Steady-state flow-sheeting of chemical plants

P. BENEDEK (EDITOR)

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OF CHEMICAL PLANTS

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PREFACE TO THE ENGLISH EDITION

The Hungarian edition of this book appeared in 1973, and was followed in 1976 by the German edition. The present book is basically the same as the earlier editions apart from being extended to include problems. These problems and their solution aim to help the reader to master the text and to gain a deeper understanding of the computerized flow-sheeting system. The authors discuss only their own flow-sheeting system. This is still up-to-date even though it was developed nearly ten years ago. The validity of the principles and solutions realized in this system are proven on the one hand by the experience gained in practical application and on the other hand by observing the developments taking place in other flow-sheeting systems.

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CHAPTER 0

SIMULATION

FUNDAMENTAL PRINCIPLES, SCOPE, REALIZATION

The intention of this book is to introduce a computer-program system which the authors hope will serve their colleagues in the chemical industry or in contact with it, as a tool which will enable them to solve problems arising from their technical and economic activity more quickly, efficiently and successfully.

The consequent structure and logic of a computer-program system requires imperatively the exact and subject-confined description of the system. We do not aim to philosophize in a general manner about mathematical modelling and simulation, nor to develop ideas and concepts, and speak about the results and failures in their realization. Considerations of this kind belong to an introduction. Nevertheless the authors concluded that the Introduction should be raised to the rank of the essential chapters and decided to write a 0th Chapter. It is thought that the generalized formulation and discussion of the problems herein will help the reader to understand and evaluate the system.

0.1 UNIT OPERATIONS

Unit operation is a basic concept of chemical engineering science, it being a subject of scientific research in this science. A unit operation consists of three components: the processing equipment, the object of work and the related human activity. The simultaneous occurrence, interrelation and combination of these three components constitute the essential condition of chemical production. The interrelation represents the operation which results in changing the chemical composition of the object of work. This type of change distinguishes the chemical production from all other kinds of production. While the object of work undergoes an essential change in the operation, the processing equipment remains practically unchanged. Human activity plays a peculiar role. The coordinates or form of the object of work may be changed using man's physical effort or equipment, but the chemical composition of the object of work cannot be changed directly by man's physical work or equipment. The chemical composition of the object of work changes spontaneously, if the conditions (temperature, pressure) are suitable. Human activity is necessary to provide the appropriate conditions, and this activity represents the intellectual activity in chemical production. Man's physical performance — although indispensable — has a secondary role in chemical production.

However, this conceptual definition of the unit operation is too general and too extensive. Its criteria can be met by the chemical industry of a country, or by a chemical factory, or by a single plant of a factory or even by a single item of equipment. We may, therefore, reasonably consider the unit operation as the simplest and all other operations as increasingly complex. It follows from this that the most practical approach is to define the unit-operation concept as clearly as possible. The best way to do this is to consider the unit operation as a system.

0.2 UNIT OPERATION AS A SYSTEM

A system we understand to be a quantity of elements and their relations which are in interaction with their surroundings. An element is part of a system, and if this part represents the whole system, then it is a single-element system. The elements of a system are interconnected and the behaviour of any one of the elements affects all other elements of the system — depending on the character of their interconnection. From the viewpoint of the behaviour of the system, two considerations are necessary: the individual behaviour of the elements — considered to be isolated — and the motivation of the individual behaviour of the elements, taking the channels which transmit the interaction into consideration. This motivation varies depending on the network of these channels. In other words: systems containing the same number of the same elements behave dissimilarly if the network connecting the elements is different.

Systems in the chemical industry are characterized by material streams connecting one element to another. There are also other types of streams. Information streams exist between the elements of a system and these relate not only to physical properties but also to economic information. Both material and information streams flow through connections: pipes, wires, etc., generally we shall call these channels.

The statement that a system is a network of elements may be expanded to the whole material world: the classification of whether or not each element of the material world belongs to a selected system can be made. Elements not belonging to the selected system represent the surroundings of the system. These surrounding elements do not need to be considered when studying the system. By definition, no element can simultaneously be part of a system and its surrounding, and contact between the system and its surroundings may only be effected through channels. It follows that both the surrounding elements and the network of the surroundings may be neglected from the point of view of the system. On the other hand, the channels connecting the system with its surroundings are of special importance. The channels leading from the surroundings to the system represent the input of the system, those leading from the system to the surroundings are its output. The system reacts to a given input with a specific output. We speak about the behaviour of a system in this sense. From the point of view of the behaviour, the surroundings represent the source of each input and the sink of each output. This follows from the definition of the system.

Further elements connected by a network in the surrounding of the system represent a second system, and another set a third system. These systems may be connected with each other. We may conclude that these systems represent the elements of a system of higher hierarchy.

Let us consider as an example the atmospheric- and vacuum-distillation units of a refinery as a system consisting of the following elements: furnaces, heat exchangers, distillation columns, etc.; the reforming unit as another system, the elements of which are furnaces, heat exchangers, distillation columns, pumps, reforming reactors, compressors, etc.; a further system is that extracting the aromatic compounds, the elements of this system being heat exchangers, distillation columns, extracting columns, pumps, etc. If these and other similar units are located together as systems, and if in addition these systems are connected by material and information streams, then it is easy to conclude that all these units represent elements — connected by a network — of a system of higher hierarchy: the refinery. The same applies to the lower levels of hierarchy. The distillation column, which has been considered as an element of various systems, has elements of its own (heat exchangers, plates, condenser, reboiler, reflux pumps etc.) which are interconnected and therefore it is a system itself. It may be deduced therefore that if further systems exist around a system, which may be circumscribed based on the same aspects and which are directly or indirectly interconnected, then these systems are at the same time elements of a system of higher hierarchy.

If we accept that all unit operations can be handled as systems, then we must question which levels of hierarchy should be distinguished among the unit operations. According to chemical engineering science, these levels may be the following:

1. Simple unit operation,
2. Combined unit operation or process step,
3. Complex operation or process, or plant,
4. Chemical factory,
5. Chemical industry.

The simple unit operation may be characterized on the basis of phenomenologic thermodynamics by the fact that all the processes taking place are spontaneous and irreversible (entropy-producing).

Mixing may be taken as an example, since two different mixtures are transformed into a third mixture whose composition differs from the first two. This process is spontaneous and produces entropy.

The combined unit operation is characterized by thermodynamically interconnected processes. If a decrease of entropy is found in the main process stream, it may be attributed only to the entropy production in the thermodynamically interconnected secondary stream, which offsets the entropy loss of the main stream. In all, the total entropy of the streams leaving the unit operation exceeds the total entropy at the entering streams. This unit operation is combined because complementary unit operations are required to produce and maintain the secondary stream. It follows that the combined unit operation is also combined as a system, including several specific elements, interconnected by a network.

Mention is made of distillation as an example of a single mixture separated into two mixtures of different composition. Since, in terms of direction separation is opposite to mixing, entropy decreases during separation and the separation process cannot take place spontaneously by itself. Even so, separation does take place because the entropy decrease is offset by the entropy production of the heat flow travelling with decreasing temperature from the reboiler to the condenser.

Chemical process engineering deals with the theory of simple and combined unit operations. The complex operation is a network consisting of simple and combined unit operations on a higher level of hierarchy, serving a prescribed (economic) object. The type of simple and combined unit operations, used to achieve this (economic) object, their number and network (recycling, feedback, etc.) are in general more sophisticated than the trivial solution. When treating such systems the thermodynamic approach is replaced by another approach, where the survey of the network dominates the determination of the behaviour of the elements. Systems engineering deals with the general theory of complex operations, whereas specialized discussion — in terms of the products — is in the realm of process engineering.

Let us refer to the synthesis of ammonia from natural gas as an example. The aim of the process (the production of a use value, namely ammonia) can equally be achieved if the unreacted synthesis gas is vented. It is, however, more effective to recycle the unreacted gas with a new unit operation: the circulating compressor sends the gas to the reactor, but it is mixed with fresh gas before entering the reactor using another unit operation (pipe mixer). This solution is — considering the number and network of the unit operations used — more sophisticated than the trivial solution already mentioned. (More similar solutions are to be found in the complete process of obtaining ammonia from natural gas. A sophisticated solution is not a direct thermodynamic necessity: it has a different cause. The industrial production of some kind of use value is simultaneously a value production and the entire process should therefore be achieved with the minimal amount of work socially required. Thus the direct need to select a more sophisticated solution has only economic reasons, which in fact determine the process.

As the level of hierarchy of process systems becomes higher, the role of economic aspects increases. The treatment of a chemical factory or the chemical industry as a unit operation is barely within the scope of natural science.

We shall consider complex operations and their mathematical modelling in the above-mentioned sense.

0.3 MATHEMATICAL MODELLING, MATHEMATICAL SIMULATION

The mathematical modelling of simple and combined unit operations is a growing trend in today's chemical-engineering science and engineering practice. This tendency was already noticeable in the development of process engineering, but in the last decade has become exact and effective, on the one hand by utilizing new scientific results of process engineering related to the internal mechanism of the processes and on the other hand by using computers. Thus, the conditions have been created where a relatively neglected area of chemical-engineering science, the complex operations can be studied. This has also been accelerated by the fact that the theory of networks has been elaborated in the field of electrotechniques and electronics, and also that in process control, results have been achieved from the study of the behaviour of similar complex systems.

The study of complex operations has become currently useful to Hungary too, since some major petro-chemical plants have recently been erected (synthesis of ammonia, naphtha cracking, production of acetylene by oxidation of methane). The rapid development of petro-chemical processes results in the partial obsolescence of the plant, after its erection and operation.

In this situation, it is not only possible, but necessary, to improve resolutely the type of process performance of the existing complex operation, to increase with change in construction size the quantity of products, to decrease the specific material requirement and to perfect the energy balance. This task can only be solved by detailed and comprehensive preparation, because of the volume of investment and size of production value. During this preparation, one type of tool which can be used is the mathematical simulation of complex operations.

Simulation and modelling generally use technical devices. The modelling consists of creating a "quasi-object" suitable for studying the behaviour of a system, from which the output of the system to a given input may be established. This type of research is termed simulation. Simulation is used to obtain by simple means and with low cost that information which could otherwise only be available by measurement on the original system. The original object is the prototype, the quasi-object serving for the research is the model.

There are different types of models. They may be material, physical constructions, but can take abstract forms.

If the quasi-object consists of mathematical objects, i.e., correlations, equations etc., then we speak about a mathematical model and we call the research which is carried out with its aid the mathematical simulation.

The mathematical model can be produced in two ways. If the prototype exists and functions, then — when sufficient coherent input-output data have been collected — a vector–vector function may be found, which best fits the available data system. This vector–vector function is the empirical mathematical model of the prototype. The mathematical model thus produced only exists in that it is valid solely for the prototype, all changes of which render it meaningless.

Such a model is eminently suitable for describing the behaviour of a complex operation if it is aimed at controlling it automatically and by optimization, but it is not sufficient to meet the technical-economic demands formulated above.

The other mode of mathematical modelling does not need a prototype, but presupposes detailed knowledge of those physical and chemical processes which form the basis of functioning of the simple and combined unit operations which are elements of the system: the complex operation. The basic knowledge allows us to set up that equation — differential equation, or partial-differential-equation system — which represents the interconnection between the variables of the given simple or combined unit operation, and whose solution warrants the requested object at given initial and marginal conditions, i.e., it reflects the behaviour of the simple or combined unit operation. This mathematical structure is the mathematical model of the unit operation based on physics and chemistry, and from these elements the mathematical model of the whole complex operation can be assembled. The mathematical model of the complex operation based on chemistry and physics satisfies our original technical and economic requirements, since it allows the type of process performance of a plant to be improved and the technical-economic consequences of change in construction size to be evaluated, without directly disturbing the prototype. Here, we are concerned with the evaluation rather than the overestimation of simulation. Each model incorporates a known and often intentional simplification of reality, which may be established in the given case by measurements on the prototype.

If it is possible to carry out a sufficiently large number of measurements, then the accuracy of the model increases significantly by fitting the model. By this, we understand that the parameters of the model — which originate from the literature or laboratory measurements — are corrected such that a quantity indicating the difference between the measured and calculated data, most frequently the sum of square errors, should be a minimum.

The models described are not yet directly suitable for simulation. If the mathematical model is completed by a sequence of statements related to the numerical calculation of the correlations, i.e., the algorithm, then in principle the calculation is possible. Since the algorithm is usually complicated and therefore calculation would be very lengthy, computers must be used. This necessitates a further task, the programming. Simulation may be carried out with digital or analog computers. We shall restrict our discussions to the former.

It follows that we have to deal also with computer techniques.

0.4 APPLICATION OF COMPUTER TECHNIQUES

The chemist and chemical engineer use in their daily work a number of objects, e.g., the burette or the mass spectrometer. The computer has entered into the realm of these objects and has found increasing application. With our daily practice of using a burette or mass spectrometer, say, we gain at least a general idea about its functioning. If we consider the computer as an object similar to those already mentioned, namely a tool used daily by the worker then it is evident that we must also become acquainted with the rough outlines of this object.

Computers have become accessible to everyone over the last 20 years. In this period we have passed through three consecutive computer generations: the first with valves, the second with transistors and the third with integrated circuits. These three generations do not only differ in the technical accomplishment, but also in the man-computer relation, in the programming of the computers, and moreover in the type of task to be solved using computer techniques.

The tasks may be classified according to their intricacy into three categories, which follow on the whole the three software generations. These may be nominated as individual calculations, combined calculations and system calculations. They have been developed in this sequence and they still exist side by side. The program for an individual calculation is prepared by a single programmer who may also be the specialist (e.g., chemist) needing the individual calculation in the course of his work. The situation differs with combined calculations. Generally several specialists have to cooperate. The first is the specialist who develops the model of any physical, chemical, economic or other task; the second is the mathematician who considers this model as a mathematical problem and develops the algorithm; this is followed by the work of the programmer who converts the algorithm into a program, which obeys the rules of programming techniques. These differently trained specialists form a team. We can, therefore, say that the programming of a combined calculation is a team work. The programming of individual calculations requires the comprehensive training and deep knowledge of a single specialist, but when programming combined calculations, a further condition of the result may be observed: the level of cooperation.

In recent years major program systems have been developed to calculate technical or economic systems, and a new kind of man-to-man relation has been born. This type of work starts with the analysis of the system determining its elements and their interconnecting network. The systems analysis is the task of the systems engineer who has also to develop the general model of the system. Further treatment of the individual elements of the model (programs or program packages) is left to suitable teams. This is a typical example of a hierarchical organization. Whereas the (simple) man-to-man relationship involved was sufficient during the programming of combined calculations, when treating program systems for major systems, a higher level of scientific organization is needed and this determines the (more complex) man-to-man relationship leading to the development of a functioning program system.

By means of a few examples, we shall examine the point in question. As an example of an individual calculation, we may refer to the calculation of the chemical equilibrium of a reacting multicomponent system. The computerized solution of this task does not require much programming work of the chemist, as each computer centre has a procedure of its own for solving the mathematical problem, i.e., the solution of a non-linear system of equations.

As an example of combined calculations, the work of the American Institute of Chemical Engineers (AIChE) may be mentioned, which presents a program package for calculating physical property values of chemical components based on their formulae. This program package can be used to calculate a fairly large range of properties as a function of the state variables. Three years were consumed in producing this program package, the costs were 300 000 $ and it may be bought on magnetic tape for $ 8000. Since, at that time, no such computer was available in Hungary on which this program could have been run, we developed the program package FISC, which is suitable for calculating a smaller range of properties. The property calculations are carried out by procedures which require some initial data, such as the critical temperature, critical pressure, etc. These data have been collected in advance for all substances which feature in the program package. The calculation is therefore not carried out on the basis of the formulae. The FISC package currently contains 210 substances.

As a third example developing a program system the so-called SIMUL system should be mentioned. It simulates complex operations (processes, plants) and has been developed by about 50 colleagues, organized in teams. The SIMUL system uses the FISC program package to calculate property values.

In the last decade, some program systems have been developed to simulate complex operations. The literature contains reviews about these (Evans et al., 1968; Gruhn et al., 1971). Until recently, these program systems or simulating languages had not been detailed. The present book aims to describe in detail the SIMUL system developed in Hungary.

0.5 IDEA, CONCEPTION, REALIZATION

The way in which a technical task can be solved divides into three phases: the idea, the conception and the realization. In each of these phases, the work is done according to fixed principles. The adherence to previously formulated principles does not exclude feedback during any of the phases but the feedback must always be within the particular phase. It would be senseless to follow a doubtful idea and to convince oneself of the negative effect in the realization phase. This attitude would increase the costs and duration of the realization.

Five principles had been formulated when we began to develop the SIMUL system. The first three are connected with the chemical engineering, the other two with the computing aspects of the problem.

It has already been mentioned that the object of work, which changes during the chemical process, has to be considered as an essential component of the unit operation. The object of work in the chemical industry is a mixture of chemical components, and it is characterized by its chemical composition and physical state. We have outlined in this relation the principle of component-independence. According to this principle, the system has to function independently of the type of components of the object of work. In order to realize this principle, we discussed in the idea phase among other things the development of a program package which could calculate the properties of any component based on the formula, the temperature and the pressure. The re-examination of this idea led us to believe that the development of this program package would demand too much work and time, and its use would require too much computer time. The result would be a system which was too general to meet practical demands. As the SIMUL system was primarily intended as a means of studying major petro-chemical plants, the program package containing property calculation of substances to be found in the petro-chemical industry itself seemed to be sufficient. The idea of the principle of the component-independence has been corrected accordingly. During the further work, difficulties arose. It would have been extremely difficult to develop a program package which was able to calculate the properties of solid substances. As the petro-chemical industry in the main handles substances in liquid or gaseous state, it is sufficient to calculate properties in these states. Having thus modified the conception, the program package FISC has been developed to calculate, in the SIMUL system, properties of pure components and their mixtures in the liquid and gaseous state.

The second essential component of the unit operation is the processing equipment. The principle of the independence of the processing equipment requires that the system should be operating independently either of the objects of work processed in the equipment or of the main dimensions of the equipment. The object of work itself combined with the processing equipment (together with the passively present personnel) already forms an actual simple or combined unit operation. In the same way that the principle of component-independence can be realized when considering the components in the SIMUL system, equally the principle of equipment-independence is realized with regard to each item of the processing equipment in the SIMUL system. Whether or not to include or omit is a practical issue and not one of principle.

That path which faithfully followed the principle of equipment-independence from the idea up to its realization led to problems which needed to be resolved and, consequently, feedback. According to the original idea, each item of equipment had to be considered as consisting of simple elements, e.g., a plate column from the feed plate and the theoretical plates. This view had to be abandoned since the networks would have been too complicated. It appeared to be more suitable to define the equipment in the manner in which it is usually done in the practice of mathematical modelling. These units are termed equipment boxes in the SIMUL system. This concept has been realized. In the course of utilization, it was found that a unit operation, e.g., the distillation, may have different significance in diverse complex operations. It is not always necessary to calculate a distillation in a very precise and detailed manner. There are cases when an approximation — needing less computer time — is quite sufficient. In the realization phase, two or more models have frequently been developed in order to use the most suitable in each case.

The demand on model accuracy varies with the object of application. The maximum possible precision must be envisaged when an equipment is simulated without prototype and experience, and the model is based only upon laboratory data and theoretical correlations. If an existing equipment has to be simulated, the model may be checked using the prototype and if the model may be fitted to the prototype by correcting some constants, less exact model is sufficient. When simulating complex operations, computer-time consumption is essential, and may be very large when optimizing because of the iterative calculation of feedbacks. We have to abandon extreme accuracy and be satisfied with simpler, less exact but less time-consuming models. If it is possible to fit the models, then these can be used for optimization, if only in a narrower interval. Even without fitting — as approximate models — they are suitable for analyzing the economic aspects of different process variants, thus providing background data.

These considerations, as well as the efficiency of the available computer, led to the conclusion that the accuracy of the models should correspond to that of the general chemical-process-design practice.

A further idea relating to processing-equipment models was the statement of the calculation sequence as a parameter. The sequence of the calculation must not coincide with the direction of the material stream, though it may be opposite, because in complex operations with recycling or information feedback, this calculation mode may be more suitable. In one part of the equipment models, such as those which calculate network modes, this idea could be maintained and has been realized. In the case of separating operations, however, the realization of this idea could have led to difficulties in principle and in practice the different calculation sequences required different algorithms, thus needlessly increasing the size of the system. The original idea was thus abandoned in such cases.

The third principle, the independence from the network, means that the system is operable independently of the flow-sheet, that is, by linking equipment and control units in any manner. This idea was found to be correct in conception and has been realized.

The fourth principle was automatic execution of the calculation, the requirement being that after the statement of the order of calculation formulated in a suitable manner, the calculation proceeds without interactive contact (if required) and the results are recorded in a form which is directly interpretable in the engineering practice. The original idea was to determine the order of calculation automatically, i.e., starting from the flow-sheet and based upon the theory of graphs, the system should be able to present the order of calculation at least suitably, if not optimally, programmed. This idea had to be abandoned because the task could not have been solved within the specified time and at that time the literature did not contain any acceptable solution. Since then, other authors have solved this problem more or less satisfactorily. We have retained our modified conception, according to which the order of calculation is formulated by the user of the SIMUL system.

The fifth principle, that of use of an independent simulation language, relates to the above formulation. The order of calculation must be composed in an independent simulation language, the SIMUL language. This means that the user of the SIMUL system does not need experience in programming, but simply has to learn some rules and concepts contained in a small handbook. Knowing these, the task to be solved can be formulated within the SIMUL system, whereafter the calculation proceeds automatically and the final results are printed. In this programming language concepts of higher-order appear such as distillation, heat exchanger, reactor, recycle, which correspond to the concepts of process engineering and are interpreted by the SIMUL system. The SIMUL system — as a program system — has been written in ALGOL. The calculating operations have to be formulated for the SIMUL system in a higher-order simulation language which uses higher-levelled operations as mathematical or logical operations. These may be described by very simple syntactical rules.

The principle just discussed was a great help in the development phase of the SIMUL system, as the equipment boxes have been elaborated and the use of the system has not yet arisen. Almost all boxes were developed by another team and all the teams were able to work independently. Since the work was carried out according to the rules of the SIMUL system, all the teams were sure that their program would not require interfacing with other programs and the system itself later.

0.6 GENERAL CHARACTERISTICS OF THE SIMUL SYSTEM

The reader may be acquainted in detail with the SIMUL system developed according to the principles discussed above. However, in the following, we have summarized the general characteristics, at least those which distinguish it from other simulating systems.

1. The SIMUL language has its own syntactics and semantics. The user is not expected to possess experience in programming.

2. In the SIMUL system, more than one stream type may be declared. It is therefore possible to handle, individually, qualitatively different objects of work figuring in complex operations.

3. The SIMUL system is operation-oriented. The user therefore need not be concerned with the determination of property values of the objects

of work, because the system calculates these automatically where and when necessary. Nor need the user to worry about the calculation of the operations: the operation computer program is available and the user has only to stipulate the sequence of the calculations, the input streams and main equipment dimensions to be used in each calculation.

4. In the SIMUL system, it is possible to formulate complex statements with the aid of some boxes (solving systems of equations or optimizing). Complex statements may be nested to any depth.

5. In the SIMUL system, references are defined. This means that with appropriate coding we may state that any parameter of a box, or any element of a stream vector, should be substituted by a value, which has been already found from calculation. The reference chain may be of any length.

6. In the SIMUL system, reference may be made to an arithmetic expression. This allows for including functions of any variables in the place of a value. (This is the way, for example, to define the objective function of the optimization.)

7. The SIMUL system may be operated automatically or interactively. The automatic order of calculation may be interrupted at completion of the calculation of a box, and it is possible to modify either the sequence of statements or the data system. Therefore, once output routines have been included, any data or data systems may be printed.

CHAPTER 1

THE PROCESS

1.1 THE PROCESS AS THE BACKGROUND OF SIMULATION

If an intellectual activity is started, resulting in the mathematical simulation of a complex operation, namely a plant or even a factory, then the basis is represented by the plant or the factory itself, with its raw materials, products, equipment and instruments.

This basis serves as a source for our information. We have to process and refine this information. The simulation obviously starts with the study of the complex operation followed by analysis of the process flow-sheet. This leads through gradual abstraction to the flow-sheet program of the simulation. On that basis the desired information — the result — is produced by the digital computer. We aim to introduce this chain of activities in this book.

In the first Chapter we shall discuss the process itself: the available information is to be analyzed, classified and selected. As an example, the catalytic isomerization of butane is introduced.

In the following chapters, the target is approached step by step. The structure of Chapters 2–5 is intentionally similar; each of these chapters consists of four parts. The first handles the subject based on the example, the second contains the terminology together with the strict rules of the SIMUL system, the third deals with conventions, and the fourth outlines the results of developing the system, as boxes, procedures, etc. It should be mentioned here that the target, the available process information, the scientific knowledge and practice needed to process this information do not unequivocally determine the system of simulation. The potential and bounds of the available computer have also to be taken into account. The character of the SIMUL system has been influenced, despite effort in the construction of the GIER computer, built by the Danish company Regnecentralen. The main characteristics of this computer are stated in Chapter 8.

1.2 INFORMATION CONTAINED IN THE PROCESS FLOW-SHEET

The chemical engineer describes a complex operation using the process flow-sheet. The process flow-sheet indicates the equipment level and true-to-scale, if this is possible. It also informs about the interconnections and defines, for individual items of equipment, the inlet and outlet streams with their chemical and physical data. The process flow-sheet includes the main process stream, and the network of the side streams necessary to follow the process, but it disregards the full piping scheme. Identical equipment items figure once the number of pieces being indicated.

The process flow-sheet accordingly indicates quantitatively the chemical composition of the material streams in the main process stream and the indicated side streams. It follows that it contains the total material flow of the complex operation, according to components and equipment. The process flow-sheet shows further the physical and thermodynamic state of the substances present in the streams. It therefore contains the total thermal energy flow of each equipment in the complex operation. In addition, it contains information about the electric power requirements of some equipment.

When simulating complex operations, the mathematical task consists of calculating the data needed for a process flow-sheet, based on data characterizing the size and thermodynamic state of the input streams and the main dimensions of the equipment.

Attention should be paid to the fact that calculating methods do not necessarily cease to function at the limits of an item of equipment. A procedure may simulate an item of equipment, part of it, or even the simultaneous functioning of a number of items of equipment. The process flow-sheet cannot therefore be the basis of a process calculation. We shall introduce later (Chapter 5) the operation-order flow-sheet, which — using a suitable identifying system — clearly presents the logical course of the simulation and contains all important computer-technical information.

To produce the operation-order flow-sheet, a simplified flow-sheet is needed, which — full enough to describe the steady-state functioning — contains only those parts of the whole process which have to be modelled. The process flow-sheet is simplified by neglecting certain equipment, pipes and instruments.

1.3 SIMPLIFYING THE FLOW-SHEET

Basically, we always have to start from the idea that the target of modelling is economic. Therefore, only those parts of the process are calculated which influence appreciably — as far as we know — the economy of production.

In the simplified flow-sheet sections of the plant, with the aim of regeneration, equipment or substances are intermittently omitted — these auxiliary operations do not affect the steady-state functioning of the plant, i.e., sufficient reserves are at hand.

It is not necessary to calculate in detail or include in the simplified flow-sheet the service systems, if their capacity may be reasonably exceeded or increased simply by multiplying. Examples of such systems are the steam supply, sewage purification, supply with compressed air, vacuum, cooling water, etc.

Of the pipe connections, all those which function periodically, as when starting up or closing down during break-downs activated for safety, but without any role in the steady-state functioning of the plant, should be omitted when producing the simplified flow-sheet.

Further, it is advisable to decrease the number of recycles. Recycle streams, which are unimportant or which can be characterized between broad process conditions with nearly constant parameters, can be replaced by constant data.

The symbols and notations of the simplified flow-sheet have the same meanings as the process flow-sheet. On the flow-sheet, data about the quality of materials and the process-performance type are generally omitted. On a separate list, the equipment and material streams, as well as the data describing the material streams should be summarized. On the flow-sheet symbols are used referring to this separate sheet.

After this introduction, let us now study the chosen example, the isomerization of butane.

1.4 FLOW-SHEET OF THE ISOMERIZATION OF BUTANE

The process flow-sheet of the catalytic isomerization of butane is displayed in Figure 1.1. The text of this figure contains the description of the process. The flow-sheet does not contain the control and measuring instruments, but contains some equipment whose function plays no essential part in the process, considering the previously discussed approach. These are the storage tanks, the pumps and some heat exchangers. The function of the heat exchanger is just to secure the prescribed inlet temperature of the stream entering reactor R1. If we do not intend to calculate the heat balance, it is sufficient to prescribe the necessary temperature of the entering stream. In the simplified flow-sheet we intend to produce, the raw material can enter reactor R1 directly. It is also unnecessary to present the storage tanks and pumps on the simplified flow-sheet, since firstly the storage does not induce a change of state, and secondly it is obvious that the flow of materials is assured by pumps. Omitting this equipment, we arrive at the simplified flow-sheet of butane-isomerization (Fig. 1.2). The heat exchanger W1 is of primary importance, as its duty is to adjust the temperature of the product leaving reactor R1 to the value required in the distillation. This heat exchanger must therefore be presented on the simplified flow-sheet. The heat exchanger W2 must also be shown, as it adjusts the temperature of the hydrocarbon stream entering reactor R2. On the basis already discussed, we omit heat exchanger W3 and storage tank B3.

For practical reasons, it is worthwhile producing a block diagram from the simplified flow-sheet. In this, we do not represent the equipment true-to-form and scale, but symbolize it by rectangles.

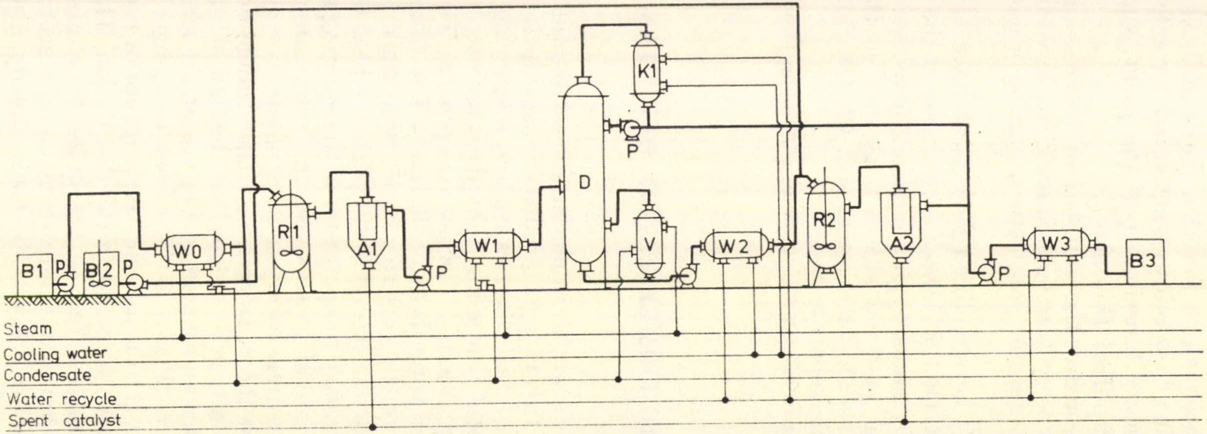


Fig. 1.1. Butane stored in liquid state under pressure (contaminated with n-pentane) in the storage tank (B1) is pumped through the heat exchanger (WO) at the prescribed temperature into the stirred reactor (R1). Before entering the reactor, catalyst suspension is added to the feed from the mixer (B2). The product leaving the reactor (R1) contains butane, i-butane and n-pentane, but also inactive catalyst. This catalyst is separated in the separator (A1). The hydrocarbons are fed into the distillation column (D) through the heat exchanger (W1), ensuring the prescribed temperature. The top product of the distillation, containing i-butane and n-butane, is cooled in the condenser (K1) below boiling point. Part of this distillate is recycled into the column with the reflux pump. The bottom product is partly fed back to the column through the reboiler (V). The remaining bottom product is fed to the second stirred reactor (R2) at the prescribed temperature through the heat exchanger (W2). Before entering the reactor, catalyst suspension is added. The spent catalyst is separated in the separator (A2). The hydrocarbon stream is mixed with the liquid top product of the distillation column (D). This mixture is cooled to storage temperature in the heat exchanger (W3) and stored in the tank (B3).

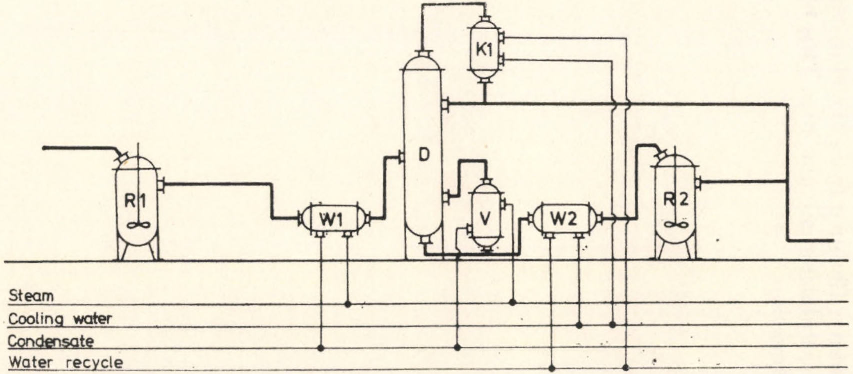


Fig. 1.2. Simplified flow-sheet of the butane isomerization

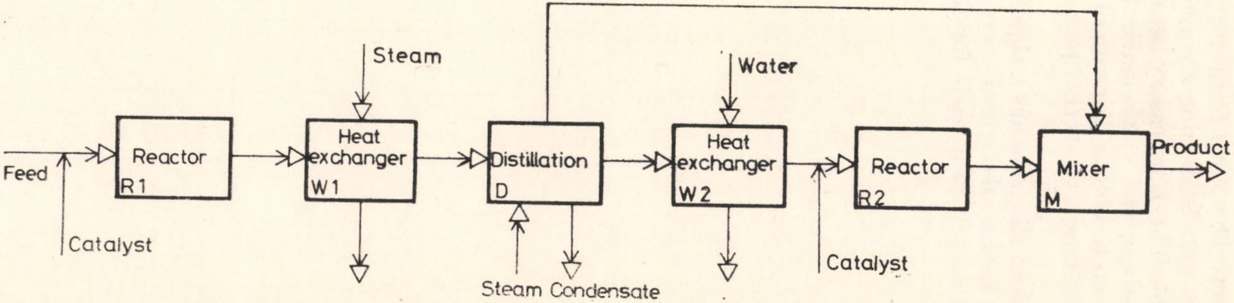


Fig. 1.3. Block diagram of the butane isomerization

The name of the operation is written in the centre of the rectangle, and in the lower left-hand corner is the position mark identical with that on the flow-sheet. The lines connecting the blocks denote material streams.

Mixing and branching are represented in the block diagram by separate rectangles. This is necessary because these processes are handled as individual operations in the mathematical model. This is why the mixing block M appears on the block diagram of butane-isomerization (Fig. 1.3). The distillation condenser, the reflux pump and the reboiler do not appear as separate blocks.

The block diagram has a significant formal difference from the flow-sheet, but it contains all elements necessary for simulating calculations. This block diagram serves as a basis for further discussion.

CHAPTER 2

STREAMS

2.1 MATERIAL FLOW IN THE SIMUL SYSTEM

The flow-sheet is a kind of representation of the complex operation. This model defines with sufficient accuracy the real flow direction of process media between the process units. We speak here of the flow of materials in the chemical sense and the purely graphic description does not specify the flow velocity, the chemical composition and the thermodynamic properties of the streams. The relevant data appear on the flow-sheet as supplementary information allocated to the graphic model. This information is indispensable for an exact description of reality. The standards of flow-sheeting define how this information should appear on the flow-sheets and which units should be used but not how much information should, could or might be presented. Engineering experience nowadays adopts a practical approach concerning the amount of information. There is an attempt, on the one hand not to list all the data necessary to define a stream completely, but only those that are considered to be important for one or other reason. On the other hand a sort of technical verbosity may be observed. Although this is done for practical reasons, it results in the same information being supplied in two different forms.

Relative to this engineering practice, from the theoretical point of view two questions have to be answered. In the first place: how much information do we need to define a complex operation with regard to the streams; in the second place: what is the number of independent data, unequivocally defining the unit operation itself. We do not intend to discuss the second question here, but we must answer the first one. The information needed to specify a complex operation with regard to its streams may be comprehensively described as stream vector. Now a further question arises, namely the number of data a stream vector must include in order to define unequivocally the given stream. This question is easy to answer starting from a thermodynamic viewpoint. The state of a homogeneous phase consisting of k components is unequivocally defined — according to the laws of thermodynamics — by $k + 2$ data.

In chemical engineering practice these $k + 2$ data are generally chosen as follows: the mass of the phase, $k - 1$ mole fractions, temperature and pressure. Of these state variables the mass of the phase is extensive, the others intensive. If the phase is flowing, then — instead of the mass of the phase — the flow may suitably be described by the flow rate (mass of the phase passing the cross section of the tube in the unit of time). This variable is the mass flow. A stream vector that includes $k + 2$ data in this sense is required and is adequate to specify a stream.

Practical considerations, nevertheless, make it essential to include some more data into the stream vector, in addition to those already enumerated, required and adequate. The mole fractions of all the components are listed; though one of them is redundant. The enthalpy stream of a homogeneous phase consisting of k components, with the mass flow w, composition z, pressure p and temperature T is adequately defined, it is, however, advisable to include this redundant data into the stream vector.

The data enumerated above also determine the physical state of the related mixture. Nevertheless, it is still suitable to define the physical state by a separate code in the stream vector. It has already been mentioned in Chapter 0 that the program package used in the SIMUL system for property calculations can handle computations in the vapour and liquid state only. Therefore the above-mentioned redundant parameter indicating the physical state is used; this may also be utilized to specify a mixed equilibrium phase.

From the thermodynamic point of view we have up to this point generally discussed streams consisting of k components. This course is correct and it implies that the composition of the stream has to be defined on a given point of the flow-sheet by k mole fractions, at the same time enumerating the components. It seems to be advantageous from practical point of view to classify the streams appearing on the flow-sheet according to their types, and to indicate the components in each type and the sequence of mole fractions in the stream vector.

Let the main process stream in our example be the 1st stream type, the sequence of its components n-butane, i-butane and n-pentane. The 2nd stream type is water, flowing through the heat exchangers.

The result of this decision may be expressed in symbols. Let us use for this purpose, on the one hand, the code of the stream type (stream-type code), on the other hand the component codes. In the above-mentioned program package for property calculations numbers are used to code the components, these are the component codes.

As the component code of n-butane is 4, of i-butane 73, of n-pentane 5, the 1st stream type is specified in a shortened form by the following feed-component declaration:

feed: 1(4, 73, 5).

It follows that by declaring the stream type-code the components and their sequence in the stream vector are simultaneously specified.

The stream vector is considered in this sense in the SIMUL system. If the values of each stream vector element are known, then the value of any physical property — admitted in the SIMUL system — of the stream can be calculated with suitable procedures, or the calculation can be prescribed.

The arrows representing the material flows in the block diagram are interrupted by small circles and the respective stream-type code is written over it. The block diagram in Chapter 1 (p. 31) was completed according to this convention and in this way we arrived at Figure 2.1. The list in the figure defines the stream types.

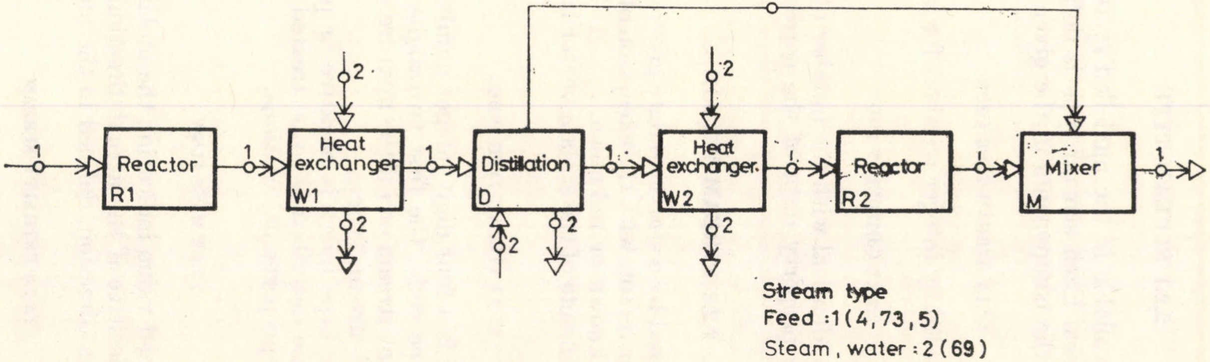


Fig. 2.1. Designation and definition of stream types

2.2 TERMINOLOGY

2.2.1 STREAM TYPE

The process streams available in the modelled system may be classified into different stream types. Each stream type is defined by enumerating the component codes of the components in the given stream.

2.2.1.1 STREAM-TYPE CODE

The stream types are coded by integer numbers for identification (stream-type code).

2.2.1.2 COMPONENT CODE

The component code is identical with the number of the row of the basic matrix storing the basic property data of the corresponding component.

2.2.2 STREAM VECTOR

Each flow is characterized by a standard date group — the stream vector. All elements of the stream vector, with the exception of the enthalpy stream, must be simultaneously known or unknown.

The sequence of the elements of the stream vector is as follows:

2.2.2.1 STREAM-TYPE INDEX

The stream-type index is a four digit integer number, the last two digits indicating the stream-type code, the first two digits being 0 if the index refers to a multicomponent stream or i if the mixture contains only the i-th component of the related stream type.

The sign of the stream type index is negative or positive depending on whether the mixture to be described is to be treated as ideal or non-ideal during the course of the property calculations.

2.2.2.2 MASS FLOW

The mass flow is a signed value indicating the molal mass velocity of the stream in kmole/s. It is positive if the actual direction of the material flow corresponds to the stream direction, defined in the model of the unit operation.

2.2.2.3 ENTHALPY STREAM

The enthalpy stream is expressed in J/s. The reference state of the molal enthalpy is chosen as the enthalpy of formation of the components in the gaseous state extrapolated to atmospheric pressure and 0 K temperature. The enthalpy of formation is negative in exothermal reactions.

2.2.2.4 TEMPERATURE

This value indicates the temperature of the fluid in K.

2.2.2.5 PRESSURE

This value indicates the static pressure of the fluid in N/m^2.

2.2.2.6 VAPOUR RATIO

The vapour ratio is a real number whose value is 0 in the liquid state, 1 in the gaseous state. Values of the vapour ratio between 0 and 1 indicate the ratio of the quantity of gas to the total quantity.

2.2.2.7 COMPOSITION

The composition is defined by a sequence of mole fractions of the components in the stream type. The sequence corresponds to the definition of the stream type.

2.3 SYSTEM OF UNITS IN THE SIMUL SYSTEM

For the sake of convenience a uniform system of units is adopted in the SIMUL system. The SI system of units was chosen and Table 2.1. lists the 7 base units. The quantity of material is expressed in kmoles instead of the moles in the SIMUL system. (At the time of drawing up the SIMUL system, the mole had not been yet included as a base unit of the SI system.)

Table 2.1
Base units and units of measure of the SI system

Units of measure	Dimension	Base units	
		Denomination	Symbol
Length	L	**meter**	**m**
Mass	M	**kilogram**	**kg**
Quantity of material	n	**mole**	**mole**
Time	T	**second**	**s**
Temperature	Θ	**kelvin**	**K**
Current intensity	—	**ampere**	**A**
Light intensity	—	**candela**	**cd**

The units of measure derived from these base units have been chosen according to the laws of physics to produce a consistent unit system. Accordingly all the derived units are expressed as products of powers of the base units, without using conversion factors.

Table 2.2

Derived units of measure

Quantity	Dimension	Units of measure		
		Expressed in base units	Denomination	Symbol
Energy	L^2MT^{-2}	m^2kg/s^2	joule	J
Force	LMT^{-2}	mkg/s^2	newton	N

Table 2.3

Variables and their units of measure in the SIMUL system

Variables	Dimension	Units of measure
Quantity of material	n	kmole
Temperature of the stream	Θ	K
Pressure of the stream	$L^{-1}MT^{-2}$	N/m^2
Molal enthalpy	$L^2MT^{-2}n^{-1}$	J/kmole
Molal density	$L^{-3}n$	$kmole/m^3$
Dynamic viscosity	$L^{-1}MT^{-1}$	Ns/m^2
Thermal conductivity	$LMT^{-3}\Theta^{-1}$	J/m s K
Surface tension	MT^{-2}	J/m^2
Isobaric molal heat	$ML^2n^{-1}T^{-2}\Theta^{-1}$	J/kmole K
Molal mass	Mn^{-1}	kg/kmole
Molal enthalpy of evaporation	$ML^2T^{-2}n^{-1}$	J/kmole

The derived variables and units are presented in Table 2.2.

The variables and units applied in the SIMUL system are listed in Table 2.3. The input and output data are supplied in these units.

2.4 PROPERTY CALCULATION OF THE STREAMS

As already mentioned in Chapter 0, the program package FISC handles the property calculations in the SIMUL system. This program package consists of procedures and a library of basic property values is available when adopting these procedures. This will be outlined in this chapter

The following abbreviations and symbols are used:

Symbols of variables:

A, B, C	Coefficients of the Antoine equation
C_p	Isobaric molal heat capacity, J/kmole
f	Fugacity, N/m^2
F	Mass flow, kmole/s
H, h	Enthalpy, J/kmole
K	Vapour-liquid phase equilibrium coefficient
L	Mass flow of the liquid phase, kmole/s
M	Molecular weight, kg/kmole
n, $ncomp$	Number of chemical components
P, p	Pressure, N/m^2
pcv	Convergence pressure, N/m^2
ΔP	$P-P_s$, N/m^2
R	Universal gas constant, Nm/kmole K
T, t	Temperature, K
V	Mass flow of the vapour, kmole/s; Molal volume, m^3/kmole
z	Mole fraction, kmole/kmole
Z	Compressibility factor
x	Mole fraction in the liquid phase, kmole/kmole
y	Mole fraction in the vapour phase, kmole/kmole

Greek letters:

λ	Thermal conductivity, J/m s K
μ	Dynamic viscosity, kg/ms
ν	Conversion factor, 1.01325×10^5, N/m^2 atm
Π	Parachor, N$^{1/4}$ m$^{11/4}$/kmole
ϱ	Molal density, kmole/m^3
σ	Surface tension, N/m

Subscripts:

b	Boiling point
corr	Correction
cr	Critical
g, v	Gas
G	Gas mixture
i, j	Component
l	Liquid
m	Mixture
p	Pseudo
r	Reduced
s	Saturated
t	Prescribed temperature
*	Ideal (as superscript)

2.4.1 SYSTEM OF BASIC MATERIAL PROPERTIES

The physical and chemical properties of the various flows are calculated using the individual basic properties of each chemical component. The data needed are available in a matrix, the rows corresponding to the components, the columns to the constants. This matrix will be termed the basic matrix of properties or in short: basic matrix.

This matrix is stored in the background store of the computer and is accessible to both the SIMUL proceduresa nd the boxes. It contains at present 214×40 elements, i.e., 214 chemical components and 40 data for each component. The assortment of procedures to calculate properties does not at present necessitate 40 data for each component. The matrix is therefore not completely filled up, the system of basic properties may be enlarged according to need. The number of rows may be increased to 999 without meeting difficulties in programming.

The columns of the basic matrix contain the following data.

Column 1
The index refers to the material features. It is a nine digit integer number structured in the following way:

Number =	*ppp*	*mmm*	*nnn*
	code referring to the polarity of the component	code referring to the molecular structure of the component	component code

The value of *ppp* is

000 if the chemical component is non-polar,
001 if the chemical component is polar and it does not contain a hydrogen bond,
002 if the chemical component is polar and contains a hydrogen bond.

The value of *mmm* is

000 if the molecular structure of the compound is "simple" (see, Section 2.4.2.3(f)),
001 if the compound is a cyclic hydrocarbon,
002 if the compound is a different hydrocarbon,
009 if the compound cannot be put in the groups mentioned above.

The value of *nnn* is

the component code, i.e., the code of the given component in the basic matrix (obviously $nnn \leq 999$).

Column 2
Molecular mass

Column 3
Critical compressibility factor

Column 4
Critical pressure

Column 5
Critical temperature

Columns 6–8
A, B and C coefficients of the Antoine equation

$$\log P = A - B/(C + \mathrm{T}),$$

which is used to calculate the saturated vapour pressure.

Column 9
Enthalpy of formation extrapolated to 0 K : HO

Columns 10–13
Coefficients *a–d* of the ideal gas enthalpy polynomial:

$$aT + bT^2 + c\,T^3 + dT^4.$$

The constant term of the enthalpy polynomial is the enthalpy of formation stored in Column 9.

Column 14
The constant term (I_s) of the entropy polynomial:

$$S(T) = I_s + a \ln T + 2bT + 3cT^2/2 + 4dT^3/3$$

Columns 15—36
The 22 coefficients of the temperature-pressure function of the vapour-liquid equilibrium coefficients (the correlation of the NGAA curves) (see, Section 2.4.2.3(m)).

Columns 37 and 38
Empty

Columns 39 and 40
Summary formula

Columns 39 and 40 of the matrix contain information about the summary formula of the compounds, namely in the form of the number of atoms of the elements in the molecule. 8 bits are reserved for each number of atoms of an element, allowing the representation of elements, occurring 255 times in the molecule. Storing capacity is provided for 10 elements in the following sequence:

Column 39:	P	J	Br	Cl	F
Column 40:	S	N	O	C	H

Table 2.4a gives the names of these components together with their serial numbers; the chemical components contained at present in the basic matrix, and their component codes and basic properties are listed in Table 2.4b.

Table 2.4a

Code and name of components

1	Methane
2	Ethane
3	Propane
4	n-Butane
5	n-Pentane
6	n-Hexane
7	n-Heptane
6	n-Octane
9	n-Nonane
10	n-Decane
11	n-Undecane
12	n-Dodecane
13	n-Hexadecane
14	2-Methylpentane
15	3-Methylpentane
16	2,2-Dimethylbutane
17	2,3-Dimethylbutane
18	Cyclopentane
19	Methylcyclopentane
20	Ethylcyclopentane
21	n-Propylcyclopentane
22	Cyclohexane
23	Methylcyclohexane
24	Ethylcyclohexane
25	n-Propylcyclohexane
26	Ethene(Ethylene)
27	Propene(Propylene)
28	1-Butene
29	1-Pentene
30	1-Hexene
31	1-Heptene
32	1-Octene
33	1-Nonene
34	1-Decene
71	Carbon Monoxide
72	Nitrogen
73	2-Methylpropane (Isobutane)
75	2,2-Dimethylpropane (Neopentane)
76	Styrene
77	2-Methyl-1,3 Butadiene (Isoprene)
78	Air
79	Sulfur
80	Sulfur Dioxide
81	Sulfur Trioxide
82	Hydrogen Sulfide
83	Carbon Disulfide
84	Carbon Oxisulfide
85	Fluorine
86	Chlorine
87	Bromine
88	Iodine
89	Hydrogen Fluoride
90	Hydrogen Chloride
91	Hydrogen Bromide
92	Hydrogen Iodide
93	Methyl Chloride
94	Methylene Chloride
95	Chloroform
96	Carbon Tetrachloride
97	Phosgene
98	Thiophosgene
99	Cyanogen
100	Hydrogen Cyanide
101	Cyanogen Chloride
102	Cyanogen Bromide
103	Cyanogen Iodide
104	Methyl Cyanide
105	Acrylonitril
142	CF_4
143	Propyon aldehyde
144	n-Butyraldehyde
145	n-Pentaldehyde
146	n-Hexaldehyde
147	n-Heptaldehyde
148	n-Octaldehyde
149	n-Nonaldehyde
150	n-Decaldehyde
151	n-Propanol
152	n-Butanol
153	n-Pentanol
154	n-Hexanol
155	n-Heptanol
156	n-Octanol
157	n-Nonanol
158	n-Decanol
159	Isopropanol
160	Tert-Butanol
161	Cyclohexanol
162	Phenol
163	Methanethiol
164	Ethanethiol
165	n-Propanethiol
166	n-Butanethiol
167	n-Pentanethiol
168	n-Hexanethiol
169	n-Heptanethiol
170	n-Octanethiol
171	n-Nonanethiol
172	n-Decanethiol
173	CH_3-S-CH_3
174	$CH_3-S-C_2H_5$
175	$CH_3-S-C_3H_7$

36 1-Dodecene
37 1-Hexadenene
38 cis-2-Butene
39 trans-2-Butene
40 2-Methylpropene (Isobutene)
41 cis-2-Pentene
42 trans-2-Pentene
43 2-Methyl-1-butene
44 3-Methyl-1-butene
45 2-Methyl-2-butene
46 Propadiene (Allene)
47 1,2-Butadiene
48 1,3-Butadiene
49 Cyclopentene
50 Cyclohexene
51 Ethyne (Acetylene)
52 Propyne (Methylacetylene)
53 1-Butine (Ethylacetylene)
54 2-Butyne (Dimethylacetylene)
55 Benzene
56 Methylbenzene (Toulene)
57 Ethylbenzene
58 n-Propylbenzene
59 1,2-Dimethylbenzene (o-Xylene)
60 1,3-Dimethylbenzene (m-Xylene)
61 1,4-Dimethylbenzene (p-Xylene)
62 Isopropylbenzene (Cumene)
63 Isopropenylbenzene
64 Oxygen
65 Nitric Oxide
66 Carbon
67 Hydrogen
68 Hydroxyl
69 Water
70 Carbon Dioxide

107 Nitrogen Dioxide
108 Dinitrogen Tetroxid
109 Formaldehyde
110 Acetaldehyde
111 Methanol
112 Ethanol
113 Ethylene Oxid
114 Ketene
115 Cyclopropane
116 Carbon Suboxide
117 Acetone
118 Allyl Alcohol
119 Chloroethene
120 1,1-Dichloroethene
121 cis-1,2-Dichloroethene
122 trans-1,2-Dichloroethene
123 Trichloroethene
124 Tetrachloroethene
125 Ammonia
126 Hydrazine
127 Methylamine
128 Dymethilamine
129 Trimethylamine
130 1-Chloroethane
131 1,1-Dichloroethane
132 1,2-Dichloroethane
133 1,1,1-Trichloroethane
134 1,1,2-Trichloroethane
135 1,1,1,2-Tetrachloroethane
136 1,1,2,2-Tetrachloroethane
137 Pentachloroethane
138 Hexachloroethane
139 CCl_3F
140 CCl_2F_2
141 $CClF_3$

177 $CH_3-S-C_5H_{11}$
178 $CH_3-S-C_6H_{13}$
179 $CH_3-S-C_7H_{15}$
180 $CH_3-S-C_8H_{17}$
181 $CH_3-S-C_9H_{19}$
182 $CH_3-S-C_{10}H_{21}$
183 $CH_3-S-S-CH_3$
184 $C_2H_5-S-S-C_2H_5$
185 $C_3H_7-S-S-C_3H_7$
186 $C_4H_9-S-S-C_4H_9$
187 $C_5H_{11}-S-S-C_5H_{11}$
186 $C_6H_{13}-S-S-C_6H_{13}$
189 $C_7H_{15}-S-S-S-C_7H_{15}$
190 $C_8H_{17}-S-S-C_8H_{17}$
191 $C_9H_{19}-S-S-C_9H_{19}$
192 $C_{10}H_{21}-S-S-C_{10}H_{21}$
193 Acetic acid
194 Acetic anhydride
195 Methyl acetate
196 Ethyl acetate
197 n-propyl acetate
198 i-Propyl acetate
199 n-Butyl acetate
200 sec-Butyl acetate
201 tert-Butyl acetate
202 n-Amyl acetate
203 Naphtalene
204 n-Methyl Styrene
205 3-Methyl Hexane
206 1-Methyl-3-Ethyl-benzene
207 Anilin

Table 2.4b
Basic matrix

column 2-8

no	M	zc	pc	Tc	A	B	C
1	16.04	.28916	46.407 E+5	191.10	8.7367	389.9	-7.16
2	30.07	.28458	48.839 E+5	305.50	8.9276	656.4	-17.16
3	44.10	.27668	42.556 E+5	370.00	8.9546	813.2	-25.16
4	58.12	.27408	37.997 E+5	425.20	8.9552	945.9	-33.16
5	72.15	.26866	33.741 E+5	469.80	8.9771	1064.6	-41.16
6	86.18	.26402	30.296 E+5	507.90	9.0027	1171.5	-48.79
7	100.21	.25949	27.358 E+5	540.20	9.0273	1268.1	-56.26
8	114.23	.25800	24.926 E+5	569.40	9.0487	1355.1	-63.64
9	128.26	.25025	22.798 E+5	595.00	9.0600	1428.8	-71.54
10	142.29	.24653	21.076 E+5	619.00	9.0786	1501.3	-78.68
11	156.31	.24131	19.454 E+5	640.00	9.1016	1572.5	-85.14
12	170.34	.23768	18.137 E+5	659.00	9.1055	1625.9	-92.85
13	226.45	.22357	14.185 E+5	725.00	9.1553	1831.3	-118.63
14	86.18	.26860	30.296 E+5	497.90	8.9640	1135.4	-46.59
15	86.18	.27295	31.208 E+5	504.70	8.9738	1152.4	-46.03
16	86.18	.27446	31.107 E+5	489.40	8.8797	1081.2	-43.82
17	86.18	.26947	31.309 E+5	500.30	8.9347	1127.2	-44.26
18	70.13	.27613	45.191 E+5	511.80	9.0117	1124.2	-41.80
19	84.16	.27290	37.896 E+5	532.80	8.9877	1186.1	-47.12
20	98.19	.26883	33.944 E+5	569.50	9.0120	1298.6	-52.48
22	84.16	.27151	40.530 E+5	553.00	8.9699	1203.5	-50.30
23	98.19	.25141	34.775 E+5	572.30	8.9518	1272.9	-51.53
26	28.05	.26757	50.662 E+5	282.40	8.8725	585.0	-18.16
27	42.08	.27558	46.204 E+5	365.00	8.9445	785.0	-26.16
28	56.11	.27674	40.226 E+5	419.60	8.9678	926.1	-33.16

column 2-8, continued

no	M	zc	pc	Tc	A	B	C
29	70.13	.26600	40.530 E+5	474.00	8.9714	1044.9	-39.64
38	56.11	.27552	41.543 E+5	428.00	8.9942	960.1	-36.16
39	56.11	.27552	41.543 E+5	428.00	8.9944	960.8	-33.16
40	56.11	.27531	40.023 E+5	417.90	8.9662	923.2	-33.16
41	70.13		40.800 E+5	475.60	8.9976	1068.0	-42.57
42	70.13		40.800 E+5	475.60	9.0307	1084.0	-40.19
43	70.13		34.240 E+5	464.80	8.9980	1053.8	-40.37
45	70.13		34.450 E+5	470.00	9.0405	1095.1	-40.32
47	54.09	.27000	43.127 E+5	422.15	9.2868	1121.0	-22.16
48	54.09	.27060	43.266 E+5	425.00	8.9843	935.5	-33.61
51	26.04	.27454	62.416 E+5	309.00	8.9498	565.7	-47.66
52	40.06	.27000	53.500 E+5	401.00	9.1245	873.4	-37.16
55	78.11	.27402	49.244 E+5	562.00	9.0306	1211.0	-52.37
56	92.14	.27312	42.151 E+5	594.00	9.0795	1344.8	-53.68
57	106.17	.26908	38.503 E+5	619.60	9.0821	1424.3	-59.95
58	120.20	.26252	32.424 E+5	638.80	9.0763	1491.3	-66.02
59	106.17	.27056	37.389 E+5	631.60	9.1238	1474.7	-59.47
60	106.17	.27643	36.477 E+5	619.00	9.1340	1462.3	-58.05
61	106.17	.25538	35.464 E+5	618.00	9.1154	1453.4	-57.85
62	120.20	.26371	32.424 E+5	635.90	9.0616	1460.8	-65.38
63	118.18	.25600	33.100 E+5	664.00	10.5171	2560.7	25.80
64	32.00	.30766	50.764 E+5	154.80	8.8660	326.2	-5.70
65	30.01	.25133	64.848 E+5	180.00			
67	2.02	.30450	12.970 E+5	33.30	8.0310	70.[illegible]	3.00
69	18.01	.23013	221.192 E+5	647.40	10.1776	1718.5	-40.20

column 2-8, continued

no	M	zc	pc	Tc	A	B	C
70	44.01	.27454	73.866 E+5	304.20	9.5750	738.3	-33.10
71	28.01	.29432	34.957 E+5	133.00	8.7110	280.1	-5.40
72	28.01	.29148	33.944 E+5	126.20	8.5395	235.3	-10.46
73	58.12	.28275	36.477 E+5	408.10	8.8730	882.8	-33.16
74	72.15	.26789	33.336 E+5	461.00	8.9146	1020.0	-40.06
75	72.15	.26899	32.019 E+5	433.80	8.8630	950.8	-36.16
76	104.15	.26100	38.200 E+5	635.00	9.9307	2038.6	-4.33
77	68.12	.24700	36.900 E+5	483.00	9.0282	1081.0	-38.49
78	28.97	.30033	38.909 E+5	132.45			
80	64.06	.26858	78.831 E+5	430.70	9.2260	996.1	-36.90
81	80.06	.26187	84.910 E+5	491.40	9.2051	858.4	-114.36
82	34.08	.28333	90.078 E+5	373.60	9.1311	747.3	-32.26
83	76.14	.29276	79.033 E+5	552.00	9.3192	1291.1	-19.86
85	38.00	.29600	53.530 E+5	144.15			
86	70.91	.27579	77.108 E+5	417.00	9.1430	904.2	-20.00
87	159.82	.26900	103.351 E+5	584.00			
88	253.81	.26800	117.160 E+5	785.00			
89	20.01	.11700	64.640 E+5	461.00			
90	36.46	.26600	82.580 E+5	324.60	9.0671	644.8	-29.16
91	80.92	.31000	85.113 E+5	363.20	9.0498	705.5	-32.36
92	127.91	.31800	82.073 E+5	423.00			
93	50.49	.27588	66.773 E+5	416.30	9.1756	920.4	-28.46
94	84.93	.27700	60.795 E+5	510.00			
95	119.38	.29435	54.715 E+5	536.60	9.3149	1284.5	-36.26
96	153.82	.27204	45.596 E+5	556.40	9.1110	1243.0	-43.30

column 2-8, continued

no	M	zc	pc	Tc	A	B	C
97	98.92	.28499	56.742 E+5	455.00	9.2211	1046.1	-32.56
99	52.04		59.782 E+5	400.00	8.9484	710.9	-73.76
100	27.03	.19733	53.905 E+5	456.70	9.1379	964.8	-64.56
106	44.01	.27171	72.650 E+5	309.70			
107	46.00	.23200	101.000 E+5	431.15			
111	32.04	.22080	79.755 E+5	506.00	10.2249	1604.9	-31.06
112	46.07	.25800	66.300 E+5	507.46	10.1954	1602.0	-43.96
113	44.05	.25515	71.941 E+5	468.00			
114	42.04	.27000	50.000 E+5	325.60	9.4380	793.5	-38.00
115	42.08	.27200	55.196 E+5	398.05			
117	58.08	.23780	47.217 E+5	508.70	9.4764	1327.5	-33.06
125	17.03	.24252	112.775 E+5	405.50	9.5880	950.9	-32.30
126	0.27		146.921 E+5	653.00			
127	31.06		74.575 E+5	430.10	9.4876	1026.5	-37.96
128	45.08		53.094 E+5	437.70	9.3055	1021.4	-43.26
129	59.11	.28719	40.733 E+5	433.30			
131	98.96		50.662 E+5	523.00			
132	98.96	.25330	53.702 E+5	561.00			
139	137.37	.27600	43.200 E+5	471.20	9.0461	1045.6	-37.66
140	120.91	.27300	39.900 E+5	384.70	8.9298	820.5	-34.06
141	104.46	.28000	39.390 E+5	302.00	8.3899	503.3	-43.46
142	88.00	.28000	38.400 E+5	227.70			
151	60.10	.25064	50.865 E+5	537.00			
152	74.12	.25900	43.740 E+5	562.95			
153	88.15		44.200 E+5	585.60			

column 2-8, continued

no	M	zc	pc	Tc	A	B	C
154	102.18		40.400 E+5	610.00			
155	116.20		37.100 E+5	638.40			
159	60.10	.27802	53.702 E+5	508.80			
161	100.16		36.100 E+5	625.00			
162	94.11	.24400	61.302 E+5	692.40	9.4584	1596.8	-95.06
163	48.11		72.100 E+5	470.00			
164	62.13		54.200 E+5	499.00			
173	62.13		54.600 E+5	503.10			
193	60.05	.27000	57.958 E+5	594.75	9.2964	1370.4	-72.20
194	102.09	.27000	46.609 E+5	569.15	9.4583	1532.2	-68.70
195	74.08	.26360	46.910 E+5	506.90	9.2900	1204.0	-50.00
196	88.10	.26160	38.300 E+5	523.30	9.1940	1228.0	-57.00
197	102.13	.25940	33.340 E+5	549.40	9.1670	1297.0	-63.00
198	102.13	.26020	34.980 E+5	540.40	9.1740	1272.0	-61.00
199	116.16	.25690	31.690 E+5	579.20	9.1760	1375.0	-70.00
200	116.16	.25910	31.410 E+5	561.20	9.1420	1325.0	-65.00
201	116.16	.26330	30.940 E+5	542.60	9.0660	1259.0	-58.00
202	132.20	.25410	28.150 E+5	601.20	9.1720	1443.0	-76.00
203	128.16	.27000	41.138 E+5	748.40	9.2517	1828.0	-60.63
204	118.17	.25200	33.944 E+5	656.00	9.1325	1461.9	-53.94
205	100.20	.26700	28.100 E+5	535.60	8.9925	1240.2	-64.65
206	120.19	.25500	31.000 E+5	636.20	9.1407	1529.2	-68.89
207	93.12	.25000	52.300 E+5	698.80	9.4265	1717.0	

column 9-13

no	HO	a	b	c	d
1	-6.6725 E+7	2.9479 E+4	6.6252	1.9184 E-2	-7.0131 E-6
2	-6.8863 E+7	2.1492 E+4	5.9641 E+1	-1.0528 E-3	-3.6685 E-6
3	-8.1284 E+7	1.6391 E+4	1.1366 E+2	-2.2610 E-2	-9.1770 E-8
4	-9.7364 E+7	2.2414 E+4	1.4877 E+2	-3.1370 E-2	4.5236 E-7
5	-1.1364 E+8	2.5150 E+4	1.8885 E+2	-4.3507 E-2	1.7881 E-6
6	-1.2901 E+8	2.8055 E+4	2.2896 E+2	-5.5941 E-2	3.2833 E-6
7	-1.4424 E+8	3.0833 E+4	2.6932 E+2	-6.8485 E-2	4.7634 E-6
8	-1.5948 E+8	3.3778 E+4	3.0910 E+2	-8.0438 E-2	6.0650 E-6
9	-1.7469 E+8	3.6777 E+4	3.4880 E+2	-9.2369 E-2	7.3642 E-6
10	-1.8991 E+8	3.9379 E+4	3.8992 E+2	-1.0588 E-1	9.2087 E-6
11	-2.0515 E+8	4.2360 E+4	4.2969 E+2	-1.1795 E-1	1.0584 E-5
12	-2.2035 E+8	4.5266 E+4	4.6965 E+2	-1.3007 E-1	1.1925 E-5
13	-2.8125 E+8	5.6742 E+4	6.3013 E+2	-1.7964 E-1	1.7772 E-5
14	-1.3429 E+8	1.8687 E+4	2.3780 E+2	-4.7241 E-2	-5.3795 E-6
15	-1.3382 E+8	3.7993 E+4	1.8229 E+2	1.2013 E-2	-2.8009 E-5
16	-1.4475 E+8	1.3669 E+4	2.4773 E+2	-5.4732 E-2	-3.2686 E-6
17	-1.3700 E+8	1.8307 E+4	2.2495 E+2	-2.5495 E-2	-1.5856 E-5
18	-4.3982 E+7	-1.7725 E+3	1.7472 E+2	-2.7733 E-2	-3.3130 E-6
19	-6.8884 E+7	2.7677 E+3	2.2028 E+2	-4.6377 E-2	3.8723 E-8
20	-8.3917 E+7	6.7406 E+3	2.5594 E+2	-5.4044 E-2	2.6930 E-7
21	-9.9529 E+7	9.6334 E+3	2.9589 E+2	-6.6192 E-2	1.6312 E-6
22	-8.2931 E+7	-1.0006 E+4	2.3555 E+2	-4.3908 E-2	-2.7026 E-6
23	-1.0939 E+8	-1.1350 E+4	2.9751 E+2	-7.5586 E-2	3.9692 E-6
24	-1.2044 E+8	-1.3643 E+4	3.5228 E+2	-1.0059 E-1	8.9752 E-6
25	-1.3594 E+8	-1.7761 E+4	4.1413 E+2	-1.3439 E-1	1.7166 E-5

column 9-13, continued

no	HO	a	b	c	d
26	6.1027 E+7	2.1414 E+4	4.5101 E+1	-2.4330 E-3	-2.3762 E-6
27	3.5667 E+7	2.0310 E+4	8.5745 E+1	-1.4361 E-2	-1.0242 E-6
28	2.2309 E+7	1.9867 E+4	1.3304 E+2	-3.2602 E-2	2.0498 E-6
29	5.0228 E+6	2.5835 E+4	1.6844 E+2	-4.1788 E-2	2.7669 E-6
30	-1.0309 E+7	2.8702 E+4	2.0799 E+2	-5.3303 E-2	3.8811 E-6
31	-2.5547 E+7	3.1638 E+4	2.4783 E+2	-6.5373 E-2	5.2335 E-6
32	-4.0777 E+7	3.4347 E+4	2.8859 E+2	-7.8423 E-2	6.9023 E-6
33	-5.5982 E+7	3.7390 E+4	3.2806 E+2	-9.0136 E-2	8.1470 E-6
34	-7.1219 E+7	4.0296 E+4	3.6799 E+2	-1.0226 E-1	9.5010 E-6
35	-8.6458 E+7	4.3223 E+4	4.0788 E+2	-1.1436 E-1	1.0857 E-5
36	-1.0165 E+8	4.6018 E+4	4.4832 E+2	-1.2714 E-1	1.2464 E-5
37	-1.6256 E+8	5.7614 E+4	6.0830 E+2	-1.7609 E-1	1.8081 E-5
38	1.6294 E+7	2.0592 E+4	1.1661 E+2	-1.6735 E-2	-2.4642 E-6
39	1.0669 E+7	2.2966 E+4	1.2565 E+2	-2.7278 E-2	7.6041 E-7
40	7.1103 E+6	1.8696 E+4	1.3893 E+2	-3.8637 E-2	3.9496 E-6
41	-2.9525 E+5	1.9475 E+4	1.6820 E+2	-3.8530 E-2	1.5401 E-6
42	-4.9617 E+6	2.2133 E+4	1.7205 E+2	-4.4989 E-2	3.7942 E-6
43	-9.4878 E+6	1.8163 E+4	1.8886 E+2	-5.9299 E-2	7.7549 E-6
44	-2.9302 E+6	1.8251 E+4	2.0112 E+2	-7.1858 E-2	1.1396 E-5
45	-1.4912 E+7	1.9965 E+4	1.6839 E+2	-3.9978 E-2	2.1884 E-6
46	1.9979 E+8	2.0288 E+4	7.9846 E+1	-2.5284 E-2	3.3120 E-6
47	1.7590 E+8	2.1714 E+4	1.1664 E+2	-3.4106 E-2	3.7777 E-6
48	1.2655 E+8	1.2123 E+4	1.4368 E+2	-5.5661 E-2	9.3746 E-6
49	5.8275 E+7	4.6080 E+3	1.4542 E+2	-2.0449 E-2	-3.9218 E-6
50	3.1734 E+7	-8.3190 E+3	2.3862 E+2	-7.4330 E-2	8.4696 E-6

column 9-13. continued

no	HO	a	b	c	d
51	2.2735 E+8	2.1641 E+4	4.7295 E+1	-2.3484 E-2	5.2212 E-6
52	1.9266 E+8	2.2748 E+4	7.5955 E+1	-2.3711 E-2	3.1533 E-6
53	1.7894 E+8	1.9944 E+4	1.2386 E+2	-4.1875 E-2	6.2064 E-6
54	1.6128 E+8	2.7534 E+4	9.7441 E+1	-1.9108 E-2	-9.0841 E-8
55	1.0081 E+8	-2.3893 E+3	1.7914 E+2	-5.7363 E-2	6.7299 E-6
56	7.3600 E+7	1.2705 E+2	2.1590 E+2	-6.6951 E-2	7.5276 E-6
57	5.8630 E+7	1.4921 E+3	2.6516 E+2	-8.8104 E-2	1.1547 E-5
58	4.1926 E+7	3.1023 E+3	3.1371 E+2	-1.1090 E-1	1.6794 E-5
59	4.6632 E+7	8.8546 E+3	2.5158 E+2	-7.9728 E-2	9.7788 E-6
60	4.6042 E+7	5.0133 E+3	2.5016 E+2	-7.5340 E-2	8.0893 E-6
61	4.6643 E+7	6.8542 E+3	2.4387 E+2	-7.0407 E-2	6.8416 E-6
62	3.9032 E+7	-1.8593 E+3	3.1910 E+2	-1.1046 E-1	1.5392 E-5
63	1.3981 E+8	7.2634 E+3	2.8294 E+2	-9.7242 E-2	1.3326 E-5
64	0.0000	2.8459 E+4	6.9999 E-1	3.5735 E-3	-1.3971 E-6
65	8.9917 E+7	3.1957 E+4	-6.2167	8.0775 E-3	-2.4258 E-6
66	0.0000	-2.9738 E+3	2.4287 E+1	-1.0213 E-2	1.6868 E-6
67	0.0000	2.8253 E+4	8.0474 E-1	-7.7435 E-5	1.6121 E-7
68	-2.8365 E+5	2.9984 E+4	-1.4292	1.2976 E-3	-8.8817 E-8
69	-2.3906 E+8	3.2889 E+4	-5.3643 E-1	5.1647 E-3	-1.5005 E-6
70	-3.9347 E+8	2.3977 E+4	2.7653 E+1	-1.0511 E-2	1.6748 E-6
71	-1.1394 E+8	2.9391 E+4	-2.3257	4.7794 E-3	-1.4687 E-6
72	0.0000	2.9476 E+4	-2.5269	4.5260 E-3	-1.3212 E-6
73	-1.0282 E+8	1.4369 E+4	1.6213 E+2	-3.9137 E-2	1.8592 E-6
74	-1.2042 E+8	1.8954 E+4	1.9529 E+2	-4.4075 E-2	1.1828 E-6
75	-1.3085 E+8	7.5457 E+3	2.2951 E+2	-7.2296 E-2	8.7576 E-6

column 9-13, continued

no	HO	a	b	c	d
76	1.7258 E+8	-1.9275 E+4	2.8930 E+2	-1.1909 E-1	2.0734 E-5
77	8.3624 E+7	1.0218 E+5	-2.2202 E+1	1.1551 E-1	-4.3500 E-5
78	-8.3293 E+6	2.6602 E+4	4.7896	-1.0947 E-3	1.0563 E-7
79	1.2502 E+8	3.0920 E+4	5.2738	-1.8381 E-3	2.3815 E-7
80	-2.9475 E+8	3.2250 E+4	1.8489 E+1	-6.1384 E-3	7.5959 E-7
81	-3.8819 E+8	1.6986 E+4	7.1199 E+1	-3.5517 E-2	7.4707 E-6
82	-1.6032 E+7	2.8212 E+4	8.5175	8.8918 E-4	-6.5423 E-7
83	1.1381 E+8	3.4207 E+4	2.5719 E+1	-1.1732 E-2	2.0987 E-6
84	-1.3709 E+8	2.3784 E+4	3.6736 E+1	-1.7732 E-2	3.3193 E-6
85	0.0000	2.7145 E+4	1.0054 E+1	-4.6464 E-3	8.1190 E-7
86	0.0000	2.3194 E+4	2.3798 E+1	-1.7338 E-2	4.5616 E-6
87	0.0000	3.4072 E+4	4.7448	-2.8266 E-3	6.7255 E-7
88	0.0000	3.5772 E+4	2.4951	-1.3790 E-3	3.2057 E-7
89	-2.7107 E+8	3.0362 E+4	-2.8048	2.4070 E-3	-4.3719 E-7
90	-9.5694 E+7	3.1063 E+4	-5.5418	5.9908 E-3	-1.5551 E-6
91	-5.2482 E+7	2.9306 E+4	-2.0561	3.6790 E-3	-9.7856 E-7
92	2.0901 E+7	2.6268 E+4	3.6840	1.7025 E-6	-1.3899 E-7
93	-7.2259 E+7	1.4158 E+4	5.0129 E+1	-1.2918 E-2	8.7842 E-7
94	-1.2470 E+8	1.8929 E+4	6.9172 E+1	-3.1086 E-2	5.9408 E-6
95	-8.5326 E+7	2.3183 E+4	9.2406 E+1	-5.4766 E-2	1.2815 E-5
96	-1.1012 E+8	5.6961 E+4	6.1699 E+1	-3.5486 E-2	7.7759 E-6
97	-2.2413 E+8	3.6540 E+4	5.5018 E+1	-3.6001 E-2	9.8974 E-6
98	2.3241 E+5	2.4930 E+4	9.9663 E+1	-8.7579 E-2	3.0260 E-5
99	3.0240 E+8	3.4348 E+4	5.0144 E+1	-3.1513 E-2	9.2006 E-6
100	1.3092 E+8	2.5362 E+4	2.2089 E+1	-8.5569 E-3	1.5979 E-6

column 9-13, continued

no	HO	a	b	c	d
101	1.4265 E+8	3.0166 E+4	3.3556 E+1	-2.1738 E-2	6.2225 E-6
102	-1.9855 E+6	3.6394 E+4	2.3130 E+1	-1.2852 E-2	3.2807 E-6
103	2.2632 E+8	3.7963 E+4	2.3750 E+1	-1.5317 E-2	4.5285 E-6
104	8.1165 E+6	1.9935 E+4	6.1507 E+1	-1.6116 E-2	9.9862 E-7
105	8.1646 E+6	1.2290 E+4	1.0714 E+2	-4.9636 E-2	1.0814 E-5
106	4.7484 E+7	2.3730 E+5	-3.3404 E+2	2.4693 E-1	-6.3055 E-5
107	3.7941 E+7	2.1892 E+4	3.0402 E+1	-1.3021 E-2	2.2823 E-6
108	2.0296 E+7	1.1878 E+4	1.8114 E+2	-1.9341 E-1	9.9903 E-5
109	-1.1003 E+8	1.8090 E+4	2.9313 E+1	-4.3704 E-3	-4.3939 E-7
1 10	-1.5358 E+8	1.4375 E+4	7.3756 E+1	-1.4614 E-2	-1.3950 E-6
111	-1.8874 E+8	1.9622 E+4	4.3521 E+1	-7.9123 E-4	-3.5879 E-6
112	-2.1808 E+8	2.0068 E+4	1.0548 E+2	-3.6472 E-2	5.8032 E-6
113	-3.3446 E+7	-1.3178 E+4	1.2432 E+2	-5.5495 E-2	1.1565 E-5
114	-5.6409 E+7	1.7668 E+4	6.1665 E+1	-2.5041 E-2	4.5070 E-6
115	7.7802 E+7	-3.5449 E+4	1.9152 E+2	-9.7005 E-2	2.2970 E-5
1 16	-4.1061 E+6	3.7076 E+4	6.0891 E+1	-2.7400 E-2	5.2011 E-6
117	-1.9692 E+8	6.1078 E+3	1.3971 E+2	-5.1918 E-2	8.5514 E-6
118	-1.0415 E+8	2.8248 E+3	1.4807 E+2	-5.8979 E-2	1.0427 E-5
119	4.0234 E+7	1.1550 E+4	8.6853 E+1	-3.6808 E-2	6.8120 E-6
120	3.7372 E+7	2.9532 E+4	8.3513 E+1	-3.9085 E-2	7.7703 E-6
121	3.3962 E+7	2.1966 E+4	9.2018 E+1	-4.3709 E-2	8.7388 E-6
122	3.6117 E+7	2.5993 E+4	8.6180 E+1	-3.9881 E-2	7.8083 E-6
123	-4.8328 E+5	4.4329 E+4	8.4908 E+1	-4.3993 E-2	9.2158 E-6
124	1.8564 E+7	6.8638 E+4	7.0885 E+1	-3.8866 E-2	8.3167 E-6
125	-3.8073 E+7	2.4446 E+4	1.8906 E+1	-1.3953 E-3	-4.2436 E-7

column 9-13, continued

no	HO	a	b	c	d
126	1.0930 E+8	2,1650 E+4	6.5211 E+1	-2.5411 E-2	4.5160 E-6
127	-1,1067 E+7	1.0975 E+4	7.8394 E+1	-2.5148 E-2	3.6996 E-6
128	-1.9864 E+6	-2.5065 E+3	1.4001 E+2	-4.9354 E-2	7.6352 E-6
129	-1.3576 E+7	-9.7280 E+3	2.0247 E+2	-7.8265 E-2	1.3299 E-5
130	-3.5836 E+7	2.4405 E+3	1.2058 E+2	-4.8295 E-2	8.4981 E-6
131	1.2620 E+7	1.9712 E+4	1.1689 E+2	-5.0407 E-2	9.4475 E-6
132	-6.9748 E+7	3.1530 E+4	9.5575 E+1	-3.6099 E-2	6.0177 E-6
133	6.3869 E+6	4.4062 E+4	1.0525 E+2	-4.7966 E-2	9.3471 E-6
134	8.8289 E+6	3.1488 E+4	1.2289 E+2	-5.8519 E-2	1.1678 E-5
135	4.4100 E+6	4.7351 E+4	1.2014 E+2	-5.8966 E-2	1.1928 E-5
136	5.4229 E+6	4.2426 E+4	1.2624 E+2	-6.2461 E-2	1.2685 E-5
137	-3.0303 E+5	6.3295 E+4	1.2202 E+2	-6.5243 E-2	1.3896 E-5
138	-6.8509 E+6	8.8180 E+4	1.1263 E+2	-6.4617 E-2	1.4237 E-5
139	-2.9235 E+8	3.2721 E+4	1,0856 E+2	-7.8476 E-2	2.2820 E-5
140	-4.6590 E+8	2.5046 E+4	1.1035 E+2	-7.4394 E-2	2.0335 E-5
141	-6.5583 E+7	1.0001 E+4	1.3523 E+2	-9.9185 E-2	3.0161 E-5
142	-9.0519 E+8	8.2709 E+3	1.1877 E+2	-7.3499 E-2	1.8739 E-5
143	-1.5307 E+8	7.5442 E+1	2.3575 E-2	-2.5181 E-5	2.0255 E-9
144	-1.6262 E+8	9.2144 E+1	6.0339 E-2	-7.3650 E-5	2,1287 E-8
145	-1.7393 E+8	1.1784 E+2	7.6782 E-2	-9.4012 E-5	2.6201 E-8
146	-1.8520 E+8	1.8450 E+2	-1.5261 E-2	7.5136 E-8	-1.0306 E-8
147	-1.9633 E+8	1.1442 E+2	2.5552 E-1	-3.0196 E-4	1.0537 E-7
148	-2.0747 E+8	1.8401 E+2	1.5968 E-1	-2.0397 E-4	6.6045 E-8
149	-2,1857 E+8	2.4337 E+2	9.5008 E-2	-1.4493 E-4	4.3964 E-8
150	-2.2971 E+8	2.3920 E+2	1.7599 E-1	-2.2356 E-4	6.7745 E-8

column 9-13, continued

no	HO	a	b	c	d
151	-2.1713 E+8	1.6114 E+1	2.2487 E-1	-2.4144 E-4	8.3051 E-8
152	-2.2999 E+8	4.8915 E+1	2.4958 E-1	-2.8627 E-4	1.0179 E-7
153	-2.4222 E+8	1.0759 E+2	1.7822 E-1	-2.1397 E-4	7.3154 E-8
154	-2.5366 E+8	1.3765 E+2	1.9405 E-1	-2.4475 E-4	8.6114 E-8
155	-2.6487 E+8	1.0251 E+2	3.5336 E-1	-4.0385 E-4	1.3877 E-7
156	-2.7601 E+8	1.4293 E+2	3.4205 E-1	-4.1049 E-4	1.4544 E-7
157	-2.8716 E+8	1.9698 E+2	2.9705 E-1	-3.7572 E-4	1.3262 E-7
158	-2.9830 E+8	2.2732 E+2	2.9496 E-1	-3.7265 E-4	1.2848 E-7
159	-2.3137 E+8	6.4313 E+1	1.2477 E-1	-1.4478 E-4	4.7847 E-8
160	-2.7199 E+8	9.6072 E+1	1.6819 E-1	-2.1293 E-4	7.5135 E-8
161	-2.2672 E+8	4.8600 E+1	3.8075 E-1	-3.9064 E-4	1.2373 E-7
162	-6.0438 E+7	5.1471 E+1	2.7151 E-1	-3.1929 E-4	1.1358 E-7
163	-6.4678 E+7	2.6106 E+2	-5.8705 E-1	6.3968 E-4	-2.4885 E-7
164	-7.9085 E+7	2.8552 E+2	-5.3721 E-1	5.7058 E-4	-2.2256 E-7
165	-9.0566 E+7	3.7210 E+2	-7.3233 E-1	8.3079 E-4	-3.4044 E-7
166	-1.0129 E+8	4.2302 E+2	-7.3400 E-1	7.7901 E-4	-3.0552 E-7
167	-1.1449 E+8	4.8857 E+2	-8.1968 E-1	8.6547 E-4	-3.3983 E-7
168	-1.2501 E+8	5.5449 E+2	-9.0762 E-1	9.5554 E-4	-3.7582 E-7
169	-1.3615 E+8	6.2020 E+2	-9.9464 E-1	1.0444 E-3	-4.1130 E-7
170	-1.4730 E+8	6.8553 E+2	-1.0791	1.1288 E-3	-4.4455 E-7
171	-1.5840 E+8	7.5125 E+2	-1.1661	1.2176 E-3	-4.8004 E-7
172	-1.6954 E+8	8.1671 E+2	-1.2514	1.3033 E-3	-5.1388 E-7
173	-6.9874 E+7	2.8552 E+2	-5.3721 E-1	5.7058 E-4	-2.2256 E-7
174	-8.2317 E+7	3.4928 E+2	-6.2083 E-1	6.5502 E-4	-2.5536 E-7
175	-9.4969 E+7	4.1521 E+2	-7.1027 E-1	7.4802 E-4	-2.9289 E-7

column 9-13, continued

no	HO	a	b	c	d
176	-1.0683 E+8	4.8076 E+2	-7.9593 E-1	8.3447 E-4	-3.2719 E-7
177	-1.1764 E+8	5.4647 E+2	-8.8298 E-1	9.2334 E-4	-3.6266 E-7
178	-1.2891 E+8	6.1219 E+2	-9.7004 E-1	1.0122 E-3	-3.9816 E-7
179	-1.4005 E+8	6.7785 E+2	-1.0560	1.0985 E-3	-4.3219 E-7
180	-1.5120 E+8	7.4349 E+2	-1.1428	1.1873 E-3	-4.6767 E-7
181	-1.6230 E+8	8.1061 E+2	-1.2374	1.2895 E-3	-5.1079 E-7
182	-1.7345 E+8	8.7596 E+2	-1.3219	1.3740 E-3	-5.4428 E-7
183	-1.1611 E+8	3.8756 E+2	-7.5480 E-1	7.8632 E-4	-3.0145 E-7
184	-1.4681 E+8	5.1904 E+2	-9.1528 E-1	9.4643 E-4	-3.6676 E-7
185	-1.7078 E+8	6.8726 E+2	-1.2004	1.2455 E-3	-4.8316 E-7
186	3.8370 E+8	8.1433 E+2	-1.3561	1.3968 E-3	-5.4177 E-7
187	-2.1863 E+8	9.6376 E+2	-1.6363	1.7646 E-3	-7.1845 E-7
188	9.4787 E+7	1.0792 E+3	-1.7144	1.7690 E-3	-6.9292 E-7
189	-2.6279 E+8	1.2105 E+3	-1.8893	1.9483 E-3	-7.6409 E-7
190	-2.8508 E+8	1.3408 E+3	-2.0557	2.1126 E-3	-8.2815 E-7
191	-3.0733 E+8	1.4773 E+3	-2.2544	2.3271 E-3	-9.1649 E-7
192	-3.2962 E+8	1.6092 E+3	-2.4309	2.5106 E-3	-9.9143 E-7
193	-4.5178 E+8	4.1366 E+4	5.6061 E+1	-8.2199 E-3	0.0000
194	-5.9715 E+8	7.6618 E+4	6.8622 E+1	1.5770 E-3	0.0000
203	1.7523 E+8	-6.0586 E+4	4.0727 E+2	-1.9770 E-1	4.1979 E-5
204	1.4206 E+8	-1.5468 E+4	3.2061 E+2	-1.2244 E-1	1.9189 E-5
205	-1.4634 E+8	-2.3376 E+4	3.7453 E+2	-1.3545 E-1	1.4002 E-5
206	3.1790 E+7	-4.2183 E+4	3.9671 E+2	-1.7712 E-1	3.5860 E-5
207	8.2480 E+7	3.0601 E+4	3.8842 E+2	-1.7778 E-1	1.2618 E-5

2.4.2 CALCULATION OF PROPERTIES

For simulation mode calculations it is necessary to know the physical and chemical properties of the streams. These properties are calculated using uniform methods in the SIMUL system. These methods are included into the system as global accessible standard procedures.

2.4.2.1 FUNDAMENTAL BASE OF THE CALCULATION METHODS

The law of corresponding states is in most cases the base for property calculations of pure substances and mixtures. According to this law the "reduced properties" of two materials are equal if their reduced state variables are identical. The law of corresponding states is valid with fair accuracy for pure substances and for mixtures also. It was obvious that the procedures for property calculations in the SIMUL system should be based on this principle.

The law of corresponding states is suitable for the estimation of all properties that are basically determined by intermolecular forces (entalphy departure). Properties deriving from intramolecular forces (enthalpy of perfect gas) cannot be calculated on the basis of the law of corresponding states. Our procedures are based upon the three-constant version of the law of corresponding states.

The three constants are the following:

critical temperature (T_{cr}),
critical pressure (P_{cr}),
critical compressibility factor (Z_{cr}) or the Riedel constant (α_{cr}).

The procedures treat the mixtures as ideal mixtures of the components. They calculate the properties of the mixtures from the critical data of a hypothetical component (as pseudo-critical data), representing the homogeneous mixture. These "pseudo-data" are calculated from the property values of the pure components by a separate procedure *(mix)*.

Some properties cannot be calculated for mixtures from pseudo-data, as the components differ from each other in behaviour and dissimilar correlations apply. The corresponding properties of the components are added in these cases according to some mixing rule. Consequently these procedures may not be adopted on condition that they result in a hypothetical state for one or more component. In the interests of universal applicability of the procedures the calculation is continued — after printing a warning message — such that the state variables inducing a hypothetical state for the given components are automatically replaced by values generating a real state during the calculation. (E.g., the vapour ratio remains constant, the temperature will be replaced by the pseudo-critical temperature, the pressure by the pseudo-critical pressure.)

When calculating the viscosity and the thermal conductivity of liquid water the law of corresponding states is not adopted, because in these cases the generalized correlations fail. Empirical and individual relations are used in their place.

The procedures do not calculate properties in the hypothetical state. If, in the temperature-pressure system of coordinates (Fig. 2.2), a point, whose coordinates are the temperature and pressure of the mixture, is located below the pseudo-vapour-pressure curve, then the calculation is carried out for the liquid state; if it is located above the curve, the calculation is carried out for the gaseous state.

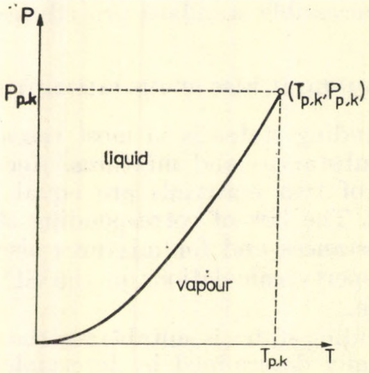


Fig. 2.2. Pseudo-vapour-pressure curve

The accuracy of the calculation methods is sufficient for technical practice; in the range

$$P < 200\times 10^5\ \mathrm{N/m^2}$$
$$T_r > 0.3$$
$$\varrho_r < 3$$

the error is between 2% and 10%. The accuracy of the individual methods used to calculate properties will be discussed in the corresponding chapters.

2.4.2.2 GENERAL DESCRIPTION OF THE PROCEDURES

The description of the procedures aims to acquaint users of the SIMUL system with the principles of the method, its accuracy and the constraints of its application.

The following factors must be introduced in advance.

(a) Formal parameters of the procedures

With the exception of the procedures *mix* and *prek*, all the procedures to be introduced are ALGOL-procedures *(real procedures)* and the calculated properties are own values of the procedure. The formal parameters of the procedures are uniformly denotated, and are called, with the exception of the block-parameters, by value.

The procedures need, besides their actual parameters, only the data of the basic matrix.

The possible formal parameters are the following:

integer *type*	stream type index
real t	temperature, K
real p	pressure, N/m^2
real *pcv*	convergence pressure, N/m^2
real v	vapour ratio
real h	molal enthalpy, J/kmol
array z [1 : *ncomp*]	overall composition, kmole/kmole
array $z_{\rm l}$ [1 : *ncomp*]	mole fractions in the liquid phase
array $z_{\rm v}$ [1 : *ncomp*]	mole fractions in the vapour phase
integer *ncomp*	number of components
boolean *first*	control parameters, calling the constants of the procedure from the background store
array c [1 : *ncomp*, 1 : 13]	array of the material constants, necessitated by the procedures
or	
array *cvapr* [1 : *ncomp*, 1:2]	

For economy the procedures do not search every time for the data of the stream type in question in the basic matrix. On evaluating the definition of the stream types, the master program selects and copies the corresponding rows of the basic matrix in advance for each stream type and stores these separately as matrices. The physico-chemical procedures place their c array parameter from this copy into the store.

With the exception of the procedures *vapr* and *bubdew* all the procedures calculate solely the properties of homogeneous phases, the value of the vapour ratio v can only be 0 or 1 with the exception of the above-mentioned two procedures.

(b) Accuracy of the procedures

The verification of the methods used in the procedures has been carried out in most cases on pure components because insufficient data were available for mixtures. The results of the control calculations are represented by the following values:

relative mean error, $H_{\rm R}$,
relative maximal error, $M_{\rm R}$,
maximal mean error, $M_{\rm A}$.

The value of the relative mean error:

$$H_{\rm R} = \frac{1}{n}\sum_{i=1}^{n} \text{abs}\left(\frac{M_i - C_i}{M_i}\right) 100, \%,$$

the relative maximal error:

$$M_{\rm R} = \max_{i}\left[\text{abs}\left(\frac{M_i - C_i}{M_i}\right) 100\right], \%,$$

the maximal mean error:

$$M_A = \frac{1}{J}\sum_{j=1}^{J} \mathrm{abs}\,(M_{R,j}),\ \%,$$

where M_i = the measured value on the i-th point,
C_i = the calculated value on the i-th point,
n = number of the measured data points,
J = number of materials for which the relative maximal error has been calculated.

The majority of the procedures have two calculation methods with different accuracy. The less accurate but much quicker method usually contains the correlations valid for ideal mixtures. The user may select the calculation method. If the sign of the stream type index — figuring among the parameters of the procedure — is negative, then the procedure handles the mixture as "ideal", in the opposite case, as a real mixture consisting of ideal components.

If the mixture contains only one component, then — as a particular case — all the procedures result in the respective property of the pure substance.

(c) Error messages

The user of the SIMUL system specifies the technology for certain streams. It may happen, however, that the state specified in some way does not exist. This is by no means caused by the inexperience of the user, but by the fact that the user cannot know in advance the results of the simulation and the value of the state variables to be calculated. In these cases, the procedures print an error message, but the calculation may be continued in most cases. This is for the user to decide. Before continuing the calculation, the conditions leading to a non-real state have to be reset.

2.4.2.3 DESCRIPTION OF THE PROCEDURES

(a) Calculation of pseudo-constants of a mixture
mix (type, t, p, z, ncomp, first, c)

The procedure *mix* calculates, using data of individual components, the pseudo-constants of the hypothetical component representing the mixture, and transfers them into array *pkr* [1 : 5]. The elements of the block *pkr* are the following:

pkr [1]	pseudo-critical temperature, K
pkr [2]	pseudo-critical pressure, N/m^2
pkr [3]	pseudo-normal boiling point, K
pkr [4]	pseudo-critical compressibility factor
pkr [5]	mean molecular mass, kg/kmole

The pseudo-critical compressibility factor is calculated by addition, weighted according to the mole fractions:

$$Z_{\mathrm{p,cr}} = \sum_{i=1}^{n} z_i Z_{\mathrm{cr},i} \tag{2.1}$$

Calculation of the pseudo-critical temperature and pseudo-critical pressure is executed through the following equations (Leland et al., 1962):

$$T_{\mathrm{p,cr}} = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j a_i a_j}{\sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j (b_i + b_j)^3}\right]^{1/\alpha}, \tag{2.2}$$

$$P_{\mathrm{p,cr}} = \frac{T_{\mathrm{p,cr}} \sum_{i=1}^{n} z_i Z_{\mathrm{cr},i}}{\sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j (b_i + b_j)^3}, \tag{2.3}$$

where

$$a_i = \left(\frac{Z_{\mathrm{cr}} T_{\mathrm{cr}}^{(\alpha+1)}}{P_{\mathrm{cr}}}\right)_i^{1/2}, \tag{2.4}$$

$$b_i = \frac{1}{2}\left(\frac{Z_{\mathrm{cr}} T_{\mathrm{cr}}}{P_{\mathrm{cr}}}\right)_i^{1/3}, \tag{2.5}$$

$$\alpha = 1 + \exp\left[-10\left(\frac{P}{\sum_{i=1}^{n} z_i P_{\mathrm{cr},i}} - 1\right)^2\right] \tag{2.6}$$

Since α is calculated from equation (2.6), it is necessary to know, at least approximately, the pressure of the mixture to calculate the pseudo-critical values. The pseudo-critical values consequently depend not only on the critical constants and the mole fractions of the components, but also slightly on the absolute pressure.

The mean molecular mass is calculated by the equation

$$M_{\mathrm{p}} = \sum_{i=1}^{n} z_i M_i, \tag{2.7}$$

the pseudo-normal boiling point by the Antoine-equation

$$T_{\mathrm{p,b}} = \frac{B_{\mathrm{p}}}{A_{\mathrm{p}} - 5.0057} - C_{\mathrm{p}} \tag{2.8}$$

The pseudo-Antoine coefficients are sums of the coefficients of the individual components, weighted according to the mole fractions:

$$A_p = \sum_{i=1}^{n} z_i A_i , \tag{2.9}$$

$$B_p = \sum_{i=1}^{n} z_i B_i , \tag{2.10}$$

$$C_p = \sum_{i=1}^{n} z_i C_i . \tag{2.11}$$

The number 5.0057 appearing in the divisor of equation (2.8) is the logarithm of the conversion factor ν. The Antoine coefficients are stored in the basic matrix according to the unit atm.

The procedure *mix* is used as an auxiliary procedure of the property calculations.

If the stream type index *type* refers to a pure component, then the procedure *mix* transfers the elements of array *c* without any calculation into array *pkr* and calculates the normal boiling point using the Antoine coefficients of the pure substance.

Array *pkr* always contains the pseudo-constants of the mixture ultimately calculated.

Array *c* [1 : *ncomp*, 1 : 13] used by procedure *mix* contains the data of columns 1–13 of the basic matrix for each component.

The pseudo-critical values calculated by procedure *mix* are suitable for the calculation of mixture properties on the basis of the law of corresponding states.

Limits of application: Pseudo-constants of all homogeneous mixtures can be calculated, and consist of components whose properties are included in the basic matrix. This is checked at the beginning of the calculation.

The pseudo-parameters of phases in equilibrium have to be calculated separately for each phase.

Error of the method: The method discussed above is a generally accepted mixing rule in chemical engineering. The error of the method cannot be indicated generally. The values of the individual mixture properties calculated on the basis of pseudo-critical data should be compared with experimental data. Since very few data relating to mixture properties were available, no detailed supervision could be performed, and therefore no numerical data on the accuracy are available.

(b) Pseudo-vapour-pressure calculation of a liquid mixture
vapp (type, t, p, z, ncomp, first, c)

The procedure *vapp* calculates the equilibrium vapour pressure of a hypothetical component representing the mixture for the case of a pure liquid component. The equilibrium vapour pressure of the hypothetical component does not correspond to the pressure of the system.

The calculation of the vapour pressure is effected using the Riedel one-constant vapour-pressure equation (Riedel, 1954), adopting pseudo-critical (critical) data:

$$\log P_{p,cr} = -\Phi(T_{p,r}) - (\alpha_{cr} - 7)\,\Psi(T_{p,r}), \tag{2.12}$$

where α_{cr} = the Riedel constant.

$$\Phi(T_{p,r}) = 0.118 \times \varphi(T_{p,r}) - 7 \times \log T_{p,r} \tag{2.13}$$

$$\Psi(T_{p,r}) = 0.0364 \times \varphi(T_{p,r}) - \log T_{p,r} \tag{2.14}$$

$$\varphi(T_{p,r}) = 36/T_{p,r} + 42 \times \ln T_{p,r} - 35 - T_{p,r}^{6}. \tag{2.15}$$

From equations (2.12)–(2.15) we obtain:

$$P_s = \exp\,[\alpha_{p,cr} \ln T_{p,r} - 0.0838 \times (\alpha_{p,cr} - 3.75) \times$$

$$\times (36/T_{p,r} - 35 - T_{p,r}^{6} + 42 \times \ln T_{p,r})] \times P_{p,cr}. \tag{2.16}$$

The pseudo-critical Riedel constant can be calculated if equation (2.16) is written for the pseudo-normal boiling point and solved for $\alpha_{p,cr}$. Knowing the numerical value of $\alpha_{p,cr}$, the equilibrium vapour pressure of the mixture can be calculated for any temperature.

Procedure *vapp* is used as an auxiliary procedure to calculate the heat of vaporization and the enthalpy, and further, to calculate the vapour pressure of pure substances. The procedure in the last case does not require the pressure value — one of the parameters — because the pressure value is only used to calculate the pseudo-critical parameters. Array *c* in this procedure is identical with that of procedure *mix*.

Procedure *vapp* uses *mix* as an auxiliary procedure.

Limits of application, error messages: the method cannot be used for temperatures above the pseudo-critical temperature of the mixture. In such an event, an error message is printed:

$$vapp : T > T_{p,cr}$$

Error of the method: The method has been tested with data of 17 pure substances (the first 8 alcanes, C_2H_4, C_3H_6, H_2, H_2O, C_2H_5–OH, N_2, NH_3, O_2, SO_2), on 183 measured data points, from 0.05×10^5 N/m² to just below the critical pressure. The relative mean error is 1.97%; with non-polar components, 5–6% relative maximal error; with polar components and hydrogen, 10%.

(c) Enthalpy of vaporization calculation of a liquid mixture
vaph (type, t, p, z, ncomp, first, c)

The procedure *vaph* calculates the enthalpy of vaporization of a pure component or a hypothetical substance representing a liquid mixture, at the equilibrium vapour pressure for the given temperature. In the last case, the enthalpy of vaporization is defined as that specific quantity of heat which is needed to vaporize all the liquid without the change of composition.

The enthalpy of vaporization is calculated using the Watson equation (Steward, 1965), which is based upon empirical correlations:

$$\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r,1}}{1 - T_{r,2}}\right)^{0.38} \tag{2.17}$$

For ΔH_1, the value of the enthalpy of vaporization at the pseudo-normal boiling point has been chosen. Therefore, we have the measurable enthalpy of vaporization at equilibrium vapour pressure:

$$\Delta H_1 = \Delta H_{p,b} \left(\frac{1 - T_{p,r}}{1 - T_{p,b,r}}\right)^{0.38} \tag{2.18}$$

The enthalpy of vaporization at the pseudo-normal boiling point of the mixture $\Delta H_{p,b}$ is calculated from the equation of Klein (1945):

$$\Delta H_{p,b} = \frac{RT_{p,b} T_{p,cr}\, k \ln \left(\frac{P_{p,cr}}{\nu}\right)}{T_{p,cr} - T_{p,b}} \left(1 - \frac{\nu}{P_{p,cr} T^3_{p,b,r}}\right)^{1/2} \tag{2.19}$$

where k represents an empirical constant:

$$k = \begin{cases} 1.02, \text{ if } T_{p,b} < 200 \text{ K} \\ 1.04, \text{ if } 200 \text{ K} \leq T_{p,b} \leq 300 \text{ K} \\ 1.045, \text{ if } T_{p,b} > 300 \text{ K} \end{cases}$$

Procedure *vaph* is used as an auxiliary procedure when calculating enthalpy, and it is further used to calculate the enthalpy of vaporization of pure components. In the latter, the procedure does not require the pressure value listed among the parameters.

Array c — which is one of the parameters of procedure *vaph* — is identical to that of *mix*. Procedure *vaph* uses *mix* as an auxiliary procedure.

Limits of application, error messages: The method cannot be used for temperatures above the pseudo-critical temperature. In such an event, an error message is printed:

$$vaph\colon\ T > T_{p,cr}$$

Error of the method: The method has been tested with data of 7 pure substances (the first 3 alcanes, C_2H_4, H_2O, N_2, NH_3) on 64 measured data points. The relative mean error was 1.82%, the relative maximal error 5.23%.

(d) Molal-density calculation of a mixture

dens (type, t, p, v, z, ncomp, first, c)

Procedure *dens* is suitable for calculating the molal density of gaseous and liquid mixtures.

The molal density of liquid mixtures is calculated according to the method of Yen and Woods (1966); for gaseous mixtures the equation of state of Redlich and Kwong (1949) is used.

