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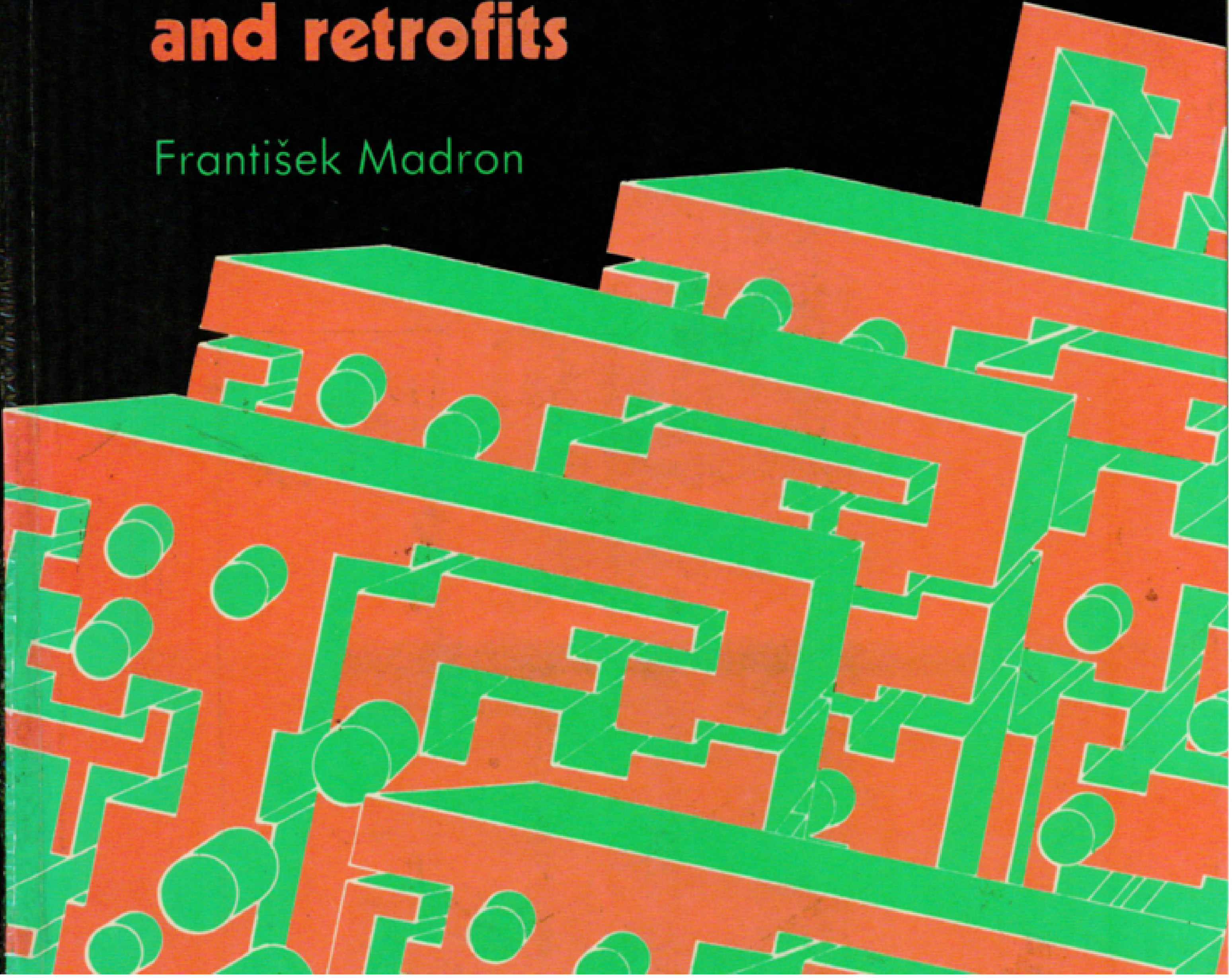
PROCESS PLANT PERFORMANCE

measurement and data processing for optimization and retrofits

František Madron



PROCESS PLANT PERFORMANCE

Measurement and Data Processing for Optimization and Retrofits

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Table of contents

Preface

Increased competition forces companies to make their plants more profitable. The need for improving existing plants is widely recognized. Attention now has to be focused on optimization, retrofitting and debottlenecking (*rationalization*) of operating plants based on a thorough chemical engineering analysis.

The objective of this book is not to present a systematic approach to rationalization. It would hardly be possible in a book of this extent, considering the diversity of techniques used in this field. There exists, however, a range of techniques common to most of the rationalization activities. By this I mean the wide range of problems connected with the analysis of the function of existing producing units based on plant measurements and experiments. The data obtained thereby represent a unique and invaluable source of information; their acquiring and processing, however, is usually not free from problems. Therefore, in this book, I have attempted to present a complex approach to plant measurements and experiments, starting from planning, through process data treatment, to interpretation of results. The structure of the book is as follows.

In the first chapter we shall acquaint ourselves with the most important activities connected with rationalization, particularly from the standpoint of plant measurements and experiments.

The aim of this book is to make the reader familiar with the possibility of a rational approach to the measurement in process plants. Generally, these problems are dealt with by the *theory of measurement* whose development has been associated primarily with the exact sciences such as physics, astronomy, or geodesy. The problems of measuring in process industries are of a rather specific character, and, therefore, the second chapter is devoted to the application of the measurement theory to process plants.

Virtually all types of information obtained by measurement are subject to errors. This is why the problem of measuring errors is dealt with in detail in the third chapter. Besides the theoretical topics such as classification of errors and their propagation in the course of their processing, practical methods for gathering information on measuring errors are also presented.

The theory of errors forms the basis for the statistical treatment of measured data which is discussed in the next chapter. After the preprocessing of data and direct calculations of unmeasured quantities, attention is focused on reconciliation of redundant data. Plant measurement could be considered to be a "battle" against gross and systematic errors of measurement. Therefore, attention is given to the important practical questions of checking the measured data from the standpoint of the occurrence of gross and systematic errors and also searching for the sources of these errors.

The fifth chapter is an introduction to the problems of the optimum design of measurement. Discussed here are the possibilities of obtaining requisite information within the shortest possible time and at minimum cost. Proper design of measurement must also reduce the probability that the only result of a measurement will be a statement that the measurement scheme used is not suitable.

The theories and methods presented up to Chapter 5 are illustrated in the text by a number of simple examples. More extensive applications are presented in the last chapter. Case studies, typical for measuring in process plants, have been selected here.

In order to comprehend the entire book, and in particular, practical applications of the presented methods, some knowledge of applied mathematics is necessary. Processing of data that are subject to random errors is based on the knowledge of probability theory and mathematical statistics. The computations proper rest upon the methods of linear algebra and for this reason the matrix notation is used extensively throughout the book. This is in tune with the current trend, since the well accepted advantages of matrices (particularly the possibility of expressing the relations among multidimensional objects) are today extended by the possibilities of using standard matrix computer software.

The enumeration of the branches of mathematics will be brought to a close with the graph theory, the usefulness of which is related to the system character of process plants.

A brief survey of concepts from the above disciplines of mathematics is presented in the Appendix. A reader who is not familiar with these branches of mathematics is advised to start this book by thumbing through the Appendix and to refer to it when necessary.

The book is intended particularly for engineers and managers responsible for improving the function of existing plants. Teams executing plant studies can also be found increasingly in research centers as well as in design and engineering companies.

A number of methods described in this book can be applied in designing the process control systems for new plants. The various aspects of an optimum design of measurement and of measured data processing are very relevant today, particularly in connection with the increasing use of automatic monitoring systems and process computers.

The problems of the theory of measurement are discussed in this book in a general way. It is not concerned exclusively with measurement in process plants. Hence the major parts of the book may also be utilized in the preparation and processing of the results of laboratory and pilot plant measurement, particularly in the sphere of chemical engineering.

Complex analysis of process data by statistical methods is not practical without computers. At the same time, much experience can be gained by answering different "what-if" questions which can occur in practice - an ideal application of the computer. To enhance study, the reader can obtain (free) computer codes on PC diskette (IBM XT/AT) in exchange for the coupon available at the end of the book. Two programs (equations solver and material balancing) will enable solving and further analysis of most of the examples presented in the book.

I owe much to all those who contributed to the writing of this book. This work has only been possible because of the co-operation with my colleagues from the Systems Engineering Department in the Research Institute of Inorganic Chemistry as well as those from other institutions and manufacturing plants. The final version of the manuscript was read in its entirety by Dr.V.Veverka and I wish to thank him for his expert criticism. The English of several chapters of the book was markedly improved by proof reading by Dr. L. Murray Rose and Peggy Temblador. The contents of the book are based on experience I have acquired during the past 15 years of my employment in the Research Institute of Inorganic Chemistry. Hence, my acknowledgements also include the Institute's management who founded the Systems Engineering Department in 1974 and supported its work even at times when the effectiveness of dealing with the tasks of plant improvement in process industries was not so obvious as it is now.

While writing this book I often pondered over the scope of the individual topics. Although I endeavoured to evaluate objectively my experience as acquired by dealing with dozens of research projects connected with plant improvement, I feel that the result is far from perfect. Therefore, I should be grateful to the readers for their comments on the book, both on the scope and on details.

Ústí nad Labem
December 1991

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List of symbols

a	adjustability
$\boldsymbol{a}$	vector of constants
$\boldsymbol{A}$	incidence matrix of a graph matrix of coefficients of measured variables
$\boldsymbol{B}$	matrix of coefficients of unmeasured variables
$\mathrm{cov}\,(X_1\,, X_2\,)$	covariance of random variables X_1 and X_2
d	gross error
$\det \boldsymbol{A}$	determinant of matrix $\boldsymbol{A}$
$\mathsf{D}\,(X)$	dispersion (variance) of random variable X
e	absolute error
$\exp\,(x)$	exponential function
F	mass flow rate
$\boldsymbol{E}$	atom matrix
$\mathsf{E}\,(X)$	mean value of random variable X
$F\,(X)$	distribution function
$F\,(\nu_1\,, \nu_2\,)$	F-distribution (Snedecor) with ν_1 and ν_2 degrees of freedom
$F_P\,(\nu_1\,, \nu_2\,)$	P % quantile (percentile) of F distribution
rank $\boldsymbol{A}$	rank of matrix $\boldsymbol{A}$
I	number of measured quantities
$\boldsymbol{I}$	unit matrix
J	number of unmeasured quantities
K	number of equations of a model
n	number of moles
$N\,(\mu\,, \sigma^2\,)$	normal (Gauss) distribution with mean value μ and variance σ^2
$N\,(0,1)$	standardized normal distribution
$N_n\,(\mu\,, \boldsymbol{F}\,)$	normal distribution of n-dimensional random vector with a vector of mean values μ and covariance matrix $\boldsymbol{F}$
p	pressure
$\mathsf{P}\,(A)$	probability of an event A
$Q_{\min}$	quadratic function (4.19)
r	rate of a chemical reaction; residual of an equation

$R(\tau)$	autocorrelation function
$R'(\tau)$	centred autocorrelation function
s	sample standard deviation
t	time
t_m	measurement time interval
$t(\nu)$	t (Student) distribution with ν degrees of freedom
$t_P(\nu)$	P % quantile (percentile) of $t(\nu)$ distribution
T	absolute (theromodynamic) temperature
u_P	P % quantile (percentile) of standarized normal distribution
v	adjustment
V	volume; volume flow
w	mass fraction
x	measured quantity; mole fraction
y	unmeasured quantity
z	standardized adjustment

Greek symbols

α	significance level of the test; confidence level
β	power of the test
γ	relative standard deviation
μ	mean value of a random variable
ν	number of degrees of freedom
ξ	extent of a chemical reaction
ρ	density
$\rho(\tau)$	standardized autocorrelation function
σ	standard deviation
σ^2	dispersion (variance) of a random variable
τ	time shift
φ	volume fraction
$\chi^2(\nu)$	chi-square distribution with ν degrees of freedom
$\chi^2_P(\nu)$	P % quantile (percentile) of distribution $\chi^2(\nu)$

Indices

g	gross error
corr	corrected value
max	maximum value
n	standard (normal) conditions
proj	project value
T	transposed matrix

-1	inverse matrix
+	measured value

Overlays

^	estimated (reconciled) value
~	real (true) value
‾	sample mean (average)

1 Introduction - rationalization of process plants

Until recently the main and practically only activities considered worthy of a chemical engineer were the research and development of new equipment and processes. This was in tune with the situation when the most common way of development of process plants was to increase their capacity by building new manufacturing units.

Lately, however, stagnant availability of raw materials and energy have led to a shift of development trends towards an improved exploitation of the existing manufacturing units by optimization.

The most frequent projects in this area are:
- economies of raw materials and energy
- structural changes involving intensification of certain processes and suppressing of others
- processing of different raw materials
- improving the product quality
- recovery of wastes.

The approach to the solution of such projects may differ considerably - from a simple optimization of process variables (temperatures, pressures etc.) to cost - intensive reconstructions. The problems encountered by a chemical engineer when dealing with such tasks are markedly different from those arising in the course of designing new plants. The maximum utilization of existing structures requires that their potential has to be known thoroughly. Hence emphasis is brought to the problems of the analysis of the function of existing equipment and systems, based on plant measurements and experimentation with adequate processing of measured data. In this way information is acquired that would otherwise not be available.

The objective of this chapter is to describe the most important rationalization activities, particularly those concerned with plant measurements and experiments.

Among them, the area referred to as "good house-keeping" represents the lowest level. In principle, this is a case of simply maintaining the plant operation in good order. In many plants this is satisfactorily done but sometimes an improvement in this sphere may bring about considerable improvement. The functioning of almost every plant can be improved by proper tuning in the values of the process variables - i.e.

by their optimization. Gains so obtained often are "free" - the improvement can be accomplished without financial investment.

Nowadays a very frequent requirement is to increase the capacity of plants (so-called *debottlenecking*). We can meet this even in companies whose production is stagnating or even declining. It is the result of the tendencies to optimize the production pattern of the whole manufacturing system by suppressing certain units, while, at the same time, increasing the production of others.

The economy of production (profit) is determined by a number of factors, some of which have already been mentioned (values of process variables, production rate). In some plants, more significant savings of raw materials and energy can be attained by changes in the structure of the respective technological system (change in the connections among equipment in separation trains, optimization of the structure of heat - exchanger networks, etc.). We speak about retrofitting, currently representing an important fraction of total investment in process industries.

1.1 GOOD HOUSEKEEPING

Maintaining the operation of a manufacturing plant in good state is the first condition for achieving good economic results. The losses as encountered in the course of plant operation may be either obvious (such as escaping materials or steam into environment) or hidden (poor utilization of heat, low conversions of chemical reactions, etc.). In modern plants which are becoming increasingly complex, it is not an easy matter to identify a malfunction of the system. A condition for maintaining favourable economic parameters of the production over a long period of time is regular *monitoring* of the plant operation (mass and energy balancing, assessing specific consumptions of raw materials and energy, evaluating products quality). A well designed monitoring system must be capable of detecting significant changes taking place in the plant, for example fouling of heat exchangers, deterioration of separation efficiency or a decrease in the activity of catalysts in reactors.

Considerable possibilities of improving plants' efficiency lie in the sphere of control. Nowadays process control computers equipped with advanced control algorithms are being installed routinely in process plants. The quality of information, on which the computer's decision-taking is based, is a critical factor. The function of a costly control system can be completely negated by the malfunction of a single measuring device. The analysis of the measured values from the standpoint of gross and systematic errors is, therefore, very important.

Because of the growing complexity of process plants, it is increasigly more difficult to determine the causes of impaired function of a plant - we speak about *detection* and *identification of abnormal states*. A valuable source of information in this respect may be detailed measurement of the plant combined with a diagnostic evaluation of the measured data (Himmelblau 1978).

Determination of specific consumptions of raw materials and energy is of particular importance when analysing the performance of plants since these variables usually determine the economy of production. The activities in which we have to deal with in this case include, for instance, performance testing of new plants, long-term examination of trends in raw materials and energy consumption, and comparison of different technological regimes.

When assessing specific consumptions, it is important that the measured values should possess the requisite precision. In the case of large-scale plants even slight deviations from the true magnitude of specific consumptions represent large values when taken absolutely. Measurements are subjected to errors and this problem has to be approached from the standpoint of the theory of measurement and of mathematical statistics. It depends on the planning of measurements, its implementation and the processing of measured values, as to whether the acquired information concerning specific consumptions is valuable or not. The same holds also for many real-life situations when the result is a difference between large numbers (for example the profit).

Measuring also plays an important role in introducing *standards (indexes) of raw materials and energy consumption* which are used mostly on higher management levels for evaluating plants performance. This means both the determination of these indexes on the basis of plant measurements and detailed analysis of the process, and the elaboration of methods suitable for long-term monitoring of specific consumption and for the measured data treatment.

In warrantable cases so-called *parametric specific consumption standards* are introduced; these are not constants but they are functions of selected external conditions (ambient temperature, raw materials quality, etc.). Setting up of a parametric consumption standard involves a series of plant measurements carried out with different values for the variables influencing the specific consumptions followed by statistical processing of measured data.

1.2 OPTIMIZING PROCESS VARIABLES

By *optimization of process variables* we usually understand the increasing of profit by reducing the specific consumptions, or improving the products quality, or the like, achieved by modifying the values of process variables. Those variables with which we can influence the value of the parameter we are concerned with, are called *optimization variables*. The dependence of such a parameter on the optimization variables is denoted as *objective function (optimization criterion)*.

When the value of a suitable parameter characterizing the functioning of a given plant (specific consumption of materials and energy, profit, and the like) are plotted against the plant age, we usually obtain a dependence whose shape is similar to the curve in Fig.1.1. The experience shows that, according to the slope of the dependence, three periods can be distinguished differing from each other in the results arrived at when improving the function of the plant.

The first period is that of putting the plant onstream, which takes 0.5 to 1 year on average. This period of the startup is characterized by removing a number of defects that are the result, in most cases, of imperfect design. The plant operation may be interrupted frequently, which brings about an increase in specific consumptions. Other losses are caused by inexperienced operators.

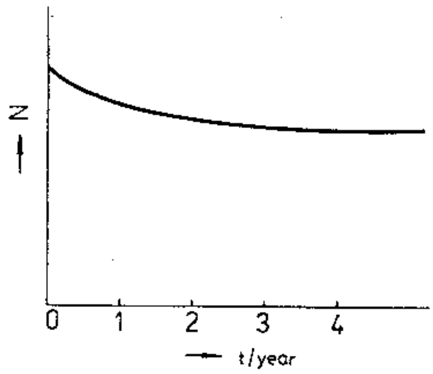


Fig.1.1 — Development of specific production costs *N*

After the startup period there is a period of stabilization that may last several years. During this period the operators are perfecting themselves and methods for the optimum control of plant operation are sought for empirically. The economic indices of production are improved markedly, maximum yields are obtained, etc. Most of the superficial reserves have been found and utilized.

A period of stable plant operation follows after a certain time. This period is the longest one and the rate of plant improvement is declining during this period. The reason is that the empirical methods of improving the functioning of the plant have already utilized most of those reserves that could be identified on the basis of information readily available in the plant.

The problem of disclosing the reserves is illustrated in Fig.1.2. The individual possibilities of improving the functioning (reserves) of a plant are presented on the x-axis in the order of their decreasing effect. The horizontal dashed line represents the usual variability of the examined index (e.g. profit) caused by slight fluctuations in the production conditions (fluctuation in the raw materials quality, imperfect control, seasonal fluctuations, and the like denoted as so-called process noise).

It is obvious that so long as the effect corresponding to a given reserve is below the noise level (reserve 4 and higher in Fig.1.2), the existence of that reserve will pass unnoticed by the operating personnel. The magnitude of the noise can only be decreased by special procedures based on the application of the measurement theory, whereby a potential for achieving further reserves emerges. This is the most significant contribution of the measurement theory to the optimization of chemical plants.

The methods of searching for the optimum process conditions differ in the degree in which the theoretical knowledge concerning the process are applied. The lowest level represent the so-called ***empirical methods of optimization***, when virtually all information is obtained from plant experiments at different values of independent variables.

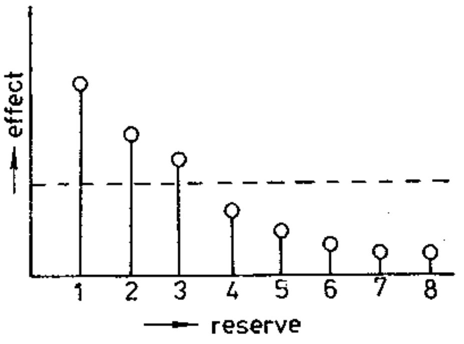


Fig.1.2 — Possibilities of reserves disclosing

In a simple, but very frequent case of optimization, two different technological regimes characterized, for instance, by different values of one process variable, are compared. The more general cases are demonstrated in Fig.1.3. If we consider a single independent variable, the question is to find an extreme (minimum of the specific production costs N) of the objective function of one variable in the interval, the so-called ***permissible region*** (Fig.1.3a). The limits of the interval usually are specified by the requirements for the product quality, by safety regulations, and the like.

Optimization of two variables is shown in Fig.1.3b. The shape of objective function in the permissible region (marked by section lining) is represented by lines of constant value of the objective function.

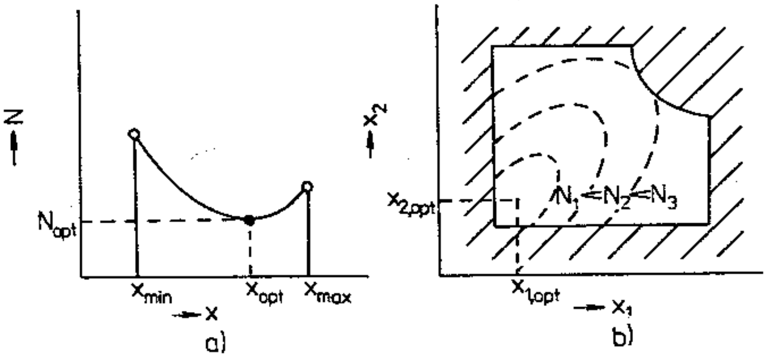


Fig.1.3 — Optimization
a) single-dimensional;
b) two-dimensional

The essence of optimization lies in an approximate determination (mapping) of the objective function in the permissible region in such a way that the values of variables, corresponding to an optimum, can be assessed.

The plans of experiments, whose objective is to determine the influence of the individual variables (*factors*) on the objective function, are similar to those of building empirical mathematical models. Generally speaking, empirical methods of building mathematical models and empirical optimization are closely connected with one another (Himmelblau, 1970).

When planning the experiments for empirical optimization, so-called *orthogonal designs* are used most frequently as these make it possible to find in the optimum way the effects of individual variables on the objective function. The simplest are two-level (so-called 2^n-*orthogonal*) designs, where n (design *dimension*) is the number of independent variables. With these designs the values of independent variables are varied on two levels, so that for the design to be complete 2^n measurements (experiments) are necessary. In the case in which n equals 2 the values of the independent variables lie in the corners of a rectangle, when n equals 3 they lie in the corners of a rectangular parallelepiped (Fig.1.4).

The application of empirical optimization methods in process industries meets with certain difficulties. This is due, for reasons that are both objective and subjective, primarily to the limited possibility of changing the process variables. Changes may be limited by safety limits, or limited ranges of measuring and controlling instruments, or the like. In some cases the source of limitation may be aversion of the personnel to interference in the plant operation.

Sometimes importance may be attributed to the costs of experiments as these can cause a decline of the production rate or a lower quality of the respective product. In order to obtain better information than would be possible in the course of routine operations, more workers may have to be engaged (for data collection, sampling, chemical analyses), which may limit the capacity of the problem solving group. The above factors may set a rigid limit to the number of possible experiments before the research project is started. In other cases the number of experiments may be limited by the time which is necessary to achieve steady state after a change in the process variable.

To identify the effect of a particular variable on the objective function, it is advantageous to use the orthogonal plans. When they are constructed, however, the dependencies among individual factors "interfere". If, for instance, we assume that the rate of conversion of ammonia oxidation by air can be affected by the volume flow rate of gas, oxygen concentration and the amount of ammonia to be oxidized, then the values of only two of these variables can be planned, while the third one follows from the material balance. A similar situation occurs when dependences among factors result from the control (for example one of the variables is a controlling and the other is a controlled variable).

To eliminate some of the drawbacks of the methods of experimental optimization, an *evolutionary optimization* method (EVOP) has been suggested (Hunter & Kittrel 1966).

The philosophy of this method can be expressed by a requirement that a manufacturing process should produce not only a material product but also information about how the process could be improved. The traditional approach to optimization mostly starts from a small number of well prepared experiments. The range of variables is chosen to be as wide as possible, and there is a tendency to execute the measurements more thoroughly than usual in the routine operation. Whereas, the EVOP method requires neither extreme changes of factors nor a detailed examination of the process (this being its greatest advantage). A higher level of noise that necessarily arises with this method, is eliminated by multiple cyclic repetitive experiments.

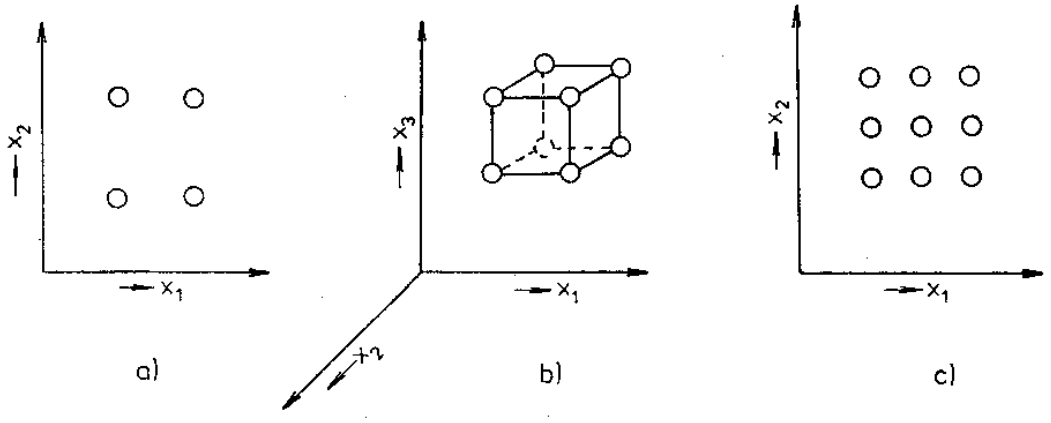


Fig.1.4 — Orthogonal factorial designs
a) two-dimensional two-level; b) three-dimensional two-level; c) two-dimensional three-level

The repetition is made possible by the fact that the method as such does not interfere with the manufacturing process and does not result in increased costs when compared with the routine operation. After an optimum is assessed within the examined region, a new region is selected and the optimization continues.

A certain disadvantage of empirical methods is that they require a considerable number of plant measurements and are comparatively time consuming. The number of plant experiments needed by factor experimental plans increases steeply with the number of variables that have to be considered. Therefore, the application of these methods in optimization of large systems is virtually out of question.

An alternative approach is optimization using a mathematical model based on laws of nature. But even in this case we can not manage without plant measurements and experiments. The number of plant experiments that have to be conducted when identifying the mathematical model is considerably smaller than in the case of empirical optimization. In this way the volume of work that has to be done in a plant can be substantially reduced and thus the time to solve the problem reduced.

Optimization based on mathematical modelling has two stages. The first one is the building of the mathematical model including the objective function to be optimized (for example to maximize profit). The second stage is to search for the extreme (maximum or minimum) of the objective function. Experience shows that the central problem and, in most cases also the bottleneck, is usually the development of the mathematical model representing all important features of the modelled object.

1.3 INCREASING THE PLANT CAPACITY - DEBOTTLENECKING

Nowadays a very frequent requirement is to increase the production on existing or only slightly modified equipment. To solve this problem, a number of questions have to be answered safety of work, wear and tear of equipment, link-up with the environment at increased rate of production, etc. However, in the following section we shall confine ourselves to the role of plant measurement and experiments in the course of debottlenecking.

In principle two types of tasks can be formulated:

- assessing the maximum attainable production rate on the given equipment, and
- finding those conditions, under which it would be possible to attain the desired production rate in the future.

When assessing the maximum attainable production rate it is usual to begin with gradually increasing the rate of raw material input and carrying out detailed measurements on different production rate levels (this method referred to cogently as "more in - more out").

It is necessary to watch carefully selected equipment where troubles can be expected at increased loads (pressure drop in columns, conversion in reactors, and the like). Particular attention needs to be given to the determination of emissions and other losses which are often extremely sensitive to production rate. The same is true as regards the product quality and specific consumptions of raw materials and energy.

The maximum attainable rate of production usually corresponds to such a state when an item of equipment or plant section reaches the limit of its operability (capacity of pumps, exceeding of admissible temperatures in reactors, fall in efficiency in separators, etc.).

The above method of debottlenecking is the most common but, in reality, the maximum production rate is not necessarily achieved in this way. Especially in the case of more complex plants the maximum attainable production can be influenced by optimally controlling the manufacturing process.

A situation where the behaviour of a plant can be influenced by the rates of raw materials input and of recycling is demonstrated in Fig.1.5. In this case the production rate is directly proportional to the feed rate of raw material. An admissible region exists in the production - recycle coordinates, within which these two variables can be varied independently (in Fig.1.5 represented by hatching). In addition, lines of constant specific costs of production are plotted within the admissible region.

The normal operating regime of the plant at 100 per cent production rate is represented by point *A*. On condition that the rate of recycling would be constant while increasing the production rate, the maximum attainable production would be given by the coordinate of point *C*. If, however, we operate at a lower rate of recycling (point *D*), even higher production rate can be reached.

Also important is the question of economy which, in our case, is represented by the lines of constant specific costs. For each level of production rate there exists a certain value of recycling rate at which the specific costs are minimum. The connecting line of the points of minimum specific costs is represented in Fig.1.5 as the dashed line. This knowledge enables the production to be increased in such a way that up to the production rate corresponding to point *B* the rate of recycling is adjusted so as to correspond to the minimum specific costs.

Thus we have formulated the problem of intensifying the production rate as one of optimization (i.e. finding the optimum process regime for each production level). The task of plant measurements and experiments in solving this more complex problem consists in finding a mathematical model representing plant behaviour at different levels of production rate.

The second task of debottlenecking, that is to find conditions under which a required production rate could be achieved (provided that this rate is too high to be attained on the existing equipment), is one of the most intricate problems a chemical engineer can be confronted with. In most cases he must supply underlying data for designing new additional equipment, replacing existing items of equipment by more efficient ones, and the like.

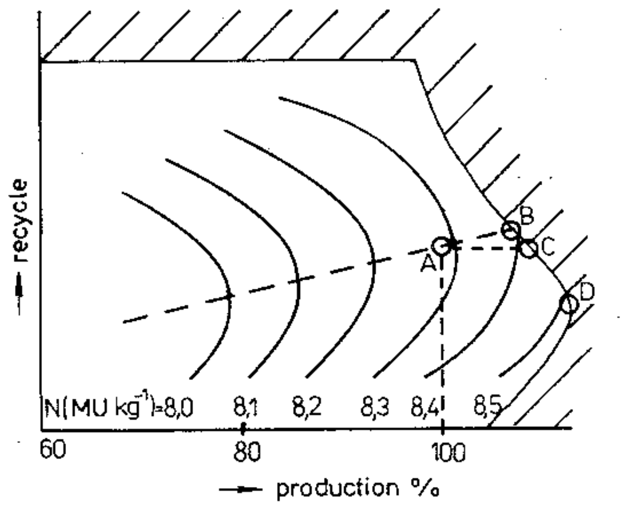


Fig.1.5 — Raising plant capacity (specific production costs *N* in money units per kg of product)

The fundamental term in the traditional approach to this problem is so-called *bottleneck of a plant*. There is usually some imbalance among the capacities of individual equipment items in a production train, for a number of reasons. The imbalance can be expressed with the aid of the capacity profile of the train, that is by expressing the capacities of individual equipment items by the same unit of measure (final production, raw material consumed, etc.). The equipment item having the lowest capacity is the bottleneck. The debottlenecking is solved either by replacing the bottleneck by more efficient equipment item or by attaching additional equipment in parallel. At the same time, it is necessary to answer the question whether, if the bottleneck were removed, another equipment item would not become a new bottleneck before the required production rate is reached.

When solving this problem, we are using plant measurements and experiments to obtain the underlying data for chemical engineering calculations for the individual equipment. In some cases, using intermediate storage tanks, we can analyze the function of equipment at throughputs higher than those corresponding to the capacity of the bottleneck.

In spite of the fact that the "bottleneck" concept may be useful in some cases, stated generally, in modern complex plants it is losing its significance.

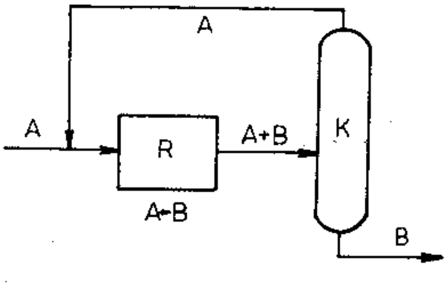


Fig.1.6 — Simple plant with recycle
R - reactor; K - distillation column

A diagram of a simple plant consisting of a reactor and a distillation column, separating the unreacted raw material from product and recycling it back to the reactor, is demonstrated in Fig.1.6. The conversion in the reactor decreases with decreasing the mean residence time of liquid in the reactor; the column load increases with increasing ratio of the unreacted component in the column feed and, at the same time, the separating efficiency of the column declines. The production rate in the above system is limited as a result of an increase in the concentration of unreacted component in the product as the feed rate to the reactor increases.

The plant capacity limitation is caused, on the one hand, by the low conversion in the reactor, and, on the other hand, by a low separating capacity of the column at higher loads. It is, therefore, not posible to state which equipment is responsible for limited production rate (the bottleneck). An increase in the plant capacity can be attained either by scaling up the reactor (resulting in high conversion even at high load, thus "relieving" the column), or by installing a new column capable of separating an increased amount of the unreacted component.

The above conception of debottlenecking is useful not only for plants with recycling but also for some linearly arranged plants as well. If, for instance, refining of a product proceeds in several steps, it is usually difficult to determine which particular step is insufficient in capacity.

In the presented examples, raising the plant capacity is based on introducing such modifications in a plant, which will ensure that the required production rate is attained. The question of which equipment is to be intensified is transferred to the region of production economy - we try to find a solution that would be the most advantageous economically. In most cases the problem formulated in this way cannot be solved without mathematical modelling (setting up material and enthalpy balances of individual equipment items under new conditions brought about by intensification, and the like).

The importance of plant measurements and experiments lies in assessing the capacity potentials and in identifying the parameters of mathematical models of individual equipment items. The methods based only on chemical engineering calculations often fail because of inaccuracies of chemical engineering correlations (in some cases errors may come up to tens of per cent of the calculated value). It is often possible in a plant to measure the maximum capacity of the equipment directly and thus to reduce investment costs of the debottlenecking to the minimum.

1.4 PROCESS RETROFITTING (REVAMPING)

Douglas (1988) defines retrofitting (sometimes termed revamping) as

1. minor changes in the inteconnections between process equipment;
2. replacement of one or more pieces of equipment by some other equipment;
3. change in the size of one or more pieces of equipment in an existing process.

Nowadays retrofitting represents an important method of plant improvement. It has been reported that in 1984 more than a half of investments in the U.K. chemical industry was directed to retrofitting of existing plants (Atkinson 1987). During recent years particular emphasis has been laid on reducing energy consumption. According to one estimate about 60% of the supplied energy in a typical refinery leaves the system in the form of heated water and air. These losses, however, are not inevitable, and they can be reduced by several tens of per cent. An important way to a better use of energy is optimization of the utilization of heat and other kinds of energy.

Particularly successful has been the application of "pinch" technology (Tjoe & Linnhoff 1986). Originally this method was developed for analyzing and optimizing heat exchange systems. In course of time pinch technology has been extended to further areas (the use of heat engines and pumps, separation systems).

The problems of optimizing the structure of separation systems represents another important field. Special attention has been given to systems of distillation columns. Distillation has been well mastered from the chemical engineering standpoint; it is the most widely used separation method and it is considerably energy intensive.

In principle, measurement plays an important role in two phases of retrofitting. During the initial stage of problem solving, measurement supplies the information about the flows of mass and energy, on which any analysis has to be based. Nowadays, when commercial programs for the analysis and synthesis of process systems are available, obtaining reliable data often represents the bottleneck in the preparation of the retrofit. It is a time consuming pursuit since frequently several process regimes under which plant operates have to be measured.

During the final stage, when the possibility of repositioning available equipment in the plant is considered, the checking and simulating of the individual equipment items are of importance. It is an advantage if the respective mathematical models can be verified using plant measurements.

2 Measurement in process industries

The following chapter is devoted to some problems that are characteristic of measuring in process industries.

There is no doubt about the importance of problems of measuring errors. Errors encountered during the measuring in process industries differ in their character from errors of measurement in other branches of science and technology. In view of their importance, the various aspects of errors will be dealt with separately in Chapter 3.

In addition, it is characteristic of the data measured in process plants that they often have to satisfy exactly valid mathematical relations expressing most frequently the laws of conservation (of mass, energy, etc.). This fact has a marked effect on the methods of data processing.

Further attributes of technological processes affecting the gathering and processing of data are the system character of process plants and variation with time (fluctuation) of the values of process variables.

Successful measurement in process plants depends not only on mastering the theory but also on solving of a number of technical problems. It is hardly possible to enumerate all the stumbling blocks that may be met when carrying out the measuring in process plants. The methods of the plant measurement proper are, therefore, discussed in the concluding part of this chapter.

2.1 BASIC CONCEPTS

Let us consider a process plant comprising several interconnected apparatuses. The state of such a system at a certain instant of time can be characterized by a set of values of the *state variables* (temperatures and pressures in the individual apparatuses, accumulation in storage tanks, composition of streams, and the like). From the standpoint of gathering information on the functioning of such a system several types of tasks may be formulated.

The basic task is to find out the performance of the plant at the given values of selected state variables. The extent of the required information may differ from case to case.

For example, it may be the case of setting up the mass balance on the basis of measurement, measuring of emissions from the plant, or there may be a demand for more detailed information, often stemming from a certain model conception of the plant function (e.g. the determination of heat transfer coefficients, plate efficiency of the distillation column, or the flow pattern of phases in selected apparatuses). Those quantities which are to be assessed by such a measurement are referred to as target quantities of the measurement.

Thus formulated task is referred to as *identification of a plant*. We might compare it to photographic documentation of the essential characteristics of the plant under conditions set beforehand.

This fundamental task is usually a part of more complex types of problems which were mentioned in the preceding chapter (optimization of the values of process variables, debottlenecking, and the like). It is important that these more complex problems can be broken down into a number of plant measurements carried out at the values of state variables that have been planned in advance.

The concept "plant identification" is always to be understood in connection with the objective stimulated before the measurement proper. For example a plant measurement aimed at assessing specific consumptions of energy will differ from that whose objective is to evaluate the possibilities for increasing the plant capacity.

When conducting the identification of a process plant we use, in principle, three kinds of information. Firstly the prior knowledge which can be called *theory of measured object*. Such information often can be expressed in the form of equations and inequalities of a *mathematical model* (balance and definition equations, calibration relations of measuring instruments, and the like). Usually, also, such prior information includes the constants exactly known beforehand (physical and mathematical constants, exactly known properties of substances, and the like).

The second source of information are the values of *directly measured* (so-called *primary*) quantities as obtained on the basis of direct measurement. These values almost always are subject to measurement errors and, therefore, in the course of their processing we make use of the third group of information, i.e. of conceptions of the measurement errors character and magnitude; what is meant is the so-called *model of measurement errors*. The mathematical model and the model of errors together form the *stochastic model* of the measured plant.

The quantities appearing in the problem can be divided in accordance with several standpoints. They may be measured directly or not and, accordingly, are divided to *directly measured quantities* and those *directly unmeasured*. The unmeasured quantities can be further divided into *observable quantities*, i.e. those which can be assessed from directly measured quantities by solving the equations of the mathematical model, contrary to *unobservable quantities*, which cannot be assessed. The observable unmeasured quantities sometimes are designated as *quantities measured indirectly* (so-called *inferential measurement*).

Unmeasured quantities may be of different nature. In some cases this is a question of *measurable* quantities (temperature, composition, and the like) whose measurement, however, has not been carried out for some reason. In other cases it is a matter of such quantities whose direct measurement is simply impossible. For example the rate of a certain chemical reaction can be found out only indirectly from the rate of changes of directly measurable quantities - concentrations. In certain circumstances the quantities may have the character of constants of mathematical models, e.g. activation energy of chemical reactions, mass transfer coefficients, or effective interfacial area in mass transfer apparatus.

Example 2.1: *Identification of a distillation column*

Fig.2.1 shows the diagram of a simple distillation column with installed measuring instruments. In addition to the directly measured flow rates of feed and bottom product we have here also the directly unmeasured flow rate of the distillate. This flow rate, however, can be calculated from the mass balance around the column. But, in principle, it could be measured (by installing another flowmeter) - hence this quantity is unmeasured but it is measurable and observable.

Somewhat different is the situation as regards the flow of vapour at a certain cross-section of the column. It is hardly possible to suggest a way to measure this

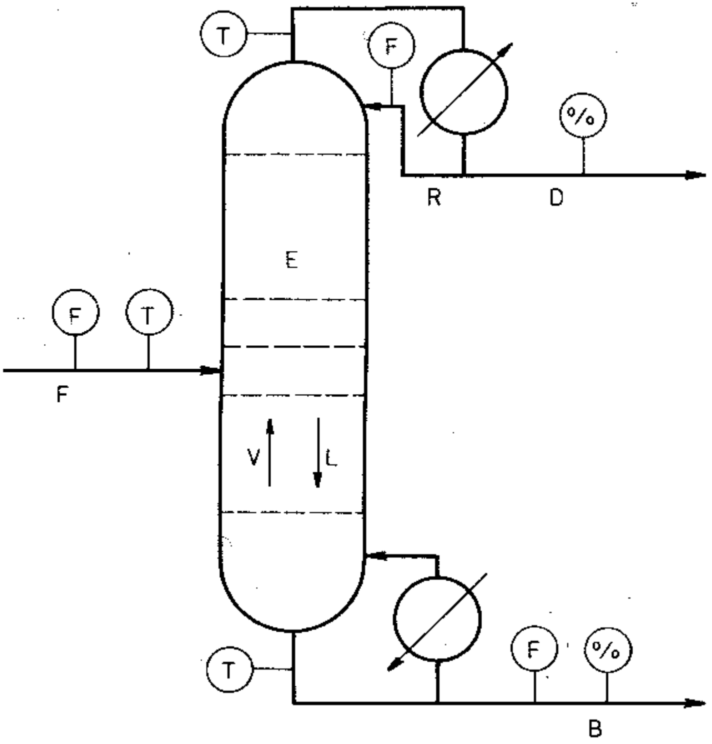


Fig.2.1 — Measurement of a distillation column

quantity directly in practice. The vapour flow, however, can be calculated, at least approximately, by solving the equations of the mathematical model of the column. In addition to the mass balance such a model would also have to incorporate the enthalpy balance and mass transfer on the column plates. Hence the vapour flow inside the column is directly unmeasurable but observable.

Somewhat diferent is the case of the next quantity - the distillation plate efficiency *E*. Unlike the vapour flow, that quantity actually does not exist. It is just a parameter of a mathematical model and cannot be measured directly. However, the efficiency can be assessed by processing the data obtained from measurements on the given column. It is, therefore, the quantity that is not measured directly but observable. But one has to realize that quite a number of distillation plate models have been defined with differently defined efficiencies. Thus the value of efficiency as assessed from the measured data is influenced by the choice of the mathematical model and by the definition of the efficiency proper.■

2.2 BUILDING OF MATHEMATICAL MODELS

By mathematical modelling we understand the expressing of the basic properties of a real object by means of a mathematical model. The mathematical model itself may be apprehended as a system of hypotheses (expressed most frequently in the form of equations and inequalities) among variables describing the modelled object. Mathematical modelling is not an end in itself but usually it is a part of the solution of a number of tasks (optimization, debottlenecking, process control and others).

2.2.1 Basic concepts

The building of a mathematical model comprises three fundamental phases. The first, preparatory phase, involves a preliminary formulation of hypotheses on the basis of previous experience with the object to be modelled, search of literature, chemical engineering calculations, and so on. At the end of this preparatory phase one or more model variants are available, representing the relations among the directly measurable quantities (temperatures, pressures, concentrations, etc.) and those quantities which cannot be measured directly. For these latter quantities the term *parameters of mathematical model* has become common; typical examples here are the coefficients of heat and mass transfer, equilibrium constants of chemical reactions, and the like. In most cases, however, this preliminary information is not sufficient for a complete solution of a given problem.

During the second phase values of directly measured quantities are collected. It may be a case of records of previous plant operation under standard regimes, or an active approach when the process is controlled so, that the maximum of information necessary for mathematical modelling can be obtained. In this case we speak about *plant experiments.*

The final phase is the statistical processing of measured data whereby the values of the mathematical model parameters are obtained. Sometimes this phase is referred to as *identification of a mathematical model.* The process of finding values of model parameters is called estimation and the values of parameters are called *estimates.*

The obtained mathematical model can be used for calculating the output quantities on the basis of pre-set (input) quantities. Then we speak about simulation of the behaviour of a real object by means of a mathematical model.

The agreement between the results of mathematical modelling and behaviour of a real object depends on the extent to which the suggested mathematical model describes the reality adequately. Part of the processing of measured data must be an evaluation of the suitability of a proposed mathematical model for a particular problem. Unless the requisite agreement between the model and reality is reached, it is necessary to go back to the first phase of mathematical modelling and modify the original modelling concepts. Sometimes it may happen that the data, on whose basis the model was identified, are not sufficient. In such a case additional measurements must be carried out in order to supplement the missing information.

The adequacy of a mathematical model is not to be understood in absolute terms but only in consideration of the objective of the modelling. It is, therefore, necessary always to define the region of values of variables that is concerned and to specify further conditions to be met if the model is to be valid. The demands made on a model (adequacy, mathematical simplicity, etc.) are the reason why the above sequence of the three phases of mathematical modelling cannot be understood to be a simple process. Confronting the results of mathematical modelling with reality mostly results in the necessity of going back to the individual phases of the modelling. In most cases, only when such an iterative procedure is adopted, will it be possible to arrive at a really useful mathematical model.

2.2.2 Classification of mathematical models

Mathematical models may be classified in accordance with a number of aspects. For our purposes it is useful to classify the models with respect to the extent in which findings of natural and engineering sciences are utilized when building the mathematical model. In this respect there exist two opposite poles.

On the one hand, there are models based exclusively on statistical evaluation of measured data. Such models are referred to as *empirical* or *regression* (the most common case being the expression of the dependence among variables by polynomial function). When building these models we do not use any prior information that would follow from physical or chemical attributes of the modelled object.

The other extreme is represented by models based on the use of laws of nature only. Sometimes these models are denoted as *mechanistic models* since a certain mechanism is assumed, according to which the changes in the modelled object proceed. In the extreme case it is possible, at least symbolically, to describe the modelled object by a system of equations expressing the laws of nature holding true under the given conditions (fundamental equations of hydrodynamics, of heat transfer, and the like).

The above two extreme cases, however, have a number of drawbacks. The empirical models require a considerable amount of measured data, and their extrapolation beyond the measured region is rather debatable. On the other hand, the purely mechanistic models depend on the values of constants that may not always be available a priori. Also, for most practical problems these models are unduly complicated and their mathematical solution is difficult. Therefore, the most frequently used models are those combining purposefully both the above approaches.

2.2.3 Empirical models

The building of empirical models has been given considerable attention in the literature from the viewpoints of measurement planning, processing of measured data (assessing the parameters of empirical equations), as well as of further applicability of models, particularly for optimization.

When selecting the model equations, the following requirements should be satisfied:
- mathematically simple form
- minimum number of parameters (constants)
- good agreement between the model and the modelled object behaviour.

The most common mathematical form of an empirical model is the dependence of a group of *dependent variables* on other variables (*independent variables*) by means of a polynomial. For a single dependent variable (y) and a single independent variable (x) the mathematical model has the following form:

$$y = a_0 + a_1 x + a_2 x^2 + \dots + a_n x^n = \sum_{i=0}^{n} a_i x^i \tag{2.1}$$

where a_i are the model parameters and n is the model order (equal to the highest exponent of the dependent variable in the power series).

The form of a first order model for m independent variables ($x_1, x_2, \dots, x_m$) is

$$y = b_0 + \sum_{i=1}^{m} b_i x_i \tag{2.2}$$

The quantity m is so-called dimension of the model.

A second-order model of dimension m is

$$y = b_0 + \sum_{i=1}^{m} b_i x_i + \sum_{j=1}^{m} \sum_{i=j}^{m} b_{ij} x_i x_j \qquad i \geq j \tag{2.3}$$

Empirical models in the polynomial form can describe any complex relation - in some cases, however, at the cost of an inadequate increase of the model order, and thus also at the cost of an increase in the number of model parameters. In practice we try to manage with polynomials of the lowest possible order. The reasons for this are numerical difficulties encountered when identifying the parameters of polynomials of higher order from measured data. Furthermore, in polynomials whose order is higher than necessary, the conditions for smoothing the data become worse.

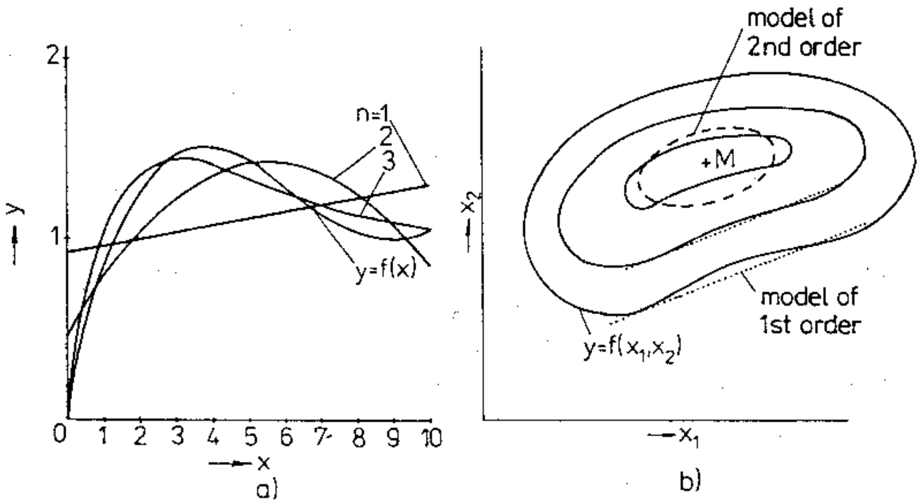


Fig.2.2 — Empirical mathematical models
a) single-dimensional 1; b) two-dimensional

An example of modelling the real dependence $y = 1 - (1 - x) \exp(-0.5x)$ by polynomials of the first to 3rd order [Eq.(2.1)] is presented in Fig.2.2a. In Fig.2.2b are demonstrated the possibilities of modelling the real dependence of a variable y on two independent variables x_1 and x_2. The function $y = f(x_1, x_2)$ represented by contour lines, i.e. lines of a constant value of the function $f(x_1, x_2)$, exhibits a maximum (point M). In the region distant from the maximum, the course of the dependence $y = f(x_1, x_2)$ can be modelled with the aid of the linear model (2.2) of dimension 2. In the proximity to a maximum (or minimum, as the case may be), however, the 1st order model is entirely unsuitable, and the 2nd order model has to be used. The shapes of the contour lines that can be expressed by the 1st and 2nd order models are demonstrated in Fig.2.3.

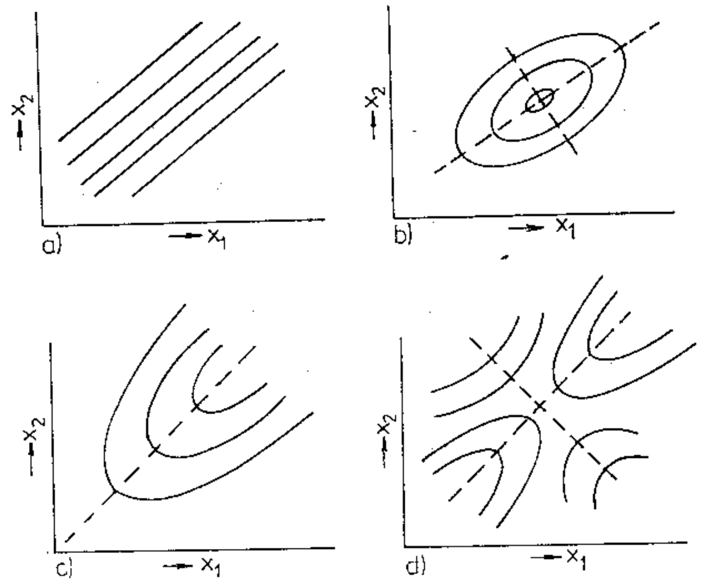


Fig.2.3 — Contour lines of polynomials of 2nd degree a) model of 1st order; b) - d) models of 2nd order

2.2.4 Models based on laws of nature

Building of mechanistic models usually is more complicated than it is in the case of empirical models. The information we start from when building mechanistic models can be divided into two groups.

The laws of conservation (of mass, energy and, provided that certain presumptions are met, of other quantities as well) belong to the first group. In most cases these laws are valid strictly and we can often use them when verifying the validity of other assumptions serving as the basis for our modelling.

In the second group are the other laws of nature, dependences assessed empirically, and the like. The validity of this type of information is not the same as that of the laws of conservation; they have rather the character of hypotheses that actually hold more or less perfectly. Typical examples are the models of chemical and phase equilibria, models of the kinetics and stoichiometry of chemical reactions, chemical engineering correlations, etc.

When compared with the applications of mathematical modelling in other branches of science and technology, the conservation laws expressed in the form of mass and energy balances are of considerable importance in building mathematical models in process industries.

Conservation laws - macroscopic balances

The diagram of the system adopted in setting up balance equations is shown in Fig.2.4.

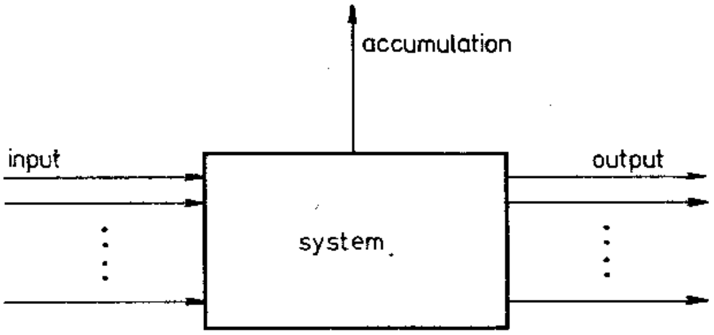


Fig.2.4 — Balanced system

The balance of any quantity over an integral period of time can be written in words:

input - output + source - consumption - accumulation = 0 (2.4)

Further, let the output be taken as negative input, consumption as negative source, and accumulation as fictitious output. Eq.(2.4) then becomes

input + source = 0 (2.5)

Generally, in the balance equation (2.5) appear the integrals of balanced quantities in time. However, the equation may also be written in terms of velocities. It may be a case of a steady-state system or it is possible to define in an appropriate way the mean integral velocities within the given time interval. Further, we shall consider steady-state systems and introduce the following notation:

m_k	mass flow rate in stream k (positive at the inlet, negative at the outlet)
n_k	substance flow rate (in moles)
x_{ki}	mole fraction of ith substance in kth stream
w_{ki}	mass fraction of ith substance in kth stream
n_{ki}	flow rate of ith substance in kth stream ($n_{ki} = n_k x_{ki}$)
m_{ki}	mass flow rate of ith substance in kth stream ($m_{ki} = m_k w_{ki}$)
H_k	flow rate of enthalpy of kth stream
h_k	specific enthalpy as related to mass ($H_k = m_k h_k$)

In practice we meet with applications of laws of conservation of mass, energy and, less frequently, of momentum. The character of these laws is absolute and the equations expressing them hold exactly. The class of models with exact validity may include also balances of those parts of molecules which are not subject to changes in a given process (atoms or stable groups of atoms) in cases concerning chemical systems with clear stoichiometry.

The law of conservation holds for the total mass and Eq.(2.5) has the following form:

$$\sum_k m_k = 0 \tag{2.6}$$

As regards the mass of individual substances, however, the law of conservation does not hold in general and the source term has to be expressed in the balance equation. Let us assume that in a system of I substances s_1 , ... , s_I J chemical reactions are taking place

$$\sum_i A_{ji}\, s_i = 0 \qquad j = 1, \dots , J \tag{2.7}$$

where A_{ji} is the stoichiometric coefficient of ith substance in jth stoichiometric equation (it holds for the products $A_{ji} < 0$).

The system of equations (2.7) can be written in the matrix form

$$\boldsymbol{A}\, \boldsymbol{s} = 0 \tag{2.8}$$

where $\boldsymbol{A}$ is the matrix of stoichiometric coefficients (A_{ji})
$\boldsymbol{s}$ is the vector of substances (s_i).

The balance equation (2.5) for individual substances then becomes

$$\sum_k n_{ki} - \sum_j A_{ji}\, r_j = 0 \tag{2.9}$$

where r_j is the rate of jth reaction; or alternatively, in the matrix form

$$\boldsymbol{N}^T\, \boldsymbol{1} - \boldsymbol{A}^T\, \boldsymbol{r} = 0 \tag{2.10}$$

where $\boldsymbol{N}$ is the matrix of flow rates of substances (n_{ki})
$\boldsymbol{1}$ is the unit column vector.

Now let us assume that the substances are composed of chemical elements E_1 , ... , E_Z . The elemental composition of ith substance is expressed by a formula

$$(E_1)_{e_{i1}} \dots (E_z)_{e_{iz}} \dots (E_Z)_{e_{iZ}} \tag{2.11}$$

where e_{iz} is the number of atoms of zth element in the molecule of ith substance. The numbers e_{iz} form the so-called atom matrix $\boldsymbol{E}$. Let us consider further that for each correctly written stoichiometric equation the law of chemical elements conservation must hold true

$$\sum_i e_{iz}\, A_{ji} = 0 \qquad z = 1, \dots , Z \tag{2.12}$$

or, in the matrix form

$$\boldsymbol{E}^T \boldsymbol{A}^T = 0 \tag{2.13}$$

Now, if Eq.(2.10) is multiplied by the matrix $\boldsymbol{E}^T$ from the left hand side, and, considering Eq.(2.13), we obtain

$$\boldsymbol{E}^T \boldsymbol{N}^T \boldsymbol{1} = 0 \tag{2.14}$$

We have thus obtained a different type of balance equation - an equation expressing the conservation of chemical elements in a balanced system. It is now necessary to raise the question about the difference between the balance equations (2.10) and (2.14).

Considering our knowledge about a given system it is obvious that working with the model (2.14) will be simpler since the information on elementary composition of substances is usually more readily available than the knowledge of all the chemical reactions taking place in the system. On the other hand, scarcity of information as used in the building of a mathematical model will manifest itself outwardly by the decrease in the number of equations of the model. The number of chemical elements occurring in the problem is frequently smaller than the number of balanced substances (take, for instance, complex mixtures of organic substances composed of a few chemical elements). Looking at Eq.(2.10) we can see that in the case when no reactions proceed in a system, the mathematical model consists of I independent equations, whereas the model (2.14) consists of only Z equations ($Z < I$). It can be proved that the two models are equivalent only in the particular case when the system of equations (2.7) contains the maximum number of independent equations that can be written in the given system (Schneider & Reklaitis 1975).

Example 2.2: *The balance model of fermentation*
Let us consider the process for the manufacture of biomass (yeast) from ethanol.

Starting materials:

1 - ethanol (elemental formula C_2H_6O),
2 - oxygen (O_2),
3 - ammonia (NH_3),
4 - mineral nutrients represented by a fictitious element Ah with relative atomic mass 1.

Products:

5 - biomass, empirical formula $C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00}$, where Ah stands for the mineral component of the biomass,

6 - acetic acid - an undesirable by-product ($C_2H_4O_2$),
7 - carbon dioxide (CO_2),
8 - water (H_2O)

The above eight substances consist of five elements, C(1), H(2), O(3), N(4), and Ah(5). The atom matrix $\boldsymbol{E}$ is shown in Table 2.1. It has the dimension of (5 x 8) and the full rank, i.e. rank($\boldsymbol{E}$) = 5. Hence, there exist only (8 - 5) = 3 linearly independent stoichiometric equations in the given system. Such a system is, for instance:

Table 2.1 — Atom matrix (Example 2.2)

substance		element				
		C	H	O	N	Ah
ethanol	(1)	2	6	1	0	0
oxygen	(2)	0	0	2	0	0
ammonia	(3)	0	3	0	1	0
mineral nutrients	(4)	0	0	0	0	1
biomass	(5)	3.83	7.00	1.94	0.64	7.00
acetic acid	(6)	2	4	2	0	0
carbon dioxide	(7)	1	0	2	0	0
water	(8)	0	2	1	0	0

1. synthesis of biomass

$$1.917\ C_2H_5OH + 1.618\ O_2 + 0.643\ NH_3 + 7\ Ah\ -$$

$$-\ C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00} - 3.214\ H_2O = 0 \tag{2.15a}$$

2. oxidation of ethanol to CO_2 (it is supposed that this reaction supplies energy for the reaction 1.)

$$C_2H_5OH + 3\ O_2 - 2\ CO_2 - 3\ H_2O = 0 \tag{2.15b}$$

3. formation of acetic acid

$$C_2H_5OH + O_2 - CH_3COOH - H_2O = 0 \tag{2.15c}$$

Any additional equation we should write would necessarily be linearly dependent on the above three equations. For instance the oxidation of acetic acid to CO_2

$$CH_3COOH + 2\ O_2 - 2\ CO_2 - 2\ H_2O = 0$$

can be expressed as the difference of equations (2.15b) and (2.15c). The matrix of stoichiometric coefficients ***A*** is presented in Tab.2.2.

Table 2.2 — Matrix of stoichiometric coefficients (2.15)

Reaction	Substance							
	ethanol	O_2	NH_3	Ah	biomass	acetic acid	CO_2	H_2O
(1)	1.917	1.618	0.646	7	-1	0	0	-3.214
(2)	1	3	0	0	0	0	-2	-3
(3)	1	1	0	0	0	-1	0	-1

The mathematical model of the biomass formation stoichiometry has the form of equations (2.10) or (2.14) where data from Table 2.1 and 2.2 are substituted for the matrices ***E*** and ***A***. Since the system (2.15) is the maximum system of linearly independent equations in the given set of substances, both the models are equivalent. In both cases at least three quantities n_i have to be measured, so that the remaining ones could be calculated from the equations of the mathematical model.

All the equations presented in this section are written by means of the quantities $n_{k\,i}$. The advantage of this lies in that the equations of the mathematical model are linear. Besides, here we could use for convenience a simple notation of the stoichiometry of chemical changes in this system of quantities.

It would not pose any problem to rewrite the equations in the system of mass flows, using the substitution $n_{k\,i} = m_{k\,i} / M_i$. More frequently, however, we need to rewrite the equations by means of mole or mass fractions. Unlike the previous quantities, these can be measured directly and also they appear in a number of physical chemistry relations. Here, too, the substitution $n_{k\,i} = n_k\, x_{k\,i}$ or $m_{k\,i} = m_k\, w_{k\,i}$ can be made. In these cases, however, the system of balance equations must be supplemented by additional relations

$$\sum_i x_{k\,i} = 1 \qquad k = 1, 2, \dots, K \tag{2.16a}$$

$$\sum_i w_{k\,i} = 1 \qquad k = 1, 2, \dots, K \tag{2.16b}$$

Balance of energy

Till now we have assumed that the streams in Fig.2.4, connected with the balanced system, represent streams of mass. For the purpose of balancing energy we have to consider also the heat and work supplied to the system. Formally this can be done in such a way that each of the streams is characterized by the following vector of stream parameters:

$$(m_k\ , w_{k\,1}\ , \ldots\ , w_{k\,J}\ , H_k\ , Q_k\ , W_k\ ) \tag{2.17}$$

where Q is the flow of heat and W flow of work, both positive if entering the system. The streams of mass have Q and W equal to zero, while the streams of heat and work have all parameters equal to zero with the exception of Q or W.

The conservation law (2.5) for energy holds in the following form

$$\sum_k (U_k + P_k V_k + E_{\text{pot}\,,\,k} + E_{\text{kin}\,,\,k} + Q_k + W_k\ ) = 0 \tag{2.18}$$

where U_k is the internal energy of the stream k, $E_{\text{pot}\,,\,k}$ is potential energy, $E_{\text{kin}\,,\,k}$ is kinetic energy.

We have neglected the other kinds of energy. When pressure energy (equal to the product PV) is merged with internal energy, we obtain the usual form using the concept of enthalpy $H = U + PV$

$$\sum_k (H_k + E_{\text{pot}\,,\,k} + E_{\text{kin}\,,\,k} + Q_k + W_k\ ) = 0 \tag{2.19}$$

After neglecting the kinetic and potential energies Eq.(2.19) is simplified to so-called balance of enthalpy

$$\sum_k (H_k + Q_k + W_k\ ) = 0 \tag{2.20}$$

In certain cases assessing the enthalpies of the streams H_k may pose a problem. The situation is simple only if a single substance occurs in the system (e.g. water in a power station system). The choice of a standard state to which enthalpy is related is arbitrary and it only remains to find the dependence of the enthalpy on temperature and pressure.

In systems with more substances there is one more problem - enthalpy of mixing - which can be neglected only in the case of ideal solutions. The most complicated situation is encountered with systems in which chemical reactions are taking place. In such a case it is not possible to select a zero level of enthalpy for all the substances present in the system but only for some subset. The number of elements of such subset is determined by stoichiometry of the chemical transformation. These special problems are dealt with in detail by Veverka & Madron (1981).

Further types of models

Balance equations represent the simplest kind of mathematical models. They are based on the laws of conservation and their validity is absolute. If they happen to be in contradiction with reality, it is not caused by invalidity of the conservation laws but it is rather a case of wrong assumptions on which the balancing has been based (for instance an escaping stream was not considered, the stoichiometry of a chemical reaction is more complex than assumed, etc.).

Balance models form the basis for more complicated models, which bring into the problem new information about the modelled process. In most cases this is a question of the principles of physical and chemical equilibria and of kinetic models of the course of chemical processes.

Equilibrium is a hypothetical state that would be established in an insulated system after an infinitely long period of time, or, in the case of a flow-through system, after infinitely long time of contact among the streams occurring in the system. In practice, however, a fairly close approach to an equilibrium can be assumed in a number of technically important cases. Equilibrium models also play a role when modelling nonequilibrium processes, too, since the driving force of those processes usually is expressed as a deviation from the equilibrium state.

As regards phase equilibria, we most frequently meet with the equilibrium in single-component two phase systems. In the former case there exists only one degree of freedom and the respective mathematical model is given by a relation between pressure and temperature

$$p = f(T) \tag{2.21}$$

In multicomponent systems each additional component means one additional degree of freedom. For an I-component mixture and the two-phase system the equilibrium at a given temperature is expressed by equations for pressure and for $I - 1$ equilibrium coefficients K_i

$$p = f(T, x) \tag{2.22}$$

$$y_i = K_i\, x_i \tag{2.23}$$

where y_i and x_i are mole fractions of ith substance in both phases at an equilibrium. The distribution coefficients K_i , generally, are function of temperature, pressure, and composition.

In a system with a single chemical reaction (2.7) the equilibrium can be expressed with the aid of the equilibrium constant of the reaction K_a .

$$K_a^{-1} = a_1^{A_1}\ a_2^{A_2}\ \dots\ a_n^{A_n} \tag{2.24}$$

where a_i is activity of ith component and A_i is stoichiometric coefficient in the equation. The equilibrium constant K_a is a function of the Gibbs free energy of the reaction, temperature, and pressure. Equilibrium in a system, in which more reactions are taking place, can be defined by analogy.

The most common form of expressing the rate of a process, in which exchange of momentum, heat and mass between two phases is taking place, is

$$rate = surface\ area \times coefficient \times driving\ force \tag{2.25}$$

In the case of heat and mass transfer we speak of heat and mass transfer coefficients. In the case of heat transfer the difference in temperatures in the bulk of the two phases is the driving force. With mass transfer, the driving force is expressed as the difference in the concentration of the substance in the bulk of one phase minus the equilibrium concentration which corresponds to the concentration of that component in the bulk of the second phase.

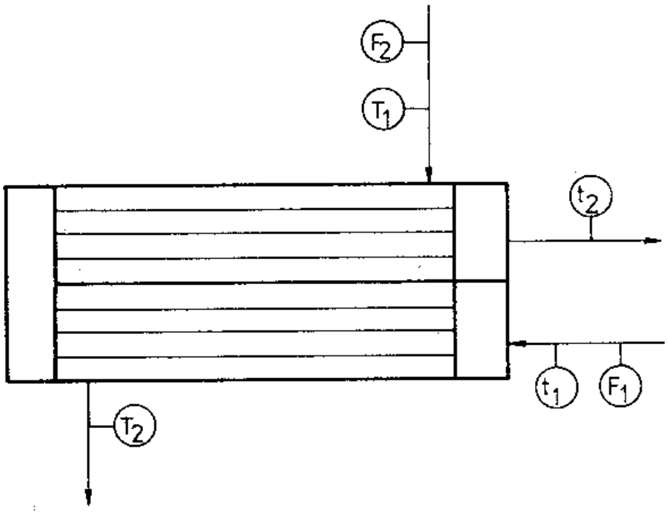


Fig.2.5 — Heat exchanger

Example 2.3: *Mathematical model of a heat exchanger*

In Fig.2.5 is presented the shell-and-tube heat exchanger with a single pass in the shell side and double pass in tubes. The equations of a simple mathematical model describing the behaviour of this exchanger are as follows:

Heat balance of the hot stream

$$Q = F_2\, c_{P2}\, (T_1 - T_2) \tag{2.26}$$

Heat balance of the cold stream

$$Q = F_1 \, c_{P1} \, (t_2 - t_1) \tag{2.27}$$

Definition equation of heat transfer

$$Q = K \, A \, \varepsilon \, \Delta t_{\mathrm{lm}} \tag{2.28}$$

Definition equation of the mean logarithmic temperature difference Δt_{lm}

$$\Delta t_{\mathrm{lm}} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\log [(T_1 - t_2) / (T_2 - t_1)]} \tag{2.29}$$

Equation of the correction cross-flow factor of the mean logarithmic temperature difference ε (Bowman, Mueller & Nagle 1940)

$$\varepsilon = \frac{M}{R - 1} \; \frac{\log [(1 - P) / (1 - RP)]}{\log \dfrac{2 / P - 1 - R + M}{2 / P - 1 - R - M}} \tag{2.30}$$

where Q is the heat flux
F mass flow
c_P specific heat capacity
K overall heat transfer coefficient
A heat transfer area
Δt_{lm} mean logarithmic temperature difference
ε cross-flow correction factor
t , T temperatures
$P = (t_2 - t_1) / (T_1 - t_1)$
$R = (T_1 - T_2) / (t_2 - t_1)$
$M = (1 + R^2)^{1/2}$

The above system of five equations represents the mathematical model among directly measured quantities (flow rates, temperatures) and directly unmeasured quantities (parameters) K , Q , ε and Δt_{lm} .

When building this mathematical model we adopted a number of simplifications:
- neglecting the loss of heat to the environment
- independence of heat capacities on temperature
- in the derivation of Eq.(2.30) it was assumed that the flow of liquid in both the shell and tube space is of piston character and that the heat transfer coefficient is constant within the whole heat exchanger.

Such simplifications restrict the possibilities of the application of this model considerably. It could be used for example for extrapolation within some region on the basis of *K* estimated from plant measurement. If we wanted to use the mathematical model of the heat exchanger for a wider range of process variables, it would have to respect the local dependence of *K* on hydrodynamic conditions and properties of substances in the exchanger.■

2.3 SYSTEM CHARACTER OF PROCESS PLANTS

A typical feature of the development of process industries during recent decades has been concentration of production into large systems comprising several complex and confusing interrelations. Process plants represent complex systems linked to one another and the environment so as to enable functioning in the most efficient way.

The complexity of modern plants that is caused by the requirement of efficient utilization of raw materials and energy (waste-free processes, energy integration, etc.) leads to increased demands on designers as well as users of plants, and on those concerned with the rationalization of operating plants.

Experience shows that it is often not possible to cope with the plant as a whole in adequate depth. The reason for this may be the limited resources of the team engaged in the analysis and optimization of the given plant (problems with carrying out a greater number of chemical analyses, limited capabilities of the computer used for measured data processing, and the like). Therefore, a multi-level system approach is adopted, consisting usually of three steps (Fig.2.6):

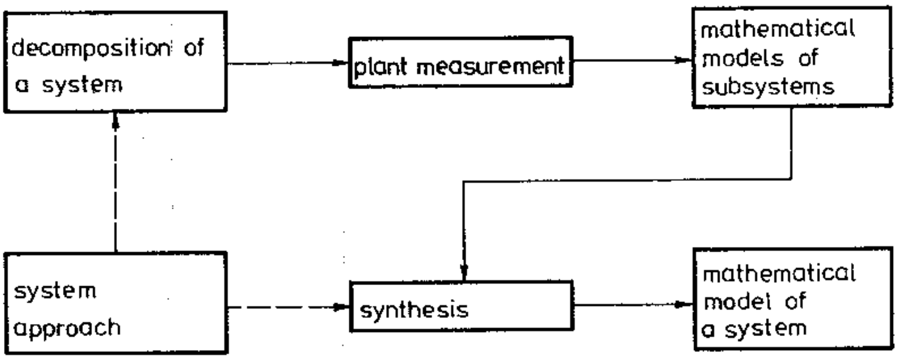


Fig.2.6 — Mathematical modelling of complex systems

- decomposition of the system into simpler subsystems (either individual apparatuses or groups thereof) that are enough simple to be dealt with without considerable problems;

- thorough analysis of functioning of the individual subsystems, based on plant measurements and experiments, published data, chemical engineering calculations, etc. The ideal situation is when the results of these activities are presented in the form of a mathematical model of a subsystem;
- re-synthesis of the system. The simplification made by decomposition of the system has to be compensated by respecting relations among elements of the system.

Applying the graph theory

The number of measured quantities, even in cases of relatively small subsystems, amounts to tens to hundreds, so that processing of the data obtained requires the use of a computer. When coding the structure of measured system for a computer we are using terms and methods of the theory of graphs (see Appendix A.5). Now let us illustrate the graph formulation of the simple system structure for purposes of computer processing of the material and energy balances.

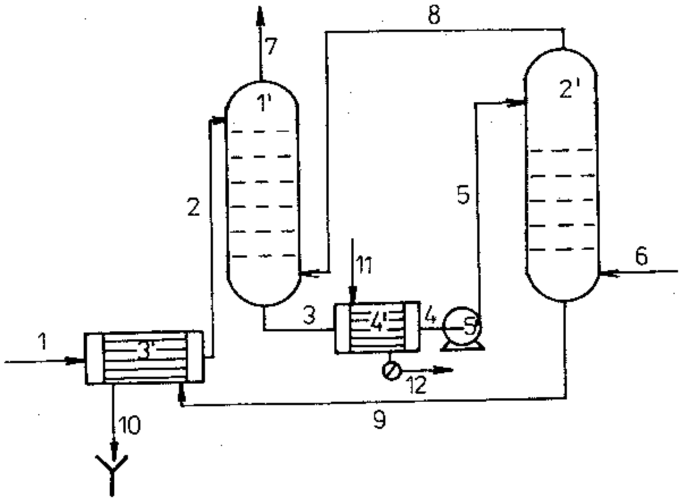


Fig.2.7 — Desorption of ammonia from water solution
Nodes: 1', 2' - desorbers; 3', 4' - heat exchangers; 5' - pump
Streams: 1 - cold ammonia solution; 2 - hot ammonia solution; 3, 4, 5 - partly desorbed solution; 6, 11 - steam; 7, 8 - ammonia and water vapors; 9, 10 - waste water; 12 - condensate

Example 2.4: *Stripping of ammonia from aqueous solution*
A part of a urea plant is shown in Fig.2.7. The purpose of this subsystem is stripping of ammonia by steam in two strippers connected in series. Besides desorption, heat exchange is taking place in two exchangers. There is also a pump, transporting the liquid between the two strippers.

It is expedient to see the exchangers, in which no mixing of streams occurs, as independent tube and shell spaces. The graph in Fig.2.8 contains two additional nodes as well as three streams of energy that are not shown in the original flowsheet (heat flows within the exchangers and mechanical energy supplied to the pump).

Such a graph containing the characteristic features of the process flowsheet is coded to a form suitable for a computer. For this purpose the notation of the graph in the form of the reduced incidence matrix (see Appendix A.5) is used.

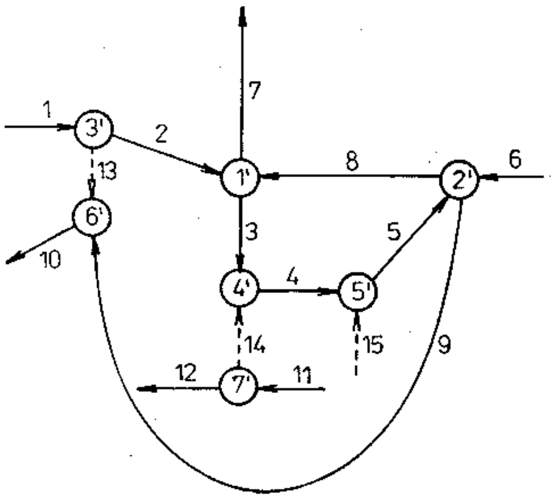


Fig.2.8 — Graph of the flowsheet in Fig.2.7
Nodes: 1', 2'- desorbers; 3', 4'- tube side of exchangers; 5'- pump; 6', 7'- shell side of exchangers
Edges: 1 - 12 - see Fig.2.7; 13, 14 - heat flux; 15 - work
— mass streams ; - - - streams of energy

When forming the incidence matrix it is necessary to realize that the node representing the environment, which will be considered as the reference node, is not, for the sake of clarity, present in the graph in Fig.2.8. In this case we obtain a reduced incidence matrix as presented in Table 2.3. So, for instance, the stream 2 represents the preheated solution of ammonia leaving the tube side of the exchanger (node 3') and entering the first stripper (node 1'). In the second column of the reduced incidence matrix, corresponding to the stream 2, there are element 1 in the first row (node 1') and element -1 in the third row (node 3').■

The reduced incidence matrix makes it possible to write in a simple way balance equations in a system described by a given graph. When balancing a certain variable that satisfies the conservation law (overall mass, energy, etc.), we write the set of balance equations around the nodes by a simple matrix equation

Table 2.3 — Reduced incidence matrix of graph (Fig.2.8)
(zero elements are omitted for simplicity)

Node	Stream														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1'		1	-1				-1	1							
2'					1	1		-1	-1						
3'	1	-1											-1		
4'			1	-1										1	
5'				1	-1										1
6'									1	-1			1		
7'											1	-1		-1	

$$\boldsymbol{A}\,\boldsymbol{v} = \boldsymbol{0} \tag{2.31}$$

where $\boldsymbol{v}$ is the vector of extensive characteristics of the individual streams (for example the vector of mass flows in the case of mass balancing). The reason for this is obvious. The balance equation around the *k*th node is formed by the scalar product of the *k*th row of matrix $\boldsymbol{A}$ with the vector $\boldsymbol{v}$.

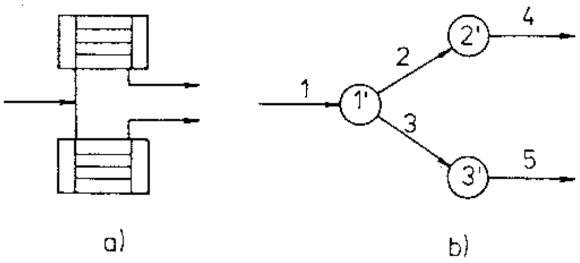


Fig.2.9 — Cooling water system
a) flowsheet; b) graph representation

The existence of balance and other constraints give rise to problems in the course of processing of measured data. Let us demonstrate it using the following simple one-component balance.

Example 2.5: *Mass balance of a cooling water network.*
Let us consider the subsystem of cooling water piping, depicted in Fig.2.9. Here the oriented edges stand for the piping, node 1' is the splitter of streams, nodes 2' and 3' are the shell sides of heat exchangers.

The flow through such a piping at a certain instant of time can be characterized by the vector $\boldsymbol{v} = (v_1, v_2, v_3, v_4, v_5)^T$ where the *i*th element of the vector represents the mass flow rate through the *i*th pipe (positive or negative, depending on whether or not the flow direction corresponds to the orientation of edges in Fig.2.9).

The set of all possible vectors $\boldsymbol{v}$ is an example of a linear space (see Appendix A.1), vectors $\boldsymbol{v}$ are the elements of this space.

In the case in which the heat exchange network is in a poor condition, water losses may take place due to leakage or, the other way round, the cooled medium may leak to the water cooling system. Under such circumstances, the flows are not constrained, and the dimension of the vector space is 5. When all the five flow rates are measured, we can analyze results and draw some conclusions as regards the extents of leakage in individual nodes; we cannot, however, judge about the reliability of measured values.

