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PHYSICAL - CHEMICAL ASPECTS OF PROCESSES IN ENVIRONMENT

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Preface

The presented set of several selected topics touching on physical chemistry, physics, and mathematics is not designed as a systematic single-discipline interpretation. The given length of 78 pages would certainly not be sufficient for that. In its reduced form, this text merely attempts to provide the reader with some non-violent insight into the processes in the environment through the perspective of the physical picture and mathematical modeling.

The starting point is the fundamental theses of equilibrium thermodynamics. The inclusion of this classical discipline is motivated by its philosophical depth, which deserves great respect. After all, the structure of the second theorem of thermodynamics, for example, can sometimes offer nooks and crannies that the reader may not have explored during their initial study. The first paper that turns directly to constructing a mathematical model is the Debye-Hückel theory of the ionic atmosphere. This topic is, of course, somewhat removed from the vast mosaic constituting the problems of physical chemistry of solutions, but it nevertheless offers a comprehensive picture of the model solution of a given type of spherically symmetric problem. Considerable attention is given in the text to the dynamical processes described by ordinary differential equations. The interpretation ranges from basic kinetic problems that are easily solved analytically to some classic examples of nonlinear dynamical systems. The principles of dynamical model construction presented are generally applicable to time-dependent processes of any type, although they have been primarily developed for chemical processes. Finally, an example of a model solution of a specific problem of ion exchange kinetics with a 1D spatial dimension is presented. This paper can perhaps broaden the viewpoint of modeling processes of the given type to some extent, although it is not of "textbook origin". An essential part of the text is the associated appendices, which contain a brief description of selected basic methods for the numerical solution of ordinary and partial differential equations.

This text relates to the course of the same name, which is taught to first-year students in the MSc in Environmental Modelling. The form of exposition is chosen to make it understandable even for the reader, who may not always have a comprehensive system of higher mathematics built into the consequences. Many times, of course, the degree of this "empathy" may seem inadequate. For example, the text also lists some treatments (substitution procedures in differential equations, etc.) that standard textbooks leave to the reader. The explanations and indications of context can often lead the reader to experience the problem intuitively rather than correctly and in a mathematical formalism. The more informed reader should show indulgence for the occasional naivety of the text.

Author

1. Basic theses of equilibrium thermodynamics

Equilibrium thermodynamics is a consistent discipline, in many aspects consistently philosophically designed.

1.1 Basic terms

Thermodynamics does not study microstructure, it distinguishes a generally specified system determined (as a whole) by state parameters. Between the system and its surroundings may proceed exchange of mass and energy.

System

- isolated does not exchange mass nor energy with surroundings
- closed does not exchange mass, exchanges energy
- open exchanges mass and energy (e.g., a living organism)
- open with steady flow.

Forms of energy exchanged between the system and its surroundings

- heat Q exchange proceeds as a result of temperature difference
- work *W* exchange proceeds by virtue of forces, i.e. work may be volume work represented by changes of volume of fluid forming the system, and mechanical work.

The initial state of the system is always subtracted from the final one (generally true - in mathematics see definite integral).

Then the following sign convention applies:

+ energy delivered to the system

- energy withdrawn from the system

W > 0 the system withdraws work

- W < 0 the system performs work
- Q > 0 the system withdraws heat endothermic process
- Q < 0 system produces heat exothermic process
- Q = 0 adiabatic process

Phases, components, state transformations of the system

The phase is a homogeneous area of the system - exhibits only continuous changes in properties in space. Therefore, the system is homogeneous or heterogeneous - composed of more phases. Every phase may be composed of more chemical substances – components. Only chemical substances can be considered as components, concentration of which can be changed independently, i.e. not substances formed of independent components by chemical reaction, or substances concentration dependent on components by means of chemical equilibrium.

Phase transformation is discontinuous change of system properties occurring at specific p,T conditions.

State of matter:

gas	liquids	
liquid		condensed state
solid subs	tance	

plasma

State and equilibrium of the system

The state of the system is determined by status quantities, it is independent at the manner by which the system gets into the given state.

For example *p*, *T*, *V*, *n*

Properties of the system expressed by state quantities:

- Extensive they have additive character (they are a sum of parts) m, V, total E
- Intensive independent at material quantity p, T, ρ , c, U

Heat Q and work W are not state quantities, they relate to thermodynamic process proceeding from the initial state to the equilibrium state.

Thermodynamic equilibrium:

- Mechanical (equilibration of pressures)
- Thermal (temperature equilibration)
- Concentration
- Phase (if state of matter changes)
- Chemical

Thermodynamic process

The system may theoretically pass to the equilibrium state either by a reversible process, which is defined as a process of infinitely small steps for infinitely long period of time, over states infinitely close to equilibrium, during which time the direction of the process may be turned over at any time - e.g. expansion of gas with infinitely slow decrease of external pressure, or by an

irreversible process, when the transition proceeds in final time, and in the system, or its surroundings, in which irreversible changes occur - e.g. expansion of compressed gas to the external environment with atmospheric pressure. Real processed in nature proceed by irreversible processes.

Types of processes:

- isothermal	constant temperature	[T]
- isobaric	constant pressure	[<i>p</i>]
- isochoric	constant volume	[V]
- adiabatic	heat is not exchanged with surroundings	Q = 0
- isenthalpic	constant enthalpy	[H]
- isentropic	constant entropy	[<i>S</i>]

1.2 Ideal gas

Ideal gas is as quite homogeneous fluid determined by state parameters:

 $f(p,T,V,n) = 0, \quad f(p,T,V_m) = 0, \quad p = p(T, V_m) \quad V_m \text{ is molar volume.}$ In mixtures: $f(p,T,V,n_i) = 0, \quad f(p,T,V_m,x_i) = 0$

In contrast to real gas, molecular structure and intermolecular interactions are entirely ignored.

State equation of ideal gas

It applies for state behaviour of ideal gas:

$$p V = n R T \quad \text{or} \quad p V_m = R T \tag{1.1}$$

 $R = 8.314 J. K^{-1}.mol^{-1}$ is gas constant

Therefore, it applies:

$p_1 V_1 = p_0 V_0 \qquad [T]$	isotherm (1	1.2)
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$$V_1 / T_1 = V_0 / T_0$$
 [p] (1.3)

$$p_1 / T_1 = p_0 / T_0$$
 [V] (1.4)

State behaviour of ideal gas

State behaviour of ideal gas can be characterized by parameters of extensibility, compressibility and expansivity.

Coefficient of isobaric extensibility:

$$\alpha_{p} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p} = \frac{1}{V} \left(\frac{\partial \frac{nRT}{p}}{\partial T} \right)_{p} = \frac{1}{T}$$
(1.5)

Coefficient of isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial \frac{nRT}{p}}{\partial p} \right)_T = \frac{1}{V} \frac{nRT}{p^2} = \frac{1}{p}$$
(1.6)

Coefficient of isochoric expansivity:

$$\beta_{V} = \left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial \frac{nRT}{V}}{\partial T}\right)_{V} = \frac{nR}{V} = \frac{p}{T}$$
(1.7)

It evidently applies:

$$\beta_V = \frac{\alpha_p}{\kappa_T} \tag{1.8}$$

For mixtures of ideal gases, Dalton's law further applies – total pressure is a sum of partial pressures of components.

$$p = n\frac{RT}{V} = \frac{RT}{V}\sum_{i=1}^{k} n_i = \sum_{i=1}^{k} \left(n_i \frac{RT}{V}\right) = \sum_{i=1}^{k} p_i$$
(1.9)

$$p_i = n_i \frac{RT}{V} = x_i n \frac{RT}{V} = x_i p \tag{1.10}$$

Amagat's law – total volume of a mixture is a sum of partial volumes of components.

$$V = n\frac{RT}{p} = \frac{RT}{p}\sum_{i=1}^{k} n_i = \sum_{i=1}^{k} \left(n_i \frac{RT}{p}\right) = \sum_{i=1}^{k} V_i$$
(1.11)

Volume work of ideal gas

 $W = F.x \tag{1.12}$

$$W = \int_{x_1}^{x_2} F dx \qquad \begin{array}{c} p = F/s \\ F = p.s \end{array}$$
(1.13)

$$dW = -p.s.dx = -p.dV \tag{1.14}$$

Volume work delivered to the system:

$$W = -\int_{V_1}^{V_2} p dV$$
(1.15)

Delivery of volume work represents reduction of operating fluid volume of the system (ideal gas). In terms of the generally valid principle, when the initial state is always subtracted from the final one, this compression is a negative change.

$$W = -p \,\Delta V \tag{1.16}$$

1.3 First law of thermodynamics

The first law thermodynamics is a universal principle, the keystone of which is recognition that the only forms of energy exchange between the system and surroundings is heat and work. Heat is microphysical – a disorderly form of energy exchange, work is macrophysical, i.e. an orderly form of energy exchange.

Internal energy increase ΔU of the closed system corresponds to delivered heat and delivered work from surroundings.

$$\Delta U = U_2 - U_1 = W + Q \tag{1.17}$$

Of course, the same applies in a differential form for infinitely small (infinitesimal) change in internal energy:

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \tag{1.18}$$

or for the case of delivered volume work:

$$\mathrm{d}U = \mathrm{d}Q - p\mathrm{d}V \tag{1.19}$$

According to the first law of thermodynamics, work and heat are equivalent, the state change of the system expressed as ΔU is independent at in what proportion both forms of energy exchange participate in it.

By definition, the following applies for a cyclic process:

$$\oint \mathrm{d}U = 0 \tag{1.20}$$

Enthalpy

However, in light of measurability of volume work, utilization of the difference of the system states given by internal energy ΔU for balance assessment of the course of chemical reactions under standard isobaric conditions (with possibility of any volume changes), is questionable.

Obvious solution is evaluation of chemical reactions on the basis of heat of reaction - enthalpy H, which is well measurable (by calorimetry). Resulting heat of reaction (released or absorbed) under constant pressure corresponds not only to change in internal energy, but also to performed or delivered (absorbed) volume work.

$$dQ = dU + d(pV) = d(U + pV) = dH$$
 (1.21)

of course, under constant pressure, pdV = d(pV) applies.

Therefore, between dQ and dH is the equal sing, and enthalpy is referred to as heat of reaction, nevertheless, it is still necessary to distinguish that enthalpy is defined as the state quantity, in contrast to heat.

For enthalpy then applies:

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V \tag{1.22}$$

or:

$$\Delta H = \Delta U + p \,\Delta V \tag{1.23}$$

Enthalpy increment is equal to heat received by the system under constant pressure, if it performs no other work than volume work. Enthalpy is advantageous for evaluation of processes (especially chemical reactions) – it is measurable.

In general, also other forms of work may be exchanged with surroundings than volume work.

Heat capacities

Heat capacity is defined on the basis of differential amount of heat dQ needed for differential temperature increase dT.

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} \tag{1.24}$$

Heat capacity is defined under constant volume - C_V , and constant pressure - C_p .

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$$C_{V} = \frac{\mathrm{d}Q_{V}}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_{V}$$
(1.25)

$$C_{p} = \frac{\mathrm{d}Q_{p}}{\mathrm{d}T} = \left(\frac{\partial H}{\partial T}\right)_{p} \tag{1.26}$$

Under constant volume, heat is not consumed for volume work - therefore, for temperature increase less heat is sufficient, i.e. $C_p > C_V$ usually applies (inequality does not apply, e.g., in water in temperature interval of $1 - 4^{\circ}$ C, when thermal contraction occurs with temperature increase).

Difference between heat capacity under constant pressure C_p and constant volume C_{ln} is expressed in numbers:

$$C_{p} - C_{V} = \left(\frac{\partial H}{\partial T}\right)_{p} - \left(\frac{\partial U}{\partial T}\right)_{V} = \left(\frac{\partial U}{\partial T}\right)_{p} + p\left(\frac{\partial V}{\partial T}\right)_{p} - \left(\frac{\partial U}{\partial T}\right)_{V}$$
(1.27)

For total differentials of state functions U, V in space of independent variables it applies:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$
(1.28)

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$
(1.29)

After substitution for dV from (1.29) to (1.28) and differentiation with respect to T, the following is obtained:

$$\left(\frac{\partial U}{\partial T}\right)_{p} = \left(\frac{\partial U}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{p} + \left(\frac{\partial U}{\partial T}\right)_{V}$$
(1.30)

Therefore, the resulting relation for difference of heat capacities has the form:

$$C_{p} - C_{V} = \left[p + \left(\frac{\partial U}{\partial V}\right)_{T} \right] \left(\frac{\partial V}{\partial T}\right)_{p}$$
(1.31)

Application of the first law of thermodynamics to ideal gas

In addition to state equation (1.1), the following applies for ideal gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{1.32}$$

Because delivered (or withdrawn) heat in isothermal expansion (or compression) is in ideal gas always equivalent to volume work, which this gas performed (or which was delivered to it), total differential of internal energy of ideal gas is then reduced to:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$$
(1.33)

or, internal energy of ideal gas depends only on temperature. Heat capacity of ideal gas at constant volume can be then expressed as:

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T} \tag{1.34}$$

With respect to differentiated form of the state equation (1.1), the relation for difference of heat capacities is in ideal gas reduced to a constant:

$$C_{p} - C_{V} = p \left(\frac{\partial V}{\partial T}\right)_{p} = nR$$
(1.35)

Of course, for a change of U and H at thermal transition from T_1 to T_2 , the following is obtained:

$$\Delta U = \int_{T_1}^{T_2} C_V \mathrm{d}T \tag{1.36}$$

$$\Delta H = \int_{T_1}^{T_2} C_p \mathrm{d}T \tag{1.37}$$

At any isothermal state change of ideal gas, its internal energy remains constant – see (1.32).

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V} dT + \left(\frac{\partial U}{\partial V}\right)_{p} dV = 0$$
(1.38)

Then :

$$dQ = pdV = nRT \frac{dV}{V}$$
(1.39)

Reversible transition of ideal gas from state 1 to state 2, i.e. isothermal change of volume or pressure can be expressed as:

$$\int_{1}^{2} dQ = \int_{1}^{2} nRT \frac{dV}{V}$$

$$Q = nRT \ln \frac{V_{2}}{V_{1}} = RT \ln \frac{p_{1}}{p_{2}}$$
(1.40)

On the contrary, it applies for the case of reverse adiabatic expansion of ideal gas according to the first law of thermodynamics (dQ = 0, dU = -pdV):

$$-pdV = C_V dT \tag{1.41}$$

While considering state equation (1.1):

$$C_V \frac{dT}{T} + nR \frac{dV}{V} = 0 \tag{1.42}$$

After integration for transition from state 1 to state 2:

$$C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0 \tag{1.43}$$

After considering (1.35):,

$$\ln\frac{T_2}{T_1} + (\gamma - 1)\ln\frac{V_2}{V_1} = 0 \qquad \gamma = \frac{C_p}{C_V}$$
(1.44)

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{(\gamma-1)}$$
(1.45)

It applies for state behaviour of ideal gas:

$$\frac{T_1}{T_2} = \frac{p_1 V_1}{p_2 V_2} \tag{1.46}$$

Thus for resulting adiabate (in space p, V) of ideal gas it is obtained from (1.45) and (1.46):

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}, \qquad p V^{\gamma} = const.$$
 (1.47)

1.4 Second law of thermodynamics

Other aspects of energy balance of processes taking place in environment (including chemical reactions) have already been related to the second law of thermodynamics, which expresses the fundamental property of spontaneous processes to proceed in direction to greater disorderliness.

E.g. bounces of a ball are absorbed at impacts on hard floor spontaneously as a result of transformation of work to heat (ball and floor heat up). A reverse process - spontaneous initiation of vertical bounces of heated ball (from heated floor) as far away as to its return to the initial point is impossible, even if the entire process is thoroughly adiabatically insulated. This impossibility, which is evident itself, is generally connected with orderliness of processes. Though arisen heat is equivalent to initial potential energy of the ball according to the first law of thermodynamics, nevertheless, the possibility that quite orderly configuration would occur leading to spontaneous bounce of the ball from the floor within the frame of chaotic thermal movement of particles (molecules) of the system, is extremely unlikely.

The second law of thermodynamics in one of many possible formulations states: It is impossible to transform heat by a spontaneous process to equivalent work.

Carnot cycle and its efficiency

Implications of this principle can be developed within the scope of description of efficiency of so-called Carnot heat engine. It concerns a purely abstract construction of cyclically operating heat engine represented by two heat reservoirs with temperatures $T_2 > T_1$ and a proper system interchanging heat with those reservoir and delivering or receiving work from surroundings. Heat flow among the system and both reservoirs does not affect by any means temperatures of reservoirs, T_2 and T_1 are constant. Within the scope of one cycle, four reversible processes run through, and measure of system disorderliness is at the end of the cycle equal to the initial. Operating fluid is ideal gas (1 mol). The Carnot cycle is described as follows:

1. Isothermal reversible expansion at temperature T_2 – gas expands from volume V_1 to V_2 , during which time it withdraws heat $+Q_2$ from heat reservoir of temperature T_2 and does (delivers to surroundings) work $-W_1$.



Fig. 1.1. Carnot cycle

2. Adiabatic reversible expansion – gas expands without exchange of heat with surroundings to volume V_3 , during which time does (delivers to surroundings) work W_2 and cools down to temperature T_1 . Isothermal reversible 3. compression at temperature T_1 –

gas is compressed by exertion of work $+W_3$ (i.e. receiving work from surroundings) to volume V_4 , during which time delivers heat to cooler reservoir $-Q_1$.

4. Adiabatic reversible compression – gas is compressed without heat interchange with surroundings by exercising work $+W_4$ back to volume V_1 , during which time warms up to initial temperature T_2 . The engine works in cycles, internal energy of operating gas after one cycle returns to starting value $\Delta U = 0$ - see (1.20).

Efficiency of this engine, which transforms heat to work, is naturally given as a ratio of performed work to heat withdrawn from the heat source (heat received by operating fluid).

$$\eta = \frac{-W}{Q_2} \tag{1.48}$$

It can be added that equation (1.48) is a general relation expressing efficiency of (non-cyclic) heat engine in dependence on size of portion of withdrawn heat, which is transformed to work -W transferred to surroundings together with residual – unused heat. It is substantial in evaluating efficiency of the Carnot cyclically operating engine that overall performed work is (according to the first law of thermodynamics) equivalent to heat balance of the operating cycle. It applies:

$$\Delta U = Q + W = Q_1 + Q_2 + W = 0 \tag{1.49}$$

$$-W = Q_1 + Q_2 \tag{1.50}$$

Expressed total work has a negative sign in (1.50), therefore, it concerns work performed by the system, which is considered in the relation for efficiency (1.48). This performed work is, with respect to the sign of Q_1 , the difference between heat delivered to the system at the first process, i.e. Q_2 , and heat transferred in the third process Q_1 (amount of heat exchanged in isothermal expansion or compression of ideal gas is of course dependent on the set temperature). I.e. work performed in the operating cycle of the Carnot heat engine is simply expressed by means of heat balance without necessity to evaluate work $-W_1$, $-W_2$, W_3 , W_4 done in individual steps.