Density of liquids: The density of liquids is calculated using the following equation:

$$\varrho = \varrho_{p,r}\,\varrho_{p,cr} \tag{2.20}$$

where

$$\varrho_{p.r} = \varrho_{p,r,s} + (\Delta\varrho_{p,r})_{27} + \delta Z_{p,cr}. \tag{2.21}$$

The method of Yen and Woods supplies the explicit formula for the reduced density of a saturated liquid ($\varrho_{p,r,s}$) as a function of $T_{p,r}$, $P_{p,r}$ and $Z_{p,cr}$:

$$\varrho_{p,r,s} = 1 + A(1 - T_{p,r})^{1/3} + B(1 - T_{p,r})^{2/3} + D(1 - T_{p,r})^{4/3}. \tag{2.22}$$

Constants A, B and D of equation (2.22) are defined by the following relations:

$$\left.\begin{aligned} A &= a_0 + a_1 Z_{p,cr} + a_2 Z_{p,cr}^2 + a_3 Z_{p,cr}^3 \\ B &= b_0 + b_1 Z_{p,cr} + b_2 Z_{p,cr}^2 + b_3 Z_{p,cr}^3 \\ D &= 0.93 - B \end{aligned}\right\}. \tag{2.23}$$

The numerical values of the coefficients are contained in Table 2.5.

If the pressure of the liquid mixture does not exceed the pseudo-equilibrium vapour pressure, then the molal density of the mixture may be calculated starting from the reduced density — calculated by equation (2.22) — and using the following formula:

Table 2.5

Coefficients of equation (2.23)

Index of coefficients	a	b	
	$Z_{p,cr}$	if $Z_{p,cr} \leq 0.26$	if $Z_{p,cr} > 0.26$
0	17.4425	−3.28257	60.2091
1	−214.578	13.6377	−402.063
2	989.625	107.4844	501.0
3	−1522.06	−384.211	641.0

$$\varrho = \frac{P_{p,cr}}{Z_{p,cr}\,RT_{p,cr}} \tag{2.24}$$

Should the pressure of the liquid mixture exceed the pseudo-equilibrium vapour pressure, then the calculation of the molal density is carried out using equation (2.21), starting from the value of $\varrho_{\mathrm{p,r,s}}$, calculated from equation (2.22).

In equation (2.21), the term $(\Delta\varrho_{\mathrm{p,r}})_{27}$ represents the increase in reduced density motivated by $\Delta P_{\mathrm{p,r}}$ if $Z_{\mathrm{p,cr}} = 0.27$.

If $0.2 \leq \Delta P_{\mathrm{p,r}} < 60$, then

$$(\Delta\varrho_{\mathrm{p,r}})_{27} = E + F \ln (\Delta P_{\mathrm{p,r}}) + G \exp (H \Delta P_{\mathrm{p,r}}). \tag{2.25}$$

If, on the other hand, $\Delta P_{\mathrm{p,r}} < 0.2$, then

$$(\Delta\varrho_{\mathrm{p,r}})_{27} = (\Delta P_{\mathrm{p,r}}/0.2) \times [(\Delta\varrho_{\mathrm{p\ r}})_{27\,\Delta P_{\mathrm{p,r}}=0.2}]. \tag{2.26}$$

If the value of the pseudo-critical compressibility factor differs from 0.27, then $\delta Z_{\mathrm{p,cr}}$ is not equal to 0 and a further correction is necessary.

If $0.2 < \Delta P_{\mathrm{p,r}} < 60$, then

$$\delta Z_{\mathrm{p,cr}} = I + J \ln \Delta P_{\mathrm{p,r}} + K \exp (L \Delta P_{\mathrm{p,r}}). \tag{2.27}$$

If $\Delta P_{\mathrm{p,r}} < 0.2$, then

$$\delta Z_{\mathrm{p,cr}} = \frac{\Delta P_{\mathrm{p,r}}}{0.2} (\delta Z_{\mathrm{p,cr}})_{\Delta P_{\mathrm{p,r}} = 0.2}. \tag{2.28}$$

The above formulae are valid in the range: $0.3 < T_{\mathrm{p,r}} < 1$.

The coefficients in equations (2.25) and (2.27) are functions of $T_{\mathrm{p,r}}$:

$$E = e_1 + e_2(1 - T_{\mathrm{p,r}})^{1/3} + e_3(1 - T_{\mathrm{p,r}})^{2/3} + e_4(1 - T_{\mathrm{p,r}}) + e_5(1 - T_{\mathrm{p,r}})^{4/3}, \tag{2.29}$$

$$F = f_1 \times T_{\mathrm{p,r}}^{\mathrm{f_2}}/[1 + f_3(-\ln T_{\mathrm{p,r}})^{\mathrm{f_4}}], \tag{2.30}$$

$$G = g_1 + g_2(g_4 - T_{\mathrm{p,r}})^{3/4} \exp [- g_3(g_4 - T_{\mathrm{p,r}})], \tag{2.31}$$

$$H = h_1 + h_2(1 - T_{\mathrm{p,r}})^{1/3} + h_3(1 - T_{\mathrm{p,r}})^{2/3} + h_4(1 - T_{\mathrm{p,r}}) + h_5(1 - T_{\mathrm{p,r}})^{4/3}, \tag{2.32}$$

$$I = i_1 + i_2(1 - T_{\mathrm{p,r}})^{1/3} + i_3(1 - T_{\mathrm{p,r}})^{2/3} + i_4(1 - T_{\mathrm{p,r}}) + i_5(1 - T_{\mathrm{p,r}})^{4/3}, \tag{2.33}$$

$$J = j_1 + j_2(1 - T_{\mathrm{p,r}})^{1/3} + j_3(1 - T_{\mathrm{p,r}})^{2/3} + j_4(1 - T_{\mathrm{p,r}}) + j_5(1 - T_{\mathrm{p,r}})^{4/3}, \tag{2.34}$$

$$K = k_1 + k_2 T_{\mathrm{p,r}} + k_3 T_{\mathrm{p,r}}^2 + k_4 T_{\mathrm{p,r}}^3, \tag{2.35}$$

$$L = l_1 + l_2(1 - T_{\mathrm{p,r}})^{1/3} + l_3(1 - T_{\mathrm{p,r}})^{2/3} + l_4(1 - T_{\mathrm{p,r}}) + l_5(1 - T_{\mathrm{p,r}})^{4/3}. \tag{2.36}$$

The values of the constants figuring in equations (2.29)–(2.36) are presented in Table 2.6.

Table 2.6

Coefficients of equations (2.29)—(2.36)

Indices	e	f	g	h
	$Z_{p,cr} = 0.27$	$Z_{p,cr} = 0.27$	$Z_{p,cr} = 0.27$	$Z_{p,cr} = 0.27$
1	0.714	0.268	0.050	−10.60
2	−1.626	2.0967	4.221	45.22
3	−0.646	0.8000	7.848	−103.79
4	3.699	0.4410	1.010	114.44
5	−2.198	—	—	−47.38

Indices	i		
	if $Z_{p,cr} = 0.29$	if $Z_{p,cr} = 0.25$	if $Z_{p,cr} = 0.23$
1	−0.0817	0.0933	0.0890
2	0.3274	−0.3445	−0.4344
3	−0.5014	0.4042	0.7915
4	0.3870	−0.2083	−0.7654
5	−0.1342	0.05473	0.3367

Indices	j		
	if $Z_{p,cr} = 0.29$	if $Z_{p,cr} = 0.25$	if $Z_{p,cr} = 0.23$
1	−0.0230	0.0220	0.0674
2	−0.0124	−0.003363	−0.06109
3	0.1625	−0.0796	0.06261
4	−0.2135	0.08546	−0.2378
5	0.08643	−0.02170	0.1665

Indices	k		
	if $Z_{p,cr} = 0.29$	if $Z_{p,cr} = 0.25$	if $Z_{p,cr} = 0.23$
1	0.05626	0.01937	−0.01393
2	−0.3518	−0.03055	−0.003459
3	0.6194	0.06310	−0.1611
4	−0.3809	0	0
5	—	—	—

Indices	l		
	if $Z_{p,cr} = 0.29$	if $Z_{p,cr} = 0.25$	if $Z_{p,cr} = 0.23$
1	−21.0	−16.0	−6.550
2	55.174	30.699	7.8027
3	−33.637	19.645	15.344
4	−28.109	−81.305	−37.04
5	26.277	47.031	20.169

If the value of $Z_{\mathrm{p,cr}}$ is not exactly 0.29, 0.25 or 0.23, then the next value must be used in the calculation.

To calculate the molal density of a liquid-state mixture characterized by the state variables T and P,*dens* first computes the density of the saturated liquid at temperature T and then adjusts this value as a function of P. If the pseudo-critical compressibility factor of the mixture differs from 0.27, then the procedure corrects the value of the density corresponding to the difference.

Vapour and gaseous state: The molal density is calculated in the vapour and gaseous state using the equation:

$$\varrho = \frac{P}{ZRT} \tag{2.37}$$

where the value of the compressibility factor Z is derived from the Redlich–Kwong equation of state:

$$Z = \frac{1}{1-h} - \frac{A^2}{B} \cdot \frac{h}{1+h}. \tag{2.38}$$

In this equation

$$h = B\frac{P}{Z}, \tag{2.39}$$

$$B = \frac{b}{RT}, \tag{2.40}$$

$$A^2 = \frac{a}{R^2T^{2,5}}, \tag{2.41}$$

$$a = 0.4278\,\frac{R^2T_{\mathrm{p,cr}}^{2,5}}{P_{\mathrm{p,cr}}}, \tag{2.42}$$

$$b = 0.0867\,\frac{RT_{\mathrm{p,cr}}}{P_{\mathrm{p,cr}}}. \tag{2.43}$$

Equations (2.38)–(2.43) enable the value of the compressibility factor Z to be determined by iteration, based on the values of the pseudo-critical pressure and the pseudo-critical temperature. Procedure *dens* uses the method of interval halving to compute Z.

If the actual value of parameter *type* is negative, then procedure *dens* calculates the compressibility factor according to the empirical equation of Hansen (1964):

$$Z = \left(\frac{1}{A} + B\right), \tag{2.44}$$

where A and B are functions of the pseudo-reduced pressure and temperature:

$$A = 1 + \sum_{i=1}^{i=9} a_i \alpha^{(2i-1)} \tag{2.45}$$

and

$$B = \frac{P_{\mathrm{p,r}}}{T_{\mathrm{p,r}}} \sum_{i=0}^{i=2} b_i \beta^i, \tag{2.46}$$

where

$$\alpha = \frac{P_{\mathrm{p,r}}}{T^3_{\mathrm{p,r}}} \tag{2.47}$$

and

$$\beta = P^{1/3}_{\mathrm{p,r}} \tag{2.48}$$

The coefficients of equations (2.45)–(2.46) are presented in Table 2.7.

The density of mixture as hypothetical component thus calculated on the basis of the pseudo-critical data practically corresponds to the weighted average of the densities of components according to mole fractions; in the case of a multicomponent mixture, this "pseudo-critical method" has the advantage of being substantially quicker.

Table 2.7
Coefficients of equations (2.45)–(2.46)

Indices	***a***	***b***
0	—	0.2595
1	0.6108	−0.0929
2	1.107	0.01437
3	0.4294	—
4	−6.747	—
5	4.211	—
6	43.44	—
7	−52.19	—
8	−40.70	—
9	57.68	—

Procedure *dens* uses *mix* and *vapp* as auxiliary procedures.

Limits of application, error messages:
The method is inapplicable

in hypothetic states,
in the range $T_r < 0.3$,
for inhomogeneous mixtures.

The corresponding error messages are as follows:

in the liquid state:

dens: hypothetical liquid state $(T > T_{\rm cr})$
dens: hypothetical liquid state $(P < P_{\rm p,s})$

in vapour or gaseous state:

dens: hypothetical gaseous state

$$(T < T_{\rm p,cr} \wedge P > P_{\rm p,s})$$

dens: $T_{\rm r} < 0.3$
dens: inhomogeneous mixture.

Error of the method: The method has been tested with density data from the Literature for H_2O, H_2, CH_4, C_2H_4, C_3H_8, NH_3 and N_2 with calculated data in the pressure range from 0.1×10^5–1×10^5 N/m^2 to 100×10^5–500×10^5 N/m^2. The temperature limit was 1000 K for H_2O and N_2, 600 K for the other substances. The test on 1012 measured data points resulted in 1.17% relative mean error. The relative mean error is 2.1% in the liquid state, but only 0.67% if the pressure is less, 40×10^5 N/m^2.

(e) Viscosity calculation of mixtures
visc (type, t, p, v, z, ncomp, first, c)

Procedure *visc* is suitable for calculating the dynamic viscosity of homogeneous mixtures. The method utilizes the correlations of Dean and Stiel (1965), Jossi et al. (1962), Stiel and Thodos (1964*a*, *b*).

The viscosity of mixtures is calculated using the correlation

$$\mu = \mu^* + \sum_{i=1}^{n} z_i \, \mu_{{\rm corr},i}, \tag{2.49}$$

where μ^* represents the viscosity of a gas mixture at low pressure ($P \leq 5 \times 10^5$ N/m^2) and $\mu_{{\rm corr},i}$ a correction factor whose value is zero if $P \leq 5 \times 10^5$ N/m^2.

The viscosity μ^* of a gas mixture at low pressure is calculated using the equation of Herning and Zipperer (1936):

$$\mu^* = \frac{\sum_{i=1}^{n} z_i (M_i T_{{\rm cr},i})^{1/2} \mu_i^*}{\sum_{i=1}^{n} z_i (M_i T_{{\rm cr},i})^{1/2}}. \tag{2.50}$$

The values of μ_i^* in equation (2.50) are calculated — depending on the type of the component — as follows:

1. The non-polar components of the mixture are considered as one hypothetical component, defined by its pseudo-critical data. For this hypo-

thetical component, the following correlations apply:

if $T_{\mathrm{p,r}} \leq 1.5$,

$$\mu_i^* = 34.0 \times 10^{-8} \times T_{\mathrm{p,r},i}^{8/9} \frac{1}{\xi}, \tag{2.51}$$

and if $T_{\mathrm{p,r}} > 1.5$,

$$\mu_i^* = 166.8 \times 10^{-8} \times (0.1338 \times T_{\mathrm{p,r},i} - 0.0932)^{5/9} \times \frac{1}{\xi}. \tag{2.52}$$

In these equations, ξ is the so-called viscosity factor:

$$\xi = \frac{T_{\mathrm{p,cr}}^{1/6}}{M_{\mathrm{p}}^{1/2} P_{\mathrm{p,cr}}^{2/3}}. \tag{2.53}$$

2. For hydrogen:

$$\mu_i^* = 90.71 \times 10^{-5} (0.1375 \times T - 1.67)^{5/8}. \tag{2.54}$$

3. For polar components containing a hydrogen bond:

$$\mu_i^* = \frac{1}{\xi_i Z_{\mathrm{cr},i}^{5/4}} (7.55 \times T_{\mathrm{r},i} - 0.55) \times 10^{-8}. \tag{2.55}$$

4. For polar components containing no hydrogen bond:

$$\mu_i^* = \frac{1}{\xi_i Z_{\mathrm{cr},i}^{2/3}} (1.90 \times T_{\mathrm{r},i} - 0.29)^{4/5} \times 10^{-7}. \tag{2.56}$$

The factor ξ_i in equations (2.55) and (2.56) is the viscosity factor calculated according to equation (2.53), but in these instances the individual data of each component must be used instead of the pseudo-data.

The residual viscosity $\mu_{\mathrm{corr},i}$ required for the correction of viscosity is calculated as follows:

1. For the hypothetical component representing the non-polar components, for hydrogen and ammonia:

$$\mu_{\mathrm{corr}\ i} = \frac{1}{\xi_i} [(a_0 + a_1 \varrho_{\mathrm{r},i} + a_2 \varrho_{\mathrm{r},i}^2 + a_3 \varrho_{\mathrm{r},i}^3 + a_4 \varrho_{\mathrm{r},i}^4)] \, 10^{-4}, \tag{2.57}$$

where in the case of a hypothetical component the pseudo-reduced density has to be used instead of the reduced density. The constants of the polynomial are presented in Table 2.8.

2. For polar components,

if $\varrho_{\mathrm{r},i} \leq 0.1$,

$$\mu_{\mathrm{corr},i} = 16.56 \times 10^{-8} \times \varrho_{\mathrm{r},i}^{1.111} \frac{1}{\xi_i}, \tag{2.58}$$

if $0.1 < \varrho_{\mathrm{r},i} \leq 0.9$,

$$\mu_{\mathrm{corr},i} = \frac{1}{\xi_i} 0.607 \times 10^{-8} \times (9.045 \times \varrho_{\mathrm{r},i} + 0.63)^{1.739}, \tag{2.59}$$

if $0.9 < \varrho_{\mathrm{r},i} < 2.6$,

$$\mu_{\mathrm{corr}\,i} = \exp\left[-\exp\left(0.6439 - 0.1005\,\varrho_{\mathrm{r},i} - \Delta\right)\right]\frac{1}{\xi_i}\,10^{-3}. \tag{2.60}$$

In this last equation Δ is calculated as follows:

if $0.9 < \varrho_{\mathrm{r},i} \leq 2.2$, then $\Delta = 0$,

if $2.2 < \varrho_{\mathrm{r},i} < 2.6$, then

$$\Delta = 4.75\times 10^{-4}(\varrho_{\mathrm{r},i}^{3} - 10.65)^{2}. \tag{2.61}$$

The viscosity of liquid water is calculated from the following individual correlation:

$$\mu = 9.81\times 10^{-6}\times \exp\left(-0.4360 + 1467.1741\times 1/T\right). \tag{2.62}$$

Table 2.8

Coefficients of equation (2.57)

Component Constant	Hypothetical component representing the non-polar component	Hydrogen	Ammonia
a_0	0.10230	0.10616	0.1067
a_1	0.023364	−0.042426	0.022655
a_2	0.058533	0.17553	0.035749
a_3	−0.040758	−0.12295	0.032153
a_4	0.0093324	0.028149	0.0089998

For mixtures considered ideal, and in those cases were the sum of the mole fractions of the non-polar components exceeds 0.98, the calculation is carried out as if all components of the mixture were non-polar.

For liquid mixtures, containing both polar and non-polar components in appreciable quantities, the method of calculation outlined above yields poor results.

Procedure *visc* uses *mix* and *dens* as auxiliary procedures.

Limits of application, error messages:

The method is inapplicable

in hypothetical states, and, further, if
$P > 200\times 10^{5}$ N/m²,
$T_{\mathrm{r}} < 0.3$,
$\varrho_{\mathrm{r}} > 3$ (if the mixture is non-polar),
$\varrho_{\mathrm{r}} > 2.6$ (if the mixture is polar).

As procedure *visc* uses procedure *dens* as an auxiliary procedure, *dens* may occur during the calculation of viscosity.

The proper error messages are the following:

visc: reduced density > 3 (non-polar mixtures)
visc: reduced density > 2.6 (polar mixtures).

Error of the method: The method has been tested with 10 pure substances (the first four alcanes, C_3H_6, H_2, N_2, H_2O, CO_2 and NH_3) on totally 453 measured data points, in the pressure range $10^5 - 500 \times 10^5$ N/m² and in the temperature range 200–1000 K. The relative mean error is 5.97%, and in the gaseous state 4.01%. With gases and in the pressure range below 5×10^5 N/m² the relative mean error is around 2%.

(f) Thermal-conductivity calculation of mixtures
hcond (type, t, p, v, z, ncomp, first, c)

Procedure *hcond* is suitable for calculating the thermal conductivity of homogeneous mixtures, consisting of hydrocarbons or simple molecule-structured substances.

The method on which procedure *hcond* is based utilizes the correlations of Misic and Thodos (1963), Stiel and Thodos (1964*a*). The first step of the calculation determines the thermal conductivity of the individual components in the gaseous state, independently of the state and pressure ($\lambda_{g,i}$), which is followed by the thermal-conductivity calculation of the gaseous mixture (λ_g). If the mixture is liquid or the pressure of the gaseous mixture exceeds 5×10^5 N/m², then the value of λ_g is corrected:

$$\lambda = \lambda_g + \sum_{i=1}^{n} z_i \lambda_{\mathrm{corr},i}, \tag{2.63}$$

$$\lambda_g = \frac{\sum\limits_{i=1}^{n} z_i \lambda_{\mathrm{g},i} \sqrt[3]{M_i}}{\sum\limits_{i=1}^{n} z_i \sqrt[3]{M_i}} \varphi. \tag{2.64}$$

If the mixture contains only non-polar components, then $\varphi = 1$ in equation (2.64), and

$$\varphi = 1 + \frac{z_j - z_j^2}{3.5} \tag{2.65}$$

applies, if the mixture also contains polar components. (In this equation z_j indicates the sum of mole fractions of the polar components.)

The thermal conductivity $\lambda_{g,i}$ of the individual components is calculated in the following way:

1. For hydrocarbons:

$$\lambda_{\mathrm{g},i} = \frac{P_{\mathrm{cr},i}^{2/3}}{M_i^{1/2} T_{\mathrm{cr},i}^{1/6}} c_{\mathrm{p},i} \Phi(T_{\mathrm{r},i}). \tag{2.66}$$

2. For hydrogen (Misic and Thodos, 1963):

$$\lambda_{\mathrm{g},i} = (\varphi_1 T_{\mathrm{r},i} - \varphi_2)^{\varphi_3} \times 10^{-5}. \tag{2.67}$$

Table 2.9

Coefficients φ of equation (2.67)

	$T_{r,i} < 1.0$	$1.0 \le T_{r,i} < 3.0$	$3.0 \le T_{r,i} \le 20.0$
φ_1	5.40	10.11	16.52
φ_2	0	2.53	12.66
φ_3	1.0	0.833	0.769

3. For other substances with simple molecular structure (e.g., Ar, Kr, Xe, N_2, O_2, CO, NO_2, Cl_2, Br_2, HCl, CS_2, H_2S, CO_2, NO, SO_2, HCN, NH_3):

$$\lambda_{g,i} = \frac{P_{cr,i}^{2/3}}{M_i^{1/2} T_{cr,i}^{1/6}} c_{p,i}^{3/4} \varphi^*(Z_{cr,i}, T_{r,i}). \tag{2.68}$$

The function Φ $(T_{r,i})$ in equation (2.66) is defined in the following way: if $3 \le T_{r,i} < 1.0$ (and also for aliphatic hydrocarbons except methane) if $0.5 \le T_{r,i} < 1.0$):

$$\Phi(T_{r,i}) = (14.52 \times T_{r,i} - 5.14)^{2/3} \times 10^{-6}. \tag{2.69}$$

For aromatic hydrocarbons and methane, the following correlation applies, if $0.5 \le T_{r,i} < 1.0$.

$$\Phi(T_{r,i}) = 0.455 \times 10^{-5} \times T_{r,i}. \tag{2.70}$$

Values of the coefficients φ in equation (2.67) are presented in Table 2.9.

The function φ^* figuring in equation (2.68) is expressed by the following correlation:

$$\varphi^*(Z_{cr,i} T_{r,i}) = [(a_1 Z_{cr,i} + a_2) T_{r,i} + a_3 Z_{cr,i} + a_4]^{a_5 - a_6 Z_{cr,i}} \times a_7. \tag{2.71}$$

Values of the coefficients are presented in Table 2.10.

Table 2.10

Coefficients of equation (2.71)

	$T_{r,i} < 1.0$	$1.0 \le T_{r,i} < 3.0$	$3.0 \le T_{r,i} < 15.0$
a_1	20.0	1.95	−18.25
a_2	1.08	−31.94	7.18
a_3	0	−82.50	10.21
a_4	0	16.83	−4.91
a_5	1.810	1.524	1.079
a_6	2.604	2.800	1.97
a_7	10^{-6}	10^{-6}	10^{-5}

The pressure correction of the thermal conductivity λ_{corr} is calculated with gaseous mixtures, whose pressure exceeds 5×10^5 N/m^2 according to the formula suggested by Stiel and Thodos (1964*a*, *b*)

$$\lambda_{\text{corr},i} = \xi_i \Psi(\varrho_{r,i}), \tag{2.72}$$

where

$$\xi_i = \frac{P_{\text{cr},i}^{2/3}}{M_i^{1/2} T_{\text{cr},i}^{1/6}} Z_{\text{cr},i}^5 . \tag{2.73}$$

The function Ψ has the following form:

$$\Psi(\varrho_{r,i}) = b_1(\exp(b_2 \times \varrho_{r,i}) + b_3) \times 10^{-8}. \tag{2.74}$$

The value of the coefficients in equation (2.74) are presented in Table 2.11.

If the pressure of the gaseous mixture does not exceed 5×10^5 N/m^2, then $\lambda_{\text{corr}} = 0$.

Table 2.11

Coefficients of equation (2.74)

	$\varrho_{r,i} \leq 0.50$	$0.50 < \varrho_{r,i} \leq 2.0$	$2.0 < \varrho_{r,i} < 2.80$
b_1	14.0	13.10	2.976
b_2	−0.535	0.67	1.155
b_3	−1.0	−1.069	2.016

If water is one of the components and the mixture is in the liquid state, then procedure *hcond* carries out the calculation for an "incomplete" mixture not containing water, and calculates the thermal conductivity of liquid water according to the formula

$$\lambda_{H_2O} = 0.001163 \times (-239.744 + 3.9598 \times T - 0.0047 \times T^2) \tag{2.75}$$

and then adds this value, weighted according to the mole fraction of water, to the thermal conductivity of the "incomplete" mixture. The mole fractions of the mixture not containing water are normed to unity before the calculation, and the value of the thermal conductivity of this mixture is multiplied with the sum of the mole fractions of the components.

Procedure *hcond* uses *cp* and *dens* as auxiliary procedures.

Limits of application, error messages:

Procedure *hcond* uses procedure *dens* as an auxiliary procedure, and is therefore inapplicable if the reduced temperature is lower than 0.3, if the pressure exceeds 200×10^5 N/m^2, or if the mixture is in a hypothetical state.

The equations used to calculate the pressure correction of the thermal conductivity ensure fair approximation only in a limited range of the reduced density.

If *type* is negative, procedure *hcond* calculates as for positive *type*, except for the calculation of density.

Procedure *hcond* may print, in addition to the error messages of procedure *dens*, the following error message *hcond: reduced density* > 2.8.

Error of the method:
The method has been tested with four binary mixtures from the first eight alcanes, hydrogen, N_2, H_2O and three multicomponent gaseous mixtures on about 200 measured data points. The relative mean error was about 6%. For liquid mixtures containing hydrocarbons it was 10%, for water 1.7%, for NH_3 25%.

(g) Surface-tension calculation of mixtures
surtens (type, t, p, z, ncomp, first, c)

Procedure *surtens* calculates the surface tension of a liquid mixture of the interface liquid/own vapour. Of the various methods used to calculatn surface tension, those which contain the parachor (Π) are generally effectivee The equation of Hammick and Andrew was chosen (1929) and consequentl. the following equation is utilized by procedure *surtens* to calculate the surface tension of liquid mixtures:

$$\sigma_{\mathrm{m}} = (\Pi_{\mathrm{m}} \varrho_{\mathrm{l}} \times 10^{-3})^4. \tag{2.76}$$

This equation was deduced from the correlation of Weinaug and Katz (1943)

$$\sigma_{\mathrm{m}}^{0.25} = 10^{-3} \sum_{i=1}^{n} \pi_i (z_{\mathrm{l},i}\, \varrho_{\mathrm{l}} - z_{\mathrm{v},i}\, \varrho_{\mathrm{v}}) \tag{2.77}$$

according to the rule of Batschinski, disregarding the molal density of the vapour mixture, in equilibrium with the liquid mixture.

Parachor Π is an additive value and practically independent of temperature:

$$\Pi_{\mathrm{m}} = \sum_{i=1}^{n} z_i \Pi_i. \tag{2.78}$$

The Π_i value in equation (2.78) is calculated according to Sugden's definition of the parachor (1924):

$$\Pi_i = \frac{\sigma_i^{0.25} \times 10^{-3}}{\varrho_{\mathrm{l}} - \varrho_{\mathrm{v}}}. \tag{2.79}$$

In equation (2.79), σ_i surface-tension values of the pure components at the temperature of the mixture are used.

σ_i can be calculated – except for water – using the equation of Brock and Bird (1955):

$$\sigma_i = (0.133 \times \alpha_{\mathrm{cr},i} - 0.281) \times (1 - T_{\mathrm{r},i})^{11/9} \times T_{\mathrm{cr},i}^{1/3} \left(\frac{P_{\mathrm{cr},i}}{v}\right)^{2/3} \times 10^{-3}. \tag{2.80}$$

In the case of water, σ_i is calculated from the equation of Katayama (Gambill, 1958), deduced from the Eötvös equation and valid over a wide temperature range:

$$\sigma_i = k(T_{\mathrm{cr},i} - T)\left(\frac{\varrho_\mathrm{l} - \varrho_\mathrm{v}}{10^3}\right)^{0.667}, \tag{2.81}$$

where $k =$ the Eötvös constant, which varies between 1.5 and 2.6, as a function of the molecular weight and the polar character of the substance. We use $k = 1.6$ for water.

The calculation of the value of $\alpha_{\mathrm{cr},i}$ in equation (2.80) is carried out in the way already introduced under procedure *vapp*. The density values required in equation (2.81) are calculated by procedure *dens*. The value of T is a parameter of the procedure, the critical data are stored in array *c*.

The procedure operates independently of the sign of *type*, apart from the calculation of density.

Procedure *surtens* uses *dens* and *vapp* as auxiliary procedures.

Limits of application, error messages:

The method is suitable for calculating the surface tension of unassociated, non-polar liquid mixtures at low pressure (far from critical).

The procedure is inapplicable to the mixture of water and organic compounds, in a hypothetical state or at reduced temperatures not exceeding 0.3. The method does not guarantee fair approximation near the pseudo-critical values of the liquid mixture, since the density of the vapour mixture — in equilibrium with the liquid — is neglected.

During the calculation, error messages of procedures *vapp* and *dens*, called by procedure *surtens*, may appear.

Error of the method: The relative mean error of the parachor calculation is 3.1% in the case of hydrocarbons containing 2–8 carbon atoms and for water.

With polar substances, the error may reach 50–100%.

(h) Enthalpy calculation of mixtures

enth (type, t, p, v, z, ncomp, first, c)

Procedure *enth* is suitable for calculating the molal enthalpy of homogeneous mixtures.

The enthalpy of real mixtures is calculated considering the enthalpy of ideal gases, the pressure correction of the enthalpy and — with liquids — the enthalpy of vaporization. The enthalpy of mixing is neglected:

$$H = H^* + H_\mathrm{corr} - \Delta H_\mathrm{s}. \tag{2.82}$$

The enthalpy of the ideal gas (H^*) is a function of intramolecular forces, its determination is therefore not possible on the basis of the law of corresponding states. The enthalpy of a mixture of ideal gases is calculated by weighted averaging of the enthalpy of the ideal gas according to mole fractions:

$$H^* = \sum_{i=1}^{n} z_i H_i^*. \tag{2.83}$$

The dependence on temperature of the ideal gas enthalpy is calculated by a fourth-order polynomial:

$$H_i^* = a_{0,i} + a_{1,i}T + a_{2,i}T^2 + a_{3,i}T^3 + a_{4,i}T^4. \tag{2.84}$$

The coefficients of equation (2.84) are stored in the basic matrix. Their values have been calculated on the basis of Rossini's data (1953). The reference state of compounds is considered as the state of the elements at 0 K; the 0th term of the polynomial is therefore the enthalpy of formation of the compound, extrapolated to 0 K. It is convenient to define the enthalpy function in this manner, because by its use the heat of reaction of any chemical reaction can be determined — without further data — as the difference of enthalpies of the product and basic materials. The pressure correction of the enthalpy equals zero with ideal mixtures of gases or with mixtures of gases, where the pressure does not exceed 5×10^5 N/m^2. It is calculated using the Redlich–Kwong equation of state and the corresponding thermodynamic correlations are found by procedure *entcorr*.

The enthalpy of a gaseous mixture, of known temperature and composition, decreases in the case of liquid mixtures with the enthalpy of vaporization, calculated by procedure *vaph*. (If the *type* is negative, then the procedure does not calculate the pressure correction, in either gaseous or liquid state. In this case the computation time is roughly halved.)

Procedure *enth* uses *vapp*, *vaph* and *entcorr* as auxiliary procedures.

Limits of application, error messages:

The limits of application of the method are defined on the one hand by the validity range of the enthalpy polynomial of gaseous mixtures (270–1770 K), and on the other hand by the restrictions of the calculation methods of procedures *entcorr* and *vaph*.

The method is inapplicable to hypothetical states, for pressures exceeding 200×10^5 N/m^2 or for reduced temperatures lower than 0.3.

The procedure *enth* may print, in addition to the error messages of the procedures called, the following error message:

enth: non-homogeneous phase.

Error of the method: No error is caused by neglecting the enthalpy of mixing with ideal mixtures. Thus, the error of procedure *enth* results from the error of polynomial-fitting and the relative mean error shall not exceed 1%.

When calculating enthalpy differences, the relative mean error may reach 2–5%.

With non-ideal mixtures when the enthalpy of mixing is considerable, the error is greater.

(i) Molal heat capacity calculation of mixtures
cp (type, t, p, v, z, ncomp, first, c)

Procedure *cp* is suitable for calculating the isobaric molal heat capacity of a homogeneous mixture, with temperature *t* and pressure *p*.

The first step is to calculate the ideal molal heat capacity (c_P^*) by differentiation of the enthalpy function of the ideal gas mixture:

$$c_P^* = \left(\frac{\partial H^*}{\partial T}\right)_P . \tag{2.85}$$

The ideal molal heat capacity is considered as the molal heat capacity of a gaseous mixture, whose pressure does not exceed 5×10^5 N/m², or which can be handled as ideal gas. With ideal gas mixtures the derivative of the pressure correction of the enthalpy with respect to the temperature must be added. This derivative is approximated by the difference quotient

$$c_{P,\mathrm{corr}} = \left(\frac{\Delta H_{\mathrm{corr}}}{\Delta T}\right)_P . \tag{2.86}$$

With liquid mixtures, the first step is to calculate the molal heat capacity (c_P) of a saturated mixture, having composition and temperature equal to that of the mixture. The calculation is carried out according to Rudd and Watson (1968):

$$c_{P,s} = c_P^* - \left(\frac{\partial H_{\mathrm{vap}}}{\partial T} + \frac{\partial (H_g^* - H_{s,g})}{\partial T}\right) . \tag{2.87}$$

The differentials are also approximated in equation (2.87) by difference quotients.

If $T_{p,r} \leq 0.8$, then the molal heat capacity of the liquid $c_{P,s}$ is modified adopting the expansion factor of Watson. Therefore

$$c_P = c_{P,s} \left(\frac{\varrho_s}{\varrho}\right)^{2.8} . \tag{2.88}$$

To calculate the density of the saturated and actual liquid mixture, procedures *dens* and *vapp* are used. If *type* is negative, then procedure *cp* calculates the weighted average of the ideal molal heat capacities of the components as the molal heat capacity of the mixture, independently of the pressure and the physical state.

Procedure *cp* uses *entcorr*, *vapp*, *vaph* and *dens* as auxiliary procedures.

Limits of application, error messages:

The limits of application of the method are determined by the validity range of the auxiliary procedures called *(entcorr, vapp, vaph, dens)* and the coefficients of the ideal enthalpy polynomial, stored in the basic matrix.

Besides the error message "non-homogeneous phase", the error messages of the auxiliary procedures may appear.

Error of the method: With ideal mixtures the relative mean error of the method is 5.73%, and if the pressure does not exceed 40×10^5 N/m², 4.21%. With hydrocarbons, water and N_2 — pressure not exceeding 40×10^5 N/m² — the relative mean error is 2.8%.

When calculating non-ideal mixtures, with considerable enthalpy of mixing, the error of procedure *cp* exceeds the values mentioned above.

(j) Calculation of the pressure correction of enthalpy

entcorr (type, t, p, z, ncomp, first, c)

Procedure *entcorr* calculates the pressure correction of the molal enthalpy of gaseous mixtures. It serves as an auxiliary procedure in procedures *enth* and *cp*.

The method is based on the thermodynamic correlation of the fugacity factor and the pressure correction of enthalpy (Reid and Sherwood, 1966):

$$H_{\mathrm{corr}} = -RT^2 \left(\frac{\partial \ln \left(\frac{f}{P} \right)}{\partial T} \right)_{\mathrm{P}} . \tag{2.89}$$

The fugacity factor in equation (2.89) is calculated from equation

$$\ln \left(\frac{f}{P} \right) = \int_0^P \frac{Z-1}{P} \mathrm{d}P \tag{2.90}$$

and the compressibility factor in equation (2.90) is found from the Redlich–Kwong equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5} V (V+b)} . \tag{2.91}$$

Substituting

$$a = 0.4278 \times R^2 \frac{T_{\mathrm{P,cr}}^{2.5}}{P_{\mathrm{P,cr}}} , \tag{2.92}$$

$$b = 0.0867 \times R \frac{T_{\mathrm{P,cr}}}{P_{\mathrm{P,cr}}} , \tag{2.93}$$

$$A^2 = \frac{a}{R^2 T^{2.5}} , \tag{2.94}$$

$$B = \frac{b}{RT} \tag{2.95}$$

we arrive at the compressibility factor Z, according to formula

$$Z = \frac{PV}{RT} \tag{2.96}$$

where the value of Z is the following:

$$Z = \frac{BP}{Z - BP} - \frac{A^2}{B} \cdot \frac{BP}{Z\left(1 + \frac{BP}{Z}\right)}. \tag{2.97}$$

Thus we obtain the integrand:

$$\frac{Z - 1}{P} = \frac{B}{Z - BP} - \frac{A^2}{B} \cdot \frac{B}{Z(1 + BP/Z)}. \tag{2.98}$$

Integrating equation (2.98) with respect to P gives the following relation:

$$\ln \frac{f}{P} = (Z - 1) - \ln (Z - BP) - \frac{A^2}{B} \ln \left(1 + \frac{BP}{Z}\right). \tag{2.99}$$

In equation (2.89), the derivative of the logarithm of the fugacity factor with respect to the temperature at constant pressure appears. From equation (2.99), this is:

$$\left(\frac{\partial \ln (f/P)}{\partial T}\right)_P = \left(\frac{\partial Z}{\partial T}\right)_P - \frac{1}{Z - BP}\left[\left(\frac{\partial Z}{\partial T}\right)_P - \left(\frac{\partial B}{\partial T}\right)_P\right] -$$

$$- \ln \left(1 + \frac{BP}{Z}\right)\left(\frac{\partial A^2/B}{\partial T}\right)_P - \frac{A^2}{B} \frac{\frac{P}{Z}\left(\frac{\partial B}{\partial T}\right)_P - \frac{BP}{Z^2}\left(\frac{\partial Z}{\partial T}\right)_P}{1 + \frac{BP}{Z}}. \tag{2.100}$$

Partial differential quotients in equation (2.100) may be calculated as follows. Differentiating equation (2.95):

$$\left(\frac{\partial B}{\partial T}\right)_P = - \frac{B}{T}. \tag{2.101}$$

Differentiating equations (2.94) and (2.95):

$$\left(\frac{\partial A^2/B}{\partial T}\right)_P = - \frac{1.5\, A^2}{BT}. \tag{2.102}$$

The differential $(\partial Z/\partial T)_P$ may be separated:

$$\left(\frac{\partial Z}{\partial T}\right)_P = \left(\frac{\partial Z}{\partial T}\right)_V + \left(\frac{\partial Z}{\partial V}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P. \tag{2.103}$$

The derivative $(\partial V/\partial T)_P$ in equation (2.103) can be transformed:

$$\left(\frac{\partial V}{\partial T}\right)_P = - \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} \tag{2.104}$$

and thus we obtain

$$\left(\frac{\partial Z}{\partial T}\right)_P = \left(\frac{\partial Z}{\partial T}\right)_V - \left(\frac{\partial Z}{\partial V}\right)_T + \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T}. \tag{2.105}$$

The partial derivatives in equation (2.105) can be expressed by differentiating with respect to the corresponding variable:

$$\left(\frac{\partial Z}{\partial T}\right)_V = 1.5\,\frac{a}{RT^{2.5}(V+b)}, \tag{2.106}$$

$$\left(\frac{\partial Z}{\partial V}\right)_T = \frac{a}{RT^{2.5}(V+b)^2} - \frac{b}{(V-b)^2}, \tag{2.107}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} + 0.5\,\frac{a}{T^{1.5}V(V+b)}, \tag{2.108}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{a}{T^{0.5}V^2(V+b)} + \frac{a}{T^{0.5}V(V+b)^2} - \frac{RT}{(V-b)^2}. \tag{2.109}$$

Substituting equations (2.100), (2.101), (2.102), (2.105), (2.106), (2.107), (2.108) and (2.109) into equation (2.89), the value of the pressure correction of the enthalpy can be calculated directly, without iteration, if the basic properties of array *c*, temperature T and pressure P – being the actual parameters – and the molal density calculated from these parameters in procedure *dens* are known.

Procedure *entcorr* uses procedure *dens* as an auxiliary procedure.

Limits of application, error messages:
The method has valid application up to pressures not exceeding 200×10^5 N/m^2, if the reduced temperature is lower than 0.3 and the substance is not in the hypothetical state.

The procedure has no error message of its own, but the error messages of procedure *dens* may appear.

Error of the method: The error of the method has not been tested since exact thermodynamic correlations are used with the exception of the Redlich–Kwong equation of state.

(k) Calculation of the temperature pertaining to the molal enthalpy of a mixture

temp (type, h, t, p, v, z, ncomp, first, c)

Procedure *temp* calculates the temperature, which pertains to the molal enthalpy, one of the actual parameters. The calculation is carried out by iteration. The independent variable of the non-linear equation which is to be solved is the temperature. During iteration the difference between the actual enthalpy and the entropy pertaining to the sought temperature is reduced to zero. The starting value of the iteration is the parameter *t* of procedure *temp*.

Procedure *temp* uses procedures *cp* and *enth* as auxiliary procedures.

Limits of application, error messages:

The procedure can only be used with homogeneous mixtures. Relating to the physical state, the value (0 or 1) *v*, one of the parameters, is considered as decisive.

Procedure *temp* may print the error messages of procedure *enth*.

If the starting value of the iteration is unfavourable, then the iteration may diverge and as a result the GIER–ALGOL error message *(spill, exp*, etc.) may be printed or an endless cycle occurs.

Error of the method: The calculated temperature value is influenced by the error of procedure *enth* called by procedure *temp*.

The tolerable error δ_t, while solving the non-linear equation is given by:

$$\delta_t = \text{abs}\left(\frac{H - H_t}{C_P}\right) < 0.05. \tag{2.110}$$

where H_t = the enthalpy at the calculated temperature, H = the indicated enthalpy, C_P = the isobaric molal heat capacity.

(l) Mean molecular weight calculation of a mixture
mol (type, z, ncomp, first, c)

Procedure *mol* is suitable for calculating the mean molecular weight of a mixture, according to equation

$$M_P = \sum_{i=1}^{n} Z_i M_i \tag{2.111}$$

(m) Equilibrium vapour ratio calculation of a mixture
vapr (type, h, t, p, pcv, z, zl, zv, ncomp, first, c)

Procedure *vapr* calculates the equilibrium vapour ratio of a mixture of given pressure and temperature, whose composition vector is *z*.

The actual value of parameter *t* may be zero. In this case the procedure calculates the equilibrium vapour ratio corresponding to the specified molal enthalpy. If *t* is not zero, then the procedure calculates the vapour ratio corresponding to $T = t$ and does not take the value of the molal enthalpy into consideration. Parameters *h* and *t* definitely correspond at the end of the calculation. (In this exceptional case, *h* and *t* are parameters, called without value.)

As parameter *pcv*, the convergence pressure has to be specified with real mixtures; the procedure does not use the value of *pcv* with mixtures, treated as ideal.

Convergence pressure is that pressure under which the vapour–liquid equilibrium coefficient of all components of the mixture converges to 1, at the temperature of the mixture. The convergence pressure is a function of the temperature of the system and the composition of the liquid. In arrays *zl* and *zv*, the procedure indicates the equilibrium composition of the liquid and vapour phases respectively.

If the mixture is homogeneous, then procedure *vapr* specifies in the array for physical state the composition z of the mixture, at the same time the elements of the array of the non-existent phase are put equal to zero.

The vapour ratio is the solution of a non-linear equation, consisting of the mass balance of the gaseous and liquid phase and of the equilibrium correlations of the components.

Denoting the molal mass flow, entering an equilibrium unity as F, its composition as z, and the molal mass flows of the emerging vapour and liquid phases as V and L respectively, then the overall mass balance is

$$F = V + L, \tag{2.112}$$

and the balance equations of the components

$$Fz_i + Vz_{\mathrm{v},i} + Lz_{1,i} = V(z_{\mathrm{v},i} - z_{1,i}) + Fz_{1,i}, \quad i = 1, 2, \ldots\ ncomp. \tag{2.113}$$

The conditions of the component equilibrium are the following:

$$z_{\mathrm{v},i} = K_i(T, P, pcv)\, z_{1,i}, \tag{2.114}$$

where $K_i\ (T,\ P,\ pcv)$ = the vapour–liquid equilibrium coefficient of the i-th component.

From equations (2.113) and (2.114) we obtain:

$$z_{1,i} = z_i \frac{1}{\dfrac{V}{F} K_i(T, P, pcv) + 1 - \dfrac{V}{F}}. \tag{2.115}$$

From this equation, since

$$\sum_{i=1}^{n} z_{1,i} = 1,$$

we obtain the non-linear equation to be solved:

$$\sum_{i=1}^{n} \left(z_i \frac{1}{v\, K_i(T, P, pcv) + 1 - v} \right) - 1 = 0, \tag{2.116}$$

where $v = V/F$.

The equation is solved by iteration, while the value of the unknown v may be between 0 and 1.

The actual value of the function $K_i\,(T, P, pcv)$ appearing in equation (2.116) can be calculated in various ways.

If the mixture is considered as ideal, then

$$K_i(T, P, pcv) = K_i(T, P) = P_i^0/P, \quad i = 1, 2, \ldots ncomp. \tag{2.117}$$

where the vapour pressure of the i-th component at temperature T is P_i^0. Procedure *vapp* is used to calculate the vapour pressure.

For hydrocarbons, the approximation of the $K_i\,(T, P, pcv)$ function, using 22 constants, is made according to the diagrams of NGAA (Equilibrium Ratio Data Book, 1961).

The curves of the NGAA diagrams are approximated by functions of the following form:

$$\ln K = x \ln x P_{1-18}(x, y, z) + [P_{19-21}(y) - z] \times \frac{c_{22} \ln x}{c_{22} \ln x - 1} - \ln x. \tag{2.118}$$

The variables x, y and z are as follows: $x = p/pcv$; $y = 1/T$; $z = \ln pcv$.

In this formula, $P_{1-18}\,(x, y, z)$ represents a polynomial, in terms of which the variable x occurs at most in linear form, the variables y and z also quadratically. $P_{19-21}\,(y)$ is a second-degree polynomial in y.

The values obtained by approximation with the formula, and those read from the NGAA diagrams result in a similar distribution (5–10%), according to our control calculations.

The procedure provides the option of considering the $K_i\,(T) - T$ value pairs as input data, and from these the $K_i(T)$ value pertaining to the actual temperature may be calculated by linear interpolation of $\ln K_i\,(T)$ according to $1/T$.

In this case, therefore, K_i is calculated from the correlation

$$K_i = \exp\,(c_{1,i} + c_{2,i}/T), \quad i = 1, 2, \ldots ncomp. \tag{2.119}$$

The required coefficients $c_{j,i}$ are calculated with procedure *prek*.

Limits of application, error messages:

The applicability of the different calculation methods depends on both the availability of necessary component data in the basic matrix, and on the possibility of using the method to calculate the vapour-liquid equilibrium coefficient for the given state of the substance.

The functions approximating the NGAA curves can be used for hydrocarbons, over a range which differs for each substance but generally fulfils the following conditions:

$$\begin{aligned} 40 \times 10^5 \text{ N/m}^2 &< pcv < 350 \times 10^5 \text{ N/m}^2 \\ 200 \text{ K} &< T < 500 \text{ K} \\ 0.7 \times 10^5 \text{ N/m}^2 &< p < pcv. \end{aligned}$$

Procedure *vapr* uses procedures *prek, bubdew, enth, temp* as auxiliary procedures.

(n) Calculation of the coefficients needed to calculate the vapour-liquid equilibrium ratio

prek (type, ta, tf, p, pcv, ncomp, cvapr)

Procedure *prek* does not calculate any physical value directly. It serves as an auxiliary procedure to those procedures which apply linear approximation to calculate the vapour-liquid equilibrium ratio for a given pressure and composition.

As a result, procedure *prek* supplies the coefficient $c_{j,i}$ for a given pressure and composition (convergence pressure) from equation:

$$K_i = \exp\left(c_{1,i} + \frac{c_{2,i}}{T}\right), \quad i = 1, 2, \ldots ncomp. \qquad (2.120)$$

The coefficients are defined such that equation (2.120) approximates for real mixtures the function $K(T, P, pcv)$, and for ideal mixtures the vapour-liquid equilibrium ratio calculated by procedure *vapp* according to the least-square method in the range $ta < t < tf$.

If the basic matrix does not contain the 22 coefficients for a component, necessary to calculate the equilibrium coefficient of a real mixture (the 36th element of the i-th row of the matrix equals zero), then procedure *prek* finds in the i-th row of the basic matrix at elements 15 and 17 two temperatures; and at elements 16 and 18 two equilibrium ratio related to the two temperatures. The coefficients of equation (2.120) are calculated by linear interpolation on the basis of these data.

Procedure *prek* uses procedure *vapp* as an auxiliary procedure.

(o) Phase equilibrium. Boiling- and dew-point calculation of a mixture

bubdew (type, t, p, pcv, v, z, zl, zv, ncomp, first, cvapr)

Procedure *bubdew* calculates the equilibrium temperature relating to a given vapour ratio. The equilibrium composition of the liquid and gaseous phases corresponding to the calculated equilibrium temperature are put into arrays *zl* and *zv* by procedure *bubdew*. The equilibrium temperature is calculated by iteration, according to equation (2.116). The starting value of the iteration is the actual value of *t*, which figures among the formal parameters of the procedure. The calculated equilibrium temperature remains the own value of the procedure. Corresponding to the vapour ratio the boiling point is calculated if $v = 0$, and the calculation of the dew point is effected if $v = 1$.

The calculation of the vapour-liquid equilibrium ratio may be carried out differently (see, the description of procedure *vapr)*.

Procedure *bubdew* uses procedure *prek* as an auxiliary procedure.

Limits of application, error messages:

The limits of application of the procedure are identical to those of procedure *vapr*.

Error of the method: The error of the method results from the inexactness of the calculated equilibrium vapour ratio and of the formulae approximating the diagrams, and the methods of approximation.

2.4.2.4 NETWORK OF PROPERTY-CALCULATION METHODS

It is characteristic of all the procedures introduced, that they receive information only
- from the basic matrix and/or
- from other procedures for property calculations and
- from stream vectors.

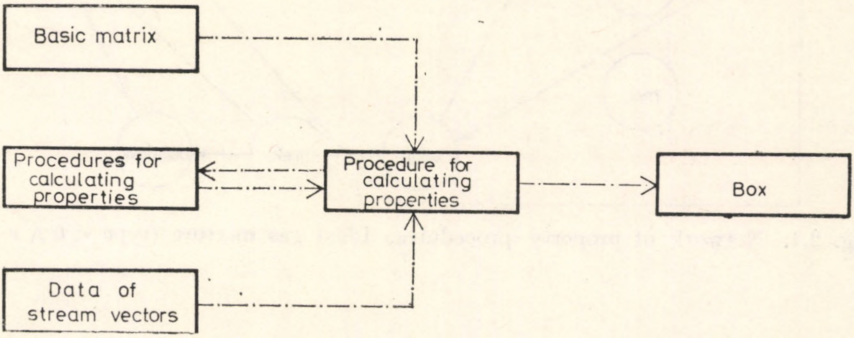


Fig. 2.3. Information streams during property calculations

In addition, they only communicate information with the boxes. This is illustrated in Figure 2.3.

Figure 2.3. also shows that the property calculation procedures form a network in the SIMUL system, which is linked with information streams. These networks differ, depending upon whether we have to calculate the properties of an ideal gaseous mixture, an ideal liquid mixture, a real gaseous mixture or a real liquid mixture. The different networks are presented in Figures 2.4–2.7.

In these figures, the procedures are symbolized by circles and the information streams by lines indicating the direction of information flow. The figures do not indicate the boxes or information sources (basic matrix, stream vectors), since the aim was only to show the internal linkage of the procedures. It may be established, from the direction of the information streams, which procedures supply information to others during calculation, and which are the procedures receiving information. (It is apparent, for example from Fig. 2.5., that procedure *dens* receives information from procedures *vapp* and *mix* and transmits it to procedure *hcond*.)

Comparing the corresponding networks for ideal and real mixtures, it is evident that the calculation is much simpler with ideal mixtures and only a few procedures are called. In order to shorten the time consumption of the calculation, it is worthwhile — provided it is permissible from physical

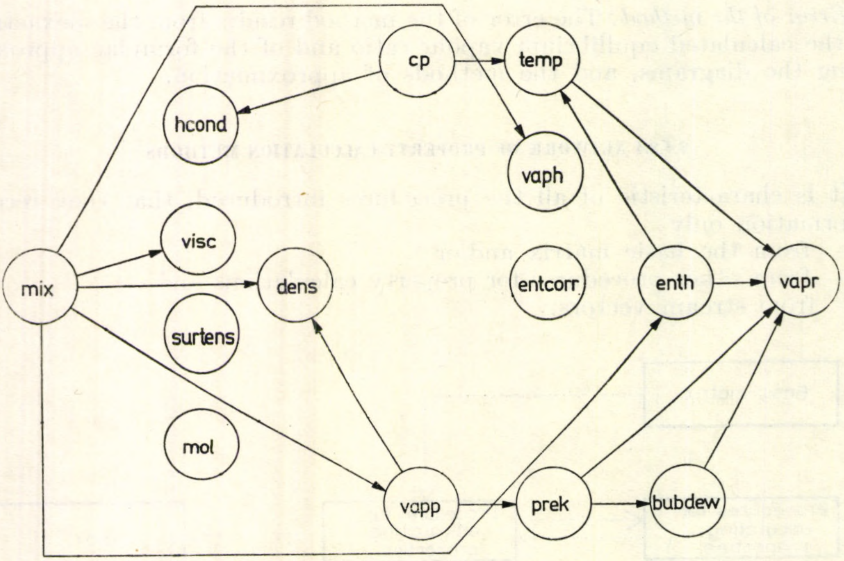
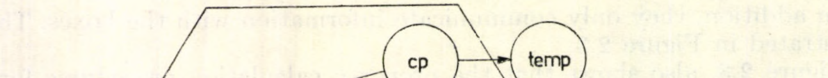


Fig. 2.4. Network of property procedures. Ideal gas mixture (type $< 0 \wedge v = 1$)



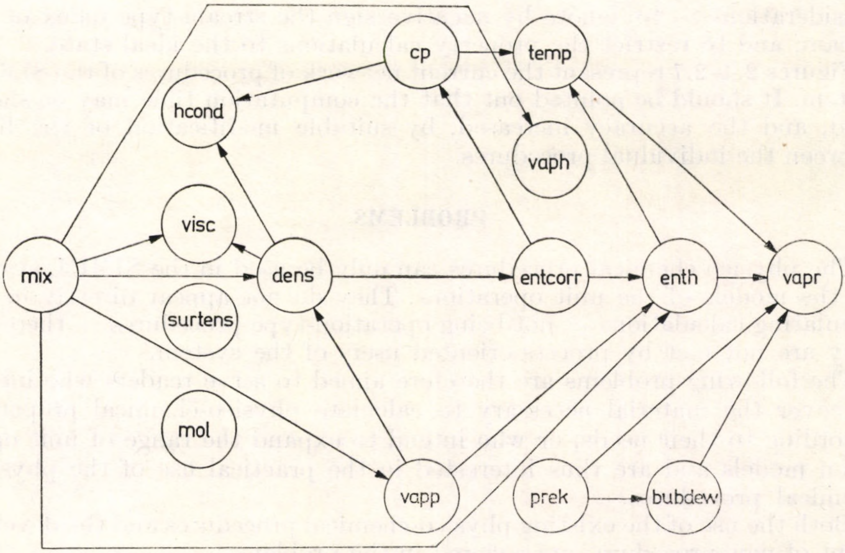


Fig. 2.6. Network of property procedures. Real gas mixture (type $< 0 \wedge v = 1$)

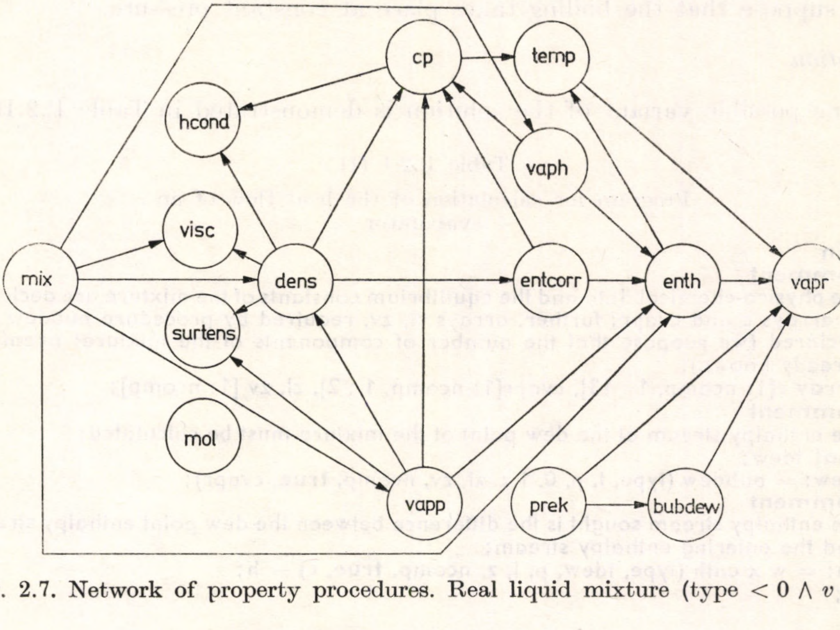


Fig. 2.7. Network of property procedures. Real liquid mixture (type $< 0 \wedge v = 0$)

considerations — to denote by negative sign the stream-type index of the stream, and to restrict the property calculations to the ideal state.

Figures 2.4–2.7 represent the current network of procedures of the SIMUL system. It should be pointed out that the computation time may be shortened, and the accuracy increased, by suitable modification of the links between the individual procedures.

PROBLEMS

The physico-chemical procedures can only be used in the SIMUL system by the models of the unit operations. They do not appear directly in the simulating calculations — not being operation-type procedures — therefore they are not met by process-oriented users of the system.

The following problems are therefore aimed to serve readers who intend to cover the material necessary to calculate physico-chemical properties according to their needs, or who intend to expand the range of unit operation models and are thus interested in the practical use of the physico-chemical procedures.

Both the use of the existing physico-chemical procedures and the development of new procedures are covered in the problems.

PROBLEM P.2.1 EVAPORATION

Program the calculation of the heat flow needed to evaporate the total quantity of a known stream entering into a boiler.

Let the entering stream be characterized by the symbols corresponding to the parameters of the procedures of package FISC: *type*, *w*, *h*, *t*, *p*, *v*, *z*. We suppose that the boiling takes place at constant pressure.

Solution

One possible variant of the solution is demonstrated in Table P.2.1(1).

Table P.2.1 (1)

Program for calculation of the heat flow of an evaporator

```
begin
  comment
  the physico-chemical data and the equilibrium constants of the mixture are declared
  in arrays c and cvapr; further, arrays zl, zv, required by procedure bubdew are
  declared (we suppose that the number of components of the mixture: ncomp is
  already known);
  array c[1: ncomp, 1 : 13], cvapr[1: ncomp, 1 : 2], zl, zv [1: ncomp];
  comment
  the enthalpy stream at the dew point of the mixture must be calculated;
  real tdew;
  tdew: = bubdew (type, t, p, 0, 1 z, zl, zv, ncomp, true, cvapr);
  comment
  the enthalpy stream sought is the difference between the dew point enthalpy stream
  and the entering enthalpy stream;
  dh: = w x enth (type, tdew, p, l, z, ncomp, true, c) — h;
end;
```

PROBLEM P.2.2 CALCULATION OF EQUILIBRIUM TEMPERATURE

Develop a program which calculates, for a stream of known composition, the temperature at which a prescribed ratio of the k-th component of the stream evaporates.

Let the known stream be characterized by the symbols corresponding to the parameters of the procedures of package FISC: *type*, *t*, *p*, *pcv*, *v*, *z*, *zl*, *zv*, *ncomp*. Let the prescribed ratio of evaporation be a $(0 < a \leq 1)$.

Solution

If the equilibrium vapour ratio and the equilibrium vapour composition are denotated by $v(T)$ and $zv(T)$ respectively, then the task requires the solution of the

$$v(T) \times zv_k(T)/z_k = a,$$

a non-linear equation.

The relations $v(T)$ and $zv(T)$ respectively, required for the numerical solution are provided in principle by procedure *vapr*. Its use is nevertheless not recommended, because it requires the solution of numerous non-linear equations. The equation might be transformed using the inverse relation supplied by procedure *bubdew:*

$$v \times zv_k(v)/z_k = a,$$

which is bound to have a solution in the interval $0 < v \leq 1$ and the condition $0 < a \leq 1$. The left-hand side of this equation is presumably a monotonous increasing function of v and therefore the interval-halving method can be used to solve the equation.

The temperature sought can be calculated according to Table P.2.2(1).

Table P.2.2 (1)

Program for the calculation of equilibrium temperature

```
begin
  array zl, zv [1: ncomp],
  cvapr [1: ncomp, 1 : 2];
  real va, vf, mr;
  comment
  set the initial values of the iteration, calculate the initial composition zv, define array
  c containing the equilibrium constants;
  va: = 0;
  vf: = 1;
  v: = 0.5;
  t: = bubdew (type, t, p, 0, v, z, zl, zv, ncomp, true, cvapr);
  comment
  solution of equation a = v×zv[k]/z[k] with a prescribed accuracy of 0.1% relative
  error;
  for[mr: v×zv [k]/z [k] − a while
            abs (mr) > 0.001 × a do
  begin
    if mr > 0 then vf: = v else va: = v;
    v: = (va + vf)/2;
    t: = bubdew (type, t, p, 0, v, z, zl, zv, ncomp, false, cvapr);
  end;
end;
```

PROBLEM P.2.3 CALCULATION OF THE HEAT OF REACTION AND THE ADIABATIC REACTION TEMPERATURE

Develop a program which calculates the heat of reaction evolved in an isenthalpic reaction of given yield (producing a known exit composition), and the temperature of the exit stream.

We suppose that the reaction takes place at constant pressure, that the entering and leaving streams are of the same stream type, and that the state of the leaving stream is known.

Solution

Let the entering stream be characterized by: *type, w0, hh, t0, p, v0, z0*, and the exit stream by: *type, w1, hh, t1, p, v1, z1.*

According to the definition of procedure *enth*, the value of the heat of reaction is supplied by the expression:

$$w1 \times enth(type,\ t0,\ p,\ v1,\ z1,\ ncomp,\ true,\ c\ ) - hh.$$

Following our assumptions, the specific enthalpy of the exit stream is: *hh/w1* and its temperature may be obtained by calling procedure *temp (type, hh/w1, t0, p, v1, z1, ncomp, false, c)*. (When calling up the second procedure, we have assumed that array *c*, containing the physico–chemical data, is already defined.)

PROBLEM P.2.4 INTERPOLATION OF MEASURED DATA AND CALCULATION OF THE THERMAL CONDUCTIVITY OF GASEOUS MIXTURES

For the interpolation of the temperature dependence of the thermal conductivity of pure gases, the following relation is recommended (Jakob, 1949):

$$\lambda(T) = \frac{a\sqrt{T}}{1 + b/T}\,(1 + cT),$$

where

T = the temperature of the gas and

$a, b, c,$ = constants, depending upon the properties of the substance

(a) Develop a program to determine the constants a_i, b_i and c_i — adhering to the components of a stream type — based on measured values.

(b) Develop a procedure calculating the thermal conductivity of gaseous mixtures based on the known values of the coefficients a_i, b_i and c_i. To calculate the thermal conductivity of the mixture the formula

$$\lambda\,\text{mixt} = \frac{\sum\limits_i \lambda_i \sqrt[3]{M_i}\, z_i}{\sum\limits_i \sqrt[3]{M_i}\, z_i}$$

has to be used (Reid and Sherwood, 1966, where M_i and 2_i represent the molecular mass and the mole ratio of the i-th component respectively.

Solution

To determine the coefficients required we need thermal conductivity values on three different temperatures for each component.

These related values are

$$\lambda_{i,j} \text{ and } T_{i,j} \qquad \begin{pmatrix} i = 1, 2, \ldots ncomp \\ j = 1, 2, 3 \end{pmatrix}.$$

Knowing these, the following linear system of equations is valid for a_i, b_i and c_i — as unknown values:

$$a_i\sqrt{T_{ij}} - b_i(\lambda_{ij}/T_{ij}) + a_i c_i T_{ij}^{3/2} = \lambda_{ij} \qquad (j = 1, 2, 3).$$

When solving this system of equations, a_i, b_i and c_i can be calculated. If it is intended to use the calculated coefficients not only in the part of the program *(box)* which derived them, but to make them available to any other box, then the coefficients have to be stored in the background store. This case is discussed in the following.

It seems to be suitable to store the coefficients in the data matrices *(ctype)*, selected for each stream type from the basic matrix. (These data matrices are selected for the purpose and duration of each simulation. See, Sections 2.4.2.2(a) and 8.2.1.3).

Although there is no empty space for that purpose in the standard basic data matrix nor thus in the derived *ctype* matrices, we may assume a modification here of our system such that, the *ctype* matrices are enlarged with further columns and the 41st, 42nd, . . . , columns are used to store the coefficients. (This modification does not apply to the basic matrix.)

A "standard" procedure may be used to place the calculated coefficients in the adequate position of the background store. This procedure does not figure among the standard procedures of the master program. Since it presupposes details of data storage, not discussed in this book, we declare it symbolically and present only an exterior specification. (This procedure is incidentally exactly analogous with procedure *cpp from drum*, which places constants from the background store into the fast store.)

The program calculating the coefficients of the interpolation formula of thermal conductivity (Problem 2.4(a)) can be seen in Table P.2.4(1).

Table P.2.4 (1)

Determination of parameters from measured values

```
begin
  comment
  in this program we suppose that we know the stream type (type), the number of its
  components (ncomp) and for all components of stream type 3–3 thermal conduc-
  tivity values at 3–3 different temperatures, in arrays La and T (we suppose that both
  are declared with index bounds 1: ncomp, 1 : 3);
  array A[1 : 3, 1 : 3], B[1 : 3, 1 : 1], chcond[1: ncomp, 1 : 3];
  boolean sing;
  integer i, j;
  for i: = 1 step 1 until ncomp do
  begin
    comment
    the coefficient matrix of the linear system of equations is prepared;
    for j: = 1,2,3 do
    begin
    A[j,1]: = sqrt(T[i,j]);
    A[j,2]: = −La[i,j]/T[i,j];
    A[j,3]: = A[j,1]×T[i,j];
    B[j,1]: = La[i,j];
    end;
    comment
    solution of the system of equations using the standard procedure matrdiv (see,
    Chapter 4.4.1.2.a)
    Result is in B;
    matrdiv (A, 3, B, 1,sing);
    if sing then error (≮ < sing ≯);
    chcond[i,1]: = B[1,1];
    chcond[i,2]: = B[2,1];
    chcond[i,3]: = B[3,1]/B[1,1];
  end;
  comment
    placing the result into the background store;
    cpp to drum (type, 43, 4, chcond);
    comment
    the procedure served to modify in part or fully the type matrix of the physico-
    chemical basic data selected for the stream type (type). The data to be placed
    into the matrix are contained in array cpp. The procedure supposes that array
    cpp is declared with index bounds 1:ncomp, 1:nc, where ncomp is the number of
    components in the stream type (type). As a result of calling the procedure, the
    columns of array cpp are placed into columns with indices ic − nc + 1,
    ic − nc + 2, . . ., ic of the matrix ctype;
 end determination of the coefficients of the interpolating formulae;
```

Using this program, the simulation may be simplified for equipment models, working in the range of validity of the interpolation formula. In addition it is possible to use measured data with standard procedures. The interpolation procedure (Problem 2.4(b)), using the results of Problem 2.4(a), has been developed after the pattern of the standard procedures of the package FISC. According to the algorithm, this procedure needs, in addition to the *chcond* coefficients already calculated and stored, the molecular mass of each component. The latter data are stored in the **2nd** column of the basic matrix. Both data groups are accessible through standard procedure *cpp from drum* and the procedure calculating the thermal conductivity reads both at the "first" call into the arrays, corresponding to the formal parameters *chcond* and M, respectively.

The interpolating procedure is found in Table **P.2.4(2)**.

Table P.2.4 (2)

Interpolation procedure to calculate thermal conductivity

```
begin
  real procedure interchcond (type, t, v, z, ncomp, first, chcond, M);
  value type, t, v, ncomp, first;
  integer type, ncomp;
  real t, v;
  boolean first;
  array z, chcond, M;
  begin
    integer i;
    real la, s, mr;
    comment
    defining arrays M and chcond when first calling the procedure;
    if first then
    begin
      cpp from drum (type, 2,1, M);
      cpp from drum (type, 43, 3, chcond);
    end;
    if v ≠ 1 then error (≮ < interchcond:
    no gaseous state ≯);
    la: = s: = 0;
    for i: = 1 step 1 until ncomp do
    begin
      mr: = M[i,1] ↑ 1/3 × z[i];
      la: = la + mr × chcond[i,1] × (1 + t × chcond[i, 3])/ (1 = chcond[i,2]/t);
    end;
    interchcond: = la × sqrt(t)/s;
  end
  comment
  for simplicity -- in contrast to other physico-chemical procedures — we have not
  allowed calculation of a single component of the stream type with the aid of the
  stream-type code to be prescribed here (see, 2.2.2.1);
  end;
```

PROBLEM P.2.5 ENTROPY CALCULATION

Develop a procedure to calculate the molal entropy of a gas.

Solution

To calculate the molal entropy

$$S^x = \int \frac{1}{T}\frac{\partial H}{\partial T} T - R\ln(P/P_0) \tag{a}$$

of an ideal gas, consisting of one component, we use the relation

$$S^x = I + a_1 \ln T + 2a_2 T + 3/2 a_3 T^2 + 4/3 a_4 T^3 - R\ln(P/P_0), \tag{b}$$

which can be obtained by integrating the polynomial (2.84) expressing the temperature dependence of the enthalpy, where

T = the temperature of the gas,
P = the pressure of the gas,
P_0 = the atmospheric pressure (101325 N/m^2).

The coefficients $a_l, \ldots, a_4$ and the I integration constant are contained in columns 10–14 of the basic matrix.

For ideal mixtures of ideal gases, we use relation (Dodge, 1944)

$$S^x_{\mathrm{mixt}} = \sum_i z_i (S^x_i - R\ln z_l), \tag{c}$$

where

z_i = the mole fraction of the i-th component and
S^x_i = the entropy of the i-th component (T temperature and P pressure).

With real mixtures the entropy correction is the following

$$S_{\mathrm{mixt}} - S^x_{\mathrm{mixt}} = \frac{H - H^x}{T} - R\int_0^P \frac{Z-1}{P}\,dp \tag{d}$$

where

Z = the compressibility factor of the mixture and
$H - H^x$ = the enthalpy correction,

and hereby we use the relations derived from the Redlich–Kwong equation of state:

$$\int_0^P \frac{Z-1}{P}\,dP = Z - 1 - \ln\left(Z - \frac{\beta P_r}{T_r}\right) - \frac{\alpha}{\beta T_r^{1.5}}\ln\left(1 + \frac{\beta P_r}{Z T_r}\right) \tag{e}$$

and

$$H - H^{\mathrm{x}} = RT\left\{Z - 1 - \frac{1.5\alpha}{\beta T_{\mathrm{r}}^{1.5}} \ln\left(1 + \frac{\beta P_{\mathrm{r}}}{Z T_{\mathrm{r}}}\right)\right\} \tag{f}$$

where P_{r} and T_{r} represent the reduced pressure and temperature respectively related to the pseudo-critical state variables of the mixture; $\alpha = 0.0867$ and $\beta = 0.4278$, the two constants of the Redlich–Kwong equation.

(The relations appearing here can be obtained by writing equation (2.99) – relating to the fugacity constant of the gas – with respect to the reduced state variables T_{r} and P_{r} or by taking into consideration, in relation (2.89) for the enthalpy correction,

$$H - H^{\mathrm{x}} = -RT^2 \frac{\partial}{\partial T} (\ln f/P)$$

not only equation (e) but also that form of the Redlich–Kwong equation which contains P_{r}, T_{r} and Z:

$$Z = \frac{Z}{Z - P_{\mathrm{r}}/T_{\mathrm{r}}} - \frac{\alpha P_{\mathrm{r}}}{T_{\mathrm{r}}^{2.5}} \frac{1}{Z + \beta P_{\mathrm{r}}/T_{\mathrm{r}}}\,. \tag{g}$$

The constants required to calculate the entropy of ideal gaseous mixtures are stored in columns 10–14 of the basic matrix, the data required for the entropy correction in columns 1–8. For the sake of simplicity the data stored in columns 1–14 are placed into the fast store.

The relation for ideal gaseous mixtures can be written as follows:

$$S_{\mathrm{mixt}}^{\mathrm{x}} = \bar{I} + \bar{a}_1 \ln(T) + 2\bar{a}_2 T + 3/2\,\bar{a}_3 T^2 + 4/3\,\bar{a}_4 T^3 - $$
$$- R\left(\sum_i z_i \ln(z_i) + \ln(P/P_0)\right) \tag{h}$$

where $\bar{I}$ and $\bar{a}_i$ are weighted values according to mole fractions.

When calculating $\sum_i z_i \ln(z_i)$ we have to omit from the summarization those components which figure in the mixture with zero mole fraction. (This is correct because $\lim_{z \to 0} z \ln z = 0$.)

Using the relations listed above, the correction required with real mixtures is the following:

$$S_{\mathrm{mixt}} - S_{\mathrm{mixt}}^{\mathrm{x}} = R\left\{\ln\left[Z\left(1 - \frac{\beta P_{\mathrm{r}}}{Z T_{\mathrm{r}}}\right)\right] - \frac{0.5\alpha}{\beta T_{\mathrm{r}}^{1.5}} \ln\left[1 + \frac{\beta P_{\mathrm{r}}}{Z T_{\mathrm{r}}}\right]\right\}. \tag{i}$$

The simplest way to calculate the compressibility factor Z is to use the standard procedure *dens*. We can make also a secondary use of procedure *dens*, and thus – as a result of the standard procedure *mix* called – the pseudocritical values of the given mixture can be found in the global array *pkr*.

Taking the above-mentioned relations into consideration, the task may be solved according to Table P.2.5(1).

Table P.2.5 (1)

Procedure to calculate entropy

```
real procedure entropy (type, t, p, v, z, ncomp, first, c);
value type, t, p, v, ncomp, first;
integer type, ncomp;
real t, p, v;
boolean first;
array z,c;
begin
  integer i, j;
  real mr, S,Z, R;
  array a [1 : 5];
  comment
  value of the R gas constant in J/kmole K;
  R: = 8314.3;
  comment
  transfer of the basic data to the store;
  if first then cpp from drum (type, 14, 14, c);
  if v = 1 then
  begin
     a[1]: = a[2]: = a[3]: = a[4]: = a[5]: = S: = mr: = 0;
     comment
     calculation of the mean values of the coefficients;
     for i: = 1 step 1 until ncomp do
     if z[i] ≠ 0 then
     begin
        for j: = 1 step 1 until 5 do
        a[j]: = a[j] + z[i] × c[i, 9 + j];
        mr: = mr + z[i] × ln(Z[i]);
        comment
        calculation of the entropy of the ideal gas mixture;
        for j: 4,3, 2 do
        S: = (S + j)(j − 1) × a[j] × t;
        comment
        Horner scheme;
        S: = S + a[1] × ln(t) + a[5] − R × (mr + ln(P/101325));
        comment
        non-ideal mixture;
        if type > 0 then
        begin
          Z: = p/R × t × dens(type, t, p, v, z, ncomp, false, c));
          write (≮ − p.ddd00₁₀ − dd ≯, Z);
          mr: = 0.0867 × p/pkr[2](Z) × pkr[1];
          S: = S + R × (ln(Z × (1 − mr)) −0.5 + 0.0167/0.4278 ×
          (pkr[1]/t↑ 1.5 × ln (1 + mr));
        end;
     end z [i] ≠ 0;
     entropy: = S;
  end else error (≮ < entropy: no gaseous state ≯);
end entropy;
```

CHAPTER 3

EQUIPMENT

3.1 THE EQUIPMENT IN THE SIMUL SYSTEM

The rectangles in the block diagram of butane isomerisation represent simple or complex unit operations. The texts show which is the unit operation in question. The instrument needed to carry out the operation is the equipment.

Each piece of equipment has inlet and outlet pipe stubs, the number of which characterizes the equipment. Each piece of equipment is characterized by one or more main dimensions (e.g., the volume of a reactor, number of plates).

Each piece of equipment (as a unit operation) possesses a certain degree of freedom, meaning that the values of certain process variables (e.g., reflux ratio) may and even has to be adjusted. These values have to be prescribed in the course of simulation mode calculations. When simulating the steady-state performance of a piece of equipment, these values are just as necessary (the main dimensions, process variables burdening the degree of freedom) as the stream vector of the flows entering the equipment. These data will be — among others — the *operating parameters*. Programs able to carry out the prescribed calculations starting from this information are named according to the terminology of the SIMUL system equipment-type boxes. The term "box" refers to the concept of the "black-box", namely that from the point of view of the entire system the inside of the box is irrelevant. There is one single requirement, that the box should produce the output stream vectors as a function of the input stream vectors, taking the main dimensions of the equipment and the parameters characterising the steady-state performance of the equipment into consideration.

The boxes do not define the unit operation in a general way, independent of their mode of execution. The distillation appearing in Figure 2.1 is not only specified by a first type stream vector entering in a defined state, but also by the type of equipment in which the distillation is carried out (plate or packed column). The box has therefore to comply with the requirement to act as an adequate model of the unit operation.

The boxes of the SIMUL system are designated by a box identifier and a box index. These define unequivocally the operation which is modelled by the box.

Let us now consider the block diagram presented in Figure 2.1 and replace all the operations indicated generally by adequate boxes chosen from the box assortment of the SIMUL system.

We begin the replacement with the last operation on the block diagram, the mixing. The physical phenomenon occurring during mixing is calculated in the SIMUL system with a box called *mixing*, the box index being 13 (see, Section 3.4.4). Its symbol is presented in Figure 3.1. This box is connected at three points *a, b* and *c* with the other elements of the block diagram. For the moment we need only point out that the box *mixing* calculates the output stream (stream vector) at connecting point *c* from the input streams (stream vectors) at connecting points *a* and *b*. This is indicated by the arrows on the lines representing the streams. This box is to calculate the operation denoted on the block diagram as position M; the word "mixing" should be changed to *mixing: 13*. It should be pointed out that this box has one operating parameter, to be indicated as *op1*. The same operation, carried out by the relevant box, may appear several times in a complex operation. It is therefore not sufficient to specify the box by the box index, but the environment in which it is appearing and the operating parameter (vector) which defines its actual functioning must be indicated. This operating parameter (vector) is characterized by index *m*, the operating index. It is therefore evident that differences in functioning are distinguished by different operating indexes. Let us say that in our case the operating index of box *mixing* should be 40 as an example. In the operation-order flow-sheets (to be introduced later), the actual operating index is written in the upper left-hand corner of the rectangle. This may all be written symbolically as follows:

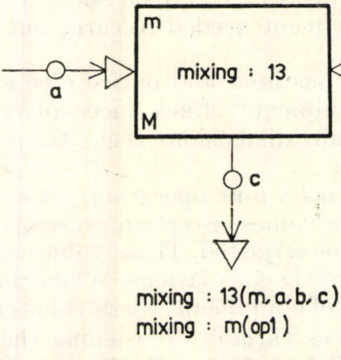


Fig. 3.1. Graphic symbol of box *mixing*

mixing: 13 (40, a, b, c)

Here we specify that, among the different operations of the process, the box *mixing* — which has index 13 and is the model of the operation characterized by the operating index 40 — handles the stream vectors at the connecting points *a*, *b* and *c*. The above symbolic sequence of indications represents — replaced by actual numbers — part of the flow-sheet program to be dealt with later. This type of data groups will be called operational declarations.

The operating index in the operational declaration ensures simultaneously the identification of the operating parameters. The operating parameters are enumerated by name when specifying the problem. The operating parameter of the box (in our example single) is stated in the following way

mixing: 40 (op1),

meaning that *op1* is the operating parameter of the operation whose operating index is 40. This type of data groups, replaced by actual operating parameters, will be part of the input data system of the simulation and will be called box declaration.

The calculation of the distillation — denoted by D on the block diagram — is carried out by box *dist1*, box index 23 or by box *dist2*, box index 26

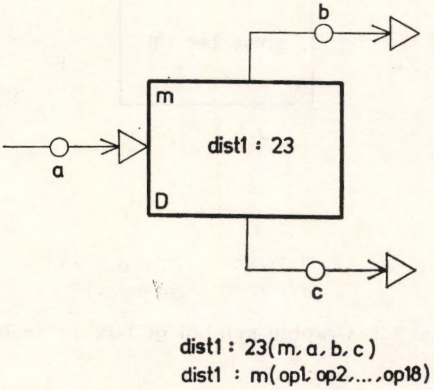


Fig. 3.2. Graphic symbol of box *dist1*

(see, Sections 3.4.9 and 3.4.10 respectively). Box *dist1* assures a rapid and fair estimation, whereas *dist2* executes a much more accurate algorithm, calculating from plate to plate, and needing more time. As *dist1* serves our purposes, this is chosen. As box *dist1* is not suitable for calculating the mass flow of the heat-carrying media, covering the calculated heat requirement of the reboiler, we will neglect it for the time being. This question is discussed in Chapter 5.

The part of the block diagram with the word "distillation" is to be substituted by the symbol of box *dist1 : 23* (Fig. 3.2). It should be noted that the number of operating parameters of box *dist1* is 18, and these have to be enumerated later. Box *dist1* is to be found once in the block diagram, the actual operating index is 30.

The statements about box *dist1* enable us, as in the case of box *mixing*, to write the following operational declaration:

dist1: 23 (30, a, b, c),

and enumerating the operating parameters we have the box declaration:

dist1: 30 (op1, op2, . . . , op18).

Heat exchangers figure twice in the block diagram (W1 and W2). We should remind the reader that according to the process description (Chapter 1) both heat exchangers are controlled, in the sense that the temperatures of the flows are set to a prescribed outlet value. From the simulation aspect, it does not matter what happens to the other flow passing the heat exchanger.

The enthalpy flow to be added to the inlet flow (type 1) is essential. It has to secure temperature T of the flow leaving the heat exchanger without change of composition, pressure or state. To accomplish this calculation, a box is chosen from the box assortment of the SIMUL system, which has a peculiar role. It is named *prescriber* and the box index is 11 (Fig. 3.3).

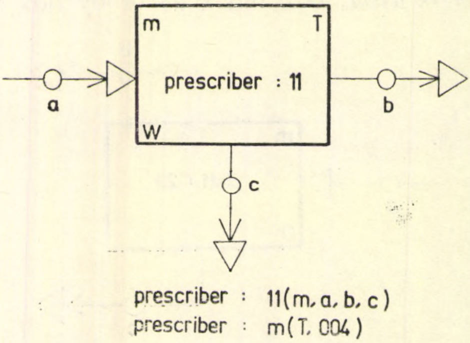


Fig. 3.3. Graphic symbol of box *prescriber*

The heat exchanger figuring twice on the block diagram is to be replaced at both places by the box *prescriber* (Section 3.4.2). The fact that the function of box *prescriber* at both places is the modification of the temperature, is indicated by the letter T written in the upper right-hand corner of the rectangle. Box *prescriber* operates at both places in a different manner, as the temperature to be adjusted is different. This is expressed by different operating indices. Let these be 20 and 21. The box *prescriber* operates in simple cases with two operating parameters, and may be specified as follows:

prescriber: 11 (20, a, b, c)
prescriber: 11 (21, a, b, c),

respectively with the operating parameters:

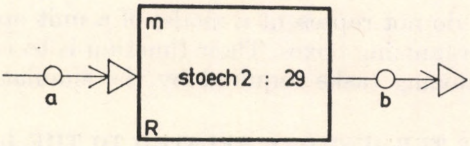
prescriber: 20 (T1, 004)
prescriber: 21 (T2, 004),

where $T1$ and $T2$ are the prescribed temperature values. The number 004 indicates that the fourth element of the stream vector at point a is to be replaced by the values of $T1$ and $T2$ (to be explained later). Remember that according to Section 2.2.3.4 the fourth element of the stream vector is the temperature. The modified stream vector will appear at point *b*. The role of point *c* will be explained when discussing this box (see, Section 3.4.2).

Reactors R1 and R2 on the block diagram have not yet been discussed. For the SIMUL system, no box has been developed which could be suitable for simulating an ideally mixed reactor. It is known, however, that in this case the conversion K of n-butane may be calculated as a function of the catalyst flow w_k and the technological flow with respect to the mass flow of type 1, using the following correlation:

$$K = \frac{Aw_k}{(Bw_k + 1)(Dw_1 + 1)}, \tag{3.1}$$

where A, B and D are constants. In our example, the values of the constants are: $A = 10^4$, $B = 10^4$ and $D = 0.5$. However, if the conversion K is known,



stoech2 : 29(m, a, b)
stoech2 : m(op1, op2,...,op7)

Fig. 3.4. Graphic symbol of box *stoech2*

then the output stream vector is easily calculated from the input stream vector. This stoichiometric-termochemical calculation is effected by box *stoech2*, whose box index is 29 (Fig. 3.4). One of the seven operating parameters (the second) is the conversion. The conversion is calculated using an arithmetic expression, and then inserted as the second operating parameter of box *stoech2:29*.

The detailed analysis of this problem would exceed the limits of this Chapter, namely the equipment-related aspects of the SIMUL system. We will deal with this question later. Here we shall only state that conversion K may be calculated from the values of w_l and w_k, and as a result the complete stream vector at point *b* is produced by box *stoech2*.

Let the operating indexes of boxes *stoech2* representing reactors R1 and R2 be 10 and 11 respectively. We can now write the following specifications:

stoech2: 29(10, a, b)
stoech2: 29(11, a, b),

and with the operating parameters:

stoech2: 10 (op1, K1, op3, . . . , op 7)
stoech2: 11 (op1, K2, op3, . . . , op7)

3.2 TERMINOLOGY

3.2.1 BOX

Computation procedures which perform simulating operations with standard date groups or elements of them are termed boxes. From these boxes — as elementary simulating operations — the model of the complex operation can be assembled.

3.2.1.1 EQUIPMENT-TYPE BOX

Boxes which represent the model of a simple or combined unit operation are termed equipment-type boxes or equipment boxes.

3.2.1.2 MATHEMATICAL AND ORGANIZING BOXES

All boxes which do not represent a model of a unit operation are termed mathematical or organizing boxes. Their function is to carry out the mathematical and organizing tasks required by the simulation.

3.2.2 TERMINOLOGY RELATED TO THE BOXES

3.2.2.1 BOX INDEX

The box index is a natural number, identifying the box.

3.2.2.2 BOX IDENTIFIER

This is identical with that of the ALGOL procedure, corresponding to the box. It is used in block diagrams, operation-order flow-sheets and in text.

3.2.2.3 OPERATING PARAMETERS

All data which determine the performance of the box, except for the input stream vectors, or those computed by the box except for the output stream vectors are termed operating parameters.

3.2.2.4 OPERATING PARAMETER VECTOR

The operating parameter vector is an ordered array of all operating parameters of a box.

3.2.2.5 OPERATING INDEX

Operating index is a natural number identifying the actual parameter vector, which determines the performance of a box in a given location. Boxes in different positions but with the same operating parameter vector may use the same operating index.

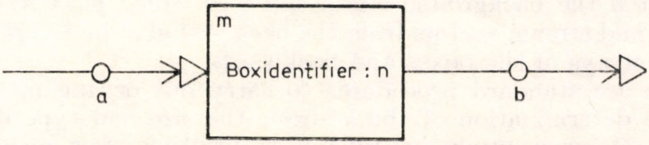
3.2.2.6 CONNECTING POINT

The identification of a flow connecting the box with the surroundings is termed connecting point.

3.3 CONVENTIONS RELATING TO THE EQUIPMENT BOXES

3.3.1 GRAPHIC SYMBOL OF THE EQUIPMENT BOXES

The equipment boxes are symbolized in the following way:



The rectangle represents the box, the number *n* after the box identifier the box index, the letter *m* in the upper left-hand corner the operating index, the arrows indicate the direction of the material flow, and letters *a* and *b* the connecting points. The small circles are symbols of the connecting points. It should be noted that in principle any number of streams may be connected to a box.

3.3.2 RULES OF DEVELOPING THE BOXES

3.3.2.1 GENERAL RULES

The boxes may be developed independently from each other. When developing a box, the existence of other boxes need not be considered. The boxes receive their input data from the background store and transfer the output data there. Information on the grouping of data is supplied by the organizing program to the box (see, Chapter 8).

The developer of a box may suppose that all input data are available in the background store.

Every box has to define the stream vectors (all their elements) which are output data and store them in the appropriate manner in the background store. In the operating-parameter vectors, input and output data may occur, in opposition to the stream vectors, whose elements are either only input data or only output data. The number and sequence of the operating parameters are defined without restriction by the developer of the box.

The output stream vectors and their elements have to ensure, that — considering the accuracy of the computer — the mass- and enthalpy-balance equations are fulfilled, the sum of the mole fractions is 1 and the correlation between the temperature, pressure and enthalpy is accomplished.

Every effort has to be made to ensure that the vapour ratio of the calculated stream corresponds to the state variables. If this is not controlled, it must be pointed out in the specification of the box.

Similarly, the box should be developed so that it prints error messages when outside its range of validity (the computation should not be terminate at the error message).

3.3.2.2 USE OF STANDARD PROCEDURES

The developer of the box can rely on the availability of certain standard procedures. These shall now be briefly considered, bearing in mind that they shall be or have been discussed elsewhere.

(1) Procedures are available which take care of the data transfer between the boxes and the background store, and also which place the operating parameters and stream vectors from the background store to specified location in the arrays of the boxes and backwards.

(2) There are standard procedures to carry out organizing operations, such as the determination of the address, the size and type of a record, defined by reference, producing references, printing error messages. These will be discussed in Chapter 8.

(3) The physical and chemical properties of a material stream may be calculated by standard procedures discussed in Chapter 2. If no standard procedure is available for the calculation of a property, this has to be solved in the box.

(4) Standard procedures are available for solving linear and non-linear systems of equations, for the numerical integration of first order differential equation systems and for finding the extreme value of multivariable functions (see, Chapter 4).

3.3.2.3 TESTING AND DOCUMENTATION OF THE BOXES

Testing of new boxes may be accomplished in two ways. One is to handle the box as an independent program, into which the standard procedures required by the organizing program are inserted in a suitable manner, or using the organizing program, into which — to shorten the translation time — only the box to be tested is inserted.

Each box has to be specified unambigously and with prescribed contents. The requirements of the user firstly govern the specification. Each box specification has the following contents:

- the box identifier and the box index,
- the graphic symbol of the box specifying the sequence of the connecting points and the direction of the technological streams,
- definition of the function of the box,
- the mathematical model represented by the box,
- the technological and computational limits of application, the accuracy (and time) of computation, and the possible directions of computation,
- the operating parameters of the box,
- the interpretation of error messages printed in the course of work of the box.

The specifications complying with the above rules are included in the documentation handbook of the SIMUL system (Mathematical Modelling, 1970).

3.4 EQUIPMENT BOXES

In the following, a short description of the boxes simulating equipment will be presented.

These descriptions contain all the information for each box which the user needs during his work: the function of the box, limits of application, list of operating parameters, and the main sources of error messages. The mathematical models (i.e., equations) are not contained in the box descriptions. The information is limited to being sufficient and necessary — according to our practice — to decide whether or not the box is suitable to simulate the functioning of the equipment in question.

To explain fully the working method of the boxes, the box descriptions are completed with an information flow diagram.

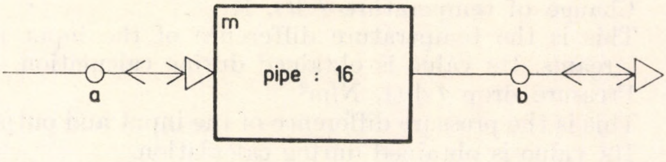
One of the simplest boxes of the available assortment, the box *pipe*, shall be treated in detail. It is considered as an example of the characteristic features of all boxes.

After describing all the boxes currently available, we shall discuss in Section 3.4.19 — based on brief information — some boxes developed to simulate factual complex operations.

3.4.1 MODEL OF THE PRESSURE DROP AND TEMPERATURE CHANGE OF A SUBSTANCE FLOWING IN A PIPE *(pipe)*

Box *pipe* is suitable for simulating the pressure drop and temperature change of a homogeneous substance flowing in a straight pipe.

The graphic symbol of the box:



Description of the operation:

pipe: 16 (m, a, b).

The box uses as initial data the geometrical and thermal data specified among the operational parameters and elements of the stream vector at one end of the pipe. As a result of the calculation the stream vector at the other end of the pipe, and among the operating parameters the heat loss of the medium, the pressure drop, temperature change, and friction factor are stated.

The calculation of the pressure drop takes place in the laminar region according to the Hagen–Poisseuille equation, and in the intermediate and turbulent region according to the Colebrook formula.

When calculating the heat loss, the thermal resistance of the pipe wall and the thermal resistance outside the wall are calculated by the box. To calculate the heat-transfer coefficient on the outside of the wall, an approximation formula is used which is valid for closed spaces and includes radiation losses. Isolation has to be taken into account by adequate selection of the thermal resistance. The calculation process is presented in information flow diagram 1.

Limits of application: The formula used to calculate the pressure drop is valid for non-compressible media in the range to be found in practice.

The box is not suitable for calculating the change of state arising from the change of pressure or temperature.

The box does not consider the change in heat-transfer coefficient along the pipe. The approximation used for the heat-transfer calculations is valid in the range 250 K $< t_{\text{outside}} <$ 400 K.

The effect of forced convection (wind) is neglected by the box when calculating the heat transfer on the outside.

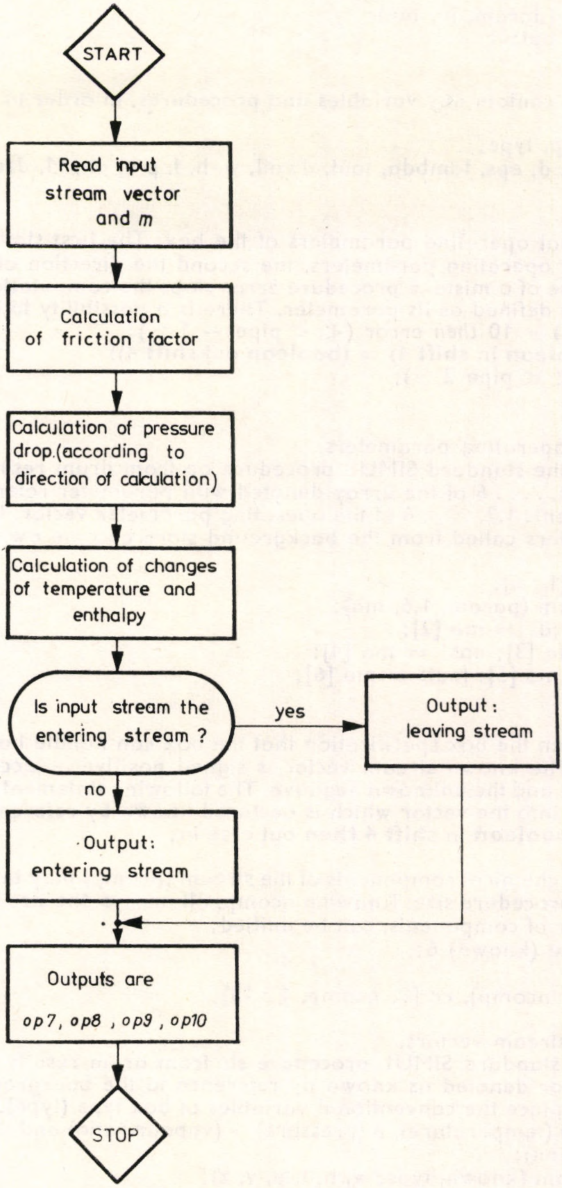
Operating parameters:

Denomination	Number	Value, significance
op1	1	Pipe length *(l)*, m
op2	1	Inner diameter of the pipe *(d)*, m
op3	1	Wall thickness (d_{wall}), m
op4	1	Pipe roughness *(eps)*, m
op5	1	Thermal conductivity of the pipe wall (λ_{wall}), J/m s K
op6	1	Outside temperature (t_{out}), K
op7	1	Heat intake (heat loss < 0), (Δh), J/s The value is obtained during calculation.
op8	1	Change of temperature (Δt), K This is the temperature difference of the input and output streams. Its value is obtained during calculation.
op9	1	Pressure drop (Δp), N/m^2 This is the pressure difference of the input and output streams. Its value is obtained during calculation.
op10	1	Friction factor (ζ). Its value is obtained during calculation.

Number of the operating parameters: 10.

Check: The box checks the number of operating parameters and the stream vectors to be calculated. If their number does not correspond to the specified number, then an error message is printed. Error message also appears, if the outlet pressure is negative.

Structure of the box: The structure of the boxes can be illustrated by taking as an example the ALGOL procedure of box *pipe*. The procedure is easy to survey based on the comments. The structure of each box is similar – being a genuine consequence of the homogeneity of the SIMUL system. Each box in the SIMUL system is declared as a procedure, and therefore starts with



Information flow diagram 1

the procedure heading. Consequently, the word *pipe* occurs as box identifier (procedure identifier). The words *m*, *in* and *out* are formal parameters, which are changed — when calling the procedure with references — with the corresponding operating index and connecting index.

```
procedure pipe (param, in, out);
real param, in, out;
begin
  comment
  the boxes may contain any variables and procedures, in order to survey the inter-
  connections;
  integer ncomp, type;
  real known, l, d, eps, lambda, tout, dwall, w, h, t, p v, dh, M, dzeta, mr, dp, a, b,
  dt, Re;
  comment
  check the actual operating parameters of the box. The first statement checks the
  number of the operating parameters, the second the direction of the information
  streams. In case of a mistake procedure error stops the computation and prints the
  error message defined as its parameter. There is a possibility to intervene;
  if size (param) ≠ 10 then error (≮ < pipe − 1 >);
  if −, (−, (boolean in shift 4) = (boolean out shift 4))
  then error (≮ < pipe 2 >);
  begin
    comment
    calling the operating parameters.
    The call of the standard SIMUL procedure op from drum results in placing the
    elements 1,2, . . . . 6 of the array denoted with parameter reference m to array
    ma as elements 1,2, . . . . 6 of the operating parameter vector. Here, the operat-
    ing parameters called from the background store become own variables of the
    box;
    array ma [1 : 6];
    op from drum (param, 1,6, ma);
    l: = ma [1];d: = ma [2];
    dwall: = ma [3]; eps: = ma [4];
    lambda: = ma [5]; tout: = ma [6];
  end;
  comment
  it is known from the box specification that the box can handle both input and out-
  put streams. The known stream vector is signed positive — according to SIMUL
  conventions — and the unknown negative. The following statement enters the known
  stream vector into the vector which is declared known by reference;
  known: = if boolean in shift 4 then out else in;
  comment
  the number of chemical components of the stream (ncomp) may be determined with
  the standard procedure size. Knowing ncomp, all arrays, the size of which depends
  on the number of components, can be unified;
  ncomp: = size (known) 6;
  begin
    array z [1: ncomp], cc [1: ncomp, 1 : 13];
    comment
    calling the stream vectors.
    Calling the standard SIMUL procedure str from drum results in the call of the
    stream vector denoted as known by reference to the background store and its
    elements replace the conventional variables of box type (type), w (mass flow), h
    (enthalpy), t (temperature), p (pressure), v (vapour ratio) and the array variable
    z (composition);
    str from drum (known, type, w, h, t, p, v, z);
    comment
    now the statements, calls and checks, follow which result in the values to be com-
    puted by the box. The entity of these statements represents the mathematical
    model of the box;
    M: = mol (type, z, ncomp, true, cc);
    comment
    computation of the pressure drop;
    Re: = 4/3.14159 x w x M/d/visc (type, t, p,v, z, ncomp, false, cc);
```

```
        if Re < 2300 then dzeta: = 64/Re else
        begin
          a: = 2.51/Re;
          b: = eps/3.72/d;
          for dzeta: = 0.1, (if dzeta + mr < a/(1 – b)
          then (dzeta + a/(1 – b))/2 else dzeta + mr)
          while abs (mr) > 0.01 × dzeta do
          mr: = dzeta × (1 + dzeta×2×0.4343×ln (a/dzeta + b));
          dzeta: = dzeta ↑2;
        end
        dp: = (if boolean out shift 4 then–1 else 1)×8/3.14159↑ 2×dzeta×1/d×
        w ↑ 2×M/(d ↑ 4×dens (type, t, p, v, z, ncomp, false, cc);
        p: = p + dp;
        if p < 0 then error (K ≮ < pipe 3 >);
        comment
        computation of the temperature change;
        b: = lambda/dwall;
        a: = 4.88–b/2 + sqrt((4.88 + b/2) ↑ 2 + 0.07×(t – tout)×b);
        a: = 1/(1/a + 1/b);
        dt: = (tout-t)×(1-exp((if boolean out shift 4 then –1 else 1)×a×(d + 2×
        dwall)×3.14159×1/w) cp (type, t, p, v, z, ncomp, false, cc)));
        t: = t + dt;
        dh: = w×enth (type, t, p, v, z, ncomp, false, cc) – h;
        h: = h + dh;
        comment
        output of the computed stream vector.
        Procedure str to drum enters the data computed by the box into the background
        store on which the unknown stream has depended;
        if known = in then str to drum (out, type, w, h, t, p, v, z)
        else str to drum (in, type, w, h, t, p, v, z);
        begin
          comment
          output of the computed operating parameters.
          As a result of the following statements, the data calculated by the box are
          entered into array ma as its elements. Procedure op to drum results in entering
          these elements as elements 7, 8, 9 and 10 of the array in the background store,
          denoted by reference m;
          array ma [7 : 10];
          ma [7]: = (if boolean in shift 4 then –1 else 1)×dh;
          ma [8]: = (if boolean in shift 4 then –1 else 1)×dt;
          ma [9]: = abs (dp); ma [10]: = dzeta;
          op to drum (param, 7, 10, ma);
      end;
    end;
end
          pipe box;
```

Mathematical model of box pipe: Knowing the elements of the specified stream vector and the data featured among the operating parameters (pipe length, inner diameter, wall thickness, pipe roughness, thermal conductivity of the pipe wall and the outside temperature) the pressure, temperature, enthalpy of the unknown stream, the heat loss, the temperature and pressure difference between the two ends of the pipe and the value of the friction factor have to be calculated.

The pressure of the unknown stream may be calculated from the known pressure by the following equation:

$$p := p \pm \Delta p. \tag{3.2}$$

The sign of the pressure drop is a function of which stream was known at the beginning of the calculation. The value of Δp is the following:

$$\Delta p = \frac{8\,\zeta\, l w^2 M}{\pi^2 d^5 \varrho}, \tag{3.3}$$

where the friction factor is the solution of equation:

$$\frac{1}{\zeta^{1/2}} = -\,2 \log \left(\frac{2.51}{\mathrm{Re}\; \zeta^{1/2}} + \frac{eps}{3.72\, d} \right). \tag{3.4}$$

The mean molecular mass in equation (3.3) is calculated by the standard procedure *mol*. The molal density *(ϱ)* of the mixture is calculated by the standard procedure *dens*. The viscosity, needed to find the Reynolds number in equation (3.4), is calculated by the standard procedure *visc*.

The temperature of the unknown stream is calculated from the temperature of the known stream by the equation:

$$\Delta t = (t_{\mathrm{out}} - t)\left[1 - \exp\left(\pm a \frac{d + 2d_{\mathrm{wall}} \pi l}{w C_{\mathrm{P}}}\right)\right], \tag{3.5}$$

where t is the temperature of the known stream, C_{F} is the molal heat capacity of the mixture, calculated with the standard SIMUL procedure *cp*. In the equation, a represents the overall heat transfer coefficient for the pipe wall and air:

$$\frac{1}{a} = \frac{1}{\alpha_{\mathrm{out}}} + \frac{d_{\mathrm{wall}}}{\lambda_{\mathrm{wall}}}. \tag{3.6}$$

The approximation formula for the outside heat-transfer coefficient

$$\alpha_{\mathrm{out}} = 4.88 - \frac{\lambda_{\mathrm{wall}}}{2\, d_{\mathrm{wall}}} + \left[\left(4.88 + \frac{\lambda_{\mathrm{wall}}}{2\, d_{\mathrm{wall}}}\right)^2 + 0.07(t - t_{\mathrm{out}}) \frac{\lambda_{\mathrm{wall}}}{d_{\mathrm{wall}}}\right]^{1/2} \tag{3.7}$$

takes the heat loss caused by radiation into consideration. The temperature of the unknown stream is therefore

$$t := t + \Delta t. \tag{3.8}$$

The enthalpy of the unknown stream is calculated as follows:

$$h := h + \Delta h, \tag{3.9}$$

where $\Delta h =$ the difference between the enthalpies of the known and calculated stream. The quantity, composition, calculated pressure and temperature of the calculated stream are known. The enthalpy is calculated by the standard procedure *enth*.

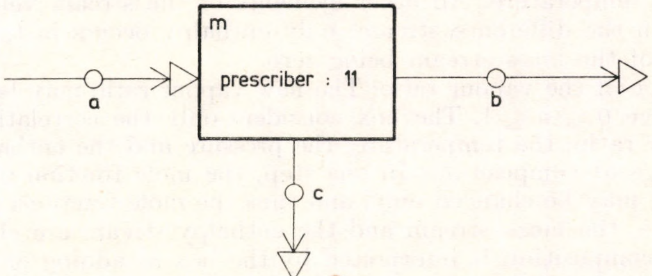
Now all elements of the stream vector are known:
the stream type has not changed *(type)*,
the mass flow is unchanged *(w)*,
the enthalpy has been calculated — equation (3.9) — *(h)*,
the temperature has been calculated — equation (3.8) — *(t)*,
the pressure has been calculated — equation (3.2) — *(p)*,
the vapour ratio remained unchanged *(v)*,
the composition remained unchanged *(z)*.