Now let us abandon the idea of the heat exchanger network being, as mentioned above, in bad state, and let us consider that the network is absolutely leakproof and, besides, no accumulation of cooling water takes place. Under these assumptions not all the flow rates are independent since among them three balance relations must be satisfied:

$$\begin{array}{llr}
\text{node 1':} & v_1 - v_2 - v_3 \qquad\qquad = 0 & \\
\text{node 2':} & \qquad v_2 \qquad - v_4 \qquad = 0 & (2.32) \\
\text{node 3':} & \qquad\qquad v_3 \qquad - v_5 = 0 &
\end{array}$$

Here only two elements of the vector $\boldsymbol{v}$ are independent, whereas the values of the remaining three elements are dependent. If v_1 and v_2 are chosen to be independent, it holds

$$\begin{aligned}
v_3 &= v_1 - v_2 \\
v_4 &= v_2 \qquad\qquad (2.33) \\
v_5 &= v_1 - v_2
\end{aligned}$$

Then the form of an arbitrary vector $\boldsymbol{v}$ has to be

$$\boldsymbol{v} = (v_1, v_2, v_1 - v_2, v_2, v_1 - v_2)$$

The dimension of thus defined vector space is no more 5 but only 2. The set of vectors describing an arbitrary flow of the cooling water (in a perfectly leakproof network without accumulation) forms a two-dimensional vector subspace of the original vector space.

Provided that we measured the flow in the above cooling network, all the final results should be within the space of dimension 2 (so-called *admissible solution*). Therefore, all the measured values have to be adjusted (reconciled) appropriately to prevent the results from being in contradiction with relations among the system elements.■

2.4 DYNAMICS OF PROCESSES

A characteristic feature of real processes of chemical technology is their variability with time. Time - dependent changes of state variables characterizing a given process either may follow from the nature of the manufacturing process proper (for example discontinuous operations), or it is a case of more or less unavoidable accompanying phenomena of continuously operating plants (start-up, shut-down, subtle fluctuations of state variables as the result of external disturbances, etc.).

To have industrial processes, including their dynamics, under control, often represents a rather difficult problem. For some purposes, such as, for instance, control, the knowledge of the process dynamics is indispensable. In other cases, however, information at a considerably lower level is sufficient and its acquisition is usually simpler, too, for instance when

- setting-up mass and energy balances over a longer period of time,
- assessing mean specific consumptions of raw materials and energy,
- determinig time - averaged values of parameters of equipment (heat transfer coefficients, and the like).

Henceforth, those data that do not contain explicitly the information on the dynamic properties of the system will be referred to as *static properties*. This may involve both the continuous and discontinuous processes. The dynamics of the processes, however, should not be ignored in these cases, too, since the precision of the measurement could be affected considerably. Therefore, the basic types of the course of technological processes will be presented.

Variability of technological processes in time

It follows from the analysis of recordings from a number of continuously operating plants that the changes of process variables in time can be divided essentially into three groups.

The first group represents *minor fluctuations* in the vicinity of nominal values, caused by random disorders, minor control actions, and the like. In these cases we say that the unit is in a *stationary* state (Fig.2.10a).

The second group covers *long-term* trends in the function of a plant brought about for example by ageing of a catalyst or by fouling of heat-exchange surfaces (Fig.2.10b). In the case that such changes do exist but can be neglected within a certain short period of time, we speak about a *quasi-stationary* state. The third group is formed by considerable changes that are a result of, for instance, change-over of the plant to a new process regime (Fig.2.10c).

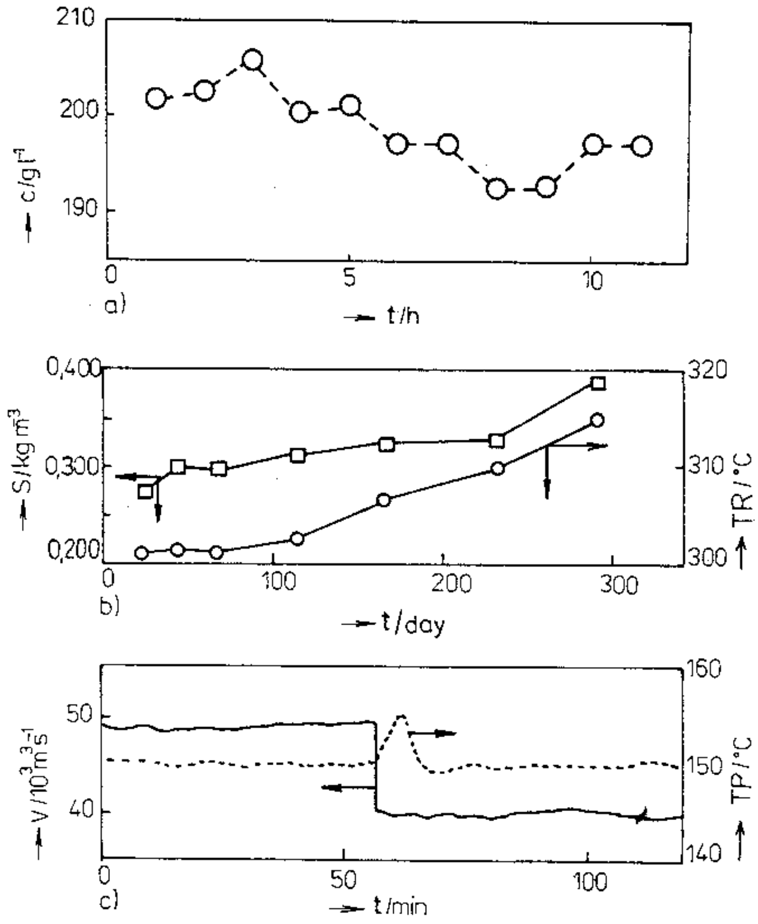


Fig.2.10 — Variability of process variables in time
a) fluctuation of product solution concentration (*c*); b) rise in specific consumption of steam (*S*) and in temperature in a reactor (*TR*) as a result of catalyst ageing; c) the changes of controlled temperature (*TP*) as a result of gas flow (*V*) drop

If the objective of measurement is, for example, assessing of the mean specific consumption over a certain period of time, the variability of manufacturing process in time is the cause of errors that are, most frequently, of a random nature, and depend particularly on the character of the time variation as well as on the measuring method used (sampling frequency, use of measuring instruments equipped with integrators, and the like).

To assess static properties, it is particularly important to carry out the measurements in plants operating under stationary or quasi-stationary state. If there occurs a more significant disruption, such measurement cannot, in most cases, be used for assessing the static properties of the process.

Fluctuation of process variables

An important feature of the planning of measurement and of processing of the results is the fluctuation of process variables around nominal values, which is an accompanying phenomenon of most continuously operating plants.

Most types of fluctuations of process variables can be classified as follows (Fig.2.11).

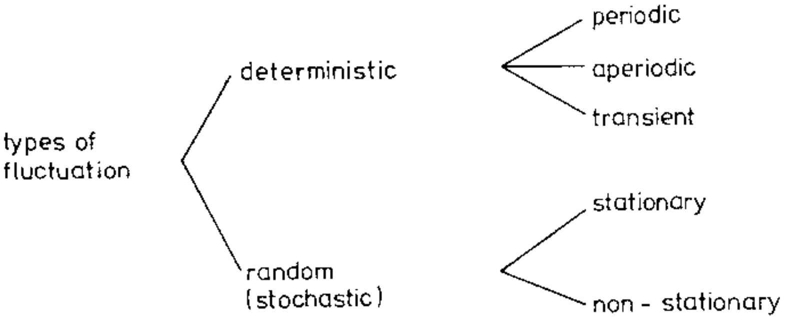


Fig.2.11 — Fluctuation of process variables

Deterministic fluctuation can be described completely by a mathematical model. Its course is determined and it is known in advance. *Periodical fluctuation* has a course recurring at a certain periodicity. Its frequency spectrum contains either a single component only (*harmonic fluctuation*) or, in addition to the fundamental component, also the overtones (*polyharmonic fluctuation*). The representative of *aperiodic fluctuation* is the *quasi-periodic* process, also having a discrete frequency spectrum, but the frequencies of its components are not integer multiplies of the lowest frequency.

Stochastic fluctuation is characterized by the fact that its next course cannot be predicted precisely even when the previous course of the fluctuating variable is known.

Let us present, for illustration, a few examples taken from continuously operating plants. The given classification is only schematic; the real courses of the process variables exhibit the characteristics of different types of fluctuation simultaneously.

A frequent source of a periodical fluctuation is poor functioning of the control system. In Fig.2.12a is presented the volume flow rate of gaseous carbon dioxide; its fluctuation, which can be considered roughly harmonic, is caused by the control of CO_2 gasification.

An interesting example of the transition process - damped harmonic fluctuation - is shown in Fig.2.12b. In the reactor producing hydrogen the temperature in the bed of catalyst TK began to oscillate without apparent reasons. At an instant of time,

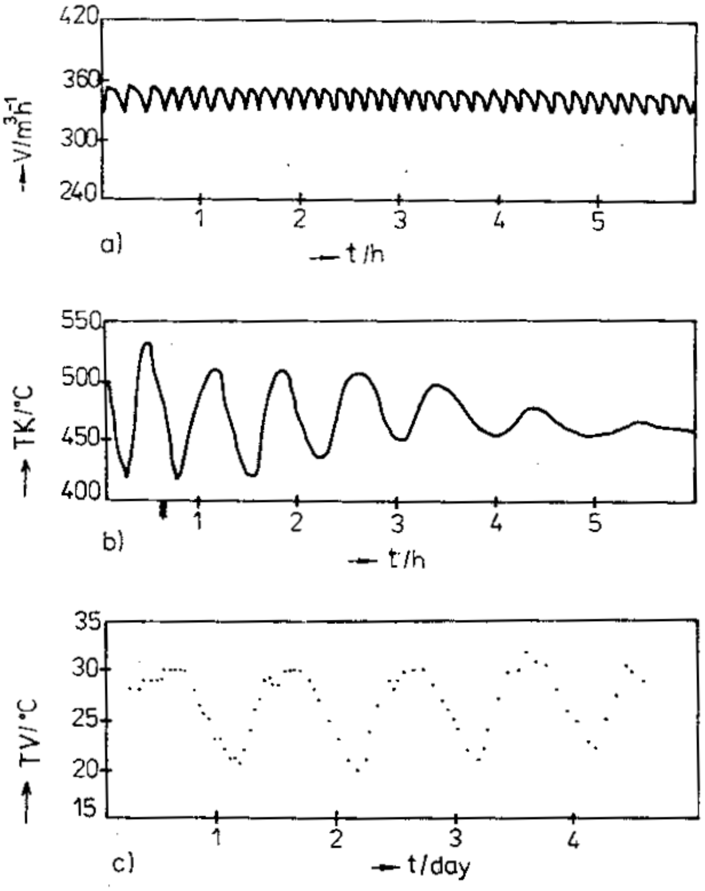


Fig.2.12 — Periodical fluctuation of process variables

marked by the arrowhead in the diagram, the gas flow through the reactor was reduced, which brought about a slow damping of the oscillations.

As may be seen in Fig.2.12c, roughly harmonic fluctuation may develop also when no control is used. The presented example refers to the course of hydrogen temperature from the chlorine and caustic soda plant. Hydrogen is cooled by water introduced at a constant rate, while the cooling water temperature is fluctuating during the day in accordance with the temperature of ambient air.

The examples of stochastic fluctuations of process variables are shown in Fig.2.13. The first one is the course of the volume flow rate of ammonium carbonate solution entering the ammonium nitrite plant. It is being adjusted manually by the operators according to the results of analyses and serves for control of ammonium carbonate concentration in the product. Such a type of fluctuation can be considered a *stochastic multilevel signal*, for which a constant value between two transitions from the first to the second level is characteristic. Its randomness consists in that it is not known in advance when the change in the level will take place, nor what the next level is going to be.

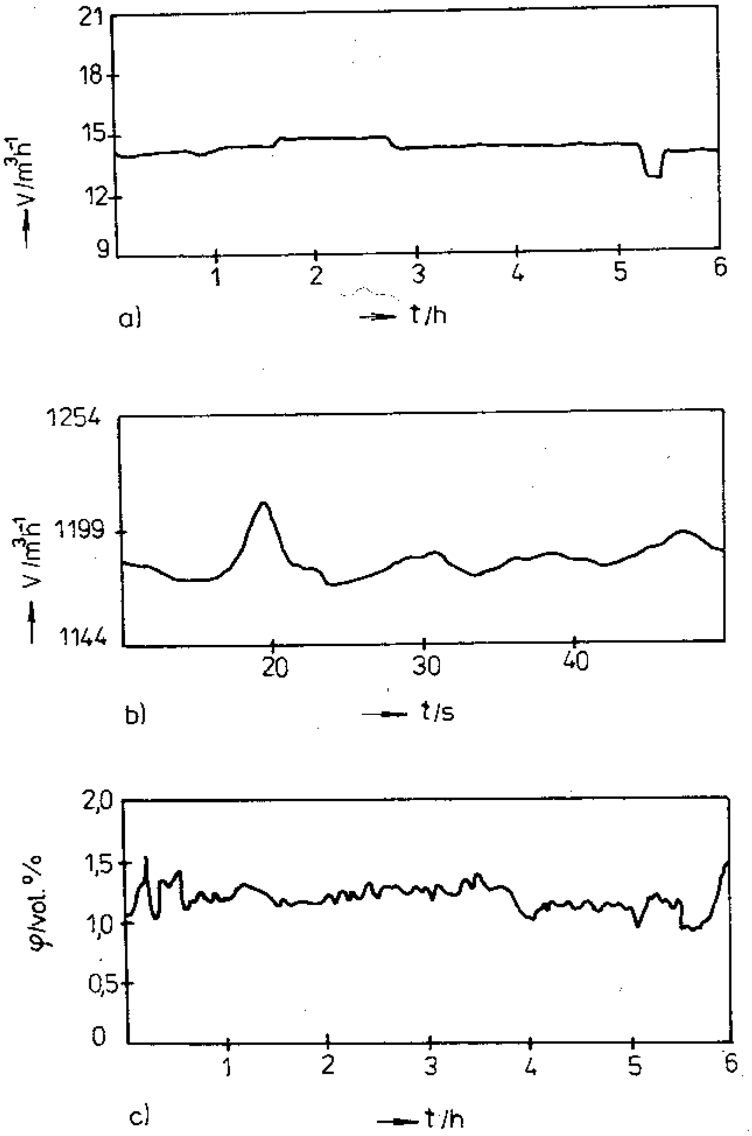


Fig.2.13 — Stochastic fluctuation of process variables

Rapid fluctuations of ammonia flow into the reactor for ammonia oxidation by air are shown in Fig.2.13b. This fluctuation results from controlling the flow rate at the requisite level.

A more complex type of fluctuation is demonstrated in Fig.2.13c, which illustrates the time dependence of concentration (expressed by the volume fraction φ in per cent) of CO_2 in gases leaving an industrial fermenter. The fluctuation of the CO_2 concentration, which has a number of causes, is the direct result of changes in microorganism respiration.

Using the theory of random processes

A suitable approach to data processing in the case of fluctuating variables is the theory of *random processes* (see Appendix A.3). Some conclusions derived from this theory can also be applied to periodical deterministic processes.

In the processing of measurements in process industries the stationary random processes play an important role, indeed, which is due to the fact that the most important process variables usually are controlled within comparatively narrow margins. When the stationarity of fluctuation of variables in process industries is impaired, it is mostly a case of breaking the assumption of the mean values constancy (trends, deterministic fluctuation). In these cases the fluctuation may be considered to be a sum of the deterministic and stationary stochastic processes.

Another important concept is the *ergodicity* of random processes. The ergodic stationary random processes are marked by the fact that the mean value and the other moments of all the other realizations at any instant of time are equal to the mean value and moments of any individual realization. By a realization in manufacturing processes we mean, for instance, the courses of repeated discontinuous operations, in continuous processes the production on identical parallel trains or production in regular cycles separated by shut-downs for equipment maintenance and cleaning. Hence the ergodicity of random processes is a certain statistical form of expressing their reproducibility, either in the course of time or in the sense of various realizations of the manufacturing equipment.

There are not many opportunities for verifying ergodicity when carrying out measurements in modern high-capacity production plants and, in most cases, the ergodicity is only assumed.

It is typical for most plants in process industries that the course of process variables is continuous with respect to time. The information about continuous processes we obtain, however, often applies only to certain instants of time. Thus discrete dependencies - *time series* - are created. The reason for the transformation of continuous processes to time series is, for example, the discrete nature of chemical analyses or discretization of analog signals for processing on digital computers. Next we shall, therefore, concentrate our attention upon the treatment of time series.

The mean value μ and variance σ^2, defined analogically as in the case of common random variables, are important statistical characteristics of random processes. On the assumption of ergodicity, these parameters can be assessed from a single realization. When, in the case of a time series, the measured values at the instants t_s , $2t_s$,...., $n\ t_s$ are x_1 , x_2 ,..., x_n , then the unbiassed estimate of the mean value μ_x is the sample mean $\bar{x}$:

$$\hat{\mu} = \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{2.34}$$

The estimate of variance σ^2 is the sample variance

$$\sigma_x^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 \tag{2.35}$$

The relation among values of a random process at various instants of time is expressed by the *autocorrelation function* $R(\tau)$, defined for a stationary process as the mean value

$$R(\tau) = \mathrm{E}\,[x(t)\,x(t+\tau)] \tag{2.36}$$

where τ is the time shift.

The autocorrelation function is presented either in the centred form $[R'(\tau)]$ or in the standardized form $[\rho(\tau)]$:

$$R'(\tau) = R(\tau) - \mu_x^2 \tag{2.37}$$

$$\rho(\tau) = R'(\tau) / \sigma_x^2 \tag{2.38}$$

The estimate of an autocorrelation function of a time series is calculated from

$$\hat{R}(r\,t_s) = \frac{1}{n-r} \sum_{i=1}^{n-r} x_i\, x_{i+r} \tag{2.39}$$

where x_i stands for the value of the time series element at time $i\,t_s$ and $r = \tau / t_s$.

The centred or standardized autocorrelation function can be calculated from the relation (2.37) and (2.38), into which the estimates as found from the relations (2.34), (2.35) and (2.39) are substituted for μ_x , σ_x^2 and $R(\tau)$. A certain drawback of this procedure is the fact that the standardization is not perfect $[\hat{\rho}(0) \neq 1]$. This disadvantage, however, is not encountered when using an alternative method where the centred autocorrelation function is estimated directly

$$\hat{R}'(r\,t_s) = \frac{1}{n-r} \sum_{i=1}^{n-r} (x_i - \bar{x})\,(x_{i+r} - \bar{x}) \tag{2.40}$$

and the standardized autocorrelation function is assessed from

$$\hat{\rho}(r\,t_s) = \hat{R}'(r\,t_v) / \hat{R}'(0) \tag{2.41}$$

For large values of n, however, the differences between the two approaches are negligible.

Hence the autocorrelation function of a time series is defined only for integer multiplies of the sampling period t_s . The course of real autocorrelation functions is approximated by empirical functions, among which for example the function

$$R\ (\tau) = a_0^2 + \sum_{i=1}^{I} \frac{a_i}{2} \cos\ (\omega_i\ \tau) + c \exp\ (\ -\ \alpha\ |\tau|) \cos\ (\beta\ \tau) \tag{2.42}$$

where a_i , c, ω_i , α and β are parameters, is capable of expressing even very complicated real courses of autocorrelation functions. The parameter a_0 represents the mean value of a random process, the second term on the right-hand side of Eq.(2.42) expresses the deterministic fluctuation (obviously in the case of purely stationary random processes this term is null).

Often we manage with an autocorrelation function in the form of the last term in Eq.(2.42):

$$R'\ (\tau) = c \exp\ (-\ \alpha\ |\tau|) \cos\ (\beta\ \tau) \tag{2.43}$$

where the parameter c is equal to the random process variance, or

$$R'\ (\tau) = c \exp\ (-\ \alpha\ |\tau|) \tag{2.44}$$

The various aspects of statistical properties of time series in process industries find their application, among others, in the analysis of errors of measurement of fluctuating process parameters (see Subsection 3.3.5).

Let us elucidate this problem further using an example.

Example 2.6: *Statistical properties of ammonia flowrate fluctuation*
A sector of the recording of the volume flowrate of gaseous ammonia is shown in Fig.2.13b. The objective is to assess the mean value, variance, and the autocorrelation function of flowrate fluctuations.

For the use of computer processing, the record was transformed into the time series by sampling at t_s = 0.968s. Besides, to make the reading easier, the value of the flowrate V proper was, during the reading, transformed into a quantity y according to

$$y = (V\ -\ 1{,}253.5)\ /\ 2.422 \tag{2.45}$$

In total, a recording 8 minutes long was processed using the above method. The mean value, variance and autocorrelation function were calculated according to relations (2.34), (2.35) and (2.40). The following values were found:

$$\hat{\mu}_y = 16.5$$

$$\hat{\sigma}_y^2 = 3.276^2$$

which correspods to

$$\hat{\mu}_V = 1{,}293 \text{ m}^3 \text{ h}^{-1}$$

$$\hat{\sigma}_V^2 = 7.93^2 \text{ m}^6 \text{ h}^{-2}$$

The calculated values of the centred autocorrelation function are plotted as points in Fig.2.14. The dependence of the centred autocorrelation function on time shift τ was approximated to by the least squares method with the aid of empirical function (2.43):

$$R'(\tau) = 7.93^2 \exp(-0.293\,|\tau|) \cos(0.267\,\tau) \tag{2.46}$$

(see the solid line in Fig.2.14).

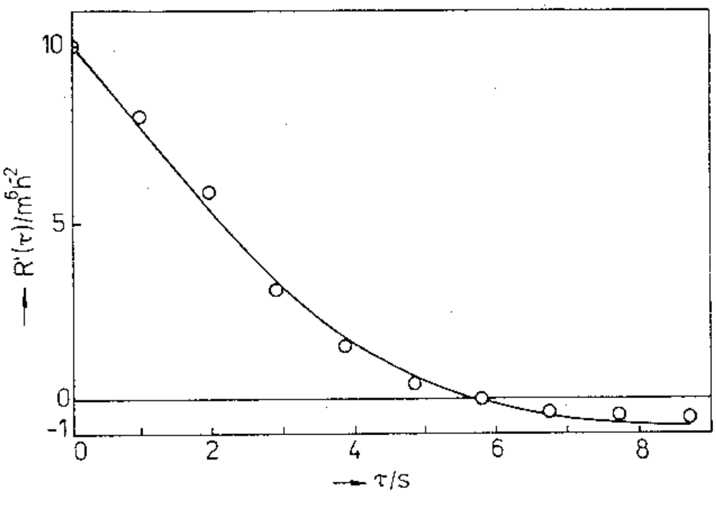


Fig.2.14 — Centred autocorrelation function of ammonia flow

It can be stated that the ammonia flowrate fluctuates in the vicinity of 1,293 m^3 h^{-1} with the standard deviation 7.93 m^3 h^{-1} , which corresponds to 0.6% of the mean value. The autocorrelation function is almost null at the time shift of 5s, which means that after that time the values of the flowrate are virtually uncorrelated.■

Verifying the process stationarity

Estimation of mean value, variance and autocorrelation function of a stationary random process does not present a serious problem, particularly when a computer is employed. The results may be distorted, however, due to the fact that a random process is not really a stationary one - most frequently a long-term trend or a deterministic periodical process are involved.

The presence of both the above influences can be assessed based on the sequence of positive and negative deviations of the time series from the mean value or median. If we denote a positive deviation from the median by + and the negative deviation by -, we may obtain, for instance, the following sequence:

+ + + - - + + - - + + + - - - + +

in which the positive and negative signs alternate regularly and all the groups are roughly equally long. In the case of such a time series we can assume that it contains a significant deterministic periodical component. On the other hand, the sequence

- - - - - - - - + - + + + + + +

gives evidence of a significant trend (growth of the time series values with time).

There exists a number of statistical tests for detecting deviations from stationarity. The simplest of these is the sign test according to Wald and Wolfowitz (Himmelblau 1970). In this test the median of time series is found first and a sequence of signs is set up in the above mentioned way. The testing criterion U^+ is defined as the number of time intervals during which there was no change in the sign. It is the random variable with a certain distribution, whose quantiles are presented in Table 2.4. The use of the Table will be elucidated using an example.

Let us consider a time series with the respective sequence of signs (median = 4.5):

5 5 6 5 3 4 5 3 5 7 4 6 6 5 3 4 5 5 3 2 3 5 4 5 5 6
+ + + + - - + - + + - + + + - - + + - - - + - + + +

In the sequence of 26 elements of this time series, altogether 13 periods occur with no change in the sign; hence $n = 26$ and $U^+ = 13$. Now we shall carry out the two-sided test for the significance level $a = 0.05$. The hypothesis of the time series stationarity is not rejected, if it holds

$$U^+_{\alpha/2} < U^+ < U^+_{1-\alpha/2} \tag{2.47}$$

In Table 2.4 we find $U^+_{0.975} = 19$ and $U^+_{0.025} = 8$. Since $8 < 13 < 19$, the hypothesis of the stationarity of the time series is not rejected.

There exist other stationarity tests (more efficient than the above mentioned simple test), which can be found in specialized literatute (Himmelblau 1970).

Table 2.4 — Quantiles of variable U^+
$\mathrm{P}[U^+ < U_P^+(n)] = P$

n/2	P					
	0.01	0.025	0.05	0.95	0.975	0.99
5	2	2	3	8	9	9
6	2	3	3	10	10	11
7	3	3	4	11	12	12
8	4	4	5	12	13	13
9	4	5	6	13	14	15
10	5	6	6	15	15	16
12	7	7	8	17	18	18
14	8	9	10	19	20	21
16	10	11	11	22	22	23
18	11	12	13	24	25	26
20	13	14	15	26	27	28
25	17	18	19	32	33	34
30	21	22	24	37	39	40
35	25	27	28	43	44	46
40	30	31	33	48	50	51
45	34	36	37	54	55	57
50	38	40	42	59	61	63
60	47	49	51	70	72	74
70	56	58	60	81	83	85
80	65	68	70	91	93	96
90	74	77	79	102	104	107
100	84	86	88	113	115	117

Further information about possible impairment of stationarity can be obtained from the analysis of autocorrelation function of the random process. It is known that with increasing time shift, the autocorrelation function of a stationary random process tends to zero. When the process contains a significant periodical component, the estimated autocorrelation function also fluctuates periodically around zero even for large values of the shift t. The autocorrelation function of a process with significant trend has also a characteristic course (Fig.2.15).

When a process includes significant deterministic components, these may be subtracted from the process, whereby a stationary random process is obtained. In most cases the deterministic part of a process is found and a properly chosen curve is fitted by the least square method (polynomial or trigonometric function). Deviations of the time series from the deterministic part represent the random component of a process.

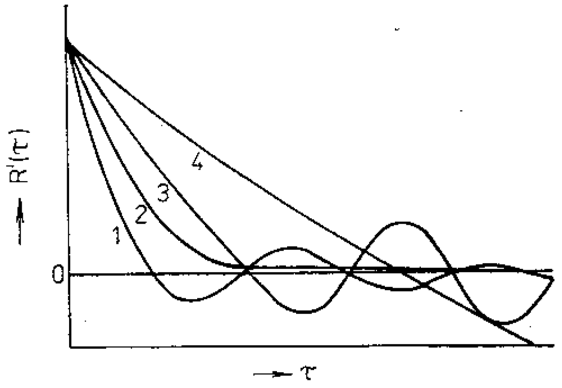


Fig.2.15 — Autocorrelation functions
1, 2 - random process; 3 - process with periodical part; 4 - process with a trend

2.5 METHODS OF MEASUREMENT IN PROCESS PLANTS

Once the target for a plant measurement has been formulated clearly, the procedure can be broken down into the three following fundamental stages:

- planning and preparation of the measurement
- the plant measurement proper
- processing of measured data and interpretation of results.

It holds true that if valuable results are to be obtained, the above sequence of activities must form a balanced entirety. Shortcomings in one stage can be eliminated only partly or cannot be rectified at all in another stage. The individual stages cannot be separated from one another, they have to be taken as inseparable parts of the process of measuring covering the overall activities from planning of the measurement to formulation of conclusions.

2.5.1 Problem formulation

The setting of the task, of which measurement forms part, is usually formulated with some degrees of freedom. It holds that the less that is known about the solution of the problem, the less concrete is also the setting of the target. The first step, therefore, must be the formulation of the problem in technical terms.

The next step is the elaboration of a global conception of the measurement. If, for instance, the problem can be formulated as the question of "*How to raise the capacity of the plant by 20%?*", we have to decide, for example, upon

- which subsystems can be measured at an increased throughput - which apparatuses can be analyzed with the aid of chemical engineering calculations;
- whether the interrelations with the adjoining plants have also to be examined.

It is necessary to specify the required precision and accuracy of the results of measurement, process regimes during the plant measurements, etc. Last but not least, the necessary capacities of the team responsible for the measurement must be evaluated including the cooperation with specialized external groups. It is likely that first-class solutions of a number of problems will be beyond the abilities of the team attempting to solve the problem. What is meant is, for example

- chemical engineering calculations and consultations concerning less common unit operations
- difficult mathematical problems
- corrosion and abrasion problems
- operational safety
- special measurement methods.

2.5.2 Measurement planning

In the next step we proceed to planning of measurements and experiments proper. Considering the availability of time, which is always limited, it is necessary to estimate the number of measurements and time needed for their execution. In addition to the capacity of the problem solving team proper, the limitations inherent in the particular plant have also to be taken into account. It is necessary to consider the dates and duration of plant shut-downs that are often essential for preparing the measurement (checking of existing measurement systems, installation of new measuring instruments, etc.).

Once it is decided when and under what conditions the individual measurements will take place, it is possible to start with their detailed planning. This is, in the first place, a matter of choosing the so-called *measuring points*. By this we do not have in mind, for instance, a decision, whether the samples of a liquid should be taken at a pump inlet or outlet (not forgetting, however, that sometimes even a detail like this may markedly affect the final result), but the selection of directly measured variables from the set of all the measurable variables.

When selecting the measured quantities we are using as a basis the characteristics of the available measuring instruments and analytical methods (in particular with respect to precision and demands on time of the measuring methods) while, at the same time, respecting the properties of the industrial system to be measured (possibilities to calculate quantities from the equations of the mathematical model, and the like).

Following the decision on the directly measured quantities, it is necessary to carry out, in particular,

- checking of existing systems of measurement
- installation of new measuring instruments

- a complex evaluation of the problem of chemical analyses including also the sampling.

During this phase it is necessary to proceed after careful deliberation since the above activities often use up the greater part of the total capacity available for the solution of the given task.

The methods of measuring as they are routinely conducted in the plant, particularly as far as process control is concerned, often do not fulfil the requirements for a satisfactory solution of the given problem. Hence the demand for carrying out measurements not conducted hitherto is justified, and to meet it, both the capacity of the problem solving group and cooperation with the plant staff are required.

The probability of our success in this respect is inversely proportional to the extent of our requirements. To achieve favourable results of our efforts, it is, therefore, necessary to select rationally the variables to be measured, making sure that only those measurements, which are really indispensable, are carried out. Such an approach may be called optimization of the selection of measuring points.

After the measurement points have been chosen we proceed to a more detailed planning of the measureemnt. It is necessary to decide various questions such as

- necessary duration of the measurement proper
- method of collecting the measured data (reading at predetermined instants of time, use of a data logging system etc.)
- detailed implementation of sampling.

In some cases even more detailed information about the plant is needed. It may be necessary to study dynamic properties of the system (extent of fluctuation of process variables), which demand, for example, an adequate frequency of readings of discretely measured variables, or of sampling. Often problems of taking representative samples have to be solved (sampling of inhomogeneous or heterogeneous streams, liquids condensing from gaseous samples, and the like).

2.5.3 Plant measurement

The concrete implementation of measurement in process industries depends on the facilities available to the problem solving group. Recently, the most common method was manual collection of data, where the readings of measuring instruments were put down in forms prepared beforehand. In cases when it was reasonable, these data could be ascertained retrospectively by evaluating strip-charts of plant instruments. A special case of manual data collection was taking of samples for chemical analysis.

The higher level of data collection, which is gaining importance nowadays, is employing automatic measuring and data processing systems (data loggers, measurement tape recorders and process computers). When those modern technical means are to be used, however, it is necessary to assess benefits obtained in the case under consideration. The use of the up-to-date data logging technology is advantageous particularly for measurements involving a great number of repetitions or when dynamic models are to be built since in this way the data can be read at high frequency and high precision of both the values and the instant of time of reading (Výborný et al. 1986). Of course, the situation is fairly simple if the plant is equipped with a process computer.

For the final success of the measurement it is important that, in addition to the measured variables proper, also the performance of the plant as the whole should be respected. In this aspect there is an important function of a measurement - coordinator who supervises the overall course of the measurement, investigates the possible defects of measuring instruments, modifies the plan of measurement in accordance with changes in the plant performance, and the like.

2.5.4 Interpretation of measurement results

The processing of plant measurements usually proceeds at several levels.

In the course of so-called *pre-processing* of data the directly measured values have to be checked for the occurrence of errors that may have arisen during the stage of data collection. It may be a case, for example, of confusions among the column forms, errors caused by defects of measuring instruments, and the like. During this stage sometimes also those data that are obviously subject to gross errors are eliminated, using statistical methods of detecting so-called outliers.

The step following after the elimination of obvious errors is so-called *correction* of measured values. The correction means a compensation of known errors (mostly of a systematic nature) that were brought about by not following the conditions set for individual measurement methods. The typical and most frequent cases in this respect are the corrections of flowmeter readings for deviation of measured liquid density from the value considered when the measuring system was designed.

Sometimes also primary data are reconciled in order not to be in contradiction with laws governing the specific measurement method. It may be a case of, for example, of normalization of the measured mass fractions whose sum must be equal to unity, or of computation of an average value for variables measured simultaneously by several different methods. A special case of data reconciliation is the smoothing of time series - so-called data *filtration.*

In some cases it is necessary to evaluate a measured process with respect to its stationarity (approach to the steady state). We start from an analysis of the time behaviour of the individual process variables, examining, for instance, the existence of trends or of periodical fluctuations. The measured time series can be processed for this purpose with the aid of methods based on the random processes theory.

In the next stage these pre-processed data are used in further calculations of required results of the measurement. The methods of data processing differ mainly in accordance with the extent of the mathematical modelling used.

In the extreme case, when no theoretical concepts of relations among the measured variables are available, the data processing is limited to the computation of mean values of variables within the time interval of the measurement, to assessing of the coefficients of empirical equations, and the like.

With the use of more advanced approaches to mathematical modelling (equations of mass and energy balances, models of unit operations), more advanced methods of data processing are used, both when assessing the quantities not directly measured, or when redundant measurements are reconciled.

An integral part of a final result of measurement should be information about potential errors of results. Most of questions that may arise in this respect can be answered using the theory of errors.

The problems of eliminating gross and systematic measurement errors are more

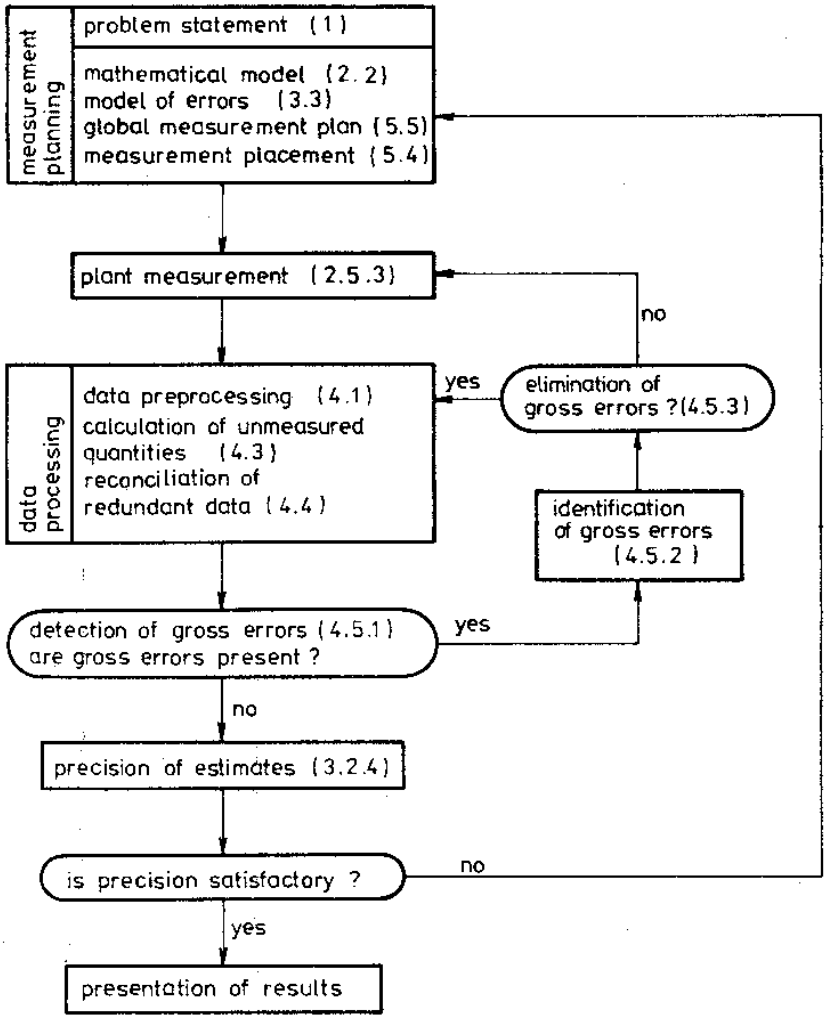


Fig.2.16 — Process plant performance assessment (numbers in parentheses refer to sections of the book)

typical in process industries than elsewhere. It is true that it is the existence of these errors that changes fairly simple questions into problems which are rather difficult to solve. Even the most careful and well thought-out preparation of the measurement does not prevent us from errors of this kind. It is, therefore, worthwhile to examine the measured data from the standpoint of gross and large systematic errors. Once the existence of such errors is proved, it is essential to eliminate the influence of gross and systematic errors on the results (elimination of data that are corrupted by gross errors, repeating or supplementing the measurements).

It would be a mistake to think that the above discussed succession of activities (planning and preparation of measurement, the measuring proper, and final processing of measured data) represent a straightforward procedure, at the beginning of which the problem is formulated and at the end it is successfully solved. More often it is true that the process of measurement in operating plant has an iterative character.

So, for example, when planning the measurement, we start from certain ideas about the extent of errors of measurement of individual quantities. Not until the measurement proper, however, can we find to what extent our ideas have been correct. It may happen that, because of the wrong assumptions during the planning of measurement, the results do not satisfy the demands made on the measurement and this has to be repeated.

Possible variants of measurements in process industries are presented in Fig.2.16, where also references are given to those parts of this book, dealing with the individual problems of plant mesurements.

2.6 RECOMMENDED LITERATURE TO CHAPTER 2

There are several good books on mathematical modelling in chemical engineering (Himmelblau & Bischoff 1968, Luyben 1973). In the first of them the system approach is emphasized, while the second is oriented to process dynamics and control. The application of graph theory to chemical engineering problems is described in a review paper by Mah (1983).

The problems of stochastic fluctuations are covered for example in books by Bendat & Piersol (1966) or Otnes & Enochson (1978).

3 Errors of measurement

Virtually all quantities obtained by measuring contain an error. Hence, the problem of errors is an important part of the treatment and interpretation of measurement results. These problems are dealt with by the theory of errors which can be divided into general theory and special theory of errors. The *general theory of errors* studies general laws governing the origin of errors, their propagation in the course of measured data processing, and methods of acquiring information on errors on the basis of the measurement proper. The *special theory of errors* applies to errors of individual measuring methods, instruments and the like.

In this Chapter the theory of errors is presented which is essential to the application of methods of measured data processing as discussed in the following chapters.

3.1 BASIC CONCEPTS AND CLASSIFICATION OF ERRORS

The *absolute error* of measurement e (henceforth referred to as error of measurement only) is defined as

$$x^+ = \tilde{x} + e \tag{3.1}$$

where x^+ is a measured value and $\tilde{x}$ is a real (true) one. The superscripts + and ~ will be used for differentiating between the measured and real values.

For assessing the precision of results the so-called *relative error* e' is suitable

$$e' = e \,/\, \tilde{x} \tag{3.2}$$

which is often expressed in percent

$$e' = 100\, e \,/\, \tilde{x} \tag{3.3}$$

In practice, it is not usually a case measuring a single quantity, but generally, of measuring I quantities (temperatures, flow rates, etc.), and so we must refer to a measured vector $\boldsymbol{x}$. The measurement of individual quantities may be either of a continuous nature as in temperature and pressure or discrete as in the determination of concentrations in collected samples. For the purpose of subsequent processing on a digital computer, continuous measurements are converted to discrete ones usually by reading a continuous signal at instants specified beforehand.

Let us assume that the measurement of a vector $\boldsymbol{x}$ was made at instants t_k, $k = 1,2,...,K$. Thus IK values of x_{ik}^+ were obtained as the result of measuring with the index ik denoting the measurement of ith quantity at time t_k. The measured values form a two-dimensional array. One dimension - that of time - is represented by index k, and the other one, relating to space is represented by index i. In practice, there are many more complex data systems. For our purposes, however, this simple scheme is sufficient, and it will be referred to hereafter. A relation analogical to Eqn.(3.1) applies to the measured values x_{ik}^+ :

$$x_{ik}^+ = \tilde{x}_{ik} + e_{ik} \tag{3.4}$$

As regards their nature, it is usual to classify errors as *random*, *systematic* and *gross*. The importance of such a classification lies in the fact that the processing of measured data is different depending mainly on how the individual types of error participate in the total error of a result of measurement.

3.1.1 Random errors

Random errors are those errors that may, under otherwise identical conditions of measuring, acquire various magnitudes and different signs. Their likely values oscillate around zero and their mean value is null. Taken individually, they do not display any regularities and are mutually independent. The individual values are both unpredictable and inexplicable. They are typical examples of random quantities.

The said properties of random errors may be expressed mathematically in terms adopted for random quantities:

zero mean value $\quad \mu_e = \mathrm{E}\,(e) = 0 \qquad (3.5)$

zero correlation $\quad \mathrm{cov}\,(e_1\,,\, e_2) = \mathrm{E}\,(e_1\, e_2) = 0 \qquad (3.6)$

Statistical independence of errors and their zero correlation are identical only in the case of errors conforming to normal distribution (for more details see Appendix A.3). In practice, however, the conditions (3.5) and (3.6) are generally accepted as the properties of random errors.

In view of the zero mean value of random errors, the mean value of a measured quantity equals the respective real value:

$$\mu_x = \mathrm{E}\,(\bar{x} + e) = \bar{x} \tag{3.7}$$

Random errors may be characterized in a similar way as random variables. In agreement with the assumption, their mean value is null and their most important characteristic is the variance defined (considering the null mean value) as

$$\mathrm{D}\,(e) = \mathrm{E}\,(e^2) = \sigma_e^2 \tag{3.8}$$

Obviously the variance of a measured quantity is the same as the variance of its random error and these two terms are sometimes confused. This holds true only in such a case, however, when the real value does not change with time. It is, therefore, necessary to differentiate the variance (e.g. fluctuating real values) from the variance of a measurement error (see Subsection 3.3.5).

More complete information about random errors is offered by the probability distribution of random error expressed by the probability density function. Of key importance in this aspect is the well known law of normal distribution (see Appendix A.3). The significance of normal distribution is clear for several reasons:

- it has been ascertained that it approximates well the behaviour of measurement in natural sciences, particularly within the range $\mu \pm 3\,\sigma$,
- an error is often the sum of a greater number of single, so-called *elementary* errors. Under conditions altogether acceptable, in accordance with the central limit theorem, the distribution of such a sum limits to normal distribution,
- in the case that the distribution of errors is not known (which is a frequent case, indeed), assuming normality of distribution, one is adding only minimum information (which moreover need not be correct) to the problem,
- the theory of normal model of errors is well developed and well treatable mathematically. The values of probability density and distribution functions of standard normal distribution are readily available in tabulated form which facilitates the solving of practical problems.

Errors complying with the normal distribution are fully characterized by the parameter of that distribution - the *standard deviation* - determining the measurement precision. The smaller the standard deviation, the more precise is the measurement. In the theory of errors also some other measures of accuracy have been adopted; assuming a normal distribution of errors, however, these may be expressed as explicit functions of standard deviation.

In earlier literature, the standard deviation is sometimes referred to as *mean quadratic error*. Its double determines the so-called width of the Gaussian curve, i.e. distance between the points of inflection of the curve.

Mean error λ is defined as a mean value of the absolute value of error

$$\lambda = \mathsf{E}\,(|e|) \tag{3.9}$$

The following relation holds between λ and σ:

$$\lambda = (2\,/\,\pi)^{1/2}\,\sigma = 0.7980\,\sigma \tag{3.10}$$

Probable error ϑ is a value for which it holds that the absolute value of a half of errors is larger than ϑ. It holds

$$\vartheta = 0.6745\,\sigma \tag{3.11}$$

Extremal error χ is defined as the triple of σ (in some papers as *n*-multiple of σ, *n* being dependent on the number of mesurements). It holds that 99.73 % of errors lie within the interval $\langle -\chi\,,\,\chi\rangle$.

Also the uniform (rectangular) distribution is of some importance in plant measurements. A typical situation where errors with uniform distribution may be observed is excessive rounding or digitization of continuous signals. This kind of error is also characteristic of balancing volumes while the accumulation is neglected.

Random errors are the simplest model of an error, but in practice, significant deviations from this model may occur particularly as the result of correlation among errors.

3.1.2 Correlated random errors

The concept of a correlated random error can be arrived at by reasoning. Let us assume that the errors of measurement of two quantities are formed by a sum of a greater number of uncorrelated random errors (so-called *elementary errors*). In the case in which no elementary error acts upon the formation of the total error of measurement simultaneously with both the quantities, then the total errors are also uncorrelated. In the opposite case, however, elementary errors occurring simultaneously in the measurement of the two quantities are responsible for the fact that the resulting errors are already correlated.

For example, let the errors of measuring of the quantities A and B be given by a sum of elementary uncorrelated errors e_1 , e_2 and e_3 with zero mean value and standard deviations σ_1 , σ_2 and σ_3 .

$$e_A = e_1 + e_2 \qquad e_B = e_1 + e_3 \tag{3.12}$$

The covariance of the errors e_A and e_B is then

$$\mathrm{cov}(e_A\,,\,e_B\,) = \mathsf{E}\,(e_A\,e_B) = \mathsf{E}\,[(e_1 + e_2)\,(e_1 + e_3)] \tag{3.13}$$

After multiplying and rearrangement we obtain

$$\mathrm{cov}(e_A , e_B) = \mathsf{E}\,(e_{12}) + \mathsf{E}\,(e_1\, e_3) + \mathsf{E}\,(e_2\, e_1) + \mathsf{E}\,(e_2\, e_3) = \sigma_{12} \tag{3.14}$$

since the elementary errors are uncorrelated, and consequently, the latter three mean values in Eqn.(3.14) are null. In this case the covariance of errors e_A and e_B is equal to the variance of error e_1 occuring simultaneously in both the total errors.

Let us first consider the *spatial correlation* of errors. This kind of errors correlation is seldom met in so far as directly measured quantities are considered. The spatial correlation is caused by the fact that individual measuring systems are not independent. For example, when measuring temperature with the aid of thermocouples, their reference ends are usually kept in a single thermostat. When the temperature in the termostat is not stabilized adequately, an elementary error thus caused manifests itself in all the measured temperatures simultaneously. Similarly, spatially correlated errors may result from fluctuations in the pressure of the air in the pneumatic measurement and control system. In chemical analyses correlated errors may be caused by taking a sample whose composition does not correspond to that of the respective main stream. For example, when in a gas sample some of its constituents condense in the sampling line, the determined concentrations of all the remaining components will be higher than the actual values.

Spatial correlation of errors, however, is encountered most frequently when calculating *secondary quantities* from quantities directly measured (*primary*).

Let us assume that the task is to measure the flow rates of substances A and B in a certain stream of liquid. The flow rate of the liquid phase is measured, a sample is taken, and in it the concentrations of the substances A and B are determined. The flow rates of the individual substances are then obtained as products of the flow rate and the respective concentrations. Although the errors of the primary quantities are uncorrelated, the errors of flow rates of the individual substances are already correlated.

The spatial correlation of errors can be expressed quantitatively with the aid of a covariance matrix of errors. If we have a vector of I measured quantities $\boldsymbol{x}$ to which belongs a vector of errors $\boldsymbol{e}$, the covariance matrix $\boldsymbol{F}$ of an $I \times I$ type has the following elements

$$F_{ij} = \mathrm{cov}\,(e_i\,, e_j\,) = \mathsf{E}\,(e_i\, e_j) \qquad \text{for } i = j \tag{3.15}$$

$$F_{ii} = \mathsf{D}\,(e_i) = \mathsf{E}\,(e_i^2) \tag{3.16}$$

The calculation of covariance matrices of errors, which belongs to the topics of random errors propagation, will be dealt with in detail in Section 3.2.

Now let us give attention to the *time correlation of errors*. Each error has its objective cause and this, in turn, has a certain physical ground. Because of inertia, it is assumed that such a cause will persist for a certain period of time. It is, therefore, only a question of the length of the time interval between two measurements whether the measurement errors in two successive instants will be dependent or almost independent. The time correlation of errors is a very frequent phenomenon, particularly in connection with the ever more extensive use of automatic measuring systems. It may be a case of measuring instruments errors varying with time, errors that are due to fluctuating process variables, and the like. The time correlation may be expressed quantitatively by an autocorrelation function (see Appendix A.3).

Example 3.1: *Autocorelation function of a time series error*
Let us assume that a single quantity x is measured at instants of time t_k, $k = 1, \dots, K$, where $t_k - t_{k-1} = \Delta t$. Thus, a time series of K measured values x_k^+ is obtained and these contain errors e_k. As for the errors, we assume that they are random variables with an equal standard deviation σ_x^2. To suppress the influence of random errors on the control of the process, we use so-called filtration of data. We calculate the quantities

$$z_i^+ = \frac{x_i^+ + x_{i-1}^+}{2} \qquad i = 2, 3, \dots, K \tag{3.17}$$

whereby a new time series comprising $(K - 1)$ elements is formed. Obviously, it holds for errors of the z_i^+

$$e_{z_i} = \frac{e_{x_i} + e_{x_{i-1}}}{2} \tag{3.18}$$

The covariances of errors of the adjacent quantities z_i and z_{i-1} then are

$$\mathrm{cov}\,(e_{z_i}, e_{z_{i-1}}) = \mathrm{E}\left[\frac{(e_{x_i} + e_{x_{i-1}})\,(e_{x_{i-1}} + e_{x_{i-2}})}{4}\right] \tag{3.19}$$

After rearrangements and considering that the errors e_{x_i} are not correlated we obtain

$$\mathrm{cov}\,(e_{z_i}, e_{z_{i-1}}) = \mathrm{E}\,(e_{x_{i-1}}^2 / 4) = \sigma_x^2 / 4$$

Analogically, we could find that the errors of quantities z_i and z_{i-2} are not any more correlated. The autocorrelation function of the time series z_i^+ defined only for integer multiples of the time interval Δt is shown in Fig.3.1.■

By way of concluding this part devoted to dependent or correlated errors, we should remark that this was a case of stochastic dependency, i.e.dependency holding true among large sets of errors. The individual errors, however, still remained random and unpredictable. Only very seldom do we find a deterministic dependency of errors in the sense of dependency of vectors in linear algebra. In such a case, one or more errors may be expressed exactly as a function of other errors. An attendant phenomenon of deterministically dependent error is that their covariance matrix is singular. This case represents a transition from random to systematic errors.

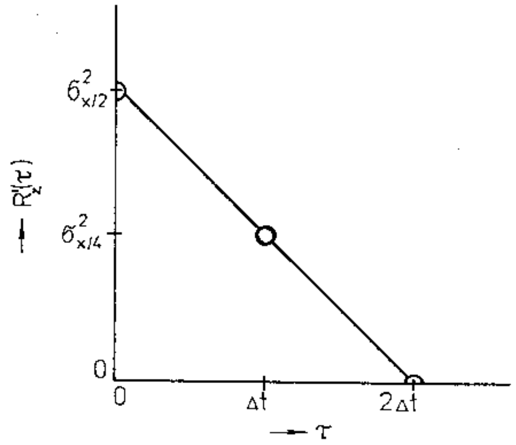


Fig.3.1 — **Autocorrelation function of time series**

3.1.3 Systematic errors

Up to now, we have understood errors as random variables. These errors either were changing quite randomly or were tied with one another stochastically. Under the concept of systematic error we understand such an error whose value is constant with time or whose behaviour is deterministic. It can be a case of an error which is due to an imperfectly adjusted instrument (constant error), error that is linearly time dependent as a result of instrument's zero drift, error with periodical variation in accordance with the daily course of ambient temperature, and the like.

Let us take notice of the relation between systematic and time correlated errors. It was stated in connection with time correlated errors that it depends exclusively on the length of the time interval between two measurements and on the dependence of the error causing factor on time, whether the errors will be time correlated or not. Reasoning in this way, we may arrive at the case when the error causing factors, compared with the time of measuring, change but insignificantly. From this point of view a constant systematic error may be considered the limit case of a time correlated error. As a matter of fact, the boundary between these two kinds of errors is not sharp, and frequently it cannot be found at all.

Similar conclusions also apply to some space correlated errors. For instance in the above example of space correlated errors of measuring temperatures with the aid of thermocouples, the total errors of the measurement of individual temperatures were the random ones since it was assumed that besides the imperfect thermostating some other elementary factors were important as well. Provided that these other factors could be neglected, knowing the error of the measurement of only one temperature, we would also be able to determine exactly the errors of the remaining temperatures. Then, the resulting error could be considered a systematic one.

Further, it is necessary to point out a random aspect of systematic errors. Let us consider a set of measuring instruments of the same type, manufactured within a certain period. Using these instruments for measuring a certain constant quantity, we would probably find that the instruments do not give absolutely identical results. The set of errors of the individual instruments form a sample space. If we select randomly (e.g. by a purchase) a single instrument and use it for measuring, we are introducing a constant systematic error into our measurements. The value of such an error, however, may be considered a sample from the given sample space. In other cases, the sample space may be hypothetical - it can be a case of a set of all the admissible methods of measuring the flow rate with an orifice gauge, where the individual methods are characterized primarily by the diameters of the pipe and the respective orifice. Having chosen a certain variant and having this measuring element made, we have made a random sample from a hypothetical sample space.

The real value of the constant systematic error is not known in the above examples, and it can be considered realization of the random variable. Comprehension of the relations between random and systematic errors is important in statistical processing of measured data. As will be shown later, solving of practical problems requires that the available information on random and systematic errors be respected in parallel in a consistent way.

Concluding the discussion of the problems of systematic errors, it is necessary to emphasize their importance in plant measurements. In the literature dealing with the theory of measurement the problems of systematic errors are often resolved by a note that systematic errors should be avoided. It is recommended that the instruments be calibrated carefully, to use standards, and the like. This approach, however, which is justified in a chemical or physical laboratory, does not solve the problem of systematic errors of plant measurements. Even if all the possible measures are taken, systematic errors will affect the final results of a measurement in a decisive way. It is, therefore, necessary to respect the existence of systematic errors and to employ the information on these errors in statistical processing of measured data as in the case of random errors.

3.1.4 Gross errors

A gross error is considered to be a sporadic large error that arises out of inattention, a fault in the measuring instrument, erroneous calculation, unforeseen events, and the like. Owing to its size it does not fit in the rank of the other errors. Its emergence as the realization of a random error would be highly unlikely. Unless its cause is removed in time, it is repeated and a *systematic gross error* arises.

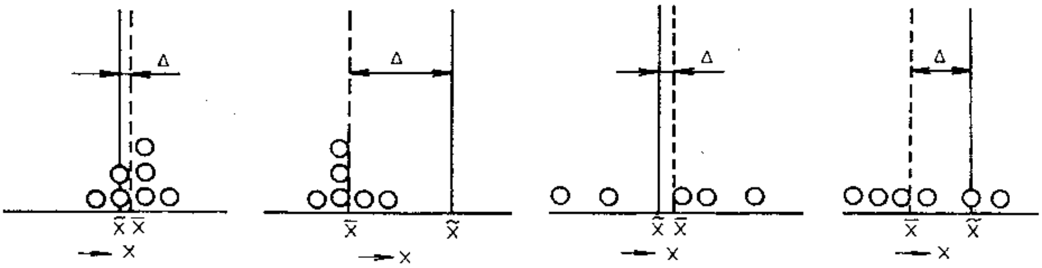
Whereas random and small systematic errors represent an inseparable constituent of the measured values and measurements containing these errors are used when presenting the results, those measurements, containing a gross error, have to be eliminated from further processing. Hence, an important aspect of obtaining good results is an analysis of measured data orientated towards tracking down and eliminating the masurements containing gross errors. These problems will be discussed in detail in Chapter 4.

3.1.5 Precision and accuracy of measurement

In connection with the occurrence of random and systematic errors, two important notions appear - precision and accuracy of measurement. *Accuracy* of a measurement means agreement between the measured and real (true) values. *Precision* of a measurement expresses agreement among several repeated measurements of the same single quantity. These two terms differ in that precision, contrary to accuracy, does not take into account systematic errors of measurement. Precision (expressed e.g. as the sample standard deviation assessed from repeated measurements) together with the potential systematic error presents a suitable criterion for the accuracy of measurement.

Precision and accuracy are shown diagrammatically in Fig.3.2. Let us assume that a single quantity x, whose real (accurate) value is $\tilde{x}$, is measured repeatedly. When the result of each measurement is represented by plotting a circle to the respective value on the x-axis, we may obtain the following characteristic cases.

In Fig.3.2a the measurement is well reproducible and the average value x is close to the real value (sometimes a precise and accurate measurement is referred to as *reliable* measurement). In Fig.3.2b again the measurement is well reproducible; the obtained values, however, deviate systematically from the real one. Hence, the measurement is precise but not accurate (the average value is not accurate). Shown in Fig.3.2c is a case where the measurement is poorly reproducible, but the average value obtained from a large number of measurements is close to the real value. In such a case we speak about a non-precise measurement with an accurate mean (for a large enough number of repeated measurements). The last and least desirable variant is a non-precise and inaccurate measurement which is badly reproducible and deviates systematically from the real value. It is obvious, however, that with this given classification the boundary is rather a matter of opinion.



a) b) c) d)

Fig.3.2 — Precision and accuracy of measurement
a) precise and accurate; b) precise and inaccurate;
c) imprecise with good average; d) imprecise and inaccurate

Comprehension of the problems of measurement precision and accuracy is important in the planning of experiments. Of course, a precise and accurate measurement would be the best one but to achieve this may sometimes be difficult. In some cases we can content ourselves with a measurement that is precise but less accurate (e.g. when only comparing the values as obtained under various process conditions - then a constant systematic error need not be important). In other cases we require the measurement to be accurate, and a lower degree of precision of the measuring method used may be set off by calculating the mean from a larger number of repeated measurements.

3.2 PROPAGATION OF ERRORS

When evaluating the results of measurements, in most cases we do not confine ourseleves to the directly measured (primary) quantities and their errors. We are asking, what will be the effect of the primary quantities errors upon those quantities which are calculated from the primary quantities (so-called *secondary* quantities)?

Next we are going to concern ourselves with three types of problems:

- what will be the errors of the secondary quantities if we know the values of the primary quantities errors?
- what will be the maximum errors of the secondary quantities if we know the maximum errors of the primary quantities?
- what probability characteristics (mean values, variances, distribution laws) will the secondary quantities possess assuming that the probability laws of the primary quantities errors are known (problems of random errors propagation)?

We shall assume that a secondary quantity z is a function of the vector of primary quantities $\boldsymbol{x} = (x_1, \dots, x_l)^{\mathrm{T}}$

$$z = f(\boldsymbol{X}) \tag{3.21}$$

The equation holds generally and can be written both for the measured values (designated by +) and real (true) values (designated by ~):

$$z^+ = f(\boldsymbol{X}^+) \tag{3.22}$$

$$\tilde{z} = f(\tilde{\boldsymbol{X}}) \tag{3.23}$$

The Equations (3.22) and (3.23) define the real value of a secondary quantity $\tilde{z}$ and the "measured" value z^+. Then the secondary quantity error is defined

$$e_z = z^+ - \tilde{z} = f(\boldsymbol{X}^+) - \mathrm{f}(\tilde{\boldsymbol{X}}) \tag{3.24}$$

3.2.1 Real value of the error of measured quantities function

Let us assume first that the function (3.21) is linear with respect to the primary quantities:

$$z = c_0 + \sum_{i=1}^{I} c_i x_i \tag{3.25}$$

where c_i are known constants.

Substituting (3.25) into (3.24), respecting at the same time, the definition relation for an error (3.1), we obtain the following relation for the secondary quantity error:

$$e_z = \sum_{i=1}^{I} c_i e_{x_i} \tag{3.26}$$

It is worth mentioning that in (3.26) no true values (usually not known to us) occur.

In the case of the relation (3.21) being nonlinear, various algebraic rearrangements are adopted to express the error of a secondary quantity.

Example 3.2: *Error in the determination of mass from measured volume and density*
Let us consider a calculation of the mass m of a liquid from the measured volume V and density ρ acording to

$$m = V \rho \tag{3.27}$$

According to (3.24) it holds

$$e = V^{+}\rho^{+} - \tilde{V}\,\tilde{\rho} = (\tilde{V} + e_V)\,(\tilde{\rho} + e_\rho) - \tilde{V}\,\tilde{\rho}$$

and after rearrangement

$$e_m = \tilde{V}\,e_\rho + \tilde{\rho}\,e_V + e_\rho\,e_V \qquad \blacksquare \tag{3.28}$$

In the case of more complex nonlinear functions we are using approximate methods based on the linearization of the function by the Taylor expansion, neglecting the second and higher order terms. It holds approximately

$$z^{+} = \tilde{z} + \sum_{i=1}^{I} \frac{\partial f(\boldsymbol{X})}{\partial x_i}\, e_{x_i} \tag{3.29}$$

the derivatives being evaluated at the point $\boldsymbol{X} = \tilde{\boldsymbol{X}}$. The error e_z is then approximately equal to

$$e_z = \sum_{i=1}^{I} \frac{\partial f(\boldsymbol{X})}{\partial x_i}\, e_{x_i} \tag{3.30}$$

thus to the total differential of the function where the differentials have been replaced by the values of errors.

Example 3.3: *Approximate error in the determination of mass from measured volume and density*

Let us revert to Example 3.2. The error in the determination of mass is found by linearization of Eqn.(3.27):

$$e_m = \frac{\partial m}{\partial V}\, e_V + \frac{\partial m}{\partial \rho}\, e_\rho$$

Since

$$\frac{\partial m}{\partial \rho} = \tilde{\rho} \qquad \text{and} \qquad \frac{\partial m}{\partial \rho} = \tilde{V}$$

$$e_m = \tilde{\rho}\,e_V + \tilde{V}\,e_\rho \tag{3.31}$$

The relation (3.31) differs from the exactly valid (3.28) in the term $e_\rho\,e_V$. E.g. for the values $\tilde{\rho} = 1000$ kg m^{-3}, $\tilde{V} = 1000$ m^3 and for positive errors of 5% of the real values (i.e. $e_\rho = 50$ kg m^{-3} , $e_V = 50$ m^3), the real value of the error $e_m = 102\,500$ kg. The approximate value from (3.31) is 100 000 kg. Hence the errors calculated according to the two methods differ by 2 500 kg which is roughly 2.5% of the accurate value of the error. Considering the total mass at 10^6 kg, however, such a difference will be negligible in most cases. ■

3.2.2 Maximum error of the measured quantities functions

Another type of problem arises if we know the maximum errors $e_{x_i}^{\max}$ of a direct measurement and are interested in what maximum errors may occur in the secondary quantity.

Let the maximum errors $e_{x_i}^{\max}$ be defined so that the measured values x_i^+ lie within the intervals

$$(\tilde{x}_i - e_{x_i}^{\max} \; ; \; \tilde{x}_i + e_{x_i}^{\max})$$

where x_i are the real (accurate) values. We are considering again a secondary quantity defined by (3.21). The maximum possible error of the quantity z is given by the following relation

$$e_z^{\max} = \max_{\boldsymbol{x} \in \mathbf{S}} | f(\boldsymbol{x}) - f(\tilde{\boldsymbol{x}}) | \tag{3.32}$$

The region **S** is the set of all the values that can be taken by the vector $\boldsymbol{x}$. In our case, to **S** belong all the vectors $\boldsymbol{x}$ whose coordinates satisfy

$$\tilde{x}_i - e_{x_i}^{\max} < x_i < \tilde{x}_i + e_{x_i}^{\max} \tag{3.33}$$

In a general case, finding the maximum possible error of a secondary quantity means to find the extreme of a function of more variables within a bounded region.

In some cases, however, the solution is simple. For example when a function $z = f(\boldsymbol{x})$ is linear in the form of (3.25), then it holds for the maximum error of a quantity z

$$e_z^{\max} = \sum_i | c_i | \, e_{x_i}^{\max} \tag{3.34}$$

The relation (3.34) differs from the similar one (3.26) only in that the coefficients of the linear function for maximum errors are present in absolute value.

With a nonlinear function an approximate solution can be obtained analogically to the preceding subsection by linearization of the function by the Taylor expansion.

Thus obtained approximate solution is an analogy to (3.30) from which it differs by absolute values of the derivatives:

$$e_z^{\max} = \sum_i \left| \frac{\partial f(\boldsymbol{X})}{\partial x_i} \right| e_{x\,i}^{\max} \tag{3.35}$$

Maximum possible errors are calculated in those cases where it is necessary to make sure that the secondary quantity error will not be outside a certain region determined beforehand (e.g. for safety reasons).

The calculation of maximum errors, however, is not convenient for routine measurements since the random character (and hence the possibility of their mutual cancelling) is not considered and the results obtained are rather pessimistic. In the cases of a greater number of primary quantities the probability that the maximum error of a secondary quantity will occur is small. From the apprehension of errors as realizations of random variables follows another type of tasks concerning the propagation of errors.

3.2.3 Propagation of random errors

From a practical point of view, the most important is the solution of the problem of how the random errors of directly measured quantities are transformed in the course of computations. In most cases, the actual values of random errors are not known, therefore, the probability properties of a result (mean value, variance, distribution) are determined provided that the probability properties of errors of the directly measured quantities are known. Frequently we confine ourselves to estimating the variance of a result or to some other measure of its precision. Based on thus obtained information, we try to construct such intervals that will cover, with a chosen probability, the real (unknown) values of results.

Mean value of the function of random variables

The mean value of the function of a vector of random variables $\boldsymbol{X}$ is defined by

$$\mu_z = \mathrm{E}\,[f(\boldsymbol{X})] = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} f(\boldsymbol{X})\; p(\boldsymbol{X})\; \mathrm{d}x_1 \ldots \mathrm{d}x_I \tag{3.36}$$

where $p(\boldsymbol{X})$ is the I-dimensional probability density of the vector $\boldsymbol{X}$. When $f(\boldsymbol{X})$ is linear [Eqn.(3.25)], it can be derived from the definition equation (3.36) that the mean value of the function will be obtained by substituting into the function for x_i the mean values

$$\mu_z = c_0 + \sum_i c_i \, \mathrm{E}\,(x_i) = c_0 + \sum_i c_i \, \mu_{x\,i} \tag{3.37}$$

In such a case, the mean value of a secondary quantity is equal to its real value. It is important that the relation (3.37) holds true irrespective of the probability distribution of the primary variables.

It holds, that the mean value of a constant is equal to the constant and that the mean value of the product of the constant and a primary quantity is equal to the product of the constant and the mean value of the primary quantity.

When the function $f\,(\boldsymbol{x})$ is not linear, it is necessary to start from the definition equation (3.36). As opposed to the preceding case, we cannnot assume that the mean value of a secondary quantity may be obtained by substituting the mean values of the primary quantities into the function. This holds only in the case of linear functions, with nonlinear functions the mean value need not be equal to the real value.

Example 3.4: *Mean value of the equilibrium constant*
Let us consider a calculation of the equilibrium constant K from the value of standard free energy $\Delta\, G°$ at temperature T:

$$K = \exp\left(- \frac{\Delta\, G^\circ}{RT}\right) \tag{3.38}$$

Let us assume further that the sole source of error is $\Delta\, G°$ having a normal distribution with the mean value μ_G and variance σ_G^2 . The task is to calculate the mean value of K.

In the case of an exponential function, it is comparatively easy to calculate the exact mean value of the quantity K by integrating (3.36) (Park & Himmelblau 1980). If we substitute into (3.36) for K from (3.38) and the probability density of normal distribution, we obtain

$$\mu_K = \int_{-\infty}^{+\infty} \exp\left(- \frac{\Delta\, G^\circ}{RT}\right) \frac{1}{(2\,\pi)^{1/2}\,\sigma_G} \exp\left[- \left(\frac{\Delta\, G^\circ - \mu_G}{\sigma_G \sqrt{2}} \right)^2 \right] \mathrm{d}\,(\Delta\, G^\circ)$$

After integration we obtain the exact expression for the mean value of K

$$\mu_K = \exp\left[- \frac{\mu_G}{RT} + \frac{1}{2}\left(\frac{\sigma_G}{RT}\right)^2 \right] \tag{3.39}$$

It is worth noting that μ_K depends on the variance σ_G^2 .

When substituting into (3.38) only the mean value, we obtain a different relation that holds only approximately:

$$\mu'_K \approx \exp\left(-\frac{\mu_G}{RT}\right)$$

Thus caused inaccuracy may be expressed by the ratio $S = \mu_K' / \mu_K$. In the following particular case of SO_2 oxidation

$$SO_2\ (g) + 1 / 2\ O_2\ (g) = SO_3\ (g)$$

it holds for the temperature dependence of ΔG° within the range 500 - 1200 K

$$\Delta G^\circ = -23\,279.6 + 10.50\,T - 0.002\,302\,T^2 + 28\,000\,T^{-1} + 4.659\,T \log(T)$$

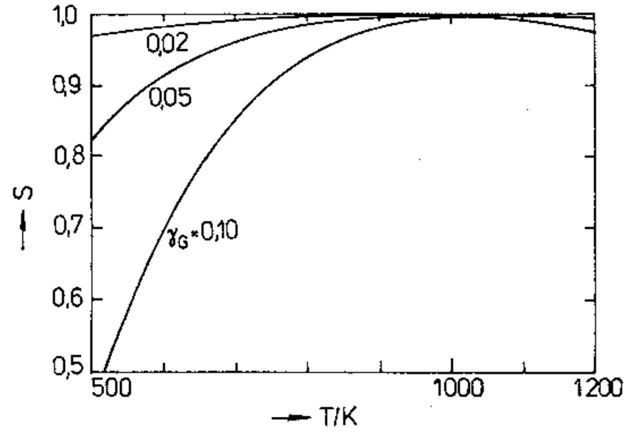


Fig.3.3 — Ratio S as a function of temperature (Example 3.4)

Fig.3.3 demonstrates the dependence of the ratio S on temperature, the parameter being the relative standard deviation $\gamma_G = \sigma_G / \Delta G^\circ$. As may be seen, the error, we would commit by simply substituting the mean value into the function, would be considerable at low temperatures when γ_G is greater than 5% .■

In some cases, it may be possible to arrange the function to a form enabling the mean value to be found without an (often rather difficult) integration of (3.36).

Example 3.5: *Mean value of the number of moles*
The amount of a given substance (in moles) n is calculated as the product of the total volume V and molar concentration of that substance c:

$$n^+ = V^+ c^+ \tag{3.40}$$

The task is to find the mean value of the number of moles of a substance on the assumption that V and c are realizations of uncorrelated random variables with zero mean value.

Substituting into (3.40) the real values and errors of measurement

$$n^+ = (\tilde{V} + e_V)(\bar{c} + e_c)$$

we can, after a rearrangement, find directly the mean value of the number of moles

$$\mathrm{E}\,(n^+) = \mu_n = \mathrm{E}\,(\tilde{V}\bar{c} + \tilde{V}e_c + \bar{c}e_V + e_V e_c) = \tilde{V}\bar{c} \tag{3.41}$$

We have made use of the fact that errors e_c and e_V have zero mean value and are uncorrelated, so that the mean value of the latter three terms in the parentheses in (3.41) is null. The mean value of the secondary quantity in this case equals the product of the primary quantities.■

Variance of the function of random variables

Further, let us concentrate upon the variance of the function of random variables $z = f(\boldsymbol{X})$ which is defined by the integral

$$\mathrm{D}\,[f(\boldsymbol{X})] = \sigma_z^2 = \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} [f(\boldsymbol{X}) - \mu_z]^2\, p(\boldsymbol{X})\, \mathrm{d}x_1 \dots \mathrm{d}x_I \tag{3.42}$$

where $p(\boldsymbol{X})$ is I-dimensional probability density function of the vector $\boldsymbol{X}$, and μ_z is the mean value of the function defined by Eqn.(3.36).

Provided that $f(\boldsymbol{X})$ is linear [Eqn.(3.25)], it is possible to prove from the definition equation (3.42) that the variance σ_z^2 is given by

$$\sigma_z^2 = \sum_{i=1}^{I} \sum_{j=1}^{I} c_i c_j \sigma_{ij} \tag{3.43}$$

where $\sigma_{ij} = \mathrm{cov}(x_i, x_j)$. Obviously $\sigma_{ii} = \sigma_i^2$ are the variances of variables x_i. Using the correlation coefficients ρ_{ij}, the relation (3.43) may also be expressed as

$$\sigma_z^2 = \sum_{i=1}^{I} \sum_{j=1}^{I} c_i c_j \sigma_i \sigma_j \rho_{ij} \tag{3.44}$$

where σ_i are the standard deviations of x_i.

If the primary quantities errors are uncorrelated, the relation (3.43) is simplified

$$\sigma_z^2 = \sum_{i=1}^{I} c_i^2 \sigma_i^2 \tag{3.45}$$

With a nonlinear function, as in the case of the mean values, the problem becomes

considerably more complex. In principle, there are three possible solutions at hand:
- integration of the definition equation (3.42),
- rearrangement of the function to a more suitable form,
- linearization of the function by Taylor expansion (approximate solution).

Example 3.6: *Calculation of the variance of the equilibrium constant by integration of definition equation*

This is a case of the calculation of the equilibrium constant as defined in Example 3.4. There is only one quantity containing an error, and the definition equation (3.42) has the folowing form:

$$\mathrm{D}\ [f(x)] = \sigma_z{}^2 = \int_{-\infty}^{+\infty} [f(x) - \mu_z\ ]^2\, p\,(x)\, \mathrm{d}x \tag{3.46}$$

Substituting K from (3.38) for $f\,(x)$ and the probability density of normal distribution for $p\ (x)$ we obtain (Park & Himmelblau 1980)

$$\sigma_K{}^2 = \int_{-\infty}^{+\infty} \left[\exp\left(-\ \frac{\Delta\, G^{\circ}}{RT} - \mu_K\right)\right]^2 \frac{1}{(2\,\pi)^{1/2}\,\sigma_G}\ \exp\left[-\left(\frac{\Delta\, G^{\circ} - \mu_G}{\sigma_G\,\sqrt{2}}\right)^2\right] \mathrm{d}\,(\Delta\, G^{\circ}) \tag{3.47}$$

After integration

$$\sigma_K{}^2 = \exp\left[-\ \frac{2\,\mu_G}{RT} + \left(\frac{\sigma_G}{RT}\right)^2\right]\left[\exp\left(\frac{\sigma_G}{RT}\right)^2 - 1\ \right] \tag{3.48}$$

In this case the variance of the secondary quantity (K) depends on the mean value of the primary quantity (G°) - compare with (3.43).■

In certain cases, the function can be rearranged to a convenient form enabling the variance to be found without a direct integration.

Example 3.7: *Determination of the variance of rearranged function*

The number of moles of a given substance is calculated as the product of the total volume V of a mixture and concentration of the substance c (see Example 3.5). The variance is then defined by

$$\mathrm{D}\ (n^{+}) = \mathrm{E}\ (c^{+}\ V^{+} - \mu_n\ )^2$$

Substituting from (3.41) for μ_n we obtain successively

$$\mathrm{D}\ (n^{+}) = \mathrm{E}\ \{\ [\ (\tilde{V} + e_V\ )\ (\tilde{c} + e_c\ ) - \tilde{V}\ \tilde{c}]^2\ \} = \mathrm{E}\ [\ (\tilde{V}\ e_c + \tilde{c}\ e_V + e_V\ e_c)^2\ ]$$

The exponentiation gives nine terms; the determination of their mean values will be shown for four typical cases:

$\mathsf{E}\,(\bar{V}^2 e_c^2) = \bar{V}^2\, \mathsf{E}\,(e_c^2) = \bar{V}^2 \sigma_c^2$ (mean value of product of the function and constant)

$\mathsf{E}\,(\bar{V}\,\bar{c}\, e_V e_c) = \bar{V}\,\bar{c}\, \mathsf{E}\,(e_V e_c) = 0$ (since e_V and e_c are uncorrelated)

$\mathsf{E}\,(\bar{V} e_c^2 e_V) = \bar{V}\, \mathsf{E}\,(e_c^2)\, \mathsf{E}\,(e_V) = 0$ (since $\mathsf{E}\,(e_V) = 0$)

$\mathsf{E}\,(e_V^2 e_c^2) = \mathsf{E}\,(e_V^2)\, \mathsf{E}\,(e_c^2) = \sigma_V^2 \sigma_c^2$

The possibility of a simplification into a product of two terms in the latter two cases follows from the definition equation (3.36) and from assumptions of uncorrelability of e_c and e_V and of normal distribution of errors.

The final relation then becomes

$$\sigma_n^2 = \bar{V}^2 \sigma_c^2 + \bar{c}^2 \sigma_V^2 + \sigma_c^2 \sigma_V^2 \quad \blacksquare$$

The methods presented hitherto are feasible only with simple functions. For general nonlinear functions, a method of linearization of the function by Taylor expansion is used [see (3.29)]. The problem is thus reduced to finding the variance of a linear function of random variables. The variance is then given approximately by the relations (3.43) or (3.44), where the coefficients are equal to partial derivatives of the function with respect to the individual primary quantities

$$c_i = \left[\frac{\partial f(\mathbf{x})}{\partial x_i} \right]_{\mathbf{x} = \hat{\mathbf{x}}}$$

Example 3.8: *Calculation of the equilibrium constant variance by linearization*
The equilibrium constant (see Example 3.6) as defined by (3.38) is linearized at the point $\Delta G^\circ = \mu_G$ to give

$$K = K_0 - \left[\frac{1}{RT} \exp\left(- \frac{\mu_G}{RT} \right) \right] e_G$$

where $K_0 = \exp[-\mu_G / (RT)]$ and e_G is the error of the quantity ΔG° .

It is then a case of a linear function of a single primary quantity, and according to (3.45) its variance is

$$(\sigma'_K)^2 = \left[\frac{\sigma_G}{RT} \exp\left(- \frac{\mu_G}{RT} \right) \right]^2 \tag{3.49}$$

Now we can compare the accuracy of the approximate relation (3.49) with that of the exact relation (3.48). We shall write the ratio of standard deviations as calculated according to both relations

$$H = \sigma_K \, / \, \sigma_K \tag{3.50}$$

In Fig.3.4, this ratio is plotted for the SO_2 oxidation (see Example 3.4), temperature being the independent variable, for different values of standard deviation of $\Delta \, G^\circ$. It may be seen that if the standard deviation is larger than 5% of $\Delta \, G^\circ$ the error due to linearization must not be neglected.■

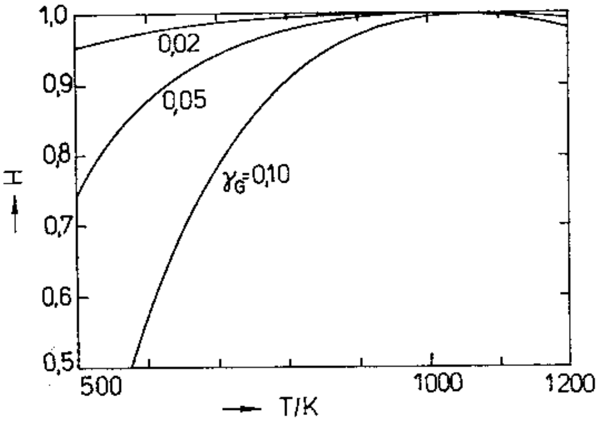


Fig.3.4 — Ratio H as a function of temperature (Example 3.8)

Example 3.9: ***Propagation of errors in flow rate measurement***

Let's consider the measurement of a flow rate F with the aid of an orifice gauge in accordance with

$$F = k \left(\frac{p_0 \, \Delta \, p}{T} \right)^{1/2} \tag{3.51}$$

Here the following quantities contain errors:

k - orifice gauge constant
$\Delta \, p$ - pressure difference on the orifice
p_0 - pressure at the orifices inlet
T - thermodynamic temperature (K).

Errors of the quantities k, $\Delta \, p$, p_0 and T are understood to be realizations of independent random variables with zero mean values and known standard deviations. The relative standard deviations of the primary quantities are, successively,

$$\gamma_k = 0.005 \qquad \gamma_{\Delta p} = 0.01 \qquad \gamma_{p_0} = 0.01 \qquad \gamma_T = 0.005$$

The task is to find the relative standard deviation of the flow rate F.