Heat Q_2 absorbed by gas in the first step corresponds to performed volume work:

$$Q_2 = -W_1 = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} RT_2 \frac{dV}{V} = RT_2 \ln \frac{V_2}{V_1}$$
(1.51)

Accordingly – heat delivered by gas Q_1 corresponds to work:

$$Q_1 = -W_3 = RT_1 \ln \frac{V_4}{V_3} \tag{1.52}$$

For reversible adiabatic processes, general relationship between volume and temperature applies for ideal gas - $TV^{\gamma-1}$ =constant ($\gamma = C_{m,p}/C_{m,V}$ is Poisson constant). So for steps 2 and 4 it can be written:

$$T_2 V_2^{\gamma - 1} = T_1 V_3^{\gamma - 1}$$

$$T_1 V_4^{\gamma - 1} = T_2 V_1^{\gamma - 1}$$
 (1.53)

I.e.:

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \tag{1.54}$$

By combination of equations (1.52) and (1.54) then comes out for Q_1 :

$$Q_1 = -RT_1 \ln \frac{V_2}{V_1} \tag{1.55}$$

Subsequently then it can be written:

$$Q_1 + Q_2 = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$
(1.56)

Efficiency can be then expressed with consideration of relations (1.49), (1.51), and (1.56) as:

$$\eta = \frac{-W}{Q_2} = \frac{Q_1 + Q_2}{Q_2} = \frac{T_2 - T_1}{T_2}$$
(1.57)

Hence it comes out that efficiency of the Carnot heat engine is determined only by temperatures of reservoirs. E.g., situation $T_2 = 2 T_1$ corresponds to 50% efficiency (100% would correspond either to $T_2 = \infty$ or $T_1 = 0$, which is in both cases impossible). Further, it should be added that relation (1.57) expresses a maximum theoretical efficiency of the heat engine operating in temperature interval T_1 to T_2 . Or maximum efficiency can be achieved only for theoretic situation, when all processes run in the reversible manner.

The following relation can be deduced from relation (1.57):

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{1.58}$$

Relation (1.58) has cardinal importance in light of studied chain of events. As already emphasized above, all four steps of the described Carnot cycle proceed in a reversible way. Or it is possible to say that if the sum of fractions at the left-hand side of equation (1.58) is equal to zero, all processes proceeding within the frame of a given cycle are reversible, and disorderliness does not rise in the system after passing the cycle.

The Carnot cycle can also be expressed as a differential with infinitesimal sections of both isotherms:

$$\frac{\mathrm{d}Q_1}{T_1} + \frac{\mathrm{d}Q_2}{T_2} = 0 \tag{1.59}$$

Generalization of relation (1.59) for any reversible cyclic process with any number of individual infinitesimal Carnot cycles leads to an integral form:

$$\oint \frac{dQ}{T} = 0 \tag{1.60}$$

If any of partial processes in the Carnot cycle proceeds in a irreversible way, the entire process is irreversible, and its overall efficiency must be lower than that of primarily considered ideal situation, when all four partial processes are reversible.

$$\eta < \frac{T_2 - T_1}{T_2} \tag{1.61}$$

This inequality can be itemized likewise relation (1.57), when the right-hand side represents temperatures T_1 , T_2 of heat reservoirs, i.e. temperatures, which the system would have (1 mol of ideal gas) at every instant of isothermal expansion or compression during their reversible course. At the irreversible course (of one or more partial processes), the system and heat reservoir are not at every instant in thermal equilibrium, and efficiency corresponding to the system itself expressed by exchanged heat is lower than that corresponding to the reversible process expressed by temperatures of external reservoirs.

$$\frac{Q_1 + Q_2}{Q_2} < \frac{T_2 - T_1}{T_2} \tag{1.62}$$

After adjustment:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0 \tag{1.63}$$

i.e. the factor corresponding to heat delivered to the system Q_2 at temperature T_2 is lower than the fraction corresponding to heat withdrawn from the system $-Q_1/T_1$. It can be said that in case of irreversible course of one or more partial processes of the Carnot cycle the system must reject more disarranged form of energy, than it would reject if all processes proceeded in a reversible manner. It means that not all received heat is made use of for work, it remains the residual. Consequently, in this sense disorderliness rises in the system, or the Carnot heat engine logically must stop. This fact can be simply shown, e.g., on adiabatic expansion, when gas would do less work at the irreversible course than it would correspond to the reversible process, and its temperature would be in connection with residual heat higher than T_1 . In the following step – isothermal compression - gas would have to deliver more heat Q_1 to heat reservoir, than if adiabatic expansion proceeded in the reversible manner. The same principle of decrease in organized forms of energy would be surely implemented even in remaining three (irreversible) processed (levelling up temperature of operating gas to temperatures T_1 and T_2 would, of course, proceed only within the frame of isothermal processes).

As well as for reversible cyclic processes, it by generalization is possible to come to an integral form of the principle expressed in (1.63). For an irreversible common cycle (when disorderliness rises in the system), therefore, the Clausius's inequality applies:

$$\oint \frac{\mathrm{d}Q}{T} < 0 \tag{1.64}$$

It can be concluded that abstract construction of the Carnot heat engine has cardinal importance for interpretation of the principle of the second law of thermodynamics in that its efficiency can be expressed as relation including only operating temperatures of isothermal processes under consideration. In this way deduced efficiency is a maximum – corresponding to reversible processes, because both temperatures are maintained outside the system by high capacity heat reservoirs and are constant. The second possibility for expressing efficiency of the Carnot engine is the relation including received and given over heats at isothermal processes, which relates to operating gas – the efficiency of the system itself is evaluated and may then include temporary imbalance with temperatures T_1 and T_2 . When comparing efficiencies defined by these two manners, it is postulated that efficiency deduced from heats is in the case of irreversibility of some of the processes of the Carnot engine lower, which hits the essence of the second law of thermodynamics. For the exact (mathematical) formulation of the second law of thermodynamics then just two basic thermodynamic quantities are available evaluating efficiency of the Carnot heat engine – heat and temperature.

Conception of entropy

In the context of facts expressed by relations (1.59) and (1.60), and in considerations in the previous section (as well as because the rate dQ/T is a total differential), it is possible to introduce a new state function named entropy – *S*, characterizing measure of disorderliness of a thermodynamic system. For a reversible process with heat exchange with the environment: it applies as follows:

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \tag{1.65}$$

Therefore, the definition of entropy means infinitesimal exchange of heat between the system and surroundings in relation to temperature of the system, which is constant.

Reversible transition of the system from state *A* to state *B* is given by:

$$\Delta S = \int_{A}^{B} \frac{\mathrm{d}Q}{T} \tag{1.66}$$

i.e. for the above analysed Carnot cycle, entropy change at reversible isothermal expansion or compression is equivalent to fraction Q_2/T_2 , or $-Q_1/T_1$, reversible adiabatic volume changes are isentropic processes (dQ =0, or ΔS = 0).

Entropy change of the system then can be simply expressed in numbers (on the basis of relation (1.66)) only for a reversible process, for an irreversible process the following inequality applies:

$$dS > \frac{\mathrm{d}Q}{T} \tag{1.67}$$

For irreversible transition from A to state B:

-

$$\Delta S > \int_{A}^{B} \frac{\mathrm{d}Q}{T} \tag{1.68}$$

If it concerns an irreversible adiabatic process, it simply applies:

$$dS > 0, \ \Delta S > 0 \tag{1.69}$$

These relations defining the entropy for irreversible processes (1.67), (1.68), (1.69) can be justified by the Clausius inequality (1.64). This inequality is valid for a cycle in which at least one of the partial processes is irreversible (the whole cycle is then irreversible). The simplest model example is a cycle in which the system goes from state A to state B irreversibly (and without heat exchange with the environment), then it must, of course, return to the initial state A by a "different path" - reversibly and with the possibility of heat exchange with the environment. The inequality expression (1.64) for this case is as follows:

$$\int_{A}^{B} \frac{\mathrm{d}Q_{ir}}{T} + \int_{B}^{A} \frac{\mathrm{d}Q_{rev}}{T} < 0$$
(1.70)

The first integral is equal to zero because at transition $A \rightarrow B$ the system is isolated and $Q_{ir} = 0$. The second integral is equal to the difference of entropies $S_A - S_B$ according to (1.61). If this difference is to be less than zero, the entropy of the system in state B must be higher than in-state A - the entropy increases during the irreversible adiabatic process $A \rightarrow B$. This conclusion would, of course, result even if the order of the processes were chosen in reverse. Thus, the validity of (1.69) is proved.

The relation (1.68) can be justified similarly if the conditions of the agencies in the model example (1.70) are considered in reverse. That is, the system goes from A to B isothermally (with heat exchange with the environment) and back - from B to A adiabatically. Thus, the second integral is equal to zero, and the transition $B \rightarrow A$ is reversible, i.e., $S_A = S_B$ must hold. The first integral for a given inequality implies $(Q_{ir}/T)_A > (Q_{ir}/T)_B$, which means that for the transition from A to B, (1.68) must hold in order to maintain entropy equality in both states ($S_A = S_B$).

Both proofs are based on integral expressions, but the principles derived are logically valid in the infinitesimal sense, i.e., relation (1.67) is also justified.

Naturally, a pattern results from these inequalities that the system entropy at the course of irreversible adiabatic process always increases (= 2^{nd} LT). Inequality (1.67), or (1.68) logically ensues from the previous. In the case of this irreversible process - with the exchange of heat with the environment, when this heat is related, for example, with the change of the internal energy of the system, the change of entropy may be positive or negative - entropy can also decrease (e.g. crystallisation under isothermal conditions); however, the factor dQ/T must be according to 2^{nd} LT (inequality 1.67) always more negative than the infinitesimal change of entropy dS (and similarly in the integral sense - inequality (1.68)).

However, it should be added that any spontaneous process can be considered isothermal only in terms of a defined local system (which exchanges heat with the environment). When the view goes beyond the scale of the local system, and its surroundings are taken into account, the process so conceived is logically adiabatic and dS > 0 (entropy increases continuously). For example, conditions on planet Earth may be considered isothermal in terms of global temperature (if actual global climate changes are disregarded), but the universe is considered an adiabatic system.

Consequences of 2^{nd} LT for irreversible thermodynamic processes with heat exchange with the environment

The following graphs outline the consequences of 2^{nd} LT for the real cyclic process with heat exchange system with the environment under isothermal conditions or in a mode that can be considered essentially isothermal.



Fig. 1.2. - The amount of heat delivered and received by the system during the cycle is equivalent. The entropy decreases during the cycle and then increases, its overall balance is necessarily positive - the entropy of the system increased after the cycle.

Fig. 1.2. Spontaneous isothermal cyclic process

Graph 1.2. demonstrates the inevitability of entropy growth after the spontaneous cyclic action of any system. In this context, as a consequence of 2^{nd} LT can be interpret even aging - the continuous degradation of objects and equipment of varying complexity, including eg a car. Similarly, the conclusions 2^{nd} LT justified the aging of living organisms, including humans.



Fig. 1.3. - During the cycle, more heat is withdrawn from the system than is delivered (Clausius's inequality applies) and less work is withdrawn than is delivered.. The cyclic process is not spontaneous. The entropy of the system may not increase after the cycle (which is generally conditioned by the application of Clausius inequality).

Fig. 1.3. Isothermal cyclic process with positive work W balance

The increase in the entropy of the system after the cycle is not generally inevitable, it can be countered by a positive work balance (and at the same time a negative heat balance), which of course means that the cyclic process is not spontaneous under these conditions - see Fig. 1.3. The situation of the positive balance of work corresponds elementally with human influence on the Earth. A trivial example is the reduction of entropy growth in interiors by regular cleaning.

It can be added that Clausius inequality is interpreted for irreversible (real) cyclic processes in systems with heat exchange with the surroundings as a balancing principle compensating the continuous increase in entropy of these processes. In this context, it is therefore clear that

Clausius inequality resulting from the balance conclusions of the Carnot cycle with one or more irreversible sub-processes directly determines the principle of a continuous increase in entropy (1.67). Simply - if more heat had to be withdrawn from the system during the cycle than it was delivered, the entropy had to increase.

Consequences of 2nd LT for irreversible adiabatic processes

Conclusions of 2nd LT for adiabatic processes do not allow the entropy of the system to decrease in any moment of the real spontaneous thermodynamic process (dS > 0 during the whole process). In terms of energy flow in the system is then a strict one-way.

For example, reference can be made to the situation of an adiabatically isolated bouncing ball described in the introduction to this chapter. In addition, one can return to the example of car operation, albeit from a different perspective. Driving a car from A to B (there is no height difference between A and B) can be considered as an adiabatic process in a system consisting of an automobile, the track it travels and the immediate external environment of a moving car. By realizing the internal energy of the fuel, work is generated with some efficiency - the car moves from A to B. By moving from A to B, the car will not gain any potential energy (the same energy would have to be spent for eventual driving back). However, energy does not disappear, so it must exist in the adiabatically isolated system in the form of frictional heat. Without consideration 2nd LT should be able to use this heat as energy to drive the car back from B to A..It can be added that the principle impossibility of reversing the flow of energy in the described system has no connection with the primary efficiency of the internal combustion engine of the car (although, of course, this is also related to the 2nd LT). According to 1th LT heat that corresponds exclusively to the work performed should be sufficient for the return drive (heat primarily generated by the combustion process with limited efficiency is not in principle part of the considered balance).

Increase in entropy of irreversible adiabatic process can be deduced also from considerations on transfer of heat between two bodies of different temperatures, which form together a thermally insulated system. For a change in entropy of this system related with transfer of heat $-dQ_1$ from a body of temperature T_1 to a body of temperature T_2 , which receives heat dQ_2 ($dQ_2 = -dQ_1$), it is possible to write:

$$dS = dS_1 + dS_2 = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dQ_1 = \frac{T_2 - T_1}{T_1 T_2} dQ_1$$

Whereof it results dS > 0, because heat transfers spontaneously (irreversibly) only from the warmer body to the cooler, i.e. $dQ_1 < 0$ at $T_2 T_1 < 0$, or on the contrary, $dQ_1 > 0$ at $T_2 T_1 > 0$; there are no other possibilities.

1.5 Gibbs energy

For the course of spontaneous process of the system (thermally not-isolated) it applies as follows:

$$\mathrm{d}S > \frac{\mathrm{d}Q}{T} \tag{1.71}$$

If this process proceeds under isothermal-isobaric conditions, it is possible to substitute dQ with enthalpy change dH. After adjustment the inequality is obtained implicating spontaneous course of the process:

$$\mathrm{d}H - T\mathrm{d}S < 0 \tag{1.72}$$

This inequality leads to introduction of thermodynamic state function consistently including common thermodynamic principles making possible to evaluate spontaneity of the course of the process under isothermal-isobaric conditions - Gibbs energy.

$$\Delta G = \Delta H - T \Delta S$$

$$dG = dH - T dS$$
(1.73)

Therefore, value ΔG is a criterion (or potential) of spontaneous course of thermodynamic processes. Chemical reaction (or any other process) will proceed, if overall balance of Gibbs energy (final process state minus the initial) is negative. In multicomponent processes, as chemical reactions and the like, the overall Gibbs energy as potential of the course (to equilibrium) in direction reactants \rightarrow products is given by difference of summary combination ΔG^o of reactants and products ($\Delta G^o_{products} - \Delta G^o_{reactants}$). Values ΔG^o for individual reaction components (compounds) are, of course, available in tables.

Negative value of Gibbs energy corresponds (in addition to entropy change) to heat released during reaction under isobaric-isothermal conditions. In real reactions heat is not generally dissipated without rest - reacting substances also warm up, nevertheless, the fact that the system is not adiabatically isolated, justifies us to talk about isothermal conditions. Gibbs energy is defined so that it reflects final thermal and entropy balances of the process, i.e. including heat consumed or released in connection with would-be volume work.

It can be added that balance relation (1.72) does not mean in principle that spontaneity of any process is automatically conditioned by increase in disorderliness ($\Delta S > 0$). This relation only says that would-be rising of orderliness of the system (decrease of entropy - minus ΔS or negative factor $T\Delta S$) is lower than the value that would correspond to negative enthalpy of the process. See the second law of thermodynamics, which does not exclude conversion of heat to work, it only says that this conversion cannot be equivalent, i.e. decrease in disorderliness - decrease in entropy is not impediment to a partial spontaneous process.

Possible decline of entropy during spontaneous partial process is conditioned by energy consumption. In partial processes, which are not doped with energy from without, the source of this consumed energy is naturally decline of internal energy $\Delta U < 0$. However, it applies for spontaneous cyclic process not receiving energy from without that the system, after completion of this cycle involving any number of partial processes, in which change in internal energy may occur and possibly to increase or decrease in disorderliness, will return to the initial state ($\Delta U = 0$) more disarranged ($\Delta G < 0$ and $\Delta S > 0$).

Helmholz energy

Helmholz free energy ΔA relates to an isochoric process, when $\Delta U = \Delta Q$ applies, i.e. volume work is not carried out.

Likewise in Gibbs energy, Helmholz energy is a potential of the course of an isothermal – isochoric process:

$$\Delta A = \Delta U - T \Delta S$$

$$dA = dU - T dS$$
(1.72)

Of course, Gibbs energy is more suitable as a criterion (potential) of the course of chemical reaction proceeding most often under atmospheric pressure, i.e. in isobaric manner.

1.6 Thermodynamic potentials

For differentials of quantities representing thermodynamic potentials -U, H, G, A, the following relations can be deduced.

Internal energy – by combination of relations resulting from the 1st and 2nd law of thermodynamics (1.19) and (1.64), or T dS = dQ (reversible process), can be obtained:

$$dU = -pdV + TdS$$
 natural variables (V, S) (1.73)

Enthalpy – according to the 1st LT, the total differential dH = dU + pdV + Vdp, by combination with relation (1.73) is obtained:

$$dH = Vdp + TdS$$
 natural variables (p, S) (1.74)

Gibbs energy – according to (1.71), the total differential is in the form dG = dH - TdS - SdT, by combination with relation (1.74) is obtained:

$$dG = Vdp - SdT$$
 natural variables (p, T) (1.75)

Helmholtz energy – according to (1.72), the total differential must be given in a form dA = dU - TdS - SdT, by combination with relation (1.73) is obtained:

$$dA = -pdV - SdT$$
 natural variables (V, T) (1.76)

Maxwell equations

Relations for thermodynamic potential (1.73 - 76) can be simply written by the help of partial differential quotients:

$$dU = \left(\frac{\partial U}{\partial V}\right)_{S} dV + \left(\frac{\partial U}{\partial S}\right)_{V} dS$$
(1.77)

$$dH = \left(\frac{\partial H}{\partial p}\right)_{S} dp + \left(\frac{\partial H}{\partial S}\right)_{p} dS$$
(1.78)

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$
(1.79)

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$
(1.80)

So that it comes out:

$$\left(\frac{\partial U}{\partial V}\right)_{S} = -p, \left(\frac{\partial U}{\partial S}\right)_{V} = T$$
(1.81)

$$\left(\frac{\partial H}{\partial p}\right)_{S} = V, \left(\frac{\partial H}{\partial S}\right)_{p} = T$$
(1.82)

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_p = -S \tag{1.83}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p, \left(\frac{\partial A}{\partial T}\right)_V = -S \tag{1.84}$$

For partial differential quotients in (1.81), it is possible to further deduce:

$$\left(\frac{\partial U}{\partial V}\right)_{S} = -p, \ -\left(\frac{\partial p}{\partial S}\right)_{V} = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_{S}\right)_{V}$$
(1.85)

$$\left(\frac{\partial U}{\partial S}\right)_{V} = T, \left(\frac{\partial T}{\partial V}\right)_{S} = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V}\right)_{S}$$
(1.86)

Order of derivations is interchangeable – Euler's reciprocal formula applies:

$$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial p}{\partial S}\right)_{V}$$
(1.87)

In the same manner other resulting Maxwell's relations are obtained:

$$\left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p} \tag{1.88}$$

$$\left(\frac{\partial V}{\partial T}\right)_{p} = -\left(\frac{\partial S}{\partial p}\right)_{T}$$
(1.89)

$$\left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T}$$
(1.90)

1.7 Third law of thermodynamics

The content of the third law of thermodynamics is the following statement: By no procedure, no matter how idealized, it is possible to achieve decrease in its temperature to absolute zero by finite number of operations in any system.

Entropy of substances at temperature of absolute zero is a limit – is gets a final lowest possible value S_0 , or according to Planck, it is zero (which probably applies only to pure substances in a state of a perfect crystal).

$$\lim_{T \to 0} S = S_0, \quad \text{or } \lim_{T \to 0} S = 0$$
(1.91)

However, in limit $T \rightarrow 0$ quite surely applies $\Delta S_0 = 0$ for any reversible process. Decrease of temperature in cooling operation (step) in limit $T \rightarrow 0$ will be zero regardless of expended energy.