In the course of the calculation, the operating parameters to be computed have been found:
op7 heat intake or loss *(Δh)*,
op8 change of temperature *(Δt)*,
op9 pressure drop *(Δp)*,
op10 friction factor calculated according to equation (3.4)—*(ζ)*.

3.4.2 BOX CHANGING ELEMENTS OF STREAM VECTORS IN A PRESCRIBED WAY *(prescriber)*

Box *prescriber* changes one or more characteristics of a process stream in such a manner that when the prescribed changes have been executed, all other characteristics of the stream should correspond to the new state and be physically real.

The graphic symbol of the box:



Description of the operation:

prescriber: 11 (m, a, b, c)

Stream *a* has to be changed, stream *b* has been changed and stream *c* represents the difference between the new and old state, i.e., *c* is a stream vector, ensuring the fulfilment of the material (component) and enthalpy balances. Stream *c* is consequently not always a genuine technological stream.

In one step, the box changes one element of the stream vector to the prescribed value and can execute any number of steps after this, according to the number of operating parameters.

The box may have the following functions — according to the sequence of stream vector elements:

1. Change of the stream-type index (stream-type change): The change means that those components of the "old" stream, which are not included in the new stream, leave with the difference stream including their mass. Temperature, pressure and vapour ratio remain unchanged. The mass and enthalpy stream corresponds to the new conditions. Components of the new stream type, which did not figure in the old one have zero mole-fraction value.

2. Change of the mass stream: Among the elements of the stream vector, the values of the mass and enthalpy streams are changed. The value of the new enthalpy stream is determined by the unchanged pressure and temperature, and the prescribed value of the mass stream.

3. Change of the enthalpy stream (heat transmission, heat loss): The temperature of the new stream corresponds to the value of the prescribed enthalpy stream. All other elements of the stream vector are unchanged. The value of the new temperature is defined by the prescribed enthalpy stream and by the unchanged pressure and mass stream. In the difference stream c, only enthalpy occurs, the value of the mass stream being zero.

4. Change of temperature: The enthalpy of the new stream shall correspond to the prescribed temperature, all other elements of the stream vector remain unchanged. In the difference stream, only enthalpy occurs, the value of the mass stream being zero.

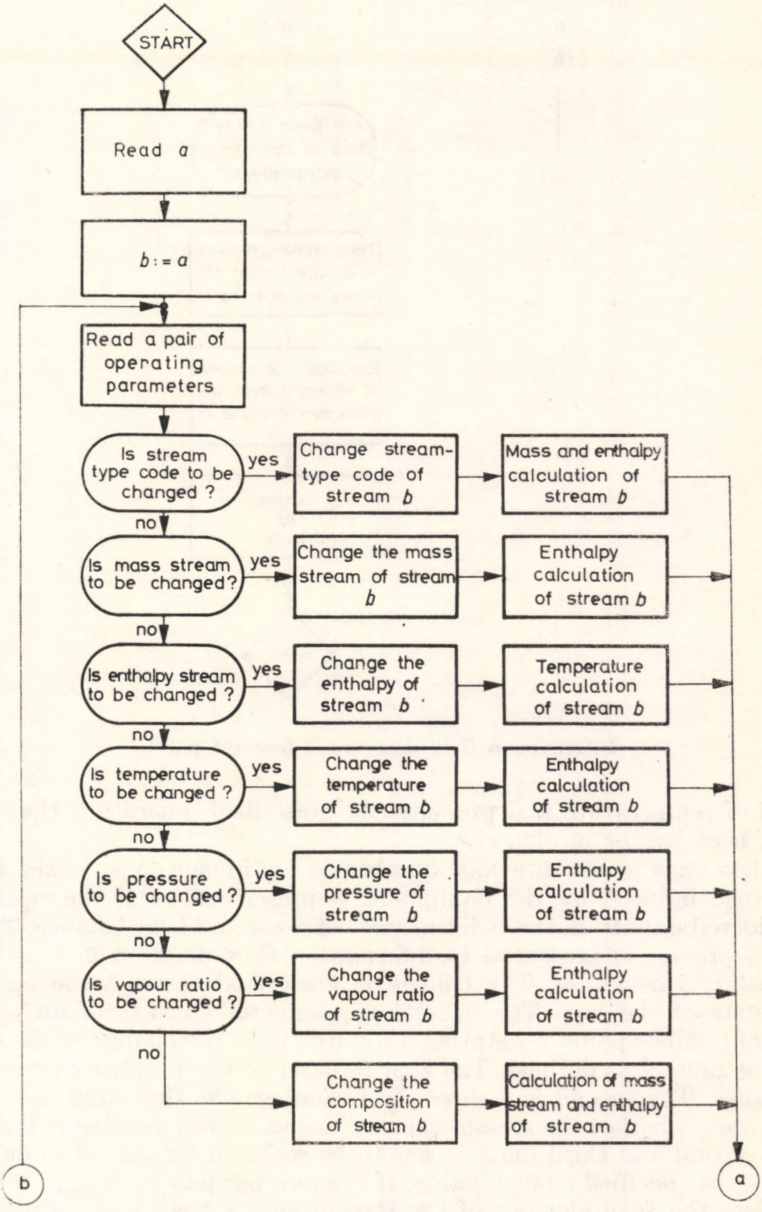
5. Change of pressure: The change of pressure is carried out isothermally, the value of the enthalpy stream changing with the pressure is therefore defined by the prescribed pressure, the unchanged mass stream and the unchanged temperature. All other elements of the stream vector are unchanged. In the difference stream, only enthalpy occurs in this case too, the value of the mass stream being zero.

6. Change of the vapour ratio: The new vapour ratio may be prescribed in the range $0 \leq v \leq 1$. The box considers only the correlation between the vapour ratio, the temperature, the pressure and the enthalpy stream.

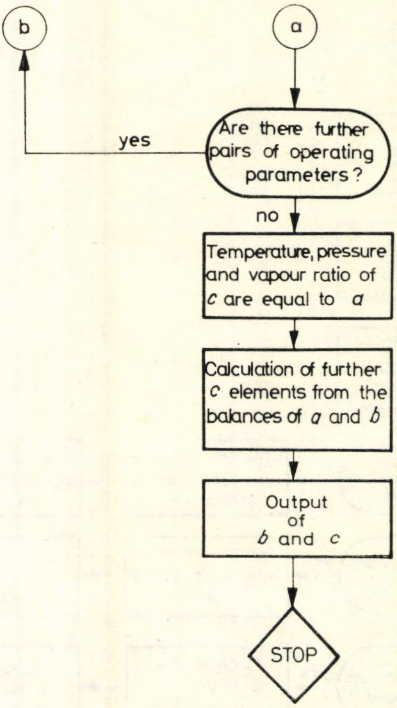
7. Change of composition: In one step, the mole fraction of one single component may be changed only, and thus the mole fractions of the other components, the mass stream and the enthalpy stream are changed. The change of composition is interpreted by the box as adding or subtracting the pure stream of the component to be modified to or from the process stream, provided that the prescribed mole-fraction value of that component is reached. The new value of the enthalpy stream is defined by the new composition and mass stream, and by the unchanged pressure and temperature.

The box *prescriber* norms before carrying out changes in the composition at points a to l.

Limits of application: The box *prescriber* is applicable in all cases where the material stream has to reach a prescribed end state. Examples are the



Information flow diagram 2 (first part)



Information flow diagram 2 (second part)

control of temperature and pressure, the prescribed separation, the simulation of heat loss or intake, etc.

The box may substitute any number of equipment-type boxes if only the change induced by the equipment is prescribed, or if the equipment is considered only from the point of view of mass and heat balance. The calculation process is presented in information flow diagram 2.

Operating parameters: The change is prescribed through the operating parameters of the box. The operating parameter consists of an optional length of number-pairs. By stating a number-pair, the change of the stream vector at point *b* is defined. The first number of the number-pair specifies the change. The second is a three digit number: the first digit is 0.1 or 2, determining whether the stream vector element — whose number is defined by the second and third digit — has to be replaced by, added to or multiplied by the specified change value. If the number-pair is, say, $(-0.8\times10^5$, $105)$, then the fifth element of the stream vector has to be decreased by 0.8×10^5 N/m^2.

The changes defined by the number-pairs are carried out in succession, progressing from left to right; each change takes the preceding changes into consideration.

The number of operating parameters is even.

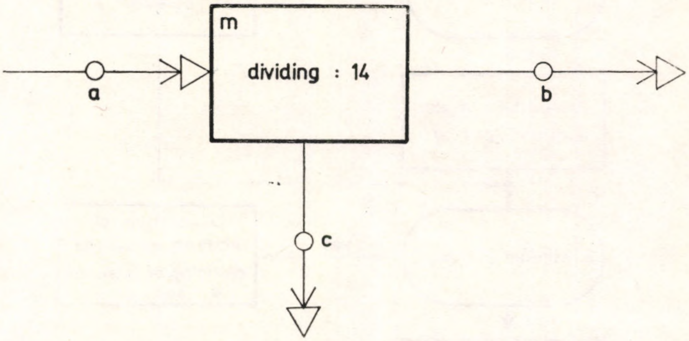
Check: The box carries out checks whilst functioning and prints error messages if

- the number of operating parameters is uneven,
- the input stream is not specified correctly,
- the change cannot be interpreted physically.

3.4.3 MODEL OF DIVIDING A HOMOGENEOUS STREAM *(dividing)*

Box *dividing* is suitable for simulating the division of a homogeneous process stream into two streams (e.g., pipe branching).

The graphic symbol of the box:



Description of the operation:

dividing: 14 (m, a, b, c).

The stream entering at a leaves at b and c. The quantity of substance leaving at b has to be specified among the operating parameters. The box calculates the mass and enthalpy streams; the pressure, temperature, vapour ratio and composition remain unchanged. The enthalpy stream leaving is proportional to the calculated mass streams.

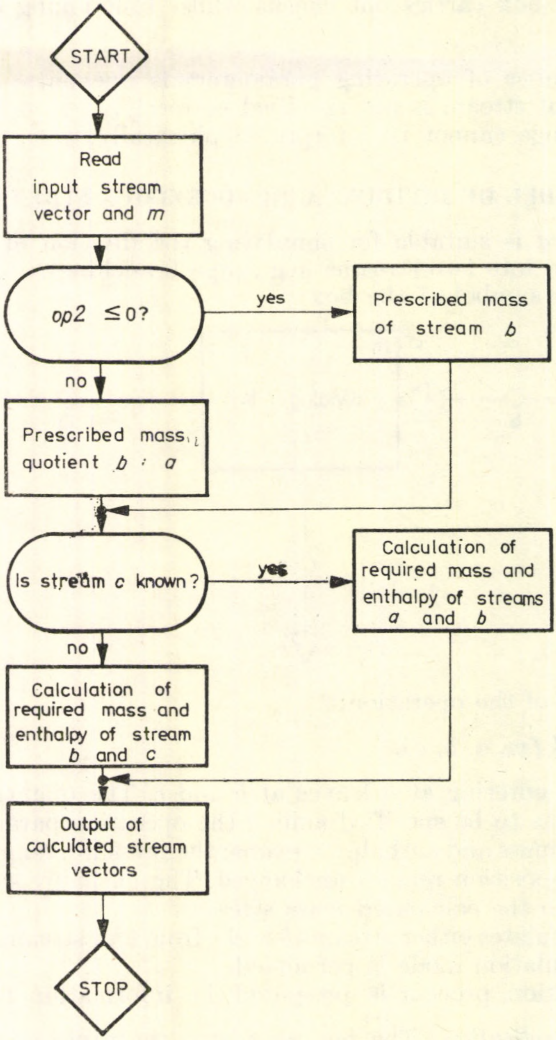
The box calculates either streams b and c from a or streams a and b from c. No other calculation mode is permitted.

The calculation process is presented in information flow diagram 3.

Limits of application: The box simulates the division of homogeneous streams. Its use as a mixer is not permitted. The prescribed stream b must not exceed input stream a.

Operating parameters:

Denomination	Number	Value, significance
op1	1	If $op2 \leq 0$, then *op1* defines the prescribed value of output stream b. If $op2 > 0$, then *op1* defines the quotient of output stream b and input stream a.
op2	1	Its value is the quotient of output stream b and input stream a.



Information flow diagram 3

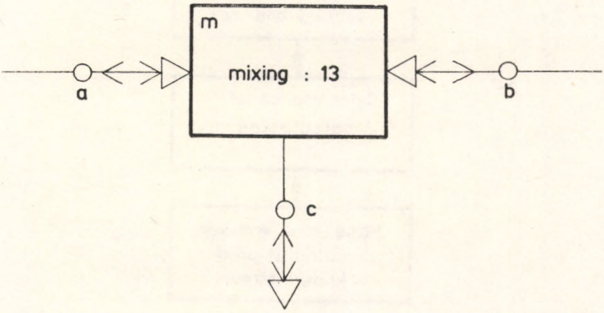
Number of the operating parameters: 2.

Check: The box prints an error message if the number of operating parameters, the mode (direction) of the calculation or the value of stream b does not correspond to the specification of the box

3.4.4 MODEL OF MIXING HOMOGENEOUS STREAMS *(mixing)*

Box *mixing* simulates the mixing without phase change of two homogeneous streams of the same pressure, state and stream type.

The graphic symbol of the box:



Description of the operation:

mixing: 13 (m, a, b, c).

From any two known stream vectors, the values of the third can be calculated. The values of the enthalpy streams — specified in the stream vectors — are not used by the box.
The calculation process is presented in information flow diagram 4.

Limits of application: The box may only be used to calculate mixing. If streams *a* and *c* are specified, then, for example, condition $w_a > w_c$ is inadmissible. The box cannot be used if the mixing of two homogeneous streams results in a multiphase stream.

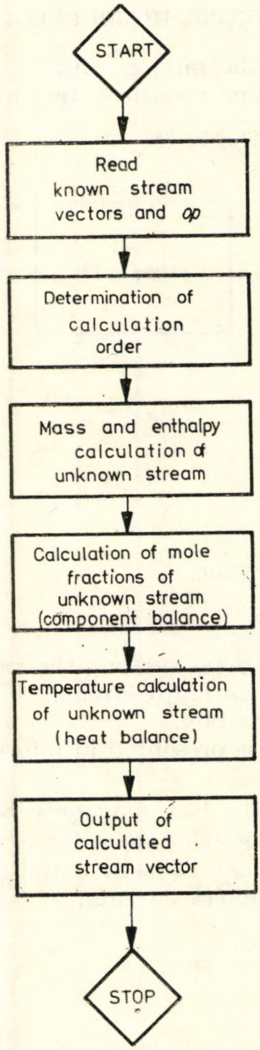
Operating parameters:

Denomination	Number	Value, significance
op1	1	The maximum allowed pressure difference of the specified two streams, N/m^2.

Number of the operating parameters: 1

Check: The box carries out checks during functioning and prints error messages, if

— the operation has been described invalidly,
— the elements of the input stream vector do not correspond to the box specification,
— the calculated mass stream is negative.

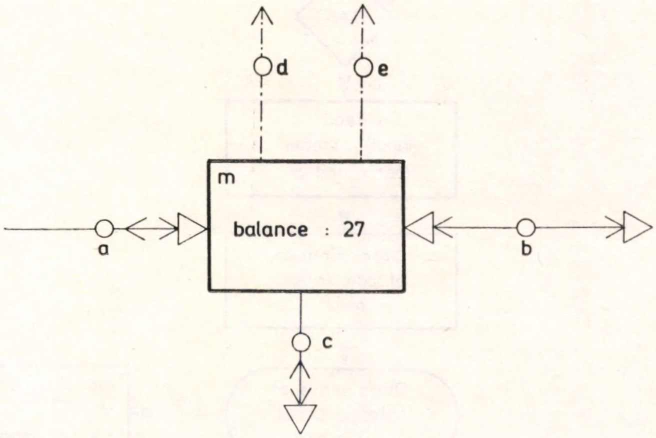


Information flow diagram 4

3.4.5 MIXING AND DIVISION MODEL OF STREAMS WITH ANY PHASES *(balance)*

Box *balance* is suitable — as a function of the actual value of the operating parameters — for simulating mixing and division of streams containing the same components. If it works as a mixer, it takes the phase change into consideration, if necessary.

The graphic symbol of the box:



Description of the operation:

balance: 27 (m, a, b, c, d, e).

If the box functions as a mixer, then the stream is directed at point *b* towards the equipment, otherwise it is in the opposite direction.

In both cases, the box calculates — knowing any two steams of *a*, *b* and *c*— the data of the unknown stream from the mass and enthalpy balances. The physical state of the known streams is immaterial. If the box functions as a mixer, then it calculates the data of the vapour and liquid phase of the leaving stream as vectors *d* and *e*.

The calculation process is presented in information flow diagram 5.

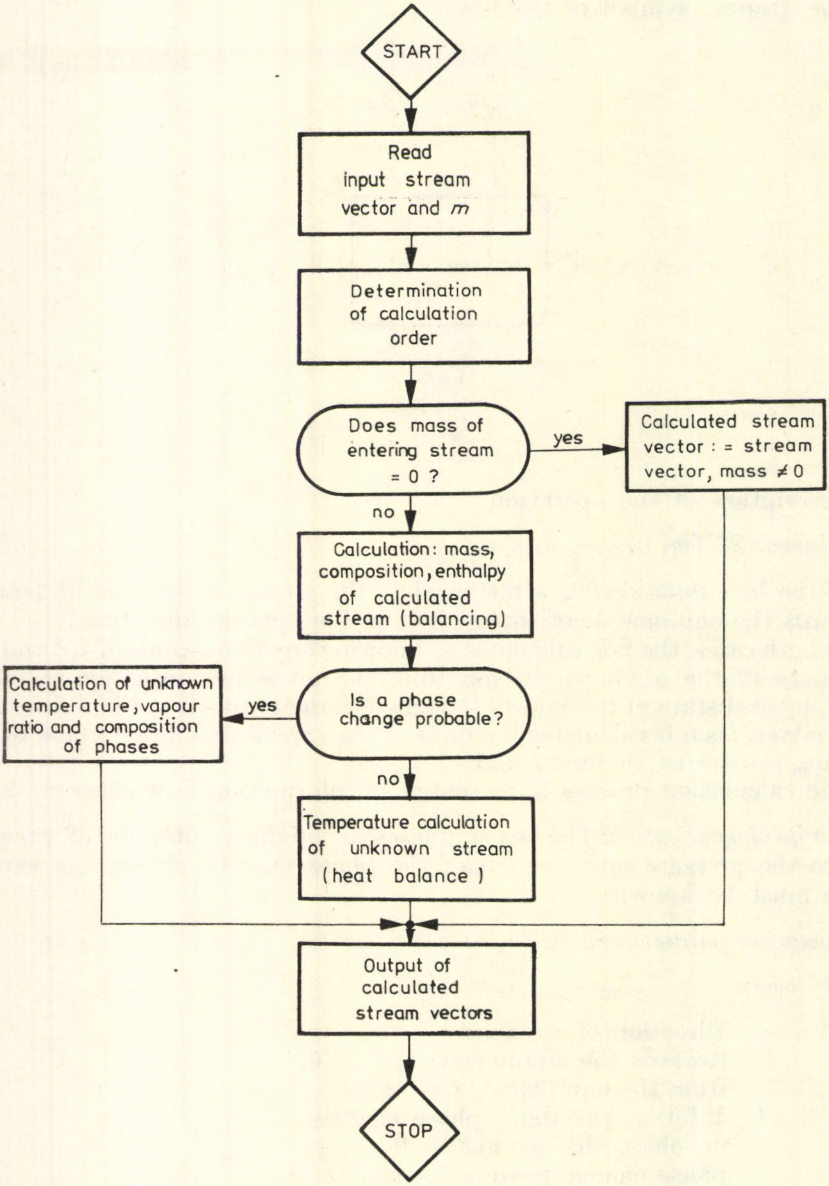
Limits of application: The box simulates the mixing or dividing of streams, where the pressure must be equal, the phase may be either, the vapour ratio must be known.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Direction of stream *b*: towards the equipment: $op1 = 0$, from the equipment: $op1 \neq 0$.
op2	1	Information about phase change: no phase change: $op2 = 0$ phase change possible: $op2 \neq 0$. If the stream type index is positive, then the convergence pressure must be stated as *op2*.

Number of the operating parameters: 2.

Check: The box checks the number and real values of the operating parameters.

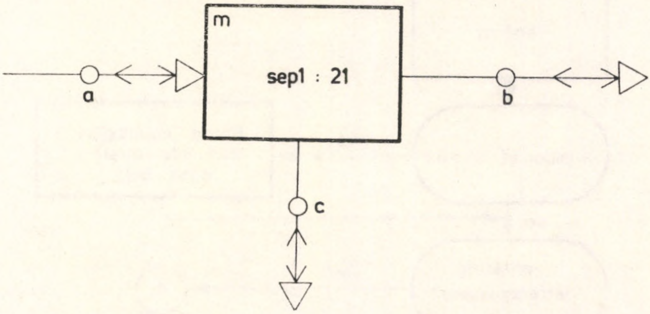


Information flow diagram 5

3.4.6 MODEL OF SEPARATION *(sep1)*

Box *sep1* is suitable for simulating the isothermal and isobaric separation of a multicomponent two-phase system.

The graphic symbol of the box:



Description of the operation:

sep1: 21(m, a, b, c).

With the knowledge of any one stream, the box calculates the data of the other two. If one of the leaving streams is assumed known, then – in order to solve the balance equations – the input mass stream must be defined.

When the model was developed, it was assumed that the geometry of the equipment would ensure perfect mechanical separation of vapour and liquid, so that the vapour and liquid phases leaving are in thermodynamic equilibrium.

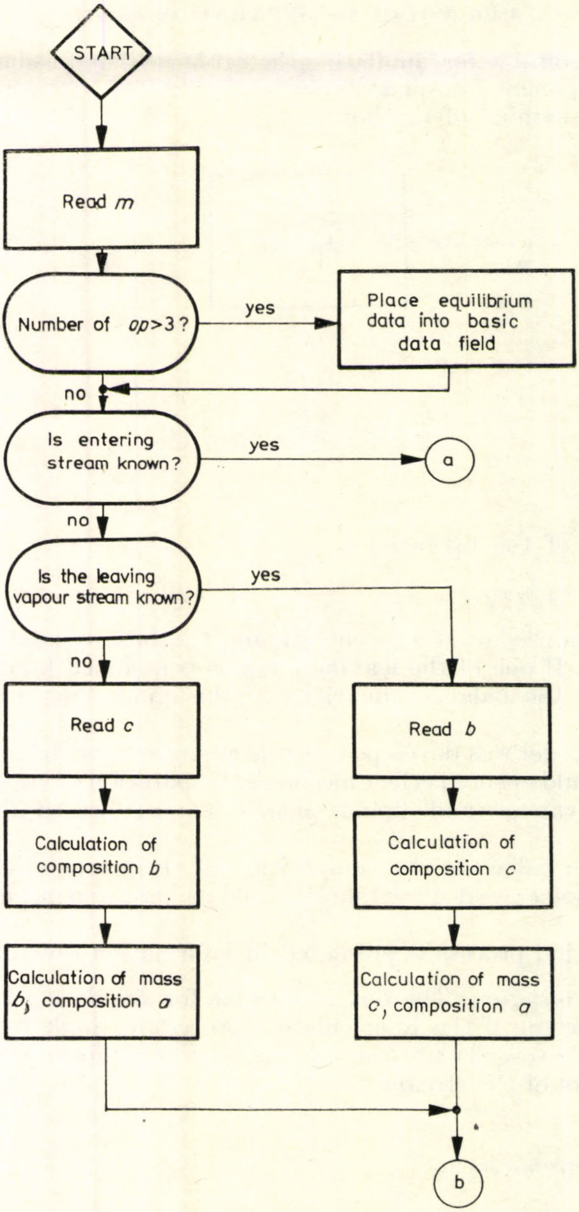
The box can calculate the composition of the streams where the mole fractions do not exceed 10^{-6} kmole/kmole as zero and norms the composition.

The calculation process is presented in information flow diagram 6.

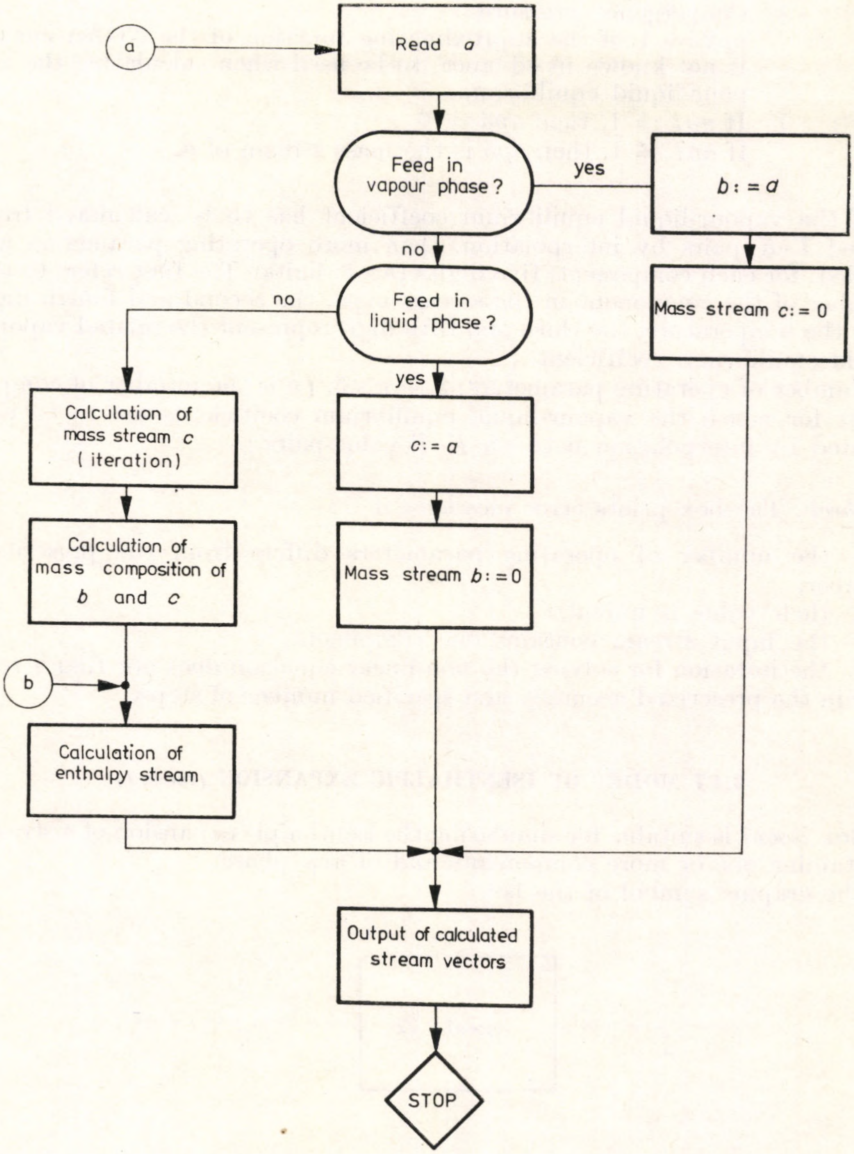
Limits of application: The box is suitable for simulating isothermal and isobaric separation, if the K calculation procedures built into the SIMUL system are able to calculate the vapour-liquid equilibrium coefficients for the components of the stream.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Information about the direction of the calculation: if *a* is known, then *op1* = 1 if *b* is known, then *op1* = 2 if *c* is known, then *op1* = 3



Information flow diagram 6 (first part)



Information flow diagram 6 (second part)

op2	1	Convergence pressure *op2* = 1, if the approximating function of the NGAA curves is not known in advance, to be used when calculating the vapour-liquid equilibrium.
op3	1	If *op1* = 1, then *op3* = 0 If *op1* $\neq$ 1, then *op3* is the mass stream of *a*.

If the vapour-liquid equilibrium coefficient has to be calculated from stated *T–K* pairs by interpolation, then more operating parameters are needed: for each component, five digits ($n \times 5$ digits). The first refers to the number of the component in the stream type, the second and fourth digit give the temperature, the third and fifth digit represent the related vapour-liquid equilibrium coefficient.

Number of operating parameters: $3 + n \times 5$. (n is the number of components for which the vapour-liquid equilibrium coefficients are to be calculated by interpolation between *K–T* value-pairs.)

Check: The box prints error messages if

— the number of operating parameters differs from the prescribed number,

— their value is unreal,

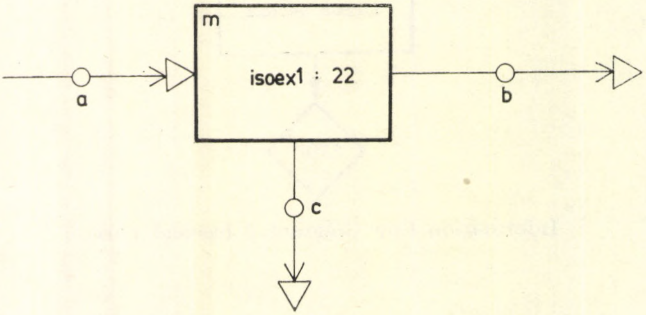
— the input stream contains one component,

— the iteration for solving the non-linear equation does not find a root within the prescribed accuracy and specified number of steps.

3.4.7 MODEL OF ISENTHALPIC EXPANSION *(isoex1)*

Box *isoex1* is suitable for simulating the isenthalpic expansion of a stream containing one or more components and of any phase.

The graphic symbol of the box:



Description of the operation:

isoex1: 22(m, a, b, c).

The mathematical model is based on the assumption that the change of state during expansion is isenthalpic.

If the stream is two-phased after expansion, then it is separated by the box, the vapour phase leaves at *b*, the liquid phase at *c*. The separation takes place according to thermodynamic equilibrium.

The box operates in two ways, depending on whether the pressure or the temperature of the leaving streams is prescribed among the operating parameters.

The calculation process is presented in information flow diagram 7.

Limits of application: The box may simulate the flow of a one- or multicomponent stream through a contraction, if the temperature and pressure of the input stream and their values after expansion are known. If the leaving stream consists of both vapour and liquid phases, then the box only functions if the vapour-liquid equilibrium coefficients of the components can be calculated with the *K*-procedures built into the SIMUL system.

Denomination	Number	Value, significance
op1	1	Information about the mode of calculation: *op1* = 1, if the output pressure is prescribed, *op1* = 2, if the output temperature is prescribed,
op2	1	If *op1* = 1, the output pressure, if *op1* = 2, the output temperature.
op3	1	Convergence pressure. In case of one component, *op3* = 1.

If the pressure of the output stream is prescribed, then the value of the vapour-liquid equilibrium coefficient may be calculated by linear interpolation between *T*–*K* value-pairs. In this case, more $(n \times 5)$ operating parameters are necessary (see, description of box *sep1)*.

Number of the operating parameters: $3 + n \times 5$.

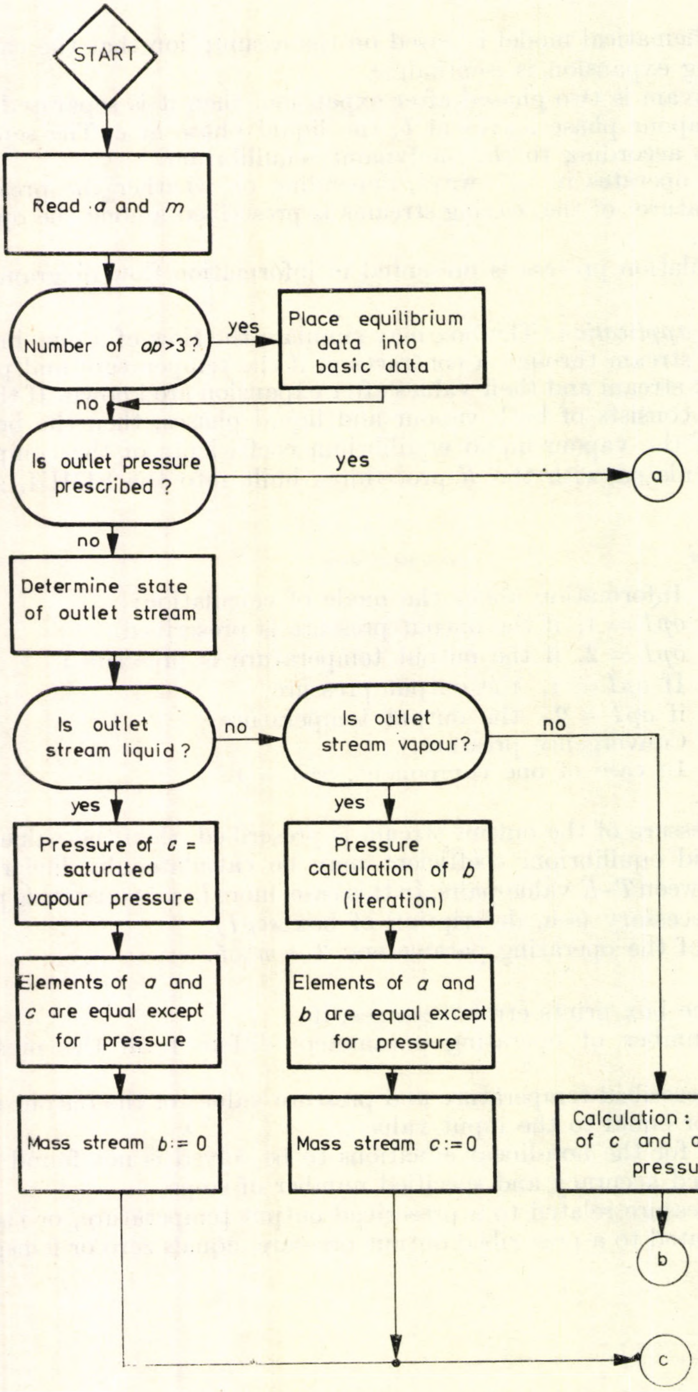
Check: The box prints error messages, if

— the number of operating parameters differs from the prescribed number;

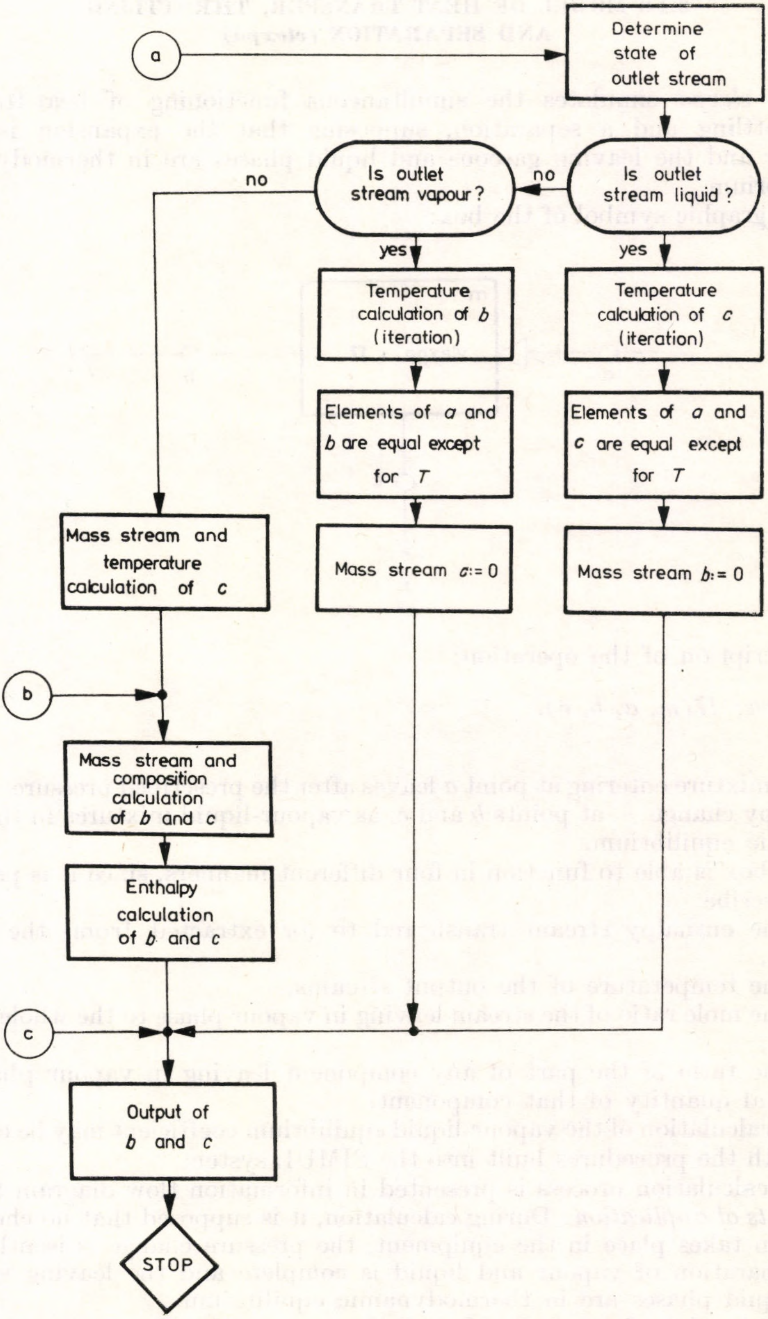
— the prescribed temperature and pressure values of the output stream are higher or equal to the input values,

— a root for the non-linear equations to be solved is not found within the prescribed accuracy and specified number of steps,

— the pressure related to a prescribed output temperature, or the temperature related to a prescribed output pressure, equals zero or is negative



Information flow diagram 7 (first part)

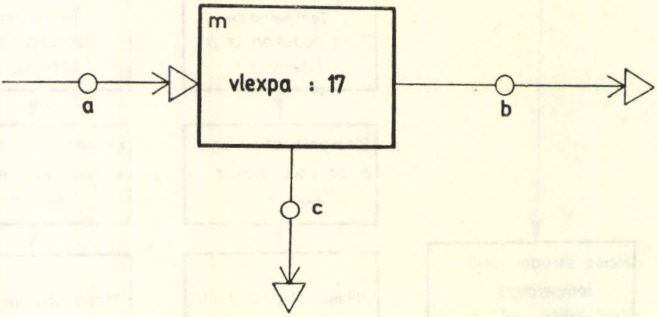


Information flow diagram 7 (second part)

3.4.8 MODEL OF HEAT TRANSFER, THROTTLING AND SEPARATION *(vlexpa)*

Box *vlexpa* simulates the simultaneous functioning of heat transfer, a throttling and a separation, supposing that the expansion is isenthalpic and the leaving gaseous and liquid phases are in thermodynamic equilibrium.

The graphic symbol of the box:



Description of the operation:

vlexpa: 17(m, a, b, c).

The mixture entering at point *a* leaves after the prescribed pressure – and enthalpy change – at points *b* and *c*, as vapour-liquid mixtures in thermodynamic equilibrium.

The box is able to function in four different manners, since it is possible to prescribe

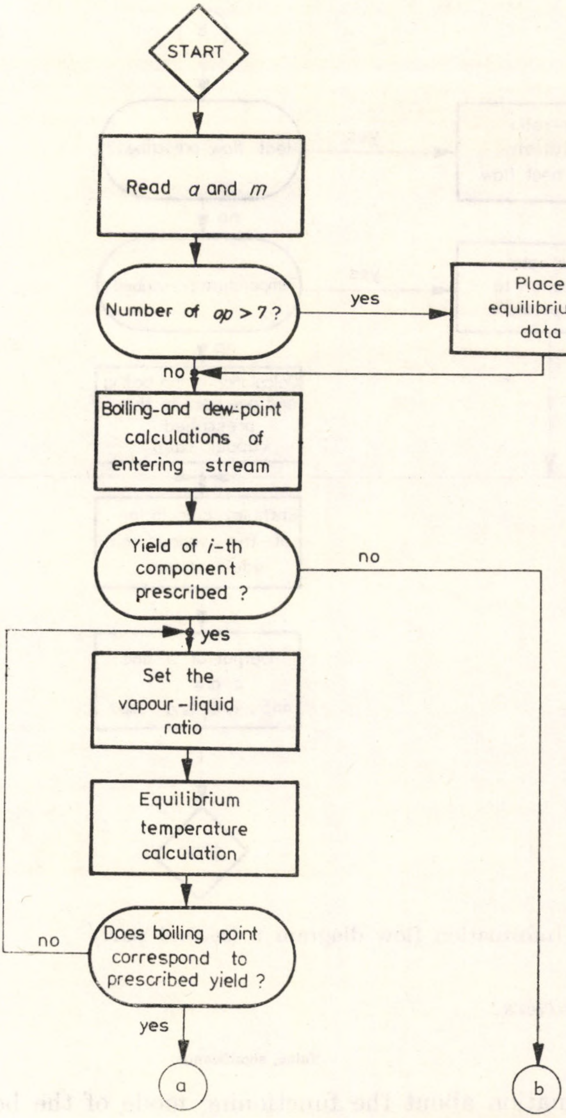
1. the enthalpy stream transferred to (or extracted from) the input stream,
2. the temperature of the output streams,
3. the mole ratio of the stream leaving in vapour phase to the whole input stream,
4. the ratio of the part of any component leaving in vapour phase to the total quantity of that component.

The calculation of the vapour-liquid equilibrium coefficient may be carried out with the procedures built into the SIMUL system.

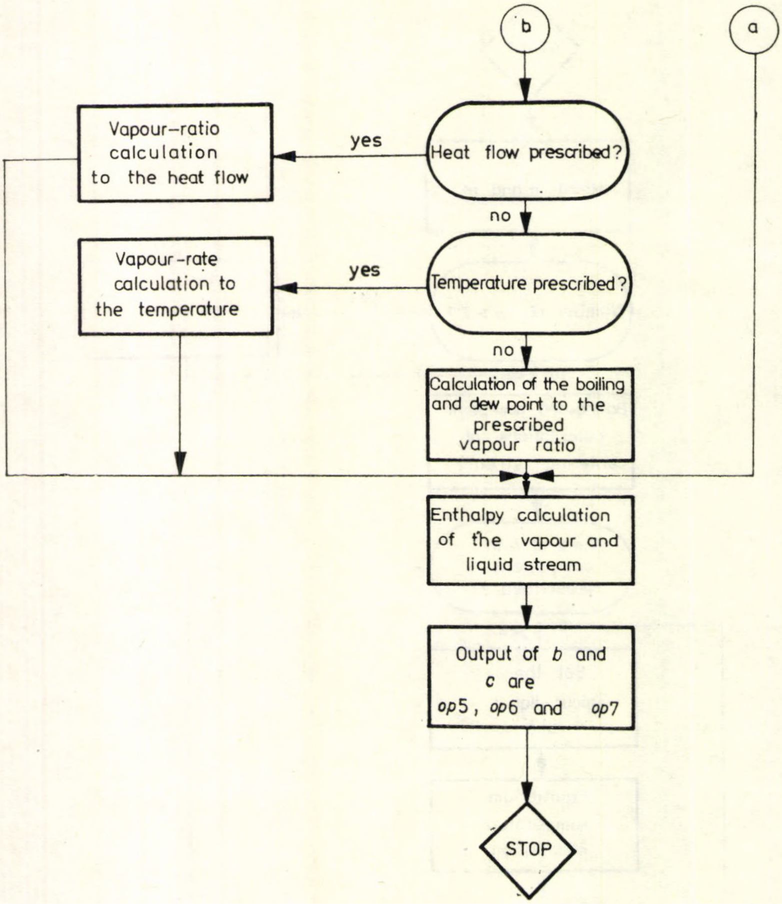
The calculation process is presented in information flow diagram 8.

Limits of application: During calculation, it is supposed that no chemical reaction takes place in the equipment, the pressure change is isenthalpic, the separation of vapour and liquid is complete and the leaving vapour and liquid phases are in thermodynamic equilibrium.

Because of the four possible functioning modes, box *vlexpa* may be widely used to simulate unit operations.



Information flow diagram 8 (first part)



Information flow diagram 8 (second part)

Operating parameters:

Denomination	Number	Value, significance
$op1$	1	Information about the functioning mode of the box: if heat-transfer is prescribed, then $op1 = 1$, if the output temperature is prescribed, then $op1 = 2$, if the output vapour ratio is prescribed, then $op1 = 3$, if the vapour ratio of the i-th component is prescribed, then $op1 = 10 \times i$.
$op2$	1	Prescribed value of the output stream: if $op1 = 1$, the transferred heat (in the case of heat loss it is negative), if $op1 = 2$, the output temperature,

		if $op1 = 3$, the quantity of the output stream in gaseous phase, related to the total input, if $op1 = 10 \times i$, then the ratio of the part of the i-th component, leaving in vapour phase related to the total input of that component.
op3	1	Convergence pressure of the input mixture (if the procedure calculating K does not need the value of the convergence pressure, then any positive number may be written here).
op4	1	Pressure of the output mixture.
op5	1	Estimated value of the dew point of the mixture at output pressure. In the output of the box, the calculated dew point appears here.
op6	1	Estimated value of the boiling point of the mixture at output pressure. In the output of the box the calculated boiling point appears here.
op7	1	The heat transferred to the equipment. The value is obtained during calculation.

The box uses the temperatures which are operating parameters 5 and 6 as initial values for the iterative calculation of the dew and boiling points.

If the vapour-liquid equilibrium has to be calculated by linear interpolation between measured values, then further operating parameters have to be stated. These number groups, consisting of five numbers, contain the number of the component and two number-pairs composed of the temperature and the related value of K (see, the description of box *sep1)*.

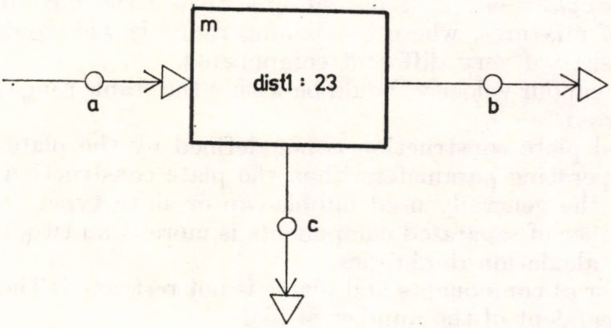
Number of the operating parameters: $7 + n \times 5$.

Check: The box checks the number of operating parameters, the sign of the connection indices and when specifying the vapour ratio, its value.

3.4.9 SIMPLIFIED MODEL OF A DISTILLATION UNIT *(dist1)*

Box *dist1* is suitable for simulating a plate column producing two products from one feed, and the simultaneous functioning of the attached condenser and reboiler.

The graphic symbol of the box:



Description of the operation:

distl: 23(m, a, b, c).

The box calculates — knowing the input stream *a* and the operating parameter vector *m* — the upper and lower product streams *b* and *c*, as well as the enthalpy streams necessary for the condensation and reboiling. The latter values will be entered among the operating parameters. The mathematical model has been developed, assuming the following simplifying conditions:

1. The relative volatility of the components may be calculated at average column temperature.
2. The molal mass flow between the plates is constant.
3. Only the key components are divided between the upper and lower products, the light components are to be found only in the upper product, the heavy components only in the lower product.
4. The feed place is optimal.
5. The correlation between the theoretical and real plates is characterized by the plate efficiency, calculated by an empirical formula.

In the model the correlations of Fenske (1932), Underwood (1948), Gilliland (1940) and O'Connell (1946) were used.

The box can operate with controlled reflux ratio, controlled top temperature or controlled condenser heat flow. The pressure drop is not calculated. The condensation and reboiling may be partial or total. In the case of partial condensation, the temperature of the reflux is the boiling point; in the case of total condensation, a different temperature may be prescribed.

If a measured value is known for the mean plate efficiency, then it may be specified; in the opposite case the box calculates it.

In calculating the composition of streams, the box substitutes zero if the value of the mole fraction does not exceed 10^{-6} kmole/kmole and norms this composition.

The box operates, if among the data of the input stream the enthalpy stream was incorrect. In this case the box corrects the input enthalpy stream after the calculations.

The calculation process is presented in information flow diagram 9.

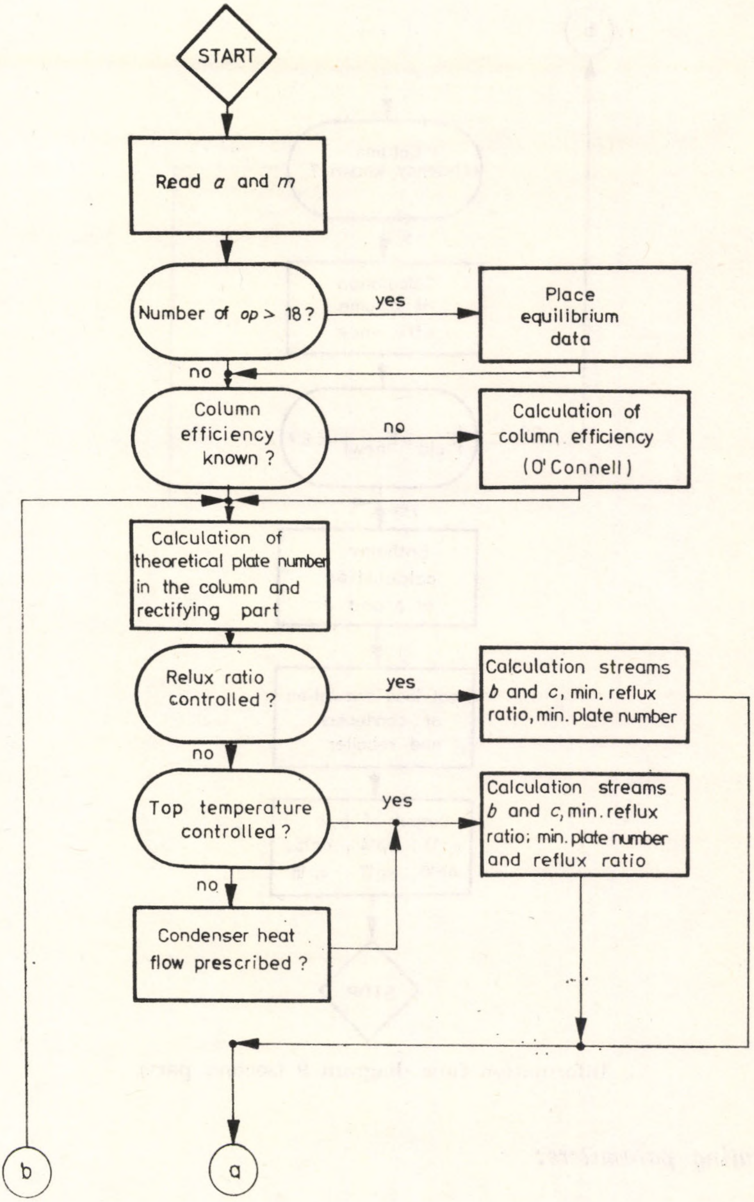
Limits of application: It is not suitable to use the box to simulate the separation of mixtures, where the boiling range is wide and/or where the mixture consists of very different components.

The linear vapour velocity should be within the stable range in the column to be simulated.

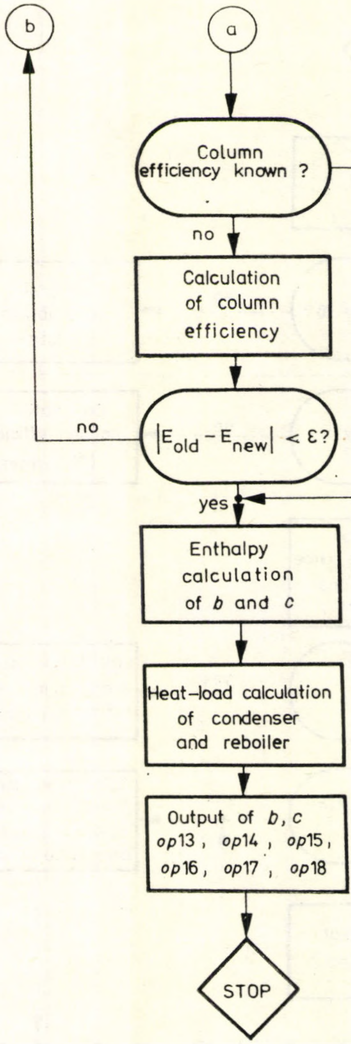
If a special plate construction is not defined by the plate efficiency, as one of the operating parameters, then the plate construction is considered to represent the generally used bubble-cap or sieve type.

If the number of separated components is more than two, then the accuracy of the calculation diminishes.

The number of components and plates is not restricted. The computation time is independent of the number of plates.



Information flow diagram 9 (first part)



Information flow diagram 9 (second part)

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of plates of the column.
op2	1	Feed entering place (number of the feed plate; counted from above, the condenser is the zeroth plate).
op3	1	Code of the light key components in the defined stream type.
op4	1	Code of the heavy key component.

op5	1	Average convergence pressure.If the calculation is not carried out by correlation of the NGAA curves to find the vapour-liquid equilibrium, then $op5 = 1$.
op6	1	Control mode of the column: $op6 = 1$, if the reflux ratio is prescribed, $op6 = 2$, if the top temperature, $op6 = 3$, if the condenser heat flow.
op7	1	Type of condensation: $op7 = 1$, if it is total, $op7 = 2$, if it is partial.
op8	1	Type of reboiling: $op8 = 1$, if it is partial, $op8 = 2$, if it is total.
op9	1	Prescribed value of the controlled parameter: if $op6 = 1$, then $op9 =$ the reflux ratio, if $op6 = 2$, then $op9 =$ the top temperature, if $op6 = 3$, then $op9 =$ the condenser heat flow.
op10	1	Reflux temperature: if $op7 = 1$, and the reflux is at boiling point, then $op10 = 0$; but in the case of reflux temperature below boiling point, then $op10 = T$; if $op7 = 2$, then $op10 = 0$, because the reflux temperature is necessarily at boiling point.
op11	1	if $op7 = 1$, then $op11 =$ the approximate value of the top temperature; if $op7 = 2$, then $op11 =$ the approximate value of the condenser temperature.
op12	1	if $op8 = 1$, then $op12 =$ the approximate value of the reboiler temperature; if $op8 = 2$, then $op12 =$ the approximate value of the bottom temperature.
op13	1	Approximate yield of the light key component in the top product (%). If known, then $0 < op13 < 100$. If unknown: $op13 = 0$. After calculation, the value of the yield of the light key component in the top product is *op13*.
op14	1	Approximate yield of the heavy key component in the bottom product (%). If known, then $0 < op14 < 100$. If unknown, the $op14 = 0$. After calculation, the value of the yield of the heavy key component in the bottom product is *op14*.
op15	1	Condenser heat flow: its value is obtained during calculation.
op16	1	Reboiler heat flow: its value is obtained during calculation.
op17	1	Reflux ratio. After calculation *op17* corresponds to the prescribed or calculated reflux ratio.

op18 1 Average column efficiency:
if known, then $0 < op18 \leq 1$,
if to be calculated, then: 0.
After calculation, *op18* corresponds to the prescribed or calculated column efficiency.

The vapour–liquid equilibrium coefficient may be calculated from the values figuring among the operating parameters. In this case further operating parameters are required as already discussed when describing box *sep1*.

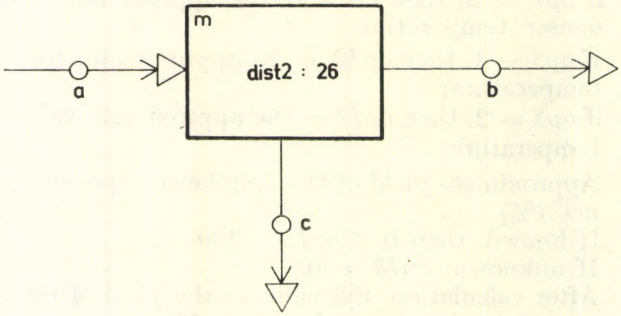
Number of operating parameters: $18 + n \times 5$.

Check: Before starting the calculation, the box checks the number of operating parameters and the reality of their value. During calculation, it prints error messages if the non-linear equations to be solved did not find a root within the prescribed accuracy and specified number of steps, and also if the calculated minimal reflux ratio had a higher value than prescribed.

3.4.10 MODEL OF A DISTILLATION UNIT CALCULATING FROM PLATE TO PLATE *(dist2)*

Box *dist2* simulates a plate column with one feed and two products, its top condenser, reboiler and feed heat exchanger. The calculation is carried out from plate to plate.

The graphic symbol of the box:



Description of the operation:

dist2: 26(m, a, b, c).

With known stream vector *a*, prescribed quantity of the distillate and geometric dimensions of the equipment, the box calculates the distillate stream *b* and the bottom stream *c;* the plate temperatures and the necessary enthalpy streams are calculated as operating parameters. (The inlet enthalpy streams are considered to be positive.)

The iterative calculation takes the mass and enthalpy balances from plate to plate into consideration. The plate temperatures are obtained from the composition of the vapour and liquid streams leaving the plates by calculating the boiling and dew points respectively.

The numbering of the plates begins with the condenser, the condenser is the zeroth plate, the plate number of the reboiler is $n + 1$.

The maximum number of iteration steps allowed is stated as an operating parameter. If the prescribed accuracy is not attained during this number, then the box presents the calculated stream vectors and operating parameters as if the calculation had been successful.

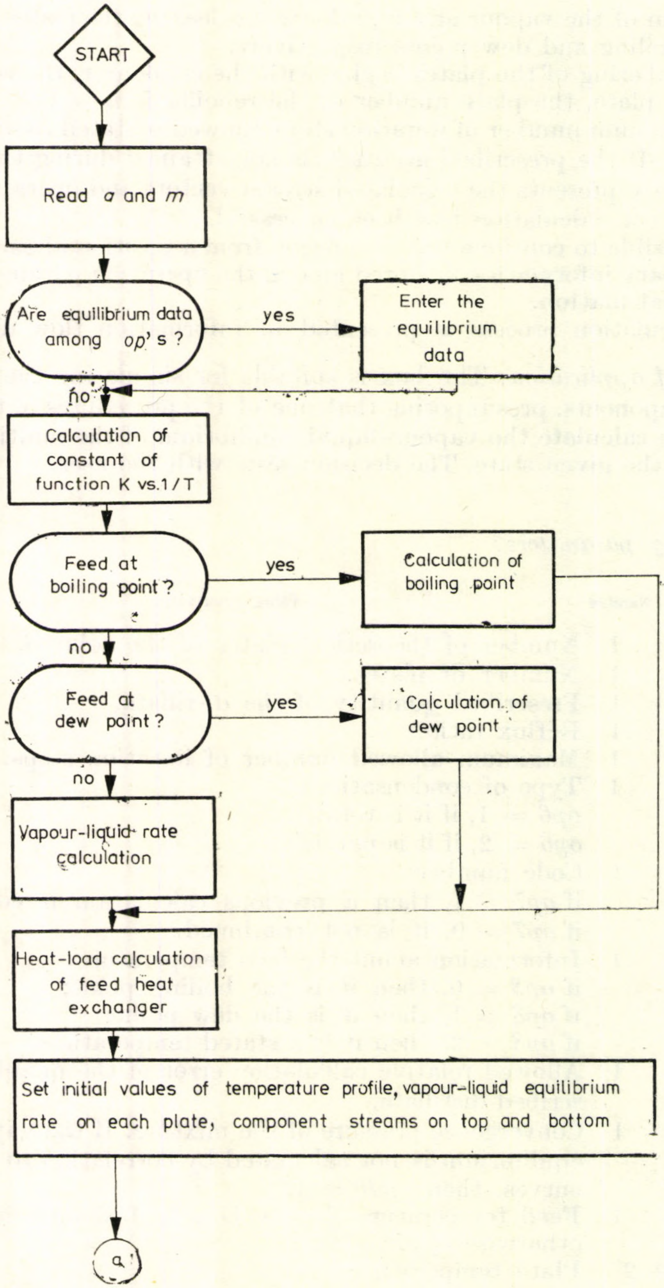
It is possible to continue the calculation from a position already reached. The necessary information is stored among the operating parameters of the previous calculation.

The calculation process is presented in information flow diagram 10.

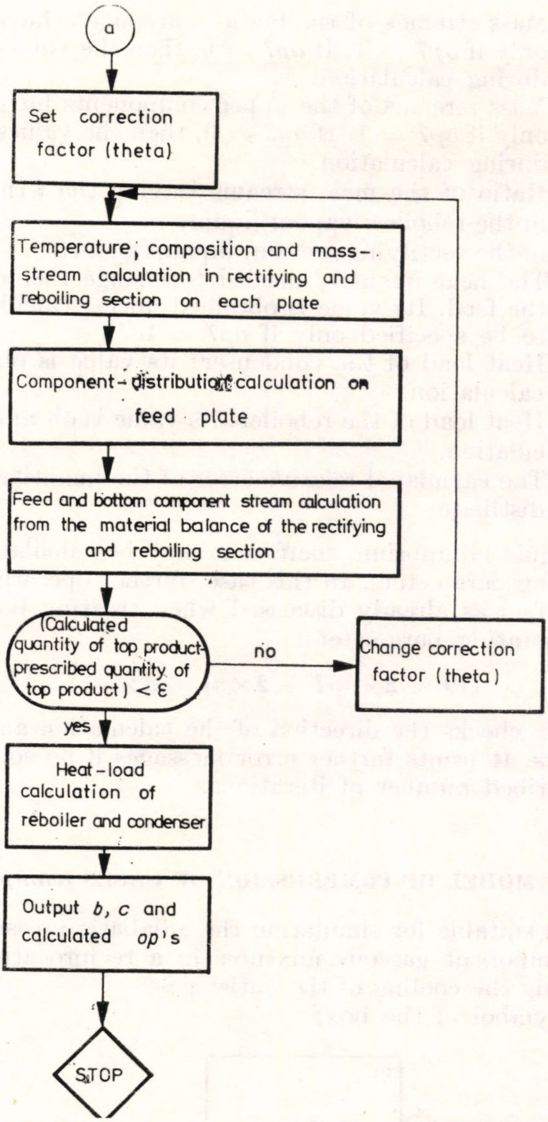
Limits of application: The box is suitable for simulating the separation of any components, presupposing that one of the procedures of the SIMUL system can calculate the vapour–liquid equilibrium of the multicomponent system in the given state. The decision rests with the user.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of theoretical plates of the column.
op2	1	Number of plates.
op3	1	Prescribed quantity of the distillate.
op4	1	Reflux ratio.
op5	1	Maximum allowed number of iteration steps.
op6	1	Type of condensation: *op6* = 1, if it is total, *op6* = 2, if it is partial.
op7	1	Code number: if *op7* = 1, then a previous calculation is continued; if *op7* = 0, it is not continued.
op8	1	Information about the feed temperature: if *op8* = 0, then it is the boiling point; if *op8* = 1, then it is the dew point; if *op8* = 2, then it is a stated temperature.
op9	1	Allowed relative calculation error of the quantity of prescribed distillate.
op10	1	Convergence pressure of the mixture. If the vapour–liquid equilibrium is not calculated by correlation to the NGAA curves, then *op10* = 1.
op11	1	Feed temperature (has to be specified only if *op8* = 2, otherwise *op11* = 0).
op12	*op1* + 2	Plate temperatures: if *op7* = 0, then only the values for index 0 and (*op1* +1) have to be stated; all other values are zero. After calculation the array contains the temperature values.



Information flow diagram 10 (first part)



Information flow diagram 10 (second part)

op13	*ncomp*	Mass streams of the lower components have to be stated only if $op7 = 1$. If $op7 = 0$, then the values are obtained during calculation.
op14	*ncomp*	Mass streams of the upper components have to be stated only if $op7 = 1$. If $op7 = 0$, then the values are obtained during calculation.
op15	*op1*+1	Ratio of the mass streams leaving the *i*-th plate: in the reboiler: vapour/liquid; in the rectifying section: liquid/vapour.
op16	1	The heat quantity needed to change the temperature of the feed. Its value is obtained during calculation and has to be specified only if $op7 = 1$.
op17	1	Heat load of the condenser: its value is obtained during calculation.
op18	1	Heat load of the reboiler: its value is obtained during calculation.
op19	1	The calculated relative error of the quantity of prescribed distillate.

The vapour–liquid equilibrium coefficient may be calculated from data, stated as operating parameters. In this case, further operating parameters have to be specified as already discussed when treating box *sep1*.

Number of operating parameters:

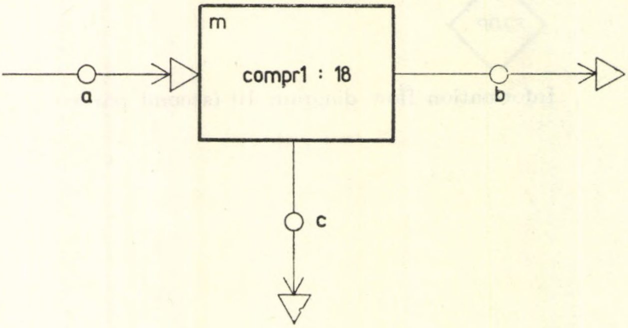
$$(19 + 2\times op1 + 2\times n) + n\times 5$$

Check: The box checks the direction of the calculation and the number of the parameters. It prints further error messages if no solution is found during the prescribed number of iterations.

3.4.11 MODEL OF COMPRESSION OF GASES *(compr1)*

Box *compr1* is suitable for simulating the adiabatic pressure increase of one- or multicomponent gaseous mixtures in a reciprocating compressor and for simulating the cooling of the outlet gas.

The graphic symbol of the box:



Description of the operation:

compr1: 18(m, a, b, c).

From the input data of the gas stream and the operating parameters, the box calculates the data of the output gas stream *b* and of the condensate stream, the electrical power needed and the work for cooling the gas. The output pressure of the gas stream has to be specified among the operating parameters.

The box is able to simulate a compressor without control, with intake control, with rotating speed control and with piston-clearance control, and thus verify the capacity.

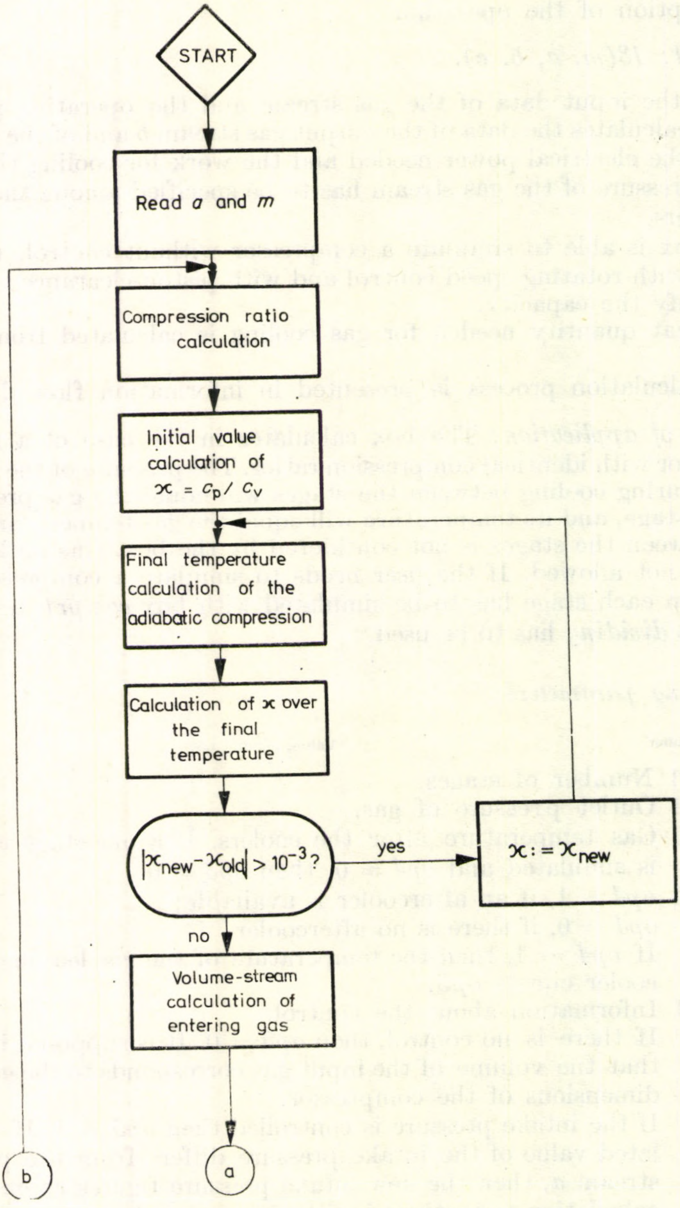
The heat quantity needed for gas cooling is calculated from the heat balance.

The calculation process is presented in information flow diagram 11.

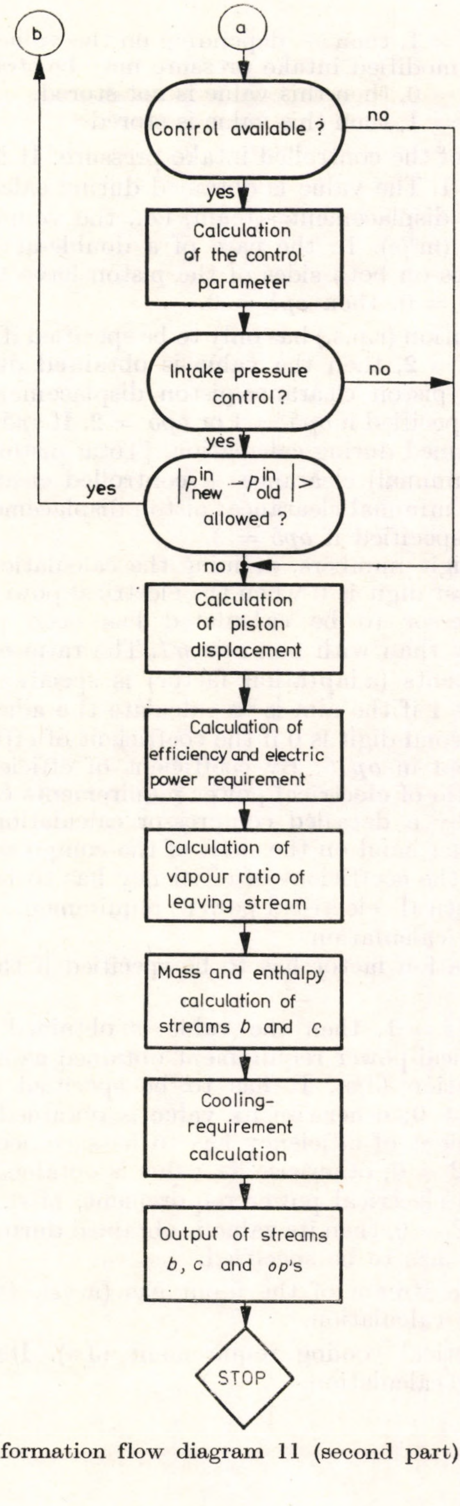
Limits of application: The box calculates in the case of a multi-stage compressor with identical compression ratios. The pressure of the condensate formed during cooling between the stages will equal the gas pressure after the first stage, and its temperature will equal the gas temperature. Pressure drop between the stages is not considered by the box. Gas outlet between stages is not allowed. If the user needs to simulate a compressor of that type, then each stage has to be simulated with box *compr1*, and between the boxes *dividing* has to be used.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of stages.
op2	1	Outlet pressure of gas.
op3	1	Gas temperature after the coolers. If a one-stage compressor is simulated and *op4* = 0, then *op3* = 0.
op4	1	*op4* = 1, if an aftercooler is available; *op4* = 0, if there is no aftercooler. If *op4* = 1, then the temperature of the gas leaving the aftercooler equals *op3*.
op5	1	Information about the control. If there is no control, then *op5* = 0. It is supposed in this case that the volume of the input gas corresponds to the geometrical dimensions of the compressor. If the intake pressure is controlled then *op5* = 1. If the calculated value of the intake pressure differs from the pressure of stream *a*, then the new intake pressure figures as *op7*, and the calculation is continued with this new value. If the rotating speed is controlled, then *op5* = **2**. The calculated rate (r.p.s.) is entered as *op9*. If the piston-clearance is controlled, then *op5* = **3**. The ratio of the piston-clearance volume to the piston-displacement volume is entered as *op10*.



Information flow diagram 11 (first part)



Information flow diagram 11 (second part)

op6	1	If $op5 = 1$, then — depending on the value of *op5* — the value of the modified intake pressure may be stored. If $op6 = 0$, then this value is not stored. If $op6 = 1$, then this value is stored.
op7	1	Value of the controlled intake pressure. It is interpreted only if $op5 = 1$. The value is obtained during calculation.
op8	1	Piston displacement stream, i.e., the volume displaced by the piston (m^3/s). In the case of a double-acting compressor, the volumes on both sides of the piston have to be added. If $op5 = 0$, then $op8 = 0$.
op9	1	Revolution (r.p.s.) has only to be specified if $op5 = 1$ or $op5 = 3$. If $op5 = 2$, then the value is obtained during calculation.
op10	1	Ratio: piston clearance/piston displacement (m^3/m^3) has only to be specified if $op5 = 1$ or $op5 = 2$. If $op5 = 3$, then the value is obtained during calculation. [Total piston clearance = cylinder (minimal) clearance + controlled clearance.]
op11	1	Ratio: minimal clearance: piston displacement (m^3/m^3) has only to be specified if $op5 = 3$.
op12	1	Two digit numbers, defining the calculation mode. The first digit is 0 when the electrical power requirement of the compressor to be calculated has been predetermined more exactly than with box *compr1*. The ratio of the two power requirements (adaptation factor) is specified in *op14*. The first digit is 1 if the aim is to calculate the adaptation factor. The second digit is 0 if the coefficient of efficiency is known and specified in *op16*. By coefficient of efficiency, we understand the ratio of electrical-power requirements calculated on the one hand by a detailed compressor calculation, and measured on the other hand on the shaft of the compressor. The second digit is 1 if the coefficient of efficiency has to be calculated.
op13	1	Theoretical electrical-power requirement. Obtains its value during calculation.
op14	1	Adaptation factor has to be specified if the first digit of *op12* is 1. If $op14 = 1$, then the value is obtained during calculation.
op15	1	Electrical-power requirement obtained as a result of a detailed calculation (J/s). It has to be specified if the first digit of $op12 \neq 0$; otherwise its value is obtained during calculation.
op16	1	Coefficient of efficiency has to be specified if the second digit of $op12 = 0$; otherwise its value is obtained during calculation.
op17	1	Actual electrical power requirement, (J/s). If the second digit of $op12 = 0$, then its value is obtained during calculation; otherwise it has to be specified.
op18	1	Volume stream of the input gas (m^3/s). Its value is obtained during calculation.
op19	1	Theoretical cooling requirement (J/s). Its value is obtained during calculation.

op20	1	Actual cooling requirement (J/s). Its value is obtained during calculation.
op21	1	Compression ratio for each stage. The value is obtained during calculation.
op22	2	Empty, and has to be specified as 0.

Number of operating parameters: 23.

Check: The box checks the number and value of the operating parameters. If the specified values are contradictory or physically non-real, then an error message is printed. The capacity of the compressor is insufficient and therefore an error message is printed, if

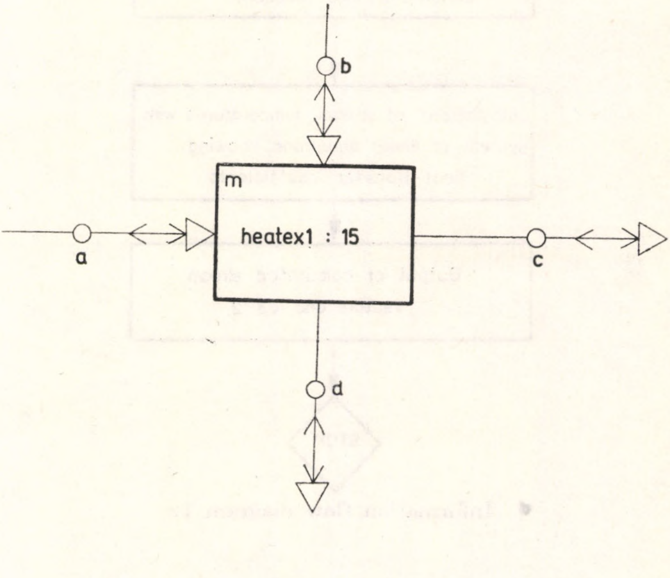
— in case of an intake pressure control, the calculated intake pressure has a higher value than that specified in the vector and the user specified that the calculation should not be restarted with the modified pressure,

— the calculated total clearance is smaller than the specified minimal clearance.

3.4.12 MODEL OF HEAT EXCHANGE WITHOUT PHASE CHANGE *(heatex1)*

Box *heatex1* is suitable for simulating a tubular heat exchanger in which no phase change occurs. The calculation of the heat exchanger is based on reference data.

The graphic symbol of the box:

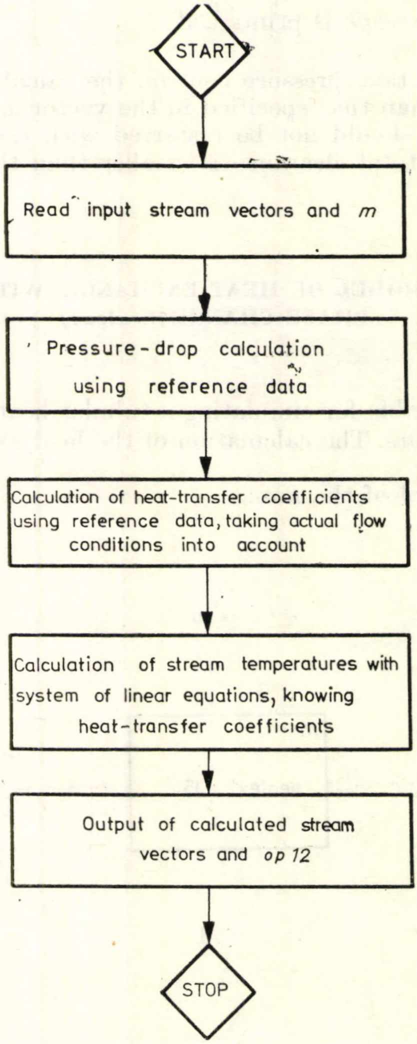


Description of the operation:
heatex1: 15(m, c, a, d, b).

To start the calculation, one stream vector on the tube side and one on the shell side must be known. The box calculates the data of both other streams. Streams on the shell side are designated with *a* and *c;* on the tube side with *b* and *d.*

The calculation process is presented in information flow diagram 12.

Limits of application: The box may be used primarily if measured heat-transfer coefficients are available. It may only be used for approximate calculations.



Information flow diagram 12

Operating parameters:

Denomination	Number	Value, significance
op1	1	Code defining the stream direction. If $op1 = 1$, the flow is parallel-current, if $op1 = 2$, the flow is counter-current, if $op2 > 1$, then *op1* contains no significant information.
op2	1	Number of passes.
op3	1	Heat-transferring surface.
op4	1	Reference mass stream on the shell side.
op5	1	Reference mass stream on the tube side.
op6	1	Reference heat-transfer coefficient on the shell side.
op7	1	Reference heat-transfer coefficient on the tube side.
op8	1	Reference pressure drop on the shell side.
op9	1	Reference pressure drop on the tube side.
op10	1	Thermal resistance of the tube wall (sm^2K/J).
op11	1	Scale resistance of the tube wall (sm^2K/J).
op12	1	Heat load. Its value is obtained during calculation.

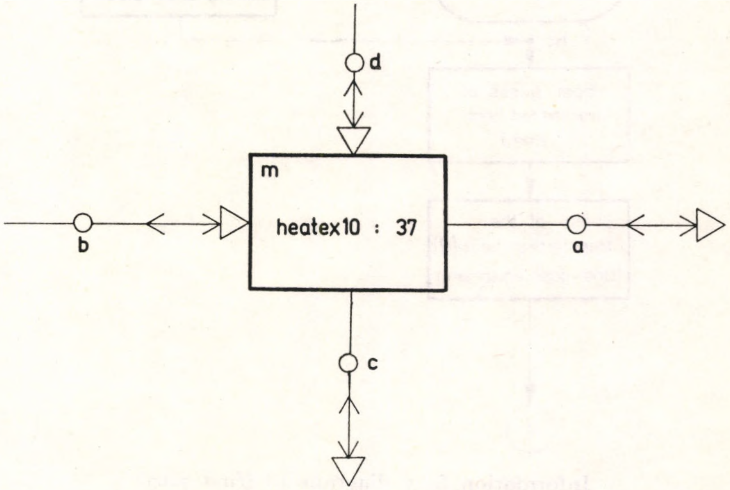
Number of operating parameters: 12.

Check: The box checks the number of operating parameters and the direction of the streams.

3.4.13 MODEL OF HEAT EXCHANGE WITH PHASE CHANGE *(heatex10)*

Box *heatex10* is suitable for simulating a parallel-current or counter current heat exchange, in which the phase of a pure component or a mixture changes on one side. In the case of a two-phase flow, it is supposed that the two phases are in thermodynamic equilibrium.

The graphic symbol of the box:

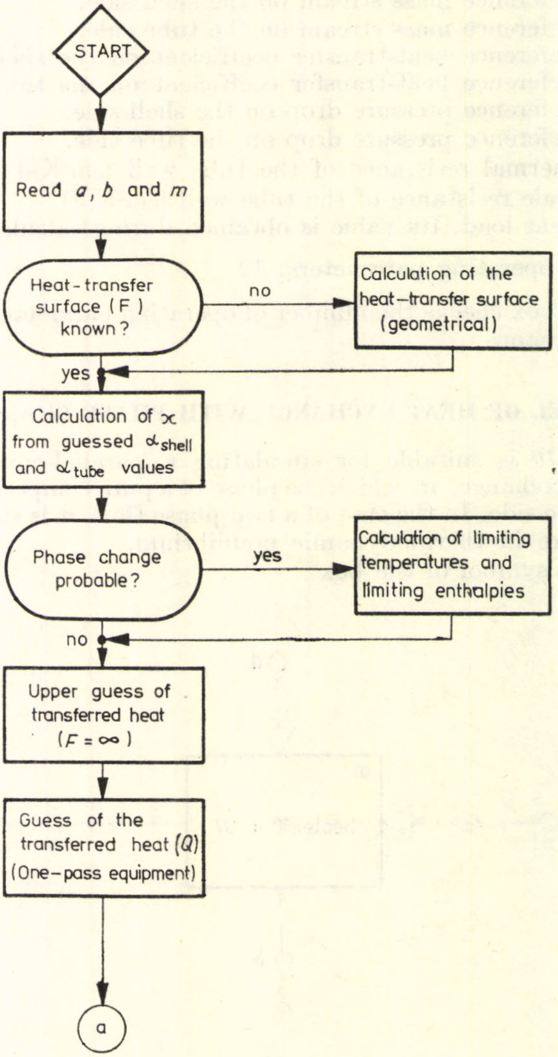


Description of the operation:

heatex10: 37 (m, a, b, c, d).

Vectors *a* and *b* designate mass flows on the shell side, *c* and *d* on the tube side. The box calculates from the data of the equipment all included into the operating parameters and from two stream vectors — one on the shell and one on the tube side — the data of the other two stream vectors.

When calculating the heat-transfer coefficients, different constructional alternatives may be taken into consideration.

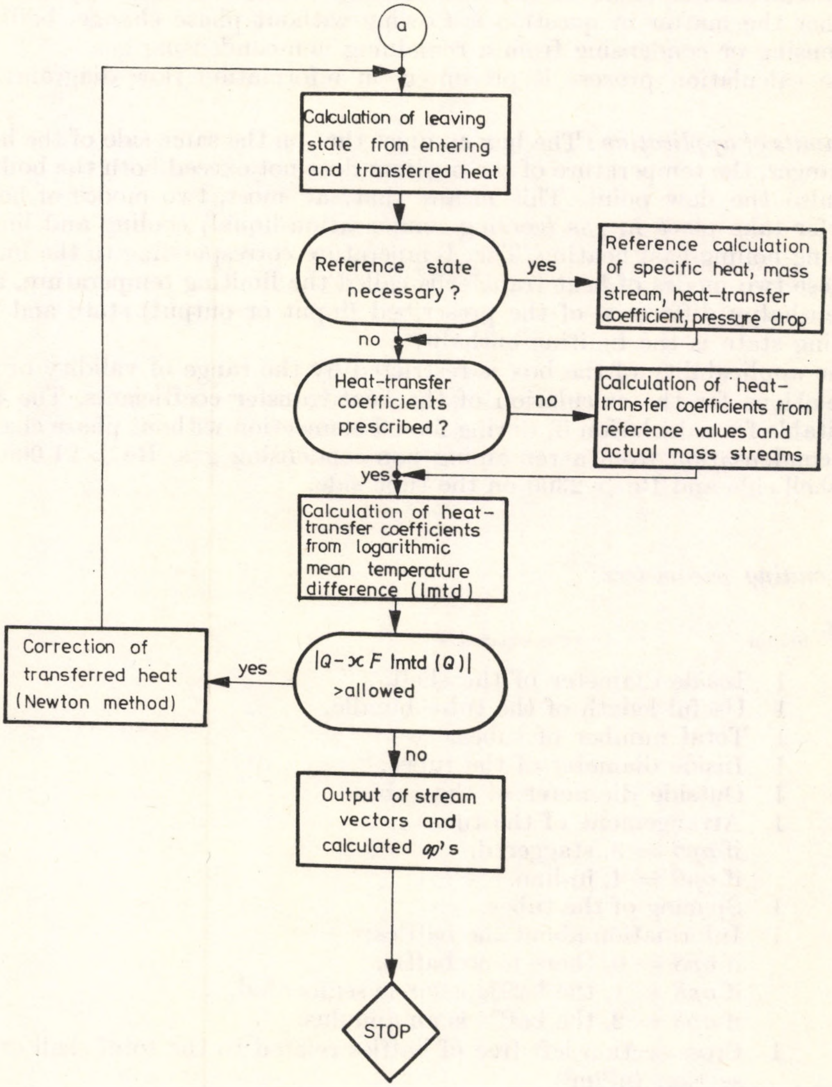


Information flow diagram 13 (first part)

On the shell side: without baffles; with vertical baffles (circle segment and annulus) and uniform baffle spacing. The tubes may be arranged in-line or staggered.

On the tube side: one or more passes, the number of tubes being equal in each pass.

For the case of more than two passes, the correction of the logarithmic mean temperature difference with respect to the number of passes is calculated as if the number were only two.



Information flow diagram 13 (second part)

The heat losses are not taken into consideration during calculation. The heat-transfer coefficient may be calculated in the three following ways:

1. iterative calculation starting from the enthalpy balance and the heat transfer equation,
2. calculation based on reference data, defined among the operating parameters,
3. calculation based on heat-transfer coefficients, defined among the operating parameters.

The calculation mode of the heat-transfer coefficient also depends on whether the matter in question is flowing without phase change, boiling, condensing or condensing from a remaining non-condensing gas.

The calculation process is presented in information flow diagram 13.

Limits of application: The box assumes that on the same side of the heat exchanger, the temperature of the medium does not exceed both the boiling and also the dew point. This means that, at most, two modes of heat-transfer take place in gas (cooling-condensation-liquid) cooling and liquid (heating-boiling-gas) heating. The temperature corresponding to the limits of these two modes of heat transfer is called the limiting temperature, and the enthalpy difference of the prescribed (input or output) state and the limiting state is the limiting enthalpy.

The applicability of the box is restricted by the range of validity of the correlations for the calculation of the heat-transfer coefficients. The box is suitable for calculation if, during forced connection without phase change and condensation from a remaining non-condensing gas, Re $>$ 21 000 on the shell side and Re $>$ 2300 on the tube side.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Inside diameter of the shell.
op2	1	Useful length of the tube bundle.
op3	1	Total number of tubes.
op4	1	Inside diameter of the tubes.
op5	1	Outside diameter of the tubes.
op6	1	Arrangement of the tubes: if *op6* = 3, staggered, if *op6* = 4, in-line.
op7	1	Spacing of the tubes.
op8	1	Information about the baffles: if *op8* = 0, there is no baffle, if *op8* = 1, the baffle is circle segmented, if *op8* = 2, the baffle is an annulus.
op9	1	Cross-section left free of baffles related to the total shell cross-section (m^2/m^2). If *op8* = 0, then *op9* = 1.

op10	1	Number of baffles.
op11	1	Number of tube rows perpendicular to the flow.
op12	1	Relative direction of the flows on the shell and tube sides. If *op12* $= 1$, it is counter-current flow, if *op12* $= -1$, it is parallel flow. If there are more than one passes, then the value of *op12* is immaterial.
op13	1	Number of passes on the tube side.
op14	1	Position of the equipment: if *op14* $= 0$, it is horizontal, if *op14* $= 1$, it is vertical.
op15	1	Thermal resistance of the tube wall and scale (m^2 K s/J).
op16	1	Heat transfer mode on the shell side. It is denoted by a two digit integer or a three digit decimal. First digit: 1, if there is forced convection without phase change, 2, if there is boiling, 3, if there is condensation, 4, if there is condensation from a remaining non-condensing gas. Second digit: 0, if the limiting temperature is the boiling point, 1, if the limiting temperature is the dew point, *.n*, if the limiting temperature relates to a vapour ratio between 0 and 1, where *.n* is the value of the vapour ratio ($0 < .n < 1$).
op17	1	Code of the heat-transfer mode on the tube side. It is specified as *op16*.
op18	1	Relative error of the calculation (relative error of the transferred heat in two consecutive calculations).
op19	2	Maximal number of reference data recalculations on the shell and tube side. If one element of *op19* is negative, then the estimated value of the heat-transfer coefficient – specified in *op31* and *op35* – is used without correction.
op20	1	Reference mass stream on the shell side.
op21	1	Reference heat transfer. Coefficient on the shell side.
op22	1	Reference pressure drop on the shell side.
op23	1	Reference mass stream on the tube side.
op24	1	Reference heat-transfer coefficient on the tube side.
op25	1	Reference pressure drop on the tube side.
op26	1	Reference mass of the condensing stream.
op27	1	Reference heat-transfer coefficient of the condensing stream.
op28	1	Specific heat of the calculated stream on the shell side.
op29	1	Change of the vapour ratio on the shell side.
op30	1	Pressure drop on the shell side.
op31	1	Heat-transfer coefficient on the shell side.
op32	1	Specific heat of the calculated stream on the tube side.
op33	1	Change of the vapour ratio on the tube side.

op34	1	Pressure drop on the tube side.
op35	1	Heat-transfer coefficient on the tube side.
op36	1	Area of heat-transfer surface of the heat exchanger.
op37	1	Logarithmic mean temperature difference.
op38	1	Overall heat-transfer coefficient.
op39	1	Exchanged heat stream.
op40	1	Limiting temperature on the shell side.
op41	1	Limiting enthalpy on the shell side.
op42	1	Limiting temperature on the tube side.
op43	1	Limiting enthalpy on the tube side.

Number of operating parameters: 44.

Of the first 14 operating parameters, *op12* and *op13* have to be specified in any case, and all others if the first digit or both of *op19* = 0 and the first digit of *op16* = 1 or 4.

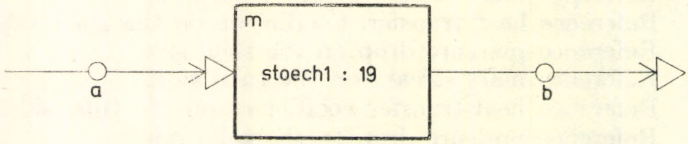
The values of *op20–op35* are calculated by the box: nevertheless, the approximate values of the specific heats and heat-transfer coefficients must be stated before calculation. If phase change occurs during heat exchange, then the box does not calculate the pressure drop, consequently the value of the parameter which stores the pressure drop, remains unchanged. *Op36* has to be specified if the first digit or both of *op19* = 0 and only *op12* and *op13* have been specified among the first 14 operating parameters. Parameters *op38–op43* obtain their value during calculation.

Check: The box checks the number of operating parameters, the reality of their values, and also whether the calculation of the heat-transfer coefficients is carried out within the range of validity of the correlations used.

3.4.14 MODEL OF CHEMICAL TRANSFORMATION *(stoech1)*

Box *stoech1* is suitable for simulating stoichiometrically possible chemical transformations in multicomponent mixtures.

The graphic symbol of the box:



Description of the operation:

stoech1 : 19 (m, a, b).

The input stream vector *a* and the output stream vector *b* are necessarily of the same stream type. The basis of the mathematical model is the application of the law of conservation of mass to chemical reactions. It is known that in a system containing *n* different chemical components,

$(n - r)$ independent chemical reactions may take place, where r represents the order of the atom-matrix (radical-matrix, compound-matrix). For all systems, the condition $n > r$ is valid. Therefore, besides the r mass conservation equations, further $(n - r)$ information data are necessary and sufficient to describe the system consisting of n components after reaction. This information may consist of $(n - r)$ component streams, mole fractions or conversions prescribed for stream b. Conversion is understood here as the relative level of transformation of a component, defined to be independent. The box considers the chemical transformations from both stoichiometric and the thermochemical point of view. Two modes of functioning are possible:

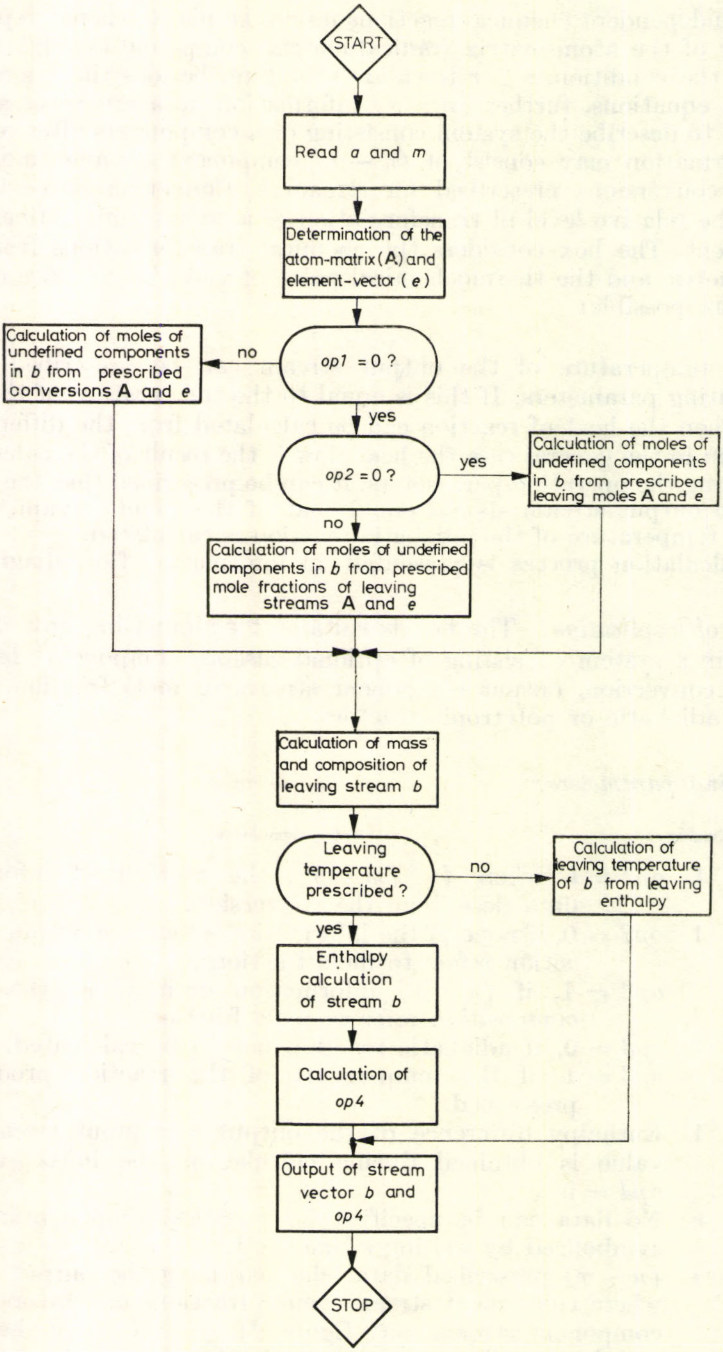
1. The temperature of the output stream can be prescribed among the operating parameters. If this is equal to the temperature of the input stream, then the heat of reaction can be calculated from the difference of enthalpies: in the general case the heat flow is the result of the calculation.
2. Among the operating parameters, it can be prescribed that the enthalpy of the output stream should equal that of the input stream. In this case, the temperature of the adiabatic reaction is calculated.

The calculation process is presented in information flow diagram 14.

Limits of application: The box is suitable for simulating any chemical reaction in a system consisting of optional gaseous components based on specified conversion, output component stream or mole fraction, in isothermal, adiabatic or polytropic reactors.

Operating parameters:

Denomination	Number	Value, significance
op1	1	$op1 = l$, where $l \leq (m - r)$, the number of information data describing the conversion.
op2	1	$op2 = 0$, if none of the information about the output composition refers to mole fractions, $op2 = 1$, if $(n - r)$ information data about the output composition refer to mole fractions.
op3	1	$op3 = 0$, if adiabatic reaction has to be calculated, $op3 = 1$, if the temperature of the reaction products is prescribed.
op4	1	Enthalpy difference of the output and input streams. Its value is obtained during calculation, the initial value is $op4 = 0$.
op5	r	No data can be specified for r outlet components: this is symbolized by writing r times -1.
op6	$n - r$	$(n - r)$ prescribed data, characterizing the output stream, where component streams, mole fractions or conversion and component stream may figure. If $op1 = 0$, then these data may be listed in any sequence, if $op1 \neq 0$, then the conversion



Information flow diagram 14

data have to appear in this information vector in the last l place.

op7 n Component codes in the sequence of the first element of vector *op5* to the last element of vector *op6*.

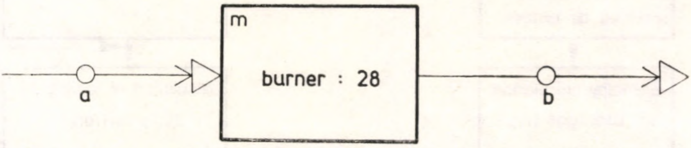
Number of operating parameters: $4 + 2\ n$.

Check: The box checks the number of operating parameters and writes an error message if the number is incorrect.

3.4.15 MODEL OF THE COMBUSTION PROCESS OF GASEOUS FUELS *(burner)*

Box *burner* is suitable for simulating the combustion process of a gaseous mixture consisting of not more than 14 components, with an oxygen-carrying gas of any $O_2 : N_2$ ratio.

The graphic symbol of the box:



Description of the operation:

burner: 28 (m, a, b).

The gas entering at *a* leaves at *b* as flue gas. The components of the flue gas are defined in each case, as total combustion is assumed.

The box calculates

— the air-excess factor, necessary to reach the ideal flame temperature

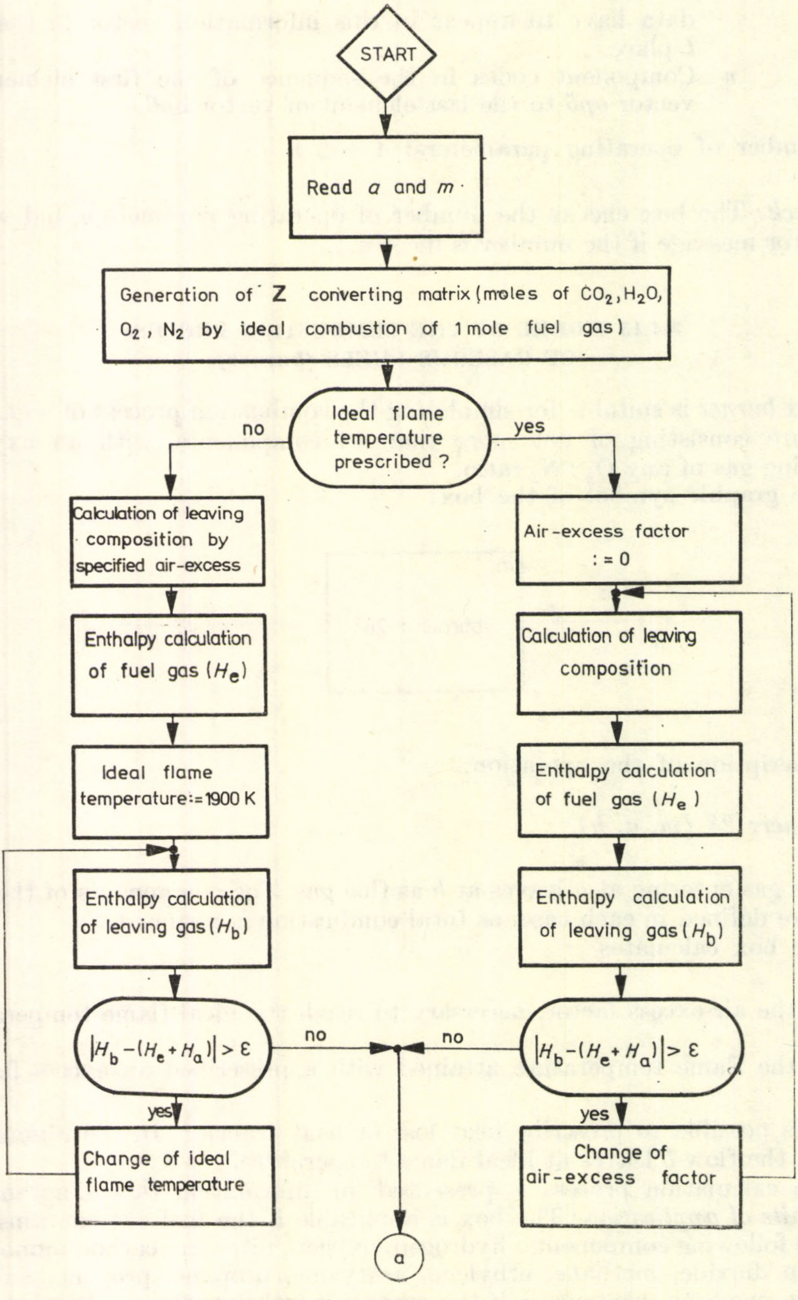
or

— the flame temperature attained with a prescribed air-excess factor.

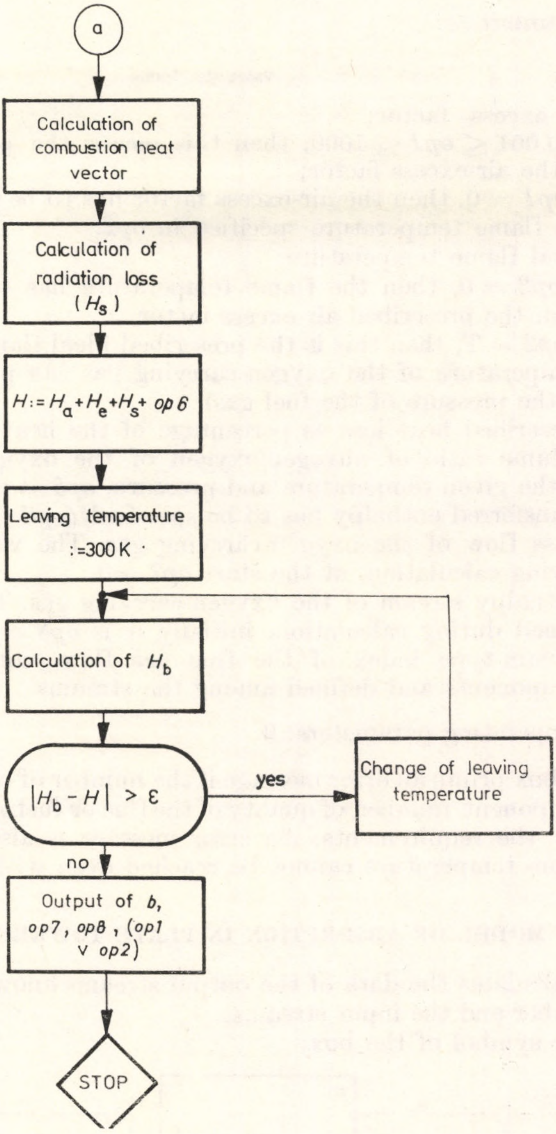
It is possible to prescribe heat loss or heat transfer. In the absence of these, the flow *b* leaves at ideal flame temperature.

The calculation process is presented in information flow diagram 15.

Limits of application: The box is applicable if the fuel gas contains any of the following components: hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethylene, acetylene, propane, propene, butane, butene, pentane, pentene — if the process is isobaric, the combustion may be modelled as total combustion — and the flue gas contains only the following components: carbon dioxide, water, nitrogen, oxygen.



Information flow diagram 15 (first part)



Information flow diagram 15 (second part)

Operating parameters:

Denomination	Number	Value, significance
op1	1	Air-excess factor: if $0.001 \leq op1 \leq 1000$, then this means the prescribed value of the air-excess factor; if $op1 = 0$, then the air-excess factor has to be calculated from the flame temperature specified in *op2*.
op2	1	Ideal flame temperature: if $op2 = 0$, then the flame temperature has to be calculated from the prescribed air-excess factor, if $op2 = \mathrm{T}$, then this is the prescribed ideal flame temperature.
op3	1	Temperature of the oxygen-carrying gas (its pressure is equal to the pressure of the fuel gas).
op4	1	Prescribed heat loss as percentage of the heat of combustion.
op5	1	Volume ratio of nitrogen/oxygen of the oxygen-carrying gas at the given temperature and pressure, $op5 \neq 0$.
op6	1	Transferred enthalpy has to be specified $(op6 \leq 0)$.
op7	1	Mass flow of the oxygen-carrying gas. The value is obtained during calculation, at the start $op7 = 0$.
op8	1	Enthalpy stream of the oxygen-carrying gas. The value is obtained during calculation, initially it is $op8 = 0$.
op9	1	Stream-type index of the flue gas flow, consisting of four components and defined among the streams.

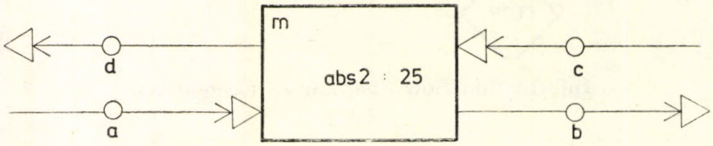
Number of operating parameters: 9.

Check: The box prints an error message if the number of operating parameters, the component number of quality of the flue or fuel gas stream vector does not meet the requirements. An error message is also printed if the prescribed flame temperature cannot be reached even without air excess.

3.4.16 MODEL OF ABSORPTION IN PLATE TOWERS *(abs2)*

Box *abs2* calculates the data of the output streams knowing the theoretical plate number and the input streams.

The graphic symbol of the box:



Description of the operation:

abs2 : 25 (m, a, c, b, d).