The relation (3.51) is linearized to the form of (3.25). The coefficients c_i are obtained by differentating the relation (3.51) with respect to the individual variables

$$c_1 = c_k = \Delta\bar{p}^{1/2}\,\bar{p}_0^{1/2}\,\bar{T}^{-1/2} = \bar{F} / \bar{k}$$

$$c_2 = c_{\Delta p} = \bar{k}\,\bar{p}_0^{1/2}\,\bar{T}^{-1/2}\,\Delta p^{-1/2} / 2 = \bar{F} / (2\,\Delta\bar{p})$$

$$c_3 = c_{p_0} = \bar{k}\,\Delta\bar{p}^{1/2}\,\bar{T}^{-1/2}\,\bar{p}_0^{-1/2} / 2 = \bar{F} / (2\,\bar{p}_0)$$

$$c_4 = c_T = -\,\bar{k}\,\Delta\bar{p}^{1/2}\,\bar{p}_0^{1/2}\,\bar{T}^{-3/2} / 2 = -\,\bar{F} / (2\,\bar{T})$$

Substituting the coefficients c_i into (3.45) yields

$$\sigma_F^2 = \frac{\bar{F}^2\,\sigma_k^2}{\bar{k}^2} + \frac{\bar{F}^2\,\sigma_{\Delta p}^2}{4\,\Delta\bar{p}^2} + \frac{\bar{F}^2\,\sigma_{p_0}}{4\,\bar{p}_0^2} + \frac{\bar{F}^2\,\sigma_T^2}{4\,\bar{T}^2}$$

Considering that $\sigma_k / k = \gamma_k$ and, analogically, with the other primary variables, we obtain the final expression for the relative standard deviation of F:

$$\gamma_F = \left(\gamma_k^2 + \frac{\gamma_{\Delta p}^2}{4} + \frac{\gamma_{p_0}^2}{4} + \frac{\gamma_T^2}{4}\right)^{1/2}$$

Substituting the respective numerical values gives

$$\gamma_F = \left(0.005^2 + \frac{0.01^2}{4} + \frac{0.01^2}{4} + \frac{0.005^2}{4}\right) = 0.0090$$

Hence the relative standard deviation of the flow rate measurement is 0.0090, i.e. 0,9% of the real value.■

Thanks to its simplicity and universality, the method of calculating the variance of function of measured quantities by linearization is applied fairly often. The relations for calculating the variance or standard deviation of the most frequent functions are summarized in Table 3.1.

Table 3.1 — Standard deviations of some functions (for noncorrelated errors)

Function z	Standard deviation σ_z	Relative standard deviation γ_z
$\sum_i x_i$	$\left[\sum_i \sigma_{x_i}^2\right]^{1/2}$	$\frac{\sigma_z}{z}$
$c\,x$	$c\,\sigma_x$	γ_x
$\sum_i c_i x_i$	$\left[\sum_i c_i^2\,\sigma_{x_i}^2\right]^{1/2}$	$\frac{\sigma_z}{z}$
$c\,x^m$	$\approx m\,c\,x^{m-1}\,\sigma_x$	$\approx m\,\gamma_x$
$c\,x_1^{m_1}\ldots x_n^{m_n}$	$\approx z\left[\sum_i m_i^2\,\sigma_{x_i}^2\,x_i^{-2}\right]^{1/2}$	$\approx\left[\sum_i m_i^2\,\gamma_{x_i}^2\right]^{1/2}$
$c\exp(k\,x)$	$\approx k\,c\exp(k\,x)\,\sigma_x$	$\approx k\,\sigma_x$
$f(x_1,\ldots,x_n)$	$\approx\left\{\sum_i\left[\frac{\partial f(\boldsymbol{x})}{\partial x_i}\right]^2\sigma_{x_i}^2\right\}^{1/2}$	$\frac{\sigma_z}{z}$

Systems of functions of measured quantities

In real problems we cannot manage with a single function of measured quantities. In the case of a greater number of functions, in addition to the characteristics already mentioned - mean values and variances - covariances among the individual functions are also to be added.

Let us assume that we have a vector of I directly measured quantities $\boldsymbol{x}$ from which the requisite results have to be calculated - a vector of R secondary quantities $\boldsymbol{z} = (z_1, \ldots, z_R)$

$$\boldsymbol{z} = \boldsymbol{f}(\boldsymbol{x}) \tag{3.52}$$

The relation (3.52) may represent e.g. an explicit solution of a set of equations with respect to $\boldsymbol{z}$, a numerical solution in the case of a system unsolvable explicitly or reconciliation when there are redundant measurements (see Chapter 4).

First let us consider a case in which the individual equations have a linear form:

$$\begin{aligned} z_1 &= C_{01} + C_{11}\, x_1 + \ldots + C_{1I}\, x_I \\ &\vdots \\ z_R &= C_{0R} + C_{R1}\, x_1 + \ldots + C_{RI}\, x_I \end{aligned} \tag{3.53}$$

which may be rewritten in the matrix form

$$\boldsymbol{z} = \boldsymbol{c}_0 + \boldsymbol{C}\boldsymbol{x}$$

If the primary quantities $\boldsymbol{x}$ have a known covariance matrix $\boldsymbol{F}_x$, then it holds that the covariance matrix of the secondary quantities vector $\boldsymbol{F}_z$ is given by

$$\boldsymbol{F}_z = \boldsymbol{C}\, \boldsymbol{F}_x\, \boldsymbol{C}^{\mathrm{T}} \tag{3.54}$$

from which one can derive the individual elements of $\boldsymbol{F}_z$ (i.e. for the individual pairs of quantities z_i, z_j).

Frequently, we deal with nonlinear functions. In such a case, it is common to linearize the function by the Taylor expansion. The covariance matrix $\boldsymbol{F}_z$ is then given approximately by the relation (3.54), where the elements of $\boldsymbol{C}$ are given by

$$C_{ri} = \left[\frac{\partial f_r(\boldsymbol{x})}{\partial x_i} \right]_{\boldsymbol{x} = \hat{\boldsymbol{x}}} \tag{3.55}$$

Now let us present a practical example of the calculation of a covariance matrix. In so doing, the results of linearization will be compared with the exact values obtained from rearranged functional relations.

Example 3.10: *Covariance in calculation of bilinear forms*

In material balancing we often find that the balanced quantities (flows of individual components) are computed as products of the measured flow rates and concentrations. In a more general case, some quantities may be defined as bilinear forms of directly measured quantities. For example, the rate of formation if *i*th substance in a chemical reactor n_i is defined at a steady state as

$$n_i = \sum_{k=1}^{K} V_k\, c_{ki} \tag{3.56}$$

where V_k is the flow rate of the *k*th stream connected with the reactor (positive in the case of an outlet stream and negative for an inlet stream), c_{ki} is the concentration of *i*th substance in *k*th stream.

For simplicity, let us confine ourselves to a case of two substances and a single stream:

$$n_1 = Vc_1 \qquad n_2 = Vc_2 \tag{3.57}$$

The primary quantities will be arranged in a vector $\boldsymbol{x} = (V\ ,\ c_1\ ,\ c_2\ )^T$ and the secondary quantities will be arranged in a vector $\boldsymbol{z} = (n_1\ ,\ n_2\ )^T$. The partial derivatives are

$$\frac{\partial n_1}{\partial V} = c_1 \qquad \frac{\partial n_1}{\partial c_1} = V \qquad \frac{\partial n_1}{\partial c_2} = 0$$

$$\frac{\partial n_2}{\partial V} = c_2 \qquad \frac{\partial n_2}{\partial c_1} = 0 \qquad \frac{\partial n_2}{\partial c_2} = V$$

Hence the linearized form of (3.57) is

$$n_1 = \tilde{n}_1 + \tilde{c}_1\, e_V + \tilde{V}\, e_{c_1}$$

$$n_2 = \tilde{n}_2 + \tilde{c}_2\, e_V + \tilde{V}\, e_{c_2}$$

Obviously the matrix $\boldsymbol{C}$ appearing in (3.54) is

$$\boldsymbol{C} = \begin{bmatrix} c_1\, V\, 0 \\ c_2\, 0\, V \end{bmatrix}$$

The measurement errors are uncorrelated and the covariance matrix $\boldsymbol{F}_x$ is diagonal with variances on the diagonal

$$\boldsymbol{F}_x = \begin{bmatrix} \sigma_V^2 & 0 & 0 \\ 0 & \sigma_{c_1}^2 & 0 \\ 0 & 0 & \sigma_{c_2}^2 \end{bmatrix}$$

On substituting into (3.54) we obtain a covariance matrix of n_1 and n_2 :

$$\boldsymbol{F} = \begin{bmatrix} \tilde{c}_1^2\, \sigma_V^2 + \tilde{V}^2\, \sigma_{c_1}^2 & , & \tilde{c}_1\, \tilde{c}_2\, \sigma_V^2 \\ \tilde{c}_1\, \tilde{c}_2\, \sigma_V^2 & , & \tilde{c}_2^2\, \sigma_V^2 + \tilde{V}^2\, \sigma_{c_2}^2 \end{bmatrix}$$

If we follow the exact procedure as described in Example 3.7, we obtain a covariance matrix

$$\boldsymbol{F} = \begin{bmatrix} \tilde{c}_1^2\, \sigma_V^2 + \tilde{V}^2\, \sigma_{c_1}^2 + \sigma_V^2\, \sigma_{c_1}^2 & , & \tilde{c}_1\, \tilde{c}_2\, \sigma_V^2 \\ \tilde{c}_1\, \tilde{c}_2\, \sigma_V^2 & , & \tilde{c}_2^2\, \sigma_V^2 + \tilde{V}^2\, \sigma_{c_2}^2 + \sigma_V^2\, \sigma_{c_2}^2 \end{bmatrix}$$

Both the covariance matrices differ only in the variances; the exact method yields variances that are higher by the term $\sigma_V^2 \sigma_{c_i}^2$. A computation with concrete values shows that for the standard deviations smaller than 5% of the respective true values, the difference between the two methods is negligible.

For completeness, the covariance matrix of the vector $\boldsymbol{n}$ as defined by (3.56) is presented as well:

$$F_{ii} = \sum_k (\tilde{V}_k^2 \sigma^2_{c_{ki}} + \tilde{c}^2_{ki} \sigma^2_{V_k} + \sigma_V^2 \sigma^2_{c_{ki}})$$

$$F_{ij} = \sum_k \tilde{V}_{ki} \tilde{c}_{kj} \sigma^2_{V_k} \qquad \text{for } i \neq j \qquad \blacksquare$$

Analysis of random errors propagation - matrices of shares

Now let us confine ourselves to a frequent case where the errors of directly measured quantities are uncorrelated. The covariance matrix $\boldsymbol{F}_x$ is then diagonal with variances σ_i^2 on the diagonal. The variances for the individual secondary quantities z_r ($r = 1, \ldots, R$) can be expressed by a set of relations

$$\sigma^2_{z_r} = C^2_{r1} \sigma_1^2 + \ldots + C^2_{ri} \sigma_i^2 + \ldots + C^2_{rI} \sigma_I^2 \tag{3.58}$$

for $r = 1, \ldots, R$, that follows from (3.45) and (3.53). This system of equations informs us of how the precision (variances) of the individual measured quantities influences the variance of secondary quantities. It can be seen here how a decrease or increase in the variance of a particular directly measured quantity manifests itself in the variance of secondary quantities.

Obviously, the described method of analysis of random errors propagation is of significance in optimization of a process of measuring. It is advantageous, however, if for these purposes the system (3.58) is further modified. After dividing each equation of (3.58) by the variance $\sigma^2_{z_r}$ and multiplying by 100, we obtain for rth secondary quantity the folowing equation:

$$100 = 100\, C^2_{r1} \sigma_1^2 / \sigma^2_{z_r} + \ldots + 100\, C^2_{rI} \sigma_I^2 / \sigma^2_{z_r} \tag{3.59}$$

in which the individual terms on the right hand side represent the percent share of the individual directly measured quantities in the rth secondary quantity variance. The terms on the right hand side of (3.59) form a matrix $\boldsymbol{H}$ of the dimension $[R \times I]$ with elements

$$H_{ri} = 100\, C^2_{ri} \sigma_i^2 / \sigma^2_{z_r} = 100\, C^2_{ri} \sigma_i^2 / \sum_i C^2_{ri} \sigma_i^2 \tag{3.60}$$

H is called the *share matrix* since its elements H_{ri} represent the share of the ith measured quantity in the rth secondary quantity variance.

The elements of a share matrix ***H*** can be interpreted in the following way: If the variance of ith measured quantity changes (decreases or increases) by $p\%$ of its original value, then the variance of the rth secondary quantity changes (decreases or increases) by

$$p\, H_{ri} \,/\, 100\ \% \tag{3.61}$$

of its original value. In a special case, if the ith quantity is measured without any error (with zero variance, which means a decrease by 100%), the variance of the rth secondary quantity will drop by H_{ri} %. From this consideration also folows the physical meaning of the elements of matrix ***H***.

Altogether, it is possible to summarize that a share matrix informs us about measured quantities representing a bottleneck as far as the accuracy is concerned. When improving the precision of direct measurements, it is necessary to concentrate our attention upon those measured quantities which correspond to large values in the respective columns of the share matrix.

Example 3.11: *Calculation of the matrix of shares*
Let a system of equations (3.53) have the form

$$\begin{aligned} z_1 &= 2x_1 & & + 3x_3 \\ z_2 &= & 3x_2 & - 5x_3 \end{aligned}$$

and the vector of variances of the directly measured quantities be $\sigma^2 = (2,2,5)^T$. Then the secondary quantities variances are

$$\begin{aligned} \sigma_{z_1}^2 &= 4\sigma_1^2 & & + 9\sigma_3^2 \\ \sigma_{z_2}^2 &= & 9\sigma_2^2 & + 25\sigma_3^2 \end{aligned}$$

Now the matrix of shares ***H*** can be calculated from (3.60):

$$\boldsymbol{H} = \begin{bmatrix} 15.1 & 0 & 84.9 \\ 0 & 12.6 & 87.4 \end{bmatrix}$$

It is obvious that the bottleneck of the precision of the whole measurement lies in the quantity x_3 (the elements of the third column of the matrix ***H*** having the highest values). If its variance could be reduced e.g. to a half, i.e. by 50%, the variance of quantity z_2 would decrease by

$50 \times 87.4 / 100 = 43.7\%$

i.e. from the value 143 to 80.5 .■

3.2.4 Intervals and regions of confidence

Until now, we have dealt with the calculations of basic characteristics of functions of directly measured quantities (mean values, variances or, as the case may be, covariances). Information of this kind may be presented in the form of confidence intervals (for a single secondary quantity) or multidimensional confidence regions (for a vector of secondary quantities). The confidence regions cover - at a specified probability level given beforehand - the values that may be taken by the secondary quantities. For constructing the confidence regions, knowledge of the secondary quantities probability distributions is essential.

As regards the manner of how the distributions of primary (directly measured) quantities are transformed in the course of calculating, it is possible to say briefly: if a function of primary quantities is linear and the primary quantities are realizations of random variables with a normal distribution, then the secondary quantities will also have a normal distribution. This fact is of fundamental importance in constructing the confidence regions.

With nonlinear functions, a deformation of the distribution takes place in general, and in most cases, it is rather difficult to find the law of distribution (an exception being e.g. a logarithmic function transforming normal distribution into the well known logarithmic normal distribution). Fortunately, errors usually are small, and quite a number of functions may be viewed as approximately linear within this limited region.

In the case where the primary quantities distribution is not normal, the situation is even more complicated. In most cases, the exact determination of the distribution of a function of primary quantities with non-normal distribution is beyond consideration. In such cases the approximate form of distribution may be assessed by the Monte Carlo method so, that the whole process of measurement and calculation of the secondary quantity is repeatedly simulated on a computer. Thus obtained results are then presented in the form of a histogram simulating the true distribution of the secondary quantity.

It will be assumed further that the primary quantities $\boldsymbol{x}$ have a normal distribution $N_I(\mu_x, \boldsymbol{F}_x)$ with a known covariance matrix $\boldsymbol{F}_x$, and that the vector of secondary quantities $\boldsymbol{z}$ is linear with respect to the primary quantities, i.e. it is in the form of (3.53). Hence the mean values of both $\boldsymbol{x}$ and $\boldsymbol{z}$ are equal to the actual (true) values. The vector $\boldsymbol{z}$ has a normal distribution $N_R(\mu_z, \boldsymbol{F}_z)$, where $\boldsymbol{F}_z$ is given by (3.54).

Let us consider first one secondary quantity z with a mean value μ_z. On the assumption that the standard deviation σ_z is known (calculated), the errors of z will, with a probability of $(1-\alpha)$, lie within the interval

$$\langle -\sigma_z\, u_{1-\alpha/2} \;;\; \sigma_z\, u_{1-\alpha/2} \rangle \tag{3.63}$$

where $u_{1-\alpha/2}$ is $100(1 - \alpha / 2)$ percent quantile of the $N(0,1)$ distribution. This information can be interpreted in two ways.

When we know the mean value μ_z , we may affirm that the measured value of a secondary quantity z^+ will, with a probability $(1 - \alpha)$, be present in the interval

$$\langle \mu_z - \sigma_z\, u_{1-\alpha/2} \;;\; \mu_z + \sigma_z\, u_{1-\alpha/2} \rangle \tag{3.64}$$

If the mean value is not known, but on the other hand the value of z^+ has been obtained by measuring, then the interval

$$\langle z^+ - \sigma_z\, u_{1-\alpha/2} \;;\; z^+ + \sigma_z\, u_{1-\alpha/2} \rangle \tag{3.65}$$

covers, with a probability $(1 - \alpha)$, the (unknown) value of the secondary quantity. In technical practice the value $(1 - \alpha)$ - coefficient of confidence - is taken mostly from the interval $\langle 0.95 \;;\; 0.995 \rangle$.

In the first case we were solving a classical problem of the theory of errors propagation. In the second one we used the measured value z^+ to estimate the respective true value and the interval (3.65) for specifying the region within which the unknown true value with a chosen probability occurs.

The above mentioned confidence intervals may be written not only for a single quantity z but also for the individual elements of a vector $\boldsymbol{z}$. It is necessary to be aware of the fact that while the interval (3.63) covers, with a probability $(1 - \alpha)$, the value of z_i error, the same assertion relating to all the errors of the vector $\boldsymbol{z}$ elements simultaneously does not generally hold true. If we want to find a region $\mathbf{S}$ in which the vector of errors $\boldsymbol{e}$ lies with a probability $(1 - \alpha)$, it is necessary to proceed in a different way.

Let us consider a vector of R secondary quantities $\boldsymbol{z}$ whose errors $\boldsymbol{e}$ have an $N_R\,(0\,,\,\boldsymbol{F}_e)$ distribution and the covariance matrix $\boldsymbol{F}_e$ is regular. Now we are searchig for a region for which it holds that the probability of $\boldsymbol{e}$ being there is equal to P. It was shown in the Appendix A.3 [Eqn.(A.43)] that such a region lies within the ellipse (ellipsoid) whose equation is

$$\boldsymbol{e}^{\mathrm{T}}\, \boldsymbol{F}_e^{-1}\, \boldsymbol{e} = \text{const} = \chi^2_P\,(R) \tag{3.66}$$

where $P = 1 - \alpha$ and $\chi^2_P\,(R)$ is the $100P$-quantile of the χ^2 distribution with R degrees of freedom. It is the so called *ellipse of errors* having its centre in the origin of coordinates. In the case of uncorrelated errors, the ellipse axes are parallel to the coordinate system. With correlated errors the ellipses axes contain non-zero angle with the coordinate axes.

Analogically with the intervals of errors (3.63) the ellipses of errors can also be interpreted in two ways. When the ellipse centre is situated in the point $\bar{\boldsymbol{z}}$ we obtain a region within which the measured vectors $\boldsymbol{z}^+$ lie with a probability $(1 - \alpha)$. If the ellipse centre is situated in the point $\boldsymbol{z}^+$, we have a region that covers the true value of the vector $\boldsymbol{z}$ with a probability $(1 - \alpha)$.

Besides, let us note that when constructing the confidence regions, we assumed regularity of the covariance matrix of secondary quantities. If, however, this is not the case, the described method of finding a confidence region cannot be applied. In such a case, the errors lie within a subspace of a lower dimension than is the number of secondary quantities (e.g. with two quantities the errors lie on a straight line, i.e. they are bound by a linear relation). This problem, however, is beyond the scope of this book, and therefore it will not be discussed. We shall state only that even in this case the above method can be used for finding the confidence region for a selected subset of secondary quantities with a regular covariance matrix.

Example 3.12: *Confidence region of mass balance residuals*
Let us consider the steady state mass balance of two nodes incident with three streams (Fig.3.5). The values of x_1 , x_2 and x_3 pertaining to streams 1, 2 and 3, resp. are measured. The following relations hold for the true values

$$\begin{aligned} \bar{x}_1 - \bar{x}_2 &= 0 \\ \bar{x}_2 - \bar{x}_3 &= 0 \end{aligned} \tag{3.67}$$

The balance equations residuals z are defined by

$$\begin{aligned} z_1^+ &= x_1^+ - x_2^+ \\ z_2^+ &= x_2^+ - x_3^+ \end{aligned} \tag{3.68}$$

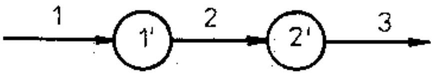


Fig.3.5 — Balance scheme (Example 3.12)

Let us assume that errors of flowmeters are realizations of random uncorrelated variables with a vector of standard deviations $\sigma_x = (1,2,1)^T$. The task is to find a region inside which will lie 95% of all the vectors of the residuals. It follows from (3.67) and (3.68) that mean values of residuals are null. The covariance matrix of residuals may be calculated from (3.54). The matrix $\boldsymbol{C}$ is

$$\boldsymbol{C} = \begin{bmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \end{bmatrix}$$

and the covariance matrix $\boldsymbol{F}_x$ is diagonal with squares of the standard deviations lying on the diagonal. Substituting into (3.54) yields

$$\boldsymbol{F}_z = \begin{bmatrix} 5 & -4 \\ -4 & 5 \end{bmatrix} \qquad \boldsymbol{F}_z^{-1} = \frac{1}{9} \begin{bmatrix} 5 & 4 \\ 4 & 5 \end{bmatrix}$$

According to (3.66) the equation of the confidence elipse is

$$\frac{1}{9} (z_1 , z_2) \begin{bmatrix} 5 & 4 \\ 4 & 5 \end{bmatrix} \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \chi_P^2 (2)$$

which may be rewritten for $P = 0.95$

$$\frac{5z_1^2 + 8z_1 z_2 + 5z_2^2}{9} = 5.991 \tag{3.69}$$

After that we are looking for the ellipse described by (3.69). This task, belonging to the sphere of analytical geometry, is not solved at this point; only the results will be presented here.

It is an ellipse in the centre of the coordinate system that is rotated through - 45°. The length of the major and the minor semi-axis is 7.34 and 2.45, resp. The ellipse is shown in Fig.3.6 together with ellipses for other values of the coefficient of confidence P. In the case that we find in the measurements residuals lying outside this ellipse, we ought to question the validity of our basic assumptions. Thus, we are getting to the problem of detection of gross errors of measurement which will be dealt with in Section 4.5.

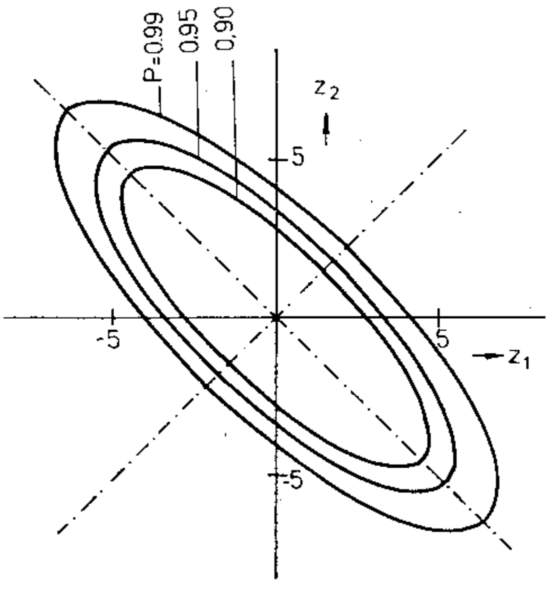


Fig.3.6 — Confidence ellipse of residuals (Example 3.12)

3.3 OBTAINING INFORMATION ON MEASUREMENT ERRORS

When solving the hitherto formulated problems one assumed that the probability properties of the primary quantities errors were known. Gathering information in this respect, however, is not an easy matter. Besides the rigorous statistical procedures, it is necessary in many cases to estimate these data on the basis of theoretical considerations, of analogy with similar cases, and the like.

Next, we shall present a general procedure for ascertaining the probability properties of primary errors. First, it is necessary to define a set of primary variables, and decompose their errors into elementary errors having, if possible, a single cause. Then, it is necessary to find out the probability properties of the elementary errors. One may take advantage of the fact that elementary errors are mostly space uncorrelated. At the same time, it is necessary to judge whether this is a case of random, time correlated or systematic errors. Once such information has been ascertained, it is possible, using the methods of errors propagation, to find the probability properties of errors of secondary quantities.

Further, we will deal with the methods for obtaining information on elementary errors. We shall concentrate upon assessing their variances the knowledge of which is of utmost importance as far as the propagation of errors is concerned. There are usually fewer opportunities for ascertaining the law of distribution (in most cases the normal distribution law is assumed).

3.3.1 Theoretical analysis

In some cases, good results may be obtained by analyzing the process causing the errors. As an example may serve errors that are due to digitization or rounding of continuous signals. On rounding a measured value in such a way that we are losing significant digits, we are committing an error that reaches a maximum value equal to half of the last valid digit order. The distribution of thus generated errors is uniform (rectangular). Errors with uniform distribution are also characteristic of balancing during which accumulation in storage tanks is neglected.

Example 3.13: *Error with uniform distribution*
Let us consider an intermediate storage tank with the horizontal section area of 2 m^2 from which a liquid is being withdrawn continuously for further processing. The tank is refilled intermittently by a pump controlled by a two-position controller of liquid level in the tank. The signal to pump is given when the liquid level in the tank recedes 10 cm below the maximum value (when this maximum level is reached, the pumping is stopped). Since there is no level indicator in the tank, when balancing, we assume that the liquid level is maintained at 5 cm below the maximum value (Fig.3.7a). Obviously, the maximum error in the determination of the liquid level is

0.05 m, and the corresponding maximum error in the determination of volume will be ±(2 × 0.05) = ±0.1 m^3. The error d has a rectangular distribution whose probability density function in accordance with Eqn.(A.33) has the following form:

$$f(d) = 1/0.2 = 0.5 \qquad \text{for } d \in \langle -0.1\ ;\ 0.1 \rangle\ m^3$$
$$f(d) = 0 \qquad \text{in other cases}$$

The distribution function of the error is shown in Fig.3.7b. The mean value of the error is null, and the variance according to (A.35) $\sigma_d^2 = 0.2^2 / 12 = 0.0033\ m^6$, corresponding to the standard deviation of 0.058 m^3. ■

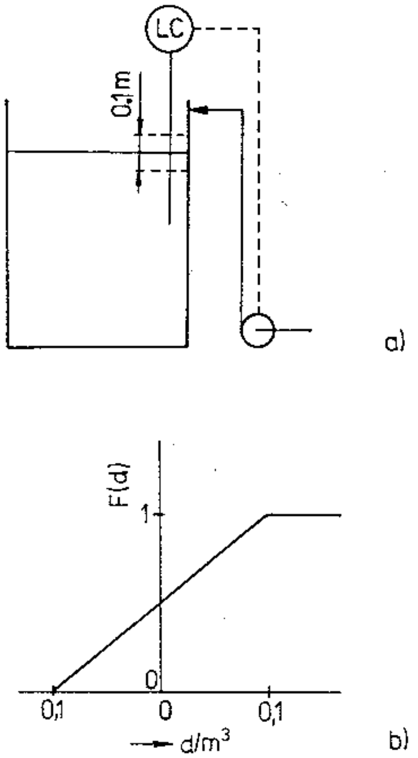


Fig.3.7 — Error in the liquid volume d (Example 3.13)
a) storage tank; b) error distribution function

3.3.2 Random measurement errors

Let us assume that errors are realizations of random variables with zero mean value and an unknown variance. On this assumption, the mean value of a measured quantity is equal to the real (true) value. In the following, the methods for estimating the mean value of a measured quantity and the variance of its error will be presented. These methods provide consistent, unbiased and efficient estimates for errors governed by the normal law of distribution. In principle, they may be applied to errors with other (particularly symmetrical) distributions as well, but at the cost of a certain decline in the estimate efficiency.

Estimation of the mean value

Let us assume that we have a number of measured values of a quantity $\boldsymbol{x}^+ = (x_1^+, \dots, x_n^+)^T$. The estimate of the mean value μ_x is the arithmetic mean $\bar{x}$:

$$\hat{\mu}_x = \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i^+ \tag{3.70}$$

The use of the arithmetic mean is advantageous for other than normal, but symmetrical, distributions as well. With small n, however, it is sensitive to distribution asymmetry (we say that it is not too *robust*).

Therefore, it is recommended for small values of n to estimate the mean value by means of the sample median which represents a value halving the set of experimental results arranged in accordance with their magnitude. In the case of sets with an odd number of elements the middle element is taken as the median, whereas in sets with an even number of elements it is the aritmetic mean of the two middle values.

Median is independent of the marginal values, so it is not sensitive to the presence of outlying results (potential gross errors). As compared with a mean, in the case of normally distributed errors the median is a less efficient estimate, its efficiency decreasing with increasing n. Hence, it is recommended to compare median with the mean; if the two values do not differ markedly, the distribution asymmetry is not too significant and the arithmetic mean may be taken as the estimate of the mean value. If they do differ considerably, however, the distribution probably is asymmetrical and median is taken as the estimate of the mean value.

Estimating the standard deviation

An estimate of the standard deviation σ is so-called *sample standard deviation*, calculated according to

$$\hat{\sigma} = s = \left[\frac{\sum_i (x_i^+ - \bar{x})^2}{n - 1} \right]^{1/2} \tag{3.71}$$

where $(n-1)$ is the number of degrees of freedom. This estimate is consistent and unbiased. But it is only asymptotically efficient, and for a reliable estimate of the standard deviation at least 15 measurements should be carried out.

But in practice such a large number of parallel measurements are usually not available. Where chemical analyses are concerned, there are normally at our disposal analyses of a large number of samples with a small number of parallel determinations of each single sample. Let us carry out analysis of K samples having similar composition and n_k parallel analyses of the kth sample. The arithmetic mean of the values obtained by the kth sample analysis will be denoted as $\bar{x}_k$. The estimate of the standard deviation, using all the measured values, is

$$\hat{\sigma} = s = \left[\frac{1}{\nu} \sum_{k=1}^{K} \sum_{i=1}^{nk} (x_{ik}^{+} - \bar{x}_k)^2 \right]^{1/2} \tag{3.72}$$

where ν is the number of the degrees of freedom, i.e.

$$\nu = \sum_{k=1}^{K} (n_k - 1) \tag{3.73}$$

For the frequent case of two parallel analyses Eqn.(3.72) is simplified to

$$\hat{\sigma} = \left[\frac{1}{2K} \sum_{k=1}^{K} R_k^2 \right]^{1/2} \tag{3.74}$$

where R_k is so-called *span*, i.e. the difference between the two determined values of the kth sample; $R_k = x_{1k}^{+} - x_{2k}^{+}$. The number of degrees of freedom is equal to K.

Elimination of outliers

When repeating the measurements of one quantity, one or more measured values may be considerably smaller or larger than the other values. The statistical procedure enabling judgement of whether this is a case of a measurement containing a gross error is referred to as *elimination of outliers*.

Let us assume that the measured values are arranged according to their magnitude:

$$x_1^+ \le x_2^+ \le .... \le x_n^+$$

The hypothesis H_0 (all the measured values are a sample from normal distribution) is tested against the H_1 hypothesis (the measurement with the highest value, i.e. x_n^+, is a realization of a random variable with a mean value greater than that of the remaining quantities).

In the most frequent case, when the standard deviation is not known, a test criterion z (Grubbs 1950) is calculated:

$$z = \frac{x_n^+ - \bar{x}}{s'} \tag{3.75}$$

where $\bar{x}$ is the arithmetic mean computed from all the values and s' is an estimate of the standard deviation

$$s' = \left[\sum_{k=1}^{n} \frac{(x_i^+ - \bar{x})^2}{n} \right]^{1/2} \tag{3.76}$$

Table 3.2 — Quantiles (z^*) of distribution of quantity
$z = (x_n^+ - \bar{x}) / s'$; P $[z < z^*] = P$

n	P			
	0.99	0.975	0.95	0.90
3	1.414	1.414	1.412	1.406
4	1.723	1.710	1.689	1.645
5	1.955	1.917	1.869	1.791
6	2.130	2.067	1.996	1.894
7	2.265	2.182	2.093	1.974
8	2.374	2.273	2.172	2.041
9	2.464	2.349	2.237	2.097
10	2.540	2.414	2.294	2.146
12	2.663	2.519	2.387	2.229
14	2.759	2.602	2.461	2.297
16	2.837	2.670	2.523	2.354
18	2.903	2.728	2.577	2.404
20	2.959	2.778	2.623	2.447
22	3.008	2.823	2.664	2.486
24	3.051	2.862	2.701	2.520

For testing, we use Table 3.2 in which the critical values z^* are presented for a given number of measurements and significance level. In the case $z^* < z$, the value x_n^+ is eliminated as an outlying one.

A similar procedure would be taken with the smallest value x_1^+, when z is calculated from

$$z = \frac{\bar{x} - x_1^+}{s'}$$

3.3.3 Errors of chemical analyses

Chemical analyses represent an important part of information obtained in measuring performance of chemical plants.

The analytical methods may be divided into absolute (*independent*) methods wherein the result is computed from the measured value and the known weighed amount of the sample, and *comparative* (*dependent*) methods, where a measured quantity is compared with a standard. With the absolute methods (e.g. with the classic gravimetric analysis) mostly good precision (reproducibility) is achieved; however, the methods have to be checked with respect to the occurrence of systematic errors. The dependent methods, among them a number of advanced instrumental methods, are more prone to the emergence of random errors. One should not forget, moreover, the possibility of systematic errors as a result of improperly prepared standards.

A positive feature of analytical methods is that in many cases the method used can be checked from the standpoint of systematic errors of measurement. That is to say - by employing a rigorous method (although it may be more tedious) it is generally possible to find the composition of a sample with an error that is negligible or to prepare a model sample whose composition is exactly known. An essential element for obtaining satisfactory results is the whole range of problems associated with random errors of measurement. Therefore, in the next part we shall confine ourselves to the problems of random errors (to the topics of precision of analyses), and to an evaluation of analytical methods from the standpoint of the occurrence of systematic errors.

The space that can be devoted to this important problem is limited and, therefore, it will not be possible to discuss a number of aspects which deserve attention. It is possible to recommend to readers the monograph by Doerffel & Eckschlager (1981), devoted to these problems.

The *reliability* of an analytical method is characterized by two aspects: the relation between the mean and real (true) values (question of the accuracy of the method) and variance (question of precision of the method). The procedure of assessing an analytical method should be roughly such as shown below.

Let us assume that we have a homogeneous sample whose composition is accurately known (either a standard or a sample analyzed by a rigorous, standard method). A number of parallel analyses is carried out with this sample. The data obtained are used for computing the estimates of the mean value and variance. In the next step, we use the statistical test for finding out whether the mean value is equal to the real (accurate) value. If it is not so, the method is subject to a systematic error and must be improved.

If there is no reason to presume the presence of a significant systematic error, we shall consider whether the precision of the method as expressed by an estimate of its variance satisfies our requirement. If the answer is "yes", the method can be used and we may assume that it is subject only to random errors with approximately known variance. In most cases, too, we can take it for granted that the distribution of errors is normal.

To estimate the mean value and variance, we use the relations presented in the preceding Section. The variance of an analytical method is ascertained from the values of parallel analyses as obtained either during day-by-day regular analyses or on the basis of a special measurement effected just for this purpose. It is necessary to ascertain that the analyses are subject to all errors which actually affect the result.

Random errors connected with sampling and pre-treatment of the sample are often on a par with the error of the analytical method itself. It is not permissible to assess the variance taking a single sample, pre-treat it as necessary and carry out a number of "parallel" determinations with thus prepared homogeneous sample. It is necessary to take several samples, pre-treat them separately and then analyze them. Hence we obtain an estimate of variance that will be conclusive for us (and will often differ markedly from the variance of the analytical method itself).

Comparing the mean with anticipated value

The accuracy of a method (i.e. absence of a systematic error) is evaluated by comparing the mean with the value we believe is accurate. In most cases, a hypothesis H_0 ($\mu_x = \tilde{x}$) is tested against the hypothesis H_1 ($\mu = \tilde{x} + a$) where a is a systematic error. The testing is carried out with the aid of the Student t-test.

The value of statistic t is calculated

$$t = \frac{\bar{x} - \tilde{x}}{s} \sqrt{n} \qquad (3.77)$$

where $\bar{x}$ and s are calculated according to (3.70) and (3.71). The statistic t has a t-distribution with (n-1) degrees of freedom (n is the number of parallel analyses used in the estimation of the standard deviation). Further, it is tested whether t originates from the given t-distribution.

We choose the significance level of the test α that is equal to the probability of a 1st kind error. The value of t is then compared with the (1 - α/2) percent quantile of the distribution t with (n-1) degrees of freedom. If it holds

$$|t| < t_{1-\alpha/2}\,(n-1) \qquad (3.78)$$

we reject the alternative hypothesis H_1 and further assume that no systemetic error is present. In the opposite case, the method is most probably subject to a systemetic error.

When testing the significance of the difference between the mean and true values we have to realize that the test can detect only systematic errors that are big enough. In statistical tables (Himmelblau 1970) the power of the test curves of the

t-test are presented indicating the probability of detecting a systematic error as a function of its magnitude.

Comparing the precision of two methods

Sometimes it is necessary to decide which of the analytical methods A and B is more precise or reproducible. In this case usually a hypothesis of equality of two variances [H_0 ($\sigma_A^2 = \sigma_B^2$)] is tested using the so-called F-test.

Let us assume that we have the estimates of variances of two analytical methods computed from parallel analyses according to (3.71). The number of the parallel analyses n_A and n_B need not necessarily be identical.

Now let the estimates of the variances be s_A^2 and s_B^2 , and let it hold that $s_A^2 > s_B^2$. Statistics F, i.e.

$$F = s_A^2 / s_B^2 \tag{3.79}$$

is the realization of a random variable with F-distribution with (n_A - 1) and (n_B - 1) degrees of freedom. The value of F is compared with the (1-α) percent quantile of the distribution F (n_A - 1 , n_B - 1). If it holds

$$F < F_{1-\alpha} (n_A - 1 , n_B - 1) \tag{3.80}$$

the difference in the precision of the two methods is not significant. In the opposite case we reject the hypothesis of variances equality and consider the method B more precise than the method A.

3.3.4 Errors of measuring instruments

Similar to errors of analyses, errors of measuring instruments can be divided into random and systematic. Contrary to the preceding case, however, here the problems of systematic errors are of key importance which makes the application of the methods of mathematical statistics difficult.

A fight against systematic errors is essential for minimizing errors of measuring instruments. For this purpose we are using calibration, adjustment and correction of measurement readings. The *calibration* is an empirical ascertaining of data as read on the instrument. By measuring a series of standards we obtain a so-called *calibration curve* (or table) which is then used for transforming the instruments readings into accurate values. *Adjustment* (*gauging*) of an instrument means its adjusting in such a way that the data on the scale corresponds with the reality. By *corrections* (*compensations*) we mean such amendments to the instrument readings that would compensate for not observing the prescribed measurement conditions. In spite of all the above provisions, in many important cases we are not able to eliminate all systematic errors substantially affecting the accuracy of the measurement results.

Example 3.14: *Correcting the readings of orifice gauges*
Measuring of the flow rates of liquids is frequently effected by means of orifices. We are often confronted with a problem of correcting the readings of a measuring instrument situated in a control room. In the following, we shall confine ourselves to correcting the reading of the orifice proper (after making sure that the signal transmission to the control room is in order).

The mass flow rate through an orifice gauge F is given by the relation (Benedict 1977)

$$F = \alpha\, \varepsilon\, \frac{\pi}{4} D^2 (2\rho\, \Delta p)^{1/2} \tag{3.81}$$

where α is the overall flow rate coefficient, ε - expansion coefficient, D - diameter of orifice opening (m), Δp - pressure difference on the orifice (Pa), ρ - density before the orifice (kg m^{-3}).

When deviations from the designed values of temperature, pressure or density at standard conditions occur, their influence on the values α, ε and D may be neglected in most cases, and these values may be considered constant. Then the relation (3.81) can be simplified to give

$$F = k\, (\rho\, \Delta p)^{1/2} \tag{3.82}$$

If we are interested primarily in measuring the volume flow rate (when measuring gas streams), it holds

$$V_n = \frac{F}{\rho_n} = \frac{k}{\rho_n} (\rho\, \Delta p)^{1/2} \tag{3.83}$$

where ρ_n is the density at standard conditions (in practice so-called "normal conditions", i.e. t = 0 °C and p = 101.3 kPa are being used almost exclusively), V_n - volume flow rate at standard conditions (m^3 s^{-1}).

Let us assume that a measuring system is without any automatic correction. In the project of the measuring system two quantities are considered - real density on the orifice ρ and density under standard conditions ρ_n . Usually both these values are given in the project documents. A reading of the flow rate V_n on the measuring instrument, being a mere transformation of the pressure difference Δp, is accurate only if the true values of ρ_n and ρ are in agreement with those given in the project documentation. When these values are different, however, a correction factor k_1 must be introduced:

$$k_1 = \left[\frac{\rho}{\rho_{\mathrm{proj}}} \right]^{1/2} \frac{\rho_{\mathrm{n,\,proj}}}{\rho_{\mathrm{n}}} \tag{3.84}$$

where the subscript proj designates a value specified in the project documentation. The correct value of a flow rate $V_{\mathrm{n,\,cor}}$ is then obtained from

$$V_{\mathrm{n,\,cor}} = k_1\, V_{\mathrm{n}} \tag{3.85}$$

The relation (3.84) represents a general form of correction and it incorporates corrections for not observing the project values of temperature and pressure and for changes in density due to changes in compositions. At the same time also an error caused by an incorrect value of the project density can be corrected (i.e. when a gas with a certain project value of standard density fails to reach the value of density on the orifice at the project values of pressure and temperature). If the latter type of error can be eliminated, for gases the relation (3.84) may be simplified to the less accurate but more frequent form

$$k_1 = \left[\frac{\rho_{\mathrm{n,\,proj}}}{\rho_{\mathrm{n}}}\; \frac{p}{T}\; \frac{T_{\mathrm{proj}}}{p_{\mathrm{proj}}} \right]^{1/2} \blacksquare \tag{3.86}$$

Static and dynamic error

With instruments measuring continuously it is important to divide errors into static and dynamic ones.

When measuring under steady state (static) conditions we assume that there exists a certain dependence between the measured quantity (x_{m}) and the measurement output value x_{v} . It is e.g. a case of the relationship between the pH value of a solution and voltage on the measuring electrode or deflection on a voltmeter measuring that voltage. At the same time, we assume that in the absence of measuring errors we obtain an exactly valid, correct correlation between the input and output quantities. We may come close to such a correct dependence if the whole measurement is performed with particular attention (all disturbing effects are eliminated). By the term *static error of measurement*, we mean the difference between a dependence existing under current conditions of measuring and the correct dependence. The magnitude of the static error depends on the conditions of the measurement proper as well as on the value of the measured quantity (Fig.3.8). Hence, a static error is defined as the difference between the measured value and the respective true value.

A *dynamic error* is generated when quantities varying in time are measured. It originates as the result of the real relationship between the measured and output quantities depending on the rate at which the measured quantity changes. The

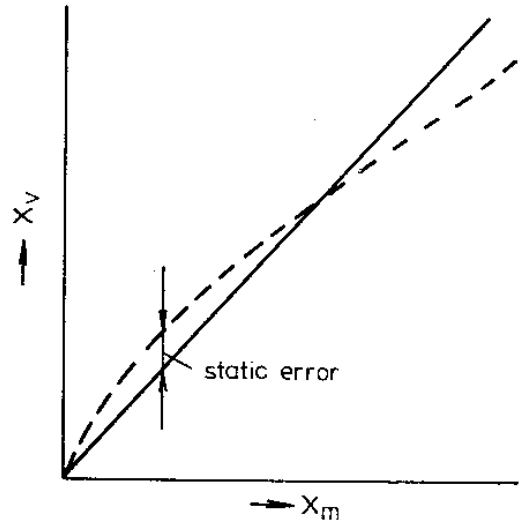


Fig.3.8 — Output of measuring instrument x_v as a function of measured quantity x_m
—— correct output; - - - real output

dynamic error is defined as the difference between the total and static errors. If the conditions of a measurement are not specified in greater detail, it is assumed that the measured value is changing at a constant rate.

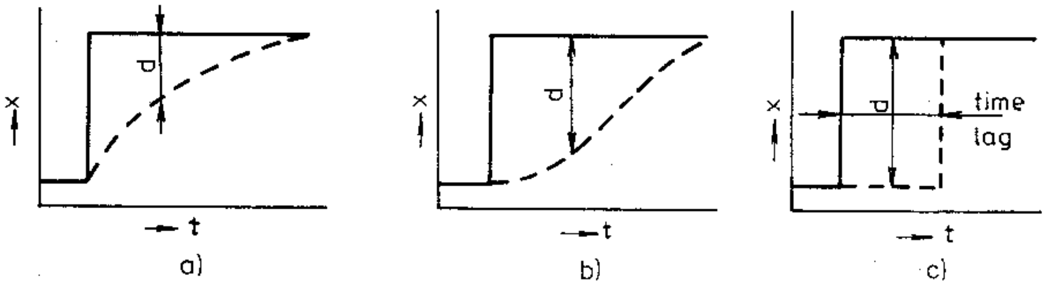


Fig.3.9 — Dynamic errors *d*
a) system of 1st order; b) system of 2nd order; c) time lag
—— measured quantity; - - - output of measuring instrument

Fig.3.9 shows some examples of the course of dynamic error. The first example demonstrates a response to a jump in the measured quantity, while the output quantity is changing in accordance with the transition curve of the first order system. The dependence between the input and output can be expressed as

$$x_v = 1 - \exp(-t / \tau)$$

where t is the time and τ is so-called *time constant* of the transition process (its numerical value is equal to the time during which the output quantity reads 63% of the steady state value). Roughly such is the course of readings of a thermometer without the thermowell. The delay in the output behind the course of the ambient temperature is caused by the thermal capacity of the thermometric sensor itself.

When the thermometer is placed in a well filled with a heat-conducting liquid, the response of the thermometer reading to a temperature jump can be described by the transition curve of the 2nd order system (Fig.3.9b).

Sometimes we meet with the occurrence of a transport delay which manifests itself in a way as shown in Fig.3.9c (so-called *time lag*). Transport delay is typical for the function of some automatic analyzers, particularly of process chromatographs.

We shall further concentrate our attention upon the problems of static errors.

Causes of errors of measuring instruments

Errors of measuring instruments may be caused by a number of factors. *Error of the method* is encountered in the case of indirect measurements and it is due to the fact that not all of the quantities influencing the reading of a measuring instrument are respected. In most cases these errors are systematic and since we can often calculate their magnitude, they can be, at least in part, eliminated by a correction (e.g. errors in weighing due to different buoyancy of air acting upon the weighed object). Those variables which influence the instrument reading but themselves are not measured by the instrument are referred to as *influencing variables.*

Error of measuring instrument is caused by an imperfection of the measuring instrument (unbalance of mechanical parts, friction, and the like). Certain elementary errors have a random character and some have a systematic character. The maximum error of a measuring instrument is guaranteed by the so-called *class of accuracy* of the measuring instrument (see below).

Errors caused by interferences are due to the action of various interfering effects within the measuring circuit. This may be a case of voltage fluctuations in the electric network, pressure fluctuations in the pneumatic control system, influence of external magnetic fields, and the like.

Errors of reading are caused by the operator who records the readings of a measuring instrument. Most often it is a matter of an incorrect reading and interpolations (particularly with multichannel recorders), errors resulting from not observing the appointed time of reading on integrating meters, etc.

Errors in standards occur when incorrect standards are used for the calibration of instruments (e.g. when adjusting gas analyzers by means of a calibration gas mixture).

As regards the dependence of an error on the magnitude of the measured quantity, the above causes of errors show themselves in various ways. Some typical dependences of the magnitude of a static error of measurement on the magnitude of the respective measured quantity are shown in Fig.3.10.

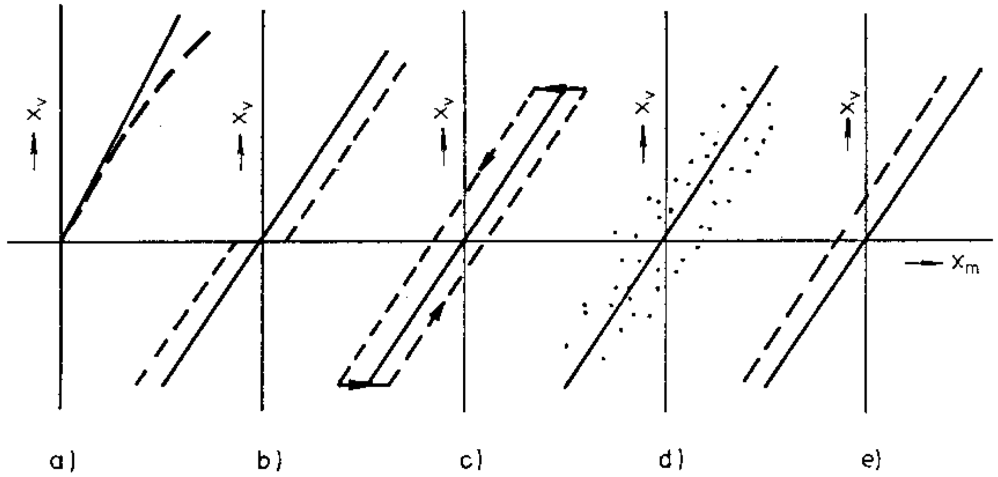


Fig.3.10 — Output of measuring instrument x_v as a function of measured quantity x_m
a) nonlinearity; b) low sensitivity; c) hysteresis; d) poor reproducibility; e) drift
——— correct output; - - - real output

Systematic deviations of the measuring instrument reading from the true value are a typical example of an error of measuring method or of the measuring instrument error. This may be a case of a moderate nonlinearity of the dependence between the measured quantity and the measuring instrument reading which for various reasons has not been respected by the manufacturer.

Error caused by low sensitivity of a measuring instrument has the character of a constant deviation between the true and measured values.

Hysteresis shows itself as an error of different sign depending on whether the measured quantity is increasing or decreasing. The reason may be e.g. excessive friction in the measuring instrument mechanism. A trivial but still rather frequent reason for this type of error can be the loosening of the writing tool of the plotter.

Zero shift (drift) with time usually is an accompanying phenomenon of measuring with electronic instruments.

Poor reproducibility, i.e. prevailing influence of random errors of measurement. This kind of error is not typical of measuring instruments. If such a case occurs, the whole measuring chain has to be checked and the fault identified (defect of a sensor, etc.).

Assessing the maximum possible error of a measuring instrument

The maximum possible error of a measuring instrument is best assessed from the class of accuracy of the instrument. *Class of accuracy* (CA) is defined as the ratio (in percent) of the maximum permissible error of an instrument to its measuring range. The maximum absolute error of a measuring instrument e_{max} is given by the relation

$$e_{\max} = \frac{X}{100}\,\mathrm{CA} \tag{3.87}$$

where X most frequently is the measuring range of the instrument. In some cases (presented below) either the measured value or length of the instrument scale is substituted for X in (3.87). When the instrument scale does not begin with zero (instruments with suppressed zero), sometimes the scale range, i.e. difference between the maximum and minimum values on the scale, is substituted for X into (3.87). The maximum error of a measuring instrument, as calculated from the class of accuracy, is sometimes called the *tolerance* of the instrument.

Example 3.15: *Maximal error of a measuring instrument*
Let us consider a measurement of electric current with an ammeter whose class of accuracy is 1.5 and the measuring range 10A. The measured value is 8A. The maximum possible error $e_{\max}$ is

$$e_{\max} = \frac{10}{100} \times 1.5 = 0.15\mathrm{A}$$

The maximum relative error of measurement for the value of the measured quantity at 8A is 0.15 × 100/8 = 1.875%. If we measured the current at 2A, the maximum relative error now would be 0.15 × 100/2 = 7.5% of the measured value. Hence in practice we try to select an instrument so that the reading is in the last third of its measuring range.■

The class of accuracy represents a guarantee by the manufacturer that the absolute error of measurement under specified conditions will not exceed the maximum error as calculated from (3.87) in any instrument and over the whole measuring range.

The conditions of measuring (so-called *reference conditions*) are given by the manufacturer of the instrument in the form of permissible values of influencing quantities. Among these belong the values (or ranges of values) of ambient temperature, air pressure and moisture, voltage and frequency in electric wiring, position (angle of inclination) and, as the case may be, also other values. The maximum error as expressed by the class of accuracy incorporates both systematic and random errors. Therefore, the reproducibility of a measuring instrument usually is better than that corresponding to the given class of accuracy. Unfortunately, in most cases the share of a systematic error on the class of accuracy is not known. Some producers may give a higher value of the class accuracy deliberately to avoid possible claims. On the other hand, sometimes the reverse is the case, e.g. with unique instruments when the user cannot be certain of the guaranteed class of accuracy.

An important term is the *additional* (*supplementary*) error. In some cases the manufacturers give the magnitude of additional errors generated as a result of the differences between the actual and prescribed conditions of the measurement. Sometimes corrections are given, corresponding to a certain change in the influencing variable (e.g. change in the instrument reading due to a 10 °C rise in ambient temperature). In such a case a correction of the instrument reading can be done, thus eliminating the measuring error caused by a change in the influencing variable. Sometimes only the absolute value of additional error is given without the respective sign. Such information serves only for increasing the tolerance that follows from the class of accuracy of the measuring instrument. In some cases both a correction and increase of the tolerance are put into effect.

The class of accuracy concept is well elaborated in the measuring of electrical variables, for which also the respective standards have been drawn up. The situation is less clear, however, in the case of non-electrical variables which is rather common in process industries. With some instruments the manufacturers give the maximum relative errors that have the character of maximum errors as calculated from the class of accuracy according to (3.87). But it is not always clear, whether the maximum error is related to the instrument range or to the measured value.

Many times we meet with the task of assessing the maximum error of measuring a flow rate with standard throttle devices (centric orifice, nozzle, Venturi tube). The question of the maximum error of measurement is solved in the respective standards by employing the tolerance by which the maximum error is understood. The standard presents, on the one hand, the basic tolerances for flow rate measurements if all the conditions as prescribed by the Standard are satisfied and, on the other hand, additional tolerances for not observing some of the prescribed conditions. Also, a method for calculating an overall tolerance from partial tolerances is given here.

Errors of complex measuring systems (chains of instruments)

So far, we have been concerned with errors of individual instruments which can be largely delimitated by the class of accuracy of the respective instrument. With the development of the measuring technique, the instruments are becoming more sophisticated, and they are designed as a more or less complex kit built-up from lower elements and subsystems. Therefore, the manufacturer is not always able to give the class of accuracy of the whole measuring system since such a system is most frequently created by the designer of the measuring and control system. Shown as an example in Fig.3.11 is the block diagram of a balancing gas flowmeter fitted with corrections for the deviations of gas temperature, pressure and density [see also the correction equation (3.86)].

If we want to assess the total error of a more complex measuring system we may, in principle, start from findings of the errors propagation theory. From the block diagram of the instrument we learn in which way errors are generated in the individual elements, how they propagate and how they ultimately manifest themselves in the result of measurement.

Finally, we face a problem of how to calculate the total error from elementary errors. In practice we sometimes meet with so-called *method of guaranteed tolerances*, giving the total maximum error as a sum of elementary maximum errors. This method guarantees that the real error will be smaller than the calculated error even if the tolerances of the individual elements of the measuring system are utilized (the most pessimistic case). It is obvious, however, that the tolerances of all the elements of the measuring system usually are not fully utilized provided that the prescribed conditions of the measurement have been satisfied. Also, errors may occur with a different sign so that their compensation takes place. For the above reasons, the method of guaranteed tolerances gives rather pessimistic results.

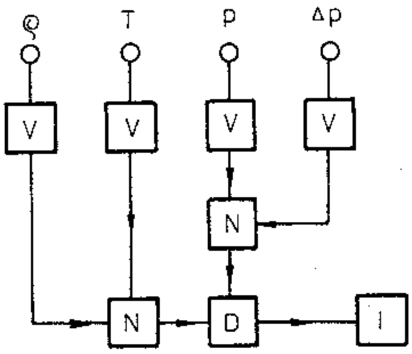


Fig.3.11 — Block diagram of balance measurement
ρ - density; T - temperature; p - pressure;
Δp pressure drop; V - transmitter;
N - multiplicator; D - divider;
I - square rooting and integration

It is more plausible to see errors of measuring instruments as realizations of random variables. It has been known that a number of errors of measuring instruments fluctuate around zero and have a random character. To these errors belong e.g. unknown drift, error in the amplifiers gain, and in some cases, error due to fluctuations of the voltage. Almost non-random are those of errors which exhibit the property of hysteresis (the sign of the error depends on the direction of the measured variable change), nonlinearity and dynamic errors. In many cases errors of this type can be corrected.

For practical purposes, a method for the calculation of the total maximum errors, presented below, may be recommended. With errors having a random character the total error is calculated using the random errors propagation method (see Section 3.2). Then absolute values of non-random errors (unless they have been eliminated by a correction) are added to this total error.

There is one more question to be answered: how to carry out the calculation of random errors propagation (for which the knowledge of variances is required) when classes of accuracy (or tolerances) of the individual instruments are known? To be able to ascribe explicitly a variance or standard deviation to a maximum error, the knowledge of the law of the measuring instrument errors distribution would be necessary. Unfortunately, in this respect the information available is rather scanty. For example, the distribution of the time and temperature drift of an operational amplifier was investigated (Sula 1971). It was stated that the distribution of the drift was normal but approximately. Moreover, it is usually not known to what extent the manufacturer utilized the permissible range as given by the class of accuracy of the respective instrument. It is plausible, however, to agree with the author's recommendation to take the standard deviation at one third to one half of the maximum error as calculated from the class of accuracy. This procedure is roughly satisfactory in the case of errors governed by the normal law of distribution (with the coefficient of confidence 0.95 - 0.99).

3.3.5 Errors of measurement of fluctuating variables

If a measured variable fluctuates and we try to measure its mean value, an error originating in the fluctuation proper appears in addition to the errors of the measuring instrument. Such an error is caused by the limited time of measuring (averaging) of the fluctuating variable. The problem of measuring the mean value of a fluctuating variable may be regarded as one of assessing the mean value of a stationary random process (Livshic & Pugatschev 1963, Kharybin 1957), see Sections A.3.6 and 2.4.

Let us assume that a variable $z(t)$ fluctuating with time is measured for a period of time t_m. The estimate of the mean value of variable z, i.e. μ_z, is its mean integral value m_z

$$m_z = \frac{1}{t_m} \int_{-\infty}^{+\infty} z(t)\, \mathrm{d}t \tag{3.88}$$

In the case that $z(t)$ is a realization of an ergodic stationary process, the following relation can be derived (Livshic & Pugatschev 1963) for the variance of the quantity m_z:

$$\hat{\sigma}_m^{\,2} = \frac{1}{t_m} \int_{-\infty}^{+\infty} \left[1 - \frac{t}{t_m} \right] R'(t)\, \mathrm{d}t \tag{3.89}$$

where $R'(t)$ is a centered autocorrelation function of a random process (see Section 2.4). For certain forms of the autocorrelation function Eqn.(3.89) can be integrated analytically. E.g. for a frequent case of the autocorrelation function as given by

$$R'(t) = \sigma^2 \exp(-\alpha\, |t|) \cos(\beta\, t) \tag{3.90}$$

we then obtain after substituting $R'(t)$ into (3.89) and integrating, the relation

$$\frac{\sigma_m^2}{\sigma^2} = \frac{1}{At_m}\left\{1 - \frac{1}{At_m}[1\text{-exp}\,(-At_m)]\right\} + \frac{1}{Bt_m}\left\{1 - \frac{1}{Bt_m}[1\text{-exp}\,(-Bt_m)]\right\} \tag{3.91}$$

where $A = \alpha + \beta j$; $B = \alpha - \beta j$ (j being the imaginary unit for which it holds $j^2 = -1$).

In so doing, we obtain the result as a ratio of the variance σ_m^2 and variance of the fluctuating variable proper σ^2. If we measure the value of the fluctuating variable at a certain instant of time, this value is realization of a random variable with variance σ^2, which is the physical meaning of the parameter σ in (3.90). The longer the fluctuating variable is averaged, the smaller the variance of thus obtained estimate of the mean value will be. Therefore, the ratio σ_m^2/σ^2 always is smaller than 1.

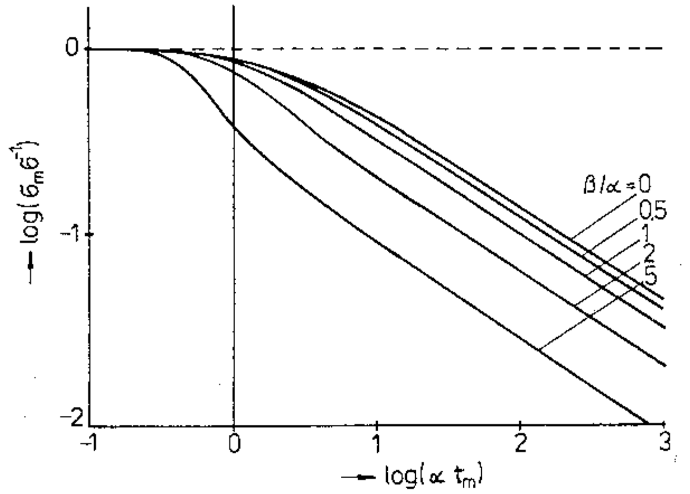


Fig.3.12 — The ratio σ_m σ^{-1} as a function of measurement interval t_m and of parameters α and β

In Fig.3.12 is demonstrated the dependence of the ratio σ_m^2/σ^2 on the quantity αt_m for different values of the ratio of parameters β/α. The following conclusions may be arrived at from Fig.3.12: the standard deviation σ_m is decreasing while increasing the time of measuring t_m and the value of frequency β. For small values of the ratio t_m/α the value of σ_m is equal approximately to the standard deviation of a random process σ. For $t_m \rightarrow \infty$ the ratio σ_m/σ tends to be zero.

In (Kharybin 1957) an even more general case is being solved, i.e. when the autocorrelation function has the form

$$R(t) = a_0^2 + \sum_i \frac{a_i^2}{2} \cos(\omega_i\, t) + c\, \exp(-\alpha\, |t|) \cos(\beta\, t) \tag{3.92}$$

where a_i , c and ω_i are parameters of the random process. It is necessary to point out that this case is not a purely random process since the autocorrelation function (3.92) describes a process which represents the superposition of a random and deterministic polyharmonic process. Hence the given procedure may also be applied to the measurement of the mean value of a deterministically fluctuating variable. Here the randomness of the determination of a mean value lies in the fact that we do not know the phase of harmonic fluctuation in advance.

Example 3.16: *Error of the determination of concentration in a mixture with fluctuating composition*

The statistical properties of fluctuations in the flow of ammonia were examined in Example 2.4. The following autocorrelation function of fluctuation around the mean value 1298 $m^3\ h^{-1}$ was found there:

$$R'(t) = 7.93^2 \exp(-0.283t) \cos(0.267t) \tag{3.93}$$

In the next step the stream of ammonia is mixed with air and fed into an oxidation reactor. The air flow rate virtually does not fluctuate; its value is 9930 $m^3\ h^{-1}$. During the mixing of the gases, backmixing may be neglected causing direct fluctuations in the gas mixture composition.

The mixture is analyzed by taking a sample into a flask and by subsequent chemical analysis. The standard deviation of the determination proper is 0.043 vol.%. This value was found on the basis of a greater number of parallel determinations of a prepared gas mixture. It is necessary to specify the time interval of taking a sample in the flask so that the standard deviation due to fluctuation is less than one half of the standard deviation of the chemical analysis proper (i.e. 0.0215 vol.%).

Let us denote the volume flow rate of ammonia by subscript 1 and volume flow rate of air by subscript 2. The volume fraction (almost equal to mole fraction) of ammonia in the obtained mixture φ_1 is given by

$$\varphi_1 = \frac{V_1}{V_1 + V_2} \tag{3.94}$$

where V_i are the respective volume flow rates. For the deviation of φ_1 from the mean value the following relation holds approximately

$$\Delta \varphi_1 = \frac{\partial \varphi_1}{\partial V_1} \Delta V_1 \tag{3.95}$$

where ΔV_1 is the deviation of V_1 from the mean value. The partial derivative of the function (3.94) is expressed numerically for the mean value of $\bar{V}_1$. On substituting (3.94) into (3.95) we obtain

$$\Delta \varphi_1 = \frac{V_2}{(V_1 + V_2)^2} \Delta V_1 = 7.90 \times 10^{-5} \Delta V_1 \tag{3.96}$$

Fluctuation of the flow rate V_1 is thus transformed roughly linearly into fluctuation of the concentration φ_1. As a result, the autocorrelation function of fluctuation in concentration φ_1 differs from the autocorrelation function (3.93) only in the standard deviation. It holds for the parameter σ in Eqn.(3.90) or (3.93) for the individual fluctuating variables

$$\sigma_\varphi = 7.90 \times 10^{-5}\, \sigma_{V_1} = 7.90 \times 10^{-5} \times 7.93 = 6.26 \times 10^{-4}$$

Thus the centered autocorrelation function of fluctuation of ammonia concentration is

$$R'(t) = 6.26^2 \times 10^{-8} \exp(-0.283t) \cos(0.267t) \tag{3.97}$$

It is a case of the model (3.90) with parameters

$\varphi = 6.26 \times 10^{-4}$
$\alpha = 0.283\ \mathrm{s}^{-1}$
$\beta = 0.267\ \mathrm{s}^{-1}$

Now the problem can be solved with the aid of Fig.3.12. According to the problem statement the value of the standard deviation must be less than 0.0215 vol. % . The ratio σ_m/σ is then $2.15 \times 10^{-4}/6.26 \times 10^{-4} = 0.343$, the ratio $\beta/\alpha = 0.267/0.283 = 0.94$. From Fig.3.12 $\alpha t_m = 7.55$ is found, the corresponding value of t_m being 27s.

In conclusion, it may be stated that if we want the standard deviation of the error in the determination of the mean value of concentration as caused by fluctuation to be less than a half of the standard deviation of the chemical analysis proper, the gas sampling must take at least 27 seconds.■

Another important problem that may be solved with the aid of the theory of stationary random processes is assessing the precision of the determination of the mean value of a fluctuating variable from values as measured in a series of equally distant instants of time. This task may be formulated as an estimation of the standard deviation of determination of a time series mean value (Livshic & Pugatschev 1963).

Let us assume that a fluctuating variable $z(t)$ is not measured continuously, but only at instants of time t_v , $2t_v$,..., nt_v , and thus the values z_1^+ , z_2^+ ,..., z_n^+ are obtained. Obviously it holds among the interval of sampling t_v , total time of measuring t_m and the number of measured values n that $t_m = nt_v$. The estimate of the mean value μ_z is the arithmetic mean m_z :

$$\hat{\mu}_z = m_z = \sum_{i=1}^{n} \frac{z_i^+}{n} \tag{3.98}$$

Now let us concern ourselves with the variance σ_m^2 of the mean value as estimated in this way. The variance σ_m^2 will depend on the interval of sampling t_v , total time of measurning t_m , the number of measured values n and on the form of the autocorrelation function of the random process in question. We feel intuitively that the precision of a mean value estimated on the basis of discrete measurement will be lower than the mean integral value (3.88) of continuous measurement over the same period of time t_m .

A quantitative relation has been derived (Livshic & Pugatschev 1963) for the dependence of σ_m^2 on the values t_v and n, and on the centered autocorrelation function $R_z'(t)$:

$$\sigma_m^2 = \frac{R_z'(0)}{n} + \frac{2}{n} \sum_{k=1}^{n-1} R_z'(kt_v) - \frac{2}{n^2} \sum_{k=1}^{n-1} kR_z'(kt_v) \tag{3.99}$$

The relation (3.99) is an analogy of (3.89) from which it would be obtained by using summation instead of integration. The importance of Eqns (3.89) and (3.99) lies in the possibility in comparing the precision of two alternative methods for measuring the mean values of fluctuating variables - integration of a continuous signal or summation of values of discrete readings. For the case of the autocorrelation function

$$R'(t) = \sigma\, 2\exp(-\alpha\, |t|) \tag{3.100}$$

Eqn.(3.99) may be rearranged to give

$$\sigma_m^2 / \sigma^2 = \frac{1}{n} + \frac{2}{n\,[\exp(A) - 1]^2} - \frac{2\exp(A)[1 - \exp(B)]}{n^2\,[\exp(A) - 1]^2} \tag{3.101}$$

where $A = \alpha t_v$ and $B = \alpha t_m$.

Fig.3.13 shows the dependence of σ_m / σ on αt_m , αt_v being the parameter. For low values of the parameter αt_v (high density of sampling), the dependence comes near to that in Fig.3.12 for $\beta/\alpha = 0$. As may be expected, the precision of the mean value measurement for a constant α is increasing with rising t_m and decreasing t_v (except for the regions with low values of αt_m and αt_v , where σ_m is limiting to σ).

Obviously the dependences in Fig.3.13 have significance only with natural n. The condition $n > 1$ also sets a limit to the range of the dependencies in the diagram.

It is instructive to observe the ratio of the precision of measuring by integration of continuous signal and by averaging of discrete readings (further distinguished by second indexes s and d, respectively). In Fig.3.14 is demonstrated the dependence of the $\sigma_{md} / \sigma_{ms}$ ratio on αt_m , the parameter being αt_v . The dependence was obtained by combining (3.99) and (3.101). It can be seen here that, in the given region and at

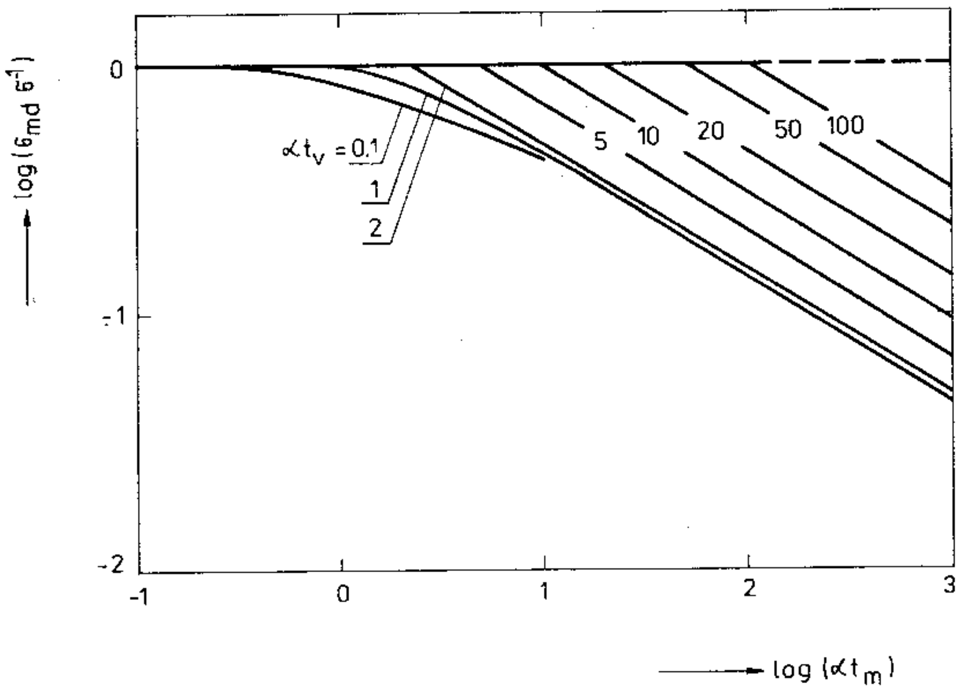


Fig.3.13 — Dependence of the ratio σ_{md} / σ on the time interval of mesurement t_m, interval of sampling t_v and the parameter α

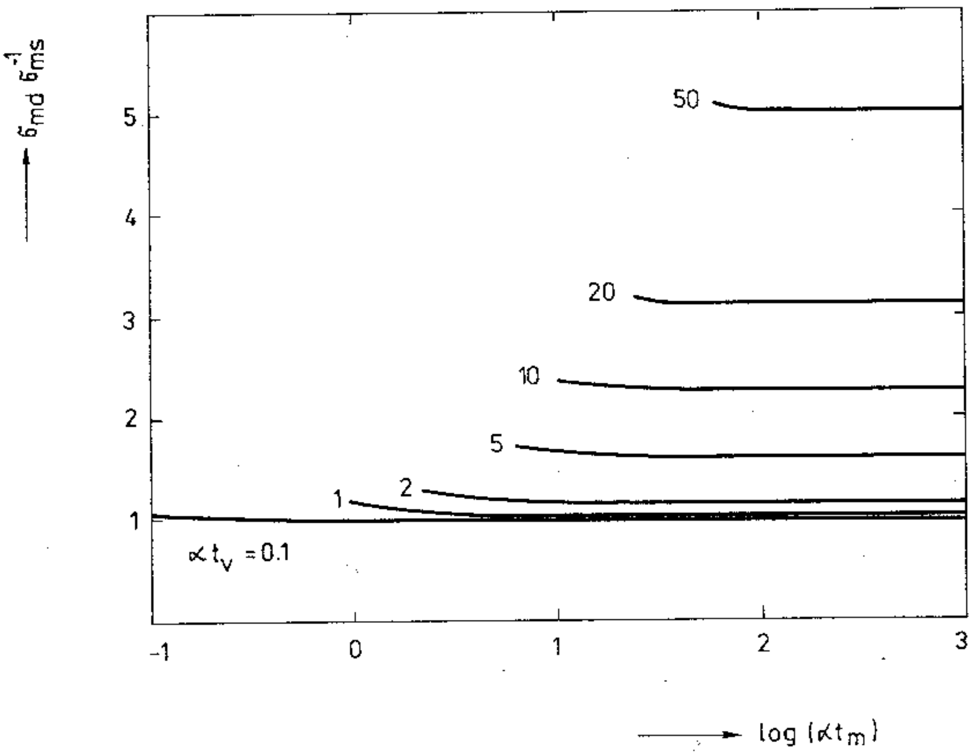


Fig.3.14 — Dependence of the ratio σ_{md} / σ_{ms} on the time interval of mesurement t_m, interval of sampling t_v and the parameter α

a constant value of α, the two measuring methods differ particularly in dependence on the value of t_v , whereas the dependence on t_m is considerably less pronounced.

Example 3.17: *Measuring losses of ammonia in waste waters*
When setting up a material balance of a nitrogenous fertilizer plant it is necessary to measure the mean concentration of ammonia in the stream of waste water leaving the plant. Ammonia concentration in the waste water is fluctuating considerably; as found by preliminary measurements, the standard deviation of fluctuation in concentration was 55 g NH_3 m^{-3} at the mean value of 130 g m^{-3}. The fluctuation can be characterized by the autocorrelation function

$$R'(t) = 55^2 \exp(-0.0427\ |t|\ ) \tag{3.102}$$

which is the model (3.100) with parameters

$$\sigma = 55 \text{ g NH}_3 \text{ m}^{-3}$$

$$\alpha = 0.0427 \text{ h}^{-1}$$

According to the plan of measurement it is assumed that samples of the waste water will be taken at eight hour intervals and analyzed in a laboratory. It is necessary to fix the requisite time of measurement, so that the standard deviation of the error as caused by fluctuation in concentration would not be higher than the standard deviation of the respective analytical method, which is 10 g m^{-3}. Further, it is necessary to consider, whether it would not be possible to shorten substantially the time of measurement by more frequent sampling (e.g. to use 4-hour interval) or by using a continuous automatic analyzer. The problem is solved with the aid of the diagram 3.13. The required standard deviation of the error in assessing the mean value as arithmetic mean of discrete readings σ_{md} is 10 and $\log(\sigma_{md} / \sigma) = \log(10/55) = -0.740$ $\alpha\, t_v = 0.0427 \times 8 = 0.34$. Now we can read in Fig.3.13 for the above values $\log(\alpha\ t_m\ ) = 1.8$ from which it follows $t_m = 1478$ h. Hence we came to a comparatively long time of measuring over a period of roughly two months.

Besides, it follows from Fig.3.13 that the time of measuring cannot be reduced by more frequent sampling since e.g. with $t_v = 4$ h $\alpha\ t_v$ becomes 0.17 but the necessary time of measuring t_m remains virtually the same (the curves for $\alpha t_v = 0.1$ and 1 in Fig.3.13 practically coincide). On the other hand, a less frequent sampling might be considered, e.g. one in 24 h, as this would not entail a considerably longer time of measurement.

Fig.3.14 enables us to evaluate also the potential contribution of a continuous analyzer. For the value $\alpha t_v = 0.34$ we find that $\sigma_{md} / \sigma_{ms}$ is only slightly higher than 1 (the lines for $\alpha t_v = 0.1$ and 1 almost coincide with the line of the equation $\sigma_{md} / \sigma_{ms} = 1$). Hence, employing a continuous analyzer in this case does not present any advantage as regards shortening of the time of measuring the mean value of concentration. It may be seen that if continuous measuring should be advantageous, the value of αt_v would have to be roughly at least five.

In conclusion it may be stated that neither the application of a continuous analyzer nor shortening of the sampling interval will reduce the length of the time of measurement that is needed for attaining the required precision. Here the reason is a low value of the parameter α whose reciprocal value gives a so-called *time constant* of the random process - 23.4 hours. The second reason is the relatively stringent demand on precision which may be considered excessive with a measurement of this type. The above example is typical of the assessment of mean emissions from a number of chemical plants.■

In this Subsection a systematic approach to the evaluation of precision of measuring the mean value of fluctuating variables is described. This is a typical problem encountered in measurements in operating plants. The methods described can be applied both in the optimum planning of measuring and for estimating the precision of measurements already executed. These methods are not too complicated, and with the use of the above diagrams, their application is fairly prompt. The most tedious part of a solution is acquiring the data on a given process and its processing (calculation of the variances and autocorrelation function). Further, it has to be emphasized that in all the methods a stationary character of the respective process was assumed (see Section 2.4). Also attention was focused only upon errors originating in the fluctuation of the measured variables. When dealing with real problems, it is necessary to consider also the other types of errors influencing the process of measuring (random and systematic errors of the measuring methods proper) and taking part in the calculation of the overall accuracy.

3.4 RECOMMENDED LITERATURE TO CHAPTER 3

The general theory of random measurement errors is treated in many books on measurement and applied statistics. The approach used in this book is based on the book by Bohm & Radouch (1978). Interesting discussions, particularly on systematic errors, may be found in some articles (Grubbs 1973, Youden 1961 and 1962).

Gathering of information about random errors of measurement is discussed in most books on applied statistics (Himmelblau 1970). Less common are the various aspects of errors in measuring fluctuating quantities; this subject is examined in sufficient extent by Livshic & Pugatschev (1963) and Kharybin (1957).

In this Chapter we have dealt largely with the general theory of errors. The problems of errors of concrete measurements (individual analytical methods, measurement of temperature, pressure, flow rate, etc.) were touched only in the Examples. The sound estimation of measuring errors requires some knowledge of individual measurement methods used in process industries. Problems of measurement of the most important quantities in process industries (including precision of individual methods) are treated in sufficient depth in some monographs (Benedict 1977, Hengstenberg, Sturm & Winkler 1980, Gatzmanga et al. 1973). Another valuable source of information about measurement errors are Standards (ASME, ISA).

Errors of chains (systems) of measuring instruments are treated thoroughly in papers by Merz (1972), Sula (1971a, 1971b) and Toman (1971).

4 Processing of measured data

The number of measured data is usually substantial, particularly when more extensive systems are measured (it can normally amount to tens of thousands). The processing of more extensive sets of data consists essentially in "condensing" the information contained in the measured data. The objective is to obtain from the data as complete information as possible as is relevant with respect to the task to be solved. We endeavour to obtain as concise results as possible but which, at the same time, will answer all the questions asked prior to the measurement. Hence the procedure of measured data processing is not simple and it is usually implemented at several levels.

4.1 PREPROCESSING OF DATA

The preprocessing of data involves, in particular:

- preliminary checking of data and their presentation in a suitable form,
- computation of the fundamental statistical characteristics of measured data (means, variances) or, as the case may be, assessing the probability distributions of random variables,
- examining the obtained time series (calculation of the autocorrelation functions, checking the stationarity),
- analysis from the viewpoint of the presence of gross measurement errors,
- corrections of measured values.

When evaluating raw data it is necessary, in the first place, to identify possible errors that could originate in the course of data collection. It may be a case of confusing the columns in a form, errors in the order, etc. Special attention must be given to data obtained with the aid of automatic measuring systems. The data must be adjusted to a suitable form, depending on the method of their further processing. If the data are to be processed completely on a computer, the transfer of data from different sources (results of chemical analyses, data from data logging systems etc.) to the computer must be ensured.

The next step is usually the computation of the fundamental statistical characteristics. The calculation of arithmetic mean and sample variance is conducted in accordance with the relations presented in Subsection 3.3.2. In the case where a greater number of measurements of one quantity is available (for instance more than 100), we can attempt to find the probability density of fluctuations of that quantity.

When a measurement is taking place for a sufficiently long interval of time, it is possible to examine the statistical properties of the obtained time series. In most cases one begins with checking the stationarity of the measured process (detection of the trend and harmonic component of fluctuations - see Section 2.4). A good picture of the character of fluctuations can be obtained by calculating the autocorrelation function of the time series, as described in Section 2.4.A more detailed information can offer the calculation of so-called spectral density, which is suitable particularly for detecting the harmonic components of fluctuation. More about this special problem can be found in (Bendat & Piersol 1966).

At all levels of data processing attention must be paid to the detection and elimination of gross errors of measurement. The problem of finding the so-called outlying values (or outliers) was examined in Subsection 3.3.2. At this stage of data processing we confine ourselves to checking the results of parallel measurements (repeated analyses, parallel measuring by several instruments). In this case we may rightly assume that a single value has been measured and that significant deviations between the parallel results are probably due to errors in measuring, sampling, or to other mistakes.