In addition to classic experiments based on isothermal compression and adiabatic expansion of operating gas, the principle of the third law of thermodynamics practically manifests itself in lowering temperature by adiabatic demagnetization of salts of rare earths elements with high values of magnetic susceptibility. By this experimental procedure, temperatures were achieved so far that may seem to be very near to absolute zero (fractions of *K*, nevertheless achieving 0K is impossible).



Curve B = Bi in Fig. 1.2 corresponds to magnetized state with oriented (i.e. organized) structure, B = 0 is a state magnetic without action of field. Adiabatic demagnetization - step $2 \rightarrow 3$ etc., is an isentropic process, i.e. increase in structural disorderliness after cut-off of magnetic field must be compensated by decrease of temperature, or structurally more disorderly state corresponds to the same entropy only after lowering of temperature. It is evident from the graph that in proximity of absolute zero (0 K), decrease of temperature achieved by demagnetizing step is close to zero.

Fig. 1.2 S - T graph of adiabatic demagnetization

2. Equilibrium constant of chemical reactions and its relation to Gibbs energy

Meaning of the term chemical equilibrium is connected with the fact that chemical reactions generally do not proceed to the entire depletion of starting substances, but they reach a steady state, when beside the products, there are present also reactants, even though often in negligible quantities.

The chemical reaction

$$A + B - X + Y$$

can be understood as two partial processes - one proceeding in direction from left to right at rate v_1 , and the second proceeding in the opposite direction at rate v_2 . If it concerns an exothermic reaction with a smooth course, it will naturally apply for the beginning of the process $v_1 >> v_2$. The equilibrium is achieved at the moment, when both rates match one with another.

These partial rates can be expressed on the basis of Guldberg-Waage law on "active mass" action. This law reflects the fact that instantaneous rate of chemical conversion of any substance must be directly proportional to its relative quantity, or concentration. For two reacting substances this rate will then logically be proportional to the product of their current concentrations (probability of meeting molecules or atoms of reacting substances determining the reaction rate is, of course, proportional to the product of their concentrations). A factor quantifying this proportion is the rate constant, which is specific for every process. It applies:

$$v_1 = k_1 c_A c_B$$

$$v_2 = k_2 c_X c_Y$$
(2.1)

For equilibrium state then:

$$k_1 c_A c_B = k_2 c_X c_Y \tag{2.2}$$

Ration of rate constants k_1/k_2 is taken as equilibrium constant for the given reaction K.

$$\frac{k_1}{k_2} = K = \frac{c_X c_Y}{c_A c_B}$$
(2.3)

Relation (2.3) can be generalized for a reaction with any stoichiometry

$$aA + bB - xX + yY$$

and transcribed to more correct form while using activities instead of concentrations.

$$K = \frac{a_X^x \cdot a_Y^y}{a_A^a \cdot a_B^b} \tag{2.4}$$

Activity describes real potential of substance behaviour in solution. In more concentrated solutions, activity more markedly deviates from molar concentration (corresponding to molar quantity of substance added to the solution) towards lower values, because every ion is in its chemical manifestations "damped" by action of opposite charged surrounding ions, i.e. effect of ionic atmospheres – see following Chapter 3.

The values of equilibrium constants for standard chemical reactions carried out under isobaric conditions are available in tables. Of course, the equilibrium constant of a chemical reaction allows to determine equilibrium concentrations (or activities) of substances participating in the reaction for various conditions designated by concentrations (activities) of other components. It can be added only that everything applies to the stable steady state only.

Higher value of *K* represents smooth reaction course from left to right, when after achieving equilibrium expressive surplus of products is present in the reaction system. Naturally, a negative difference in Gibbs energy of equilibrium (final) and starting states appertains to this case. This connection implies evident link between *K* and ΔG . Derivation of relationship between Gibbs energy and reaction constant comes out from relation (1.71), from which it results for isothermal conditions that change in Gibbs energy at pressure change is equivalent to volume - see (1.83)

$$\left(\frac{\mathrm{d}G}{\mathrm{d}p}\right)_T = V$$

When considering (1.1), it comes out for isothermal conditions:

$$dG = nRT\frac{dp}{p}$$
(2.5)

For transition of gas from the standard state (i.e. the state under standard pressure of 101.325 kPa) characterized by quantities G^{o} and p^{o} to any other state expressed as G, p, it applies:

$$G - G^{o} = nRT \int_{p^{o}}^{p} \frac{\mathrm{d}p}{p} = nRT \ln\left(\frac{p}{p^{o}}\right) = nRT \ln p_{r}$$
(2.6)

i.e. ratio p/p^{o} is expressed as relative pressure p_{r} .

Equation (2.6) can be generalized for a mixture of k components - ideal gases, which will chemically react together.

$$\Delta G_r - \Delta G_r^0 = RT \sum_{i=1}^k v_i \ln p_{r,i}$$
(2.7)

In this case it does not already concern transition of the system to an arbitrary state. The final state characterized by term ΔG_r corresponds to a reaction mixture of ideal gases in equilibrium, i.e. after completion of reaction, when the chemical process achieved the minimum energy. The initial state is expressed by a balance of starting energy states, i.e. standard combination of Gibbs energy ΔG_{sl}^o of individual components of the reaction mixture. During the process reactants are consumed - their ΔG_{sl}^o is then calculated with a minus sign.

$$\Delta G_r^0 = \sum_{i=1}^l v_i \Delta G_{slu\check{c}.prod.,i}^0 - \sum_{i=1}^m v_i \Delta G_{slu\check{c}.reakt.,i}^0$$
(2.8)

Term ΔG_r^o means standard reaction Gibbs energy (potential of the reaction course), which is related to 1 mol of basic reaction turnovers, i.e. symbol *n* designating number of mols in equation (2.7) does not feature any more. On the contrary, stoichiometric coefficients v_i of individual components were added for reaction mixture.

Equation (2.7) then describes a process, on beginning of which there is a mixture of k ideal gases, starting partial pressures p_{i}^{o} of which correspond to a unity (and of course, relative partial pressures $p_{r,i}$ too, at the beginning $p_i = p_i^{o}$). In case $\Delta G_r^{o} < 0$, partial pressures of components, which are taken as products, will increase, and $p_{r,i}$ of reactants will decrease. Under gradual lowering of the rate of chemical conversions, the process will tend towards the equilibrium state, instantaneous Gibbs energy of the process ΔG will retreat from initial value ΔG_r^{o} , moving towards zero (from below).

It applies for the equilibrium state $\Delta G_r = 0$ (with constant *T* and *p*). In consideration of balance equation (2.8), it is possible to write:

$$\Delta G_{r}^{0} = -RT \left(\sum_{i=1}^{l} v_{i} \ln p_{r.prod,i} - \sum_{i=1}^{m} v_{i} \ln p_{r.reakt,i} \right)$$
(2.9)

Whereas relative partial pressures of the reaction components p_r in equation (2.9) correspond to final equilibrium state. Chemical conversion of every component (ideal gas) of the reaction mixture can be then taken as an independent process with change of partial pressure corresponding to $\Delta G^o_{sluč}$ of this component. Of course, relation (2.9) can be converted into a form:

$$\Delta G_{r}^{0} = -RT \ln \frac{p_{r.prod,1}^{v_{1}} \cdots p_{r.prod,l}^{v_{l}}}{p_{r.reakt,1}^{v_{1}} \cdots p_{r.reakt,m}^{v_{m}}} = -RT \ln K_{p}$$
(2.10)

The result is then relation of standard reaction Gibbs energy and equilibrium reaction constant K_p (for chemical reactions in gaseous state).

For reaction in a solution also constancy of pressure can be considered - isobaric conditions, in addition to isothermal conditions. Both terms resulting from definition of dG as general thermodynamic potential (1.79) are then zero for isothermal processes in solution. In connection with chemical changes, change in Gibbs energy is equivalent to change of mol amounts of individual substances n in product with their chemical potential μ .

$$dG = -SdT + Vdp + \sum_{i=1}^{\infty} \mu_i dn_i = \sum_{i=1}^{\infty} \mu_i dn_i \ [T, p]$$
(2.11)

It applies for a change in mol quantity of a reaction component:

$$dn_i = v_i d\xi_i \tag{2.12}$$

 ξ is a scope of reaction defined as a ratio of substance quantity of any reaction component formed or consumed to its stoichiometric coefficient.

$$\xi_i = \frac{\Delta n_i}{\nu_i} \tag{2.13}$$

i.e.:

$$dG = \left(\sum_{i=1}^{n} v_i \mu_i\right) d\xi \quad [T, p]$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T, p} = \sum_{i=1}^{n} v_i \mu_i \qquad (2.14)$$

It applies for equilibrium:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$$

$$\left(\sum_{i=1}^{r} v_i \mu_i\right)_{rown} = 0 = \Delta G_r$$
(2.15)

It applies for chemical potential of a substance a_i (reaction component) as for equivalent of Gibbs energy - see (2.11):

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{2.16}$$

Relation (2.16) is an analogue of (2.6) (activity in solution corresponds to relative pressure in mixture of gases).

It is possible to write for activities of reaction components:

$$\Delta G_r = \sum_{i=1}^k v_i \left(\mu_i^0 + RT \ln a_i \right) = \sum_{i=1}^k v_i \mu_i^0 + RT \ln \prod_{i=1}^k a_i^{v_i} = \Delta G_r^0 + RT \ln \prod_{i=1}^k a_i^{v_i}$$
(2.17)

Considering sign convention expressed in (2.8), resulting relation is obtained between standard reaction Gibbs energy ΔG^{o}_{r} and equilibrium constant K_{a} for chemical reaction in solution:

$$\Delta G_r^0 = -RT \ln \frac{a_{prod,1}^{v_1} \cdots a_{prod,l}^{v_l}}{a_{reakt,1}^{v_1} \cdots a_{reakt,m}^{v_m}} = -RT \ln K_a$$
(2.18)

In the context of the above mentioned, standard reaction Gibbs energy ΔG^{o}_{r} can be determined as the change of free energy, which occurs at chemical reaction of components, initial activities of which equal to one (or they are such that the fraction in (2.18) equals to one).

It is also possible to say that the standard combination Gibbs energy of compounds - i.e. of individual reaction components ΔG^o_{sl} , which serve to balance derivation of ΔG^o_r , are defined as Gibbs energies (related to 1 mol of basic reaction turnovers) for reactions, by which the given substances were formed directly from elements. The starting referential state are then elements, ΔG^o_{sl} of which is logically zero.

Logarithmic relation (2.18) is naturally valid also for dissociation processes. For dissociation of water

$$H_2O - H^+ + OH$$

it applies:

$$\Delta G_r^0 = -RT \ln \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = -RT \ln K_v$$
(2.19)

 K_{ν} is dissociation constant of water. The rate of dissociation of pure water is very low (under standard conditions, activity - concentration H^+ and OH gets near to the value of 10^{-7} mol.l⁻¹). Activity of non-dissociated molecule is then practically maximum, i.e. = 1. It was measured for dissociation constant of water:

$$K_v = a_{H^+} a_{OH^-} = 10^{-14}$$

Of course, the constant value of this ionic product is valid also for all water solutions in equilibrium under standard conditions.

It can be seen from the mentioned facts that the suitable parameter for balance evaluation of chemical and physico-chemical processes is always a function characterizing the state of the given system, which is logarithmically dependent on a parameter determined by relative quantity (molar) of each of the components. In this connection and also from practical reasons given by the measured value of dissociation constant of water (whole negative power of number 10), a parameter $pH = -\log a_{H^+}$ was introduced, which characterizes the state of aqueous solutions in light of measure of acidity or alkalinity. For slightly acidic or slightly alkaline environment, it is possible to replace activity H^+ with concentration - it is possible to write: $pH = -\log [H^{+}]$. Analogous parameter is often used for description of the state properties of alkaline solutions $pOH = -\log a_{OH}$, or $pOH = -\log [OH^-]$.

3. Selected aspects of behaviour of ions in solutions

3.1 Activity and activity coefficient

Definition of ideal solution, physico-chemical state of which is determined by equations of thermodynamic equilibria (e.g. $\Delta G_0 = -RT \ln K$) involving directly concentrations of dissolved substances, is in reality approached only in diluted solutions of nonelectrolytes, where Coulombic interactions have no effect.

Solutions of electrolytes, i.e. substances in water dissociable to ions, are non-ideal solutions. Equations of thermodynamic equilibria here apply for activities of components (ions) of these non-ideal solutions.

Activity *a* means real (consistent with thermodynamic equations) action of dissolved substance *i* (ion) corresponding to its concentration corrected by inclusion of "shielding" Coulombic interactions expressed by the activity coefficient γ .

$$a_i = c_i \gamma_i \tag{3.1}$$

At infinite dilution of solution of electrolyte $\gamma \rightarrow 1$ and the solution is getting close to the ideal. The relation of activity coefficient and Gibbs energy (i.e. state quantity) results from comparison of chemical potential of *i*-th component of ideal and non-ideal solutions.

$$\mu_i^{id} = \mu_i^0 + RT \ln c_i$$

$$\mu_i = \mu_i^0 + RT \ln c_i + RT \ln \gamma_i$$
(3.2)

Term *RT* ln γ_i corresponds to a change of molar Gibbs energy ΔG of *i*-th component (ion) of the solution in transition from ideal to non-ideal state (ΔG of the equilibrium process is in solutions equivalent to chemical potential multiplied by stoichiometric coefficient), γ_i is an individual ionic activity coefficient. From measurement or calculation it is possible, with respect to electroneutrality (naturally both ions are always present), to obtain mean activity coefficient $\gamma \pm$ of the given electrolyte.

Change of Gibbs energy for transition of 1 mol of general electrolyte

$$K_x A_y \longleftrightarrow x K^{z_{\kappa}} + y A^{z_{\kappa}}$$

from ideal to non-ideal state - so-called additional Gibbs energy is expressed as:

$$\Delta G = RT \left(x \ln \gamma_+ + y \ln \gamma_- \right) \tag{3.3}$$

or

$$\Delta G = RT(x+y)\ln\gamma_{\pm} \tag{3.4}$$

Relation for mean activity coefficient of electrolyte results from comparison of (3.3) and (3.4):

$$\gamma_{\pm} = \left(\gamma_{\pm}^{x}, \gamma_{-}^{y}\right)^{l/(x+y)}$$
(3.5)

Mean activity and molar concentration are established likewise mean activity coefficient:

$$a_{\pm} = \sqrt[x+y]{a_{\pm}^{x} . a_{-}^{y}} = c_{\pm} \gamma_{\pm}$$
(3.6)

$$c_{\pm} = \sqrt[x+y]{c_{\pm}^{x}.c_{-}^{y}} = c \times \sqrt[x+y]{x^{x}.y^{y}}$$
(3.7)

In more diluted solutions, mean activity coefficient of strong electrolyte is not dependent on a type of ions, but only on concentration c_i and charge number z_i of all ions in solution. In this connection, ionic strength is established for expression of effect of ions in solution I_c :

$$I_{c} = \frac{1}{2} \sum_{i} c_{i} z_{i}^{2}$$
(3.8)

Dependence between mean activity coefficient and ionic strength is for diluted electrolytes expressed by Debye-Hückel's limit law:

$$-\log \gamma_{\pm} = \overline{A} |z_{\rm K} z_{\rm A}| \sqrt{I_c}$$
(3.9)

3.2 Debye-Hückel theory of ionic atmosphere

Debye-Hückel theory derives analytical relation for calculation of potential of ionic atmosphere φ' (additional potential), on the basis of which it is possible to calculate additional Gibbs energy of electrolyte solution, i.e. φ' is the exact basis for numeration of activity coefficient.



Fig. 3.1 Central positive ion (cation) surrounded by ionic atmosphere of negative and positive ions. All ions have radius a. The described model (Debye-Hückel theory) calculates additional potential at the point of central ion, or in distance *a* from the centre.

The primary solution is Poisson equation describing relation of potential φ to volume density of charge ρ for spherical symmetrical arrangement.

$$\frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right) = -\frac{\rho}{\varepsilon_0 \varepsilon_r} \tag{3.10}$$

Charge density in the surrounding of the central ion is not naturally constant for the situation being solved - it is dependent on potential of all ions that operate in the given place by its reach. It is then necessary to find appropriate dependence $\rho = f(\varphi)$. Applicable solution is Boltzmann theorem (3.11) determining number of particles of *i*-th type C'_i with energy higher by value of *E* than the average energy, which corresponds to thermal motion kT (if E = 0, $C'_i = C_i$).

$$C_i' = C_i \mathrm{e}^{-E/kT} \tag{3.11}$$

while C_i is a mean number of ions of *i*-th type in volume unit of solution. Application of (3.11) to situation being solved assumes that energy *E* may correspond to work needed for bringing ion of charge *Q* to the point of potential φ , i.e. product of $Q\varphi$.

$$C_i' = C_i e^{-Q_i \varphi/kT} \tag{3.12}$$

Relation (3.12) then determines number of ions of *i*-th type (related to the volume unit) acting with its potential in the surrounding of the central ion delimited by ionic atmosphere. Charge density then equals to the total charge of all acting ions (charge is summed over all types of ions).

$$\rho = \sum C'_i Q_i = \sum C_i Q_i e^{-Q_i \varphi/kT}$$
(3.13)

After substitution (3.13) to (3.10) it can be obtained:

$$\frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right) = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum C_i Q_i \mathrm{e}^{-Q_i \varphi/kT}$$
(3.14)

The sought function for potential of the central ion and ionic atmosphere $\varphi = f(r)$ can be obtained by solving this spherical symmetrical differential equation. To preserve possibilities of finding analytical solution, which is the goal of the described model, however, it is necessary to introduce certain simplifications into equation (3.14), which is non-linear. Exponential factor on the right hand side of (3.14) can be, with respect to relation $Q_i\varphi \ll kT$ valid for diluted solutions, approximate using Taylor series.

$$e^{-Q_i\varphi/kT} = 1 - \frac{Q_i\varphi}{kT} + \frac{1}{2!} \left(\frac{Q_i\varphi}{kT}\right)^2 - \dots$$
(3.15)

When neglecting all higher terms of series (3.15), except the first two, a linear dependence on potential (with negative slope) comes out for charge density.

$$\rho = \sum C_i Q_i - \frac{\varphi}{kT} \sum C_i Q_i^2 \tag{3.16}$$

Moreover, in connection with electro-neutrality, the first term is zero. Expression of ion charge Q_i by means of a charge number $z_i \times$ elementary charge *e* then leads to simple relation:

$$\rho = -\frac{e^2\varphi}{kT}\sum C_i z_i^2 \tag{3.17}$$

By substitution of this simplified linear dependence of charge density on potential (3.17) to (3.10), a linearized Poisson-Boltzmann equation is obtained:

$$\frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right) = \frac{e^2 \varphi}{\varepsilon_0 \varepsilon_r kT} \sum C_i z_i^2$$
(3.18)

Parameters, which are constant in light of the sought solution of Poisson-Boltzmann equation, can be summarized as parameter b.

$$\frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\varphi}{\mathrm{d}r} \right) = b^2 r^2 \varphi \tag{3.19}$$

$$b^{2} = \frac{e^{2}}{\varepsilon_{0}\varepsilon_{r}kT}\sum C_{i}z_{i}^{2}$$
(3.20)