The mathematical model calculates according to the algorithm introduced by Owens and Maddox (1968), and includes the following simplifications:

— the column is divided with respect to the calculation into three parts: the uppermost plate, the middle part and the bottom plate. These are considered as calculation units;

— the mass and enthalpy balances are fulfilled in all calculation units;

— the temperature dependence of the equilibrium coefficients used to calculate the composition is determined by an equation of the following type:

$$K_i = \exp\,(C_{1,i} + C_{2,i}/T);$$

— 80 % of the mass transfer takes place on both extreme plates, all other plates are calculated with the average absorption coefficient;

— the temperature dependence of the enthalpy of the components is considered as linear in the column;

— the least volatile component of the liquid does not pass into the gas on the uppermost plate;

— a temperature equalization occurs on the top and bottom plates;

— the temperature of the gas reaching the uppermost plate may be calculated as if the temperature distribution in the column were uniform.

The value of the equilibrium coefficient is calculated by the standard procedure *prek*.

The linear enthalpy function is calculated by linear interpolation between two enthalpy values, which have been computed by the standard procedure *enth* and which belong to temperatures near the working temperature of the column.

If, apart from the heat of condensation, another type of heat source is available, then this has to be specified among the operating parameters by the user. In this case, the heat of absorption is equal to the sum of the specified heat transmission and the heat of condensation.

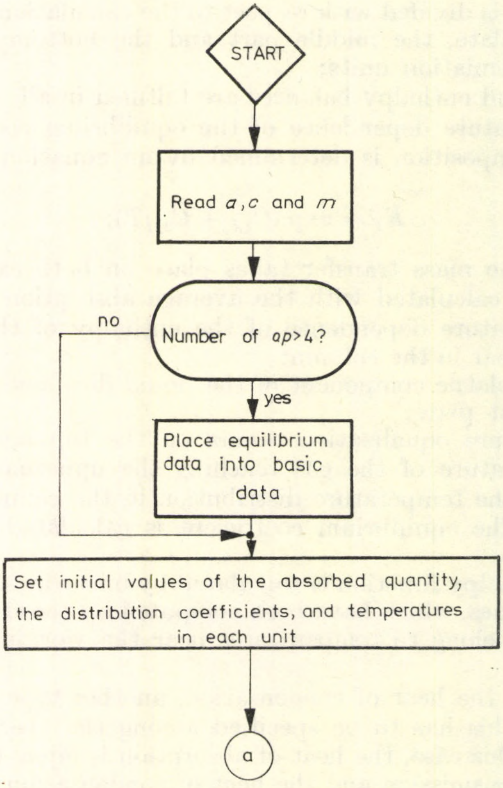
For practical computing reasons, the least volatile component has to figure in the last place when defining the stream type.

The calculation process is presented in information flow diagram 16.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of theoretical plates.
op2	1	Allowed maximum error of the calculation (%). The error relates at the same time to the temperature, mass quantity and enthalpy.
op3	1	Convergence pressure of the mixture.
op4	*n*	*op4* = 0, if there is no major heat effect besides the heat of condensation, otherwise *op4* has to be specified as the heat transmission, which is to be added to the heat of condensation to arrive to the heat of absorption.

The equilibrium coefficient can be calculated from the values specified among the operating parameters. In this case, further operating parameters are needed, as outlined in the description of box *sep1*.



Information flow diagram 16 (first part)

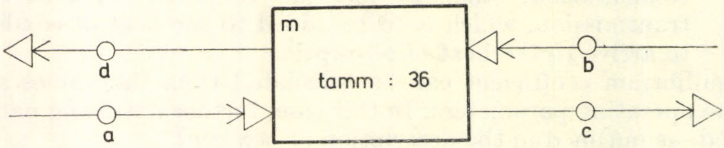
Number of operating parameters: $4 + n \times 6$.

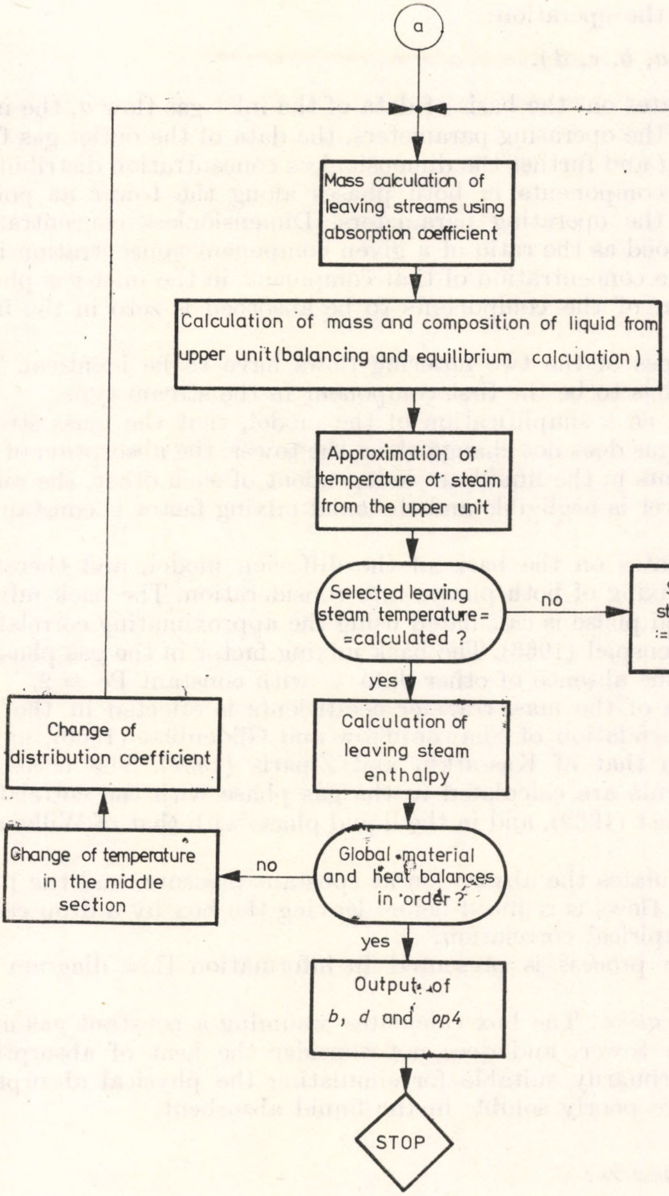
Check: The box checks the direction of the streams, the reality of the values of the input stream elements and the number of operating parameters.

3.4.17 MODEL OF A PACKED ABSORBER *(tamm)*

Box *tamm* is suitable for simulating the multicomponent, isothermal, isobaric, counter-current physical absorption in a packed tower, if the absorbent consists of one component.

The graphic symbol of the box:





Information flow diagram 16 (second part)

Description of the operation:

tamm : 36 (m, a, b, c, d).

The box calculates on the basis of data of the inlet gas flow *a*, the inlet liquid flow *b* and the operating parameters, the data of the outlet gas flow *c* and liquid flow *d* and further the dimensionless concentration distribution of the absorbed components in both phases along the tower at points specified among the operating parameters. Dimensionless concentration has to be understood as the ratio of a given component concentration in a given phase to the concentration of that component in the inlet gas phase. The concentration of the components to be absorbed is zero in the inlet liquid phase.

The stream types of the two entering flows have to be identical. The liquid absorbent has to be the first component in the stream type.

It is supposed, as a simplification of the model, that the mass stream of the liquid and gas does not change along the tower, the absorption of the gaseous components in the liquid are independent of each other, the radial mixing in the tower is negligible and the axial mixing factor is constant in the tower.

The box calculates on the basis of the diffusion model, and therefore takes the back mixing of both phases into consideration. The back mixing factor in the liquid phase is calculated using the approximating correlation of Sater and Levenspiel (1966). The back mixing factor in the gas phase is calculated — in the absence of other data — with constant Pe = 2.

The calculation of the mass-transfer coefficients is effected in the gas phase with the correlation of Shaworonkow and Gildenblat (1960), in the liquid phase with that of Kassatkin and Ziparis (1952). The necessary diffusion coefficients are calculated in the gas phase with the correlation of Chen and Othmer (1962), and in the liquid phase with that of Wilke and Chang (1955).

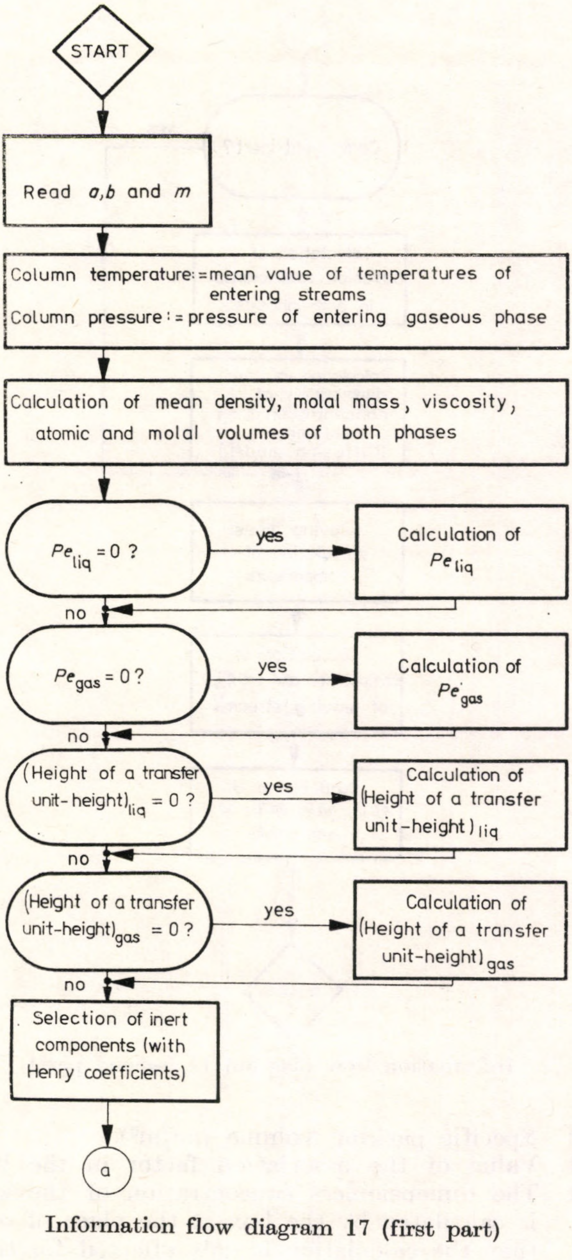
The model calculates the absorption at constant pressure, and the pressure of the outlet flows is reduced before leaving the box by a drop calculated with an empirical correlation.

The calculation process is presented in information flow diagram 17.

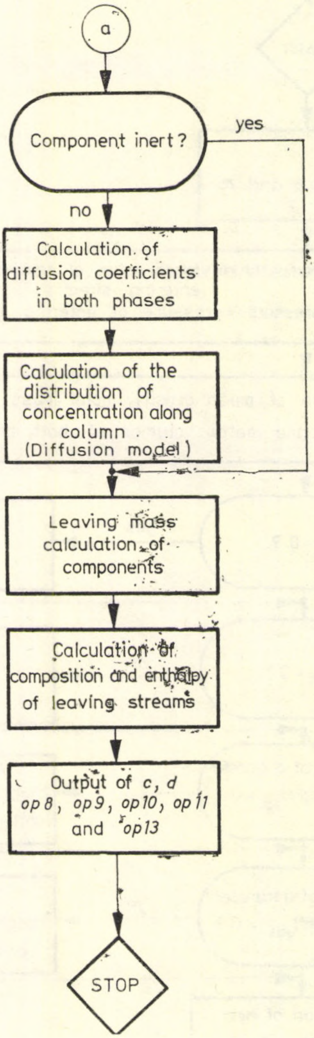
Limits of application: The box calculates assuming a constant gas-mass stream along the tower, and does not consider the heat of absorption. It is therefore primarily suitable for simulating the physical absorption of gases which are poorly soluble in the liquid absorbent.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Height of the packed section.
op2	1	Diameter of the packed section.
op3	1	Equivalent diameter of the packing.
op4	1	Specific packing surface (m^2/m^3).



Information flow diagram 17 (first part)



Information flow diagram 17 (second part)

op5	1	Specific packing volume (m^3/m^3).
op6	1	Value of the association factor in the Wilke equation.
op7	1	The dimensionless concentration of the key components is calculated by the box at the place of *op7*. If $op7 = 1$, then the calculation is only effected for the outlet point.
op8	1	Height of the gas-phase mass-transfer unit. Obtains its value during calculation, the initial value is $op8 = 0$. If it is possible to specify this value before calculation, then $op8 \neq 0$.

op9	1	Height of the liquid-phase mass-transfer unit. Obtains its value during calculation, but it is possible to specify it in advance.
op10	1	Péclet number of the liquid phase. Obtains its value during calculation, but it is possible to specify it in advance.
op11	1	Péclet number of the gaseous phase. If *op11* = 0, then the box calculates with Pe = 2.
op12	n	Henry coefficients (N/m^2). (For non-absorbed components $op12_i = 0$.) The Henry coefficients have to be specified at the pressure of the tower.
op13	$2 \times n \times (op7 + 1)$	Dimensionless concentration values of the absorbed components in both phases, at the points specified by parameter *op7* and at the inlet point. Obtain their value during calculation, at the start they are zero. The non-absorbed components obtain no value during calculation.

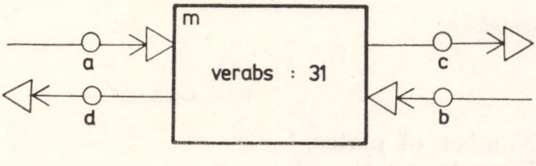
Number of operating parameters: $11 + n \times (2 \times op7 + 3)$.

Check: The box checks the number and value of the operating parameters. If physically non-real data are found, then an error message is printed.

3.4.18 MODEL OF ABSORPTION AND CHEMICAL REACTION IN A PLATE TOWER *(verabs)*

Box *verabs* is suitable for simulating the physical and/or the instant first-order chemical reaction accompanying the absorption of a multicomponent mixture in a plate tower.

The graphic symbol of the box:



Description of the operation:

verabs : 31 (m, a, b, c, d).

The box calculates on the basis of data of the inlet gas flow *a*, the inlet liquid flow *b* and the operating parameters, the data of the outlet gas flow *c* and liquid flow *d*, and further the heat of absorption on each plate.

The model contains the following simplifications:

1. The quantity of liquid and gas remains unchanged along the tower;
2. The temperature is unchanged along the tower. (Each plate has the same temperature, presupposing that the heat formed is removed by heat exchange);

3. The pressure in the tower is constant;
4. The gaseous and liquid phases are in thermodynamical equilibrium on each plate;
5. The mixing on each plate is equal;
6. The equilibrium and operating curves are straight;
7. The chemical reactions are first-order and instantaneous.

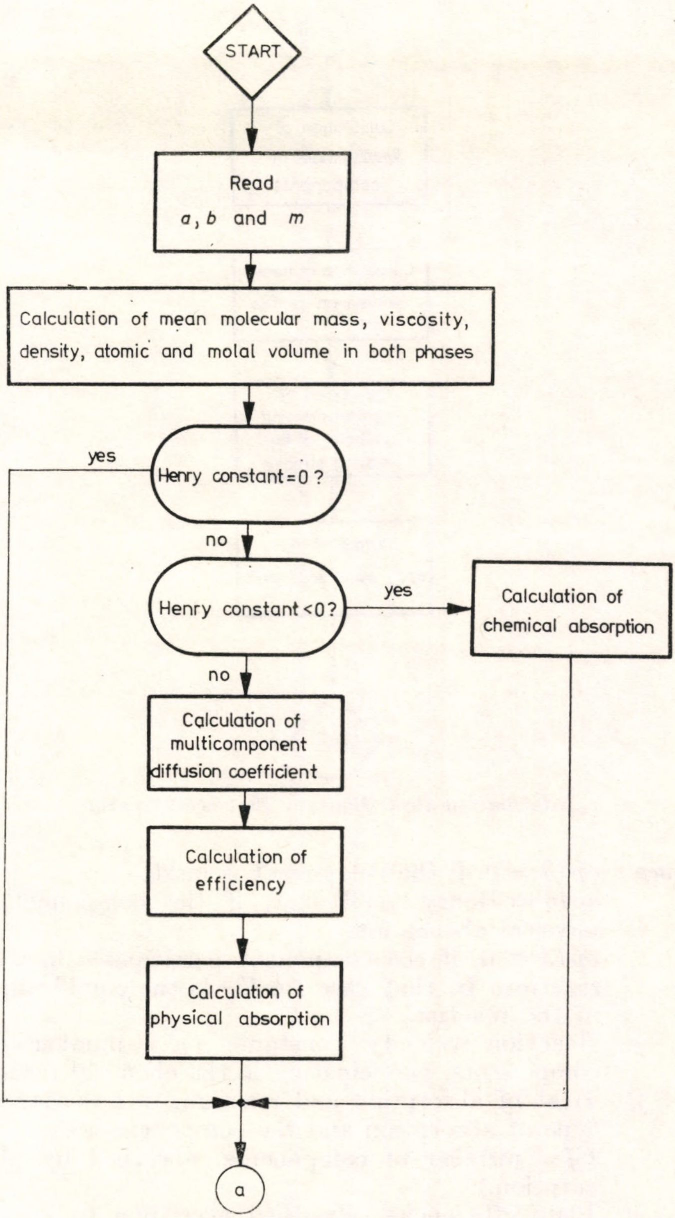
It is characteristic of the model that the components participating in the physical and chemical absorption are handled separately. The box calculates the absorption, accompanied by chemical reaction, according to the method of Jeffreys (1964), the physical absorption according to Kremser (1930) and Souders and Brown (1932). The plate efficiency is calculated based on the method proposed in AIChE Bubble Tray Design Manual (1958). If the values are outside the limits of application of this method, then the course proposed by O'Connell (1946) is followed. The diffusion coefficients in the gas phase are calculated according to the equations of Ning Hsing and Othmer (1972), in the liquid phase according to Wilke and Chang (1955).

The calculation process is presented in information flow diagram 18.

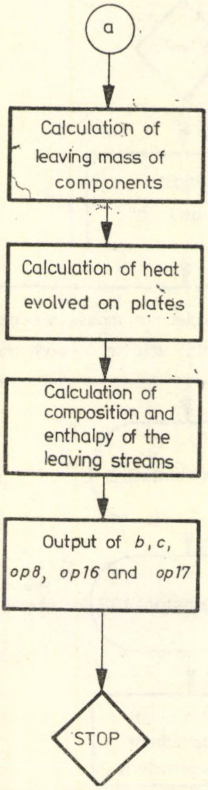
Limits of application: As the box calculates with a gas mass stream, which is unchanged along the tower, it is suitable for simulating the absorption of gaseous components which are poorly soluble or present in small concentration. If the absorption is accompanied by the evolution of heat, then heat exchangers maintain the nearly uniform temperature. The dimensions of the heat exchangers may be derived from the heat evolution calculated by the box.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of plates.
op2	1	Diameter of the plate, m.
op3	1	Liquid flow width, m.
op4	1	Seal, m.
op5	1	Cap diameter, m.
op6	1	Bubbling region width, m.
op7	1	Skirt clearance, m.
op8	1	Mean tower temperature, k.
op9	1	Value of the association factor in the Wilke equation.
op10	1	Height of liquid layer on the plate, m.
op11	1	Code of the liquid component, participating in the chemical reaction.
op12	1	Code of liquid component, resulting in the chemical reaction.



Information flow diagram 18 (first part)



Information flow diagram 18 (second part)

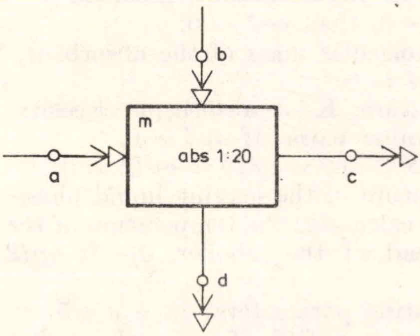
op13	*ncomp*	*op13* = 0, if the component is inert, *op13* = Henry coefficient, if the component undergoes physical absorption; *op13* $<$ 0, if the component participates in the chemical reaction. In that case *(op13)* is the equilibrium constant of the reaction.
op14	*jv*	Reaction velocity constants *(jv* = number of gaseous components, participating in the chemical reaction), (s^{-1}).
op15	*jv* + *jf*	Heat of absorption and reaction, in accordance with the type of absorption and the component code. *(jf* = number of components, absorbed by physical absorption.)
op16	*jv* + *jf*	Plate efficiencies, classified according to the chemically and physically absorbed components. (If for a physically absorbed component this value is specified as zero, then the box calculates it.)
op17	*op1*	Heat of absorption, evolved on the plates. The values are obtained during calculation.

Check: The box prints error messages if the pressure difference of the two inlet flows exceeds 1 atm; if the number of operating parameters is wrong; if the number of plates, their diameter, the liquid flow width, the seal, the cap diameter, the bubbling region width, the skirt clearance, the mean tower temperature, the association factor are negative or if they exceed prescribed limits and if *op11* or *op12* are undefined codes.

3.4.19 MODEL OF GAS ABSORPTION OR DESORPTION *(abs1)*

Box *abs1* is suitable for the simplified simulation of the absorptive separation of hydrocarbon gases in a plate column or the regeneration of the absorbent with inert gas.

The graphic symbol of the box:



Description of the operation:

abs1 : 20 (m, a, b, c, d)

The box calculates the data of the leaving streams based on the data of the entering gas flow *a*, the entering liquid flow *b* and the operating parameters.

The mathematical model has been developed on the basis of the relations of Kremser (1930), Souders and Brown (1932), and Horton and Franklin (1940). The computation time does not depend upon the number of plates. The heat balance calculation uses the method of Hull and Raymond (1953), the column efficiency that of O'Connell (1946). The vapour–liquid equilibrium coefficients are calculated through relation

$$K_i = \exp\left(C_{i1} + \frac{C_{i2}}{T}\right).$$

The value of the coefficients is determined from the standard procedure *prek*.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Code, *op1* = 0 if absorption, *op1* = 1 if desorption is modelled.
op2	1	Number of real plates.

op3	1	$op3 =$ convergence pressure, N/m^2, if the phase equilibrium is calculated with the approximating function of the NGAA diagrams. $op3 = 1$, if the vapour–liquid equilibrium has to be calculated from $T-K$ pairs – figuring among the operating parameters – by interpolation.
op4	1	Average column efficiency. $op4 = 0$, if the column efficiency is to be calculated. The known column efficiency: $0 < op4 < 1$,
op5	1	Code of the key component in the declaration of the stream type. If $op4 = 0$, then $1 \leq op5 \leq (\mathrm{k} - 1)$. If $op4 \neq 0$, then $op5 = 0$.
op6	1	Density of the absorbent, kmole/m^3. If $op4 \neq 0$, then $op7 = 0$.
op7	1	Mean molecular mass of the absorbent, kg/kmole. If $op4 \neq 0$, then $op7 = 0$.
op8 ⋮ *op11*	1	Temperature, K – absorbent viscosity, Ns/m^2 value pairs. If $op4 \neq 0$, then $op8 = op9 = op10 = op11 = 0$.
op12	1	Temperature of the leaving liquid phase, K. If $op12 = 0$, then the box calculates the temperature of the leaving liquid stream.
op13	1	Heat load of the reboiler, J/s. If $op12 \neq 0$, then $op13 = 0$.

Number of operating parameters: $13 + n \times 5$.
$n \times 5$ data are to be specified, if $op3 = 1$, as discussed when describing box *sep1*.

Limits of application: Box *abs1* is particularly suitable for simulating the oil wash of a hydrocarbon gas mixture and the regeneration of the wash oil.

In general use it is applicable, if:

– the absorbent is practically non-volatile,

– the pseudocritical temperature of the hypothetic mass stream consisting of components which are absorbed (desorbed) on the first theoretical plate counted from the top exceeds that of the plate,

– the pressure in the column is between 3 . . . 60.10^5 N/m^2,

– the weight ratio of the absorbent/gas is between 1 and 5 (the relations are not valid if the weight ratio is lower than 0.8),

– the component representing the absorbent is declared in the last place in the corresponding stream type. This is necessary for computational reasons.

Check: the box prints an error message, if

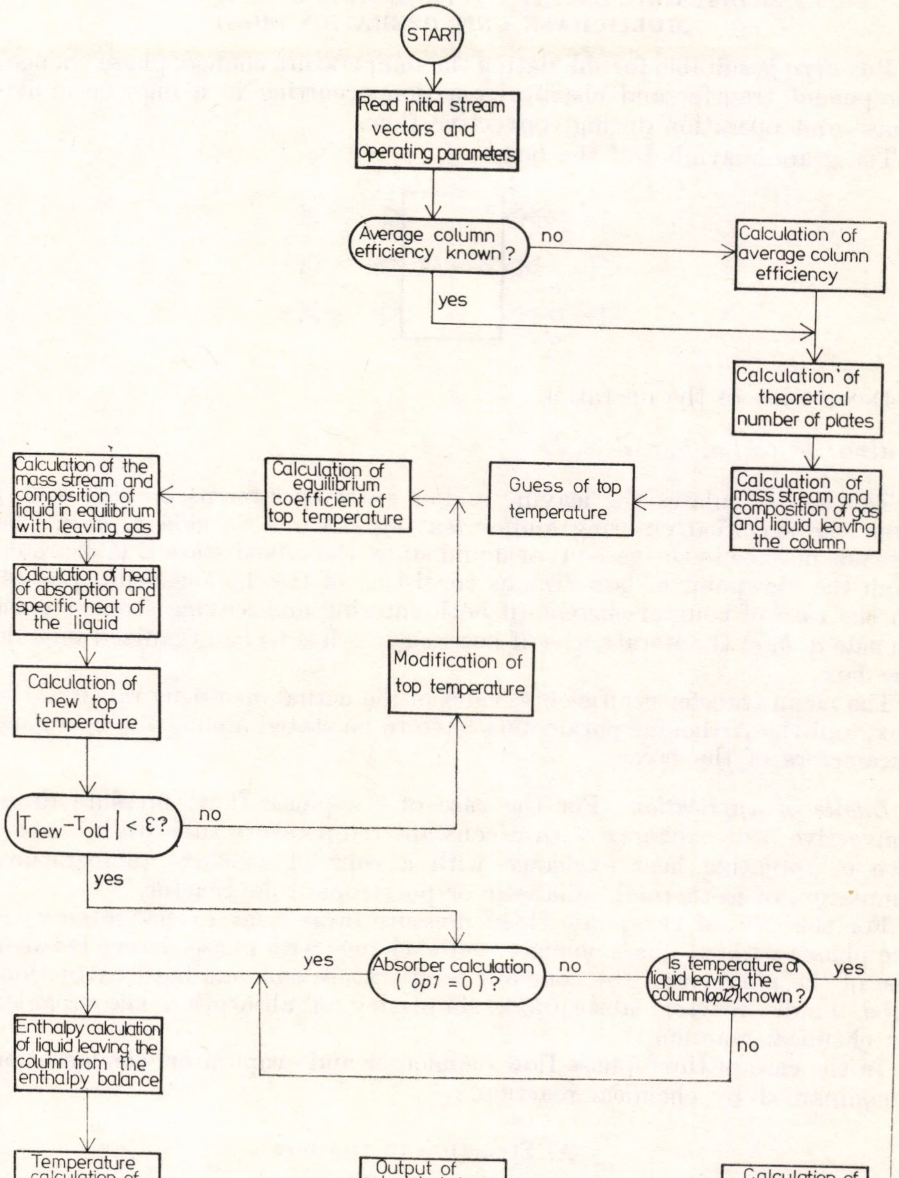
– the type of entering streams is different,

– the state of the entering streams is not adequate,

– the pressure difference of the entering streams exceeds 0.1×10^5 N/m^2.

– It is not possible to perform the iterative calculation of the temperature of the gas leaving the top plate under the given conditions.

The calculation process is presented in information flow diagram 19.

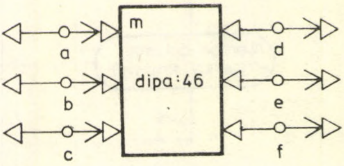


Information flow diagram 19

3.4.20 DISTRIBUTED PARAMETRAL MODEL OF A ONE- OR MULTIPHASE UNIT OPERATION *(dipa)*

Box *dipa* is suitable for simulating the temperature change, phase change, component transfer and chemical reaction occurring in a one- or multiphase unit operation during convective flow.

The graphic symbol of the box:



Description of the operation:

dipa: 46 (m, a, b, c, d, e, f)

The box calculates the **leaving** and/or entering streams on side *d, e, f* from the specified entering and/or leaving streams on side *a, b, c*. The streams may be in the gaseous or liquid state, the mixed state is interpreted from the viewpoint of box *dipa* as consisting of two homogeneous phases. In the case of counter-current (if both entering and leaving streams exist on side *a, b, c*) the iteration — if necessary — has to be organized outside the box.

The mean transfer coefficients, valid in the actual operating range of the box, and the Arrhenius parameters have to be stated among the operating parameters of the box.

Limits of application: For the case of one-phase flow: pressure drop; convective heat exchange with a constant temperature tube wall; convective or radiating heat exchange with a zone of constant temperature; simulation of isothermal, adiabatic or polytropic tube reactor.

For the case of two-phase flow: pressure drop; heat exchange between the phases without phase change; heat exchange with phase change between one of the phases and the constant temperature surroundings; extraction; tube bundle reactor; absorption; simulating of absorption accompanied by chemical reaction.

In the case of three-phase flow: condenser and evaporator; condensation accompanied by chemical reaction.

A. Structure of the box

Box *dipa* is suitable for describing streams, in contact with each other and their surroundings. The composition, temperature, pressure and flow cross-section may change along the axis, parallel to the flow (length as independent variable). The reason for these changes may be chemical reaction, prescribed linear pressure change, component transfer, evaporation or condensation, heat transfer or radiation.

These changes are described as inhomogeneous first-order systems of differential equations written for all component streams, the temperature and the flow cross-section as dependent variables.

We suppose that each stream is homogeneous and that phase change is only allowed between streams 1 and 2. The interactions between the streams take place on the phase interface, that between the streams and the surroundings through the wall of the equipment. Not more than three streams are considered.

The serial numbers of the 1st and 2nd stream are interchangeable. Component transfer is only allowed between these two streams. The component transfer from the 3rd stream to the 1st and 2nd streams is prohibited.

The scheme of interactions (Fig. 3.5) includes all allowed interactions and so is valid with the following restrictions:

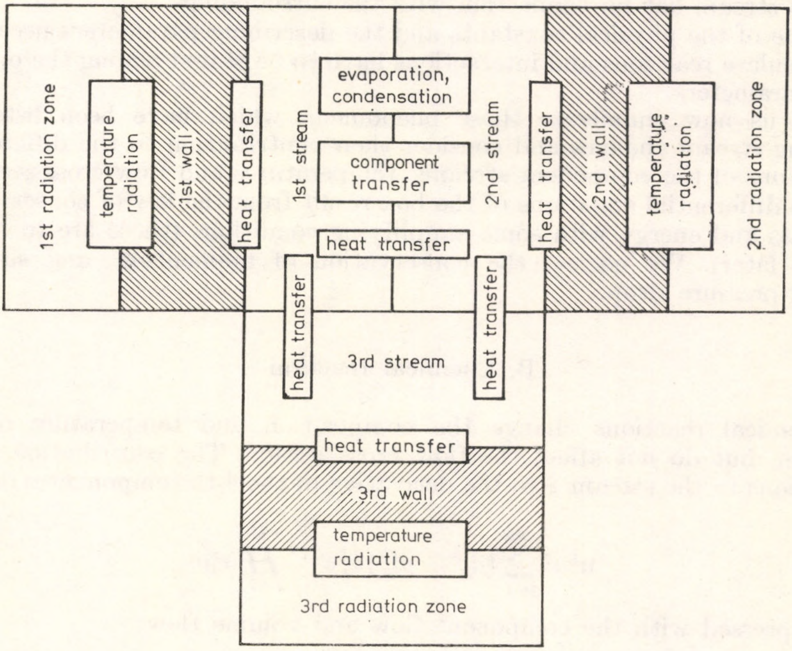


Fig. 3.5. Allowed interactions in box *dipa*

1. If a phase change occurs between the 1st and 2nd streams, then both streams must contain the same component, and the state of the same component is different. In this case the chemical reaction in the 1st and 2nd streams, as well as any other interaction between the two streams is prohibited. The pressure of the streams is constant.

2. If component transfer exists between the 1st and 2nd streams, then the stream type of both streams have to agree.

3. It is necessary to explain the relation between a stream and the related radiation zone. We suppose that we can coordinate a $T^{f\xi}_{(x)}$ wall temperature to the wall between the ξ stream ($\xi = 1, 2, 3$) and the radiation zone, according to relation

$$F^{s\xi}\,\sigma^{\xi}(T^{s\xi 4} - T^{f\xi 4}) = F^{f\xi}\,\chi^{f\xi}(T^{f\xi} - T^{\xi}), \tag{3.10}$$

where

F = the heat transfer area,
σ = the effective thermal radiation coefficient,
χ = the heat transfer coefficient.

Equation (3.10) indicates that the radiation heat flow transferred to the wall and the heat transferred from the wall to the stream are equal.

If the radiation area does not join one of the streams then the heat exchange occurs either between a constant-temperature wall and the stream or the stream has no connection with the surroundings.

Some of the physical constants and the describing parameters necessary to calculate reactions and interactions have to be stated among the operating parameters.

Let us now enumerate those phenomena which have been listed as causing stream changes and consider their contribution to the differential equations of the component streams, temperatures and flow cross-sections.

The differential equations of the box result from the law of conservation of mass and energy with some simplifying conditions (these are to be detailed later). We neglect the conservation of momentum, and suppose linear pressure drop.

B. Chemical reaction

Chemical reactions change the composition and temperature of the stream, but do not affect the flow cross-section. The contribution of all reactions in the stream ξ to the derivative of the i-th component stream is

$$\mathrm{u}^{\xi} a^{\xi} \sum_{j=1}^{m\xi} (\mu_{ij}^{\xi+} - \mu_{ij}^{\xi-})\, k_j^{\xi}\, e^{\frac{Ej}{RT^{\xi}}} \prod_{l=1}^{n^{\xi}} c_l^{\nu_{lj}^{\xi}} \tag{3.11}$$

or expressed with the component flow and volume flow:

$$\mathrm{u}^{\xi} a^{\xi} \sum_{j=1}^{m\xi} (s_{ij}^{\xi} e^{\frac{Ej}{RT^{\xi}}}\, \varphi^{\xi-\nu_j^{\xi}}) \prod_{l=1}^{n^{\xi}} j_l^{\nu_{lj}^{\xi}} \tag{3.12}$$

where

$$s_{ij}^{\xi} = (\mu_{ij}^{\xi+} - \mu_{ij}^{\xi-})\, k_j^{\xi} \text{ and } \nu_j^{\xi} = \sum_{l=1}^{n^{\xi}} \nu_{lj}^{\xi}$$

The chemical reactions do not affect the enthalpy stream of the phase because of the enthalpy convention adopted in the SIMUL system; the temperature changes because of the change of the composition. The effect of chemical reactions leading to temperature change are discussed in section 3.4.20.F.

A chemical reaction has to be defined for box *dipa* in the form of a number serial:

$$\mu^{-}_{p_1j}, p_1, \nu_{p_1j}, \ldots, \mu^{-}_{p_mj}, p_m, \nu_{p_mj}, 0, k_j, E_j, \mu^{+}_{q_1j}, q_1, \ldots, \mu^{+}_{q_mj}, q_m, 0, \qquad (3.13)$$

where $p_1, \ldots, p_m$ are the reaction sites and $q_1, \ldots, q_m$ are the produced components in the declaration of the stream type,

μ = the stoichiometrical number of the component defined by its subscript in the j-th reaction $j = 1,2, \ldots, m\xi$.
ν = the order with respect to the i-th reacting component defined by its subscript in the j-th reaction,
k_j = the pre-exponential coefficient of the j-th reaction,
E_j = the activation energy of the j-th reaction.

C. Component transfer

The contribution of the component transfer to the derivative of the i-th component stream of the ξ stream (ξ 1,2):

$$\mathrm{u}^{\xi} F^{12}(\omega_i^{\eta\xi} c_i^{\eta} - \omega_i^{\xi\eta} c_i^{\xi}) \qquad (3.14)$$

where η denotes the other stream. The contribution in stream η is the negative value of (3.14). Equation (3.14) expresses that the driving force of the component transfer is the difference between the suitably weighted concentrations.

Substituting our variables into (3.14):

$$\mathrm{u}^{\xi} F^{12}\left(\frac{\omega_i^{\eta\xi}}{\varphi^{\eta}} j_i^{\eta} - \frac{\omega_i^{\xi\eta}}{\varphi^{\xi}} j_i^{\xi}\right) \qquad (3.15)$$

The component transfer changes the enthalpy stream of the phases. The contribution of the component transfer to the derivative of the enthalpy stream of stream ξ is:

$$\mathrm{u}^{\xi} F^{12} \sum_{i=1}^{n\xi}\left(\frac{\omega_i^{\eta\xi}}{\varphi^{\eta}} j_i^{\eta} h_i^{\eta} - \frac{\omega_i^{\xi\eta}}{\varphi^{\xi}} j_i^{\xi} h_i^{\xi}\right) \qquad (3.16)$$

The component transfer may also change the flow cross-section of the 1st and 2nd streams. We suppose that this change has no other cause.

The overall cross-section of the two streams is constant:

$$a^{\xi} + a^{\eta} = a \qquad (3.17)$$

It is known that

$$a^{\xi} v^{\xi} \varrho^{\xi} = \sum_{i=1}^{n\xi} j_i^{\xi} \qquad (3.18)$$

and $\varrho^{\xi} > \varrho^{\eta}$. We differentiate (3.18) with respect to x:

$$v^{\xi}\varrho^{\xi}\frac{da^{\xi}}{dx} + a^{\xi}\frac{d(\varrho^{\xi}v^{\xi})}{dx} = \sum_{i=1}^{n^{\xi}}\frac{dj_i^{\xi}}{dx} \tag{3.19}$$

As

$$\frac{dj_i^{\xi}}{dx} = \frac{dj_i^{\xi}}{dx}\bigg|_{\text{reactions}} + \frac{dj_i^{\xi}}{dx}\bigg|_{\text{component transfer}} \tag{3.20}$$

and supposing that the contribution of the component transfer is negligible in the derivatives of $\varrho^{\xi}\, v^{\xi}$, we may write the following equation:

$$v^{\xi}\varrho^{\xi}\frac{da^{\xi}}{dx} = \sum_{i=1}^{n^{\xi}}\frac{dj_i^{\xi}}{dx}\bigg|_{\text{component transfer}} \tag{3.21}$$

Taking equation (3.15) into consideration, we arrive at the differential equation of a^{ξ}.

$$\mathrm{u}^{\xi}\frac{da^{\xi}}{dx} = F^{12}\frac{a^{\xi}}{\varphi^{\xi}\varrho^{\xi}}\sum_{i=1}^{n^{\xi}}\left(\frac{\omega_i^{\eta\xi}}{\varphi^{\eta}}j_i^{\eta} - \frac{\omega_i^{\xi\eta}}{\varphi^{\xi}}j_i^{\xi}\right). \tag{3.22}$$

Actual value of a^{η} may be calculated from equation (3.17).

D. Evaporation, condensation

Both streams contain the same component as different phases. The pressure and temperature of the streams are constant. The common temperature is the boiling point of the component on the given pressure.

The overall component stream of the two streams is constant, therefore

$$\frac{dj^1}{dx} + \frac{dj^2}{dx} = 0 \tag{3.23}$$

The overall enthalpy stream of the two streams:

$$H^{12} = j^1h^1 + j^2h^2 \tag{3.24}$$

The overall enthalpy stream of the two streams is influenced only by an external heat source, namely the 3rd stream that is, the thermal connection between the first two streams and the wall. We may therefore write the following:

$$\frac{dH^{12}}{dx} = u^1\{(\chi^{13} + \chi^{23})(T^3 - T) + \chi^{f_1}(T^{f_1} - T) + \chi^{f_2}(T^{f_2} - T)\} \tag{3.25}$$

where $\chi = \mathrm{F}\ \varkappa$ = specific heat transfer area × heat transfer coefficient.

Differentiate (3.24) with respect to x and make use of the fact that the molal enthalpies (h^1, h^2) do not depend on x, since pressure and temperature are constant:

$$\frac{dH^{12}}{dx} = h^1 \frac{dj^1}{dx} + h^2 \frac{dj^2}{dx} \tag{3.26}$$

Since (3.25) and (3.26) are equal, we obtain, using (3.23):

$$\frac{dj^1}{dx} = \frac{u^1}{h^1 - h^2} \{(\chi^{13} + \chi^{23})(T^3 - T) + \chi^{f_1}(T^{f_1} - T) + \chi^{f_2}(T^{f_2} - T)\} \tag{3.27}$$

and the derivative of the component stream of the 2nd stream may be obtained from (3.23) knowing (3.27).

Equation (3.27) expresses that the rate of the phase change is controlled by the rate of heat transfer.

E. Differential equation of the component streams

For the sake of general discussion, let us introduce the δ_R^ξ, δ_A^ξ, δ_F^ξ zero-one variables:

$$\delta_R^\xi = \begin{cases} 1, & \text{if there is chemical reaction in the } \xi \text{ stream} \\ 0, & \text{otherwise.} \end{cases}$$

$$\delta_A^\xi = \begin{cases} 1, & \text{if there is component transfer between the 1st and 2nd streams and} \\ & \xi = 1,2 \\ 0, & \text{otherwise} \end{cases}$$

$$\delta_F^\xi = \begin{cases} 1, & \text{if there is phase change between the 1st and 2nd streams and} \\ & \xi = 1,2. \\ 0, & \text{otherwise.} \end{cases}$$

The reason for the component stream changes may be the chemical reaction, the component transfer or the phase change. Considering the contributions listed in B, C and D to the derivatives of the component streams, we may write the following equation using δ_R^ξ, δ_A^ξ, and δ_F^ξ:

$$u^\xi \frac{dj_i^\xi}{dx} = \delta_R^\xi a^\xi \sum_{j=1}^{m^\xi} s_{ij}^\xi e^{\frac{E_j}{RT^\xi}} \varphi^{\xi - \nu_j^\xi} \prod_{l=1}^{n^\xi} j_l^{\nu_{lj}^\xi} + \delta_A^\xi F^{12} \left(\frac{\omega_i^{\eta\xi}}{\varphi^\eta} j_i^\eta - \frac{\omega_i^{\xi\eta}}{\varphi^\xi} j_i^\xi \right) +$$

$$+ \frac{\delta_F^\xi}{h^\xi - \eta^\xi} \{(\chi^{\xi 3} + \chi^{\eta 3})(T^3 - T) + \chi^{f\xi}(T^{f\xi} - T) + \chi^{f\eta}(T^{f\eta} - T)\} \tag{3.28}$$

$\xi = 1, 2, 3$ and $\eta = 3 - \xi$, $i = 1, 2, \ldots, n^\xi$. If δ in (3.28) equals zero, then this must be omitted with its coefficient and in such cases this coefficient may be insignificant (e. g., for $\xi = 3$, $\eta = 0$ although this does not matter since here $\delta_A^3 = \delta_F^3 = 0$ has to be fulfilled).

F. Differential equations for the temperature

Let us formulate the enthalpy stream change of stream ξ using the δ defined in E. Since the cause of the enthalpy stream change may be the component transfer or the heat transfer (we previously discussed the phase change):

$$\mathrm{u}^{\xi}\frac{dH^{\xi}}{dx} = \chi^{\xi\eta}(T^{\eta} - T^{\xi}) + \chi^{\xi\zeta}(T^{\zeta} - T^{\xi}) + \chi^{\xi f}(T^{f} - T^{\xi}) +$$

$$\delta_{\mathrm{A}}^{\xi} F^{12} \sum_{i=1}^{n^{\xi}} \left(\frac{\omega_i^{\eta\xi}}{\varphi^{\eta}} j_i^{\eta} h_i^{\eta} - \frac{\omega_i^{\xi\eta}}{\varphi^{\xi}} j_i^{\xi} h_i^{\xi} \right) \tag{3.29}$$

$\xi = 1, 2, 3$ and $\eta = 3 - \xi$. The enthalpy of ideal mixtures

$$H^{\xi} = \sum_{i=1}^{n^{\xi}} h_i(T^{\xi}) j_i^{\xi} \tag{3.30}$$

Differentiate (3.30) with respect to x, h_i, $(T^{\xi}) = h_i^{\xi}$ indirectly through T^{ξ}:

$$\frac{dH^{\xi}}{dx} = \sum_{i=1}^{n^{\xi}} h_i^{\xi} \frac{dj_i^{\xi}}{dx} + \frac{dT^{\xi}}{dx} \sum_{i=1}^{n^{\xi}} j_i^{\xi} \frac{dh_i^{\xi}}{dT^{\xi}} \tag{3.31}$$

Taking into consideration (3.28), with $\delta^{\xi} = 0$, and further the equality of (3.29) and (3.31):

$$u^{\xi}\frac{dT^{\xi}}{dx} = \Big\{ \chi^{\xi\eta}(T^{\eta} - T^{\xi}) + \chi^{\xi\zeta}(T^{\zeta} - T^{\xi}) + \chi^{\xi f}(T^{f} - T^{\xi}) +$$

$$+ \delta_{\mathrm{A}}^{\xi} \frac{F^{12}}{\varphi^{\eta}} \sum_{i=1}^{n^{\xi}} \omega_i^{\eta\xi} j_i^{\eta} (h_i^{\eta} - h_i^{\xi}) +$$

$$+ \delta_{\mathrm{R}}^{\xi} a^{\xi} \sum_{i=1}^{n^{\xi}} h_i^{\xi} \sum_{j=1}^{m^{\xi}} s_{ij}^{\xi} e^{\frac{E_j}{RT^{\xi}}} \varphi^{\xi - \nu_j^{\xi}} \prod_{l=1}^{n^{\xi}} j_l^{\nu_{lj}} \Big\} \Big/ \sum_{i=1}^{n^{\xi}} j_i^{\xi} \frac{dh_i^{\xi}}{dT^{\xi}} \tag{3.32}$$

$\xi, \eta, \zeta = 1{,}2{,}3$ but $\xi \neq \eta$, $\xi \neq h$, $\eta \neq h$. There is component transfer if $\xi = 1$ or 2, $\eta = 3 - \xi$ and $\delta_{\mathrm{A}}^{\xi} \neq 0$.

Operating parameters:

It is evident from the structure of box *dipa* that it is the generator of a system of differential equations. From the operating parameters, this generator obtains information about the dependent variables for which differential equations have to be generated. These variables figure on the right-hand side of these equations. The parameters of the differential equation must also be stated among the operating parameters. Since, however, the number of operating parameters depends on the number and right-hand sides of the differential equations to be generated, it is not judicious to state the number and sequence of the operating parameters in the form used so far. When using box *dipa*, the sequence of operating parameters is determined by the following dialogue, where operating parameters from *op000* to *op015* define the conditions for terminating the integration.

Terminating the integration and the exit from the box may be effected in one of four ways:

1. The upper bound of the integration — that is, the independent variable — has been attained. This is the normal exit.

2. One of the component streams stated in *op105*, *op205* and *op305* has fallen below the value stated in *op014*.

3. The temperature of one of the components has approximated, within the accuracy defined in *op013*, the upper or lower temperature bound stated in *op104*, *op204* and *op304*.

4. The temperature of one of the streams has exceeded, from below or above, the boiling point. The integration stops in cases (2), (3) and (4) at the last step in accordance with exit conditions and the box only records any contradiction with exit conditions. The last x value accepted is stored in *op004*, the next (unaccepted) one in *op005*. The difference between these two x values is Δx, or the corresponding differences of the temperature or the component stream may be $\Delta_{r\xi}$ or $\Delta_{j\xi}$.

The operating parameter *op000* is an input and output parameter. If at the input $op000 = 0$, then the integration limits are $x = op010$ and $x = op011$, otherwise $x = op004$ and $x = op005$. At the first exit conditions or if $\Delta x < op006 = (op011 - op010)\ x\ op12$, the output value of *op000* is 0, otherwise 1.

Operating parameters *op100*, *op200* and *op300* contain information about what is taking place in the 1st, 2nd and 3rd streams. These parameters are interpreted as sums of powers of two. The significance of these powers is the following:

16 = there is component transfer between the 1st and 2nd streams,
8 = there is phase change between the 1st and 2nd streams,
4 = there is heat exchange between streams ξ and η,
2 = the ξ stream is in thermal relation with the radiation zone through a wall,
1 = there is heat transfer between stream ξ and the constant temperature wall.

In operating parameters *op100*, *op200*, *op300* a sum of powers can be stated, which takes the conditions of Chapter E into consideration and its value may be optional. For the 1st stream $op100 = 22$ is allowed for example, but $op100 = 23$ is not allowed, since $23 = 16 + 4 + 2 + 1$, and the number 2 (radiation zone) and 1 (constant wall temperature) cannot occur simultaneously.

Operating parameters:

Condition of branching	Label of continuation	Label	Denomination	Value, significance; comments
			op000	In the first step of the general and repeated call 0.
			op001	Its input value — 0 if $op000 = 0$ — changes with change of enthalpy stream of the 1st stream.

			op002	Its input value — 0 if *op000* $= 0$ — changes with change of enthalpy stream of the 2nd stream.
			op003	Its input value — 0 if *op000* $= 0_z$ — changes with change of enthalpy stream of the 3rd stream.
			op004	New lower bound of integration. Output.
			op005	New upper bound of integration. Output.
			op006	Allowed error of the integration interval, working variable. Its input value is irrelevant.
			op007	0
			op008	0
			op009	If test output $= -1$, otherwise any value.
			op010	Lower integration bound.
			op011	Upper integration bound.
			op012	Accuracy of the integration.
			op013	Temperature accuracy (exit condition).
			op014	Allowed minimal value of the chosen component streams (exit condition).
			op015	Suggested initial step length of integration.
op016 ≤ 0	L1		*op016*	≤ 0, if there is no chemical reaction, otherwise the maximal number of components on the left-hand side of the reactions.
			op017	Maximal number of components on the right-hand side of the reactions.
op100 < 0	L2	L1:	*op100*	< 0, the 1st stream does not exist, ≥ 0, number, characterizing the stream.
			op101	1 or -1, flow direction of the 1st stream.
			op102	Cross section of the 1st stream.
			op103	Longitudinal pressure drop of the 1st stream in the flow direction (per meter).
			op104	Allowed maximal temperature or the negative minimal temperature of the 1st stream.
op016 ≤ 0	L2		*op105*	The subscript of the chosen component of the 1st stream.

$op106 = 0$	L2		*op106*	Number of chemical reactions in the 1st stream. Description of chemical reaction *op106*, see, eqn. (3.13).
$op200 < 0$	L3	L2:	*op200*	< 0, the 2nd stream does not exist, ≥ 0, number, characterizing the stream.
			op201	1 or − 1, flow direction of the 2nd stream.
			op202	Cross-section of the 2nd stream.
			op203	Longitudinal pressure drop of the 2nd stream in the flow direction (per meter).
			op204	Allowed maximal temperature or the negative minimal temperature of the 2nd stream.
$op016 \leq 0$	L3		*op205*	The subscript of the chosen component of the 2nd stream.
$op206 = 0$	L3		*op206*	Number of chemical reactions in the 2nd stream. Description of chemical reaction *op206*, see, eqn. (3.13).
$op300 < 0$	L4	L3:	*op300*	< 0, the 3rd stream does not exist. ≥ 0, number, characterizing the 3rd stream.
			op301	1 or − 1, flow direction of the 3rd stream.
			op302	Cross-section of the 3rd stream.
			op303	Longitudinal pressure drop (per meter) of the 3rd stream in the flow direction.
			op304	Allowed maximal temperature or the negative minimal temperature of the 3rd stream.
$op016 \leq 0$	L4		*op305*	The subscript of the chosen component of the 3rd stream.
$op306 = 0$	L4		*op306*	Number of chemical reactions in the 3rd stream. Description of chemical reaction *op306*, see, eqn. (3.13).
$op100 < 16$	L5	L4:		If there is no component transfer.
			op120	Component transfer area per meter.
			op121	Component transfer coefficient pairs: 1st → 2nd,
	L6			In the sequence 2nd → 1st, 2× *ncomp* 1.

op100 mod $16 < 8$	L6	L5:		There is no evaporation, condensation in 1st, 2nd.
	L7			There is evaporation or condensation in 1st, 2nd.
op100 mod $8 < 4$	L8	L6:		The 1st stream has no thermal contact with 2nd, 3rd.
			op122	Heat transfer area per meter: 1st ↔ 2nd.
			op123	Heat transfer coefficient: 1st ↔ 2nd.
op300 mod $8 < 4$	L9	L7:		The 3rd stream has no thermal contract with the 1st.
			op132	Heat transfer area per meter: 1st ↔ 3rd.
			op133	Heat transfer coefficient: 1st ↔ 3rd.
op200 mod $8 < 4$	L9	L8:		The 3rd stream has no thermal contact with the 2nd.
			op232	Heat transfer area per meter: 2nd ↔ 3rd.
			op233	Heat transfer coefficient: 2nd ↔ 3rd.
op100 mod $4 < 2$	L10	L9:		The 1st stream is isolated from a radiating zone.
			op108	Constant temperature of the 1st radiating zone.
			op109	Area of the 1st radiating zone per meter.
	L11		*op110*	Radiation coefficient of the 1st radiating zone.
op100 mod $2 < 1$	L12	L10:		No heat transfer between the 1st stream and its wall.
			op111	Constant wall temperature of the 1st stream.
		L11:	*op112*	Heat transfer area per meter 1st ↔ 1st wall.
			op112	Heat transfer coefficient: 1st ↔ 1st wall.
op200 mod $4 < 2$	L13	L12:		The 2nd stream is isolated from a radiating zone.
			op208	Constant temperature of the 2nd radiating zone.

			op209	Area of the 2nd radiating zone per meter.
	L14		*op210*	Radiation coefficient of the 2nd radiating zone.
op200 mod $2 < 1$	L15	L13:		No heat transfer between the 2nd stream and its wall.
			op211	Constant wall temperature of the 2nd stream.
		L14:	*op212*	Heat transfer area per meter: 2nd $\leftrightarrow$ 2nd wall.
			op213	Heat transfer coefficient: 2nd $\leftrightarrow$ 2nd wall.
op300 mod $4 < 2$	L16	L15:		The 3rd stream is isolated from a radiating zone.
			op308	Constant temperature of the 3rd radiating zone.
			op309	Area of the 3rd radiating zone per meter.
	L17		*op310*	Radiation coefficient of the 3rd radiating zone.
op300 mod $2 < 1$	L18	L16:		No heat transfer between the 3rd stream and its wall.
			op311	Constant wall temperature of the 3rd stream.
		L17:	*op312*	Heat transfer area per meter: 3rd $\leftrightarrow$ 3rd wall.
			op313	Heat transfer coefficient: 3rd $\leftrightarrow$ 3rd wall.
		L18:		End of listing of the operating parameters.

Check:

Error message	Explanation of error messages
dipa1	The overall component in the streams ≤ 0, stream vectors not defined.
dipa2	Number of operating parameters < 19, task unintelligible.
dipa3	Number of operating parameters is fewer than expected from the operating parameters already read.
dipa4	Number of components on the right-hand side of chemical reactions ≤ 0.

dipa5	The accuracy of integration $< 10^{-10}$.
dipa6	The accuracy of temperature $< 10^{-3}$, at the exit condition.
dipa7	Output level of the chosen components $< 10^{-10}$.
dipa8	Suggested initial step length $< 10^{-10}$.
dipa9	Lower bound of integration < 0.
dipa10	Integration interval zero or negative.
dipa11	Flow direction of the 1st stream is prescribed differently in the stream vector and the op.
dipa12	Flow direction of the 2nd stream is prescribed differently in the stream vector and the op.
dipa13	Flow direction of the 3rd stream is prescribed differently in the stream vector and the op.
dipa14	The interrelation of the 1st and 2nd streams is contradictory.
dipa15	Stoichiometric constant of the left-hand side of the reaction is negative.
dipa16	The index of the component, appearing on the left-hand side of the reaction, is negative.
dipa17	Order with respect to one of the components in one of the reactions < 0.
dipa18	Pre-exponential coefficient of the reaction ≤ 0.
dipa19	Stoichiometric constant of the right-hand side of the reaction is negative.
dipa20	The index of the component, appearing on the right-hand side of the reactions is negative or 0.
dipa21	All streams are empty.
dipa22	Interrelation contradictory, 1st ↔ 2nd.
dipa23	Component transfer area ≤ 0, 1st ↔ 2nd.
dipa24	Component transfer coefficient negative.
dipa25	Entering mass stream of the 1st stream $= 0$ and it does not obtain mass from the 2nd stream as either component transfer, or as phase change.
dipa26	Entering mass stream of the 2nd stream $= 0$ and it does not obtain mass from the 1st stream as either component transfer or phase change.
dipa27	Interrelation stated contradictory. Phase change, 1st ↔ 2nd.
dipa28	Interrelation stated contradictory. Heat transfer between streams.
dipa29	Heat transfer area < 0, or heat transfer coefficient < 0, 1st ↔ 2nd.
dipa30	Heat transfer area < 0, or heat transfer coefficient < 0, 1st ↔ 2nd.
dipa31	Heat transfer area < 0, or heat transfer coefficient < 0, 2nd ↔ 3rd.
dipa32	One of parameters of radiation zone and/or wall < 0, 1st stream.
dipa33	One of parameters of radiation zone and/or wall < 0, 2nd stream.
dipa34	One of parameters of radiation zone and/or wall < 0, 3rd stream.
dipa35	Component stream or flow direction of the 1st stream does not correspond to that of the 2nd stream nor do their states correspond. Phase change 1st ↔ 2nd.

dipa36	Pressure or temperature of the 1st stream is not equal to that of the 2nd stream, or the slope of pressure drop is not 0. Phase change 1st ↔ 2nd.
dipa37	The stream does not exist and the mass stream $\neq 0$ (in the stream vector), or the mass stream $= 0$ and the stream exists. 1st, 2nd, 3rd stream.
dipa38	Flow direction of any stream not $+ 1$ or $- 1$.
dipa39	Flow cross-section of any stream ≤ 0.
dipa40	Index of chosen component of any stream is wrong. Exit condition.
dipa41	Number of chemical reactions negative in any stream.
dipa42	Radiation zone exists, but radiating area and/or radiation coefficient ≤ 0. 1st, 2nd, 3rd stream.

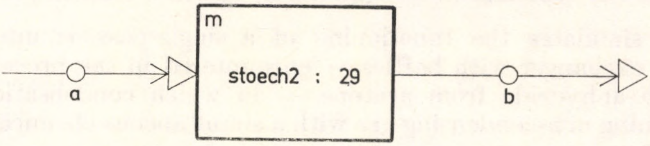
3.4.21 SPECIAL BOXES WITH RESTRICTED APPLICABILITY

The boxes described in the following simulate unit operations of particular designation. The limits of application of these boxes is restricted.

(a) Model of a particular chemical reaction *(stoech2)*

Box *stoech2* is suitable for simulating the isomerization of two components from a three-component mixture in the gaseous phase.

The graphic symbol of the box:



Description of the operation:

stoech2 : 29 (m, a, b)

The box calculates on the basis of the input stream vector *a* and the operating parameter vector *m*, the output vector *b*. Streams *a* and *b* are necessarily of the same stream type.

It is possible to prescribe the temperature and/or the pressure of the outlet stream. The difference between enthalpies of the inlet and outlet streams in this case appears among the operating parameters.

Limits of application: The box may be used to simulate isomerization, if the desired value of the conversion is known before the calculation, and if one component of the three-component mixture does not participate in the reaction.

(b) Model of heat-transfer by radiation *(rad)*

Box *rad* is suitable for simulating heat-transfer in the radiating zone at the flue gas side of a rotary kiln.

Description of the operation:

rad : 33 (m, a, b).

The mathematical model has been developed based on the method of Lobo and Evans (1939). During calculation, the box takes the heat-transfer by radiation and convection and the heat losses into consideration.

Box *rad* has been developed to model the pyrolitic cracking of acetone. It is not applicable to general cases.

(c) Model of the reactor for the pyrolitic cracking of acetone *(acreakt)*

Box *acreakt* is suitable for simulating the pyrolitic cracking of acetone, proceeding on the tube side of the furnace.

Description of the operation:

acreakt : 32 (m, a, b).

Based on the conversion and the temperature of the product, and the number and size of the tubes, the box calculates the unknown elements of the output stream vector, the tube length required to attain the prescribed conversion of the reaction and the temperature of the tube wall considered to be constant.

(d) Model of condensation accompanied by chemical reaction *(cond)*

Box *cond* simulates the functioning of a single-pass, counter-current tubular heat exchanger with baffles — encountered in the process of producing acetic anhydride from acetone — in which condensation occurs from a remaining non-condensing gas with a simultaneous chemical reaction during cooling.

Description of the operation:

cond : 35 (m, a, b, c, d, e).

Cooling water flows on the shell side, and the reacting mixture on the tube side of the heat exchanger. The box presents the gaseous and liquid products as separate stream vectors. The distribution between the phases satisfies the thermodynamical equilibrium.

The box is exclusively suitable for calculating the reaction producing acetic anhydride from ketene and acetic acid.

(e) Model of the partial oxidation of methane *(po)*

Box *po* simulates the partial oxidation of methane in a flame reactor.

Description of the operation:

po : 12 (m, a, b, c, d).

In order to achieve the maximal acetylene yield, the reaction is quenched with water spray. The products of the reaction are therefore not in equilibrium. Thus the calculation proceeds in two stages:

1. The reaction zone, where high-temperature products are formed from the inlet gas as a result of the reaction.
2. The quench zone, where the products are cooled by evaporating part of the cooling water.

It is assumed that the inlet gas flow contains only methane, oxygen and nitrogen, the outlet flow only hydrogen, carbon monoxide, carbon dioxide, ethylene, acetylene, methylacetylene, nitrogen and water. The inlet liquid flow contains only water. When calculating the reaction zone, it is assumed that

— the reaction is adiabatic,

— the reaction occurs according to a given stoichiometry,

— the concentration of acetylene leaving the reactor may be considered as an empirical function of the inlet gas composition and the temperature of the preheater,

— the concentration of carbon monoxide, water, carbon dioxide and hydrogen in the product corresponds to the chemical equilibrium of the producer gas,

— the quantity of ethylene and methylacetylene in the product flow is proportional to the quantity of acetylene produced.

The box has two calculation modes:

1. Based on the data of the inlet gas and cooling water, the data of the reaction product and remaining cooling water are calculated.
2. Based on the inlet gas flow, the inlet water temperature and the prescribed outlet temperature, the outlet gas flow and the quantity of cooling water are calculated.

(f) Model of a foam column (*foamco*)

Box *foamco* is suitable for simulating the heat exchange and partial condensation of a hydrocarbon mixture and water — originating from naphtha cracking — in the foam phase, occurring in a perforated plate equipment.

Description of the operation:

foamco : 30 (m, a, b, c, d).

The box simulates the process occurring on one plate of the foam column. It is assumed that the gas and liquid leaving the plate have identical temperatures, that there is not more than one volatile component in the liquid phase, which saturates the gas phase with its vapour, and that the liquid mixture is ideal. The box calculates the pressure drop of the gas, the height of the foam layer and the data of the outlet stream vectors.

(g) Model of hydrocarbon cracking *(reaktl)*

Box *reaktl* is suitable for simulating the process on the tube side of a polytropic tubular cracker in homogeneous gas phase.

Description of the operation:

reaktl : 24 (m, a, b).

In addition to data of stream vector *b* among the operating parameters, the box calculates the linear gas velocity, the Re number, the density of the gas mixture and the conversion — if it is less than 100 % at the outlet. In the opposite case, the tube length necessary for 100 % conversion is presented. The mathematical model applies stoichiometry to characterize the reactions, calculating the constants from laboratory results.

To solve the differential equation system, the standard procedure *rkm2* is used. The box does not calculate the heat balance, it is supposed that the longitudinal temperature distribution of the following phase is known and has the form of a polynomial of not more than third order.

Because of the limits of validity of the reaction-kinetic correlations, the box can only be used if the inlet gaseous mixture consists of only one hydrocarbon component and water.

(h) Model of packed cooling tower *(quench)*

Box *quench* is suitable for simulating a rapid counter-current cooling, effected in a packed tower.

Description of the operation:

quench : 34 (m, a, b, c, d).

Based on the data of the inlet gaseous and liquid flows, the box calculates the outlet flows. It is possible to prescribe the temperature of the outlet flow. In this case the box calculates the quantity of inlet liquid flow.

The box has been developed to simulate the quench tower used to produce acetic anhydride. The general use is therefore restricted.

PROBLEMS

In the SIMUL system, the simulation consists of consecutively running suitable boxes in the right sequence. It is the chemical-engineering task of the user to select the boxes and prescribe the sequence. The simulation may be efficiently composed by the user only if he knows the routines available, and the field of application of the boxes, though in principle he need not know the contents of the boxes. The facility of the computer-aided flow-sheeting is based on this fact.

The following problems have been prepared for readers who want to learn more about the application of the boxes, or have decided to develop new boxes and wish to have practical advice.

The first ten problems represent examples of application, the 11th introduces the development of a new box, whilst the 12th demonstrates in a detailed case the elaboration of the operating parameters.

The reader should already know that a box is an ALGOL procedure which can be only run as part of a program. This is the SIMUL master program, discussed in a later chapter.

In solving the following problems, we had to use the SIMUL master program. It is now sufficient for the reader to know the simple application rules of the SIMUL master program. We recommend that Sections 4.1 and 5.1.1 are read before the problems are tackled. This will enable the reader to understand the SIMUL formulation of the problem and to comprehend the printed results.

PROBLEM P.3.1 DISTILLATION

A mixed-phase mixture containing saturated normal hydrocarbons ($C_2 - C_6$) has to be separated so that the propane yield in the top product and the butane yield in the bottom product should be approximately 99.5 %.

The number of theoretical plates of the column is 20, the feed plate being the 10th plate. The controlled reflux rate is 6.82, and the reflux temperature is the bubble point. Condensation and reboiling are partial. Entering mass flow is 0.1 kmole/s, its temperature 381 K, the average column pressure 17×10^5 N/m^2.

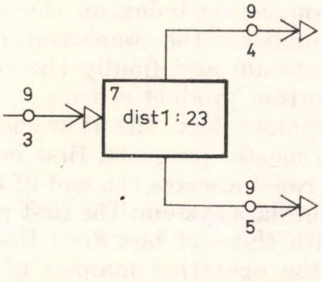
The composition of the feed entering the column is as follows: 3 mole % ethane, 20 mole % propane, 37 mole % butane, 35 mole % pentane, 5 mole % hexane.

Calculate the stream vectors of the top and bottom products, the heat load of the condenser and the reboiler, and the column efficiency.

Solution

Box *dist1* is used for the calculation.

The operation-order flow-sheet is the following:



The first row of the flow-sheet program (Table P.3.1 (1)) contains the denomination of the task in brackets. The job number figures in the second row which has no influence on the solution. The third row indicates that the declaration of the stream type follows. The fourth row contains in succession the denomination of the stream as a comment: a colon; the stream type index; and in parentheses separated by commas the component codes.

The + sign in the fifth row indicates that the enumeration of the stream types is complete.

Table P.3.1 (1)

Flow-sheet program and input data system of problem [dist1 : 23]

[dist1 : 23]
0123
stream type
hydrocarbon mixture :9(2,3,4,5,6)J
+
operation
distillation of
hydrocarbon mixture :23(7,3,−4,−5)
print :2(8)
stop :4(9)
+
data set number :1
controlled reflux
distillation :7(20,10,2,3,$61_{10}5$,1,2,1,
6.82,0,320,400,99.9,99.9,4*0)
print :8(6,3s,4s,5s, < 13 = 18 > e < 7 > b)
+
input stream :3(9,100_{10}−3,0,381,$17_{10}5$,0.13,
0.03,0.2,0.37,0.35,0.05)

The operations are enumerated in the second paragraph. Any comment relating to a box may be written before the colon followed by the box index, and a number sequence in parentheses. The first element is the operating index of the box which is followed by a list of the connection indices, whose sequence is specified by the box. In our case the comment consists of the box identifier with the number after the colon (:23) being the box index. The first number in parentheses designates the operating index. This is followed by the connection index on the connecting point of the input stream. The third number is the connection index on the connecting point of the top product stream and finally the connection index on the connecting point of the bottom product stream.

Besides the single equipment box, the flow-sheet program necessarily contains two boxes of the master program, first box *print*, then box *stop*.

The + sign in the next row indicates the end of the flow-sheet program. This is followed by the input data system. The first part contains the operating parameter vectors, with those of box *dist1* first. The comment before the colon now refers to the operating manner of the box. The colon is followed by the operating index, then the operating-parameter vector in parentheses. For their elements see the enumeration of the operating parameters in Section 3.4.9. This is followed by box *print:* the elements of its operating parameter vector are listed in Section 4.4.2.5. The enumeration of the operating parameter vectors is terminated by a + sign in the next row. The second part of the input data system refers to the input streams. The comment before the colon refers now to the entering position of the stream. The input data system is ended by sign +.

Table P.3.1 (2)

Calculation results of problem [disl : 23]

```
dist1: 23 −1
:        3s(   9.00000       ,    100.000  10− 3,    −8.64112 10+ 6,
             381.000         ,      1.70000  + 6,   166.766   10− 3,
              30.0000  10− 3,    200.000  10− 3,   370.000   10− 3,
             350.000   10− 3,     50.0000 10− 3)
:        4s(   9.00000       ,     23.0808 10− 3,    −1.52311 10+ 6,
             318.014         ,      1.70000 10+ 6,    1.00000        ,
             129.978   10− 3,    863.093  10− 3,     6.92832 10− 3,
               0.00000       ,      0.00000       )
:        5s(   9.00000       ,     76.9192  10− 3,   − 6.86183 10+ 6,
             406.052         ,      1.70000 10+ 6,    0.00000        ,
               0.00000       ,      1.02851 10− 3,   478.945   10− 3,
               0.00000       ,      1.02851 10− 3,
             455.023   10− 3,     65.0033  10− 3)
:     13e7b(   99.6044        )
:     14e7b(   99.5678        )
:     15e7b(  −2.05241 10+ 6)
:      16e7b(   2.30859 10+ 6)
:     17e7b(    6.82000        )
:     18e7b(  745.267   10− 3)
+
end dist1:23
```

The result of the calculation is presented in Table P.3.1 (2). The number before parentheses is the connection index. The data of the stream vector is found in sequence between the parentheses. After the input — top and bottom products — stream, some data of the column, i. e., some operating parameters of box *dist1* may be found. Their interpretation is contained in Section 3.4.9.

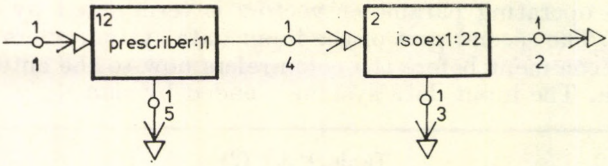
PROBLEM P.3.2 ISENTHALPIC EXPANSION

A liquid mixture, containing $C_3 - C_6$ normal hydrocarbons, whose pressure and temperatures are 30×10^5 N/m^2 and 339 K respectively passes through a pressure-control valve whereby its pressure is reduced to 10^5 N/m^2. The mass stream is 0.100 kmole/s, the mole fraction of the components: propane = 0.20, butane = 0.15, pentane = 0.15, hexane = 0.50.

Calculate the vapour ratio of the expanded mass stream and the data describing the phases.

Solution

The task may be solved by either box *isoex1* or box *vlexpa*. Selecting box *isoex1*, the operation-order flow-sheet is as follows:



Box *prescriber* is used to calculate the enthalpy of the entering stream, such that the user can print it.

The flow-sheet program and the results are presented in Tables P.3.2 (1), and P.3.2 (2) respectively. The data describing the gaseous phase are listed after 2s, those of the liquid phase after 3s.

We may observe that the sum of enthalpies of the two leaving streams (3e2s and 3e3s) equals the enthalpy of the entering stream (3e4s), proving that the operation is isenthalpic.

Table P.3.2 (1)

Flow-sheet program and input data system of problem [isoex1 : 22]

```
[isoex1:22]
1,22
stream type
C3−C6:1(3,4,5,6)
+
operation
prescriber:11(12,1,−4,−5)
isoex1:22(13,4,−2,−3)
print:2(14)
stop:4(15)
+
no:2
box
prescriber:12(0,104)
isoex1:13(1,1₁₀5,50₁₀5)
print:14(6,3e4s,2s,3s)
+
stream
C3−C6:1(0001,100₁₀3,0,339,30₁₀5,0,0.20,0.15,0.15,0.50)
+
```

Table P.3.2 (2)

Calculation results of problem [isoex1 : 22]

```
Isoex1:22  −2
:       3e4s(    −10.7940  ₁₀+ 6)
:         2s(      1.00000      ,         35.2219  ₁₀− 3,       −2.75469 ₁₀+ 6,
                 300.653        ,        100.000   ₁₀+ 3,        1.00000        ,
                 468.874   ₁₀− 3,        242.519   ₁₀− 3,      125.301   ₁₀− 3,
                 163.305   ₁₀− 3)
:         3s(      1.00000      ,         64.7781  ₁₀− 3,       −8.03919 ₁₀+ 6,
                 300.653        ,        100.000   ₁₀+ 3,        0.00000        ,
                  53.8055  ₁₀− 3,         99.6945  ₁₀− 3,      163.429   ₁₀− 3,
                 683.071   ₁₀− 3)
+
end  isoex1:22
```

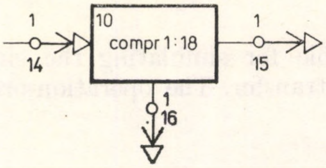
PROBLEM P.3.3 COMPRESSION

Air is needed at a pressure of 60×10^5 N/m² and temperature of 308 K. A three-stage piston compressor equipped with an after-cooler is available, whose intake pressure is 10^5 N/m². The mass stream of the inlet air (temperature 293 K) is 0.064×10^{-3} kmole/s. The compressor efficiency is 0.75.

Calculate the effective cooling performance to cool the compressed air to 308 K, and the required effective electric power.

Solution

The calculation is carried out by box *compr1.* The operation-order flow-sheet is the following:



The flow-sheet program and results are presented in Tables P.3.3 (1) and P.3.3 (2) respectively. Effective cooling performance 20e10b, effective electric power 17e10b.

Table P.3.3 (1)

Flow-sheet program and input data system of problem [comprl : 18]

```
[compr1:18]
1,18
stream type
air:1(64,72,70)
+
operations
compr:18(10,14,−15,−16)
print:2(30)
stop:4(31)
+
no:3
box
compr:10(3,60₁₀5,308,1,7×0,00,0,1,0,0.75,7×70)
print:3₀(6, <17 = 21 > e < 1₀ > b)
+
stream
air:14(0001,0.064₁₀ − 3,0,293,1.01₁₀5,1,0.2090,0.7814,0.0096)
+
```

Table P.3.3 (2)

Calculation results of problem [comprl : 18]

```
compr1:18  −3
: 17e 10b(    1.06763₁₀+  3)
: 18e 10b(    1.49394₁₀−  3)
: 19e 10b( 782.431         )
: 20e 10b(    1.06214₁₀+  3)
: 21e 10b(    3.90190      )
+
end compr1:18
```

PROBLEM P.3.4 CONDENSATION AND HEAT TRANSFER

A liquid mixture containing methane, ethylene and ethane, having temperature and pressure 265 K and 30 × 10^5 N/m^2 respectively, passes through a control valve and heat exchanger and flows in the liquid state with 4 × 10^5 N/m^2 pressure drop. The mass stream is 23 × 10^{-3} kmole/s, the mole fraction of the components in the sequence of their listing above: 0.85, 0.1498 and 0.0002.

Calculate the temperature of the saturated liquid leaving the heat exchanger and the heat load of the heat exchanger.

Solution

Box *vlexpa* is suitable for simulating the simultaneous modelling of condensation and heat transfer. The operation-order flow-sheet is the following:

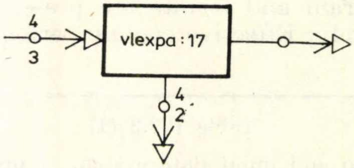


Table P.3.4 (1)

Flow-sheet program and input data system of problem [vlexpa : 17]

```
[vlexpa:17]
2,17
stream type
mix:4(1,26,2)
+
operation
vlexpa:17(3,3,−4,−2)
print:2(10)
stop:4(11)
+
no:4
box
vlexpa:3(3,0,205,26₁₀5,300,250,0,
        1,243,3.803,253,4.346,
        2,243,0.865,253,1.000,
        3,243,0.558,253,0.654)
print:10(6,2e2s,4e2s,5e2s,7e3b)
+
stream
mix:3(0004,23₁₀−3,0,265,3₁₀5,0,0.8500,0.1498,0.0002)
+
```

Table P.3.4 (1) contains the flow-sheet program and the input data system. Since *op1* = 3 and *op2* = 0 (the prescribed vapour ratio in the leaving stream is zero), *op7* contains the heat load required to reach the prescribed conditions after the calculation.

The number of operating parameters of box *vlexpa* is 7 + 4 × 5 because the vapour-liquid equilibrium coefficients are calculated by interpolation, using the stated K—T value-pairs.

Table P.3.4 (2) presents the results of the calculation.

Table P.3.4 (2)

Calculation results of problem [vlexpa : 17]

```
vlexpa:17 —4
: 2e  2s(     23.0000 10—  3)
: 4e  2s(   178.943          )
: 5e  2s(       2.60000 10+  6)
: 7e 3b(—234.531    10+  3)
+
end vlexpa: 17
```

The leaving stream is really a saturated liquid because 2e3s = 2e2s, temperature of the leaving liquid: 4e2s, calculated heat load: 7e3b.

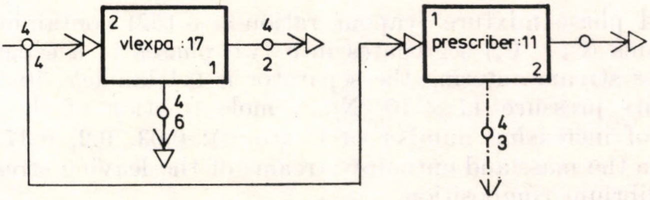
PROBLEM P.3.5 COOLING OF GAS MIXTURES

A gas mixture, at a pressure of 32×10^4 N/m^2 and a temperature of 253 K, consisting of hydrogen and methane, has to be cooled to 220 K. Mass stream: 30 mole/s, mole fraction of both components: 0.5.

Calculate the energy consumption of the cooler.

Solution

Since no phase change occurs during cooling, the task may be solved by either box *prescriber* or *vlexpa*. Both solutions will be demonstrated. The operation-order flow-sheet is as follows:



The flow-sheet program and results are presented in Tables P.3.5 (1) and P.3.5 (2). The power required for the cooling is contained in parameter 7 of box *vlexpa* and the 3rd element of the difference stream of box *prescriber* respectively.

Table P.3.5 (1)

Flow-sheet program and input data system of problem
[vlexpa : 17, presciber : 11]

```
[vlexpa:17,prescriber:11]
1,17
stream type
H2CH4:1(67,1)
+
operation
vlexpa:17(2,4,−5,−6)
prescriber:11(1,4,−2,−3)
print:2(3)
stop:4(4)
+
no:5
box
vlexpa:2(2,220,1,32₁₀5,250,200,0,
         1,200,30,300,80,
         2,213,1.75,361,7.187)
prescriber:1(220,004)
print:3(6,7e2b,3e3s,2e5s,4e5s,2e2s,4e2s)
+
stream
in:4(0001,30₁₀−3,0,253,32₁₀5,1,0.5,0,5)
+
```

Table P.3.5 (2)

Calculation results of problem [vlexpa : 17, presciber : 11]

```
vlexpa:17, prescriber:11 −5
: 7e 2b(−33.9414₁₀+ 3)
: 3e 3s(  33.9414₁₀+ 3)
: 2e 5s(  30.0000₁₀− 3)
: 4e 5s( 220.000       )
: 2e 2s(  30.0000₁₀− 3)
: 4e 2s( 220.000       )
+
end vlexpa:17, prescriber:11
```

PROBLEM P.3.6 SEPARATION

A mixed phase mixture (vapour ration = 0.152) containing saturated hydrocarbons ($C_2 - C_6$) segregates into two phases in a separator.

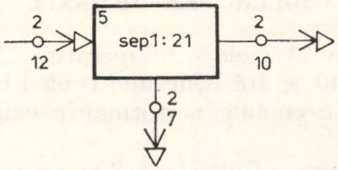
The mass stream entering the separator is 0.1 kmole/s, its temperature 380.4 K, its pressure 17×10^5 N/m^2, mole fraction of the components (in order of increasing number of C atoms): 0.03, 0.2, 0.37, 0.35, 0.05.

Calculate the mass and enthalpy streams of the leaving streams, further their equilibrium composition.

Solution

Boxes *balance*, *sep1*, *vlexpa* are suitable for solving the problem. We shall use box *sep1*.

The operation-order flow-sheet is the following:



The flow-sheet program is presented in Table P.3.6 (1). The number of operating parameters of box *sep1* is 3, because the vapour-liquid equilibrium is to be calculated with the approximating functions of the NGAA curves.

Table P.3.6 (1)

Flow-sheet program and input data system of problem [sepl : 21]

```
[sep1:21]
1,21
stream type
C2—C6:2(2,3,4,5,6)
+
operation
sep1:21(5,12,—10,—7)
print:2(6)
stop:4(7)
+
no:6
box
sep1:5(1,61₁₀5,0)
print:6(6,10s,7s)
+
stream
In:12(0002,100₁₀—3,1.1546₁₀6,380.4,17₁₀5,0.152,0.03,0.20,0.37,0.35,0.05)
+
```

The result is presented in Table P.3.6 (2). The data describing the gaseous phase leaving the separator are contained in 10s, those of the liquid phase in 7s.

Table P.3.6 (2)

Calculation results of problem [sepl : 21]

```
sep1:21  —6
:        10s(     2.00000          ,     15.0279  ₁₀— 3,    —1.03031 ₁₀+ 6,
               380.400             ,      1.70000 ₁₀+ 6,     1.00000        ,
                83.9715  ₁₀— 3,         347.340   ₁₀— 3,   366.484   ₁₀— 3,
               188.321   ₁₀— 3,          13.8831  ₁₀— 3)
:         7s(     2.00000          ,     84.9721  ₁₀— 3,    —7.64389 ₁₀+ 6,
               380.400             ,      1.70000 ₁₀+ 6,     0.00000        ,
                20.4548  ₁₀— 3,         173.942   ₁₀— 3,   370.622   ₁₀— 3,
               378.594   ₁₀— 3,          56.3875  ₁₀— 3)

+
end sep1:21
```

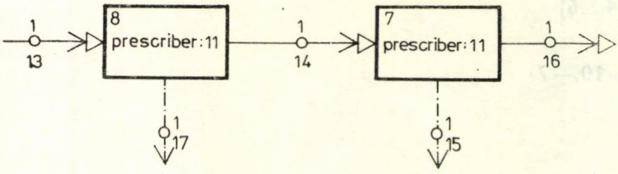
PROBLEM P.3.7 CALCULATION OF TEMPERATURE FROM KNOWN COOLING PERFORMANCE

Ethylene (mass stream 78 mole/s, temperature 313 K) was compressed from 5.5×10^5 N/m^2 to 40×10^5 N/m^2 and cooled in an after-cooler to the original temperature. The cooling performance calculated by box *compr1* was 457 000 J/s.

Calculate the temperature of ethylene leaving the compressor (entering the after-cooler).

Solution

The problem may be solved with box *prescriber* such that we prescribe the enthalpy of the mass stream leaving box *prescriber*. The box calculates the temperature pertaining to the prescribed enthalpy stream. The prescribed enthalpy stream is the sum of the enthalpy of the compressed and cooled mass stream plus the cooling power. The operation-order flow-sheet is the following:



The enthalpy of the entering stream is calculated by a separate box *prescriber*, because it is thus possible to print it.

Table P.3.7 (1)

Flow-sheet program and input data system of problem [prescriber : 11]

```
[prescriber:11]
1,11
stream type
ethylene:1(26)
+
operations
pres:11(8,13,−14,−17)
prescriber:11(7,14,−16,−15)
print:2(20)
stop:4(21)
+
no:7
box
prescriber:8(1,204)
prescriber:7(457₁₀3,103)
print:20(6,3e14s,3e16s,3e15s,4e16s)
+stream
gas:13(0001,78₁₀−3,0,313,40₁₀5,1,1)
+
```

Table P.3.7 (2)

Calculation results of problem [prescriber : 11]

```
prescriber:11  −7
: 3e 14s(      5.47512₁₀+ 6)
: 3e 16s(      5.93212₁₀+ 6)
: 3e 15s(−457.000   ₁₀+ 3)
: 4e 16s(  408.542          )
+
end prescriber:11
```

The flow-sheet program and the results are presented in Tables P.3.7 (1) and P.3.7 (2). Temperature of ethylene, entering the after-cooler: 4e16s.

PROBLEM P.3.8 DISTILLATION

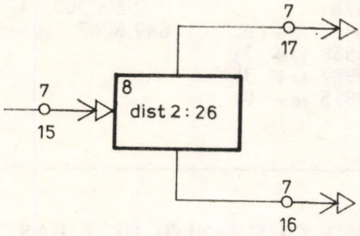
Ethylene, contaminated by methane and ethane has to be separated by distillation, such that the distillate stream should be 51×10^{-6} kmole/s from 23×10^{-3} kmole/s feed.

The column contains 21 plates, the feed plate being the fifth from above. The controlled reflux rate is 55, the condensation and reboiling is partial. The feed temperature is 256 K, average pressure in the column is 26×10^5 N/m^2. The mole fraction of ethane in the feed: 0.15, that of methane 0.00002.

Calculate the data describing the top and bottom product streams and the heat load of the condenser and reboiler.

Solution

The problem may be solved by either box *dist1* or *dist2*. In this example, box *dist2* has been used. The operation-order flow-sheet is the following:



The flow-sheet program and results are presented in Tables P.3.8 (1) and P.3.8 (2).

Heat load of the condenser: 64e8b

Heat load of the reboiler: 65e8b

Top product stream: 17s

Bottom product stream: 16s

Table P.3.8 (1)

Flow-sheet program and input data system of problem [dist2 : 26]

```
[dist2:26]
1,26
stream type
MEE:7(1,26,2)
+
operation
dist2:26(8,15,−17,−16)
print:2(10)
stop:4(11)
+
no:8
box

dist2:8(21,5,51 10−6,55,25,0,0,2,1 10−6,1,256,253,21×0,258,
      3×0,3×0,22×0,4×0,
      1,243.2,3.808,253.2,4.346,
      2,243.2,0.865,253.2,1.000,
      3,243.2,0.558,253.2,0.654)
print:10(7,15s,17s,16s,64e8b,65e8b,66e8b)
+
stream
in:15(0007,23 10−3,0,256,26 10 5,0,2 10−5,0.84998,0.15000)
+
```

Table P.3.8 (2)

Calculation results of problem [dist2 : 26]

```
dist2:26  −8
:          15s(     7.000000        ,      23.00000 10− 3,        0.000000      ,
                  256.0000          ,       2.600000 10+ 6,        0.000000      ,
                    20.00000 10− 6,      849.9800  10− 3,      150.0000  10− 3)
:          17s(     7.000000        ,      51.00000 10− 6,        3.317089 10+ 3,
                  253.5041          ,       2.600000 10+ 6,        1.000000      ,
                     4.085854 10− 3,     981.9396  10− 3,       13.97456 10− 3)
:          16s(     7.000000        ,      22.94900 10− 3,      916.6893  10+ 3,
                  257.0516          ,       2.600000 10+ 6,        0.000000      ,
                    10.96437 10− 6,      849.6867  10− 3,      150.3023  10− 3)
:        64e8b(   −22.83558 10+ 3)
:        65e8b(    25.69987 10+ 3)
:        66e8b(    31.20815 10− 9)
+
end  dist2:26
```

PROBLEM P.3.9 HEATING OF A GAS MIXTURE

We intend to heat a gas mixture (temperature 323 K, pressure 40×10^5 N/m^2), containing light hydrocarbons, in a counter-current, one-pass, heat exchanger with water. The water is flowing in the shell side, the gas mixture in the tubes.

The heat transfer area is 198 m^2 , the thermal resistance of the wall 86×10^{-6} sm^{2}K/J, and the scale resistance 0.4×10^{-3} sm^{2}K/J.

The following reference data are known:

	tube side	shell side
mass stream, kmole/s	0.12	0.06
heat transfer coefficient, J/m²sK	886	735
pressure drop, N/m²	0.02×10^5	0.01×10^5

The two entering mass streams are known:

	water	gas mixture
mass stream, kmole/s	57×10^{-3}	118×10^{-3}
temperature, K	413	323
pressure, N/m²	6×10^5	40×10^5

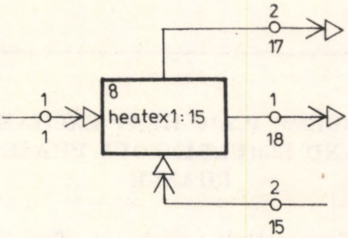
Composition, mole fractions

water	1	—
methane	—	0.56
ethylene	—	0.29
ethane	—	0.05
propylene	—	0.06
propane	—	0.00
n-butane	—	0.02
n-pentane	—	0.00

Calculate the temperature of the leaving streams and the heat load.

Solution

The solution of the problem is presented in box *heatex1*. The operation-order flow-sheet is the following:



The flow-sheet program and the results are presented in Tables P.3.9 (1) and P.3.9 (2):

temperature of the leaving water: 4e17s
temperature of the leaving gas mixture: 4e18s
heat load: 12e8b

Table P.3.9 (1)

Flow-sheet program and input data system of problem [heatex1 : 15]

```
[heatex1:15]
1,15
stream types
gas:1(1,26,2,27,3,4,5)
water:2(69)
+
operations
heatex1:15(8,−17,15,−18,1)
print:2(50)
stop:4(51)
+
no:9
box
heatex:8(2,1,198,0.06,0.12,735,886,0.01₁₀5,0.02₁₀5,86₁₀−6,0.4₁₀−3,0)
print:50(6,18s,17s,12e8b)
+
streams
gas:1(0001,118₁₀−3,0,323,40₁₀5,1,
     0.562,0.296,0.053,0.065,0.003,0.020,0.001)
water:15(0002,57₁₀−3,0,413,6₁₀5,0,1)
+
```

Table P.3.9 (2)

Calculation results of problem [heatex1 : 15]

```
heatex1:15  −9
:        18s(      1.00000         ,      118.000  ₁₀− 3,     −1.33005 ₁₀+ 6,
                 363.391           ,        3.99806 ₁₀+ 6,      1.00000         ,
                 562.000   ₁₀− 3,         296.000  ₁₀− 3,      53.0000  ₁₀− 3,
                  65.0000  ₁₀− 3,           3.00000 ₁₀− 3,      20.0000  ₁₀− 3,
                   1.00000 ₁₀− 3)
:        17s(      2.00000         ,       57.0000  ₁₀− 3,    −15.1663  ₁₀+ 6,
                 383.728           ,      599.093  ₁₀+ 3,       0.00000         ,
                   1.00000         )
:      12e8b(  −150.669    ₁₀+ 3)
+
end heatex1:15
```

PROBLEM P.3.10 HEAT EXCHANGE AND SIMULTANEOUS PHASE CHANGE

The bottom product of the ethylene column of an ethylene plant is ethane. In order to save energy, 70 % of this bottom product is recycled to a counter-current, one-pass, tube heat exchanger in which hydrocarbon gas mixture (temperature 293 K, pressure 4×10^5) flows on the shell side. The aim is to cool this gas mixture.

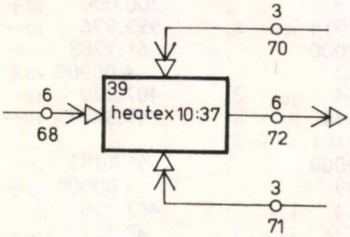
The bottom product and the gas to be cooled are described by the following data:

	bottom product	**gas mixture**
mass flow, kmole/s	0.0020162	0.0611283
temperature, K	196.773	293.16
pressure, N/m^2	2×10^5	40×10^5
Composition, mole fractions		
hydrogen	—	0.1950
methane	—	0.4072
ethylene	0.0001	0.2920
ethane	0.9999	0.0515
propylene	—	0.0494
propane	—	0.0023
butadiene	—	0.0026

Calculate the temperature of the streams leaving the heat exchanger.

Solution

The bottom product used as cooling medium is a saturated liquid. Therefore, a phase change — boiling — is bound to occur on the tube side during cooling. Box *heatex10* is therefore suitable for simulating the operation. The operation-order flow-sheet is the following:



The functioning of box *heatex10* is prescribed in the following manner:

op16 = 11, meaning that there is forced convection without phase change on the shell side and the dew point is the limiting temperature.
op17 = 20, meaning that there is boiling on the tube side and the boiling point is the limiting temperature.

We have stated the heat-transfer area of the equipment and the initial values of the reference data.

The flow-sheet program and the results are presented in Tables P.3.10 (1) and P.3.10 (2).

Temperature of the leaving ethane: 4e71s,
temperature of the cooled hydrocarbon mixture: 4e72s.

Table P.3.10 (1)

Flow-sheet program and input data system of problem [heatex10 : 37]

```
[heatex10:37]
1,37
stream type
gas:3(67,1,26,2,27,3,48)
ethane:6(26,2)
+
operation
heatex10:37(39,−71,70,−72,68)
print:2(40)
stop:4(41)
+
no:10
box
heatex10:39(11×0,1,1,0,0.05⏨−3,11,20,0.1,−1,−1,
        0,100,5×0,1500,3⏨4,2×0,100,3⏨4,2×0,
        1500,10,7×0)
print:40(6,68s,70s,71s,72s,40e39b,39e39b)
+
stream
gas:70(0003,61.1283⏨−3,0,293.16,40⏨5,1,194.954⏨−3,407.229⏨−3,
     292.013⏨−3,51.4644⏨−3,49.3774⏨−3,2.31974⏨−3,2.64181⏨−3)
ethane:68(0006,2.20162⏨−3,0,196.773,2⏨5,0,4.34914⏨−6,999.996⏨−3)
+
```

Table P.3.10 (2)

Calculation results of problem [heatex10 : 37]

```
heatex10:37  −10
:        68s(      6.00000        ,          2.20162 ⏨− 3,     −169.122    ⏨+ 3,
                 196.773          ,        200.000   ⏨+ 3,        0.00000       ,
                   4.31914 ⏨−  6,        999.996   ⏨− 3)
:        70s(      3.00000        ,         61.1283  ⏨− 3,        0.00000       ,
                 293.160          ,          4.00000 ⏨+ 6,        1.00000       ,
                 194.954   ⏨−  3,        407.229   ⏨− 3,      292.013    ⏨− 3,
                  51.4644  ⏨−  3,         49.3774  ⏨− 3,        2.31974  ⏨− 3,
                   2.64181 ⏨−  3)
:        71s(      3.00000        ,         61.1283  ⏨− 3,     −169.797    ⏨+ 3,
                 279.409          ,          4.00000 ⏨+ 6,        1.00000       ,
                 194.954   ⏨−  3,        407.229   ⏨− 3,      292.013    ⏨− 3,
                  51.4644  ⏨−  3,         49.3774  ⏨− 3,        2.31974  ⏨− 3,
                   2.64181 ⏨−  3)
:        72s(      6.00000        ,          2.20102 ⏨− 3,     −128.680    ⏨+ 3,
                 275.693          ,        200.000   ⏨+ 3,        1.00000       ,
                   4.34914 ⏨−  6,        999.996   ⏨− 3)
:        40e39b(  40.4424  ⏨+  3)
:        39e39b(  97.1764         )
+
end heatex 10:37
```

PROBLEM P.3.11 THEORETICAL FLAME TEMPERATURE

Develop a box which calculates the theoretical flame temperature of a fuel gas, which is defined by the air excess coefficient as operating parameter.

Use this box to calculate the air stream necessary to burn the fuel gas specified below, with 20 % air excess, and calculate the stream vector of the flue gas.

The data of the fuel gas and air streams are as follows:

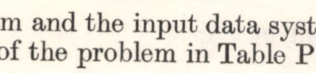
		fuel gas	**air**
molal flow	kmole/s	14.696	
temperature	K	313	313
pressure	N/m^2	101×10^3	101×10^3
Composition, mole fractions			
methane		0.60615	
ethylene		0.10174	
carbon monoxide		0.16998	
carbon dioxide		0.083644	
hydrogen		0.038486	

Solution

Let us choose the identifier of the box, calculating the theoretical flame temperature as *flame*, box index: 47. We suppose that the burning is perfect, i. e., the carbon content of any component in the fuel gas appears as carbon dioxide, and the hydrogen content as water vapour in the flue gas. The description of the stoichiometry of burning is restricted to the following components: methane, ethylene, carbon monoxide, carbon dioxide, hydrogen. The product of the vectors of the component streams of the fuel gas and the [A] atom-matrix is a vector, whose elements are the component streams of the flue gas — when burning without air excess — in the following sequence: carbon dioxide, water, oxygen, nitrogen. From this — based on a given air excess — both the air stream used for burning, and the actual component streams of the flue gas may be calculated:

$$[A] = \begin{array}{c|c|c|c|c|l} CH_4 & C_2H_4 & CO & CO_2 & H_2 & \\ \hline 1 & 2 & 1 & 1 & & CO_2 \\ 2 & 2 & & & 1 & H_2O \\ 2 & 3 & 0.5 & & 0.5 & O_2 \\ 7.5 & 11.25 & 1.875 & & 1.875 & N_2 \end{array}$$

The enthalpy stream of air can be calculated by procedure *enth.* After calculating the mole flow and the enthalpy stream of the leaving flue gas, the flame temperature can be calculated with procedure *temp.* The commented ALGOL description of procedure *flame* is presented in Table P.3.11 (1). The box is specified in Table P.3.11 (2). The second part of the problem is solved with box *flame.* The operation-order flow-sheet is the following:



The flow-sheet program and the input data system are presented in Table P.3.11 (3), the solution of the problem in Table P.3.11 (4).

Table P.3.11 (1)

```
procedure flame(mi,a,b);
real mi,a,b;
begin
  integer i,i1,j,mo,k;
  real c,c1,c2,c3,wa,ha,ta,pa,va;
  array A[1:4,1:5],P[1:9],za,K[1:5],zb,T[1:4],
    cb[1:4,1:13];
  comment
  error message if the number of components in the entering stream differs from five
  or if the number of operating parameters differs from nine;
  if size(a) = 11vsize(mi) ≠ 9 then
  errc (≮ flame ≯);
  comment
  calling the input stream vector;
  str from drum(a,j,wa,ha,ta,pa,va,za);
  comment
  calling the operating parameter vector;
  op from drum(mi,1,9,P);
  comment
  filling the stoichiometric matrix. The a[i,j] element of the matrix indicates how much
  mole component i result in the flue gas from one mole of component j when burning
  without air excess;
  A[1,1]: = A[1,3]: = A[1,4]: = A[2,5]: = 1;
  A[1,5]: = 0:
  A[1,2]: = 2;
  A[3,2]: = 3;
  A[3,3]: = 0.5;
  A[4,1]: = 7.5;
  A[4,2]: = 11.25
  A[4,3]: = A[4,5]: = 1.875;
  comment
  preparation of the vector containing the component streams of the flue gas;
  for i: = 1,2,3,4,5 do
  K[i]: = za[i]xwa;
  comment
  multiplying the stoichiometric matrix by the vector of the component streams.
  Result in vector T;
  for i: = 1,2,3,4 do
  begin
    c: = 0;
    for i1: = 1,2,3,4,5 do
    c: = c + A[i,i1]×K[i1];
    T[i]: = c;
  end i;
  comment
  multiplying factor, considering the air excess factor;
  c3: = 1 + 10 − 2×P[1];
  comment
  calculation of the air requirement and positioning in the seventh operating param-
  eter;
  P[7]: = T[3] + T[4]×c3;
  comment
  calculation of the molal enthalpy of oxygen on the temperature of the entering air;
  zero(4,zb,1);
  zb[1]: = 1;
  j: = −abs P[9];
  c1: = enth(j,P[3],pa,va,zb,4,true,cb);
  comment
```

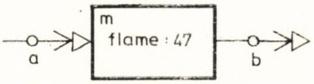
Table P.3. 11 (1) (cont.)

```
calculation of the molal enthalpy of nitrogen on the temperature of the entering
air;
zero(4,zb,1);
zb[4]: = 1;
c2: = enth(j,P[3],pa,va,zb,4,true,cb);
comment
enthalpy of the entering air;
P[8]: = (T[3]×c1 + T[4]×c2)×c3;
comment
the output flue-gas stream;
wa: = T[1] + T[2] + (c3−1)×T[3] + c3×T[4];
comment
the output enthalpy stream;
ha: = ha + P[8];
comment
pressure of the output gas;
pa: = ₁₀5;
comment
state of the output gas;
va: = 1;
comment
mole fraction calculation of CO2,H2O,O2,N2 in the flue gas;
zb[1]: = (c3 − 1)×T[3]/wa;
zb[2]: = T[2]/wa;
zb[3]: = T[1]/wa;
zb[4]: = T[4]×c3/wa;
comment
suggested initial temperature for procedure temp;
ta: = P[2];
comment
calculation of flue-gas temperature with procedure temp;
ta: = temp(j,ha/wa,ta,pa,va,zb,4,true,cb);
comment
output of the modified operating parameter vector;
op to drum(mi,1,9,P);
comment
output of the leaving stream vector;
str to drum
end
flame box;
finis
```

Table P.3.11 (2)

Model of burning of a fuel gas with five components *(flame)*

Box *flame* is suitable for simulating the complete burning of a fuel gas consisting of five components with any air excess.
The graphic symbol of the box:



Description of the operation:
flame: 47 *(m, a, b)*
The entering fuel gas *a* leaves at *b* as flue gas.
The flue gas consists of four components.

Table P.3.11 (2) (cont.)

The box is suitable for calculating the flame temperature, taking the prescribed air excess factor into consideration. It is not possible to consider radiation losses or other type of heat transfer.

Limits of application.

The box can be used if

— the fuel gas contains the following components: methane, ethylene, carbon monoxide, carbon dioxide, hydrogen,

— the operation proceeds at atmospheric pressure,

— the burning is complete, i. e., the flue gas contains only the following components: carbon dioxide, water, oxygen, nitrogen.

Operating parameters:

Denomination	Number	Value, signification
op1	1	air-excess factor to be stated in %.
op2	1	estimated value of the flame temperature
op3	1	air temperature
op4	1	working cell. *op4* = 0
op5	1	working cell. *op5* = 3.85
op6	1	working cell. *op6* = 0
op7	1	Mass stream of air. Obtains its value during calculation, initial value *op7* = 0.
op8	1	Enthalpy stream of air. Obtains its value during calculation, initial value *op8* = 0.
op9	1	Stream type code of flue gas. *op9* = 5. This means that the flue gas: 5(70,69,64,72) must be declared among the streams.

Number of operating parameters: 9.

Check: The box prints an error message if the number of components of the fuel gas differs from five, or the number of operating parameters differs from nine.

Table P.3.11 (3)

Flow-sheet program and input data system of problem [Theoretical flame temperature]

```
[Theoretical flame temperature]
A 770405
streams
fuel gas: 4 (1, 26, 71, 70, 67)
flue gas: 5 (70, 69, 64, 72)
+
Operations
flame: 47 (1,1, −3)
print: 4 (2)
stop: 2 (3)
+
no: 11
box
flame: 1(20,1350, 313, 0, 3.85, 0,0,0, 5)
print: 2 (5,1s, 3s,1b)
+
stream
fuel gas: 1(4, 14.696, 0, 313, 101₁₀3, 1, 0.60615,
            0.10174, 0.16998, 0.083644, 0.038485)
+
```

Table P.3.11 (4)

Calculation results of problem [Theoretical flame temperature]

```
Theoretical flame temperature —11
:         1s(     4.000          ,     14.696           ,      —1.1255  10+ 9,
                313.00           ,    101.00    10+ 3,         1.0000       ,
                606.15   10— 3,       101.74    10— 3,       169.98   10— 3,
                 83.644  10— 3,        38.486   10— 3)
:         3s(   —5.000           ,    149.01            ,    110.43   10+ 6,
                  2.1684 10+ 3,       100.00    10+ 3,         1.0000       ,
                 31.988  10— 3,       143.42    10— 3,       104.86   10— 3,
                719.73   10— 3)
:         1b(    20.000          ,      1.3500  10+ 3,       313.00         ,
                  2.0000         ,      3.8000          ,      0.           ,
                135.85           ,      1.2359  10+ 9,         5.0000       )
+
end Theoretical flame temperature
```

PROBLEM P.3.12 TUBE REACTOR

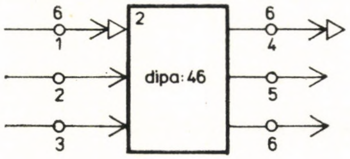
Acetone, preheated to 468 K, is pyrolyzed in a tube reactor. In the main reaction, ketene and methane are formed. This is accompanied by a side reaction producing carbon monoxide, carbon dioxide and hydrogen. The primary product, the ketene, decomposes in a further reaction to carbon monoxide and ethylene.

The length of the reactor is 66 m, its area 0.3194 m^2/m. The tube reactor is placed in the radiation zone (temperature 1020 K) of a furnace. The acetone feed is 1.053×10^{-2} kmole/s.

Calculate the stream vector at the exit of the tube reactor.

Solution

Box *dipa* is used to solve this problem. The operation-order flow-sheet is as follows:



The most important feature of using box *dipa* is the elaboration of the operating-parameter vector.

This is demonstrated now;

	The first ten operating parameters are zero	10 × 0,
op010	lower bound of integration	0,

op011	upper bound of integration	66,
op012	accuracy of integration	10^{-3},
op013	accuracy of temperature (exit condition)	2,
op014	Allowed minimal value of selected component streams (exit condition)	10^{-4},
op015	Suggested initial step length of integration	1,
op016	There is chemical reaction, the maximal number of components on the left-hand side of the reactions	2,
op017	Maximal component number on the rigth-hand side of the reactions	3,
op100	Number which characterizes the 1st phase to be found from the following search	2.

	Question	Answer
16	Is component transfer between the 1st and 2nd streams?	No
8	Is phase change between the 1st and 2nd streams?	No
4	Is heat transfer between the 1st and 2nd and/or the 3rd stream?	No
2	Is the 1st stream in thermal connection through a wall with its radiation zone?	Yes
1	Is heat transfer between the 1st stream and its constant temperature wall?	No

Now we can continue to elaborate the operating parameters related to the 1st stream:

op101	Flow direction is the x-axis direction	1,
op102	Cross section of the 1st stream	4.56×10^{-3},
op103	Pressure drop per meter of the 1st stream in the flow direction	-1591,
op104	Max. allowed temperature of the 1st stream	1500,
op105	Serial number of the selected component of the 1st phase in the stream vector	1,
op106	Number of chemical reactions in the 1st stream	3.

