

Physics of Processes

Changes and development of systems

Changes and development of systems

Chemical kinetics

- chemical reactions take place at very different speeds (whole years vs. supersonic speeds for combustion)
- the basic information in chemical kinetics is, in addition to time, the concentration of substance c and its rate of change over time dc/dt

Chemical equation: $A + mB \rightarrow AB_m$ (m – substance quantity - number of moles)

The time changes in the concentration of each component in the substance are expressed as:

$$-\frac{d[A]}{dt} = -\frac{1}{m} \frac{d[B]}{dt} = \frac{d[AB_m]}{dt}$$

Chemical kinetics

1st order kinetic equations

- the rate of change of individual components in a substance depends on their concentration
- this dependence is called the kinetic equation of the reaction
- the most important property of this equation is the order of the reaction:

The chemical equation is given: $A + B \rightarrow C$.

The time evolution of the concentration of component A is described by the equation:

$$-\frac{d[A]}{dt} = k[A]^i[B]^j \quad (1), \text{ where } i > j; i, j \text{ are integers and } k \text{ is a real number}$$

- i values determine the order of the reaction according to the component A
- if we put $[A] = c$ a $i = 1 \Rightarrow j = 0$, then equation (1) takes the form:

$$\frac{dc}{dt} = -kc \quad (2) - \text{1st order kinetic equation, where}$$

k - kinetic parameter - a measure of the reaction rate

c - component concentration

Chemical kinetics

1st order kinetic equations

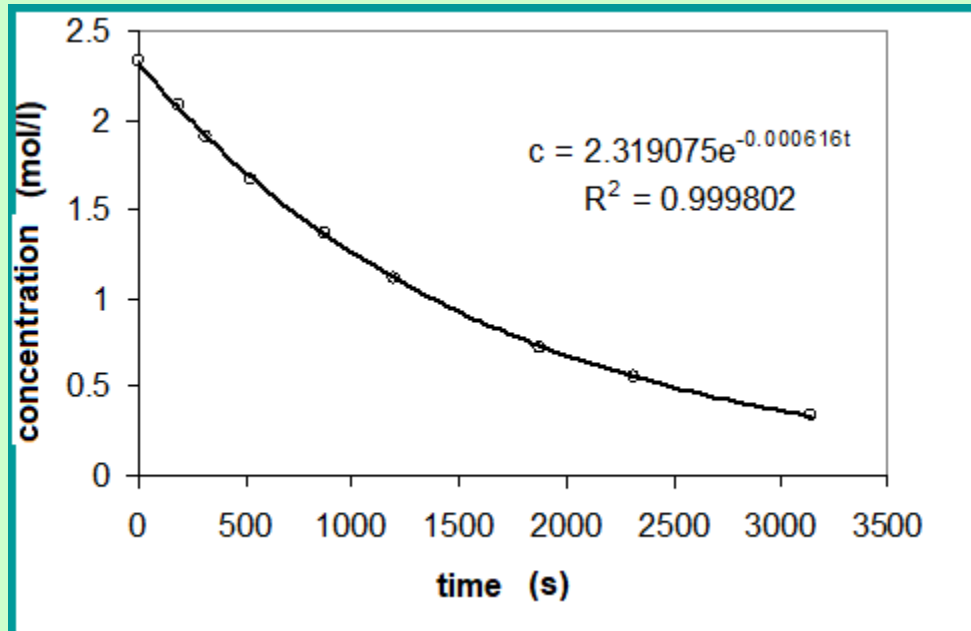
- by integrating (2) we obtain $c = c_0 e^{-kt}$ (3), where c_0 – initial concentration of the component

- after substituting $c = c_0 / 2$ do (3) obdržíme poločas reakce we obtain the half-life of the reaction:

$$t_{1/2} = \frac{\ln 2}{k}$$

- the time it takes for the initial concentration to drop by half

Exponential decrease in concentration:



Decrease in N_2O_5 concentration in CCl_4 (carbon tetrachloride) solution due to decomposition (Daniels, Alberty, 1961)

Chemical kinetics

example of a 2nd order kinetic equation

The chemical equation is given: $A + B \rightarrow C$.