By substitution $u = r \varphi$, equation (3.19) passes to form:

$$\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} = b^2 u \tag{3.21}$$

Because:

$$\frac{\mathrm{d}u}{\mathrm{d}r} = \frac{\mathrm{d}r\varphi}{\mathrm{d}r} = \varphi + r\frac{\mathrm{d}\varphi}{\mathrm{d}r}, \qquad \qquad \frac{\mathrm{d}\varphi}{\mathrm{d}r} = \frac{1}{r}\left(\frac{\mathrm{d}u}{\mathrm{d}r} - \varphi\right),$$

the right-hand side of (3.19) is then:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^{2}\frac{\mathrm{d}\varphi}{\mathrm{d}r}\right) = \frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}u}{\mathrm{d}r} - r\varphi\right) = \frac{\mathrm{d}u}{\mathrm{d}r} + r\frac{\mathrm{d}^{2}u}{\mathrm{d}r^{2}} - \varphi - r\frac{\mathrm{d}\varphi}{\mathrm{d}r} =$$
$$= \frac{\mathrm{d}u}{\mathrm{d}r} + r\frac{\mathrm{d}^{2}u}{\mathrm{d}r^{2}} - \varphi - \frac{\mathrm{d}u}{\mathrm{d}r} + \varphi = r\frac{\mathrm{d}^{2}u}{\mathrm{d}r^{2}}$$

General form of (3.21) allows looking for its solution in a form generally suitable to the given equation:

$$u = Ae^{-br} + Be^{br} \tag{3.22}$$

For original (3.19) is then available the following form:

$$\varphi = \frac{A}{r} e^{-br} + \frac{B}{r} e^{br}$$
(3.23)

Constants of integration A and B will ensue from boundary conditions. Deduction of B is trivial:

For $r \to \infty$ it must apply $\varphi = 0$, i.e. $0 = \frac{A}{\infty}e^{-\infty} + \frac{B}{\infty}e^{\infty}$, which applies only for B = 0. The applicable solution is then in the form:

 $\varphi = \frac{A}{r} e^{-br}$

Calculation of *A* is based on expression of charge density
$$\rho = f(r)$$
. After substitution of (3.24) as the calculated function of dependence on potential φ on *r* to (3.17), and in consideration of (3.20), it is obtained for charge density as function *r*:

$$\rho = -\frac{Ab^2 \varepsilon_0 \varepsilon_r}{r} e^{-br}$$
(3.25)

Relation (3.25) reflects charge density in ionic cloud under consideration (in dependence on r). Total charge of ionic cloud, i.e. integral over spherical surfaces surrounding the central ion (see Fig. 3.1) in distance interval from a to infinite, then must be equal to a charge of the central ion, except for the sign:

$$\int_{a}^{\infty} 4\pi r^2 \rho(r) \mathrm{d}r = -z_i e \tag{3.26}$$

After substitution of the expression for charge density (3.25)

$$Ab^{2}\varepsilon_{0}\varepsilon_{r}4\pi\int_{a}^{\infty}r\mathrm{e}^{-br}\mathrm{d}r = z_{i}e$$
(3.27)

and value of constant A is obtained by integration from this model consideration.

$$A = \frac{z_i e}{4\pi\varepsilon_0 \varepsilon_r} \frac{e^{ba}}{1+ba}$$
(3.28)

It then comes out for the resulting potential from (3.24) and (3.28):

(3.24)

$$\varphi = \frac{z_i e}{4\pi\varepsilon_0 \varepsilon_r} \frac{e^{ba}}{1+ba} \frac{e^{-br}}{r}$$
(3.29)

Calculated potential φ includes Coulombic contribution of the central ion itself $\varphi_c = \frac{z_i e}{4\pi\varepsilon_0 \varepsilon_r r}$, and contribution of ionic atmospheres φ' . It results for φ' : from relation $\varphi = \varphi_c + \varphi'$

$$\varphi' = \frac{z_i e}{4\pi\varepsilon_0 \varepsilon_r r} \left(\frac{e^{ba}}{1+ba} e^{-br} - 1 \right)$$
(3.30)

For potential of ionic atmospheres at the point of central (shielded) ion it comes out after substitution r = a (*a* is a minimum possible distance corresponding to radius of the central ion).

$$\varphi_{r=a}' = \frac{-z_i e}{4\pi\varepsilon_0 \varepsilon_r} \frac{b}{1+ba}$$
(3.31)

For extremely diluted solutions $ba \ll 1$ applies and expression (3.31) can be simplified:

$$\varphi_{r=a}' = \frac{-z_i e b}{4\pi\varepsilon_0 \varepsilon_r} \tag{3.32}$$

Calculated additional potential φ' determined by ionic atmosphere corresponds with additional Gibbs energy of electrolyte solution, i.e. it is in relation with activity coefficient.

Additional ΔG for charging an ion with "shielding" charge corresponding to the effect of ionic atmospheres is expressed:

$$\Delta G = \int_{o}^{ze} \varphi' dQ = \int_{o}^{ze} \frac{-bQ}{4\pi\varepsilon_0\varepsilon_r} dQ = -\frac{z^2 e^2 b}{8\pi\varepsilon_0\varepsilon_r}$$
(3.33)

It applies for additional Gibbs energy for one ion:

$$\Delta G = kT \ln \gamma_i \tag{3.34}$$

Relation (3.34) in principle corresponds to (3.4), which is though related to the molar quantity. By combining (3.33) and (3.34), it comes out:

$$\ln \gamma_i = -\frac{z^2 e^2 b}{8\pi \varepsilon_0 \varepsilon_r kT} \tag{3.35}$$

Relation (3.20) for parameter *b* can be converted into a form for molar concentration of represented ions ($R = N_A k$, $c_i = C_i / N_A$ applies).

$$b = \left(\frac{N_A^2 e^2}{\varepsilon_0 \varepsilon_r RT} \sum c_i z_i^2\right)^{1/2} = B\sqrt{I}$$
(3.36)

By combining (3.35) and (3.36) and other adjustments, a standard form of Debye-Hückel limit law comes into being (3.9), describing dependence of mean activity coefficient on ionic strength and charge numbers of cation and anion of the electrolyte.

$$-\log\gamma_{\pm} = \overline{A}|z_{\rm K}z_{\rm A}|\sqrt{I_c}$$

The derived parameter includes only general constants – within the frame of simplification under consideration applicable for extremely diluted solutions the activity coefficient is not dependent on radius of present ions.

4. Oxidation – reduction processes, relation of Gibbs energy and oxidation-reduction potential

Standard reaction Gibbs (free) energy ΔG^{o}_{r} is thermodynamic potential of the course of chemical processes. In oxidation-reduction reactions connected with exchange of electrons, potential of the process course manifests oneself in a form of electric voltage, which is measurable in specific arrangement as an electrochemical cell.

For example, oxidation-reduction reaction

$$Zn^{o} + CuSO_{4} \rightarrow Cu^{o} + ZnSO_{4}$$

running from left to right can be arranged so that its course entailing exchange of electrons will be limited by (large) resistance on voltmeter attached to the electrodes from metals in question - see Fig 3.2. This effect is achieved by that the running partial oxidation-reduction processes Zn^{2+}/Zn° a Cu^{2+}/Cu° are separated by semipermeable diaphragm, i.e. reaction may proceed only by means of electrons transferred by external conductor with voltmeter. This electrochemical cell is described as a Daniel cell.



Fig. 4.1 Daniel cell

Electric voltage has dimension of energy – it applies for relationship between oxidation-reduction potential and Gibbs energy as general thermodynamic potential:

$$\Delta G = -nfE \tag{4.1}$$

Therefore, if activities of Cu^{2+} and Zn^{2+} in the presented Daniel cell equal to one (or if their ratio equals to one; activities of metals Zn° and Cu° forming the electrodes are maximum, i.e. equal to one), voltage measured on voltmeter (with infinite resistance) will correspond to standard Gibbs energy of the given reaction ΔG_r° divided by Faraday constant and number two (2 exchanged electrons).

For electric voltage, which can be measured for oxidation- reduction reaction in a described way, i.e. for instantaneous redox potential of this reaction apply the same basic starting points as for Gibbs energy ΔG . I.e. in the initial state, to which activity of reaction components of one unit corresponds, applies $E = -\Delta G^o_r/nf$, and in equilibrium (the final state, which gets stabilized, if electrodes are interconnected with a conductor), redox potential of the reaction equals to zero - the cell is discharged. It means that for general oxidation-reduction reaction with *m* reactants and *l* products, Nernst equation applies:

$$E = E^{0} - \frac{RT}{nf} \ln \frac{a_{prod,1}^{v_{1}} \cdots a_{prod,l}^{v_{l}}}{a_{reakt,1}^{v_{1}} \cdots a_{reakt,m}^{v_{m}}}$$
(4.2)

or:

$$E^{0} = -\frac{\Delta G_{r}^{0}}{nf} = \frac{RT}{nf} \ln K_{a}$$
(4.3)

Evaluation of the course of oxidation- reduction processes is carried out by balancing potentials of partial semi-cells, i.e. electrode reactions.

Within the frame of the above mentioned reaction, two partial processes proceed:

$$Zn^{2+} + 2e^{-} - Zn$$
 -0.7628 V
 $Cu^{2+} + 2e^{-} - Cu$ +0.337 V

On the right hand side, standard electrode potentials E° of both electrode reactions are given. Values E° can be found by measurement of individual semi-cells (electrode made of appropriate metal immersed into the solution of its cation of unit activity) compared to standard hydrogen electrode, standard electrode potential of which is taken as equal to zero.

Electrode reactions are conventionally written in the direction of reduction. Zinc tends to pass to an oxidized form (to the solution), ΔG^o_r of this electrode reaction for this element (written in the direction of reduction) is positive - the reaction in the given conventionally designated direction will not proceed. Standard electrode potential E^o for this reaction according to (4.3) is negative. Copper is a noble metal - it has no tendency to oxidize (dissolve), i.e. the electrode reaction in question will proceed in the given direction - $\Delta G^o_r < 0$, $E^o > 0$.

Oxidation- reduction reaction running in Daniel cell includes electrode reaction of zinc in the opposite direction. In balance calculation of the standard electromotive tension of this cell will then be included $E_{\text{Zn+/Zn}}^{o}$ with opposite sign (+0.7628 + 0.337 = 1.0998 V). The stated value corresponds to voltage, which will be measured, if activities of Zn²⁺ and Cu²⁺ equal to one.

Generally, for individual electrode reactions, it is possible to write:

$$E = E^{0} - \frac{RT}{nf} \ln \frac{a_{red,1}^{v_{1}} \cdots a_{red,l}^{v_{l}}}{a_{ox,1}^{v_{1}} \cdots a_{ox,m}^{v_{m}}}$$
(4.4)

Most of electrode reactions (for metals all) include only two components in the reaction mixture reduced and oxidized forms, whereas stoichiometric coefficients of both equal to one. For this type of processes Nernst equation can be written in a simplified form:

$$E = E^0 + \frac{RT}{nf} \ln \frac{a_{ox}}{a_{red}}$$
(4.5)

Or if reduced form is formed of metal (i.e. a semi-cell with an electrode from the appropriate metal), activity of which is a maximum - equal to one, it is possible to write:

$$E = E^0 + \frac{RT}{nf} \ln a_{ox} \tag{4.6}$$

Oxidation - reduction potential of environment - Eh

Oxidation-reduction processes in environment (natural water) are represented by a complicated system formed of greater number of individual counterions (Fe^{3+}/Fe^{2+} , Mn^{4+}/Mn^{2+} , PO_4^{3-}/PO_3^{3-} , etc.) - semi-cells. For such environment a general - summary oxidation- reduction potential is instituted, referred to as *Eh*. *Eh* value could be expressed in numbers as a sum of all partial electrode potentials calculated for individual counterions, while substituting currently found concentrations of these ions into the given equation. Finding *Eh* of any aqueous environment is practically carried out by measurements - with an electrode of bright finished platinum interconnected with a suitable reference electrode. Generally a non-zero value is measured, *Eh* > 0 represents oxidation properties and vice versa.

Natural (aqueous) environment is especially in flowing water considered to be steady in equilibrium. However, for equilibrium conditions $\Delta G = 0$, Eh = 0 generally applies (system in equilibrium has no potential – it is "discharged"). This principle ($\Delta G_r = 0$, $E_{equil} = 0$) relates to general opinion on chemical processes, when initial activities of the reaction components are considered as one, or having with respect to stoichiometry such values that the fraction on the left hand side of (4.4) equals to one. For the initial state it theoretically applies: $\Delta G = \Delta G^o$, $E = E^o$, " $Eh = Eh^o$ ". In aqueous systems in natural environment this general solution naturally is not observed, and zero value E_{equil} cannot be achieved for the state, when fraction on the left hand side of (4.4) corresponds to equilibrium, .

Measured Eh > 0 of a real system corresponds as a rule to the concentration excess of dissolved oxygen. The system is in its energy minimum, however, it cannot achieve the general equilibrium state $\Delta G = 0$, i.e. Eh = 0 in connection with concentration disproportion of oxidizable components compared with dissolved O₂.

5. Kinetics of physico-chemical (and other) processes in environment

5.1 Rate, scope and order of processes

Kinetics of processes in environment, especially of chemical reactions, studies the course of these possible processes in time in view of thermodynamics, i.e. their rate. Generally, one isolated process or more simultaneous processes may proceed in the system, as are reversible, side, and subsequent processes. The processes are further distinguished (especially chemical reaction) as homogenous, when all components of the system are in one phase, and heterogeneous processes, e.g. controlled diffusion on phase interface.

The attributes in question – rate, order, and scope, are primarily instituted for chemical reactions – in the following text terminology relating to chemical processes is then observed. Nevertheless, the described principles have more general importance and correspond also with other types of dynamic processes in environment (nuclear, biological, physico-chemical, etc.).

For general reaction:

$$\alpha A + \beta B > \eta Y + \omega Z$$

a differential of the scope of reaction is defined - see (2.13):

$$d\xi = -\frac{dn_A}{\alpha} = -\frac{dn_B}{\beta} = +\frac{dn_Y}{\eta} = +\frac{dn_Z}{\omega}$$
(5.1)

 α , β , η , ω are stoichiometric coefficients, n_A , n_B , n_X , n_Z are substance quantities of reaction components. The following applies for infinitesimal time change in the scope of reaction, i.e. reaction rate w

$$w = \frac{d\xi}{dt} = -\frac{1}{\alpha} \frac{dn_A}{dt} = -\frac{1}{\beta} \frac{dn_B}{dt} = +\frac{1}{\eta} \frac{dn_Y}{dt} = +\frac{1}{\omega} \frac{dn_Z}{dt}$$
(5.2)

Relation of w to the unit volume leads to definition of rate of standard reaction in solution vv.

$$v = w/V = \frac{d\xi}{V dt} = -\frac{1}{\alpha} \frac{dc_A}{dt} = -\frac{1}{\beta} \frac{dc_B}{dt} = +\frac{1}{\eta} \frac{dc_Y}{dt} = +\frac{1}{\omega} \frac{dc_Z}{dt}$$
(5.3)

Instantaneous concentration of the reacting substance is connected with its initial concentration by relation:

$$c_i = c_i^0 + v_i x \tag{5.4}$$

where $x = \xi/V$ is the scope of reaction related to volume unit and v_i is stoichiometric coefficient of the substance *i*. Stoichiometric coefficients are taken for starting substances as negative, for products as positive. I.e.:

$$c_A = c_A^0 - \alpha x, \quad c_B = c_B^0 - \beta x, \quad c_Y = c_Y^0 + \eta x, \quad c_Z = c_Z^0 + \omega x$$
 (5.5)

For reaction rate (proceeding in constant volume) it then applies:
$$v = \frac{1}{v_i} \frac{\mathrm{d}c_i}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{1}{\alpha} \frac{\mathrm{d}c_A}{\mathrm{d}t} = -\frac{1}{\beta} \frac{\mathrm{d}c_B}{\mathrm{d}t} = +\frac{1}{\eta} \frac{\mathrm{d}c_Y}{\mathrm{d}t} = +\frac{1}{\omega} \frac{\mathrm{d}c_Z}{\mathrm{d}t}$$
(5.6)

Reaction rate is dependent on temperature and concentrations of reacting substances. Under isothermal conditions it applies:

$$v = kc_A^r c_B^s \tag{5.7}$$

Reaction rate is proportional to the power of instantaneous concentrations of reacting substances.

An important term is the order of reaction, which is defined as a sum of exponents of instantaneous concentrations of reacting substances found by measurement of reaction rate. It may be emphasized that the exponents determining the reaction rate are in general independent on stoichiometry.

5.2 Dynamic processes of the zeroth and first orders

In processes of zeroth order the rate during an action is constant and independent at concentration of reacting materials.

$$v = -\frac{\mathrm{d}c_A}{\mathrm{d}t} = k \tag{5.8}$$

Therefore, for the time course of concentration (generally of relative amount) of material A being consumed (starting material), it applies as follows:

$$c_A = c_A^0 - kt \tag{5.9}$$

Processes of the first order proceed at a speed depending on instantaneous concentration (relative amount) of a component being consumed (starting). It concerns speed of degradation of this component A, i.e. with a minus sign.

$$A \xrightarrow{k} Y$$

$$-\frac{dc_A}{dt} = kc_A$$
(5.10)

The simplest possible common differential equation (5.10) may be easily integrated after separation of variables.

$$\int \frac{dc_A}{c_A} = -\int kt \tag{5.11}$$

$$\ln c_A = -kt + C \tag{5.12}$$

The constant of integration is simply expressed in numbers in point t = 0. It applies in the beginning of the process as follows:

$$C = \ln c_A^0 \tag{5.13}$$

And the resulting solution is in the form:

$$\ln \frac{c_A^0}{c_A} = kt \tag{5.14}$$

Or:

$$c_A = c_A^0 \exp(-kt) \tag{5.15}$$

It applies for the instantaneous concentration of initial component A, expressed generally by the help of (5.4) as follows:

$$\ln \frac{c_A^0}{\left(c_A^0 - x\right)} = kt \tag{5.16}$$

$$x = c_A^0 (1 - \exp(-kt))$$
(5.17)

Of course, in addition to the time course of concentration of initial components A, the function for concentration of product Y is also expressible.

$$c_{Y} = c_{A}^{0} (1 - \exp(-kt)) + c_{Y}^{0}$$
(5.18)

Another parameter, which is often solved for dynamic processes, is a half-life, i.e. the time, in which the concentration of the initial component is exactly half compared to the initial value:

$$c_A = 0.5 c_A^0 \tag{5.19}$$

After substitution of (5.19) to (5.14), it is obtained for the half-life as follows:

$$\frac{\ln 2}{k} = t_{1/2} \tag{5.20}$$

Dynamic processes of the second order 5.3

Dynamic processes of the second order for two reactants

$$A + B \xrightarrow{k} produkty$$

The unit exponents in equation (5.7) correspond to this category of kinetic processes, and the reaction rate depends on the instantaneous concentration of both starting components. With regard to the two initial reactants, the speed of the process is expressed generally in the sense (5.6), ie:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \left(c_A^0 - x \right) \left(c_B^0 - x \right) \tag{5.21}$$

After separation of variables:

$$\frac{\mathrm{d}x}{\left(c_A^0 - x\right)\left(c_B^0 - x\right)} = k\mathrm{d}t \tag{5.22}$$

The integration of the left side (5.22) is conditioned by the decomposition into partial fractions.

$$\frac{1}{(c_A^0 - x)(c_B^0 - x)} = \frac{M}{c_A^0 - x} + \frac{N}{c_B^0 - x} = \frac{M(c_B^0 - x) + N(c_A^0 - x)}{(c_A^0 - x)(c_B^0 - x)}$$
(5.23)

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From (5.23) the equality follows:

$$1 = M(c_B^0 - x) + N(c_A^0 - x)$$
(5.24)

The enumeration (5.24) for the initial state x = 0 represents:

$$Mc_B^0 + Nc_A^0 = 1 (5.25)$$

Therefore, for any x > 0, with respect to (5.24) (multiplied) and (5.25):

$$M + N = 0 \tag{5.26}$$

The combination of (5.25) and (5.26) gives:

$$N = \frac{1}{\left(c_A^0 - c_B^0\right)} = -M \tag{5.27}$$

The form of the right side (5.21) is already suitable for integration after substituting (5.27) into (5.23)

$$-\int \frac{1}{(c_A^0 - c_B^0)} \frac{dx}{(c_A^0 - x)} + \int \frac{1}{(c_A^0 - c_B^0)} \frac{dx}{(c_B^0 - x)} = \int k dt$$
(5.28)

Which (including the right-hand side (5.28)) follows after a trivial substitution in the form:

$$\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\ln\left(c_{A}^{0}-x\right)-\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\ln\left(c_{B}^{0}-x\right)=kt+C$$
(5.29)

As with first-order processes, the integration constant is simply calculated using the initial state t=0.

$$C = \frac{1}{(c_A^0 - c_B^0)} \ln c_A^0 - \frac{1}{(c_A^0 - c_B^0)} \ln c_B^0$$
(5.30)

It is now possible to return from the general range of the reaction (relative to the unit volume) x to the concentrations of the reactants - $c_A^0 - x = c_A$, $c_B^0 - x = c_B$. I.e.:

$$\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\left(\ln c_{A}-\ln c_{A}^{0}\right)-\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\left(\ln c_{B}-\ln c_{B}^{0}\right)=kt$$

$$\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\ln \frac{c_{A}}{c_{A}^{0}}-\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\ln \frac{c_{B}}{c_{B}^{0}}=kt$$
(5.31)

The resulting formula including the time course of the concentrations of the reactants in the second order process is thus in the form:

$$\frac{1}{\left(c_{A}^{0}-c_{B}^{0}\right)}\ln\frac{c_{B}^{0}c_{A}}{c_{A}^{0}c_{B}}=kt$$
(5.32)

Of course, the instantaneous concentrations of the reactants are not independent of each other - see (5.5).

