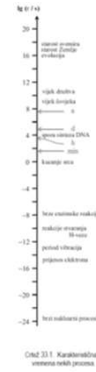


Kemijska kinetika

bavi se

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



KLJUČNI POJMOVI

brzina konverzije
(prirast dosegaja reakcije)

$$\dot{\zeta} = \frac{d\zeta}{dt}$$

brzina kemijske
reakcije

$$v = \frac{dx}{dt} \quad v_c = \frac{1}{\nu_B} \frac{dc_B}{dt}$$

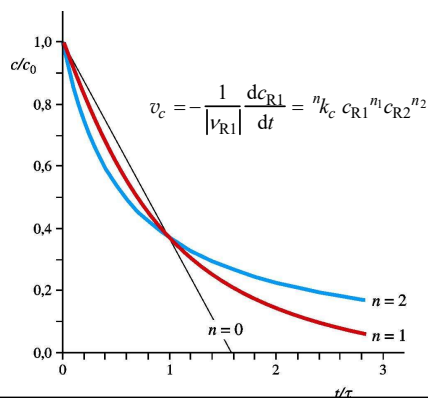
brzina trošenja / nastajanja

$$v_R = -\frac{dc_R}{dt} \quad v_P = \frac{dc_P}{dt}$$

KLJUČNI POJMOVI

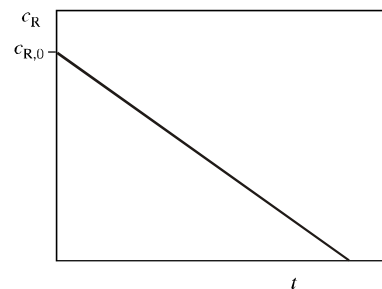
- molekularnost
- red reakcije
- koeficijent (konstanta) brzine reakcije
- mehanizam kemijske reakcije

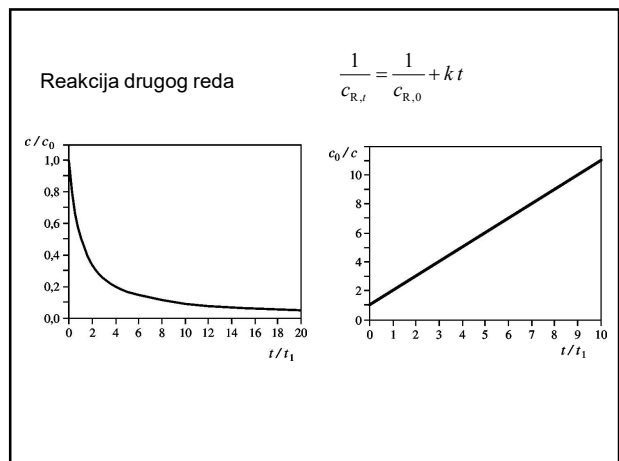
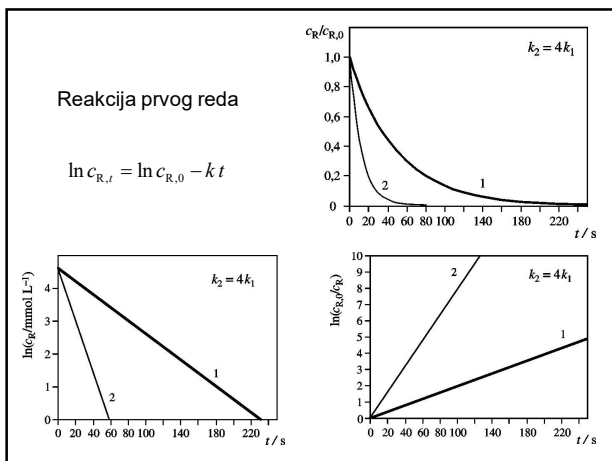
Zakoni brzina kemijskih reakcije