The time increment of component **C** is described by the equation:

$$\frac{d[C]}{dt} = k([A_0] - [C])([B_0] - [C]) \quad (4) \text{ - index "0" indicates the initial concentration}$$

- 1st order reaction with respect to components **A** and **B** but 2nd order reaction with respect to **C**

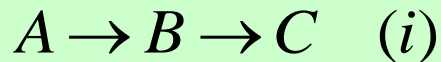
- simplifying designation $c = [C]$, $a_0 = [A_0]$ a $b_0 = [B_0]$

- then solution (4) is:

$$t = \frac{1}{k(a_0 - b_0)} \ln \frac{1 - c/a_0}{1 - c/b_0} \quad \text{pro} \quad a_0 \neq b_0 \quad \text{a} \quad t = \frac{1}{ka_0} \frac{c/a_0}{1 - c/a_0} \quad \text{pro} \quad a_0 = b_0$$

Chaining of chemical reactions

- just as there is a chaining of chemical reactions, there is also a chaining of their description through differential equations
- an example is the combination of two subsequent reactions:



- in the first reaction, component A changes to B with kinetic parameter k_1
- in the second reaction the component B changes to C with kinetic parameter k_2
- mathematical description of the reaction by differential equations:

$$\frac{d[A]}{dt} = -k_1[A] \quad (a) \quad \frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (b) \quad \frac{d[C]}{dt} = k_2[B] \quad (c)$$

with initial conditions: $[A_0] > 0$, $[B_0] = 0$, $[C_0] = 0$

Solution:

(a) in integral form: $[A] = [A_0]e^{-k_1t} \quad (a')$

- after inserting (a') into (b): $[B] = \frac{k_1[A_0]}{k_2 - k_1} [e^{-k_1t} - e^{-k_2t}] \quad (b')$

- the sum of the material components of (i) is conserved, then:

$$[C] = [A_0] - [A] - [B] = [A_0] \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1t} - k_1 e^{-k_2t}) \right] \quad (c')$$

Chaining of chemical reactions

Fig.: Time dependence of components concentration

- the concentration of component B peaks in time

$$t_{Bm} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (d)$$

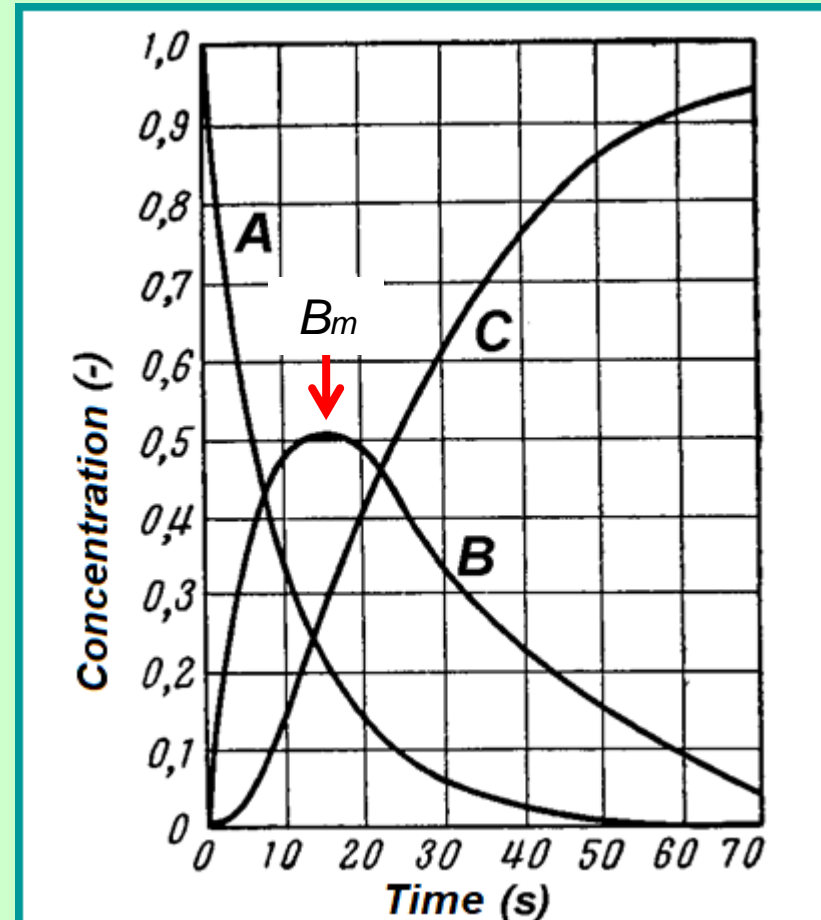
- after inserting (d) into (b') is the max. concentration B:

$$[B_{\max}] = [A_0] \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}}$$

The course of concentration of components.
Reaction according to the equation with
initial conditions

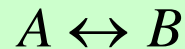
$$[A_0] = 1; k_1 = 0,1 \text{ s}^{-1}; k_2 = 0,05 \text{ s}^{-1}$$

$$t_{Bm} = 13,86 \text{ s and } [B_{\max}] = 0,5.$$



Reversible reactions

- reactions proceeding in the reverse direction of the initial reaction. Example:



- a reaction takes place where component A changes with kinetic parameter k_1 into component B and at the same time a reaction where component B changes into component A with kinetic parameter k_2

- differential equations describing the course of reactions: $\frac{d[A]}{dt} = -k_1[A] + k_2[B]$

- equation takes on a special significance in the state of equilibrium, when

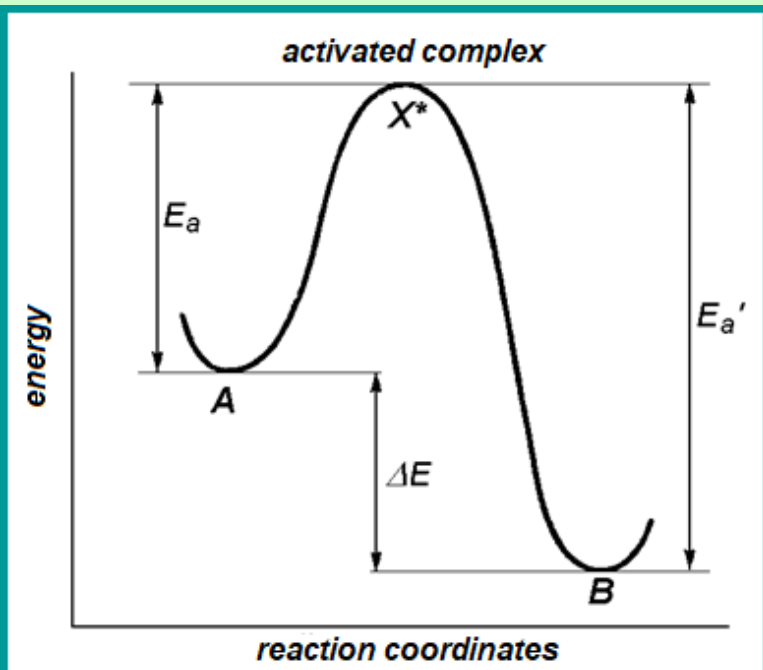
$$d[A]/dt = d[B]/dt = 0$$

- and for the ratio of the equilibrium concentrations of the two components ($[B_r]$ and $[A_r]$):

$$\frac{[B_r]}{[A_r]} = \frac{[A_0] - [A_r]}{[A_r]} = \frac{k_1}{k_2} = K, \text{ where } K \text{ is the equilibrium constant}$$