Dynamic processes of the second order with a single starting substance

Naturally, processes of the second order may also concern degradation of a single component, when this action is generally subject to interaction of two particles of the same component A.

$$2A \xrightarrow{k} products$$

Accordingly, it applies for degradation rate of component A:

$$-\frac{1}{2}\frac{\mathrm{d}c_A}{\mathrm{d}t} = kc_A^2 \tag{5.33}$$

The factor of one-half on the left-hand side is related to the fact that the loss of starting substance A must, by definition, correspond to an increase in the extent of reaction *x* that is half the actual second-order concentration loss of substance A in the process $- dx = \frac{1}{2} dc_A$.

After integration and numeration of the constant of integration (at point t = 0) it is obtained as follows:

$$\frac{1}{c_A} = 2kt + \frac{1}{c_A^0}$$

$$\frac{c_A^0 - c_A}{c_A^0 c_A} = 2kt$$
(5.34)

The half-life of the initial components A is then:

$$\frac{1}{2c_A^0 k} = t_{1/2}$$

Dynamic processes of the *n*-th order

General kinetic relation for processes of any order n = r + s + ..., which (*the order*) is considered as a variable, may be valid only for the situation, when initial concentrations of reacting components exactly correspond to stoichiometry of the process (e.g. chemical reaction). Only in this case the ratios of instantaneous concentrations of reacting components remain constant in time.

E.g. for reaction: $\alpha A + \beta B + \gamma C \xrightarrow{k}$ products

it is possible to write

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \frac{\left(c_A^0 - \alpha x\right)}{\alpha} \frac{\left(c_B^0 - \beta x\right)}{\beta} \frac{\left(c_C^0 - \gamma x\right)}{\gamma}$$
(5.35)

i.e. the general relation for the process of n-th order

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \left(c^0 - x\right)^n \tag{5.36}$$

may apply only to the described condition valid for the initial concentrations of the reactive components, i.e.:

$$c^{0} = c_{A}^{0} / \alpha = c_{B}^{0} / \beta = c_{C}^{0} / \gamma$$
(5.37)

(5.36) may be simply integrated after trivial separation of variables

$$\int \frac{\mathrm{d}x}{\left(c^0 - x\right)^n} = \int k \mathrm{d}t \tag{5.38}$$

Of course, the constant of integration is expressed in numbers through initial condition (t = 0).

$$\frac{1}{n-1} \left(c^0 - x \right)^{(1-n)} = kt + \frac{1}{n-1} \left(c^0 \right)^{(1-n)}$$
(5.39)

The following general relation for any order of the process is obtained after adjustment.

$$\frac{1}{n-1} \left[\frac{1}{c^{(n-1)}} - \frac{1}{(c^0)^{(n-1)}} \right] = nkt$$
(5.40)

The multiplication by order of the process *n* on the right-hand side of (3.40) is related to the same general assumptions as in relations (5.33) and (5.34). Going to relation (5.40), where the concentration decay of the starting substance(s) is no longer expressed in general terms - via the extent of *x* (as in (5.39), the ratio of the infinitesimal change in extent to the actual concentration decay must be taken into account - dx = dc/n.

5.4 Simultaneous dynamic processes

Within simultaneous processes, it is generally possible to talk about lateral, reversible and subsequent processes (reactions).

Lateral dynamic processes



b)
$$A + B \xrightarrow{k_1} Y$$
$$A + C \xrightarrow{k_2} Z$$

c)
$$B \xrightarrow{+A} Y$$

 $C \xrightarrow{+A} Z$

Lateral dynamic processes can take place as branched - a), competitive - b), or. independent - c). It applies for the case of branched processes:

$$\frac{dx}{dt} = k_1 (c_A^0 - x) + k_2 (c_A^0 - x) \equiv -\frac{dc_A}{dt} = c_A (k_1 + k_2)$$
(5.43)

It then results for the concentration of starting material A as follows:

$$-\ln c_{A} = (k_{1} + k_{2})t - \ln c_{A}^{0}$$

$$\ln \frac{c_{A}^{0}}{c_{A}} = (k_{1} + k_{2})t$$
(5.44)

Within the frame of the first order under consideration, the growth rate of product concentrations is in both processes proportional to c_A .

$$\frac{\mathrm{d}c_Y}{\mathrm{d}t} = k_1 c_A \tag{5.45}$$

$$\frac{\mathrm{d}c_Z}{\mathrm{d}t} = k_2 c_A$$

When considering (5.44):

$$dc_{Y} = k_{1}c_{A}^{0}e^{-(k_{1}+k_{2})t}dt$$

$$dc_{Z} = k_{2}c_{A}^{0}e^{-(k_{1}+k_{2})t}dt$$
(5.46)

Relations (5.46) expressed in numbers are no longer differential equations, but only equations of independent derivations. It is obtained after integration and numeration of the constant of integration as follows:

$$c_{Y} = \frac{k_{1}c_{A}^{0}}{k_{1} + k_{2}} \left[1 - e^{-(k_{1} + k_{2})t} \right]$$

$$c_{Z} = \frac{k_{2}c_{A}^{0}}{k_{1} + k_{2}} \left[1 - e^{-(k_{1} + k_{2})t} \right]$$
(5.47)

Whereas the constant of integration in the form of

$$C = \frac{k_1 c_A^0}{k_1 + k_2}$$
(5.48)

is expressed in numbers for the initial conditions c_Y , $c_Z = 0$, at t = 0.



Fig. 5.1 Possible trend of concentrations of components of branched process at $k_2 > k_1$

Reversible dynamic processes

$$A \xrightarrow[k_2]{k_1} B$$

The first order is considered for both directions of the process. For the equilibrium state, a significant excess of product B or the starting component A is not assumed. The corresponding equation is logically in the form:

$$\frac{dx}{dt} = k_1 (c_A^0 - x) - k_2 (c_B^0 + x)$$
(5.49)

The definition of the reverse process practically corresponds to the principle of defining the equilibrium state, which can be used to quantify one of the rate constants using the equilibrium constant, which is often available. The following applies to equilibrium:

$$k_1 (c_A^0 - x)_{rov} = k_2 (c_B^0 + x)_{rov}$$
(5.50)

With regard to (2.3):

$$\frac{\left(c_B^0 + x\right)_{rov}}{\left(c_A^0 - x\right)_{rov}} = \frac{k_1}{k_2} = K$$
(5.51)

Substituting (2.3), (respectively (5.51)) into (5.49) allows to obtain a form suitable for simple integration.

$$\frac{dx}{dt} = k_2 \left(K c_A^0 - K x - c_B^0 - x \right) = k_2 \left(K + 1 \right) \left(\frac{K c_A^0 - c_B^0}{(K+1)} - x \right)$$

$$\frac{dx}{\left(\frac{K c_A^0 - c_B^0}{(K+1)} - x \right)} = k_2 \left(K + 1 \right) dt$$
(5.52)

After integration and enumeration of the integration constant (for t = 0, x = 0):

$$-\ln\left(\frac{Kc_{A}^{0}-c_{B}^{0}}{(K+1)}-x\right) = k_{2}(K+1)t - \ln\left(\frac{Kc_{A}^{0}-c_{B}^{0}}{(K+1)}\right)$$

$$-\ln\left(1-\frac{(K+1)}{Kc_{A}^{0}-c_{B}^{0}}x\right) = k_{2}(K+1)t$$

(5.54)

The resulting relation for x = f(t) is in the form:

(5.53)



Subsequent dynamic processes

$$A \xrightarrow{k_1} B \xrightarrow{k_2} Y$$

Degradation of starting components A with formation of component B is considered as the first order process, i.e.:

$$-\frac{\mathrm{d}c_A}{\mathrm{d}t} = k_1 c_A, \quad c_A = c_A^0 \mathrm{e}^{-k_1 t}$$

It then applies for time change *c*_B:

$$-\frac{\mathrm{d}c_B}{\mathrm{d}t} = k_2 c_B - k_1 c_A = k_2 c_B - k_1 c_A^0 \mathrm{e}^{\cdot k_1 t}$$
(5.56)

Formation of final product Y is similarly considered as a simple process of the first order, therefore it must apply:

$$\frac{\mathrm{d}c_Y}{\mathrm{d}t} = k_2 c_B \tag{5.57}$$

Equation (5.56) is easily analytically solvable, even though here it is impossible to carry out simple separation of variables as in the previous cases. The solution results as an application of substitution of $c_B \equiv u \cdot v$.

$$\frac{\mathrm{d}c_{\scriptscriptstyle B}}{\mathrm{d}t} = \left(uv\right)' = u'v + uv'$$

It results from comparison with (5.56) as follows:

$$u'v = -k_{2}c_{B}, \quad uv' = k_{1}c_{A}^{0}e^{-k_{1}t}$$
$$u'v = -k_{2}uv, \quad u' = -k_{2}u, \quad u = C_{1}e^{-k_{2}t}$$
$$v' = \frac{k_{1}c_{A}^{0}e^{-k_{1}t}}{u} = \frac{k_{1}c_{A}^{0}e^{-k_{1}t}}{C_{1}e^{-k_{2}t}} = \frac{k_{1}c_{A}^{0}}{C_{1}}e^{(k_{2}-k_{1})t}$$
$$v = \frac{k_{1}c_{A}^{0}}{C_{1}}\int e^{(k_{2}-k_{1})t}dt = \frac{k_{1}c_{A}^{0}}{C_{1}(k_{2}-k_{1})}e^{(k_{2}-k_{1})t} + C_{2}$$

The resulting function is then in a form of:

$$uv = c_B = e^{-k_2 t} \left(\frac{c_A^0 k_1}{k_2 - k_1} e^{(k_2 - k_1)t} + C \right)$$
(5.58)

Naturally, the constant of integration $C = C_1 C_2$ is obtained for t = 0.

$$C = -\frac{c_A^0 k_1}{k_2 - k_1}$$

It then applies for the time course of concentration of component B as follows:

$$c_B = \frac{c_A^0 k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$
(5.59)

Relation (5.59) is then substituted to (5.57), and for growth of concentration of the resulting product Y it is possible to write:

$$\frac{\mathrm{d}c_Y}{\mathrm{d}t} = k_2 \frac{c_A^0 k_1}{k_2 - k_1} \left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t} \right)$$
(5.60)

Rate equation (5.60) is of the same type as (5.46) and may be easily integrated.

$$c_{Y} = k_{2} \frac{c_{A}^{0} k_{1}}{k_{2} - k_{1}} \left(\frac{1}{k_{2}} e^{-k_{2}t} - \frac{1}{k_{1}} e^{-k_{1}t} \right) + C$$

 $C = c_A^0$ ai t = 0, i.e.:

$$c_{Y} = c_{A}^{0} \left(1 - \frac{k_{2}}{k_{2} - k_{1}} e^{-k_{1}t} + \frac{k_{1}}{k_{2} - k_{1}} e^{-k_{2}t} \right)$$
(5.61)



Fig. 5.3 Possible trend of concentrations of components of subsequent process.

6. Non-linear dynamic systems described by a set of common differential equations

Oscillating Belousov-Zabotinsky chemical reaction

Within the research of chemical or biological dynamic processes, chaotic behavior was observed in some specific cases, characterized by the time oscillation of some parameters. A significant breakthrough in the field of chemical kinetics was the discovery of an oxidation-reduction reaction system showing a continuous concentration oscillation of some reactants. The so-called the oscillating reaction named after its discoverers as the Belousov-Zabotinsky reaction is very complex. In one modification of this reaction, the following main processes can be estimated:

 $\begin{aligned} CH_2(COOH)_2 + 6 Ce^{4+} + 2 H_2O &\rightarrow 2 CO_2 + HCOOH + 6 Ce^{3+} + 6 H^+ \\ 10 Ce^{3+} + 2 HBrO_3 + 10 H^+ &\rightarrow 10 Ce^{4+} + Br_2 + 6 H_2O \\ CH_2(COOH)_2 + Br_2 &\rightarrow CHBr(COOH)_2 + HBr \end{aligned}$

The observed oscillation course generally did not correspond to the assumption that the concentrations of the reacting components of the chemical system should return to an equilibrium steady state within clearly definable trends, as discussed in the previous chapter. Of course, the general thermodynamic principles also apply here. The equilibrium state associated with the end of the $Ce^{3+}\leftrightarrow Ce^{4+}$ oscillation occurs at a time when the starting components are predominantly consumed. The oscillating behavior of this chemical system corresponds to a state far from equilibrium. It can be said that the time course of concentrations of some components of the system is chaotic on the way to equilibrium.

Brusselator model

In connection with an effort for clarification of experimentally found oscillating (or chaotic) character of system behaviour of oscillatory chemical reaction, a simplified kinetic model, or dynamic system was designed:

- I. $A \longrightarrow X$
- II. $2X + Y \xrightarrow{k_1} 3X$
- III. $B + X \xrightarrow{k_2} Y + C$
- IV. $X \longrightarrow D$

If components A, B are taken as constants, to which their large surplus would correspond in real (i.e. the kinetic model concerns the condition remote from equilibrium), it is possible to express the mentioned scheme by two differential equations.

$$\dot{\mathbf{X}} = 1 - (k_2 + 1)\mathbf{X} + k_1\mathbf{X}^2\mathbf{Y}$$
 (6.1)

$$\dot{\mathbf{Y}} = k_2 \mathbf{X} - k_1 \mathbf{X}^2 \mathbf{Y} \tag{6.2}$$

For the speed of the processes I. and IV., it is then calculated with a constant equal to one for simplification, constant concentrations of components A and B are also taken as ones. Time derivations on left-hand sides are expressed in short - by notation, which is most frequently used. Symbols designating system components X, Y, A, B, C, D have in equations meaning directly of their concentrations, or more generally, relative quantities

This model is referred to as Brusselator according to the place of its origin. Both equations contain a non-linear terms, and analytical solution of this system is not offered. Numerical solution is not a problem, the result being the oscillatory course of parameters X and Y, really corresponding to experimental findings.



Fig. 6.1 The resulting oscillating course of variables X, Y obtained by numerical solution of Brusselator model (6.1), (6.2).

The principle of this complicated dynamic behaviour is non-linearity of the set of common differential equations to be solved. Therefore, the models of this type are referred to as non-linear dynamic systems, and their solution exhibits oscillating (or chaotic) nature. If systems of equations do not contain any parameter with in advanced determined time course, these systems are referred to as autonomous.

Oregonator model

Oregonator model, the name of which is also connected with the place of origin (the University of Oregon), was also developed as theoretical analogy to oscillating chemical reaction, even though it is evident that its meaning is more general likewise in Brusselator model. The model kinetic scheme consists of five partial actions, in which three variables operate, other initial or produced components are considered constant likewise in the previous case.

I.	$A + Y \xrightarrow{k_1} X$
II.	$X + Y \xrightarrow{k_2} P$
III.	$B+X \xrightarrow{k_3} 2X+Z$
IV.	$2X \xrightarrow{k_4} Q$
V.	$Z \xrightarrow{k_5} fY$

Therefore, the corresponding set of differential equations has the following form:

$$\dot{\mathbf{X}} = k_1 \mathbf{A} \mathbf{Y} - k_2 \mathbf{X} \mathbf{Y} + k_3 \mathbf{B} \mathbf{X} - k_4 \mathbf{X}^2$$
 (6.3)

$$\dot{\mathbf{Y}} = -k_1 \mathbf{A} \mathbf{Y} - k_2 \mathbf{X} \mathbf{Y} + k_5 \mathbf{Z} \tag{6.4}$$

$$\dot{\mathbf{Z}} = k_3 \mathbf{B} \mathbf{X} - k_5 \mathbf{Z} \tag{6.5}$$

The symbol of the system components have in the equations meaning directly of their concentrations, or more generally, relative quantities. Non-linearity of equations (6.3) and (6.4) results in typical oscillatory nature of the solution. Likewise in the previous case of non-linear dynamic system, the solution of Oregonator model exhibits antagonistic oscillation parameter X, with respect to Y, while variable Z imitates X.



Fig.6.2 The resulting oscillating course of variables X, Y, Z obtained by numerical solution of Oregonator model (6.3), (6.4), (6.5).

Lorentz model of convection in the atmosphere

This model, which is considered a pioneering work in the field of nonlinear dynamical systems, describes convection in the Earth's atmosphere at a slightly supercritical value of the Rayleigh number, ie a problem, in contrast to previous cases, purely physical. Briefly, this nonlinear

dynamical system consisting of three ordinary differential equations, ie comprising three variables X, Y, Z, was created by applying Galerkin's method (see ... of this text) to the initial nonlinear equations for thermal convection in a fluid (derived with general NS equations) in the space of three wave modes characterizing the idealized image of convective (ie vertical temperature gradient conditioned) processes in a fluid. The variable X corresponds to the convective flow velocity, Y is equivalent to the temperature difference between the rising and falling flow in the fluid heated from below and Z reflects the deviation of the vertical temperature profile from the linear profile.

$$\dot{\mathbf{X}} = -\boldsymbol{\sigma}\mathbf{X} + \boldsymbol{\sigma}\mathbf{Y} \tag{6.6}$$

$$\dot{\mathbf{Y}} = -\mathbf{X}\mathbf{Z} + r\mathbf{X} - \mathbf{Y} \tag{6.7}$$

$$\dot{\mathbf{Z}} = \mathbf{X}\mathbf{Y} - b\mathbf{Z} \tag{6.8}$$

For completeness, it can be added that σ is the Prandtl number, *r* is the ratio of the Rayleigh number to its critical value Ra/Ra_{krit} (the elaboration of specific physical or meteorological aspects of atmospheric convection is beyond the scope of this text). At this critical value, a fluid with a certain vertical temperature profile becomes unstable and convective movements occur.

The results of the numerical solution of the Lorentz model are standardly displayed as a so-called phase portrait, ie (phase) solution course in the space of three parameters X, Y, Z. The time axis is not displayed by default as in previous cases, it is actually parallel to the trajectory of the phase course of the solution. The phase portrait of the Lorenz model as a nonlinear dynamic system is the so-called chaotic (it is also referred to as a strange) attractor - see Fig. 6.3. The display of the chaotic oscillation course of individual parameters in the time axis - as in the previous cases, is of course also easily imaginable.

Lorentz's model was created in his time (1962) as part of an analysis of the problem of numerical weather forecasting. The results clearly show the basic property of the behavior of nonlinear dynamical systems (describing not only convective processes in the atmosphere or fluids in general) and the extreme sensitivity of the solution course to the initial conditions.