These three reactions are now described:

First reaction

acetone → ketene + methane

Stoichiometric number of acetone	1,
Serial number of acetone in the stream vector	1,
Reaction order with respect to acetone	1,
Stoichiometric number of the second reacting component	0,

Pre-exponential coefficient of the reaction	8.2×10^{14},
Activation energy of the reaction (with negative sign)	-2.85×10^{8}
Stoichiometric number of ketene	1,
Serial number of ketene in the stream vector	2,
Stoichiometric number of methane	1,
Serial number of methane in the stream vector	3,
Stoichiometric number of the third product	0.

The number sequences characterizing the second and third reactions are similarly assembled:

2,2,2,0,8, 2×10^{14}, -2.85×10^{8}, 1,4,2,5,0
1,1,1,0,8, 2×10^{13}, -2.85×10^{8}, 1,5,1,6,2,7,0,

op200	The 2nd stream does not exist, therefore and to be continued at L3	-1,
op300	The 3rd stream does not exist, therefore and to be continued at L4	-1,
	No component transfer, therefore to be continued at L5	
	No evaporation, therefore to be continued at L6	
	The 1st stream has no thermal interrelation with the 2nd and 3rd streams, therefore to be continued at L8	
	The 3rd stream has no thermal interrelation with the 2nd stream, therefore to be continued at L9	
	The 1st stream is in thermal relation with the radiation zone, therefore	
op108	Temperature of the radiating zone	1020,
op109	Heat transfer area per meter	0.3194,
op110	Radiation coefficient, to be continued at L11	4,
op112	Heat transfer area per meter	0.1394,
op113	Heat transfer coefficient between the wall and the 1st stream	550.

The flow-sheet program and input data system are presented in Table P.3.12 (1), the result in Table P.3.12 (2). Output stream vector: 4s

Table P.3.12 (1)

Flow-sheet program and input data system of problem [Tube reactor]

```
[Tube reactor]
A 770314
stream type
pyrolysis gas: 6(117, 114, 1, 26, 71, 70, 67)
+
operations
dipa: 46(2,1,2,3 −4, −5, −6)
print: 2 (4)
stop: 4 (9)
+

data set number: 12
operating parameters of boxes
dipa: 2(10−O, 0, 66, ₁₀−3, 2, ₁₀−4, 1,2,3,2,
         1,4.56₁₀−3, −1591, 1500, 1,3,
         1,1,1,0,8.2₁₀−14, −2.85₁₀8, 1,2,1,3,0,
         2,2,2,0,8.2₁₀14, − 2.85₁₀8, 1,4,1,5,0,
         1,1,1,0, 8.2₁₀13, −2.85₁₀8, 1,5,1,6,2,7,0,
         −1,−1, 1020, 0.3194, 4, 0.3194, 550)
print: 4 (5, 1s, 4s)
+
stream
acetone: 1(6,1.053, 0, 468, 3₁₀5, 1,1, 6×0)
+
```

Table P.3.12 (2)

Calculation results of problem [Tube reactor]

```
Tube reactor −12
:        1s(   6.0000           ,    10.530  ₁₀− 3,       0.0000        ,
              468.00            ,   300.00   ₁₀+ 3,       1.0000        ,
               1.0000           ,     0.0000       ,      0.0000        ,
               0.0000           ,     0.0000       ,      0.0000        ,
               0.0000           )
:        4s(   6.0000           ,    14.821  ₁₀− 3,    −826.68   ₁₀+ 3,
               1.0016   ₁₀+ 3,      194.99   ₁₀+ 3,       1.0000        ,
              465.69    ₁₀− 3,      222.15   ₁₀− 3,     222.55   ₁₀− 3,
              195.83    ₁₀− 6,       22.646  ₁₀− 3,      22.255  ₁₀− 3,
               44.509   ₁₀− 3)

+
end Tube reactor
```

CHAPTER 4

NETWORK

4.1 THE NETWORK OF COMPLEX OPERATIONS

The complex operation consists of interconnected elements, representing a system. Information and streams flow through the interconnections. To define a complex operation besides specifying the stream types and enumerating stationary functioning elements (simple or complex operations or boxes) and their operating parameters, we must also declare the interconnection mode of the elements, i. e., the network of material and information streams of the complex operation must be described. This is easily solved by means of connection indices.

The circles situated in the arrows of the block diagram are numbered in any sequence for this purpose, these numbers are termed connection indices. The connection index has to be written under the circle, as the stream-type index is positioned above. Each circle is simultaneously the connecting point of an output stream of a box and the input stream of another box. Consider Figure 4.1 as an example. In this case, the connecting point with connection index 6 is connected to box *stoech2 : 29* with operating index 11 and connecting point *b*, and also to box *mixing : 13* with operating index 40 and connecting point *a*. This type of interconnection is described thus:

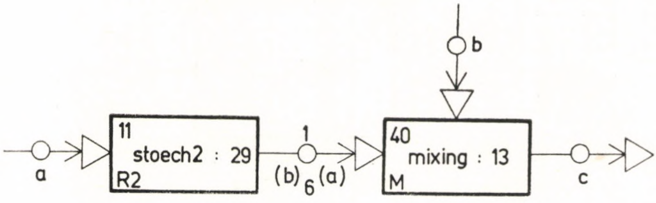


Fig. 4.1. Designation of the connecting points

stoech2 : 29 (11, a, – 6)
mixing : 13 (40, 6, b, c).

It may be observed that the connection index figures at the place of the connecting points, and has a positive sign if the stream enters the box, and negative if it leaves the box. If this is then carried out, then the network is described from the point of view of material streams, and all streams passing a connecting point are enumerated at the same time.

We wish to describe the network of butane isomerization with respect to the information streams, and must thus define the terms, and reference and arithmetic expressions.

In Chapter 3.1. we discussed the fact that box *stoech2* calculating the reactor requires the conversion as an operating parameter. The value of the conversion is unknown when starting the calculation, and no other box calculates it. Nevertheless, as the calculation starts with box *stoech2*, the values of mass flows w_l and w_K are available and the conversion may be calculated from these using equation (3.1). In this case, equation (3.1) may be presented as an arithmetic expression and reference must be made to it among the operating parameters at the conversion site. The reference results in calculating the conversion before the box starts to work, and this enables box *stoech2* to calculate the data of the mass flow leaving the reactor.

The arithmetic expression is therefore not an independent box, but just an additional instrument, enabling us to define in the form of formulae the input data of a box which is interconnected to the operating parameters or the stream vector of another box by means of information streams. The arithmetic expression is defined among the operating parameter vectors and therefore yields an operating index. This index appears in the relevant reference.

The arithmetic expression is presented as a rectangle in Figure 4.2. It is attached to the symbol of box *stoech2*, since the expression is used during the functioning of box *stoech2*. The arithmetic expression receives one input information stream whose value is the independent variable w_1. But w_1 is the second element of the stream vector passing through the point with connection index 1. (It should be remembered that the mass velocity is the second element of the stream vector.) It is therefore sufficient to refer directly in the arithmetic expression to the following symbol instead of w_1 *: 2els*, indicating that it is the second element of the stream, passing through the first connecting point.

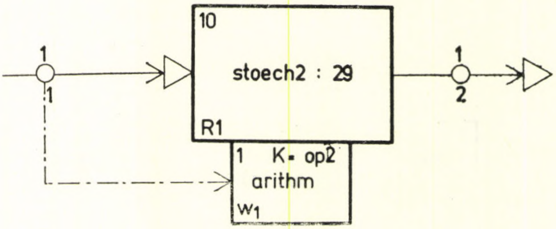
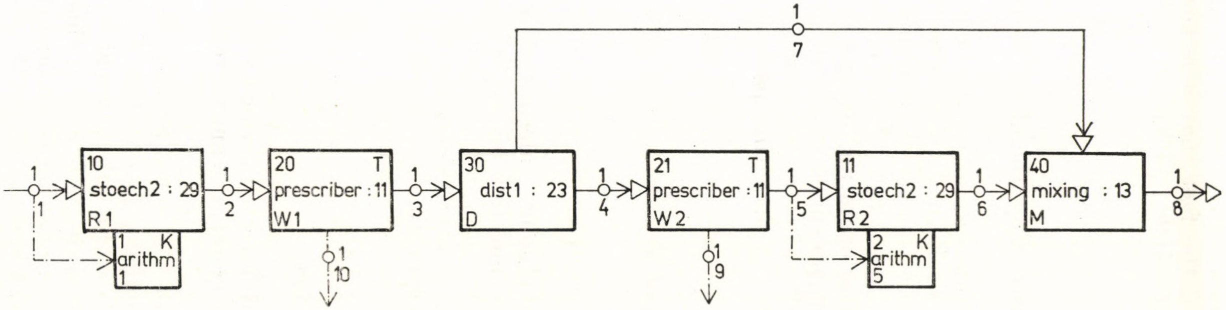


Fig. 4.2. Graphic symbol of the arithmetic expression

The value w_k of the catalyst stream, needed to calculate the conversion, is written directly into the arithmetic expression. In the rectangle representing the arithmetic expression, the operating index figures in the upper left-hand corner and the value of the input information in the lower left-hand corner. Since one of the two independent variables of the arithmetic



Operations

stoech2 : 29(10, 1,-2)
prescriber : 11(20, 2,-3,-10)
dist1 : 23(30, 3,-7,-4)
prescriber : 11(21, 4,-5,-9)
stoech2 : 29(11, 5,-6)
mixing : 13(40, 6, 7,-8)

Operating parameters of the boxes

prescriber : 20(T1, 004)
prescriber : 21(T2, 004)
arithm : 1(...2e1s...)
arithm : 2(...2e5s...)
stoech2 : 10(op1, 1b, op3, . . . , op7)
stoech2 : 11(op1, 2b, op3, . . . , op7)
dist1 : 30(op1, op2, . . . , op18)
mixing : 40(op1)

Fig. 4.3. New block diagram of the butane isomerization

expression is defined by reference, the other directly, the calculation can be carried out. The result of the arithmetic expression with operating index 1 is referred to by reference *1b* and the fact that it is the second operating parameter of box *stoech2* (operating index 10) has to be described in the following manner:

stoech2 :10 (. . . , 1b, ...).

The network of the information streams may therefore be described by references.

Consequently carrying out these instructions, we arrive at the new block diagram of butane isomerization (Fig. 4.3). Formal parameters are seen on this figure, in the first column the boxes, their identifiers and indices, operating indices and connecting indices, in the second column the symbols of the arithmetic expressions and the operating parameters of the boxes. We shall handle the arithmetic expressions in detail in Section 5.2.1 (c). The information network is specified by the references, featuring in the arithmetic expressions and among the operating parameters.

4.2 TERMINOLOGY

4.2.1 CONNECTION INDEX

The connection index is an integer whose absolute value serves to identify the connecting points formed by the interconnection of two boxes and the streams passing through them.

The connection index in the operational declaration of the box is positive if the stream passing the given connecting point is the input of the box, and negative if the stream is the output.

4.2.2 REFERENCE

A declaration consisting of numbers and letters is termed the reference, which identifies the operating parameter vectors, stream vectors and their elements figuring in the calculation.

The operating and connection indices of the boxes are also references, although they are defined by integer numbers, in order to simplify the description. It is to be noted that on the place of a value, to which reference has been made, another reference may be positioned, and in this manner reference chains of any length may originate. Care has to be taken to break this chain, to avoid the formation of closed loops, because the organizing program does not carry out any control in this respect.

4.2.3 ARITHMETIC EXPRESSIONS

Arithmetic expressions are constituted from references and numbers using the four basic arithmetic processes and elementary functions. The indication of the arithmetic expression is effected in the so-called reversed Polish system of notation (see, Section 5.2.1 (c)). In the input data system of the simulation the arithmetic expression has to be specified as an operating parameter vector. The result of the expression is represented by a reference, referring to this operating parameter vector.

The arithmetic expressions may refer to other arithmetic expressions. According to the definition given above the arithmetic expression is analogous to the unconditional arithmetic expression defined in the ALGOL-report (ed. by Naur, 1964).

4.3 NUMBERING OF THE CONNECTING INDICES AND THE OPERATING PARAMETER VECTORS

As regards the connection indices and operating indices there is no restriction. (There is one exception when using arithmetic expressions, see, Section 5.2.3.1). Thus the possibility of compliance with technological conventions is guaranteed.

The organizing program of the SIMUL system reserves the necessary storage space in the background store conforming with the stream vectors, denoted different connection indices. In order to save storage space, it is permissible to use the same connection index several times. In this case, the ultimately calculated stream vector is coordinated with the connection index.

Proceeding in this manner, the connection indices are insufficient to describe the network unequivocally, and the sequence of calculation is also needed for this purpose.

"Unused" indices cause each one of the cells of the background store to remain unutilized (see, Section 8.2.1.2).

4.4 MATHEMATICAL AND ORGANIZING PROCEDURES, BOXES

Simulating complex operations not only demands the simulation of individual elements but also requires the fulfillment of conditions arising on the one hand from the recycling in the system and on the other hand from requirements which cannot be specified with the input stream vectors or the operating parameters (e. g., the process control securing a prescribed type of process performance). Such problems may arise during the designing of a box or when using the available box for modelling. Therefore, standard mathematical procedures are available for box composers, and mathematical boxes for the users of the SIMUL system. Similarly, organizing procedures and organizing boxes are available for solving organizational tasks.

4.4.1 STANDARD PROCEDURES

The organizing program contains the following global procedures which are also available for the organizing program and all boxes.

4.4.1.1 DATA TRANSFER PROCEDURES

To place the operating parameters, and the relevant stream vectors of a box from the background store into the declared arrays, the procedures *op from drum* and *str from drum* are available. It is unnecessary to describe these in detail, as they act in the same way for the box, as an input procedure does for an independent program. These procedures also search for those data which have been defined by references or reference chains, and they carry out the evaluation of the arithmetic expressions which may exist. Procedure *str from drum* calculates the enthalpy stream not included in the input data system of the stream vectors (see, Section 2.2.5.3).

A separate procedure — *cpp from drum* — serves to call the basic property values from the background store. This procedure places constants of components defined by the stream type into the declared array of the box. It is an auxiliary procedure of the procedures calculating properties. The procedure *cpp from drum* is not generally used directly by the boxes.

The stream vectors and operating parameters calculated by the boxes are placed into the background store by means of procedures *str to drum* and *op to drum*. These output procedures correspond to the input procedures with the exception that they do not consider the references. It follows that — with the exception of a few organizing boxes — the boxes only modify the contents of their respective arrays, independently of whether they contained numbers or references.

If a box calculates a stream vector which has not yet been defined, then procedure *str to drum* simultaneously defines the place of this stream vector in the background store and the reference needed to find this stream vector. This reference is included in the reference list (see, Section 8.2.1.2).

4.4.1.2 MATHEMATICAL PROCEDURES

During development of the SIMUL system, mathematical procedures have been elaborated on the basis of procedures of companies Regnecentralen and Haldor Topsøe Chemical Engineers.

(a) Solution of simultaneous systems of linear equations

matrdiv (A, n, B, l, sing)

Procedure *matrdiv* solves simultaneous systems of equations of the type

$$\mathbf{A}\,\mathbf{X} = \mathbf{B}$$

by Gauss elimination. The resulting matrix **x** is entered in place of matrix **B**. During calculation the array containing the coefficient matrix **A** changes. The procedure is suitable for solving a linear system of equations if there is one right-hand side, and for inversion if **B** = **I** is known.

Formal parameters of the procedure:

array A [1 : n, 1 : n]:	Coefficient matrix **A** of the system of equations.
integer n:	Number of rows of the coefficient matrix **A**.
array B [1 : n, 1 : n]:	The right-hand side **B** of the system of equations.
integer l:	Number of right-hand sides.
boolean *sing*:	Parameter defining the singularity of the coefficient matrix. When leaving the procedure, its value is **true** or **false** depending on, whether or not the determinant of the coefficient matrix of the system of equations was 0.

Limits of application: It is impractical to use the procedure to solve equation systems containing more than 15 unknowns. (Equation systems of this size are hardly to be expected in the boxes.)

(b) Finding the root of non-linear equation systems

noleq (var, countit, countcyc, maxit, maxcyc, outside, first, del0x, delx, xact, opsx, yact, epsy, yold, y0, inveps, maxstepfac, FOUND, ERROR)

Procedure *noleq* solves non-linear equation systems of the pattern

$$\mathbf{y}\,(\mathbf{x}) = \mathbf{0}$$

by multi-dimensional Newton–Raphson iteration. Accordingly:

$$\Delta\,\mathbf{x} = \mathbf{x}^{(k-1)} - \mathbf{x}^{(k)} = \mathbf{D}\cdot\mathbf{y}^{(k)},$$

where $\mathbf{D} = -\,(\mathrm{d}\mathbf{y}/\mathrm{d}\mathbf{x})^{-1}$, i. e., the inverse of the Jacobi matrix formed from the partial derivatives. Superscript k denotes the value obtained at the k-th iteration. The partial derivatives are determined by approximation with difference quotients.

Matrix **D** may also be prescribed. It is also possible to use procedure *noleq* for direct iteration. If we choose

$$\mathbf{D} = \mathbf{I} \text{ (unit matrix)}$$

then the iteration is accomplished according to

$$\mathbf{x}^{(k+1)} - \mathbf{x}^{(k)} = \mathbf{y}^{(k)},$$

corresponding to the equation

$$\mathbf{x} = \mathbf{x} + \mathbf{y}\,(\mathbf{x}).$$

The procedure only sets the values of the independent variables. The user's program has to attend to calculation of the related dependent variables and the organization of the interation cycles.

Formal parameters of the procedure:

integer *var*:	Number of unknowns and equations.
integer *countit*:	Working cell of the procedure used for different purposes. Its value is 0 if, when first calling procedure *noleq*, the function values relating to starting values *xact* are found in *yact*; otherwise it is 1. The parameter obtains its value during calculation.
integer *countcyc*:	Working cell, containing the number of cycles already started. Its initial value is 0 or 1, depending on whether the actual value of parameter *first* is **true** or **false.** The parameter obtains its value during calculation.
integer *maxit*:	Number of iterations to be calculated with unchanged derivatives.
integer *maxcyc*:	Maximum number of the cycles to be calculated. One cycle consists of the calculation of function values (whose number is *var*) needed to calculate the derivatives, and of iteration steps, (whose number is *maxit*), using the calculated derivatives.
boolean *outside*:	A logical variable or procedure depending upon *xact*, enabling the user to define the permissible range of the independent variables. Its value is **false** in the permissible range, and **true** outside.
boolean *first*:	Working cell, controlling the procedure. Its initial value is **false** if, instead of the inverse of the derivative matrix, a given **D** matrix is used; otherwise it is **true.** The parameter obtains its value during calculation.
array *del*0*x* [1 : *var*]:	The increment of the independent variables when forming difference quotients.
array *delx* [1 : *var*]:	The final calculated increments of the independent variables. The calculation is effected in the procedure.
array *xact* [1 : *var*]:	Contains — when leaving the procedure — the last approximation of the values of the independent variables sought (the unknowns). Initially, estimated values have to be used.

array *epsx* [1 : *var*]:	The allowed error of the independent variables.
array *yact* [1 : *var*]:	When calling the procedure, *yact* has to contain function values corresponding to the independent variables contained in array *xact*. There is one exception: the first call of the procedure, — i.e., *countit* = 0 — when the contents of array *yact* may be undefined.
array *epsy* [1 : *var*]:	The allowed error of the dependent variables.
array *yold* [1 : *var*, 1 : *var*]:	Array containing the prevailing matrix of difference quotients and its negative inverse. When first calling the procedure, if *first* = **false**, initial values have to be given. Otherwise the values are obtained during calculation.
array *y*0 [1 : *var*]:	Series of function values, calculated during the preceding call and stored in *yact*.
real *inveps*:	Allowed singularity of the matrix of difference quotients. In practice it is proposed that the following value be used: $10^{-5} \times \max \; (y[i]/x[j])$ $(i, j = 1, 2, \ldots, var)$
real *maxstepfac*:	Restriction of the Δx step length, calculated in the procedure.
label *FOUND*:	Label to which procedure *noleq* jumps if the conditions of exactitude are satisfied. This jump is effected after the calculation (control) of the function values pertaining to the system of values accepted as solution.
label *ERROR*:	Label to which procedure *noleq* jumps, if no solution has been found during the number of cycles specified in *maxcyc*, or if the matrix of derivatives has become singular (the equations are linearly related). This procedure has been developed by reshaping procedure NOLEQ5 from the program library of Haldor Topsøe Chemical Engineers.

(c) Numerical integration of system of first-order differential equations

rkm2 (ny, f, x0, xl, dx, y0, yl, dy)

Procedure *rkm2* serves for the numerical integration of differential equation systems by the Runge–Kutta method. The type of equation is the following:

$$dy\,[i]\,/dx = f\,(i,x,y\,[1], y\,[2]\,, \ldots, y\,[ny]\,(i = 1,2, \ldots, ny).$$

The procedure adjusts the step length automatically so that the allowed error is not exceeded in steps or variables.

Procedure *rkm2* allows constraints to be placed on both the independent and the dependent variables. The solution functions therefore occupy a range which is limited by following conditions:

$$x0 \leq x \leq x1$$

$$y0\,[i] \leq y\,[i] \leq y1\,[i], \quad (i = 1,2, \ldots, ny),$$

where

$x0$ and $y0\,[i]$ = initial values of the independent and dependent variables, respectively

$x1$ and $y1\,[i]$ = bounds of the respective variables.

The integration proceeds from given initial conditions until the independent variable reaches $x\,[i]$ bound, or the dependent variable has approximated its bound within the prescribed accuracy. As a result of the integration, the bounds cannot be overstepped. No assumptions are made about the numerical values of the bounds; $x1$ and $y1\,[i]$ are the upper and lower bound of the respective variables, depending on whether the relations

$$x0 < x1, \; y0\,[i] < y1\,[i] \text{ or}$$

$$x0 > x1, \; y0\,[i] > y1\,[i]$$

were valid at the entry.

Formal parameters of the procedure:

integer *ny*:	Number of independent variables.
real procedure *f*:	Function procedure to calculate the values of derivatives d$y[i]$/dx. Procedure *f* has to be declared outside *rkm2* in the form $f(i, x, y)$, where i = index of the dependent variables, x = array of the independent variables, y = array of the dependent variables.
real $x0$:	Independent variable. When calling the procedure the initial values must appear — as must the final values when leaving the procedure.
real $x1$:	Bounds of the independent variables.
real dx:	Integration step length. When calling the procedure, the estimated initial step length has to appear. When leaving the procedure, the last calculated step length value has to be returned.
array $y0\ [1 : ny]$:	Array of the dependent variables. When calling the procedure it has to contain the initial values of the variables; when leaving the procedure it contains their final values.
array $y1\ [1 : ny]$:	Bounds of the dependent variables.

array d*y* [1 : *ny*]:	Allowed error of the dependent variables in one integration step. The values defined here also determine when to stop the integration, when the values of the dependent variables have been approximated within a prescribed range.

(d) Optimization

optsimp7 (var, count1, count2, cmax, return, step, xnew, xold, x, y, ynew, eps, start, outside, out)

Procedure *optsimp7* enables the minimum value of a scalar function with *n* variables to be found (objective function). The procedure only sets the system of values of the independent variables. After calling the procedure, we must test whether, depending upon the value of parameter *out*, the system of values (**x**) set by the procedure are within the permitted range, i. e., the objective-function values *(ynew)* related to **x** have to be calculated. Then procedure *optsimp7* has to be called again, until parameter *out* indicates either the optimum has been found or else failure.

Finding the optimum takes place with the aid of a series of regular simplexes in *n*-dimensional space. In two-dimensional space, these simplexes are triangles, in three-dimensional space tetrahedrons. The procedure systematically reflects the apexes of the simplexes. If the reflected image is more favourable than the foregoing system, then the reflected image is entered to replace the foregoing system. Near the minimum, the size of the simplexes is halved, provided the differences between the independent variables and the related values of the objective functions have attained a prescribed limit.

Procedure *optsimp7* seeks the minimum value of the objective function in an allowed range of the independent variables. This range may be defined by a scalar-vector-function, whose value is 0 in the allowed range, positive outside the allowed range, having no local minimum there. This last restriction is required in those cases where the given initial value is outside the boundaries of the allowed range. In this case, procedure *optsimp7* seeks the suitable initial value by minimizing function *G*.

If the objective function has more than one local minima in the allowed range, then the procedure finds one of these by chance, depending upon the initial value.

Formal parameters of the procedure:

integer *var*:	Number of independent variables.
integer *count1*:	Number of successful optimization steps. The initial value is 0. Obtains its value during calculation.
integer *count2*:	Working cell to count the apexes of the simplexes. Obtains its value during calculation.
integer *cmax*:	Allowed maximum value of parameter *count1*.

integer *return*:	Control parameter of the procedure. Obtains its value during calculation.
array *step* [1 : *var*]:	Initial step length prescribed for the independent variables.
array *xnew* [1 : *var*]:	System of values pertaining to the prevailing best value of the objective function. The initial value is the system of initial values of the independent variables. The array obtains its value in the procedure.
array *xold* [0 : *var*, 1 : *var*]:	Array containing the coordinates of the actual simplex apexes. Obtains its value during calculation.
array *x* [1 : *var*]:	Actual value-system of the independent variables. Obtains its value during calculation.
array *y* [0 : *var*]:	Function values pertaining to the simplex apexes. Obtain their value during calculation.
real *ynew*:	Value of the objective function pertaining to value-system **x**. The value of *ynew* has to be set outside the procedure.
array *eps* [1 : *var* + 1]:	Allowed error of the dependent variables (from *eps* [1] to *eps[var]*) and of the objective function (*eps[var* + 1]).
boolean *start*:	Control parameter. Its value is **false** until the procedure finds a point in the allowed range. Its value is obtained during calculation.
real *outside*:	Parameter, defining the allowed range, and positive outside it.
integer *out*:	Control parameter. If *out* = 1, the value of *outside*, if *out* = 2, the value of the parameter *ynew* has to be set outside the procedure, if *out* = 3, then the procedure has found no minimum in *cmax* steps, if *out* = 4, then the optimum has been found (the optimizing cycle has been left).

4.4.1.3 ORGANIZING PROCEDURES

(a) Printing of error messages

error (text)

Procedure *error* controls the printing of error messages. The message contained in the parameter *text*, the index of the operation where the error occurred and the relevant box index are printed. After printing an error message, the computation may be continued — it is the user's decision — from the point where the error message was printed or by jumping to the simulating operation.

(b) Reference procedures

Procedures organizing references will be discussed in detail after outlining the references in Section 8.2.1.1. Here we shall list them:

Address of the reference: *address (ref)*
Size of the reference: *size (ref)*
Type of the reference: *type (ref)*
Declaration of the reference: *ref (type, size, address)*
Data search by reference: *from ref (ref)*

4.4.2 MATHEMATICAL AND ORGANIZING BOXES

4.4.2.1 BOX FOR THE SOLUTION OF A NON-LINEAR SYSTEM OF EQUATIONS (*soleqs*)

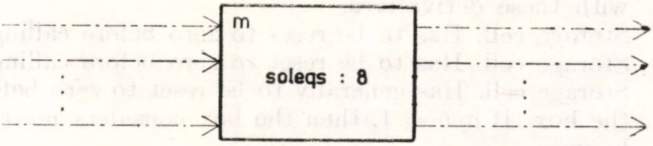
Box *soleqs* allows a non-linear system of equations of the type

$$y_i\,(\mathbf{x}) = z_i\,(\mathbf{x}),\ (i = 1,2, \ldots, n)$$

by iteration, where

$$\mathbf{x} = [x_1,\ x_2, \ldots,\ x_i, \ldots,\ x_n].$$

The graphic symbol of the box:



Description of the operation:
soleqs : 8 (m)
$\wedge$
A sequence of operations,
leading to the values
of the dependent
variables.
$\vee$

The box sets only the value-system of the x_i variables. The calculation of **y** and **z** values pertaining to **x** has to be effected outside the box. The sequence of the operations leading to **y** and **z** have to be specified after *soleqs : 8* between the signs $\wedge$ and $\vee$.

The x_i independent variables (unknowns) may be any quantities of the simulation (stream vector elements, operating parameters), y_i, z_i may be defined as quantities depending in any way on the unknowns. These have to be defined among the operating parameters of the box, and the independent ones as references.

The box seeks the root of the equation inside a prescribed range of the independent variables. If there are more roots inside this range, then — depending on the initial value — one of the roots is found by chance.

The accuracy of the solution may be prescribed for both the independent and the dependent variables. Standard procedure *soleq* allows solution of the system of equations.

Limits of application: The box provides mainly for solving system of equations, whose derivatives may be determined analytically in the range of the independent variables, and where the initial estimate of the roots is fairly good.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Number of unknowns *(n)*.
op2	1	Number of iterations to be performed with unchanged value of derivatives.
op3	1	Maximum number of cycles to be calculated. One cycle consists of *n* function-value calculations to determine the partial derivatives, and of *op2* iterations to be calculated with these derivatives.
op4	1	Storage cell. Has to be reset to zero before calling the box.
op5	1	Storage cell. Has to be reset to zero before calling the box.
op6	1	Storage cell. Has generally to be reset to zero before calling the box. If *op6* = 1, then the box considers matrix *op18* as known.
op7	*n*	References to the independent variables.
op8	*n*	Actual values of the independent variables (x_i). As initial values, estimates of the x_i solutions have to be stated. The estimates must be within the allowed range of the variables.
op9	*n*	Lower bound of the independent variables.
op10	*n*	Upper bound of the independent variables.
op11	*n*	Step length of the independent variables when forming difference quotients.
op12	*n*	Cells storing the last adjusted step length of the independent variables. The initial value does not affect the calculation.
op13	*n*	Acceptable error of the independent variables.
op14	*n*	References to the new dependent variables.
op15	*n*	References to the z_i dependent variables.
op16	*n*	Storage cells. Their initial content in optional.
op17	*n*	Acceptable error of the dependent variables.
op18	$n \times n$	Negative inverse of the matrix of the partial derivatives — the Jacobi matrix — in row sequence. If the initial value of *op6* = 0, then these values are not used. If *op6* = 1, then the box handles and uses these values as the inverse of the matrix of partial derivatives.

Number of operating parameters: $n \times (n + 11) + 6$.

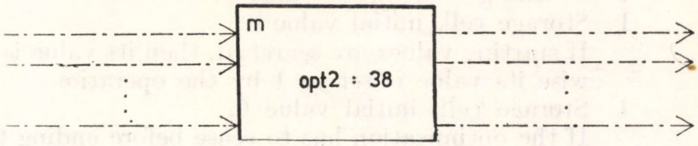
Check: The box checks the following:

- number of the operating parameters,
- initial value of the independent variables (whether they are in the permissible range),
- singularity of the matrix of derivatives,
- number of iterations.

4.4.2.2 OPTIMIZING BOX (opt2)

Box *opt2* provides for optimizing (minimizing) any parameter of a model, consisting of one or more boxes.

The graphic symbol of the box:



Description of the operation:

opt2 : 38 (m)

$\wedge$

Sequence of the operations,
calculating the value of
the objective function
and the constraints.

$\vee$

The box sets the value system of the decision variables. The relevant values of the objective functions, as well as the values of the constrained variables, have to be calculated outside the box after operation *opt2 : 38(m)*, in those operations which are defined between $\wedge$ and $\vee$.

The decision variables may be any quantities of the simulation (elements of stream vectors, operating parameters); the objective function and the constrained variables may be stated as quantitites, depending upon the decision variables. All these have to be defined among the operating parameters of box *opt2* as references. The box repeats — changing the value of the independent variable — the operations between $\wedge$ and $\vee$ until the minimum is reached within a prescribed accuracy.

The box is built in the procedure *optsimp7*, working as outlined in the description of the procedure.

The last cycle is calculated with the independent variables adhering to the minimum. Then the calculation is continued after mark $\vee$.

Box *opt2* is suitable for considering bounded conditions. These may relate to the decision variables, as well as to their functions.

The constrained variables may be divided into two groups:

1. External constrained variables: quantities, depending upon the decision variables and calculated in the cycle marked ∧ and ∨.

2. Internal constrained variables: quantities to be calculated from the values of the decision variables without carrying out simulating operations.

If the initial values of the decision variables lie outside the allowed range, then the initial values are determined by an optimizing algorithm.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Counting cell, initial value 0.
op2	1	Storage cell, initial value 0. If starting values are searched, then its value is 0, otherwise its value is set to 1 by the operation.
op3	1	Storage cell, initial value 0. If the optimization has to cease before ending the cycle, then its value must be set by box *read* to 1. Hereafter, the action of the box ceases, and the least value found is considered as minimum.
op4	1	Storage cell, initial value 0.
op5	1	Storage cell, initial value 0.
op6	1	Maximum allowed number of cycles.
op7	1	Number of independent variables.
op8	1	Number of the internal constrained variables, $op8 \leq op7$.
op9	1	Number of the external constrained variables, their number is unlimited.
op10	1	Counting cell. Initial value 0.
op11	1	If the error of the objective function – defined in *op17* – is to be considered as an absolute error, then $op11 = 0$.
op12	1	Reference relating to the objective function.
op13	*op7*	References relating to the decision variables.
op14	*op7*	Values of the decision variables pertaining to the least value of the objective function. As initial values, those of the decision variables must be stated.
op15	*op7*	Initial step length of the decision variables. The step length decreases automatically during calculation.
op16	*op7*	Allowed maximum relative error of the decision variables.
op17	1	Allowed maximum error of the objective function.
op18	*op8*	References relating to the internal constrained variables.
op19	*op8*	Lower bounds of the internal constrained variables.
op20	*op8*	Upper bounds of the internal constrained variables.
op21	*op9*	References relating to the external constrained variables.
op22	*op9*	Lower bounds of the external constrained variables.
op23	*op9*	Upper bounds of the external constrained variables.

op24	$(op7)^2 + op7 + 1$	Calculated values of the objective function in the region of the simplex apexes. Initial value 0.
op25	$(op7)^3 + (op7)^2 + op7$	Values of decision variables, pertaining to the stored objective function values. Initial value 0.
op26	$(op7)^2 + op7$	Values of decision variables of the actual simplex apexes. Initial value 0.
op27	$op7 + 1$	Calculated objective functions in the actual simplex apexes. Initial value 0.

Number of operating parameters:

$$(op7)^3 + 3 \times (op7)^2 + 8 \times op7 + 3 \times op8 + 3 \times op9 + 15.$$

Check: The box checks the number of operating parameters and the reality of the constraints. In addition, an error message is printed if the minimum has not been attained within the prescribed accuracy in the allowed maximum step number. In this case, the least value is considered as minimum when continuing the simulation.

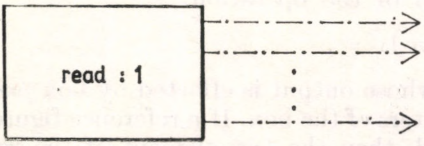
4.4.2.3 ORGANIZING BOX FOR DYNAMIC OPTIMIZATION *(bellman)*

Box *bellman* provides the dynamic optimization of complex systems and organizes one step of the optimization. The box is to be discussed in Section 7.3.2.2.

4.4.2.4 DATA MODIFIER BOX *(read)*

Box *read* enables data or data groups to be modified by input.

The graphic symbol of the box:



Description of the operation:

read : 1 (m).

Box *read* prints the text *read (m)* on the consol typewriter when it first functions: thereafter it is optional to select the input mode. The letter *m* in the text is the operating index in the flow-sheet program, and identifies the operation.

The data group, whose input is effected by box *read*, may consist of any number of records. Each record starts with a comment containing any characters except ∧, ∨, +, :. Between the semicolon (;) ending the comment and the character (indicating the beginning of the record, the reference has to be inserted.

The reference relates to the data or arrays to be modified. The number of the data following must equal the number of data designated by the reference. The record is ended with character). The formal rules of presenting the data are identical to those of data input. The data group *read* is closed by character +.

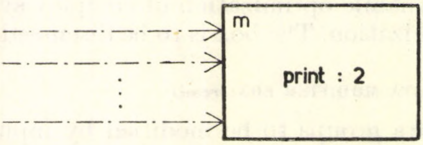
Operating parameters: The box has no operating parameters. Therefore, no operating parameter group, denoted by the operating index of box *read*, appears in the input data system.

Check: The box checks whether
- a reference follows the character ; ,
- the character (follows the reference,
- the referred data are defined,
- the number of input and referred data are equal.

4.4.2.5 OUTPUT BOX *(print)*

Box *print* provides for the output of operating parameters, stream vectors and their elements.

The graphic symbol of the box:



Description of the operation:

print : 2 (m).

The data whose output is effected by box *print*, are defined by the operating parameters of the box. If a reference figures in the place of a quantity to be printed, then the last element of the reference chain is printed. If this refers to an arithmetic expression, then the value of that expression is printed.

The result is printed by the box in format A4, with a title page, each page having identical heading. Besides standard text, the title page contains the denomination of the job, the serial number of the data system, the data of computation and the file number. The numbering of the pages is continuous in each job. The output produced by box *print* on punched tape can formally serve as the input to box *read*.

Operating parameters: The number of operating parameters of the box is unrestricted in principle. The first parameter is an integer, defining the number of significant figures to be printed.

In the remaining parameters, the output data or data groups must be stated as references.

Number of operating parameters: ≥ 2.

Check: The box checks whether

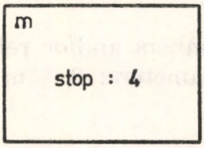
— the number of the operating parameters ≥ 2,

— the parameters, except the first, are references or reference chains.

4.4.2.6 BOX FOR INTERRUPTION *(stop)*

Box *stop* enables a simulation-mode computation to be interrupted and organizational tasks to be carried out in the course of computation.

The graphic symbol of the box:



Description of the operation:

stop : 4 (m).

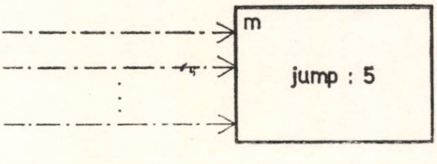
When calling box *stop*, the denomination of the job and the message *stop* is written on the typewriter. The user can decide whether to run the same flow-sheet program with a new data system or to start another computation.

Operating parameters: No operating parameter relates to box *stop*. The operating index *m* has no function, but must be stated for formal reasons.

4.4.2.7 BOX CHANGING THE SEQUENCE OF CALCULATION *(jump)*

Box *jump* allows the sequence of simulating operations to be changed, depending upon the fulfillment of certain conditions.

The graphic symbol of the box:



Description of the operation:

jump : 5 (m).

As a consequence of using box *jump*, the organizing program considers the next operation of the process program to be that operation which is defined by the first operating parameter of box *jump*. This function of box *jump* depends upon the fulfillment of conditions defined among the other operating parameters.

Limits of validity: The box organizes cycles and causes the repetition or abandoning or certain parts of the calculation by manual intervention.

Operation parameters:

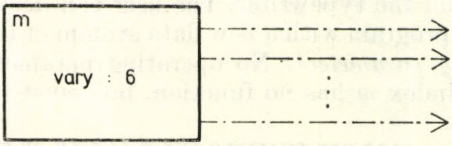
Denomination	Number	Value, significance
op1	1	Calculation serial number of the operation, following box *jump*.
op2	1	If $op2 \geq 0$, then the box only functions if all checked quantities are positive, if $op2 < 0$, then the box only functions if at least one of all checked quantities is non-positive.
op3	*m*	Checked quantities.

Op2 and *op3* may be numbers and/or references.
Number of operating parameters: $2 + m$ ($m \geq 1$).

4.4.2.8 DATA SYSTEM VARYING BOX *(vary)*

Box *vary* serves to organize the repeated execution of a calculation, consisting of one or more operations, with different initial values.

The graphic symbol of the box:



Description of the operation:

vary : 6 (m)

∧

Sequence of the operations
to be repeated

∨

Box *vary* repeats the operations figuring between marks ∧ and ∨. When starting each cycle, the box provides new initial values to the quantities enumerated among the operating parameters. If all data systems have been used, then the calculation is continued with the operation figuring under mark ∨.

The parameter, adjusted by box *vary*, may be the operating parameter of another box or any stream-vector element. The parameters to be varied have to be defined as references among the operating parameters.

The box functions according to three modes:

1. For each parameter varied the values to be adopted are prescribed and box *vary* carries out the calculation with all possible variations of the system of values.

The number of cycles is equal in this case to the number of possible variations, i. e., the product of the number of permissible values of each variable. If fewer cycles were prescribed, then the box calculates with systems of values, chosen randomly from among the possible systems.

2. The sequence of the related parameter system values is defined.

3. The expected value and the standard deviation are defined for each parameter varied and box *vary* sets data systems with normal distribution in a random manner, corresponding to the parameters.

Operating parameters:

Denomination	Number	Value, significance
op1	1	Cycle variable. Its value defines at the exit from box *vary* the serial number of the following cycle. 0 is generally stated as the initial value of *op1*. If the initial value i differs from 0, then the next cycles to run are those, which have indices $i + 1, i + 2, \ldots$ *op2*.
op2	1	Number of cycles to run or their expected value *(ncycle)*.
op3	1	Number of varied parameters *(nvar)*.
op4	1	Digit defining the mode of functioning of the box. Its value is 1, 2 or 3 depending on, whether it is intended to use the box in the mode (a), (b) or (c), described above.
op5	*nvar*	Sequence of the references, defining the parameters varied.

The number and significance of the following operating parameters depend upon the value of *op4*.

If $op4 = 1$:

op5	*nvar*	Number of the values of the varied parameters (nx_i) to be set in a sequence, corresponding to the elements of *op5*.
op6	nx_1	Sequence of the values of the first parameter (x_1) to be set.
op7	nx_2	Sequence of the values of the second parameter (x_2) to be set.
.	.	.
.	.	.

If *op4* = 2: *op5* *ncycle* × *nvar*	Sequence of the vectors containing *ncycle* elements of the variables to be varied $(x_1, x_2, \ldots, x_{nvar})$.
If *op4* = 3: *op5* 2 × *nvar*	Sequence of number pairs containing *nvar* elements, formed from the expected values and standard deviations of the varied parameters.

Number of operating parameters

$$\text{If } op4 = 1 : 4 + 2 \times nvar + \sum_{i=1}^{nvar} nx_i$$

$$\text{If } op4 = 2 : 4 + nvar + nvar \times ncycle$$

$$\text{If } op4 = 3 : 4 + 3 \times nvar$$

Check: The box checks the number of operating parameters in each case.

PROBLEM

In the previous chapter we demonstrated the application of equipment boxes on problems which, with the intervention of the SIMUL master program (together with boxes *print* and *stop*), have been used to present interpretable results from the viewpoint of chemical engineering. This chapter deals with boxes performing mathematical and organizing functions. Because of their character, these boxes cannot be used in isolation. Their placing and functioning when calculating networks needs careful consideration, to be discussed in Chapters 6 and 7. There is one exception, namely the box *vary*, whose use may already be demonstrated, since this box organizes the repetition of calculations with one or more varied parameters.

PROBLEM P.4.1 SERIAL CALCULATION

Summarize in tabular form the change of flame temperature arising when burning a fuel gas of given composition, as a function of the air excess.

Solution

Box *burner* is used to calculate the flame temperature, the serial calculation is organized by box *vary*, and the table is printed by box *print*.

The operation-order flow-sheet is the following: The air excess factor is selected to be 10^{-3}, 1, 10, 20, 30. The flow-sheet program and input data system are presented in Table P.4.1 (1), the results of the calculation in Table P.4.1 (2).

Table P.4.1 (1)

Flow-sheet program and input data system of problem
[Serial calculation]

```
[Serial calculation]
A 770412
stream types
fuel gas: 4(1, 26, 71, 70,67)
flue gas: 5(64, 69, 70, 72)
+
operations
∧
vary: 6 (1)
burner: 28 (2,2, — 3)
print: 2 (3)3
∨
stop: 4 (4)
+
data set number: 41
operating parameters of the boxes
vary: 1 (0,5, 1, 1, 1e2b, 5, 10^-3, 1, 10,20, 30)
print: 3 (5, 1e2b, 4e3s)
burner: 2 (10^-3, 0, 313, 2, 3.8, 0, 0, 0,5)
+
stream
fuel gas: 2 (4, 14.696, 0, 313, 101⏨3, 1, 0.60615,
             0.10174, 0.16998, 0.083644, 0.038486)
+
```

Table P.4.1 (2)

Calculation results of problem [Serial calculation]

```
Serial calculation  — 41
:    1e2b(      1.000⏨-3)
      4e3s(     2.5083⏨+3)
+
:    1e2b(      1.0000)
      4e3s(     2.4865⏨+3)
+
:    1e2b(    10.000)
      4e3s(     2.3175⏨+3)
+
:    1e2b(    20.000)
      4e3s(     2.1684⏨+3)
+
:    1e2b(    30.000)
      4e3s(     2.0455⏨+3)
+
end Serial calculation
```

CHAPTER 5

PROCESS SIMULATION

5.1 SIMULATION OF BUTANE ISOMERIZATION

5.1.1 PLANNING AND PROGRAMMING OF THE CALCULATION

Having studied the first four chapters, we may now proceed to define the calculation order simulating butane isomerization. This can be followed easily from Figure 4.3. As the material and information streams are not directional in the complex operation, for example, the calculation order is definitely determined, and no decision on the calculation order is required.

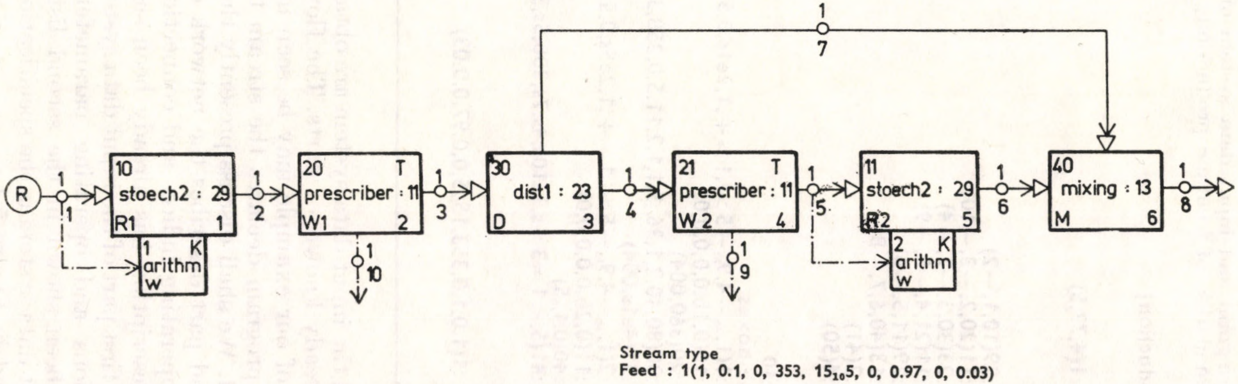
It is obvious that the entering raw-material flow has to be defined as a stream vector. The fact that this stream vector represents the input of the calculation, is symbolized by the character R in a circle in Figure 5.1, which is developed as the operation-order flow-sheet.

The calculation starts with box *stoech2* (Section 3.4.18), as the stream leaving the first reactor has to be determined first. Accordingly, the number 1, the calculation serial number, is written in the right-hand lower corner of the graphic symbol of the box.

As already mentioned, in this case there arises the problem that among the operating parameters of box *stoech2 : 29* the conversion K is unknown and has therefore to be calculated with the arithmetic expression (3.1). Given this knowledge, the outlet stream vector of the reactor can be calculated. The second step of the calculation can be just the calculation of the heat exchanger (W1), and the third exclusively the calculation of the distillation (D). Although a separation follows in the system (in the direction of the distillate and bottom-products flows), there is no choice as to the order of calculation, since the calculation of *mixing : 13* presupposes the calculation of the heat exchanger (W2) and the reactor (R2). The fourth step must therefore be the calculation of the heat exchanger (W2). After this the technique already used when calculating the first reactor is repeated; as the fifth step, the conversion is calculated with the arithmetic expression and the stoichiometric and thermochemical calculation of the output stream vector of the reactor is effected using box *stoech2*. (Calculation of the mixer can now take place as both entering flows are known.

This calculation order corresponds exactly to the thinking of the chemical engineer, as he calculates on paper with pencil and slide rule. As the chemical engineer finishes his calculations, he sums up the important results (the significant data of the streams at the connecting points) in tables. The SIMUL system accomplishes this with box *print : 2*, outlined in the previous chapter.

The information contained in the operation-order flow-sheet have to be transcribed in order to use them in the SIMUL system. As a result, the



Stream type
Feed : 1(1, 0.1, 0, 353, $15_{10}5$, 0, 0.97, 0, 0.03)

Fig. 5.1. Operation-order flow-sheet of the butane isomerization

Table 5.1

Flow-sheet program and input data system of problem [Simulation of i-butane production]

```
[Simulation of i-butane production]
D97001
stream type
feed                      :1(4,73,5)
+
operations
stoech2                   :29(10,1,−2)
prescriber                :11(20,2,−3,−10)
dist1                     :23(30,3,−7,−4)
prescriber                :11(21,4,−5,−9)
stoech2                   :29(11,5,−6)
mixing                    :13(40,6,7,−8)
print                     :2(41)
stop                      :4(50)
+
data-system serial number:10
operating parameters of the boxes
arithm                    :1(1,₁₀−4,9₁₀−5>/,1>+,1,2e1s,0.5>×>+>×>/)
stoech2                   :10(0,1b,0,0,0,0,0)
prescriber                :20(360,004)
dist1                     :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,98,98,0,0,0,0)
prescriber                :21(4e1s,004)
arithm                    :2(1,₁₀−4,9₁₀−5>/,1>+,1,2e5s,0.5>×>+>×>/)
stoech2                   :11(0,2b,0,0,0,0,0)
mixing                    :40(0.1₁₀5)
print                     :41(5,<1=3>s,3e10s,4s,7s,30b,5s,3e9s,<6,8>s)
+
stream
feed                      :1(1,0.1,0,353,15₁₀5,0,0.97,0,0.03)
+
```

flow-sheet program and the input data system are obtained. Each of these is divided into two — already known — parts. The flow-sheet program and the input data system of our example may be seen in Table 5.1. The first part of the flow-sheet program declares the stream types, as has already been done in Figure 2.1. We shall discuss presently the function of the 2nd stream type. The second part describes the network of the material flows with the box indices, operating indices and connection indices figuring in the calculation. This description has already been seen as part of Figure 4.3, as the first list. The first part of the input data system is the enumeration of arithmetic expressions and operating parameters. The structure of this enumeration has been shown in the second list of Figure 4.3. The second part of the input data system is the specification of the input stream vector. It may be found in Figure 5.1.

With the flow-sheet program produced in this manner, it is possible to calculate the stream vectors for different types of process performance, at all connecting points, and also conversion of the isomerizating reactions

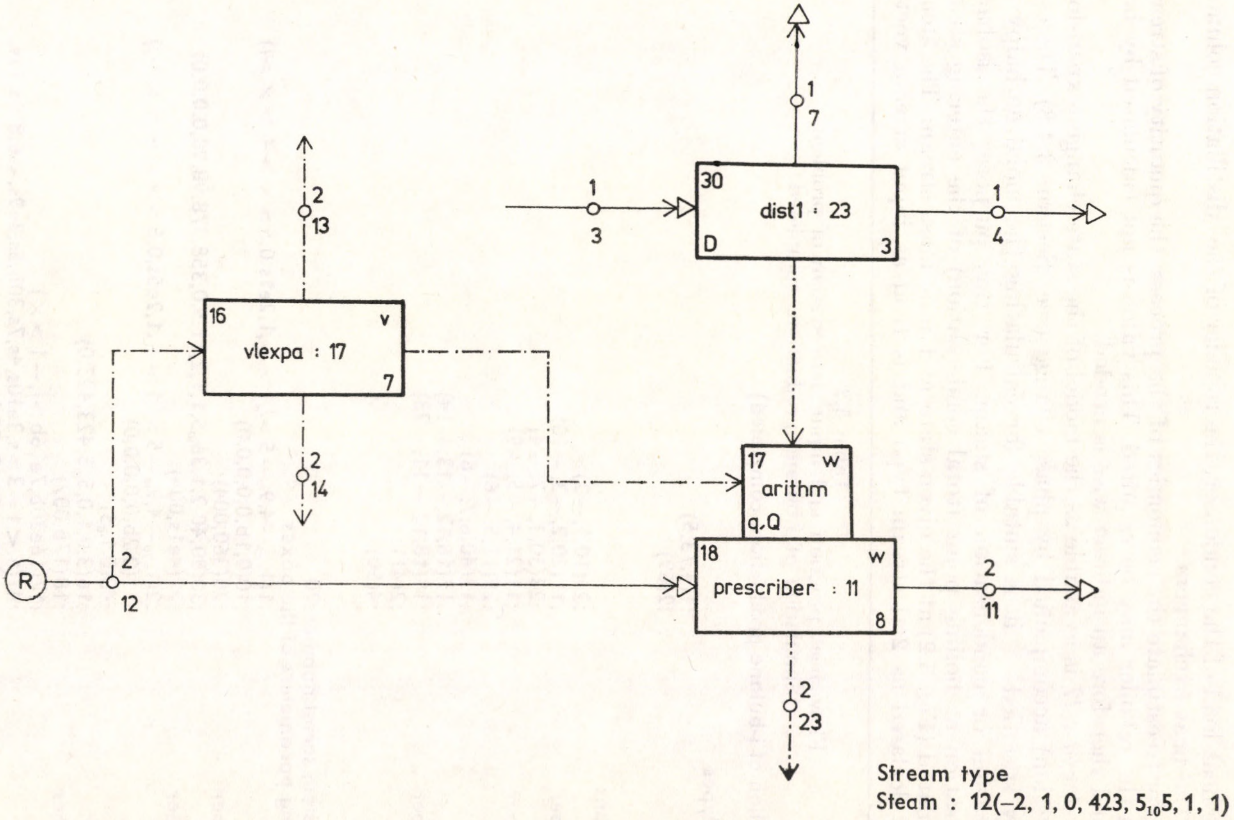


Fig. 5.2. Complete operation-order flow-sheet for calculating the steam consumption of the reboiler

and the heat load of the condenser, the reboiler of the distillation column, and of the heat exchangers.

In order to estimate the economics of the process, the quantity of stream used in the reboiler may be required. This value is not calculated by box *dist1*, and therefore an indirect way is needed.

Box *vlexpa : 17* is available as the model of the state change (expansion, compression) accompanied by phase change (see, Section 3.4.8). Thus — suitably specified — it is suitable for calculating the molal enthalpy of vaporization or condensation of steam. For this purpose, the isobaric condensation at boiling point (total condensation) of the entering steam is calculated (Fig. 5.2) at the given state and unit mass stream. The steam flow is declared as 2nd stream type and is read as input stream vector

Table 5.2
Flow-sheet program and input data system of problem
[Simulation of i-butane production, completed]

```
[Simulation of i-butane production, completed]
D97001
stream types
feed                        :1(4,73,5)
steam                       :2(69)
+
operations
stoech2                     :29(10,1,-2)
prescriber                  :11(20,2,-3,-10)
dist1                       :23(30,3,-7,-4)
prescriber                  :11(21,4,-5,-9)
stoech2                     :29(11,5,-6)
mixing                      :13(40,6,7,-8)
vlexpa                      :17(16,12,-13,-14)
prescriber                  :11(18,12,-11,-23)
print                       :2(41)
stop                        :4(50)
+
data-system serial number:20
operating parameters of the boxes
arithm                      :1(1,₁₀-4,9₁₀-5 >/,1 >+,1,2e1s,0.5 > × >+ > × >/)
stoech2                     :10(0,1b,0,0,0,0,0)
prescriber                  :20(360,004)
dist1                       :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,98,98,0,0,0,0)
prescriber                  :21(4e1s,004)
arithm                      :2(1,₁₀-4,9₁₀-5 >/,1 >+,1,2e5s,0.5 > × >+ > × >/)
stoech2                     :11(0,2b,0,0,0,0,0)
mixing                      :40(0.1₁₀5)
vlexpa                      :16(3,0,1.0,5₁₀5,423,423,0)
prescriber                  :18(17b,002)
arithm                      :17(16e30b,7e16b >/,-1 > ×)
print                       :41(5,<1=3 >s,3e10s,4s,7s,30b,5s,3e9s,<6,8 >s,12s,
                               7e16b,11s,2e23s)
+
stream
feed                        :1(1,0.1,0,353,15₁₀5,0,0.97,0,0.03)
steam                       :12(-2,1,0,423,5₁₀5,1,1)
+
```

into stream vector 12. After calculating the condensation, box *vlexpa : 17* (operating index: 16, calculation serial number: 7) places the enthalpy into its operating parameters. Since the mass stream was of unit value, this is then the molal enthalpy of vaporization. The quantity of steam entering the reboiler of the distillation column is calculated as the quotient of the heat load of the reboiler (16e30b) and the molal enthalpy of vaporization of the steam (7e16b). This value has to be multiplied by $_{-1}$ because of the sign convention of the enthalpy streams of the boxes. The result is the mass stream of stream 11 (2e11s). This value may be calculated by box *prescriber : 11*, as has already been discussed. The arithmetic expression is referred to among the operating parameters of the box. As the operating index of the arithmetic expression was 17, the reference is symbolized by 17b. The arithmetic expression itself is written as :

```
arithm: 17 (<< 16e30b, 7e16b >/, > − 1 >×).
```

Here, every arrangement for calculating the steam consumption of the distillation column is made. The cooling water consumption of the condenser could be calculated accordingly but may be disregarded because of the negligible economic effect.

The operation-order flow-sheet is still valid, but it is completed with the part shown in Figure 5.2. The flow-sheet program in Table 5.1 is also valid but must also be completed. The completed flow-sheet program is shown in Table 5.2.

The flow-sheet program has to comply with certain syntactical rules to be detailed later. A short tape-checking program, which is independent of the SIMUL system, checks for syntactic errors in the flow-sheet program. If there are none, then the mathematical simulation of the complex operation described in the flow-sheet program may begin in the SIMUL system.

5.1.2 RESULTS AND THEIR DISCUSSION

The printed results of the completed calculation are shown in Table 5.3. The table contains two parts. One of them is compact, the other more detailed. Let us consider the first part. Selection of data and their tabulation is due to the functioning of box *print*.

It must be read line by line. After the delimiter, the identifier follows, stating which stream vector or which operating parameter and which element of a stream vector or operating parameter respectively are to be found between the following brackets. If the identifier is not a reference to an element, then all elements of the related vectors are printed in lines. The sequence of the elements of a stream vector is — as already discussed — prescribed. Starting from the seventh element (mole fractions), it corresponds to the definition of the stream type. The sequence of elements in the operating parameter vector corresponds to the specification of the box.

However it should be noted that the number of characters to be printed has been prescribed among the operating parameters of box *print*, and

Table 5.3

Calculation results of problem [Simulation of i-butane production, completed]
(first part)

```
Simulation of i-butane production, completed — 20
:       1s(    1.0000        ,        100.00  ₁₀− 3,      −8.9797 ₁₀+ 6,
             353.00          ,          1.5000 ₁₀+ 6,      0.0000       ,
             970.00   ₁₀− 3,            0.0000      ,     30.000  ₁₀− 3)
:       2s(    1.0000        ,        100.00  ₁₀− 3,      −9.1871 ₁₀+ 6,
             353.00          ,          1.5000 ₁₀+ 6,      0.0000       ,
             532.41   ₁₀− 3,          437.59  ₁₀− 3,      30.000  ₁₀− 3)
:       3s(    1.0000        ,        100.00  ₁₀− 3,      −9.0376 ₁₀+ 6,
             360.00          ,          1.5000 ₁₀+ 6,      0.0000       ,
             532.41   ₁₀− 3,          437.59  ₁₀− 3,      30.000  ₁₀− 3)
:    3e10s(    0.1495 ₁₀+ 6)
:       4s(    1.0000        ,         56.226  ₁₀− 3,      −4.8222 ₁₀+ 6,
             373.47          ,          1.5000 ₁₀+ 6,      0.0000       ,
             945.31   ₁₀− 3,            1.3383 ₁₀− 3,     53.356  ₁₀− 3)
:       7s(    1.0000        ,         43.774  ₁₀− 3,      −4.0603 ₁₀+ 6,
             358.34          ,          1.5000 ₁₀+ 6,      0.0000       ,
               2.0448 ₁₀− 3,          997.96  ₁₀− 3,       0.0000       )
:      30b(   80.000         ,         40.000       ,      2.0000       ,
               1.0000        ,          3.6000 ₁₀+ 6,      1.0000       ,
               1.0000        ,          1.0000      ,     11.500        ,
             358.34          ,        358.00        ,    378.00         ,
              99.828         ,         99.832       ,     −7.2685 ₁₀+ 6,
               7.4235 ₁₀+ 6,           11.500       ,    903.46   ₁₀− 3)
:       5s(    1.0000        ,         56.226  ₁₀− 3,      −5.0716 ₁₀+ 6,
             353.00          ,          1.5000 ₁₀+ 6,      0.0000       ,
             945.31   ₁₀− 3,            1.3383 ₁₀− 3,     53.356  ₁₀− 3)
:     3e9s(  249.38   ₁₀+ 3)
:       6s(    1.0000        ,         56.226  ₁₀− 3,      −5.1880 ₁₀+ 6,
             353.00          ,          1.5000 ₁₀+ 6,      0.0000       ,
             509.77   ₁₀− 3,          436.87  ₁₀− 3,      53.356  ₁₀− 3)
:       8s(    1.0000        ,        100.00  ₁₀− 3,      −9.2483 ₁₀+ 6,
             355.47          ,          1.5000 ₁₀+ 6,      0.0000       ,
             287.52   ₁₀− 3,          682.48  ₁₀− 3,      30.000  ₁₀− 3)
:      12s(   −2.0000        ,          1.0000      ,      0.0000       ,
             423.00          ,        500.00  ₁₀+ 3,       1.0000       ,
               1.0000        )
:    7e16b(  −36.637  ₁₀+ 6)
:      11s(   −2.0000        ,        200.62  ₁₀− 3,      45.571  ₁₀+ 6,
             423.00          ,        500.00  ₁₀+ 3,       1.0000       ,
               1.0000        )
:    2e23s( −797.38   ₁₀− 3)
+
end Simulation of i-butane production, completed — 20
```

Table 5.3

Calculation results of problem [Simulation of i-butane production, completed] (second part)

```
SIMUL print
i-butane production  -20
D97001

stream (1)

   stream type                                1
   mass stream                           360.00        kmole/h
   enthalpy                      -          7.7212×10^6 kcal/h
   temperature                            79.8         °C
   pressure                               14.7         atm
   vapour ratio                             0.0000     kmole/kmole
   n-butane                                 0.9700     kmole/kmole
   2-methyl-propane                         0.0000     kmole/kmole
   n-pentane                                0.0300     kmole/kmole

stream (2)

   stream type                                1
   mass stream                           360.00        kmole/h
   enthalpy                      -          7.8995×10^6 kcal/h
   temperature                            79.8         °C
   pressure                               14.8         atm
   vapour ratio                             0.0000     kmole/kmole
   n-butane                                 0.5324     kmole/kmole
   2-methyl-propane                         0.4376     kmole/kmole
   n-pentane                                0.0300     kmole/kmole

stream (3)

   stream type                                1
   mass stream                           360.00        kmole/h
   enthalpy                      -          7.7709×10^6 kcal/h
   temperature                            86.8         °C
   pressure                               14.8         atm
   vapour ratio                             0.0000     kmole/kmole
   n-butane                                 0.5324     kmole/kmole
   2-methyl-propane                         0.4376     kmole/kmole
   n-pentane                                0.0300     kmole/kmole

stream (10)

   enthalpy                              128.55×10^3    kcal/h

stream (4)

   stream type                                1
   mass strean                           202.41        kmole/h
   enthalpy                      -          4.1463×10^6 kcal/h
   temperature                           100.3         °C
   pressure                               14.8         atm
   vapour ratio                             0.0000     kmole/kmole
   n-butane                                 0.9453     kmole/kmole
   2-methyl-propane                         0.0013     kmole/kmole
   n-pentane                                0.0534     kmole/kmole
```

Table 5.3 (cont.)

```
stream (7)

  stream type                                           1
  mass stream                                        157.59            kmole/h
  enthalpy                                        —    3.4912 × 106    kcal/h
  temperature                                         85.2             °C
  pressure                                            14.8             atm
  vapour ratio                                         0.0000          kmole/kmole
  n-butane                                             0.0020          kmole/kmole
  2-methyl-propane                                     0.9980          kmole/kmole
  n-pentane                                            0.0000          kmole/kmole

dist 1 (30)

  number of plates                                    80
  feed plate                                          40
  code of the light key component                      2
  code of the heavy key component                      1
  average convergence pressure                        35.5 atm
  control mode of column                             reflux specification
  type of condensation                               total
  type of reboiling                                  total
  value of the controlled parameter                   11.500
  reflux temperature                                  85.2             °C
  top temperature                                     84.8             °C
  bottom temperature                                 104.8             °C
  yield of key component in the bottom product        99.8%
  condenser heat flow                             —    6.287 × 106     kcal/h
  reboiler heat flow                                   6.383 × 106     kcal/h
  calculated reflux ratio                             11.500
  average column efficiency                          903.46 × 10−3

stream (5)

  stream type                                           1
  mass stream                                        202.41            kmole/h
  enthalpy                                        —    4.3608 × 106    kcal/h
  temperature                                         79.8             °C
  pressure                                            14.8             atm
  vapour ratio                                         0.0000          kmole/kmole
  n-butane                                             0.9453          kmole/kmole
  2-methyl-propane                                     0.0013          kmole/kmole
  n-pentane                                            0.0534          kmole/kmole

stream (9)

  enthalpy                                           214.43 × 103      kcal/h

stream (6)

  stream type                                           1
  mass stream                                        202.41            kmole/h
  enthalpy                                        —    4.4609 × 106    kcal/h
  temperature                                         79.8             °C
  pressure                                            14.8             atm
  vapour ratio                                         0.0000          kmole/kmole
  n-butane                                             0.5098          kmole/kmole
  2-methyl-propane                                     0.4369          kmole/kmole
  n-pentane                                            0.0534          kmole/kmole
```

Table 5.3 (cont.)

stream (8)		
stream type	1	
mass stream	360.00	kmole/h
enthalpy	-7.9521×10^6	kcal/h
temperature	82.3	°C
pressure	14.8	atm
vapour ratio	0.0000	kmole/kmole
n-butane	0.2875	kmole/kmole
2-methyl-propane	0.6825	kmole/kmole
n-pentane	0.0300	kmole/kmole
stream (12)		
stream type	−2	
mass stream	3.60000×10^3	kmole/h
enthalpy	0.0000	kcal/h
temperature	149.8	°C
pressure	4.9	atm
vapour ratio	1.00	kmole/kmole
water	1.00	kmole/kmole
vlexpa (16)		
transferred heat	-31.502×10^6	kcal/h
stream (11)		
stream type	−2	
mass stream	722.23	kmole/h
enthalpy	39.184×10^6	kcal/h
temperature	149.8	°C
pressure	4.9	atm
vapour ratio	1.00	kmole/kmole
water	1.0000	kmole/kmole
stream (23)		
mass stream	-2.8706×10^3	kmole/h

therefore they do not contain information about the accuracy of the results. In this respect the evaluation is not programmed, it is the task of the user of the SIMUL system.

A program, independent of the SIMUL system, is able to print the calculated data in a more readable form. In this the SI units are also converted. The second part of Table 5.3 contains the relevant data as described here, under the heading "SIMUL print".

From the point of view of process evaluation, the functioning of the two reactors and the distillation column is the most important. In the stream leaving the first reactor, the mole fraction of i-butane (8e2s) is 0.42, corresponding to around 45 % conversion. This value cannot be considered as sufficiently high for a reaction of this type. The reason may be found in the quantity of catalyst which is relatively low. The distillation equipment performs a good separation using 0.3 kmole/s (2e11s) steam, corresponding to the heat load of the reboiler (16e30b). The n-butane content of the top product (7e7e) is 0.2 %, the i-butane content of the bottom product (8e4s) 0.13 %. The feed entering the second reactor contains 94.5 % n-butane (7e5s). The n-butane content of the leaving flow (7e6s) is around 50 %, far from the quality of commercial i-butane. It is therefore understandable that in the final product, obtained by mixing the distillate and the product of the second reactor, the i-butane content (8e8s) is not more than 68 %. The conclusion may be drawn that the simulated type of process performance procedures only one useful product: the distillate. Immediately the question arises whether a more favourable type of process performance can be found.

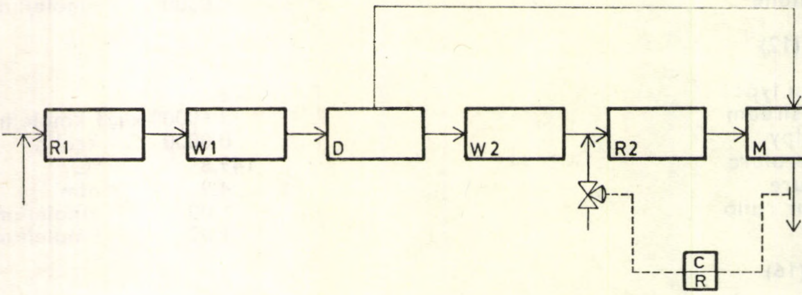


Fig. 5.3. **Process block diagram of the butane isomerization (control of product quality)**

The answer is readily found without entering into the economic aspects of the question. It is obvious that the conversion of n-butane must be increased in the reactors and this may be achieved by increasing the catalyst flow in both reactors.

In practice, the catalyst flow needed to manufacture products of prescribed quality is regulated by control loops (one or more) built into the complex operation. The process block diagram is enlarged if the elements of the control loop are symbolized too (Fig. 5.3). The analyser built into the product pipeline measures the concentration of i-butane. This information arrives through the feedback (dotted line) to C/R controller. This compares the actual concentration of i-butane with the prescribed value and establishes the difference. If the actual concentration is less (greater) than the prescribed concentration, then the controller relays the instruction to the final control element (through the feedback, denoted by the dotted line) to increase (decrease) the catalyst flow. As a consequence, the concentration of i-butane increases in the product. After a certain time, the actual value of the i-butane concentration is measured again by the analyser and thus a new control cycle starts. In the course of these cycles, the actual value approaches the prescribed value and the actual value is corrected provided it approaches the prescribed value, taking the allowed error into consideration. The difference between prescribed and actual values is a function, whose actual value permits the quasi-steady-state functioning of the complex operation in each cycle to be evaluated. During controlling, the minimum of the absolute value of this function is sought. This description is a simplified illustration of control, but nevertheless it reflects the main features of control mechanism.

Considering the results of the calculation (Table 5.3), we have compared the concentration of i-butane with the prescribed value of the commercial product (0.94). We conclude that the catalyst flow has to be increased in the second reactor chosen for control purposes (Fig. 5.3). If we define the new value, then the simulation may be repeated. A second computing cycle is required, after which the new concentration of i-butane in the product is obtained. Comparing this value with the prescribed one, a new decision may be made which is followed by the third computing cycle. After each cycle the actual value approaches the prescribed value. The number of subsequent computing cycles is the number necessary to arrive at the prescribed value within the allowed error. At this stage, the sequence of cycles is terminated and the value of the catalyst flow obtained in the last cycle ensures that the concentration of i-butane is within the limits of error.

It is obvious that we have simulated the functioning of a control loop. It seems that all computation cycles have to be calculated with the same flow-sheet program, but with modified input data systems. The SIMUL system can organize successive computation cycles automatically, and based on a sensible strategy, can simulate the functioning of a control loop. Without entering into details (this is done in Chapter 6), the final result of the calculation is as follows: in the system represented in Figure 5.3 the value of the catalyst flow in the second reactor is 0.00034 kmole/s. It is evident that the load on both reactors is rather unequal: the conversion is 45 % in the first and about 93 % in the second. It is qualitatively evident to the technologist that increase of the catalyst flow in the first reactor and decrease in the second would decrease the overall catalyst flow without endangering the quality of the product. Simulation of other different types of process performance and selection of the most favourable one do not introduce difficulties. We consider a process performance as the most favourable when the cost sum of the overall catalyst consumption plus the cost of steam used in the distillation are minimal. We have thus defined the objective function which evaluates any type of process performance from the economic point of view. We shall select that type of process performance which induces the minimal value of the objective function. The search for this type of process performance is the optimization which may be carried out automatically and with a suitable strategy in the SIMUL system. The block diagram of the above optimization is presented in Figure 5.4.

Without entering into details about the solution of the task (this will be done in Chapter 7), the significant results are the following. In the optimal case (assuming the validity of the catalyst and steam prices used) the catalyst flow is 0.000500 kmole/s in the firts reactor and 0.000619 kmole/s in the second. The overall catalyst flow is therefore 0.001119 kmole/s. This value was about three times as much (0.00347 kmole/s) in the non-optimal case discussed above. The steam consumption on the other hand had doubled.

Both the control and the optimization have a common feature: the direction of the material and some information streams were opposed, therefore one or more closed loops were formed in the information network. The information network is described by references in the SIMUL system,

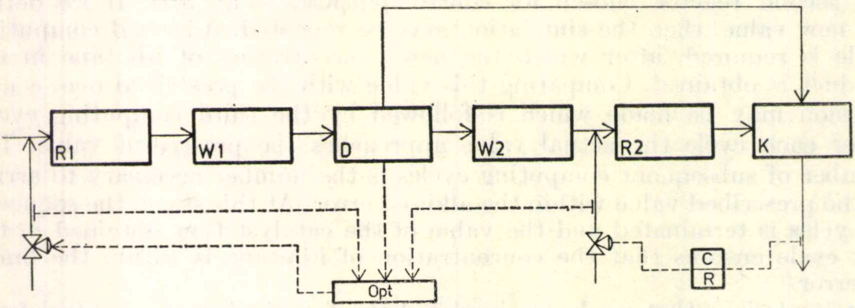


Fig. 5.4. Process block diagram of the butane isomerization (control of product quality, optimization)

and it is a strict requirement that the reference chain must not form loops. Actually, no loops occur in a calculation cycle. A calculation cycle signifies the calculation of a hypothetical steady-state type of process performance with an open reference chain from which, according to a suitable plan we automatically switch over to the next hypothetical type of process performance, provided a hypothetical type of process performance, which corresponds to the required real (controlled or optimized) type, is obtained.

The problem raised and dealt with here occurs in a second aspect when simulating complex operations. The material streams in the three cases discussed above were non-directional. To produce i-butane another scheme is conceivable (Fig. 5.5). Here a single reactor is used whose product is separated by distillation into two flows. The bottom product, consisting mainly of non-reacted n-butane is recycled to the mixer and mixed with

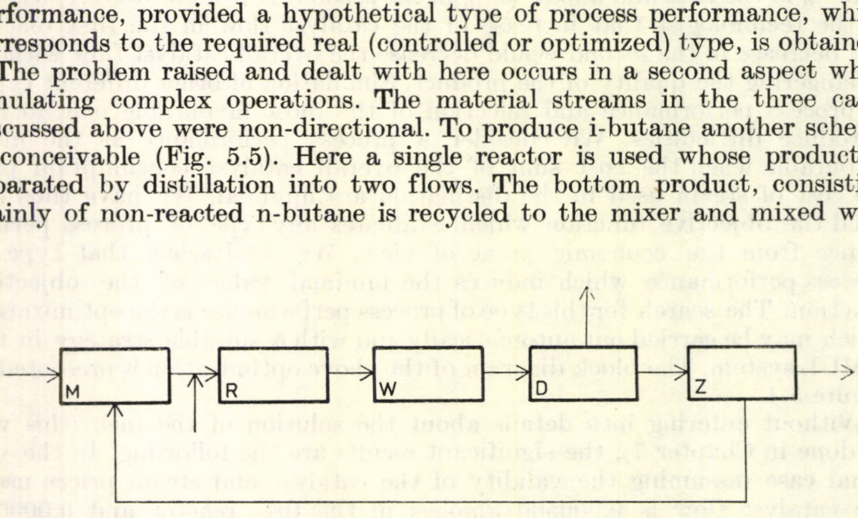


Fig. 5.5. Process block diagram of the butane isomerization (bottom product recycle)

the raw material. Part of the recycled flow is blown off in order to adjust the concentration of the unreacted n-pentane to a stationary value. This network is new in every aspect, as a loop appears in the network of material streams. The problem does not differ in principle from controlling (information feedback), but it is more general in two aspects. In order to follow this train of thought, let us interrupt the recycled flow and consider the two separate flows formed (Fig. 5.6). An analyzer is placed into the flow originating from the branch, which determines $k + 2$ independent process variables. These actual values are entered into a *($k + 2$)* dimensional controller. This controller considers the actual $k + 2$ values of the flow entering the mixer as the actual prescribed value of the $k + 2$ qualities of the flow arriving from the divider.

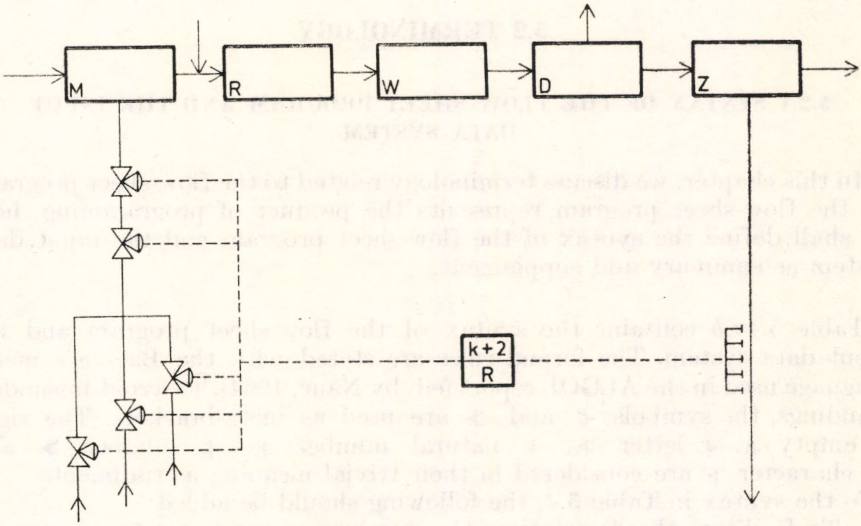


Fig. 5.6. Analogy between recycle and control

The controller compares the two vectors – each containing $k + 2$ elements – and relays the instruction to the final control element to eliminate the differences. This leads to a new type of process performance in which the controlled and controlling stream vectors differ again. New cycles follow, provided the two vectors agree, within the limits of the allowed error.

This consideration leads to the following results:

1. the problem of loops in the network of material streams does not differ from controlling, nevertheless it is more general, since
2. it is not related to a single quantity but to the vector of independent quantities of a stream and
3. it is interpreted with a changing base-value vector.

The computational solution is again to break the loop in each calculation cycle. A calculation cycle implies computation of a hypothetical, steady-state, feed-back-free type of process performance from which, according to a suitable plan, we automatically switch over to the next hypothetical type of process performance, provided a hypothetical process-performance type is obtained, which corresponds to the required real type. This question will be discussed in more detail in Chapter 6.

5.2 TERMINOLOGY

5.2.1 SYNTAX OF THE FLOW-SHEET PROGRAM AND THE INPUT DATA SYSTEM

In this chapter, we discuss terminology related to the flow-sheet program. As the flow-sheet program represents the product of programming, here we shall define the syntax of the flow-sheet program and the input data system as summary and supplement.

Table 5.4*a*,*b* contains the syntax of the flow-sheet program and the input data system. The formal rules are stated with the Backus's meta-language used in the ALGOL report (ed. by Naur, 1964). To avoid misunderstandings, the symbols ⊀ and ⊁ are used as meta-brackets. The signs ⊀ empty ⊁, ⊀ letter ⊁, ⊀ natural number ⊁, ⊀ number ⊁ and ⊀ character ⊁ are considered in their trivial meaning as rudiments.

To the syntax in Table 5.4, the following should be added:

1. To facilitate the description, the number-sequence statement may be used in the flow-sheet program and in the input data system. The formal number-sequence statement is the following:

⊀ Number sequence statement ⊁ : : =
⊀ delimiter ⊁ ⊀ number ⊁ = ⊀ delimiter ⊁
⊀ number ⊁ | ⊀ delimiter ⊁ ⊀ integer ⊁ × ⊀ delimiter ⊁ ⊀ number ⊁.

The number sequence statement $p = q$ means a number sequence from p till q, where each difference is 1.

The number sequence statement $i \times p$ means i times the same value (p).

More rigorously the number sequence statement of the type $p = q$ means

$$\begin{aligned} &\text{if } p \leq q\text{, then p, } p+1, \ldots, p+k \\ &\text{if } p > q\text{, then } p, p-1, \ldots, p-k \end{aligned}$$

numerical values, where k is the rounded-off value of $(q - p)$.

The number sequence statement $i \times p$ means a number sequence:

$$p, p, \ldots, p$$

containing i elements.

Table 5.4a

Syntax of the flow-sheet program

```
≮ flowsheet program ≯ : : = ≮ task identifier ≯ ≮ job number ≯ ≮ stream type data group ≯ ≮ comment ≯ +
  ≮ data group of operation order ≯ ≮ comment ≯ +
      ≮ task identifier ≯ : : = [ ≮ text ≯ ]
          ≮ text ≯ : : = ≮ any character sequence not containing ] character ≯
      ≮ job number ≯ : : = ≮ start ≯ ≮ natural number ≯
      ≮ stream type data group ≯ : : = ≮ empty ≯ | ≮ stream type data group ≯ ≮ stream type record ≯
          ≮ stream type record ≯ : : = ≮ comment ≯ : ≮ stream type code ≯ ≮ component code list ≯
              ≮ comment ≯ : : = ≮ empty ≯ | ≮ any character sequence not containing characters : or ∧ or ∨ or + ≯
              ≮ stream type code ≯ : : = ≮ natural number ≯
              ≮ component code list ≯ : : = ≮ start ≯ ≮ component code ≯ / ≮ component code list ≯ ≮ delimi-
              ter ≯ ≮ component code list ≯
                  ≮ start ≯ : : = ≮ empty ≯ | ≮ delimiter ≯
                  ≮ component code ≯ : : = ≮ natural number ≯
                  ≮ delimiter ≯ : : = ≮ letter ≯ | ∨ | / |; | [ | ] | | ↗ | < |, | : | CR | ≮ delimiter ≯
                      ≮ delimiter ≯
      ≮ operation order data group ≯ : : = ≮ empty ≯ | ≮ operation order data group ≯ ≮ operational declaration ≯
                      | ≮ operation order data group ≯ ≮ | loop ≯
          ≮ operational declaration ≯ : : = ≮ comment ≯ : ≮ box index ≯ ( ≮ operating index ≯
                      ≮ connection index list ≯ )
              ≮ box index ≯ : : = ≮ natural number ≯
              ≮ operating index ≯ : : = ≮ start ≯ ≮ natural number ≯
              ≮ connection index list ≯ : : = ≮ empty ≯ | ≮ connection index list ≯ ≮ delimiter ≯
              ≮ connection index ≯
                  ≮ connection index ≯ : : = ≮ natural number ≯
              ≮ loop ≯ : : = ≮ operational declaration ≯ ≮ comment ≯ ∧ ≮ operation order data group ≯
                  ≮ comment ≯ ∨
```

Table 5.4b
Syntax of the input data system

≮ input data system ≯ : : = ≮ data system serial number ≯ b ≮ box data group ≯ ≮ comment ≯ + s ≮ stream data group ≯ ≮ comment ≯ +
≮ data system serial number ≯ : : = ≮ natural number ≯
≮ box data group ≯ : : = ≮ empty ≯ | ≮ box data group ≯ ≮ box declaration ≯
≮ box declaration ≯ : : = ≮ comment ≯ : ≮ operating index ≯ (≮ operating parameter vector ≯) | ≮ comment ≯ : operating index ≯ (≮ arithmetic expression ≯)
≮ operating parameter vector ≯ : : = ≮ start ≯ operating parameter ≯ | ≮ operating parameter vector ≯ ≮ delimiter ≯ ≮ operating parameter ≯
≮ operating parameter ≯ : : = ≮ number ≯ | ≮ reference ≯ | ≮ operating parameter ≯ ≮ stored delimiter ≯
≮ reference ≯ : : = ≮ array reference ≯ | ≮ array element reference ≯ | ≮ reference code ≯ r
≮ array reference ≯ : : = ≮ natural number ≯ b | ≮ natural number ≯ s
≮ array element reference ≯ : : = ≮ natural number ≯ e ≮ array reference ≯
≮ reference code ≯ : : = ≮ natural number ≯
≮ stored delimiter ≯ : : = > ≮ character ≯
≮ arithmetic expression ≯ : : = ≮ number ≯ | ≮ reference ≯ | ≮ arithmetic expression ≯ | ≮ one-argument operation symbol ≯ | > ≮ arithmetic expression ≯ ≮ arithmetic expression ≯ > ≮ two-argument operation symbol ≯
≮ one-argument operation symbol ≯ : : = 1 | e | s | o | g | a | i
≮ two-argument operation symbol ≯ : : = + | − × | / | ∧
≮ stream data group ≯ : : = ≮ empty ≯ | ≮ stream data group ≯ ≮ stream record ≯
≮ stream record ≯ : : = ≮ comment ≯ : ≮ connection index ≯ (≮ stream vector ≯)
≮ stream vector ≯ : : = ≮ start ≯ ≮ stream vector element ≯ | ≮ stream vector ≯ ≮ delimiter ≯ ≮ stream vector element ≯
≮ stream vector element ≯ : : = ≮ number ≯ ≮ reference ≯

In both the flow-sheet program and the input data system, the corresponding number sequence statement may be inserted everywhere, where a number sequence of this kind appears.

2. Letters *s* and *b* in the array identifier define the type of the array. In case of *b*, the identified array is the operating parameter vector of a box or an arithmetic expression; in case of *s* it is a stream vector.

The number is the array declarer (operating index and connection index) In a reference to an array element, the number situated before the letter *e* is the serial number of the element.

3. In the description of the arithmetic expression, the so-called reversed Polish notation is used.

Accordingly, the calculation of the numerical values of the expression is effected from right to left, and all operation symbols relate to the numerical value of the argument situated before the symbol. In an operation with two arguments, the evaluation of the right-hand argument is made first and the left-hand argument follows.

The operation symbols in the arithmetic expressions are the following, using ALGOL notation:

$$
\begin{aligned}
&< \mathrm{x} > \mathrm{l} && = \ln x \\
&< \mathrm{x} > \mathrm{i} && = \text{entier } x \\
&< \mathrm{x} > \mathrm{e} && = \exp x \\
&< \mathrm{x} > \mathrm{s} && = \sin x \\
&< \mathrm{x} > \mathrm{c} && = \cos x \\
&< \mathrm{x} > \mathrm{g} && = \arctan x \\
&< \mathrm{x} > \mathrm{a} && = \text{abs } x \\
&< \mathrm{x,y} > + && = x + y \\
&< \mathrm{x,y} > - && = x - y \\
&< \mathrm{x,y} > \times && = x * y \\
&< \mathrm{x,y} > / && = x / y \\
&< \mathrm{x,y} > \wedge && = x \uparrow y
\end{aligned}
$$

It should be noted that an array reference in an arithmetic expression may refer only to another arithmetic expression.

It should also be noted, that the symbol $>$ in the syntactic definition of the arithmetic expression is only present for clarification. Assuming or dropping it does not influence the course of calculation.

5.2.2 FLOW-SHEET PROGRAM

The flow-sheet program is a description with prescribed structure, defining unequivocally the stream types figuring in the calculation and the course of calculation. The organizing program (Chapter 8.2), based on the flow-sheet program, activates the boxes in the required sequence and with the necessary stream vectors, using the operating parameter vectors of the boxes and the stated stream vectors as input.

5.2.2.1 PARTS OF THE FLOW-SHEET PROGRAM

The flow-sheet program contains the definition of the stream types in the system modelled and the description of the course of the calculation.

(a) Definition of the stream types

The stream types are defined by records. Each record defines a stream type. The first data of the record is the stream-type index, followed by the component codes of the first, second, etc., components.

Proper selection of the stream types may save storage capacity and computation time because the components figuring incidentally in the following mixtures with zero mole fraction, participate in reserving storage capacity, as is the case in property calculations.

(b) Description of the course of calculation

The course of calculation is described by records. Each record defines a simulating operation, in short: operation. The first datum of the record is the box index, followed by the operating index indicating the operating parameters of the box and the connection index denoting the streams which join the box.

The operations are carried out in the order of their description, except when an organizing program prescribes another sequence.

Some organizing boxes allow the cyclic repetition of an operation sequence consisting of one or more operations. The records of the operations to be repeated should be stated after the operation, organizing the cycle between symbols $\wedge$ and $\vee$. If during calculation, the operation preceding the symbol $\vee$ is carried out, then the box organizing the cycle functions again, provided the box organizing the cycle does initiate the operation following the symbol $\vee$. The operation organizing the cycle and the repeated operations may be considered as a unified operation, which – as much – may figure as an element of an operation sequence to be repeated. This is why it is possible to arrange any intermeshed cycles.

The operations are considered to have serial numbers in the sequence of their description – these are the calculation serial numbers.

The calculation serial number is to be found related to operations modifying the sequence of operations (e. g., *jump*). The calculation serial number does not figure in the flow-sheet program.

5.2.3 INPUT DATA SYSTEM

The input data system contains the operating parameters of the boxes figuring in the calculation, and then the data groups of the input stream vectors.

Both the operating parameters and the data groups of the stream vectors consist of records. The records, defining the operating-parameter vector and the stream vector begin with the operating index and the connection index respectively. The sequence of records in a data group is discretional. The number, the meaning and the sequence of the operating parameters linked to each box are defined in their specification (see, Chapters 3.4 and 4.4).

In place of any data of the input data system, a reference may appear, referring to other data or arithmetic expression (see, Section 4.4.2), which — when called — represents the actual value of that quantity.

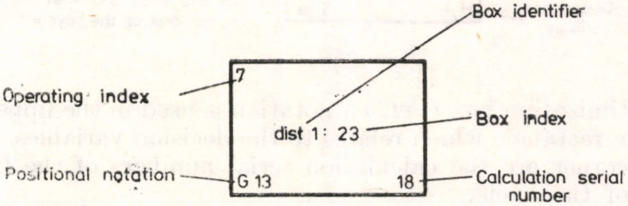
The operating index of a record, defining an arithmetic expression, has to be smaller than the highest operating index featured in the flow-sheet program. If an input stream is in the gaseous or liquid state (not in mixed state), then the enthalpy stream need not be stated, and zero may be written on its place. In this case procedure *str from drum* completes the stream vector with the value of the enthalpy at the given temperature, pressure, state and composition. Otherwise, the relations between the values of the enthalpy, temperature, pressure and vapour ratio have to be fulfilled.

5.3 SYMBOLS AND NOTATIONS IN THE OPERATION-ORDER FLOW-SHEETS

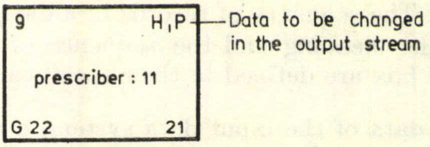
The accepted symbol system of the operation-order flow-sheet is — as already discussed — suitable for representing clearly all the information needed to simulate a process. This system of symbols was discussed in detail in the previous chapters. We shall recall these conventions.

The simulating operations are symbolized by rectangles. In the middle the identifier of the box is written, and after a colon, the box index. The operating index of the box is in the upper left-hand corner and the calculation serial number is given in the lower right-hand corner.

The symbol of the equipment-type boxes contains the positional notation of the equipment on the flow-sheet in the lower left-hand corner of the rectangle.

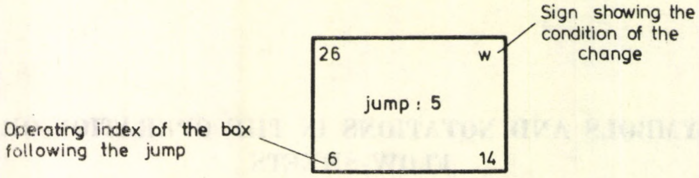


In the symbol of the box prescribing the change of the output stream *(prescriber)*, the elements to be modified by the stream vector are indicated in the upper right-hand corner of the rectangle.

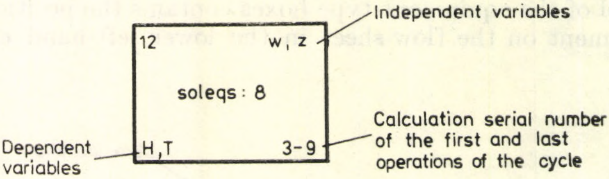


Denoting the box which modifies the order of calculation *(jump)* a character is used in the upper right-hand corner of the rectangle, which refers to the condition of the modification. The operating index of the box which has to be used to continue the calculation, figures in the lower left-hand corner.

The letter w has the meaning that the change in the calculation order is a function of the mass stream *(w)*.

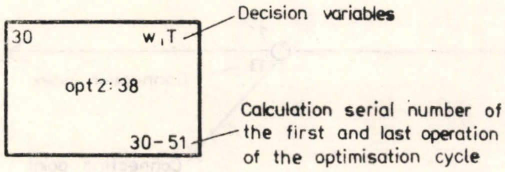


Among the mathematical boxes, the rectangle symbolizing the box for solving non-linear systems of equations *(soleqs)* contains in the upper right-hand corner notations referring to the independent variables of the equation-system, whilst the notations of the dependent variables figure in the lower left-hand corner. In the lower right-hand corner are the calculation serial numbers of the first and last operations of the cycle.



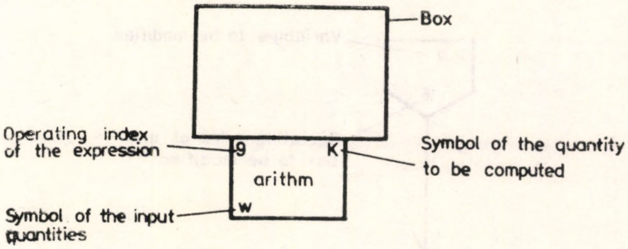
In the optimization box *(opt2)* a notation is used in the upper right-hand corner of the rectangle which relates to the decision variables. In the lower right-hand corner are the calculation serial numbers of the first and last operations of the cycle.

Before beginning the computation, the input of the entering stream vectors is effected by the organizing program. These are denoted in the calculation flow-sheet as *R*.

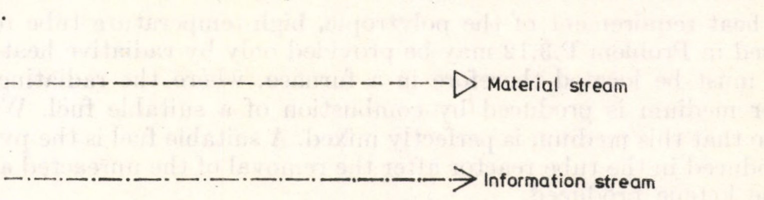


The arithmetic expressions used in the course of computation are also symbolized by rectangles in the operation-order flow-sheet. To underline the fact that an arithmetic expression is always used simultaneously with an optimizing operation, the rectangle which symbolizes the arithmetic expression adjoins the rectangle of the related operation.

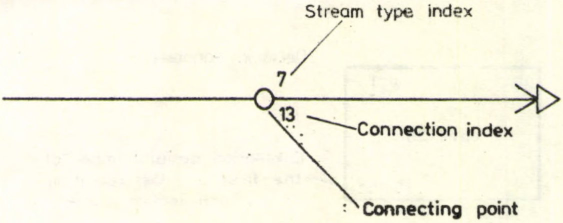
The operating index of the arithmetic expression is written in the upper left-hand corner of the rectangle, the notations of the input quantities are in the lower left-hand corner. The notation of the quantity to be computed is in the upper right-hand corner.



The symbol of the streams flowing between the boxes is a direct line, which may be solid, dashed or dotted, depending on material and information, only material, or only information is flowing between the connected points. The arrow, showing the direction of the information stream is open; it ends with a triangle if it denotes the direction of a material stream.

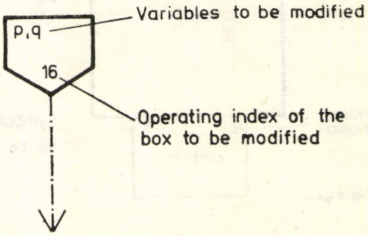


The mode of notation of the stream-type index, of the connection index and of the connecting point is as follows:



The controlled process variables are designated by squares, in which the parameters are written:

The modification of operating parameters or elements of stream vectors by a box is symbolized by a pentagon, containing the operating index of the modifying box and the variables to be modified. The information stream starting from the pentagon is directed to the site where the modification is carried out.



PROBLEM

PROBLEM P.5.1 RADIATION ZONE OF A PIPE STILL

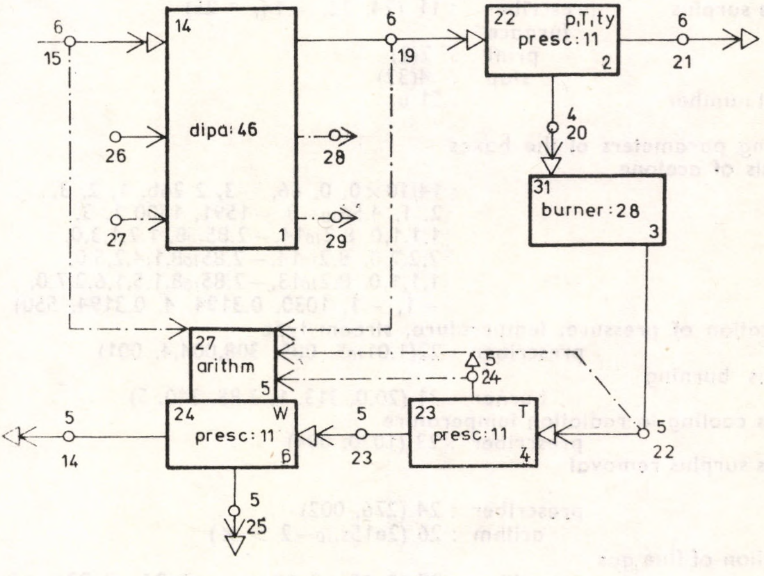
The heat requirement of the polytropic, high-temperature tube reactor, discussed in Problem P.3.12 may be provided only by radiative heat-transfer. It must be located therefore in a furnace, where the radiating heat-transfer medium is produced by combustion of a suitable fuel. We may suppose that this medium is perfectly mixed. A suitable fuel is the pyrolysis gas produced in the tube reactor after the removal of the unreacted acetone and the ketene produced.

Calculate the stream vector of the pyrolysis gas and the flue gas using the geometrical and feed data of Problem P.3.12, with a 1030 K radiation temperature.

Solution

The tube reactor is simulated by box *dipa*, as for Problem P.3.12. The pressure, temperature and stream type of the gas leaving the tube reactor are set by box *prescriber*. The stream leaving box *prescriber* is fuel gas; the acetone and ketene content of the pyrolysis gas leave in the difference stream. Burning of the fuel gas with 20 % air excess simulated by box *burner*, which is followed by setting the temperature of the flue gas to 1030 K by box *prescriber*. The mole stream of the flue gas is set by the next box *prescriber*, but calculated from an arithmetic expression, based on the following consideration. The difference enthalpy stream of box *prescriber* setting the temperature of the flue gas, divided by the mass stream of the entering fuel gas, results in the molal enthalpy decrease of the flue gas due to heat-transfer.

On the other hand the difference in enthalpy streams between the inlet and outlet of the pipe still is exactly the heat load taken up by heat transfer. It follows that the quotient of the heat load and the molal enthalpy decrease equals the mole stream of the flue gas. The operation-order flow-sheet is as follows:



It has to be checked that the order of operations is unidirectional, i. e., no loops exist in the graph of the information streams. The result of the check should indeed be positive.

The flow-sheet program and input-data system are presented in Table P.5.1 (1), the results of the calculation in Table P.5.1 (2).

Table P.5.1 (1)

Flow-sheet program and input data system of problem [Furnace]

```
[Furnace]
A 770305
stream types
pyrolysis gas                          : 6 (117, 114,1, 26, 71, 70,67)
acetone, ketene, methane,
ethylene, carbon dioxide,
hydrogen
fuel gas                               : 4 (1,26, 71, 70,67)
methane, ethylene,
carbon monoxide,
carbon dioxide,
hydrogen
flue gas                               : 5 (64,69, 70, 72)
oxygen, water,
carbon dioxide,
nitrogen
operations                    +
tube reactor                 dipa      : 46 (14, 15, 26, 27,−19,−28,−29)
print reactor side          print      : 2 (1)
fuel gas burning           burner      : 28 (31,20, −22)
heat transfer          prescriber      : 11 (23, 22, −23, −24)
flue gas surplus       prescriber      : 11 (24, 23, −14, −25)
print                     furnace
side                        print      :  2(2)
                             stop      :  4(32)
data set number                        : 51 u

operating parameters of the boxes
pyrolysis of acetone
  dipa                                 : 14/10×0, 0, 66, −3, 2 26b, 1, 2, 3,
                                         2, 1, 4.56₁₀−3 −1591, 1500 1, 3,
                                         1,1,1,0, 8.2₁₀14,−2.85₁₀8, 1,2,1,3,0,
                                         2,2,2,0, 8.2₁₀14,−2.85₁₀8,1,4,2,5,0,
                                         1,1,1,0, 8.2₁₀13,−2.85₁₀8,1,5,1,6,2,7,0,
                                         −1, −1, 1030, 0.3194, 4, 0.3194, 550)
Modification of pressure, temperature, stream type
                       prescriber      : 22(1.01₁₀5, 005, 308,004,4, 001)
fuel gas burning
                           burner      : 31 (20,0, 313, 1, 3.85, 3*0, 5)
fuel gas cooling to radiation temperature
                       prescriber      : 23 (1030, 004)
flue-gas surplus removal

                       prescriber      : 24 (276, 002)
                           arithm      : 26 (2e15s,₁₀−2 > ×)
calculation of flue gas
                           arithm      : 27 (3e15s, 3e19s > − 3e24s, 2e22s > / > /)
after calculating the tube reactor
                            print      : 1 (5, 15s, 19s)
after calculating the radiating zone
                            print      : 2 (5, 14s, < 19 = 25 > s)
                                         +
streams
                     aceton input      : 15 (6, 1.053₁₀−2,0, 468,3₁₀5,1,1, 6*0)
                                         +
```

Table P.5.1 (2)

Calculation results of problem [Furnace]

```
Furnace 51—
:        15s(     6.0000           ,     10.530  10− 3,        0.0000          ,
               468.00              ,    300.00   10+ 3,        1.0000          ,
                  1.0000           ,      0.0000       ,       0.0000          ,
                  0.0000           ,      0.0000       ,       0.0000          ,
                  0.0000           )
:        19s(     6.0000           ,     15.542  10− 3,     −785.93    10+ 3,
                  1.0093   10+ 3,       194.99   10+ 3,        1.0000          ,
               404.92      10− 3,       247.22   10− 3,      247.82    10− 3,
               303.01      10− 6,        25.388  10− 3,       24.782   10− 3,
                 49.564    10− 3)
:   63e14b(       1.0300   10+ 3)
+
:        14s(    −5.0000           ,     19.097  10− 3,     −774.75    10+ 3,
                  1.0300   10+ 3,       100.00   10+ 3,        1.0000          ,
                 31.841    10− 3,       162.72   10− 3,       89.018   10− 3,
               716.42      10− 3)
:        19s(     6.0000           ,     15.542  10− 3,     −785.93    10+ 3,
                  1.0093   10+ 3,       194.99   10+ 3,        1.0000          ,
               404.92      10− 3,       247.22   10− 3,      247.82    10− 3,
               303.01      10− 6,        25.388  10− 3,       24.782   10− 3,
                 49.564    10− 3)
:        20s(     4.0000           ,      5.4064 10− 3,     −399.88    10+ 3,
               308.00              ,    101.00   10+ 3,        1.0000          ,
               712.42      10− 3,       871.07   10− 6,       72.984   10− 3,
                 71.242    10− 3,       142.48   10− 3)
:        21s(     6.0000           ,     10.135  10− 3,     −386.04    10+ 3,
                  1.0093   10+ 3,       194.99   10+ 3,        1.0000          ,
               620.92      10− 3,       379.08   10− 3,        0.0000          ,
                  0.0000           ,      0.0000       ,       0.0000          ,
                  0.0000           )
:        22s(    −5.0000           ,     52.133  10− 3,       30.520   10+ 3,
                  2.1253   10+ 3,       100.00   10+ 3,        1.0000          ,
                 31.841    10− 3,       162.72   10− 3,       89.018   10− 3,
               716.42      10− 3)
:        23s(    −5.0000           ,     52.133  10− 3,       −2.1149  10+ 6,
                  1.0300   10+ 3,       100.00   10+ 3,        1.0000          ,
                 31.841    10− 3,       162.72   10− 3,       89.018   10− 3,
               716.42      10− 3)
:        24s(    −5.0000           ,      0.0000       ,       2.1455  10+ 6,
                  2.1253   10+ 3,       100.00   10+ 3,        1.0000          ,
                 31.841    10− 3,       162.72   10− 3,       89.018   10− 3,
               716.42      10− 3)
:        25s(    −5.0000           ,     33.035  10− 3,       −1.3402  10+ 6,
                  1.0300   10+ 3,       100.00   10+ 3,        1.0000          ,
                 31.841    10− 3,       162.72   10− 3,       89.018   10− 3,
               716.42      10− 3)
+
end Furnace
```

CHAPTER 6

INFORMATION FEEDBACK

The recycles and control loops are feedback from the viewpoint of information streams when simulating networks defined by unit operations and material streams flowing between them. Therefore — when calculating the unknown stream vectors — not only do the model equations of the consecutive unit operations have to be solved, but also those systems of equations which are defined by the relations of the output and input of some groups of unit operations. As the mathematical models represented by the boxes are generally non-linear, the task to be solved when calculating feedbacks consists mainly of solving single non-linear equations or systems of them.

In practice this is equivalent to saying that during simulation the output stream vector cannot be obtained from the input ones by calculating the network once, but it is necessary to iterate, returning several times if necessary to the same unit operation.

6.1 RECYCLE

Figure 6.1 shows the process block diagram consisting of A, B and C unit operations, where a material stream is recycled from C to A.

When starting the simulation, only the input stream data are known. Therefore, if we start to calculate with unit A, initial trial values must be substituted for the missing data of the recycle. After these values are assumed, we simulate A, B and C in turn, obtaining the calculated value of each stream as a result. The assumed and calculated data of the recycling stream probably differ. Our task is to determine the data of the stream entering A such that they are equal to the calculated data of the stream leaving C.