- the last two equations express the principle of dynamic equilibrium

Arrhenius equation



Arrhenius found an empirical equation for the temperature dependence of the kinetic parameters of chemical reactions k expressed in the simplest form as:

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

where ν - frequency factor (s^{-1}), E_a - activation energy ($J \cdot mol^{-1}$), R - molar gas constant ($J \cdot K^{-1} \cdot mol^{-1}$) and T - absolute temperature
- knowledge of the characteristic quantities of a given reaction (E_a and ν) allows to determine the magnitude of the kinetic parameter for different reaction temperatures

- a chemical reaction is a process involving an internal restructuring of the reacting components
- this restructuring is associated with changes in the internal energy of the components; it is also called the formation of the activation complex X^* - intermediate steps between components A and B: $A \leftrightarrow X^* \leftrightarrow B$

Temperature-activated processes

- activation energy - energy required for the formation of the activation complex
- the whole process of transition from component A to component B can be described schematically in a graph, where the "coordinates of change" are plotted on the "x" axis and the energy of the changing unit on the "y" axis - see Fig.
- states A and B correspond to local energy minima
- between A and B there is at least one state with maximum energy - the so-called activated complex
- component B - steady state with the lowest energy
- component A - only metastable, it is at an energy level ΔE higher than B \Rightarrow at the same frequency factor, the ratio of the kinetic parameters of the forward and

reverse reaction :

$$\frac{k_{AB}}{k_{BA}} = e^{\frac{\Delta E}{RT}}$$

- with increasing temperature the ratio of the two kinetic parameters decreases, but their values according to the Arrhenius equation increase
- the rate of change of the kinetic parameter with temperature change is most often expressed by the modified Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Survival curves

application of kinetic equations

- the first-order kinetic equation finds great application in many descriptions of phenomena - e.g. exponential decrease in amplitude of damped oscillations with decrement of damping δ :

$$x(t) = Ae^{-\delta t} \sin(\tilde{\omega}t + \varphi) = Ae^{-\frac{t}{\tau}} \sin(\tilde{\omega}t + \varphi) , \delta \text{ acts here as a kinetic parameter}$$

$$\tau = \frac{1}{\delta} \text{ - damping time constant}$$

- the time period over which the amplitude of the oscillations is reduced to a value e - times smaller

- analogous definition of response half-life - the time it takes for the amplitude of oscillations to drop to half of the initial value:

$$t_{1/2} = \frac{\ln 2}{\delta} = \tau \ln 2$$

- similar equations are used to describe the decay or lifetime of various products, substances, living organisms - e.g. the decay of radioactive elements

Decay of nuclides

Half-life of selected nuclides

Nuclid **Type of decay** **Half-life (s)**

^{37}Ca	β^+	0,175
^{37}K	β^+	1,23
^{16}N	β^-	7,2
^{19}Ne	β^+	17,2
^{220}Fr	α	27,5
^{53}Fe	β^+	511
^{42}K	β^-	44600
^{198}Au	β^-	$2,32 \cdot 10^5$
^{222}Rn	α	$3,3 \cdot 10^5$
^{131}I	β^-	$6,97 \cdot 10^5$
^{32}P	β^-	$1,24 \cdot 10^6$

^{60}Co	β^-	$3,15 \cdot 10^7$
^3H	β^-	$3,87 \cdot 10^8$
^{90}Sr	β^-	$8,86 \cdot 10^8$
^{137}Cs	β^-	$9,53 \cdot 10^8$
^{226}Ra	α	$5,05 \cdot 10^{10}$
^{14}C	β^-	$1,81 \cdot 10^{11}$
^{239}Pu	α	$7,69 \cdot 10^{11}$
^{233}U	α	$5,13 \cdot 10^{12}$
^{235}U	α	$2,24 \cdot 10^{16}$
^{238}U	α	$1,42 \cdot 10^{17}$