As can be seen, the course of solving the Lorentz model is drawn into a certain form, respectively the oscillations of individual parameters show a certain order and regularity. On the other hand, even a slight change in the initial conditions leads to a completely different position of a point in the trajectory of the solution in the phase space X, Y, Z after a small number of oscillations (or cycles). This fundamental property of nonlinear dynamical systems, referred to as deterministic chaos, is the essence of, for example, the practical impossibility of long-term weather forecasting.

For the sake of completeness, it can be added that the possibilities for the formulation of nonlinear dynamical systems are of course countless, the three cases presented here are perhaps most well-known next to the Lotka-Volterr model describing the biological (or ecological) predator-prey system. This simplest nonlinear dynamic system showing an oscillating course of parameters was formulated as early as 1925 (it can be found, for example, in *Begon, Harper: Ecology*).

7. Example of solution of ion exchange kinetics at flow through a path with active surface

Physical problems solved in the space of Cartesian coordinates (ie R2, R3) and in time are generally described by partial differential equations. The problem of ion exchange kinetics when flowing through an active surface path does not require this approach with respect to one spatial dimension and the considered



Fig. 7.1 Considered notion of flow of profile elements through path x

The formulation of the task is presented in Fig. 7.1. The solution containing the exchanged ions, i.e. hydrogen cations H^+ and metal cations Me^+ , flows at a velocity v in a 1D path of length X with an active surface (indicated by dots) with bound H^+ , Me^+ referred to in this context as H^S and Me^S . Thus, ion exchange is considered between the flowing solution and the static active surface:

$$Me^{s} + H^{+} \xrightarrow{k_{1}} Me^{+} + H^{s}$$

Fixation of ions on the active surface, which is really related to sorption factors, is expressed in the considered formulation of the problem simply as a general second-order process dependent on the concentration of these ions in solution and the relative number of (sorption) exchange sites on the active surface, ie sites occupied by the exchanged ion - c_{Me^S} , c_{H^S} . I.e. can be written:

$$\frac{\mathrm{d}c_{\mathrm{Me}^{+}}}{\mathrm{d}t} = k_{1}c_{\mathrm{H}^{+}}c_{\mathrm{Me}^{S}} - k_{2}c_{\mathrm{Me}^{+}}c_{\mathrm{H}^{S}}$$
(7.1)

The model calculation of the resulting course $c_{Me^+} = f(x,t)$ and the functions derived from it for other components of the indicated ion exchange can in this case be based on the idea of a profile element of width dx flowing in the path x and interacting with the active surface - see Fig. 7.1. With regard to the constant flow rate v, the time step can be "measured" by a corresponding displacement of the profile element in the path dx = vdt. The change in the metal concentration in the solution filling the profile element can then be expressed as a function of the displacement in the path:

$$\frac{dc_{Me^+}}{dx} = \frac{1}{v} \left(k_1 c_{H^+} c_{Me^S} - k_2 c_{Me^+} c_{H^S} \right)$$
(7.2)

To solve this initial equation, it is of course necessary to eliminate the unknown on the right. The concentration of hydrogen cations in the profile element can be expressed with a simple balance with regard to the considered ion exchange (which takes place during the passage of this element through the path with the active surface):

$$c_{\rm H^+}(x,t) = c_{\rm H^+}(0,t) + \alpha \left(c_{\rm Me^+}(0,t) - c_{\rm Me^+}(x,t) \right)$$
(7.3)

The factor α reflects the possible relative loss of H⁺ in the solution associated with the possible displacement of other metals from the active surface into the solution in parallel with the metal Me⁺, the concentration of which is calculated. The degree of this parallel elution of metals is identical to the behavior of Me⁺ within the simplification used.

From the point of view of the static active surface, the given displacement of the profile element represents the change of the state of this surface (determined by c_{Me^S} a c_{H^S}) in the spatial step dx = vdt by the time step dt. Therefore, the following applies throughout the flow path:

$$\frac{\mathrm{d}c_{\mathrm{Me}^{\mathrm{S}}}}{\mathrm{d}t} = -v \frac{\mathrm{d}c_{\mathrm{Me}^{\mathrm{+}}}}{\mathrm{d}x}$$
(7.4)

The total change of the "concentration" of the metal ion in the active surface c_{Me^S} in the whole path $x \in \langle 0, X \rangle$ in the time step thus corresponds to an increase or decrease (due to back fixation) of the concentration c_{Me^+} in the profile element that flowed through this path.

$$\frac{d\int_{0}^{X} c_{Me^{S}} dx}{dt} = c_{Me^{+}}(0,t) - c_{Me^{+}}(X,t)$$
(7.5)

The following profile element represents the next time step for the active surface. - see Fig. 7.1. Then the value $c_{Me^{S}}$ fixed at point *x* in the flow path corresponds to the total time $t = \tau$, which is "measured" by the integral of the flowing (and ion-exchanging) profile elements.

$$c_{\rm Me^{S}}(x,\tau) = c_{\rm Me^{S}}^{0} - v \int_{0}^{\tau} \frac{\mathrm{d}c_{\rm Me^{+}}(x,t)}{\mathrm{d}x} \mathrm{d}t$$
(7.6)

For the initial $c_{Me^{S}}^{0}$ and $c_{H^{S}}^{0}$, constant values over the entire path x are considered. Similarly, $c_{u^{S}}(x,\tau)$ can be expressed:

$$c_{\rm H^{S}}(x,\tau) = c_{\rm H^{S}}^{0} + \alpha v \int_{0}^{\tau} \frac{\mathrm{d}c_{\rm Me^{+}}(x,t)}{\mathrm{d}x} \mathrm{d}t$$
(7.7)

Substituting (7.3), (7.6) and (7.7) the initial differential equation is created, the solution of which, ie the course of c_{Me^+} (via a profile element) in the path *x* corresponding to one time step, is sought:

$$\frac{\mathrm{d}c_{\mathrm{Me}^{+}}}{\mathrm{d}x} = \frac{1}{\nu} \begin{bmatrix} k_1 \Big(c_{\mathrm{H}^{+}}^{}(0,t) + \alpha \Big(c_{\mathrm{Me}^{+}}^{}(0,t) - c_{\mathrm{Me}^{+}}^{} \Big) \Big) \Big(c_{\mathrm{Me}^{S}}^{0} - \nu \int_{0}^{\tau} \frac{\mathrm{d}c_{\mathrm{Me}^{+}}^{}}{\mathrm{d}x} \mathrm{d}t \Big) - \\ k_2 c_{\mathrm{Me}^{+}}^{} \Big(c_{\mathrm{H}^{S}}^{0} + \alpha \nu \int_{0}^{\tau} \frac{\mathrm{d}c_{\mathrm{Me}^{+}}^{}}{\mathrm{d}x} \mathrm{d}t \Big) \end{bmatrix}$$
(7.8)

After adjustment:

$$\frac{\mathrm{d}c_{\mathrm{Me}^{+}}(x,\tau+1)}{\mathrm{d}x} = \frac{1}{v}k_{1}\left(c_{\mathrm{H}^{+}}(0,\tau+1) + \alpha c_{\mathrm{Me}^{+}}(0,\tau+1)\right)\left(c_{\mathrm{Me}^{S}}^{0} - v_{0}^{\tau}\frac{\mathrm{d}c_{\mathrm{Me}^{+}}(x,t)}{\mathrm{d}x}\mathrm{d}t\right) - c_{\mathrm{Me}^{+}}\left[\alpha\left(k_{2}-k_{1}\right)\int_{0}^{\tau}\frac{\mathrm{d}c_{\mathrm{Me}^{+}}(x,t)}{\mathrm{d}x}\mathrm{d}t + \frac{1}{v}\left(\alpha.k_{1}c_{\mathrm{Me}^{S}}^{0} + k_{2}c_{\mathrm{H}^{S}}^{0}\right)\right]$$
(7.9)

The integrals over the time interval <0, τ > (corresponding to (7.6) and (7.7)) refer to the current state of the active surface (at point x), which will interact with the solved profile element, ie the element represented by the derivative of c_{Me^+} on the left side of (7.9). This current state of the surface was created by interaction with profile elements "flowed" in front of the solved element. I.e. the time integrals read the changes of c_{Me^-} at point x represented by the derivatives of c_{Me^+} into a state at time τ , while the derivative of $c_{Me^+}(x, \tau+1)$ on the left of (7.9) already expresses the state at the next time step. Integrals over a time interval can therefore be taken in (7.9) in general as independent functions of x, and this equation therefore corresponds to an ordinary differential equation of the type:

$$y' = g(x) - yf(x)$$
 (7.10)

The general solution of equation (7.10) is obtained by a simple procedure using the substitution y = uv (see the procedure in chapter 5.5 - Subsequent processes):

$$y(x) = e^{-F(x)} \int g(x) e^{F(x)} dx, \quad F(x) = \int f(x) dx$$
 (7.11)

The analytical solution of the integrals v (7.11) for the specific functions f(x), g(x) of course leads to the subsequent enumeration of the respective integral constants. Within the general form, these integrals can be rewritten to certain, while the integration interval (on the *x*-axis) <0, x_l > will correspond to the point in the argument of computed $y(x_l)$. For the integral curve going through the point [x_0 , y_0] then follows:

$$y(x_l) = e^{-F(x_l)} \left(y_0 + \int_0^{x_l} g(x) e^{F(x)} dx \right), \ F(x_l) = \int_0^{x_l} f(x) dx$$
(7.12)

Based on (7.12), the solution (7.9) sought for the course of c_{Me^+} in a flowing profile element in the path *x* can be written in the form:

$$c_{\mathrm{Me}^{+}}(x_{l},\tau+1) = e^{-z(x_{l},\tau)} \begin{bmatrix} c_{\mathrm{Me}^{+}}(0,\tau+1) + \\ \frac{1}{v}k_{1}(c_{\mathrm{H}^{+}}(0,\tau+1) + \alpha . c_{\mathrm{Me}^{+}}(0,\tau+1)) \times \\ \int_{0}^{x_{l}} \left(c_{\mathrm{Me}^{S}}^{0} - v_{0}^{\tau} \frac{\mathrm{d}c_{\mathrm{Me}^{+}}(x,t)}{\mathrm{d}x} \mathrm{d}t \right) e^{z(x,\tau)} \mathrm{d}x \end{bmatrix}$$
(7.13)

Whereas:

$$z(x_{l},\tau) = \int_{0}^{x_{l}} \left[\alpha \left(k_{2} - k_{1}\right) \int_{0}^{\tau} \frac{dc_{Me^{+}}(x,t)}{dx} dt + \frac{1}{\nu} \left(\alpha . k_{1} c_{Me^{S}}^{0} + k_{2} c_{H^{S}}^{0} \right) \right] dx =$$

= $\alpha . \left(k_{2} - k_{1}\right) \int_{0}^{\tau} c_{Me^{+}}(x_{l},t) - c_{Me^{+}}(0,t) dt + \frac{1}{\nu} \left(\alpha . k_{1} c_{Me^{S}}^{0} + k_{2} c_{H^{S}}^{0} \right) x_{l}$ (7.14)

The primitive function to the integrand in (7.13) containing the derivative of the unknown function in the product with e^z cannot be expressed in contrast to the integral in (7.14) (where only this derivative appears), ie only an adjustment can be made:

$$\int_{0}^{x_{l}} \left(c_{Me^{S}}^{0} - v_{0}^{\tau} \frac{dc_{Me^{+}}(x,t)}{dx} dt \right) e^{z(x,\tau)} dx =$$

$$c_{Me^{S}}^{0} \left(\frac{1}{z'(x_{l},\tau)} e^{z(x_{l},\tau)} - \frac{1}{z'(0,\tau)} \right) - v_{0}^{x_{l}} e^{z(x,\tau)} \int_{0}^{\tau} \frac{dc_{Me^{+}}(x,t)}{dx} dt dx$$
(7.15)

The form (7.15) reflects (7.14), or the zero value z at the point of the beginning of the path - x =0. The solution of the problem (7.13) in the path x therefore takes the form:

$$c_{Me^{+}}(x_{l},\tau+1) = e^{-z(x_{l},\tau)}c_{Me^{+}}(0,\tau+1) + k_{1}\left(c_{H^{+}}(0,\tau+1) + \alpha.c_{Me^{+}}(0,\tau+1)\right)\left[\frac{1}{v}c_{Me^{S}}^{0}\left(\frac{1}{z'(x_{l},\tau)} - e^{-z(x_{l},\tau)}\frac{1}{z'(0,\tau)}\right) - e^{-z(x_{l},\tau)}\int_{0}^{1}\int_{0}^{1}\frac{dc_{Me^{+}}(x,t)}{dx}dt e^{z(x,\tau)}dx\right]$$
(7.16)

Where of course:

$$z'(x,\tau) = \alpha \left(k_2 - k_1\right) \int_0^\tau \frac{\mathrm{d}c_{\mathrm{Me}^+}(x,t)}{\mathrm{d}x} \mathrm{d}t + \frac{1}{\nu} \left(\alpha . k_1 c_{\mathrm{Me}^S}^0 + k_2 c_{\mathrm{H}^S}^0\right)$$
(7.17)

Equation (7.16) (incl. (7.14) and (7.17)) of course relates only to the time step $\tau + 1$, ie it expresses the course of $c_{Me^+}(x, \tau+1)$ in the profile element in the path x, which is in the state τ after the "flow" of the previous element represented by $c_{Me^+}(x,\tau)$, respectively derivatives of $c_{Me^+}(x,\tau)$. This situation therefore corresponds to recurrence. The initial course of $c_{Me^+}(x,1)$ (+ derivation) for the first profile element interacting with the path surface in the initial homogeneous state is easily expressed:

$$c_{\mathrm{Me}^{+}}(x,1) = \frac{K_{2}}{K_{1}} + e^{-\frac{1}{\nu}K_{1}x} \left(c_{\mathrm{Me}^{+}}(0,1) - \frac{K_{2}}{K_{1}} \right)$$
(7.18)

$$\frac{\mathrm{d}c_{\mathrm{Me}^{+}}(x,1)}{\mathrm{d}x} = \frac{1}{\nu} \mathrm{e}^{-\frac{1}{\nu}K_{1}x} \left(K_{2} - K_{1}c_{\mathrm{Me}^{+}}(0,1) \right)$$
(7.19)

W

There:
$$K_1 = \alpha . k_1 c_{\text{Me}^S}^0 + k_2 c_{\text{H}^S}^0$$
, $K_2 = c_{\text{Me}^S}^0 k_1 (c_{\text{H}^+}(0,1) + \alpha . c_{\text{Me}^+}(0,1))$

The relatively "usable" analytical form with the enumerated primitive function of the integrand in (7.15) can also be obtained for the following time step:

$$c_{Me^{+}}(x,2) = e^{-z(x,1)}c_{Me^{+}}(0,2) + k_{1}\left(c_{H^{+}}(0,2) + \alpha \cdot c_{Me^{+}}(0,2)\right) \left[\frac{1}{v}c_{Me^{S}}^{0}\left(\frac{1}{z'(x,1)} - \frac{e^{-z(x,1)}}{z'(0,1)}\right) - k_{1}\left(k_{2} - K_{1}c_{Me^{+}}(0,1)\left(\frac{e^{-\frac{1}{v}K_{1}x}}{z'(x,1) - \frac{1}{v}K_{1}} - \frac{e^{-z(x,1)}}{z'(0,1) - \frac{1}{v}K_{1}}\right) \right]$$
(7.20)

Where:

$$z(x,1) = \alpha \cdot \left(k_2 - k_1\right) \left[\frac{K_2}{K_1} + e^{-\frac{1}{v}K_1 x} \left(c_{Me^+}(0,1) - \frac{K_2}{K_1}\right) - c_{Me^+}(0,1)\right] + \frac{1}{v}K_1 x$$
$$z'(x,1) = \alpha \left(k_2 - k_1\right) \frac{1}{v} e^{-\frac{1}{v}K_1 x} \left(K_2 - K_1 c_{Me^+}(0,1)\right) + \frac{1}{v}K_1$$

It is obvious that the analytical form for the *n*th time step is theoretically expressible in the form of a binary tree. If a generalized structure of the problem in the time axis is introduced, where the course of c_{Me^+} in the profile element in the *n*th time step can be simply referred to as c_n and the corresponding function (ie solution) (7.13), resp. (7.16) as f_n , it is possible to write in the sense of a given recurrence:

$$c_n = f_n(\sum_{i=1}^{n-1} c_i)$$
(7.21)

 c_i figure on the right-hand side of (7.13) and (7.16) of course also as the sum of their derivatives in the path *x*, however, this is a detail not reflected in its structure within the considered generalization. E.g. the solution for c_3 is simply given by:

$$c_3 = f_3(f_2(c_1) + c_1)$$

Then:

$$c_{4} = f_{4}(f_{3}(f_{2}(c_{1}) + c_{1}) + f_{2}(c_{1}) + c_{1})$$

$$c_{5} = f_{5}(f_{4}(f_{3}(f_{2}(c_{1}) + c_{1}) + f_{2}(c_{1}) + c_{1}) + f_{3}(f_{2}(c_{1}) + c_{1}) + f_{2}(c_{1}) + c_{1})$$
(7.22)

etc. Ie. the structure of the solution in the time axis corresponds to a binary tree of type (7.22). Finding an explicit analytical form of the solution for the *n*th time step is obviously not practical.

The total number of occurrences of functions corresponding to individual time steps in a given binary tree for expressing c_n is calculated as (of course $c_1 = f(c_0)$):

$$m_{f_i} = 2^{n-i-1}, \quad i = 1, n-1$$
 (7.23)

In practical applications of this concept, recurrent reading in the time axis is solved in numerical form on a computer (as a recurrent sequence with an initial value of c_1). This is not a numerical approximation - step dx is with respect to the existence of the analytical solution (7.16) in the path x infinitesimal, ie dt according to (7.4) as well. The numerical approximation generating inaccuracy must be used only for the calculation of the integral (7.15), whose explicitly expressed integrand has the form of a binary tree (7.22).

It can be added that the developed concept providing a semi-analytical solution of ion exchange kinetics at the flow of a 1D path with an active surface depending on the inflow concentrations of exchanged ions is generally applicable to a number of real processes. In laboratory conditions, of course, it is about modeling interactions in columns of various types, in the natural environment, the model is very well applicable, for example, for simulations of acidification or other episodes in watercourses.

Appendix A - Basic numerical methods of problem solving with initial conditions, i.e. of common differential equations and their sets

It concerns systems with collected parameters, which are described by sets of common differential equations for state variables in dependence on time.

Euler's explicit single-step method

Numerical solution of a common exercise with an initial condition expressed by a common differential equation

$$y'(t) = f(t, y(t))$$
 (A.1)
 $y(t_0) = y_0$

is based on approximation of derivative of the function in search on the left hand side of (A.1) by its difference in the selected time step h.

$$y'(t) \approx \frac{y(t+h) - y(t)}{h} \tag{A.2}$$

It means:

$$y(t+h) \approx y(t) + h f(t, y(t)) \tag{A.3}$$

For calculation of a new value y(t+h) then the known value present itself of y(t), or f(t,y(t)) from the previous step, which is the principle of the Euler's explicit method.

$$y_{n+1} = y_n + h f(t_n, y_n)$$
 (A.4)

Therefore, numeric approximation gets near to the exact solution at $h\rightarrow 0$. It is possible to add that (A.4) puts the equal sign between difference $(y_{n+1}-y_n)/h$ and the right-hand side function at point t_n , y_n . The nature of this error connected with this fact is shown in Fig. A.1. The value of the right-hand side function at point $t_{n+1/2}$, $y_{n+1/2}$, which would evidently correspond best to the given difference, is not available, indeed.



Fig. A.1 The error arising in numerical solution using Euler's single-step explicit method. The difference in the first step is for the given form of the function of accurate solution overestimated, which is demonstrated even in the following steps – the sequence of numerical solution is "unaware" at all, that accurate solution is below. After the fourth step the situation is then opposite.