Let us tear the recycling stream. Let $\mathbf{x}$ be the assumed vector, $\mathbf{y}$ the calculated vector, both consisting of m independent elements:

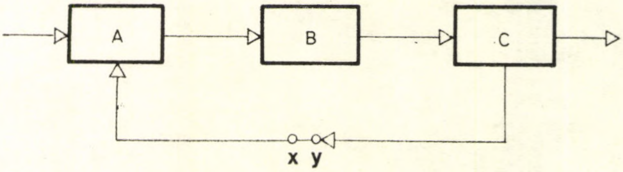


Fig. 6.1. Simple recycle loop

$$\mathbf{x} = [x_1, x_2, \ldots, x_m]\,,$$

$$\mathbf{y} = [y_1, y_2, \ldots, y_m]\,.$$

Their relation is:

$$\mathbf{y} = f(\mathbf{x})\,. \tag{6.1}$$

The calculation of the recycle may be considered as solved if the condition

$$\mathbf{y} = \mathbf{x} \tag{6.2}$$

is fulfilled with sufficient accuracy. From equations (6.1) and (6.2) we obtain vector equation

$$F(\mathbf{x}) = \mathbf{x} - f(\mathbf{x}) = \mathbf{0} \tag{6.3}$$

Expanding this correlation, the following system of non-linear equations evolves:

$$\begin{aligned} F_1(x_1, x_2, \ldots, x_m) &= 0 \\ F_2(x_1, x_2, \ldots, x_m) &= 0 \\ &\vdots \\ F_m(x_1, x_2, \ldots, x_m) &= 0 \end{aligned}$$

Solution of this system of equations — containing m variables — yields the data of the recycling stream.

The feedback, presented in Figure 6.2, is more sophisticated: two streams are recycled and unit C appears in both recycle loops.

From the previous example it may be concluded that this network is also unsuitable for direct calculation. Let us again tear the recycling streams and in addition to vectors $\mathbf{x}$ and $\mathbf{y}$ let us define $\mathbf{u}$ and $\mathbf{v}$ vectors, consisting of n independent elements, where

$$\mathbf{u} = [u_1, u_2, \ldots, u_n]\,,$$

$$\mathbf{v} = [v_1, v_2, \ldots, v_n]\,.$$

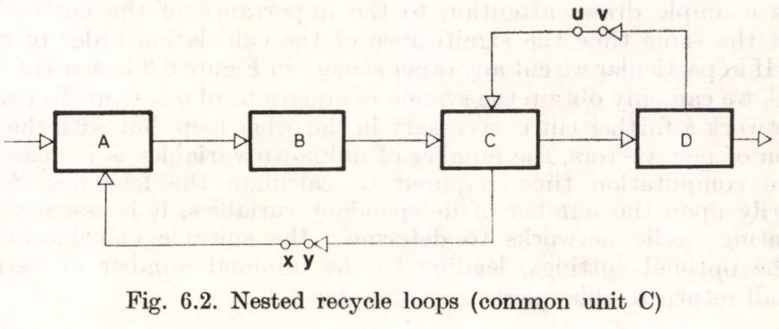


Fig. 6.2. Nested recycle loops (common unit C)

Here the relations arising from the recycling are:

$$\mathbf{y} = f_1(\mathbf{x}, \mathbf{u}), \tag{6.4}$$

$$\mathbf{v} = f_2(\mathbf{x}, \mathbf{u})\,. \tag{6.5}$$

As with the simple recycle, we also obtain the solution if the conditions

$$\mathbf{y} = \mathbf{x}, \tag{6.6}$$

$$\mathbf{v} = \mathbf{u} \tag{6.7}$$

are fulfilled. Relations (6.4), (6.5) (6.6) and (6.7) may be written – by analogy to (6.3) – as the vector equation:

$$\Phi(\mathbf{x}, \mathbf{u}) = \mathbf{0} \tag{6.8}$$

Expanding (6.8), we obtain the data of the recycling streams by solving the system of equations containing $m + n$ variables

$$\begin{aligned}
&\Phi_1(x_1, x_2, \ldots, x_m, u_1, u_2, \ldots, u_n) = 0\\
&\Phi_2(x_1, x_2, \ldots, x_m, u_1, u_2, \ldots, u_n) = 0\\
&\vdots\\
&\Phi_{m+n}(x_1, x_2, \ldots, x_m, u_1, u_2, \ldots, u_n) = 0,
\end{aligned}$$

Figure 6.3 demonstrates a process network, in which units B and C figure in both recycle loops. If we tear stream B → C and again describe the two streams by vectors **x** and **y**, then the feedback is again solved by a non-linear vector equation of m variables.

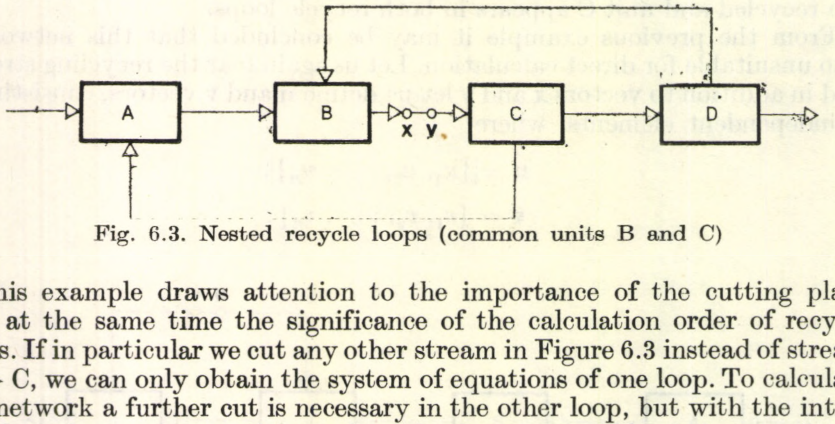


Fig. 6.3. Nested recycle loops (common units B and C)

This example draws attention to the importance of the cutting place and at the same time the significance of the calculation order of recycle loops. If in particular we cut any other stream in Figure 6.3 instead of stream B → C, we can only obtain the system of equations of one loop. To calculate the network a further cut is necessary in the other loop, but with the introduction of new vectors, the number of unknown variables is increased too. As the computation time required to calculate the feedback depends primarily upon the number of independent variables, it is essential when calculating cyclic networks to determine the suitable calculation order and the optimal cuttings, leading to the minimal number of variables. We shall return to this question in Chapter 6.4.

6.2 CONTROL

Figure 6.4 demonstrates a simple block diagram, consisting of unit operation A and control device AC. The information feedback is directed from the leaving stream to that entering.

Without control, the simulation task could be formulated in this case such that the data of the leaving stream have to be calculated from the data of the stream entering A. Giving the manipulated parameters suitable values we have to keep the controlled parameters to the prescribed value. If the values of the manipulated parameters can be expressed explicitly from the model equations as a function of the prescribed values, then the calculation may be carried out directly.

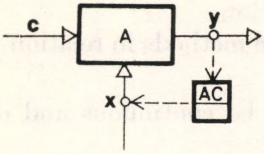


Fig. 6.4. Simple control loop

The boxes of the SIMUL system do not generally allow rearrangement of these equations, and therefore iteration must be adopted. When starting the calculation, we use initial trial values in place of the still unknown data of the entering streams. Thereafter we calculate unit A, resulting in calculated data for the leaving stream. The prescribed and calculated values of the controlled parameters probably differ. The task is to set the values of the manipulated parameters such that the prescribed and calculated values of the controlled parameters coincide.

Let **x** be the vector of the assumed value, **y** that of the calculated value, **c** that of the prescribed value. The following function exists between the manipulated and controlled variables:

$$\mathbf{y} = f(\mathbf{x}). \tag{6.9}$$

The calculation of the control loop is solved if

$$\mathbf{y} = \mathbf{c} \tag{6.10}$$

From (6.9) and (6.10) we obtain the system of equations

$$F(\mathbf{x}) = \mathbf{c} - f(\mathbf{x}) = \mathbf{0}, \tag{6.11}$$

whose solution yields the values of the manipulated parameters to be set.

When we solve using SIMUL system tasks, in which we find the prescribed value of the streams leaving the unit operation by prescribing the geometric parameters, e. g., main dimensions, which figure among the operating parameters of the box (design), then we use similar techniques to those used when calculating a control loop. The discussions in this chapter therefore also relate to the control in a broader sense.

6.3 SOLUTION OF SYSTEM OF EQUATIONS

When calculating networks, numerical procedures may be used for the iterative solution of the systems of equations arising from the feedbacks. Simplicity, stability and quick convergence are the main requirements. Nevertheless, there is no method suitable for solving the wide variety of tasks arising in the practice of a chemical engineer. It is therefore necessary — depending upon the character of the tasks — to utilize several methods or their combination.

The requirements of these methods in relation to the systems of equations are:

1. The functions should be continuous and differentiable in the neighbourhood of the solution.
2. The number of independent variables and independent equations should be equal.
3. There should be at least one real solution. These requirements are generally met when modelling steady-state chemical-process networks.

Depending upon the initial guess of the independent variables, several solutions are often obtained as the result of the iteration. In these cases, the values representing the "engineering" solution of the task have to be selected with an understanding of the physico-chemical phenomena taking place in the simulated system.

In order to discuss the principles of the solving methods, let us return to the general form (6.3) of the system of non-linear equations with m variables:

$$\boldsymbol{F}(\mathbf{x}) = \mathbf{x} - f(\mathbf{x}) = 0.$$

This can be solved by iteration such that we produce in a finite number of steps a convergent series $\mathbf{x}^0, \mathbf{x}^1, \ldots \mathbf{x}^k, \ldots$ of $\mathbf{x}$ independent variables, where superscripts $0, 1, \ldots, k$ represent the serial number of the approximate steps. Subsequent solutions are always obtained as a function of the previous solution. The procedure may be illustrated with the general iteration formula:

$$\mathbf{x}^{k+1} = \mathbf{x}^k + \mathbf{G}(\mathbf{x}^k). \qquad (6.12)$$

The methods differ in forming the correction vector $\mathbf{G}$.
Relation (6.12) may be written equivalently as:

$$\mathbf{x}^{k+1} = \mathbf{x}^k + t^k \mathbf{A}^k F(\mathbf{x}^k) \qquad (6.13)$$

Thus the task is to select values of scalar t and matrix $\mathbf{A}$ such that the series of approximate roots of the system of the equations (6.3) should be convergent.

The accuracy of the approximate solution obtained as a result of iteration may be characterized by

$$\boldsymbol{\delta} = \boldsymbol{F}(\mathbf{x}),$$

where the Euclidean norm of the error vector is:

$$\|\boldsymbol{\delta}\| = (\delta T \delta)^{1/2}$$

In this case we consider the system of equations to be solved if

$$\|\boldsymbol{\delta}\| \leq \eta$$

The established value of η depends on the task to be simulated.

The convergence rate is characteristic of the iterative methods. If the error of approximate solution is defined as the deviation of independent variables **x** from the exact solution **x***,

$$\boldsymbol{\epsilon} = \mathbf{x} - \mathbf{x}^*,$$

then the rate is determined with k sufficiently by the correlation:

$$\|\boldsymbol{\epsilon}^{k+1}\| \simeq c\, \|\boldsymbol{\epsilon}^{k}\|^{p},$$

where c is constant and p is the order characterizing the rate. The use of higher-ordered methods has to be considered because of the bigger computation effort and the eventual instability, although the convergence rate is higher.

The iterative methods used to calculate networks may be divided into three groups:

1. Direct iteration and acceleration methods
2. Newton–Raphson-type methods
3. Gradient methods.

Of the mathematical boxes of the SIMUL system, the simple direct iteration, the Newton–Raphson method and a modification of it are available.

6.3.1 DIRECT ITERATION AND ACCELERATION METHODS

Carrying out the substitution $t^k = 1$ and $\mathbf{A}^k = \mathbf{I}$ in the general iteration formula (6.13) we obtain the well-known recurrence formula

$$\mathbf{x}^{k+1} = \mathbf{x}^{k} + F(\mathbf{x}^{k}) \tag{6.14}$$

or

$$\mathbf{x}^{k+1} = f(\mathbf{x}^{k})$$

of the *simple direct iteration* (**I** = identity matrix).

The main advantage of this method is that it requires the calculation of only a few values of the function. On the other hand, the convergence rate is of first order, i. e., it is relatively slow. The solution is uncertain in the case of interaction between variables (e. g., non-ideal mixtures), and it often fails to converge if the initial guess was poor. The *damped direct iteration* can avoid the divergence in some cases. For this purpose, the $\mathbf{A} = \mathbf{I}$ substitution is effected in (6.13) and in the relation

$$\mathbf{x}^{k+1} = \mathbf{x}^k + t^k \mathbf{I} F(\mathbf{x}^k) \tag{6.15}$$

the damping factor t is selected in the range $0 < t^k \leq 1$ such that the value of the norm $\|\boldsymbol{\delta}\|$ should decrease or be minimal in all iterations. The previous task may be solved by heuristic search, the latter by optimum search methods.

The convergence of direct iteration is accelerated by the *method of Wegstein* (Lapidus, 1962). For this purpose, the value of t in equation (6.15) is calculated from the $(k-1)$-th and k-th iterations in the following manner (Batstone et al., 1971):

$$t^k = \left[1 - \frac{\|f(\mathbf{x}^k) - f(\mathbf{x}^{k-1})\|}{\|\mathbf{x}^k - \mathbf{x}^{k-1}\|}\right]^{-1},$$

where the Euclidean norm of the respective difference vectors appears on the right-hand side.

The order characterizing the rate of the method is 1.6, and therefore it is substantially quicker than the simple direct iteration. The method converges in many cases where the simple direct iteration would be divergent.

The method of *dominant eigenvalue* (Orbach and Crowe, 1971) also accelerates the convergence. For this purpose, the value of t from (6.15) is determined from the $(k-1)$-th and k-th iterations with the following relation (Batstone et al., 1971):

$$t^k = \left[1 - \frac{\|f(\mathbf{x}^k) - \mathbf{x}^k\|}{\|f(\mathbf{x}^{k-1}) - \mathbf{x}^{k-1}\|}\right]^{-1}.$$

The direct iteration and its variants may be organized simply in modular simulating systems by conditional branching instructions.

6.3.2 NEWTON-RAPHSON-TYPE METHODS

In addition to direct iteration, there are widespread methods based on the local linearization of the system of equations to be solved. These are the variants of the Newton–Raphson method.

Let us start from the derivative of relation (6.13) according to $\mathbf{x}^k$. If we suppose that $\mathbf{x}^k$ is close to the solution vector, then $F(\mathbf{x}^k) \cong 0$ and rearranging the derived relation results in the following term for matrix $\mathbf{A}$:

$$\mathbf{A}^k = \left[1 - t^k \frac{\partial F(\mathbf{x})^k}{\partial \mathbf{x}^k}\right]^{-1}, \tag{6.16}$$

where

$$\left[\frac{F(\mathbf{x})^k}{\mathbf{x}^k}\right] = \mathbf{J}^k,$$

the Jacobian matrix. Substituting (6.16) into (6.13) and selecting the value of t as unity, we arrive at the general form of the Newton–Raphson method (Cavett, 1963):

$$\mathbf{x}^{k+1} = \mathbf{x}^k - (\mathbf{J}^k)^{-1} F(\mathbf{x}^k). \tag{6.17}$$

In every step of the iteration, the approximate root is the solution of the system of linear equations (6.17).

Specifying the identity matrix in (6.17) instead of the inverse matrix of the partial derivatives — $(\mathbf{J}^k)^{-1} = \mathbf{I}$ — we reobtain the simple direct iteration (6.14):

$$\mathbf{x}^{k+1} = \mathbf{x}^k + F(\mathbf{x}^k).$$

The Newton–Raphson method is a second-order iterative process and therefore converges more quickly in principle than the direct iteration. In general, function F (x) is not analytically differentiable when calculating networks. Instead, we approximate, the elements of the Jacobian matrix with partial difference quotients. This requires calculation in each iteration step of $m + 1$ values of the function. Therefore with several variables, because of the calculation and inversion of the Jacobian matrix, the computation effort may exceed that of the methods based on direct iteration.

The stability of the method depends on several conditions, but it certainly converges if they are fulfilled. The reason for eventual divergence is generally an incorrect guess of the initial values of the independent variables, or the singular or ill-conditioned Jacobian matrix. To avoid divergence, we have to repeat the calculation with modified initial values. If there is no result, then as a further attempt, the interaction may be decreased by omitting those variables which are not fully independent based on the revision of the variables to be iterated. Otherwise, another iteration method has to be selected, less sensitive to the overdetermination of the system of equations.

Several variants have been developed to decrease the computation effort and to improve the convergence of the method.

If, using the iteration formula (6.17), the Jacobian matrix is only calculated at the beginning of the iteration or during selected steps, we obtain the *modified Newton–Raphson method* (Kehat and Shacham, 1973)

$$\mathbf{x}^{k+1} = \mathbf{x}^k - (\mathbf{J}^{\varphi(k)})^{-1} F(\mathbf{x}^k).$$

If the Jacobian matrix is only evaluated once, at the beginning of the iteration, i. e., $\varphi(k) = 0$, then the method is of first order. If $0 < \varphi(k) < k$, the convergence rate is between first and second order. If during consecutive iteration steps the value of the Jacobian matrix changes only slightly, then this method leads to considerable decrease of computation time in the case of several variables.

The divergence of the Newton–Raphson method may be avoided in some cases by using (6.17) in such a form as to iterate, in which the scalar factor t is not constant:

$$\mathbf{x}^{k+1} = \mathbf{x}^k - (t^k \mathbf{J}^k)^{-1} F(\mathbf{x}^k).$$

This variant is the *damped Newton–Raphson method*. The value of t is calculated according to Section 6.3.1 (Wilde, 1964; Broyden, 1965).

6.3.3 GRADIENT METHODS

The solution of the system of equations $F(\mathbf{x}) = 0$ may be equivalently formulated as the optimization of the function

$$\psi(\mathbf{x}) = \sum_{i=1}^{m} (F_i(\mathbf{x}))^2.$$

If the value of the minimum is zero, then the location minimum is simultaneously the solution of the system of equations. If the Jacobian matrix is singular or ill-conditioned because of the interaction between the variables or for other reasons, and the Newton–Raphson-type methods fail to give results, then this kind of task modification may be advantageous.

The *gradient method* may be used to locate the minimum. If the negative gradient of the value of the function, the $-(\mathbf{J}^k)^T$ transpose of the Jacobian matrix, is substituted in relation (6.13) in place of matrix **A** determining the direction of the correction, then we obtain the iteration formula of the gradient method:

$$\mathbf{x}^{k+1} = \mathbf{x}^k - t^k (\mathbf{J}^k)^T F(\mathbf{x}^k). \tag{6.18}$$

The relatively high computation time is a disadvantage of the method, and therefore it seems wise to combine it with the Newton–Raphson method. The *Marquardt method* (Himmelblau, 1973) is a combined method of this type. Its iteration formula is developed from (6.18) if we substitute

$$-(2(\mathbf{J}^k)^T \mathbf{J}^k + t^k \mathbf{I})^{-1} 2(\mathbf{J}^k)^T$$

in place of the negative gradient (Kehat and Shacham, 1973):

$$\mathbf{x}^{k+1} = \mathbf{x}^k - (2(\mathbf{J}^k)^T \mathbf{J}^k + t^k \mathbf{I})^{-1} 2(\mathbf{J}^k)^T F(\mathbf{x}^k).$$

With small values of t the Newton–Raphson method is preferable, but with big t values the gradient method is better.

6.4 SIMULATION OF COMPLEX SYSTEMS

It has been already emphasized in Chapter 6.1 that the calculation order of the unit operations, i. e., the strategy of the calculation, is essential in order to decrease the computation effort, when simulating networks consisting of intricate, nested or intertwined loops. This strategy may be divided into two objectives:

1. Partitioning of the network
2. Cutting of the cycles.

The first objective consists of the analysis of the network and in this relation the location of those parts of the network between which no feedback takes place. The second objective includes the establishing of a suitable calculation order, to prepare the use of the methods discussed in Chapter 6.3, to solve systems of equations.

The breakdown may be carried out intuitively with sufficient experience, and with networks which are too complex. This way of processing is often more reasonable than using an automatic method, because previous experience gained from similar problems may be utilized. However, the decomposition algorithms are not always effective with extremely complex networks, and therefore they frequently play a guiding role in determining the strategy of calculation. Experience proves that a significant part of the methods developed up to the present is specific of some network type.

As a result of this experience, there is no standardized or built-in decomposition method in the SIMUL system, but the system presupposes the possession of an intuitive or algorithmic method by the user, enabling the calculation order to be determined before writing the flow-sheet program. Thus the most suitable method may be used without any restriction, just to suit the task, when preparing the simulation.

We shall discuss briefly a few decomposition methods.

6.4.1 PARTITIONING OF THE NETWORK

It is practicable and usual when analysing networks to represent them according to the graph theory and to describe the structure of the graphs with matrices. Chemical-process networks may be mapped by directed graphs, where the nodes correspond to unit operations or their models, and the directed edges correspond to mass or information streams.

The graph of networks can be described by Boolean matrices. If the analysis is cycle location then frequently the

$$\mathbf{C} = c_{ij}$$

Associated matrix is used, whose size is $n \times n$, where n equals the number of nodes in the graph and $C_{ij} = 1$ if an edge exists in the graph which is directed from edge i to j. Otherwise $C_{ij} = 0$.

The storage requirement of the *Associated matrix* may be decreased by replacing it by the *Index matrix*, whose size is $2n$, and which contains only the coordinates of the non-zero elements (Kehat and Shacham, 1973).

The methods leading to the network partitioning may be divided into two groups:

1. Path-searching methods
2. Methods based on the powers of the *Associated matrix*.

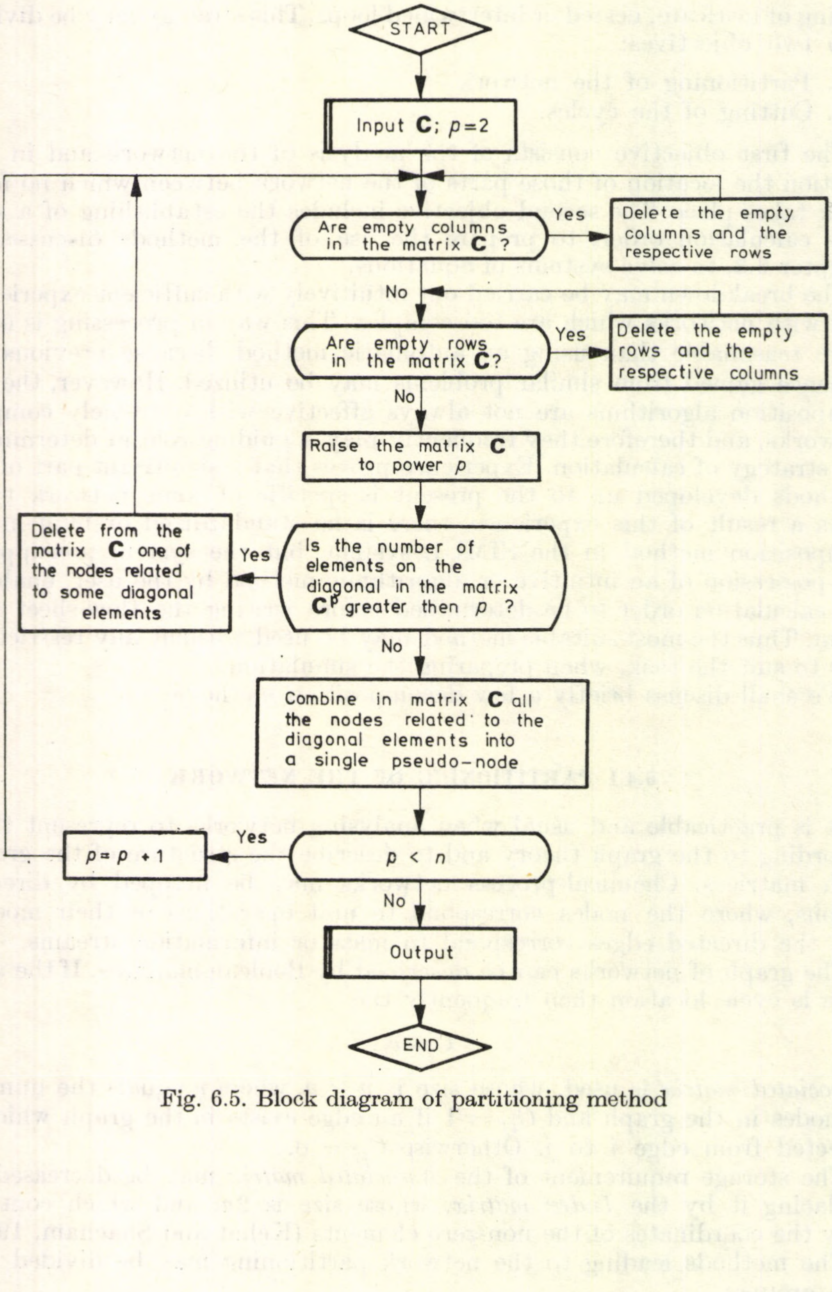


Fig. 6.5. Block diagram of partitioning method

Location of the cycles is effected by the methods of the first group such that we proceed opposite to the edges of the graphs, until a node, already touched, is reached. The cycle so found is replaced by a single node, and thus we proceed up to the last node (Steward, 1962; Sargent and Westerberg, 1964; Billingsley, 1967; Christensen and Rudd, 1969; Forder and Hutchinson, 1969). The reduced calculation effort is an advantage of this method, but its drawback is the difficult programming.

The methods belonging to the second group utilize the property of the *Associated matrix* that the elements of the $\mathbf{C}^p$ powers describe relations involving **p** nodes. Among them, the $C_{ii} = 1$ elements on the diagonal represent a cycle consisting of **p** nodes (Harary, 1959; 1960; 1962).

If the number of elements on the diagonal exceeds **p**, then more cycles of the same size have been found. If any element of the diagonal exceeds 1, then this means that the corresponding mode appertains simultaneously to a number of cycles. The independent cycles may be identified in these cases by omitting these nodes individually from the *Associated matrix* and repeating each time cycle-searching, raising to the power (Ravicz and Norman, 1964; Norman, 1965).

By using the corresponding *Index matrix* instead of the *Associated matrix*, the operation may be simplified (Kehat and Shacham, 1973) further by omitting from the matrix those nodes which are just connected with one other node (Marimont, 1959).

The advantages of this method are the easy programming and exactness; its drawback is the large computation effort.

Figure 6.5 presents the block diagram of the algorithm based on the powers of the matrix (Kehat and Shacham, 1973).

6.4.2 CUTTING OF THE CYCLES

Establishing the calculation order in parts of networks containing cycles or cycle-systems must be optimized by one of the following possible aims:

1. Minimum number of cut information streams.
2. Minimum number of independent variables of the cut information streams.
3. Minimum number of weighted independent variables.

The effective computation effort needed to solve the systems of equations arising from the feedbacks, decreases in the order enumerated above.

It is known that the independent variables influence the convergence of the solution diversely. The system of equations is most sensitive to weighted independent variables.

The algorithms used to cut the cycles can hardly be systematized because of the diversity of the methods and their numerous variants. The perspicuity is influenced by the rarity of publications containing comparative analysis — therefore the user can only rely on the conclusions of the authors on the efficiency of their methods.

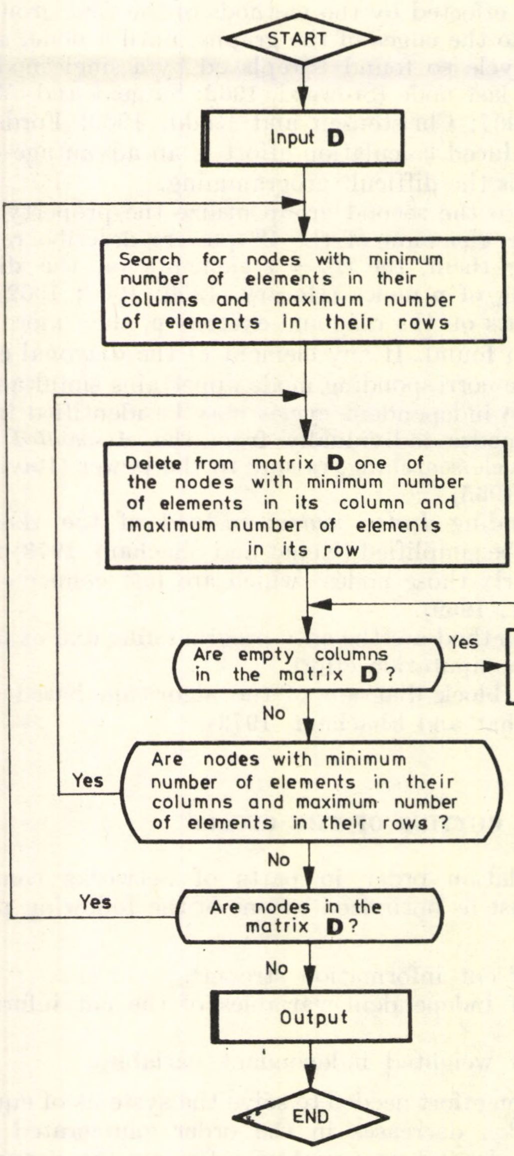


Fig. 6.6. Block diagram of cutting method

A simple but rather time-consuming method consists of comparing all combinations resulting from the cuts (Crowe et al., 1971); this is effective if the cycles are small, but is not economic for networks containing many units. The efficiency of this method has been increased with dynamic programming, without deviation from the basic concept (Sargent and Westerberg, 1964; Upadhye and Grens, 1972). This variant is mainly advantageous for systems containing a small number of unit operations and involute feedbacks.

Another significant group of algorithms is based on operations with different Boolean matrices describing the network (Associated matrix, triangular matrix, cycle matrix, etc.) (Forder and Hutchinson, 1969; Rubin, 1962; Lee and Rudd, 1966; Jänicke and Biess, 1974). A new variant of these methods also performs sensitivity analysis (Kevorkian and Snoek, 1973).

In addition to the groups already discussed, other algorithms are known, which could not be classified among the previous groups. These are based on the integer programming (Piehler, 1972), the graph operations (Pho and Lapidus, 1973), the "branch and bound" techniques (Wilde and Atherton, 1973), and other special methods.

We shall now introduce a readily programable searching method based upon the block diagram in Figure 6.6, resulting in a minimal number of cut streams. The originally stream-oriented algorithm (Kehat and Shacham, 1973) has been modified such that the network should be described by an *Associated matrix*. When using this method, we start from the matrix obtained by partitioning the network with respect to an independent cycle or cycle-system. The first step is to seek those unit operations which have a minimal number of input and maximal number of output streams. The input streams of these units represent the set of the streams which may be cut. One of the streams is now cut and we investigate which units may be calculated as a result of this action. More cuts and investigations are carried out if necessary, and we proceed in this manner as long as there exist streams to cut in the set. If units which cannot be calculated directly still exist in the network, we search again — as prescribed — for streams to cut and we repeat the whole operation.

We arrive at the list of the cutting places and a possible calculation order of the units.

6.5 CALCULATION OF FEEDBACKS IN THE SIMUL SYSTEM

When calculating process networks with the SIMUL system, the systems of equations — produced from the feedbacks — are solved by direct iteration or a Newton–Raphson-type method. Box *jump* (see, Section 4.4.2.7) is suitable for handling the direct iteration, while box *soleqs* (see, Section 4.4.2.1) contains the Newton–Raphson method and its modified variant. Box *soleqs* is also suitable for handling the direct iteration, if the inverse matrix $(\mathbf{J}^i)^{-1}$ figuring in (6.13) is specified as identity matrix, when specifying the box data.

In the following chapters, we shall introduce the calculation of a few feedback systems, based on our process example in its developed form.

6.5.1 RECYCLE

The process block diagram of the butane isomerization in Figure 5.5 deals with the case where the unchanged n-butane is separated from the reacted mixture and recycled into the feed. In order to avoid the enrichment of the inert n-pentane, part of the recycling stream is released into the atmosphere. The quantity of catalyst fed into the reactor is constant, and the distillation column operates with the prescribed pressure and reflux ratio. When simulating this type of process performance, the first step needed to organize the calculation, is to investigate the independence of the elements of the vector describing the recycling stream. This has been already discussed in Chapter 2.1, and it has been stated that the degree of freedom of a material stream is $k + 2$ in the general case. In the example, there are four constraints: the conversion in the reactor, the prescribed feed temperature, the pressure of the distillation column and the bubble point of the bottom product. As $k = 3$, the recycling stream has only one degree of freedom. Therefore a non-linear equation with one variable has to be solved to calculate the recycle — all other elements of the stream vector follow as dependent variables.

First, the direct iteration is presented. The operation-order flow-sheet is shown in Figure 6.7, and the flow-sheet program in Table 6.1.

We set the mass stream of the recycle as independent variable (2e2s). The mass balance is the non-linear equation to be solved, written with SIMUL references as

$$2\text{e1s} - 2\text{e7s} - 2\text{e9s} = 0, \tag{6.19}$$

where

$$2\text{e7s} = f1(2\text{e2s})$$

$$2\text{e9s} = f2(2\text{e2s}).$$

Reading the known and assumed data of the recycling stream into the stream vector with connection index 2, the calculation proceeds from *mixing* (calculation serial number 1) to box *dividing* (calculation serial number 5). The result is the stream vector calculated at connecting point 2. Depending on the result of the arithmetic expression with operating index 9, *jump* instructs the cycle to be repeated or stopped. After having reached the prescribed accuracy, box *vlexpa* (serial number 7) and box *prescriber* (serial number 8) follow, and the calculation finishing after printing the results with box *print*.

Let us now use the Newton–Raphson method to solve the same problem. The operation-order flow-sheet is shown in Figure 6.8, the flow-sheet program in Table 6.2.

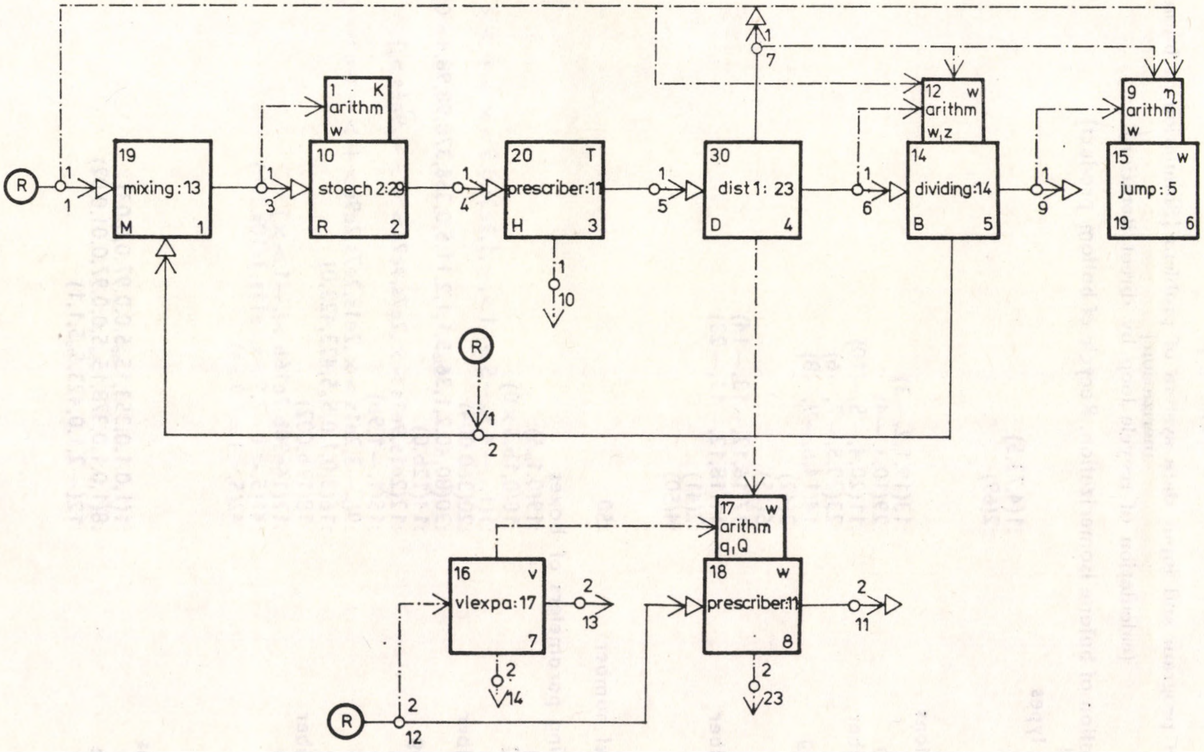


Fig. 6.7. Operation-order flow-sheet for butane isomerization (calculation of recycle loop by direct iteration)

Table 6.1

Flow-sheet program and input data system of problem [Simulation of butane isomerization]
(calculation of recycle loop by direct iteration)

```
[Simulation of butane isomerization, Recycle of bottom product]
D97001
stream types
feed                        :1(4,73,5)
steam                       :2(69)
+

operations
mixing                      :13(19,1,2,−3)
stoech2                     :29(10,3,−4)
prescriber                  :11(20,4,−5,−10)
dist1                       :23(30,5,−7,−6)
dividing                    :14(14,6,−9,−8)
print                       :2(42)
jump                        :5(15)
vlexpa                      :17(16,12,−13,−14)
prescriber                  :11(18,12,−11,−23)
print                       :2(41)
stop                        :4(50)
+

data set number             :50
b
operating parameters of     boxes
mixing                      :19(0.1⏨5)
stoech2                     :10(0,1b,5×0)
arithm                      :1(1,⏨−4,9⏨−5>/,1>,+,1,2e3s,0.5>×>+>×>/)
prescriber                  :20(360,004)
dist1                       :30(80,40,2,1,36⏨5,1,1,2,11.5,0,358,378,98,98,4×0)
dividing                    :14(12b,0)
arithm                      :12(2e1s,9e1s>×,2e7s,9e7s>×>−,9e6s>/)
jump                        :15(1,−1,9b)
arithm                      :9(⏨−3,2e1s>×,2e1s,2e7s,2e9s>+>−>a>−)
vlexpa                      :16(3,0,1.0,5⏨5,423,423,0)
prescriber                  :18(17b,002)
arithm                      :17(16e30b,7e16b>/,−1>×)
print                       :41(5,<1=7,9>s,2e11s,3e10s,30b)
print                       :42(5,<1=7,9>s)
+

s
streams
feed                        :1(1,0.1,0,353,15⏨5,0,0.97,0,0.03)
recycle                     :8(1,0.1,0,378,15⏨5,0,0.97,0.01,0.02)
steam                       :12(−2,1,0,423,5⏨5,1,1)
+
```

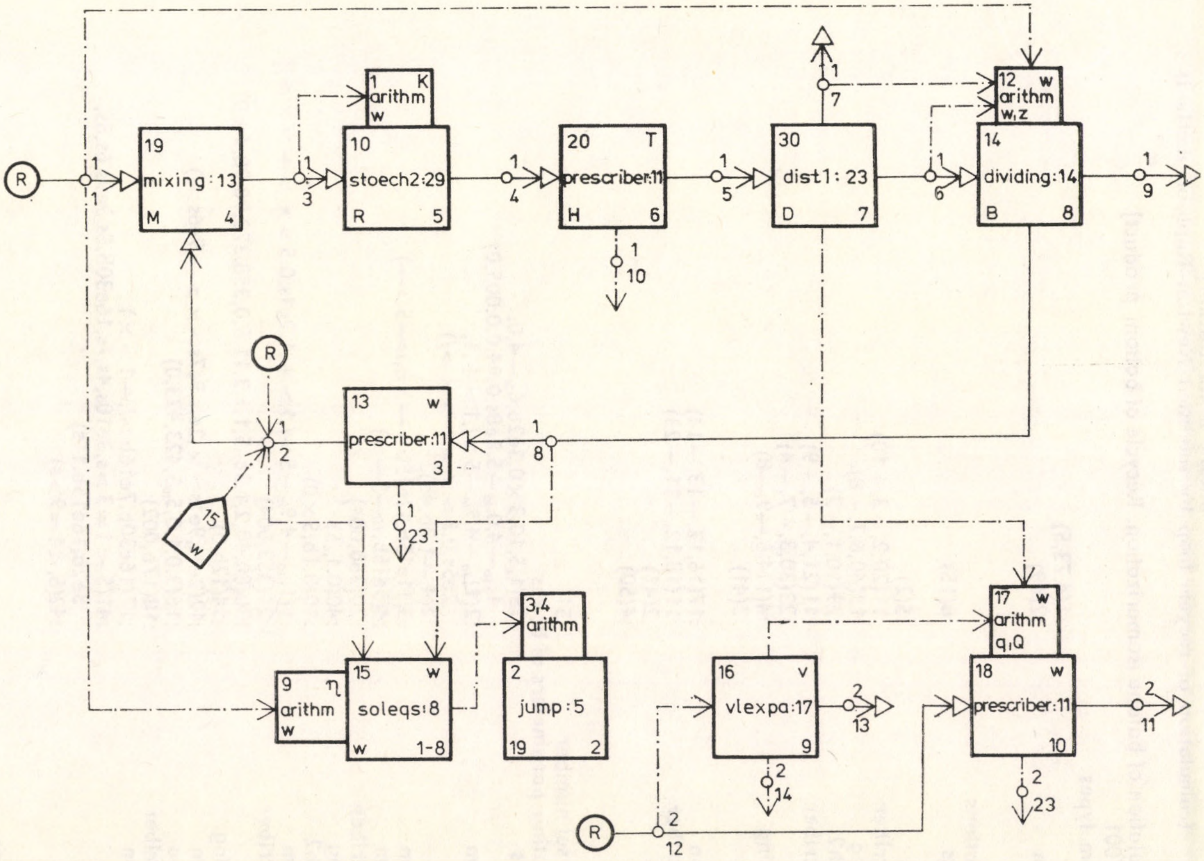


Fig. 6.8. Operation-order flow-sheet for butane isomerization (calculation of recycle loop by modified Newton–Raphson method

Table 6.2

Flow-sheet program and input data system of problem [Simulation of butane isomerization]
(calculation of recycle loop by modified Newton–Raphson method)

```
[Simulation of butane isomerization. Recycle of bottom product]
D 97001
stream types
feed                      :1(4,73,5)
steam                     :2(69)
+

operations
soleqs                    :8(15)
 ∧
jump                      :5(2)
prescriber                :11(20,2,−3,−10)
mixing                    :13(40,6,7,−8)
stoech2                   :29(10,1,−2)
prescriber                :11(21,4,−5,−9)
dist1                     :23(30,3,−7,−4)
dividing                  :4(114,6,—9,—8)
print                     :2(41)
 ∨
vlexpa                    :17(16,12,−13,−14)
prescriber                :11(18,12,−11,−23)
print                     :2(41)
stop                      :4(50)
+

data set number           :51
operating parameters of boxes
soleqs                    :15(1,5,10,3×0,3e2b,6⏨−4,0,
                            1,⏨−4,0,⏨−5,8e8s,0.94,0,0.005,0)
arithm                    :2(1,⏨−4,9⏨−5>/,1>+,1,
                            2e5s,0.5>×>+>×>/)
jump                      :2(4,—1,3b,4b)
arithm                    :3(11e15b,12e15b>—>a,⏨—5>—)
arithm                    :4(5e15b,⏨—5—>)
prescriber                :20(360,004)
mixing                    :40(0.1⏨5)
stoech2                   :10(0,1b,5×0)
arithm                    :1(1,⏨−4,9⏨−5>/,1>+,1,2e1s,0.5>×>+>×>/)
prescriber                :21(353,004)
dist1                     :30(80,40,2,1,36⏨5,1,1,2,11.5,0,358,378,98,98,4×0)
dividing                  :14(12b,0)
arithm                    :12(2e1s,9e1s>×,2e/s,9e7s>×>—,9e6s>/)
vlexpa                    :16(3,0,1.0,5⏨5,423,423,0)
prescriber                :18(17b,002)
arithm                    :17(16e30b,7e16b>/,−1>×)
print                     :41(5,<1=3>s,3e10s,4s,7s,16e30b,5s,3e9s,6s,8s,
                            3e2b,16e15b,11s)
print                     :42(5,<1=9>s)
+

streams
feed                      :1(1,0.1,0,353,15⏨5,0,0.97,0,0.03)
recycle                   :2(1,0.1,0,378,15⏨5,0.97,0.01,0,02)
steam                     :12(−2,1,0,423,5⏨5,1,1)
+
```

The non-linear equation to be solved is again the mass stream, this time relating to the cut recycle stream:

$$2e2s - 2e8s = 0 \tag{6.20}$$

where

$$2e8s = f(2e2s).$$

The initial stream vector is read into the stream vector with connection index 2. After box *soleqs* has determined a value for the independent variable – again the mass stream of the recycle – the cycle starts at box *jump* (calculation serial number 2) continuing until box *dividing* (calculation serial number 8). As a result we obtain the stream vector at connecting point 8. Hereafter, box *soleqs* changes the initial trial value of the independent variable to the prescribed amount and the cycle is repeated. From the values of the function thus obtained, the box produces the linear approximation of equation (6.20). By solving this, a new, approximate root is found for the independent variable. In our example, the linear model is used unaltered to calculate five subsequent roots. Repeating the operation a solution is obtained corresponding to the accuracy prescribed with the arithmetic expression (operating index 9).

Prescriber (serial number 3) has the task of changing, during the iteration steps, the value of stream vector 2 with recycling stream vector 8 and the mass stream, influenced by *soleqs* and the interrelated box *jump*: this leads to approximate solutions. After the recycle has been solved, boxes *vlexpa* (serial number 9) and *prescriber* (serial number 10) are calculated and the computation ends with the printing of results.

6.5.2 CONTROL

The block diagram of butane isomerization without recycle was shown in Figure 5.3. This differs in principle from the block diagram 1.3 in that the i-butane concentration (8e8s), characterizing the product quality, is set to the prescribed value by controlling the quantity of the catalyst (3e2b) entering the second reactor.

The non-linear equation, arising from the feedback, is again solved by the Newton–Raphson method. The operation-order flow-sheet is shown in Figure 6.9, the flow-sheet program in Table 6.3. The equation to be solved is:

$$z_0 - 8e8s = 0 \tag{6.21}$$

where

$$8e8s = f(3e2b),$$

and z_0 represents the prescribed i-butane concentration.

Calculation of the operations using box *stoech2* (calculation serial number 1) up to box *prescriber* (serial number 4) is carried out only once. Afterwards we repeat the modification of the independent variable in the arithmetic expression (operating index 2), and then the calculation with box

Table 6.3

Flow-sheet program and input data system of problem [Simulation of butane isomerization]

(calculation of control loop by modified Newton–Raphson method)

```
[Simulation of butane isomerization. Control of product quality]
D97001
stream types
feed                          : 1(4,73,5)
steam                         : 2(69)
+
operations
stoech2                       :29(10,1,−2)
prescriber                    :11(20,2,−3,−10)
dist1                         :23(30,3,−7,−4)
prescriber                    :11(21,4,−5,−9)
soleqs                        :8(15)
∧
stoech2                       :29(11,5,−6)
mixing                        :13(40,6,7,−8)
print                         : 2(42)
∨
vlexpa                        :17(16,12,−13,−14)
prescriber                    :11(18,12,−11,−23)
print                         : 2(41)
stop                          : 4(50)
+
data set number               :52
b
operating parameters of boxes
stoech2                       :10(0,1b,5×0)
arithm                        : 1(1,₁₀−4,9₁₀−5 >/,1 > +,1,2e1s,0.5 >× > +× >/)
prescriber                    :20(360,004)
dist1                         :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,356,376,98,98,4×0)
prescriber                    :21(353,004)
soleqs                        :15(1,5,10,3×0,3e2b,₁₀−3,0,1,₁₀−4,0,1,6e8s,0.94,
                               0,0.005,0)
arithm                        : 2(1,₁₀−4,₁₀−3 >/,1 > +,1,2e5s,0.5 >× > + >× >/)
stoech2                       :11(0,2b,5×0)
mixing                        :40(0.1₁₀5)
vlexpa                        :16(3,0,1.0,5₁₀5,423,423,0)
arithm                        :17(16e30b,7e16b >/,−1 >×)
prescriber                    :18(17b,002)
print                         :41(5, > 1 = 8 > s,2e11s,3e2b,30b)
print                         :42(5,3e2b)
+
s
streams
feed                          : 1(1,0.1,0,353,15₁₀5,0,0,97,0,0.03)
steam                         :12(−2,1,0,423,5₁₀5,1,1)
+
```

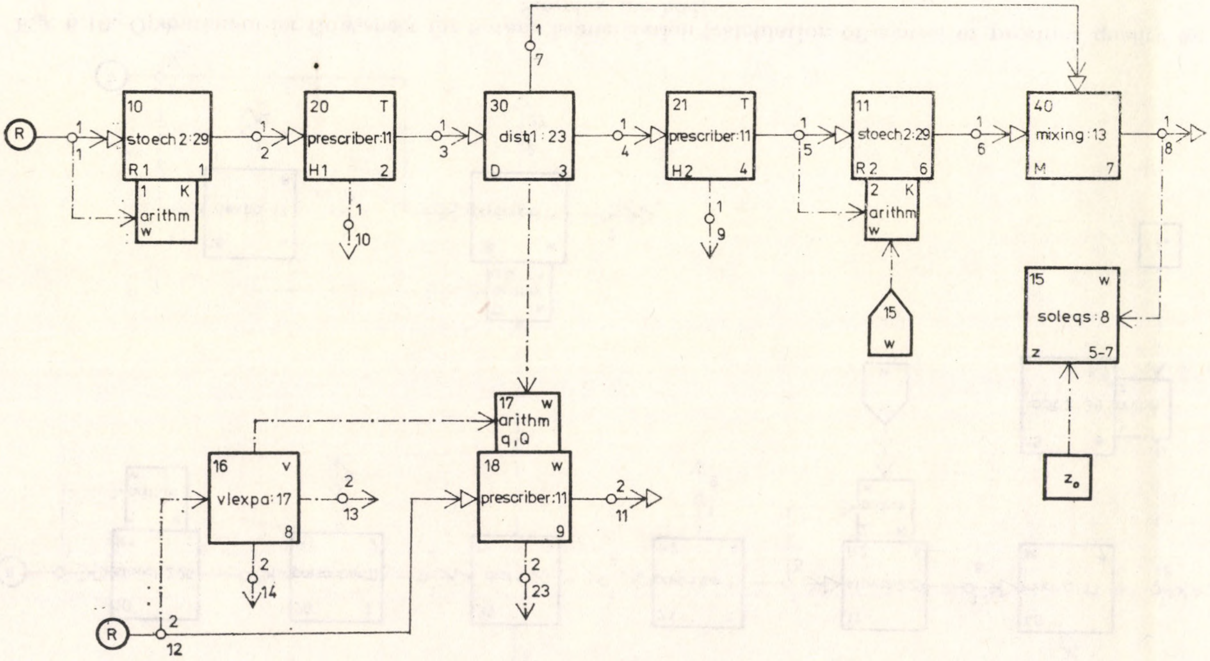


Fig. 6.9. Operation-order flow-sheet for butane isomerization (calculation of control of product quality by modified Newton–Raphson method)

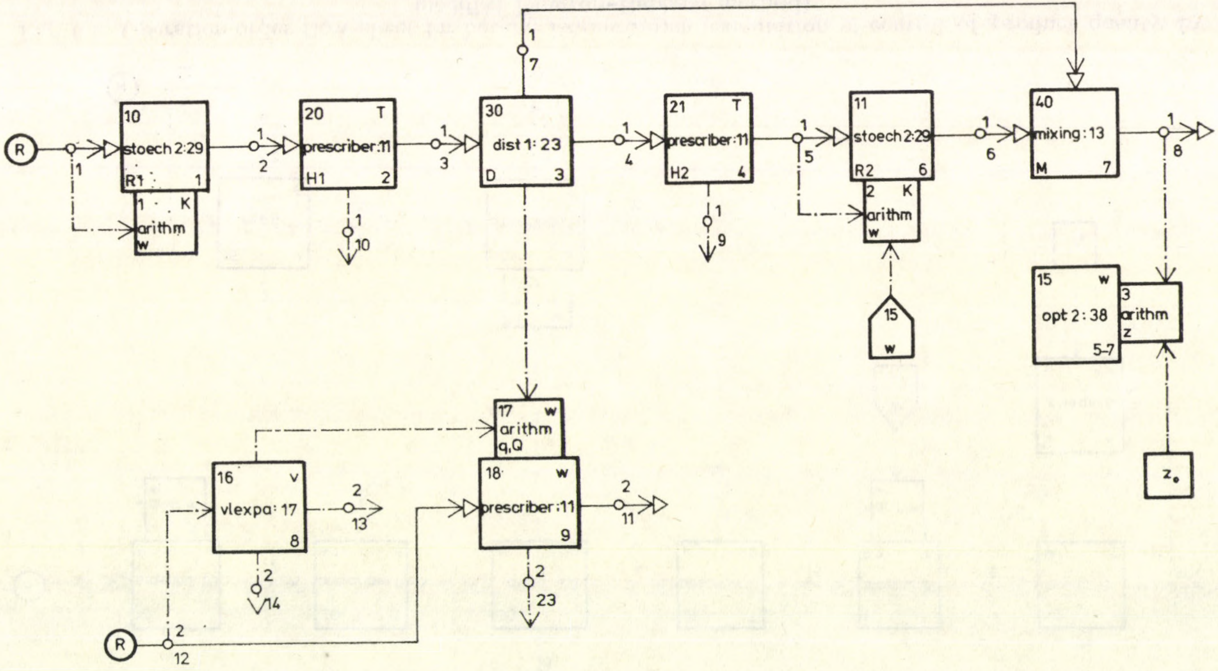


Fig. 6.10. Operation-order flow-sheet for butane isomerization (calculation of control of product quality by Simplex method)

Table 6.4

Flow-sheet program and input data system of problem [Simulation of butane isomerization] (calculation of control loop by Simplex method)

```
[Simulation of butane isomerization. Control of product quality]
D97001
stream types
feed                         : 1(4,73,5)
steam                        : 2(69)
+
operations
stoech2                      :29(10,1,−2)
prescriber                   :11(20,2,−3,−10)
dist1                        :23(30,3,−7,−4)
prescriber                   :11(21,4,−5,−9)
print                        : 2(43)
opt2                         :38(15)
∧
stoech2                      :29(11,5,−6)
mixing                       :13(40,6,7,−8)
print                        : 2(42)
∨
vlexpa                       :17(16,12,−13,−14)
prescriber                   :11(18,12,−11,−23)
print                        : 2(41)
stop                         : 4(50)
+
data set number              :55
b
operating parameters of boxes
stoech2                      (10 0,1b,5×0)
arithm                       :1(1,₁₀−4,9₁₀−5 >/,1 > +,1,2e1s,0.5 >× > + >× >/)
prescriber                   :20(360,004)
dist1                        :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,98,98,4×0)
prescriber                   :21(353,004)
opt2                         :15(5×0,10,2×1,3×0,3b,3e2b,₁₀−3,0.5₁₀−3,1,2.5₁₀
                                 −5,3e2b,0,1,10×0)
arithm                       : 3(8e8s,0.94 > −,2 > ∧)
arithm                       : 2(1,₁₀−4,₁₀−3 > /,1 > +,1,2e5s,0.5 >× > + >× >/)
stoech2                      :11(0,2b,5×0)
mixing                       :40(0.1₁₀5)
vlexpa                       :16(3,0,1.0,5₁₀5.423,423,0)
arithm                       :17(16e30b,7e16b > /,−1 >×)
prescriber                   :18(17b,002)
print                        :41(5, < 1 = 8 > s,2e1s,3e2b,30b)
print                        :42(5,3e2b,8e8s)
print                        :43(5, < 1 = 5,7 > s)
+
s
streams
feed                         : 1(1,0.1,0,353,15₁₀5,0,0.97,0,0.03)
steam                        :12(−2,1,0,423,5₁₀5,1,1)
+
```

stoech2 (serial number 6) and box *mixing* (serial number 7) until the accuracy prescribed for the dependent variable is reached. The calculation terminates as described in Section 6.5.1.

As discussed in Section 6.3.3, the task may be interpreted as optimum-search. If the square of equation (6.21) is considered as an objective function, then the location of the minimum is simultaneously the solution of the equation:

$$(z_0 - 8e8s)^2 = 0 \tag{6.22}$$

where

$$8e8s = f(3e2b).$$

Optimum searching is carried out with box *opt2*, working according to the sequential simplex method. The corresponding operation-order flow-sheet appears in Figure 6.10, the flow-sheet program in Table 6.4.

The operation order is essentially identical to that in Figure 6.9. Box *opt2* changes the value of the independent variables (3e2b) in the arithmetic expression (operating index 2) with suitable strategy as long as the value of the objective function (6.22), described by the arithmetic expression (operating index 3) remains below a prescribed limit.

6.5.3 RECYCLE AND CONTROL

Figure 6.11 represents the process block diagram of butane isomerization including recycle and control. The concentration of i-butane in the mixture leaving the reactor is controlled by the quantity of catalyst. The unreacted n-butane is recycled from the distillation column to the feed.

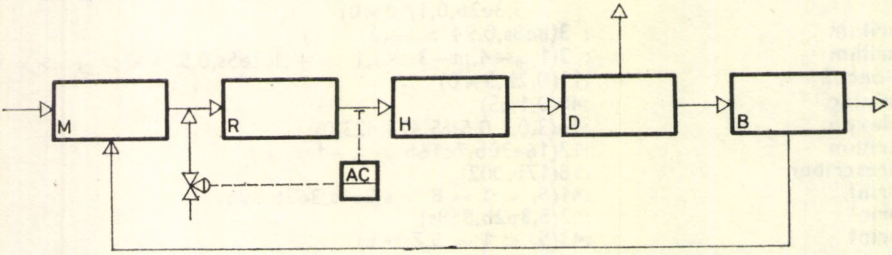


Fig. 6.11. Process block diagram for butane isomerization (recycle of bottom product and control of reactor outlet quality)

The corresponding operation-order flow-sheet appears in Figure 6.12, the flow-sheet program in Table 6.5.

Using the considerations outlined in Section 6.5.1, the mass stream (2e2s) is again set as independent variable in the recycling stream, the independent variable of the control being the mass stream of the catalyst

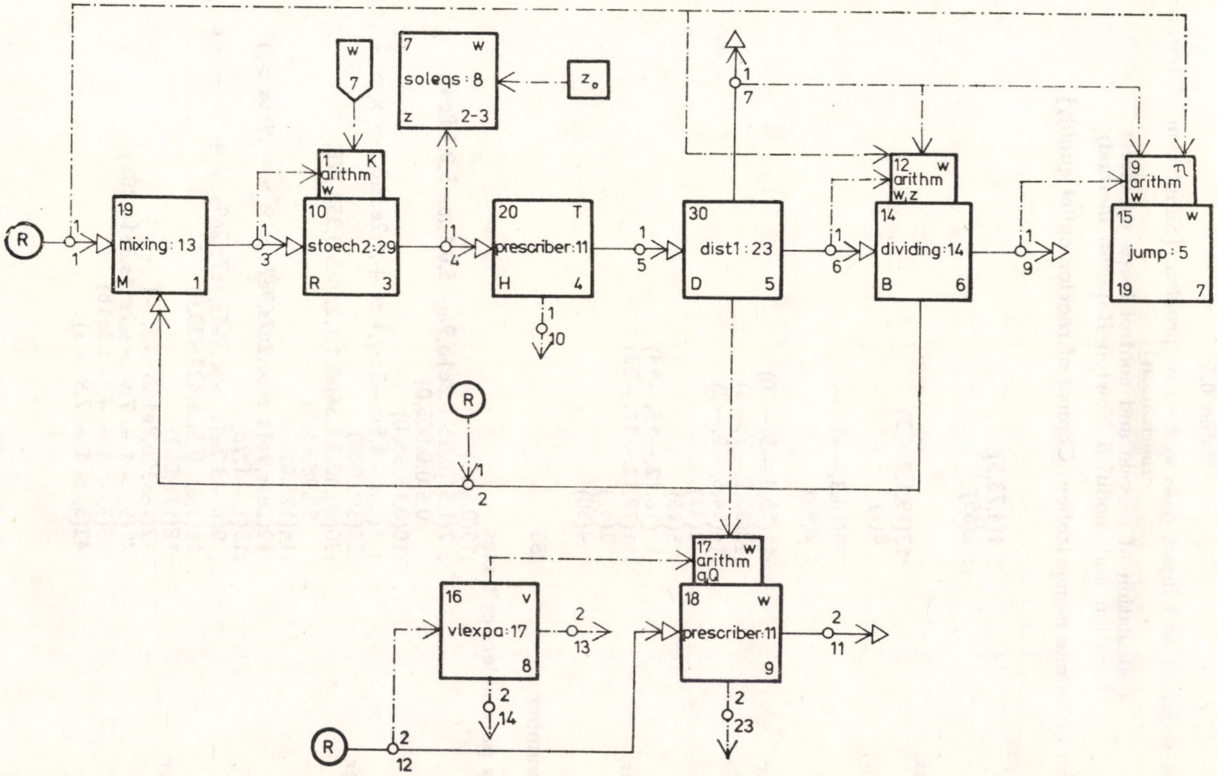


Fig. 6.12. Operation-order flow-sheet for butane isomerization (calculation of recycle loop and control of reactor outlet quality by direct iteration and modified Newton–Raphson method)

Table 6.5

Flow-sheet program and input data system of problem [Simulation of butane isomerization]
(calculation of recycle and control loops by direct
iteration and modified Newton–Raphson method)

```
[Simulation of butane isomerization. Control of reactor outlet quality]
D97001
stream types
feed                          : 1(4,73,5)
steam                         : 2(69)
+
operations
mixing                        :13(19,1,2,−3)
soleqs                        : 8(7)
∧
stoech2                       :29(10,3,−4)
print                         : 2(40)
∨
prescriber                    :11(20,4,−5,−10)
dist1                         :23(30,5,−7,−6)
dividing                      :14(14,6,−9,−2)
print                         : 2(42)
jump                          : 5(15)
vlexpa                        :17(16,12,−13,−14)
prescriber                    :11(18,12,−11,−23)
print                         : 2(41)
stop                          : 4(50)
+
data set number               :53
b
operating parameters of boxes
mixing                        :19(0.₁₀15)
soleqs                        : 7(1,5,10,3×0,3e1b,9₁₀−5,0.1,₁₀−5,0,1,8e4s,
                                  0.5,0,0.005,0)
stoech2                       :10(0,1b,5×0)
arithm                        : 1(1,₁₀−4,9₁₀−5>/,1 > +,1,2e3s,0,5 > × > + > × >/)
prescriber                    :20(360,004)
dist1                         :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,
                                  98,98,4×0)
dividing                      :14(12b,0)
arithm                        :12(2e1s,9e1s >×,2e7s,9e7s >× > −,9e6s >/)
jump                          :15(1,−1,9b)
arithm                        : 9(₁₀−3,2e1s >×,2e1s,2e7s,2e9s > + > − > a > −)
vlexpa                        :16(3,0,1.0,5₁₀5,423,423,0)
prescriber                    :18(17b,002)
arithm                        :17(16e30b,7e16b > /,−1 >×)
print                         :41(5, > 1 = 7,9 > s,2e11s,3e1b,30b)
print                         :40(5, < 1 = 4 > s,3e1b)
print                         :42(5, > 1 = 7,9 > s)
+
s
streams
feed                          : 1(1,01,0,353,15₁₀5,0,0.97,0,0.03)
recycle                       : 2(1,0.1,0,378,15₁₀5,0,0.97,0.01,0.02)
steam                         :12(−2,1,0,423,5₁₀5,1,1)
+
```

(3e1b). The system of equations to be solved is:

$$2\text{e1s} - 2\text{e7s} - 2\text{e9s} = 0 \tag{6.23a}$$

$$z_0 - 8\text{e4s} = 0, \tag{6.23b}$$

where

$$2\text{e7s} = f_1(2\text{e2s}),$$

$$2\text{e9s} = f_2(2\text{e2s}),$$

$$8\text{e4s} = f_3(3\text{e1b}),$$

and z_0 equals the prescribed value of i-butane concentration.

The system of equations (6.23) may be solved simultaneously or consecutively. Related to the recycle, the control presents a smaller problem, since it can be solved by repeated calculation of a single box. It therefore seems suitable to solve equation (6.23b) consecutively, embedded in the iteration cycle of (6.23a).

Recycle is calculated by direct iteration organized by box *jump*, according to Section 6.5.1. The calculation of the control is effected by box *soleqs*, using the Newton–Raphson method according to Section 6.5.2. The simulation is effected by repeatedly solving the inner loop which consists of box *soleqs* (serial number 2) and box *stoech2* (serial number 3) in each step of the iterating calculation of the external loop which consists of box *mixing* (serial number 1) up to *dividing* (serial number 6).

On the operation-order flow-sheet (Fig. 6.13) and flow-sheet program (Table 6.6) the simultaneous solution of recycle and control is demonstrated. The mass balance resembles (6.20) rather than (6.23a):

$$2\text{e2s} - 2\text{e8s} = 0 \tag{6.24a}$$

$$z_0 - 8\text{e4s} = 0, \tag{6.24b}$$

where

$$2\text{e8s} = f_1(2\text{e2s})$$

$$8\text{e4s} = f_2(3\text{e1b}).$$

This system of equations with two variables is solved using the Newton–Raphson method. The course of calculation is similar to the simulation of the recycle discussed in Section 6.5.1 and shown in Figure 6.8. There is one difference: the values of both independent variables (2e2s and 3e1b) are set during iteration by box *soleqs* (operating index 15) and the solution is obtained, since the prescribed accuracy is fulfilled simultaneously for both equations.

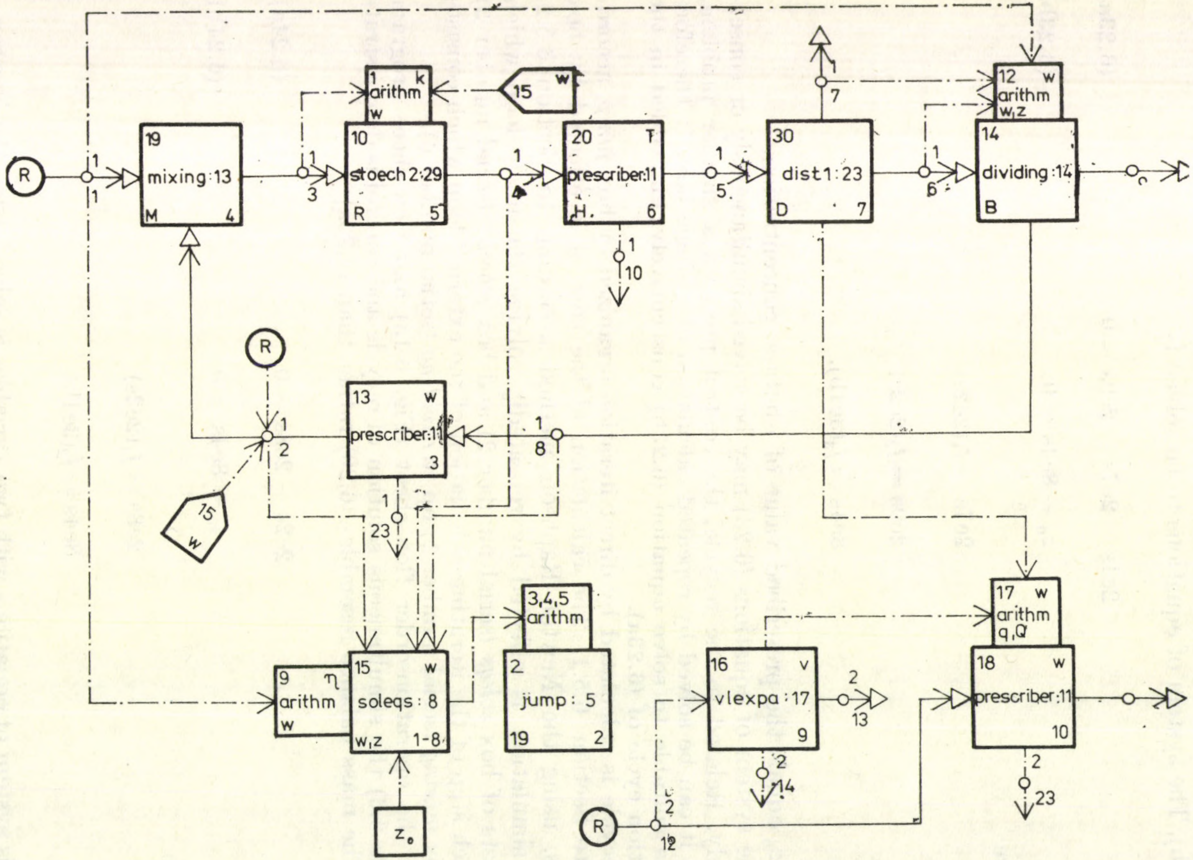


Fig. 6.13. Operation-order flow-sheet for butane isomerization (calculation of recycle loop and control of reactor outlet quality by modified Newton–Raphson method)

Table 6.6

Flow-sheet program and input data system of problem [Simulation of butane isomerization]
(calculation of recycle and control loops by modified
Newton–Raphson method)

```
[Simulation of butane isomerization. Control of reactor outlet]
D97001
stream types
feed                          : 1(4,73,5)
steam                         : 2(69)
+
operations
soleqs                        : 8(15)
∧
jump                          : 5(2)
prescriber                    :11(13,8,-2,-23)
mixing                        :13(19,1,2,-3)
stoech2                       :29(10,3,-4)
prescriber                    :11(20,4,-5,-10)
dist1                         :23(30,5,-7,-6)
dividing                      :14(14,6,-9,-8)
print                         : 2(42)
∨
vlexpa                        :17(16,12,-13,-14)
prescriber                    :11(18,12,-11,-23)
print                         : 2(41)
stop                          : 4(50)
+
data set number               :54
b
operating parameters of boxes
soleqs                        :15(2,5,10,3×0,2e2s,3e1b,0.1,9₁₀-5,2×0,2×1,₁₀-2,
                                 ₁₀-5,2×0,2×1,2e8s,8e4s,2e2s,0,5,2×0,9b,0.005,
                                 4×0)
arithm                        : 9(₁₀-3,2e1s >×)
jump                          : 2(4,-1,3b,4b,5b)
arithm                        : 3(15e15b,17e15b > - > a,₁₀-5 > -)
arithm                        : 4(5e15b,₁₀-5 > -)
arithm                        : 5(16e15b,18e15b > - > a,₁₀-8 > -)
prescriber                    :13(9e15b,002)
mixing                        :19(0.1₁₀5)
stoech2                       :10(0,1b,5×0)
arithm                        : 1(1,₁₀-4,9₁₀-5 >/,1 > +,1,2e3s,0.5 >× > + >×
                                 >/)
prescriber                    :20(360,004)
dist1                         :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,98, 98,4×0)
dividing                      :14(12b,0)
arithm                        :12(2e1s,9e1s >×,2e7s,9e7s >× > -,9e6s >/)
vlexpa                        :16(3,0,1.0,5₁₀5,423,423,0)
prescriber                    :18(17b,002)
arithm                        :17(16e30b,7e16b >/,-1 >×)
print                         :41(5, <1 = 9 > s,2e11s,3e1b,30b)
print                         :42(5, <1 = 9 > s,3e1b)
+
s
streams
feed                          : 1(1,0.1,0,353,15₁₀5,0,0.97,0,0.03)
recycle                       : 2(1,0.1,0,378,15₁₀5,0,0.97,0.01,0.02)
steam                         :12(-2,1,0,423,5₁₀5,1,1)
+
```

PROBLEMS

PROBLEM P.6.1

Simulate the process containing a recycle loop and demonstrated in Figure 5.5 with the aid of the SIMUL flow-sheet programs figuring in Tables 6.1 and 6.2. Compare the convergence rate of the direct iteration and the Newton–Raphson methods used to solve the problem.

In order to make comparison, let us start in both cases from the same input stream (1s) and initial guess (2s). We use the modified Newton–Raphson method such that the recalculation of the linear model is effected after every fifth step. The value of the function has therefore to be calculated in the zeroth step, and thereafter 1.2 times, on average, in each iteration step.

The result of the calculation is shown in Tables 6.7 and 6.8.

Table 6.7

Calculation results of problem [Simulation of butane isomerization. Recycle of bottom product] (calculation of recycle loop by direct iteration)

```
Simulation of butane isomerization. Recycle of bottom product — 50
:      1s(    1.0000       ,      100.00 10− 3,      0.0000       ,
              353.00       ,      1.5000 10+ 6,      0.0000       ,
              970.00 10− 3,      0.0000       ,      30.000 10− 3)
:      2s(    1.0000       ,      29.694 10− 3,     −2.6723 10+ 6,
              363.40       ,      1.5000 10+ 6,      0.0000       ,
              930.73 10− 3,      1.9146 10− 3,      67.353 10− 3)
:      3s(    1.0000       ,      129.73 10− 3,     −11.801 10+ 6,
              355.42       ,      1.5000 10+ 6,      0.0000       ,
              961.02 10− 3,      438.93 10− 6,      38.541 10− 3)
:      4s(    1.0000       ,      129.73 10− 3,     −12.087 10+ 6,
              355.42       ,      1.5000 10+ 6,      0.0000       ,
              533.53 10− 3,      427.93 10− 3,      38.541 10− 3)
:      5s(    1.0000       ,      129.73 10− 3,     −10.000 10+ 6,
              360.00       ,      1.5000 10+ 6,      1.0000       ,
              533.53 10− 3,      427.93 10− 3,      38.541 10− 3)
:      6s(    1.0000       ,      74.236 10− 3,     −6.6808 10+ 6,
              363.40       ,      1.5000 10+ 6,      0.0000       ,
              930.73 10− 3,      1.9146 10− 3,      67.353 10− 3)
:      7s(    1.0000       ,      55.496 10− 3,     −5.4567 10+ 6,
              338.82       ,      1.5000 10+ 6,      0.0000       ,
              2.1969 10− 3,      997.80 10− 3,      0.0000       )
:      9s(    1.0000       ,      44.541 10− 3,     −4.0085 10+ 6,
              363.40       ,      1.5000 10+ 6,      0.0000       ,
              930.73 10− 3,      1.9146 10− 3,      67.353 10− 3)
:   2e11s(    229.37 10− 3)
:   3e10s(   −106.81 10+ 3)
:     30b(    80.000       ,      40.000       ,      2.0000       ,
              1.0000       ,      3.6000 10+ 6,      1.0000       ,
              1.0000       ,      2.0000       ,      11.500       ,
              338.82       ,      358.00       ,      378.00       ,
              99.744       ,      99.824       ,     −10.704 10+ 6,
              8.5663 10+ 6,      11.500       ,      855.75 10− 3)
+
end Simulation of butane isomerization. Recycle of bottom product
```

Table 6.8

Calculation results of problem [Simulation of butane isomerization. Recycle of bottom product] (calculation of recycle loop by modified Newton–Raphson method)

```
Simulation of butane isomerization. Recycle of bottom product — 51
:        1s(    1.0000          ,      100.00   10− 3,       0.0000        ,
                353.00          ,        1.5000 10+ 6,       0.0000        ,
                970.00   10− 3,          0.0000        ,     30.000   10− 3)
:        2s(    1.0000          ,       17.172  10− 3,      −1.5445  10+ 6,
                363.10          ,        1.5000 10+ 6,       0.0000        ,
                937.48   10− 3,          1.8439 10− 3,      60.675   10− 3)
:        3s(    1.0000          ,      117.17   10− 3,     −10.670   10+ 6,
                354.50          ,        1.5000 10+ 6,       0.0000        ,
                965.23   10− 3,        270.22   10− 6,      34.496   10− 3)
:        4s(    1.0000          ,      117.17   10− 3,     −10.931   10+ 6,
                354.50          ,        1.5000 10+ 6,       0.0000        ,
                533.32   10− 3,        432.18   10− 3,      34.496   10− 3)
:        5s(    1.0000          ,      117.17   10− 3,      −9.0304  10+ 6,
                360.00          ,        1.5000 10+ 6,       1.0000        ,
                533.32   10− 3,        432.18   10− 3,      34.496   10− 3)
:        6s(    1.0000          ,       66.552  10− 3,      −5.9860  10+ 6,
                363.10          ,        1.5000 10+ 6,       0.0000        ,
                937.43   10− 3,          1.8335 10− 3,      60.733   10− 3)
:        7s(    1.0000          ,       50.620  10− 3,      −4.9773  10+ 6,
                338.82          ,        1.5000 10+ 6,       0.0000        ,
                  2.0211 10− 3,        997.98   10− 3,       0.0000        )
:        8s(    1.0000          ,       17.155  10− 3,      −1.5430  10+ 6,
                363.10          ,        1.5000 10+ 6,       0.0000        ,
                937.43   10− 3,          1.8335 10− 3,      60.733   10− 3)
:        9s(    1.0000          ,       49.396  10− 3,      −4.4429  10+ 6,
                363.10          ,        1.5000 10+ 6,       0.0000        ,
                937.43   10− 3,          1.8335 10− 3,      60.733   10− 3)
:     2e11s(    209.65   10− 3)
:     3e10s(   −115.54   10+ 3)
:       30b(     80.000         ,       40.000         ,      2.0000         ,
                  1.0000        ,        3.6000 10+ 6,        1.0000         ,
                  1.0000        ,        2.0000        ,     11.500          ,
                338.82          ,      358.00          ,    378.00           ,
                 99.759         ,       99.836         ,     −9.7626  10+ 6,
                  7.8297 10+ 6,         11.500         ,    855.75    10− 3)
+
end Simulation of butane isomerization. Recycle of bottom product
```

Solution

The accuracy of the approximate solutions is characterized by the error of the mass balance, which, for the case of direct iteration, is:

$$\delta = |\, 2\mathrm{e}1\mathrm{s} - 2\mathrm{e}7\mathrm{s} - 2\mathrm{e}9\mathrm{s}\,|,$$

and with the Newton–Raphson method

$$\delta = |\, 2\mathrm{e}2\mathrm{s} - 2\mathrm{e}8\mathrm{s}\,|.$$

The prescribed accuracy is:

$$\eta = 0.0001 \text{ kmole/s}.$$

Table 6.9

Iteration steps in Problem P.6.1

Number of iteration steps	Direct iteration				Modified Newton-Raphson method		
	2e1s	2e7s	2e9s	$\delta \times 10^3$	2e2s	2e8s	$\delta \times 10^3$
Start	0.10000	0.084497	0.069302	53.80	0.100000	0.046201	53.80
1		0.062364	0.050302	12.67	0.043421	0.031406	12.02
2		0.057089	0.045868	2.96	0.018148	0.017684	0.46
3		0.055851	0.044836	0.69	0.017172	0.017155	0.02
4		0.055563	0.044597	0.16			
5		0.055496	0.044541	0.04			

$\eta = 0.0001$

The data of mass balance and the balance errors following the iteration closely are demonstrated in Table 6.9, the convergence in Figure 6.14.

To solve the problem, 6 steps were required with direct iteration, 3 steps when using the Newton–Raphson method. Therefore the latter is quicker in principle. In practice, however, the efficiency of a method is characterized by the computation effort required and not by the number of iteration steps. The computation effort is proportional to the number of function

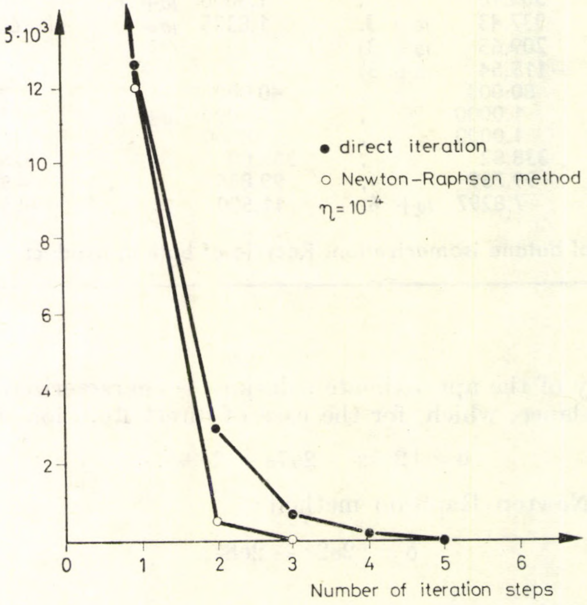


Fig. 6.14. Comparison of rate of convergence for direct iteration and modified Newton–Raphson method

values determined during the operation. In this aspect, there is no significant difference between the two methods. There are 6 values of the function to be calculated using direct iteration, and 5 with the Newton–Raphson method.

PROBLEM P.6.2

Simulate the process containing a control loop and demonstrated in Figure 5.3 with the aid of the SIMUL flow-sheet programs figuring in Tables 6.3 and 6.4. Starting from the same input data, compare the convergence rate of the modified Newton–Raphson and the Simplex method which are used to solve the problem. The conditions of functioning of the Newton–Raphson method should be the same as for Problem P.6.1, i.e., all linear models should be used in 5 iteration steps.

The results of the calculations appear in Tables 6.10 and 6.11.

Table 6.10

Calculation results of problem [Simulation of butane isomerization. Control of product quality] (calculation of control loop by modified Newton–Raphson method)

```
Simulation of butane isomerization, Control of product quality — 52
:    1s(   1.0000       ,   100.00 10− 3,    0.0000       ,
           353.00       ,   1.5000 10+ 6,    0.0000       ,
           970.00 10− 3,    0.0000       ,   30.000 10− 3)
:    2s(   1.0000       ,   100.00 10− 3,   −9.3509 10+ 6,
           353.00       ,   1.5000 10+ 6,    0.0000       ,
           532.41 10− 3,    437.59 10− 3,    30.000 10− 3)
:    3s(   1.0000       ,   100.00 10− 3,   −7.7059 10+ 6,
           360.00       ,   1.5000 10+ 6,    1.0000       ,
           532.41 10− 3,    437.59 10− 3,    30.000 10− 3)
:    4s(   1.0000       ,   56.283 10− 3,   −5.0594 10+ 6,
           362.76       ,   1.5000 10+ 6,    0.0000       ,
           944.51 10− 3,    2.1920 10− 3,    53.302 10− 3)
:    5s(   1.0000       ,   56.283 10− 3,   −5.1578 10+ 6,
           353.00       ,   1.5000 10+ 6,    0.0000       ,
           944.51 10− 3,    2.1920 10− 3,    53.302 10− 3)
:    6s(   1.0000       ,   56.283 10− 3,   −5.4130 10+ 6,
           353.00       ,   1.5000 10+ 6,    0.0000       ,
           59.276 10− 3,    887.42 10− 3,    53.302 10− 3)
:    7s(   1.0000       ,   43.717 10− 3,   −4.2987 10+ 6,
           338.81       ,   1.5000 10+ 6,    0.0000       ,
           1.8526 10− 3,    998.15 10− 3,    0.0000       )
:    8s(   1.0000       ,   100.00 10− 3,   −9.7117 10+ 6,
           346.90       ,   1.5000 10+ 6,    0.0000       ,
           34.172 10− 3,    935.83 10− 3,    30.000 10− 3)
: 2e11s(   181.54 10− 3)
: 3e10s(  −125.24 10+ 3)
:   30b(   80.000       ,   40.000       ,    2.0000       ,
           1.0000       ,   3.6000 10+ 6,    1.0000       ,
           1.0000       ,   2.0000       ,    11.500       ,
           338.81       ,   358.00       ,    378.00       ,
           99.718       ,   99.848       ,   −8.4323 10+ 6,
           6.7800 10+ 6,    11.500       ,    855.63 10− 3)
+
end Simulation of butane isomerization, Control of product quality
```

Table 6.11

Calculation results of problem [Simulation of butane isomerization. Control of product quality] (calculation of control loop by Simplex method)

```
Simulation of butane isomerization, Control of product quality — 55
:        1s(     1.0000          ,      100.00   10— 3,       0.0000         ,
                353.00           ,       1.5000  10+ 6,       0.0000         ,
                970.00   10— 3,          0.0000        ,     30.000    10— 3)
:        2s(     1.0000          ,      100.00   10— 3,      —9.3509   10+ 6,
                353.00           ,       1.5000  10+ 6,       0.0000         ,
                532.41   10— 3,        437.59    10— 3,      30.000    10— 3)
:        3s(     1.0000          ,      100.00   10— 3,      —7.7059   10+ 6,
                360.00           ,       1.5000  10+ 6,       1.0000         ,
                532.41   10— 3,        437.59    10— 3,      30.000    10— 3)
:        4s(     1.0000          ,       56.283  10— 3,      —5.0594   10+ 6,
                362.76           ,       1.5000  10+ 6,       0.0000         ,
                944.51   10— 3,          2.1920  10— 3,      53.302    10— 3)
:        5s(     1.0000          ,       56.283  10— 3,      —5.1578   10+ 6,
                353.00           ,       1.5000  10+ 6,       0.0000         ,
                944.51   10— 3,          2.1920  10— 3,      53.302    10— 3)
:        6s(     1.0000          ,       56.283  10— 3,      —5.4152   10+ 6,
                353.00           ,       1.5000  10+ 6,       0.0000         ,
                 55.488  10— 3,        891.21    10— 3,      53.302    10— 3)
:        7s(     1.0000          ,       43.717  10— 3,      —4.2987   10+ 6,
                338.81           ,       1.5000  10+ 6,       0.0000         ,
                  1.8526 10— 3,        998.15    10— 3,       0.0000         )
:        8s(     1.0000          ,      100.00   10— 3,      —9.7140   10+ 6,
                346.90           ,       1.5000  10+ 6,       0.0000         ,
                 32.040  10— 3,        937.96    10— 3,      30.000    10— 3)
:      2e11s(   181.54   10— 3)
:       3e2b(     3.0000 10— 3)
:        30b(    80.000          ,       40.000        ,      2.0000         ,
                  1.0000         ,        3.6000 10+ 6,       1.0000         ,
                  1.0000         ,        2.0000       ,     11.500          ,
                338.81           ,      358.00         ,    378.00           ,
                 99.718          ,       99.848        ,     —8.4323   10+ 6,
                  6.7800 10+ 6,          11.500        ,    855.63     10— 3)
+
end Simulation of butane isomerization. Control of product quality
```

Solution

The accuracy of the approximate solutions is characterized by the difference of the prescribed and calculated concentration of i-butane in the product

$$\delta = |z_0 - 8e8s|.$$

The prescribed accuracy is:

$$\eta = 0.005 \text{ kmole/kmole}.$$

The concentrations and the deviation from the prescribed value, following the iteration closely, are demonstrated in Table 6.12, the course of convergence in Figure 6.15.

Table 6.12

Iteration steps in Problem P.6.2

Number of iteration steps	Modified Newton-Raphson method			Simplex method		
	z_0	8e8s	$\delta \times 10^3$	z_0	8e8s	$\delta \times 10^3$
Start	0.94000	0.907638	32.36	0.94000	0.90764	32.36
1		0.927801	12.20		0.92232	17.68
2		0.934537	8.46		0.93002	9.98
3		0.933572	6.43		0.93475	5.25
4		0.934894	5.11		0.93796	2.04
5		0.935831	4.17			
$\eta = 0.005$						

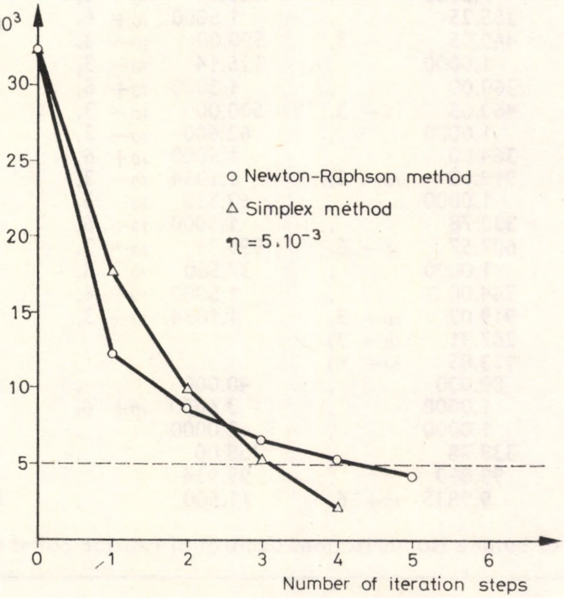


Fig. 6.15. Comparison of rate of convergence for modified Newton–Raphson and Simplex methods

Both the Newton–Raphson and the Simplex methods converge in 5 iteration steps. Considering the number of values of the function, the Simplex method is more efficient since 5 values of the function have to be calculated compared with 7 needed by Newton–Raphson method.

PROBLEM P.6.3

Simulate the process containing recycle and control loop, and demonstrated in Figure 6.11, with the aid of the SIMUL flow-sheet programs figuring in Tables 6.5 and 6.6. Starting from the same input data, compare the convergence rate of the two variants: first the consecutively used direct

Table 6.13

Calculation results of problem [Simulation of butane isomerization. Control of reactor outlet quality] (calculation of recycle and control loops by direct iteration and modified Newton–Raphson method)

```
Simulation of butane isomerization. Control of reactor outlet quality — 53
:       1s(   1.0000          ,   100.00   10— 3,    0.0000        ,
             353.00           ,     1.5000 10+ 6,    0.0000        ,
             970.00   10— 3,     0.0000        ,   30.000   10— 3)
:       2s(   1.0000          ,    25.040  10— 3,  —2.2556  10+ 6,
             364.00           ,     1.5000 10+ 6,    0.0000        ,
             919.02   10— 3,     1.1034  10— 3,   79.872   10— 3)
:       3s(   1.0000          ,   125.14   10— 3, —11.390   10+ 6,
             355.25           ,     1.5000 10+ 6,    0.0000        ,
             959.82   10— 3,   221.97    10— 6,   39.956   10— 3)
:       4s(   1.0000          ,   125.14   10— 3, —11.712   10+ 6,
             355.25           ,     1.5000 10+ 6,    0.0000        ,
             460.05   10— 3,   500.00    10— 3,   39.956   10— 3)
:       5s(   1.0000          ,   125.14   10— 3,  —9.7114  10+ 6,
             360.00           ,     1.5000 10+ 6,    1.0000        ,
             460.05   10— 3,   500.00    10— 3,   39.956   10— 3)
:       6s(   1.0000          ,    62.600  10— 3,  —5.6390  10+ 6,
             364.00           ,     1.5000 10+ 6,    0.0000        ,
             919.02   10— 3,     1.1034  10— 3,   79.872   10— 3)
:       7s(   1.0000          ,    62.538  10— 3,  —6.1501  10+ 6,
             338.78           ,     1.5000 10+ 6,    0.0000        ,
             607.57   10— 6,   999.39    10— 3,    0.0000        )
:       9s(   1.0000          ,    37.560  10— 3,  —3.3834  10+ 6,
             364.00           ,     1.5000 10+ 6,    0.0000        ,
             919.02   10— 3,     1.1034  10— 3,   79.872   10— 3)
:    2e11s(  267.31   10— 3)
:     3e1b(  123.85   10— 6)
:      30b(   80.000          ,    40.000         ,    2.0000        ,
               1.0000         ,     3.6000 10+ 6,    1.0000        ,
               1.0000         ,     2.0000        ,   11.500         ,
             338.78           ,   358.00          ,  378.00          ,
              99.890          ,    99.934         , —12.061   10+ 6,
               9.9835 10+ 6,    11.500          ,  859.00   10— 3)
+
end Simulation of butane isomerization. Control of reactor outlet quality
```

---

iteration and modified Newton–Raphson method, and second the Newton–Raphson method with two variables.

Compared with the previous problems, the difference in utilizing the Newton–Raphson method with two variables consists of increasing the computation effort, because after the zeroth step the function has to be evaluated on average 1.4 times after each step.

The results of the calculation appear in Tables 6.13 and 6.14.

The accuracy of the approximation is characterized by the error of the mass balance in the external iteration cycle of the consecutive method, and in the inner cycle by the difference of the prescribed and calculated concentration of i-butane in the mixture leaving the reactor:

$$\delta_1 = |\,2\mathrm{e1s} - 2\mathrm{e7s} - 2\mathrm{e9s}\,|$$

$$\delta_2 = |\,z_0 - 8\mathrm{e4s}\,|.$$

Table 6.14

Calculation results of problem [Simulation of butane isomerization. Control of reactor outlet quality] (calculation of recycle and control loops by modified Newton–Raphson method)

```
Simulation of butane isomerization. Control of reactor outlet — 54
:         1s(   1.0000          ,      100.00   10− 3,      0.0000     ,
                353.00          ,      1.5000   10+ 6,      0.0000     ,
                970.00   10− 3, ,      0.0000        ,      30.000  10− 3)
:         2s(   1.0000          ,      10.673   10− 3,     −960.39  10+ 3,
                363.36          ,      1.5000   10+ 6,      0.0000     ,
                932.64   10− 3,        1.2952   10− 3,      66.067  10− 3)
:         3s(   1.0000          ,      110.67   10− 3,     −10.086  10+ 6,
                354.02          ,      1.5000   10+ 6,      0.0000     ,
                966.40   10− 3,        124.91   10− 6,      33.478  10− 3)
:         4s(   1.0000          ,      110.67   10− 3,     −10.370  10+ 6,
                354.02          ,      1.5000   10+ 6,      0.0000     ,
                466.68   10− 3,        499.85   10− 3,      33.478  10− 3)
:         5s(   1.0000          ,      110.67   10− 3,     −8.5808  10+ 6,
                360.00          ,      1.5000   10+ 6,      1.0000     ,
                466.68   10− 3,        499.85   10− 3,      33.478  10− 3)
:         6s(   1.0000          ,      55.383   10− 3,     −4.9836  10+ 6,
                363.40          ,      1.5000   10+ 6,      0.0000     ,
                931.93   10− 3,        1.1659   10− 3,      66.901  10− 3)
:         7s(   1.0000          ,      55.291   10− 3,     −5.4370  10+ 6,
                338.82          ,      1.5000   10+ 6,      0.0000     ,
                646.78   10− 6,        999.35   10− 3,      0.0000     )
:         8s(   1.0000          ,      10.540   10− 3,     −948.47  10+ 3,
                363.40          ,      1.5000   10+ 6,      0.0000     ,
                931.93   10− 3,        1.1659   10− 3,      66.901  10− 3)
:         9s(   1.0000          ,      44.842   10− 3,     −4.0351  10+ 6,
                363.40          ,      1.5000   10+ 6,      0.0000     ,
                931.93   10− 3,        1.1659   10− 3,      66.901  10− 3)
:      2e11s(   235.59   10− 3)
:       3e1b(   120.12   10− 6)
:        30b(   80.000          ,      40.000        ,      2.0000     ,
                1.0000          ,      3.6000   10+ 6,      1.0000     ,
                1.0000          ,      2.0000        ,      11.500     ,
                338.82          ,      358.00        ,      378.00     ,
                99.885          ,      99.931        ,     −10.634  10+ 6,
                8.7988   10+ 6,        11.500        ,      855.75  10− 3)
+
end Simulation of butane isomerization. Control of reactor outlet
```

The accuracy of the approximation is defined in the simultaneous method by the Euclidean norm of the error vector, constructed from the former δ components:

$$\|\delta\| = (\delta_1^2 + \delta_2^2)^{1/2}$$

In our example the prescribed accuracy for the mass balance is:

$$\eta_1 = 0.0001 \text{ kmole/s},$$

for the concentration:

$$\eta_2 = 0.0005 \text{ kmole/kmole}.$$

From these data, we obtain as the maximal permissible (rounded) value of the norm:

$$\eta_n = 0.005$$

In this problem the size of the inner iteration cycle of the consecutive variant is negligible compared with the external cycle. Comparison of the convergence rate of the two variants is therefore only reasonable if we compare the change of $\|\boldsymbol{\delta}\|$ with that of δ_1.

The data characterizing the iteration are presented in Table 6.15, the course of convergence in Figure 6.16.

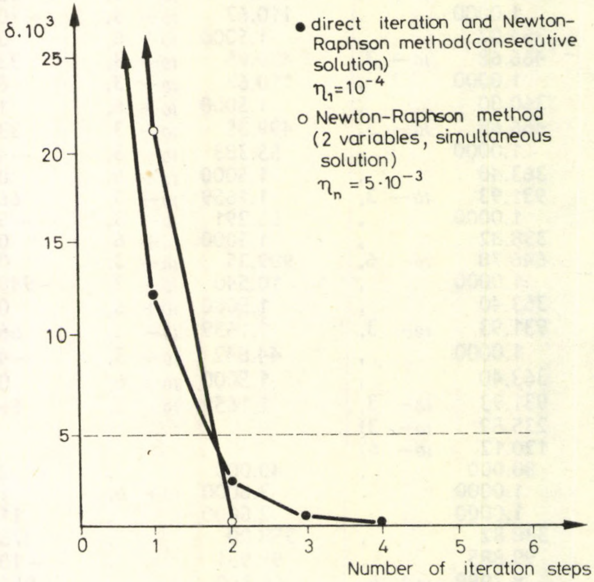


Fig. 6.16. Comparison of rate of convergence for consecutive and simultaneous solutions

Table 6.15

Iteration steps in Problem P.6.3

Number of iteration steps	Direct iteration and modified Newton-Raphson method (consecutive)					
	2e1s	2e7s	2e9s	z_0	8e4s	$\delta_1 \times 10^3$
Start	0.10000	0.099547	0.060272	0.50000	0.49799	59.82
1		0.070024	0.042094		0.49978	12.12
2		0.063994	0.038441		0.49996	2.44
3		0.062782	0.037707		0.49999	0.49
4		0.062538	0.037560		0.50000	0.01

Table 6.15 (cont.)

Number of iteration steps	Modified Newton-Raphson method (simultaneous)				
	2e2s	2e8s	z_0	8e4s	$\|\|\delta\|\| \times 10^3$
Start	0.10000	0.046201		0.42270	94.18
1	0.038621	0.026365		0.48250	21.37
2	0.010673	0.010540	0.50000	0.49985	0.20
3					
4					

$\eta_1=0.0001$
$\eta_2=0.005$
$\eta_n=0.005$

Solution

The solution was reached in the consecutive case in 5 iteration steps, correspondingly by calculating 5 values of the function. In the simultaneous method the iteration already converges by the second step, but for this purpose the function had to be evaluated 5 times. The two modes of operation are therefore equivalent when solving this problem.

CHAPTER 7

OPTIMIZATION

SIMUL system has been developed to simulate complex operations and to prepare for economic-technical decisions. If this decision is related to the production of a given product, then it generally requires the evaluation of alternative processes.

Developing alternative processes needs human creative activity and engineering intuition. It is, certainly today, inconceivable to use a computer for this development. The computer has a much bigger role when comparing and economically evaluating different possibilities. A reliable comparison of alternatives demands much work, and is unsolvable without the use of a computer. The comparison of two process alternatives not only requires simulation of the two alternatives with one data system each and evaluation of the economy of the result. Both alternatives usually contain a number of optional parameters, and as they have been chosen by estimation, we cannot know to what extent these data secure the optimum of the process alternative.

It may happen that, when comparing alternatives based on arbitrarily chosen data systems, one of the alternatives appears less advantageous, although this one would be the most favourable when properly determining the conditions of the process. The conclusion can be drawn that when choosing alternatives it is only rational to compare results optimized according to a given objective function. The optimization of complex operations is almost without exception a task with a number of variables and subsidiary conditions. The value of the objective function can be determined generally by a sequence of simulating operations with different value systems of the variables. Nothing else can be assumed about the mathematical features of the objective functions, characterizing the different tasks, except their continuity.

7.1 SEARCH METHODS IN OPTIMIZATION

In order to preserve the general applicability, an optimization box was necessary in the SIMUL system, which — based upon the value of the objective function, calculated by a sequence of simulating operations — seeks the optimum, but assumes the minimum about the relationship of the objective function and its variables, and takes the subsidiary conditions into consideration.

It is evident that only the numerical methods of optimization need to be considered. These may be divided into two groups, according to whether or not, during the search for an optimum, it is necessary to know the gradient of the objective function. The gradient methods belong to the first group, the direct-search methods to the second. There are many variants in both groups, differing to some extent in the search techniques. We do not choose to discuss and analyse these methods here. There are some comprehensive works in this field, among others the publications of Beveridge and Schechter (1970) and Wilde and Beightler (1967).

The direct-search methods are more suitable for the SIMUL system than the gradient methods, because no explicit correlation can be assumed in calculating the gradients, and to reach these correlations via partial derivatives consumes much computer time and is sometimes not accurate enough.

The direct-search methods may be divided into three groups:

- methods which search in the direction of the axes (univariant search),
- sequential simplex methods,
- methods using a more sophisticated search strategy.

The best known in the last group are Powell's method (1964), using conjugated directions and Rosenbrock's method (1960), which operates by transforming the coordinate system.

We disregarded the method which searches for the direction of coordinates because it converges slowly and inaccurately with a large number of variables. The sequential simplex method has been found to be suitable because of its simplicity. It is less sensitive to the area of the objective function and the subsidiary conditions can be taken into account more simply and with minimal computing. As favourable results have been already achieved with this method, it is now preferred to the methods of Powell and of Rosenbrock, mainly because of its simple algorithm.

The method has been improved in so far as the search for the optimum is continued automatically with reduced step length, provided the procedure has reached the prescribed accuracy for both the optimum and the modification of the objective function.

It is also possible to add to the box assortment an other optimizing box, using a different search method.

We have not yet mentioned that these methods find local optima. All algorithms are similar in this respect. It is unfortunate that no method is known which can find a practical, unequivocal global optimum. If more local optima have to be predicted, then roughly reliable information about the global optimum may be obtained only by repeated local optimizations approached from different starting points.

7.2 OPTIMIZATION OF BIG SYSTEMS

Complex operations normally assume numerous degrees of freedom, that is to say, the number of optional parameters to be optimized is large. This often results in insoluble difficulties regarding the practical execution of the optimization, because the computer time increases steeply with the number of independent variables. According to the estimation of Rudd and Watson (1968), the number of values to be computed increases exponentially with the number of independent variables.

It follows that, in order to arrive at practical results, the number of variables to be optimized must be reduced. Thus, those variables must be selected to which the objective function is most sensitive. This selection depends above all on intuition and experience. Principally, the variables may be ordered on the basis of calculations according to the sensitivity of the objective function, but if any interrelation is allowed, the calculation becomes practically impossible because of the immense number of possible combinations. If the number of these variables cannot be sufficiently reduced by intuition or experience, then a sensitivity check may be needed, which takes no interrelation or only simple interrelations into consideration.

As regards the number of variables to be optimized no generally valid limit may be stated, since it depends on the technical problem and the computer. In our experience we have already dealt with a task where the computer-time needed for optimation reached several hours, although the number of variables was only three.

If the number of variables to be optimized cannot be reduced by process considerations, then in order to permit the use of search methods, decomposition of the task must be attempted.

The complex operations are combined systems from the systems engineering aspect. Therefore, the structure of the SIMUL model provides the possibility of decomposing the system into sub-systems as each SIMUL box, modelling a piece of equipment, may be considered as a sub-system of the whole system. For combined systems the "principle of optimality" applies, according to which the optimal system can only be composed from optimal sub-systems (Kaufmann, 1964).

Optimization methods are based on this principle: the system is first decomposed into sub-systems and knowing the optima of the sub-systems, the optimum of the entire system is sought. Many variants of these decomposition methods are known. These may be divided into two main groups, depending on whether the decomposed parts are solved with fixed (optimal) values of the variables connecting the decomposed parts or as a function of them. As example of the first group, we refer to the decomposition methods of Dantzig and Wolfe (1960), and of the second group, to the dynamic optimization according to Bellman and Dreyfus (1962) and Roberts (1964).

If the decomposed parts are solved with fixed values of the connecting variables, then the decomposition method requires at least one iteration; the optimization of the connecting variables and the solution of the related parts is carried out by iteration.

If the decomposed parts are solved as a function of the connecting variables, then the solution of the parts is generally presented in tabular form and the whole task is solved in a manner to be discussed later, by "embedment" of the partial solutions.

The search methods already mentioned are in principle also suitable for optimizing complex operations. As the number of variables increases, the use of a decomposition method becomes more favourable. The nested or parallel use of these methods may also be considered (Almásy et al., 1971).

The different methods and combinations require different computation times to carry out a given optimization. The selection of the best strategy may therefore significantly reduce the computer costs.

The box assortment of the SIMUL system currently contains only the box *bellman* of decomposition methods. It is suitable for the dynamic optimization of a system, containing sub-systems connected in series.

7.3 OPTIMIZATION IN THE SIMUL SYSTEM

7.3.1 OPTIMIZATION WITH BOX *(opt2)*

The box assortment of the SIMUL system contains box *opt2*, which corresponds to the sequential simplex method (Jenson and Jeffreys, 1963). It should be noted that this method is not identical with the simplex method used to solve linear optimization problems. The functioning of this box was described in Section 4.4.2.2.

The algorithm described defines a single local optimum. If there are more local optima in the allowed range, then the procedure finds one of these — depending on the input data system — in a random manner.

The calculation following the operation-order flow-sheet in Figure 7.1 is an example of the use of box *opt2*. This figure formulates the optimization problem discussed in Section 5.1.2 using the symbols of the SIMUL system. It may be observed that the calculation order is practically identical to that of Figure 6.7, with the single exception that, before the simulating calculation, operation *opt2 : 38 (49)* is carried out in order to obtain the optimal value of the catalyst stream entering reactor R1. All calculation serial numbers are therefore increased by 1.