Survival curves of microorganisms

- the above mechanism for describing decay and lifetime is also used to describe the survival of a collection of organisms or substances under defined condition

- DRT (decimal reduction time) is used instead of the kinetic parameter k :

$$D = \ln(10)/k = \ln(10)\tau$$

- D is the length of time over which the concentration of individuals in a given environment and under given conditions falls by (to one tenth of the original number) one order of magnitude

- in the medical and food industry, sterilisation results in a reduction of several D

- 12 D procedures are used for food sterilisation - they reduce the pathogenic microorganism content by 12 orders of magnitude

- the dependence of the natural logarithm of the concentration of organisms on the time of action is the so-called "survival line"

Survival curves of microorganisms

generalization - application of the Arrhenius equation

- now we are looking for the such operating times t_T (critical time of action) which at different temperatures lead to the same reduction of the concentration of the substance c/c_0
- is therefore $c/c_0 = \text{konst.} = \exp(-kt_T) \Rightarrow kt_T = \ln(c_0/c)$ is also constant

Survival curves of microorganisms

generalization - application of the Arrhenius equation

In the last equation we add k from the Arrhenius equation:

$$kt_T = ve^{-\frac{E_a}{RT}} t_T = \ln\left(\frac{c_0}{c}\right) \Rightarrow t_T = \frac{1}{v} \ln\left(\frac{c_0}{c}\right) e^{\frac{E_a}{RT}} \Rightarrow E_a = RT \ln \frac{t_T}{\frac{1}{v} \ln\left(\frac{c_0}{c}\right)} \Rightarrow$$

$$\Rightarrow T = -\frac{E_a}{R} \ln \frac{t_T}{\frac{1}{v} \ln\left(\frac{c_0}{c}\right)} = -\frac{E_a}{R} \ln t_T + \frac{E_a}{R} \ln \left[\frac{1}{v} \ln\left(\frac{c_0}{c}\right) \right] = -K_s \ln t_T + q$$

- equations for the relationship between temperature and heating time during thermoinactivation (in the case of enzymes and micro-organisms) or destruction (in the case of positive components, e.g. vitamins)
- thermoinactivation results in preservation by heating

Application of the Arrhenius equation

(continued)

- the equivalent temperature T (i.e. the temperature at which there is a constant decrease in the concentration of the substance) decreases as a logarithmic function with increasing critical time of action t_T

- the direction of T dependence on t_T , ($K_s = E_a/R$) depends on the respective reduction mechanism (E_a), but does not depend on the level of reduction (c_0/c)

- the constant term q depends not only on the respective reduction mechanism (E_a), but also on the level of reduction (c_0/c):

$$q = \frac{E_a}{R} \ln \left[\frac{1}{\nu} \ln \left(\frac{c_0}{c} \right) \right]$$

- as the ratio c_0/c increases, the value of q increases and therefore the reduction temperature corresponding to the same level of action