Reakcija nultog reda

$$c_{R,t} = c_{R,0} - kt$$





Reakcije pseudo-*n*-tog reda

primjer $A + B \rightarrow P$

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

reakcija drugog reda $\frac{1}{c_{R,t}} = \frac{1}{c_{R,0}} + k t$

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

$$t_{1/2} = \frac{\ln 2}{|v_A|k} \quad t_{1/2} = \frac{1}{k|v_A|c_{R,0}}$$


Zakoni brzina iz pretpostavljenih mehanizama reakcije

$$A + B \rightleftharpoons C + D$$

$$v_1 = k_1 c_A c_B \quad K_c = \frac{c_C c_D}{c_A c_B}$$

$$v_{-1} = k_{-1} c_C c_D$$

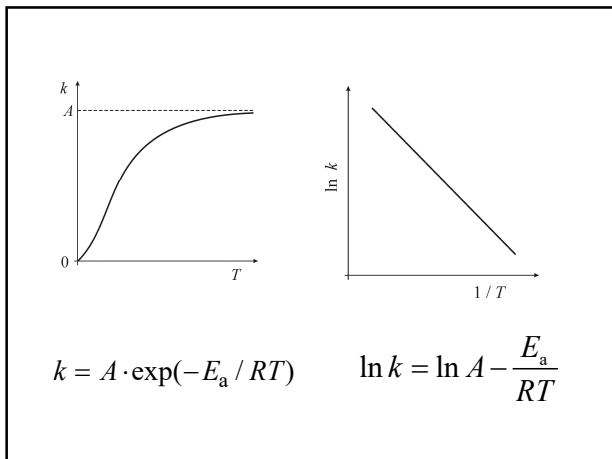
Temperaturna ovisnost brzine reakcije



$$k = A \cdot \exp(-E_a / RT)$$

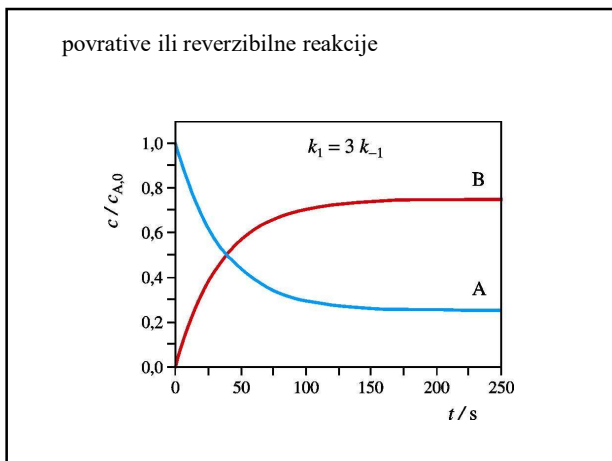
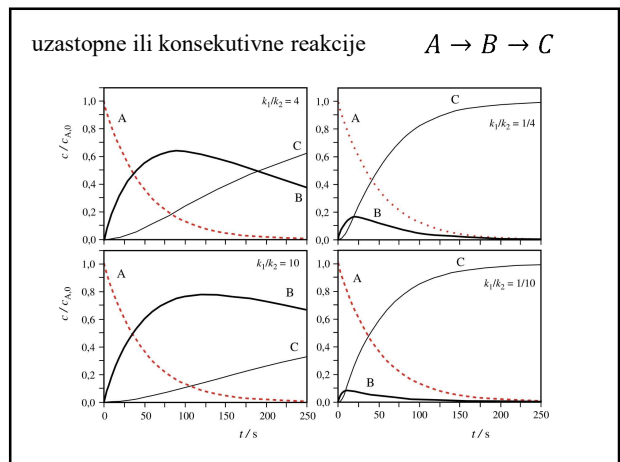
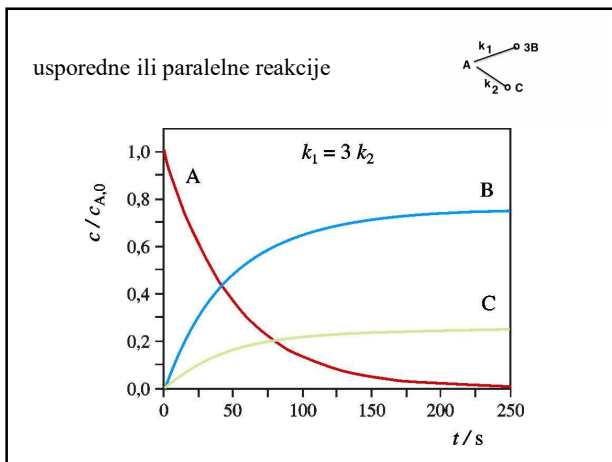
$$\ln k = \ln A - \frac{E_a}{RT}$$

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



MECHANIZAM REAKCIJE

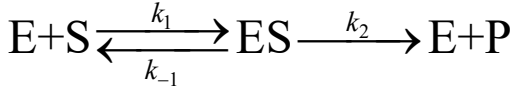
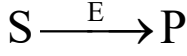
- usporedne ili paralelne reakcije
- uzastopne ili konsekutivne reakcije
- povratne ili reverzibilne reakcije



