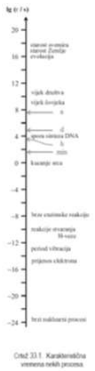
Kemijska kinetika

bavi se

- proučavanjem brzina kemijskih reakcija
- proučavanjem mehanizama kojima se te reakcije odvijaju

$$R \rightarrow P$$



KLJUČNI POJMOVI

brzina konverzije (prirast dosega reakcije)

$$\dot{\zeta} = \frac{\mathrm{d}\zeta}{\mathrm{d}t}$$

brzina kemijske reakcije

$$v = \frac{\mathrm{d}x}{\mathrm{d}t} \qquad v_c = \frac{1}{\nu_\mathrm{B}} \frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t}$$

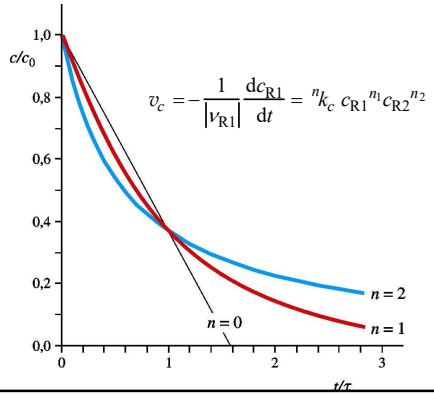
brzina trošenja / nastajanja

$$v_\mathrm{R} = -\frac{\mathrm{d}c_\mathrm{R}}{\mathrm{d}t} \qquad v_\mathrm{P} = \frac{\mathrm{d}c_\mathrm{P}}{\mathrm{d}t}$$

KLJUČNI POJMOVi

- molekularnost
- red reakcije
- koeficijent (konstanta) brzine reakcije
- mehanizam kemijske reakcije

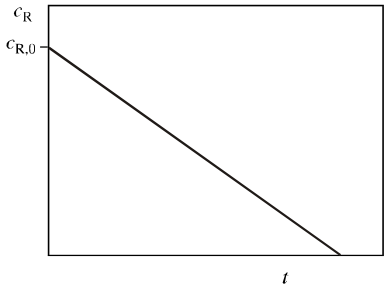
Zakoni brzina kemijskih reakcije



$$v_c = -\frac{1}{|\nu_{\mathrm{R}1}|} \frac{\mathrm{d}c_{\mathrm{R}1}}{\mathrm{d}t} = {}^{n}k_c \, c_{\mathrm{R}1}{}^{n_1} c_{\mathrm{R}2}{}^{n_2}$$

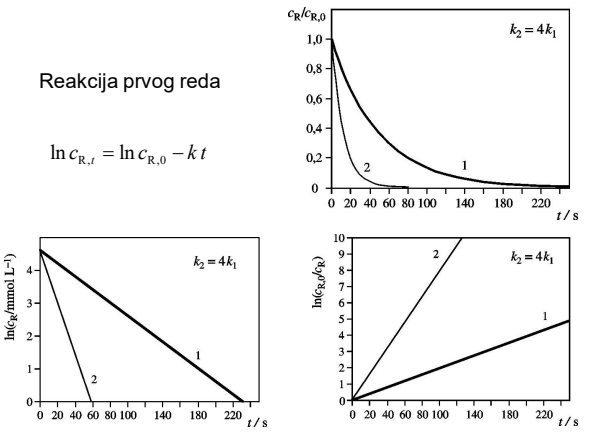
Reakcija nultog reda

$$c_{R,t} = c_{R,0} - k\,t$$



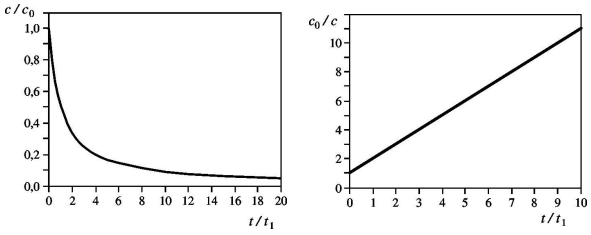
Reakcija prvog reda

$$\ln c_{\mathrm{R},t} = \ln c_{\mathrm{R},0} - k\,t$$



Reakcija drugog reda

$$\frac{1}{c_{\mathrm{R},t}} = \frac{1}{c_{\mathrm{R},0}} + k\,t$$



Reakcije pseudo-*n*-tog reda

primjer A + B → P

- koncentracija B značajno veća od koncentracije A, reakcija će biti prvog reda u odnosu na A i neće ovisiti o koncentraciji B
- reakcija pseudo-prvog reda