Sometimes there is a tendency to apply the methods of eliminating outlying observations to the values of time series. Besides measurement errors, the variability of results can be brought about also by the objectively existing larger fluctuations of measured variables. Elimination of so originated values is not justifiable as it can affect adversely the estimation of the mean value of a fluctuating quantity. It may be said generally that the elimination of outliers is a double-edged weapon. It is, therefore, recommended not to apply the tests of outlying values directly (that is not to eliminate the outliers immediately) but rather to make use of them in a detailed examination of their possible causes.

Corrections of the measured data are made in order to reduce to the least possible degree the influence of systematic measuring errors. It is a matter of principle that any detectable factor influencing the results of a measurement should be taken into account. In most cases this is a matter of correction of deviations of the real conditions from reference conditions when measuring instruments are used. These problems are discussed in detail in Subsection 3.3.4. Experience shows that when a computer is employed, implementing of corrections is very effective (the amount of work needed for programming the correction relations usually is considerably smaller than that needed for improving the precision and accuracy of the measuring instruments and methods proper).

4.2 TYPES OF MEASURED DATA PROCESSING AND CLASSIFICATION OF VARIABLES

Let us assume that we are dealing with preprocessed data. During a measurement taking place under stationary or quasi-stationary conditions these are the estimates of mean values within the measured period. With measurements in non-stationary state (for example in the case of batch operations) the data may be the integral values of quantities characterizing inputs and outputs, accumulation, etc.

Further, a mathematical model is known, represented by a system of linearly independent equations, in which appear quantities measured directly, directly unmeasured, and those known exactly in advance (constants). Let us assume first that the mathematical model is linear with respect to individual variables, i.e. it can be written in the form

$$\boldsymbol{A}\boldsymbol{x} + \boldsymbol{B}\boldsymbol{y} + \boldsymbol{a} = 0 \tag{4.1}$$

where $\boldsymbol{x}$ is the vector of directly measured quantities, $\boldsymbol{y}$ - vector of unmeasured quantities, and the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ as well as the vector $\boldsymbol{a}$ are exactly known beforehand. Hereafter in this Chapter the following notation will be used:

I - number of directly measured quantities (vector $\boldsymbol{x}$)
J - number of unmeasured quantities (vector $\boldsymbol{y}$)
K - number of equations of the mathematical model.

Example 4.1: *Mass balance*

Fig.4.1 represents a simple balance scheme consisting of six nodes (node number 7 - environment - is not shown in the diagram) and twelwe streams, out of which six

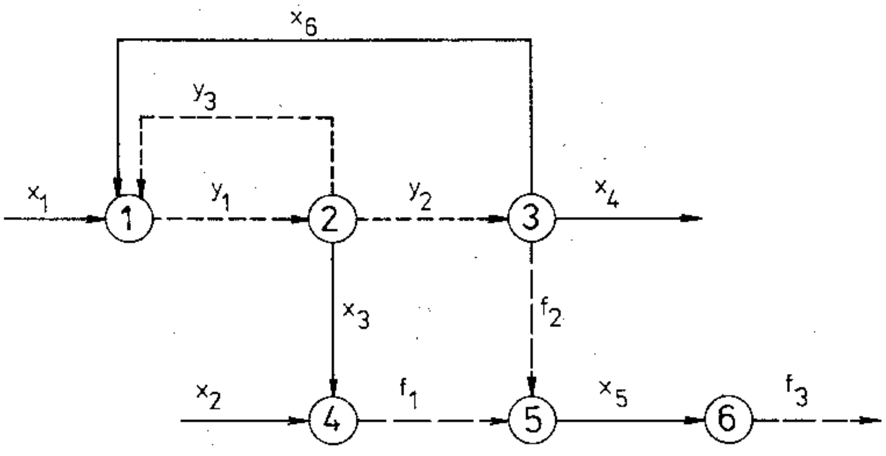


Fig.4.1 — Balance scheme

are measured (the flows are denoted x), three unmeasured streams (denoted by y), and three streams with flow rates that are exactly known (denoted f), which have the character of constants. It is necessary to remark at this point that it is not typical to regard flow rates as constants, i.e. as quantities that are not subjected to errors (in practice we should hardly find a method enabling us to measure the flow rate with only a negligible error). We have introduced such flow rates here, so that later we might use this simple example for demonstrating the role of constants in the processing of measured data.

We shall write 7 balance equations around the individual nodes (the seventh equation being the balance around the environment).

$$\begin{aligned}
&y_1 - y_3 - x_1 - x_6 &&= 0\\
&-y_1 + y_2 + y_3 + x_3 &&= 0\\
&-y_2 + x_4 + x_6 + f_2 &&= 0\\
&-x_2 - x_3 + f_1 &&= 0\\
&x_5 - f_1 - f_2 &&= 0\\
&-x_5 + f_3 &&= 0\\
&x_1 + x_2 - x_4 - f_3 &&= 0
\end{aligned} \tag{4.2}$$

The system (4.2) can be written in the matrix form (4.1), where

$$\boldsymbol{A} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & -1\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 1\\ 0 & -1 & -1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & -1 & 0\\ 1 & 1 & 0 & -1 & 0 & 0 \end{bmatrix} \qquad \boldsymbol{B} = \begin{bmatrix} 1 & 0 & -1\\ -1 & 1 & 1\\ 0 & -1 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0 \end{bmatrix} \qquad \boldsymbol{a} = \begin{bmatrix} 0\\ 0\\ f_2\\ f_1\\ -f_1 \ -f_2\\ f_3\\ -f_3 \end{bmatrix}$$

The elements of matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are, at the same time, coefficients in balance equations and the elements of the vector $\boldsymbol{a}$ are sums of the exactly known flow rates.■

First we shall examine the most important variants that can occur in the course of data processing. We shall use as the basis the mathematical model (4.1), which will be converted into canonical form by elementary matrix rearrangements (see Appendix A.2.4). It will be assumed that the reader is conversant with the Gauss–Jordan elimination method for transforming matrices to a form having the unit submatrix in the upper left-hand corner of the original matrix (see Appendix A.2.4).

Let us form a composed matrix (further denoted as *macro-matrix*) $\boldsymbol{M}$ from the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ and from the column vector $\boldsymbol{a}$ according to the scheme presented in Fig.4.2a. It is obvious that the first J columns of the macro-matrix $\boldsymbol{M}$ correspond to the unmeasured quantities, the next I columns to the measured ones, and the last column is formed by the vector $\boldsymbol{a}$. Now let us apply to the matrix $\boldsymbol{M}$ the Gauss - Jordan elimination, using for pivoting, first,only the columns belonging to the unmeasured quantities. After completing the elimination we obtain the matrix shown in Fig.4.2b. It might happen that during the elimination an interchange in the order of the unmeasured quantities or equations in the macro-matrix could take place (interchanging of the matrix columns or rows). It is also obvious that the submatrix in the intersection of the first horizontal and second vertical bands need not have been formed.

In the next phase we apply the elimination to the submatrix formed by the horizontal band 2 in Fig.4.2b. The matrix resulting after this second elimination step is shown in Fig.4.2c. Further we shall try to create zero fields in the submatrices $\boldsymbol{M}_{1,2}$, $\boldsymbol{M}_{2,4}$ and $\boldsymbol{M}_{3,5}$ by rearranging the rows and columns of the macro-matrix. The final (canonical) form of the macro-matrix $\boldsymbol{M}$ is shown in Fig. 4.2d.

It is important to realize that, from the viewpoint of data processing, the canonical form is equivalent to the original form, and the conclusions arrived at from the canonical form hold true for the original form of the matrix, or for the model (4.1) as well.

Let us take note of the horizontal band 3 first. If it contains non-zero elements in the last column, it means that the task is not solvable since the mathematical model contains contradictory equations (of the type non-zero constant = zero), regardless of the values of variables. We shall not concern ourselves with this case any more.

When the horizontal band does not contain non-zero elements, the equations in this band are linearly dependent on the remaining equations and may be ignored further without influencing the results. In the case in which the horizontal band 3 is not formed during the macro-matrix elimination, the mathematical model consists of a set of linearly independent equations. Since such a form can always be arrived at by leaving out the dependent equations, further in this Chapter we shall confine ourselves to just such a type of model.

If in the course of elimination the vertical band 2 is formed, there are nonobservable unmeasured quantities present (those that can not be calculated unambiguously from the model). The nonobservable variables belong to columns in the vertical bands 1b and 2. With a view to having the task fully solvable, a certain number of unmeasured variables would have to be measured additonally (the simplest way would be to measure variables that belong to the vertical band 2). When, however, the additional measurement is not possible, there is no other possibility but to eliminate from the problem those equations which correspond to the horizontal band 1b, along with the nonobservable unmeasured variables. Then only observable unmeasured variables from the vertical band 1a remain in the problem solved. The way how to calculate them is obvious.

Now let us pay attention to the horizontal band 2 in which only measured quantities occur. If this band has been formed, there are so-called redundant measured quantities present in the problem (for example, the variables belonging to the vertical

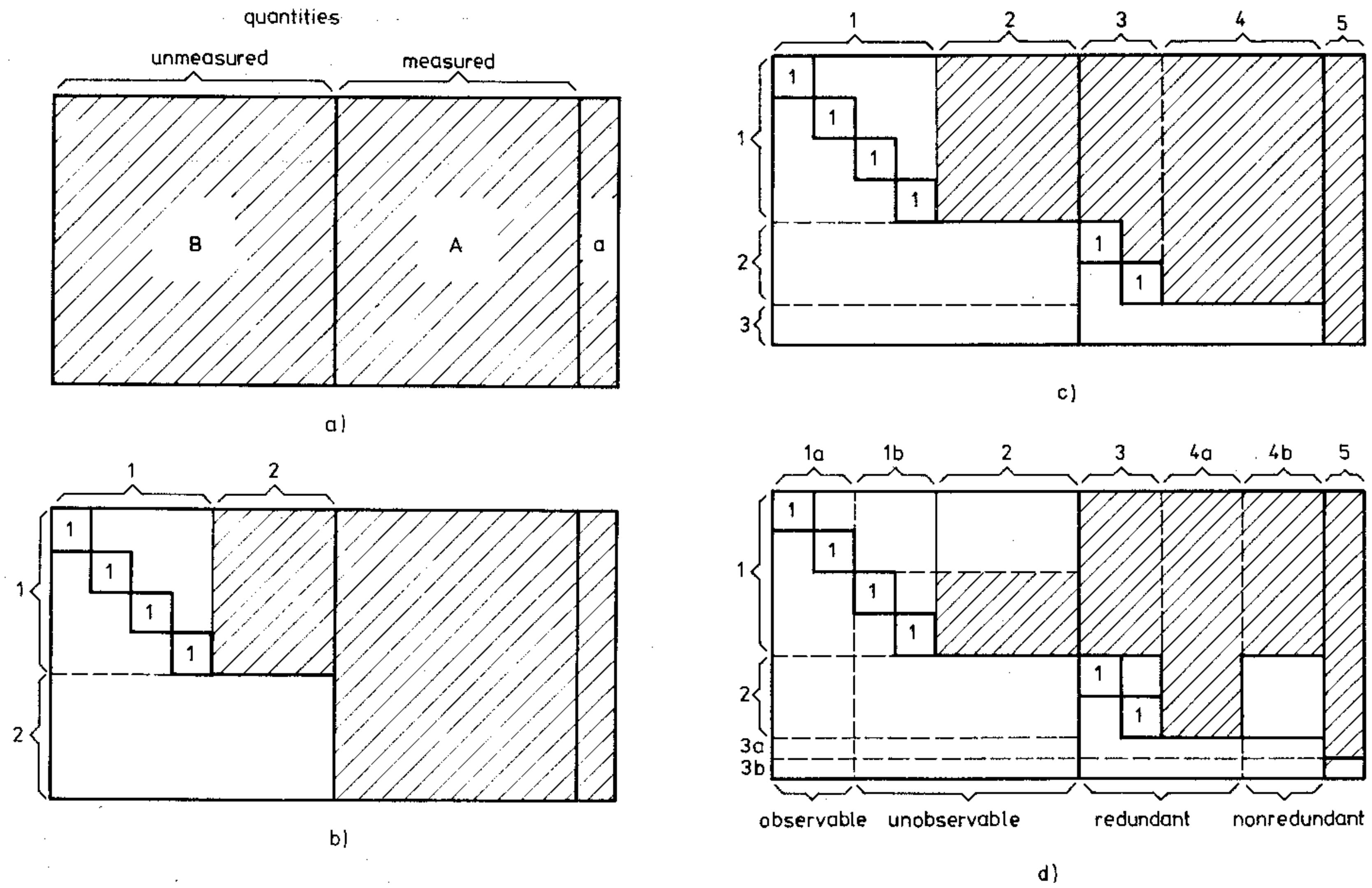


Fig.4.2 — Macro-matrix ***M***

band 3 can be calculated from remaining measured quantities - their measurement was not indispensible).

Since the measured quantities are subject to measurement errors, it is almost certain that the set of equations belonging to the horizontal band 2 will not be satisfied exactly. The means of solving this problem is the adjustment (so-called *reconciliation*) of measured values, so that the set of equations might be satisfied exactly. This problem will be dealt with in detail in Subsection 4.4.1. Redundancy, however, does not concern those measured quantities that belong to the vertical band 4b, since these quantities are not present in equations of the horizontal band 2. These measured quantities are *nonredundant* (or just *determined*), in contrast with redundant variables in vertical bands 3 and 4a.

The case presented in Fig.4.2a represents the so-called *general linear model* involving all the variants that may be met with in data processing. It is also useful to discern certain special cases. When no redundant quantities are present in a problem, we speak about *calculating the unmeasured quantities from a system of equations* (formed by the horizontal band 1a). This case is dealt with in Section 4.3. When unmeasured quantities are not present, it is a question of reconciling the directly measured quantities, which is discussed in Subsection 4.4.1. A general linear model is handled in Subsection 4.4.3. The canonical form of the macro-matrix in Fig.4.2d further points to certain important relations among the measured and unmeasured quantities. If we include an unmeasured nonobservable quantity with the measured ones, the resulting measured quantity is always nonredundant, and vice versa. On the other hand, if a redundant measured quantity is included among unmeasured quantities, this is always observable.

The necessary and sufficient conditions for the solvability of equations, observability and redundancy can be expressed also by means of the rank of matrices $\boldsymbol{A}$, $\boldsymbol{B}$ and of the vector $\boldsymbol{a}$, and of matrices composed thereof.

Condition of solvability:

$$\text{rank}\,(\boldsymbol{A}, \boldsymbol{B}) = \text{rank}\,(\boldsymbol{A}, \boldsymbol{B}, \boldsymbol{a}) \tag{4.3}$$

Linear independence of the model equations:

$$\text{rank}\,(\boldsymbol{A}, \boldsymbol{B}) = K \tag{4.4}$$

Observability of all the unmeasured quantities:

$$\text{rank}\,(\boldsymbol{B}) = J \tag{4.5}$$

Presence of redundant quantities:

$$\text{rank}\,(\boldsymbol{B}) < \text{rank}\,(\boldsymbol{A}, \boldsymbol{B}) \tag{4.6}$$

The rearrangement of the macro-matrix $\boldsymbol{M}$ to a canonical form represents the decomposition of the whole problem into two comparatively independent subproblems:

1. Reconciliation of redundant measurements using a subset of equations corresponding to the horizontal band 2 in Fig.4.2d.
2. Computation of the values of observable unmeasured quantities from equations corresponding to the horizontal band 1a, into which the reconciled values obtained in the preceding step are substituted. This second step is the so-called *cooptation.*

The conversion of a system of equations of a mathematical model into the canonical form thus represents not only a method for classifying the quantities but also a way of transforming this problem to a uniform and readily solvable form. In addition the historical development as well as the special form of some types of frequently used mathematical models have given rise to some other approaches that will be dealt with in a greater detail in the next two Sections. The classification of quantities is depicted in Fig.4.3.

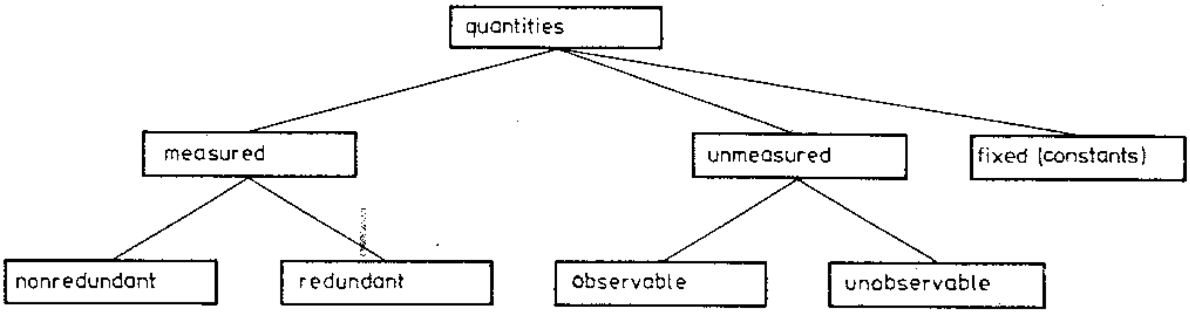


Fig.4.3 — Classification of quantities

Example 4.2: *Conversion of a system of equations to a canonical form*
Let us revert to the system of equations describing a mass balance, which was created in Example 4.1. The fundamental macro-matrix of the system is presented in Fig.4.4a (see matrices $\boldsymbol{A}$, $\boldsymbol{B}$ and vector $\boldsymbol{a}$ in Example 4.1). Note that zero elements of the matrix $\boldsymbol{M}$ are not printed here for simplicity.

It was first partly converted into the canonical form, using only the unmeasured quantities (the result is shown in Fig.4.4b). In the next step the columns corresponding to the measured quantities were used (Fig.4.4c). Let us note here that it was necessary to exchange the columns corresponding to measured streams Nos.3 and 5.

Fig.4.4 — Macro-matrix ***M*** (Example 4.2)

	unmeas.			measured						fixed
Equation	1	2	3	1	2	3	4	5	6	
1	1		-1	-1					-1	
2	-1	1	1			1				
3		-1					1		1	f_2
4					-1	-1				f_1
5								1		$-f_1\ -f_2$
6								-1		f_3
7				1	1		-1			$-f_3$

Fig.4.4a — Original macromatrix ***M***

	unmeas.			measured						fixed
Equation	1	2	3	1	2	3	4	5	6	
1	1		-1	-1					-1	
2		1		-1		1			-1	
3				-1		1	1			f_2
4					-1	-1				f_1
5								1		$-f_1\ -f_2$
6								-1		f_3
7				1	1		-1			$-f_3$

Fig.4.4b — ***M*** after elimination of unmeasured quantities

	unmeas.			measured						fixed
Equation	1	2	3	1	2	5	4	3	6	
1	1		-1	-1					-1	
2		1		-1		1			-1	
3				1			-1	-1		$-f_2$
4					1			1		$-f_1$
5						1				$-f_1\ -f_2$
6										$-f_1\ -f_2\ +f_3$
7										$f_1\ +f_2\ -f_3$

Fig.4.4c — ***M*** after elimination of measured quantities

Equation	unmeasured				measured						fixed
	1	2	4	3	1	2	5	4	3	6	
1	1			-1	-1					-1	
2		1			-1		1			-1	
6			1								$-f_1$ $-f_2$
3					1			-1	-1		$-f_2$
4						1			1		$-f_1$
5							1				$-f_1$ $-f_2$
7											

Fig.4.4d — ***M*** after setting f as unmeasured No.4 and making all eliminations

Equation	unmeasured				measured						fixed
	2	4	1	3	1	2	5	4	3	6	
2	1			0	-1		1		-1	-1	
6		1		0							$-f_1$ $-f_2$
1			1	-1	-1				-1	-1	
3					1			-1	-1	0	$-f_2$
4						1			1	0	$-f_1$
5							1			0	$-f_1$ $-f_2$
7	0	0	0	0	0	0	0	0	0	0	0

Fig.4.4e — ***M*** after final rearrangements

Before we proceed to further rearrangements of the matrix in Fig.4.4c, we shall pay heed to its last two rows. These rows mean that certain linear combinations of constants equals zero. That is to say - if these constants are chosen independently, then in the course of solving we shall arrive at contradictory equations of the form non-zero constant equal zero. Hence there would be no solution of the system. Such a situation can be handled in two ways. Either we shall, before the solution proper, ask that the values of constant flow rates should satisfy the relations of the mathematical model, i.e.

$$f_1 + f_2 - f_3 = 0 \; .$$

or we can include some of the constant flow rates among the unmeasured quantities, whereby the relations among constant flow rates will be respected automatically in the course of the solution. When the constant flow rate f_3 is included among the unmeasured quantities and designated as y_4 , we obtain, after converting the new system into the canonical form, the macro-matrix presented in Fig.4.4d.

And now we can carry out the final rearrangements and analyze the problem. The result is demonstrated in Fig.4.4e. Three zero submatrices have been created here, marked by zeros. The conclusions are then as follows:

1. The equation 7 is linearly dependent on the remaining equations and need not be further considered (this fact is obvious to those experienced in balancing since the equation of the balance of environment always is linearly dependent on the system of balance equations around the individual nodes).
2. There are two unmeasured unobservable quantities y_1 and y_3 in the system, the other quantities are observable.
3. The directly measured quantity x_6 is nonredundant, the remaining quantities are redundant.■

Before we proceed to the individual estimation methods, we shall set out the assumptions, concerning the errors of directly measured quantities. In this Chapter we shall assume that errors are realizations of random variables with zero mean values

$$\mathrm{E}(\boldsymbol{e}_x) = \boldsymbol{0} \tag{4.7}$$

and with a regular covariance matrix $\boldsymbol{F}_x$ for whose elements it holds

$$F_{ij} = \mathrm{cov}\,(e_{x_i}, e_{x_j}) = \mathrm{E}\,(e_{x_i} e_{x_j}) \tag{4.8}$$

In most cases the assumption of the matrix $\boldsymbol{F}_x$ regularity can be accepted (in principle it means that there does not exist any exactly valid deterministic dependence among errors). We assume further that we know either the matrix $\boldsymbol{F}_x$ or at least a matrix $\boldsymbol{W}$, proportional to it according to

$$\boldsymbol{F}_x = \sigma^2\, \boldsymbol{W} \tag{4.9}$$

where σ^2 is an unknown coefficient. With the matrix $\boldsymbol{W}$ the most common case is that we know the ratios of precision of the individual measurements.

When the measuring errors are uncorrelated (this being the most frequent case in the processing of primary quantities), the matrix $\boldsymbol{F}_x$ is diagonal with squares of standard deviations of errors on the diagonal. In the case that all the measurements are equally precise and the errors are uncorrelated, $\boldsymbol{W}$ is a unit matrix.

In some cases (particularly when assessing the confidence intervals of results) it is necessary to know the probability distribution of random errors of measurement. We shall further assume that the errors have an I-dimensional normal distribution $N_I\,(\boldsymbol{0},\boldsymbol{F}_x)$.

Further we shall discuss the most important methods of measured data processing. We shall always present the method of point estimation of both the directly measured and unmeasured quantities, including the calculation of the covariance matrix of estimates (which is sufficient for estimation of confidence intervals of results). The confidence regions (ellipsoids) will be described only for vectors with a regular covariance matrix.

Two variants will always be considered - we know either the covariance matrix $\boldsymbol{F}_x$ or a matrix $\boldsymbol{W}$ that is proportional to it according to Eq.(4.9). In the latter case also the estimate of the unknown parameter σ^2 will be given. The matrix $\boldsymbol{F}_x$ will be then estimated in accordance with

$$\hat{\boldsymbol{F}}_x = \hat{\sigma}^2 \boldsymbol{W} \tag{4.10}$$

We shall use consistently the superscript + for a measured value, the sign ~ above a symbol for a true value, and the sign ^ above a symbol for estimates (reconciled values).

The remaining part of Chapter 4 has been drawn up with regard to practical problem solving. Considering the extent of the studied problems, however, it has not been possible to include here the derivations or proofs of the relations presented further. The literature dealing with the data processing problems is quite extensive. It has not been possible to describe all the published methods and approaches. The survey of recommended literature at the end of this Chapter can serve the interested readers for further studies.

4.3 DIRECT CALCULATION OF UNMEASURED QUANTITIES

In the following Section we shall deal with the case when a system of equations of a mathematical model is just sufficient for calculating the quantities directly unmeasured. This means that the number of unmeasured quantities in the general linear model (4.1) is equal to the number of equations and, at the same time, to the rank of matrix $\boldsymbol{B}$. We shall rearrange the model (4.1) into the form

$$\boldsymbol{B}\boldsymbol{y} = -\boldsymbol{A}\boldsymbol{x} - \boldsymbol{a} \tag{4.11}$$

Since $\boldsymbol{B}$ is a square and regular matrix, we obtain the solution by multiplying the Equation (4.11) by the matrix $\boldsymbol{B}^{-1}$ from the left hand side.

$$\hat{\boldsymbol{y}} = -\boldsymbol{B}^{-1}\boldsymbol{A}\boldsymbol{x}^{+} - \boldsymbol{B}^{-1}\boldsymbol{a} \tag{4.12}$$

This form could be arrived at also by converting the system (4.11) into the canonical form using the elimination as described in the Section 4.2. Since the vector $\boldsymbol{a}$ is known exactly, it holds for the errors of vector $\hat{\boldsymbol{y}}$

$$\boldsymbol{e}_{\hat{y}} = - \boldsymbol{B}^{-1} \boldsymbol{A} \boldsymbol{e}_x \tag{4.13}$$

where $\boldsymbol{e}_x$ is the vector of errors of directly measured quantities. It is a case of errors propagation during a linear transformation of a random vector, and it holds for the covariance matrix of vector $\hat{\boldsymbol{y}}$ [see Eqs (3.54) and (A.4)]:

$$\boldsymbol{F}_{\hat{y}} = \boldsymbol{B}^{-1} \boldsymbol{A} \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} (\boldsymbol{B}^{-1})^{\mathrm{T}} \tag{4.14}$$

Eq.(4.12) gives the point estimates of unmeasured quantities. On assumption that the distribution of errors $\boldsymbol{e}_x$ is normal, errors $\boldsymbol{e}_{\hat{y}}$ have the distribution $N_J(\boldsymbol{0}, \boldsymbol{F}_{\hat{y}})$, and we can construct the interval estimates for the true values of unmeasured quantities. The confidence intervals, within which the true values $\tilde{y}_j$ occur with the probability $(1 - \alpha)$, are

$$\langle \hat{y}_j - u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \quad ; \quad \hat{y}_j + u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \rangle \tag{4.15}$$

where $u_{1-\alpha/2}$ is the $100(1 - \alpha/2)$ percentile of the standardized normal distribution, and $\sigma_{\hat{y}_j} = (F_{\hat{y}_{jj}})^{1/2}$.

The intervals (4.15) hold for the components $\tilde{y}_j$ individually but do not hold for the whole vector $\boldsymbol{y}$ (see Subsection 3.2.3). When $\boldsymbol{F}_{\hat{y}}$ is regular, we can construct the confidence ellipsoid whose equation is

$$(\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}} \boldsymbol{F}_{\hat{y}}^{-1} (\boldsymbol{y} - \hat{\boldsymbol{y}}) = \chi^2_{1-\alpha}(J) \tag{4.16}$$

where $\chi^2_{1-\alpha}(J)$ is the $100(1 - \alpha)$ percentile of the distribution χ^2 with J degrees of freedom. When there is the sign < instead of = in Eq.(4.16), the true vector $\tilde{\boldsymbol{y}}$ occurs inside the confidence ellipsoid with probability $(1 - \alpha)$.

The confidence ellipsoid can be used when solving the question, whether or not the results of a measurement differ considerably from the previous assumptions. If, prior to the measurement, we considered that the true value of $\boldsymbol{y}$ was $\boldsymbol{y}^*$ (hypothesis H_0), after the measurement we substitute into (4.16) $\boldsymbol{y}^*$ for $\boldsymbol{y}$. If the left hand side is greater than the right hand side, the hypothesis H_0 is rejected and we say that the results of the measurement differ from the presumption. In the opposite case we state that, at the chosen significance level, there is no reason to think that the result differs from the assumption.

When the matrix $\boldsymbol{F}_x$ is not known but we know the matrix $\boldsymbol{W}$ from Eq.(4.9), the estimation is made according to Eq.(4.12). In this case, however, neither the intervals nor the ellipsoid of confidence can be constructed.

Example 4.3: *Calculation of unmeasured quantities of the fermentation process*
A mathematical model of the material balance of the process of manufacturing

biomass from ethanol was presented in Example 2.2 [see Eq.(2.14) and Table 2.1]. Let us assume that the three following quantities were measured: the main product - biomass, the ethanol consumed, and the acetic acid formed. Additional five unmeasured quantities should be calculated, i.e. amounts of further produced and consumed substances.

The substances are numbered as follows:

- measured substances: biomass 1, ethanol 2, acetic acid 3;
- unmeasured substances: oxygen 1, carbon dioxide 2, ammonia 3, water 4, mineral nutrients 5.

The balance equations (2.14) can be written for changes in the amounts of measured substances (vector $\boldsymbol{n}_1$) and unmeasured substances (vector $\boldsymbol{n}_2$):

$$\boldsymbol{E}_1^{\mathrm{T}}\,\boldsymbol{n}_1 + \boldsymbol{E}_2^{\mathrm{T}}\,\boldsymbol{n}_2 = 0$$

where $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ are the atom matrices of the measured and unmeasured, resp., substances. When we alter the notation $\boldsymbol{E}_1^{\mathrm{T}} \to \boldsymbol{A}$, $\boldsymbol{E}_2^{\mathrm{T}} \to \boldsymbol{B}$, $\boldsymbol{n}_1 \to \boldsymbol{x}$ and $\boldsymbol{n}_2 \to \boldsymbol{y}$, we obtain the model (4.1) where the vector $\boldsymbol{a}$ is the zero vector. The solution of the problem is then given by (4.12).

The columns of the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ from Eq.(4.12) are formed by selecting those columns of the matrix presented in Table 2.1 that belong to the measured and unmeasured quantities in the above indicated order. Hence the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are

$$\boldsymbol{A} = \begin{bmatrix} 3.83 & 2 & 2 \\ 7.00 & 6 & 1 \\ 1.94 & 1 & 2 \\ 0.64 & 0 & 0 \\ 7.00 & 0 & 0 \end{bmatrix} \qquad \boldsymbol{B} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 3 & 2 & 0 \\ 2 & 2 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

The measured values published by Madron, Veverka & Vanecek (1977) will be used as input data. It was found here that the increments in the amount of measured substances are for the biomass, ethanol and acetic acid, respectively, $x_1^+ = 350$, $x_2^+ = -1\ 089$, $x_3^+ = 3.2$ kmol. Also, using the errors propagation method, also the covariance matrix of the measured quantities errors was assessed (Madron, Veverka & Vanecek 1977).

$$\boldsymbol{F}_x = \begin{bmatrix} 29.9 & 0 & 0.0277 \\ 0 & 39.7 & 0 \\ 0.0277 & 0 & 0.00131 \end{bmatrix}$$

On substituting $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{x}^+$ into (4.12) we obtain the vector of estimates of increments of the amount of components during fermentation:

$$\hat{\boldsymbol{y}} = (-1\ 815\ ;\ 831\ ;\ -224\ ;\ 2\ 372\ ;\ -2\ 450)^T \text{ kmol}$$

The order of elements of the vector corresponds to the numbering of the unmeasured substances (i.e. oxygen, carbon dioxide, ammonia, water, and mineral nutrients).

We obtain the covariance matrix of computed quantities errors by substituting $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{F}_x$ into (4.14):

$$\boldsymbol{F}_{\hat{y}} = \begin{bmatrix} 868 & -712 & -79 & -671 & -865 \\ -712 & 598 & 73 & 529 & 802 \\ -79 & 73 & 12 & 49 & 134 \\ -671 & 529 & 49 & 550 & 532 \\ -865 & 802 & 134 & 532 & 1465 \end{bmatrix}$$

For example the interval estimate for substance amount of the generated oxygen is obtained by substituting $\hat{y}_1 = -1\ 815$ kmol and $\sigma_{\hat{y}_1} = 868^{1/2} = 29.5$ kmol into (4.15). When we choose $\alpha = 0.05$, $u_{0.975} = 1.96$. The confidence interval for the oxygen formed is

$$\langle -1\ 815 - 29.5 \times 1.96\ ;\ -1\ 815 + 29.5 \times 1.96 \rangle$$

that is

$$\text{P}\ [\tilde{y}_1 \in \langle -1\ 873\ ;\ -1\ 757 \rangle \text{ kmol}] = 0.95 \qquad \blacksquare$$

In Subsection 3.2.3 we have introduced the concept of share matrices. The share matrices are convenient for the analysis of how the random measuring errors manifest themselves in the calculation [according to Eq.(4.12)] of unmeasured quantities. When calculating the share matrix Eq.(3.60) is used, where it holds for the matrix $\boldsymbol{C}$:

$$\boldsymbol{C} = -\boldsymbol{B}^{-1} \boldsymbol{A} \tag{4.17}$$

We often meet with a case when the mathematical model is nonlinear with respect to the quantities occurring in it. The unmeasured quantities cannot be calculated simply according to Eq.(4.12) but a proper numerical method has to be used. Most frequently the Newton-Raphson method is adopted, in which the system of nonlinear equations is linearized by expansion into Taylor series while neglecting the second and higher order terms. Thus linearized it has the form of Eq(4.11) and for the solution the procedure described earlier can be used. This range of problems will be discussed in detail in Subsection 4.4.5 in connection with the identification of the nonlinear model parameters in the presence of redundant measurements.

4.4 DATA PROCESSING IN THE PRESENCE OF REDUNDANT MEASUREMENTS

By reconciliation of redundant measurements we have in mind their adjustment in such a way that they do not contradict with the mathematical model. The reconciliation of redundant measurements in the processing of measured data obtained in process plants has a dual sense.

Firstly, the reconciliation of data enables the complete information that is available to be utilized. In the case in which we excluded the redundant data from further data treatment and confined ourselves to direct computation of unmeasured quantities as discussed in the preceding Section, we would lose the information contained in the redundant data. In the course of processing, the data become more precise, which manifests itself by lowering the standard deviation of the reconciled quantity when compared with the measured ones.

The second, and perharps even more important advantage of redundant data processing, consists in the fact that, owing to measuring errors, the redundant data are, to a certain extent, inconsistent with the presumed mathematical model. A detailed analysis of this inconsistency enables one to judge, whether a mathematical model including the assumed model of errors is in order (i.e. whether the existing inconsistency between the measured values and the model can be explained within the framework of the assumed measuring errors). The latter problem will be dealt with in detail in Section 4.5.

Despite the mentioned importance of redundant data reconciliation we do not meet with it often in practice. The reason may be that in most cases reconciliation - when compared with direct calculation of unmeasured quantities - is more demanding as regards numerical computations. It is true, however, that, particularly in modern plants usually well equipped with measuring instruments, redundant measurements are often available.

The reconciliation of redundant measurements means, in principle, finding adjusted values of the measured quantities and, at the same time, also the calculation of directly unmeasured quantities when these are present. The adjusted values $\hat{\boldsymbol{x}}$ are defined as

$$\hat{\boldsymbol{x}} = \boldsymbol{x}^{+} + \boldsymbol{v} \tag{4.18}$$

where the elements of the vector $\boldsymbol{v}$ (so-called *adjustments*) possess the following properties:

1. the equations of the mathematical model are fulfilled exactly with the adjusted values,
2. the adjusted values differ from the measured ones "as little as possible", i.e. the magnitude of adjustments is, in a certain way, minimal.

In practice there are two approaches adopted most frequently for reconcilation -- the *least squares method* and the principle of *maximum likelihood*. It is esential that, in the case of normal distribution of errors, both the principles are equivalent as far as the results are concerned.

The criterion of adjustments minimization is the quadratic form Q:

$$Q = \boldsymbol{v}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{v} \tag{4.19}$$

where $\boldsymbol{F}_x$ is the covariance matrix of measurement errors. Those adjustments, with which the value of Q takes a minimum ($Q_{\min}$) - while with thus adjusted values the equations of a mathematical model are satisfied exactly - represent the solution of the problem of redundant data reconciliation (so-called *general method of least squares*). Hence, it is a case of minimizing the quadratic function (4.19), when the variables have to satisfy the mathematical model.

We shall assume further that (see Section 4.2)

1. all the unmeasured quantities are observable, i.e. the selection of the measured quantities enables estimation of all unmeasured quantities,
2. at least some of the measured quantities are redundant. The conditions of satisfying the assumptions 1 and 2 will be examined with individual types of mathematical models.

4.4.1 Reconciliation of directly measured quantities

The task is the estimation of a vector $\boldsymbol{x} = (x_1 ,..., x_I)^{\mathrm{T}}$, whose elements are measured directly, but they have to satisfy K equations. Unmeasured quantities are not present and, in this case, the general linear model (4.1) has the following form:

$$\boldsymbol{a} + \boldsymbol{Ax} = \boldsymbol{0} \tag{4.20}$$

Let it hold for the rank of the matrix $\boldsymbol{A}$ (K x I) that rank $\boldsymbol{A} = K < I$. If the matrix $\boldsymbol{A}$ had not a full rank, i.e. it would hold rank $\boldsymbol{A} < K$, the linearly dependent rows of the matrix would be eliminated from the mathematical model.

On the above assumptions it holds for adjustments

$$\boldsymbol{v} = -\boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} (\boldsymbol{AF}_x \boldsymbol{A}^{\mathrm{T}})^{-1} (\boldsymbol{a} + \boldsymbol{Ax}^{+}) \tag{4.21}$$

where $\boldsymbol{v}$ has the distribution $N_T (\boldsymbol{0}, \boldsymbol{F}_v)$, and $\boldsymbol{F}_v = \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} (\boldsymbol{AF}_x \boldsymbol{A}^{\mathrm{T}})^{-1} \boldsymbol{AF}_x$ has the rank K (is singular).

The quantity $Q_{\min}$ calculated from the relation (4.19) is, on the assumption of normal distribution of errors, a realization of a random variable with χ^2 distribution with K degrees of freedom.

Substituting the vector of adjustments into (4.18) gives

$$\hat{\boldsymbol{x}} = \boldsymbol{x}^{+} + \boldsymbol{v} = -\boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}}\,(\boldsymbol{A}\boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}})^{-1}\,\boldsymbol{a} + [\boldsymbol{I} - \boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}}\,(\boldsymbol{A}\boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}})^{-1}\,\boldsymbol{A}]\,\boldsymbol{x}^{+} \tag{4.22}$$

where $\boldsymbol{I}$ is unit matrix. The vector $\hat{\boldsymbol{x}}$ calculated from (4.22) is an unbiased estimate of the vector $\tilde{\boldsymbol{x}}$. Its elements are realizations of random variables with distribution $N_I\,(\tilde{\boldsymbol{x}}\,,\,\boldsymbol{F}_{\hat{x}})$, where

$$\boldsymbol{F}_{\hat{x}} = \boldsymbol{F}_{x} - \boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}}\,(\boldsymbol{A}\boldsymbol{F}_{x}\,\boldsymbol{A}^{\mathrm{T}})^{-1}\,\boldsymbol{A}\boldsymbol{F}_{x} \tag{4.23}$$

has the rank $(I - K)$, what means that it is singular. It is possible to form the confidence intervals covering, at a chosen probability, the real values, i.e. elements of the vector $\tilde{\boldsymbol{x}}$. It holds that the intervals

$$\langle \hat{x}_i - u_{1-\alpha/2}\,\sigma_{\hat{x}_i}\ ;\ \hat{x}_i + u_{1-\alpha/2}\,\sigma_{\hat{x}_i} \rangle \tag{4.24}$$

where $\sigma_{\hat{x}_i} = (F_{\hat{x}_{ii}})^{1/2}$, cover real values $\tilde{x}_i$ with the probability $(1 - \alpha)$.

So far we have assumed that the covariance matrix $\boldsymbol{F}_x$ is known. When we know only the matrix $\boldsymbol{W}$ from Eq.(4.9) but not the value of the coefficient σ^2 , we proceed in the following way: σ^2 is estimated from

$$\hat{\sigma}^2 = \boldsymbol{v}^{\mathrm{T}}\,\boldsymbol{W}^{-1}\,\boldsymbol{v}/K \tag{4.25}$$

The estimate of the covariance matrix $\hat{\boldsymbol{F}}_x$ is then given by Eq.(4.10). After substituting $\hat{\boldsymbol{F}}_x$ instead of $\boldsymbol{F}_x$ into (4.23) we obtain also an estimate of the covariance matrix of adjusted values $\hat{\boldsymbol{F}}_{\hat{x}}$. Estimates of the variances of reconciled values are on the matrix $\hat{\boldsymbol{F}}_{\hat{x}}$ diagonal and we can use them for the construction of confidence intervals for individual elements of the vector $\tilde{\boldsymbol{x}}$. The interval

$$\langle \hat{x}_i - t_{1-\alpha/2}\,(K)\,\hat{\sigma}_{\hat{x}_i}\ ;\ \hat{x}_i + t_{1-\alpha/2}\,(K)\,\hat{\sigma}_{\hat{x}_i} \rangle \tag{4.26}$$

where $\hat{\sigma}_{\hat{x}_i} = (\hat{F}_{\hat{x}_{ii}})^{1/2}$ and $t_{1-\alpha/2}\,(K)$ is the 100 $(1 - \alpha/2)$ percentile of t (Student) distribution with K degrees of freedom, covers the real values with a probability $(1 - \alpha)$.

Example 4.4: *Reconciliation of a mass balance* ($\boldsymbol{F}_x$ is known)
Fig.4.5 shows a flowsheet of residual oil flow. The oil is pumped from the distillation column into two storage tanks, A and B (streams 1 and 2). The oil from the tanks is pumped further into a mixer (streams 3 and 4). In addition, oil is also pumped from the storage tank B to black water treatment plant (stream 5). From the mixer the oil is fed into a residual oil gasification unit (streams 6 through 10). Accumulations in the tanks are shown in the flowsheet as the fictitious streams 11 and 12.

The flow rates of all the above streams are measured. The task is to reconcile the measured values so that they should satisfy the balance equations around the individual nodes. Since the residual oil density is constant, the balance may be set up on the volume basis (integrals of flow rates and accumulation).

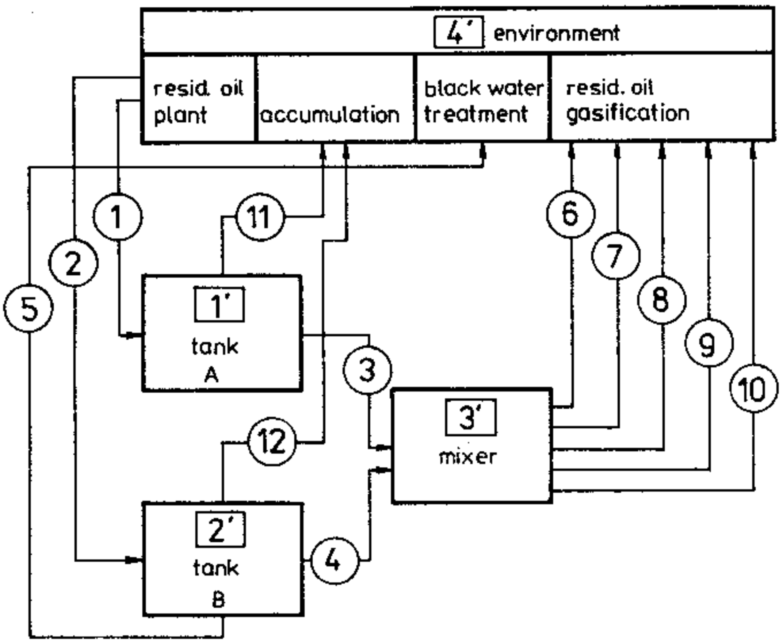


Fig.4.5 — Measurement of residual oil flows (Example 4.4)

A total of three independent equations among the measured quantities can be written - around the storage tank A (node 1'), tank B (node 2'), and the mixer (node 3'). The balance is written for the elements of the vector $\boldsymbol{x}$, for whose elements it holds $x_i = V_i$, where V_i is the volume flow of the ith stream during the balance interval.

$$x_1 - x_3 - x_{11} = 0$$

$$x_2 - x_4 - x_5 - x_{12} = 0 \qquad (4.27)$$

$$x_3 + x_4 - x_6 - x_7 - x_8 - x_9 - x_{10} = 0$$

The balance around the node 4' (environment) would already be dependent on the above three balance equations.

The equations (4.27) can be written in the form of the model (4.20), while $\boldsymbol{a} = \boldsymbol{0}$. The matrix $\boldsymbol{A}$ is

$$\boldsymbol{A} = \begin{bmatrix} 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 1 & 0 & -1 & -1 & -1 & -1 & -1 & 0 & 0 \end{bmatrix}$$

It is possible to make certain here that $\boldsymbol{A}$ is a reduced incidence matrix of the graph presented in Fig.4.5 (the environment being the reference node).

Table 4.1 — Input data and results to Example 4.4

i	x_i^+	$\sigma_{x_i^+}$	$F_{x_{ii}}$	v_i	$\hat{x}_i$	$\sigma_{\hat{x}_i}$	a_i
1	3849	19.24	370.3	14.83	3864	9.87	0.49
2	1848	9.24	85.3	-14.51	1833	5.87	0.36
3	3825	19.12	365.7	-9.45	3816	9.40	0.51
4	1362	6.81	46.3	8.54	1371	5.39	0.21
5	359	3.59	12.8	2.19	362	3.42	0.05
6	1022	5.11	26.1	-0.37	1022	4.92	0.04
7	1021	5.11	26.1	-0.37	1021	4.91	0.04
8	1033	5.17	26.7	-0.38	1033	4.97	0.04
9	1048	5.24	27.5	-0.39	1048	5.03	0.04
10	1064	5.32	28.3	-0.40	1064	5.10	0.04
11	49	4.20	17.6	-0.71	48.3	4.13	0.02
12	101	2.10	4.41	0.75	101.8	2.07	0.02

The values measured in the course of 96 h balance period are shown in the first column of Table 4.1. The streams 1 through 10 are integrals of the flow rates of individual streams over the whole time period, the values x_{11}^+ and x_{12}^+ are accumulations, i.e. volume differences in the storage tanks at the end and beginning of the balance period.

First the standard deviations of the individual measurements are assessed. The flow rates of the streams 1 through 4 and 6 through 10 were measured with positive displacement flowmeters whose standard deviation is equal to 0.5 per cent of the measured value (a half of the maximum measurement error). The stream 5 is measured by an orifice gauge with the standard deviation equal to 1 per cent of the measured value. In the case of accumulations the standard deviations in assessing the volume increments were 4.2 and 2.1 m^3 in the tanks A and B, resp. The errors of measurement are uncorrelated, so that the covariance matrix $\boldsymbol{F}_x$ is diagonal with squares of the standard deviations of the measurement errors on the diagonal. The standard deviations $\sigma_{x_i^+}$ as well as the matrix $\boldsymbol{F}_x$ diagonal are presented in Table 4.1.

Substituting $\boldsymbol{A}$, $\boldsymbol{F}_x$ and $\boldsymbol{x}^+$ into (4.21) and (4.22) yielded the adjustments $\boldsymbol{v}$ and reconciled values $\hat{\boldsymbol{x}}$. Besides, the covariance matrix of reconciled quantities $\boldsymbol{F}_{\hat{x}}$ was calculated according to Eq.(4.23). The adjustments, reconciled values and roots of the diagonal elements of the matrix $\boldsymbol{F}_{\hat{x}}$, representing the standard deviations of reconciled values $\sigma_{\hat{x}_i}$, are presented in the section of results of Table 4.1.

Shown in the last column of the Table are the expressions

$$a_i = 1 - \sigma_{\hat{x}_i} / \sigma_{x_i^+}$$

which are a measure of improving the precision of measured values in the course of reconciliation (a is so-called *adjustability*). If the improvement in precision is significant, the adjustability approaches 1, in the opposite case the adjustability is near zero. In other words, the adjustability represents the improvement of precision caused by reconciliation, and can be expressed in percent.

A considerable improvement in precision was accomplished only with the quantities 1 through 4, which exhibit the highest standard deviations of measurements as well.■

Example 4.5: *Reconciliation of concentrations in streams incident with a chemical reactor* ($\boldsymbol{F}_x$ is unknown)

Let us consider a continuous flow reactor for methane chlorination. Fed into the reactor are Cl_2, CH_4, CH_3Cl, CH_2Cl_2 and $CHCl_3$. In addition to these substances also HCl and CCl are present at the reactor outlet; their concentration at the inlet is almost zero (Fig.4.6).

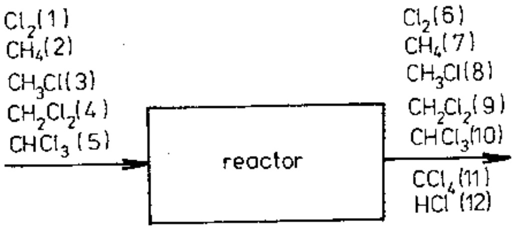


Fig.4.6 — A chlorination reactor (Example 4.5)

Steady state concentrations (molar fractions) of the substances are measured at the reactor inlet and outlet, i.e. a total of 12 quantities, whose numbering is obvious from Fig.4.6, are measured. In the chlorination reactor the number of moles is conserved, and, therefore, the molar flow rates at the inlet and outlet are equal. Also, the conservation law holds for the three chemical elements : C(1), H(2) and Cl(3). Our task is the reconciliation of measured concentrations to satisfy the following conditions:

- the reconciled values satisfy the law of chemical elements conservation,
- the sum of molar fractions in both streams equals 1.

Let us form a vector of the measured quantities $\boldsymbol{x}$ in such a way that the first five elements of the vector will consist of molar fractions of the substances 1 through 5 at the reactor inlet, the other seven elements then will be the concentrations of the substances 6 through 12 at the outlet. The elements conservation law can be written as

$$\sum_{j=1}^{12} A_{ij}\, x_j = 0 \qquad i = 1,2,3 \tag{4.28}$$

because the total number of moles remains constant.

The absolute values of the coefficients A_{ij} are equal to the number of atoms of the ith element in the formula of the substance of jth measured concentration. The signs of the elements A_{ij} are plus for $j < 5$ (inlet stream) and minus for $j > 5$ (outlet stream).

Equations (4.28) are further complemented by conditions for the sums of molar fractions:

$$\sum_{j=1}^{5} x_j - 1 = 0 \tag{4.29}$$

$$\sum_{j=6}^{12} x_j - 1 = 0 \tag{4.30}$$

The system of equations (4.28) - (4.30) can be written schematically as

$$\boldsymbol{Ax} + \boldsymbol{a} = \boldsymbol{0} \tag{4.31}$$

where the matrix $\boldsymbol{A}$ and vector $\boldsymbol{a}$ are

$$\boldsymbol{A} = \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 0 & -1 & -1 & -1 & -1 & -1 & 0 \\ 0 & 4 & 3 & 2 & 1 & 0 & -4 & -3 & -2 & -1 & 0 & -1 \\ 2 & 0 & 1 & 2 & 3 & -2 & 0 & -1 & -2 & -3 & -4 & -1 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \tag{4.32}$$

$$\boldsymbol{a} = (0, 0, 0, -1, -1)^{T}$$

By a more detailed examination we find that the matrix $\boldsymbol{A}$ does not have the full rank, rank $\boldsymbol{A} = 4$. Therefore, we eliminate the condition (4.30), which is linearly dependent on the preceding equations. The mathematical model is then formed by Eq.(4.31) where the matrix $\boldsymbol{A}$ contains only four rows of the matrix defined by Eq.(4.32), and the vector $\boldsymbol{a} = (0, 0, 0, -1)^{T}$.

So much about the mathematical model whose form is (4.20). As regards the measuring errors, we assume that they are uncorrelated, and that their standard deviations are directly proportional to the measured value (hence the concentrations are measured with the same relative precision). Then the covariance matrix of the measured quantities errors can be written in the form of Eq.(4.10). The matrix $\boldsymbol{W}$ is diagonal with squares of measured values on the diagonal:

$$W_{ij} = 0 \qquad \text{for } i \neq j \quad \text{and } W_{ii} = (x_i^+)^2 \tag{4.33}$$

Now we can proceed to the reconciliation proper. The measured values of concentrations x_i^+ are in the first column of Table 4.2, the matrix $\boldsymbol{W}$ diagonal is in the second column. The reconciliation is carried out according to (4.21) and (4.22), where the the matrix $\boldsymbol{W}$ is substituted for the covariance matrix $\boldsymbol{F}_x$. The results of the reconciliation - the vectors of adjustments $\boldsymbol{v}$ and of reconciled values $\hat{\boldsymbol{x}}$ - are also demonstrated in Table 4.2.

Table 4.2 — Input data and results to Example 4.5

i	x_i^+	W_{ii}	v_i	$\hat{x}_i$	$\hat{\sigma}_{x_i^+}$	$\hat{\sigma}_{\hat{x}_i}$	a_i
1	0.621	3.85E-1	-8.53E-3	0.612	6.35E-3	4.76E-4	0.92
2	0.269	7.23E-2	-6.65E-4	0.268	2.75E-3	7.61E-4	0.72
3	0.108	1.16E-2	-3.09E-4	0.108	1.10E-3	1.05E-3	0.05
4	0.00775	6.00E-5	-2.63E-6	0.00775	7.93E-5	7.92E-5	0.00
5	0.00376	1.41E-5	-8.63E-7	0.00376	3.84E-5	3.84E-5	0.00
6	0.0155	2.40E-4	6.86E-6	0.0155	1.58E-4	1.58E-4	0.00
7	0.0157	2.46E-4	3.85E-6	0.0157	1.60E-4	1.60E-4	0.00
8	0.0683	4.66E-3	1.54E-4	0.0685	6.98E-4	6.85E-4	0.02
9	0.248	6.15E-2	3.09E-3	0.251	2.53E-3	8.38E-4	0.67
10	0.0482	2.32E-3	1.57E-4	0.0484	4.93E-4	4.76E-4	0.03
11	0.593	3.51E-1	3.96E-3	0.597	6.06E-3	4.85E-4	0.92
12	0.00393	1.54E-5	1.31E-6	0.00393	4.02E-5	4.01E-5	0.00

To evaluate the precision of the reconciled values we substitute the vector $\boldsymbol{v}$ into (4.25) and thus we obtain an estimate of the proportionality constant from Eq.(4.10): $\hat{\sigma}^2 = 1.048 \times 10^{-4}$. Substituting σ^2 into Eq.(4.10) yields an estimate of the covariance matrix of the measurement $\hat{\boldsymbol{F}}_x$. The roots of the matrix $\hat{\boldsymbol{F}}_x$ diagonal elements, representing an estimate of standard deviations of the directly measured quantities errors $\hat{\sigma}_i$, are also presented in Table 4.2.

The covariance matrix of reconciled values $\boldsymbol{F}_{\hat{x}}$ is estimated by substituting $\hat{\boldsymbol{F}}_x$ for $\boldsymbol{F}_x$ into (4.23). The roots of matrix $\hat{\boldsymbol{F}}_{\hat{x}}$ diagonal elements (denoted $\hat{\sigma}_{\hat{x}_i}$) represent the estimates of standard deviations of the reconciled values. In the last column of Table 4.2 is the adjustability of the measured values (see Example 4.4). It can be seen here that all the quantities are adjustable but only in four of them (quantities 1,2,9 and 11) the adjustability is significantly greater than zero.■

4.4.2 Estimation of unmeasured quantities from redundant measurements

A vector of quantities $\boldsymbol{y} = (y_1 , \dots , y_J)^{\mathrm{T}}$ that are not measured directly is to be estimated. These quantities, however, are related to directly measured quantities $\boldsymbol{x} = (x_1 , \dots , x_I)^{\mathrm{T}}$ through K independent linear equations

$$\boldsymbol{B}\boldsymbol{y} = \boldsymbol{x} \tag{4.34}$$

This is the special case of the general linear model (4.1), where the vector $\boldsymbol{a}$ is the zero vector and $\boldsymbol{A}$ is the negative unit matrix. This special form of a model is met with very often in practice (polynomial regression of quantities $\boldsymbol{x}$ on parameters $\boldsymbol{y}$).

We assume that $I = K$ and rank $\boldsymbol{B} = J < I$. Supposing that it held rank $\boldsymbol{B} < J$, the vector $\boldsymbol{y}$ would be nonobservable. A case when $I = J$ would be that of the direct calculation of unmeasured quantities, which was dealt with in Section 4.3.

The objective of data processing in this case is, on the one hand to estimate the values of vector $\boldsymbol{y}$, and, on the other hand, to carry out the reconciliation of the directly measured values $\boldsymbol{x}^+$. Let us assume first that the covariance matrix of the measured quantities $\boldsymbol{F}_x$ is known.

The estimate $\hat{\boldsymbol{y}}$ is calculated by solving a system of so-called *normal equations*

$$\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{B}\hat{\boldsymbol{y}} = \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{x}^+ \tag{4.35}$$

which can be written

$$\hat{\boldsymbol{y}} = (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{x}^+ \tag{4.36}$$

the distribution of $\hat{\boldsymbol{y}}$ being $N_K (\tilde{\boldsymbol{y}} , \boldsymbol{F}_{\hat{y}})$, where the regular matrix

$$\boldsymbol{F}_{\hat{y}} = (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{B})^{-1} \tag{4.37}$$

Further we can form confidence intervals for individual elements of the vector $\tilde{\boldsymbol{y}}$. The intervals

$$\langle \hat{y}_j - u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \ ; \quad \hat{y}_j + u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \rangle \tag{4.38}$$

where $\sigma_{\hat{y}\,j} = (F_{\hat{y}})_{jj}^{1/2}$ cover the true values $\hat{y}_j$ with the probability (1 - α).

The confidence ellipsoid whose equation is

$$(\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_{\boldsymbol{x}}^{-1} \boldsymbol{B} (\boldsymbol{y} - \hat{\boldsymbol{y}}) = \chi^2_{1-\alpha}(J) \tag{4.39}$$

covers the true vector $\bar{\boldsymbol{y}}$ with the probability (1 - α).

The vector of reconciled values of the measured quantities $\hat{\boldsymbol{x}}$ is obtained when $\hat{\boldsymbol{y}}$ is substituted into (4.34):

$$\hat{\boldsymbol{x}} = \boldsymbol{B}\hat{\boldsymbol{y}} = \boldsymbol{B}(\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_{\boldsymbol{x}}^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_{\boldsymbol{x}}^{-1} \boldsymbol{x}^{+} \tag{4.40}$$

$\hat{\boldsymbol{x}}$ has the distribution $N_I(\bar{\boldsymbol{x}}, \boldsymbol{F}_{\hat{\boldsymbol{x}}})$, where the singular matrix

$$\boldsymbol{F}_{\hat{\boldsymbol{x}}} = \boldsymbol{B}(\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_{\boldsymbol{x}}^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \tag{4.41}$$

Obviously, the vector of adjustments is $\boldsymbol{v} = \hat{\boldsymbol{x}} - \boldsymbol{x}^{+}$. The value $Q_{\min}$, defined by Eq.(4.19), is, assuming a normal distribution of errors, a realization of a random variable with the distribution χ^2 and $(I - J)$ degrees of freedom.

When the covariance matrix of the measuring errors $\boldsymbol{F}_{\boldsymbol{x}}$ is not known but we know the matrix $\boldsymbol{W}$ from Eq.(4.9), $\hat{\boldsymbol{y}}$ and $\hat{\boldsymbol{x}}$ can be calculated according to Eqs (4.36) and (4.40), substituting $\boldsymbol{W}$ for $\boldsymbol{F}_{\boldsymbol{x}}$. The unknown coefficient σ^2 is estimated according to

$$\hat{\sigma}^2 = \boldsymbol{v}^{\mathrm{T}} \boldsymbol{W}^{-1} \boldsymbol{v} / (I - J) \tag{4.42}$$

The estimate of the vector $\hat{\boldsymbol{y}}$ covariance matrix is

$$\hat{\boldsymbol{F}}_{\hat{\boldsymbol{y}}} = \hat{\sigma}^2 (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{W}^{-1} \boldsymbol{B})^{-1} \tag{4.43}$$

The confidence intervals for individual elements of the vector $\bar{\boldsymbol{y}}$ covering the values $\bar{y}_j$ with the probability (1 - α) are

$$\langle \hat{y}_j - \hat{\sigma}_{\hat{y}\,j} t_{1-\alpha/2}(I - J) \;\; ; \;\; \hat{y}_j + \hat{\sigma}_{\hat{y}\,j} t_{1-\alpha/2}(I - J) \rangle \tag{4.44}$$

where $\hat{\sigma}_{\hat{y}_j} = (F_{\hat{y}})_{jj}^{1/2}$.

The confidence ellipsoid, covering the vector of true values $\bar{\boldsymbol{y}}$, with probability 1 - α has the equation

$$(\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_{\boldsymbol{x}}^{-1} \boldsymbol{B} (\boldsymbol{y} - \hat{\boldsymbol{y}}) / J = F_{1-\alpha}(J, I - J) \tag{4.45}$$

where $F_{1-\alpha}(J, I - J)$ is 100 (1 - α) percentile of the distribution $\boldsymbol{F}$ with J and $(I - J)$ degrees of freedom.

So far we have not concerned ourselves with assessing the confidence intervals and regions for quantities $\hat{\boldsymbol{x}}$. We shall meet with them now when solving a more general problem. Let us consider a vector $\tilde{\boldsymbol{h}}$ of the dimension $(m \times 1)$, which is a linear transformation of a vector $\boldsymbol{y}$:

$$\tilde{\boldsymbol{h}} = \boldsymbol{G}\boldsymbol{y} \tag{4.46}$$

where $\boldsymbol{G}$ is a known matrix of dimension $(m \times J)$. The vector $\boldsymbol{h}$ is called *parametric function.*

The estimate of the vector $\tilde{\boldsymbol{h}}$ is the vector $\hat{\boldsymbol{h}}$ defined

$$\hat{\boldsymbol{h}} = \boldsymbol{G}\hat{\boldsymbol{y}} = \boldsymbol{G}\,(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{F}_{\boldsymbol{x}}^{-1}\,\boldsymbol{B})^{-1}\,\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{F}_{\boldsymbol{x}}^{-1}\,\boldsymbol{x}^{+} \tag{4.47}$$

where $\hat{\boldsymbol{h}}$ is an unbiased estimate of $\tilde{\boldsymbol{h}}$; the covariance matrix of the vector $\hat{\boldsymbol{h}}$ is

$$\boldsymbol{F}_{\hat{h}} = \boldsymbol{G}\,(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{F}_{\boldsymbol{x}}^{-1}\,\boldsymbol{B})^{-1}\,\boldsymbol{G}^{\mathrm{T}} \tag{4.48}$$

In the case in which we do not know the matrix $\boldsymbol{F}_{\boldsymbol{x}}$ but do know the matrix $\boldsymbol{W}$ and the estimate of the coefficient σ^2 from Eq.(4.9), the covariance matrix $\boldsymbol{F}_{\hat{h}}$ is estimated according to

$$\hat{\boldsymbol{F}}_{\hat{h}} = \hat{\sigma}^2\,\boldsymbol{G}\,(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{W}^{-1}\,\boldsymbol{B})^{-1}\,\boldsymbol{G}^{\mathrm{T}} \tag{4.49}$$

Similarly, $\hat{\boldsymbol{h}}$ is estimated according to Eq.(4.47) where $\boldsymbol{W}$ is substituted for $\boldsymbol{F}_{\boldsymbol{x}}$.

The confidence intervals covering the true values $\tilde{h}_j$ with the probability $(1 - \alpha)$, are

$$\langle \hat{h}_j - u_{1-\alpha/2}\,\sigma_{\hat{h}\,j} \;\; ; \;\; \hat{h}_j + u_{1-\alpha/2}\,\sigma_{\hat{h}\,j} \rangle \tag{4.50}$$

where $\sigma_{\hat{h}j} = (F_{\hat{h}})_{jj}^{1/2}$ when the matrix $\boldsymbol{F}_{\boldsymbol{x}}$ is known, and

$$\langle \hat{h}_j - \hat{\sigma}_{\hat{h}j}\;t_{1-\alpha/2}\,(I - J) \quad ; \quad \hat{h}_j + \hat{\sigma}_{\hat{h}j}\;t_{1-\alpha/2}\,(I - J) \rangle \tag{4.51}$$

where $\hat{\sigma}_{\hat{h}j} = (\hat{F}_{\hat{h}})_{jj}^{1/2}$ when only the matrix $\boldsymbol{W}$ is known in advance.

When constructing the confidence ellipsoids we shall confine ourselves to a case of the matrix $\boldsymbol{F}_{\hat{h}}$ or its estimate being regular. The necessary condition of the matrix $\boldsymbol{F}_{\hat{h}}$ regularity is that it should hold rank $\boldsymbol{G} = m \le J$. This means that the number of the vector $\boldsymbol{h}$ elements must not be higher than the number of parameters $\boldsymbol{y}$ and, in addition, $\boldsymbol{G}$ must have the full rank. Since we assume that it holds for the number of directly measured quantities $I = K > J$, the covariance matrix $\boldsymbol{F}_{\hat{\boldsymbol{x}}}$ is singular and the confidence ellipsoid cannot be constructed simply (see Subsection 3.2.4).

On condition that the covariance matrix of the parametric function is regular, the confidence ellipsoid covering the vector of true values $\tilde{\boldsymbol{h}}$ with the probability (1 - α) has the following form:

$$(\boldsymbol{h} - \hat{\boldsymbol{h}})^{\mathrm{T}} \boldsymbol{F}_{\hat{h}}^{-1} (\boldsymbol{h} - \hat{\boldsymbol{h}}) = \chi^2_{1-\alpha}(m) \tag{4.52}$$

in the case that $\boldsymbol{F}_x$ is known beforehand, and

$$(\boldsymbol{h} - \hat{\boldsymbol{h}})^{\mathrm{T}} \hat{\boldsymbol{F}}_{\hat{h}}^{-1} (\boldsymbol{h} - \hat{\boldsymbol{h}}) \,/\, m = F_{1-\alpha}(m, I - J) \tag{4.53}$$

when only the matrix $\boldsymbol{W}$ is known beforehand.

Example 4.6: *Reconciliation of the material balance of fermentation* ($\boldsymbol{F}_x$ is known) The process for the manufacture of biomass from ethanol was described in Example 2.2 (Subsection 2.2.4). Steady state rates of formation in the fermenter of the following substances were measured: biomass (substance 1), ethanol (2), acetic acid (3), oxygen (4), and carbon dioxide (5). Some of the measurements are redundant and the task is to reconcile the measured values so that the reconciled values should satisfy the material balance.

In the same Example was described the balance model, in which the microbial conversion was expressed by the system of three stoichiometric equations:

$$\begin{aligned}
&1.\ 1.917\ C_2H_5OH + 1.618\ O_2 + 0.643\ NH_3 + 7\ Ah\ - \\
&\quad -\ C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00} - 3.214\ H_2O = 0 \\
&2.\ C_2H_5OH + 3\ O_2 - 2\ CO_2 - 3\ H_2O = 0 \\
&3.\ C_2H_5OH + O_2 - CH_3COOH - H_2O = 0
\end{aligned} \tag{4.54}$$

When we denote the number of moles of the substance as n_i , where the index i corresponds to the numbering of substances as given previously, and the extents of chemical reactions as ξ_j , where the index j corresponds to the number of the reaction, we can write the component balances by the following system of equations:

$$\begin{aligned}
n_1 &= \xi_1 \\
n_2 &= -1.917\,\xi_1 - \xi_2 - \xi_3 \\
n_3 &= \xi_3 \\
n_4 &= -1.618\,\xi_1 - 3\xi_2 - \xi_3 \\
n_5 &= +\ 2\xi_2
\end{aligned} \tag{4.55}$$

or in the matrix form

$$\boldsymbol{n} = \boldsymbol{B}\,\xi$$

where

$$\boldsymbol{B} = \begin{bmatrix} 1 & 0 & 0 \\ -1.917 & -1 & -1 \\ 0 & 0 & 1 \\ -1.618 & -3 & -1 \\ 0 & 2 & 0 \end{bmatrix}$$

It is possible to make certain that $-\boldsymbol{B}$ is a submatrix of the transpose of the matrix of stoichiometric coefficients, which was defined in Subsection 2.2.4. The columns of the matrix $\boldsymbol{B}$ are formed by stoichiometric coefficients of the substances appearing in the individual equations (positive in the case of products and negative for the starting substances).

The following number of moles of the substances formed were measured:

$$\boldsymbol{n}^+ = (0.3500, -1.0890, 0.0032, -1.7712, 0.7857)^{\mathrm{T}}$$

Besides, the covariance matrix of errors of the vector $\boldsymbol{n}^+$ is known (Madron, Veverka & Vanecek 1977):

$$\boldsymbol{F}_n = \begin{bmatrix} 2.99\times10^{-5} & 0 & 2.77\times10^{-8} & 0 & 0 \\ 0 & 3.97\times10^{-5} & 0 & 0 & 0 \\ 2.77\times10^{-3} & 0 & 1.31\times10^{-9} & 0 & 0 \\ 0 & 0 & 0 & 9.60\times10^{-3} & 5.30\times10^{-4} \\ 0 & 0 & 0 & 5.30\times10^{-4} & 1.61\times10^{-3} \end{bmatrix}$$

When we change notation ($\boldsymbol{n} \rightarrow \boldsymbol{x}$ and $\xi \rightarrow \boldsymbol{y}$), we obtain the model (4.34). The following calculation will be done with the original notation, i.e. with vectors $\boldsymbol{n}$ a ξ. The vector of the chemical reactions rates is estimated according to Eq.(4.36):

$$\xi = (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_n^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_n^{-1} \boldsymbol{n}^+ \tag{4.56}$$

and the reconciled vector $\hat{\boldsymbol{n}}$ according to (4.40)

$$\hat{\boldsymbol{n}} = \boldsymbol{B}\,\xi \tag{4.57}$$

We are further interested in the variances of the reconciled values $\hat{\boldsymbol{n}}$. Their covariance matrix is obtained from Eq.(4.41):

$$\boldsymbol{F}_{\hat{n}} = \boldsymbol{B}\,(\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_n^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \tag{4.58}$$

The matrix $F_{\hat{n}}$ diagonal, i.e. the vector $\sigma_{\hat{n}}$, is

$$\sigma_{\hat{n}} = (2.2 \times 10^{-5}\,,\ 3.6 \times 10^{-5}\,,\ 1.3 \times 10^{-9}\,,\ 5.8 \times 10^{-4}\,,\ 3.9 \times 10^{-4}\,)^{\mathrm{T}}$$

Comparing the matrices F_n and $F_{\hat{n}}$ diagonals we can judge on the change of the higher precision brought about by reconciliation.■

Example 4.7: *Linear regression* (**F_x** is not known)
The dependence of an electrolyzer voltage on current intensity was measured . The values of current intensity (I), in kA, and voltage (U), in volt, measured at ten steady states, are presented in Table 4.3. The task is to assess the values of the parameters of linear dependence between the current and voltage.

Table 4.3 — Input data and results to Example 4.7

j	I_j	U_j^+	$\hat{U}_j$	$\sigma_{\hat{U}_j}$	Δ
1	2.701	4.305	4.297	0.00375	0.00865
2	2.808	4.341	4.346	0.00242	0.00559
3	2.905	4.390	4.390	0.00207	0.00477
4	3.002	4.433	4.435	0.00287	0.00662
5	3.052	4.464	4.458	0.00352	0.00813
6	3.006	4.446	4.437	0.00292	0.00673
7	2.907	4.391	4.391	0.00207	0.00479
8	2.803	4.341	4.344	0.00247	0.00570
9	2.704	4.300	4.298	0.00370	0.00855
10	2.955	4.403	4.413	0.00237	0.00547

We assume that only the voltage measurement is subject to a substantial error caused by fluctuations in the process variables (electrode gap, electrolyte composition); this is where the main error is concentrated. We assume further that the errors are independent, with a constant (unknown) variance.

The mathematical model is

$$U = b_0 + b_1\, I \tag{4.59}$$

where b_0 and b_1 are unknown coefficients. Eq.(4.59) can be written for the individual measured regimes

$$U_j = b_0 + b_1\, I_j\,,\quad j = 1\ ,\ \dots\ ,\ 10 \tag{4.60}$$

or in the matrix form

$$\boldsymbol{U} = \boldsymbol{B}\boldsymbol{b} \tag{4.61}$$

where matrix $\boldsymbol{B}$ is of dimension (10×2), its jth row equals $(1\ ,\ I_j\ )$, and the vector of parameters $\boldsymbol{b} = (b_0\ , b_1\ )^{\mathrm{T}}$. If we change the notation ($\boldsymbol{b} \rightarrow \boldsymbol{y}$ and $\boldsymbol{U} \rightarrow \boldsymbol{x}$) in Eq.(4.61), we have the model (4.34). In the subsequent calculations the notation $\boldsymbol{U}$ will be used for the measured quantities and $\boldsymbol{b}$ for parameters.

Estimates of the parameters will be obtained from (4.36) by substituting the matrix $\boldsymbol{W}$ for $\boldsymbol{F}_x$. In this case the covariance matrix of measuring errors can be expressed in the form

$$\boldsymbol{F}_x = \sigma^2\ \boldsymbol{W} = \sigma^2\ \boldsymbol{I} \tag{4.62}$$

where $\boldsymbol{I}$ is unit matrix. Since $\boldsymbol{W}$ is unit matrix, Eq.(4.36) can be rewritten in a simpler form

$$\hat{\boldsymbol{b}} = (\boldsymbol{B}^{\mathrm{T}}\ \boldsymbol{B})^{-1}\ \boldsymbol{B}^{\mathrm{T}}\ \boldsymbol{U}^{+} \tag{4.63}$$

where $\boldsymbol{U}^{+}$ obviously is a vector of the measured values of voltage. Then the estimates of the parameters are

$$\begin{aligned} \hat{b}_0 &= 3.059\ \mathrm{kA} \\ \hat{b}_1 &= 0.458\ 4\ \mathrm{kA\ V^{-1}} \end{aligned} \tag{4.64}$$

The covariance matrix of parameters estimates is assessed from (4.43). First we calculate reconciled values from Eq.(4.40), whose form in this case is

$$\hat{\boldsymbol{U}} = \boldsymbol{B}\ (\boldsymbol{B}^{\mathrm{T}}\ \boldsymbol{B})^{-1}\ \boldsymbol{B}^{\mathrm{T}}\ \boldsymbol{U}^{+} \tag{4.65}$$

The reconciled values of voltage are presented in Table 4.3. The vector of adjustments $\boldsymbol{v} = \hat{\boldsymbol{U}} - \boldsymbol{U}^{+}$ is calculated next. The proportionality constant σ^2 is estimated from Eq.(4.42), which can be rearranged to

$$\hat{\sigma}^2 = \frac{\boldsymbol{v}^{T}\ \boldsymbol{v}}{(I - J)} = \frac{\Sigma v_i^2}{(10 - 2)} = 4.165 \times 10^{-5}$$

(where I is the number of directly measured quantities, i.e. the number of measured steady states).

According to Eq.(4.43) the estimate of the covariance matrix of the parameters estimates is

Table 4.4 — Input data and results to Example 4.8

i	x_i^+	$\sigma_{x_i}^+$	v_i	$\hat{x}_i$	$\sigma_{\hat{x}_i}$	a_i
1	100.1	1.0	-0.942	99.2	0.60	0.40
2	41.1	0.8	0.000	41.1	0.80	0.00
3	79.0	0.8	0.349	79.4	0.60	0.25
4	30.6	0.4	-0.063	30.5	0.39	0.02
5	108.3	2.0	1.590	109.9	0.69	0.65
6	19.8	0.1	0.009	19.8	0.10	0.00

$$\hat{\boldsymbol{F}}_{\hat{b}} = \hat{\sigma}^2 (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{B})^{-1} = 4.164 \times 10^{-5} \begin{bmatrix} 58.989 & -20.417 \\ -20.417 & 7.079 \end{bmatrix}$$

The confidence intervals for the parameters b_0 and b_1 for $(1 - \alpha) = 0.95$ are, according to Eq.(4.44):

$$\hat{b}_0 = 3.059 \pm (4.165 \times 10^{-5} \times 58.989)^{1/2} \times 2.306$$

$$\tilde{b}_0 \in \langle 2.945, 3.173\rangle$$

$$\hat{b}^1 = 0.458\ 4 \pm (4.165 \times 10^{-5} \times 7.079)^{1/2} \times 2.306$$

$$\tilde{b}_1 \in \langle 0.418\ 8, 0.498\ 0\rangle$$

since

$$\hat{\sigma}_{\hat{b}_0} = (\hat{F}_{\hat{b}_{11}})^{1/2}$$

$$\hat{\sigma}_{\hat{b}_1} = (\hat{F}_{\hat{b}_{22}})^{1/2}$$

and

$$t_{0.975}(8) = 2.306$$

Further, we shall find the confidence ellipse covering the vector of true values of parameters $\boldsymbol{b}$ with probability 0.95. According to (4.45) the ellipse equation is

$$(\boldsymbol{b} - \hat{\boldsymbol{b}})^{\mathrm{T}} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{B} (\boldsymbol{b} - \hat{\boldsymbol{b}}) = 2\sigma^2 F(2,8)$$

since

$$\hat{\boldsymbol{F}}_{\hat{b}} = \hat{\sigma}^{-2} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{B}$$

$$\boldsymbol{B}^{\mathrm{T}}\boldsymbol{B} = \begin{bmatrix} 10.000 & 28.843 \\ 28.843 & 88.333 \end{bmatrix}$$

and, after the matrix operations, we obtain the ellipse equation in the form

$$10b'^2_0 + 2 \times 28.843b'_0\, b'_1 + 88.333b'^2_1 = 3.714 \times 10^{-4} \tag{4.66}$$

In so doing we made the substitution $\boldsymbol{b} - \hat{\boldsymbol{b}} = \boldsymbol{b}'$, whereby the origin of coordinates was shifted into the ellipse centre. For details of an analysis of Eq.(4.66) the reader is referred to textbooks of analytical geometry, here only the results will be presented. It is a case of an ellipse rotated in the coordinate system through an angle -19.09°. The length of the major and minor semiaxes is 0.1566 and 1.995×10^{-3}, resp. The ellipse is plotted in Fig.4.7, where dashed lines mark the confidence intervals for the individual parameters (here the intervals create bands that are symmetrical around the individual coordinates). The ellipse area (given as the product πab , where a and b stands for the semiaxes lengths) is 9.82×10^{-4}.

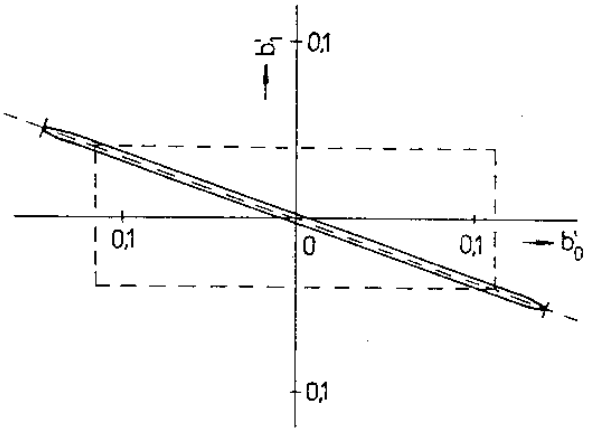


Fig.4.7 — The confidence ellipse (Example 4.7)

The area of the confidence ellipse is considerably smaller than the area of a rectangle formed as the intersection of the bands corresponding to the individual reliability intervals. It is obvious, too, that the reliability coefficient for that rectangle is smaller than the reliability coefficient for the individual bands and ellipse, i.e. 0.95. It is, therefore, convenient to use the reliability regions (ellipsoids) for a greater number of variables.

Further, let us note the elongated shape of the ellipse. Together with the ellipse inclination it means that the estimates are strongly correlated. It is important that the whole set of pairs of the parameters values, centred around the ellipse major axis, is in good agreement with the measured values. Otherwise, it means that the parameters cannot be precisely assessed separately but only in combination with one another. Of course, this is undesirable from the viewpoint of estimating the individual parameters. The whole problem, however, is not caused by the precision of the measurement itself but by an improper choice of the values of current intensity at which the measurement was carried out. We shall concern ourselves with this problem once again in Chapter 5, dealing with optimum planning of measurement.

In conclusion let us discuss the question of the precision of calculating the value of voltage for a given current intensity from the regression equation (4.59). Let the Eq.(4.59) be written in a matrix form:

$$\boldsymbol{O} = (1\ ,\ I)\begin{bmatrix}\hat{b}_0\\ \hat{b}_1\end{bmatrix} \tag{4.67}$$

This is the case of a parametric function (4.46), so that (4.51) can be used for the construction of the confidence interval. The estimate of the variance of an assessed value of the voltage U is obtained from Eq.(4.49), where the matrix $\hat{\boldsymbol{F}}_{\hat{h}}$ has a single element equal to the variance of the calculated voltage

$$\hat{\sigma}_{\hat{U}}^2 = \hat{\sigma}^2\,(1\ ,\ I)\,(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{B})^{-1}\begin{bmatrix}1\\ I\end{bmatrix} \tag{4.68}$$

where $\hat{\sigma}^2$ is given by (4.42).

The confidence interval is obtained by substituting $\hat{\sigma}_{\hat{U}}$ into (4.51). The interval covering the true value of voltage with the probability of 0.95 is

$$\langle \hat{U} - \hat{\sigma}_{\hat{U}}\, t_{0.975}\,(8)\quad ;\quad \hat{U} + \hat{\sigma}_{\hat{U}}\, t_{0.975}\,(8)\rangle \tag{4.69}$$

The calculation was made for the individual measured values of current intensity. Hence, for example for the first measurement $I_1 = 2.701$ kA the value of $\hat{U} = 4.297$ V. Substituting into (4.68) we obtain $\hat{\sigma}_{\hat{U}} = 3.751\times10^{-3}$ V and the confidence interval is

$$\langle 4.297 - 3.751\times10^{-3}\times2.306\ ;\ 4.297 - 3.751\times10^{-3}\times2.306\rangle$$

that is

$$\langle 4.288\ ;\ 4.306\rangle$$

where 2.306 is $t_{0.975}\,(8)$.