The objective function of the complex operation quoted as an example is, as discussed previously the total cost of the overall catalyst stream and the steam. In order to determine these values, the whole model has to be calculated with fixed catalyst stream of reactor R1. All operations following *opt2 : 38 (49)* are placed between symbols $\wedge$ and $\vee$, indicating that the calculation of the whole model is necessary to arrive at each value of the objective function. The objective function is denoted by operating index 3,

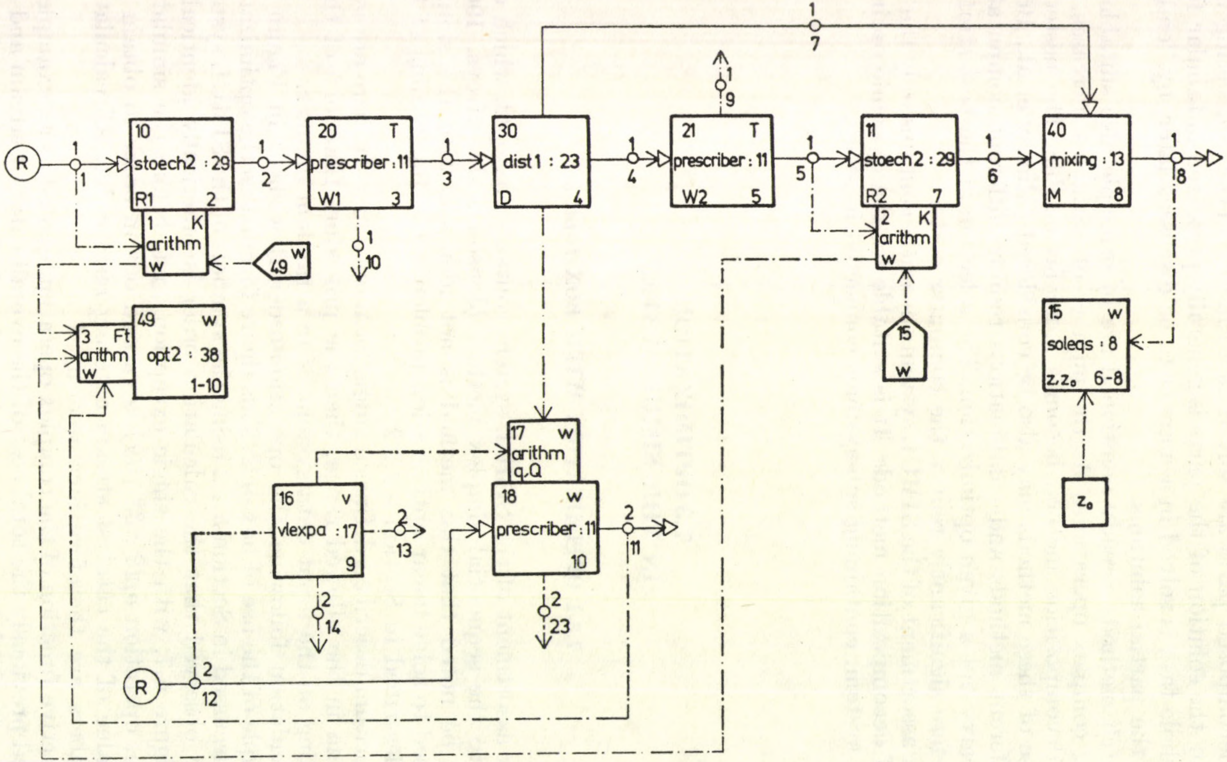


Fig. 7.1. Operation-order flow-sheet of the butane isomerization (optimization of the system with product–quality control)

specified as an arithmetic expression among the operating parameters of box *opt2*. The catalyst stream (coefficients of the arithmetic expressions with operating indices 1 and 2) and the mass stream of the stream vector with connection index 23 are the input data of this calculation. As the catalyst stream of reactor R1 is the decision variable, box *opt2* intervenes through the coefficient corresponding to the catalyst stream in the arithmetic expression (operating index 1). If operation *print: 2*, which prints the results of the calculation, is written outside the bracket symbols, then only the results are printed, when operation *opt2*, i.e. the optimization, is complete.

The flow-sheet program of the above task is presented in Table 7.1. The result of the calculation is presented in Table 7.2.

Table 7.1

Flow-sheet program and input data system of problem
[Simulation of i-butane production, optimized]

```
[Simulation of i-butane production, optimized]
D97001
stream types
feed                          :1(4,73,5)
steam                         :2(69)
+
operations
opt                           :38(49)
 ∧
stoech2                       :29(10,1,−2)
prescriber                    :11(20,2,−3,−10)
dist1                         :23(30,3,−7,−4)
prescriber                    :11(21,4,−5,−9)
soleqs                        :8(15)
 ∧
stoech2                       :29(11,5,−6)
mixing                        :13(40,6,7,−8)
print                         :2(41)
 ∨
print                         :2(42)
 ∨
vlexpa                        :17(16,12,−13,−14)
prescriber                    :11(18,12,−11,−23)
print                         :2(43)
stop                          :4(50)
+
data set number               :81
operating parameters of the boxes
opt                           :49(5×0,10,1,1,0,0,1,3b,3e1b,3₁₀−4,1₁₀−4,1,0.5,
                                 3e1b,0,1,10×0)
stoech2                       :10(0,1b,5×0)
arithm                        :1(1,₁₀−4,9₁₀−5>/,1>+,1,2e1s,0.5>×>+>×>/)
arithm                        :3(9₁₀—5,1>×)
prescriber                    :20(360,004)
dist1                         :30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358,378,98,98,4×0)
soleqs                        :15(1,5,10,0,0,0,3e2b,6₁₀−4,0,1,₁₀−4,0,₁₀−5,8e8s,
                                 0.94,0,0.005,0)
```

Table 7.1 (cont.)

```
prescriber      :21(350,004)
arithm          :2(1,₁₀−4,9₁₀−5>/,1>+,1,2e5s,0.5>×>+>×>/)
arithm          :3(3e1b,3e2b>+,2₁₀4>×,2e11s>+)
arithm          :5(1e3b,1e4b>+)
stoech2         :11(0,2b,5×0)
mixing          :40(0.1₁₀5)
vlexpa          :16(3,0,1.0,5₁₀5,423,423,0)
arithm          :17(16e30b,7e16b>/,−1>×)
prescriber      :18(17b,002)
print           :41(5,<3>e<1=2>b,2e11s,12e49b,8s)
print           :42(5,<11=14>s,23s,11b)
print           :43(5,<1=8>s,11b,15,49b)
+
stream
feed            :1(1,0.1,0,353,15₁₀5,0,0.97,0,0.03)
steam           :12(−2,1,0,423,5₁₀5,1,1)
+
```

Table 7.2

Calculation results of problem [Simulation of i-butane production, optimized]
(controlled product quality and optimization)

```
Simulation of i-butane production, optimized — 81
:       11s(   −2.0000           ,    333.65  ₁₀− 3,     −75.038  ₁₀+ 6,
               423.00            ,    500.00  ₁₀+ 3,      1.0000        ,
                1.0000           )
:       12s(   −2.0000           ,     1.0000       ,      0.0000        ,
               423.00            ,    500.00  ₁₀+ 3,      1.0000        ,
                1.0000           )
:       13s(   −2.0000           ,     0.0000       ,      0.0000        ,
               423.22            ,    500.00  ₁₀+ 3,      1.0000        ,
                1.0000           )
:       14s(   −2.0000           ,     1.0000       ,    −262.25  ₁₀+ 6,
               423.22            ,    500.00  ₁₀+ 3,      0.0000        ,
                1.0000           )
:       23s(   −2.0000           ,    666.35  ₁₀− 3,    −149.87  ₁₀+ 6,
               423.00            ,    500.00  ₁₀+ 3,      1.0000        ,
                1.0000           )
:       11b(    0.0000           ,    872.33  ₁₀− 3,      0.0000        ,
                0.0000           ,     0.0000       ,      0.0000        ,
                0.0000           )
+
:        1s(    1.0000           ,    100.00  ₁₀− 3,      0.0000        ,
               353.00            ,     1.5000 ₁₀+ 6,      0.0000        ,
               970.00   ₁₀− 3,         0.0000       ,     30.000  ₁₀− 3)
:        2s(    1.0000           ,    100.00  ₁₀− 3,     −9.5027  ₁₀+ 6,
               353.00            ,     1.5000 ₁₀+ 6,      0.0000        ,
               234.72   ₁₀− 3,       735.28   ₁₀− 3,     30.000  ₁₀− 3)
:        3s(    1.0000           ,    100.00  ₁₀− 3,     −7.9126  ₁₀+ 6,
               360.00            ,     1.5000 ₁₀+ 6,      1.0000        ,
               234.72   ₁₀− 3,       735.28   ₁₀− 3,     30.000  ₁₀− 3)
:        4s(    1.0000           ,     26.497 ₁₀− 3,     −2.3932  ₁₀+ 6,
               365.54            ,     1.5000 ₁₀+ 6,      0.0000        ,
               885.68   ₁₀− 3,         1.1016 ₁₀− 3,    113.22   ₁₀− 3)
:        5s(    1.0000           ,     26.497 ₁₀− 3,     −2.4534  ₁₀+ 6,
               353.00            ,     1.5000 ₁₀+ 6,      0.0000        ,
```

```
          885.68  10- 3,      1.1016 10- 3,     113.22  10- 3)
:    6s(    1.0000     ,     26.497  10- 3,     -2.5586 10+ 6,
          353.00       ,      1.5000 10+ 6,      0.0000       ,
          113.08  10- 3,    773.70   10- 3,    113.22   10- 3)
:    7s(    1.0000     ,     73.503  10- 3,     -7.2283 10+ 6,
          338.81       ,      1.5000 10+ 6,      0.0000       ,
           61.153 10- 6,    999.94   10- 3,      0.0000       )
:    8s(    1.0000     ,    100.00   10- 3,     -9.7869 01+ 6,
          342.67       ,      1.5000 10+ 6,      0.0000       ,
           30.007 10- 3,    939.99   10- 3,     30.000  10- 3)
:   11b(    0.0000     ,    872.33  10- 3,       0.0000       ,
            0.0000     ,      0.0000      ,      0.0000       ,
            0.0000     )
:   15b(    1.0000     ,      5.0000      ,     10.000        ,
            0.0000     ,      0.0000      ,      0.0000       ,
          761.21  10- 6,    761.21   10- 6,      0.0000       ,
           10.000 10- 3,     80.000  10- 6,     -2.5811 10- 6,
           30.000 10- 6,    939.99   10- 3,    940.00   10- 3,
            7.0296 10- 6,     5.0000 10- 3,     35.199  10- 3)
:   49b(   11.000      ,      1.0000      ,      7.0000       ,
            0.0000     ,      0.0000      ,     10.000        ,
            1.0000     ,      0.0000      ,      0.0000       ,
            3.0000     ,      0.0000      ,      1.1512  10- 3,
          390.00  10- 6,    390.00   10- 6,     30.000  10- 6,
           10.000 10- 6,     50.000  10- 3,      1.1796 10- 3,
            1.1538 10- 3,     1.2157 10- 3,    360.00   10- 6,
          390.00  10- 6,    330.00   10- 6,    360.00   10- 6,
          390.00  10- 6,      1.1796 10- 3,      1.1538 10- 3)
+
end Simulation of i-butane production, optimized
```

7.3.2 OPTIMIZATION WITH BOX *(bellman)*

Box *bellman* is not as universally applicable as box *opt2*, but there are systems — namely those consisting of sub-systems, connected in series — where its use may be recommended.

7.3.2.1 GENERAL OUTLINES OF THE BELLMAN METHOD

The principle of optimality is valid with sub-systems connected in series, for an objective system function such as $H = H_1$, which can be formed by the recursive formula

$$H_i = H_i(\mathbf{f}_i, \mathbf{y}_i, H_{i+1}), H_{n+1} \equiv 0 \quad (i = n, n-1, \ldots, 1) \tag{7.1}$$

where

i = the serial number of the sub-systems, increasing in the direction of the information stream,
n = the number of sub-systems,

$\mathbf{f}_i$ = the connecting variables of the i-th sub-system, connecting it to the $(i-1)$-th sub-system,
$\mathbf{y}_i$ = decision parameters and
H_i = the objective sub-system function of the i-th step, containing the $i, i+1, \ldots, n$ sub-systems.

These interconnections are demonstrated in Figure 7.2. The objective sub-system function of the n-th (last) sub-system depends only on the variables, connecting it with the $(n-1)$-th sub-system and on the decision parameters related to the n-th sub-system ($H_{n+1} = 0$). If the optimal value of these parameters is determined, then the optimal value of the objective function is solely a function of connecting variable $\mathbf{f}_n$:

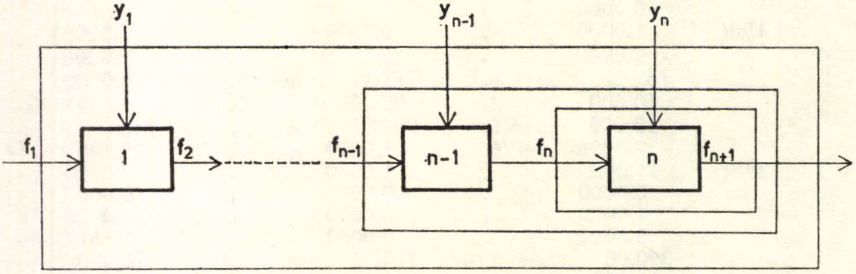


Fig. 7.2. Optimization of a system consisting of sub-systems connected in series

$$H_n^{\text{opt}} = H_n^{\text{opt}}(\mathbf{f}_n) = \underset{y_n}{\text{opt}}(H_n). \tag{7.2}$$

Connecting the $(n-1)$-th sub-system to the n-th, we arrive at the $(n-1)$-th step of the dynamic optimization.

Substituting (nesting) into the objective function of the $(n-1)$-th step:

$$H_{n-1} = H_{n-1}(\mathbf{f}_{n-1}, \mathbf{y}_{n-1}, H_n) \tag{7.3}$$

the function

$$H_n = H_n^{\text{opt}}(\mathbf{f}_n), \tag{7.4}$$

we obtain the new objective function of the $(n-1)$-th step. As the output of the $(n-1)$-th sub-system is

$$\mathbf{f}_n = \mathbf{F}_{n-1}(\mathbf{f}_{n-1}, \mathbf{y}_{n-1}) \tag{7.5}$$

H_{n-1} will be solely a function of the connecting variables ($\mathbf{f}_{n-1}$) of the $(n-1)$-th sub-system and the decision variables respectively. H_{n-1}^{opt} will be solely a function of variables $\mathbf{f}_{n-1}$.

The operation is continued until the optimum value of the objective function relating to the first step, and so the optimum of the whole system, is found.

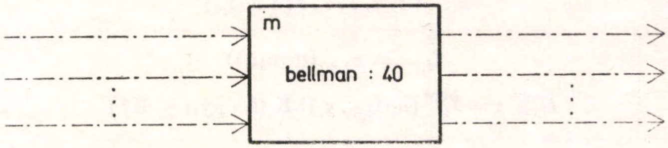
The $\mathbf{f}_1$ input variables of the first step are given, defining the optimal decision parameters $\mathbf{y}_i$ of the first sub-system and the connecting variables $\mathbf{f}_2$ with the second sub-system. Thus, the optimal input variables of the second step are known in this manner the optimal decision parameters of the second and likewise all the subsequent sub-systems can be determined.

7.3.2.2 DESCRIPTION OF BOX *(bellman)*

We have already discussed the mathematical boxes of the SIMUL system (Chapter 4.4). It would have been impractical to introduce box *bellman* in that chapter without having first outlined the general concept of dynamic optimization.

Box *bellman* provides for the dynamic optimization of complex systems and also optimizes one step.

The graphic symbol of the box:



Description of the operation:

bellman: 40 (m_1)
$\wedge$
S_1
$\vee$

bellman: 40 (m_2)
$\wedge$
S_2
$\vee$
⋮

describing the optimization of a complex system. S is the sequence of simulating operations, related to the i-th sub-system.

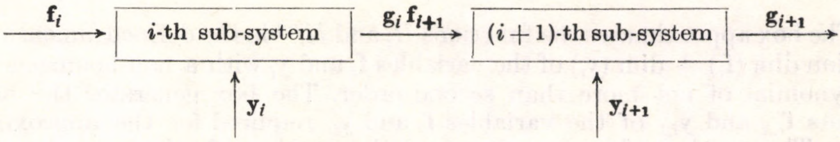


Fig. 7.3

In each sub-system, input variables ($\mathbf{f}_i$), decision variables ($\mathbf{y}_i$) and output variables ($\mathbf{g}_i$) are taken into consideration (Fig. 7.3).

The basic principle of the calculation is demonstrated in Figure 7.4.

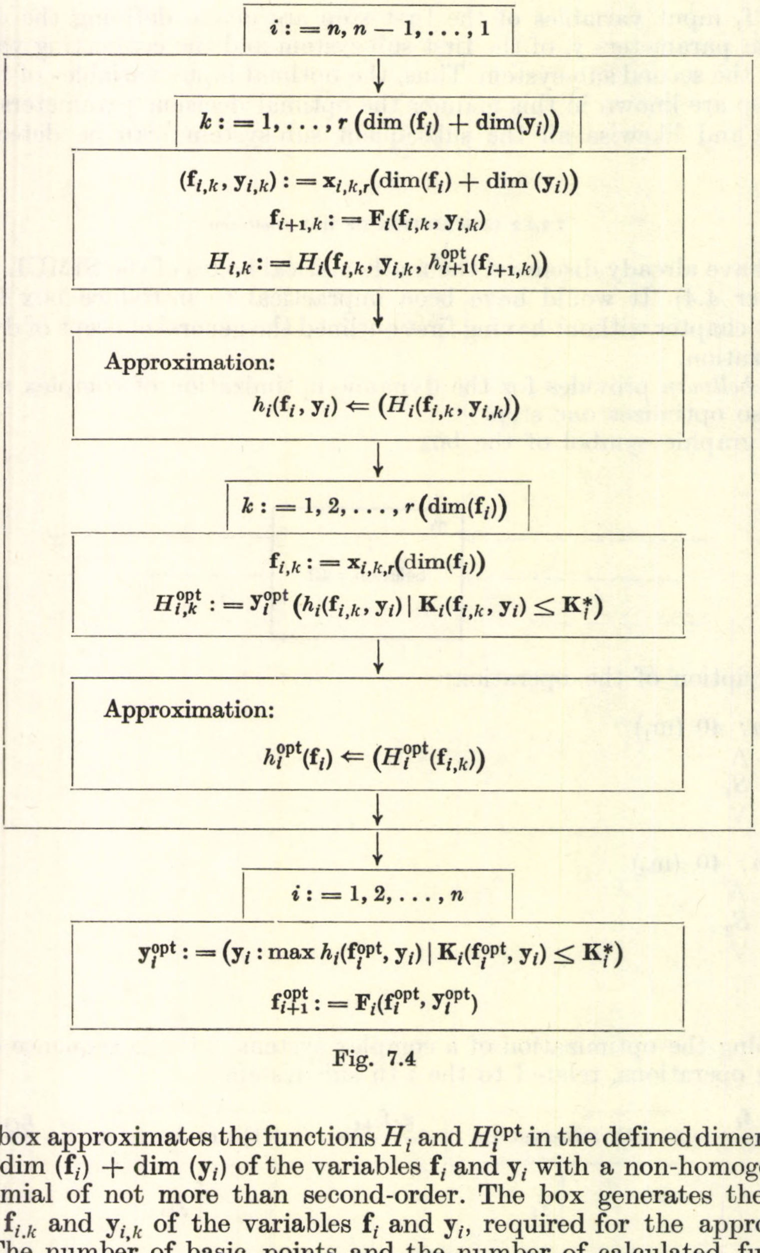


Fig. 7.4

The box approximates the functions H_i and H_i^{opt} in the defined dimensional region $\dim(\mathbf{f}_i) + \dim(\mathbf{y}_i)$ of the variables $\mathbf{f}_i$ and $\mathbf{y}_i$ with a non-homogeneous polynomial of not more than second-order. The box generates the basic points $\mathbf{f}_{i,k}$ and $\mathbf{y}_{i,k}$ of the variables $\mathbf{f}_i$ and $\mathbf{y}_i$, required for the approximation. The number of basic points and the number of calculated function values

$$v = \begin{cases} (d-1)(d+2) + 4, & \text{if } d < 4 \\ (d+1)(d+2) & \text{otherwise} \end{cases}$$

Here

$$d = \begin{cases} \dim(\mathbf{f}_i) + \dim(\mathbf{y}_i) & \text{approximating } H_i \\ \dim(\mathbf{f}_i) & \text{approximating } H_i^{\text{opt}}. \end{cases}$$

If $d \geq 4$, the basic points $\mathbf{x}_i = [\mathbf{f}_i, \mathbf{y}_i]$ and $\mathbf{x}_i = \mathbf{f}_i$ are the centres of the 0-, 1- and $(d - 1)$-dimensional elements of a d-dimensional regular simplex around the prescribed mean value of the variables, considering the prescribed intervals as unity.

The optimization is carried out in two phases. In the first phase, starting from the n-th sub-system, which determines the overall objective function and progressing backwards over the sub-systems, the $h_i\,(\mathbf{f}_i, \mathbf{y}_i)$ and $h_i^{\text{opt}}\,(\mathbf{f}_i)$ functions are calculated by minimizing the square errors. These functions approximate the H_i and H_i^{opt} objective functions. In the second phase we progress starting from the first sub-system, the input values of $\mathbf{f}_i$ are substituted into function $h_i\,(\mathbf{f}_i, \mathbf{y}_i)$ and the optima of the $\mathbf{y}_i$ decision variables of each sub-system are determined. This repeated optimization in the second phase differs from the usual techniques.

The optimum of the control variables is found by the box in the prescribed range either when calculating $H_i^{\text{opt}}\,(\mathbf{f}_i)$, or when calculating $\mathbf{y}_i^{\text{opt}}$ in the second phase by the gradient method. The possible constraints

$$K_i(\mathbf{f}_i, \mathbf{y}_i) \leq K_i^* \tag{7.6}$$

are considered by "punitive functions".

Operating parameters:

Denomination	Number	Value, significance	Note
op1	1	Cycle variable	Storage cell, initial value to be set to 0.
op2	1	Number of input variables (*nf*)	
op3	1	Number of decision variables (*ny*)	
op4	1	Number of output variables (*ng*)	
op5	1	Continuation point	Serial number of the next "bellman operation" in the flow-sheet program in the course of the "backwards calculation". It is zeroed at the end of the partial optimization. In the case of the first part, optimized finally, the serial number of the starting operation has to be specified.

op6	1		In the case of the part optimized finally, this value is 1.
op7	1	Value of the objective function of the previous step	In the arithmetic expression which calculates the objective function in the actual step, reference should be made to this variable.
op8	1	Reference of the coefficients of function $h_{i+1}^{\mathrm{opt}}(\mathbf{f}_i + 1)$	Reference to the 11th operating parameter of box *bellman*, optimizing the previous step.
op9	1	Actual objective function	Reference to the arithmetic expression defining the objective function of the actual step.
op10	1	Reference of the coefficients of function $h(\mathbf{f}, \mathbf{y}) \approx H$	Obtains its value in the box.
op11	1	Reference of the coefficients of function $h^{\mathrm{opt}}(\mathbf{f})$	Obtains its value in the box.
op12	*nf*	Reference of the input variables	
op13	*nf*	Mean value of the input variables	
op14	*nf*	Deviation of the input variables	
op15	*ny*	Reference of the decision variables	
op16	*ny*	Mean value of the decision variables	
op17	*ny*	Deviation of the decision variables	
op18	*ng*	Reference of the output variables	
op19	*ng*	Mean value of the output variables	
op20	*ng*	Deviation of the output variables	
op21	1	Beginning of the store location of the objective function values	Obtains its value during calculation.
op22	1	Value of the objective function obtained when calculating forwards	Obtains its value during calculation.
op23	1	Value of $h(\mathbf{f}^{\mathrm{opt}}, \mathbf{y}^{\mathrm{opt}})$ obtained when calculating forwards	Obtains its value during calculation.
op24	1	Value of $h^{\mathrm{opt}}(\mathbf{f}^{\mathrm{opt}})$ obtained when calculating forwards	Obtains its value during calculation.
op25	*ny*	Optimal decision variables obtained when calculating forwards	Obtain their values during calculation.

op26	*ng*	Calculated mean values of the dependent variables	Obtain their values during calculation.
op27	1	Mean deviation of the dependent variables	Obtains its value during calculation.

Check: The box prints an error message if the dimension of the task is too big $(ny + nf) > 30$, if the measured range of the output variables differs from the estimated range, if the value of the objective function $h_i^{\mathrm{opt}}(\mathbf{f}_i^{\mathrm{opt}})$ differs in the optimum from the calculated $H_i(\mathbf{f}_{i+1}^{\mathrm{opt}}, \mathbf{y}_i^{\mathrm{opt}}, h_{i+1}^{\mathrm{opt}})$-value, and if the error in the approximation of $h(\mathbf{f}, \mathbf{y})$ or $h_i^{\mathrm{opt}}(\mathbf{f})$ exceeds the allowed limit.

7.3.2.3 EXAMPLE OF APPLICATION

In this chapter we discuss an example demonstrating in particular the decomposition of a system.

The sub-system of the dynamic optimization in the SIMUL system does not necessarily consist of a single box. The decomposition into suitable sub-systems is just a favourable set-up for utilizing the described operation.

We shall discuss the use of box *bellman* on the example of butane-isomerization. Since selection of the parameters was arbitrary to some extent during our calculations, we have not yet exhausted all the possible variants. One may ask for example, whether the economy could be improved by increasing the separating efficiency of the distillation. It may be supposed that when the efficiency of separation is increased and obtaining unchanged *i*-butane content, the cost of the catalyst might decrease. It is evident that the increase in steam consumption should be taken into account. If the number of plates is fixed, then the separation can be improved by changing the reflux ratio. We must therefore consider the reflux ratio as a decision variable.

If we decide to optimize our system either according to the catalyst stream of reactor R1, or according to the reflux ratio, then the optimization may be carried out with either box *opt2* or box *bellman*. The organization of the calculation differs little in the first case from the operation-order flow-sheet (Fig. 7.1); we have only to specify the reference to the operating parameters of box *dist1* among the parameters of box *opt2*.

The use of box *bellman* in apparently obvious in this case, because the whole system can easily be divided at connecting point 3 into two sub-systems, each containing only one decision variable.

The box *bellman*, built into the SIMUL system, describes the dependence of the objective functions in each step from the connecting and decision variables — differing somewhat from the generally used techniques — with a second order approximation. This approximation is carried out in a previously fixed variable range.

In order to decrease the calculation work, only those function values are used for the approximation which are limited to the point system of the field of the variables, fixed by the box. The number of points is about one and a half time as great as the number of the function values, required to define a second-order polynomial. We have to calculate far fewer function values compared with their number if taken from tables which contain the values of the objective functions for each variable in two steps.

PROBLEM

PROBLEM P.7.1 ISOMERIZATION OF BUTANE

Solve the process problem outlined in Section 7.3.1 using a different calculation philosophy and interpret the result from the process viewpoint.

Solution

We have used box *soleqs* to simulate the loop controlling the product quality in the operation order presented in Section 7.3.1; it was not the task of box *opt2* to set the quality of the product, i.e., 8e8s., A different operation order may be followed if 8e8s is a constrained external variable of box *opt2*, whose lower bound is 0.94. Box *soleqs* may therefore be abandoned from the flow-sheet program, since box *opt2* is able to organize the total operation order with two independent variables (the two catalyst streams) and an external variable. The flow-sheet program and input data system of this solution is presented in Table P.7.1 (1), the results in Table P.7.1. (2).

Some partial results of the optimization with one variable have been compiled in Table P.7.1 (3), those of the optimization with two variables in Table P.7.1 (4). Comparison of these tables shows that the two results differ. This is the consequence of the prescribed step length and the accuracy requirement.

Table P.7.1 (1)

Isomerization of butane with controlled product quality and optimization. Optimization with two variables and one external variable. Flow-sheet program and input data system of problem [Simulation of butane isomerization, optimized]

```
[Simulation of butane isomerization, optimized]
A 770319
Stream types
feed     : 1(4,73,5)
steam    : 2(69)
+
operations
opt      : 38(15)
Λ
stoech2  : 29(10,1,−2)
presc    : 11(20,2,−3,−10)
dist1    : 23(30,3,−7,−4)
presc    : 11(21,4,−5,−9)
stoech2  : 29(11,5,−6)
mixing   : 13(40,6,7,−8)
print    : 2(42)
V
vlexpa   : 17(16,12,−13,−14)
presc    : 11(18,12,−11,−23)
print    : 2(41)
stop     : 4(50)
+
Data set number: 80
operating parameters of the boxes
opt      : 15(5×0,10,2,0,1,0,0,5b,1e3b,1e4b,9₁₀−5,₁₀−3,₁₀−4,₁₀−4,
           5₁₀−5,5₁₀−5,0.05,8e8s,0.94.1,30×0)
stoech2  : 10(0,1b,5×0)
arithm   : 1(1,₁₀−4,3b >/1 > +,1,2e1s,0.5 > × > × >/)
arithm   : 3(9₁₀−5,1 > ×)
presc    : 20(360,004)
dist1    : 30(80,40,2,1,36₁₀5,1,1,2,11.5,0,358.378,98,98,4×0)
presc    : 21(253,004)
arithm   : 2(1,₁₀−4,4b >/,1 > +,1,2e5s,0.5 > × > + > ×/)
arithm   : 4(₁₀−3,1 > ×)
arithm   : 5(1e3b,1e4b > +)
stoech2  : 11(0,2b,5×0)
mixing   : 40(₁₀4)
vlexpa   : 16(3,0,1,5₁₀5,423,423,0)
arithm   : 17(16e30b,7e16b >/,−1 > ×)
presc    : 18(17b,002)
print    : 42(5, < 1 = 10 > s,1e3b,1e4b,15b,30b)
print    : 41(5, < 11 = 14 > s,23s,11b)
+
streams
feed     : 1(1,0.1,0,353.15₁₀5,0,0,97,0,0.03)
steam    : 12(−2,1,0,423,5₁₀5,1,1)
+
```

Table P.7.1 (2)

Isomerization of butane with controlled product quality and optimization. Optimization with two variables and one external variable. Calculation results of problem [Simulation of butane isomerization, optimized]

```
Simulation of butane isomerization, optimized -80
:      1s(    1.0000         ,     100.00   10- 3,        0.0000      ,
             353.00          ,       1.5000 10+ 6,        0.0000      ,
             970.00   10- 3,       0.0000       ,       30.000   10- 3)
:      2s(    1.0000         ,     100.00   10- 3,       -9.4918 10+ 6,
             353.00          ,       1.5000 10+ 6,        0.0000      ,
             256.15   10- 3,     713.85     10- 3,       30.000   10- 3)
:      3s(    1.0000         ,     100.00   10- 3,       -7.8978 10+ 6,
             360.00          ,       1.5000 10+ 6,        1.0000      ,
             256.15   10- 3,     713.85     10- 3,       30.000   10- 3)
:      4s(    1.0000         ,      28.638  10- 3,       -2.5848 10+ 6,
             365.15          ,       1.5000 10+ 6,        0.0000      ,
             894.26   10- 3,     986.56     10- 6,      104.76    10- 3)
:      5s(    1.0000         ,      28.638  10- 3,       -3.1030 10+ 6,
             253.00          ,       1.5000 10+ 6,        0.0000      ,
             894.26   10- 3,     986.56     10- 6,      104.76    10- 3)
:      6s(    1.0000         ,      28.638  10- 3,       -3.2162 10+ 6,
             253.00          ,       1.5000 10+ 6,        0.0000      ,
              99.622  10- 3,     795.62     10- 3,      104.76    10- 3)
:      7s(    1.0000         ,      71.362  10- 3,       -7.0178 10+ 6,
             338.81          ,       1.5000 10+ 6,        0.0000      ,
              72.550  10- 6,     999.93     10- 3,        0.0000      )
:      8s(    1.0000         ,     100.00   10- 3,      -10.234  10+ 6,
             315.64          ,       1.5000 10+ 6,        0.0000      ,
              28.581  10- 3,     941.42     10- 3,       30.000   10- 3)
:      9s(    1.0000         ,       0.0000       ,      518.23   10+ 3,
             365.15          ,       1.5000 10+ 6,        0.0000      ,
             894.26   10- 3,     986.56     10- 6,      104.76    10- 3)
:     10s(    1.0000         ,       0.0000       ,     -125.75   10+ 3,
             353.00          ,       1.5000 10+ 6,        0.0000      ,
             256.15   10- 3,     713.85     10- 3,       30.000   10- 3)
:    1e3b(   340.00   10- 6)
:    1e4b(   913.40   10- 6)
:     15b(     8.0000        ,       1.0000       ,        7.0000      ,
               0.0000        ,       2.0000       ,       10.000       ,
               2.0000        ,       0.0000       ,        1.0000      ,
               3.0000        ,       0.0000       ,        1.2534  10- 3,
             340.00   10- 6,     913.40     10- 6,      340.00    10- 6,
             913.40   10- 6,      36.788    10- 6,       36.788   10- 6,
              50.000  10- 6,      50.000    10- 6,       50.000   10- 3,
             941.42   10- 3,     940.00     10- 3,        1.0000      ,
               1.2534 10- 3,       1.2902   10- 3,        1.3037  10- 3,
               0.0000        ,       0.0000       ,        0.0000      ,
               0.0000        ,     340.00     10- 6,      913.40    10- 6,
             376.79   10- 6,     913.40           ,        0.0000      ,
             945.26   10- 6,       0.0000         ,        0.0000      ,
               0.0000        ,       0.0000       ,        0.0000      ,
               0.0000        ,       0.0000       ,        0.0000      ,
             358.39   10- 6,     945.26     10- 6,      376.79    10- 6,
             913.40   10- 6,     340.00     10- 6,      913.40    10- 6,
               1.3037 10- 3,       1.2902   10- 3,        1.2534  10- 3)
      30b(    80.000         ,      40.000        ,        2.0000      ,
               1.0000        ,       3.6000 10+ 6,        1.0000      ,
               1.0000        ,       2.0000       ,       11.500       ,
             338.81          ,     358.00         ,      378.00        ,
```

Table P.7.1. (2) (cont.)

```
                99.960      ,        99.980         ,      −13.757   10+ 6,
                12.052  10+ 6,       11.500         ,      855.63    10− 3)
+
:       11s(   −2.0000      ,        322.71   11− 3,       −72.578   10+ 6,
                423.00      ,        500.00   10+ 3,        1.0000      ,
                1.0000      )
:       12s(   −2.0000      ,         1.0000        ,       0.0000      ,
                423.00      ,        500.00   10+ 3,        1.0000      ,
                1.0000      )
:       13s(   −2.0000      ,         0.0000        ,       0.0000
                423.22      ,        500.00   10+ 3,        1.0000      ,
                1.0000      )
:       14s(   −2.0000      ,         1.0000        ,      −262.25   10+ 6,
                423.22      ,        500.00   10+ 3,        0.0000      ,
                1.0000      )
:       23s(   −2.0000      ,        677.29   10− 3,      −152.32    10+ 6,
                423.00      ,        500.00   10+ 3,        1.0000      ,
                1.0000      )
:       11b(    0.0000      ,        888.60   10− 3,        0.0000      ,
                0.0000      ,         0.0000        ,       0.0000      ,
                0.0000      )
+
end Simulation of butane isomerization, optimized
```

Table P.7.1 (3)

Isomerization of butane with controlled product quality and optimization. Optimization with one variable, quality control with the Newton–Raphson method

Serial number of optimizing step	Number of Newton-Raphson steps	Catalyst stream into the first reactor	Mole fraction of i-butane in the first reactor	Catalyst stream into the second reactor	Conversion in the second reactor	Mole fraction of i-butane in the second reactor	Value of the objective function	Mole fraction of i-butane in the product
		× 10³	8e2s	× 10³	2e11b	8e6s	× 10³	8e8s
1.	12	90	0.437	3423	945	0.894	3513	0.93997
2.	11	120	0.503	2363	936	0.879	2483	0.939
3.	10	150	0.554	1858	925	0.865	2008	0.940
4.	6	180	0.593	1554	920	0.852	1734	0.940
5.	5	210	0.625	1324	912	0.839	1534	0.939
6.	5	240	0.652	1191	905	0.827	1431	0.939
7.	4	270	0.674	1061	899	0.816	1331	0.940
8.	4	300	0.692	965	892	0.805	1265	0.940
9.	4	330	0.708	885	885	0.794	1215	0.940
10.	4	360	0.722	819	879	0.784	1179	0.940
11.	4	390	0.735	763	872	0.774	1153	0.940
12.	3	390	0.735	761	872	0.773	1151	0.93999

Table P.7.1 (4)

Isomerization of butane with controlled product quality and optimization. Optimization with two variables and one external variable

Serial number of optimizing step	Catalyst stream into the first reactor	Mole fraction of i- butane in the first reactor	Catalyst stream into the second reactor	Mole fraction of i-butane in the se cond reactor	Value of the objective function	Mole fraction of i-butane in the product
	$\times 10^3$	8e2s	$\times 10^3$	8e6s	$\times 10^3$	8e8s
1.	90	0.532	1000	0.837	1090	0.907
2.	190	0.605	1000	0.823	1190	0.930
3.	140	0.538	1086	0.836	1226	0.924
4.	240	0.652	1086	0.822	1326	0.938
5.	290	0.686	1000	0.809	1290	0.940
6.	340	0.713	1086	0.808	1425	0.945
7.	390	0.735	1000	0.795	1390	0.945
8.	340	0.713	913	0.795	1253	0.941
9.	240	0.652	913	0.809	1153	0.933
10.	440	0.752	913	0.782	1353	0.946
11.	376	0.730	913	0.790	1289	0.943
12.	358	0.722	945	0.795	1303	0.943
13.	340	0.713	913	0.795	1253	0.941

CHAPTER 8

ORGANIZING PROGRAM

The reader now possesses a conception, based on the previous chapters, of how to produce from the process flow-sheet, by analyzing, simplifying and elaborating all the stream-, equipment- and network-characteristics of a complex operation, the operation-order flow-sheet. This flow-sheet shows, how the flow-sheet program and the input data system which determine the functioning of the computer should be written. We have discussed these questions from the user's point of view and no mention has been made about the internal organization and management of the computation.

The computation is governed by an organizing program, which processes the flow-sheet program and the input data system.

When developing the SIMUL system, we aimed at achieving a computer-independent system. Of the characteristics of the available computer, almost always the auxiliary store with medium access time was sufficient to store the input data and the calculated results. Of course, we had to comply with the bounds of the given computer.

In order to judge the structure of the organizing program, we should describe briefly the characteristics of the available computer.

8.1 THE COMPUTER

The system has been developed on the GIER computer. Its efficiency is only medium, or even considered rather small nowadays. It was developed for general use, its cycle time is 6.6 μs, possesses a floating-point arithmetic (the computer time needed to carry out the basic operations is between 29 and 267 μs), the direct-access ferrite store has a capacity of 1 K words. The word length is 42 bit.

The auxiliary stores are the following:

1	supplementary ferrite store, (4 K words)
2	drum stores (capacity of each 12 800 words, transfer speed 20 ms/40 words),
1	disk store (capacity 2000×600 words, transfer speed 30–150 ms/600 words),
1	magnetic tape store.

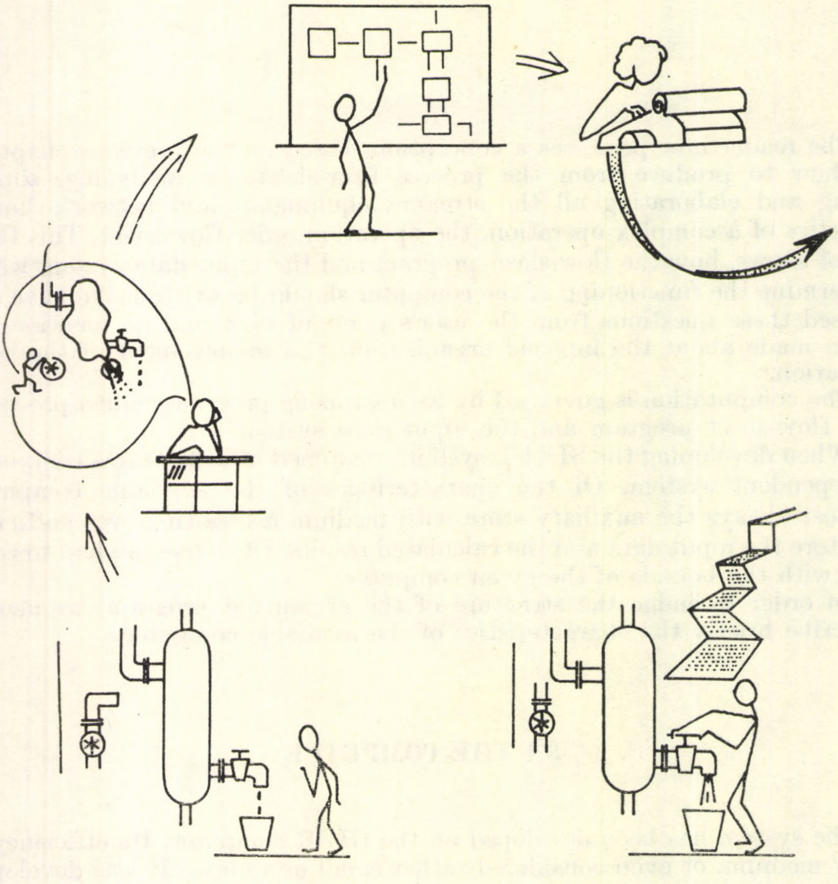


Fig. 8.1. Functioning of the SIMUL system

The input and output peripheral equipment consists of the following:

1 paper tape reader (speed 2000 signals/s)
1 tape puncher (speed 150 signals/s)
1 alphanumerical printer (number of positions: 160, speed 12 lines/s)
1 consol typewriter (speed 12 lines/s).

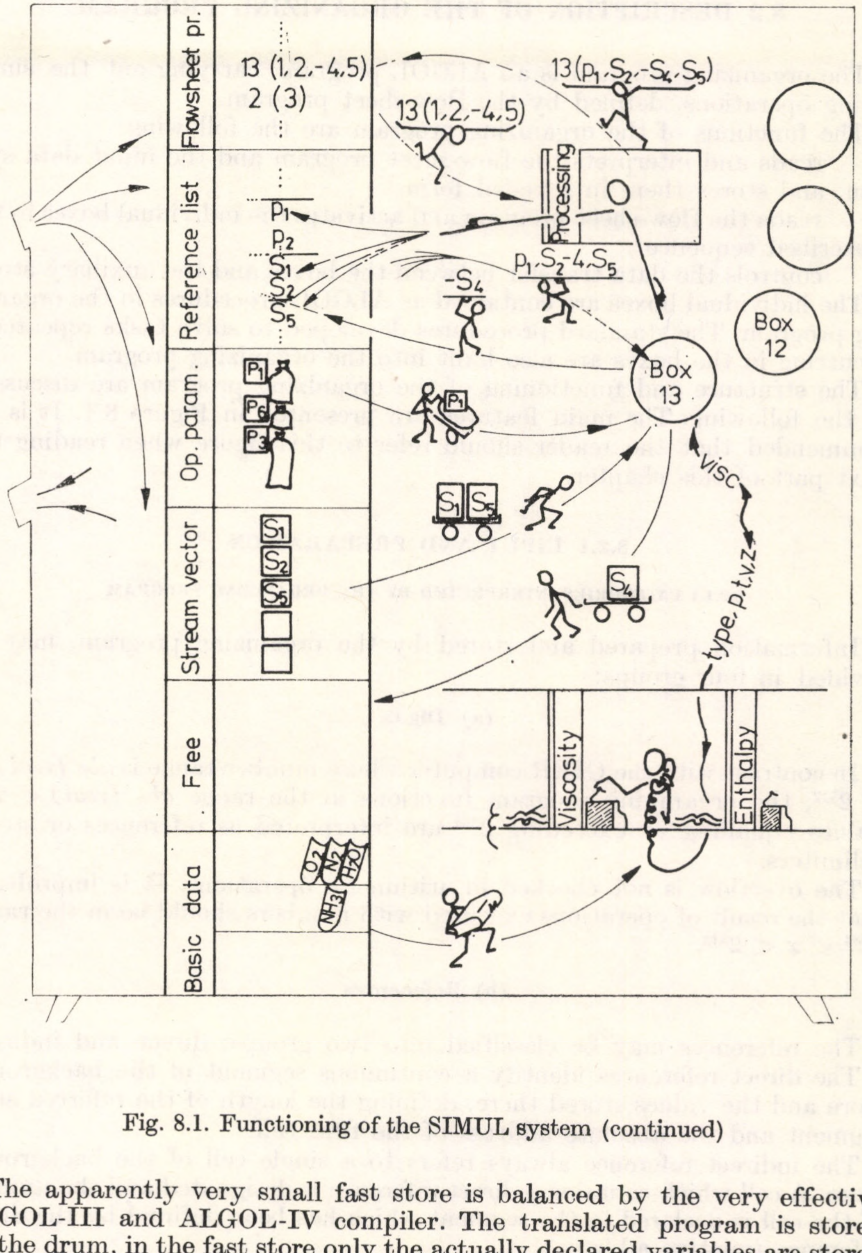


Fig. 8.1. Functioning of the SIMUL system (continued)

The apparently very small fast store is balanced by the very effective ALGOL-III and ALGOL-IV compiler. The translated program is stored on the drum, in the fast store only the actually declared variables are stored (when using the ALGOL-IV compiler only the scalar variables), and some part of the running program is stored (Naur, 1965).

8.2 DESCRIPTION OF THE ORGANIZING PROGRAM

The organizing program is an ALGOL program, carrying out the simulating operations, defined by the flow-sheet program.

The functions of the organizing program are the following:

– reads and interprets the flow-sheet program and the input data system, and stores them in a coded form,

– reads the flow-sheet program and activates the individual boxes in the prescribed sequence,

– controls the data transfer between the boxes and the auxiliary store.

The individual boxes are contained as ALGOL procedures in the organizing program. The standard procedures developed to solve tasks repeatedly occurring in the boxes are also built into the organizing program.

The structure and functioning of the organizing program are discussed in the following. The main features are presented in Figure 8.1. It is recommended that the reader should refer to this figure when reading the next part of this chapter.

8.2.1 INPUT AND PREPARATION

8.2.1.1 CATEGORIES INTERPRETED BY THE ORGANIZING PROGRAM

Information prepared and stored by the organizing program, may be divided in four groups:

(a) Digits

In contrast with the GIER computer whose number range is *abs (real)* $<$ $< 2^{512}$, the organizing program functions in the range *abs (real)* $< 2^{384}$. Values equalling or exceeding 2^{384} are interpreted as references or stored delimiters.

The overflow is not checked in arithmetic operations. It is improbable that the result of operations executed with numbers should be in the range $2^{384} < x < 2^{512}$.

(b) References

The references may be classified into two groups: direct and indirect.

The direct references identify a continuous segment of the background store and the values stored there, defining the length of the referred store segment and the absolute address of the first cell.

The indirect reference always refers to a single cell of the background store. A cell which contains a direct reference is designated and the number of the cell is declared in the segment which has been defined by the direct reference (relative address).

The references are represented by a single real number, which is the product of a positive integer and 2^{384}. (In the case of references, the sign is used for designating other information.)

The value of the multiplicator factor in the references has been chosen according to following considerations:

— To avoid rounding errors, integer powers of 2 have been used, since then the multiplication only modifies the exponent,

— In the binary notation of the multiplier, the form of the exponent is 110 000 000, and therefore the extra bits may be used for other purposes.

When representing the references in this manner, we intended to make full use of ALGOL. Other solutions based on special features of another computer may often prove more suitable.

We may have access to the information contained in the references by standard procedures. Procedure *address (ref)* supplies the address, *size (ref)* the size, *type (ref)* the type of a reference. Procedure *ref (type, size, address)* is used to produce references.

The search for a referred value is carried out by procedure *from ref (ref)*.

(c) Stored delimiters

From the structure of references — not detailed here — it follows that the range

$$abs\ (r) > 10\,000 \times 2^{384}$$

is provided for the numerical value of the reference r. To encode the so-called stored delimiters, the following range

$$2^{384} < t < 256 \times 2^{384}$$

is used (see, Section 5.2.1).

The organizing program stores in this manner, e.g., the operation symbols of the arithmetic expressions, specified in the input data system, as the numerical value of the given character multiplied by 2^{384}. This can also be utilized to designate the coherent data groups figuring in boxes and their operating parameters (see, e.g., box *print)*.

(d) Texts

The organizing program reads only texts relating to the verbal definition of the task in its actual state. The output of the results with an accompanying text requires a separate program.

8.2.1.2 DATA STORAGE

The flow-sheet program, the input data and calculated data are stored in the background store. The fast store contains only the data of the box just processed. The storage capacity therefore does not limit the number of simulating operations (boxes).

The actual values of quantities required to control the computation are also stored in the background store. The computation can therefore be interrupted after each simulating operation (box), as all information necessary

to continue the computation is available in the background store. The stored data may be divided into four groups:
— physical property values of the components in the stream types, defined in the flow-sheet program;
— records of the individual simulating operations contained in the flow-sheet program;
— operating parameters;
— the input and calculated stream vectors.

All data groups consist of records, corresponding to the individual stream types, operations, boxes and stream vectors. The records are not stored in tabulated form, because their length is different and no restriction on the identifying index of the records need to be made. The records in each data group are stored in the sequence of their input and their calculation in subsequent rows. The place and the number of elements of each record is denoted by a reference: these references are collected and stored together. The segment of the auxiliary store which stores the references to the stream-type declarations and simulates operations, parameter vectors of the boxes and the stream vectors is termed the reference index.

In the reference index, the references are contained in the sequence of the identifying index of the records.

8.2.1.3 PROCESSING OF THE FLOW-SHEET PROGRAM AND THE INPUT DATA SYSTEM

After the input of the flow-sheet program and the input data system, a syntactic check is carried out by the organizing program. At the same time, the direct references to the records are written into the reference index.

(a) The organizing program first reads the stream-type definitions. Based on the component codes, the basic property data of the components of the defined stream type are read from the basic matrix. The basic data of the individual components are stored in the background store in the sequence of the components in the stream type. As the organizing program searches for the basic data in the basic matrix of each component, it also signals if any should be missing. If the missing data are not required during the calculation, then the computation may still be carried out. If the basic matrix does not contain one of the components, then the organizing program prints an error message.

(b) After processing the data groups defining the stream types, the data groups of the simulating operations contained in the flow-sheet program are read into the background store. After that, as almost a second translation, the following function is carried out by the organizing program:

(ba) Based on the largest operating index and connection index, the size of the reference index, relating to the operating parameters and stream vectors is determined and these segments are filled up with 10×2^{384} numbers. By considering these, the organizing program later decides whether or not an operating parameter group and a stream vector have been defined. These values cannot be obtained by any other operation.

(bb) Before each operational declaration contained in the flow-sheet program, and directly preceding the box index, the reference to the record of the next operation is placed. The operations are normally processed in the sequence of their description. The exception is the last operation of a cycle, which is followed by the cycle-controlling operation (see, Section 5.2.1).

(bc) If a cycle-controlling operation is necessary, then a further reference has to be inserted two places before the box index. This determines the operation following the cycle.

(c) The organizing program reads the input data system without a specific statement. The characters of the input data system (number sequence statements, references) are interpreted and the related data groups are defined. There is no check during input on the number and content of the data. Such checking is the task of the boxes.

8.2.2 PROCESSING

Processing of the flow-sheet program starts after the input of the input data system. The organizing program hereby carries out the following operations in cycles:

(a) Based on the reference of the following operation, the declaration of the actual operation is called from the background store. The reference of the next operation is sent to the fast store.

(b) If the simulating operation is carried out the first time, then the operating and connection indices are replaced by references. These references relate — if the given record is already defined (operating parameter vector or stream vector) — directly to the records, otherwise to those places of the reference index where the references of the records will be found later.

(c) After the preparatory stage described above under (a) and (b), the organizing program jumps to a label determined by the box index, where the procedure representing the box is called. Among the actual parameters, the box is supplied with the references of the operating parameters and stream vectors related to the box. Hereupon, the box uses standard data-transfer procedures for the input of the input data and — after completing the computation — the output of the results. The evaluation of the references among the input data and the search for the referred data is carried out by standard input procedures.

(d) At the end of an operation, the change of the declarations is amended in the background store by the organizing program. (Before the first calling of the box at the place of the reference of the stream vectors, only the reference to the reference index appears. After carrying out the operation at this site, the direct reference to the related stream vector is found.)

The bounds of the free part of the background store and the reference to the next operation are transferred by the organizing program after each box call to the background store. This is followed by jumping to the start of the next operation and all operations enumerated from (a) are repeated.

(e) After ending each simulating operation, the organizing program allows the intervention into the flow-sheet program. If the intention to intervene is communicated from the consol, then the input of any simulating operation and a group of operating parameters (corresponding to the rules of syntax) is possible. This simulating operation is carried out as if it were the next operation on the flow-sheet program. Afterwards the computation proceeds according to the flow-sheet program.

The intervention may also be used to interrupt the computation.

8.2.3 BOX ASSORTMENT

The equipment and organizing boxes are introduced into the organizing program — after they are developed independently from the other boxes and from the organizing program itself — and they represent the assortment of elementary operations available to the user.

8.3 ORGANIZING PROGRAM VARIANTS SIMUL-1 AND SIMUL-2

The organizing program has been developed initially in GIER-ALGOL-III language. After the access of a new compiler, it was rewritten in GIER-ALGOL-IV. The SIMUL-1 program, written in GIER-ALGOL-III, is closer to the reference language ALGOL-60. The SIMUL-2 program, written in GIER-ALGOL-IV, is more suited to the given computer.

The SIMUL–2 organizing program contains a diagnostic program, which offers the possibility of printing the actual content of the related cells of the background store after each simulating operation.

Selection of SIMUL–1 or SIMUL–2 is the user's choice. The computation is carried out by either, using the same data system.

CHAPTER 9

FLOW-SHEETING

Simulation of the gas-separating section of a naphtha cracker. We intend to simulate the gas-separating section of a naphtha cracker characterized by furnace cracking and low-temperature gas separation. The pyrolysis gas is compressed and purified in the separating section followed by partial liquefaction at low temperature and separation by distillation to ethylene, ethane, hydrogen-methane and C_{3+} fractions.

9.1 SHORT PROCESS DESCRIPTION OF THE GAS-SEPARATION UNIT

The simplified flow-sheet is presented in Figure 9.1. After separating the heavy residues formed in the cracking process, the gas enters the buffer container G1 at ambient temperature and atmospheric pressure. Here the gas streams from separators G2 and G19 are admixed. The piston compressor increases the pressure of the gas in two stages to 7×10^5 N/m^2. The gas is cooled after each stage by after-coolers G7 and G16. The liquid, condensed during the cooling of the gas, is separated in separators G8 and G17. The condensate leaving separators G8 and G17 through level-controller valves expands and separates to gaseous and liquid phases in separators G2 and G19 respectively. The gaseous phase is recycled to G1. The liquid phase is the pyrolysis naphtha. The separation of pentane and higher hydrocarbons from the gas leaving the separator G17 is effected in the plate column G21 by oil wash.

The gas leaving the column G21 is mixed in container G36 with the gas from separator G18, then it enters the two-stage compressor G39, where its pressure is increased to 40×10^5 N/m^2. The gas is cooled in after-coolers G40 and G49, the condensate and gas separates in separators G41 and G50. The condensate leaves through level-controller valves to separator G18, where its expansion takes place. The gas is recycled to G36, the liquid phase consists mainly of C_4 hydrocarbons. (The gas is desulphurized, freed from acetylene and dried at 40×10^5 N/m^2 pressure. Since these operations are not to be simulated, they were not included in the simplified process flow-sheet. Similarly we have omitted the wash-oil regeneration, the cooling cycles, and the condensers and reboilers of the rectifying columns.)

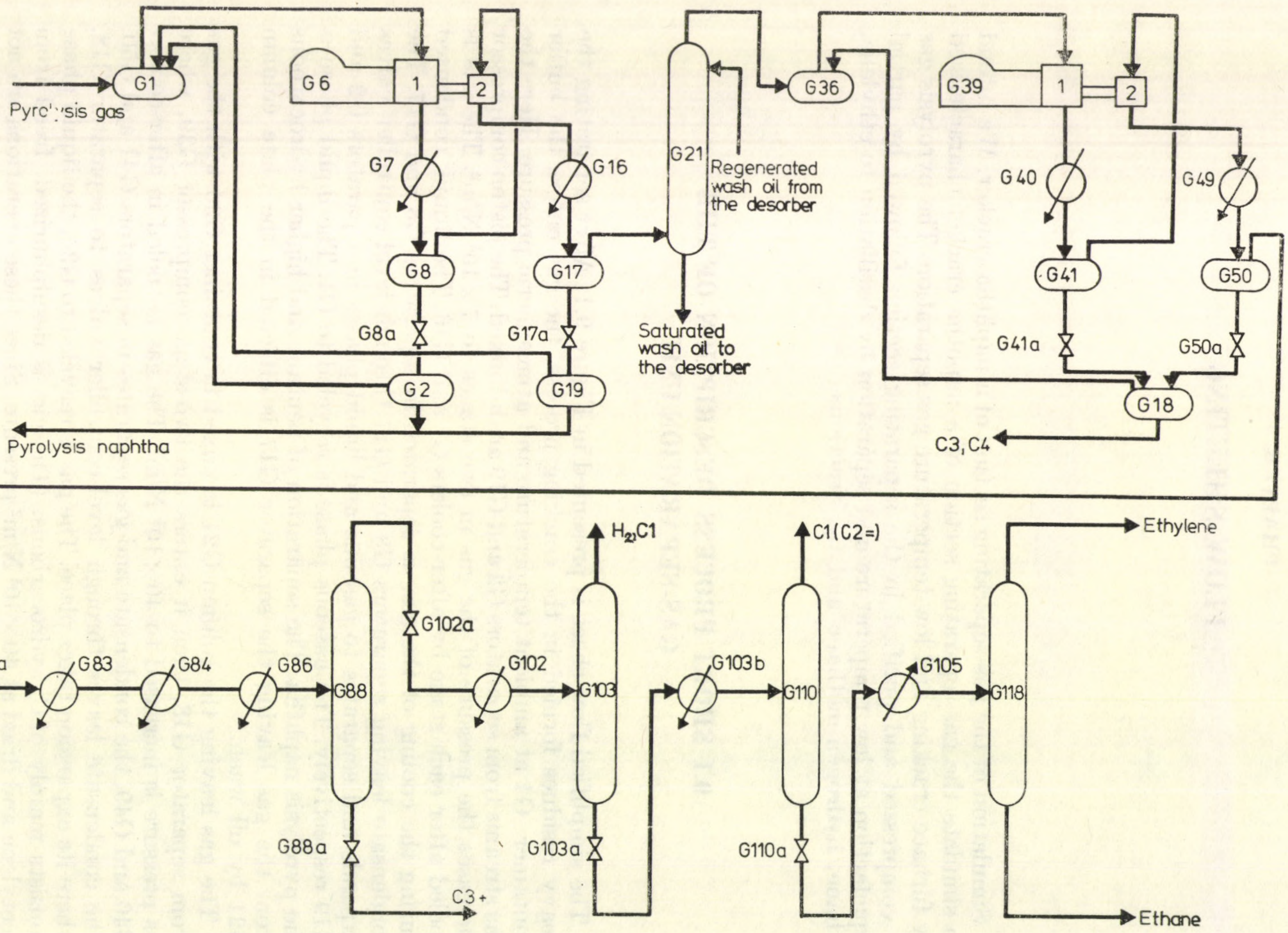


Fig. 9.1. Simplified process flow-sheet of the gas separation of a naphta cracker

The dried gas is cooled in heat exchangers G83, G84 and G86 to 253 K at 40×10^5 N/m^2 pressure, then it enters the rectifying column G88 in a partly condensed state. The bottom product of this column consists of C_{3+} hydrocarbons. The gaseous top product is partly condensed in heat exchanger G102, before entering the rectifying column G103. The top product of this column consists of hydrogen and methane, the bottom product contains ethylene, ethane and methane contamination. This is fed into the rectifying column G110 through heat exchanger G103 b in order to remove the methane contamination. The top product of column G110 consists of methane, containing a small amount of ethylene, the bottom product is the ethane-ethylene fraction. This bottom product is totally evaporated in heat exchanger G105 and in this state it enters the rectifying column G118. The distillate is ethylene (product), and the bottom product is ethane.

9.2 AIM OF THE SIMULATION

The aim is flow-sheeting, i.e., to quantify the flow-sheet presented in Figure 9.1. This means that knowing the main dimensions of the equipment, we intend to characterize the output streams of the equipment with adequate stream vector.

9.3 INITIAL DATA FOR THE FLOW-SHEETING

Entering mass streams

Pyrolysis gas

mass velocity	0.0695 kmole/s
temperature	293 K
pressure	1.1×10^5 N/m^2
composition	kmole/kmole
hydrogen	0.1715
methane	0.3635
ethylene	0.2765
ethane	0.0494
propylene	0.0618
propane	0.0030
butadiene	0.0306
1-pentene	0.0209
benzene	0.0162
toluene	0.0048
styrene	0.0008
methyl-styrene	0.0010

Wash oil

mass velocity	0.0150 kmole/s
temperature	293 K
pressure	7×10^5 N/m^2
composition	kmole/kmole
n-hexadecane	1.000

Characteristics of the equipment

Compressor G6
two-stage piston compressor, with covling after each stage. Intake pressure 1.1×10^5 N/m^2, pressure after the first stage 2.6×10^5 N/m^2, after the second stage 7×10^5 N/m^2.

Compressor G39
two-stage piston compressor, with cooling after each stage. Intake pressure 7×10^5 N/m^2, pressure after the first stage 17×10^5 N/m^2, pressure after the second stage 40×10^5 N/m^2.

Wash tower G21
plate column, number of plates: 39. The gas enters at the bottom, the wash oil at the top.

Rectifying columns
with bubble-cap plates. Characteristics of the columns are presented in Table 9.1.

Table 9.1

Characteristics of the distillation columns

Position number of column	Number of plates	Serial number of feed plate (from the top)	Condensation	Reboiling
G88	49	27	partial	partial
G103	30	13	partial	partial
G110	15	5	partial	partial
G118	79	41	partial	total

Heat exchangers
are tube-bundle exchangers. We suppose that their heat-transfer area is sufficient. The geometric data are not required.

Separators
their geometric data are not required, as the separation is near to thermodynamic equilibrium.

Pipelines
the pressure drop in the pipelines is negligible.

Process conditions, controlled parameters

Temperature of the gas leaving heat exchangers G7, G16, G40 and G49 is 293 K.

The controlled parameters of the distilling columns are presented in Table 9.2.

Table 9.2

Controlled parameters of the distillation columns

Position number of column	Controlled parameter		Prescribed for input stream	
		value	Temperature K	Pressure N/m^2
G88	reflux ratio	1.0	253	32×10^5
G103	reflux ratio	1.3	231	30×10^5
G110	reflux ratio	55.0	257	26×10^5
G118	reflux ratio	2.2	saturated vapour	2×10^5

The prescribed value of the top-product quantity in column G110 is 0.00005 kmole/s.

Prescribed pressure of the C_{3+} fraction entering the propylene separating section is 17×10^5 N/m^2.

9.4 MODELLING OF GAS SEPARATION, CHOICE OF BOXES

Figure 9.2 shows the block diagram of the gas-separating section, based on the simplified process flow-sheet. As the first step in modelling, we have to determine which boxes are suitable for simulating each unit operation and/or equipment, taking into account the available box assortment.

We have written in the rectangles of the block diagram the positional number of that equipment to be simulated with the box also denoted in the rectangle. Numbers identifying the box also appear in the upper left corner of the rectangles — these are to be used later as operating indices.

Since three mass streams have to be mixed in container G1, we need two boxes *mixing* (1,2) for the modelling. Compressor G6 is modelled as two one-stage compressors (4,7). To model heat exchanger G7 and separator G8 after the first stage, and heat exchanger G16 and separator G17 after the second stage, one box *vlexpa* for each complex equipment (5,8) is suitable. Boxes *vlexpa* (6,9) are again used for simultaneous modelling of expansion G8a and separator G2, and of G17a and G19. The liquid phase of separators G2 and G19 leave in a common pipe — their mixing is modelled by box *mixing* (16). Box *abs1* (10) is suitable for modelling the oil wash.

Mixing of the purified gas and the recycle stream (G36) is simulated by box *mixing* (11). The functioning of the two-stage compressor is simulated in this case by one box *compr1* (12). This includes the calculation of the after-coolers (G40, G49) and also the separation of the gaseous and liquid phase (G41, G50). Separator G18 and the expansions G41a and G50a are simultaneously simulated by a single box *vlexpa* (13).

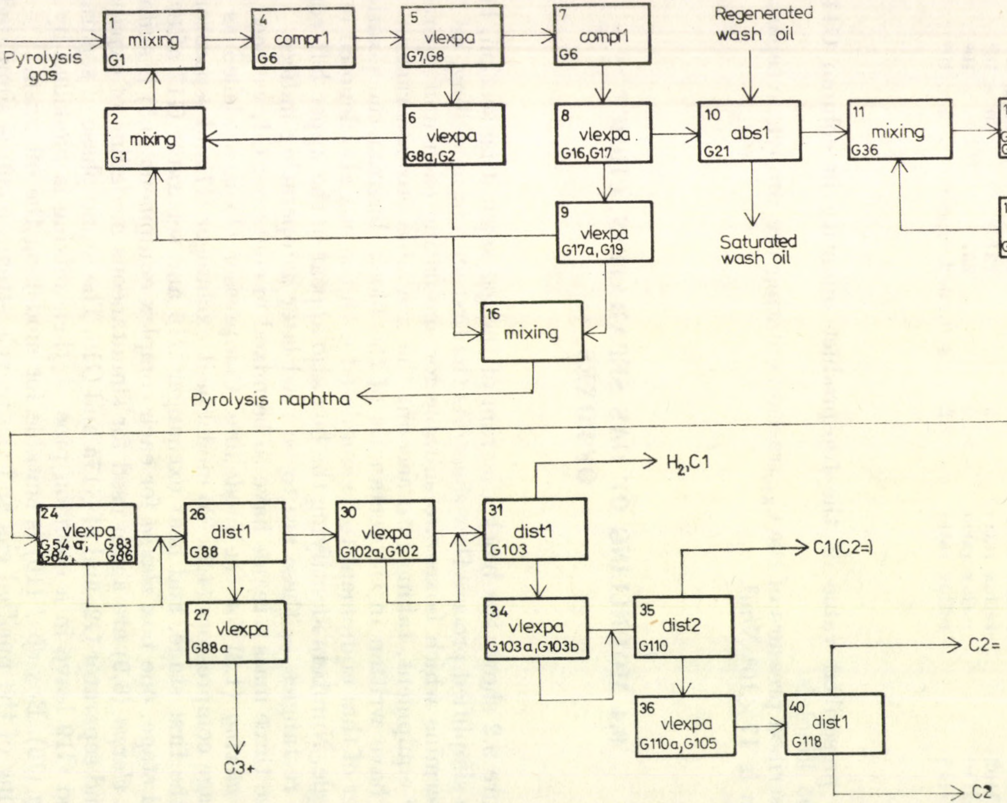


Fig. 9.2. Block diagram of the gas separation

The pressure of the gas leaving separator G50 is set by valve G54a, its temperature is by heat exchangers G83, G84 and G86. These are again simultaneously simulated by box *vlexpa* (24).

Distillation columns G88, G103 and G118 are simulated by box *dist1* (26, 31, 40), but distillation G110 with box *dist2* (35) in order to demonstrate its use. Box *vlexpa* (30, 34, 36) is used to simulate the expansion of the bottom products (G103a, G110a), the feed heat exchangers (G103b, G105) and the expansion and cooling of the top product of column G88.

There are two recycles in the process, around compressors G6 and G39.

9.5 DESIGNATION OF STREAM TYPES

Table 9.3

Distribution of chemical components in the process

Component codes	Operating indices																					
	1	4	5	6	7	8	9	2	16	10	11	12	13	24	26	30	31	27	34	35	36	40
67	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×					
1	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×		×	×		
26	×	×	×	×	×	×	×	×	×		×	×	×	×	×	×	×	×	×	×	×	×
2	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
27	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
3	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×			×				
48	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×			×				
29	×	×	×	×	×	×	×	×	×	×												
55	×	×	×	×	×	×	×	×	×	×												
56	×	×	×	×	×	×	×	×	×	×												
76	×	×	×	×	×	×	×	×	×													
63	×	×	×	×	×	×	×	×	×													
13										×												

Table 9.4

Stream types declared in the process

Stream type code	Component code	Operating indices of boxes using this type
1	67,1,26,2,27,3,48,29,55,56,76,63	1,4,5,6,7,8,9,2,16
2	67,1,26,2,27,3,48,29,55,56,13	10
3	67,1,26,2,27,3,48	11,12,13,24,26
4	67,1,26,2,27	30,31
5	26,2,27,3,48	27
8	1,26,2,27	34,35
6	26,2,27	36,40

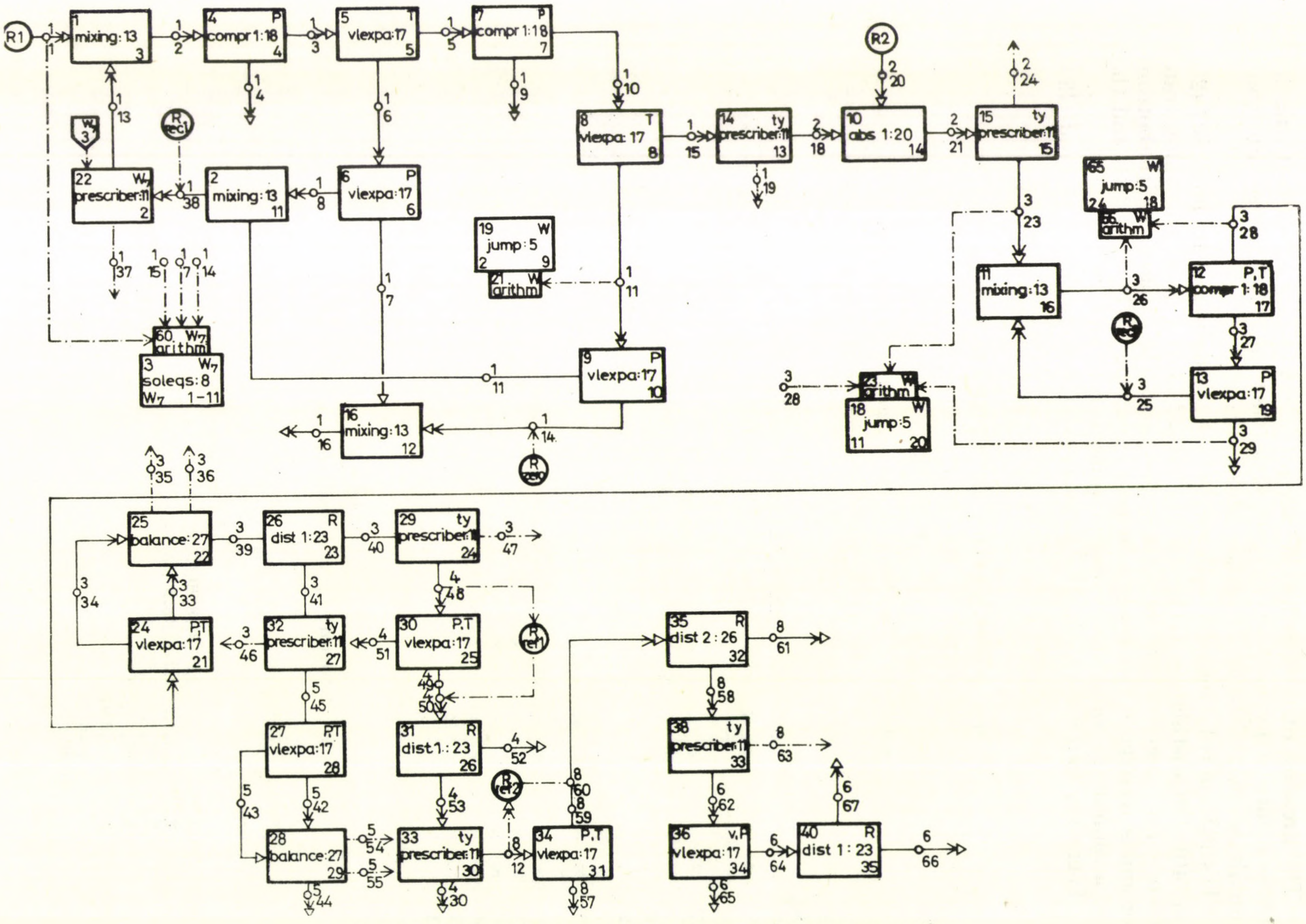


Fig. 9.3. Operation-order flow-sheet of the gas separation

Columns of Table 9.3 represent the operating indices of the boxes, identified in Figure 9.2. The rows are the chemical components. In a given position of the matrix, the sign × means that the mole fraction of the given chemical component in that box is probably not zero. It is evident from the table that it is suitable to declare several stream types. The stream types demonstrated in Table 9.4 were declared when solving the problem.

9.6 OPERATION-ORDER FLOW-SHEET

The operation-order flow-sheet developed from the block diagram (Fig. 9.2) of the gas separation is demonstrated in Figure 9.3. The two figures only differ in that Figure 9.3 also contains information necessary to simulate the process. In order to facilitate the comparison of the block diagram and the operation-order flow-sheet, the numbers used in Figure 9.2 have been chosen to be the operating indices of the boxes. Preparation of the operation-order flow-sheet and its system of denotation has been discussed in Chapter 5.3; here we shall just consider some particular details.

From the technological description (Chapter 9.1), it is evident that the process starts with the recycle loop around compressors G6a and G6b, modelled by

compr1: 18(4,2, −3, −4) and

compr1: 18(7,5, −10, −9),

which unite streams from two branches. It is therefore expedient after joining, i.e.,

mixing: 13 (2, 8, 11, −38)

to tear up the recycle stream at the position whose connection index is 38.

This tearing has three consequences:

1. the input stream 38s has to be provided for,
2. we have to provide a box which organizes the iteration,
3. care has to be taken to carry out the instructions of the box, organizing the iteration in each iteration step.

In fulfillment of requirement (a), the estimated initial values of stream 38s

recycle 1:38 (−1, $0.1_{10^{-3}}$, 0.293, 16, $1.1_{10^{5}}$, 1, 0.05, 0.05, 0.3, 0.05, 0.2, 0.01, 0.2, 0.1, 0.03, 0.003, 0.003, 0.004)

must figure among the streams.

This stream vector is overridden by the output stream vector of *mixing:* 13(2, 8, 11, −38) after each iteration. Requirement (b) is fulfilled by introducing as the first operation of the flow-sheet program box

soleqs: 8(3).

The independent variable of the non-linear equation resulting from the recycle is the butadiene component stream of the recycle stream, the dependent variable is the deficit of the butadiene component stream in the recycle loop. The iteration continues as long as this deficit stays below 1% of the butadiene component stream entering the recycle. This is expressed in the following manner:

arithm: 60 (2e15s, 13e15s>×, 2e7s, 13e7s>×, 2e14s, 13e14s>×, >+>+>2e1s, 13e1s>×>/)

The actual substitution value of this arithmetic expression is the 14th operating parameter vector of box *soleqs*. The operating parameter vector of box *soleqs* is therefore the following:

soleqs: 3 (1.1, 10, 3×0, 1e22b, 0.13, 0, 1, 0.005, 0, 10^{-3}, 60b, 1, 0, 10^{-2}, 0)

Requirement (c) is fulfilled by box

prescriber: 11 (22, 38, −13, −37)

carrying out the modification by box *soleqs* on stream 38s and hereby a new iteration cycle starts.

The second recycle may be found from

comprl: 18 (12, 26, −28, −27)

The tearing is effected at the position with connection index 25 and the calculation is carried out with box

jump: 5 (65)

by direct iteration. The recycling mass stream is the independent variable of the non-linear equation. The dependent variable, the deficit of the mass stream, is calculated by

arithm: 66 (2e26s, 2e28s >−, 10^{-6} >−)

Attention should be drawn to the fact that box *vlexpa* does not function if the value of the input stream is zero, which may happen in the first step of any iteration cycle. In the first recycle previously discussed, for example, the 11s output stream of

vlexpa, G16, G17: 17 (8, 10, −15, −11)

or the 27s output stream of the second recycle

comprl: 18 (12, 26, −28, −27)

may be zero when starting the calculation.

The result would be that in the first loop

vlexpa: 17 (9, 11, −11, −14)

and/or in the second loop

vlexpa: 17 (13, 27, −25, −29)

would become ineffective and the calculation would stop with an error message. To avoid this, we calculate the input stream of *vlexpa* in the first loop with

arithm: 21 (10^{-8}, 2e11s >−)

and in the second with *arithm:* 66, discussed previously.

If it is smaller than 10^{-8}, then

jump: 5(18)

and

jump: 5 (65), respectively,

take care of the continuation of the calculation by passing box *vlexpa*. However, in this case 14s would be undefined in the first loop and this again would hinder the functioning of box

mixing: 13 (16, 14, 7, −16)

since this box stops with an error message if the input stream is zero. A trick may be used here to overcome this difficulty. We include among the input mass streams, the stream vector of the mass stream R_{zero}: 14s, containing values declared zero, thus rendering the continuous calculation of the first loop possible.

The second part of the operation-order flow-sheet contains box

dist1: 23 (26, 39, −40, −41).

The input 39s stream of this box may be mixed-phase in principle, the temperature and pressure of which are set by box

vlexpa: 17 (24, 28, −34, −33.)

At the same time, it divides the input stream into two homogeneous streams which have to be mixed before entering one mixed-phase stream. This is accomplished by box

balance: 27 (25, 33, 34, −39, −35, −36).

Such difficulties may be overcome in another way: we may, e.g. define the input stream of

dist1: 23 (31, 50, −52, −53)

among the input streams. The vector elements of stream refl cannot be chosen arbitrarily. The mole stream and the mole fractions are equal to the corresponding elements of 48s. The corresponding elements of 49s figure in place of the temperature and pressure, and in place of the enthalpy stream the sum of the two exit enthalpy streams of box *vlexpa* must figure. This calculated from arithmetic expression

enthalpy: 61(3e49s, 3e51s > +).

Therefore

Refl: 50 (4,2e48s, 61b, 4e49s, 5e49s, 0.5, 7e48s, 8e48s, 9e48s, 10e48s, 11e48s).

We may similarly define the input stream 60s of box *dist2*.

9.7 THE FLOW-SHEET PROGRAM

Writing the operations in the flow-sheet program does not present any difficulty based on the operation-order flow-sheet and the related general and specific information. The operating parameters of the boxes and the input streams may be stated using the data enumerated in Chapter 9.3.

The flow-sheet program of the gas-separating section is presented in Table 9.5.

Table 9.5

Flow-sheet program and input data system of the gas separation of problem [Ethylene plant, Var. 5.]

```
[Ethylene plant, Var.5.]
1976
stream types
pyrolysis gas 1                   : 1(67,1,26,2,27,3,48,29,55,56,76,63)
pyrolysis gas 2                   : 3(67,1,26,2,27,3,48)
oil                               : 2(67,1,26,2,27,3,48,29,55,56,13)
pyrolysis gas 3                   : 4(67,1,26,2,27)
pyrolysis gas 4                   : 5(26,2,27,3,48)
```

Table 9.5 (cont.)

```
C1C2C3                                  : 8(1,26,2,27)
C2                                      : 6(26,2,27)
+
operations
 1 soleqs                               : 8(3)
∧
 2 prescriber                           :11(22,38,−13,−37)
 3 mixing, G1                           :13(1,1,13,−2)
 4 compr1, G6a                          :18(4,2,−3,−4)
 5 vlexpa, G7,G8                        :17(5,3,−5,−6)
 6 vlexpa, G8a,G2                       :17(6.6,−8,−7)
 7 compr1, G6b                          :18(7,5,−10,−9)
 8 vlexpa, G16,G17                      :17(8,10,−15,−11)
 9 jump                                 : 5(19)
10 vlexpa, G19a,G19                     :17(9,11,−11,−14)
11 mixing, G1                           :13(2,8,11,−38)
∨
12 mixing                               :13(16,14,7,−16)
13 prescriber                           :11(14,15,−18,−19)
14 absorber, G21                        :20(10,20,18,−22,−21)
15 prescriber                           :11(15,21,−23,−24)
16 mixing, G36                          :13(11,25,23,−26)
17 compr1, G39,G40,G41,G49,G50          :18(12,26,−28,−27)
18 jump                                 : 5(65)
19 vlexpa, G41a,G50a,G18                :17(13,27,−25,−29)
20 jump                                 : 5(18)
21 vlexpa, G54a,G83,G84,G86             :17(24,28,−34,−33)
22 balance                              :27(25,33,34,−39,−35,−36)
23 dist1, G88                           :23(26,39,−40,−41)
24 prescriber                           :11(29,40,−48,−47)
25 vlexpa, G102a,G102                   :17(30,48,−49,−51)
26 dist1, G103                          :23(31,50,−52,−53)
27 prescriber                           :11(32,41,−45,−46)
28 vlexpa, G88a                         :17(27,45,−43,−42)
29 balance                              :27(28,42,43,−44,−54,−55)
30 prescriber                           :11(33,53,−12,−30)
31 vlexpa, G103a,G103b                  :17(34,12,−57,−59)
32 dist2,G110                           :26(35,60,−61,−58)
33 prescriber                           :11(38,58,−62,−63)
34 vlexpa, G110a,G105                   :17(36,62,−64,−65)
35 dist1,G118                           :23(40,64,−67,−66)
36 print                                : 2(70)
37 stop                                 : 4(99)
+
data set no                             :76
operational parameters of boxes
soleqs                                  : 3(1,1,10,3×10,1a22b,0.13,0,1,0.005,0.⏨−3,
                                            60b,1,0,⏨−2,0)
arithm                                  :60(2e15s,13e15s > ×, < 2e7s,13e7s >×,
                                             < 2e14s,13e14s >× > + > +,
                                             < 2e1s,13e1s >× > /)
prescriber                              :22(0,013)
mixing                                  : 1(0.1⏨5)
mixing                                  : 2(0.⏨15)
compr1                                  : 4(1,2.6⏨5,9×0.00,0,1,0,0.8,7×0)
vlexpa                                  : 5(2,293,16,1,5e3s,350,250,0)
vlexpa                                  : 6(1,0,1.1⏨5,350.250,0)
compr1                                  : 7(1,7⏨5,9×0,00,0,1,0,0,8,7×0)
```

Table 9.5 (cont.)

```
vlexpa          : 8(2,293,16,1,5e10s,350,250,0)
vlexpa          : 9(1,0,1,1.1₁₀5,350,250,0)
jump            :19(11,1,21b)
arithm          :21(₁₀−8,2e11s > −)
mixing          :16(0.1₁₀5)
prescriber      :14(0002,001)
absorber        :10(0,39,1,0,8,3.245,277,293,0.02216,323,
                     0.00675,0,0,
                     1,  333,1749,273,1565,
                     2,  300,27.00,325,44.00,
                     3,  300,  5.70,325,  9.70,
                     4,  300,  4.70,325,  7.30,
                     5,  300,  1.40,325,  2.70,
                     6,  300,  1.30,325,  2.50,
                     7,  300,  0.38,325,  0.83,
                     8,  300,  0.09,325,  0.26,
                     9,  300,0.018,325,  0.05,
                    10,  300, ₁₀−5,  325, 2₁₀−5,
                    11,  300, ₁₀−10.325, 2₁₀−5)
prescriber      :15(0003,001)
mixing          :11(0.1₁₀5)
compr1          :12(2,40₁₀5,293.16,1,7×0,00,0,1,0.0.8,7×0)
jump            :65(21,−1,66b)
arithm          :66(2e26s,2e28s > −,₁₀−6 > −)
vlexpa          :13(1,0,110₁₀5,7₁₀5,480,350,0,
                      1,261,120,297,150,
                      7,320,0,71,349,1.43)
jump            :18(16,−1,23b)
arithm          :23(2e23s,₁₀−3 > ×,2e23s,2e28s,2e29s
                     > + > − > a > −)
vlexpa          :24(2,253.16,1,32₁₀5,300,250,0,
                     1,200,30,300,80,
                     2,213,1,750,361,7.187,
                     3,213,0.350,361,2.781,
                     4,213,0.194,361,2.188,
                     5,213,0.038,361,1.172,
                     6,213,0.031,361,1.078,
                     7,249,0.033,361,0.563)
balance         :25(0,1)
dist1           :26(49,27,4,5,1,1.2,1,1,0,0,230,370,99.9,99,
                     4×0)
prescriber      :29(0004,001)
vlexpa          :30(2,231.16,1,30₁₀5,250,200,0,
                      1,200,30,300,80,
                      2,153,0.583,273,4.667,
                      3,153,0.033,273,1.233,
                      4,172,0.033,273,0.833,
                      5,211,0.037,273,0.333)
dist1           :31(30,13,2,3,1,2,2,1,1,3,0,150,250,99.9,99.9,
                     4×0)
prescriber      :32(0005,001)
vlexpa          :27(2,350,49₁₀5,17₁₀5,400,300,0,
                     5,317,0,329,385,1.088)
balance         :28(0,49₁₀5)
enth            :61(3e49s,3e51s > +)
prescriber      :33(0008,001)
vlexpa          :34(2,257,52₁₀5,26₁₀5,300,250,0,
                     1,187,48,227,70,
```

Table 9.5 (cont.)

```
                                   2,243.2,3.808,253.2,4.346,
                                   3,243.2,0.865,253.2,1.00,
                                   4,243.2,0.558,253.2,0.654,
                                   5,243.2,0.146,253.2,0.200)
dist2                           :35(15,5,0.05₁₀−3,55,15,0,0,2,₁₀−3,1,257,
                                   253,15×0,257,4×0,4×0,16×0,4×0,
                                   1,243,2,3.808,253,2,4.346,
                                   2,243.2,0.865,253.2,1.00,
                                   3,243,2,0.558,253,2,0.654,
                                   4,243,2,0.146,253,2,0.200)
prescriber                      :38(0006,001)
vlexpa                          :36(3,1,1,2₁₀5,190,185,0,
                                   1,183.2,1.10,203.2,2.60,
                                   2,188.7,0.65,203.2,1.375,
                                   3,227.6,0.575,233.2,0.725)
dist1                           :40(79,41,1,2,1,1,2,2,2,2,0,183,199,99.9,99.9,
                                   3×0,0.70)
enth                            :17(3e57s,3e59s > +)
gi                              :20(2e57s,2e12s >/)
print                           :70(6, < 1 = 3 > s,2e4s, < 5 = 8 > s,
                                   2e9s,10s,11s, < 13 = 16 > s,37s,38s,3b,
                                   13e4b,17e4b,18e4b,20e4b,21e4b,
                                   < 5 = 7 > e < 5 = 6 > b,13e7b,
                                   17e7b,18e7b,20e7b,21e7b, < 5 = 7 >
                                   e < 8 = 9 > b,22b, < 18 = 24 > s,
                                   26s,2e27s,28s,4e10b,13e12b,17e12b,
                                  18e12b,20e12b,21e12b,< 5 = 7 > e
                                   < 13 > b,34s,33s, < 5 = 7 > e
                                   < 24 > b,35s,36s,39s,40s,41s,26b,49s,
                                   51s, < 5 = 7 > e < 30 > b,50s,52s,
                                   53s,31b,45s,43s,42s, < 5 = 7 > e
                                   < 27 > b,44s,12s,57s,59s,< 5 = 7 >
                                   e < 34 > b,60s,61s,58s,54e35b,55e35b,
                                   56e35b, < 62 = 65 > s, < 5 = 7 > e
                                   < 36 > b,67s,66s,40b)
+
streams
pyrolysis gas                   : 1(−0001,69.5₁₀−3,0,293,16,1.1₁₀5,1,
                                   0.1715,0.3635,0.2765,0.0494,0.0618,
                                   0.0030,0.0306,0.0209,0.0162,0.0048,
                                   0.0008,0.0010)
recycle 1                       :38(−0001,0.1₁₀−3,0,293.16,1,1₁₀5,1,
                                   0.05,0.05,0.30,0.05,0.20,0.01.
                                   0.20,0.10,0.03,0.003,0.003,0.004)
zero                            :14(−0001,17×0)
oil                             :20(0002,15₁₀−3,0,293,16,7₁₀5,0,0,0,0,0,0,0,0,
                                   0,0,0,1)
recycle 2                       :25(0003,₁₀−6,0,293.16,7₁₀5,1,0.1,0.1,0.1,0.2.
                                   0.2,0.2,0.1)
ref1                            :50(0004,2e48s,61b,4e49s,5e49s,0.5,
                                   7e48s,8e48s,9e48s,10e48s,11e48s)
ref2                            :60(0008,2e12s,17b,4e59s,5e59s,20b,7e12s,
                                   8e12s,9e12s,10e12s)
+
```

9.8 RESULT OF FLOW-SHEETING

The printed output of the computation is presented in Table 9.6. The data of the main streams are shown in Table 9.7, and the heat load of the heat-transfer units in Table 9.8.

Table 9.6

Calculation results of the gas separation of problem [Ethylene plant, Var. 5.]

```
Ethylene plant, Var. 5. — 76
:          1s(   −1.00000        ,     69.5000  10− 3,      0.00000        ,
                 293.169         ,    110.000   10+ 3,      1.00000        ,
                 171.500   10− 3,     363.500   10− 3,    276.500   10− 3,
                  49.4000  10− 3,      61.8000  10− 3,      3.00000 10− 3,
                  30.6000  10− 3,      20.9000  10− 3,     16.2000  10− 3,
                   4.80000 10− 3,     800.000   10− 6,      1.00000 10− 3)
:          2s(   −1.00000        ,     69.5826  10− 3,    543.991   10+ 3,
                 293.149         ,    110.000   10+ 3,      1.00000        ,
                 171.297   10− 3,     363.148   10− 3,    276.584   10− 3,
                  49.4492  10− 3,      61.9870  10− 3,      3.00989 10− 3,
                  30.7290  10− 3,      20.9806  10− 3,     16.2197  10− 3,
                   4.79801 10− 3,     799.138   10− 6,    998.859   10− 6)
:          3s(   −1.00000        ,     69.5826  10− 3,    701.192   10+ 3,
                 340.666         ,    260.000   10+ 3,      1.00000        ,
                 171.297   10− 3,     363.148   10− 3,    276.584   10− 3,
                  49.4492  10− 3,      61.9870  10− 3,      3.00989 10− 3,
                  30.7290  10− 3,      20.9806  10− 3,     16.2197  10− 3,
                   4.79801 10− 3,     799.138   10− 6,    998.859   10− 6)
:        2e4s(    0.00000        )
:          5s(   −1.00000        ,     69.1405  10− 3,    494.288   10+ 3,
                 293.160         ,    260.000   10+ 3,      1.00000        ,
                 172.392   10− 3,     365.459   10− 3,    278.280   10− 3,
                  49.7434  10− 3,      62.2825  10− 3,      3.02318 10− 3,
                  30.7150  10− 3,      20.6282  10− 3,     14.0253  10− 3,
                   3.05749 10− 3,     222.857   10− 6,    171.022   10− 6)
:          6s(   −1.00000        ,    442.080   10− 6,     32.8933  10+ 3,
                 293.160         ,    260.000   10+ 3,      0.00000        ,
                   1.26904 10− 6,       1.69447 10− 3,     11.3098  10− 3,
                   3.43092 10− 3,      15.7749  10− 3,    932.554   10− 6,
                  32.9279  10− 3,      76.0982  10− 3,    359.418   10− 3,
                 277.013   10− 3,      90.9286  10− 3,    130.471   10− 3)
:          7s(   −1.00000        ,    438.338   10− 6,     32.7483  10+ 3,
                 292.560         ,    110.000   10+ 3,      0.00000        ,
                 463.333   10−12,     316.946   10− 6,      7.59879 10− 3,
                   2.67560 10− 3,      14.7545  10− 3,    883.785   10− 6,
                  32.6128  10− 3,      76.3447  10− 3,    362.213   10− 3,
                 279.318   10− 3,      91.7005  10− 3,    131.582   10− 3)
:          8s(   −1.00000        ,       3.74199 10− 6,   144.989          ,
                 292.560         ,    110.000   10+ 3,      1.00000        ,
                 149.871   10− 6,     163.058   10− 3,    446.015   10− 3,
                  91.9104  10− 3,     135.300   10− 3,      6.64536 10− 3,
                  69.8394  10− 3,      47.2260  10− 3,     32.0226  10− 3,
                   6.94345 10− 3,     502.997   10− 6,    386.415   10− 6)
:        2e9s(    0.00000        )
:         10s(   −1.00000        ,     69.1405  10− 3,    676.202   10+ 3,
                 348.665         ,    700.000   10+ 3,      1.00000        ,
                 172.392   10− 3,     365.459   10− 3,    278.280   10− 3,
                  49.7434  10− 3,      62.2825  10− 3,      3.02318 10− 3,
```

Table 9.6 (cont.)

```
               30.7150 ₁₀− 3,    20.6282 ₁₀− 3,    14.0253 ₁₀− 3,
               3.05749 ₁₀− 3,    222.857 ₁₀− 6,    171.022 ₁₀− 6)
:       11s(  −1.00000      ,    78.8363 ₁₀− 6,    4.07861 ₁₀+ 3,
               286.452      ,    110.000 ₁₀+ 3,    1.00000      ,
               48.1269 ₁₀− 6,    62.4857 ₁₀− 3,    342.543 ₁₀− 3,
               90.7832 ₁₀− 3,    223.343 ₁₀− 3,    11.5589 ₁₀− 3,
               142.624 ₁₀− 3,    90.7944 ₁₀− 3,    32.8010 ₁₀− 3,
               2.94177 ₁₀− 3,    53.7258 ₁₀− 6,    22.5253 ₁₀− 6)
:       13s(  −1.00000      ,    82.5817 ₁₀− 6,    4.22378 ₁₀+ 3,
               286.697      ,    110.000 ₁₀+ 3,    1.00000      ,
               52.7366 ₁₀− 6,    67.0423 ₁₀− 3,    347.230 ₁₀− 3,
               90.8341 ₁₀− 3,    219.355 ₁₀− 3,    11.3364 ₁₀− 3,
               139.327 ₁₀− 3,    88.8206 ₁₀− 3,    32.7655 ₁₀− 3,
               3.12305 ₁₀− 3,    74.0825 ₁₀− 6,    39.0139 ₁₀− 6)
:       14s(  −1.00000      ,    1.01414 ₁₀− 3,    62.6435 ₁₀+ 3,
               286.452      ,    110.000 ₁₀+ 3,    0.00000      ,
               164.158 ₁₀−12,    137.208 ₁₀− 6,    6.65676 ₁₀− 3,
               3.02779 ₁₀− 3,    28.6417 ₁₀− 3,    1.81461 ₁₀− 3,
               81.6899 ₁₀− 3,    186.428 ₁₀− 3,    500.080 ₁₀− 3,
               165.834 ₁₀− 3,    14.3745 ₁₀− 3,    11.3149 ₁₀− 3)
:       15s(  −1.00000      ,    68.0475 ₁₀− 3,    394.239 ₁₀+ 3,
               293.160      ,    700.000 ₁₀+ 3,    1.00000      ,
               175.161 ₁₀− 3,    371.255 ₁₀− 3,    282.254 ₁₀− 3,
               50.3921 ₁₀− 3,    62.5972 ₁₀− 3,    3.03130 ₁₀− 3,
               29.8256 ₁₀− 3,    18.0759 ₁₀− 3,    6.75963 ₁₀− 3,
               631.686 ₁₀− 6,    12.1452 ₁₀− 6,    5.11230 ₁₀− 6)
:       16s(  −1.00000      ,    1.45248 ₁₀− 3,    95.3989 ₁₀+ 3,
               289.455      ,    110.000 ₁₀+ 3,    0.00000      ,
               254.445 ₁₀−12,    191.450 ₁₀− 6,    6.94105 ₁₀− 3,
               2.92150 ₁₀− 3,    24.4508 ₁₀− 3,    1.53370 ₁₀− 3,
               66.8791 ₁₀− 3,    153.207 ₁₀− 3,    458.474 ₁₀− 3,
               200.082 ₁₀− 3,    37.7103 ₁₀− 3,    47.6097 ₁₀− 3)
:       37s(  −1.00000      ,    2.58365 ₁₀− 9,    363.327 ₁₀− 3,
               286.697      ,    110.000 ₁₀+ 3,    1.00000      ,
               0.00000      ,    0.00000      ,    0.00000      ,
               0.00000      ,    0.00000      ,    0.00000      ,
               1.00000      ,    0.00000      ,    0.00000      ,
               0.00000      ,    0.00000      ,    0.00000      )
:       38s(  −1.00000      ,    82.5783 ₁₀− 6,    4.22360 ₁₀+ 3,
               286.697      ,    110.000 ₁₀+ 3,    1.00000      ,
               52.7374 ₁₀− 6,    67.0431 ₁₀− 3,    347.232 ₁₀− 3,
               90.8343 ₁₀− 3,    219.354 ₁₀− 3,    11.3363 ₁₀− 3,
               139.326 ₁₀− 3,    88.8201 ₁₀− 3,    32.7657 ₁₀− 3,
               3.12311 ₁₀− 3,    74.0843 ₁₀− 6,    39.0148 ₁₀− 6)
:        3b(   1.00000      ,    1.00000      ,    10.0000      ,
               0.00000      ,    0.00000      ,    0.00000      ,
               139.327 ₁₀− 3,    139.327 ₁₀− 3,    0.00000      ,
               1.00000      ,    5.00000 ₁₀− 3,   −18.9992 ₁₀− 6,
               1.00000 ₁₀− 3,    1.00000      ,    1.00000      ,
              −286.847 ₁₀− 9,    10.0000 ₁₀− 3,    22.1741      )
:     13e4b(   157.421 ₁₀+ 3)
:     17e4b(   196.776 ₁₀+ 3)
:     18e4b(   1.49212      )
:     20e4b(   39.5751 ₁₀+ 3)
:     21e4b(   2.36364      )
:      5e5b(   307.604      )
:      6e5b(   31.2322      )
:      7e5b(  −174.011 ₁₀+ 3)
```

Table 9.6 (cont.)

```
:     5e6b(  395.941          )
:     6e6b(  254.442          )
:     7e6b( −122.070    10−  6)
:    13e7b(  182.259    10+  3)
:    17e7b(  227.823    10+  3)
:    18e7b(  627.292    10−  3)
:    20e7b(   45.9091   10+  3)
:    21e7b(    2.69231        )
:     5e8b(  315.191          )
:     6e8b(   37.0546         )
:     7e8b( −215.241    10+  3)
:     5e9b(  361.137          )
:     6e9b(  216.258          )
:     7e9b( −244.141    10−  6)
:      22b(  139.327    10−  3,     13.0000          )
:      18s(    2.00000        ,     68.0463  10−  3,     394.026   10+  3,
             293.160          ,    700.000   10+  3,       1.00000        ,
             175.164    10−  3,    371.261   10−  3,     282.259   10−  3,
              50.3930   10−  3,     62.5983  10−  3,       3.03135 10−  3,
              29.8261   10−  3,     18.0762  10−  3,       6.75975 10−  3,
             631.696    10−  6,      0.00000         )
:      19s(   −1.00000        ,      1.17419 10−  6,     213.177          ,
             293.160          ,    700.000   10+  3,       1.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,    703.802   10−  3,     296.198   10−  3)
:      20s(    2.00000        ,     15.0000  10−  3,       0.00000        ,
             293.160          ,    700.000   10+  3,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      1.00000        )
:      21s(    2.00000        ,     61.1273  10−  3,     −75.9384  10+  3,
             295.229          ,    700.000   10+  3,       1.00000        ,
             194.951    10−  3,    407.225   10−  3,     292.010   10−  3,
              51.4608   10−  3,     49.3738  10−  3,       2.31645 10−  3,
               2.64015  10−  3,     55.0768  10−  9,       0.00000        ,
               0.00000        ,      6.84363 10−12)
:      22s(    2.00000        ,     21.9190  10−  3,      −3.86850 10+  6,
             291.730          ,    700.000   10+  3,       0.00000        ,
             109.153    10−  6,     16.8985  10−  3,      61.9053  10−  3,
              12.9291   10−  3,     56.6402  10−  3,       2.95059 10−  3,
              85.2306   10−  3,     56.1164  10−  3,      20.9852  10−  3,
               1.96106  10−  3,    684.336   10−  3)
:      23s(    3.00000        ,     61.1273  10−  3,     −75.9402  10+  3,
             295.229          ,    700.000   10+  3,       1.00000        ,
             194.956    10−  3,    407.234   10−  3,     292.016   10−  3,
              51.4620   10−  3,     49.3749  10−  3,       2.31650 10−  3,
               2.64021  10−  3)
:      24s(    2.00000        ,      3.18804 10−  9,       1.82446        ,
             295.229          ,    700.000   10+  3,       1.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      0.00000        ,       0.00000        ,
               0.00000        ,      1.00000        ,       0.00000        ,
               0.00000        ,      0.00000        )
:      26s(    3.00000        ,     61.1283  10−  3,     −75.9395  10+  3,
             295.229          ,    700.000   10+  3,       1.00000        ,
```

Table 9.6 (cont.)

```
                194.954   10− 3,      407.229   10− 3,      292.013   10− 3,
                 51.4644  10− 3,       49.3774  10− 3,        2.31974 10− 3,
                  2.64181 10− 3)
:       2e27s(    0.00000      )
:         28s(    3.00000       ,      61.1283  10− 3,     −129.355   10+ 3,
                293.160         ,       4.00000 10+ 6,        1.00000       ,
                194.954   10− 3,      407.229   10− 3,      292.013   10− 3,
                 51.4644  10− 3,       49.3774  10− 3,        2.31974 10− 3,
                  2.64181 10− 3)
:       4e10b(  216.814   10− 3)
:      13e12b(  282.929   10+ 3)
:      17e12b(  353.661   10+ 3)
:      18e12b(  207.448   10− 3)
:      20e12b(  407.077   10+ 3)
:      21e12b(    2.39046      )
:       5e13b(  480.000        )
:       6e13b(  350.000        )
:       7e13b(    0.00000      )
:         34s(    3.000000      ,      60.25200 10− 3,     −254.7020  10+ 3,
                253.1600        ,       3.200000 10+ 6,       1.000000      ,
                197.7380  10− 3,      411.1737  10− 3,      290.8405  10− 3,
                 50.72379 10− 3,       45.47722 10− 3,        2.103203 10− 3,
                  1.943263 10− 3)
:         33s(    3.000000      ,     876.3010  10− 6,       17.38565 10+ 3,
                253.1600        ,       3.200000 10+ 6,       0.000000      ,
                  3.553259 10− 3,     136.0178  10− 3,      372.6396  10− 3,
                102.3891  10− 3,      317.5414  10− 3,       17.18727 10− 3,
                 50.67169 10− 3)
:       5e24b(  255.4113       )
:       6e24b(  123.3344       )
:       7e24b( −107.9614  10+ 3)
:         35s(    3.000000      ,     878.0096  10− 6,       17.41718 10+ 3,
                253.1558        ,       3.200000 10+ 6,       0.000000      ,
                  3.553494 10− 3,     136.0268  10− 3,      372.6624  10− 3,
                102.3944  10− 3,      317.5260  10− 3,       17.18599 10− 3,
                 50.65102 10− 3)
:         36s(    3.000000      ,      60.25029 10− 3,     −254.7336  10+ 3,
                253.1558        ,       3.200000 10+ 6,       1.000000      ,
                197.7435  10− 3,      411.1814  10− 3,      290.8378  10− 3,
                 50.72225 10− 3,       45.46973 10− 3,        2.103094 10− 3,
                  1.942183 10− 3)
:         39s(    3.000000      ,      61.12830 10− 3,     −237.3455  10+ 3,
                253.1558        ,       3.200000 10+ 6,     985.6366  10− 3,
                194.9543  10− 3,      407.2293  10− 3,      292.0131  10− 3,
                 51.46443 10− 3,       49.37738 10− 3,        2.319736 10− 3,
                  2.641807 10− 3)
:         40s(    3.00000       ,      57.8066  10− 3,     −431.782   10+ 3,
                229.176         ,       3.20000 10+ 6,        1.00000       ,
                206.157   10− 3,      430.630   10− 3,      308.793   10− 3,
                 54.4204  10− 3,        0.00000       ,       0.00000       ,
                  0.00000      )
:         41s(    3.000000      ,       3.321721 10− 3,     134.0205  10+ 3,
                351.8312        ,       3.200000 10+ 6,       0.000000      ,
                  0.000000      ,       0.000000      ,       0.000000      ,
                 22.73435 10− 6,      908.6720  10− 3,       42.68916 10− 3,
                 48.61611 10− 3)
:         26b(   49.00000       ,      27.00000       ,       4.000000      ,
                  5.000000      ,       1.000000      ,       1.000000      ,
```

```
              32.2912  10− 6,      850.140  10− 3,       149.828  10− 3,
               0.00000      )
:      59s(    8.00000       ,       0.00000       ,       0.00000       ,
             257.000         ,       2.60000 10+ 6,        0.00000       ,
               0.00000       ,       0.00000       ,       0.00000       ,
               0.00000      )
:    5e34b(  192.262        )
:    6e34b(  178.568        )
:    7e34b(  155.748   10+ 3)
               0.00000       ,       0.00000       ,       0.00000       ,
               0.00000       ,       0.00000      )
:    5e30b(  227.003        )
:    6e30b(  121.528        )
:    7e30b(   10.3990  10+ 3)
:      50s(    4.00000       ,      57.8066  10− 3,     −421.381   10+ 3,
             231.160         ,       3.00000 10+ 6,        1.00000       ,
             206.157   10− 3,      430.630  10− 3,       308.793   10− 3,
              54.4204  10− 3,        0.00000      )
:      52s(    4.00000       ,      36.8101  10− 3,       −1.51779 10+ 6,
             158.770         ,       3.00000 10+ 6,        1.00000       ,
             323.749   10− 3,      676.243  10− 3,         7.70822 10− 6,
               0.00000       ,       0.00000      )
:      53s(    4.00000       ,      20.9965  10− 3,       855.622  10+ 3,
             264.044         ,       3.00000 10+ 6,        0.00000       ,
               0.00000       ,      32.2912  10− 6,       850.140  10− 3,
             149.828   10− 3,        0.00000      )
:      31b(   30.0000        ,      13.0000        ,       2.00000       ,
               3.00000       ,       1.00000       ,       1.00000       ,
               2.00000       ,       1.00000       ,       1.30000       ,
             158.770         ,     150.000         ,     250.000         ,
              99.9973        ,      99.9984        ,    −263.115   10+ 3,
              22.3285  10+ 3,        1.30000       ,     537.752   10− 3)
:      45s(    5.00000       ,       3.32172 10− 3,      134.020   10+ 3,
             351.830         ,       3.20000 10+ 6,        0.00000       ,
               0.00000       ,      22.7343  10− 6,      908.672   10− 3,
              42.6892  10− 3,      48.6161  10− 3)
:      43s(    5.00000       ,       3.32172 10− 3,      168.971   10+ 3,
             350.000         ,       1.70000 10+ 6,        1.00000       ,
               0.00000       ,      22.7343  10− 6,      908.672   10− 3,
              42.6892  10− 3,      48.6161  10− 3)
:      42s(    5.00000       ,       0.00000       ,       0.00000       ,
             350.000         ,       1.70000 10+ 6,        0.00000       ,
               0.00000       ,       0.00000       ,       0.00000       ,
               0.00000       ,       0.00000      )
:    5e27b(  314.063        )
:    6e27b(  316.598        )
:    7e27b(   34.9515  10+ 3)                   3
:      44s(    5.00000       ,       3.32172 10− 3,      168.971   10+ 3,
             350.000         ,       1.70000 10+ 6,        1.00000       ,
               0.00000       ,      22.7343  10− 6,      908.672   10− 3,
              42.6892  10− 3,      48.6161  10− 3)
:      12s(    8.00000       ,      20.9965  10− 3,      855.623   10+ 3,
             264.044         ,       3.00000 10+ 6,        0.00000       ,
              32.2912  10− 6,      850.140  10− 3,       149.828   10− 3,
               0.00000      )
:      57s(    8.00000       ,      20.9965  10− 3,        1.01137 10+ 6,
             257.000         ,       2.60000 10+ 6,        1.00000       ,
               2.000000      ,       1.000000      ,       1.000000      ,
```

Table 9.6 (cont.)

```
                229.1760       ,     230.0000         ,     370.0000        ,
                 99.99760      ,     100.0000         ,    −578.0083  ₁₀+ 3,
                517.5914  ₁₀+ 3,       1.000000       ,     802.3583  ₁₀− 3)
:       49s(      4.00000      ,      57.8066  ₁₀− 3,      −421.381   ₁₀+ 3,
                231.160        ,       3.00000 ₁₀+ 6,         1.00000       ,
                206.157   ₁₀− 3,     430.630   ₁₀− 3,       308.793   ₁₀− 3,
                 54.4204  ₁₀− 3,       0.00000      )
:       51s(      4.00000      ,       0.00000        ,       0.00000       ,
                231.160        ,       3.00000 ₁₀+ 6,         0.00000       ,
:       60s(      8.00000      ,      20.9965  ₁₀− 3,         1.01137 ₁₀+ 6,
                257.000        ,       2.60000 ₁₀+ 6,         1.00000       ,
                 32.2912  ₁₀− 6,     850.140   ₁₀− 3,       149.828   ₁₀− 3,
                  0.00000      )
:       61s(      8.00000      ,      49.9798  ₁₀− 6,         3.23648 ₁₀+ 3,
                253.377        ,       2.60000 ₁₀+ 6,         1.00000       ,
                  6.33423 ₁₀− 3,     979.730   ₁₀− 3,        13.9355  ₁₀− 3,
                 10.0000  ₁₀− 9)
:       58s(      8.00000      ,      20.9465  ₁₀− 3,       837.087   ₁₀+ 3,
                257.046        ,       2.60000 ₁₀+ 6,         0.00000       ,
                 17.2544  ₁₀− 6,     849.831   ₁₀− 3,       150.152   ₁₀− 3,
                 10.0239  ₁₀− 9)
:    54e35b(    −22.4092  ₁₀+ 3)
:    55e35b(     22.8934  ₁₀+ 3)
:    56e35b(    403.600   ₁₀− 6)
:       62s(      6.00000      ,      20.9462  ₁₀− 3,       837.109   ₁₀+ 3,
                257.046        ,       2.60000 ₁₀+ 6,         0.00000       ,
                849.846   ₁₀− 3,     150.154   ₁₀− 3,        10.0240  ₁₀− 9)
:       63s(      8.00000      ,     361.366   ₁₀− 9,       −21.7363        ,
                257.046        ,       2.60000 ₁₀+ 6,         0.00000       ,
                  1.00000      ,       0.00000        ,       0.00000       ,
                  0.00000      )
:       64s(      6.00000      ,      20.9462  ₁₀− 3,       982.152   ₁₀+ 3,
                184.892        ,     200.000     + 3,         1.00000       ,
                849.846   ₁₀− 3,     150.154   ₁₀− 3,        10.0240  ₁₀− 9)
:       65s(      6.00000      ,       0.00000        ,       0.00000       ,
                184.892        ,     200.000   ₁₀+ 3,         0.00000       ,
                713.218   ₁₀− 3,     286.782   ₁₀− 3,       162.083   ₁₀− 9)
:     5e36b(    184.892        )
:     6e36b(    183.076        )
:     7e36b(    145.043   ₁₀+ 3)
:       67s(      6.00000      ,      17.8010  ₁₀− 3,         1.17804 ₁₀+ 6,
                181.224        ,     200.000   ₁₀+ 3,         1.00000       ,
                  1.00000      ,       0.00000        ,       0.00000       )
:       66s(      6.00000      ,       3.14517 ₁₀− 3,      −241.603   ₁₀+ 3,
                196.773        ,     200.000     + 3,         0.00000       ,
                  4.34914 ₁₀− 6,     999.996   ₁₀− 3,         0.00000       )
:       40b(     79.0000       ,      41.0000         ,       1.00000       ,
                  2.00000      ,       1.00000        ,       1.00000       ,
                  2.00000      ,       2.00000        ,       2.20000       ,
                181.224        ,     183.000          ,     199.000         ,
                 99.9999       ,     100.000          ,    −512.607   ₁₀+ 3,
                466.890   ₁₀+ 3,       2.20000        ,     700.000   ₁₀− 3)
+
end Ethylene plant, Var. 5.
```

Table 9.7

Results of the simulation.
Stream vectors

Connection index	W $\times 10^3$ kmoles/s	T K	P $\times 10^5$ N/m^2	state	Composition, mole %											
					67	1	26	2	27	3	48	29	55	56	76	63
1	69.500	293	1.1	G	17.15	36.35	27.65	4.94	6.18	0.30	3.06	2.09	1.62	0.48	0.08	0.10
2	69.583	293	1.1	G	17.13	36.31	27.66	4.95	6.20	0.30	3.07	2.10	1.62	0.48	0.08	0.10
3	69.583	340.5	2.6	G	17.13	36.31	27.66	4.95	6.20	0.30	3.07	2.10	1.62	0.48	0.08	0.10
5	69.140	293	2.6	G	17.24	36.55	27.83	4.97	6.23	0.30	3.07	2.06	1.40	0.31	0.02	0.02
10	69.140	348.5	7	G	17.24	36.55	27.63	4.97	6.23	0.30	3.07	2.06	1.40	0.31	0.02	0.02
15	68.048	293	7	G	17.52	37.13	28.23	5.04	6.26	0.30	2.98	1.81	0.67	0.06	0	0
16	1.452	289	1.1	L	0	0.02	0.69	0.29	2.45	0.15	6.69	15.32	45.85	20.00	3.77	4.76
21	61.127	295	7	G	19.50	40.72	29.20	5.15	4.94	0.23	0.26	0	0	0	—	—
26	61.128	295	7	G	19.50	40.72	29.20	5.15	4.94	0.23	0.26	—	—	—	—	—
28	61.128	293	40	G	19.50	40.72	29.20	5.15	4.94	0.23	0.26	—	—	—	—	—
29	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
39	61.128	253	32	M	19.50	40.72	29.20	5.15	4.94	0.23	0.26	—	—	—	—	—
40	57.807	229	32	G	20.62	43.06	30.88	5.44	0	0	0	—	—	—	—	—
41	3.321	351.7	32	L	0	0	0	0.00	90.87	4.27	4.86	—	—	—	—	—
44	3.321	350	17	G	—	—	0	0.00	90.87	4.27	4.86	—	—	—	—	—
5v	57.807	231	30	G	20.62	43.06	30.88	5.44	0	—	—	—	—	—	—	—
52	36.810	158.6	30	G	32.374	67.624	0.001	0	0	—	—	—	—	—	—	—
53	20.997	264	30	L	0	0.003	85.014	14.983	0	—	—	—	—	—	—	—
60	20.997	257	26	G	—	0.003	85.014	14.983	0	—	—	—	—	—	—	—
61	0.050	253.2	26	G	—	0.633	97.973	1.394	0	—	—	—	—	—	—	—
58	20.947	257	26	L	—	0.002	84.983	15.015	0	—	—	—	—	—	—	—
64	20.947	184.7	2	G	—	—	84.985	15.015	0	—	—	—	—	—	—	—
67	17.801	181	2	G	—	—	100.000	0	0	—	—	—	—	—	—	—
66	3.145	196.6	2	L	—	—	0.0004	99.9996	0	—	—	—	—	—	—	—

Table 9.8

Result of the simulation.
Heat load of the heat-transfer units

Position number of the heat-transfer units	Heat load 10^{-3} J/s
G7	174.011
G16	215.241
G40, G49	296.482
G83, G84, G86	107.961
G88 condenser	578.008
G88 reboiler	517.591
G102	10.399
G103 condenser	263.115
G103 reboiler	22.329
G103 b	155.748
G110 condenser	22.409
G110 reboiler	22.893
G105	145.043
G118 condenser	512.607
G118 reboiler	466.890

CHAPTER 10

COMPUTER-AIDED PROCESS DESIGN

The concept of computer-aided process design includes any part of process design, whether solved by calculator and/or computer. Carried out consequently and *ad extremum* it leads to automatic process design. By this, we understand a process design, all parts of which are solved by computer, using a comprehensive program system. We know of no program system able to perform automatic process design in this sense, but in neither chemical engineering nor computer science need we await scientific results, the conceptual precondition of such a program system. This program system is likely to include as a sub-system something like the SIMUL flow-sheeting program outlined in this book. If this supposition is correct, then we may consider what further steps may be taken on the road leading to automatic process design, with typical and atypical use of the SIMUL flow-sheeting program. This question may be formulated in another way: which strategy must be selected for the process design, using the simulator as the available tool.