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



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 HUDSON SANDERSON HALDANE. (From the Biochemical and Biophysical 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 $A \rightarrow B$, simultaneous in regard to A , and catalysed by an enzyme. Suppose one molecule of A to combine reversibly with one of enzyme, the compound thus changing irreversibly into free enzyme and B , where B may represent several molecules. We may represent this as:

$$A + E \rightleftharpoons^k_1 \underset{k_{-1}}{AE} \xrightarrow{k_2} B + E$$

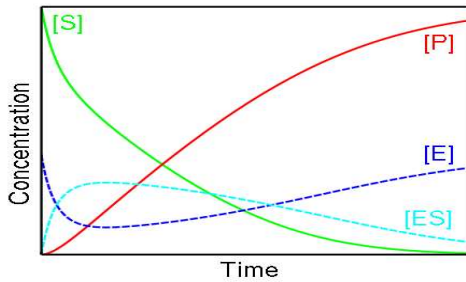
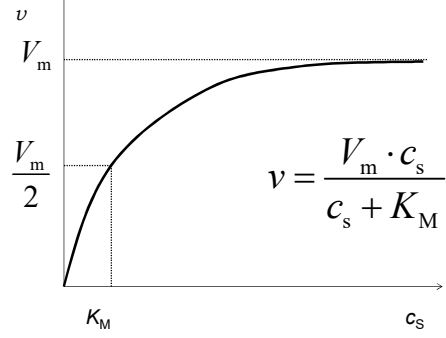
Now let a be the initial concentration of A , e the total concentration of enzyme, x the concentration of B produced after time t , and p the concentration of enzyme combined with substrate at time t . We suppose a and p to be negligibly small compared with a and e . Then by the laws of mass action:

$$\frac{dx}{dt} = k_1(a-x)(e-p) - k_{-1}ep - k_2p$$

where k_1, k_2, k_{-1} are the velocity constants of the reaction $A + E \rightleftharpoons AE, AE \rightarrow A + E$, and $AE \rightarrow B + E$, 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 itself.

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 $-\frac{dx}{dt}$ is less than $\frac{a}{t}$. And provided t 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 cease to be a simple reaction. Even if the enzyme concentration is so unusually large that the inversion of a strong sucrose solution is half completed in 10 minutes, t cannot be less than 120,000, and if $-\frac{dx}{dt}$ attained 1% of the value of $\frac{a}{t}$ for 1 second the

Michaelis & Menten



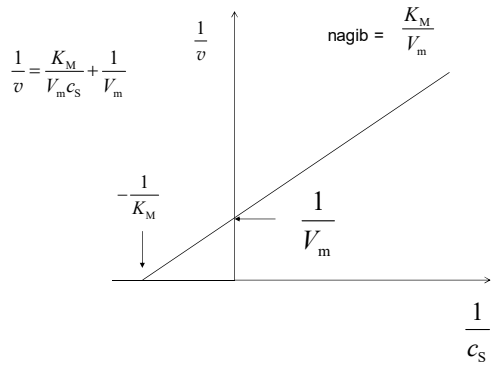
Lineweaver, H and Burk, D. (1934). "The Determination of Enzyme Dissociation Constants", *Journal of the American Chemical Society* 56 (3): 658-666.

658 HENRY LINWEAVER AND DAVID BURK Vol. 56
Determination of the Fractional Inhibition of Enzyme by Carbonyl and Sulfhydryl Compounds

The Determination of Enzyme Dissociation Constants

Kinetic studies of enzyme reactions have been based on the theory of equilibrium intermediate compounds. The dissociation constants of the enzyme-substrate complex and of the enzyme-inhibitor complex have been determined by Lineweaver and Burk (1934) and by other workers. The dissociation constants of the enzyme-substrate complex have been determined by Lineweaver and Burk (1934) and by other workers. The dissociation constants of the enzyme-inhibitor complex have been determined by Lineweaver and Burk (1934) and by other workers. The dissociation constants of the enzyme-substrate complex have been determined by Lineweaver and Burk (1934) and by other workers. The dissociation constants of the enzyme-inhibitor complex have been determined by Lineweaver and Burk (1934) and by other workers.

H. Lineweaver i D. Burk



G. S. Eadie