The results are presented in the last column of Table 4.3 in the form of $\Delta = \hat{\sigma}_{\hat{U}}\, t_{0.975}\,(8)$ values, these being the half-widths of the confidence intervals. In Fig.4.8 the confidence intervals are presented as the two curves marking off a region in the regression line vicinity. The confidence band in Fig.4.8 can be interpreted as follows: if we choose a value of current intensity within the measuring range (for instance I_0) we obtain, after substituting into the regression equation, the value U which obviously lies on the regression line. The true (unknown) value of U_0 lies, with the probability of 95%, on the line segment intercepted by the confidence band on the straight line $I = I_0$.■

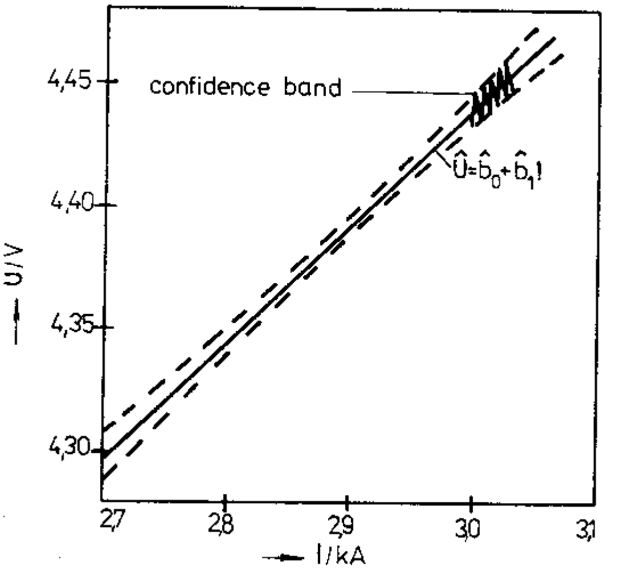


Fig.4.8 — Regression of voltage U on current intensity I (Example 4.7)

4.4.3 General linear model

The hitherto discussed two types of mathematical models enable a number of important practical problems to be solved but they are not applicable in all cases. An important generalization is represented by the general linear model

$$\boldsymbol{a} + \boldsymbol{A}\boldsymbol{x} + \boldsymbol{B}\boldsymbol{y} = 0 \tag{4.70}$$

whose simplification gives the models presented earlier.

Let us assume that all the quantities are observable and at least some of the measured quantities are redundant. These assumptions are equivalent to the validity of the following relations:

$$\begin{aligned} &\operatorname{rank}\,(\boldsymbol{A}\,,\,\boldsymbol{B}) = K \\ &\operatorname{rank}\,\boldsymbol{B} = J \\ &I > K - J > 0 \end{aligned} \tag{4.71}$$

where I is the number of measured quantities, J is the number of unmeasured quantities, K being the number of equations of the mathematical model. Obviously, the matrices types are $\boldsymbol{A}$ $(K \times I)$ and $\boldsymbol{B}$ $(K \times J)$.

Estimates $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$ are obtained by solving the system of equations

$$\begin{bmatrix} \boldsymbol{A}\boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}} & , & \boldsymbol{B} \\ \boldsymbol{B}^{\mathrm{T}} & , & \boldsymbol{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{k} \\ \hat{\boldsymbol{y}} \end{bmatrix} + \begin{bmatrix} \boldsymbol{a} + \boldsymbol{A}\boldsymbol{x}^{+} \\ \boldsymbol{0} \end{bmatrix} = \boldsymbol{0} \tag{4.72}$$

$$\boldsymbol{v} = \boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}}\boldsymbol{k} \tag{4.73}$$

$$\hat{\boldsymbol{x}} = \boldsymbol{x}^{+} + \boldsymbol{v} \tag{4.74}$$

where $\boldsymbol{k}$ is the vector of Lagrange's multipliers.

First, Eq.(4.72) is solved with respect to $\boldsymbol{k}$ and $\hat{\boldsymbol{y}}$:

$$\begin{bmatrix} \boldsymbol{k} \\ \hat{\boldsymbol{y}} \end{bmatrix} = - \begin{bmatrix} \boldsymbol{A}\boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}} & , & \boldsymbol{B} \\ \boldsymbol{B}^{\mathrm{T}} & , & \boldsymbol{0} \end{bmatrix}^{-1} \begin{bmatrix} \boldsymbol{a} + \boldsymbol{A}\boldsymbol{x}^{+} \\ \boldsymbol{0} \end{bmatrix} \tag{4.75}$$

The partitioned matrix in (4.75) is divided into blocks $\boldsymbol{Q}$:

$$\begin{bmatrix} \boldsymbol{A}\boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}} & , & \boldsymbol{B} \\ \boldsymbol{B}^{\mathrm{T}} & , & \boldsymbol{0} \end{bmatrix}^{-1} = \begin{bmatrix} \boldsymbol{Q}_{11} & , & \boldsymbol{Q}_{12} \\ \boldsymbol{Q}_{21} & , & \boldsymbol{Q}_{22} \end{bmatrix} \tag{4.76}$$

The individual blocks are of the types $\boldsymbol{Q}_{11}$ $(K \times K)$, $\boldsymbol{Q}_{12}$ $(K \times J)$, $\boldsymbol{Q}_{21}$ $(J \times K)$ and $\boldsymbol{Q}_{22}$ $(J \times J)$. The solution is then

$$\boldsymbol{k} = - \boldsymbol{Q}_{11}(\boldsymbol{a} + \boldsymbol{A}\boldsymbol{x}^{+}) \tag{4.77}$$

$$\hat{\boldsymbol{y}} = - \boldsymbol{Q}_{21}(\boldsymbol{a} + \boldsymbol{A}\boldsymbol{x}^{+}) \tag{4.78}$$

$$\boldsymbol{v} = \boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}}\boldsymbol{k} = - \boldsymbol{F}_x\boldsymbol{A}^{\mathrm{T}}\boldsymbol{Q}_{11}(\boldsymbol{a} + \boldsymbol{A}\boldsymbol{x}^{+}) \tag{4.79}$$

$$\hat{\boldsymbol{x}} = \boldsymbol{x}^{+} + \boldsymbol{v} \tag{4.80}$$

$\hat{\boldsymbol{y}}$ is a random vector with $N_J(\hat{\boldsymbol{y}}, \boldsymbol{F}_{\hat{y}})$ distribution, where

$$\boldsymbol{F}_{\hat{y}} = - \boldsymbol{Q}_{22} \tag{4.81}$$

The matrix $\boldsymbol{F}_{\hat{y}}$ rank is J at the most. When it holds, besides the conditions (4.71), that $I > K = \operatorname{rank} \boldsymbol{A}$, the matrix $\boldsymbol{F}_{\hat{y}}$ rank is just equal to J, and this matrix is regular.

The intervals

$$\langle \hat{y}_j - u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \quad ; \quad \hat{y}_j + u_{1-\alpha/2}\, \sigma_{\hat{y}_j} \rangle \tag{4.82}$$

where $\sigma_{\hat{y}_j} = (F_{\hat{y}_{jj}})^{1/2}$, cover the true values with the probability $(1 - \alpha)$.

For the regular matrix $\boldsymbol{F}_{\hat{y}}$, the ellipsoid

$$(\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}} \boldsymbol{F}_{\hat{y}}^{-1} (\boldsymbol{y} - \hat{\boldsymbol{y}}) \leq \chi^2_{1-\alpha}(J) \tag{4.83}$$

covers the vector of the true values with the probability $(1 - \alpha)$.

The vector of adjustments $\boldsymbol{v}$, expressed by Eq.(4.79), has the distribution $N_I(\boldsymbol{0}, \boldsymbol{F}_v)$, where the singular matrix $\boldsymbol{F}_v = \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} \boldsymbol{Q}_{11} \boldsymbol{A} \boldsymbol{F}_x$. Assuming the normal distribution of errors, the value $Q_{\min}$ defined by (4.19) is a realization of random variable with χ^2 distribution with $(K - J)$ degrees of freedom. The vector of reconciled values $\hat{\boldsymbol{x}}$ given by Eq.(4.80) has the distribution $N_I(\bar{\boldsymbol{x}}, \boldsymbol{F}_{\hat{x}})$, where the singular matrix

$$\boldsymbol{F}_{\hat{x}} = \boldsymbol{F}_x - \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} \boldsymbol{Q}_{11} \boldsymbol{A} \boldsymbol{F}_x \tag{4.84}$$

has the rank $[I - (K - J)]$.

The intervals

$$\langle \hat{x}_i - u_{1-\alpha/2}\, \sigma_{\hat{x}_i} \quad ; \quad \hat{x}_i + u_{1-\alpha/2}\, \sigma_{\hat{x}_i} \rangle \tag{4.85}$$

where $\sigma_{\hat{x}_i} = (F_{\hat{x}_{ii}})^{1/2}$, cover the real values with the probability $(1 - \alpha)$.

When the covariance matrix of measuring errors $\boldsymbol{F}_x$ is not known but the matrix $\boldsymbol{W}$ is known, we shall present the results for a frequent case when it holds rank $\boldsymbol{A} = K < I$. The estimates $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$ are calculated according to (4.78) and (4.80), substituting $\boldsymbol{W}$ for $\boldsymbol{F}_x$. The unknown coefficient σ^2 from (4.9) is estimated from

$$\hat{\sigma}^2 = \frac{\boldsymbol{v}^{\mathrm{T}} \boldsymbol{W}^{-1} \boldsymbol{v}}{K - J} \tag{4.86}$$

The covariance matrix of measured quantities $\boldsymbol{F}_x$ is estimated according to (4.10). The estimates of the vectors $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$ covariance matrices are

$$\hat{\boldsymbol{F}}_{\hat{y}} = -\hat{\sigma}^2 \boldsymbol{Q}_{22} \tag{4.87}$$

$$\hat{\boldsymbol{F}}_{\hat{x}} = \hat{\sigma}^2 (\boldsymbol{W} - \boldsymbol{W} \boldsymbol{A}^{\mathrm{T}} \boldsymbol{Q}_{11} \boldsymbol{A} \boldsymbol{W}) \tag{4.88}$$

The confidence intervals for the individual elements of the vector $\bar{\boldsymbol{y}}$ are

$$\langle \hat{y}_j - \hat{\sigma}_{\hat{y}_j} t_{1-\alpha/2}\ (K-J) \quad ; \quad \hat{y}_j + \hat{\sigma}_{\hat{y}_j} t_{1-\alpha/2}\ (K-J) \rangle \tag{4.89}$$

where $\hat{\sigma}_{\hat{y}_j} = (\hat{F}_{\hat{y}_{jj}})^{1/2}$

The equation of confidence ellipsoid is

$$(\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}}\, \hat{\boldsymbol{F}}_{\hat{y}}^{-1}\, (\boldsymbol{y} - \hat{\boldsymbol{y}}) / J = F_{1-\alpha}(J, K-J) \tag{4.90}$$

The confidence intervals for the individual elements of the vector $\hat{\boldsymbol{x}}$ are

$$\langle \hat{x}_i - \hat{\sigma}_{\hat{x}_i} t_{1-\alpha/2}\ (K-J) \quad ; \quad \hat{x}_i + \hat{\sigma}_{\hat{x}_i} t_{1-\alpha/2}\ (K-J) \rangle \tag{4.91}$$

where $\hat{\sigma}_{\hat{x}_i} = (\hat{F}_{\hat{x}_{ii}})^{1/2}$. The confidence intervals (4.89) and (4.91) correspond to the probability $(1 - \alpha)$.

Improving the precision of measured quantities as the result of reconciliation

Let us examine Eq.(4.84) in detail. The second term on the right-hand side of the equation represents the covariance matrix of adjustments $\boldsymbol{F}_v$. Then (4.84) can be rewritten

$$\boldsymbol{F}_x = \boldsymbol{F}_{\hat{x}} + \boldsymbol{F}_v \tag{4.92}$$

from which it follows

$$\sigma_i^2 = \sigma_{\hat{x}_i}^2 + \sigma_{v_i}^2 \tag{4.93}$$

These important relations follow from statistical independence of the vectors $\hat{\boldsymbol{x}}$ and $\boldsymbol{v}$ (Kubáček & Pázman 1979). An important inequality between the variances of measured and reconciled values follows from (4.93):

$$\sigma_i^2 \geq \sigma_{\hat{x}_i}^2 \tag{4.94}$$

Then it is obvious that the precision of a quantity cannot become worse as the result of reconciliation. In the limiting case, when the precision remains unchanged, i.e. when it holds $\sigma_i^2 = \sigma_{\hat{x}_i}^2$, the variance of the adjustment must be zero. Since it holds, at the same time, that the mean value of the adjustment is null, the value of the adjustment must be null as well, irrespective of measured values. Such quantities are called nonadjustable. If the errors of measurement are independent (diagonal covariance matrix), the *nonadjustable* quantities are identical with nonredundant (just determined) quantities.

The expression

$$a_i = 1 - \sigma_{\hat{x}_i} / \sigma_i \qquad a_i \in \langle 0 ; 1 \rangle \tag{4.95}$$

has already been referred to as the adjustability (see Example 4.4). The adjustability of nonadjustable quantities is equal to zero, the adjustability of significantly adjustable quantities limits to one (the precision of those quantities is significantly influenced by the measurement of other variables). The observable unmeasured quantities can be understood as fully adjustable ($a_i = 1$).

Example 4.8: *A mass balance* (**F_x** is known)
The diagram of a single-component balance is presented in Fig.4.9 (for the sake of clarity the node representing environment is not shown). There are four nodes and eight streams, out of which only six are measured. The measured flow rates, including their standard deviations, are in the first part of Table 4.4. The task is to assess the values of the unmeasured flows and, besides, to reconcile the measured ones.

Table 4.4 — Input data and results to Example 4.8

i	x_i^+	$\sigma_{x_i^+}$	v_i	$\hat{x}_i$	$\sigma_{\hat{x}_i}$	a_i
1	100.1	1.0	-0.942	99.2	0.60	0.40
2	41.1	0.8	0.000	41.1	0.80	0.00
3	79.0	0.8	0.349	79.4	0.60	0.25
4	30.6	0.4	-0.063	30.5	0.39	0.02
5	108.3	2.0	1.590	109.9	0.69	0.65
6	19.8	0.1	0.009	19.8	0.10	0.00

When the ith measured quantity is denoted as x_i and the jth unmeasured quantity as y_j, the balance equations around the individual nodes are

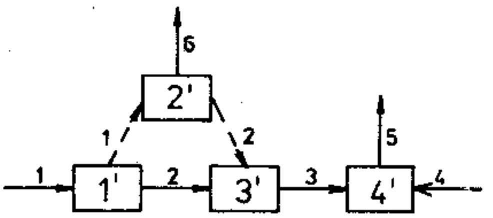


Fig.4.9 — Mass balance
—— measured streams; - - - unmeasured streams

$$\begin{array}{rrrrrrrrrrrl}
x_1 & - & x_2 & & & & & & - & y_1 & & = 0 \\
 & & & & & & - & x_6 & + & y_1 & - \; y_2 & = 0 \\
 & & x_2 & - & x_3 & & & & & & + \; y_2 & = 0 \\
 & & & & x_3 & + & x_4 & - \; x_5 & & & & = 0
\end{array}$$

or, in the matrix form

$$\boldsymbol{Ax} + \boldsymbol{By} = 0$$

where

$$\boldsymbol{A} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & -1 & 0 \end{bmatrix} \qquad \boldsymbol{B} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}$$

We point out that $\boldsymbol{A}$ and $\boldsymbol{B}$ are reduced incidence matrices of the graphs of measured and unmeasured streams.

This is a case of the model (4.70) where the vector $\boldsymbol{a} = \boldsymbol{0}$. The problem solution is: vectors $\hat{\boldsymbol{y}}$ and $\boldsymbol{k}$ are calculated from Eqs.(4.77) and (4.78).

$$\hat{\boldsymbol{y}} = (58.06\ ,\ 38.25)^T$$

$$\boldsymbol{k} = (-0.9416\ ,\ -0.9416\ ,\ -0.3964\ ,\ -0.9416)^T$$

After substituting $\boldsymbol{k}$ into (4.79) and (4.80) we obtain the vector of adjustments $\boldsymbol{v}$ and vector of reconciled values $\hat{\boldsymbol{x}}$. The vectors $\boldsymbol{v}$ and $\hat{\boldsymbol{x}}$ are presented in Tab.4.4.

The covariance matrices of the vectors $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$ are assessed from Eqs (4.81) and (4.84). The vector of standard deviations of $\hat{\boldsymbol{y}}$ (roots of the matrix $\boldsymbol{F}_{\hat{y}}$ diagonal) is $\sigma_{\hat{y}} = (1.032\ ;\ 1.013)^T$. Standard deviations of the reconciled quantities $\hat{x}_i$ (roots of the matrix $\boldsymbol{F}_{\hat{x}}$ diagonal elements) are shown in Table 4.4. The adjustability $\boldsymbol{a}$ is in the right hand side of the Table. The measured stream 2 has the adjustability equal to zero (see also the zero value of its adjustment). In this case of the nonredundant variable the reconciliation does not lead to a higher precision when compared with direct measurement.■

4.4.4 Reducing the dimension of the problem

When solving the problems of reconciliating redundant measurements, in practice we may often meet with the case when the dimension of the problem to be solved (number of equations and variables) exceeds the capacity of the computer which is available. With the growing dimension of a task also the demands on computer time are growing, and even problems of numerical nature may be encountered (stability of the solution of large systems of equations). One of the possibilities of how to avoid these difficulties lies in dividing the problem into several smaller ones and solving them separately. A drawback of this approach, however, is that those quantities appearing in more subproblems simultaneously acquire different values, so that the resultant solution is not consistent. There exist, however, other possibilities of reducing the dimension of a problem solved.

The fundamental problem usually is the solution of the system (4.72), where the inverse of matrix whose dimension is $(J + K) \times (J + K)$ occurs. But the problem need not be solved globally. In Section 4.2 the decomposition by transforming a system of equations to the canonical form was described. In that case reconciliation can be carried out using the method described in Subsection 4.4.1, where the matrix $\boldsymbol{A}$ appearing in Eq.(4.20) is identical with the matrix formed as the intersection of the horizontal band 2 and vertical bands 3 and 4 in Fig.4.2d.

Let us introduce the following notation for the submatrices from Fig.4.2d (the submatrices indices stand for the numbers of the horizontal and vertical bands in Fig.4.2d).

$$\boldsymbol{A} = \boldsymbol{M}_{2,\,(3+4)}$$

$$\boldsymbol{a} = \boldsymbol{M}_{2,5}$$

$$\boldsymbol{B} = \boldsymbol{M}_{1\boldsymbol{a},\,(3+4)}$$

$$\boldsymbol{b} = \boldsymbol{M}_{1\boldsymbol{a},\,5}$$

The results of reconciliation, including the information about errors propagation, are then expressed by Eqs (4.21) and (4.26).

Calculation of the observable unmeasured quantities $\boldsymbol{y}$ and of their covariance matrices is conducted according to

$$\begin{aligned} \hat{\boldsymbol{y}} &= -\boldsymbol{B}\hat{\boldsymbol{x}} - \boldsymbol{b} \\ \boldsymbol{F}_{\hat{y}} &= \boldsymbol{B}\boldsymbol{F}_{\hat{x}}\,\boldsymbol{B}^{\mathrm{T}} \end{aligned} \tag{4.96}$$

With the decomposition made in the way described in Section 4.2, the simplification of the numerical side of the solution is obvious.

In Example 4.2 the decomposition of the mathematical model of a mass balance was done. Then it follows from Fig.4.4e that

$$\boldsymbol{A} = \begin{bmatrix} 1 & 0 & 0 & -1 & -1 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \qquad \boldsymbol{a} = \begin{bmatrix} -f_2 \\ -f_1 \\ -f_1 \quad -f_2 \end{bmatrix}$$

$$\boldsymbol{B} = \begin{bmatrix} -1 & 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \boldsymbol{a} = \begin{bmatrix} & 0 & \\ -f_1 & & -f_2 \end{bmatrix}$$

There are also other possibilities of reducing the dimension of the problem. If the matrix $\boldsymbol{A}$ in the model (4.70) satisfies the conditions (quite frequent in practice) $I \geq K$ and rank $\boldsymbol{I} = K$, it is possible to make use of the existence of the null submatrix in Eq.(4.76) and carry out decomposition of the system. Then the submatrices $\boldsymbol{Q}_{ij}$ from (4.76) can be obtained by means of inversion of the $(J \times J)$ and $(K \times K)$ dimension matrices (Kubacek & Pazman 1979, Knepper & Gorman 1980).

$$\boldsymbol{Q}_{22} = -(\boldsymbol{B}^{\mathrm{T}} \boldsymbol{G}^{-1} \boldsymbol{B})^{-1} \tag{4.97}$$

$$\boldsymbol{Q}_{12} = -\boldsymbol{G}^{-1} \boldsymbol{B}\boldsymbol{Q}_{22} \tag{4.98}$$

$$\boldsymbol{Q}_{11} = \boldsymbol{G}^{-1} - \boldsymbol{Q}_{12} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{G}^{-1} \tag{4.99}$$

where $\boldsymbol{G} = \boldsymbol{A}\boldsymbol{F}_{\boldsymbol{x}} \boldsymbol{A}^{\mathrm{T}}$

Another way of reducing the dimension of a problem is the elimination of unmeasured variables from the equations of a mathematical model. Let us assume that we want to eliminate P unmeasured variables from a general linear model (let us suppose, for example, that we are not interested in the values of these variables). The system (4.70) is written so, that the matrices $\boldsymbol{A}$, $\boldsymbol{B}$ and the vector a are properly divided into submatrices

$$\begin{bmatrix} \boldsymbol{A}_1 \\ \boldsymbol{A}_2 \end{bmatrix} \boldsymbol{x} + \begin{bmatrix} \boldsymbol{B}_{11}, \boldsymbol{B}_{12} \\ \boldsymbol{B}_{21}, \boldsymbol{B}_{22} \end{bmatrix} \begin{bmatrix} \boldsymbol{y}_1 \\ \boldsymbol{y}_2 \end{bmatrix} + \begin{bmatrix} \boldsymbol{a}_1 \\ \boldsymbol{a}_2 \end{bmatrix} = \boldsymbol{0} \tag{4.100}$$

where the vector $\boldsymbol{y}_1$ of dimension $(P \times 1)$ contains unmeasured variables we want to eliminate. We assume that the matrix $\boldsymbol{B}_{11}$ has the full rank, i.e rank $\boldsymbol{B}_{11} = P$. Thus the system (4.100) is decomposed into two systems of equations

$$\boldsymbol{A}_1 \boldsymbol{x} + \boldsymbol{B}_{11} \boldsymbol{y}_1 + \boldsymbol{B}_{12} \boldsymbol{y}_2 + \boldsymbol{a}_1 = 0 \tag{4.101}$$

$$\boldsymbol{A}_2 \boldsymbol{x} + \boldsymbol{B}_{21} \boldsymbol{y}_1 + \boldsymbol{B}_{22} \boldsymbol{y}_2 + \boldsymbol{a}_2 = 0 \tag{4.102}$$

From the system (4.101) the vector $\boldsymbol{y}_1$ can be expressed

$$\boldsymbol{y}_1 = -\boldsymbol{B}_{11}^{-1} (\boldsymbol{A}_1 \boldsymbol{x}_1 + \boldsymbol{B}_{12} \boldsymbol{y}_2 + \boldsymbol{a}_1) \tag{4.103}$$

and substituted back into the system (4.102). Rearranging we obtain the system of equations that does not contain the vector $\boldsymbol{y}_1$.

$$\boldsymbol{A}'\boldsymbol{x} + \boldsymbol{B}'\boldsymbol{y}_2 + \boldsymbol{a}' = \boldsymbol{0} \tag{4.104}$$

The following relations hold among the original and new matrices

$$\boldsymbol{A}' = \boldsymbol{A}_2 - \boldsymbol{B}_{21}\,\boldsymbol{B}_{11}^{-1}\,\boldsymbol{A}_1$$

$$\boldsymbol{B}' = \boldsymbol{B}_{22} - \boldsymbol{B}_{21}\,\boldsymbol{B}_{11}^{-1}\,\boldsymbol{B}_{12}$$

$$\boldsymbol{a}' = \boldsymbol{a}_2 - \boldsymbol{B}_{21}\,\boldsymbol{B}_{11}^{-1}\,\boldsymbol{a}_1$$

When doing reconciliation with the new model (4.104) according to (4.72) to (4.74), the matrix (4.76) dimension is reduced from the original value $[(J + K) \times (J + K)]$ to $[(J + K - 2P) \times (J + K - 2P)]$. With each eliminated parameter the number of rows and columns of the inverted matrix (4.76) is reduced by two.

The above procedure is particularly advantageous when some of the parameters appearing in the mathematical model are not needed. But even if some or all the eliminated variables are needed, they may be calculated from the system (4.103) after the reconciliation has been done.

Sometimes the elimination of unmeasured variables is referred to as reduction of a mathematical model, and the model (4.104) is called a reduced model. In this case it is essential that the reduction does not mean a loss of generality of the model, and that it does not cause any loss of information. Reduction is widely used in the cases of extensive problems as encountered, for instance, when carrying out balancing of complex plants. The principle to be observed here is: *to reconcile redundant data with the aid of the reduced model first, and only then calculate the observable unmeasured variables.*

4.4.5 Nonlinear models

In many practical cases we cannot limit ourselves to models discussed hitherto, which are linear with respect to both the measured and unmeasured quantities.

It is necessary to state beforehand that the measured data, obeying nonlinear models, cannot be processed rigorously. It is caused, in the first place, by problems associated with random errors propagation in nonlinear functions, dealt with in Subsection 3.2.3. In most cases it is possible, however, to find a solution suitable for technical purposes by introducing the concept of so-called *quasilinear model.*

It would be possible to introduce the quasilinear form of the model for all the types of models discussed so far. Because of the limited extent of this Chapter we shall limit ourselves further to so-called *general quasilinear model* corresponding to the general linear model solved in the Subsection 4.4.3. The quasilinear forms of other types of models would be created analogically.

We shall call a model *general quasilinear model* (henceforth simply *quasilinear model*) when it differs from a linear model so, that instead of the set of equations (4.70) there are K equations

$$\mathbf{f}(\mathbf{x}, \mathbf{y}) = \mathbf{0} \tag{4.105}$$

where the elements of the column vector $\mathbf{f}$ of dimension $(K \times 1)$ generally are nonlinear functions of vectors $\mathbf{x}$ and $\mathbf{y}$ elements. We assume further:

1. The functions $f_k(\mathbf{x}, \mathbf{y})$; $k = 1, \ldots, K$ have continuous second partial derivatives with respect to x_i and y_j .
2. We know vectors $\mathbf{x}_0$ and $\mathbf{y}_0$ which are so close to the true vectors $\tilde{\mathbf{x}}$ and $\tilde{\mathbf{y}}$ that in the Taylor expansion

$$\mathbf{f}(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}) = \mathbf{f}(\mathbf{x}_0, \mathbf{y}_0) + \mathbf{C}\,\Delta\,\mathbf{x} + \mathbf{D}\,\Delta\,\mathbf{y} + \ldots\ldots. \tag{4.106}$$

where $\tilde{\mathbf{x}} = \mathbf{x}_0 + \Delta\,\mathbf{x}, \quad \tilde{\mathbf{y}} = \mathbf{y}_0 + \Delta\,\mathbf{y}$
$\mathbf{C} = [C_{k\,i}] = [\partial f_k / \mathrm{d}x_i]$
$\mathbf{D} = [D_{k\,j}] = [\partial f_k / \mathrm{d}y_j]$

the second and higher order terms can be neglected (the matrices $\mathbf{C}$ and $\mathbf{D}$ are evaluated at the points $\mathbf{x}_0$ and $\mathbf{y}_0$). If we introduce the notation

$$\mathbf{a} = \mathbf{f}(\mathbf{x}_0, \mathbf{y}_0), \quad \mathbf{A} = \mathbf{C}, \quad \mathbf{B} = \mathbf{D} \tag{4.107}$$

and write in Eq.(4.106) $\mathbf{x}$ and $\mathbf{y}$ instead of $\Delta\,\mathbf{x}$ and $\Delta\,\mathbf{y}$, resp., Eq.(4.106) becomes identical with (4.70).

The processing of all the data proceeds as follows:

1. first guesses of $\mathbf{x}_0$ and $\mathbf{y}_0$ are assessed; obviously $\mathbf{x}_0 = \mathbf{x}^+$,
2. vector $\mathbf{a}$ and matrices $\mathbf{A}$ and $\mathbf{B}$ defined by (4.106) and (4.107) are calculated,
3. reconciliation in accordance with Eqs (4.72) to (4.74) is carried out,
4. vectors $\mathbf{x}_0$ and $\mathbf{y}_0$ are assigned the values acording to
   $\mathbf{x}_0 + \hat{\mathbf{x}} \rightarrow \mathbf{x}_0$
   $\mathbf{y}_0 + \hat{\mathbf{y}} \rightarrow \mathbf{y}_0$
5. the sequence of the steps 2 to 4 is repeated so long as there are in the individual cycles significant increments $\Delta\,\mathbf{x}$ or $\Delta\,\mathbf{y}$, or the residuals of equations $\mathbf{f}(\mathbf{x}_0, \mathbf{y}_0)$, which should limit to null vectors.

The general task of reconciling measured values is, in its quasilinear form, of considerable importance when solving the problems encountered in the course of processing plant data. In most cases the limitations imposed on the equations of a mathematical model are acceptable.

Example 4.9: *Reconciling the material balance of an absorber*
Let us consider an absorption unit shown schematically in Fig.4.10, where also the directly measured (primary) variables are presented. The inlet gas stream 1,

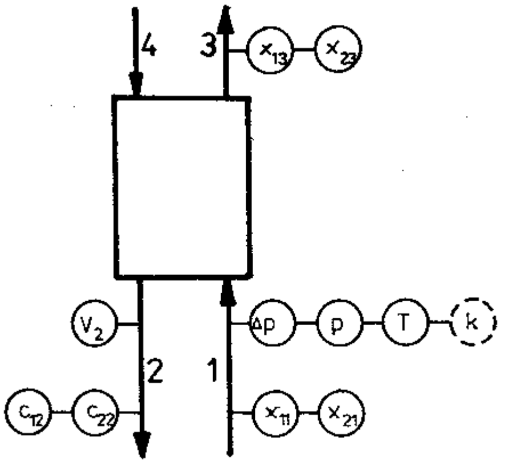


Fig.4.10 — Measurement of an absorber (Example 4.9)

containing besides inerts two substances to be absorbed, is contacted with a pure absorption liquid (stream 4). The concentration of absorbent vapours in the gaseous phase may be neglected.

Ten primary quantities are measured:

x_{ij} $i = 1, 2; j = 1, 3$, where x_{ij} is the molar fraction of ith substance in jth stream,

c_{ij} $i = 1, 2$, where c_{i2} is ith substance concentration in stream 2 (kmol/m^3),

V_2 flow rate of stream 2 (m^3/h)

Δp pressure difference on the gas flow measuring orifice (Pa)

T temperature at the measuring orifice (K)

p gas pressure at the measuring orifice (Pa).

The orifice coefficient k can be considered another primary quantity (as it has its own error). The molar flow rate of the stream 1, denoted n_1 is given by the expression

$$n_1 = k\,(p\,\Delta p\,\rho_n^{-1}\,T^{-1}) \tag{4.108}$$

where ρ_n is the stream 1 density under standard conditions (101.3 kPa, 273 K). The density is given as a function of substances 1,2 and inerts (substance 3) densities under standard conditions.

$$\rho_n = 1.34\,x_{11} + 1.27\,x_{21} + 1.29\,x_{31} \tag{4.109}$$

There are four unmeasured quantities appearing in the problem: n_1 , n_3 , x_{31} and x_{33} -- that is molar flow rates and molar fractions of the inerts in streams 1 and 3.

A total of six independent equations satisfying the conditions of the model (4.105) can be written among the measured and unmeasured quantities:

Table 4.5a — Material balance of an absorber - Example 4.9
(the course of calculation)

i	var.	γ_i	x_i^+	$x_i^{(1)}$	$x_i^{(2)}$	$x_i^{(3)}$
1	x_{11}	0.03	3.120E-2	3.2288E-2	3.2262E-2	3.2262E-2
2	x_{21}	0.03	5.600E-3	5.5154E-3	5.5178E-3	5.5178E-2
3	x_{13}	0.04	1.800E-2	1.7355E-2	1.7371E-2	1.7371E-2
4	x_{23}	0.04	6.000E-4	6.0172E-4	6.0167E-4	6.0167E-4
5	c_{12}	0.02	4.113E+0	4.0809E+0	4.0817E+0	4.0817E+0
6	c_{22}	0.02	1.312E+0	1.3200E+0	1.3198E+0	1.3198E+0
7	V_2	0.02	3.100E-1	3.0948E-1	3.0949E-1	3.0949E-1
8	Δp	0.03	2.000E+3	2.0013E+3	2.0013E+3	2.0013E+3
9	T	0.02	2.810E+2	2.8091E+2	2.8091E+2	2.8091E+2
10	P	0.02	9.730E+4	9.7329E+4	9.7328E+4	9.7328E+4
11	k	0.01	1.131E-1	1.1311E-1	1.1311E-1	1.1311E-1
12	n_1	-	8.000E+1	8.2885E+1	8.2883E+1	8.2883E+1
13	n_3	-	8.000E+1	8.1206E+1	8.1212E+1	8.1206E+1
14	x_{31}	-	9.600E-1	9.6219E-1	9.6222E-1	9.6222E-1
15	x_{33}	-	9.800E-1	9.8204E-1	9.8202E-1	9.8202E-1
-	Q	-	-	2.6664E+0	2.5359E+0	2.5359E+0
-	Q_1	-	-	2.6664E+0	1.6400E-3	3.3154E-16
-	Q_2	-	1.133E+1	3.0335E-5	2.9132E-15	7.3599E-20

1. Expressing the stream 1 flow rate with the aid of Eq.(4.108)
2. balance of the substance 1:

$$n_1\, x_{11} - V_2\, c_{12} - n_3\, x_{13} = 0 \tag{4.110}$$

3. balance of the substance 2:

$$n_1\, x_{21} - V_2\, c_{22} - n_3\, x_{23} = 0 \tag{4.111}$$

4. equation for stream 1 molar fractions:

$$x_{11} + x_{21} + x_{31} - 1 = 0 \tag{4.112}$$

5. equation for stream 3 molar fractions:

$$x_{13} + x_{23} + x_{33} - 1 = 0 \tag{4.113}$$

6. balance of inerts:

$$n_1\, x_{31} - n_3\, x_{33} = 0 \tag{4.114}$$

Table 4.5b — Material balance of an absorber - Example 4.9 (results)

i	var.	γ_i	x_i^+	$\hat{x}_i$	$\sigma_{\hat{x}_i}$	a_i
1	x_{11}	0.03	3.120E-2	3.2262E-2	6.2847E-4	0.33
2	x_{21}	0.03	5.600E-3	5.5178E-2	1.2038E-4	0.28
3	x_{13}	0.04	1.800E-2	1.7371E-2	5.9717E-4	0.17
4	x_{23}	0.04	6.000E-4	6.0167E-4	2.3885E-5	0.00
5	c_{12}	0.02	4.113E+0	4.0817E+0	7.9872E-2	0.03
6	c_{22}	0.02	1.312E+0	1.3198E+0	2.3970E-2	0.07
7	V_2	0.02	3.100E-1	3.0949E-1	5.6073E-3	0.10
8	Δp	0.03	2.000E+3	2.0013E+3	5.6860E+1	0.05
9	T	0.02	2.810E+2	2.8091E+2	5.4909E+0	0.02
10	P	0.02	9.730E+4	9.7328E+4	1.9013E+3	0.02
11	k	0.01	1.131E-1	1.1311E-1	1.1050E-3	0.02
12	n_1	-	8.000E+1	8.2883E+1	1.6574E+0	-
13	n_3	-	8.000E+1	8.1206E+1	1.6471E+0	-
14	x_{31}	-	9.600E-1	9.6222E-1	6.6632E-4	-
15	x_{33}	-	9.800E-1	9.8202E-1	5.9798E-4	-

The balance of the absorbent is not presented here as its flow belongs among unobservable quantities.

The process of calculation is presented in Table 4.5. The relative standard deviations of the directly measured quantities x_{11} through k are in the column γ_i. The values of the ith quantity in jth iteration are presented in the columns denoted $x_i^{(j)}$. For the zero iteration these are the values of directly measured values obtained by measuring, and initial guesses of unmeasured quantities. In each of the iterations the values of Q, Q_1 and Q_2 were calculated. Q is the value of the quadratic form (4.19). Q_1 is the sum of squares of the measured quantities increments divided by the respective variances of the measurements. Q_2 is the sum of squares of the residuals of mathematical model equations.

The calculation was terminated when the difference of Q in two consecutive iterations dropped below 0.001 (iteration No.3). In the next column of the Table there are standard deviations of the reconciled values $\sigma_{\hat{x}_i}$, and the adjustability a_i of measured quantities.■

Reconciliation of measured data with the aid of the quasilinear model has an advantage in operating with directly measured quantities without having to modify the mathematical model considerably to achieve the linearity. It may happen in some cases, however, that the process of iteration is diverging, which manifests itself by increasing residuals of mathematical model equations in the course of iterations. This problem can often be overcome by reducing the $\boldsymbol{x}$ and $\boldsymbol{y}$ increments in an iteration step (e.g. by a half) for so long as the decrease in the sum of squares of the mathematical model residuals is attained.

A further drawback of the iteration method may be its demand on computing time (which may be a limiting factor in on-line applications). Therefore, in Subsection 4.4.6 we shall concern ourselves with the possibility of converting a nonlinear model to a linear one by proper transformations of variables. Before doing so, however, we shall add a few concluding remarks about the problems of processing data governed by nonlinear mathematical models.

As already stated in the opening of this Subsection, working with nonlinear models brings about, in addition to numerical problems, serious theoretical problems as well. Virtually all the statistical methods available in the literature are based on the assumption of the mathematical model linearity. In that case the measuring errors with normal distribution are transformed into random variables whose distribution is normal, too, which facilitates the problem markedly. The nonlinearity of a problem can impair this assumption considerably. Problems may arise in the following spheres:

1. The method based on linearization of a mathematical model, as described in general terms so far, does not lead to reaching the minimum of the least squares function, in spite of the fact that the process of iteration has been completed and all the conditions of its termination have been satisfied.
2. Even if the minimum value of the least squares function is reached (e.g. by some nonlinear programming method), the unbiasedness of the estimates is not reached (the mean values of estimates differ from true values). This is analogous to the case dealt with in Example 3.4.
3. All the other methods of advanced data processing (confidence intervals and regions, etc.) are only approximate.

The question to what extent the model nonlinearity devaluates the conclusions, resulting from the processing of data, cannot be answered in a general way. Important factors here are, in particular, the degree of the model nonlinearity and magnitude of measuring errors. These problems are dealt with in a case study in Section 6.4.

4.4.6 Transforming a model to linear form

Linearizing a mathematical model by expansion in Taylor series we alter the model character fundamentally. In some cases it is possible, however, to linearize a model using a less drastic method. For example, it is possible to make use of the fact that often we are not interested in primary quantities but in their functions. So, for instance, measuring of temperature, pressure and pressure drop is only a means for the determination of a flow rate. Another equation can be linearized by introducing new variables, for example $z = \ln(x)$, x being a primary quantity.

With multicomponent balances nonlinearities of the type of two quantities product occur frequently (for instance $n_j x_{ij}$, where n_j is the molar flow rate of the jth stream and x_{ij} is the molar fraction of ith substance in jth stream). Such nonlinearities can be eliminated by introducing an appropriate system of secondary variables (for example $n_{ij} = n_j x_{ij}$, where n_{ij} is the flow rate of ith substance in jth stream). Both ways of balancing (nonlinear and linearized) were compared by Serth, Weart & Heenan (1989) with finding the superiority of nonlinear approach with primary variables (total flow rates and compositions) used in reconciliation. The use of secondary variables for reconciliation can affect the gross errors detection adversely.

It is true that the above transformations make a mathematical model simpler but, on the other hand, they bring about complications as far as the model of errors is concerned. While the primary quantities errors are usually independent, this is no more true with secondary quantities. Then the data processing procedure must include also calculation of the covariance matrix of transformed quantities from the primary quantities standard deviations.

The demands on computing time usually are smaller with a linearized model than with a nonlinear one, the ratio of the computing time depending on the rate of the iteration process convergence.

Demands on computer memory cannot be assessed explicitly since in some cases certain saving achieved with a linearized model may be offset by the necessity of storing a nondiagonal covariance matrix.

Linearization of mathematical models by means of suitable transformations of variables used to be applied particularly before the advent of computers, when it was often the necessary condition for solving a problem. With the advance of computers, however, its importance is declining and a trend towards nonlinear models can be seen.

4.4.7 Share matrices

With all the models discussed hitherto, share matrices, introduced in Subsection 3.2.3, can be calculated readily; they enable a detailed analysis of the imprecision of the measurement results. Share matrices elements are calculated according to (3.60), where it holds for the matrix $\boldsymbol{C}$ for the individual models:

Reconciliation of directly measured quantities (4.22)

$$\boldsymbol{C}_{\hat{x}} = \boldsymbol{I} - \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} (\boldsymbol{A}\boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}})^{-1} \boldsymbol{A} \tag{4.115}$$

Estimation of unmeasured quantities from redundant measurements

a) unmeasured quantities (4.36)

$$\boldsymbol{C}_{\hat{y}} = (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \tag{4.116}$$

b) reconciled values (4.40)

$$\boldsymbol{C}_{\hat{x}} = \boldsymbol{B} (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \boldsymbol{B})^{-1} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{F}_x^{-1} \tag{4.117}$$

General linear model
a) unmeasured quantities (4.78)

$$\boldsymbol{C}_{\hat{y}} = \boldsymbol{Q}_{21} \boldsymbol{A} \tag{4.118}$$

b) reconciled values (4.79) and (4.80)

$$\boldsymbol{C}_{\hat{x}} = \boldsymbol{I} - \boldsymbol{F}_x \boldsymbol{A}^{\mathrm{T}} \boldsymbol{Q}_{11} \boldsymbol{A} \tag{4.119}$$

In all these cases, however, there is a certain change in the interpretation when compared with the case described in Subsection 3.2.3. It still holds that a share matrix informs us about the share of individual measured variables in the variance of measurement results. It does not hold true, however, that there exists a direct proportionality between the decrease of the variance of directly measured quantities on the one hand, and of a secondary quantity (observable unmeasured or reconciled) on the other hand.

The reason is that a change in the measured quantity variance entails a change in the matrix transforming the measured values into secondary quantities. It is a case of matrices whose elements are not constants, and depend on the variances of measured quantities. Now the simple reasoning presented in Subsection 3.2.3 is not valid any longer. It is possible to prove, however, the validity of the following statement:

If the variance of the ith measured quantity decreases by p% of its original value, the variance of the rth secondary quantity decreases at least by

$$pH_{ri} \,/\, 100\ \% \tag{4.120}$$

of its original value.
(H_{ri} in (4.120) is an element of the share matrix belonging to *i*th measured and *r*th secondary quantity.)

Example 4.10: *Matrices of shares*
Let us continue with Example 4.8 dealing with the mass balance. The share matrices of measured and unmeasured variables are as follows (F_i is the flow of *i*th stream):

	F_1	F_2	F_3	F_4	F_5	F_6
F_1	36	0	54	0	8	1
F_2	0	100	0	0	0	0
F_3	35	0	56	0	8	0
F_4	0	0	0	96	3	0
F_5	24	0	38	25	12	0
F_6	0	0	0	0	0	99
F_7	14	64	20	1	3	1
F_7	13	65	21	1	3	1

It can be observed here, that in the case of directly measured flows, the bottleneck of their precision is mostly their direct measurement (especially in the case of F_2 which is nonredundant and its precision is given solely by its direct measurement). The exceptions are F_1 and F_5 whose precision can be improved preferably by other directly measured flows (F_3 , F_1 and F_4). As far as unmeasured flows F_7 and F_9 are concerned, the key variable in their determination is the flow F_2 .

Let us study further the possibilities of improving the precision of results. If we are, for example, interested especially in the vaule of flow F_1 , we could focus attention on the measurement of F_3 and F_1 . If the standard deviation of F_3^+ is cut by 50% (i.e. to 0.4), the standard deviation of $\hat{F}_1$ is lowered from 0.60 to 0.38. On the other hand, if the standard deviation of F_1^+ is cut by 50%, the standard deviation of $\hat{F}_1$ is 0.42, which corresponds well with the share matrix of reconciled quantities.

The best way of improving the precision of unmeasured flows F_7 and F_9 lies in improving the measurement of flow F_2 . If its standard deviation is cut by 50%, the standard deviations of both F_7 and F_9 are lowered from 1.00 to 0.72. On the other hand, if the standard deviation of F is cut by 50%, the improvement of precision of F_7 and F_9 is negligible (standard deviations 0.97 and 0.96, resp.).■

4.5 ELIMINATION OF GROSS AND SYSTEMATIC ERRORS

In the preceding Section it was pointed out that reconciliation brings about higher precision of the reconciled values when compared with the measured ones. This statement holds true, however, only if both the mathematical model and the model of errors are in agreement with the reality. On the other hand, if this is not the case, reconciliation may lead to the deterioration of precision of reconciled values and unmeasured parameters. This occurs particularly in those cases when the data contain one or more gross errors. In the process of reconciliation gross errors are dispersed among a great number of reconciled values and thus even a single gross error can devaluate the results of the measurement.

So if we use reconciliation during data processing, the data should be analyzed with respect to the presence of gross and systematic errors. If these errors have been detected, it is necessary to find out what are their causes and to eliminate them from the process of measurement.

The *elimination* of gross errors can be divided into three stages. In the first stage (*detection of gross errors*) we are ascertaining, whether gross errors are present. If yes, the causes of these errors are looked for (*identification of gross errors*), which means that probable sources of errors are found out. Then follows the *elimination of gross errors* proper.

4.5.1 Detection of gross and systemetic errors

This process begins with comparing the measured data with the available information about the examined problem. Calculations based on the measured data may give such values of parameters that are considered either improbable or impossible (for example extremal values of a transfer coefficient, negative values of concentrations).

The occurrence of an unreal value need not necessarilly be a proof of the presence of a gross error. For instance, if the calculated value of mass fraction (that should lie within the interval $\langle 0, 1 \rangle$) has the confidence interval $\langle -0.5, 0.7 \rangle$, the unrealistic value of concentration in the interval $\langle -0.5, 0 \rangle$ can be attributed fully to random errors of measurement.

In the analysis of measured data the most important method concerning the occurrence of gross and systematic errors is the confrontation of data with exactly valid mathematical models. By this term we mean balance equations; exceptionally it may refer to reliable thermodynamic data (phase equilibria) and, as the case may be, other information as well.

Further we shall confine ourselves to those cases when the model is represented by a system of algebraic and transcendental equations. It is necessary to point out here that, when processing measured data, we start not only at the mathematical model proper but also at the model of measuring errors. Considering this, errors may be divided into two groups.

Included in the first group are *errors of the mathematical model*. Most frequently the reasons lie in our imperfect knowledge of the measured process (the model does not describe the reality adequately). It may be a case of leakage of substances (the leaking stream is not considered in the model), unknown byproducts are formed in the course of chemical reactions, and the like.

In the second group there are *errors in the model of errors*. We assume that measuring errors are realizations of random variables with multidimensional normal distribution and with a given covariance matrix. The existence of a large gross error is inconsistent with this model. Such a type of error occurs most frequently, and when we speak about gross and systematic errors without a more detailed specification, we mean just these deviations from the assumed model of errors.

Before we proceed to the method of eliminating errors itself, let us formulate two more assumptions we shall use further. The first one is the assumption that the model of errors is known. It will be assumed further that the errors are uncorrelated and have a normal distribution with zero mean values and known variances. The assumption of the knowledge of errors variances may seem to be too demanding. Unless we have an idea about random measurement errors, however, it is virtually impossible to define what the gross errors are, and their detection is meaningless.

The second assumption will be that in the mathematical model a certain part of measured data is redundant.

Residuals of equations and adjustments in the presence of random errors only

Let us assume a mathematical model expressed by the system of equations

$$\boldsymbol{Ax} + \boldsymbol{By} + \boldsymbol{a} = \boldsymbol{0} \tag{4.121}$$

discussed in a greater detail in Subsection 4.4.3 [Eq.(4.70)]. In Section 4.2 we described the decomposition of the system (4.121) yielding a subsystem of equations among directly measured quantities only. From the viewpoint of the redundant measurements analysis it is, therefore, possible to confine ourselves to the case of processing directly measured quantities described in Subsection 4.4.1. In this case the mathematical model is

$$\boldsymbol{Ax} + \boldsymbol{a} = \boldsymbol{0} \tag{4.122}$$

where the matrix $\boldsymbol{A}$ and vector $\boldsymbol{a}$ in (4.122) are not identical with the matrices in (4.121) but originated from them in the process of decomposition from the matrices appearing in Eq.(4.121).

Substituting directly measured values into (4.122) we obtain the vector of residuals of the system of equations $\boldsymbol{r}$:

$$\boldsymbol{r} = \boldsymbol{A}_{\boldsymbol{x}}^{+} + \boldsymbol{a} \tag{4.123}$$

It is obvious that if errorless values were substituted into (4.123), the vector of residuals would be null. With the growing magnitude of errors also a growth of the residuals absolute values can be expected.

Now let us assume that the measured data were reconciled by the method described in Subsection 4.4.1 whereby we obtained the vectors of adjustments $\boldsymbol{v}$ and of reconciled values $\hat{\boldsymbol{x}}$. Considering that with the reconciled values the system (4.122) is satisfied exactly

$$\boldsymbol{A}\hat{\boldsymbol{x}} + \boldsymbol{a} = \boldsymbol{0} \tag{4.124}$$

after subtracting (4.124) from (4.123) we obtain the relation between the vectors $\boldsymbol{r}$ and $\boldsymbol{v}$:

$$\boldsymbol{r} = \boldsymbol{A}\,(\boldsymbol{x}^{+} - \hat{\boldsymbol{x}}) = -\,\boldsymbol{A}\boldsymbol{v} \tag{4.125}$$

The adjustments and residuals are functions of measured values and, therefore, they are realizations of random variables with zero mean values. When they are examined it is useful to know their covariance matrices. As set out in Subsection 4.4.1, the covariance matrix of the vector $\boldsymbol{v}$ is given by

$$\boldsymbol{F}_{\boldsymbol{v}} = \boldsymbol{F}_{\boldsymbol{x}}\,\boldsymbol{A}^{\mathrm{T}}\,(\boldsymbol{A}\boldsymbol{F}_{\boldsymbol{x}}\,\boldsymbol{A}^{\mathrm{T}})^{-1}\,\boldsymbol{A}\boldsymbol{F}_{\boldsymbol{x}} \tag{4.126}$$

From (4.125) and (4.126), and considering (3.54), it follows for the covariance matrix of residuals

$$\boldsymbol{F}_{\boldsymbol{r}} = \boldsymbol{A}\boldsymbol{F}_{\boldsymbol{x}}\,\boldsymbol{A}^{\mathrm{T}} \tag{4.127}$$

The same result would be arrived at if we used as the basis the definition equation of residuals (4.123).

The hitherto discussed properties of the random vectors $\boldsymbol{v}$ and $\boldsymbol{r}$ can be summed up as follows:

1. they are vectors with zero mean values and known covariance matrices,
2. on the assumption of normal distribution of measuring errors, the vectors $\boldsymbol{v}$ and $\boldsymbol{r}$ will have normal distribution as well,
3. vector $\boldsymbol{r}$ is a function of vector $\boldsymbol{v}$. Hence any information contained in the vector $\boldsymbol{v}$ is contained in the vector $\boldsymbol{r}$ (the opposite statement does not hold true).

An important function of the vector of adjustments is the quadratic function Q_{min} defined by

$$Q_{\mathrm{min}} = \boldsymbol{v}^{\mathrm{T}}\,\boldsymbol{F}_{\boldsymbol{x}}^{-1}\,\boldsymbol{v} \tag{4.128}$$

The quantity Q_{min} has the χ^2 distribution with the number of degrees of freedom equal to the number of the matrix $\boldsymbol{A}$ rows (i.e. number of independent equations). In a similar way we can write the quadratic function of residuals

$$Q_1 = \boldsymbol{r}^{\mathrm{T}}\,\boldsymbol{F}_{\boldsymbol{r}}^{-1}\,\boldsymbol{r} \tag{4.129}$$

It can be shown, however, that the random quantities Q_{min} and Q_1 are identical.

Presence of gross errors

The characteristics of the vectors $\boldsymbol{v}$ and $\boldsymbol{r}$ discussed so far hold true provided that the measurement errors are realizations of random variables with zero mean values and normal distribution. This model of errors can be written as Eq.(3.1). Now let us assume that the model (3.1) is not valid - that a gross error of the constant magnitude d is present:

$$x^{+} = \tilde{x} + d + e \tag{4.130}$$

Such a gross error (particularly when it is a large one) will result in changes in the properties of the vectors $\boldsymbol{v}$ and $\boldsymbol{r}$ and of the quantity $Q_{\min}$. It can be expected intuitively that their values will rise with raising the gross error magnitude. Hence these quantities are suitable indicators of the presence of a gross error.

The procedure for detecting a gross error belong to the sphere of testing statistical hypotheses (see Appendix A.4.2). The null hypothesis H_0 is: *no gross error is present*, expressed mathematically

$$d = 0 \tag{4.131}$$

The alternative hypothesis H_1 has the form

$$d \neq 0 \tag{4.132}$$

The hypothesis H_0 is then rejected or not in accordance with the value of the statistics (in our case the quantity $Q_{\min}$ or elements of the $\boldsymbol{r}$ and $\boldsymbol{v}$ vectors).

In the case of the quantity $Q_{\min}$ the H_0 hypothesis is rejected if the value of $Q_{\min}$ exceeds the critical value of the χ^2 distribution for the given number of degrees of freedom ν

$$Q_{\min} > \chi^2_{1-\alpha}(\nu) \tag{4.133}$$

If the inequality (4.133) is satisfied, the presence of a gross error has been detected.

Let us mention here that when testing the hypothesis we can commit errors of the first and second kind. In our case these errors can be defined as follows:

Error of the Ist kind: *the presence of a gross error has been detected though actually this does not exist*

Error of the IInd kind: *an existing gross error has not been detected*

The probability of the Ist kind error is equal to the significance level of the test α in Eq.(4.133). The probability of the error of IInd kind depends on the magnitude of the gross error and it will be discussed later.

But first let us concern ourselves with the case when we want to use elements of the vectors $\boldsymbol{v}$ or $\boldsymbol{r}$ instead of $Q_{\min}$ for the testing. It should be stated beforehand, however, that in this case the testing is considerably more difficult than with the quantity $Q_{\min}$. The problem will be demonstrated by an example when we try to test the magnitude of the vector $\boldsymbol{v}$ elements.

Let us assume that we are carrying out a test at the significance level α, and no gross error is present. Since the adjustments v_i are normally distributed, the standardized adjustments v_i / σ_{v_i} have standardized normal distribution. This distribution is symmetrical; therefore, individual adjustments will lie, with the probability $1 - \alpha$, within the interval

$$\langle -u_{1-\alpha/2} \; ; \; u_{1-\alpha/2} \rangle \tag{4.134}$$

It is thus possible to assume that, even in the absence of a gross error, on the average 100α% of standardized adjustments will be outside the interval (4.134). If we consider a real case involving hundreds of directly measured quantities, and α = 5%, we find that a number of standardized adjustments will lie always outside the interval (4.134).

It follows from the above that, in this case, the probability of an error of the Ist kind is considerably higher than 5%. To satisfy the overall significance level of 5%, we have to choose for the testing the critical value greater than that corresponding to the required probability of the Ist kind error α. The null hypothesis is rejected, if it holds

$$|v_i / \sigma_{v_i}|_{\max} > u_{1-\alpha'/2} \tag{4.135}$$

The term on the left hand side of (4.135) is the standardized adjustment with the maximum absolute value. There is the problem, however, how to assess the value of α'. It holds approximately (Mah 1990)

$$\alpha' = 1 - (1 - \alpha)^{1/S} \tag{4.136}$$

where S is the number of adjustable variables with different adjustments [if there exists a group of two or more variables with identical adjustments (irrespective of the sign), such a group is considered a single variable].

It should be mentioned, however, that this test is only an approximate one, and that the probability of the Ist kind error is lower than the value of α in Eq.(4.136); we say the test is *conservative*. If the above problems are taken into account, the testing based on $Q_{\min}$ (so-called *global test*) seems to be more advantageous than testing the maximum adjustment or residual.

We have considered so far that the mathematical model is linear and that decomposition has been made, so that no unmeasured quantities occur in the problem. It is true, however, that the decomposition is not necessary. It is essential to know the values of adjustments, of their standard deviations , and the $Q_{\min}$ quantity including the number of degrees of freedom (see, for example, Subsection 4.4.3 in the case of the general linear model). In this case, however, we cannot use for the detection of gross errors the residuals of the equations since they are defined only when all the variables are measured (the analysis of residuals is important particularly in the case of balance models, where the residuals possess a clear physical meaning). Furthermore, it is necessary to realize that, in the discussed case, nonadjustable quantities occur and these are not subject to analysis of adjustments (the adjustments are null and so are their standard deviations, and the standardized adjustments are not defined).

In the matter of nonlinear models a complete decomposition is often not possible, so that the residuals cannot be analyzed. It is further necessary to realize in this case that testing for the presence of gross errors is only approximate (see the discussion in Subsection 4.4.5).

Example 4.11: *Detection of the presence of a gross error*
This Example is the continuation of Example 4.8, in which reconciliation of measured data was carried out. It was the case with 2 degrees of freedom (4 equations and 2 unmeasured quantities). Presented in the second column of Table 4.6 are the values of $Q_{\min} = 1.74$ and the maximum absolute value of the standardized adjustment 1.18.

Now let us test the hypothesis of the absence of a gross error at the significance level $\alpha = 0.05$. The critical value of the χ^2 distribution with 2 degres of freedom $\chi^2_{0.95}(2) = 5.99$. Since

$$1.74 < 5.99$$

we state that no gross error was detected [see the inequality (4.133)]. Next we shall test the maximum absolute value of the standardized adjustment. There are five redundant measured quantities (streams 1, 3, 4, 5, 6) appearing in the problem. Also, it was found that the absolute values of standardized adjustments of the streams 1 and 4 are identical with the same quantities belonging to the streams 6 and 5, resp. Hence three independent adjustments occur in the problem, and S in Eq.(4.136) equals 3. After substituting S and α into (4.136) we obtain $\alpha' = 0.01695$, the corresponding value of $u_{1-\alpha'/2}$ being 2.39. Again, no presence of a gross error was detected, since

$$1.18 < 2.39$$

In the next step the detection of gross errors in the individual quantities was studied. A gross error equal to tenfold the standard deviation of the respective measurement was added in turn to the measured values presented in Table 4.4 and the data were reconciled. The assessed values of $Q_{\min}$ and of the maximum standardized adjustments are presented in Table 4.6 (index i indicates the number of the stream corrupted by the gross error). It can be seen from the results that the presence of a gross error was detected correctly in the cases of flows 1, 3, 4 and 5, and that by testing both $Q_{\min}$ and the maximum standardized adjustments.

Table 4.6 — Detection of gross error (Example 4.11)

i		1	2	3	4	5	6
d_i	0	10	8	8	4	20	1
z_1	**-1.18**	**-9.17**	-1.18	4.36	-1.60	0.95	-0.38
z_2	0	0	0	0	0	0	0
z_3	0.66	7.33	0.66	**-5.98**	0.01	3.90	-0.01
z_4	-0.85	-2.66	-0.85	-3.14	-2.72	**8.53**	-0.66
z_5	0.85	2.66	0.85	3.14	2.72	**-8.53**	0.66
z_6	1.18	**9.17**	1.18	-4.36	1.60	-0.95	0.38
$Q_{\min}$	1.74	**84.5**	1.74	**37.1**	**8.43**	**73.8**	0.49
$\lvert z_j' \rvert_{\max}$	1.18	**9.17**	1.18	**5.98**	**2.72**	**8.53**	0.66

On the other hand, with streams 2 and 6 the detection of a gross error was not successful. In the case of stream 2 this is logical, since it is not redundant (its value does not affect the values of tested quantities). In the case of stream 6 the values of both $Q_{\min}$ and the standardized adjustments even decreased. This can be explained in, that the gross error is offset by random errors of the other quantities.■

As may be seen from the above example, the chance of detecting a gross error depends not only on its magnitude but also on the variable that is subjected to the gross error. It is, therefore, useful to concern ourselves with the power of testing the presence of gross error in individual quantities.

Power of the test for gross errors detection

When we try to analyze data with respect to the occurrence of gross errors, we should realize, what is the power of the test we use. In other words - how small can a gross error be, so that the test still might protect us against it.

Let us consider the general linear mathematical model (4.121). Let us consider further that only a single gross error, affecting the jth quantity, is present. Hence, the form of the model of errors is

$$x_1^+ = \bar{x}_i + d_i + e_i \qquad d_i = 0 \qquad \text{for} \qquad i \neq j \tag{4.137}$$

We shall limit our attention to the case in which the global test based on $Q_{\min}$ is used.

The key problem of the following analysis is finding the distribution of $Q_{\min}$ in the presence of a gross error. This problem was solved by Madron (1985a) and those interested in more details are referred to this paper. Here only the information necessary for understanding the practical procedure will be presented.

In the presence of a gross error the $Q_{\min}$ does not have the usual (central) χ^2 distribution but the noncentral one (see Appendix A.3.5). Then the non-centrality parameter δ is a simple function of the gross error

$$\delta = d_j \, \sigma_{v_j} \, / \, \sigma_j^2 = q_j \, \sigma_{v_j} \, / \, \sigma_j \tag{4.138}$$

where the dimensionless gross error q_j was introduced:

$$q_j = d_j \, / \, \sigma_j \tag{4.139}$$

Let us denote the probability of the IInd kind error by γ and the power of the test by β. Obviously it holds

$$\beta = 1 - \gamma$$

Now let us devote ourselves to the construction of the power characteristics of the test, i.e. to the dependence of the test power on the gross error magnitude (see Fig.4.11).

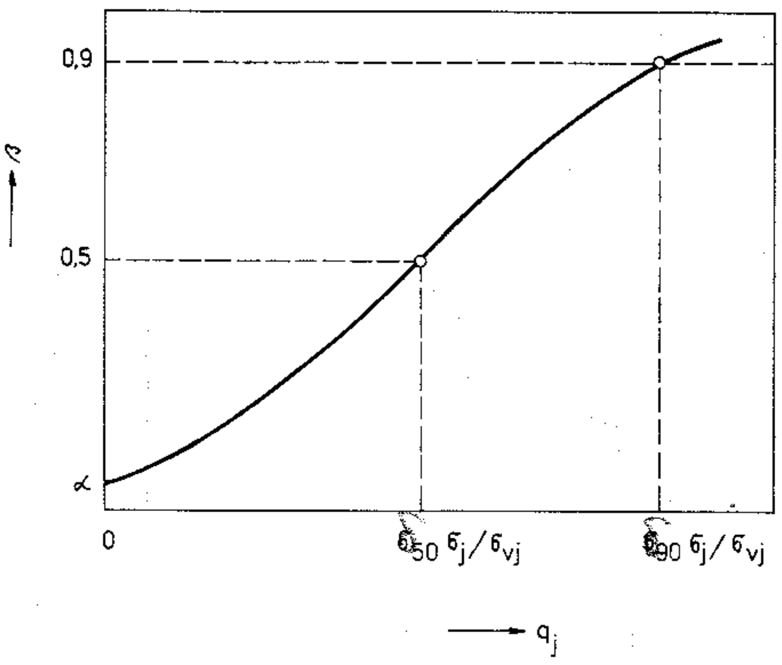


Fig.4.11 — Construction of the power characteristics

In the q_j - β coordinates the power characteristics run through three important points.

For $q_j = 0$ (absence of a gross error) obviously $\beta = \alpha$. The coordinates of the other two points are ($q_{j,50}$; 0.5) and ($q_{j,90}$; 0.9). Here $q_{j,50}$ and $q_{j,90}$ are such values of a dimensionless gross error that the power of the test is 50 and 90%, resp. These values are then easily calculated from

$$q_{j,50} = \delta_{50}\, \sigma_j / \sigma_{v_j} \tag{4.140}$$

$$q_{j,90} = \delta_{90}\, \sigma_j / \sigma_{v_j} \tag{4.141}$$

The only unknowns in Eqs (4.140) and (4.141) are the constants δ_{50} and δ_{90}. These values are functions of the number of degrees of freedom ν and significance level α. For $\alpha = 0.05$ and $\nu = 1, 2, \ldots, 20$ these constants were tabulated in (Madron 1985a) and are presented in Table 4.7. For the computer implementation the following empirical relation can be adopted for calculation of δ_{90} (ν , 0.05):

$$\begin{aligned}\delta_{90}(\nu, 0.05) &= 3.2403 + 0.4334 \ln(\nu) + 0.02692 \ln^2(\nu) \\ &\quad + 0.01229 \ln^3(\nu)\end{aligned} \tag{4.142}$$

Table 4.7 — Table of values of δ_{50} and δ_{90}

ν	δ_{50}	δ_{90}	ν	δ_{50}	δ_{90}
1	1.96	3.24	11	3.09	4.60
2	2.23	3.56	12	3.15	4.67
3	2.40	3.76	13	3.20	4.74
4	2.53	3.93	14	3.25	4.80
5	2.64	4.06	15	3.30	4.86
6	2.74	4.17	16	3.34	4.91
7	2.82	4.28	17	3.38	4.96
8	2.90	4.37	18	3.42	5.02
9	2.97	4.45	19	3.46	5.06
10	3.03	4.53	20	3.50	5.11

Using the above procedure it is comparatively easy to construct the power characteristics for any redundant quantity. In real problems, however, where hundreds of redundant quantities are involved, constructing the power characteristics is not practical. However, the power of the test may be fairly well characterized by a single number - the value of $q_{j,90}$ or $d_{j,90} = q_{j,90}\, \sigma_j$ - that is, by the value of a gross error which will be detected with the probability of 90%. The $d_{j,90}$ value is called "*the threshold value*" and $q_{j,90}$ is called "*the dimensionless threshold value*".

It is quite illustrative to draw the dependence of $q_{j,90}$ on the ratio $\sigma_{\hat{x}_j} / \sigma_j$, which follows from combination of Eqs (4.141) and (4.93)

$$q_{j,90} = \frac{\delta_{90}\,(\nu\ ,\ 0.05)}{(1\ -\ \sigma_{\hat{x}_j}^2\ /\ \sigma_j^2\ )^{1/2}} \tag{4.143}$$

The dependence (4.143) for $\alpha = 0.05$ and different degrees of freedom is shown in Fig.4.12. It can be seen here that when the ratio $\sigma_{\hat{x}_j} / \sigma_j$ is greater than 0.7 (or the adjustability is less than 0.3), the efficiency of the test for the detection of gross error is decreasing steeply. It is logical that in the cases of nonadjustable quantities, where the adjustability equals zero, no gross error can be detected.

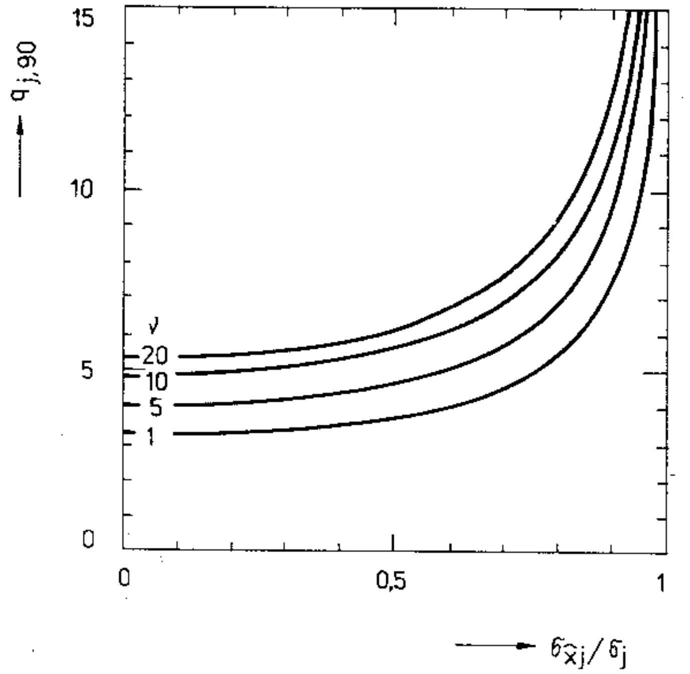


Fig.4.12 — Dependence of dimensionless threshold value q_{90} on the ratio $\sigma_{\hat{x}_j} / \sigma_j$

Example 4.12: *Threshold values for mass balance reconciliation*
Let us continue with the analysis of the mass balance from Example 4.11. The calculation of the threshold values is demonstrated in Table 4.8. It is the case of two degrees of freedom, so that we find in Table 4.7 the corresponding value of $\delta_{90} = 3.56$. By a calculation according to Eq.(4.141) we arrive at the values present in the last two columns of the Table 4.8.

Table 4.8 — Threshold values (Example 4.12)

j	σ_j	σ_{v_j}	$q_{j,90}$	$d_{j,90}$
1	1.0	0.779	4.570	4.57
2	0.8	0.0	∞	∞
3	0.8	0.531	5.363	4.29
4	0.4	0.0750	18.987	7.60
5	2.0	1.875	3.797	7.60
6	0.1	0.00799	44.56	4.45

Let us note that the calculation is carried out with the known standard deviations only; we do not need to know the values of the measured quantities. Hence the analysis of the power of the test can be done prior to the measurement proper.

The results presented in Table 4.8 conform well with those of Example 4.11. Indeed, it is not possible to expect that a gross error could be detected in the case of stream 6 since the gross error introduced is considerably smaller than the threshold value for this quantity, which equals 4.45. In the case of streams 1,3 and 5 gross errors were detected without any problem because the gross errors were approximately twice the respective threshold values. Accordingly, also the values of $Q_{\min}$ are more than ten times higher than the critical value of the test.

It may be rather confusing that the gross error detected in the case of stream 4 is somewhat smaller than the threshold value (4 versus 7.595). Here it is caused by the values of random errors that were present in this case. It is probable that, in a repeated measurement, this gross error would not be detected (let us note that the value of $Q_{\min}$ is but slightly higher than the critical value of the test - 8.43 and 5.99, resp.).■

Effect of gross errors on results of measurement

From the practical point of view a comparison of the power characteristics of the test for detecting gross error with the effect of a gross error on quantities that are the target of the measurement is more important than the power characteristics proper.

If the deviation of the target quantity from the true value exceeds a required value, we say that this target quantity is in gross error. Then the following phenomena can be defined:

phenomenon **B** - gross error was detected
phenomenon **A** - a gross error occurred in the target quantity
phenomenon **C** - non (**B**) $\cap$ **A** - no gross error was detected and, at the same time, a gross error occurred in the target quantity.

It is instructive to plot the dependences of the phenomena **A**, **B** and **C** on the gross measurement error magnitude. In the case of phenomenon **B** this has already been done since such dependence is identical with the power characteristics of the test (Fig.4.11).

Typical dependences of the probability of the occurrence of a gross error in the target quantity (phenomenon **A**) on the gross error magnitude are demonstrated in Fig.4.13a. The individual dependences may differ from one another considerably in accordance with the form of the relation between primary and target quantities. We can meet with strong dependences where even a small gross error manifests itself as a gross error in the target quantity (curve 1), as well as with the case where the target quantity is independent of a certain primary quantity (straight line 3).

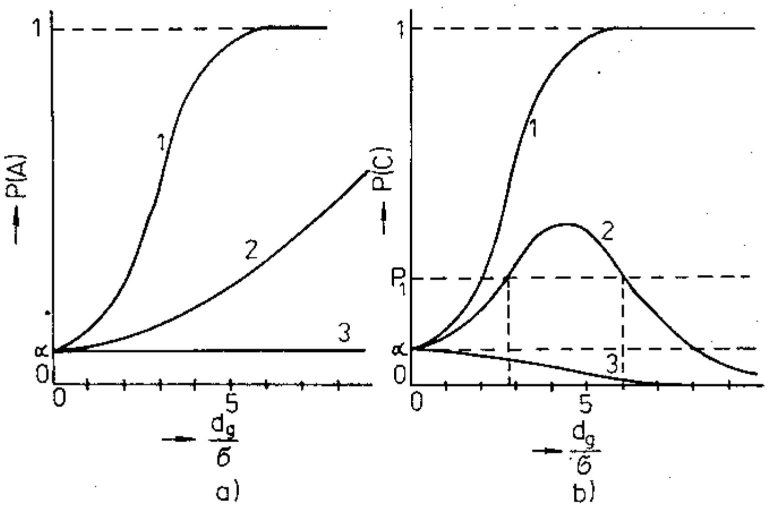


Fig.4.13 — Probabilities of events **A** and **C**

Similar dependences for the probability of the case when no gross error in a primary quantity was detected - while in the target quantity a gross error occurred (phenomenon **C**) - are presented in Fig.4.13b. There are three typical dependences that can be met with. The curve 1 represents a case when, from a certain magnitude of a primary quantity gross error, the probability of phenomenon **C** is high. Such an unfavourable case occurs when the primary quantity is nonadjustable and affects the target quantity. The curve 2 runs through a maximum, the value of the function in the maximum being greater than the given value P_1 . The probability of the phenomenon **C** is considerable only within a certain range of the primary quantity gross error. The last case (curve 3) is the most favourable one. The curve either tends to the horizontal axis or runs through a not very distinct maximum. Here the probability of the phenomenon **C** is low irrespectively of the magnitude of the primary quantity gross error.

As regards practical consequences, it is necessary to avoid particularly the phenomenon **C**, which means that a result is subject to a gross error, while we take it as being correct. Henceforth we shall refer to the phenomenon **C** as an *error of kind* C. The error of kind C differs from an error of the IInd kind in that it does not consider those cases when a gross error, though existing, has not been detected and, at the same time, no gross error occurred in the target quantity (which is essential).

Example 4.13: *Detection of gross errors in the material balance of an absorber*
Let us consider the absorption unit described in Example 4.9. Regarded as the target quantities will be the degrees of absorption of substances 1 and 2 (s_1 and s_2) defined as

$$\begin{aligned} s_1 &= n_{12} / n_{11} \\ s_2 &= n_{22} / n_{21} \end{aligned} \tag{4.144}$$

where n_{ij} is the flow of ith component in jth stream.

The efficiency of the material balance analysis from the viewpoint of the occurrence of gross errors was simulated on a computer using the Monte Carlo method. Randomly generated uncorrelated errors with zero mean value and relative standard deviations, shown in the Table 4.5, were added to the values of the primary quantities that satisfied the balance equations exactly and represented the real values. In addition, a gross error of constant magnitude was always added to one primary quantity. A hundred of thus simulated measurements were conducted for each primary quantity and magnitude of gross error using the method described in Example 4.9. The H_0 hypothesis was tested by the $Q_{\min}$ statistics.

The results of the study are presented in Figs 4.14 to 4.16. Empirically assessed power characteristics of testing the H_0 hypothesis are shown in Fig.4.15. These are relative frequencies of detecting a gross error (rejection of H_0) for the individual measured quantities in dependence on its magnitude. The gross errors in primary quantities are expressed in a dimensionless form (divided by their standard deviations). It may be seen from Fig.4.14 that the power characteristics for the individual primary quantities differ markedly from one another. While, for example, the power characteristics for the primary quantities 1 and 2 are favourable, it holds for the quantity 4 that any gross error will probably not be detected, even if it is considerable in reality.

Let us further define the concept of the gross error in the target quantity. If we start from the true values of primary quantities, we arrive at the true values of the degrees of absorption $s_1 = 0.4968$ and $s_2 = 0.8907$. If we take into consideration the standard deviations of the primary quantities shown in Table 4.5 and carry out the reconciliation, we find the standard deviations of thus assessed degrees of absorptions $\sigma_{s_1} = 0.0122$ and $\sigma_{s_2} = 0.0046$. Assuming normal distribution, we can construct for the degrees of absorption the confidence intervals whose limits (for $\alpha = 0.05$) are

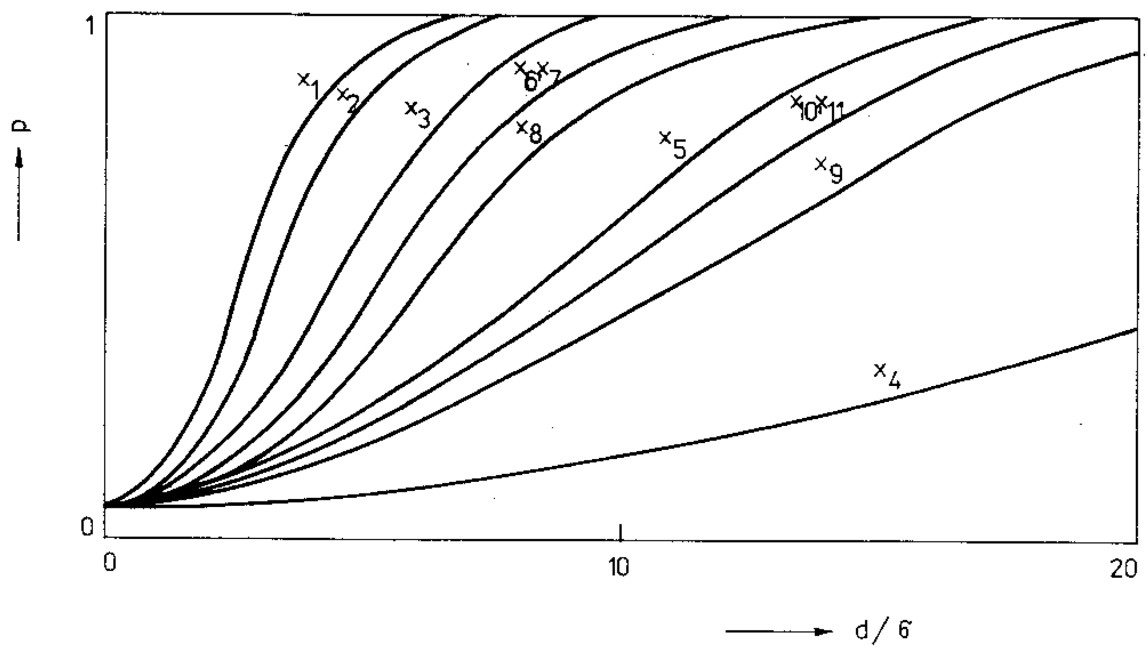


Fig.4.14 — Power characteristics of gross error detection test (Example 4.13)

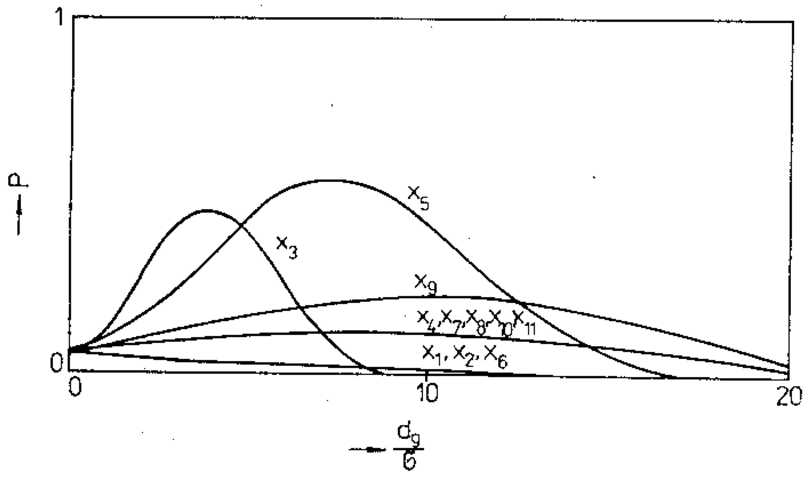


Fig.4.15 — Probabilities of error of type C for quantity s_1

⟨0.4729 , 0.5206⟩ for s_1 and ⟨0.8817 , 0.8997⟩ for s_2 . If the degrees of absorption found in the individual simulated measurements lie outside these intervals, we will state that this target quantity (degree of absorption) is corrupted by a gross error.

Empirically assessed probabilities of errors of type C are shown in Figs 4.15 and 4.16. These are relative frequencies of the case when a gross error occurred in one of the target quantities, which, however, has not been detected (the hypothesis H_0 has

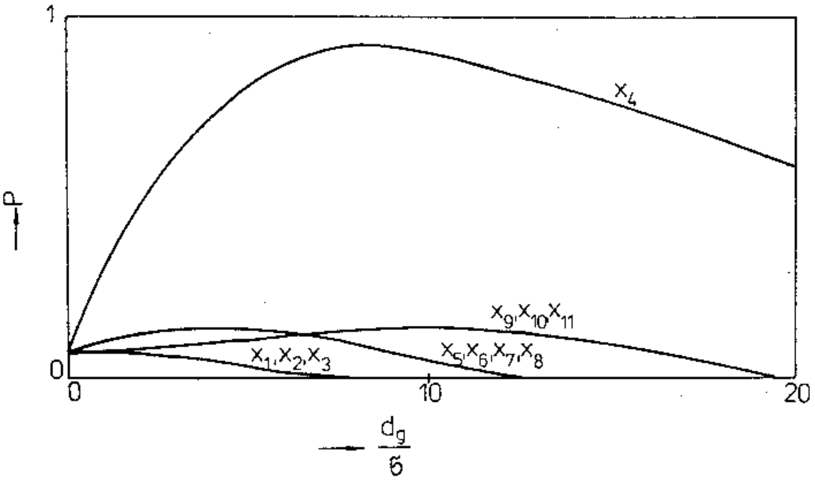


Fig.4.16 — Probabilities of error of type C for quantity s_2

not been rejected). It follows from the diagrams that in a limited number of the primary quantities a gross error within a certain range may cause, with a high probability, that the target quantity will be subject to an undetected gross error (primary quantities 3 and 5 in the case of s_1 and 4 in the case of s_2). With the other primary quantities such danger is negligible.