Euler's implicit (backward) single-step method

Within the frame of Euler's single-step method, it is also possible to come out from the right-hand side function at point t_{n+1} , y_{n+1} .

$$y(t+h) \approx y(t) + h f(t+h, y(t+h))$$
(A.5)

$$y_{n+1} = y_n + h f(t_{n+1}, y_{n+1})$$
(A.6)

Unknown y_{n+1} is now contained also in the right-hand side of (A.6). The value of the right-hand side function obtained after expression of unknown y_{n+1} in the left-hand side is, of course, available for any point in the time axis (i.e. also for t_{n+1}).



Fig. A.2 The error arising in numerical solution using Euler's single-step implicit method. The situation is logically quite opposite to the explicit scheme.

The same differential approximation (Euler's explicit and implicit ones) may also be, of course, used in case of the set of common differential equations. In the equation being currently solved of the set, it is possible for the right-hand side function, which includes other variables as a rule, to select for some of these variables between the state from the previous step n and state n+1, which is already available, if it concerns parameters calculated from equations preceding the one being currently solved.

Runge – Kutta methods

Again, it concerns a single-step approach, however, which provides significantly more accurate numerical solution compared to the Euler's elemental method. This conception, the principle of which is sophisticated estimation of the value of the right-hand side function at the point properly corresponding to approximating difference, was designed by German mathematicians Carle David Tolme Runge and Martin Wilhelm Kutta.

The initial numerical scheme of the common differential equation being solved, is in a form of y' = f(t, y):

$$y_{n+1} = y_n + h\Phi(t_n, y_n, h)$$
 (A.7)

Whereas $\Phi(t_n, y_n, h)$ is the sought for estimation of the right-hand side function. A local error relating to (A.7) as to a common single-step method may be expressed as follows:

$$L(y(t);h) = y(t+h) - y(t) - h\Phi(t, y(t),h)$$
(A.8)

The relative increment of the exact solution may be in a discreet form given by the difference of the left-hand side at the non-zero step h.

$$\Delta(t, y, h) = \frac{y(t+h) - y(t)}{h}, \quad h \neq 0$$
(A.9)

Of course, in general (h = 0) it corresponds to the right-hand side function:

$$\Delta(t, y, h) = f(t, y), \quad h = 0 \tag{A.10}$$

It then applies for the local error:

$$L(y(t);h) = h [\Delta(t, y(t),h) - \Phi(t, y(t),h)]$$
(A.11)

With respect to (A.10), the step increment of the accurate solution $h\Delta(t,y,h)$ corresponds to Taylor expansion of the right-hand side function f(t,y(t)) through individual powers of step h.

$$h\Delta(t, y, h) = y(t+h) - y(t) = hf(t, y) + \frac{1}{2}h^2 f' + \dots + \frac{1}{p!}h^p f^{(p-1)}(t, y) + O(h^{p+1})$$
(A.12)

 $O(h^{p+1})$ is the residual error in the order of the respective power *h*. It then applies for the relative increment of the exact solution:

$$\Delta(t, y, h) = \frac{y(t+h) - y(t)}{h} = f(t, y) + \frac{1}{2}hf' + \dots + \frac{1}{p!}h^{p-1}f^{(p-1)}(t, y) + O(h^p)$$
(A.13)

The best estimation of the right-hand side function is then the following expansion:

$$\Phi(t, y, h) = f(t, y) + \frac{1}{2}hf' + \dots + \frac{1}{p!}h^{p-1}f^{(p-1)}(t, y)$$
(A.14)

Numeration of respective derivations f(t,y) in (A.14) (expressed by an index in parentheses) is not available within the frame of a single-step method.

The optimum value of the right-hand side function for numeration of the relative increment of exact solution is naturally f(t,y) at point t_{opt} , $y(t_{opt})$ lying in interval $t_n \le t_{opt} \le t_{n+1}$. Therefore, Φ may be sought for as a linear combination of functional values f of this interval. If these functional values are expressed as terms k_i , it is possible to write:

$$\Phi(t, y, h) = \sum_{i=1}^{s} w_i k_i$$
(A.15)

Of course, within the frame of the starting numerical scheme of the single-step method only value y_n is available (from the step *n* currently expressed in numbers), i.e. the right-hand side function *f* is enumerated at point t_n , y_n . The principle of Runge-Kutta method is recurrent structure of approximating terms of the values of the right-hand side function k_i . The primary starting value $f(t_n, y_n)$ is known (hereinafter f(t,y)). It means:

$$k_1 = f(t, y) \tag{A.16}$$

Other approximating terms are designed in accordance with the following principle:

$$k_{i} = f(t + \alpha_{i}h, y + h\sum_{j=1}^{i-1} \beta_{ij}k_{j}), \qquad i = 2,...,s$$
(A.17)

This scheme directly results from the definition of the differential equation, because common step displacement in axis y is given as $y + \beta hy'$, i.e. $y + \beta hf(t, y)$, $f(t, y) = k_1$ etc. Or in k_i is nested i - 1 (within the frame of the sum in the argument also i - 2, ..., 1) cycles of a predictor – corrector type.

It is possible to add that one of the established methods of numerical solution of common differential equations is just predictor – corrector progress, when starting value is y_{n+1} , which is calculated using the standard Euler's explicit method, and subsequently substituted to the right-hand side function f(t,y), and a new corrected value y_{n+1} is expressed in numbers. This cyclic progress may be repeated, e.g., until the selected convergent criterion is achieved.

The approximating values of the right-hand side function k_i in the proposed form of (A.17) are enumerable within the frame of the calculated step, with respect to recurrent nature ($k_1 = f(t,y)$ is available), providing the values of factors α_i , β_{ij} can be found. Further, it is necessary to deduce values of weighted factors w_i so that sought for $\Phi(t,y,h)$ could be expressed in numbers. It is evident that the criterion of correctness of values of these factors is conformity of Φ expressed according to (A.15) with Taylor expansion Φ (A.14) as its best estimation. Or w_i and their products with α_i , β_{ij} should be equivalent to factors 1/p! for terms representing the relevant powers h^{p-1} in (A.14). In individual k_i 's, h, α_i , β_{ij} are a part of the argument, and may be converted to required form of coefficients by (Taylor) expansion of functions k_i for given displacement $t + \alpha_i h$, $y + \beta h k_{i-1}$.

Therefore, for k_2 the following may be written with respect to the form of the total first and second derivations of the equation being solved:

$$y'' = f_{t}(t, y) + f_{y}(t, y)y' = f_{t}(t, y) + f_{y}(t, y)f(t, y)$$

$$y''' = \left(f_{t}(t, y) + f_{y}(t, y)y'\right)' =$$

$$f_{tt}(t, y) + f_{ty}(t, y)y' + f_{yt}(t, y)y' + f_{yy}(t, y)y'^{2} =$$

$$f_{tt}(t, y) + 2f_{ty}(t, y)f(t, y) + f_{yy}(t, y)f(t, y)^{2}$$
(A.18)
(A.18)

(derivations y' formed from argument f(t,y) are constants):

$$k_{2} = f(t + \alpha_{2}h, y + \beta_{21}hk_{1}) = f(t + \alpha_{2}h, y + \beta_{21}hf(t, y)) = f(t, y) + h\left[\alpha_{2}f_{t}(t, y) + \beta_{21}f_{y}(t, y)f(t, y)\right] +$$

$$\frac{h^{2}}{2}\left[\alpha_{2}^{2}f_{tt}(t, y) + 2\alpha_{2}\beta_{21}f_{ty}(t, y)f(t, y) + \beta_{21}^{2}f_{yy}(t, y)f(t, y)^{2}\right] + O(h^{3})$$
(A.20)

The relevant derivations are expressed by lower indices. The simplest application of Runge - Kutta approach is numeration of w_i , α_i , β_{ij} for second order, i.e. the linear combination:

$$\Phi(t, y, h) = w_1 k_1 + w_2 k_2 \tag{A.21}$$

In this case expansion of k_2 is sufficient in order h^1 , i.e.:

$$\Phi(t, y, h) = w_1 f(t, y) + w_2 f(t + \alpha_2 h, y + \beta_{21} h f(t, y)) = (w_1 + w_2) f(t, y) + w_2 h [\alpha_2 f_t(t, y) + \beta_{21} f_y(t, y) f(t, y)]$$
(A.22)

It results from comparison of corresponding terms of powers h (ie. h^0 , h^1) of Taylor expansion:

$$w_1 + w_2 = 1, \quad w_2 \alpha = \frac{1}{2}, \qquad w_2 \beta = \frac{1}{2}$$
 (A.23)

The set of three equations (A.23) containing four unknowns has, of course, infinite number of solutions. For each of these solutions, there is arbitrary $p \neq 0$, or the solution is given by setting of this parameter. It is possible to write:

$$w_1 = 1 - p, \quad w_2 = p, \quad \alpha = \frac{1}{2p}, \quad \beta = \frac{1}{2p}$$
 (A.24)

Parameter *p* is most often selected as $p_1 = 1$ and $p_2 = \frac{1}{2}$, from which results as follows:

$$\Phi_1 = f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}hf(t_n, y_n))$$
(A.25)

$$\Phi_2 = \frac{1}{2}f(t_n, y_n) + \frac{1}{2}f(t_n + h, y_n + hf(t_n, y_n))$$
(A.26)

Or:

$$y_{n+1} = y_n + hf(t_n + \frac{1}{2}h, y_n + \frac{1}{2}hf(t_n, y_n))$$
(A.27)

$$y_{n+1} = y_n + \frac{1}{2}h[f(t_n, y_n) + f(t_n + h, y_n + hf(t_n, y_n))]$$
(A.28)

The enumeration of the coefficients w_i , α_i , β_{ij} for higher orders of the Runge - Kutta methods is already more extensive. For the third order can be written:

$$k_{3} = f(t + \alpha_{3}h, y + h(\beta_{31}k_{1} + \beta_{32}k_{2})) = f(t, y) + h[\alpha_{3}f_{t} + (\beta_{31}k_{1} + \beta_{32}k_{2})f_{y}] + (A.29)$$

$$\frac{h^{2}}{2} [\alpha_{3}^{2}f_{tt} + 2\alpha_{3}(\beta_{31}k_{1} + \beta_{32}k_{2})f_{ty} + (\beta_{31}k_{1} + \beta_{32}k_{2})^{2}f_{yy}] + O(h^{3})$$

Derived terms f_t , f_y , f_{tt} , f_{ty} , f_{yy} are taken in (A.29) as independent of a specific point in the interval $\langle t_n, t_n + h \rangle$, and $\langle y(t_n), y(t_n + h) \rangle$ respectively. This point, to which the derivative of *f* relates, appears in the product with f_y (ie in the form of the derivative of the compound function *f*), where $y' = (\beta_{31}k_1 + \beta_{32}k_2)$, and $(y')^2 = (\beta_{31}k_1 + \beta_{32}k_2)^2$ respectively in the product with f_{yy} etc. It can be also written:

$$k_{3} = f(t, y) + h\left[\alpha_{3}f_{t} + (\beta_{31} + \beta_{32})f_{y}f(t, y) + \beta_{32}hf_{y}(\alpha_{2}f_{t} + \beta_{21}f_{y}f(t, y))\right] + \frac{h^{2}}{2}\left[\alpha_{3}^{2}f_{tt} + 2\alpha_{3}(\beta_{31} + \beta_{32})f_{ty}f(t, y) + (\beta_{31} + \beta_{32})^{2}f_{yy}f(t, y)^{2}\right] + O(h^{3})$$
(A.30)

I.e. in the term of k_3 development in h^1 the development of k_2 is also considered in the order h^1 . In the next term of k_3 development (in h^2), k_2 is "developed" only to h^0 , is here is $k_2 = k_1 = f(t,y)$ - then it holds:

$$\left(\beta_{31}k_1 + \beta_{32}k_2\right)^2 f_{yy} = \left(\beta_{31} + \beta_{32}\right)^2 f_{yy} f(t, y)^2$$

This gradual reduction of the development of k_2 appearing in k_3 is logical in connection with the fact that for Runge-Kutta the third order methods are sufficient terms of the development (A.14) to h^2 . For k_3 , after the clarification (A.30), the following applies:

$$k_{3} = f(t, y) + h\left[\alpha_{3}f_{t} + (\beta_{31} + \beta_{32})f_{y}f(t, y)\right] +$$

$$h\left[\alpha_{3}f_{t} + (\beta_{31} + \beta_{32})f_{y}f(t, y)\right] +$$

$$h^{2}\left[\beta_{32}\alpha_{2}f_{t}f_{y} + \beta_{32}\beta_{21}f_{y}^{2}f(t, y) + \frac{1}{2}(\beta_{31} + \beta_{32})^{2}f_{yy}f(t, y)^{2}\right] + O(h^{3})$$
(A.31)

The approximating function of the right-hand side Φ for the third order of the Runge-Kutta methods can be expressed on the basis of (A.20) and (A.31):

$$\Phi(t, y, h) = w_{1}k_{1} + w_{2}k_{2} + w_{3}k_{3} = w_{1}f(t, y) + \left\{ f(t, y) + h\left[\alpha_{2}f_{t} + \beta_{21}f_{y}f(t, y)\right] + \right\} \\ w_{2} \left\{ \frac{f(t, y) + h\left[\alpha_{2}f_{t} + \alpha_{2}\beta_{21}f_{y}f(t, y) + \frac{1}{2}\beta_{21}^{2}f_{yy}f(t, y)^{2}\right] \right\} +$$

$$\left\{ h^{2}\left[\frac{1}{2}\alpha_{2}^{2}f_{tt} + \alpha_{2}\beta_{21}f_{y}f(t, y) + \frac{1}{2}\beta_{21}^{2}f_{yy}f(t, y)\right] + \right\} \\ w_{3} \left\{ h^{2}\left[\beta_{32}\alpha_{2}f_{t}f_{y} + \beta_{32}\beta_{21}f_{y}^{2}f(t, y) + \frac{1}{2}\left(\beta_{31} + \beta_{32}\right)^{2}f_{yy}f(t, y)^{2}\right] \right\}$$
(A.32)

The following breakdown is useful:

$$\Phi(t, y, h) = (w_1 + w_2 + w_3)f(t, y) + h\{w_2[\alpha_2 f_t + \beta_{21}f_y f(t, y)] + w_3[\alpha_3 f_t + (\beta_{31} + \beta_{32})f_y f(t, y)]\} + h^2 \begin{cases} w_2[\frac{1}{2}\alpha_2^2 f_{tt} + \alpha_2\beta_{21}f_{ty}f(t, y) + \frac{1}{2}\beta_{21}^2 f_{yy}f(t, y)^2] + \\ w_3[\beta_{32}\alpha_2 f_t f_y + \beta_{32}\beta_{21}f_y^2 f(t, y) + \\ \frac{1}{2}\alpha_3^2 f_{tt} + \alpha_3(\beta_{31} + \beta_{32})f_{ty}f(t, y) + \frac{1}{2}(\beta_{31} + \beta_{32})^2 f_{yy}f(t, y)^2] \end{cases} =$$

$$= (w_{1} + w_{2} + w_{3})f(t, y) + h \begin{cases} (w_{2}\alpha_{2} + w_{3}\alpha_{3})f_{t} + \\ [w_{2}\beta_{21} + w_{3}(\beta_{31} + \beta_{32})]f_{y}f(t, y) \end{cases} + h^{2} \begin{cases} \frac{1}{2}(w_{2}\alpha_{2}^{2} + w_{3}\alpha_{3}^{2})f_{tt} + \\ [w_{2}\alpha_{2}\beta_{21} + w_{3}\alpha_{3}(\beta_{31} + \beta_{32})]f_{yy}f(t, y) + \\ \frac{1}{2}[w_{2}\beta_{21}^{2} + w_{3}(\beta_{31} + \beta_{32})^{2}]f_{yy}f(t, y)^{2} + \\ w_{3}\beta_{32}\alpha_{2}f_{t}f_{y} + w_{3}\beta_{32}\beta_{21}f_{y}^{2}f(t, y) \end{cases}$$
(A.33)

The comparison (A.33) with (A.14) therefore gives:

$$w_1 + w_2 + w_3 = 1 \tag{A.34}$$

$$w_2 \alpha_2 + w_3 \alpha_3 = \frac{1}{2}$$
(A.35)

$$w_2 \beta_{21} + w_3 (\beta_{31} + \beta_{32}) = \frac{1}{2}$$
(A.36)

$$w_2 \alpha_2^2 + w_3 \alpha_3^2 = \frac{1}{3} \tag{A.37}$$

$$w_2 \alpha_2 \beta_{21} + w_3 \alpha_3 (\beta_{31} + \beta_{32}) = \frac{1}{6}$$
(A.38)

$$w_2 \beta_{21}^2 + w_3 (\beta_{31} + \beta_{32})^2 = \frac{1}{3}$$
(A.39)

$$w_3 \alpha_2 \beta_{32} = \frac{1}{6} \tag{A.40}$$

$$w_3 \beta_{21} \beta_{32} = \frac{1}{6} \tag{A.41}$$

From (A.40) and (A.41)) the equality follows:

$$\alpha_2 = \beta_{21} \tag{A.42}$$

I.e. for (A.35) and (A.36) the identity follows and the following applies:

$$\alpha_3 = \beta_{31} + \beta_{32} \tag{A.43}$$

Thus, (A.37) and (A.39) are identical, and (A.38) contradicts (A.39) or (A.37) and cannot be used to calculate unknown parameters. This contradiction (A.38) is not without context - this equation (and of course it also (A.63), (A.39)) does not figure in the final form when it is with relations (A.42), (A, 43) is already calculated when deriving k_2 , k_3 and Φ . This more correct statement Φ takes the form of:

$$\Phi(t, y, h) = (w_{1} + w_{2} + w_{3})f(t, y) + h_{2}\{\alpha_{2}f_{t} + \beta_{21}f_{y}f(t, y)\} + w_{3}[\alpha_{3}f_{t} + (\beta_{31} + \beta_{32})f_{y}f(t, y)]\} + h_{2}\{w_{2}\left[\frac{1}{2}\alpha_{2}^{2}f_{tt} + \alpha_{2}\beta_{21}f_{ty}f(t, y) + \frac{1}{2}\beta_{21}^{2}f_{yy}f(t, y)^{2}\right] + h^{2}\left\{w_{3}\left[\frac{1}{2}\alpha_{3}^{2}f_{tt} + \alpha_{3}(\beta_{31} + \beta_{32})f_{ty}f(t, y) + \frac{1}{2}(\beta_{31} + \beta_{32})^{2}f_{yy}f(t, y)^{2} + \frac{1}{\beta_{32}}\beta_{21}f_{y}^{2}f(t, y)\right]\right\} = (A.44)$$

$$= (w_1 + w_2 + w_3)f(t, y) + h[(w_2\alpha_2 + w_3\alpha_3)F] + h^2 \begin{bmatrix} \frac{1}{2}(w_2\alpha_2^2 + w_3\alpha_3^2)G + \\ w_3\beta_{32}\alpha_2F \end{bmatrix}$$

Whereas:

$$F = f_t + f_y f(t, y), \quad G = f_{tt} + 2f_{ty} f(t, y) + f_{yy} f(t, y)^2$$

So there are four equations (A.34), (A.35), (A.37), (A.40) with six unknowns (w_{1-3} , α_1 , α_2 , β_{32}) - the solution is similar to Runge - Kutta second order methods ambiguous. It is possible to occur, for example:

$$w_1 = \frac{1}{4}, \ w_2 = \frac{1}{2}, \ w_3 = \frac{1}{4}, \ \alpha_2 = \beta_{21} = \frac{2}{3}, \ \alpha_3 = \frac{2}{3}, \ \beta_{31} = -\frac{1}{3}, \ \beta_{32} = 1$$
 (A.45)

$$w_1 = \frac{1}{6}, w_2 = \frac{2}{3}, w_3 = \frac{1}{6}, \alpha_2 = \beta_{21} = \frac{1}{2}, \alpha_3 = 1, \beta_{31} = -1, \beta_{32} = 2$$
 (A.46)