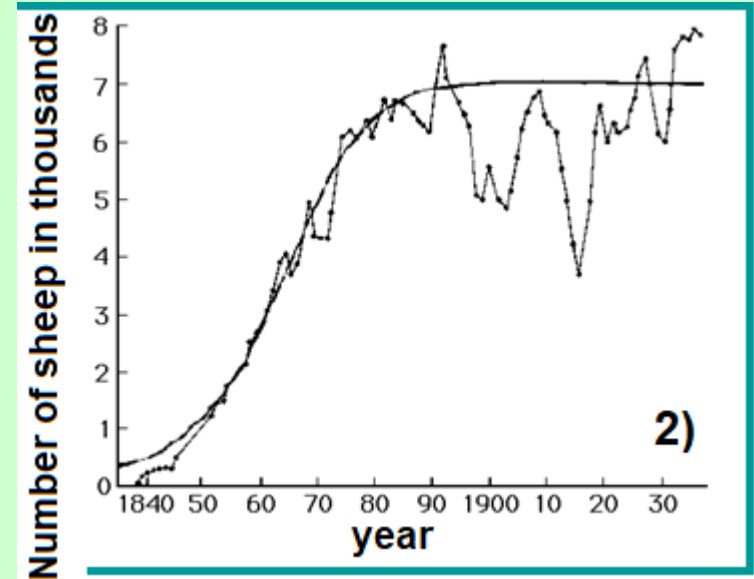
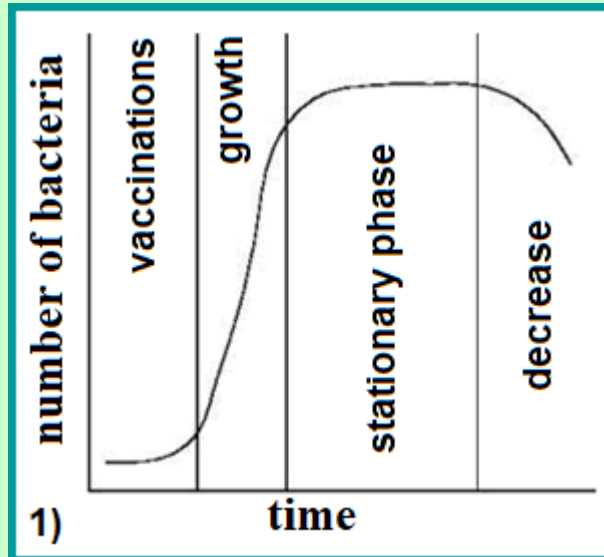
Growth curves - GC

- dependencies describing the temporal evolution of systems
- are based on observation (empirical)
- GC phases: increasing, stationary, possibly decreasing

Examples - see graphs:

- 1) Growth of bacterial colonies after their inoculation into the substrate
- 2) Evolution of sheep numbers in South Australia - sigmoidal GC

- GCs with only a growth and stationary part are referred to as sigmoidal - they can be described by the logistic function P (which has been proposed to describe population growth)

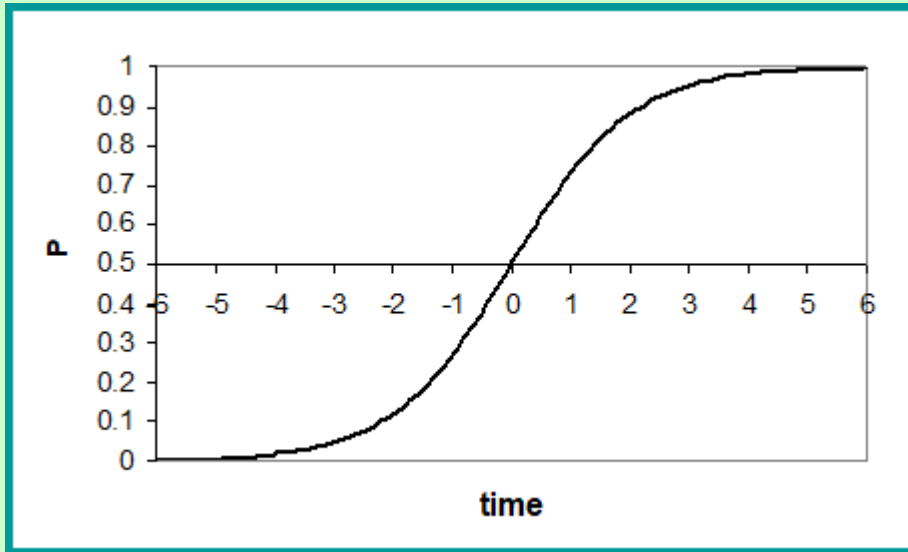


Logistics function

- $P(t)$ is defined for all $t \in \mathbb{R}$
- practically but just use $t \in \langle -6, 6 \rangle$