The conclusion that can be drawn from the above finding is that the statistical analysis of material balance inconsistency in combination with independent checking of the results of measurements 3, 4 and 5 (using parallel independent measurements, frequent revisions of measuring instruments, and the like) can, with high probability, exclude the possibility of any of the target quantities being corrupted by gross errors.■

Detection of systematic errors

Let us assume that we have a series of measurements of a certain process, for example a number of material balances set up on the basis of the day-to-day evaluation of the plant operation. Series of results so obtained make it possible not only to deal separately with the analysis of the individual sets of measurements, but also to examine the resulting time series with respect to the occurrence of systematic errors. Hence a more extensive volume of data enables one to detect smaller errors than was so in the cases discussed earlier.

Let us consider a series of adjustments of a single quantity obtained as the result of data reconciliation. If systematic errors are not present, these adjustments should behave as realizations of a random variable, which means that they should fluctuate around zero. The examination of such a time series from the viewpoint of a systematic occurrence of positive or negative values, or of a certain trend, can direct our attention to the fact that systematic errors may be present. Other methods for the examination of this problem (problem of the analysis of residuals in regression) are discussed in the book (Draper & Smith 1966).

4.5.2 Searching for the source of gross errors

Finding out that a gross error is probably present in the measured data represents only the first step in solving the problem of eliminating the gross error from the data. In principle, it is possible to proceed so that all the sources of measured values are checked up (measuring instruments, analytical methods, sampling practices, etc.). The extent of work associated with an action of this kind is usually enormous and, besides, in many cases the checking of plant measuring instruments cannot be done without breaking up the plant operation (disassembling of flowmeters, and the like).

It is, therefore, useful to concern ourselves with the possibility of finding out the source of a gross error on the basis of the analysis of measured data inconsistencies. Such an approach to the searching for the gross error source need not lead to an explicit determination of the error source but can reduce considerably the amount of measurements that would need to be made on site.

Preliminary considerations

As an introduction it is necessary to state that the identification of a measurement that is subject to a gross error is more complicated than a mere detection of a gross error. The reason for this is that the problem of errors identification often cannot be simply formulated mathematically. In its solution methods of mathematical statistics and logic have to be combined with information on the measured process we have acquired previously.

In publications dealing with statistical treatment of measurements some problems of the measured data analysis are solved with a view to identifying the so-called *outliers*. In Subsection 3.3.2 a method was set out for identifying a gross error in a series of repeated measurements of the same value. Methods are also known for identifying a measurement departing significantly from a regression line. In most of these cases, however, this concerns measurements of a single variable, with roughly the same precision. The structure of the mathematical model usually is simple, which makes the problem considerably easier. When carrying out measurements in process plants we meet simultaneously with different measuring precision, and the measured quantities usually are interrelated with one another in a rather complex way. In such a case it is necessary to adopt procedures differing, to a certain degree, from those hitherto commonly presented in textbooks on applied mathematical statistics.

Now let us start from the assumption that a significant inconsistency between the measured data and the mathematical model was ascertained. Such inconsistency may be caused by a number of factors, which, as mentioned earlier, can be divided into two groups: the inadequacy of the mathematical model and the inadequacy of the model of measuring errors (presence of gross measurement errors). Further we shall focus on the inconsistency caused by gross errors of measurement.

The basic way of searching for the measurement (measurements) corrupted by gross errors, can be taken over from the evaluation of controversial statements -

similarly as it is done in daily life. If there are statements of several persons available and one of them is in contradiction with the rest, then, on the assumption of their independence, only that statement is considered incorrect.

In more complex cases the credibility of the individuals is also taken into account. These two principles, of which the first one can be named principle of *minimizing the number of sources of gross errors* and the second principle of *credibility*, will be applied to the identification of gross errors. This means practically that we shall try to explain a gross inconsistency as being caused by a gross error in a minimum number (preferably only one) of the measurements, and, if we have to select among two or more measured quantities, we shall choose the one, whose measurement we distrust more.

First let us concern ourselves with selecting a set of measured quantities among which we shall look for the source of a gross error. A reasonable requirement with respect to such a set is that it should contain quantities with uncorrelated measuring errors. This requirement follows the principle of minimizing the number of sources of gross error since the correlation in its consequences means that a gross error from a single source will appear simultaneously in two or more quantities with correlated errors. Therefore, a suitable basis for gross errors identification usually is the set of primary quantities.

Further information on potential sources of gross errors is given by the power characteristics of the test used for gross errors detection. It is obvious that if the detection of a gross error in a given quantity is not probable, then the existence of a detected gross error caused by that particular quantity is also not probable. In this respect the limiting cases are the nonredundant quantities which can obviously be counted out completely from the list of suspects.

A number of methods has been suggested for selecting measurements that are subject to a gross error. Four of them will be briefly described further.

Analysis of standardized adjustments

It is known that the value of so-called *standardized adjustment*

$$z_i = v_i / \sigma_{v_i} \tag{4.145}$$

is a good indicator of the presence of a gross error. It is possible to prove that when only one gross error is present, in the absence of random errors, the standardized adjustment of that quantity is greater or equal (in the absolute value) to the standardized adjustments of the other quantities. Even when the presence of random errors in other quantities may distort the situation to a certain extent, the standardized adjustment of a quantity that is corrupted by a gross error always belongs among the greatest ones (in the absolute value).

As mentioned earlier, the standardized adjustment is not defined for nonadjustable quantities whose adjustments are identically equal to zero. In practice, however, we can meet with quantities which are "almost nonadjustable". It is characteristic for these quantities that their adjustments as well as the standard deviations of their adjustments are close to zero. In theory even in this case the standardized adjustment may serve for identifying a gross error. However, it is a quotient of two very small numbers and, therefore, the resulting value has to be accepted with caution (it may be affected by numerical problems during computing).

The functioning of this method can be studied on results of Example 4.11 (see Table 4.6). It can be observed here that the variable with a gross error is always among suspects with the largest values of standardized adjustments z_i (boldface entries in the Table). However, only in the case of stream 3 this method gives the unequivocal answer. In the remaining cases also some other flows are found suspect. This situation is typical of many real cases from industry.

Analysis of the residuals of equations

In the case when the unmeasured quantities are not present, or when a system of equations can be decomposed so that such a subsystem of equations is formed, an analysis of the individual equations residuals can be useful. If we form standardized residuals, i.e. quotients of the residuals and their standard deviations [see Eq.(4.127)], we may find equations having values of residuals so high that they cannot be ascribed only to the presence of random errors of quantities appearing in that particular equation. If we find the measured quantity in all equations that exhibit significantly large residuals, the said quantity will be suspected as the source of a gross error. The above method has been worked out especially for single-component balances in complex systems (Mah, Stanley & Downing 1976), where significant residuals possess an obvious physical meaning (so-called *imbalances*).

There is a problem here, however, that different equations are sensitive to the formation of a significant residual in a different way. It may happen that a gross error in a certain quantity will not cause a significant residual of all equations in which the quantity appears (Madron 1985b). Such situation reduces somewhat the efficiency of this method.

Elimination of measured quantities

Let us suppose that we regard all the redundant quantities - successively one by one - as being unmeasured, and carry out the gross error detection procedure. If we have included among the unmeasured quantities one that is subject to a gross error, it may be expected that, in this case, the gross error will not be detected. Then we shall declare suspicious all those quantities, whose inclusion among the unmeasured quantities has not led to detecting the presence of a gross error.

With this method it is necessary to realize that besides the processing of the fundamental set of measured data, so many additional runs of data processing have to be conducted, dependent on how many adjustable quantities there are. Even when this need not concern all the redundant quantities (it is possible to focus only upon suspicious quantities with high standardized adjustments), the computation time may be prohibitive. It is, therefore, important that there have been developed procedures (for linear models) that do not require complete reconciliation in each elimination step. In these cases the results of the base case are corrected only as a result of the inclusion of the measured quantity among those unmeasured ones (Ripps 1961, Romagnoli & Stephanopoulos 1981, Crowe 1988).

Measurement credibility

When the method of elimination of measured quantities is applied to the detection of gross errors, it is possible to meet with the following phenomenon. When a measured quantity is included among the unmeasured ones, its value is obtained as the result of the coaptation. If the value thus calculated differs extremely from the measured value, we may raise objections against it.

In most cases we are informed about the maximum possible gross error which can occur in the course of the measurement. For instance, we may know the reading of some other, though less precise, but quite reliable instrument. The accumulation in a storage tank must be greater than zero but cannot exceed the tank capacity. The flow rate of a liquid is limited by the capacity of the respective pump. It would certainly be possible to find out other kinds of prior information about the maximum possible error of an individial measurement.

The above kind of reasoning is the basis of the following method for gross errors identification. It can be divided into four steps:

1. A value of the maximum gross error (in absolute value), which cannot be exceeded, is assessed for each measured quantity. This value, denoted for *i*th measured quantity as $d_{i,\max}$, may be rather large in some cases. It may even make sense if $d_{i,\max}$ is within the range of hundreds of per cents of the measured value.
2. Based on the value of the gross error detection testing criterion $Q_{\min}$ one estimates the value of the gross error of the individual quantities (that could cause the found value of $Q_{\min}$). These estimates will be denoted $|\hat{d}_i|$, the method of their calculation will be described later.
3. From among the measured quantities a subset **B** is chosen for which it holds

$$|\hat{d}_i| > d_{i,\max} \tag{4.146}$$

Thus we have selected a subset of quantities which we do not regard as the source of a gross error since the estimate of their gross error is greater than the assumed values $d_{i,\max}$.

4. Now the set of quantities suspicious as the source of a gross error (set **C**) is found as the difference between the set of suspicious quantities assessed by traditional methods (set **A**) and the set of quantities satisfying the inequality (4.146) (set **B**).

$$\mathbf{C} = \mathbf{A} - \mathbf{B} \tag{4.147}$$

Estimating absolute value of a gross error

It holds for the mean value of the non-central χ^2 distribution

$$E\,[\chi^2\,(\nu\,,\,\delta)] = \nu + \delta^2 \tag{4.148}$$

The value of $Q_{\min}$ is the realization of a random quantity with χ^2 (ν , δ) distribution. If no other information is avaliable, $Q_{\min}$ can be considered an estimate of mean value and used for estimating the parameter δ of noncentral χ^2 distribution according to

$$\hat{\delta} = (Q_{\min} - \nu)^{1/2} \tag{4.149}$$

Respecting Eq.(4.138) we obtain, after the rearrangement, an expression for estimating the gross error d_j :

$$|\,\hat{d}_j\,| = (Q_{\min} - \nu)^{1/2}\,\sigma_j^2\,/\,\sigma_y \tag{4.150}$$

Example 4.14: *Estimating a gross error magnitude*
In Example 4.11 a case of a mass balance was dealt with. Gross errors equal to tenfold the standard deviation of the random measuring errors were added to the individual measured values. Using the global test, the presence of a gross error was detected in the quantities 1, 3, 4 and 5.

Table 4.9 — Estimation of the gross errors magnitude (Example 4.14)

j	d_j	$Q_{\min}$	σ_j	σ_{v_j}	$\lvert\hat{d}_j\rvert$
-	0	1.74	-	-	-
1	10	84.5	1.0	0.799	11.3
3	8	59.7	0.8	0.531	9.2
4	4	8.43	0.4	0.075	5.4
5	20	73.8	2.0	1.875	18.1

The values of the gross errors and of $Q_{\min}$ for the individual cases are presented in Table 4.9. The estimates of the gross errors, calculated from (4.150), are shown in the last column of the Table. It can be seen from the results that the agreement between the gross error true value and its estimate is fairly good.■

Example 4.15: *The identification of a gross error*
The detection of the gross error presence in a mass balance was examined in Example 4.11. Let us apply the methods of a gross error identification to the case when the gross error (10 per cent of the measured value) was added to the measured

quantity x_1 . The course of the identification is shown in Table 4.10. The value of $Q_{min} = 41.2$ was found after reconciliation, which is more than the critical value 5.99. The values of standardized adjustments z_i are also present there. The highest values of z_i belong to the quantities 1, 3 and 6. The quantity No.3 has the standardized adjustment a little smaller than the others but the difference is not significant.

Next the method of elimination of measured quantities was used. Successively the quantities No.1, 3 and 6 were regarded as unmeasured ones and the reconciliation was carried out. Then the values Q_{min} were compared with the critical value of the χ^2 distribution for $\alpha = 0.05$ and one degree of freedom, which is equal to 3.84 (the transfer of one quantity among unmeasured ones cuts the number of degrees of freedom by one).

Table 4.10 — Identification of a gross error (Example 4.15)
$Q_{min} = 84.5$

i	z_i	Q_{min}	$d_{max,i}$ (%)	$d_{est,i}$
1	**-9.17**	**0.35**	**20**	**11**
2	-			
3	**7.33**	30.7		
4	-2.66			
5	2.66			
6	**9.17**	**0.35**	30	57

It can be seen from Table 4.10 that the quantity No.3 can be omitted from the list of suspects since, contrary to the quantities 1 nad 6, the presence of a gross error is detected even when it is added to the unmeasured quantities.

Now it is necessary to arbitrate between the quantities 1 and 6. Based on the evaluaion of the measured process, gross errors greater than 20 and 30% of the measured values of x_1 and x_6 , resp., are not possible. Further, gross errors at 11% and 54% of the measured values were estimated from Q_{min} with the aid of Eq.(4.150). Since the estimated value of the gross error for the quantity x_6 is considerably greater than the maximum error (30%) set beforehand, x_1 remains the only suspect quantity.■

The presence of more gross errors

The methods of gross errors identification presented so far can be used also in cases when more than one gross errors is present.

As the starting point can serve the set of quantities with large values of standardized adjustments. If standardized adjustments differ significantly in absolute values, the method of successive elimination can be used. The quantity with the largest absolute standardized adjustment is put among unmeasured quantities and the reconciliation is done with the reduced set of measured variables. If the presence of some further gross error is detected, the whole procedure is repeated. The whole procedure ends if no gross error is detected, or if there remain no redundant quantities.

This approach looks very promising, but the practical implementation faces serious problems. Quite often there are more than one candidates for elimination in individual elimination steps (remember the previous example). In some cases some other information can be taken into account. For example Serth and Heenan (1986) proposed to analyze if the results after the elimination of suspect quantities are realistic (positive concentrations, reasonable values of flow rates etc.). If it is not the case, the respective suspect quantity is not eliminated. However, even in this case the probability of eliminating good measurement and retaining the bad one is quite high.

4.5.3 Elimination of gross errors

When eliminating gross errors, we distinguish, essentially, between two different cases. The first one occurs when we can use as the basis only the measured data and cannot repeat the measurement, neither can we examine the properties of the measuring instruments used, and the like. In this case it is a matter of a mere elimination of values that are subject to gross errors (which can be done automatically by a computer). As follows from our long term experience, this problem can only exceptionally be solved with success. The reason is that the methods for gross errors identifications only rarely give unambiquous results (especially when more gross errors are present). We say that these methods are not selective enough. More often they define a set of suspect quantities.

The other case, in which the analysis of measured data takes place simultaneously with their acquisition (for example when the data processing is on-line), is considerably more favourable. Then the set of measured quantities can be divided into two sets, the first one containing those quantities, which are checked by procedures for gross errors detection (the quantities with low threshold values). If a gross error is detected, it can be identified and eliminated by a combination of gross error identification procedures and on site checking of measuring instruments.

In the second group there are quantities for which the gross error detection is not efficient (high values of threshold values). If these quantities influence significantly the targets of the whole measurement (see Subsection 4.5.1 - an error of type C), they should be checked independently on-site (by adjusting the instruments more frequently, doubling the measurements, and the like). Only such complex approach can yield really reliable results. On the other hand, the reliance on automatic elimination of gross errors by a computer may result in false confidence in results.

Even very sophisticated data analysis methods cannot substitute the responsible approach to the measuring process, maintenance of instruments, and the like.

4.6 RECOMMENDED LITERATURE TO CHAPTER 4

Reconciliation of measured values based on the least-squares principle was devised independently by Gauss, Legendre and Andrain at the beginning of the 19th century (Bohm & Radouch 1978). Since then thousands of papers and many books on this topic have been published. Reconciliation had been widely used mostly in astronomy and geodesy long before the advent of computers (for example the reconciliation of measured angles in triangular nets used in geodesy to obey 180° sum in every triangle).

First such activities in process engineering emerged in the early sixties (Ripps 1961, Kuehn & Davidson 1961). Since then many applications in chemical and refinery processes, pulp industry, ore processing and others have been described in the literature.

The basics of reconciliation and parameters estimation can be learned, for example, from papers by Britt & Luecke (1973), Knepper & Gorman (1980) or from books (Mah 1990, Bard 1974).

The basis of almost all chemical engineering models is formed by mass, component and enthalpy balances. Processing of data obeying mass (single-component) balances is treated well in papers by Vaclavek (1969a), and Mah, Stanley and Downing (1976). Multicomponent balances are discussed e.g. by Vaclavek, Kubicek & Loucka (1975).

There is quite voluminous literature on variables classification, mostly in connection with mass balances (Vaclavek 1969a, Mah, Stanley & Downing 1976, Stanley & Mah 1981b, Crowe, Campos & Hrymak 1983) or component balances (Vaclavek, Bilek & Karasiewicz 1972, Vaclavek, Kubicek & Loucka 1976, Romagnoli & Stephanopoulos 1980, Kretsovalis & Mah 1987a, Crowe 1989a). Papers by Kretsovalis & Mah cover also chemical reactors and energy balances (1988a, 1988b). Most of the classification algorithms are graph-oriented, some are equations-oriented.

Attention is given also to problems of gross errors detection. After the first works in this area (Reily & Carpani 1963, Almasy & Sztano 1975, Mah, Stanley and Downing 1976) many others were published (Madron, Veverka & Vanecek 1977, Romagnoli & Stephanopoulos 1980, Tamhane 1982, Mah & Tamhane 1982, Madron 1983a, Serth & Heenan 1986, Heenan & Serth 1986, Serth, Valero & Heenan 1987, Crowe 1989b). Some gross errors detection procedures were evaluated by Iordache, Mah & Tamhane (1985).

The identification of gross errors has also received much attention. After pioneer works by Ripps (1961), Nogita (1972) and Mah, Stanley & Downing (1976) this problem was investigated e.g. by Madron (1985a, 1985b), Narasimhan & Mah (1987) and Crowe (1988). All the above procedures are based on the assumption that the covariance matrix of measuring errors is known. A quite different approach based on so-called Studentized residuals was described by Jongenelen, Hrijer & Zee (1988). Also worth mention are the methods of estimating the covariance matrix of measurement errors (Kubacek 1983, Almasy & Mah 1984).

An efficient solution of large-scale problems is facilitated by the decomposition of data processing into reconciliation and coaptation described in Section 4.2. Widely used are the graph-oriented approach presented by Mah, Stanley and Downing (1976) and equations-oriented matrix projection method by Crowe, Campos & Hrymak (1983) and Crowe (1986).

The identification of nonlinear models in this book was based on linearization of the system of equations. Another approach based on nonlinear programming has been studied by Pai & Fisher (1988), Ramamurthi & Bequette (1990), Tjoa & Biegler (1990).

There are also numerous papers on data processing of specific unit operations, such as chemical reactors and bioreactors (Vaclavek 1969a, Murthy 1973, 1974, Madron, Veverka & Vanecek 1977, Madron 1981, Wang & Stephanopoulos 1983), distillation problems (Rose & Hyka 1984, Horakova & Madron 1987, MacDonald & Howat 1988, Kuncir & Madron 1990), rigorous models of unit operations (Nair & Iordache 1990) and heat exchangers (Madron, Horakova & Hostalek 1986, Pang et al. 1990). Reconciliation can also be applied to utilities systems (Serth & Heenan 1986, Stephenson & Schindler 1990).

Important experience can be gained from the implementation of modern data processing methods in operating plants (Umeda, Nishio & Komatsu 1971, Holly, Cook & Crowe 1989, Raza et al. 1989, Leung & Pang 1990).

The important problem of the choice of directly measured quantities (the measurement placement) was dealt with by Vaclavek (1969b), Vaclavek & Loucka (1976), and Madron & Vybomy (1983).

A common assumption applied so far concerned a steady-state of the measured process. The data processing under dynamic conditions is studied by Wells (1971), Vaclavek (1974) and Stanley & Mah (1977). A good analysis of this problem was presented by Almasy (1990). The detection of changes in steady states was studied by Narasimhan et al. (1986).

5 Rational approach to measurement planning

As already stated in Chapter 2, the individual stages of the process of measurement, i.e. preparation of a measurement, the measurement proper and evaluation of results, have to compose a balanced whole. The first precondition for obtaining good-quality results are responsible planning and preparation of the measurement that include decision-taking at several levels, from a global conception of the measurement to details of chemical analyses, sampling methods, and the like.

The problems of measurement planning are more complex than those we have dealt with so far. They require that we cope with a number of spheres of the measurement theory (problems of errors, measured data processing) and, therefore, we can concern ourselves with them only at this place, although, taken from the viewpoint of methodology, this Chapter should have been inserted at the beginning of the book.

The measurement can be effected in various ways differing in their efficiency. Hence the planning of measurement may be formulated as a problem of optimization (how to obtain the required information at minimum costs, within the shortest possible time, etc.). Since this presents a complex problem, it would be extremely difficult to solve it as a single whole. A more favourable prospect of succeeding has the approach based upon optimization of partial problems at individual levels, or on comparison among several different alternatives. Although in most cases such an approach does not lead to the overall optimum, it makes it possible to obtain a satisfactory, technically feasible solution.

5.1 DETAILS OF PLANT MEASUREMENT

The typical questions met in the course of detailed planning of plant measurements are, for instance:

- choosing the places where samples are taken,
- analytical methods used,
- number of parallel determinations of samples composition,
- sampling frequency.

A number of questions of this kind may be answered on the basis of intuition or of analogy with similar cases the researcher has already met with. In other cases it is possible to make use of theoretical knowledge based on, for example:
- theory of random errors propagation,
- character of measuring errors (systematic and random errors),
- theory of stationary random processes (measuring of fluctuating variables).

This range of problems also covers some of the questions discussed in the preceding Chapters of this book. So, for instance, the choice of the time interval of taking a sample from the stream, whose composition is fluctuating, represents an example of optimization in this respect (see Example 3.16). Similarly, by using a method based on the theory of fluctuating signals processing, it is possible to choose between a continuous measurement (or use of an instrument equipped with an integrating device), or measurement at discrete instants of time (see Subsection 3.3.5).

Problems often arise in the course of selecting the analytical method. Usually there are more methods available, differing in laboriousness, precision, accuracy, and other aspects. Since the obtaining of a more precise result is usually contingent on more extensive work, we try to choose a method whose precision is just adequate for our needs. The working capacity thus saved can be devoted to more useful matters (carrying out the chemical analyses more frequently, analyzing of other samples in order to obtain redundant measurements, and the like). The same is true as far as the optimum (or minimum necessary) number of parallel analytical determinations is concerned. A suitable approach to the solution of the said problems is the application of the *theory of information* to the problems of analytical methods, which is described, for example, in (Eckschlager & Stepanek 1979).

5.2 APPLICATION OF THE ERRORS PROPAGATION THEORY

The theory of errors propagation can be applied in virtually all spheres of the measurement planning. At this point we shall study the possibilities of selecting conditions of measuring in an optimal way, so as to reduce the influence of random measurement errors on the errors of final results.

The results obtained by studying the propagation of random errors (see Tab.3.1) enable one to formulate certain simple rules that have to be adhered to when minimizing errors of results. So, for example, when a result is given as the sum of a series of directly measured quantities, the precision of the result is affected mostly by the precision of the measurement with the highest variance; such measurements have to be focused upon when improving precision of the result. Analogically, when a result is a product of directly measured quantities, maximum attention must be given to the measurement with the greatest relative standard deviation.

The course of optimization of measurement conditions is as follows: that quantity, which is the objective of the measurement, is expressed as the function of directly measured quantities and other quantities, characterizing the measurement conditions.

Those quantities, which can be varied freely and which affect the precision of results, represent for us the optimization variables. A suitable measure of the precision of a result (most frequently the standard deviation) is expressed with the aid of random errors propagation theory as a function of the optimization variables. When doing so, we must often consider the influence of optimization variables on the precision of primary quantities measurement. The task of measurement optimization is then solved as minimization of standard deviation of the result with respect to the set of admissible values of optimization variables.

Example 5.1: *Optimization of ammonia losses measurement*
A mixture of air and ammonia is leaving the plant via a stack. It is necessary to determine the ammonia flow rate in the stack. However, due to the character of streaming in the stack, conventional methods of flow rate measurement cannot be used. A method has been suggested, based on the fact that the flow through the stack in time is virtually constant. Ammonia concentration is measured under normal operation conditions and then a measured amount of secondary air is fed to the stack bottom. After stabilization ammonia concentration at the stack outlet is measured. Ammonia flow rate can be computed on the basis of component mass balance. The task is to find such flow rate of secondary air, at which the standard deviation of the assessed ammonia flow is minimal.

It is known that the total mass flow through the stack is roughly 300 kg h^{-1} and the ammonia mass fraction 0.05. The standard deviations of the individual measurements are 6 kg h^{-1} and 0.0025 for the secondary air flow rate and ammonia fraction, resp.

Let us introduce the following symbols:
F_0 - flow rate through the stack at the beginning of the measurement (kg h^{-1}),
F_1 - mass flow rate of secondary air, the optimization variable (kg h^{-1}),
w - ammonia mass fraction at the beginning of the measurement,
w_1 - ammonia mass fraction after the dilution by secondary air
$F = F_0\, w$ - mass flow rate of ammonia, the target quantity,
σ_{F_1}, σ_w - standard deviations of measurements of the secondary air mass flow rate and of ammonia mass fractions.
The fundamental balance equation is

$$F_0\, w = (F_0 + F_1)\, w_1 \;, \text{ or}$$

$$F_0 = \frac{F_1\, w_1}{w - w_1} \tag{5.1}$$

The mass flow rate of ammonia is expressed by means of directly measured quantities F_1, w and w_1 :

$$F = F_0\, w = \frac{F_1\, w_1\, w}{w - w_1} \tag{5.2}$$

For use of the calculation of random errors propagation, we linearize the nonlinear relation (5.2) by expanding in the Taylor series while neglecting the terms of the second and higher orders. The function is expanded at the point of the assumed values of quantities F_0 and w:

$$F = F_0\, w + \frac{w_1\, w}{w - w_1}\, \Delta F_1 - \frac{F_1\, w_1^2}{(w - w_1)^2}\, \Delta w + \frac{F_1\, w^2}{(w - w_1)^2}\, \Delta w_1 \tag{5.3}$$

We assume that the errors of measuring are non-correlated; then the variance of the ammonia flow rate σ_F^2 is expressed by the following relation [see equation (3.45)]:

$$\sigma_F^2 = \frac{w_1^2\, w^2}{(w - w_1)^2}\, \sigma_{F_1}^2 + F_1^2\, \frac{w_1^4 + w^4}{(w - w_1)^4}\, \sigma_w^2 \tag{5.4}$$

since $\sigma_w^2 = \sigma_{w_1}^2$.

The relation (5.4) is evaluated for the values $F_0 = 300$ kg h^{-1} and $w = 0.05$. The mass fraction depends on the other quantities:

$$w_1 = \frac{F_0\, w}{F_0 + F_1} \tag{5.5}$$

The flow rate F_1 is considered to be an independent variable.

The dependence of σ_F on the ratio F_1 / F_0 is demonstrated as curve 1 in Fig.5.1. The minimum value of σ_F is attained for the flow rate of secondary air equal to approximately 1.1× multiple of the flow rate through the stack, i.e. for $F_1 =$ 330 kg h^{-1}. At this optimum value the standard deviation of the ammonia mass flow rate equals 3.1 kg h^{-1}, which is 20.6 % of the measured value. In addition, it follows from Fig.5.1 that the secondary air flow rate can be chosen at a somewhat higher than optimum value without any significant adverse effect. If, on the other hand, the flow rate is lower than optimal, the precision of measurement decreases steeply.

Let us examine also the effect of standard deviations of direct measurements on standard deviation of the result. If the standard deviation of ammonia concentration measurement is reduced to a half, we obtain the dependence 2 in Fig.5.1. When the standard deviation of the measurement of secondary air flow rate is reduced to a half, however, σ_F remains virtually unchanged (dropping by only 0.3% at the minimum), so that the dependence of σ_F on the ratio F_1 / F_0 coincides with the original curve 1. Hence, if we want to improve the measurement of F significantly, we have to focus our attention on reducing the variance of ammonia concentration measurement.■

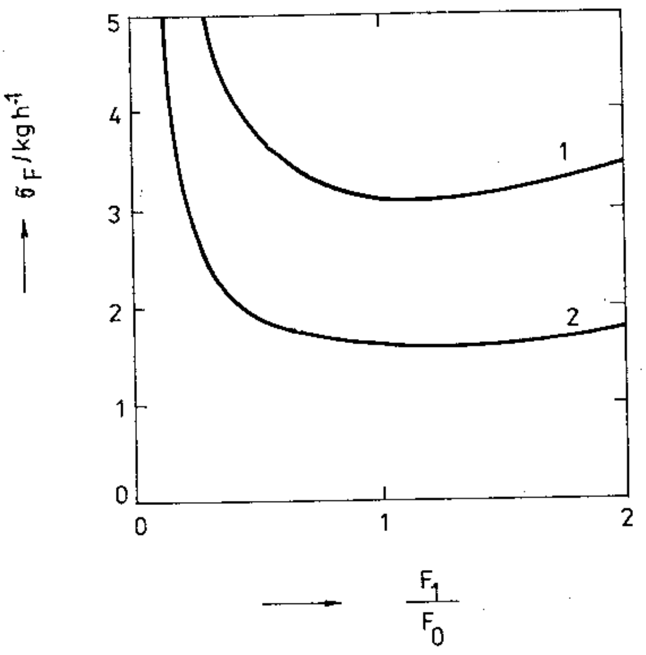


Fig.5.1 — Precision of ammonia flow rate measurements (Example 5.1)

The method described above can be generalized to the case of a greater number of variables with the use of share matrices introduced in Chapters 3 and 4.

5.3 OPTIMUM ESTIMATION OF MATHEMATICAL MODELS PARAMETERS

The generalization of the problem solved in Example 1 is the choice of such conditions of the measurement as will ensure that the whole set of unmeasured quantities (parameters of the mathematical model) are estimated with the highest possible precision.

First it is necessary to choose a criterion that will be used as the measure of the parameters precision. The following quantities are minimized most frequently:
- volume of the confidence region (ellipsoid) of parameters,
- sum of variances,
- weighted sum of variances,
- maximum variance.

Solutions of some of the problems can be found e.g. in the monograph (Bandemer et al. 1977). Next we shall outline, how this task is dealt with when the volume of the confidence ellipsoid of models parameters is minimized. In this case we take advantage of the fact that the volume of the confidence ellipsoid V is directly proportional to the root of the determinant of the covariance matrix of estimates of models parameters $\boldsymbol{y}$.

$$V \sim [\det \boldsymbol{F}_{\hat{y}}]^{1/2} = [\det \boldsymbol{F}_{\hat{y}}^{-1}]^{-1/2} \tag{5.6}$$

It is, therefore, sufficient to find such a method of measurement that will minimize the determinant of $\boldsymbol{F}_{\hat{y}}$ or maximize the determinant of $\boldsymbol{F}_{\hat{y}}^{-1}$.

Further we shall confine ourselves to a model of estimating the directly unmeasured quantities from redundant measurements (see Subsection 4.4.2).

The mathematical model is

$$\boldsymbol{By} = \boldsymbol{x} \tag{5.7}$$

We shall assume that the measurements of the directly measured quantities $\boldsymbol{x}$ are equally precise, and the matrix $\boldsymbol{F}_x$ is not known in advance. The estimate of the covariance matrix of parameters estimate is given by (see Example 4.7)

$$\hat{\boldsymbol{F}}_{\hat{y}} = \hat{\sigma}^2 (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{B})^{-1} \tag{5.8}$$

On the given assumption the estimate of the covariance matrix $\boldsymbol{F}_{\hat{y}}$ is a function of the matrix $\boldsymbol{B}$ only and it holds that

$$\det \boldsymbol{F}_{\hat{y}}^{-1} \sim \det (\boldsymbol{B}^{\mathrm{T}} \boldsymbol{B}).$$

By choosing the matrix $\boldsymbol{B}$ (referred to as the *design matrix*) we can influence the covariance matrix of estimates of directly unmeasured variables, which is used when the optimum conditions of the measurement are searched for.

Let us assume that the model (5.7) represents the expression of the measured dependent variable x as a polynomial function of an independent variable t. For the individual values of t_i and x_i Eq.(5.7) has the following form:

$$y_1 + t_i y_2 + t_i^2 y_3 + \dots t_i^{k-1} y_k = x_i \qquad i = 1, \dots, I \tag{5.9}$$

and the ith row of the matrix $\boldsymbol{B}$ obviously is $(1, t_i, \dots, t_i^{k-1})$. The values of the independent variable t_i (supposed to contain no error) are so-called *node points of measurement*. Obviously the volume of the confidence ellipsoid of $\hat{\boldsymbol{y}}$ is, for a given number of measurements I, a function of the choice of node points t_i that are, in this case, optimization variables. When an interval is given within which the t_i may be selected, the two following tasks can be formulated.

How can one choose t_i, $i = 1, \dots, I$ so that the confidence ellipsoid of y be as small as possible? It is essentially a case of the selection of node points of measurement and of assessing the number of repetitions of measurements at the individual node points.

The second problem arises if a number of measurements is already available but we are not satisfied with the result (the confidence intervals for the parameters are too wide). We carry out additional measurements so that we always measure one pair x_i , t_i , evaluate the result, and repeat this until the confidence region is reduced to the required size. In this case the task is to choose t_i in each successive measurement, so that the decrease in the confidence region is maximal (the procedure is referred to as *sequential* method).

Example 5.2: *Improving the estimation of linear function parameters*
In Example 4.7 we have estimated parameters of a linear function of an electrolytic cell voltage in dependence on current intensity. The confidence ellipse parameters b_0 and b_1 were markedly elongated. Therefore, supplementary measurement is required to make the estimates of parameters more precise (to reduce the area of the confidence ellipse to less than one fifth of its original value). The independent variable - current intensity - can be chosen from the interval $\langle 0.5, 3 \rangle$ kA. We may assume that the precision of voltage measurement does not depend on the value of current.

The task is to suggest further measurement (that is to select such values of current intensity), so that the required reduction of the confidence ellipse area might be achieved with the least possible number of measurements. To do so, we will use the method of maximization of the matrix $(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{B})$ determinant. In Example 4.7, ten measurements have already been made and we are now planning the eleventh measurement. Hence the matrix $\boldsymbol{B}$ will have eleven rows. The first ten rows have already been fixed (by the measurement carried out previously), the eleventh row $(1, I_{11})$ contains the optimization variable, i.e. the current intensity during the supplementary measurement.

Table 5.1 — Results of Example 5.2

I_{11}	D	$D^{-1/2}$	$S \times 10^4$	$\hat{\sigma}_{b_0} \times 10^2$	$\hat{\sigma}_{b_1} \times 10^2$
-	1.412	0.842	9.818	4.96	1.72
0.5	58.40	0.131	1.296	0.73	0.26
1.0	37.06	0.164	1.628	0.92	0.33
1.5	20.72	0.220	3.152	1.49	0.53
2.0	9.374	0.327	3.324	1.86	0.66
2.5	3.031	0.574	6.167	3.44	1.21
3.0	11.688	0.770	7.998	4.61	1.59

In Table 5.1 the values are presented of $D = \det(\boldsymbol{B}^{\mathrm{T}}\,\boldsymbol{B})$ and of the reciprocal value of the D root (proportional to the area S of the confidence ellipse) for various values of I_{11} within the range 0.5 - 3 kA. It may be seen that the area of the confidence ellipse will be minimal when the current intensity during the subsequent measurement is at the lowest limit of the admissible interval, i.e. 0.5 kA.

To verify the above conclusion, a series of measurements was simulated by a computer for the values of current intensity as given in the first column of Table 5.1. Using the methods described in Example 4.5 the values of parameters were evaluated and also the confidence ellipses were assessed. Areas of the ellipses as well as the estimates of standard deviation parameters for the individual cases are presented in the next columns of Table 5.1.

It follows from the results that the optimal value of current intensity during the supplementary measurement ensures that the initial requirement (to reduce the area of the confidence ellipse to 1/5 of its original value 9.818×10^{-4}) is met since the reduction was actually by the factor 7.6. On the other hand, if the supplementary measurement were carried out at $I = 3$ kA, the ellipse area would have decreased only by the factor 1.2, so that additional measurements would be necessary.■

5.4 SELECTING DIRECTLY MEASURED QUANTITIES

The problem of optimizing the selection of directly measured quantities can be formulated mathematically in the following way. We assume that a mathematical model, represented by a system of equations among the quantities occurring in the given problem, is known. The set of all the quantities not known beforehand can be divided into subsets of *measurable* and *unmeasurable*, and further into subsets of *required* (representing the objective of the measurement) and *non-required* quantities. The task is to select from the set of measurable quantities a subset of quantities that will be measured, so that the desired quantities can be estimated at a required accuracy, and, at the same time, an extreme of the optimization criterion (for example the minimum cost of measurement) is attained. Hence we are trying to meet the objective of the measurement at the minimum cost, within the shortest possible time, with the lowest consumption of labour, and the like.

There is no doubt that thus formulated the problem is interesting theoretically but, in most cases, its significance is purely academic. The reasons for this statement are as follows.

The notion of accuracy of a result is rather complex. In addition to precision, it involves also the question of systematic errors of measurement and of protecting the results against the influence of gross errors of measurement. In spite of the fact that methods for solving such partial problems do exist, in the end it is difficult to evaluate exactly the individual variants of measurement with respect to accuracy of the obtained results.

Further problems may arise when forming an objective function which is to be optimized. There is often a number of methods available for measuring of a certain variable, which differ from one another as regards the occurrence of random, systematic and gross errors (for example, the flow rate can be measured by flowmeters of various types, each of which can have several modifications). Information concerning the cost of individual variants is usually rather incomplete.

The set of admissible methods of measurement usually is fairly extensive. As will be shown later, the number of various possibilities of selecting the measured quantities is quite high even in comparatively simple cases.

It would be possible to present more reasons for claiming that the task of optimum selection of measured quantities cannot be solved rigorously for the time being. This knowledge, however, should not prevent us from applying the findings of the theory of measurement to solving the partial problems we meet when selecting the measured quantities.

Next we shall try to outline the solution of some topical problems in this area. We shall confine ourselves to the selection of directly measured quantities (which is sometimes formulated as a dual problem of selection of unmeasured quantities) so that a just solvable set of equations for unmeasured quantities is formed. The case of optimal selection of redundant measurements (for instance with a view to detection of gross errors) has not yet been solved.

5.4.1 Classification of quantities

We are often confronted with the task of carrying out the measurement of a plant equipped with some instrumentation, and where analyses of certain streams are conducted routinely. We want to know whether all the quantities, required as the result of plant measurement, are observable (i.e. belong among the directly measured or can at least be estimated by solving the equations of the mathematical model). If it is not so, we need to know, which quantities, hitherto unmeasured, have to be measured so that all the required quantities might be determined. Therefore, the first stage consists in dividing the unmeasured quantities into observable and unobservable ones. In the second stage unmeasured quantities are selected as measured in the future. It is useful to classify, at the same time, the directly measured variables as redundant and nonredundant (since only redundant variables can be analyzed as concerns the occurrence of gross errors).

Thus formulated the problem can be solved easily for a one-component mass balance. Let us assume that we have a flowsheet expressed in the form of a connected oriented graph. Let us assume further that we want to assess the flow rates of all the streams. For use of classification it is advantageous to take the graph as disoriented, that is, not to consider the orientation of the graph edges.

For the classification of unmeasured streams as observable and unobservable, the following rule is applicable (Mah 1990):

The stream is unobservable if and only if it occurs in a circuit of unmeasured streams.

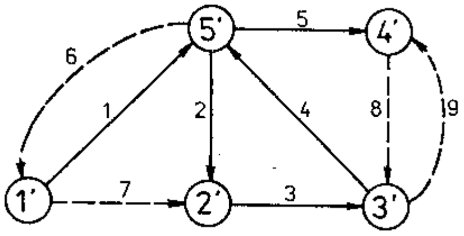


Fig.5.2 — The graph of mass balance schema

In the diagram (Fig.5.2) there is only one circuit formed by unmeasured streams 8 and 9. The flow rates of these streams are nonobservable. It is obvious, too, how to proceed when selecting additional measurements in order to make all the unmeasured streams observable - we select unmeasured streams with a view to break the circuits of unmeasured streams. In our particular case we are choosing between streams 8 and 9. By including one of these streams among the measured ones we are breaking up the circuit of unmeasured streams and all the flow rates are thus observable.

Similarly, there exists a simple method for classifying directly measured flow rates as redundant and nonredundant ones. The following rule (Mah 1990) holds true:

> *Let a stream i connecting the nodes j and k, be measured. The measurement of the stream i is redundant if and only if the nodes are not connected by a path of unmeasured streams.*

Hence, for example, the measurement of the stream 2 in Fig.5.2 is nonredundant since the unmeasured streams 6 and 7 connect the nodes 5' and 2' (initial and terminal nodes of the stream 2).

When we want to find all the redundant quantities we proceed so, that we gradually reduce the original graph by merging the nodes connected by unmeasured stream (or streams), and ignore the resulting loops. The procedure is illustrated in Fig.5.3. Successively we combine the nodes 1' and 5' (streams 1 and 6 drop out), nodes 3' and 4' (streams 8 and 9 drop out), and finally we merge the node 2' with that obtained by merging of nodes 1' and 5'. The resulting graph contains only the streams 3, 4 and 5, which are, at the same time, redundant.

In a general case, when we work with a general mathematical model, the clasification of quantities is more difficult. If the mathematical model is linear, we can use the method described in Section 4.2. The information about variables classification was obtained there as a by-product of problem decomposition into reconciliation and coaptation. If the mathematical model is nonlinear, the problem of classification is much more complicated. If we apply this method on the linearized form of the model, the solution is only approximate. There have also been developed other methods of classification, mostly applicable to systems of balance equations. These methods which are efficient, but rather complicated, will be mentioned in Section 5.6.

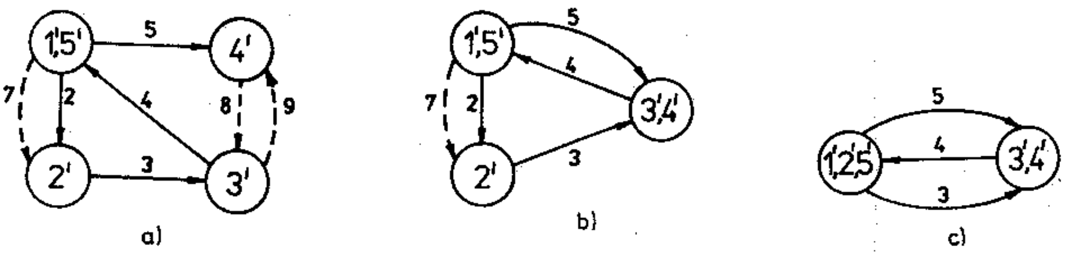


Fig.5.3 — Reduction of a graph when looking for redundant measurements

In most cases the above procedures enable the task of variables classification to be solved without major problems. Yet, there may be a reservation as regards this approach. Practical experience shows that the results of classification should not be overvalued. It often happens that the precision of a quantity, which is observable in theory, is so poor (its standard deviation is so high) that it is nonobservable in practical terms. Similarly, a measured quantity may be redundant in theory, but not so in practice (low adjustability resulting in bad precision if calculated). It is, therefore, useful to look at the problem of variables classification from a practical point of view.

Let us introduce the following terms: *Nonobservable in practice* is such a quantity, whose standard deviation is greater than the value predetermined for that quantity. Note that this term covers both estimates of directly measured and unmeasured quantities.

A quantity is *redundant in practice* when the adjustability is greater than the set value A:

$$a = 1 - \sigma_{\hat{x}} / \sigma_{x^+} > A$$

A being from the interval $\langle 0,1 \rangle$.

The following procedure proved to be applicable when classifying variables in practice. All the quantities are considered to be measured directly. The data are processed using the method described in Section 4.4.1 [where we are interested particularly in the relation (4.23) for the covariance matrix of reconciled values $\mathbf{F}_{\hat{x}}$]. The standard deviations of reconciled values (roots of the diagonal elements of the matrix $\mathbf{F}_{\hat{x}}$) are sufficient for the classification of variables in practice. There remains one problem, however, of what should be substituted into Eq.(4.23) for the variances of unmeasured values.

In virtually all cases we are capable of assessing the interval within which the value of an unmeasured quantity must occur. So, for instance, a number of quantities in plants are measured only by instruments with low precision, such as local thermometers, manometers. In most cases we do not take these readings into consideration when processing the data since we regard them as not precise enough; they can, however, serve as a rough specification of the range within which the respective quantity will lie. Another time the interval is given by the physical meaning of the measured quantity - for example the concentration fraction must lie within the interval $\langle 0,1 \rangle$. The flow rate of gas in a pipeline is limited by reaching the speed of sound, or by the capacity of pumps. Pressure limit is given by adjusted values on safety valves, and the like.

By an unmeasured quantity we may understand a random variable acquiring values from the interval $\langle a , b \rangle$, and whose value can be written in the form $(a + b) / 2 \pm (b - a) / 2$. If the distribution of this variable were uniform, it would hold for the standard deviation $\sigma = (b - a) / (2 \sqrt{3})$. To avoid possible mistakes it may be recommended to choose the value of σ somewhat higher, equal to a half of the interval width, that is

$$\sigma = (b - a) / 2$$

From the practical standpoint, the above method enables the problem of classification to be solved in a simple way. This method has a sound statistical basis because the introduction of intervals for unmeasured quantities is common in so-called Bayesian approach (Beck & Arnold 1977) as the introduction of prior information. However, it should not be used for strongly nonlinear models.

Example 5.3: *Classification of variables in a single-component balance*
Reconciliation of a single-component balance in the case in which all the streams were measured was discussed in Example 4.4. Let us now assume that the streams 3, 10, and 11 have not been measured (the respective diagram is in Fig.5.4a). The task is to classify , both theoretically and practically, the quantities with respect to their observabilty and redundancy.

It can be seen from Fig.5.4a that the unmeasured streams form a single circuit (for example from node 4' we can come back through nodes 1' and 3' by streams 10, 3, and 11). The flow rates of these three streams are, therefore, nonobservable. Now, we shall gradually merge the nodes 1', 3', and 4'. The resulting graph is in Fig.5.4b. The streams 2, 4, 5, and 12 are redundant. The other streams, eliminated in the course of nodes merging (1, 6, 7, 8, and 9), are nonredundant.

Now let us do the classification from a practical point of view. First we shall specify the intervals, within which the unmeasured quantities must occur. The stream 3 flow rate must lie within the interval $\langle 0;4\,000 \rangle$ m^3 ; the upper limit is given by the maximum capacity of the pump. The interval for the flow rate of stream 10, which has to be within the interval $\langle 0;1000 \rangle$ m^3 , is assessed analogically. The stream 11 represents accumulation in a storage tank whose volume is 100 m^3 . Hence, accumulation has to be within the interval $\langle 0;100 \rangle$ m^3 .

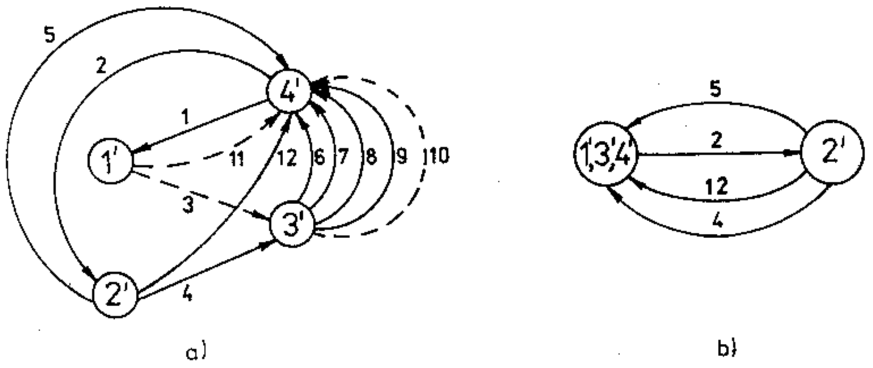


Fig.5.4 — Graph of a balance schema (Example 5.3)
a) original graph; b) reduced graph

Quantities, whose relative standard deviation exceeds 3% of the reconciled value (i.e. $\sigma_{\hat{x}} / \hat{x} > 0.03$), will be considered practically nonobservable. Those quantities, where reconciliation resulted in a decrease in the standard deviation by less then 10% of its original value (i.e. $\sigma_{\hat{x}} / \sigma_{x^+} > 0.9$ or the adjustability $a < 0.1$) will be considered practically nonredundant.

Table 5.2 — Input data and results of Example 5.3

i	x_i^+	$\sigma_{x_i^+}$	$\hat{x}_i$	$\sigma_{\hat{x}_i}$	a_i	$\sigma_{\hat{x}_i} / x_i$
1	3.85E+3	1.92E+1	3.85E+3	1.92E+1	0.001	0.0049
2	1.85E+3	9.24E+0	1.83E+3	6.04E+0	0.347	0.0032
3	2.00E+3	2.00E+3	3.79E+3	5.33E+1	0.974	0.0140
4	1.36E+3	6.81E+0	1.37E+3	5.65E+0	0.171	0.0041
5	3.59E+2	3.59E+0	3.61E+2	3.43E+0	0.045	0.0094
6	1.02E+3	5.11E+0	1.02E+3	5.11E+0	0.001	0.0049
7	1.02E+3	5.10E+0	1.02E+3	5.10E+0	0.001	0.0049
8	1.03E+3	5.17E+0	1.03E+3	5.16E+0	0.001	0.0049
9	1.05E+3	5.24E+0	1.05E+3	5.24E+0	0.001	0.0049
10	6.00E+2	6.00E+2	1.04E+3	5.46E+1	0.909	0.0524
11	5.00E+2	2.10E+1	5.42E+1	4.98E+1	0.004	0.9194
12	1.01E+2	2.10E+0	1.02E+2	2.07E+0	0.015	0.0203

The results of data processing are presented in Table 5.2. The measured values and their standard deviations are given in the first part of the Table (in the cases of unmeasured quantities the centres of the presented intervals are considered to substitute measured values). In the right-hand part of the Table there are the results of the reconciliation, in particular the ratio $\sigma_{\hat{x}} / \hat{x}$ and the adjustability a, which decide, whether a quantity is observable and redundant. It follows from the results that the flow rates of the streams 10 and 11 are practically unobservable, while only the flow rates of streams 2 and 4 are practically redundant.

The classification gives markedly different results, depending on whether it is done from the theoretical or practical point of view. The set of practically redundant quantities has a smaller number of elements than the set of quantities redundant theoretically; as we have already mentioned, the redundancy, particularly with quantities measured with high precision, often is negligible.

Somewhat surprising is the finding that the flow rate of the stream 3, theoretically unobservable, is classified as practically observable. This can be explained as that the accumulation (stream 11) is so small when compared with the other streams, that it can be neglected without any significant consequence.■

5.4.2 Comparison of all possible variants

As mentioned earlier, measurement of required quantities can be effected by various methods. A possible way of finding the optimum solution is the comparison of all the possibilities available. Let us evaluate this task using a single-component balance.

Let us have a closed connected graph representing the flow rates among individual nodes. The task is to find all the possible variants of choosing directly measured quantities, enabling full observability of unmeasured quantities (a directly solvable system of equations for the values of unmeasured quantities is formed).

In the preceding Subsection an assertion was presented that the necessary and sufficient condition for the observability of all the streams is that the unmeasured streams must not form a circuit. In addition, the number of directly measured streams, on condition that all the flow rates are observable, must be minimal (if it were not so, there would be more directly measured quantities than necessary, which means redundant measurements). Hence a subgraph of unmeasured streams must contain as many edges as possible, these, however, must not form a circuit. It was shown in Appendix 5 that each spanning tree of the graph posssesses such a property.

The task of finding all the possible choices of directly measured quantities is thus identical with finding all the spanning trees of the respective graph. There exist several algorithms and computer codes for solving this problem on a computer. An advantage of most of these algorithms is that they are capable of finding all these spanning trees without repeating (no solution has to be examined twice). Searching for all the graphs spanning trees exceeds the scope of this book by its complexity and the reader is therefore referred to literature (Chen 1971). For illustrative purposes a simple graph with all its spanning trees is shown in Fig.5.5. In the case that the graph

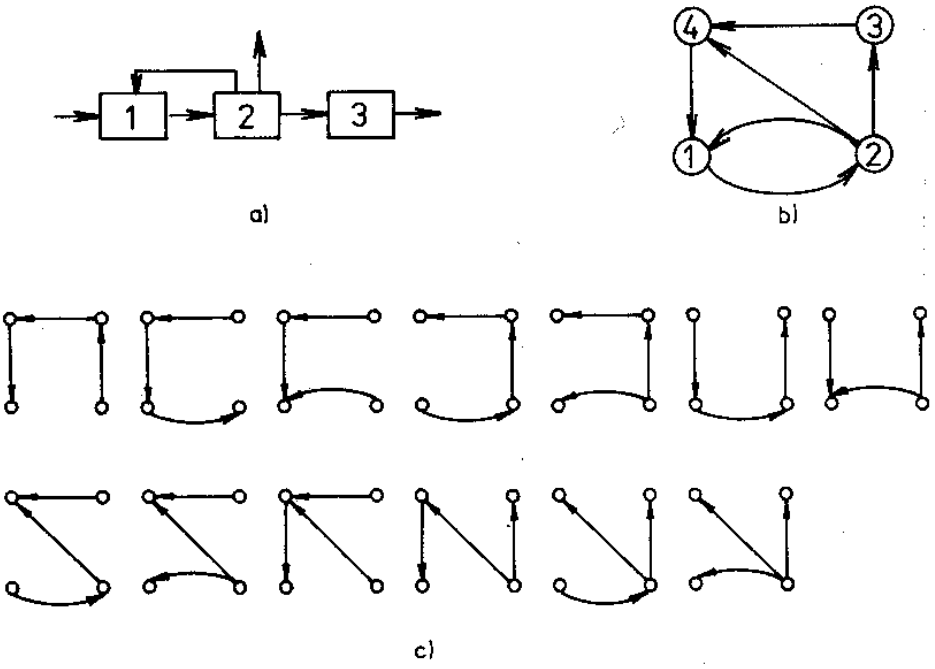


Fig.5.5 — Selection of unmeasured streams
a) flowsheet; b) graph; c) all spanning trees

represents a scheme for a mass balance, the spanning trees represent all the possible variants of the choice of unmeasured quantities.

The problem can be solved analogically when selecting directly measured quantities in a general linear model that can be written

$$\boldsymbol{C}\,\boldsymbol{p}+\boldsymbol{a}=\boldsymbol{0} \tag{5.10}$$

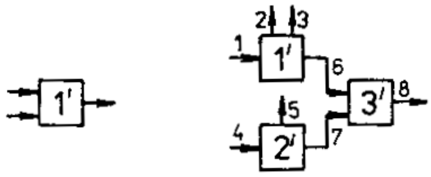
where $\boldsymbol{C}$ is a matrix of coefficients whose dimension is $m \times n$ ($n > m$), $\boldsymbol{a}$ is a vector of constants and $\boldsymbol{p}$ is a vector of unknown quantities present in the problem. The task is to divide the vector $\boldsymbol{p}$ into to two subvectors, one of measured and the other of unmeasured quantities. Eq.(5.10) can be now rewritten in the form of Eq.(4.1). In order that we may calculate the unmeasured quantities according to Eq.(4.12), the matrix of coefficients of the unmeasured quantities must obviously be regular. Hence the problem of finding out all possible variants of the selection of directly measured quantities can be formulated as a problem of finding all the possible regular square matrices of dimension $m \times m$ from a given rectangular matrix of dimension $m \times n$. Also this task can be programmed on a computer, those interested are referred to literature (Chen 1971).

In principle the method of comparing all the possible variants is viable; its drawback, however, is that quite often there are a great number of variants that have to be compared.

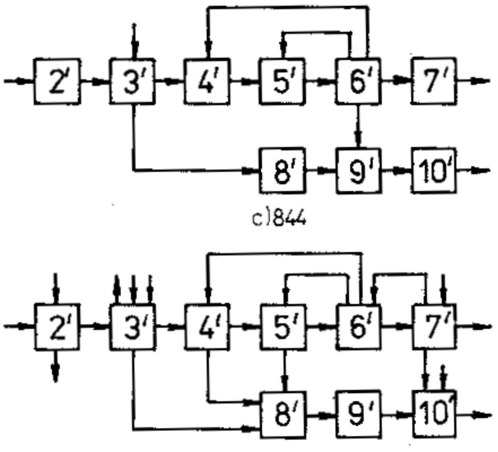
Example 5.4: *Number of variants in the selection of directly measured quantities in a mass balance*

In the textbooks of the theory of graphs the following lemma is frequently presented:

Let $\mathbf{L} = \mathbf{A}\,\mathbf{A}^{\mathrm{T}}$, *where* $\mathbf{A}$ *is a reduced incidence matrix of an oriented graph. The number of different spanning trees of this graph equals the matrix* $\mathbf{L}$ *determinant.*



a) 3 spanning trees b) 29



c) 844

d) 100 862

Fig.5.6 — Flowsheets to Example 5.4

The calculation of the number of graph spanning trees is demonstrated as an example for the graph in Fig.5.6b. The node 4' (environment), which is not shown in Fig.5.6b., is considered the reference node, and the reduced incidence matrix is

$$\mathbf{A} = \begin{bmatrix} 1 & -1 & -1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & -1 \end{bmatrix}$$

and the matrix $\mathbf{L}$

$$\boldsymbol{L} = \begin{bmatrix} 4 & 0 & -1 \\ 0 & 3 & -1 \\ -1 & -1 & 3 \end{bmatrix}$$

Let us note that the matrix $\boldsymbol{L}$ can be built simply even without matrix multiplication. On its diagonal there is the number of edges connected with the given node, elements lying outside the diagonal L_{ij} are equal to the number (with minus sign) of edges connecting the *i*th and *j*th nodes.

In our case the determinant of the matrix L equals 29; this means that there exist 29 different spanning trees in the given graph. In a mass balance according to scheme in Fig.5.6b there exist 29 different variants of selecting the directly measured quantities in such a way that the unmeasured quantities could be assessed explicitly by solving the balance equations. Presented in Fig.5.6 are four graphs of increasing complexity, together with the number of different spanning trees. It can be seen that the number of spanning trees grows steeply with increasing complexity of the graphs. A comparison of all the variants is real only for the first three cases. The fourth case is already at the limit of possibility even if a high-speed computer is available. In Section 6.3 the single-component balance of a chemical plant is examined (17 nodes, 49 streams); the number of the graph spanning trees is 7.76×10^9. Obviously, such a case can no more be coped with by the method of comparison of all the variants.■

The conclusion similar to that arrived at in the preceding example holds also for the case of the general linear model (5.10). Optimal selection of measured quantities in real cases requires some optimization procedure. For the case of single-component balance such procedure will be presented in Section 6.3.

5.4.3 Improving the measurement precision

It follows from the examples presented so far that the problems of optimum choice of directly measured quantities are rather complex. It is, therefore, advisable to confine oneself, in practical terms, to selecting one or a few acceptable variants, and to their improvement when time allows.

A suitable basis for this is usually the practical classification of the quantities from the viewpoint of their observability as described in Subsection 5.4.1. We can see from the data concerning the precision of individual quantities, in which cases the requisite precision was achieved using the existing method of measurement, and which quantities have to be measured more precisely. There are two most common ways of improving the precision of measurement - perfection of the existing measurement or installation of new measurements. The boundary between these two methods need not be sharp. In the course of perfecting an existing measuring instrument a qualitatively new measurement may be created.

The question usually arises, upon which of the directly measured quantities should we concentrate our attention? The methods of errors propagation enable the precision of results to be expressed by means of the standard deviations of directly measured quantities. To solve this problem in an efficient and systematic way, so-called matrices of shares have been introduced in Chapters 3 and 4.

It is obvious that if we are able to formulate in a certain way the objective function characterizing overall precision of the measurement (for example the sum of variances of requisite quantities), we can readily select those directly measured quantities that affect the precision of results most significantly.

It follows from the considerations presented that the search for a good solution of practical problems proceeds in two phases. In the first place the *first variant* of the choice of directly measured quantities is to be found. Such first variant still need not meet all the requirements put on the measurement but we endeavour to make it as good as possible (so-called *suboptimal solution*). In the second phase the initial variant is further improved. It is difficult to give any general directions as to how to proceed since the methods may vary in accordance with a number of circumstances (problem formulation, information about measuring errors, etc.). The whole range of these problems will be illustrated in detail in Section 6.3 by an example of optimal choice of measuring points when balancing a chemical plant.

5.5 FURTHER PROBLEMS OF MEASUREMENT PLANNING

As may be seen from the problems discussed so far, the difficulty in finding out the optimum plan of measurement grows with the level at which the measurement is planned and prepared. Whereas until now we have been capable of at least approximate mathematical formulation of the problem, when a global conception of measurement is looked for, even this very first step brings about considerable difficulties. At the same time, a proper orientation of the whole research is of key importance as regards the obtaining of results applicable in practice. It seems that the leading role in looking for a good (when not just the optimal) strategy of measurement belongs to the experience of those solving the problem, to a certain kind of intuition acquired when dealing with previous problems. Further we shall present the fundamental questions that have to be answered when solving the most frequent tasks in plant measurement.

When looking for optimum process regimes:

- selecting the optimization variables,
- region within which the optimization variables can be varied,
- approach to optimization (relation between empirical methods and mathematical modelling),
- the applied method of optimization (plan of factor experiments).

Building of mathematical models:
- choosing the mathematical model type (empirical models or models based on laws of nature),
- depth of mathematical description (microscopic or macroscopic models);
- methods of assessing the parameters of mathematical models (the share of published data, laboratory and plant measurements).

When increasing plant capacity (debottlenecking):
- choice of throughputs at which the measurement will be effected,
- scope of checking chemical engineering calculations,
- way of solving special problems (wear of equipment due to higher production rate, safety of work, etc.).

The above enumeration demonstrates the complexity and variety of questions forming the global strategy of measurement. A more or less qualified answer can be given to a number of them on the basis of experience from the previous plant operation (e.g. admissible ranges of process variables). Another times also the knowledge and methods of the theory of measurement may be applied. As an example in this respect it is possible to give the Section 6.2, where a rational approach to assessing the specific consumptions of raw materials and energy in a complex plant is described.

5.6 RECOMMENDED LITERATURE TO CHAPTER 5

The problems discussed in this Chapter belong to the area of *optimization of experiments*. The problems of experiments optimization are dealt with by the mathematically oriented monograph (Bandemer et al. 1977). Out of publications focused upon experiments in industrial processes it is possible to recommend the book by Himmelblau (1970) compiling a number of methods and examples hitherto published mostly by periodicals. Optimization of chemical analyses can be studied in the book by Doerffel & Eckschlager (1981).

Somewhat beyond problems dealt with by standard literature on experiments optimization is the problem of optimum choice of measured variables. This area, especially in connection with the classification of variables, is mentioned in Section 4.6.

6 Case studies

The following chapter contains four more extensive examples to document the application of the hitherto presented approaches and methods. Although it is not possible to go into great detail because of the scope and complexity of these cases, we will see solutions of actual tasks as commonly encountered when carrying out measurements in chemical plants.

6.1 MATERIAL BALANCE OF SYNTHESIS GASES PRODUCTION

The task is to set up a consistent (reconciled) material balance of the production of hydrogen and synthesis gases on the basis of measured data.

6.1.1 Process description

Hydrogen and the synthesis gases are produced by the gasification of residual oil and by further processing of the resulting gas (Fig.6.1).

Residual oil (stream no.1) is gasified by partial oxidation in a mixture with oxygen (2) and steam (3) in the subsystem 1'. Carbon particles and hydrogen sulphide are separated from the resulting gas. Four exit streams are in the subsystem 1': furnace black (4), excess water (5), hydrogen sulphide gas (6) and so-called desulphurized gas (7) which is further branched (streams No. 8, 9, 10).

The desulphurized gas (8) is fed into subsystem 2' where the shift conversion of CO proceeds according to

$$CO + H_2O - CO_2 - H_2 = 0 \tag{6.1}$$

and most of the carbon dioxide is separated by triethanolamine absorption. Leaving the subsystem 2' are CO_2 (11) and processed gas - so-called raw hydrogen (12) which is split into two streams (13) and (14).

CO and CO_2 are removed from the stream (13) by methanation in subsystem 4'

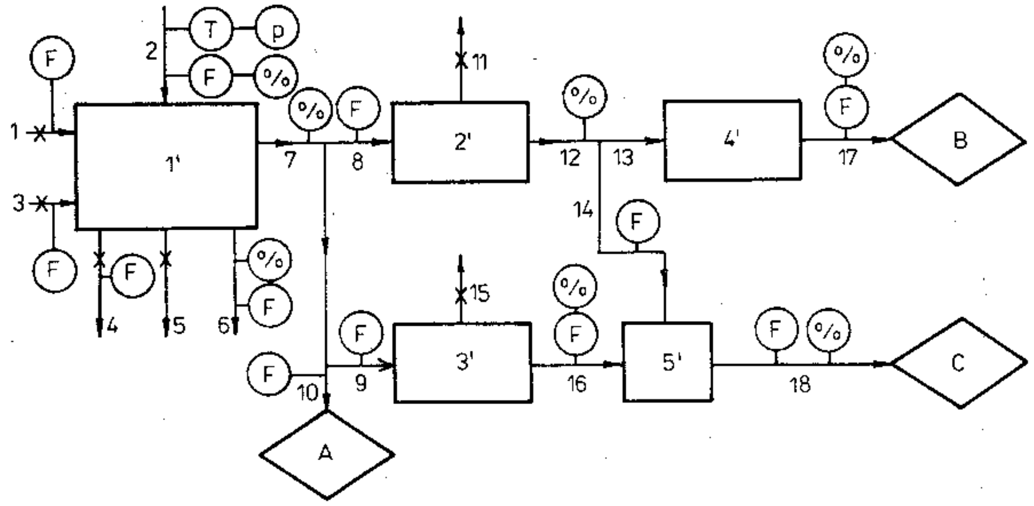


Fig.6.1 — Measurement of hydrogen and synthesis gases production
Nodes (subsystems): 1' - gasification and desulphurization, 2' - CO conversion and CO_2 washing, 3' - CO_2 washing, 4' - methanation, 5' - mixing;
Streams: 1 - residual oil, 2 - oxygen, 3 - steam, 4 - furnace black, 5 - water, 6 - hydrogen sulphide gas, 7, 8, 9, 10 - desulphurized gas, 11, 15 - CO, 12, 13, 14 - raw hydrogen, 16 - washed gas, 17 - pure hydrogen, 18 - synthesis gas;
Measurement: F - flowmeter, % - analysis, T - thermometer, p - manometer, * - stream with exactly known composition

$$CO + 3\,H_2 - CH_4 - H_2O = 0 \tag{6.2}$$

$$CO_2 + 4\,H_2 - CH_4 - 2\,H_2O = 0 \tag{6.3}$$

One of the products is so-called pure hydrogen (17) suitable for the production of ammonia.

Carbon dioxide is removed from the desulphurized gas (9) by scrubbing in subsystem 3'. CO_2 is vented to atmosphere (15) while the so-called washed gas (16) is combined with raw hydrogen (14) in a mixer 5'. Synthesis gas thus obtained (18) is fed into a methanol plant.

6.1.2 Measured and required quantities

The disposition of the available measuring instruments is shown in Fig.6.1. The flowmeters, with the exception of that designed for measuring the stream (2), are equipped with an automatic correction for temperature, pressure and density under standard conditions, so that the volume flow rate of the gas is given as at 0 °C and 101.3 kPa.

The required quantities are all the measured ones, and, in addition to these, the unmeasured flows of the streams (5) and (13).

6.1.3 Mathematical model

The mathematical model will be formed by a set of balance equations. A few pieces of information are needed before we proceed to the construction of such a model.

Table 6.1 contains data on the substances present in the individual streams. The manufacturing process takes place at a high pressure and the content of water vapour in the gas streams may be neglected. Several unmeasured streams of water (serving primarily as a direct exchange of heat) not shown in Fig. 6.1 are connected with the individual subsystems. The flow rates of these streams are not measured, but as will be shown later, these are not essential for assessing the required quantities.

Table 6.1 — The occurrence of substances in streams (+ substance is present, - absent, ++ the concentration is complement to 100%; S - streams 7, 8, 9, 10, 12, 13, 14, 16, 18)

Substance	Stream							
	1	2	3,5	4	6	S	11,15	17
residual oil	+	-	-	-	-	-	-	-
water	-	-	+	-	-	-	-	-
carbon black	-	-	-	+	-	-	-	-
CO	-	-	-	-	-	+	-	-
CO_2	-	-	-	-	++	+	+	-
CH_4	-	-	-	-	-	+	-	+
H_2	-	-	-	-	-	++	-	++
N_2	-	++	-	-	-	+	-	+
H_2S	-	-	-	-	+	-	-	-
O_2	-	+	-	-	-	-	-	-

The gases are analyzed and their composition is given in volume fractions; the fraction of one of the components is always obtained as the difference between unity and the sum of the remaining fractions. Hence that concentration is not a directly measured quantity and the calculated difference from 1 is used instead of it in the mathematical model (see Tab. 6.1).

Residual oil is a complex raw material, but it will be considered a chemical individuum. Its elementary composition (C-84.92, H-10.90, S-2.92, N-0.56 and O-0.70 % by mass) will be considered free of error. It will be assumed further that the values of fuel oil density as well as of the molecular and atomic weights and densities of gases under standard conditions are virtually free of errors.

Next, let us introduce the following notation:

$w_{1,A}$	mass fraction of element A in residual oil
$\varphi_{i,A}$	volume fraction of substance A in the *i*th stream
M_A	molar mass of element or substance A (kg kmol^{-1})
v_A	volume of 1 kmole of substance A under standard conditions (0 °C, 101.3 kPa)
V_i	with gaseous streams - flow rate at standard conditions; with residual oil - volume flow rate at density 915 kg m^{-3} (m^3 h^{-1})
ρ_i	*i*th stream density (kg m^{-3})
m_i	*i*th stream mass flow rate (kg h^{-1})

For the sake of clarity, when constructing the mathematical model, the measured quantities will be denoted by the superscript ', the unmeasured ones by an asterisk * and the exactly known values (constants) will be without designation.

Node 1' Balance

The mechanism of partial oxidation of residual oil is not known exactly. Hence the balance will be written on the basis of conservation of chemical elements.

Balance of carbon:

$$V'_1\, \rho_1\, w_{1,C} / M_C - m'_4 / M_C - (V'_8 + V'_9 + V'_{10})\, (\varphi'_{7,CO_2} / v_{CO_2} + \varphi'_{7,CO} / v_{CO} +$$

$$+ \varphi'_{7,CH_4} / v_{CH_4}) - V'_6\, (1 - \varphi'_{6,H_2S}) / v_{CO_2} = 0 \tag{6.4}$$

Balance of hydrogen:

$$V'_1\, \rho_1\, w_{1,H} / M_H + 2(m'_3 - m^*_5) / M_{H_2O} - 2V'_6\, \varphi'_{6,H_2S} / v_{H_2S} -$$

$$- (V'_8 + V'_9 + V'_{10})\, (4\varphi'_{7,CH_4} / v_{CH_4} + 2\varphi'_{7,H_2} / v_{H_2}) = 0 \tag{6.5}$$

Balance of nitrogen:

$$V'_1\, \rho_1\, w_{1,N} / M_N + 2(1 - \varphi'_{2,O_2})\, V'_2 / v_{N_2} -$$

$$- (V'_8 + V'_9 + V'_{10})\, \varphi_{7,N_2}' / v_{N_2} = 0 \tag{6.6}$$

Balance of sulphur:

$$V'_1 \rho_1 w_{1,S} / M_S - V'_6 \varphi_{6,H_2S} / \nu_{H_2S} = 0 \tag{6.7}$$

Balance of oxygen:

$$V'_1 \rho_1 w_{1,O} / M_O + (m'_3 - m^*_5) / M_{H_2O} + 2V^*_2 \varphi'_{2,O_2} / \nu_{O_2} - (V'_8 + V'_9 + V'_{10})$$
$$(\varphi'_{7,CO} / \nu_{CO} + 2\varphi'_{7,CO_2} / \nu_{CO_2}) - 2V^*_6 (1 - \varphi'_{6,H_2S}) / \nu_{CO_2} = 0 \tag{6.8}$$

Further, it is necessary to introduce a correction to the stream (2) flow rate with respect to the temperature, pressure and density of the gas at standard conditions. In Eq. (6.8) the stream (2) flow rate appears as an unmeasured quantity. It can be expressed from measured quantities with the aid of the correction (3.86)

$$V^*_2 = V'_2 \left[\frac{\rho_{n,proj}}{\rho'_n T'_2} \quad \frac{T_{proj}\, p'_2}{p_{proj}} \right]^{1/2} \tag{6.9}$$

In this case, ρ'_n is not measured directly but it can be expressed from a direct measurement of the gas composition and tabulated values of the gases density under standard conditions

$$\rho'_n = \varphi'_{2,O_2} \rho_{n,O_2} + (1 - \varphi'_{2,O_2}) \rho_{n,N_2} \tag{6.10}$$

where ρ_{n,O_2} and ρ_{n,N_2} are the densities of oxygen and nitrogen under standard conditions.

Node 2' Balance

In node 2' the chemical reaction (6.1) takes place. Since the stoichiometry of the chemical conversion is known, the increments and decrements of the substances may be expressed by means of the rate r_1 of this reaction. The balance is written for the flows of the individual substances (kmole h^{-1}).

Balance of CO_2 :

$$[V'_8 \varphi'_{7,CO_2} - V^*_{11} - (V^*_{13} + V'_{14}) \varphi'_{12,CO_2}] / \nu_{CO_2} + r^*_1 = 0 \tag{6.11}$$

Balance of CO:

$$[V'_8 \varphi'_{7,CO} - (V^*_{13} + V'_{14}) \varphi'_{12,CO}] / \nu_{CO} - r^*_1 = 0 \tag{6.12}$$

Balance of CH_4 :

$$[V'_8 \varphi'_{7,CH_4} - (V^*_{13} + V'_{14}) \varphi'_{12,CH_4}] / \nu_{CH_4} = 0 \tag{6.13}$$

Balance of N_2 :

$$[V'_8 \varphi'_{7,N_2} - (V^*_{13} + V'_{14}) \varphi'_{12,N_2}] / \nu_{N_2} = 0 \tag{6.14}$$

Balance of H_2 :

$$[V'_8\,\varphi'_{7,H_2} - (V^*_{13} + V'_{14})\,\varphi'_{12,H_2}]\,/\,\nu_2 + r^*_1 = 0 \tag{6.15}$$

Node 3' Balance

No chemical reactions are present in this node and hence the form of the balance equations is simple.

Balance of CO_2 :

$$V'_9\,\varphi'_{7,CO_2} - V'_{16}\,\varphi'_{16,CO_2} - V^*_{15} = 0 \tag{6.16}$$

Balance of CO:

$$V'_9\,\varphi'_{7,CO} - V'_{16}\,\varphi'_{16,CO} = 0 \tag{6.17}$$

and analogically for CH_4 , N_2 and H_2 .

Node 4' Balance

Here two reactions proceed with stoichiometric equations (6.2) and (6.3). The respective changes in the number of moles are expressed with the aid of the rates of the individual reactions r_2 and r_3 .

Balance of CO_2 :

$$V^*_{13}\,\varphi'_{12,CO_2}\,/\,\nu_{CO_2} - r^*_3 = 0 \tag{6.18}$$

Balance of CO:

$$V^*_{13}\,\varphi'_{12,CO}\,/\,\nu_{CO} - r^*_2 = 0 \tag{6.19}$$

Balance of CH_4 :

$$(V^*_{13}\,\varphi'_{13,CH_4} - V'_{17}\,\varphi'_{17,CH_4})\,/\,\nu_{CH_4} + r^*_2 + r^*_3 = 0 \tag{6.20}$$

Balance of N_2 :

$$V^*_{13}\,\varphi'_{13,N_2} - V'_{17}\,\varphi'_{17,N_2} = 0 \tag{6.21}$$

Balance of H_2 :

$$(V^*_{13}\,\varphi'_{13,H_2} - V'_{17}\,\varphi'_{17,H_2})\,/\,\nu_{H_2} - 3r^*_2 - 4r^*_3 = 0 \tag{6.22}$$

Node 5' Balance

The forms of the balance equations are identical for all the substances involved. When any of the substances is denoted as A, then the balance equations for all the five substances assume the following form:

$$V'_{16}\,\varphi'_{16,A} + V'_{14}\,\varphi'_{14,A} - V'_{18}\,\varphi'_{18,A} = 0 \tag{6.23}$$

The set of equations (6.4) through (6.23) together with further equations mentioned above represents 26 equation among 34 measured and 8 non-measured quantities. Out of unmeasured quantities (F^*_5, V^*_2, V^*_{13}, V^*_{11}, V^*_{15}, r^*_1, r^*_2, r^*_3), only the first three are required. The dimension of the problem is reduced by eliminating those unmeasured quantities that are not required (e.g. r^*_1 is expressed from Eq. (6.11), and substituted to Eqs (6.12) and (6.15)). Thus, the final set of 21 equations among 34 measured and 3 unmeasured quantities is obtained. This mathematical model will be used hereinafter for the treatment of the measured data.

6.1.4 Measurement errors

Now let us concentrate on the creation of a model of errors of the measurements of the gas streams flow rates and concentrations which occur most frequently in our case. A similar line would be followed when estimating the errors of the other measured quantities.

Measuring of gaseous streams flow rates

In the case under study, we meet with both measuring equipment with automatic correction for gas temperature, pressure and density at standard conditions, and equipment without such a correction.

A block diagram for measuring the flow rate without correction is shown in Fig. 6.2. The diagram represents a certain transformation of the orifice pressure difference. This is transformed into a unified signal in the pressure difference transmitter V and the value of the signal is square-rooted in the next element O. The output signal is then registered by the instrument R. The block diagram presents also multiplication N of the square-rooted signal by a proportionality factor K (whose value depends primarily on the design of the orifice and is a source of certain error). Hence the

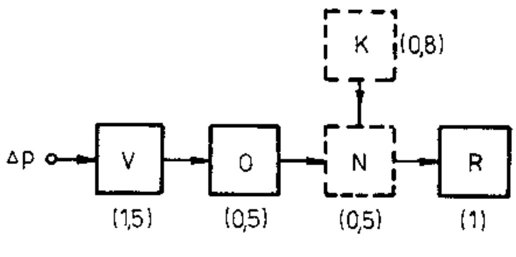


Fig.6.2 — Block diagram of flow measurement without correction

blocks N and K are shown here only for respecting the errors of the orifice proper and of the measuring system adjustment. The parenthesized numbers in Fig.6.2 indicate the maximum relative errors (classes of accuracy) of the individual blocks.

The maximum error of the given measuring system is estimated on the assumption of a random character of the primary errors.

When gain of the individual members of the measuring chain in Fig.6.2 is denoted A with the corresponding indices, the final reading on the registering instrument x_C may be approximated by

$$x_C = (A_C \, \Delta p)^{1/2} A_O \, A_N \, A_K \, A_R \tag{6.24}$$

In so doing we may assume that the errors are contained in the gains of the individual members (i.e. A_V , A_O , A_N , A_K and A_R). The total errors in the registering instrument reading can be estimated using the method of random errors propagation. The term on the right-hand side of Eq.(6.24) represents a product of powers of quantities subjected to errors and the relative standard deviation of the registering instrument reading γ_C can be expressed by the relation (see Table 3.1)

$$\gamma_C = \left[\frac{\gamma_V^2}{4} + \gamma_O^2 + \gamma_N^2 + \gamma_K^2 + \gamma_R^2 \right]^{1/2} \tag{6.25a}$$

It is also possible to substitute into Eq.(6.25a) maximum relative errors instead of the relative standard deviations whereby an estimate of the maximum relative error in the final result e_C is obtained

$$e_C = (1.5^2 / 4 + 0.5^2 + 0.5^2 + 0.8^2 + 1^2)^{1/2} = 1.6\% \tag{6.25b}$$

Thus the maximum error of the whole measuring system has been estimated at 1.6% of the measuring range (class of accuracy 1.6%). It has to be pointed out that this is a case of an error in a non-corrected value; additional errors are introduced by corrections for temperature, pressure and density of the gas. These errors, however, are respected automatically in the mathematical model, see Eq.(6.9).

It has to be considered further that the maximum relative error as given by Eq. (6.25b) holds only for the upper limit of the measuring range. The measured value actually fluctuates around 80 % of the measuring range, and hence, the maximum relative error is increased in the proportion of 100/80. The maximum relative error of the flow rate measurement is thus roughly 2% of the measured value.