vrijeme polureakcije $t_{1/2}$

reakcija prvog reda

$$\ln c_{\mathrm{R},t} = \ln c_{\mathrm{R},0} - k\,t$$

reakcija drugog reda

$$\frac{1}{c_{\mathrm{R},t}} = \frac{1}{c_{\mathrm{R},0}} + k\,t$$

ako vrijedi: $t = t_{1/2}$ $c_{R,t} = \frac{1}{2} c_{R,0}$

$$t_{1/2} = \frac{ln2}{|\nu_A| k}$$

$$t_{1/2} = \frac{ln2}{k|\nu_A| c_{R,0}}$$

Zakoni brzina iz pretpostavljenih mehanizama reakcije

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} + \mathrm{D}$$

$$v_1 = k_1 c_{\mathrm{A}} c_{\mathrm{B}} \qquad K_c = \frac{c_{\mathrm{C}} c_{\mathrm{D}}}{c_{\mathrm{A}} c_{\mathrm{B}}}$$

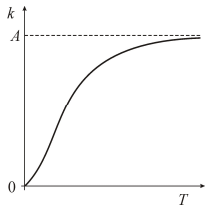
$$v_{-1} = k_{-1} c_{\mathrm{C}} c_{\mathrm{D}}$$

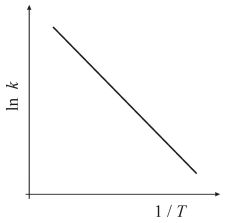
Temperaturna ovisnost brzine reakcije

Slika 33.2 Svante Arrhenius švedski kemičar (1859 - 1927) i dobitnik Nobelove nagrade za kemiju 1903. za teoriju elektrolitne disocijacije.

$$k = A \cdot \exp(-E_{\mathrm{a}} / RT)$$

$$\ln k = \ln A - \frac{E_{\mathrm{a}}}{RT}$$



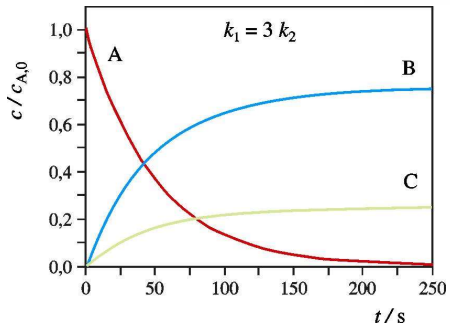


$$k = A \cdot \exp(-E_a / RT) \qquad \ln k = \ln A - \frac{E_a}{RT}$$

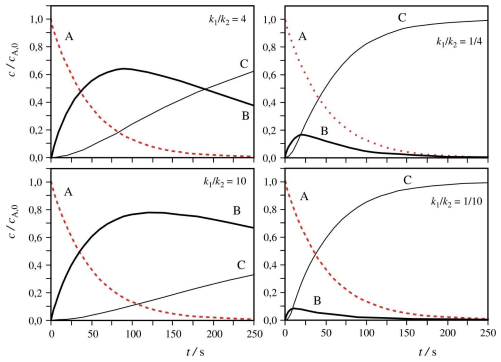
MEHANIZAM REAKCIJE

- usporedne ili paralelne reakcije
- uzastopne ili konsekutivne reakcije
- povrative ili reverzibilne reakcije

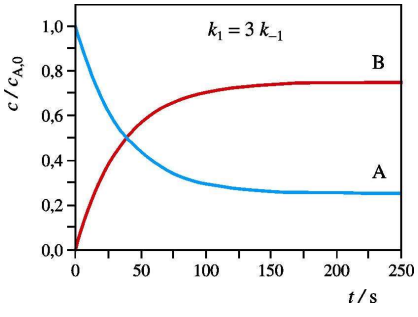
usporedne ili paralelne reakcije



uzastopne ili konsekutivne reakcije $A \rightarrow B \rightarrow C$



povrative ili reverzibilne reakcije



Teorije brzina reakcija

- Teorija sudara

  sudarni presjek
  gustoća učestalosti sudara
  energijski prag

- Teorija prijelaznog stanja (teorija aktiviranog kompleksa, teorija apsolutnih brzina reakcija)

  prijelazno stanje (aktivirani kompleks)

ENZIMSKA KINETIKA

$$S \xrightarrow{E} P$$

$$E+S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E+P$$

Michaelis&Menten (1913)

Leonor Michaelis (1875 –1949)

Maud Leonora Menten (1879 –1960)

Briggs, G.E.; Haldane, J.B.S. (1925). "A note on the kinematics of enzyme action". *Biochem J* **19** (2): 338–339.

L. A NOTE ON THE KINETICS OF ENZYME ACTION.

By GEORGE EDWARD BRIGGS and JOHN BURDON SANDERSON HALDANE.

