

C6320 Chemická kinetika:

Historie chemické kinetiky

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Ref: "The World of Physical Chemistry," by K. J. Laidler, Oxford Univ. Press, 1993)

- **•1850: Wilhelmy (Germany) studied the rate of inversion of sucrose (hydrolysis into D-(+)-glucose and D-(-)-fructose in the presence of an acid) and found it to be proportional to the concentrations of both the sugar and the acid. (viz experimentální úloha v praktiku fyzikální chemie)**
- **•1864: Guldberg and Waage (Norway) formulated their "law of mass action," according to which the reaction "forces" are proportional to the product of the concentrations of the reactants: $K = \frac{[R]^r [S]^s}{[A]^a [B]^b}$ where a, b, r and s are the stoichiometric coefficients in the chemical equation $A + B = R + S$. So the rate of the forward reaction is proportional to $[A]^a [B]^b$ and that of the reverse reaction is proportional to $[R]^r [S]^s$.**

- **•1865: Harcourt and Esson (UK) analyzed the reactions between H₂O₂ and HI and between KMnO₄ and (COOH)₂. They wrote the corresponding differential equations, integrated them and determined the concentration vs. time relationships. They also proposed an equation for the temperature dependence of the reaction rate, $k = A TC$.**
- **•1884: van't Hoff (The Netherlands) published his "Studies of Chemical Dynamics" (Études de dynamique chimique), in which he generalized and further developed the work of Wilhelmy,**

- **Harcourt and Esson.** In particular, he introduced the differential method of analysis. He also analyzed the temperature dependence of the equilibrium constant (now called the "van't Hoff equation") and of forward and reverse reaction rates.
- **•1887: Ostwald (Germany; Latvia) introduces the terms "reaction order" and "half-life" in his "Lehrbuch der allgemeinen Chemie.,,**
- **•1889: Arrhenius (Sweden) further analyzed the temperature dependence of reaction rate, $k = A \exp(-B/T)$, and gave it an "energy barrier" interpretation; this is now called the "Arrhenius equation."**

- **Mentenová (Maude Lenora Menten)**
Michaelis-Menten equation (1912), enzymová kinetika (profesorkou v 60-ti letech)



Termodynamika



No such criterion can be applied to *all* processes. If we restrict the conditions sufficiently, however, there is a state function whose change for the *system* predicts spontaneity. This new state function is called **free energy (G)** and is defined by Equation 13-6:

$$\text{Free energy} = G = H - TS \quad (13-6)$$

where H is enthalpy, T is temperature, and S is entropy.*

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- The American J. Willard Gibbs introduced free energy into chemical thermodynamics. A professor of mathematical physics at Yale University from 1871 until his death in 1903, Gibbs was the first to show how the laws of thermodynamics apply to chemical processes. Because Gibbs published in a little-known American journal at a time when most scientific work was being done in Europe, his outstanding contributions to chemical thermodynamics were not recognized until 13 years after they were first published. In the 1890s, however, his 400 pages of elegant mathematical development of this subject were translated into French and German, and European scientists quickly recognized the greatness of his work. To commemorate Gibbs, free energy is symbolized G and is sometimes called *Gibbs free energy*.

Shrnutí poznatků z historie

- Řada pojmů a představ se kterými se setkáváme v chemické kinetice je již dlouho známých.
- Získání některých kinetických informací je velmi náročné (mechanismy reakcí, reakční koordináta,...)
- Moderní kinetika je interdisciplinární (biochemická kinetika, molekulová dynamika , kvantová chemie)

Literatura

Významné ženy a muži vědy:

<http://jchemed.chem.wisc.edu/JCEWWW/Features/eChemists/Bios/Menten.html>