Most often, however, the sequence is applied:

$$w_1 = \frac{1}{4}, w_2 = 0, w_3 = \frac{3}{4}, \alpha_2 = \beta_{21} = \frac{1}{3}, \alpha_3 = \frac{2}{3}, \beta_{31} = 0, \beta_{32} = \frac{2}{3}$$
 (A.47)

I.e.:

$$y_{n+1} = y_n + \frac{1}{4}hf(t_n, y_n) + \frac{3}{4}hf(t_n + \frac{2}{3}h, y_n + \frac{2}{3}hf(t_n + \frac{1}{3}h, y_n + \frac{1}{3}f(t_n, y_n)))$$
(A.48)

The reader himself can perform deriving of the parameters of Runge- Kutta methods of fourth order, which is most effective for numerical solution of differential equations (higher orders does not mean significant improvement any longer). The resulting scheme is as follows:

$$y_{n+1} = y_n + \frac{1}{6}h(k_1 + 2k_2 + 2k_3 + k_4)$$

$$k_1 = f(t_n, y_n)$$

$$k_2 = f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}hk_1)$$

$$k_3 = f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}hk_2)$$

$$k_4 = f(t_n + h, y_n + hk_3)$$
(A.49)

Of course, the values of derived parameters in (A.49) represent only one out of an infinite number of possible solutions (the solution is ambiguous even for the fourth order), nevertheless, it is frequently used. In software applications for numerical solution of differential equations (or their sets), an option of the following set of parameters is also often available:

$$y_{n+1} = y_n + \frac{1}{8}h(k_1 + 3k_2 + 3k_3 + k_4)$$

$$k_1 = f(t_n, y_n)$$

$$k_2 = f(t_n + \frac{1}{3}h, y_n + \frac{1}{3}hk_1)$$

$$k_3 = f(t_n + \frac{2}{3}h, y_n - \frac{1}{3}hk_1 + hk_2)$$

$$k_4 = f(t_n + h, y_n + hk_1 - hk_2 + hk_3)$$
(A.47)

Appendix B - Numerical solution of partial differential equations – approximation using Galerkin's method

General starting data

A common partial differential equation can be expressed in the following form:

$$A\tilde{u} - f = 0 \tag{B.1}$$

Where \tilde{u} is the exact solution, i.e. a function, e.g. in space \mathbb{R}^3 , *f* is any function of threedimensional coordinates (e.g. in \mathbb{R}^3) or in time (in parabolic differential equations), in a number of cases (hyperbolic and some elliptic equations) is $f \equiv 0$. *A* is a differential operator, i.e., e.g.:

$$\frac{\partial}{\partial x}\mathbf{e}_{x} + \frac{\partial}{\partial y}\mathbf{e}_{y} + \frac{\partial}{\partial z}\mathbf{e}_{z} \equiv \nabla$$
(B.2)

Nabla operator in physical \mathbf{R}^3 space, \mathbf{e}_x , \mathbf{e}_y , \mathbf{e}_z are unit vectors in this space.

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \equiv \nabla^2 \equiv \Delta$$
(B.3)

Laplace's operator in \mathbb{R}^3 .

When describing time-dependent actions, corresponding differential operators are applied:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \equiv \Box$$
(B.4)

D'Alembert's operator operating in equations of a wave expanding with a speed of light c.

$$\frac{\partial}{\partial t} + u_x \frac{\partial}{\partial x} + u_y \frac{\partial}{\partial y} + u_z \frac{\partial}{\partial z}$$
(B.5)

Non-linear operator, which is part of equations describing a vector field of flux and other actions in liquids.

Discretization of partial differential equations (hereinafter PDE) is within the frame of conception of so-called weighted residues, where Galerkin's method belongs to, based on that the exact solution is in region Ω approximated by linear combination of a finite number of selected functions. It means that spectrum of these so-called base functions would be designed so that their specific linear combination could approach the exact solution.

$$\widetilde{u} \approx u = \sum_{i=1}^{n} u_i \varphi_i \tag{B.6}$$

These functions φ_i forming the base are, therefore, linearly independent, i.e. none of them may be expressible as a linear combination of others. Fulfilment of this condition is guaranteed by orthogonality of the base functions φ_i . It then applies for the scalar product expressed by integral over region Ω in \mathbf{R}^3 , in which base functions φ_i are established:

$$\left(\varphi_{i},\varphi_{j}\right) = \int_{\Omega} \varphi_{i}\varphi_{j} d\Omega = \delta_{ij}$$
(B.7)

 δ_{ij} je Kronecker's delta, which takes the value 1 for i = j and 0 for $i \neq j$. The functions of the base are then standardized ((φ_i , φ_i) = 1) and conform to requirement:

$$\sum_{i=1}^{n} \varphi_i = 1 \tag{B.8}$$

Condition (B.8) is met for any triplet (if Ω is considered in \mathbf{R}^3) of values of local variables in the region Ω substituted to the base functions.

It is possible to state more precisely that the base functions are orthonormal with respect to (B.7) and (B.8). This orthonormal base is in this respect defined in Hilbert's space **H**, where it forms the final subspace of base functions of dimension n, or the approximating solution of PDE u is sought for in this subspace of base functions in **H**. The solution (sought for according to (B.6)) in commonness will approximate the exact solution depending on abundance of the selected base, i.e. the dimension of subspace of base functions in **H**.

Approximate solution *u is* not exact for PDE (B.1), i.e. it is possible to write:

$$Au - f \neq 0$$

$$Au - f = r$$
(B.9)

Where *r* is the residuum expressing the "measure" of inaccuracy *u*. Solution *u* in form (B.6) will then come mostly close to the exact solution at finding the set of coefficient values u_i representing the smallest possible residuum in sense of (B.9) (i.e. coefficients u_i would give in commonness larger weight to the base functions approaching the exact solution and vice versa). Residuum *r* is naturally the function of relevant coordinates in region Ω , and in its evaluation or minimization, it is possible only to start from the principles applicable to space of functions **H**. In particular, the residuum can be "weighed" through scalar product (on region Ω) with selected socalled weight function *w*, when this scalar product of two functions (in **H**) is put equal to zero.

$$(w,r) = (w,Au-f) = 0$$

i.e.:

$$\int_{\Omega} w (Au - f) \, \mathrm{d}\Omega = 0 \tag{B.10}$$

Therefore, this condition means orthogonality of the residuum and weight functions w - see (B.7), or stated simply, the residuum and weighting functions do not "overlap" in region Ω (for any (3D) coordinate in region Ω , one of the functions is always zero, and the whole integral of their product is then zero). Besides, the fact should not be forgotten that equation (B.10) would be met also in the event that the function representing the residuum would be zero in the entire region Ω , and u would then be exact solution (w is non-zero in any case).

Generally, the following equation then applies:

$$\int_{\Omega} w (Au - f) \, \mathrm{d}\Omega = \int_{\Omega} w (A\tilde{u} - f) \, \mathrm{d}\Omega = 0 \tag{B.11}$$

Relation (B.10) then conforms to given PDE (B.1) in integral sense, or function u expressed from (B.10) is so-called weak (or generalized) solution of (B.1) in region Ω .

Of course, in terms of (B.10) one weigh function w may only "displace" residuum outside its non-zero value in region Ω . For finding solution u close to the exact solution, a possibility is certainly offered to weigh the residuum multiple times using more selected functions w_i , or if a number of weight functions corresponds to dimension n of subspace of base functions φ_i , a closed system is available of n integral equations (in case of time independent operator A) for calculation of n unknown coefficients u_i , and also for finding approximate solution u. J-th row of the given matrix is then in the form:

$$\int_{\Omega} w_j \left(A \left(\sum_{i=1}^n u_i \varphi_i \right) - f \right) d\Omega = \left(\sum_{i=1}^n u_i \int_{\Omega} w_j A \varphi_i d\Omega \right) - \int_{\Omega} w_j f d\Omega = 0$$
(B.12)

Of course, weight functions w_i must be suitably selected. Primarily, the logical condition is offered for this choice that the resulting residuum was "displaced" by "weighing" with n functions w_i outside the subspace of base functions φ_i . Then it is assured that the weak solution u in form (B.6) will be within the frame of dimension n of this subspace the best possible – most approaching the exact solution, or that given set of base functions already cannot offer a better variant of solution.

Solution of system (B.12) (i.e. calculation of set u_i , i = 1, ..., n) leads to the residuum, which must be orthogonal with all w_i 's. It is evident that if the base functions are directly used as weight functions $w_i = o_i$, (i = 1, ..., n), by solving (B.12) the desirable "displacement" of residuum outside the subspace of base functions is achieved. This variant of method of weighted residua $(w_i = \varphi_i)$ is called Galerkin's method after its author.
Weak solution u in form (B.6) is a generally applicable approximation at the level of numerical solution of discretized PDE within the frame of step corresponding to region Ω (identified with the final element). Of course, a possibility arises, especially when solving PDE with non-linear operators – e.g. (B.5), that the exact solution \tilde{u} will get within the frame of criteria Ω complicated fluctuating course, which will not be caught by weak solution u (suitable in integral sense of criterion Ω) in any case. Or the resulting residuum (function in **H** except subspace of base functions) will acquire not negligible functional values in region Ω .

Stationary exercises

The resulting system of algebraic equations formed by application of Galerkin's method on time independent PDE is in the form:

$$u_{1}\int_{\Omega}\varphi_{1}A\varphi_{1}d\Omega \quad \cdots \quad u_{n}\int_{\Omega}\varphi_{1}A\varphi_{n}d\Omega = \int_{\Omega}\varphi_{1}fd\Omega$$

$$\vdots \quad \ddots \quad \vdots \qquad \vdots$$

$$u_{1}\int_{\Omega}\varphi_{n}A\varphi_{1}d\Omega \quad \cdots \quad u_{n}\int_{\Omega}\varphi_{n}A\varphi_{n}d\Omega = \int_{\Omega}\varphi_{n}fd\Omega$$

(B.14)

Functions $A\varphi_i$ created by operation of differential operator A on base functions are not orthogonal with weight (i.e. base) functions φ_i , and individual integrals are generally non-zero (max. value = 1). In the same way *f*, i.e. integrals of their products with φ_i , form a non-zero vector of the right-hand side function (if it does not concern a type of PDE not containing *f*).

It should be added that the resulting set of linear equations (B.14) allowing us calculation of values u_i after numeration of individual integrals, e.g. by Gaussian elimination, corresponds to time independent linear operator A (i.e. it concerns a solution of a stationary problem). For a non-linear operator (time independent), e.g. products $u_i u_j$ would appear within the frame of individual terms of the resulting system – it would concern a system of non-linear equations solvable by a suitable iterative procedure.

Time dependent exercises

In time dependent PDE application of Galerkin's method leads to a system of equations in the form:

$$\frac{\partial u_1}{\partial t} \int_{\Omega} \varphi_1 \varphi_1 d\Omega + u_1 \int_{\Omega} \varphi_1 A \varphi_1 d\Omega \quad \cdots \quad u_n \int_{\Omega} \varphi_1 A \varphi_n d\Omega = \int_{\Omega} \varphi_1 f d\Omega$$

$$\vdots \qquad \ddots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$\frac{\partial u_n}{\partial t} \int_{\Omega} \varphi_n \varphi_n d\Omega + u_1 \int_{\Omega} \varphi_n A \varphi_1 d\Omega \quad \cdots \quad u_n \int_{\Omega} \varphi_n A \varphi_n d\Omega = \int_{\Omega} \varphi_n f d\Omega$$
(B.15)

Sought for coefficients u_i are then variables in time. Of course, a term representing time derivation appears only once on every line (with respect to (B.7)). Integrals for scalar products (φ_i, φ_i) in this term are equal to one, and need not have to be written at all. Therefore, (B.15) represents a set of common differential equations (hereinafter ODE). For parabolic PDE it concerns ODE of a standard type, for hyperbolic PDE, system of ODE type is created. Therefore, application of Galerkin's method converts time dependent PDE to a set of common differential equations providing weak solution for region Ω , i.e.:

$$u(t,\xi,\eta,\zeta) = \sum_{i=1}^{n} u_i(t)\varphi_i(\xi,\eta,\zeta)$$
(B.16)

where ξ, η, ζ are local three-dimensional coordinates in Ω . Again, it is necessary to add that the non-linear operator will lead to a system of non-linear ODE. The set in form (B.15) will not also be suitable for PDE containing the second time derivation, or the first and the second one simultaneously. Analysis of these events is already over the frame of this text.

Possibilities of numerical solution of systems of type (B.15) are already outlined in the previous chapter (numerical methods of solution of ODE systems). In this place, it is possible to very briefly mention other possible alternatives. One of these is an analytical solution applicable for the system of linear ODE with zero vector of the right-hand side. This system, which is a result of discretization of linear PDE with first time derivation and $f \equiv 0$ using Galerkin's method, has the following form:

$$\frac{\partial u_1}{\partial t} + u_1 \int_{\Omega} \varphi_1 A \varphi_1 d\Omega \quad \cdots \quad u_n \int_{\Omega} \varphi_1 A \varphi_n d\Omega = 0$$

$$\vdots \quad \ddots \quad \vdots \quad \vdots$$

$$\frac{\partial u_n}{\partial t} + u_1 \int_{\Omega} \varphi_n A \varphi_1 d\Omega \quad \cdots \quad u_n \int_{\Omega} \varphi_n A \varphi_n d\Omega = 0$$
(B.17)

The solution represented by *n* functions of the time course of individual u_i may be anticipated in a form of products of time averaged \overline{u}_i with generally convenient function of time:

$$u_i(t) = \overline{u}_i e^{-\lambda t}$$
, $(i = 1, ..., n)$ (B.18)

After substitution of (B.18) into (B.17) (and cancelling out) a homogeneous system of *n* linear algebraic equations for unknown components of the eigenvector $\overline{\mathbf{u}}$ is obtained:

$$\overline{u}_{1}\left(-\lambda+\int_{\Omega}\varphi_{1}A\varphi_{1}d\Omega\right) \cdots \overline{u}_{n}\int_{\Omega}\varphi_{1}A\varphi_{n}d\Omega = 0$$

$$\vdots \cdots \overline{u}_{n}\left(-\lambda+\int_{\Omega}\varphi_{n}A\varphi_{n}d\Omega\right) = 0$$
(B.19)

Detailing of (B.19) corresponds to a matrix record:

$$(\mathbf{A} - \lambda \mathbf{E})\mathbf{\overline{u}} = \mathbf{0} \tag{B.20}$$

Where element A_{ij} of matrix **A** is equal to $\int_{\Omega} \varphi_i A \varphi_j d\Omega$ and **E** is a unit matrix. Equation (B.20) is in the form of a problem of eigen numbers λ of matrix **A**, because it applies as follows:

$$\mathbf{A}\overline{\mathbf{u}} = \lambda\overline{\mathbf{u}} \tag{B.21}$$

For a non-zero solution of the homogeneous system (B.19) the eigen number λ must be selected so that:

$$\det(\mathbf{A} - \lambda \mathbf{E}) = \mathbf{0} \tag{B.22}$$

Expression of determinant (B.22) leads to a characteristic equation of matrix **A** for unknown λ . Roots of the characteristic equation are generally *n* values λ , i.e. *n* eigen numbers λ_i of matrix **A**. A partial result is then *n* possible time courses of the vector $\overline{\mathbf{u}}$, which is available in *n* forms as a solution of (B.19) for individual eigen numbers λ_i , therefore as *n* eigenvectors of matrix **A**. If the obtained vectors $\overline{\mathbf{u}}_i$ are normalized to the unit size, i.e. if the following applies:

$$\left(\overline{\mathbf{u}}_{i},\overline{\mathbf{u}}_{i}\right)=1\tag{B.23}$$

It is possible to express the general solution of system (B.17):

$$\mathbf{u}(t) = \sum_{i=1}^{n} \overline{\mathbf{u}}_{i} \mathbf{e}^{-\lambda_{i}t} = \overline{\mathbf{u}} \mathbf{e}^{-\lambda t}$$
(B.24)

The weak solution of linear PDE generating system (B.17) for region Ω is then in the form:

$$u(t,\xi,\eta,\zeta) = e^{-\lambda t} \sum_{i=1}^{n} \overline{u}_{i} \varphi_{i}(\xi,\eta,\zeta)$$
(B.25)

The resulting forms of (B.24) and (B.25) represent identical evolution for time dependent parameters u_i within the frame of general solution (in time). This situation documents linearity, or the result of this type would not come into consideration for a non-linear problem.

Another possible alternative for solution of time dependent PDE is assignment of time axes to spatial dimensions of region Ω , i.e. introduction of base functions, which include dependence on time. The time course of the solution *u* (of course only for local time interval of region Ω) is then

calculated directly within the frame of discretization of PDE using Galerkin's method, and not subsequently, as it is in the above developed approaches. More detailed description of this conception already exceeds the frame of this text.

Expansion to finite elements

On solving practical problems in \mathbb{R}^3 , especially modelling of transport processes, the need arises as a rule of expansion of numerical solution of PDE to more regions. This requirement is reflected by introduction of so-called finite elements. The Finite Element Method constructs individual local regions Ω as elements, which fill the entire global region of the solution – they are introduced through a grid. The Galerkin's discretization of PDE (or PDE system) in the entire global region, the shape of which is given by physical assignment, then generates a large thin system with non-zero terms in the proximity of the diagonal.

Basic procedures of grid formation lead in 2D physical space to triangular or tetragonal elements. Tetrahedral and hexahedral elements correspond to them in 3D. Problems of construction of finite elements and to them appertaining base functions are considerably wide. Within the frame of the focus of this text, only selected (practically the simplest) example may be brought in.

Tetragonal element in 2D



The element is instituted in the local three-dimensional coordinates ξ , η , which need not correspond with global Cartesian coordinate system with respect to possible non-orthogonal form of the element. On discretization of PDE, which are formulated in Cartesian coordinate system, it is necessary to carry out relevant transformation operations among local and global coordinates.

It is possible to introduce a linear isoparametric base in 2D local coordinates:

$$L_{1}(\xi) = \frac{1}{2}(1-\xi), \ L_{2}(\xi) = \frac{1}{2}(1+\xi), \ L_{1}(\eta) = \frac{1}{2}(1-\eta), \ L_{2}(\eta) = \frac{1}{2}(1+\eta)$$
(B.26)

Therefore, functions (B.26) are designed as the simplest polynomials of the first order with functional value <0,1> in the region of the element - see Fig. B.1. Naturally, the base functions, which are "offered" for the possible course of PDE solution, must be functions of two spatial variables in 2D application. From (B.26) is then derived bilinear base:

$$\varphi_1 = L_1(\xi)L_1(\eta) = \frac{1}{4}(1-\xi)(1-\eta)$$
(B.27)

$$\varphi_2 = L_2(\xi)L_1(\eta) = \frac{1}{4}(1+\xi)(1-\eta)$$
(B.28)

$$\varphi_3 = L_2(\xi)L_2(\eta) = \frac{1}{4}(1+\xi)(1+\eta)$$
(B.29)

$$\varphi_4 = L_1(\xi)L_2(\eta) = \frac{1}{4}(1-\xi)(1+\eta)$$
(B.30)

It means that base functions (B.27 – 30) have in respective corner points the value of one. It follows from Fig. 4.1 that the even such a simple base of four functions "offers" basic possibilities of variability of the three-dimensional course of the solution u in the region of element Ω . For practical calculations more complex types of bases are available. E.g. biquadratic base, which is derived from three basic types of the polynomials of the second order, which generally leads for a square element in 2D to nine base functions, whereas this number may be purposefully reduced (eight functions – so-called serendipian element). The base function may likewise be derived from Lagrangian or Hermitian polynomials, then it concerns Lagrangian and Hermitian elements.

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