(*From the Botanical and Biochemical Laboratories, Cambridge.*)

(*Received March 9th, 1925.*)

The equation of Michaelis and Menten [1913] has been applied with success by Kuhn [1924] and others to numerous cases of enzyme action. It is therefore desirable to examine its theoretical basis. Consider the irreversible reaction $A \rightarrow B$, unimolecular as regards A, and catalysed by an enzyme. Suppose one molecule of A to combine reversibly with one of enzyme, the compound then changing irreversibly into free enzyme and B, where B may represent several molecules. We may represent this as:

$$A + E \rightleftharpoons AE \rightarrow B + E.$$

$(a - x)$ $(e - p)$ p x

Now let a be the initial concentration of A, e the total concentration of enzyme, x the concentration of B produced after time t, and p the concentration of enzyme combined with substrate at time t. We suppose e and p to be negligibly small compared with a and x. Then by the laws of mass action

$$\frac{dp}{dt} = k_1 (a - x)(e - p) - k_2 p - k_3 p,$$

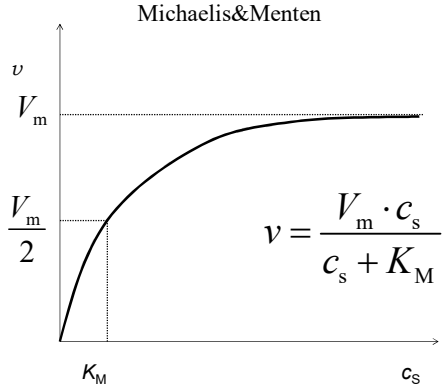
where k_1, k_2, k_3 are the velocity constants of the reactions

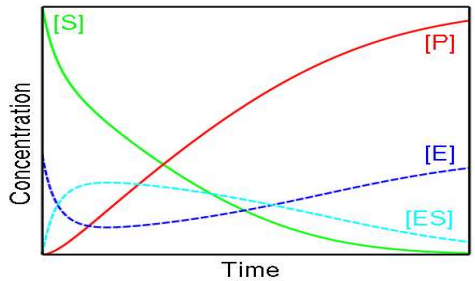
$$A + E \rightarrow AE, \quad AE \rightarrow A + E, \quad \text{and} \quad AE \rightarrow B + E,$$

respectively. Now since p is always negligible compared with x and $a - x$, its rate of change must, except during the first instant of the reaction, be negligible compared with theirs.

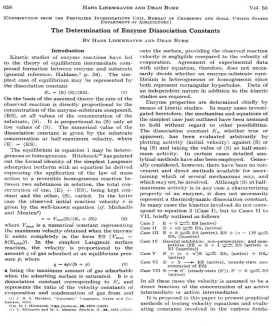
For during the remainder of the reaction p diminishes from a value not exceeding e to zero, whilst x increases from zero to a. Thus the average value of $-\frac{dp}{dt} + \frac{dx}{dt}$ is less than $\frac{e}{a}$. And provided $\frac{e}{a}$ is small it is clear that if the amount of combined enzyme decreased for a measurable time at a rate comparable with that of its substrate the reaction would come to an end. To take a concrete example Kuhn [1924] calculates that a yeast saccharase molecule at 15° and p_H 4·6 can invert 100 or more molecules of sucrose per second. Even if the enzyme concentration is so unusually large that the inversion of a strong sucrose solution is half completed in 10 minutes, $\frac{e}{a}$ cannot be less than 120,000, and if $-\frac{dp}{dt}$ attained 1 % of the value of $\frac{dx}{dt}$ for 1 second the

Michaelis&Menten





Lineweaver, H and Burk, D. (1934). "The Determination of Enzyme Dissociation Constants", *Journal of the American Chemical Society* **56** (3): 658–666.



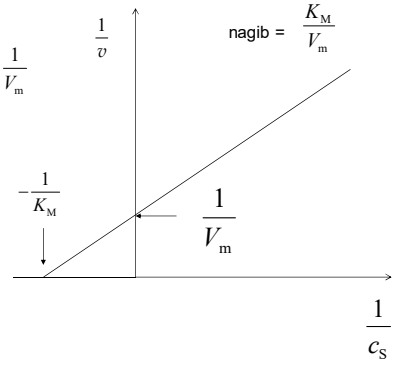
The Determination of Enzyme Dissociation Constants

By Hans Lineweaver and Dean Burk

Introduction

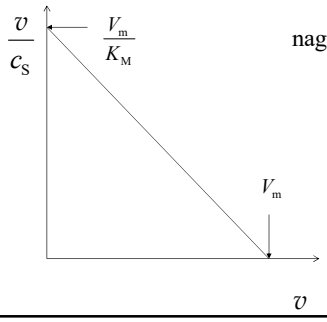
H. Lineweaver i D. Burk

$$\frac{1}{v} = \frac{K_M}{V_m c_S} + \frac{1}{V_m}$$



G. S. Eadie

$$\frac{v}{c_S} = -\frac{v}{K_M} + \frac{V_m}{K_M}$$



$$\text{nagib} = -\frac{1}{K_M}$$