A block diagram of gas flow rate measuring with correction for temperature, pressure and density of the gas at standard conditions is shown in Fig. 6.3. Calculation of the maximum errors of this measuring system is rather complex and will not be presented here. Those interested in this problem are referred to the paper

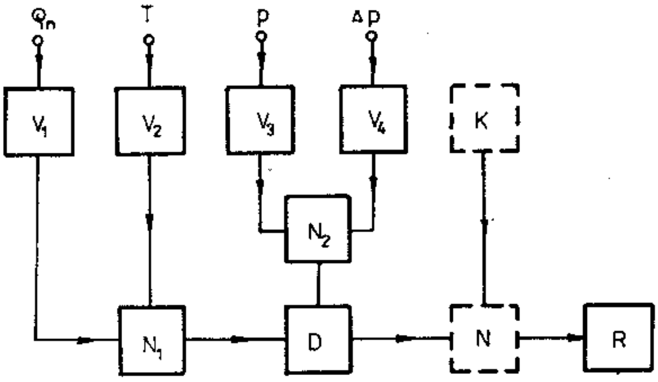


Fig.6.3 — Block diagram of flow measurement with corrections for temperature, pressure and density under standard conditions

by Toman (1971) where the design of a given measuring system is discussed in detail inclusive of the measuring errors. In this paper the maximum measuring error is estimated at 2% of the measured value within the 50 - 100 % range of the maximum flow rate.

Analyses of gaseous streams

Most of the gas streams (all with the exception of streams (2) and (6) that were analyzed by traditional analytical methods) were analyzed by gas chromatography. To estimate errors in the determined concentrations the following two runs of measurements were designed.

Altogether, three sets of five samples were taken in the plant at a single sampling point. Each of the samples was analyzed separately. Sample standard deviation of the determination of individual concentrations was calculated according to Eq.(3.72) (measurement I).

A standard gas mixture whose composition was close to that of the gas streams in the plant was analyzed eight times by different analysts during several days. Sample standard deviation was calculated from the assessed data using Eq.(3.71) (measurement II). The results are presented in Table 6.2.

Whereas the measurement I implies the repeatability of an analytical procedure as conducted by a single analyst on an instrument and adjusted in a certain way (inclusive of the sampling proper), the measurement II takes into account the human factor as well as adjustment of the instrument (reproducibility). It follows from Table 6.2 that the influence of the latter two factors is markedly greater than the effects of factors involved in the measurement I. It may be seen further that the standard deviations depend on the absolute value of the measured concentration.

The relative standard deviations for individual ranges of the volume fractions as estimated on the basis of the results of measurement II are given in Table 6.3. The given values that will be used in the measured data processing are more pessimistic than optimistic. The mean values over the balancing period represent an average of nine values, while partial elimination of the measuring errors may take place.

Maximum errors and standard deviations of the other directly measured quantities were assessed analogically. In the case in which the maximum errors were known (i.e. measuring by instruments), standard deviations equal to 50% of the respective maximum error were ascribed to the measurements. The data relating to the accuracy of all the measurements and expressed as relative standard deviations are presented in the third columm of Table 6.4.

Table 6.2 — Sample standard deviations of volume fractions

Substance	CO_2	CO	CH_4	N_2
volume fraction	0.0380	0.4700	0.0022	0.0130
s_I	0.0004	0.005	0.0001	0.0003
s_{II}	0.0012	0.045	0.0001	0.0005

Table 6.3 — Estimates of relative standard deviations (γ) of gases analyses

Volume fraction	γ %
0.002 - 0.004	5
0.01 - 0.02	4
0.03 - 0.04	3
0.30 - 0.50	1

Table 6.4 — Input data and results to Section 6.1
(V - m^3 h^{-1}; F - kg h^{-1}; φ - vol.%)

x	x^+	γ_{x^+}	v/σ_v	$\hat{x}$	$\gamma_{\hat{x}}$	a
V_1	1.799E+1	0.005	-2.855	1.797E+1	0.0035	0.29
V_2	1.237E+4	0.010	-0.050	1.248E+4	0.0077	0.21
φ_{2,O_2}	9.660E+1	0.005	-2.357	9.551E+1	0.0010	0.80
F_3	8.670E+3	0.020	-0.000	8.670E+3	0.0200	0.00
V_8	4.045E+4	0.010	-2.162	4.012E+4	0.0053	0.47
V_9	8.760E+3	0.010	-0.873	8.713E+3	0.0063	0.37
φ_{7,CO_2}	3.840E+0	0.030	-1.386	3.794E+0	0.0281	0.08
$\varphi_{7,CO}$	4.747E+1	0.010	-1.729	4.687E+1	0.0042	0.58
φ_{7,CH_4}	2.200E-1	0.050	0.217	2.223E-1	0.0246	0.50
φ_{7,N_2}	1.310E+0	0.040	-0.956	1.262E+0	0.0177	0.57
F_4	2.330E+2	0.050	-2.642	2.329E+2	0.0498	0.01
V_{10}	7.300E+2	0.010	-2.951	7.299E+2	0.0099	0.00
V_6	7.530E+2	0.010	9.447	7.526E+2	0.0099	0.00
φ_{6,H_2S}	3.900E+1	0.010	9.544	-	-	-
V_{14}	3.670E+3	0.010	-0.509	3.669E+3	0.0092	0.08
φ_{12,CO_2}	1.200E-1	0.050	1.240	1.213E-1	0.0487	0.01
$\varphi_{12,CO}$	3.400E-1	0.030	1.165	3.434E-1	0.0286	0.04
φ_{12,CH_4}	2.400E-1	0.050	-0.897	2.307E-1	0.0246	0.55
T_2	3.180E+2	0.003	0.050	3.179E+2	0.0029	0.01
φ_{16,CO_2}	6.200E-1	0.050	0.323	6.269E-1	0.0367	0.26
$\varphi_{16,CO}$	4.890E+1	0.010	-1.419	4.841E+1	0.0038	0.62
φ_{16,CH_4}	2.300E-1	0.050	-0.065	2.296E-1	0.0246	0.51
φ_{16,N_2}	1.290E+0	0.040	0.349	1.303E+0	0.0177	0.55
V_{16}	8.470E+3	0.010	-0.689	8.436E+3	0.0062	0.38
φ_{18,CO_2}	4.800E-1	0.050	-0.363	4.736E-1	0.0339	0.33
$\varphi_{18,CO}$	3.360E+1	0.010	0.467	3.384E+1	0.0047	0.52
φ_{18,CH_4}	2.200E-1	0.050	1.028	2.299E-1	0.0246	0.49
φ_{18,N_2}	1.350E+0	0.040	-0.857	1.306E+0	0.0177	0.57
V_{18}	1.200E+4	0.010	0.840	1.210E+4	0.0049	0.50
V_{17}	3.433E+4	0.010	-0.972	3.444E+4	0.0061	0.38
φ_{17,CH_4}	7.500E-1	0.050	-1.259	7.062E-1	0.0180	0.66
φ_{17,N_2}	1.350E+0	0.040	-0.350	1.330E+0	0.0177	0.56
p_2	4.020E+0	0.009	-0.050	4.034E+0	0.0086	0.04

6.1.5 Measured data processing

The measured values, mathematical model and model of errors represent a basis for solving the given problem. New knowledge obtained during statistical treatment of the measured data will be presented next. The measured values are shown in the second column of Table 6.4, being mean values obtained during a 72 hour balance measurement. Plant operation was fairly stable during that period and the influence of the process parameters fluctuation on the measured values may be neglected.

Gross errors detection

The mathematical model represents a set of 21 independent equations for 3 unknown quantities. Eighteen measured quantities are redundant and they may be used for evaluating the measured data from the viewpoint of possible occurrence of gross errors in the measurement (see Section 4.5).

During the first stage all the measured values were reconciled so as to fulfil exactly the equations of the mathematical model. Essentially this was a case of solving the problem of identifying a general quasi-linear model as described in Subsection 4.4.5. The value of Q_{min} as defined by Eq.(4.19) was then calculated from the adjustments. The obtained value of $Q_{min} = 108.7$ is the realization of a random quantity with χ^2 distribution and 18 degrees of freedom. The 95% quantile of distribution χ^2 (18) is 28.9. That is to say, that the probability of Q_{min} being larger than 28.9 is only 5%. It is, therefore, possible to reject, on the 5% significance level, the hypothesis that only random measuring errors are present.

When searching for a potential source of errors we first focused our attention on the analysis of adjustments as described in Subsection 4.5.2. Standardized adjustments of the individual quantities are presented in the fourth column of Table 6.4. It can be seen here that the magnitudes of adjustments of the quantities V_6 and φ_{6,H_2S} (flow rate and concentration of hydrogen sulphide in the stream No. 6) differ from those of the other standardized adjustments.

Both these measurements were verified. We found no discrepancies in the system of flow rate measuring. Hydrogen sulphide concentration is assessed by absorption into solution, and by subsequent analytical determination. This method was compared with the determination by gas chromatography. It was found that the results obtained by the former method were significantly lower than those obtained by the chromatographic method.

To verify the hypothesis that measuring of the hydrogen sulphide concentration in the stream No. 6 is the only source of gross errors, the method of a measured quantity elimination as described in Subsection 4.5.2 was applied. Hydrogen sulphide concentration was considered to be an unmeasured quantity and the data were reconciled once more (whereby the number of redundant data decreased to 17). The value of $Q_{min} = 16.5$ was calculated. In this case, Q_{min} has the distribution χ^2 (17), the 95% quantile of this distribution being 27.6. Since $16.5 < 27.6$, there is no reason to believe that there might be any other gross error present.

Final results of measured data processing

The results are summarized in the respective segments of Tables 6.4 (measured quantities) and 6.5 (unmeasured quantities). Reconciled values of directly measured quantities are presented in the 5th column of Table 6.4. Relative standard deviations (standard deviations/reconciled values) are in the 6th column. The last column of Table 6.4 gives the adjustability of directly measured quantities. As the result of reconciliation, the standard deviation dropped below 50% of the original value in the case of 13 quantities (i.e. 39% of their total number) and below 80% of the original value in the case of 23 (i.e. 70%) quantities. One quantity (F_3), however, was nonadjustable. On the average, the reconciliation resulted in a decrease to 65% of the original value of the standard deviations.

The values of quantities not measured directly and their relative standard deviations (coefficients of variance) are presented in Table 6.5. The calculations were effected on a programmable calculator Wang 2200 with the aid of the universal computer code. The input data were the measured values, their standard deviations and the set of equations of the mathematical model.

Table 6.5 — Estimates of unmeasured quantities

y	$\hat{y}$	$\gamma_{\hat{y}}$ %
F_5	5 298	4.1
V_{13}	34 971	0.6
$(V_2)_{cor}$	12 282	0.8
φ_{6,H_2S}	44.66	1.1

The reconciled values are presented in Table 6.6 corresponding with the flowsheet in Fig.6.1. The complete set of flow rates and concentrations of the streams under study represent the solution of the given problem.

Table 6.6 — Reconciled values of flows and concentrations

Quantity		Stream						
		1	2	3	4	5	6	8
F	kg h^{-1}	16445	-	8670	233	5298	-	-
V	m^3 h^{-1}	17.973	12382	-	-	-	735	40115
res. oil	mass %	100	0	0	0	0	0	0
carb. black	mass %	0	0	0	100	0	0	0
H_2O	mass %	0	0	100	0	100	0	0
CO_2	vol.%	0	0	0	0	0	55.34	3.79
CO	vol.%	0	0	0	0	0	0	46.87
CH_4	vol.%	0	0	0	0	0	0	0.22
H_2	vol.%	0	0	0	0	0	0	47.86
N_2	vol.%	0	4.49	0	0	0	0	1.26
H_2S	vol.%	0	0	0	0	0	44.66	0
O_2	vol.%	0	95.51	0	0	0	0	0

Quantity		Stream						
		9	10	13	14	16	17	18
F	kg h^{-1}	-	-	-	-	-	-	-
V	m^3 h^{-1}	8713	730	34971	3669	8436	34442	12104
res. oil	mass %	0	0	0	0	0	0	0
carb. black	mass %	0	0	0	0	0	0	0
H_2O	mass %	0	0	0	0	0	0	0
CO_2	vol.%	3.79	3.79	0.12	0.12	0.63	0	0.47
CO	vol.%	46.87	46.87	0.34	0.34	48.41	0	33.84
CH_4	vol.%	0.22	0.22	0.23	0.23	0.23	0.71	0.23
H_2	vol.%	47.86	47.86	98.00	98.00	49.43	97.96	64.15
N_2	vol.%	1.26	1.26	1.31	1.31	1.30	1.33	1.31
H_2S	vol.%	0	0	0	0	0	0	0
O_2	vol.%	0	0	0	0	0	0	0

6.2 DETERMINATION OF SPECIFIC CONSUMPTION OF RAW MATERIALS AND ENERGY IN A COMPLEX CHEMICAL PLANT

Specific consumptions of raw materials and energy are probably the most important characteristics of chemical plants. Their determination, based on measurements carried out in operating plants, belongs to methods frequently employed to evaluate chemical processes. Whereas the consumption of a whole system is usually readily determinable, the distribution of the total consumption among individual products may present a rather difficult task (Boustead & Hancock 1979). The following section is devoted to the optimization of procedures used for assessing specific consumptions in complex systems on the basis of industrial measurements (Madron & Veverka 1981).

6.2.1 Problem analysis

One of the features of modern technological processes is their complexity, associated with the formation of a number of main products and by-products as well as of secondary energy. Consequently, typical systems problems such as the exchange of energy between individual subsystems or the distribution of consumptions among separate streams are encountered in the determination of specific consumptions. The prerequisite for assessing specific consumptions in such systems is their decomposition into independently balanced subsystems for which the specific consumptions of raw materials and energy are to be determined separately. On the one hand, such a decomposition must be detailed enough to enable the specific consumptions to be determined. On the other hand, with an increasing number of subsystems balanced independently, demands on the installation and maintenance of measuring instruments will grow, and so will demands on the working capacity associated with the measuring and data treatment.

Two problems will be discussed further: computer-based calculations of specific consumptions and minimization of the number of balanced subsystems.

6.2.2 General considerations

Let us consider a chemical plant consisting of K subsystems among which mass and energy exchange is taking place (Fig.6.4). All the streams occurring in the plant may be divided into two groups. The first group comprises those streams for which the defining of specific consumptions of raw materials and energy makes sense (products and intermediates). Hereafter such streams will be referred to as *reference streams*. The second group comprises the other streams, i.e. raw materials and energies consumed and secondary energies and by-products generated. It is typical of chemical plants that, in many cases, it is not possible to draw a dividing line between raw materials and energy. The manufacture of ammonia may serve as an example: the

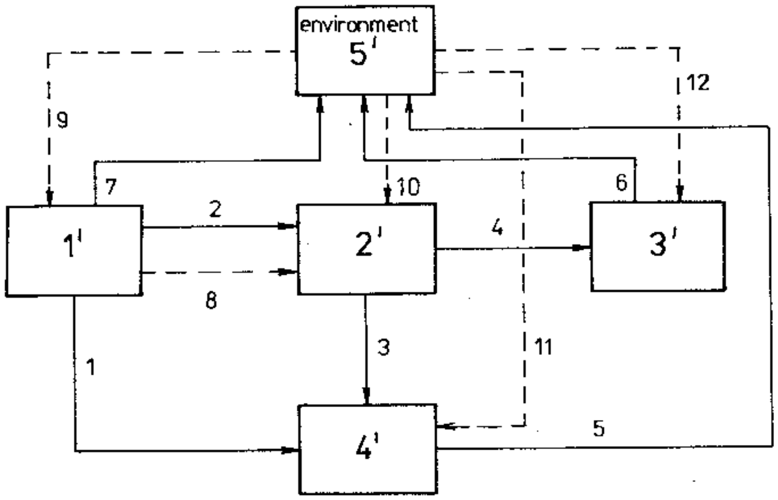


Fig.6.4 — Diagram of a chemical process system
——— products and intermediate products (reference streams);
- - - - - raw materials and energy (energy streams)

essential raw material - natural gas - may also be considered as the source of energy. Hereafter, all such streams will be designated generally as *streams of energy*.

During the formation of individual reference streams a certain amount of energy must be transformed. The amount of interchanged energy is usually expressed in terms of the consumption of its carriers. Thus one speaks about consumption of cooling water, steam at a given temperature and pressure, and the like. To be able to assign the amount of consumed energy carriers to the individual reference streams, we shall introduce also streams of energy carriers consumed, referred to, for simplicity, as streams of *consumed energy*. Then one stream of consumed energy belongs to each reference stream and its value is equal to that amount of the energy carrier which was consumed during the formation of the respective reference stream. When more than one energy carrier is involved in a problem, the stream of consumed energy is characterized by a vector with the number of elements equal to the number of energy carriers (and raw materials). It is necessary to bear in mind, however, that these are only fictitious streams introduced for the purposes of calculation and used for cumulating the consumed energy on the account of the respective streams. The energy streams and streams of consumed energy will hereafter be referred to as *streams of generalized energy*.

The situation can be demonstrated by means of oriented graphs in which the individual subsystems are nodes of the graph and the streams are their oriented edges. Shown in Figs 6.5 - 6.7 are graphs of flow of energy, consumed energy and generalized energy corresponding to the block diagram in Fig.6.4. It is obvious that the graphs of reference streams and graphs of consumed energy are identical.

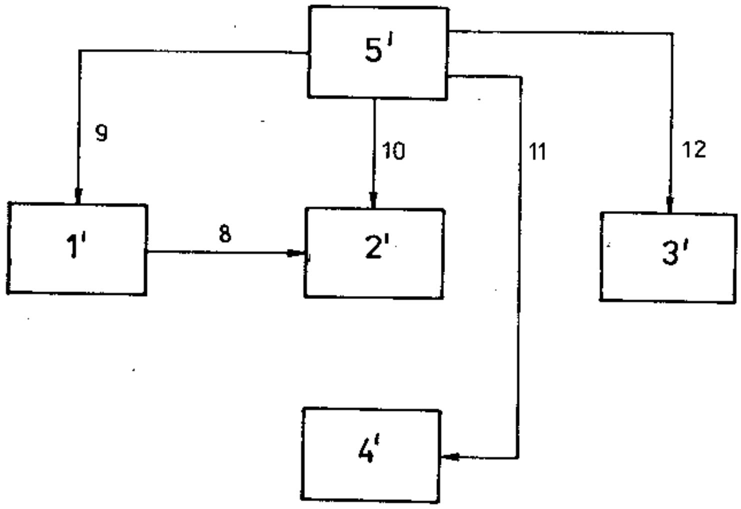


Fig.6.5 — Graph of energy flow G_1

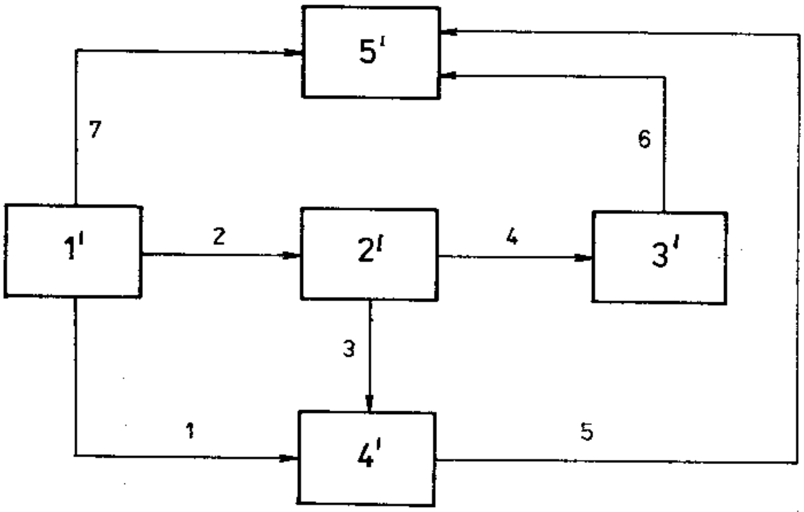


Fig.6.6 — Graph of consumed energy flow G_2

When solving practical problems, one has to deal most frequently with graphs having the following properties: (i) the reference streams are not outgoing streams of the environment, (ii) the graph of reference streams is connected and there exists an oriented path from any node (except for the node of environment) to the node of environment.

The above properties, with obvious physical meanings, are prerequisites for the determination of specific consumptions. Their validity will be presumed henceforth.

On introducing the union of the consumed energy graph (G_2) and the graph of energy flow (G_1) as a graph whose set of nodes is the union of sets of nodes of the

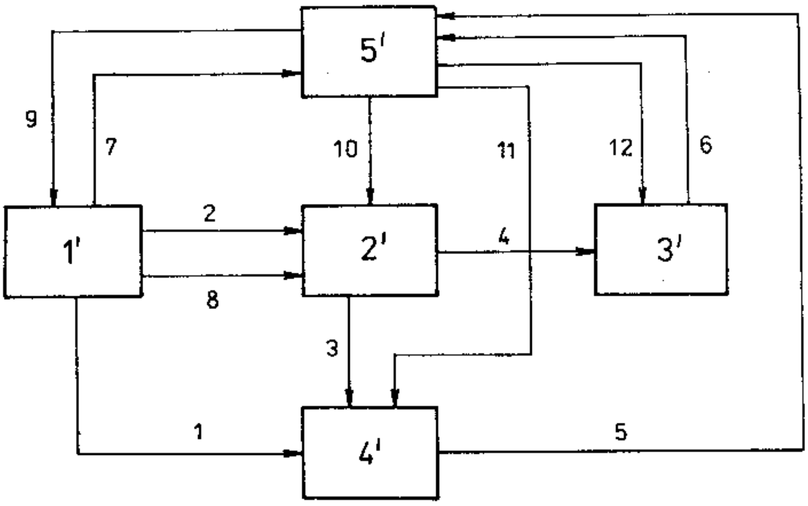


Fig.6.7 — Graph of generalized energy flow G_3

graphs G_1 and G_2, and the set of edges the union of sets of edges of the graphs G_1 and G_2, the graph of generalized energy flow (G_3) is obtained as the union of the graphs G_1 and G_2.

The specific consumption of energy must be assessed separately for each type of energy. It is, therefore, possible to limit the first step to the determination of the specific consumption of only one kind of energy without any loss of generality.

6.2.3 Specific consumption calculations

Let us assume further that the magnitudes of flow of all the reference streams and energy streams have been measured or are otherwise known. Calculation of the consumed energy flows will be based on equations for the generalized energy conservation. The balance of generalized energy around the individual subsystems can be written in the matrix form

$$\boldsymbol{A}\boldsymbol{v} = \boldsymbol{0} \tag{6.26}$$

where $\boldsymbol{A}$ is the reduced incidence matrix of the graph of generalized energy flow (the balance of the environment is deleted) and $\boldsymbol{v}$ is the vector of generalized energy flows.

Matrix $\boldsymbol{A}$ can be decomposed into incidence matrix of the graph of consumed energy flow $\boldsymbol{A}_r\,(K, J_r)$ and incidence matrix of the graph of energy flow $\boldsymbol{A}_e\,(K, J_e)$ (the environment node being deleted). The balance equations of generalized energy then can be expressed by the flows of energy ($\boldsymbol{v}_e$) and flows of consumed energy ($\boldsymbol{v}_r$), the latter being the objective of the calculation:

$$[\boldsymbol{A}_r, \boldsymbol{A}_e] \begin{bmatrix} \boldsymbol{v}_r \\ \cdot \\ \boldsymbol{v}_e \end{bmatrix} = \boldsymbol{0}, \quad \text{resp. } \boldsymbol{A}_r \boldsymbol{v}_r = - \boldsymbol{A}_e \boldsymbol{v}_e \tag{6.27}$$

When the graph of reference streams has no splitters, it contains just K streams (Chen 1971). The matrix $\boldsymbol{A}_r$ is then square and regular, and (6.27) is sufficient for calculating the unknown $\boldsymbol{v}_r$ according to

$$\boldsymbol{v}_r = - \boldsymbol{A}_r^{-1} \boldsymbol{A}_e \boldsymbol{v}_e \tag{6.28}$$

If, however, the graph of reference streams contains splitters (i.e. nodes with two or more outgoing edges), the number of balance equations is smaller than the number of unknown streams of consumed energy. The difference d between the number of unknown values and equations is given (Chen 1971) by Eq.(6.29)

$$d = \sum_{k=1}^{K} (d_k - 1) \tag{6.29}$$

where d_k is the number of outgoing streams of consumed energy from the kth node. Equation (6.27) has to be complemented by d additional relations characterizing the splitters.

Let m reference streams v_j go out from the kth node, $j = q_1, q_2, \dots, q_m$. Information on the distribution of the consumed energy among these m outgoing streams may be written using a set of $m - 1$ independent equations:

$$\begin{aligned} v_{q_1} a_{kq_2} - v_{q_2} a_{kq_1} &= 0 \\ &\vdots \\ v_{q_1} a_{kq_m} - v_{q_m} a_{kq_1} &= 0 \end{aligned} \tag{6.30}$$

where a_{kq_j} is the distributing ratio, i.e. the ratio of the consumed energy leaving the node k in the stream q_j to the total amount of consumed energy leaving the node k. Obviously, for the distributing ratios it holds

$$\sum_{j=1}^{m} a_{kq_j} = 1 \tag{6.31}$$

Equations (6.30) are written for all the splitters. The resulting set of d equations is written in the matrix form

$$\boldsymbol{M}\,\boldsymbol{v}_r = \boldsymbol{0} \tag{6.32}$$

The set (6.27) is complemented with the set (6.32) to give

$$\begin{bmatrix} \boldsymbol{A}_r \\ \boldsymbol{M} \end{bmatrix} \boldsymbol{v}_r = - \begin{bmatrix} \boldsymbol{A}_e \\ \boldsymbol{0} \end{bmatrix} \boldsymbol{v}_e \tag{6.33}$$

with the solution

$$\boldsymbol{v}_r = - \begin{bmatrix} \boldsymbol{A}_r \\ \boldsymbol{M} \end{bmatrix}^{-1} \begin{bmatrix} \boldsymbol{A}_e \\ \boldsymbol{0} \end{bmatrix} \boldsymbol{v}_e = \boldsymbol{B}\,\boldsymbol{v}_e \tag{6.34}$$

A detailed algebraic analysis has shown that, under the previously made assumptions, the set (6.33) has a unique solution.

The specific consumptions of energy p_j associated with the formation of the jth stream are given by the following relations:

$$p_j = v_{rj} / z_j \qquad j = 1, 2, \dots, J_r \tag{6.35}$$

where v_{rj} is the jth element of the vector v_r and z_j is the jth element of the reference streams flow vector $\boldsymbol{z}$.

If more than one kind of energy is involved in the problem, the above procedure may be applied separately to each kind. This approach, however, makes it necessary to find a specific transformation matrix $\boldsymbol{B}$ for each type of energy. When the distributing ratios do not depend on the type of energy, which assumption can be accepted in most cases, only one transformation matrix may be set up for all kinds of energy. The relation for calculating the consumed energy (6.34) is then extended to the case of I kinds of energy

$$\boldsymbol{V}_r = \boldsymbol{B}\,\boldsymbol{V}_e \tag{6.36}$$

where $\boldsymbol{V}_e$ is the energy flow matrix, whose elements V_{eji} represent the flow of the ith kind of energy in the $(j + J_r)$th stream of energy, and $\boldsymbol{V}_r$ is the matrix of consumed energy, whose elements V_{rji} represent the flow of the ith type of energy in the jth stream.

When $V_{eji} = 0$, the ith type of energy is not present in the $(j + J_r)$th stream. If $V_{eji} < 0$, the flow of the ith type of energy is in a reverse direction relative to the orientation of the $(j + J_r)$th edge.

6.2.4 Minimizing the number of balanced subsystems

A proper approach to the decomposition of a system into separately balanced subsystems may often reduce considerably the work necessary for the determination of specific consumptions. Minimization of the number of balanced subsystems not only simplifies the mathematical treatment of the results of industrial measurements, but what is even more important, reduces the number of measuring instruments that have to be checked or newly installed.

When minimizing the number of balanced subsystems, it is advisable to start from a detailed flow chart in which the flows of both reference streams and energy streams are given. The essential requirement for such an initial flow diagram is that the origin of the outgoing streams of the reference stream splitters must be clearly seen. It is advantageous to simplify this initial diagram further by combining the individual elements into larger subsystems. It is necessary, however, still to be able to assess specific consumptions for all the required outgoing streams (products).

An analysis of the solvability of the set of equations (6.33) has shown that, in principle, any two neighbouring subsystems may be combined, except for combining a splitter with a node linked to it by an outgoing stream of that splitter. The latter method of combining is admissible only in those cases when the combination results in the vanishing of the splitter. Two such cases are demonstrated in Fig.6.8, i.e. parallel reference streams linked with a splitter (b) and a simple recycle (a).

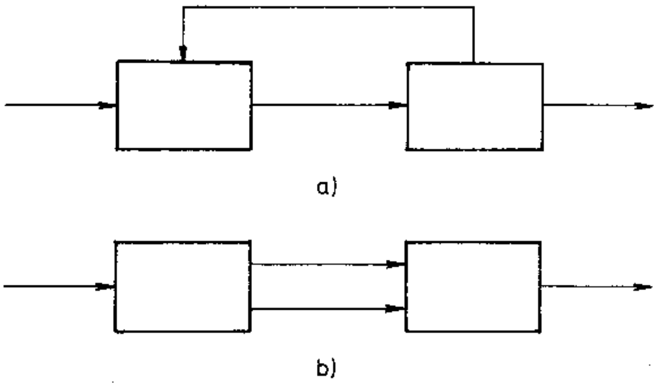


Fig.6.8 — Admissible combining of a splitter with the next node

6.2.5 Determination of specific consumptions in hydrogen and synthesis gases production by residual oil gasification

Consider a process whose reference streams diagram is shown in Fig.6.9. Residual oil is gasified by a reaction with oxygen and steam, and the resulting mixture is further processed by desulphurization and conversion of carbon monoxide into hydrogen. Three main products are produced: desulphurized gas, hydrogen and synthesis gas. Specific consumptions of the following kinds of energy are to be assessed: residual oil (1), cooling water (2), electricity (3), and steam (4).

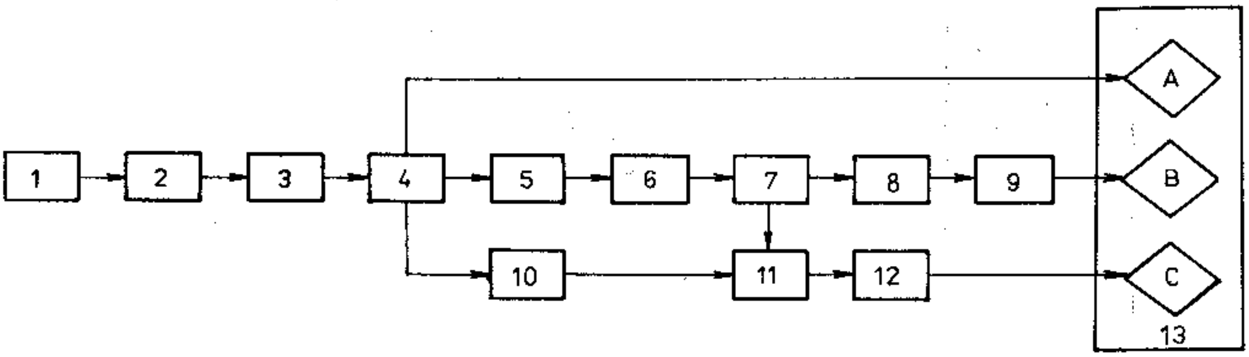


Fig.6.9 — Diagram of reference streams flow. Production of hydrogen and synthesis gases by residual oil gasification
1 - production of oxygen; 2 - residual oil gasification; 3 - desulphurization; 4, 7 - gas separators; 5 - high - temperature CO conversion; 6 - low - temperature CO conversion; 8 - methanation; 9, 12 - compression; 10 - CO_2 scrubbing; 11 - gas mixer; 13 - environment;
A - desulphurized gas; B - hydrogen; C - synthesis gas

In the first stage, the minimization of the number of independently balanced subsystems is carried out by combining successively pairs of subsystems. This procedure is shown in Fig.6.10. The original number of 12 subsystems could be reduced to four. Also shown in Fig.6.10c is the new way of numbering the subsystems.

A simplified diagram of the manufacturing plant, corresponding to the reference streams diagram in Fig.6.10c, is given in Fig.6.11. In addition to the enumerated reference streams flows, flows of the individual types of energy are also indicated (for the sake of clarity the energy flows are not connected with the environment completely).

The graphs of flow of energy, consumed energy, and generalized energy corresponding to Fig.6.11 are shown in Figs 6.5 - 6.7. The number of flows of reference streams $J_r = 7$, the number of energy streams $J_e = 5$, and the number of types of energy $I = 4$. The matrices necessary for calculating the specific consumptions are (see Figs. 6.5 and 6.6):

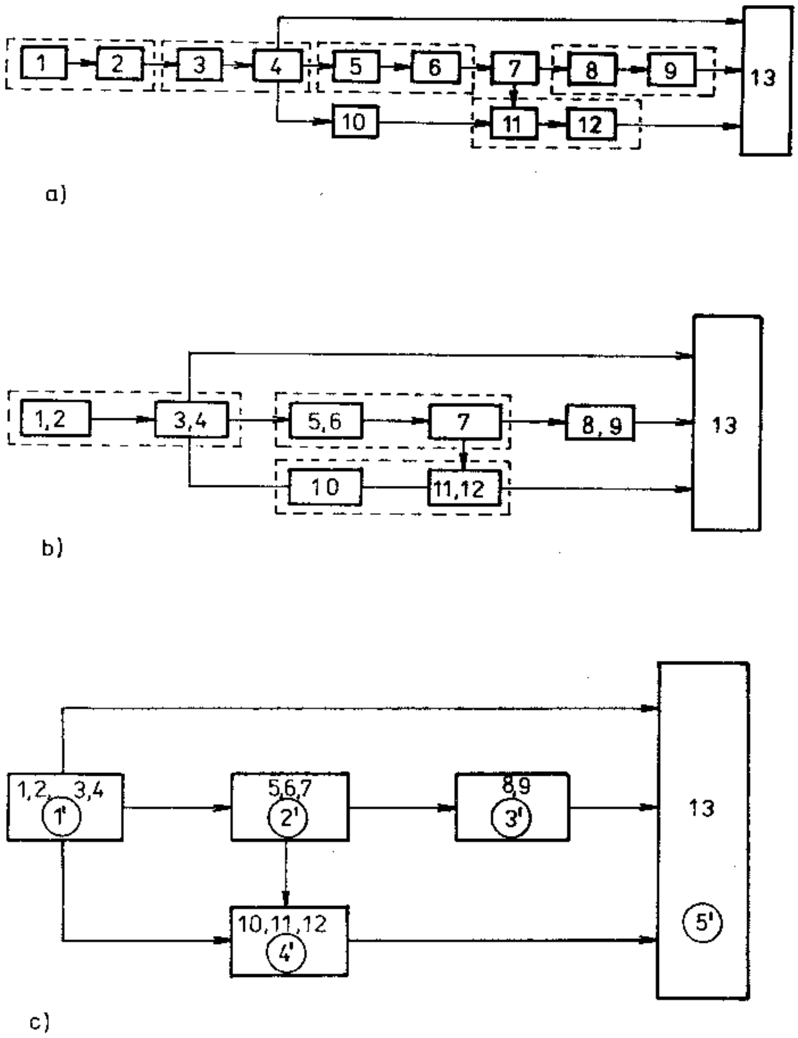


Fig.6.10 — Minimization of the number of balanced subsystems

$$A_r = \begin{bmatrix} -1 & -1 & 0 & 0 & 0 & 0 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & -1 & 0 \\ 1 & 0 & 1 & 0 & -1 & 0 & 0 \end{bmatrix}.$$

$$A_e = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 \end{bmatrix}$$

Further, the following data were measured: z, the vector of flows of reference streams $z^T = [7.62, 40.47, 3.68, 34.27, 11.06, 33.77, 1.14] \times 10^3\ \mathrm{m}^3\ \mathrm{h}^{-1}$ and V_e, the energy flow matrix,

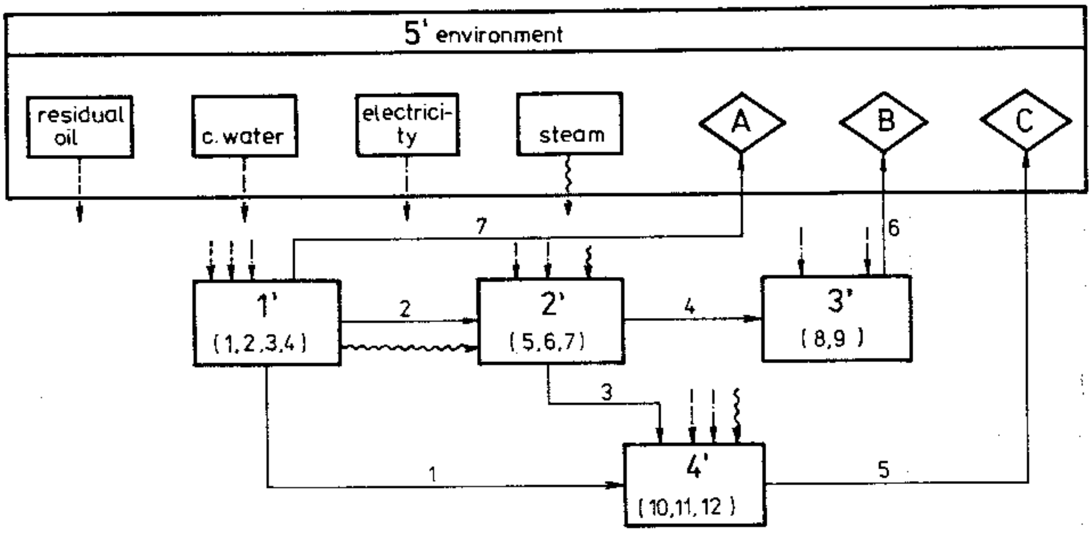


Fig.6.11 — Simplified balance diagram of the manufacture of hydrogen and synthesis gases

$$\begin{array}{ccc}
 & \begin{array}{c}\text{Stream}\\ \text{No}\end{array} & \begin{array}{cccc}\begin{array}{c}\text{Residual}\\ \text{oil}\\ (\times10^3\ \text{kg h}^{-1})\end{array} & \begin{array}{c}\text{Cooling}\\ \text{water}\\ (\text{m}^3\ \text{h}^{-1})\end{array} & \begin{array}{c}\text{Electricity}\\ \\ (\text{MW})\end{array} & \begin{array}{c}\text{Steam}\\ \\ (\times10^3\ \text{kg h}^{-1})\end{array}\end{array} \\
V_e = & \begin{array}{c}8\\ 9\\ 10\\ 11\\ 12\end{array} & \left[\begin{array}{cccc}0 & 0 & 0 & 7.51\\ 18.33 & 3120 & 13.2 & 0\\ 0 & 890 & 1.24 & 12.62\\ 0 & 176 & 1.46 & 1.12\\ 0 & 626 & 4.55 & 0\end{array}\right]
\end{array}$$

The consumed energy leaving the splitters (subsystems 1 and 2) is to be divided in proportion to the amounts of the outgoing reference streams of the splitters. In this case, for the *k*th splitter (see Eq. (6.30))

$$a_{kq_j} = z_{q_j} \,/ \sum_{j=1}^{m} z_{q_j} \qquad (6.37)$$

For example, for subsystem 2,

$m = 2$, $q_1 = 3$ and $q_2 = 4$

$a_{23} = 3.68 \,/\, (3.68 + 34.27) = 0.0970$

$a_{24} = 34.27 \,/\, (3.68 + 34.27) = 0.9030$

Then the matrix $\boldsymbol{M}$ (see Eqn.(6.32)) is

$$\boldsymbol{M} = \begin{bmatrix} 0.8221 & 0.1548 & 0 & 0 & 0 & 0 & 0 \\ 0.0232 & 0 & 0 & 0 & 0 & 0 & 0.154 \\ 0 & 0 & 0.9030 & 0.0970 & 0 & 0 & 0 \end{bmatrix}$$

$\boldsymbol{A}_r$, $\boldsymbol{A}_e$ and $\boldsymbol{M}$ were substituted into (6.34) and, after the matrix $\boldsymbol{B}$ had been calculated from (6.36), the matrix of consumed energy flows $\boldsymbol{V}_r$ was computed:

$$\boldsymbol{V}_r = \begin{bmatrix} 2.84 & 483 & 2.04 & -1.16 \\ 15.07 & 2565 & 10.85 & -6.17 \\ 1.46 & 334 & 1.17 & 1.35 \\ 13.61 & 3120 & 10.92 & 12.60 \\ 4.30 & 994 & 4.68 & 1.31 \\ 13.61 & 3746 & 15.47 & 12.60 \\ 0.42 & 72 & 0.31 & -0.17 \end{bmatrix}$$

The elements of the specific consumption matrix $\boldsymbol{P}$ are defined by analogy with (6.35):

$$P_{ji} = V_{rji} \,/\, z_j \tag{6.38}$$

where P_{ji} is the specific consumption of the ith kind of energy for generating the jth reference stream:

$$\boldsymbol{P} = \begin{bmatrix} 0.372 & 63.4 & 0.268 & -0.153 \\ 0.372 & 63.4 & 0.268 & -0.153 \\ 0.397 & 91.0 & 0.319 & 0.368 \\ 0.397 & 91.0 & 0.319 & 0.368 \\ 0.389 & 89.9 & 0.423 & 0.119 \\ 0.403 & 110.9 & 0.458 & 0.373 \\ 0.372 & 63.4 & 0.268 & -0.153 \end{bmatrix}$$

In the matrix the jth row represents the specific consumptions belonging to the jth reference stream. Thus the following specific consumptions were assessed, e.g. for the produced hydrogen (stream 6):

Residual oil (energy no. 1)	403 kg/1000 m^3 of gas
Cooling water (2)	110.9 m^3 / 1000 m^3 of gas
Electricity (3)	458 kWh / 1000 m^3 of gas
Steam (4)	373 kg / 1000 m^3 of gas

Negative values occurring with specific consumptions (last column of matrix $\boldsymbol{P}$) indicate that steam is generated when streams 1, 2 and 7 are formed.

6.2.6 Analysis of the method used

The procedure for the analysis of specific consumptions of raw materials and energy in complex systems as described in the present Section enables the specific consumptions to be assessed with a minimum number of measurements and minimum treatment of the measured data.

Minimization of the number of subsystems that have to be balanced independently can be performed either directly in the graph of the consumed energy flow or in the respective incidence matrix, where the addition of the matrix rows stands for the combining of neighbouring nodes. The procedure for minimizing the number of balanced subsystems by adapting the incidence matrix can be programmed for a computer without difficulty.

When assessing the specific consumptions, a certain problem may arise out of an unsteady operation of the plant, represented by an accumulation of intermediate products. Such an accumulation can be incorporated in the balance diagram as a stream between a storage tank and the environment, thus solving the given problem theoretically. In practice, however, the existence of significant accumulations complicates the determination of specific consumptions considerably. A storage tank with accumulation represents a splitter connected with the environment by one outgoing stream which may markedly reduce the possibilities of minimizing the number of balanced subsystems.

Another important question that has not been studied systematically in the present work is the problem of distributing the consumed energy among the outgoing streams of splitters. In fact, a number of splitters can often be eliminated when minimizing the number of balanced subsystems. Nevertheless, one or more splitters may be left in the reference streams diagram and these must be taken into consideration when analyzing the consumption of energy. Here we distinguish between simple splitters and separators. With simple splitters the outgoing streams occur in the same state, whereas the outgoing streams of separators differ in their state (temperature, pressure, composition, phase). With simple splitters it is logical to distribute the consumed energy in proportion to the sizes of the outgoing reference streams of the simple splitter. In the case of separators, however, the situation is more complex. A possible approach to the solution of this problem is an exergetic analysis (Baehr et al. 1965) of the separator. This problem has not yet been solved satisfactorily.

6.3 OPTIMAL SELECTION OF MEASURING POINTS WHEN BALANCING A COMPLEX CHEMICAL PLANT

6.3.1 Problem statement

A chemical plant consists of a number of mutually interconnected process units (Fig.6.12). As concerns mass exchange among the individual units and between the plant and environment, it is interesting to know the flows of sulphur, which appears in various forms (elemental sulphur, sulphur oxides, solutions of sulphurous substances) in all the streams of the flowsheet in Fig.6.12.

Now the task is to evaluate possibilities of monitoring the flow of sulphur in individual streams. In substance all the streams can be measured directly. The accuracy of measurement, however, differs by orders (balance measurements of raw materials and products are most accurate while the flows of off-gases and waste waters are measurable with the lowest accuracy). In addition, the individual types of measurement differ in investment costs (some measurement facilities are already installed and used) and in laboriousness. The data concerning the investment and operating costs (maintenance of the measurement device) are roughly known.

6.3.2 Input data

The information available in advance is summarized in Table 6.7. Approximate flow rates (column 2) are known from earlier works as are the estimates of relative standard deviations of measurements (column 3). In addition, investment costs I_i needed for installation of *i*th measurement are presented (in the cases of measurement facilities already installed these investments are zero). In the next column the estimates of operating costs of measuring including the costs of necessary maintenance are presented in the form of time needed for measuring one value t_i . It is assumed that each measurement is made once per shift and that the yearly working time is 8000 hours (hence each measurement is taken a thousand times a year).

6.3.3 Finding the first solution

Further, we shall confine ourselves to selecting directly measured quantities (selection of measuring points) in such a way that a system of solvable equations for unmeasured quantities is formed (redundant measurements are not present). It was shown in Section 5.4 that unmeasured (i.e calculated) streams in a one-component balance have to create the spanning tree of the graph of the balance flowsheet. However, there is a great number of graph spanning trees (e.g. the graph in Fig.6.12 has 7.76×10^9 different spanning trees), and, therefore, the selection of measurement points should be optimized. Before doing so we shall introduce the term costed graph.

An *edge-costed* graph is a graph having a certain real number (cost) assigned to each of its edges. The graph of a balance scheme can be costed in a number of ways; it is possible to assign to each of the edges the presumed flow rate, standard deviation of measurement or investment needed for executing the measurement. The latter two types of costing are of particular importance for us from the standpoint of optimizing the measurement points selection.

Table 6.7 — Input data to Example 6.3

i	F_i	γ_{F_i}	I_i	t_i	i	F_i	γ_{F_i}	I_i	t_i
	kg h^{-1}	-	MU	min		kg h^{-1}	-	MU	min
1	8000	0.01	0	1	26	100	0.05	30	10
2	40	0.05	0	30	27	3	0.01	0	15
3	3500	0.01	10	1	28	150	0.02	0	30
4	2500	0.01	0	1	29	7	0.25	500	60
5	2000	0.01	0	1	30	300	0.05	0	10
6	60	0.05	20	10	31	60	0.05	20	10
7	30	0.50	15	10	32	6	0.00	0	1
8	120	0.02	0	20	33	200	0.05	10	15
9	60	0.07	0	5	34	60	0.10	0	60
10	400	0.02	0	15	35	500	0.01	20	1
11	500	0.02	0	5	36	12	0.10	0	20
12	150	0.05	10	10	37	10	0.02	50	10
13	60	1.00	50	15	38	360	0.05	200	10
14	380	0.25	100	10	39	20	0.02	100	15
15	400	0.03	60	40	40	170	0.02	0	10
16	2500	0.02	0	5	41	300	0.02	0	5
17	2000	0.03	10	5	42	100	0.02	10	10
18	8	0.00	0	1	43	100	0.25	100	10
19	700	0.01	0	1	44	120	0.10	40	5
20	5000	0.02	15	5	45	580	0.02	100	10
21	400	0.02	0	10	46	700	0.01	100	10
22	1	0.02	0	1	47	1000	0.01	0	20
23	80	0.05	80	15	48	50	0.03	20	10
24	170	0.02	0	1	49	1300	0.02	0	15
25	90	0.50	200	5					

Next, we shall introduce the terms *minimum* and *maximum spanning tree*. The *minimum (maximum) spanning tree* of a costed graph is a spanning tree, for which the sum of costs of its edges is the minimum (maximum) one of all the spanning trees of a given graph. Now it is possible to conjecture the connection between the optimization of selecting the measurement point and the task of finding out the maximum or minimum spanning tree of a graph.

When selecting measured quantities so as to ensure the minimum investment needed for the measurement, we shall try to include the quantities with high costs of

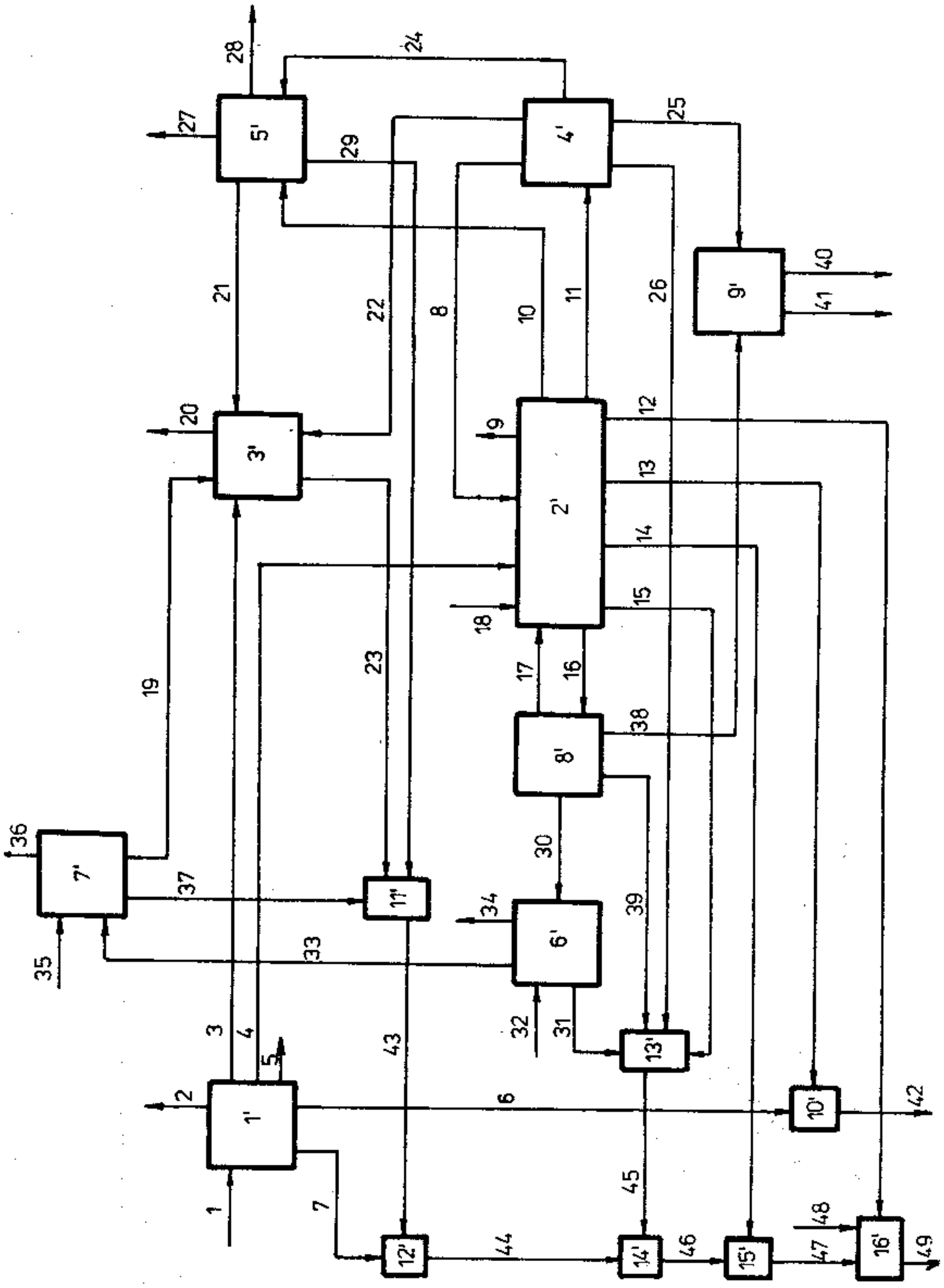


Fig.6.12 — Scheme of a chemical plant

measurement among the unmeasured ones (by including a quantity among the calculated ones we actually save money needed for carrying out its direct measurement). Obviously the total saving will be maximal if a spanning tree formed by unmeasured streams is maximal (on the assumption that the graph edges are costed by costs of measuring the respective streams).

Further, we shall describe the algorithm for finding the maximum spanning tree (in the case of the minimum spanning tree the procedure will be analogical). The procedure is based on a step-by-step formation of the graph tree from which the expected spanning tree appears in the last step.

1. The graph edges are arranged according to decreasing costs (the graph edge with the highest cost has the number 1, etc.).
2. The edge with the lowest number (i.e. with the maximum cost) is taken as the basis of the maximum spanning tree; this edge represents an initial tree to which further edges will be added.
3. The set of the graph nodes is divided into two subsets; the subset **A** contains nodes that are constituents of the tree as formed up to the present time; the subset **B** contains the remaining nodes. When the subset **B** is empty (does not contain any node), the tree is then the maximum spanning tree and the search ends.
4. We shall create a list *S* of all the edges connected (i.e. having one node in common) with the hitherto created tree (the edges forming the tree do not belong to *S*).
5. From the list *S* we choose the edge with the highest cost. If the only one node of this edge belongs to the subset **A**, we connect this edge to the tree and return to the step 3. When both nodes of the edge belong to the subset **A**, this edge is deleted from the list *S* and we shall return to the start of step 5 (let us notice that we delete those edges that would form circles with the previously chosen edges).

The described algorithm enables the maximum spanning tree of the graph to be found by a finite number of steps. If more edges have the same cost, then there can exist more maximum spanning trees with the same cost.

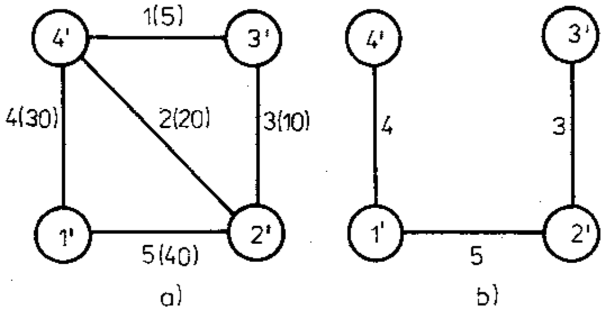


Fig.6.13 — A costed graph (a) and its spanning tree (b)

Let us demonstrate the creation of the maximum spanning tree with the aid of a simple graph in Fig.6.13 where the parenthesized numbers are costs of the edges. We shall proceed according to the individual steps as given in the algorithm:

1. arranging the edges: 5, 4, 2, 3, 1
2. edge 5 forms the first tree
3. **A** = (1', 2'); **B** = (3', 4')
4. S = (2, 3, 4)
5. selecting edge 4; a new tree is formed by edges 5,4
3. **A** = (1', 2', 4'); **B** = (3')
4. S = (1, 2, 3)
5. selecting edge 2. This edge is not suitable since both of its nodes (2', 4') are from the subset **A** (its attaching to the tree would result in a circle). Edge 2 is deleted from the list S
5. S = (1, 3). We select edge 3 and attach it to the tree which is formed by edges 5, 4, 3
3. now, the subset **B** contains no element; the formed tree is the maximum spanning tree of the graph. The spanning tree cost is 40 + 30 + 10 = 80

In the cases of larger graphs with tens or even hundreds of edges, it is necessary to code the above algorithm for a computer.

Thus we have covered the selection of measuring points by the method of maximum spanning tree. Individual variants of selecting the unmeasured streams differ according to the costing of the graph. In the following three methods of costing will be presented.

Let us denote the costing of the ith edge as h_i :

$$(h_i)_1 = I_i \tag{6.39}$$

where I_i is the investment cost of measurement of ith stream, in MU (money unit),

$$(h_i)_2 = m\, t_i\, \frac{1000}{60} \tag{6.40}$$

in MU per year, where m is the cost of one hour of the measurement (in further considerations the value m = 20 MU/hour will be used), t_i = time needed for effecting the ith measurement (in minutes). The number 1000 represents the number of measurements per year,

$$(h_i)_3 = 0.08\,(h_i)_1 + (h_i)_2 \tag{6.41}$$

in MU per year.

The first method costs the stream by the investment needed for the installation of measurement, the second one by operating costs of the measurement and the third method by the total cost of one year of measurement (at eight percent depreciation rate).

Next, we shall present the results of the optimal selection of measuring points. The maximum spanning trees found by the jth method of graph costing minimizes the objective function H_j defined by

$$H_j = \sum_i (h_i)_j \qquad j = 1, 2, 3 \tag{6.42}$$

where in the course of summation the index i passes over the number of all the measured streams. Obviously the objective functions for $j = 1, 2, 3$ represent the investment, operating and total costs, resp., needed for implementing the measurement system.

The information can be completed by mentioning the precision of the measurement system as a whole, expressed as the mean relative standard deviation γ_S , defined as

$$\gamma_S = \left[\sum_{i=1}^{n} \gamma_i^2 / n \right]^{1/2} \tag{6.43}$$

where γ_i is the relative standard deviation of measuring the flow of sulphur in the ith stream (in the cases of unmeasured flows, γ_i is calculated by the method of propagation of random errors) and n is the total number of streams.

Table 6.8 — Optimum selection of measuring point

costing of streams	H_1	H_2	H_3	γ_S
	MU	MU/a	MU/a	-
1	170 000	129 667	143 267	2.345
2	680 000	70 000	124 400	2.835
3	330 000	80 000	106 400	2.823
	unmeasured streams (maximum spanning trees)			
1	6, 13, 14, 23, 25, 29, 31, 35, 37, 38, 39, 43, 44, 45, 46, 48			
2	2, 8, 10, 13, 15, 23, 28, 29, 34, 36, 38, 39, 43, 45, 47, 49			
3	2, 10, 13, 14, 15, 23, 25, 28, 29, 34, 37, 38, 39, 43, 45, 47			

The results are demonstrated in Table 6.8. A universal computer code was written for the solution of the task. The calculation performed on a WANG 2200 computer (finding one maximum spanning tree including its costing and solution of the system of balance equations) took 30 seconds.

The optimal selection of measuring points in the case of a single-component balance by the method of finding the maximum spanning tree is applicable even when we are not able to assign costs to streams exactly. Sometimes it is possible to arrange the streams in accordance with our wish to measure them directly. The order in such a series (number one is ascribed to the stream that can be measured in the easiest way) is so-called *priority of measuring*. If the graph edges are costed by the priorities of the respective streams measuring, the maximum spanning tree represents the selection of unmeasured streams for which the sum of priorities is maximal (those streams we do not want to measure directly are preferentially ranked among the unmeasured ones).

6.3.4 Optimal measurement placement from the standpoint of measurement precision

The hitherto mentioned variants of measurement are optimal from the point of view of measurement costs (investment or operating costs). An important factor that has been omitted until now is the measurement accuracy. The mean relative standard deviation as defined by Eq.(6.43) obtained in the individual cases (see Tab.6.8) is rather unfavourable. The high value of γ_S is caused by extremely high values of relative standard deviations of several quantities (standard deviations equal to thousands of percent of the measured values).

This fact can be explained in this way: Measuring of streams of off-gases and waste waters belong among the most cost-intensive activities. At the same time, these measuring systems must be usually newly installed and the measurement proper is rather tedious. Therefore, these streams are preferentially included among unmeasured streams. In these cases, however, the flows usually are considerably smaller than with other streams (raw materials, intermediates and products). Since they are computed as a difference between large numbers, their relative precision is poor.

Next we shall try to optimize the selection of measurement points from the viewpoint of minimizing the function (6.43). Contrary to the previous cases where the optimized function was a simple linear function of streams costs, it will not be possible to find the optimum by simply finding the maximum spanning tree of the graph. It will be possible to apply this method to find only the first, suboptimum solution which will have to be further improved. A method, based on looking for a better solution in the neighbourhood of the initial spanning tree, has been developed for solving the problem of optimizing the selection of measuring points in a general case.

In textbooks on the theory of graphs the *distance between spanning trees* is defined. At this point we shall only mention that spanning trees of distance 1 differ from one another by a single edge, the other edges being identical. All the spanning trees of distance 1 from a given spanning tree are found so that we go successively through all the edges of the initial spanning graph, and try to substitute them by those graph edges which are not parts of the spanning tree. Demonstrated in Fig.6.14 is the initial spanning tree and all the spanning trees of distance 1 from it. In practice, the number of spanning trees of the distance 1 from a given spanning tree may vary from several tens to several thousands.

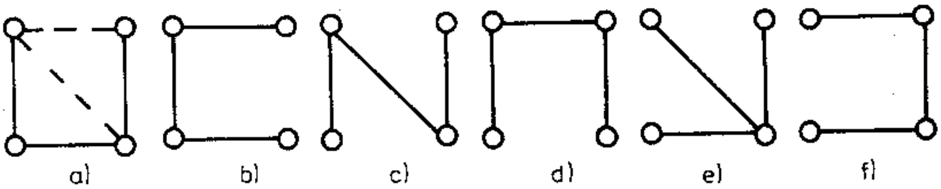


Fig.6.14 — Spanning trees of the graph from Fig.6.13a
a) starting spanning tree; b) - f) spanning trees of distance 1
——— spanning trees

The optimization method based on spanning trees of distance 1 is as follows. The first step consists in finding out the initial spanning tree, for which the value of the objective function is calculated. Spanning trees of distance 1 are then generated and the values of their objective functions are calculated. When a spanning tree so formed is better than the initial spanning tree, such a spanning tree is now considered the initial spanning tree and the whole procedure is repeated. The search is ended when there is no better solution in distance 1 from a given spanning tree (the spanning tree represents the local optimum).

The above procedure was used for solving the task of selection of measured streams that would minimize the objective function (6.43). The initial solution was found as the maximum spanning tree when edges of the graph in Fig.6.12 were costed by the relative standard deviations of measurements.

A total of 428 spanning trees had to be evaluated to find the optimum. The calculation was implemented on a Wang 2200 computer with the aid of a universal program. The calculation including the finding of the initial spanning tree took two hours. The most important results are presented below, where in addition to the function (6.43) also other characteristics (6.42) are given. The initial spanning tree is formed by the following edges (unmeasured streams)

7, 9, 12, 13, 14, 23, 25, 27, 29, 30, 31, 34, 36, 38, 43, 44

$H_1 = 555\ 000$ MU

$H_2 = 108\ 333$ MU / a

$H_3 = 152\ 733$ MU / a

$\gamma_S = 7.99$

The optimum spanning tree is formed by edges

1, 4, 7, 10, 13, 14, 15, 17, 20, 25, 30, 33, 38, 43, 45, 49

$H_1 = 1\ 010\ 000$ MU

$H_2 = 139\ 300$ MU / a

$H_3 = 220\ 133$ MU / a

$\gamma_S = 0.086$

Hence it was possible to improve the measurement precision expressed by the mean relative standard deviation by two orders of magnitude.

6.3.5 Further considerations

The optimization method as described is not confined to a particular form of the objective function, and may be applied to the solution of a number of practical problems connected with the selection of measuring points in single-component balancing. In the above case its use resulted in a considerable decrease in the value of the objective function in comparison with the initial solution. In spite of this, however, there may be certain reservations from the practical standpoint.

The selection concerned only the measuring points without redundant measurements. The solution which was found could be improved by choosing the unmeasured streams whose measuring is not cost and labour intensive, and including these among the measured streams (selection of redundant measurements). In addition, it would certainly be useful to consider the possibility of improving the precision of the whole measurement by improving the precision of selected measurements. But on which measurements should such attention be concentrated? This could be found by expressing the objective function in dependence on standard deviations of directly measured streams (see the method of share matrices in Section 3.2). The reader will certainly find other possibilities of further improving the suggested variants of selecting measuring points. The quality of the final solution thus depends to a large extent on time available for solving the problem.

6.4 MEASURING THE HEAT TRANSFER COEFFICIENT OF AN INDUSTRIAL HEAT EXCHANGER

The overall heat transfer coefficient K is the most important quantity characterizing the function of heat exchangers and we can meet with its measurement in a number of activities. Measuring the value of K in new types of exchangers serves as the source of underlying data for evaluating their function. Also useful is the measurement of K on standard exchangers in order to obtain more precise design correlations. Measurement of K is essential in the monitoring of fouling of heat exchange surfaces. When improving the structure of existing plants, we often meet with the problem of placement of an existing heat exchanger under new conditions. In such a case the measurement of K and its comparison with the theoretically predicted value may be an asset.

The objective of the following subsection is to point out certain problems connected with the measurement of K in industrial shell-and-tube exchangers. We have encountered these problems during the measurement of heat exchangers in a number of process plants, when we have found marked discrepancies between the measured and theoretically predicted values. It turned out that, in some cases, this discrepancy could be explained by propagation of errors in the course of the calculation of K from measured data.

The mathematical model of a heat exchanger is a typical nonlinear model. One important theoretical problem is discussed in the concluding part of this section: errors we commit by the linearization of a mathematical model.

6.4.1 Mathematical model

Hereinafter we shall confine ourselves to an industrial shell-and-tube exchanger with one pass in the shell space and two passes in the tube side. A simple mathematical model describing the behaviour of this exchanger has already been presented in Subsection 2.2.4 (Example 2.3), together with the respective diagram (Fig.2.5). By an analysis of degrees of freedom we find that the number of unmeasured variables is lower by one than the number of equations. It is, therefore, a case with one redundant measurement, which can be processed by the method described in Section 4.4.

6.4.2 Propagation of random errors during measurement of K

Before we start with the measurement of K proper, let us pay attention to the simulation calculation of the functioning of the heat exchanger.

The input values for the calculation are the flow rates of both streams, their inlet temperatures, K, heat exchange area and specific heat capacities of both streams. The outputs are the outlet temperatures of both streams, transferred heat, Δt_{lm} and the cross-flow correction factor ε.

The simulation can be expressed symbolically as the transformation of vector of input variables $\boldsymbol{x}$ to vector of output variables $\boldsymbol{y}$:

$$\boldsymbol{y} = \boldsymbol{f}(\boldsymbol{x}) \quad , \quad \text{where}$$

$$\boldsymbol{x}^{\mathrm{T}} = (F_1 \, , F_2 \, , t_1 \, , T_1 \, , c_{\mathrm{p1}} \, , c_{\mathrm{p2}} \, , A, K)$$

$$\boldsymbol{y}^{\mathrm{T}} = (t_2 \, , T_2 \, , Q, \Delta \, t_{\mathrm{lm}} \, , \varepsilon)$$

The results of simulation for three values of the heat exchange area A are presented in Table 6.9. It may be seen here that with increasing the exchange area (in the case in which the heat exchanger is seriously overdesigned), the value of ε decreases. The simulation calculation carried out so far, which was actually the solution of the set of equations of the mathematical model with respect to the output variables, has yielded consistent values of variables that can be considered true values, being not subject to any errors.

Table 6.9 — Heat exchanger simulation for different heat exchange transfer area A

$F_1 = 150$ kg s^{-1} $\quad$ $K = 600$ W m^{-2} K^{-1}
$F_2 =.50$ kg s^{-1} $\quad$ $t_1 = 19.0$ °C
$c_{\mathrm{P}} = 4\ 180$ J kg^{-1} K^{-1} $\quad$ $T_1 = 56.5$ °C

Quantity		A (m^2)		
		500	1000	1500
t_2	°C	27.4	29.0	29.4
T_2	°C	31.4	26.4	25.4
ε	1	0.896	0.683	0.504
$\Delta\, t_{\mathrm{lm}}$	°C	19.6	15.3	14.3
Q	W	5.26×10^6	6.28×10^6	6.50×10^6
$K\varepsilon$	W m^{-2} K^{-1}	537.5	409.7	302.4

The task, however, can also be set out in the opposite way. The outlet temperatures as given in Table 6.9 may serve as the input variables for calculating the model parameters.

$\boldsymbol{y} = \boldsymbol{f}(\boldsymbol{x})$, where

$\boldsymbol{x}^{\mathrm{T}} = (F_1 , F_2 , t_1 , t_2 , T_1 , T_2 , c_{\mathrm{p1}} , c_{\mathrm{p2}} , A)$

$\boldsymbol{y}^{\mathrm{T}} = (K, Q, \Delta\, t_{\mathrm{lm}} , \varepsilon)$

This calculation simulates the identification of the model parameters from the "measured" flow rates and temperatures. Since the values of "measured" variables taken from Table 6.9 satisfy exactly the model equations (are not subject to errors), the values of calculated parameters will be identical with those shown in Table 6.9. The values of "unmeasured" variables assessed in this way represent the true values that would be approached if we eliminated the errors of measurement.

When calculating the model parameters from exact values of flow rates and temperatures we can find the scatter of parameters around the true (mean) values. Based on the theory of random errors propagation, it is possible to calculate the intervals within which the calculated unmeasured variables will occur at a certain probability.

The maximum deviations of calculated unmeasured variables from true values are presented in Table 6.10. They were calculated on the basis of maximum errors of directly measured quantities given in the same Table (standard deviation used in this calcuation were taken as maximum errors divided by 1.96). These results can be interpreted so, that when we repeat the measurement many times under the same conditions, about 95% of the individual calculated values will be subject to an error smaller than is shown in Table 6.10.

Table 6.10 — Maximum errors of unmeasured quantities
Maximum errors of measured quantities are:
F_1 , F_2 ± 5% A ± 0.5%
t_1 , t_2 , T_1 , T_2 ± 0.5 °C c_{p} ± 0.2%

Quantity		A(m^2)					
		500		1000		1500	
K	W m^{-2} K^{-1}	39.6	(6.6%)	78.8	(13.0%)	227	(37.9%)
ε	1	0.01	(1.1%)	0.05	(7.7%)	0.16	(32.6%)
$\Delta\, t_{\mathrm{lm}}$	°C	0.54	(2.7%)	0.60	(3.9%)	0.63	(4.3%)
Q	W	2.6×10^5	(4.9%)	2.9×10^5	(4.6%)	3.0×10^5	(4.6%)
$K\varepsilon$	W m^{-2} K^{-1}	30.5	(5.6%)	24.8	(6.0%)	19.0	(6.2%)

It may be seen from Table 6.10 that the precision of K and ε depends considerably on the exchanger size (overdesign). When the heat-exchange area is 1500 m^2, the maximum error of measuring is so large that the measurement makes no sense. At the same time, the other quantities (Q, Δt_{lm} as well as the product $K\ \varepsilon$) are ascertained comparatively accurately. The problem can be elucidated by constructing the ellipse defining the region within which 95% of the K and ε values occur. Such an ellipse, which is shown in Fig.6.15, was constructed from covariance matrice by the method described in Section 4.4 [see Eq.(4.83)]. It can be seen from Fig.6.15 that, owing to strong correlation between K and ε, the ellipse shape is markedly elongated and, consequently, these parameters cannot be identified separately but only as a product.

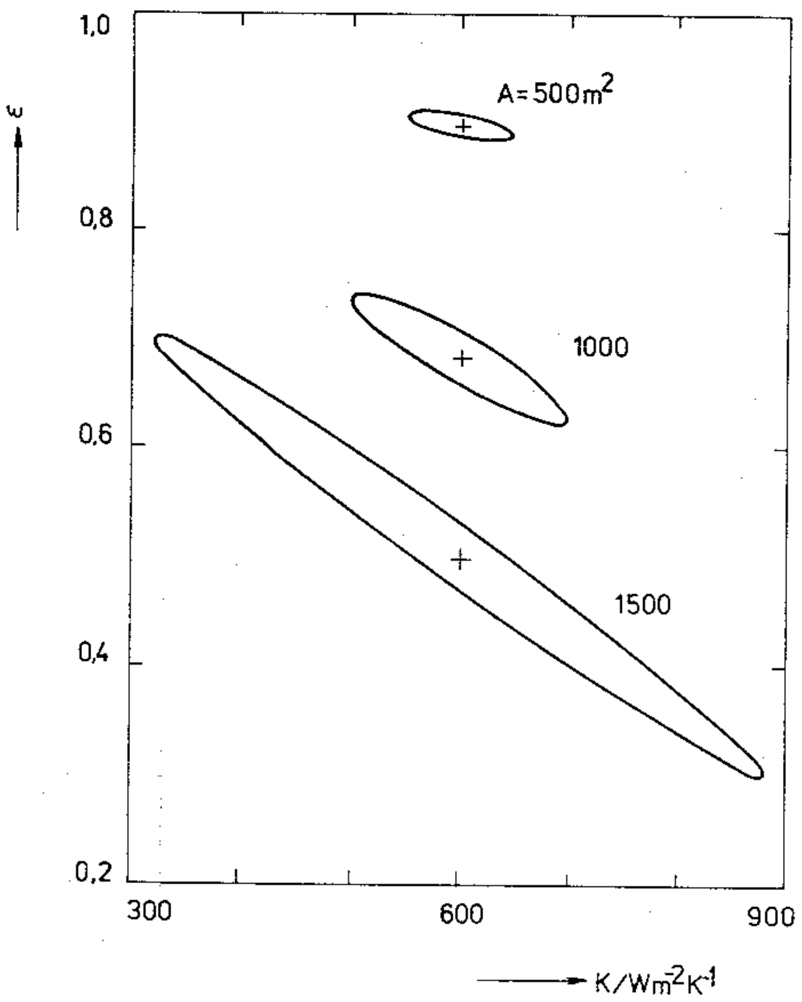


Fig.6.15 — Propagation of errors in calculation of K and ε
(Ellipses covering with 95% probability calculated values of K and ε.
+ represents true values)

Further, it is useful to examine in a greater detail the propagation of errors in the course of calculation of calculated unmeasured variables. The matrix of shares for the exchanger area $A = 1500\ \mathrm{m}^2$ is presented in table 6.11. It follows from this that in the case under consideration the imprecision of K depends particularly on the measurement of temperatures t_2 and T_1, which contribute to the variance of K by 32 and 60%, resp. Hence, if we tried to reduce the variance of K, it would be necessary to measure these temperatures more precisely.

Table 6.11 — Share matrice of unmeasured quantities
$A = 1500\ \mathrm{m}^2$

Quantity	Directly measured quantities							
	F_1	F_2	A	c_p	t_1	t_2	T_1	T_2
K	0	1	0	0	6	32	60	0
ε	0	0	0	0	7	32	61	0
Δt_{lm}	2	2	0	0	31	15	41	9
Q	10	58	0	0	10	10	6	6
$K\varepsilon$	11	22	1	0	3	25	39	0

6.4.3 Processing of measured data

The method of measured data processing is identical to that used in the preceding Subsection. The only difference is that, whereas in the preceding case the input data were precise (satisfying exactly the mathematical model), now the data will be subject to random measuring errors. Data, made up from the consistent (accurate) values to which randomly generated random errors were added, are presented in Table 6.12. These data were processed by the method described in Subsection 4.4.5 and the results are shown in Table 6.12 (Δ denotes the maximum errors of results).

The results are similar to those in the preceding Subsection (Table 6.10), their interpretation, however, is different. In this case the values Δ do not represent the maximum errors of results but define, together with the parameters $\hat{x}$, the intervals $\hat{x} \pm \Delta$ within which the unknown values of parameters occur with the probability of 95% (so-called confidence intervals). It may be seen here again that, in the case of large heat-exchange areas, the confidence intervals are rather wide, witnessing a poor precision of the measurement of K.

In Fig.6.16 are so-called confidence ellipses for K and ε, having their centres at points, whose coordinates are (K, ε), and defining the region within which the true

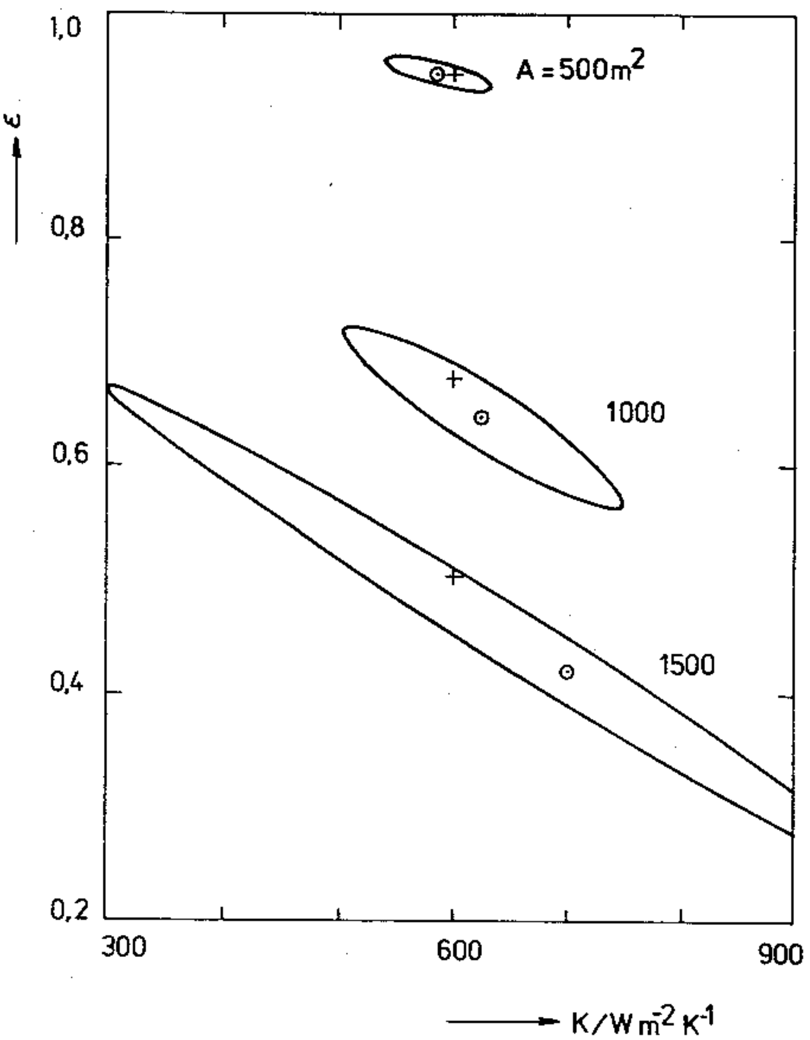


Fig.6.16 — Confidence ellipses covering the true values with 95% probability (o - estimate; + - true value)

values of K and ε occur with the probability of 95%. In practice the true values are not known. In our case, however, when the data were generated, the true values are known (see Table 6.9).

As in the preceding Subsection, it would be possible to introduce here the matrix of shares. The results, however, would be analogical with those in Table 6.11.

The detailed statistical analysis of the problem of identifying the overall coefficient of heat transfer as made hitherto concerned a tubular exchanger with a single pass in the shell space and two passes in the tube space. The same conclusions hold approximately also for exchangers with one pass in the shell side and an even number of passes in the tube side. A similar analysis could be made for other types of exchangers provided that the mathematical dependence of the correction factor ε on other variables is known.

Table 6.12 — Processing of measured data
Measured quantities: F_1 , F_2 , A, c_p , t_1 , t_2 , T_1 , T_2

Quantity		$A = 500\ \mathrm{m}^2$			$A = 1000\ \mathrm{m}^2$			
		x^+	$\hat{x}$	Δ	x^+	$\hat{x}$	Δ	d_{90}
F_1	kg s^{-1}	151.5	149.4	4.6%	151.5	149.0	4.5%	17%
F_2	kg s^{-1}	40.0	46.6	4.5%	46.0	46.7	4.4%	17%
A	m^2	498	498	0.5%	996	996	0.5%	-
c_p	J kg^{-1} K^{-1}	4183	4183	0.2%	4183	4183	0.2%	-
t_1	°C	19.3	19.5	0.4 °C	19.3	19.5	0.4 °C	1.8 °C
t_2	°C	27.6	27.4	0.4 °C	29.2	29.0	0.4 °C	1.8 °C
T_1	°C	31.2	31.1	0.5 °C	26.2	26.2	0.5 °C	5.3 °C
T_2	°C	56.6	56.7	0.5 °C	56.6	56.7	0.5 °C	5.3 °C
K	W m^{-2} K^{-1}	-	584	6.7%	-	626	15.9%	-
ε	1	-	0.894	1.2%	-	0.647	10.4%	-
Δt_{lm}	°C	-	19.1	2.8%	-	14.8	4.2%	-
Q	MW	-	4.97	4.9%	-	5.96	4.6%	-
$K\varepsilon$	W $\mathrm{m}^{-2}\mathrm{K}^{-1}$	-	522	5.7%	-	406	6.2%	-

It has been shown that when the value of ε is low, the determination of K may be subject to a considerable error. In such cases it is necessary to carry out a detailed statistical analysis of the measured data,whereby the possible error in the results can be estimated. When the precision of the results is unsatisfactory, it is possible to examine, whether measuring some variables more precisely can result in considerably better precision of K. It may turn out in some cases that it is impossible to assess the value of K with required precision even if very precise measurement methods are used.

The fundamental cause of problems, from the viewpoint of chemical engineering, are the low values of the cross-flow correction factor ε. The textbooks usually state that ε should not be smaller than 0.7 - 0.8. It is true, however, that in industrial practice exchangers whose ε is smaller than 0.5 can occur sometimes. There are a number of reasons for this, from overdesign of the exchanger in the design stage to its operating outside the design conditions region.

As with most real problems, the procedure used in the present work could not be absolutely rigorous. The mathematical model itself is based upon a number of simplifying assumptions. The adopted method of data processing holds true exactly only with linear models. Hence the confidence intervals and regions are only approximative.

