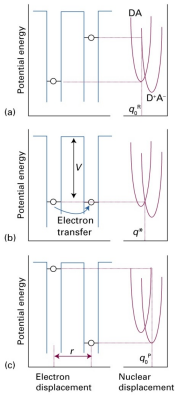


Prijenos elektrona

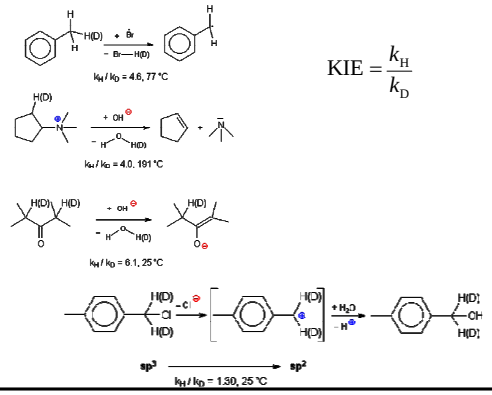
$$D + A \rightleftharpoons D^+ + A^-$$

$$k_{et} \propto e^{-\beta r} \cdot e^{-\frac{\Delta^\ddagger G}{RT}}$$

Marcusova jednadžba za konstantu brzine kod prijenosa elektrona, r je udaljenost između **D**onora i **A**kceptora, β ovisi o mediju kroz koji elektron prelazi.



Kinetički izotopni efekti



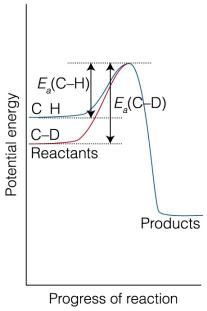
$$KIE = \frac{k_H}{k_D}$$

Primarni KIE

$$D\text{-}\mathbf{H} + A \xrightarrow{k_H} D + \mathbf{H}\text{-}A$$

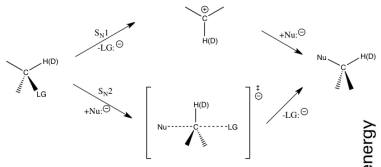
$$D\text{-}\mathbf{D} + A \xrightarrow{k_D} D + \mathbf{D}\text{-}A$$

$$KIE = \frac{k_H}{k_D}$$

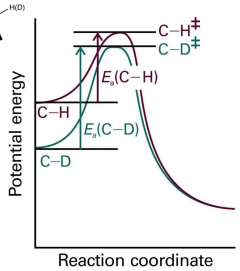


$$D\text{-}\mathbf{H(D)} + A \longrightarrow D\cdots\mathbf{H(D)}\cdots A^\ddagger \longrightarrow D + \mathbf{H(D)}\text{-}A$$

Sekundarni KIE



$$\mathrm{KIE} = \frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}$$



Normalni KIE: 1 < KIE < ≈ 2

Inverzni KIE: KIE < 1

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