Valid: $P(t) = \frac{1}{1+e^{-t}}$ a $\frac{dP}{dt} = \frac{e^{-t}}{(1-e^{-t})^2} = P(t)[1-P(t)] = P(t)P(-t),$

because equality applies $1 - P(t) = P(-t)$



- the theoretical waveform is given with negative time and symmetry around the point $[0;0,5]$
- important is the asymptotic behaviour for small and high values of time, where the value of the derivative of the function with respect to time is close to zero

Logistics function

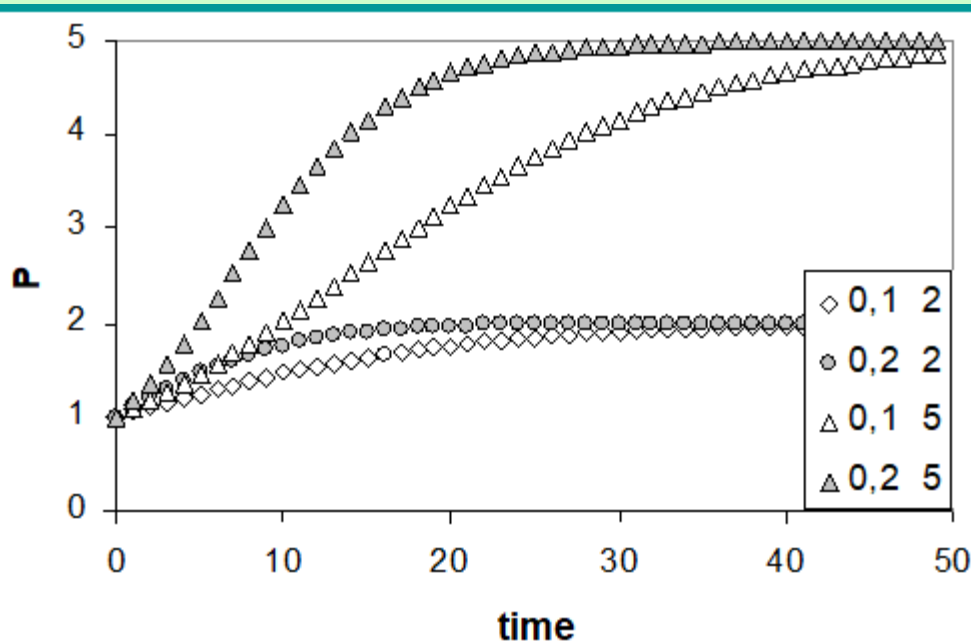
(practical form)

- a logistic function in a practical form is used to describe growth:

$$\frac{d(P/K)}{dt} = r \frac{P}{K} \left(1 - \frac{P}{K}\right),$$

where r - growth rate and K - achievable capacity – see Fig.

- for $P(0) = P_0$ the solution of the equation is $P(t) = \frac{KP_0 e^{rt}}{K + P_0(e^{rt} - 1)}$



- this equation describes the growth from an initial value of P_0 , to a finite value of K for infinite time

Overview of growth functions

There are a number of growth functions:

A review of growth functions used to describe increments in forest stands (Li Feng-ri et al. 2000)

Equation name	Basic form	Components	
		Growth	Decrease
Logistics			
L	$P = \frac{A}{1 + ce^{-bt}}$	$\frac{bc}{A} P^2$	e^{-bt}
Mitscherlich			
M	$P = A(1 - ce^{-bt})$	Abc	e^{-bt}
Gompertz			
G	$P = Ae^{-be^{-ct}}$	bcP	e^{-ct}
Chapman-Richards			
	$P = A(1 - e^{-bt})^c$	$\frac{1}{A^c} bcP^{\frac{c-1}{c}}$	e^{-bt}
Korf			
K	$P = Ae^{-bt^{-c}}$	bcP	$t^{-(c+1)}$