6.4.4 Errors caused by linearizing the mathematical model

One of the causes of potential errors during the processing of data, described in this Section so far, is the fact that the methods used have been applied to the linearized form of the model. Hence the character of the solution is only approximative and thus may differ considerably from the reality. There have been very few studies, however, dealing with these problems (Pazman 1966, Ramamurthy & Bequette 1990). The solution is not a simple one, indeed - in this case it is not possible to arrive at conlusions that are valid generally. Any new knowledge acquired here will always hold true only for a particular class of models depending on their nonlinearity and other characteristics. In spite of this, further studies in this respect are desirable if the confidence in mathematical modelling of real technological processes is to be improved. Therefore, the remaining part of this Section will be devoted to studying the above problem.

Let us concentrate our attention upon the impact of nonlinearity of a model on the confidence intervals and regions and on testing of model adequacy according to (4.83).

The fundamental problem consists in the fact that the described constructions and tests are based on the assumption of normal distribution of measuring errors, which, in the case of a linear model, implies normality in the calculated unmeasured variables. The nonlinearity of the model, however, causes a deformation of the normal distribution, so that the presented constructions are approximative. The most appropriate way for studying these problems is the Monte Carlo method, where repeated simulation of the measurement on a computer yields results that can be compared with the approximative linearized solution. Further we shall give attention to two unmeasured variables - K and ε (the remaining two - Q and $\Delta\, t_{\mathrm{lm}}$ - will be eliminated from the model).

Now, let us proceed to the simulation of measuring the K and ε using the Monte Carlo method. In the first place, the "true" values are found by a simulation calculation of the exchanger. The values A, K, F_1 , F_2 , t_1 , T_2 and c_p (c_p being the same for both streams) are set as input and the remaining ones, i.e. t_2 , T_2 and ε are calculated. Further, in the phase of Monte Carlo simulation randomly generated errors are added to the values so obtained. The following maximum errors were assumed: flow rates - 5%, temperatures - 0.5 °C (1 °C in one particular case), heat exchange area - 0.5%, c_p - 0.2%. Standard deviations were taken as the maximum error/1.96.

Altogether three cases were evaluated:

1) exchanger with heat exchange area 500 m^2,
2) exchanger with exchange area 1000 m^2,
3) same as in case 2, only the maximum error in temperature measurement was increased to 1 °C.

For each of the above variants 1000 sets of "measurements" were generated and these data sets were processed. The results were examined as concerns the following quantities and phenomena:

- sample mean of parameters K and ε as identified from the individual sets of measurement (evaluation of the bias of estimates),
- relative frequency of cases when the interval (4.82) which did not cover the the "true" values of the parameters,
- relative frequency of cases when the region (4.83), i.e. the confidence ellipse, did not cover the "true" vector,
- relative frequency of cases when the inequality (4.133) was not satisfied.

The results are presented in Table 6.13. The following conclusions can be arrived at from this Table: As far as the bias of estimates is concerned, the situation is fairly good. The maximum deviation of the mean of estimated parameters was found in the case of K, variant No.3. (reality 600 kW m^{-2} K^{-1}, found - 604.4 kW m^{-2} K^{-1}). Even in this case, however, this disproportion is negligible when compared with the confidence interval for K (±150 kW m^{-2} K^{-1}).

Table 6.13 — Results of Monte-Carlo simulation

Quantity		Variant		
		1	2	3*
A	m^2	500	1000	1000
K	kW m^{-2} K^{-1}	600	600	600
ε	1	0.896	0.683	0.683
ΔK	kW m^{-2} K^{-1}	39.7	77.8	150
$\Delta \varepsilon$	1	0.010	0.052	0.103
$\bar{K}$	kW m^{-2} K^{-1}	599.1	601.3	604.4
$\bar{\varepsilon}$	1	0.896	0.682	0.682
P'[K outside (4.82)]	%	5.2	5.2	7.6
P'[ε outside (4.82)]	%	5.3	4.5	7.2
P'[K,ε outside (4.83)]	%	5.2	5.6	9.4
P'[Q_{min} outside (4.133)]	%	6.1	5.5	6.2

Remarks:
* - max. error of measuring temperatures 1 K
ΔK, $\Delta \varepsilon$ - half of confidence interval width
$\bar{K}$, $\bar{\varepsilon}$ - average values from 1000 simulations
P'[] - relative frequency

The relative frequency of cases where the inequality (4.133) was not satisfied (gross error was detected, even if it was not present) was fairly close to the theoretical probability 5%.

Obviously, this finding is in relation to the fact that the task is but very little overdetermined - practically by a single redundant equation only (enthalpy balance of the exchanger), which is, moreover, only slightly nonlinear.

The largest deviations of relative frequencies from theoretical probabilities occurred in the case of the coverage of "true" values by intervals or, as the case may be, by the coverage of "true" vectors by ellipses of confidence. The maximum disproportions were observed in the variant 3, where the relative frequencies were markedly higher than the theoretical probabilities 5%. This is obviously due to the non-normality of parameters distribution caused by nonlinearity of the model (the confidence region has no more the shape of an ellipse). Yet, even in this worst case the situation is not entirely unacceptable. It is necessary to consider here that, in the given case, the accuracy of measurement is altogether poor (a half of the confidence interval width for K is 150 kW m^{-2} K^{-1}, i.e. 25% of the assessed value). In such a case the worth of the whole measurement is rather questionable and its optimization is necessary.

It follows from the study executed that the statistical methods of processing the measured data, as developed for linear models, are, in principle, applicable to nonlinear models as well. We have arrived at this conclusion when studying the identification of the mathematical model of a heat exchanger. To confirm this opinion, further studies on other unit operations will be needed.

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Appendix: Mathematical Tools

The appendix briefly summarizes the mathematical concepts which are necessary for understanding this book. In most cases, the survey does not exceed the graduate range of knowledge; it is supposed that it will serve the reader mainly for brushing up what has been learnt before.

A.1 VECTOR SPACES

An ordered set of n numbers $\mathbf{x} = (x_1 \dots x_n)$ is called a vector of n-dimensional space and the numbers $x_1, \dots, x_n$ are called the coordinates of the vector $\mathbf{x}$. Vectors will be denoted by ***boldface small letters***, the coordinates by *italics*.

As examples of vectors may serve instantaneous values of flow rates at different places of a pipeline network or the sequence of yields of a chemical reaction obtained in a series of subsequent batch operations.

Two vectors $\mathbf{x}$ and $\mathbf{y}$ are equal when and only when the corresponding coordinates are equal.

The *sum of vectors* $\mathbf{x}$ and $\mathbf{y}$ is vector $\mathbf{z} = \mathbf{x} + \mathbf{y}$ whose coordinates equal $z_i = x_i + y_i$ for $i = 1, 2, \dots, n$. For the sum of vectors, the following laws of 1.commutativity and 2.associativity hold

1/ $\mathbf{x} + \mathbf{y} = \mathbf{y} + \mathbf{x}$

2. $(\mathbf{x} + \mathbf{y}) + \mathbf{v} = \mathbf{x} + (\mathbf{y} + \mathbf{v})$

The product of scalar k and vector $\mathbf{x}$ is vector $\mathbf{z} = k\mathbf{x}$ whose coordinates equal $z_i = kx_i$ for $i = 1, 2, \dots, n$.

For vectors $\mathbf{x}$, $\mathbf{y}$ and real numbers a, b, one defines the *linear combination* $a\mathbf{x} + b\mathbf{y}$ as the vector of coordinates $ax_i + by_i$. The notion of a linear combination can be extended to the sum of an arbitrary number of products of a scalar with a vector.

A *linear space* **P** is a set of vectors having the following properties. If $\mathbf{x}$ and $\mathbf{y}$ are two arbitrary elements of **P** and c is an arbitrary real number, then also $\mathbf{x} + \mathbf{y}$ and $c\mathbf{x}$

belong to the linear space **P**. An example of a linear space is the set of all vectors in a plane. The vectors $\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n$ are *linearly dependent* if there exist some numbers $c_1, \ldots, c_n$ of which at least one is different from zero, and such that we have

$$c_1 \boldsymbol{x}_1 + \ldots + c_n \boldsymbol{x}_n = \boldsymbol{0} \tag{A.1}$$

where $\boldsymbol{0}$ is the zero vector (the vector whose all coordinates equal zero). In the opposite case, the vectors are linearly independent. The vectors are linearly dependent if and only if one of them is a linear combination of the other vectors.

A linear space is called n-dimensional if it contains n linearly independent vectors while any more than n vectors of the space are linearly dependent. The number n is called the *dimension* of the linear space.

A linear subspace **L** of a linear space **P** is a subset of elements of **P** having all the properties of a linear space. There holds that all elements belonging to **L** also belong to **P**, but not necessarily conversely.

A.2 MATRICES

A.2.1 Basic concepts

We shall call a matrix an array of $m \times n$ real numbers arranged as a rectangle scheme of m rows and n columns

$$\boldsymbol{A} = \begin{bmatrix} A_{11}, A_{12}, & \ldots\ldots\ldots\ldots, & A_{1n} \\ A_{21}, A_{22}, & \ldots\ldots\ldots\ldots, & A_{2n} \\ & \ldots\ldots\ldots\ldots & \\ & \ldots\ldots\ldots\ldots & \\ A_{m1}, A_{m2}, & \ldots\ldots\ldots\ldots, & A_{mn} \end{bmatrix} \tag{A.2}$$

We say a matrix of m rows and n columns is of *type* $m \times n$; if necessary, it is written as $\boldsymbol{A}$ $(m \times n)$. If $m = n$, it is called a *square matrix of order n*. A matrix of type $1 \times n$ is called *row matrix* or *row vector*. A matrix of type $n \times 1$ is called *column matrix* or *column vector*. A vector without the type specification will further be considered as a column vector. A number (scalar) can be considered as a 1×1 matrix.

The elements A_{ii} $(i = 1, \ldots , n)$ of a square matrix form the *main diagonal* (abridged: diagonal) of the matrix. A square matrix with nonnull elements in the main diagonal and with all elements below (above) the diagonal equal to zero, is called *upper (lower) triangular matrix*. A square matrix with nonnull elements in the diagonal and with all off-diagonal elements equal to zero, is called a *diagonal matrix*. A diagonal matrix is thus a particular example of a triangular matrix. If all diagonal elements of a diagonal matrix equal unity, it is called ***unit (identity) matrix*** and denoted $\boldsymbol{I}$. A matrix whose all elements equal zero is called ***zero matrix*** and denoted by $\boldsymbol{O}$.

A symmetric matrix is a square matrix whose elements satisfy $A_{ij} = A_{ij}$ $(i = 1, \dots, n; j = 1, \dots, n)$; thus the elements placed symmetrically with respect to the diagonal are equal. The basic kinds of matrices are illustrated on Fig.A.1.

If a matrix $\boldsymbol{A}$ $(m \times n)$ is divided by horizontal lines in number $(p - 1)$ and by vertical lines in number $(q - 1)$ between the rows and between the columns, respectively, one obtains a ***partitioned matrix*** (also called ***composed*** or ***block matrix***) whose elements in number pq are matrices (see Fig.A.2 for examples).

$$\begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \quad \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \quad (x\ x\ x\ x) \quad \begin{bmatrix} x \\ x \\ x \\ x \end{bmatrix} \quad \begin{bmatrix} z & x & x & x \\ 0 & x & x & x \\ 0 & 0 & x & x \\ 0 & 0 & 0 & x \end{bmatrix}$$

a) b) c) d) e)

$$\begin{bmatrix} z & 0 & 0 \\ x & z & 0 \\ x & x & z \end{bmatrix} \quad \begin{bmatrix} z & 0 & 0 \\ 0 & z & 0 \\ 0 & 0 & z \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} x & 5 & 1 \\ 5 & x & 7 \\ 1 & 7 & x \end{bmatrix}$$

f) g) h) i) j)

Fig.A.1 — Basic kinds of matrices (x - real number, z - non-zero number)
a) rectangular, b) square, c) row, d) columm (vector), e) upper triangular, f) lower triangular, g) diagonal, h) unit, i) zero, j) example of a symmetric matrix

$$\boldsymbol{A} = (5) \qquad \boldsymbol{B} = (2\ 3) \qquad \boldsymbol{C} = \begin{bmatrix} 7 \\ 9 \end{bmatrix} \qquad \boldsymbol{D} = \begin{bmatrix} 5 & 6 \\ 2 & 4 \end{bmatrix}$$

$$(\boldsymbol{A}\ \boldsymbol{B}) = (5\ 2\ 3) \qquad \begin{bmatrix} \boldsymbol{A} \\ \boldsymbol{C} \end{bmatrix} = \begin{bmatrix} 5 \\ 7 \\ 9 \end{bmatrix} \qquad \begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{C} & \boldsymbol{D} \end{bmatrix} = \begin{bmatrix} 5 & 2 & 3 \\ 7 & 5 & 6 \\ 9 & 2 & 4 \end{bmatrix}$$

Fig.A.2 — Examples of partioned (block) matrices

One of the basic concepts is that of the *rank* of a matrix. One says matrix $\boldsymbol{A}$ is of rank h if in the set of its rows, there exist at most h linearly independent rows. It can be shown that the same rank is obtained when considering the set of the columns instead of the rows of the matrix. If rank $(\boldsymbol{A}) = \min(m, n)$ where m and n are the dimensions of the matrix, then the matrix is said to be of full rank.

A square matrix whose rank equals its order is called *regular*. If the rank of a square matrix is lower than its order, then the matrix is called *singular*.

A.2.2 Matrix operations

Two matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are equal (one writes $\boldsymbol{A} = \boldsymbol{B}$) if they are of the same type and if the corresponding elements are equal, thus $A_{ij} = B_{ij}$ for $i, j = 1, 2, \ldots$.

The *transposed matrix* $\boldsymbol{A}^{\mathrm{T}}$ (transpose of $\boldsymbol{A}$) is obtained from matrix $\boldsymbol{A}$ by interchanging the rows and the columns while preserving their order (i.e. by "turning the matrix over" round the main diagonal). For the elements of matrices $\boldsymbol{A}$ and $\boldsymbol{A}^{\mathrm{T}}$, we have $A_{ij} = A_{ji}^{\mathrm{T}}$ for all i and j.

The sum of matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ is the matrix $\boldsymbol{C}$ whose elements equal the sum of the corresponding elements of $\boldsymbol{A}$ and $\boldsymbol{B}$, thus $C_{ij} = A_{ij} + B_{ij}$ for all i and j. The matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ must be of the same type, thus also $\boldsymbol{C}$ is of the same type.

The product of scalar c and matrix $\boldsymbol{A}$ is the matrix $\boldsymbol{B} = c\boldsymbol{A}$ whose elements satisfy $B_{ij} = cA_{ij}$ for all i and j. In the special case of $c = -1$, $\boldsymbol{B}$ is called *opposite* to matrix $\boldsymbol{A}$.

One of the most important matrix operations is matrix multiplication. Let $\boldsymbol{A}$ be of type $m \times n$ and $\boldsymbol{B}$ of type $n \times p$. The product $\boldsymbol{AB}$ is the matrix $\boldsymbol{C}$ of type $m \times p$ whose elements satisfy

$$C_{ik} = \sum_{j=1}^{n} A_{ij} B_{jk} \quad (i = 1, \ldots, m;\ k = 1, \ldots, p) \tag{A.3}$$

The product $\boldsymbol{AB}$ is defined only if the number of columns of $\boldsymbol{A}$ equals the number of rows of $\boldsymbol{B}$ (one says that $\boldsymbol{A}$ and $\boldsymbol{B}$ are *conformable*). The product of a matrix with the unit matrix (from the left or the right) equals the original matrix.

Further relevant properties of the matrix product are: Matrix multiplication is generally not commutative, but it is associative.

non-comutativity: $\boldsymbol{AB}$ is not always equal to $\boldsymbol{BA}$

associativity: $\boldsymbol{ABC} = (\boldsymbol{AB})\,\boldsymbol{C} = \boldsymbol{A}\,(\boldsymbol{BC})$

The associativity of a greater number of matrices enables to calculate the product as a sequence of products of two matrices.

Let $\boldsymbol{A} = \boldsymbol{A}_1 \boldsymbol{A}_2 \ldots \boldsymbol{A}_p$. For the rank of $\boldsymbol{A}$ there holds that it equals at most the rank of matrix $\boldsymbol{A}_i$ of minimum rank

$$\operatorname{rank}(\boldsymbol{A}) \leq \min \operatorname{rank}(\boldsymbol{A}_i) \quad \text{for } i = 1, \ldots, p$$

The transposed matrix product equals

$$(\boldsymbol{A}_1 \boldsymbol{A}_2 \ldots \boldsymbol{A}_p)^{\mathrm{T}} = \boldsymbol{A}_p^{\mathrm{T}} \ldots \boldsymbol{A}_2^{\mathrm{T}} \boldsymbol{A}_1^{\mathrm{T}} \tag{A.4}$$

Important is the notion of inverse matrix introduced for square matrices. For a given square matrix $\boldsymbol{A}$, let there exist a matrix $\boldsymbol{A}^{-1}$ such that simultaneously

$$\boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{I} \quad \text{and} \quad \boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{I}$$

where $\boldsymbol{I}$ is the unit matrix. Then $\boldsymbol{A}^{-1}$ is unique, and it is called the *inverse* of matrix $\boldsymbol{A}$. For the existence of the inverse matrix, it is sufficient and necessary that the original matrix is regular.

The inversion of a product of regular square matrices follows an analogous scheme as the transposition

$$(\boldsymbol{A}_1 \boldsymbol{A}_2 \ldots \boldsymbol{A}_p)^{-1} = \boldsymbol{A}_p^{-1} \ldots \boldsymbol{A}_2^{-1} \boldsymbol{A}_1^{-1} \tag{A.5}$$

A.2.3 Linear, bilinear, and quadratic forms

In the application of matrix algebra, linear, bilinear and quadratic forms are of frequent use.

A *linear form* in n variables is a polynomial defined as

$$f(\boldsymbol{x}) = a_1 x_1 + a_2 x_2 + \ldots. + a_n x_n$$

where a_i are given numbers, the so-called coefficients of the linear form. Having m linear forms

$$\begin{aligned} f_1(\boldsymbol{x}) &= A_{11} x_1 + \ldots + A_{1n} x_n \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ f_m(\boldsymbol{x}) &= A_{m1} x_1 + \ldots + A_{mn} x_n \end{aligned} \tag{A.6}$$

this system of linear forms can be written as the matrix scheme

$$\boldsymbol{f} = \boldsymbol{A}\boldsymbol{x} \tag{A.7}$$

here, $\boldsymbol{f}\,(m \times 1)$ and $\boldsymbol{x}\,(n \times 1)$ are column vectors and $\boldsymbol{A}\,(m \times n)$ is the matrix of the system of linear forms.

Let us now have $2n$ variables $(x_1, \ldots, x_n)$ and $(y_1, \ldots, y_n)$. A *bilinear form* in $2n$ variables is a polynomial of the 2nd degree whose any member is linear in x_i as well as in y_i, for $i = 1, \ldots, n$:

$$f(\boldsymbol{x}, \boldsymbol{y}) = \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} x_i y_j \tag{A.8}$$

In matrix expression

$$f(\boldsymbol{x}, \boldsymbol{y}) = \boldsymbol{x}^{\mathrm{T}} \boldsymbol{A} \boldsymbol{y} \tag{A.9}$$

where $\boldsymbol{A}$ is the matrix of the bilinear form.

A *quadratic form* in n variables $(x_1, \ldots, x_n)$ is a polynomial of the second degree defined as

$$f(\boldsymbol{x}, \boldsymbol{x}) = \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} x_i x_j \qquad \text{where } A_{ij} = A_{ji} \tag{A.10}$$

or in matrix expression

$$f(\boldsymbol{x}, \boldsymbol{x}) = \boldsymbol{x}^{\mathrm{T}} \boldsymbol{A} \boldsymbol{x} \qquad \text{where } \boldsymbol{A} = \boldsymbol{A}^{\mathrm{T}} \tag{A.11}$$

The (symmetric) matrix $\boldsymbol{A}$ is called the matrix of the quadratic form.

For example the quadratic trinomial $x_1^2 + 4x_1 x_2 + x_2^2$ can be written according to Eqn.(A.11) where $\boldsymbol{x}^{\mathrm{T}} = (x_1, x_2)$ and with the symmetric matrix

$$\boldsymbol{A} = \begin{bmatrix} 1 & 2 \\ 2 & 1 \end{bmatrix}$$

A.2.4 Elementary matrix rearrangements

The basic elementary rearrangements are:

1. The multiplication of a row (or column) of the matrix by a number different from zero.
2. The interchange of two rows (or columns) of the matrix.
3. The addition of a row (column) to another row (column). The elementary rearrangements are those composed of the rerrangements 1 through 3.

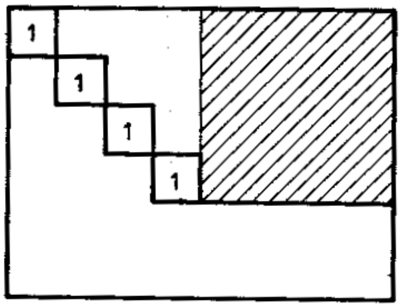


Fig.A.3 — Canonical form of a matrix

By elementary rearrangements, any (generally) rectangular matrix can be transformed to the so-called *canonical form* (see Fig.A.3). In the canonical form , in the left upper corner of the matrix one has the unit matrix while the other rows , if present, equal zero.

Transforming the matrix to the canonical form is a convenient method of determining the rank of the matrix. The rank then equals the order of the unit submatrix in the canonical expression.

A.2.5 Matrices and systems of linear equations

The system of m linear equations in n unknowns $x_1 , \dots , x_n$

$$\begin{aligned} A_{11} x_1 \; + \; \dots\dots \; + A_{1n} x_n &= c_1 \\ A_{m1} x_1 \; + \; \dots\dots \; + A_{mn} x_n &= c_m \end{aligned} \qquad \text{(A.12)}$$

can be written in matrix form

$$\boldsymbol{Ax} = \boldsymbol{c} \qquad \text{(A.13)}$$

The matrix $\boldsymbol{A}$ is called the *matrix of the system* (of equations), the composed matrix $\boldsymbol{A}_r$

$$\boldsymbol{A}_r = [\boldsymbol{A}, \boldsymbol{c}] \qquad \text{(A.14)}$$

is called the *extended matrix* of the system. A convenient method for the discussion of the solvability as well as for the solution proper is transforming the extended matrix of the system to the canonical form. Three basic cases which can thus occur are shown in Fig.A.4

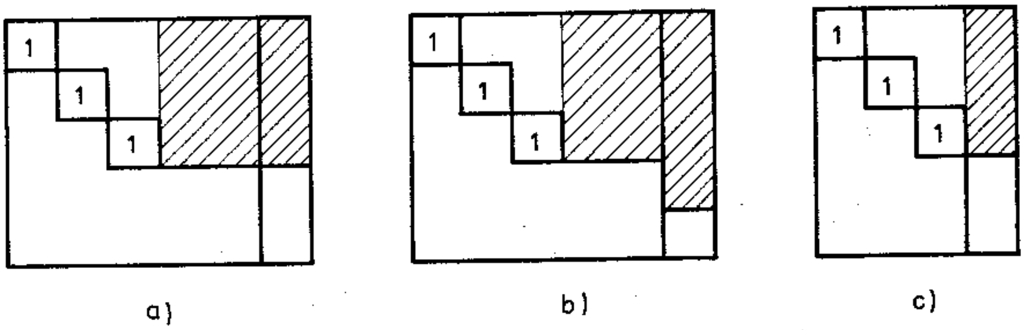


Fig.A.4 — Solvability of linear equations

a) a solvable undetermided system (having an infinity of solutions)
b) a non-solvable system (having no solution)
c) a solvable system with unique solution.

It is essential that the solutions of the original system and that of the system corresponding to the canonical form are identical. On this principle is based the well-known Gauss-Jordan method of elimination for a system of linear equations.

Another method of solution for a system of equations with a regular square matrix makes use of the inverse of matrix $\boldsymbol{A}$

$$\boldsymbol{x} = \boldsymbol{A}^{-1}\,\boldsymbol{c} \tag{A.15}$$

as follows from the multiplication of Eqn.(A.13) from the left by matrix $\boldsymbol{A}^{-1}$.

A.3 CONCEPTS OF PROBABILITY

A.3.1 Random events and their probabilities

Let us suppose that the rate of a chemical reaction depends on the temperature and composition of the reacting solution. If we now fix the temperature and composition in the reactor and measure the reaction rate several times at given conditions, the results will probably differ slightly from case to case. The reasons may be for example the fact that the actual conditions in the reactor differ slightly from the fixed values, that the reaction rate depends also on other, uncontrolled factors or that we have committed certain errors in the reaction rate measurement proper.

The result of the experiment, the measured value of the reaction rate, is a *random event* because this value though can, still need not have been obtained in the given case. More generally, a random event need not be just the finding of a specific value but for example the fact, that the measured value lies in a certain, a priori chosen interval. The laws a random event obeys are *probabilistic (stochastic) laws.*

In this book, we shall meet only cases where the random event will be occurence of a value in an interval (or of a vector in a multidimensional region). The respective intervals (regions) can be conceived as sets; for random events, set concepts and operations can then be introduced. For example if an interval assigned to event A is a part of the interval of event B, one says event A is a part of event B (from event A follows event B). For events one can introduce the notions of equality, union, intersection etc.; the notions refer to the sets assigned to individual events.

Two events which can not occur simultaneously are called *disjoint*. A set of random events is disjoint if the events are two-by-two disjoint. An event S which always occurs under the given set of conditions, is a *sure* event. Important is the notion of a complete set of disjoint events, whose union is a sure event. Dividing the interval (region) assigned to a sure event into a set of not-overlapping intervals (regions), one clearly obtains a complete set of disjoint events.

To any random event A is assigned its probability, i.e. a number $\mathsf{P}(A)$ satisfying the following axioms

a) the probability is nonnegative

$$\mathsf{P}(A) \geq 0$$

b) the probability of a union of disjoint events equals the sum of the probabilities of the events

$$A \text{ and } B \text{ disjoint: } \mathsf{P}(A + B) = \mathsf{P}(A) + \mathsf{P}(B)$$

c) the probability of a sure event equals unity

$$\mathsf{P}(S) = 1$$

To the determination of the numerical value of the probability, one can apply the so-called classical definition of probability. If an experiment is n-times independently repeated and if event A occurs m-times, then its relative frequency equals m/n. If, increasing the number n of repeated experiments the relative frequency converges to a certain number, this number is considered an estimate of the probability $\mathsf{P}(A)$.

A.3.2 Random variables

There is a variety of random events which are encountered in the probability theory. The mathematical treatment requires transforming the random events to so-called *random variables*. In this book, one will meet only the cases where the results of an experiment (measurement) are certain measured values or their functions. In such cases, as the value of a random variable is considered directly the measured value or its function. Here, one has to make a distinction between the random variable and its concrete value (the so-called *realization* of the random variable) obtained as the result of a concrete experiment.

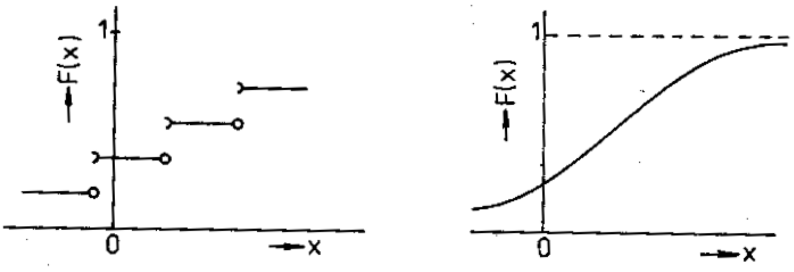
According to whether the random variables can assume only discrete values or can vary continuously, they are divided into discrete and continuous ones. The values obtained from measurements are always given (rounded off) to a certain number of decimal places. For the sake of easier mathematical treatment and also because the actual character of a measured value is usually continuous, we shall regard the measured results as realizations of continuous random variables.

A.3.3 Distribution of random variables

For computing the probability that a random variable assumes a certain value or a value lying in a certain interval, of basic importance is the concept of the *distribution function*. The latter assigns to any real number the probability that the random variable will assume a value lower than this number. The mathematical expression is

$$F\,(x) = \mathrm{P}\,(X < x) \tag{A.16}$$

where X is the random variable, x is a real number and $F\,(x)$ is the distribution function. For examples of distribution functions see Fig.A.5.



a) b)

Fig.A.5 — Distribution functions
a) discrete random variable; b) continuous random variable

The distribution function is non-decreasing and it satisfies $F\,(-\infty) = 0$ and $F\,(+\infty) = 1$. Relevant is the fact that the probability of the occurrence of the random variable in the interval $(x_1\,, x_2\,)$ equals the difference of distribution function values

$$\mathrm{P}\,(x_1 \leq X < x_2\,) = F\,(x_2\,) - F\,(x_1\,) \tag{A.17}$$

For continuous distribution functions, we have

$$\mathrm{P}\,(x_1 < X < x_2\,) = \mathrm{P}\,(x_1 \leq X < x_2\,) = \mathrm{P}\,(x_1 < X \leq x_2\,)$$

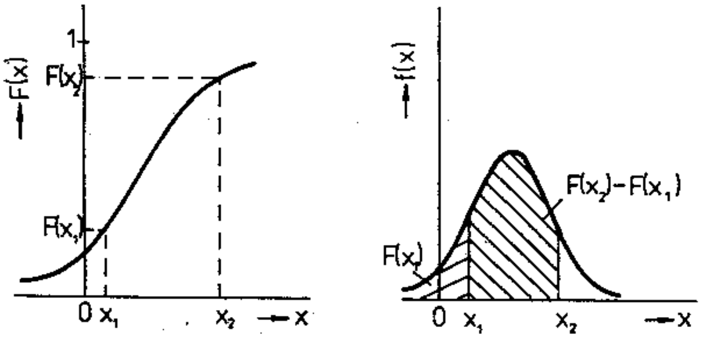
If the distribution function is continuous, the probability distribution law for a random variable can also be expressed in terms of the probability density. A function $f\,(x)$ is the *probability density function* of random variable X at point x, if it is related to the distribution function according to

$$F\,(x) = \int_{-\infty}^{x} f\,(t)\;\mathrm{d}t \tag{A.18}$$

For the probability that the random variable assumes a value from the interval $\langle x_1 , x_1)$, there holds

$$P\,(x_1 \leq X < x_2\,) = \int_{x_1}^{x_2} f\,(t)\;\mathrm{d}t \tag{A.19}$$

The relation illustrates the probabilistic interpretation of the propability density. The relation between the probability density and the distribution function is illustrated in Fig.A.6 [see also Eqns (A.16) through (A.19)].



a) b)

Fig.A.6 — Distribution function (a) and probability density function (b)

One can thus express the probability distribution law for a continuous random variable, using either the distribution function or the probability density; for frequently encountered distributions, both can be found in tables. Of practical importance are so-called *quantiles* of a distribution which are also often tabulated. The *P-quantile* of a given distribution is the value x_P of the argument of the distribution function satisfying the condition:

The probability that the value of a continuous random variable belongs to the interval $(-\infty\ , x_P\ )$ *equals* P; thus

$$\int_{-\infty}^{x_P} f\,(t)\;\mathrm{d}t = F\,(x_P\,) = P$$

The probability P is often given in percent (%). For example, the 95% quantile of a distribution is the value of the argument giving the value of the distribution function equal to 0.95.

Multidimensional random variables

In practical applications of the probability theory, it is often not sufficient to restrict oneself to one random variable only; it is necessary to take into account a vector of random variables simultaneously, i.e. to consider a multidimensional random variable. In the case of n random variables $(X_1 , \ldots , X_n)$, one formulates the probability distribution law for an n-dimensional random variable using a joint distribution function. The function gives the probability that the value of each random variable X_i is simultaneously lower than the respective argument (a real number) x_i of the distribution function. Thus

$$F (x_1 , \ldots , x_n) = \mathrm{P} (X_1 \leq x_1 , \ldots , X_n \leq x_n) \tag{A.20}$$

The n-dimensional joint probability density of continuous random variables $X_1 , \ldots , X_n$ is the function $f (x_1 , \ldots , x_n)$ related to the corresponding distribution function as follows

$$F (x_1 , \ldots , x_n) = \int_{-\infty}^{x_n} \ldots \int_{-\infty}^{x_1} f (t_1 , \ldots , t_n) \, \mathrm{d}t_1 \ldots \mathrm{d}t_n \tag{A.21}$$

In addition to the joint probability density, the so-called marginal probability densities for individual random variables are introduced. Thus, the *marginal density* for variable X_1 is by definition

$$f_1 (x_1) = \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} f (x_1 , t_2 , \ldots , t_n) \, \mathrm{d}t_2 \ldots \mathrm{d}t_n \tag{A.22}$$

The marginal distribution function $F_1 (x_1)$

$$F_1 (x_1) = \int_{-\infty}^{x_1} f_1 (t_1) \, \mathrm{d}t_1 \tag{A.23}$$

gives the probability that a value of the random variable X_1 will be lower than x_1, irrespective of the values of other random variables.

The notions of marginal probability density and of marginal distribution function can also be extended to arbitrary couples of random variables. For example the two-dimensional marginal distribution function $F_{ij} (x_i , x_j)$ satisfies the relation

$$F_{ij} (x_i , x_j) = \mathrm{P} (X_i < x_i , X_j < x_j) \tag{A.24}$$

irespective of the values of other random variables.

Of particular importance is the notion of the statistical independence of two random variables. Two random variables are *statistically independent* if the value of one random variable is independent of the value other variable has assumed. A necessary and sufficient condition for the independence of random variables X_i and X_j is the validity of the equation

$$F_{ij}(x_i, x_j) = F_i(x_i)\,F_j(x_j) \tag{A.25}$$

For independent random variables, the two-dimensional marginal distribution function is thus always equal to the product of the respective one-dimensional marginal distribution functions.

A.3.4 Characteristics of random variables and of their functions

The distribution law of a random variable, as expressed by the distribution function, describes the behaviour of the random variable completely, but it is not always sufficiently lucid. The characteristics of a random variable are numbers characterizing in a straitforward manner certain selected properties of its distribution. In what follows let us confine ourselves to two such characteristics, *viz.* the position characteristics, which is the mean, and the variability characteristics, which is the variance (dispersion) of the random variable.

The mean of a continuous random variable X, denoted $\mathsf{E}\,(X)$ or μ_x is defined by

$$\mathsf{E}\,(X) = \int_{-\infty}^{+\infty} x\,f(x)\,\mathrm{d}x \tag{A.26}$$

where $f(x)$ is the probability density of the random variable X. In addition to the mean value, there exist also other position characteristics; best known are the median and the modus. The *median M* is the value for which there holds $\mathsf{P}\,(X \leq M) = 1/2$. The *modus* of a discrete or continuous random variable is the value giving the maximum probability or probability density, respectively.

The *variance* of a continuous random variable is defined by

$$\mathsf{D}\,(X) = \int_{-\infty}^{+\infty} [x - \mathsf{E}\,(X)]^2 f(x)\,\mathrm{d}x \tag{A.27}$$

The variance is also denoted by σ_X^2 and its square root is called the *standard deviation.*

For multivariate random variables, one can define the mean values and variances of separate random varibles by the equations (A.26) and (A.27); here, for the probability density one substitutes the marginal probability density of the given random variable.

The notions of mean and variance can be generalized for functions of random variable X, for example $Y = y(X)$. The mean and the variance of the function are, respectively

$$\mathrm{E}(Y) = \int_{-\infty}^{+\infty} y(t) f(t)\, \mathrm{d}t \tag{A.28}$$

$$\mathrm{D}(Y) = \int_{-\infty}^{+\infty} [y(t) - \mathrm{E}(Y)]^2 f(t)\, \mathrm{d}t \tag{A.29}$$

Let us now consider an n-dimensional random variable $x = (X_1, \ldots, X_n)$. Besides the previously defined mean values and variances of separate vector components, a measure of statistical independence of the components, the so-called covariance is important. The *covariance* of two random variables X_i and X_j is denoted cov (X_i, X_j) and is defined by

$$\mathrm{cov}(X_i, X_j) = \mathrm{E}\{[X_i - \mathrm{E}(x_i)][X_j - \mathrm{E}(X_j)]\} \tag{A.30}$$

For random variables X_i and X_j with two-dimensional marginal probability density $f_{ij}(x_i, x_j)$ we have

$$\mathrm{cov}(X_i, X_j) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} t_i t_j f_{ij}(t_i, t_j)\, \mathrm{d}t_i\, \mathrm{d}t_j - \mathrm{E}(X_i)\,\mathrm{E}(X_j) \tag{A.31}$$

With the covariance is closely connected the *correlation coeficient* $\rho(X_i, X_j)$, a dimensionless measure of the correlatedness of two random variables

$$\rho(X_i, X_j) = \frac{\mathrm{cov}(X_i, X_j)}{\sigma_{x_i}\sigma_{x_j}} \tag{A.32}$$

The correlation coefficient takes its values from the interval $\langle -1, 1\rangle$. If the coefficient is null, the variables are called *uncorrelated.* If $|\rho| = 1$, there is a deterministic linear relation between the random variables.

The covariances and the correlation coefficients of an n-dimensional random vector x can be arranged into the so-called *covariance matrix* and *correlation matrix*, respectively. These matrices of type $n \times n$ are symmetric and the elements in the ith row and jth column equal cov (X_i, X_j) and $\rho(X_i, X_j)$, respectively. The elements of the diagonal of the covariance matrix are the variances of the components of the random vector. On the diagonal of the corelation matrix, one has unities.

An important relation is that between the correlatedness and the statistical independence of random variables. If two random variables are statistically independent, they are also uncorrelated. A converse assertion (that the correlatedness implies the independence) does not hold generally for any type of distribution of random variables; but it holds true in the most frequent case where the random variables have the multidimensional normal distribution. Therefore, in practice, the covariances or correlation coefficients are employed as a measure of independence of random variables, and one often makes no distinction between the notions of uncorrelatedness and independence.

A.3.5 Important distributions of random variables

In what follows, we shall restrict ourselves to those distributions of continuous random variables which are important from the standpoint of measured data processing.

Uniform distribution

The distribution of a random variable is called *uniform* (*rectangular*), if the probability density is constant on the whole interval of values the variable can assume. Thus if the range of values of the random variable is the interval $\langle a , b\rangle$ then the probability density equals

$$\begin{aligned} f(x) &= 1 / (b - a) && \text{for } x \in \langle a , b\rangle \\ f(x) &= 0 && \text{otherwise} \end{aligned} \tag{A.33}$$

and the distribution function is

$$\begin{aligned} &0 && \text{for } x < a \\ F(x) &= (x - a) / (b - a) && \text{for } a \le x \le b \\ &1 && \text{for } x > b \end{aligned}$$

Both functions are depicted on Fig.A.7. The basic characteristics satisfy

$$\mathsf{E}(x) = (a + b) / 2 \tag{A.34}$$

$$\mathsf{D}(x) = (b - a)^2 / 12 \tag{A.35}$$

Normal (Laplace - Gauss) distribution

The *normal distribution* is the most important distribution of a continuous random variable; under certain circumstances, also some other distributions can be approximated as normal. The probability density of the normal distribution is given by the function

$$f(x) = \frac{1}{\sigma (2\pi)^{1/2}} \exp\left[- \frac{(x - \mu)^2}{2 \sigma^2} \right] \tag{A.36}$$

The function is characterized by two prameters, μ and σ, where μ equals the mean and σ the standard deviation of the random variable. The normal distribution is written briefly as $N(\mu\ ,\ \sigma^2\ )$. Examples of probability densities are given in Fig.A.8a.

If $\mu = 0$ and $\sigma = 1$, one speaks of the *standard normal distribution* $N\ (0{,}1)$ and the random variable is denoted by U. The quantiles of the standard normal distribution, denoted as u_p , are given in Tab. A.1 (see also Fig. A.8b). The importance of the standard normal distribution consists in the universality of its application. It is obtained from a random variable X, normally distributed as $N\ (\mu\ ,\ \sigma^2)$, by the transformation $U = (X - \mu)\ /\ \sigma$. The distribution of the random variable U is then $N\ (0{,}1)$.

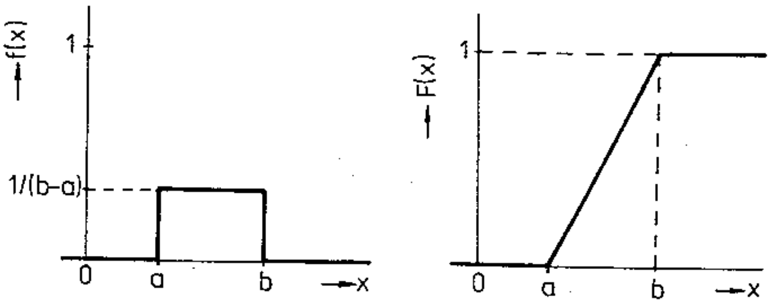


Fig.A.7 — Uniform (rectangular) distribution
[probability density function $f\ (x)$ and distribution function $F\ (x)$]

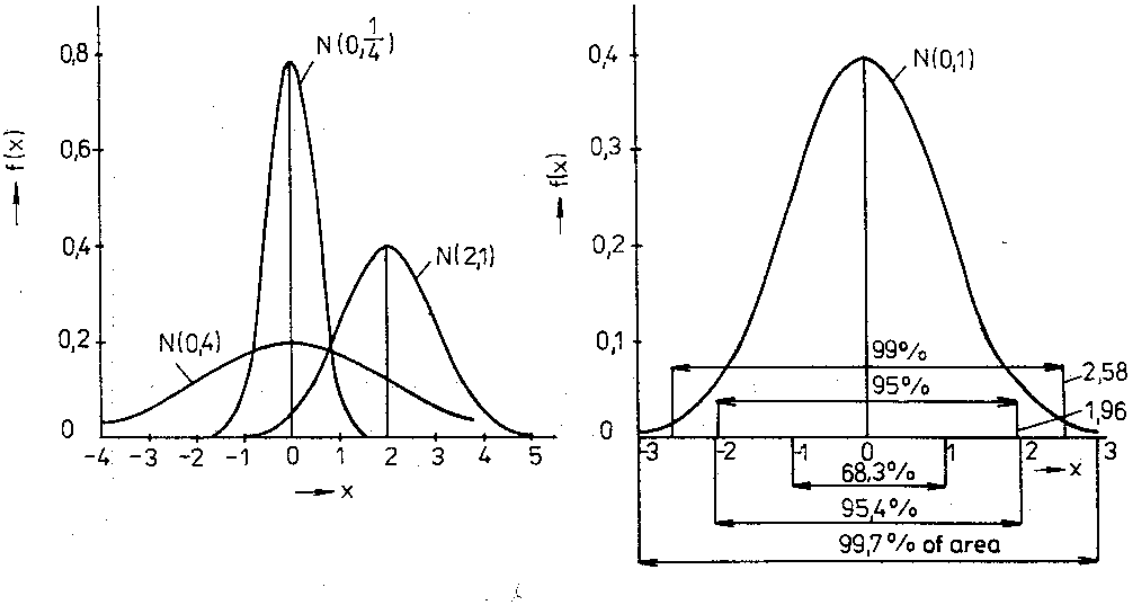


Fig.A.8 — Probability density function of a normal distribution

Table A.1 — Quantiles of standard normal distribution
$\mathrm{P}\,(U < u_P\,) = P$

P	0.500	0.900	0.950	0.975	0.990	0.995	0.999
u_P	0.000	1.282	1.645	1.960	2.326	2.576	3.090

If a quantile of the distribution $N\,(\mu\,,\sigma^2\,)$ is to be found, one proceeds as follows. From Tab. A.1 one takes the respective quantile u_P of the standard normal distribution and the sought-for quantile x_P follows from the relation $x_P = \mu + \sigma\, u_P$.

The normal distribution is symmetric; hence the probability density, the distribution function and the quantiles satisfy the respective relations

$$f\,(u) = f\,(-u) \tag{A.37}$$

$$F\,(u) = 1 - F\,(-u) \tag{A.38}$$

$$u_P = -\,u_{1\,-\,P} \tag{A.39}$$

It is important to know that the values $\alpha < 0.5$ satisfy

$$\mathrm{P}\,\{\,|U| < u_{1\,-\,\alpha/2}\,\} = 1 - \alpha \tag{A.40}$$

Multivariate normal distribution

The distribution of n-dimensional random variable $x = (X_1\;,\;\ldots\;,\;X_n\;)$ is called *n-variate normal distribution* of random vector $\boldsymbol{x}$ if its joint probability density equals

$$f\,(\boldsymbol{x}) = k\,\exp\,(-q\,/\,2) \tag{A.41}$$

where

$$k = (2\pi)^{-n/2}\,[\det\,\boldsymbol{F}]^{-1/2}$$

and

$$q = (\boldsymbol{x} - \mu)^{\mathrm{T}}\,\boldsymbol{F}^{1}\,(\boldsymbol{x} - \mu)$$

here, μ is the vector of mean values $\mathrm{E}\,(\boldsymbol{x})$ and $\boldsymbol{F}$ is the covariance matrix of the random vector $\boldsymbol{x}$. One supposes $\boldsymbol{F}$ to be regular. The distribution is denoted $N_n\,(\mu\,,\boldsymbol{F})$.

The loci of constant probability density satisfy the equation

$$q = (\boldsymbol{x} - \mu)^{\mathrm{T}}\,\boldsymbol{F}^{-1}\,(\boldsymbol{x} - \mu) = \mathrm{const} \tag{A.42}$$

which is the equation of n-dimensional ellipsoid ($n = 2$: ellipse, $n > 3$: hyperellipsoid).

It is important to know the probability that the realization of a random vector will occur inside a given ellipsoid. Let us have a random vector with distribution $N_n(\mu, \boldsymbol{F})$; then the ellipsoid whose equation is

$$q = (\boldsymbol{x} - \mu)^{\mathrm{T}} \boldsymbol{F}^{-1} (\boldsymbol{x} - \mu) = \chi^2_{1-\alpha}(n) \qquad \text{(A.43)}$$

contains the variables with the probability $(1 - \alpha)$. The expression $\chi^2_{1-\alpha}(n)$ denotes here the 100 $(1 - \alpha)$ percent quantile of the χ^2 distribution with n degrees of freedom (see below).

Example A.1: *Bivariate normal distribution*

Let us consider the distribution $N_2(\boldsymbol{0}, \boldsymbol{F})$ where $\boldsymbol{F} = \begin{bmatrix} 4 & 0 \\ 0 & 1 \end{bmatrix}$. In this case, the probability density is given by the equation

$$f(x_1, x_2) = \{ \exp [-(x_1^2/4 + x_2^2) / 2]\} / (4\pi) \qquad \text{(A.44)}$$

The equation of the ellipse of constant probability density is obtained by taking the logarithm and by a rearrangement of the equation (A.44)

$$(x_1 / 2)^2 + x_2^2 = - 2 \ln (4\pi) - 2 \ln [f(x_1, x_2)] = K^2 \qquad \text{(A.45)}$$

The equation (A.45) can be rearranged to yield the standard equation of an ellipse

$$[(x_1 / (2K)]^2 + (x_2 / K)^2 = 1 \qquad \text{(A.46)}$$

where the values $2K$ and K are the lengths of the respective semi-axes. The ellipses for probability equal to 0.04, 0.01 and 0.001 are presented in Fig.A.9.

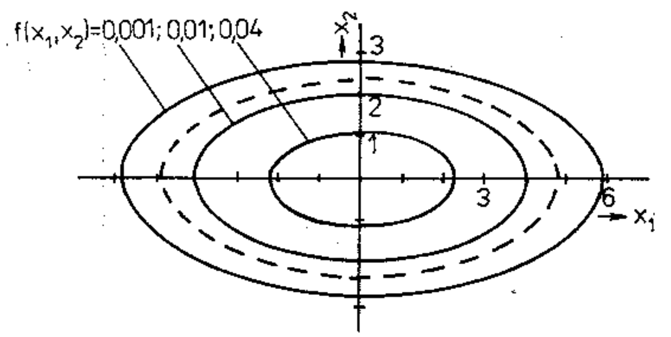


Fig.A.9 — Contours of probability density of two-dimensional normal distribution (Example A.1)
—— constant probability density
- - - 95% realizations inside the ellipse

Let us search further for the ellipse inside which is contained 95% realizations of the random vector. According to (A.43) its equation reads

$$(x / 2)^2 + x_2^2 = \chi^2_{0.95}(2) = 5.99 \tag{A.47}$$

The ellipse is depicted by the dashed curve on Fig.A.9.■

The χ^2 distribution

Let us have ν random variables $U_1, \dots, U_\nu$, mutually uncorrelated, each of them having the distribution $N(0, 1)$. The random variable χ^2 defined as the sum of squares of the random variables

$$\chi^2 = U_1^2 + \dots + U_\nu^2 \tag{A.48}$$

has the *chi-square* distribution with ν degrees of freedom, denoted by $\chi^2(\nu)$. The diagrams of the probability densities of the χ^2 distributions are shown in Fig.A.10, for several degrees of freedom. The quantiles are given in Tab.A.2.

Table A.2 — Quantiles of χ^2 distribution
$P[\chi^2 < \chi_P^2(\nu)] = P$

ν	P			ν	P		
	0.90	0.95	0.99		0.90	0.95	0.99
1	2.71	3.84	6.64	16	23.54	26.30	32.00
2	4.61	5.99	9.21	17	24.77	27.59	33.41
3	6.25	7.82	11.35	18	25.99	28.87	34.81
4	7.78	9.49	13.28	19	27.20	30.14	36.19
5	9.24	11.07	15.09	20	28.41	31.41	37.57
6	10.65	12.59	16.81	21	29.62	32.67	38.93
7	12.02	14.07	18.48	22	30.81	33.92	40.29
8	13.36	15.51	20.09	23	32.01	35.17	41.64
9	14.68	16.91	21.67	24	33.20	36.15	42.98
10	15.99	18.31	23.21	25	34.38	37.65	44.31
11	17.28	19.58	24.73	26	35.56	38.89	45.64
12	18.55	21.03	26.22	27	36.74	40.11	46.96
13	19.81	22.36	27.69	28	37.92	41.34	48.28
14	21.06	23.69	29.14	29	39.09	42.56	49.59
15	22.31	25.00	30.59	30	40.26	43.77	50.89

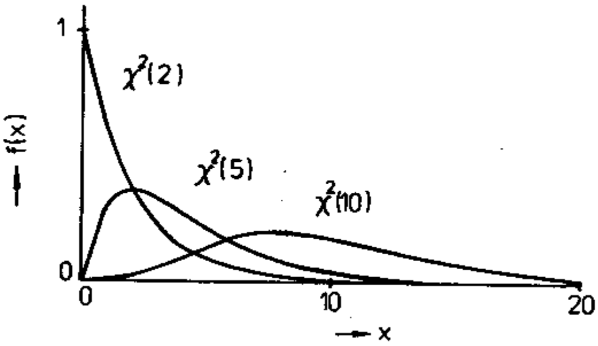


Fig.A10 — Probability density function of χ^2 distribution

The mean and the variance satisfy the relations

$$\mathrm{E}\,[\chi^2\,(\nu)] = \nu \tag{A.49}$$

$$\mathrm{D}\,[\chi^2\,(n)] = 2\nu \tag{A.50}$$

Noncentral χ'^2 distribution

Let us have ν random variables $U_1\,, \dots\,, U_\nu$ which are mutually uncorrelated, the distribution of the ith variable being $N\,(\mu_i\,, 1)$. The random variable χ'^2 defined as the sum of squares of these variables

$$\chi'^2 = U_1^2 + \dots + U_\nu^2 \tag{A.51}$$

has the *noncentral chi-square* distribution with ν degrees of freedom and with noncentrality parameter δ; it is denoted by $\chi'^2\,(\nu\,, \delta)$. The noncentrality parameter δ is determined by the relation

$$\delta = \left[\,\sum_{i=1}^{\nu} \mu_i^2\right]^{1/2} \tag{A.52}$$

(The terminology is not unique. In certain papers, as the noncentrality parameter is designated the quantity $\lambda = \delta^2$). If the noncentrality parameter equals zero, one obtains the usual (central) χ^2 distribution defined by Eqn. (A.48). If a χ^2 distribution is given without more precise denotation, the central χ^2 distribution is meant. For the mean and variance we have

$$\mathrm{E}\,[\chi'^2\,(\nu\,, \delta)] = \nu + \delta^2 \tag{A.53}$$

$$\mathrm{D}\,[\chi'^2\,(\nu\,, \delta)] = 2\nu + 4\delta^2 \tag{A.54}$$

The t (Student) distribution

Let us have two independent random variables U and χ^2. Let U have the distribution N (0,1) and let χ^2 have the distribution χ^2 (ν) . The random variable t

$$t = \frac{U}{(\chi^2 / \nu)^{1/2}} \tag{A.55}$$

has the distribution t with ν degrees of freedom, written as t (ν).

The probability density for several degrees of freedom is in Fig.A.11. The quantiles of the distribution, denoted by t_P (ν), are in Tab.A.3. The distribution is symmetric. It thus satisfies relations analogous to the relation (A.37) through (A.40), in particular

Table A.3 — Quantiles of t distribution
$P\,[t < t_P\,(\nu)] = P$

ν	P			ν	P		
	0.95	0.975	0.995		0.95	0.975	0.995
1	6.31	12.71	63.66	14	1.76	2.15	2.98
2	2.92	4.30	9.93	15	1.75	2.13	2.95
3	2.35	3.18	5.84	16	1.75	2.12	2.92
4	2.13	2.78	4.60	17	1.74	2.11	2.90
5	2.02	2.57	4.03	18	1.73	2.10	2.88
6	1.94	2.45	3.71	19	1.73	2.09	2.86
7	1.90	2.37	3.50	20	1.73	2.09	2.85
8	1.86	2.31	3.36	25	1.71	2.06	2.79
9	1.83	2.26	3.25	30	1.70	2.04	2.75
10	1.81	2.23	3.17	40	1.68	2.02	2.70
11	1.80	2.20	3.11	60	1.67	2.00	2.66
12	1.78	2.18	3.06	120	1.66	1.98	2.62
13	1.77	2.16	3.01		1.65	1.96	2.58

$$P\,\{\,|t| < t_{1-\alpha/2}\,(\nu)\} = 1 - \alpha \tag{A.56}$$

Increasing the number of degrees of freedom, the t distribution converges to the N (0,1) distribution.

The *F* (Snedecor) distribution

Let us have two independent random variables χ_1^2 and χ_2^2 having distributions $\chi^2(\nu_1)$ and $\chi^2(\nu_2)$, respectively. The random variable F

$$F = \frac{\chi_1^2 / \nu_1}{\chi_2^2 / \nu_2} \qquad \text{(A.57)}$$

has the distribution F with ν_1 and ν_2 degrees of freedom, denoted by $F(\nu_1, \nu_2)$.

The diagrams of the probability density are shown in Fig.A.12. The quantiles of the distribution, denoted by $F_P(\nu_1, \nu_2)$, are in Tab.A.4. The quantiles satisfy the relation

$$F_{1-P}(\nu_1, \nu_2) = 1 / F_P(\nu_2, \nu_1) \qquad \text{(A.58)}$$

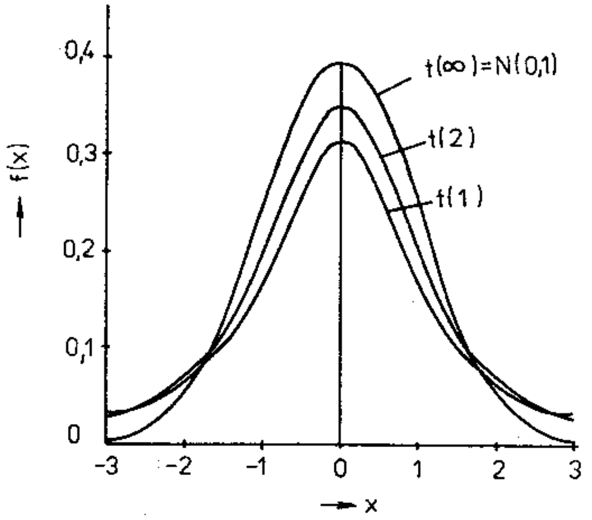


Fig.A.11 — Probability density function of *t* distribution

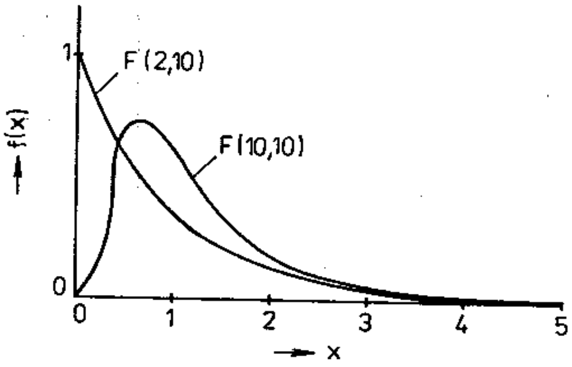


Fig.A.12 — Probability density functions of *F* distribution

A.3.6 Random (stochastic) processes

A random (stochastic) process is a generalization of the concept of a random variable. From the mathematical point of view, this process is a random function of time; from the physical point of view, it means a process whose course in time is random.

As an example, let us consider the course of the temperature of gaseous ammonia at the outlet from a pre-heater. Although this quantity is controlled, it fluctuates around the desired value due to extraneous perturbations. In Fig.A.13 are depicted four realizations of the course of the temperature in time. Observing the individual realizations we see that their courses are different, although they belong to the same random process. The knowledge of the course of a realization in the past does not allow us to determine its future course. The properties of a random process can only be described by statistical means.

Mathematically, a random process can be defined as the set of all possible realizations with common statistical properties (the analogy to a random variable and its realization being obvious).

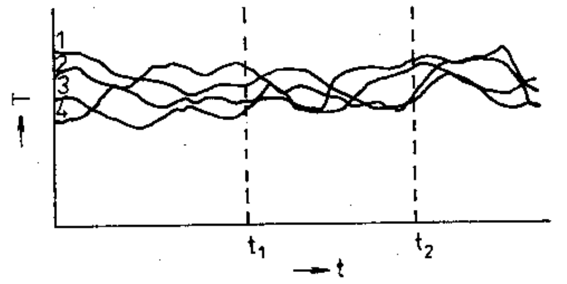


Fig.A.13 — Repeated measurements of ammonia temperature

Statistical properties of random processes

Suppose we dispose of the set of all possible realizations of a random process. In analogy to the case of a random variable, one can define the distribution function or the probability density function. At a certain time instant t, individual realizations of the random process may assume different values. The distribution of the values is characterized by the distribution function $F(x, t)$ which is generally a function of time.

For a brief description of random processes, in the same manner as for random variables different characteristics are employed. Most frequent are the mean and the variance. Important is the fact that the numerical characteristics can be defined either as the characteristics of all realizations of a random process at a given time instant, or as the characteristics in time for a unique realization of the process.

Table A.4 — Quantiles of F distribution
$P\,[F < F_P\,(\nu_1\,,\nu_2\,)] = 0.95$

ν_1	ν_2									
	1	2	3	4	5	6	7	8	9	10
1	161	18.51	10.13	7.71	6.61	5.99	5.59	8.32	5.12	4.96
2	200	19.00	9.55	6.94	5.79	5.14	4.74	4.46	4.26	4.10
3	216	19.16	9.28	6.59	5.41	4.76	4.35	4.07	3.86	3.71
4	225	19.25	9.12	6.39	5.19	4.53	4.12	3.84	3.63	3.48
5	230	19.30	9.01	6.26	5.05	4.39	3.97	3.69	3.48	3.33
6	234	19.33	8.94	6.16	4.95	4.28	3.87	3.58	3.37	3.22
7	237	19.36	8.88	6.09	4.88	4.21	3.79	3.50	3.29	3.14
8	239	19.37	8.84	6.04	4.82	4.15	3.73	3.44	3.23	3.07
9	241	19.38	8.81	6.00	4.78	4.10	3.68	3.39	3.18	3.02
10	242	19.39	8.78	5.96	4.74	4.06	3.63	3.34	3.13	2.97
11	243	19.40	8.76	5.93	4.70	4.03	3.60	3.31	3.10	2.94
12	244	19.41	8.74	5.91	4.68	4.00	3.57	3.28	3.07	2.91
14	245	19.42	8.71	5.87	4.64	3.96	3.52	3.23	3.02	2.86
16	246	19.43	8.69	5.84	4.60	3.92	3.49	3.20	2.98	2.82
20	248	19.44	8.66	5.80	4.56	3.87	3.44	3.15	2.93	2.77
24	249	19.45	8.64	5.77	4.53	3.84	3.41	3.12	2.90	2.74
30	250	19.46	8.62	5.74	4.50	3.81	3.38	3.08	2.86	2.70
40	251	19.47	8.60	5.71	4.46	3.77	3.34	3.05	2.82	2.67
50	252	19.47	8.58	5.70	4.44	3.75	3.32	3.03	2.80	2.64
75	253	19.48	8.57	5.68	4.42	3.72	3.29	3.00	2.77	2.61
100	253	19.49	8.56	5.66	4.40	3.71	3.28	2.98	2.76	2.59
200	254	19.49	8.54	5.65	4.38	3.69	3.25	2.96	2.73	2.56
500	254	19.50	8.54	5.64	4.37	3.68	3.24	2.94	2.73	2.55
∞	254	19.50	8.53	5.63	4.36	3.67	3.23	2.93	2.71	2.54

There is a property of random process which, in contrast to the preceding ones, has no analogy in case of random variables; it is the so-called autocorrelation function. The *autocorrelation function* $R\,(t_1\,,t_2\,)$ of the set of realizations of random process $X\,(t)$, for two different time instants t_1 and t_2, equals

$$R\,(t_1\,,t_2\,) = \mathsf{E}\,[X\,(t_1\,)\,X\,(t_2\,)] = \mathsf{E}\,[X\,(t_1\,)\,X\,(t_1 + \tau)] \tag{A.59}$$

here, $\tau = t_2 - t_1$ is the so called *time shift*. It is thus the mean value of the product of the random functions at times t_1 and t_2.

Of particular importance are random processes whose autocorrelation function depends only on the shift τ:

$$R\ (t_1\ ,\ t_2 + \tau) = R\ (\tau)$$

for all t_1 .

Types of random processes

According to the statistcal properties, random processes are divided into several groups. A process whose all statistical properties are constant in time is called *stationary* (in the *strict sense*). A less strict form of stationarity is the stationarity in the *wide sense*; here, only the constant character of the mean and variance and further the dependence of the autocorrelation function on the shift only are required. In practice, one frequently assumes the stationarity in the strict sense for processes where only the stationarity in the wide sense has been proved.

An important subgroup of stationary random processes are *ergodic processes*. They are characterized by the property that the statistical characteristics of all realizations at any moment equal the the respective statistical characteristics of any realization in time. For the determination of the properties of an ergodic random process, it is therefore not necessary to know all its realizations; one suffices. Physical stationary random processes met in practice can usually be considered as ergodic.

Nonstationary random processes have statistical properties variable in time. In Fig.A.14 are shown the most important types of nonstationary random processes.

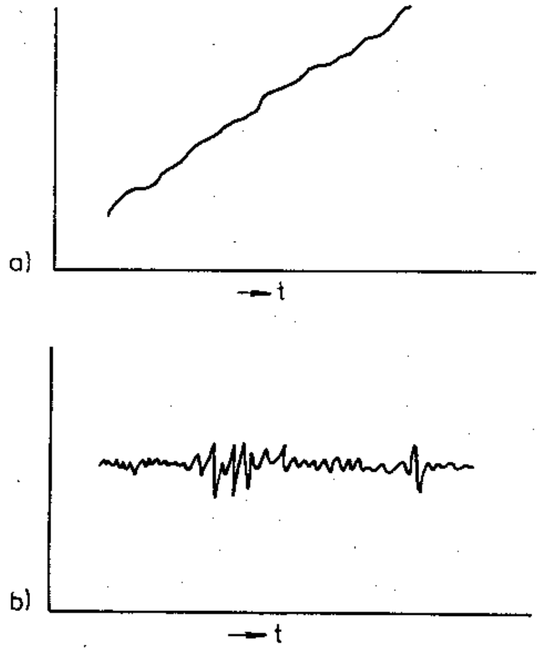


Fig.A.14 — Realizations of random processes
a) variable mean value; b) variable dispersion

Random processes can also be divided according to other criteria. If a random variable can assume continuously all possible values, one speaks of a continuous random process. If the variable can assume only certain values, a discrete random process is involved. A random process defined only in certain time instants is the so-called *random time series.*

A.4 MATHEMATICAL STATISTICS

A.4.1 Basic concepts

Mathematical statistics is concerned with processing measured or otherwise obtained data under the assumption that they are realizations of random variables. It is based upon the theory of probability and it employs its concepts.

The basic concepts of mathematical statistics are the basic ensemble and the random sample.

The *basic ensemble* is the set of events we dispose of in the discussion of a given problem. The basic ensemble can be actual or hypothetical. Let us for example assume we have to determine the mean concentration of the certain substance in the delivery of a raw material. From the material of mass 1000 kg we take samples of mass 10 g and we carry out the chemical analysis. In the total, one could take 10^5 samples and the same number of results could be obtained from the analysis. The results could be regarded as random events. In the given example, the basic ensemble represented by the set of all possible samples was actual and finite (it had a finite number of elements).

Let us further suppose we examine the accuracy of some given analytical method carried out under prior defined conditions, in the manner that we shall repeat the determination of the substance in identical samples prepared in advance. The basic ensemble represented by possible future analyses is then hypothetical and infinite (the number of possible future analyses is not bounded).

In most cases, it is not possible to measure all elements of the basic ensemble. Mathematical statistics judges on the properties of the basic ensemble from those of its part, the so-called *sample.* The sample should have the properties close to those of the basic ensemble (it should be *representative*). A *random* sample is such that all elements of the basic ensemble have the same probability of being included in the sample. Within the process industries, a random sampling means, for example, to take a sample from any place or, in continuous processes, at any time.

From the variables identified using the random sampling one computes their functions, the so-called *statistics* (*sample statistics*). Examples of statistics are the sample mean or the sample variance. A characteristic feature of statistics is the fact that computing them does not involve unknown parameters of the distribution of random variables in the random sample. The statistics are themselves random variables with a certain distribution which can be deduced from the distribution of the random sample and from the functional relationship between the random sample and the statistics.

In the statistical processing of a random sample, the most frequent task is gathering information on unknown parameters of the distribution of the basic ensemble. One speaks of the parameter *estimates* which can be either point or interval estimates.

A *point estimate* is a statistic considered further as a sought-for parameter. Since the statistic itself is the realization of a random variable, this estimate is usually not identical to the sought-for parameter, it only approaches its value. Important properties of point estimates are unbiasedness, efficiency and consistency.

An estimate is called *unbiased* if its mean value equals the actual value of the parameter.

An estimate is called *efficient* if it is unbiased with minimum variance for any sample size and for any admissible value of the parameter; if it holds only in the limit for sample size $n \to \infty$, it is called *asymptotically efficient*.

An estimate is *consistent* if, for $n \to \infty$, it converges in probability to the true value of the parameter. That means that with a sufficiently large sample the probability that the estimate value will differ from the true parameter value by less than an arbitrary small difference, will approach unity.

According to the criteria mentioned above, the estimates obtained on the basis of the *maximum likelihood* principle show very good properties. For details of the method of maximum likelihood, see the literature (Hines & Montgomery 1980).

The other type of estimate is the interval which with a certain prior chosen probability contains the sought-for parameter (the so-called *interval estimate*). If more parameters are estimated simultaneously, a point estimate is a vector in a multidimensional space; an analogy to the interval estimate is, in this case, a *region* in the multidimensional space, viz the region where the actual vector of parameters occurs with a chosen probability.

With the notion of interval estimates is closely connected the notion of confidence interval. Suppose the result of the interval estimate of parameter Θ is the interval with extreme points h_1 and h_2. The interval is called the 100 (1 - α) percent *confidence interval* for the parameter Θ if we have

$$\mathsf{P}\,(h_1 \le \Theta < h_2) = 1 - \alpha \tag{A.60}$$

The number $(1 - \alpha)$ is called the confidence coefficient. The relation (A.60) says that the interval $\langle h_1, h_2 \rangle$ covers the actual value of the parameter Θ with probability $(1 - \alpha)$. The confidence coefficient is usually chosen close to unity, in engineering problems most frequently 0.95.

A.4.2 Testing of statistical hypotheses

Sometimes we are interested in whether a certain assertion concerning properties of the basic ensemble holds true; for example whether the mean value equals a given, prior fixed value. Such assertions are called *statistical hypotheses*.

The procedure of deciding on the validity of a postulated hypothesis is the so-called testing of a statistical hypothesis. The hypothesis whose validity is being tested is called the *null hypothesis*, the hypothesis confronted with the former is the *alternate hypothesis*. The test of the null hypothesis H_0 against the alternate hypothesis H_1 leads, on the basis of examining a random sample, either to rejecting H_0 or to not-rejecting H_0 (i.e. to rejecting H_1). Here, the nonrejection of H_0 cannot be identified with its acceptance, although the practical consequences of both are usually the same. The nonrejection of a hypothesis simply means that on the basis of available information, there is no reason to doubt the validity of the hypothesis.

In testing a hypothesis one proceeds as folows. One postulates a certain hypothesis on the basic ensemble. One takes a sample of size n, i.e. a vector $\boldsymbol{X} = (X_1 , \dots , X_n)$. One chooses an appropriate statistic $T = T(X_1 , \dots , X_n)$ which in this case is called the *testing criterion*. One finds the distribution of the random variable T under the assumption that the null hypothesis holds. The interval, where the statistic can be contained [for example $(-\infty ; +\infty)$], is divided into two intervals, the interval R and its complement R'. R is chosen in the manner that under the validity of H_0 the statistics T assumes a value from this interval with probability $(1 - \alpha)$. The interval R is most frequently chosen such that for given α, its length is minimum. The value of α is chosen sufficiently small (for example 0.05) and it is called the *level of significance*. The region R' is called the *critical region*. From the random sample one now computes the statistic T. If T assumes a value from the critical region R', the hypothesis H_0 is rejected.

In testing hypotheses one can commit basically two kinds of errors.

An error of the *first kind* consists in rejecting the hypothesis on the basis of a random sample while the hypothesis, in fact, holds true. The probability of an error of the first kind is the significance level α.

If the hypothesis H_0 does not hold but is not rejected on the basis of a random sample, one speaks of an error of the *second kind*. The probability of an error of the second kind is denoted by β, and the value $(1 - \beta)$ is called the *power* of the test.

While the probability of an error of the first kind for a given test was a single number (equal to the significance level), the power of the test depends on how much the null hypothesis deviates from the reality. If we are able to measure this deviation in some way, the dependence of β on the deviation is called the *operating characteristic* of the test. If the hypothesis can be tested by two or more tests (with the same significance level), the test yielding the smallest value of probability of an error of the second kind is called the *strongest* (*most powerful*) test.

Let us now illustrate the most important problems of testing statistical hypotheses with the help of a simple example.

Example A.2: *Testing a statical hypothesis*
A liquid flows through a pipe with a volume flow rate V. On the pipe, two flowmeters are installed: A and B. For the values V_A and V_B measured by the respective flowmeters we have

$$V_A = V + d_A \qquad V_B = V + d_B$$

where d_A and d_B are the respective random errors of measurement. We suppose the errors behave as normally distributed random variables with zero mean and with variances σ_A^2 and σ_B^2, respectively. The flowmeter A is prone to give a systematic error; our aim is to judge, on the basis of the measured values, whether such an error actually arises in flowmeter A.

Let us formalize the problem mathematically. The above equations are rewritten as

$$V_A = V + d_S + d_A \qquad V_B = V + d_B$$

where d_S is the systematic error of flowmeter A. The hypothesis that the flowmeter A is not subjected to a systematic error will be written in the form $d_S = 0$ (hypothesis H_0), the alternate hypothesis reads $d_S \neq 0$.

Let us now carry out a sampling, which in our case is represented by measuring the values of V_A and V_B. As a statistic, let us take the difference of the measured values

$$T = V_A - V_B = d_S + d_A - d_B$$

Assuming the validity of H_0 (i.e. $d_S = 0$), T equals the sum of two random variables with zero mean and with normal distribution and it also has a normal distribution $N(0\ ,\ \sigma_A^2 + \sigma_B^2)$. It can thus take the values from the interval $(-\infty\ ,\ +\infty)$.

Let us further choose the significance level α and the corresponding interval R. In Fig.A.15a, we have the probability density of the statistic T. Because T has a normal distribution with zero mean, let us take the interval R symmetric with respect to zero

$$R = \langle -\sigma_T\, u_{1-\alpha/2}\ ,\ \sigma_T\, u_{1-\alpha/2} \rangle$$

where $\sigma_T = (\sigma_A^2 + \sigma_B^2)^{1/2}$ and $u_{1-\alpha/2}$ is the quantile of the distribution $N(0,1)$.

Let us now assume H_0 holds, thus $d_S = 0$. In 100 α percent of cases the value of T falls into the interval R' and the hypothesis H_0 will be unduly rejected. The probability of this error of the first kind is depicted by the hatched area in Fig.A.15a.

Let us further assume $d_S \neq 0$. The statistic T has, in this case, the mean value d_S and the distribution illustrated on Fig.A.15b. The hatched area here represents the probability of an error of the second kind (T falls into the interval R and the hypothesis H_0 is not rejected). Clearly, the probability of the error of the second kind decreases rapidly with increasing value of d_S .■

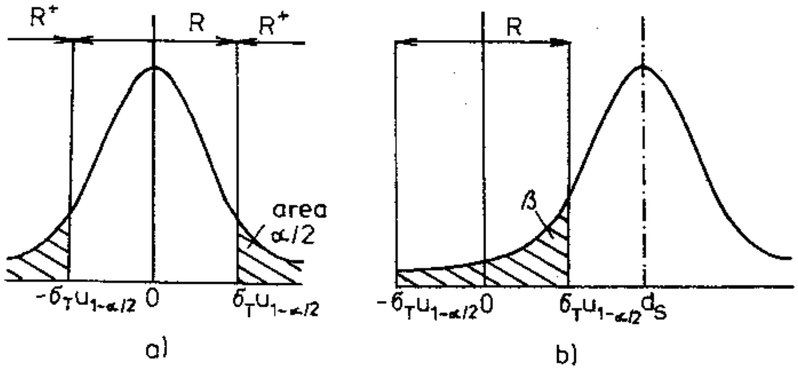


Fig.A.15 — Magnitude of errors of Ist kind (α) and of IInd kind (β)
a) $d_S = 0$; b) $d_S = 0$

A.5 GRAPH THEORY

The notion of a graph is frequently used with different interpretations (most frequently, it means a graphical representation of some relation). In engineering practice, another type of graphs is often met; such a graph is formed by a set of points and by a set of lines connecting the points. The graph theory is concerned with the mathematical expression of different relations in such a system of points and lines.

A.5.1 Basic notions

In order to define a graph (say **G**), two sets have to be given: the set of nodes N (the aforementioned points) and the set of edges E (the aforementioned lines). In addition to these sets, the graph is determined by a rule which for any edge determines the nodes the edge connects.

The nodes connected by a given edge (i.e. those with which it is incident) are called the *endpoints* of the edge. If the edge is oriented, one speaks of the *initial* node and *terminal* node of the edge. A graph whose all edges are oriented, respectively unoriented, is an *oriented* (*directed*), respectively *unoriented* (*undirected*) graph. Examples of an oriented and of an unoriented graph are given in Fig.A.16. To any oriented graph clearly corresponds a unique unoriented graph arising by neglecting the orientation (the so-called *disoriented* graph). A converse assignment is, however, no more unique. An edge issuing from and ending at a single node is called a *self loop*.

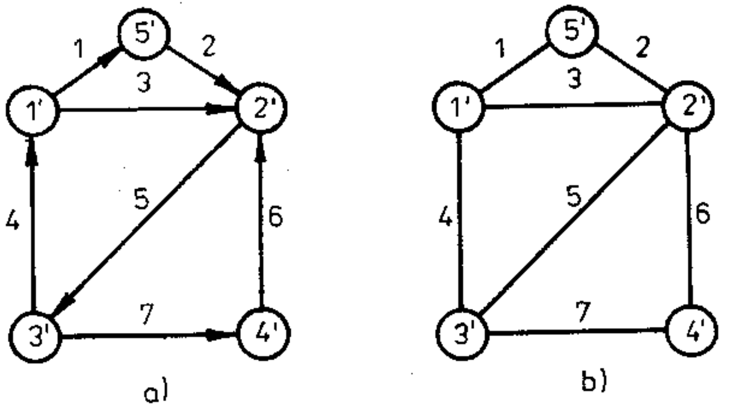


Fig.A.16 — a) oriented graph; b) unoriented graph

Let **G** [N, E] be an unoriented graph. A *path* is such sequence of edges (E_1 , ... , E_n) that one of the endpoints of edge E_i ($i = 2, 3, \dots, n - 1$) is also incident with edge E_{i-1} and the other endpoint is incident with edge E_{i+1} . For the extreme edges of the path, one of the respective endpoints need not be generally incident with any edge of the sequence. A path whose first and last node coincides is called a *circuit*. Examples of paths and circuits of the graph Fig.A.16 are given in Fig.A.17. A graph whose any two nodes can be connected by a path is called *connected*. An unoriented connected graph which contains no circuit is called a *tree* and its edges are called *branches*. The number of the branches of a tree is smaller by one than the number of its nodes.

If $\mathbf{G}_1$ [N_1 , E_1] and $\mathbf{G}_2$ [N_2 , E_2] are graphs, one says $\mathbf{G}_2$ is a *subgraph* of $\mathbf{G}_1$ if and only if N_2 is a subset of N_1 and E_2 is a subset of E_1 preserving the incidence; if $\mathbf{G}_2$ contains all nodes of $\mathbf{G}_1$, it is called a *factor* of graph $\mathbf{G}_1$, and if it is a tree, then $\mathbf{G}_2$ is called a *spanning tree* of graph $\mathbf{G}_1$. An important property of a spanning tree of a graph is that the spanning tree connects all nodes of the original graph by the minimum number of branches. The edges of the graph which do not belong to the spanning tree are called chords.

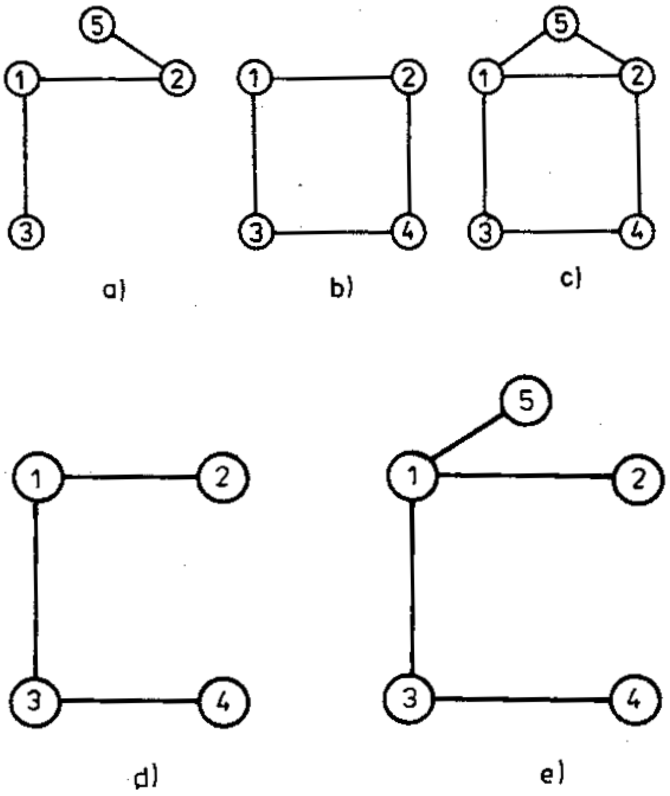


Fig.A.17 — Subgraphs of the graph in Fig.A.16b
a) path; b) circuit; c) factor; d) tree; e) spanning tree

A.5.2 Graphs and matrices

Operations with graphs, in particular when using a computer, require an exact mathematical specification of the graph. An oriented graph without self-loops can be fully characterized by its incidence matrix. Let us assume an oriented graph **G** $[N, E]$ with n nodes and b oriented edges. The incidence matrix $\mathbf{A}_a$ of type $n \times b$ has its elements A_{ij} equal to 0, 1 or -1 according to the following rule:

$A_{ij} = -1$ if node N_i is the initial node of edge E_j
$A_{ij} = 1$ if node N_i is the terminal node of edge E_j
$A_{ij} = 0$ if node N_i is not incident with edge E_j

The incidence matrix of the oriented graph in Fig.A.16 is

$$\mathbf{A}_a = \begin{bmatrix} -1 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

An important property of any incidence matrix is the fact that each column contains just two nonzero elements, 1 and -1, so that the sum of all rows of the matrix is the vector zero. From here it follows that the incidence matrix is not of full rank (for a connected graph, its rank equals the number of nodes minus 1). It is also obvious that any row of the matrix can be computed from the remaining ones. All information on a connected graph is thus also contained in a matrix obtained by deleting one of its rows. Such a matrix is called a *reduced* incidence matrix and the node corresponding to the deleted row is called the *reference* node. Similarly, a simplified way of drawing a graph consists of deleting a reference node while some edges of the graph are then incident with one node only. Recall, however, that this is only a simplifying convention while in fact, each edge must be incident with a node at both of its endpoints.

A.6 RECOMMENDED LITERATURE

The mathematical concepts necessary for following the book can be found in a number of textbooks on mathematics. The reader may find also a more detailed description in specialized books dealing with linear and matrix algebra (Noble 1969), probability and mathematical statistics (Hines & Montgomery 1969) and graph theory (Chen 1971, Mah 1983). Somewhat beyond the general level of mathematical knowledge are the problems of random processes; as a convenient source may serve the book by Bendat & Piersol (1966).

Index

Credit

Section 6.2 of this book is based on the paper *Determination of specific consumption of energy and raw materials in complex chemical plants* (Madron & Veverka,1981).

Figs 6.4 - 6.11 were reprinted with permission from *Taylor & Francis Ltd, London.*