It is evident from the previous chapters of this book, that the simulator is only able to function if the process as a network and all the equipment included is identified by its operating parameters. It follows that before the simulator may start functioning in automatic process design, the following steps have to be carried out:

— identification of the network, which is described in the SIMUL flow-sheet program,

— provisional identification of the operating parameters of all equipment contained in the network and the declaration of the input streams of the network; all these figure in the input data system. (We should remember here that the mathematical boxes organizing the calculation figure in the flow-sheet program, and their operating-parameter vectors in the input data system. This was discussed in Chapter 6). We must speak about provisional identification, because design in the case of a previously established network is simply calculation of the optimal operating parameters, which may be carried out automatically when using the SIMUL system by optimizing boxes included suitably in the flow-sheet program.

10.1 PROCESS-CONCEPT GENERATOR TO IDENTIFY THE NETWORK

Developing a process concept is today an accepted task for the experienced chemical engineer. With a knowledge of the raw material and the quality and quantity of the required product, he has to develop the network, using the *a priori* knowledge gained by experience, i.e. has to specify a poorly defined processing problem as a network, for the time being. The problem differs entirely from flow-sheeting, because the matter in hand this time is not the calculation but the logical planning.

Undoubtedly, a number of algorithms may be found to identify the network. Research has been started on this subject (Lee et al. 1970; Siirola and Rudd, 1971; Siirola et al. 1971; Hendry and Hughes, 1972; Hendry et al., 1973; Rudd et al., 1973; Mahalec and Motard, 1977), and remarkable results have been achieved in two special fields in the algorithmic identification of the network. These are the handling of the heat-exchange blocks (Pho and Lapidus, 1973) and the separating blocks (Thomson and King, 1972; Rathore et al., 1974; Rodrigo and Seader, 1975; Stephanopoulos and Westberg, 1975). These two fields arise because the elements of the network are identical operations and therefore we can omit the step of the identification of a network which leads to selection of operations.

Before further discussion of the selection of operations, the reader should return to Chapter 0.2, where we discussed the functioning of the process from the thermodynamic viewpoint.

Let us now introduce the concept of *the main process stream*. The main process stream is that which enters the complex operation as raw material and leaves as product. The main stream undergoes a change when passing through equipment, because at appropriate places it encounters side streams and/or auxiliary streams which changes the main stream state, initiating spontaneous alteration or, conversely, it can exclude a undesirable change.

The side stream is a mass stream which may contact the main stream directly, whereas the auxiliary stream is only in contact through a wall (with the purpose of heat transfer).

Thus it is understandable that the drawing up of the state change of the main stream is the first step in the course of automatic process design. Drawing up of the side stream(s) must be completed at one time. The auxiliary streams may be dealt with later.

When embarking on a process design, the quantitatively and qualitatively defined product stream and the raw material stream — at least partly defined — are known (Fig. 10.1*a*).

From these we have information about the different chemical components of the input (raw material) and the output (product) of the main stream. This is only possible if chemical reactions occur in one or more sections of the main stream. The programmed search of the reaction sequence, based on the composition of the input and output, is an interesting problem in itself, independent of the automatic process design, several solutions of which are known.

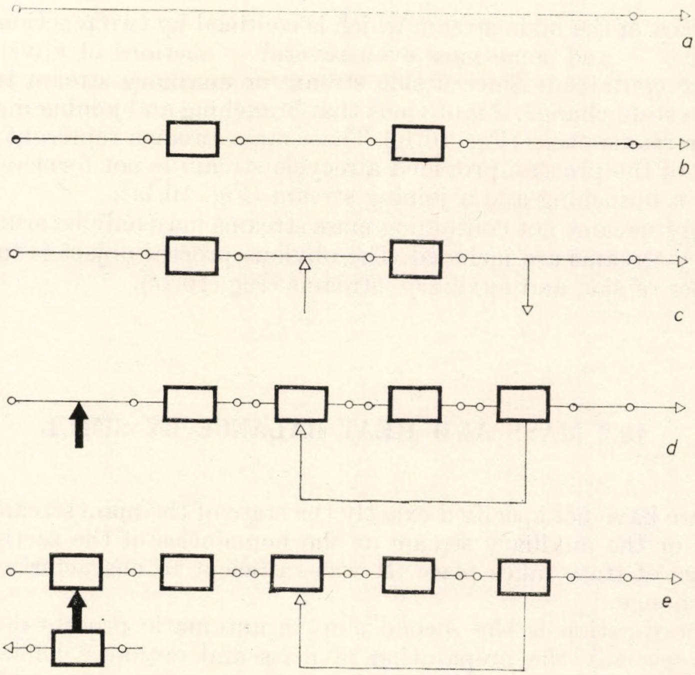


Fig. 10.1. Indication of the sections of the main process stream

Since these programs are large, it is practicable to carry out the search of the reaction sequence independently of the automatic process design, and to consider its result from the viewpoint of process design as *a priori* knowledge.

This tells us that the consecutive reaction sections along the main stream may be indicated by specifying the state of the main stream at the entry and exit points of every section (Fig. 10.1*b*). Thus in every section the equilibrium conditions, incidentally limiting the chemical transformation (e.g., ammonia synthesis) or selectivity conditions, (e.g., pyrolysis of acetone) have to be taken into consideration. The state at exit of each section may be estimated using preliminary reaction kinetics calculations. Thus the main stream contains several reaction sections, and entry and exit states are fairly well specified in every case. We may observe that the state at the exit point of a reaction section and — advancing along the main stream — the state at the entry point of the next reaction section differ from each other: between these two states at least one section must figure as the place of the operation inducing the difference of states between the exit stream of the former reaction section and the entry stream of the next reaction section. If the temperatures of the streams differ then the operation is heat exchange, if their pressures differ then the operation increases or decreases the pressure of the stream. In the case of concentration difference, separation or admixture must be provided for.

In the part of the main stream which is confined by two reaction sections, at least one — and sometimes even several — sections of physical state-change are contained. Since a side stream or auxiliary stream is adopted to induce a state change, it is obvious that branching and joining mass and/or enthalpy streams occur (Fig. 10.1*c*). These mass streams represent the input or output of the process, provided a recycle stream is not formed by short-circuiting a branching and a joining stream (Fig. 10.1*d*).

Enthalpy streams not containing mass streams may only be accomplished if auxiliary streams are included. The obvious process object is to decrease the number of side and auxiliary streams (Fig. 10.1*e*).

10.2 MASS AND HEAT BALANCE BY SIMUL

So far we have not specified exactly the state of the main stream, the side stream(s) or the auxiliary stream at the boundaries of the sections where the change of state takes place. It was sufficient to characterize the type of state change.

This specification is the second step in automatic process design. This step is essentially the preparation of mass and enthalpy balances in all sections. Balances are always produced by thermodynamic calculations. Just now we are interested in discovering, how the SIMUL flow-sheeting program may be used for this purpose.

The preparation of mass and enthalpy balances is based on the calculation of states and state differences. The route and time consumption on changing states is irrelevant in this respect. In other words, it is not necessary to know equipment dimensions which determine the residence time.

To calculate mass and enthalpy balances we may therefore use all SIMUL boxes where such data is absent from the operating parameters.

The direction of the balance calculation does not necessarily concur with that stream which characterizes most SIMUL boxes. Our precise problem is not to calculate the exit condition from an entering state, but to know the difference between entering and exit states. In such cases we use either iteration, or an atypical SIMUL practice: we have to supplement the box to enable it to perform the operation with arithmetic expressions. In this respect, the ability of the SIMUL system to develop reference chains and to refer in arithmetic expressions to an element of a stream vector or an operating parameter at the site of variables is a great advantage.

If we take all this into consideration, then the production of mass and enthalpy balances consists of formulating such a flow-sheet program and input data system corresponding to the conditions mentioned. This activity is not automated, but this would not be difficult to arrange.

On the other hand, the calculation of the mass and enthalpy balance is naturally carried out automatically after formulation of the flow-sheet program and the input data system.

10.3 SELECTION OF THE EQUIPMENT, EVENTUAL DEVELOPMENT OF NEW EQUIPMENT MODELS

The mass and enthalpy balances take quantitative aspects into consideration, when the equipment carrying out the prescribed state change is selected bearing in mind the unit operations. This activity leads to the process flow-sheet which does not include stream vectors yet.

If the actual box assortment of the SIMUL system contains boxes able to simulate all equipment — after all, this is the requirement of the automatic design — then the formulation of the flow-sheet program presents no difficulties. For the purpose of flow-sheeting, formulation of the input data system is also necessary. Among the elements of the operating-parameter vector, this contains the main dimensions of the equipment. We need now to estimate these, on the basis of mass and enthalpy balance data. The computed estimation presents no difficulties. Although the estimation of the main dimensions is specific for any operation (box), nevertheless it may be carried out on the basis of simple relations originating from unit operations. For example, we refer to

— distillation, where the minimal number of plates and minimal reflux ratio, i.e., the minimal values of the two main dimensions, are calculated from the mass balance data,

— heat exchange, where the heat transfer area, the main dimension of the heat exchange, is calculated from the enthalpy balance data.

If at least one box, able to simulate a piece of equipment, is missing from the actual assortment of the flow-sheeting system, then it must be developed before starting the automatic design. It is not easy to formulate general rules about development of boxes. When preparing the box assortment of the SIMUL system, two practical problems were encountered:

— the one-to-one correspondence of the equipment and the box was a major aim when developing the box assortment of the SIMUL system. Nevertheless, the situation can arise where a piece of equipment needs to be simulated by several boxes, and this has to be organized in the flow-sheet program. In other cases, a single box has been constructed to simulate several items of strongly interconnected equipment. This non-correspondence represents two techniques which were exploited for practical reasons.

— The choice between a box being generally and a specially usable depends on the actual case in hand. An extremely general box, such as box *dipa*, actually serves as a mathematical framework, and a large number of parameters has to be defined when creating it. The use of a general box is tedious because of this preparatory work. This does not arise when using special boxes, although a box of this type infringes the principle of the independence of the components and it is only justified when connected with repeated problems. Special boxes in this sense were discussed in Chapter 3.4.20.

10.4 FLOW-SHEETING

Flow-sheeting is the next step in automatic process design. It is not necessary to discuss this subject further. The result of flow-sheeting is a feasible solution of the process design.

10.5 PROCESS OPTIMIZATION BY FLOW-SHEET SIMULATION

The last step of automatic process design consists of setting the optimum of the process variables (e.g., recycle rate) and the main dimensions of the equipment (Gaines and Gaddy, 1976). The optimum is an economic concept — the values of the process variables and the actual main dimensions of the equipment are considered to be optimal if the objective function of these adopts extreme value.

We do not intend to consider the objective function here, but just to state that

— the elaboration of the form and coefficients of the objective functions is one of the tasks of cost engineering (Guthrie, 1969),

— cost engineering defines the investment cost of any equipment as a function of the main dimension, but anyway, the main dimensions are described among the elements of the operating-parameter vector.

Cost engineering produces that knowledge needed to calculate the coefficients of the objective function in a manner which is easy to handle, but the formulation of the economic sense of the objective function does not relate to the activities to be automated.

The library of the SIMUL flow-sheeting system contains two optimizing boxes. These were discussed in Chapter 7. We should remember here that these two boxes

— *opt38* (which use the simplex algorithm) — may be recommended for calculating networks which contain loops, when the optimum of the recycle ratio and the purge is sought (Adelman and Stevens, 1972),

— box *bellman:* 40 is, on the contrary, chiefly suitable for calculating the optimal state at connecting points between series-coupled boxes, if the decision variables are the main dimensions of the box before and follow the connecting point.

Optimization of course requires enlargement of the flow-sheet program by these boxes as discussed in Chapter 7.

If an integer occurs in the decision variables (e.g., the number of plates of a column) then the design has to be carried out in principle by integer programming. In such cases — taking the present condition of the SIMUL system into consideration — the interactive course of work may be recommended, and the values of the integer variables may be set by box *vary*.

PROBLEMS

In the following problems one single design task is to be solved — in detail — on the previous lines of approach. 20 000 tons of acetic anhydride (technical quality) containing not more than 5 weight % contaminating acetic acid have to be produced in 8000 working hours. The row material is acetone and acetic acid (Jeffreys, 1964).

PROBLEM P.10.1 THE MANUFACTURE OF ACETIC ANHYDRIDE. INITIAL DESIGN OF THE CHEMICAL PROCESSING SYSTEM

For the main process stream of the plant, make a sequence fulfilling the above-mentioned production requirements of the characteristic states. Designate those side and auxiliary streams, whose interaction brings about the required state changes step by step in the main stream.

The production task is indicated in Figure 10.2*a*.

The *a priori* knowledge from chemistry is: acetone decomposes to ketene and methane at around 1000 K, with a fairly short residence time:

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4$$

This means that in Figure 10.2*b*, on line A–C, representing the main process stream, a point D must occur, which is characterized by the presence of ketene and methane, as a result of the above-mentioned reaction.

It is also known that acetone decomposes in a side reaction at the given temperature and residence time:

$$CH_3COCH_3 \rightarrow 3H_2 + CO + 2C.$$

It should be considered that the ketene produced is a reactive compound, decomposing at the given temperature and residence time:

$$2\,CH_2CO \rightarrow C_2H_4 + 2\,CO.$$

All these three reactions are endothermic.

Consequently, at point D of the main process stream a pyrolysis gas is present, containing all the above-listed components.

It is also obvious that in the main process stream, point E and the corresponding state must appear, containing pure acetone in gaseous phase at a temperature not sufficient to cause decomposition. The first reaction zone of the main process stream is therefore on section $\overline{ED}$ (Fig. 10.2*c*).

According to *a priori* knowledge, ketene reacts with acetic acid in homogeneous liquid phase, in a considerably exothermic reaction and produces acetic anhydride:

$$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O$$

It follows that on line $\overline{AC}$, on the right-hand side of point D, a point G must occur, where the state of the main process stream is characterized by the low temperature (liquid phase is needed) and by the presence of acetic anhydride.

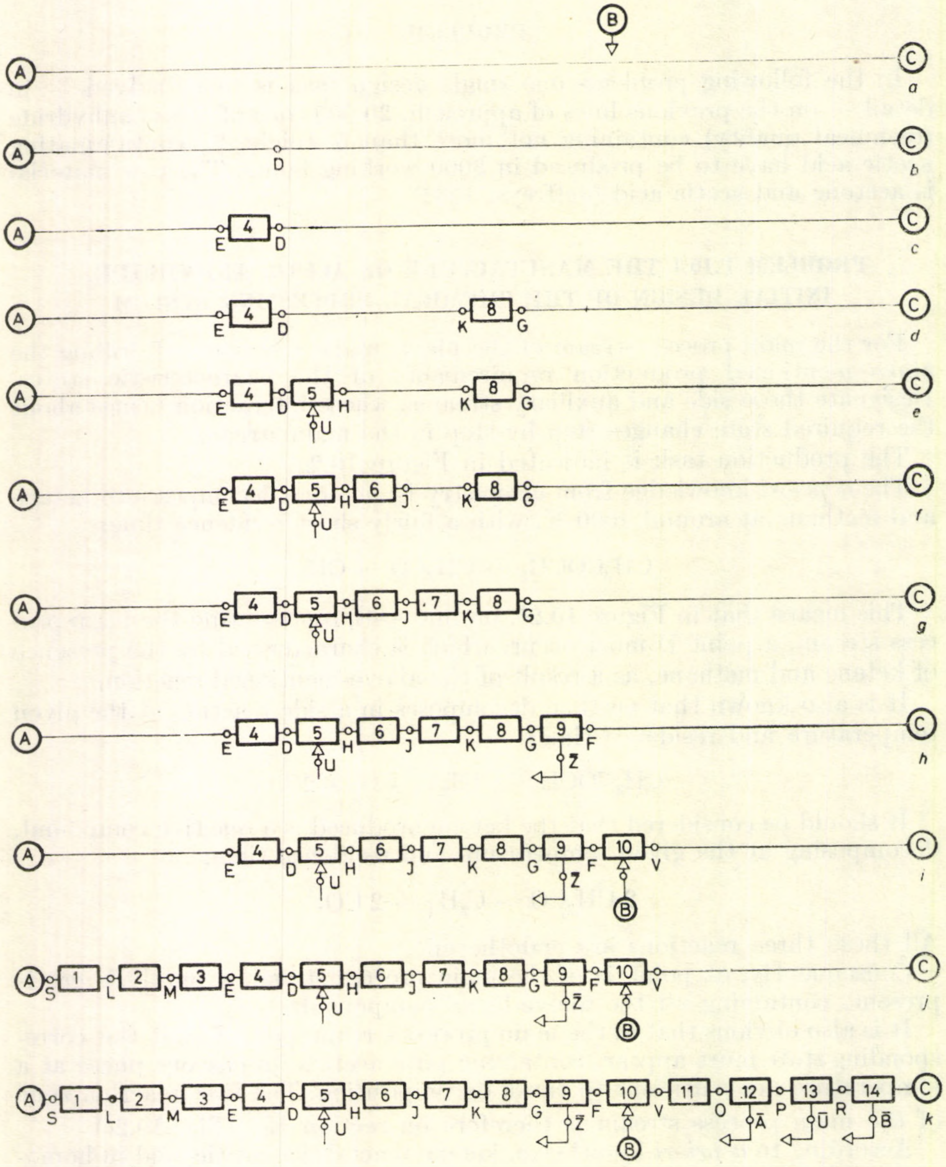


Fig. 10.2. Manufacture of acetic anhydride. Design of the main process stream

On the left-hand side of point G is point K, where the stream is liquid, but does not contain acetic anhydride. $\overline{KG}$ represents the second reaction section (Fig. 10.2*d*). There are no more reaction sections between A and C, because acetic anhydride has been formed at G.

The process stream between D and H is characterized by the sharp decrease of temperature. Cooling has to be particularly effective between D and H, in order to stop the decomposition of ketene instantaneously. For this purpose a cool, liquid, side stream U has to be injected into the warm (1000 K) main stream (Fig. 10.2*e*).

This injected side stream has to be acetic acid stream, in equivalent quantity with the ketene stream. If this does not reduce the temperature sufficiently, it is practical to add acetic anhydride.

As the main stream is still above the dew point, it has to be cooled further to its dew point in a later section. On line $\overline{AC}$, the gas at its dew point is characterized by point J. On the cooling section $\overline{HJ}$, the main stream has to be brought into contact with a heat-carrying medium, whose temperature is lower than that of the main stream (Fig. 10.2*f*). The main stream passing point J is at its dew point, and as it is cooled further, part of it condenses and therefore a mixed phase passes point K (Fig. 10.2*g*). In section $\overline{GF}$, therefore, a gaseous side stream leaves the main process stream. This side stream contains the following components: CH_4, H_2, CO, CO_2, C_2H_4 (Fig. 10.2*h*). As this gas is warm, it must be cooled by a cooling medium. Acetic acid (B) is used: it enters the main stream when cooling is complete (Fig. 10.2*i*).

In region $\overline{AE}$, before the first reaction section, the main stream (consisting of undecomposed acetone) has to pass through the following state changes:

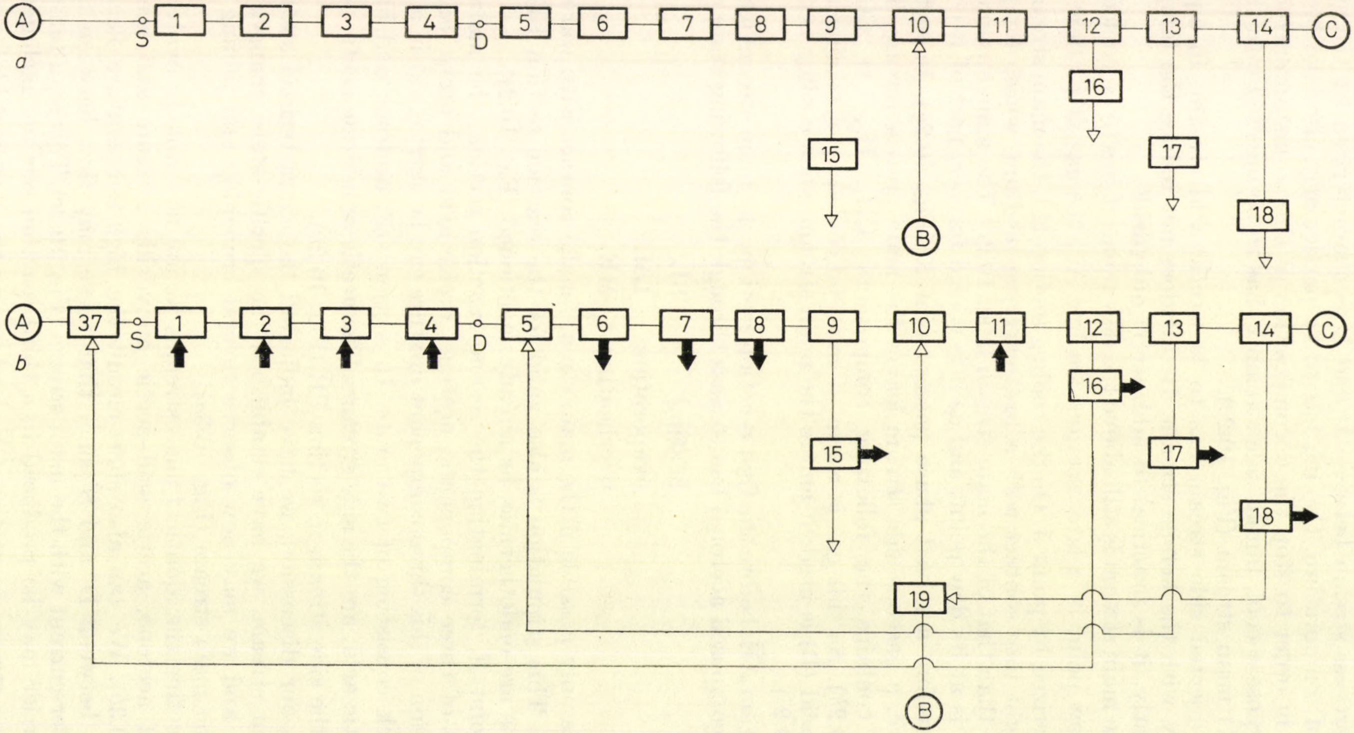
heating	$\overline{SL}$,
evaporation	$\overline{LM}$,
overheating	$\overline{ME}$.

This is only possible if the main stream make contact with warmer heat carriers. This stipulation is also valid for the reaction section $\overline{ED}$, as the reactions are endothermic, as already mentioned (Fig. 10.2*j*).

At point F, terminating the second reaction section, the main stream consists of three components: acetone, acetic acid and acetic anhydride. Separation of this three-component mixture can be carried out in a separating block consisting of two units. In section $\overline{OP}$, acetone, and in section $\overline{RC}$ acetic acid, are the side streams. The acetic anhydride-acetic acid mixture is the side stream in section $\overline{PR}$ (Fig. 10.2*k*).

From our discussion, we have indicated the characteristic states along the main stream, we have established the specific state changes in each section, and we may now observe several branching and joining streams along the main stream (Fig. 10.3*a*).

Connecting the identical mass streams we are now able to evolve recycle loops of acetone, acetic acid–acetic anhydride mixture and acetic acid (Fig. 10.3*b*). We can also short-circuit the high-temperature heat-carrier streams between D′ and S′ such that these may flow between S and D in counter-current with the main stream (Fig. 10.3*c*). This high-temperature heat carrier may be produced in a third reaction section, included in the branching stream in section $\overline{GF}$, by burning the combustible components


A
S
D
C
B
a
b
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
37

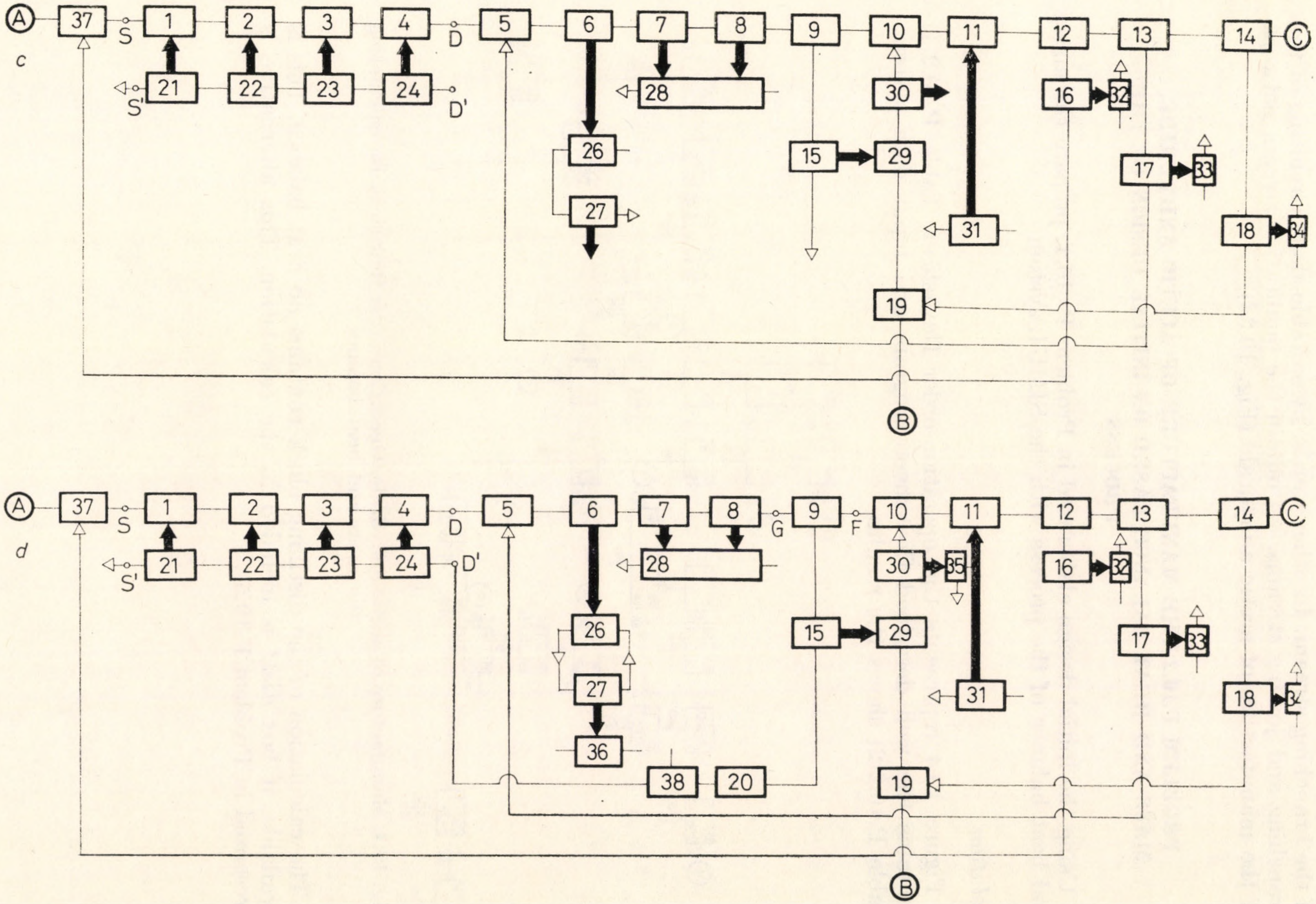


Fig. 10.3 a, b, c, d. Manufacture of acetic anhydride. Design of side and auxiliary streams and recycle loops

of the branching stream. In other words, by suitable short-circuiting of the branching and joining streams, we obtain the qualitative stream network of the manufacture of acetic anhydride (Fig. 10.3*d*).

PROBLEM P.10.2 THE MANUFACTURE OF ACETIC ANHYDRIDE. MASS AND HEAT BALANCE BASED ON INITIAL DESIGN OF THE PROCESS

Using the initial design elaborated in Problem P. 10.1, prepare the mass and heat balance of the process with the SIMUL system.

Solution

Figure 10.4 represents the operation-order flow-sheet. Table P.10.2(1) contains the well described flow-sheet program and input data system. Table P.10.2(2) shows the results.

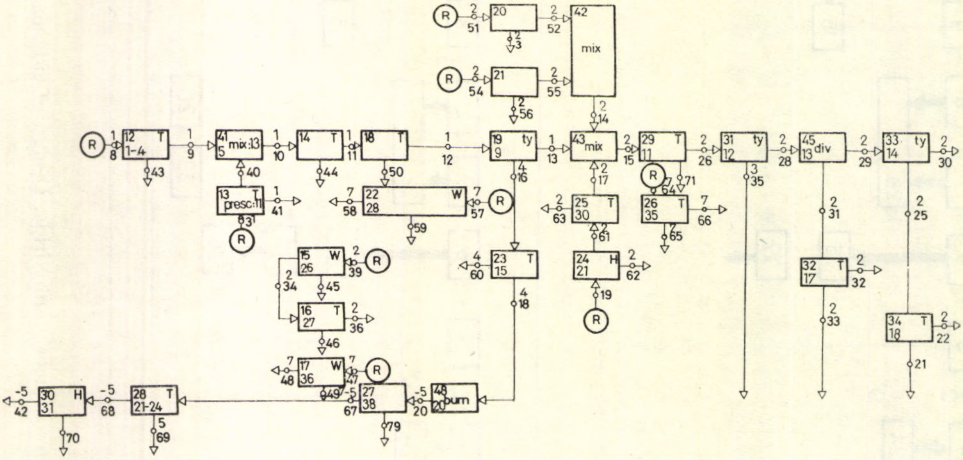


Fig. 10.4. Manufacture of acetic anhydride. Operation-order flow-sheet for calculating the mass and heat balance

The calculation of the distilling block contains no heat balance. This is available, if box *dist1* is included in the calculation. This alternative is presented in Problem P.10.5.

Table P.10.2 (1)

Manufacture of acetic anhydride. Flow-sheet program and input data system of problem [Mass- and heat-balance calculation]

```
[Mass and heat balance of the manufacture of acetic anhydride]
A 770218

STREAM TYPES

general stream
acetone, acetic acid, acetic
anhydride, ketene,
methane, ethylene, CO,
CO2, hydrogen                          :1(117,193,194,114,1,26,71,70,67)
mixture
acetone, acetic acid,
acetic anhydride                       :2(117,193,194)
acetone                                :3(117)
fuel gas
methane, ethylene, CO, CO2,
hydrogen                               :4(1,26,71,70,67)
flue gas
oxygen, water, CO2, nitrogen           :5(64,69,70,72)
pyrolysis gas
acetone, ketene, methane,
ethylene, CO, CO2, hydrogen            :6(117,114,1,26,71,70,67)
water                                  :7(69)
+
operations

PRELIMINARY CALCULATIONS

product stream calculation with arithmetic expression
  prescriber                           :11(1,1,−30,−41)
molal enthalpy of the cold mixture used in the injector, 313 K
  prescriber                           :11(2,2,−2,−41)
same as the exit temperature of the injector, 783 K
  prescriber                           :11(3,3,−3,−41)
molal enthalpy of the mixture after quenching, 373 K
  prescriber                           :11(2,39,−39,−41)
  prescriber                           :11(2,5,−5,−75)
  prescriber                           :11(7,7,−7,−75)
  prescriber                           :11(6,6,−6,−77)
calculation of the exit pyrolysis gas from the furnace, 987 K, with arithmetic expression
  prescriber                           :11(8,8,−8,−76)

QUENCH OF THE PYROLYSIS GAS IN THE MAIN STREAM

cool the furnace exit gas to 783 K
  prescriber                           :11(12,8,−9,−43)
acetone feed quantity — calculated with arithmetic expression — heated to 783 K
  prescriber                           :11(13,3,−40,−41)
mixture of the two streams is the exit stream of the injector
  mixing                               :13(41,9,40,−10)

COOLING THE MAIN STREAM TO DEW POINT

set the temperature of the main stream to 422 K
  prescriber                           :11(14,10,−11,−44)
fresh mixture quantity — calculated with arithmetic expression — heated to 373 K
```

Table P.10.2 (1) (cont.)

```
   prescriber                                    :11(15,39,−34,−45)
cooling the warm mixture to 313 K
   prescriber                                    :11(16,34,−36,−46)
calculation of the required cooling water stream with arithmetic expression
   prescriber                                    :11(17,47,−48,−49)

LIQUEFYING THE MAIN STREAM

cooling the main stream to 344 K
   prescriber                                    :11(18,11,−12,−50)
separation of the uncondensed fuel gas
   prescriber                                    :11(19,12,−16,−13)
calculation of the condensed acetone stream with arithmetic expression
   prescriber                                    :11(20,51,−52,−53)
calculation of the condensed anhydride stream with arithmetic expression
   prescriber                                    :11(21,54,−55,−56)
extraction of the heat of condensation with cooling water
   prescriber                                    :11(22,57,−58,−59)
liquid main stream
   mixing                                        :13(42,52,55,−14)

COOLING THE FUEL GAS

cooling the fuel gas to 313 K
   prescriber                                    :11(23,16,−18,−60)
calculation of the cooling-acetone stream with arithmetic expression
   prescriber                                    :11(24,19,−61,−62)
cooling acetic acid to 313 K
   prescriber                                    :11(25,61,−17,−63)
required cooling-water stream
   prescriber                                    :11(26,64,−65,−66)
main stream: mixture of the condensed stream and acetic-acid stream
   mixing                                        :13(43,14,17,−15)
calculation of the amount of fuel gas
   burner                                        :28(48,18,−20)
setting the flue-gas temperature
   prescriber                                    :11(27,20,−67,−79)
flue gas cooling, acetone preheating
   prescriber                                    :11(28,67,−68,−69)
preheating the main stream to distillation temperature
   prescriber                                    :11(29,15,−26,−71)
temperature drop of the flue gas due to preheating the mixture
   prescriber                                    :11(30,68,−42,−70)

SEPARATION OF THE MAIN STREAM

separation of acetone
   prescriber                                    :11(31,26,−35,−28)
recycle
   dividing                                      :14(45,28,−31,−29)
cooling the recycle stock to 313 K
   prescriber                                    :11(32,31,−33,−32)
separation of acetic acid and exit of the product
   prescriber                                    :11(33,29,−30,−25)
cooling of acetic acid
   prescriber                                    :11(34,25,−21,−22)

END OF CALCULATION

   print                                         :2(47)
   stop                                          :8
+
```

Table P.10.2 (1) (cont.)

```
data set number: 10
operating parameters of boxes
calculation of product stream with arithmetic expression
   prescriber                          :1(51b,002)
empty statements to calculate correct stream vectors
   prescriber                          :2(0,106)
   prescriber                          :6(0,106)
   prescriber                          :7(0,106)
calculation of pyrolysis-gas stream of the furnace with arithmetic expression
   prescriber                          :8(52b,002)
setting the temperature of the exit pyrolysis-gas stream
   prescriber                          :12(783,004)
calculation of the fresh-mixture stream with arithmetic expression
   prescriber                          :13(54b,002,1,001)
setting the main stream
   mixing                              :41(_{10}4)
cooling the main stream to dew point
   prescriber                          :14(442,004)
calculation of the cooling-mixture
stream with arithmetic expression
   prescriber                          :15(56b,002)
cooling the mixture
   prescriber                          :16(313,004)
calculation of cooling-water stream with arithmetic expression
   prescriber                          :17(55b,002)
cooling the main stream to liquefaction
   prescriber                          :18(344,004)
separation of the non-condensing fuel gas with change of stream type
   prescriber                          :19(4,001)
empty statements to calculate correct stream vectors
   prescriber                          :20(0,106)
   prescriber                          :21(0,106)
extraction of the heat of condensation with cooling water. Calculation of the cooling-
water stream with arithmetic expression
   prescriber                          :22(63b,002)
   mixing                              :42(_{10}4)
cooling the fuel gas
   prescriber                          :23(313,004)
calculation of the acetic-acid stream temperature
   prescriber                          :24(3e60s,103)
cooling acetic acid
   prescriber                          :25(313,004)
cooling-water-stream calculation with arithmetic expression
   prescriber                          :26(55b,002)
   mixing                              :43(_{10}4)
burning the fuel gas
   burner                              :48(20,1350,313,2,3.8,0,0,−5)
setting the flue-gas temperature
   prescriber                          :27(1100,004)
calculation of the required flue-gas
stream with arithmetic expression
   prescriber                          :28(68b,002,69b,103)
heating the mixture
   prescriber                          :29(350,004)
flue gas cooling as a result of heating the mixture
   prescriber                          :30(3e71s,003)
separation of acetone with change of stream type
```

Table P.10.2 (1) (cont.)

```
  prescriber                                    :31(3,001)
recycle
  dividing                                      :45(2e40s,—1)
cooling the recycle stock
  prescriber                                    :32(313,004)
separation of the product with prescribed composition
  prescriber                                    :33(8e30s,008)
cooling acetic acid
  prescriber                                    :34(313,004)
ARITHMETIC EXPRESSIONS
conversion of the standard mole stream of the product from conventional units of
measure                                         :51(106,3.6103,8103 > ×/,1,60.02 > /,19,
                                                 102.09 > / > + >×)
calculation of the pyrolysis-gas stream of the furnace is based on the loss-free
transformation of its ketene content to the product acetic anhydride
                                                :52(2e30s,9e30s > ×10e8s > /)
molal enthalpy difference of the mixture with temperatures 783 and 313 K
                                                :53(3e3s,3e2s > —)
heat of cooling the pyrolysis gas is used to heat the mixture
                                                :54(3e43s > a,53b > /)
molal-enthalpy difference of the mixture used to cool the main stream
                                                :55(3e39s,3e2s > —)
heat of cooling the main stream to its dew point is used to heat the mixture
                                                :56(3e44s > a,55b > /)
molal enthalpy of heating the cooling water
                                                :57(3e47s,3e6s > —)
heat of cooling the mixture is used to heat the cooling water
                                                :58(3e46s > a,57b > /)
acetone condensate
                                                :3(2e13s,7e13s > ×)
besides containing the anhydride originally present, the anhydride condensate also
contains that formed from ketene
                                                :4(2e13s,9e13s > ×,2e13s,10e13s > × > +)
heat of condensation. Sum of heat extraction from the main stream by cooling and
evaporation and the enthalpy stream of the acetone and anhydride condensate dif-
fers to the same extent as the extraction with the cooling medium
                                                :61(3e50s > a,3e13s > a > + > 3e52s > a,
                                                 3e55s > a > + > —)
molal-enthalpy stream of heating the cooling medium
                                                :62(3e57s,3e6s > —)
extracted heat when condensing the main stream is used to heat the cooling medium
                                                :63(61b,62b > / > a)
acetic-acid stream used to cool the fuel gas equals that quantity which after mixing to
the condensate ensures the prescribed ratio of acetone and anhydride
                                                :64(4b,8e2s > ×,9e2s > /)
prescribed temperature rise of the water stream cooling the warm acetic acid
                                                :65(3e63s > a,62b > /)
acetone input can be calculated from the composition of the pyrolysis gas
                                                :66(2e8s,7e8s > ×,1.33 > ×)
heat load of the radiation zone of the furnace
                                                :67(3e8s,3e7s > —)
fuel-gas stream is the quotient of the heat load and the molal-enthalpy decrease of
the flue gas
                                                :68(67b,3e79s > a > /)
heat load of the convective zone to heat acetone
                                                :69(66b,3e5s > ×,66b,3e7s > × —)
  print                                         :47(5, < 1 = 18,20 = 22,25 = 36,39,40,
+                                                   42 = 62 > s)
```

Table P.10.2 (1) (cont.)

streams
pyrolysis gas leaving furnace
: 8(1,1,0,987,$101_{10}3$,1,
0.578,0,0,0.134,0.189,0.062,
0.030,0.025,0.012)
product : 1(2,1,0,313,$101_{10}3$,0,
0,0.08213,0.91787)
mixture
—fresh : 2(2,1,0,313,$101_{10}3$,0,
0,062964,0.37036)
—high temperature : 3(2,1,0,783,$101_{10}3$,1,
0,062964,0.37036)
—warm :39(2,1,0,373,$101_{10}3$,0,
0,062964,0.37036)

acetone
—fresh : 5(3,1,0,313,$101_{10}3$,0,1)
—evaporated : 7(3,1,0,468,$101_{10}3$,1,1)
—condensed :51(2,1,0,344,$101_{10}3$,0,
1,0,0)

anhydride
—condensed :54(2,1,0,344,$101_{10}3$,0,
0,0,1)

acetic acid
—fresh :19(2,1,0,313,$101_{10}3$,0,
0,1,0)

cooling water
—warm 353K :47(7,1,0,353,$101_{10}3$,0,1)
—warm 323K :57(7,1,0,323,$101_{10}3$,0,1)
—warm 323K :64(7,1,0,323,$101_{10}3$,0,1)
—fresh : 6(7,1,0,303,$101_{10}3$,0,1)
+

Table P.10.2 (2)

Manufacture of acetic anhydride. Calculation results of problem
[Mass- and heat-balance calculations]

```
Mass- and heat-balance of the manufacture of acetic anhydride - 10
:       1s(    2.0000          ,     1.0000           ,         0.0000       ,
             313.00            ,   101.00     10+ 3,            0.0000       ,
               0.0000          ,    82.130    10- 3,          917.87    10- 3)
:       2s(    2.0000          ,     1.0000           ,      -531.43    10+ 6,
             313.00            ,   101.00     10+ 3,            0.0000       ,
               0.0000          ,   629.64     10- 3,          370.36    10- 3)
:       3s(    2.0000          ,     1.0000           ,      -428.05    10+ 6,
             783.00            ,   101.00     10+ 3,            1.0000       ,
               0.0000          ,   629.64     10- 3,          370.36    10- 3)
:       4s(    0.0000          )
:       5s(    3.0000          ,     1.0000           ,      -213.95    10+ 6,
             313.00            ,   101.00     10+ 3,            0.0000       ,
               1.0000          )
:       6s(    7.0000          ,     1.0000           ,      -272.99    10+ 6,
             303.00            ,   101.00        + 3,           0.0000       ,
               1.0000          )
:       7s(    3.0000          ,     1.0000           ,      -168.48    10+ 6,
             468.00            ,   101.00     10+ 3,            1.0000       ,
:       8s(    1.0000          ,    48.227    10- 3,           -3.2027  10+ 6,
             987.00            ,   101.00     10+ 3,            1.0000       ,
             578.00   10- 3,         0.0000           ,         0.0000       ,
             134.00   10- 3,       189.00     10- 3,           32.000   10- 3,
              30.000  10- 3,        25.000    10- 3,           12.000   10- 3)
:       9s(    1.0000          ,    48.227    10- 3,           -4.3680  10+ 6,
             783.00            ,   101.00     10- 3,            1.0000       ,
             578.00   10- 3,         0.0000           ,         0.0000       ,
             134.00   10- 3,       189.00     10- 3,           32.000   10- 3,
              30.000  10- 3,        25.000    10- 3,           12.000   10- 3)
:      10s(    1.0000          ,    59.499    10- 3,           -9.1929  10+ 6,
             782.99            ,   101.00     10+ 3,            1.0000       ,
             468.50   10- 3,       119.28     10- 3,           70.164   10- 3,
             108.61   10- 3,       153.19     10- 3,           25.938   10- 3,
              24.317  10- 3,        20.264    10- 3,            9.7266  10- 3)
:      11s(    1.0000          ,    59.499    10- 3,          -11.359   10+ 6,
             422.00            ,   101.00     10+ 3,            1.0000       ,
             468.50   10- 3,       119.28     10- 3,           70.164   10- 3,
             108.61   10- 3,       153.19     10- 3,           25.938   10- 3,
              24.317  10- 3,        20.264    10- 3,            9.7266  10- 3)
:      12s(    1.0000          ,    59.499    10- 3,          -11.720   10+ 6,
             344.00            ,   101.00     10+ 3,            1.0000       ,
             468.50   10- 3,       119.28     10- 3,           70.164   10- 3,
             108.61   10- 3,       153.19     10- 3,           25.938   10- 3,
              24.317  10- 3,        20.264    10- 3,            9.7266  10- 3)
:      13s(    1.0000          ,    45.610    10- 3,          -10.725   10+ 6,
             344.00            ,   101.00     10+ 3,            1.0000       ,
             611.17   10- 3,       155.61     10- 3,           91.351   10- 3,
             141.69   10- 3,         0.0000           ,         0.0000       ,
               0.0000          ,     0.0000           ,         0.0000       )
:      14s(    2.0000          ,    38.512    10- 3,          -12.418   10+ 6,
             334.89            ,   101.00     10+ 3,            0.0000       ,
             723.80   10- 3,         0.0000           ,       276.20    10- 3)
:      15s(    2.0000          ,    56.596    10- 3,          -21.045   10+ 6,
             328.60            ,   101.00     10+ 3,            0.0000       ,
             492.53   10- 3,       319.52     10- 3,          187.95    10- 3)
:      16s(    4.0000          ,    13.889    10- 3,         -994.68    10+ 3,
```

Table P.10.2 (2) (cont.)

```
             344.00          ,    101.00     10+ 3,       1.0000        ,
             656.25   10− 3,      111.11     10− 3,     104.17    10− 3,
              86.806  10− 3,       41.667    10− 3)
:     17s(     2.0000        ,     18.084    10− 3,      −8.6371  10+ 6,
             313.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,      1.0000        ,       0.0000        )
:     18s(     4.0000        ,     13.889    10− 3,      −1,0114  10+ 6,
             313.00          ,    101.00     10+ 3,       1.0000        ,
             656.25   10− 3,      111.11     10− 3,     104.17    10− 3,
              86.806  10− 3,       41.667    10− 3)
:     20s(    −5.0000        ,    148.95     10− 3,     226.54    10+ 3,
               2.1615 10+ 3,      100.00     10+ 3,       1.0000        ,
              32.054  10− 3,      147.00     10− 3,      99.725   10− 3,
             721.22   10− 3)
:     21s(     2.0000        ,     10.408    10− 3,      −4.9712  10+ 6,
             313.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,      1.0000        ,       0.0000        )
:     22s(     2.0000        ,      0.0000        ,      84.687   10+ 3,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,      1.0000        ,       0.0000        )
:     25s(     2.0000        ,     10.408    10− 3,      −4.8865  10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,      1.0000        ,       0.0000        )
:     26s(     2.0000        ,     56.596    10− 3,     −20.870   10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
             492.53   10− 3,      319.52     10− 3,     187.95    10− 3)
:     27s(     0.0000        )
:     28s(     2.0000        ,     28.721    10− 3,     −15.051   10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     29s(     2.0000        ,     17.449    10− 3,      −9.1443  10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     30s(     2.0000        ,      7.0407   10− 3,      −4.2578  10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,     82.130    10− 3,     917.87    10− 3)
:     31s(     2.0000        ,     11.272    10− 3,      −5.9071  10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     32s(     2.0000        ,      0.0000        ,      83.122   10+ 3,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     33s(     2.0000        ,     11.272    10− 3,      −5.9903  10+ 6,
             313.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     34s(     2.0000        ,    216.50     10− 3,    −112.89    10+ 6,
             373.00          .    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     35s(     3.0000        ,     27.875    10− 3,      −5.8184  10+ 6,
             350.00          ,    101.00     10+ 3,       0.0000        ,
               1.0000        )
:     36s(     2.0000        ,    216.50     10− 3,    −115.06    10+ 6,
             313.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     39s(     2.0000        ,      1.0000        ,    −521.43    10+ 6,
             373.00          ,    101.00     10+ 3,       0.0000        ,
               0.0000        ,    629.64     10− 3,     370.36    10− 3)
:     40s(     1.0000        ,     11.272    10− 3,      −4.8249  10+ 6,
```

Table P.10.2. (2) (cont.)

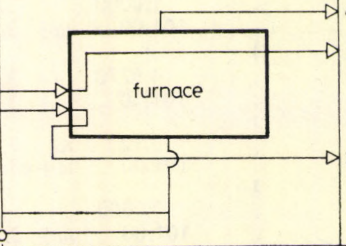
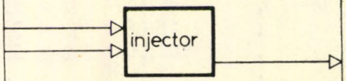
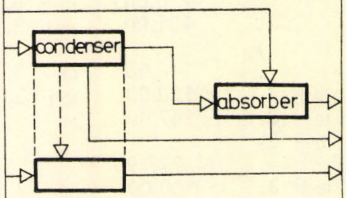
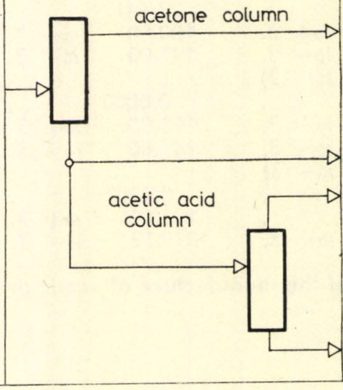
```
              783.00       ,     101.00   10+ 3,      1.0000        ,
              0.0000       ,     629.64   10− 3,     370.36   10− 3,
              0.0000       ,     0.0000        ,      0.0000        ,
              0.0000       ,     0.0000        ,      0.0000        )
:     42s(   −5.0000       ,     27.790        ,    −185.09   10+ 3,
              2.1171 10+ 3,     100.00   10+ 3,      1.0000        ,
              32.054 10− 3,     147.00   10− 3,      99.725        ,
              721.22 10− 3)
:     43s(    1.0000       ,     0.0000        ,      1.1653  10+ 6,
              987.00       ,     101.00   10+ 3,      1.0000        ,
              578.00 10− 3,     0.0000        ,      0.0000        ,
              134.00 10− 3,     189.00   10− 3,      32.000  10− 3,
              30.000 10− 3,     25.000   10− 33      12.000  10− 3)
:     44s(    1.0000       ,     0.0000        ,      2.1658  10+ 6,
              782.99       ,     101.00   10+ 3,      1.0000        ,
              468.50 10− 3,     119.28   10− 3,      70.164  10− 3,
              108.61 10− 3,     153.19   10− 3,      25.938  10− 3,
              24.317 10− 3,     20.264   10− 3,      9.7266  10− 3)
:     45s(    2.0000       ,     783.50   10− 3,    −408.53   10+ 6,
              373.00       ,     101.00   10+ 3,      0.0000        ,
              0.0000       ,     629.64   10− 3,     370.36   10− 3)
:     46s(    2.0000       ,     0.0000        ,      2.1658  10+ 6,
              373.00       ,     101.00   10+ 3,      0.0000        ,
              0.0000       ,     629.64   10− 3,     370.36   10− 3)
:     47s(    7.0000       ,     1.0000        ,      0.0000        ,
              353.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       )
:     48s(    7.0000       ,     10.003   10+ 6,     −2.6883  10+15,
              353.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       )
:     49s(    7.0000       ,    −10.003   10+ 6,      2.6883  10+15,
              353.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       )
:     50s(    1.0000       ,     0.0000        ,     361.17   10+ 3,
              422.00       ,     101.00   10+ 3,      1.0000        ,
              468.50 10− 3,     119.28   10− 3,      70.164  10− 3,
              108.61 10− 3,     153.19   10− 3,      25.938  10− 3,
              24.317 10− 3,     20.264   10− 3,      9.7266  10− 3)
:     51s(    2.0000       ,     27.875   10− 3,      0.0000        ,
              344.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       ,     0.0000        ,      0.0000        )
:     52s(    2.0000       ,     27.875   10− 3,     −5.8427  10+ 6,
              344.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       ,     0.0000        ,      0.0000        )
:     53s(    2.0000       ,     0.0000        ,      0,0000        ,
              344.00       ,     101.00   10+ 3,      0.0000        ,
              1.0000       ,     0.0000        ,      0.0000        )
:     54s(    2.0000       ,     10.637   10− 3,      0.0000        ,
              344.00       ,     101.00   10+ 3,      0.0000        ,
              0.0000       ,     0.0000        ,      1.0000        )
:     55s(    2.0000       ,     10.637   10− 3,     −6.5750  10+ 6,
              344.00       ,     101.00   10+ 3,      0.0000        ,
              0.0000       ,     0.0000        ,      1.0000        )
```

Table P.10.2. (2) (cont.)

```
:      56s(   2.0000          ,    0.0000          ,    0.0000          ,
              344.00          ,    101.00    10+ 3,    0.0000          ,
              0.0000          ,    0.0000          ,    1.0000          )
:      57s(   7.0000          ,    1.0000          ,    0.0000          ,
              323.00          ,    101.00    10+ 3,    0.0000          ,
              1.0000          )
:      58s(   7.0000          ,    4.8770    10- 3,   -1.3233    10+ 6,
              323.00          ,    101.00    10+ 3,    0.0000          ,
              1.0000          )
:      59s(   7.0000          ,    995.12    10  3,   -270.00    10+ 6,
              323.00          ,    101.00    10+g3,    0.0000          ,
              1.0000          )
:      60s(   4.0000          ,    0.0000          ,    16.739    10+ 3,
              344.00          ;    101.00    10+ 3,    1.0000          ,
              656.25    10- 3,    111.11    10- 3,    104.17    10- 3,
              86.806    10- 3,    41.667    10- 3)
:      61s(   2.0000          ,    18.084    10- 3,   -8.6204    10+ 6,
              319.90          ,    101.00    10+ 3,    0.0000          ,
              0.0000          ,    1.0000          ,    0.0000          )
:      62s(   2.0000          ,    0.0000          ,   -16.739    10+ 3,
              313.00          ,    101.00    10+ 3,    0.0000          ,
              0.0000          ,    1.0000          ,    0.0000          )
:      63s(   2.0000          ,    0.0000          ,    16.739    10+ 3,
              319.90          ,    101.00    10+ 3,    0.0000          ,
              0.0000          ,    1.0000          ,    0.0000          )
:      64s(   7.0000          ,    1.0000          ,    0.0000          ,
              323.00          ,    101.00    10+ 3,    0.0000          ,
              1.0000          )
:      65s(   7.0000          ,    10.003    10+ 6,   -2.7141    10+15,
              323.00          ,    101.00    10+ 3,    0.0000          ,
              1.0000          )
:      66s(   7.0000          ,   -10.003    10+ 6,    2.7141    10+15,
              323.00          ,    101.00    10+ 3,    0.0000          ,
              1.0000          )
:      67s(  -5.0000          ,    148.95    10- 3,   -5.7208    10+ 6,
              1.1000    10+ 3,    100.00    10+ 3,    1.0000          ,
              32.054    10- 3,    147.00    10- 3,    99.725    10- 3,
              721.22    10- 3)
:      68s(  -5.0000          ,    27.790          ,   -1.0690    10+ 9,
              1.0984    10+ 3,    100.00    10+ 3,    1.0000          ,
              32.054    10- 3,    147.00    10- 3,    99.725    10- 3,
              721.22    10- 3)
:      69s(  -5.0000          ,   -27.641          ,    1.0633    10+ 9,
              1.1000    10+ 3,    100.00    10+ 3,    1.0000          ,
              32.054    10- 3,    147.00    10- 3,    99.725    10- 3,
              721.22    10- 3)
:      70s(  -5.0000          ,    0.0000          ,   -1.0688    10+ 9,
              1.0984    10+ 3,    100.00    10+ 3,    1.0000          ,
              32.054    10- 3,    147.00    10- 3,    99.725    10- 3,
              721.22    10- 3)
:      71s(   2.0000          ,    0.0000          ,   -185.09    10+ 3,
              328.60          ,    101.00    10+ 3,    0.0000          ,
              492.53    10- 3,    319.52    10- 3,    187.95    10- 3)
+
end Mass- and heat-balance of the manufacture of acetic anhydride
```

Table P.10.3. (1)

The manufacture of acetic anhydride. Selection of unit operations

stream in	mass flow x 10^3	temperature	enth flow x 10^{-6}	connect index	mass and heat balance on	connect index	mass flow x 10^3	temperature	enth flow x 10^{-6}	stream out
					 furnace	42	93.400		-4.6583	stack gases
						8	48.227	873	-3.2027	pyrolysis gas
acetone cold	36.559	313	-7.8200	66b						
still feed (cold)	56.596	328.6	-21.005	15s						
						26	56.596	350	-20.870	still feed (warm)
fuel gas	9.1500	313	-0.6905	18						
air	91.000	313	0.82600	6e8b						
pyrolysis gas	48.227	873	-3.2027	8	 injector					
quench spray	11.272	313	-2.9902	40		10	59.499	782.99	-9.1929	main stream
					 quench tower	11	59.499	422	-11.359	main stream
main stream	59.499	782.99	-9.1929	10						
quench liquid (cold)	216.50	313	115.25	39		34	216.50	373	-112.89	quench liquid (warm)
quench liquid (warm)	216.50	373	-112.89	34	 heat exchanger	36	216.50	313	-115.25	quench liquid (cold)
cooling water		303		47		48		353	2.36	cooling water
acetic acid	18.084	313	-8.6371	19	 condenser absorber					
main stream	59.499	422	-11.359	11						
						18	13.889	313	-1.0114	fuel gas
						15	56.596	328.6	-21.055	still feed cold
cooling water		303		57		58		323	2.07	cooling water
					 acetone column acetic acid column	35	27.875	350	-5.8184	acetone
still feed (warm)	56.596	350	-20.870	26						
						31	11.272	350	-5.9071	recycle stock
						25	10.408	350	-4.8865	acetic acid
						30	7.0407	350	-4.2578	product

PROBLEM P.10.3 THE MANUFACTURE OF ACETIC ANHYDRIDE. SELECTION OF UNIT OPERATIONS BASED ON THE MASS AND HEAT BALANCE

Using the mass and heat balances calculated in the previous problem, select those unit operations which can perform the prescribed state changes.

Solution

If we examine the data of the mass and heat balance along the main process stream together with the side and/or auxiliary streams bringing out the prescribed state change, we can identify the operations (equipment) belonging to the network of the process. The result is summarized in Table P.10.3(1).

As a result, we can prepare the block diagram and the flow-sheet of the process (Fig. 10.5*a*, *b*).

PROBLEM P.10.4 THE MANUFACTURE OF ACETIC ANHYDRIDE. FLOW-SHEETING

From the viewpoint of flow-sheeting, the block including various heat exchangers (furnace, injector, quench column, condenser, absorber) is the most delicate part. In this problem, the flow-sheeting of the heat exchanger block has to be resolved. With the exception of the absorber, all heat exchangers are described with a distributed parametral model. (Flow-sheeting of distillation is left to the next problem.)

Solution

The operation-order flow-sheet is presented in Figure 10.6. The calculation starts with the simulation of the pyrolysis of acetone. (Remember that a four-chamber furnace is needed for constructional reasons, although the calculation relates to one chamber.) We already dealt with a pyrolysis reactor in Problem P.3.12

The box, simulating the reactor

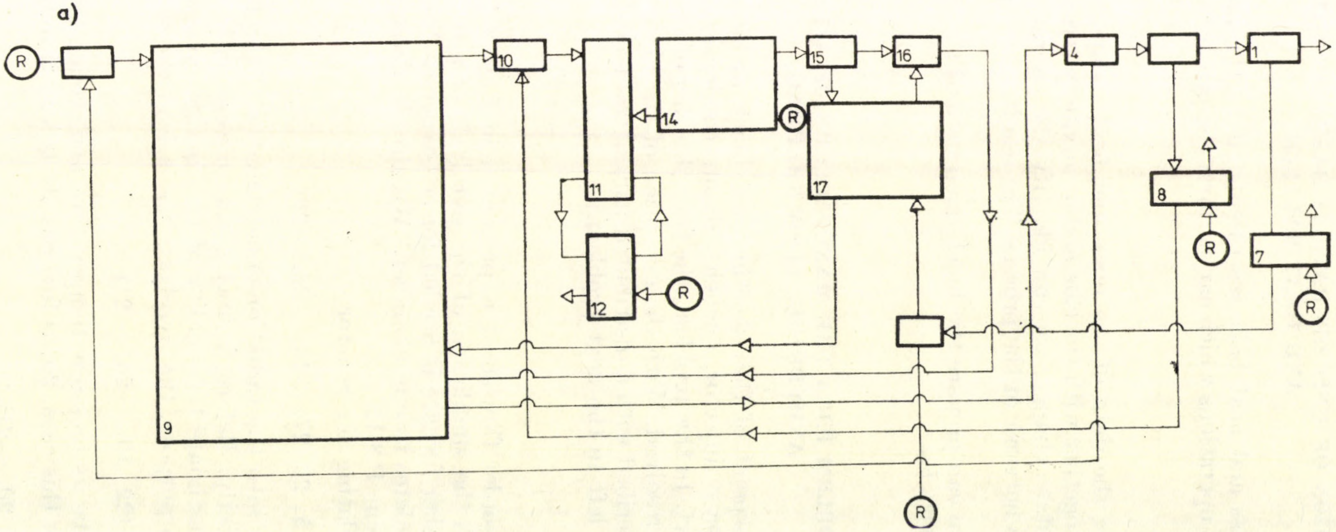
dipa: 46 (14, 15, 26, 27, −19, −28, −29)

has to be placed into the radiation-zone chamber of the furnace. We calculate this indirectly. Before following the process path of the pyrolysis gas (19s), let us estimate the quality of the fuel gas available to heat the furnace. For this purpose, the pyrolysis gas is lead through box

prescriber: 11 (22, 19, −20, −21)

where we prescribe its pressure, temperature and stream type: the latter is to be fuel gas. In this case, 20s is fuel gas. It is lead through box

burner: 28 (31, 20, −21),


a)
R
10
11
14
R
15
16
17
4
1
8
R
7
R
12
R
9
R

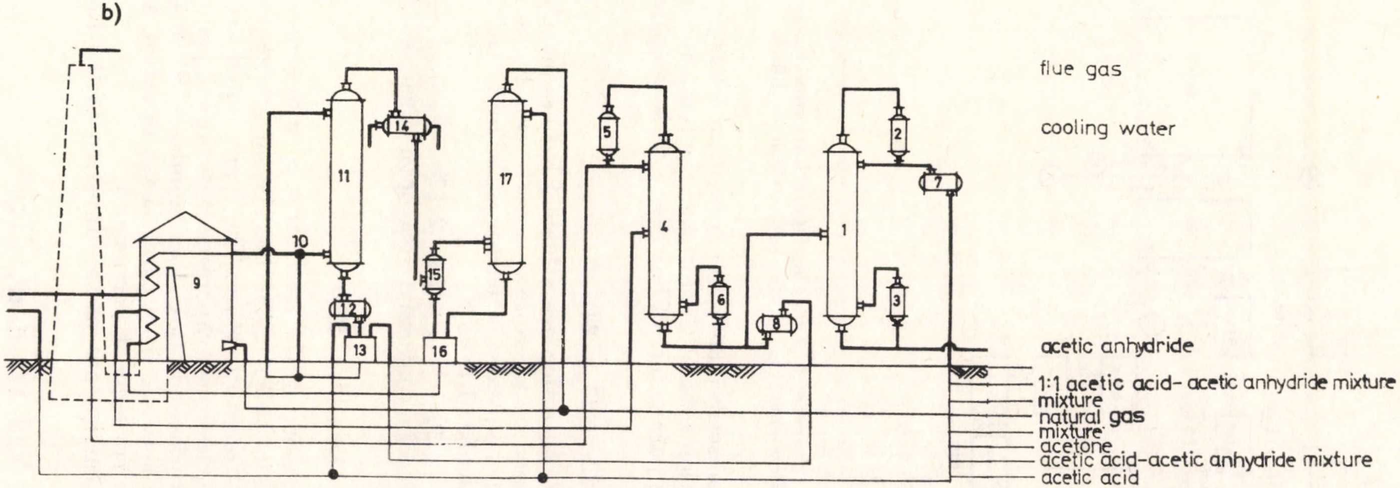


Fig. 10.5. Manufacture of acetic anhydride. *a* Block dia gram of the process. *b*. Flowsheet

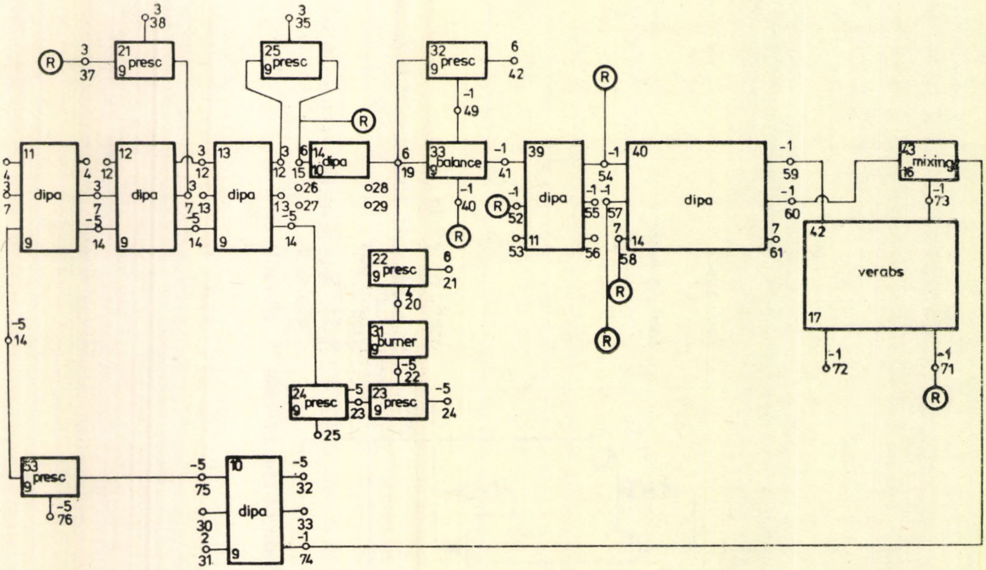


Fig. 10.6. Manufacture of acetic anhydride. Operation-order flow-sheet relating to the flow-sheeting of the heat-exhanger block

and burned with the prescribed 30% air excess it produces high-temperature flue gas. In the radiation zone of the furnace, the temperature is prescribed (among the operating parameters of box *dipa)*. This temperature has to be set by box

prescriber: 11 (23, 22, −23, −24).

The third element of the difference stream 24 consequently indicates the quantity of heat released by the total flue gas stream by radiation. We also know the heat load of the pyrolysis reactor. It follows that the *required* flue gas stream can be calculated from

arithm: 27 (3e15s, 3e19s > −, 3e24s, 2e22s >/>/).

This stream passing into the convective zone of the furnace can be prescribed by box

prescriber: 11 (24, 23, −14, −25).

The flue gas moves along in the convective zone in counter-current with the acetone streaming in the tube. On the tube side, three phenomena occur in succession in the stream direction. The input liquid acetone is heated to its boiling point, the acetone evaporates at its boiling point and the evaporated acetone is overheated. Box *dipa* simulates all these phenomena. We therefore form a network from three boxes in series, and these serve to simulate the three consequent phenomena.

The calculation is carried out in the direction of the flow of flue gas, beginning with box

dipa: 46 (13, −12, −13, 14, 12, 13, −14).

The acetone is overheated in the first phase, the second phase is empty, and flue gas flows in the third phase. Integration is interrupted when the temperature of acetone decreases below 348 K. The initial value of this last step of the integration (performed using the Bunge–Kutta method) is therefore lower than the bound of the independent variable (the length), but the final value bypasses it. Box *dipa* stores these two values of the independent variable in its 5th and 6th operating parameters, and if the step length exceeds the value prescribed in the 7th operating parameter, then a new calculation is required, and is carried out with lower step length. In this case the first operating parameter of box *dipa* is 1. The calculation has to be repeated if the step length becomes lower than the prescribed value, the first operating parameter of box *dipa* shall be 0.

Now the sequence of the calculation must change in order to move to the next box. This is accomplished by box

jump: 5(8),

when the first operating parameter of box *dipa* becomes zero. Calculation of the tube length required to evaporate the acetone now follows using box

dipa: 46 (12, −12, −7, 14, 12, 7, −14).

The calculation is again organized by box

jump: 5(9).

The next box

dipa: 46 (11, −4, −7, 14, 4, 7, −14)

simulates the heating of acetone to boiling point.

This time the integration proceeds to the upper bound of the independent variable (tube length). At the termination of the integration, a value of the temperature of the input acetone, is obtained which may or may not correspond to the initial process data. If it does not, the dimension of the equipment (the tube length) was incorrect and a new calculation is necessary. This recalculation may be effected by a program step, but we have disregarded this here.

The calculation of the convective zone of the furnace is not yet complete, because the hot flue gas may be used to heat some other liquid. This other liquid is the mixture which must be separated in the distilling block. We do not yet know anything about this mixture. Calculation of the convective zone is therefore interrupted and continued with the simulation of processing the gas (19s), leaving the pyrolysis reactor. This gas passes box

prescriber: 11 (32, 19, −49, −42)

which performs computational tasks and enters box

balance: 27 (33, 49, 40, −41, −48, −43) simulating the injector. Here, the main process stream passes box

dipa: 46 (39, 41, −52, 53, −54, 55, −56)

which simulates a packed quench tower. The cooled gas enters the condenser, simulated by box

dipa: 46 (40, 54, 57, 58, −59, −60, −61)

from which a gas (59s) and a liquid phase (60s) exit. The gaseous phase is washed with acetic acid in the next column, simulated by box

verabs: 31 (42, 59, 71, −72, −73).

The fuel gas (72s) leaves this column, whereas the condensed and reacting components (disregarding losses) leave in the liquid stream 73s.

This stream, together with liquid leaving the condenser, constitutes the cold still feed, passing box

mixing: 13 (41, 73, 60, −74),

This feed can be preheated in the convective zone of the furnace. This is again simulated by box

dipa: 46 (10, 75, 30, −34, −32, 33, 74).

The direction of the integration again coincides with the flow direction of the flue gas. The exit temperature of the still feed has to be subjected to the initial conditions of integration. Also the calculated entering temperature of the still feed has to be checked for agreement with the exit temperature of the stream, leaving box *mixing*. This agreement can be achieved by programming, by suitable selection of the relevant parameter of the last box *dipa*.

The flow-sheet program and input data system are presented in Table P.10.4(1), and the results of the calculation in Table P.10.4(2).

Table P.10.4 (1)

Manufacture of acetic anhydride. Flow-sheet program and input data system of problem [Manufacture of anhydride of acetic acid]

```
[Manufacture of anhydride of acetic acid]
B 77 05 12
  stream types
  general          : 1(117,193,194,114,1,26,71,70,67)
  mixture          : 2(117,193,194)
  acetone          : 3(117)
  fuel gas         : 4(1,26,71,70,67)
  flue gas         : 5(64,69,70,72)
  pyrolysis gas    : 6(117,114,1,26,71,70,67)
  water            : 7(69)
+
operations
```

Table P.10.4 (1) (cont.)

```
REACTOR

    dipa           :46(14,15,26,27,-19,-28,-29)
    print          : 2(5)

RADIATION ZONE

    prescriber     :11(22,19,-20,-21)
    burner         :28(31,20,-22)
    prescriber     :11(23,22,-23,-24)
    prescriber     :11(24,23,-14,-25)
    prescriber     :11(25,15,-12,-35)
    print          : 2(6)

CONVECTIVE ZONE

    dipa           :46(13,-12,-13,14,12,13,-14)
    print          : 2(2)
    jump           : 5(8)
    prescriber     :11(21,37,-7,-38)
    dipa           :46(12,-12,  -7,14,12,7,-14)
    jump           : 5(9)
    print          : 2(3)
    dipa           :46(11,-4,-7,14,4,7,-14)
    print          : 2(4)

MIXTURE PREHEATER IN THE CONVECTIVE ZONE

    prescriber     :11(53,14,-75,-76)
    dipa           :46(10,75,30,-34,-32,-33,74)
    prescriber     :11(32,19,-49,-42)

INJECTOR

    balance        :27(33,49,40,-41,-48,-43)
    print          : 2(34)

QUENCH

    dipa           :46(39,41,52,53,-54,-55,-56)
    print          : 2(35)

CONDENSER

    dipa           :46(40,54,57,58,-59,-60,-61)
    print          : 2(36)

ABSORBER

    verabs         :31(42,59,71,-72,-73)
    print          : 2(37)
    mixing         :13(42,73,69,-74)
    print          : 2(38)
   stop            : 4(82)
+
```

Table P.10.4 (1) (cont.)

data set number: 014
operating parameters of the boxes

```
dipa   :14(  10×0,
              0,       66,         ₁₀−3,        2,      26b,      1,    2, 3,
              2,        1,      4.56₁₀−3,   −1591,     1500,      1,    3,

              1,1,1,0,8.2₁₀14,−2.85₁₀8,1,2,1,3,0,
              2,2,2,0,8.2₁₀14,−2.85₁₀8,1,4,2,5,0,
              1,1,1,0,8.2₁₀13,−2.85₁₀8,1,5,1,6,2,7,0,

             −1,       −1,         1001,   0.3194,        4, 0.3194,    550)
dipa   :13(  10×0,
              0,    168.6,        3₁₀−3,      0.2,     ₁₀−4,      2,      0,
              4,       −1,     2.83₁₀−3,    −1591,   −347.9,      1,
             −1,
              4,        1,        3₁₀−3,        0,   −347.9,      1,
          0.099,    43.13)
dipa   :12(  10×0,
          5e13b,    168.6,        3₁₀−3,      0.2,     ₁₀−4,      2,      0,
             12,       −1,     2.83₁₀−3,        0,   −347.9,      1,
             12,       −1,     2.83₁₀−3,        0,   −347.9,      1,
              4,        1,        3₁₀−3,        0,   −347.9,      1,
              0,        0,        0.250,       35,    0.250,     35)
dipa   :11(  10×0,
          5e12b,    168.6,        3₁₀−3,        2,     ₁₀−4,      2,      0,
             −1,
              4,       −1,     2.83₁₀−3,    −1591,     −200,      1,
              4,        1,        3₁₀−3,        0,     −200,      1,
          0.099,    43.13)
dipa   :10(  10×0,
              0,       50,         ₁₀−3,        2,     ₁₀−4,      1,      0,
              4,        1,     5.66₁₀−3,    −1591,     −200,      1,
             −1,
              4,       −1,        3₁₀−3,        0,     −200,      1,
           0.14,    43.13)
dipa   :39(  10×0,
              0,    2.042,         ₁₀−3,        2,     ₁₀−8,  5₁₀−3,      0,
             20,        1,        1.066,        0,     −300,      1,
             20,       −1,         0.41,        0,     −250,      2,
             −1,
         121.16,        0,            0,    8₁₀−3,        0,  2₁₀−2,   13×0,
         121.16,    30.26)
dipa   :40(  10×0,      0,         8.53,
           ₁₀−4,        2,         ₁₀−8,     ₁₀−3,        2,      1,
             20,        1,        0.217,        0,     −273,      5,      0,
             20,        1,         ₁₀−4,        0,     −273,      0,      1,
          1,2,1,    1,4,1,      0, ₁₀3,0,     1,3,        0,
              4,       −1,       0,1152,        0,     −273,      1,      0,
          23.94,     ₁₀−2,            0,     ₁₀−2,        0,   ₁₀−2,      0,
           ₁₀−2,        0,         10×0,    23.94,        0,  23.94,  73.53,
          23.94,    73.53)

verabs  :41(12,1.067,0.907,6.35₁₀−2,7.62₁₀−2,0.762,0.508,
           313,2,0.0762,2,3,0.22,0.0,0,−2.5×0,
           0.075,5919,5216.36,0,0.4,12×0)

mixing  :42(₁₀4)
```

Table P.10.4 (1) (cont.)

```
prescriber     :21(0,106)
prescriber     :22(1.01V5,005,308,004,4,001)
prescriber     :23(63e14b,004)
prescriber     :24(27b,002)
prescriber     :25(3,001)
prescriber     :32(101₁₀3,005,4,202,−1,001)
balance        :33(0,2)
burner         :31(30,1350,313,1,3.85,0,0,0,5)
jump           : 8(9,1,28b)
jump           : 9(13,1,29b)
print          : 1(5,54s, < 57 = 61 > s,40b)
print          : 2(5, < 12 = 15 > s,35s,13b)
print          : 3(5,7s,12s,14s,37s,38s,12b)
print          : 4(5,4s,7s,14s,11b)
print          : 5(5,14s,15s,19s, < 26 = 29 > s,14b)
print          : 6(5,14s, < 19 = 25 > s,31b)
print          : 7(5,59s,60s, < 68 = 70 > s)
print          :34(5,19s, < 40 = 43 > s,48s,49s)
print          :35(5,41s, < 52 = 56 > s,39b >
print          :36(5,14s,30s, < 32 = 34 > s, < 74 = 76 > s,10b)
print          :51(5, < 48 = 50 > s,54s,74s, < 77 = 84 > s,48b,50b)
print          :52(5,62s,69s,73s,74s,42b)
               :55(5,59s, < 71 = 73 > s,42b)
arithm         :26(2e15s,V−2 > ×)
arithm         :27(3e15s,3e19s > −3e24s,2e22s > ₂ > ₂)
arithm         :28(1e13b,₁₀−4 > −)
arithm         :29(1e12b,₁₀−4 > −)
arithm         :44(2e54s,₁₀−3 > ×)
arithm         :45(3e54s,₁₀−3 > ×)
+
streams
aceton rad     :15(6,1.053₁₀−2,0,468,3₁₀5,1,1,6 × 0)
aceton f.      :37(3, ₁₀−12,₁₀−12,3 × 0,1)
feed stiel     :31(2,1.5,0,348.5,1.52₁₀6,0,0.533,0.294,0.173)
cold liquid    :40(−1,11.272₁₀−3,0,313,101₁₀3,0,0,0.62964,0.37036,6 × 0)
liquid         :52(1,0.26532,0,375.6,101325,0,
                   0,062955,0.37045,6 × 0)
water          :58(7,5.43,0,320,101325,0,1)
condens        :57(1,44b,45,4e58s,5e54s,0,0,0,1,6 × 0)
cooled gas     :54(1,62.619₁₀−3,−9.7627₁₀6,460,02.101325,1,507.92₁₀−3,
                   97.731₁₀−3,23.300₁₀−3,118.21₁₀−3,165.83₁₀−3,27.925₁₀−3,
                   46.805₁₀−3,2.2322₁₀−3,10.045₁₀−3)
acetic acid    :71(1,18.084₁₀—3,0,313,101325,1,1,1,7 × 0)
+
```

Table P.10.4 (2)

Manufacture of acetic anhydride. Calculation results of problem [Manufacture of acetic anhydride −14] flow-sheeting the heat-exchanger block

```
Manufacture of acetic anhydride -14
:        15s(     6.0000          ,     10.530    10- 3,      0.0000         ,
                468.00            ,    300.00     10+ 3,      1.0000         ,
                  1.0000          ,      0.0000        ,      0.0000         ,
                  0.0000          ,      0.0000        ,      0.0000         ,
                  0.0000          )
:        19s(     6.0000          ,     13.582    10- 3,   -899.32    10+ 3,
                987.00            ,    194.99     10+ 3,      1.0000         ,
                585.24    10- 3,       172.63     10- 3,    172.79    10- 3,
                 75.570   10- 6,        17.430    10- 3,     17.279   10- 3,
                 34.557   10- 3)
:     63e14b(     1.0010  10+ 3)
+
:        14s(    -5.0000          ,     23.840    10- 3,   -871.17    10+ 3,
                  1.0010  10+ 3,       100.00     10+ 3,      1.0000         ,
                 44.403   10- 3,       151.39     10- 3,     82.663   10- 3,
                721.55    10- 3)
:        19s(     6.0000          ,     13.582    10- 3,   -899.32    10+ 3,
                987.00            ,    194.99     10+ 3,      1.0000         ,
                585.24    10- 3,       172.63     10- 3,    172.79    10- 3,
                 75.570   10- 6,        17.430    10- 3,     17.279   10- 3,
                 34.557   10- 3)
:        20s(     4.0000          ,      3.2885   10- 3,   -243.39    10+ 3,
                308.00            ,    101.00     10+ 3,      1.0000         ,
                713.62    10- 3,       312.11     10- 6,     71.986   10- 3,
                 71.362   10- 3,       142.72     10- 3)
:        21s(     6.0000          ,     10.293    10- 3,   -655.94    10+ 3,
                987.00            ,    194.99     10+ 3,      1.0000         ,
                772.21    10- 3,       227.79     10- 3,      0.0000         ,
                  0.0000          ,      0.0000        ,      0,0000         ,
                  0.0000          )
:        22s(    -5.0000          ,     34.117    10- 3,     40.289   10+ 3,
                  2.0064  10+ 3,       100.00     10+ 3,      1.0000         ,
                 44.403   10- 3,       151.39     10- 3,     82.663   10- 3,
                721.55    10- 3)
:        23s(    -5.0000          ,     34.117    10- 3,     -1.2467  10+ 6,
                  1.0010  10+ 3,       100.00     10+ 3,      1.0000         ,
                 44.403   10- 3,       151.39     10- 3,     82.663   10- 3,
                721.55    10- 3)
:        24s(    -5.0000          ,      0.0000        ,      1.2870  10+ 6,
                  2.0064  10+ 3,       100.00     10+ 3,      1.0000         ,
                 44.403   10- 3,       151.39     10- 3,     82.663   10- 3,
                721.55    10- 3)
:        25s(    -5.0000          ,     10.277    10- 3,   -375.53    10+ 3,
                  1.0010  10+ 3,       100.00     10+ 3,      1.0000         ,
                 44.403   10- 3,       151.39     10- 3,     82.663   10- 3,
                721.55    10- 3)
:        12s(     3.0000          ,     10.530    10- 3,     -1.7763  10+ 6,
                468.00            ,    300.00     10+ 3,      1.0000         ,
                  1.0000          )
+
:        12s(     3.0000          ,     10.530    10- 3,     -1.8713  10+ 6,
                379.25            ,    366.11     10+ 3,      1.0000         ,
                  1.0000          )
:        14s(    -5.0000          ,     23.840    10- 3,   -963.73    10+ 3,
                891.61            ,    100.00     10+ 3,      1.0000         ,
```

Table P. 10.4. (2) (cont.)

```
                44.403   10− 3,     151.39   10− 3,      82.663   10− 3,
               721.55    10− 3)
:      13b(      1.0000       ,     −95.069  10+ 3,       0.0000       ,
               −92.563   10+ 3,      41.551       ,      64.227        ,
               505.80    10− 3,       0.0000      ,       0.0000       ,
                 0.0000       ,       0.0000      ,     168.60         ,
                 3.0000  10− 3,     200.00   10− 3,     100.00    10− 6,
                 2.0000       ,       0.0000      ,       4.0000       ,
                −1.0000       ,       2.8300 10− 3,      −1.5910  10+ 3,
              −347.90         ,       1.0000      ,      −1.0000       ,
                 4.0000       ,       1.0000      ,       3.0000  10− 3,
                 0.0000       ,    −347.90        ,       1.0000       ,
                99.000   10− 3,      43.130       )
:    5e13b(     41.551        )
+
:      12s(      3.0000       ,      10.530  10− 3,      −1.8880  10+ 6,
               361.84         ,     378.13   10+ 3,       1.0000       ,
                 1.0000       )
:      14s(     −5.0000       ,      23.840  10− 3,    −980.23    10+ 3,
               871.83         ,     100.00   10+ 3,       1.0000       ,
                44.403   10− 3,     151.39   10− 3,      82.663   10− 3,
               721.55    10− 3)
:      13b(      1.0000       ,    −111.74   10+ 3,       0.0000       ,
               −16.496   10+ 3,      49.109       ,      60.443        ,
               505.80    10− 3,       0.0000      ,       0.0000       ,
                 0.0000   −   ,       0.0000      ,     168.60         ,
                 3.0000  10− 3,     200.00   10− 3,     100.00    10− 6,
                 2.0000       ,       0.0000      ,       4.0000       ,
                −1.0000       ,       2.8300 10− 3,      −1.5910  10+ 3,
              −347.90         ,       1.0000      ,      −1.0000       ,
                 4.0000       ,       1.0000      ,       3.0000  10− 3,
                 0.0000       ,    −347.90        ,       1.0000       ,
                99.000   10− 3,      43.130       )
:    5e13b(     49.109        )
+
:      12s(      3.0000       ,      10.530  10− 3,      −1.8957  10+ 6,
               352.94         ,     384.14   10+ 3,       1.0000       ,
                 1.0000       )
:      14s(     −5.0000       ,      23.840  10− 3,    −988.45    10+ 3,
               861.94         ,     100.00   10+ 3,       1.0000       ,
                44.403   10− 3,     151.39   10− 3,      82.663   10− 3,
               721.55    10− 3)
:      13b(      1.0000       ,    −119.41   10+ 3,       0.0000       ,
                −8.2174  10+ 3,      52.887       ,      58.554        ,
               505.80    10− 3,       0.0000      ,       0.0000       ,
                 0.0000       ,       0.0000      ,     168.60         ,
                 3.0000  10− 3,     200.00   10− 3,     100.00    10− 6,
                 2.0000       ,       0.0000      ,       4.0000       ,
                −1.0000       ,       2.8300 10− 3,      −1.5910  10+ 3,
              −347.90         ,       1.0000      ,      −1.0000       ,
                 4.0000       ,       1.0000      ,       3.0000  10− 3,
                 0.0000       ,    −347.90        ,       1.0000       ,
                99.000   10− 3,      43.130       )
:    5e13b(     52.887        )
+
:      12s(      3.0000       ,      10.530  10− 3,      −1.8994  10+ 6,
               348.43         ,     387.15   10+ 3,       1.0000       ,
                 1.0000       )
```

Table P.10.4. (2) (cont.)

```
:     14s(     -5.0000          ,     23.840   10- 3,   -992.55   10+ 3,
               856.99           ,     100.00   10+ 3,    1.0000        ,
                44.403   10- 3,       151.39   10- 3,    82.663   10- 3,
               721.55    10- 3)
:     13b(      1.0000          ,    -123.15   10+ 3,    0.0000        ,
               -4.1024   10+ 3,       54.776        ,    57.610        ,
               505.80    10- 3,       0.0000        ,    0.0000        ,
                0.0000          ,     0.0000        ,    168.60        ,
                3.0000   10- 3,       200.00   10- 3,    100.00    10- 6,
                2.0000          ,     0.0000        ,    4.0000        ,
               -1.0000          ,     2.8300   10- 3,   -1.5910    10+ 3,
             -347.90            ,     1.0000        ,   -1.0000        ,
                4.0000          ,     1.0000        ,    3.0000    10- 3,
                0.0000          ,    -347.90        ,    1.0000        ,
               99.000    10- 3,       43.130        )
:   5e13b(     54.776           )
+
:     12s(      3.0000          ,     103.75   10- 6,   -18.715    10+ 3,
               348.43           ,     387.15   10+ 3,    1.0000        ,
                1.0000          )
:      7s(      3.0000          ,     10.426   10- 3,   -2.1787    10+ 6,
               348.43           ,     387.15   10+ 3,    0.0000        ,
                1.0000          )
:     14s(     -5.0000          ,     23.840   10- 3,   -1.2923    10+ 6,
               478.40           ,     100.00   10+ 3,    1.0000        ,
                44.403   10- 3,       151.39   10- 3,    82.663    10- 3,
               721.55    10- 3)
:     12b(      0.0000          ,     1.8807   10+ 6,   -2.1787    10+ 6,
             -478.01            ,     115.86        ,    116.17        ,
               341.47    10- 3,       0.0000        ,    0,0000        ,
                0.0000          ,     54.776        ,    168.60        ,
                3.0000   10- 3,       200.00   10- 3,    100.00    10- 6,
                2.0000          ,     0.0000        ,    12.000        ,
               -1.0000          ,     2.8300   10- 3,    0.0000        ,
             -347.90            ,     1.0000        ,    12.000        ,
               -1.0000          ,     2.8300   10- 3,    0.0000        ,
             -347.90            ,     1.0000        ,    4.0000        ,
                1.0000          ,     3.0000   10- 3,    0.0000        ,
             -347.90            ,     1.0000        ,    0.0000        ,
                0.0000          ,     250.00   10- 3,    35.000        ,
               250.00    10- 3,       35.000        )
:   5e12b(    115.86            )
+
:      7s(      3.0000          ,     10.426   10- 3,   -2.2275    10+ 6,
               315.27           ,     471.06   10+ 3,    0.0000        ,
                1.0000          )
:     14s(     -5.0000          ,     23.840   10- 3,   -1.3209    10+ 6,
               440.29           ,     100.00   10+ 3,    1.0000        ,
                44.403   10- 3,       151.39   10- 3,    82.663    10- 3,
               721.55    10- 3)
:     11b(      0.0000          ,     0.0000        ,   -48.816    10+ 3,
              -28.668    10+ 3,       168.60        ,    168.60        ,
                0.0000          ,     0.0000        ,    0.0000        ,
                0.0000          ,     115.86        ,    168.60        ,
                3.0000   10- 3,       2.0000        ,    100.00    10- 6,
                2.0000          ,     0.0000        ,   -1.0000        ,
                4.0000          ,    -1.0000        ,    2.8300    10- 3,
               -1.5910   10+ 3,      -200.00        ,    1.0000        ,
```

Table P.10.4. (2) (cont.)

```
                   4.0000          ,       1.0000          ,         3.0000  10− 3,
                   0.0000          ,    −200.00            ,         1.0000       ,
                  99.000   10− 3,         43.130           )
:    5e11b(      168.60            )
+
+
:      19s(        6.0000          ,      13.582    10− 3,      −899.32    10+ 3,
                 987.00            ,     194.99     10+ 3,         1.0000       ,
                 585.24    10− 3,        172.63     10− 3,       172.79    10− 3,
                  75.570   10− 6,         17.430    10− 3,        17.279   10− 3,
                  34.557   10− 3)
:      40s(       −1.0000          ,      11.272    10− 3,         0.0000       ,
                 313.00            ,     101.00     10+ 3,         0.0000       ,
                   0.0000          ,     629.64     10− 3,       370.36    10− 3,
                   0.0000          ,       0.0000          ,       0.0000       ,
                   0.0000          ,       0.0000          ,       0.0000       )
:      41s(       −1.0000          ,      65.599    10− 3,       −9.5869   10+ 6,
                 802.14            ,     101.00     10+ 3,         1.0000       ,
                 484.68    10− 3,        908.19     10− 3,        63.640   10− 3,
                 142.97    10− 3,        143.10     10− 3,        62.585   10− 6,
                  14.435   10− 3,         14.310    10− 3,        28.619   10− 3)
:      49s(       −1.0000          ,      54.327    10− 3,       −3.5967   10+ 6,
                 987.00            ,     101.00     10+ 3,         1.0000       ,
                 585.24    10− 3,          0.0000          ,       0.0000       ,
                 172.63    10− 3,        172.79     10− 3,        75.570   10− 6,
                  17.430   10− 3,         17.279    10− 3,        34.557   10− 3)
+
:      41s(       −1.0000          ,      65.599    10− 3,       −9.5869   10+ 6,
                 802.14            ,     101.00     10+ 3,         1.0000       ,
                 484.68    10− 3,        108.19     10− 3,        63.640   10− 3,
                 142.97    10− 3,        143.10     10− 3,        62.585   10− 6,
                  14.435   10− 3,         14.310    10− 3,        28.619   10− 3)
:      52s(        1.0000          ,     265.32     10− 3,         0.0000       ,
                 375.60            ,     101.00     10+ 3,         0.0000       ,
                   0.0000          ,     620.00     10− 3,       380.00    10− 3,
                   0.0000          ,       0.0000          ,       0.0000       ,
                   0.0000          ,       0.0000          ,       0.0000       )
:      53s(        0.0000          )
:      54s(       −1.0000          ,      58.832    10− 3,       −8.6760   10− 6,
                 450.42            ,     101.00     10+ 3,         1.0000       ,
                 540.43    10− 3,         62.733    10− 3,        13.838   10− 3,
                 159.41    10− 3,        159.56     10− 3,        69.783   10− 6,
                  16.095   10− 3,         15.956    10− 3,        31.911   10− 3)
:      55s(        1.0000          ,     285.55     10− 3,      −139.20    10+ 6,
                 274.37            ,     101.00     10+ 3,         0.0000       ,
                   0.0000          ,     623.05     10− 3,       376.95    10− 3,
                   0.0000          ,       0.0000          ,       0.0000       ,
                   0.0000          ,       0.0000          ,       0.0000       )
+
:      54s(       −1.0000          ,      58.832    10− 3,       −8.6760   10+ 6,
                 450.42            ,     101.00     10+ 3,         1.0000       ,
                 540.43    10− 3,         62.733    10− 3,        13.838   10− 3,
                 159.41    10− 3,        159.56     10− 3,        69.783   10− 6,
                  16.095   10− 3,         15.956    10− 3,        31.911   10− 3)
:      57s(        1.0000          ,       1.0000   10−12,         0.0000       ,
                 450.42            ,     101.00     10+ 3,         1.0000       ,
                   0.0000          ,       1.0000          ,       0.0000       ,
                   0.0000          ,       0.0000          ,       0.0000       ,
```

Table P.10.4. (2) (cont.)

```
              0.0000          ,      0.0000          ,      0.0000          )
:     58s(    0.0000          )
:     59s(   −1.0000          ,     23.340    10− 3,     −2.6348    10+ 6,
            450.42            ,    101.00     10+ 3,      1.0000          ,
            303.76     10− 3,       35.261    10− 3,      7.7780    10− 3,
             89.603    10− 3,      402.19     10− 3,    175.90      10− 6,
             40.571    10− 3,       40.219    10− 3,     80.436     10− 3)
:     60s(    1.0000          ,     35.495    10− 3,     −6.0451    10+ 6,
            450.42            ,    101.00     10+ 3,      0.0000          ,
            696.03     10− 3,       80.810    10− 3,     17.838     10− 3,
            205.32     10− 3,        0.0000          ,      0.0000          ,
              0.0000          ,      0.0000          ,      0.0000          )
+
:     59s(   −1.0000          ,     23.340    10− 3,     −2.7922    10+ 6,
            337.00            ,    101.00     10+ 3,      1.0000          ,
            303.76     10− 3,       35.261    10− 3,      7.7780    10− 3,
             89.603    10− 3,      402.19     10− 3,    175.90      10− 6,
             40.571    10− 3,       40.219    10− 3,     80.436     10− 3)
:     71s(    1.0000          ,     18.084    10− 3,      0.0000          ,
            313.00            ,    101.00     10+ 3,      0.0000          ,
              0.0000          ,      1.0000          ,      0.0000          ,
              0.0000          ,      0.0000          ,      0.0000          ,
              0.0000          ,      0.0000          ,      0.0000          )
:     72s(   −1.0000          ,     14.189    10− 3,   −101.22      10+ 6,
            313.00            ,    101.00     10+ 3,      1.0000          ,
              2.0896   10− 3,       58.003    10− 3,     12.794     10− 3,
             30.499    10− 6,      661.59     10− 3,    289.35      10− 6,
             66.736    10− 3,       66.159    10− 3,    132.31      10− 3)
:     73s(    1.0000          ,     25.144    10− 3,   −415.33      10+ 6,
            313.00            ,    101.00     10+ 3,      0.0000          ,
            280.79     10− 3,      636.06     10− 3,     83.157     10− 3,
              0.0000          ,      0.0000          ,      0.0000          ,
              0.0000          ,      0.0000          ,      0.0000          )
:     74s(    1.0000          ,     53.351    10− 3,
            313.00            ,    101.00     10+ 3,      0.0000          ,
            464.00     10− 3,      388.00     10− 3,    148.00      10− 3,
+
end Manufacture of acetic anhydride
```

PROBLEM P.10.5 MANUFACTURE OF ACETIC ANHYDRIDE. FLOW-SHEETING OF THE DISTILLATION BLOCK AND DIMENSIONING OF THE ACETONE COLUMN

Simulate the distillation block as the last part of the process discussed. Consider that part of the acetic acid–acetic anhydride mixture leaving the acetone column has to be utilized as recycle stock. Assume that the plate efficiency is unity, when flow-sheeting. Starting from the results of the preliminary flow-sheeting, find more favourable values for the number of plates and the reflux ratio of the acetone column. Consider the column efficiency in these calculations.

Solution

The operation-order flow-sheet is presented in Figure 10.7, the flow-sheet program and input data system in Table P.10.5(1), and the results of the calculation in Table P.10.5(2).

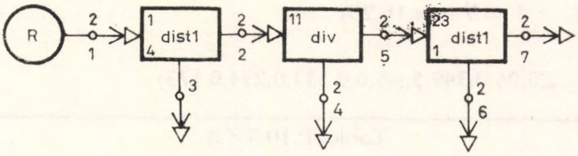


Fig. 10.7. Manufacture of acetic anhydride. Operation-order flow-sheet relating to the flow-sheeting of the distilling block

When dealing with the dimensions of the acetone column, a series of calculations have to be executed. This is organized by box *vary*, for four different numbers of plates and in each case with three different reflux ratios. The flow-sheet program of this calculation is presented in Table P.10.5(3), and the results of the calculation in Table P.10.5(4). The most important results are summarized in Table P.10.5(5).

It is apparent that the conditions regardingt he quality of the top product determine the range of feasible solutions. If no more than 1% acetic acid is allowed in the acetone, then a column with 8 plates is useless. The reflux ratio has to be 2 with 12 plates, 1 with 16 plates and 0.5 with 20 plates.

If, however, the contamination of acetone should not exceed 0.5%, then the reflux ratio must be 5 with 12 plates, 2 with 16 plates and 1 with 20 plates.

Provided we do not define an objective function to evaluate the economy of distillation, there is no meaning in an optimal solution.

In such cases, the unprogrammed decision rests with chemical engineering considerations, also examining a number of aspects which have not been discussed.

Table P.10.5 (1)

Manufacture of acetic anhydride. Flow-sheet program and input data system of problem [distilling block]

```
[Distilling block]
A770128
Stream types
mixture       : 2(117,193,194)
+
operations
distl        :23(1,1,−3,−2)
div:         :14(11,2,−4,−5)
dist         :23(2,5,−6,−7)
print         :2(21)
stop          : 4(30)
+
data set number: 01,
boxes
operating parameters
distl         : 1(16,9,1,2,5×1,330,330,393,4×0,1,1)
div          :11(0.0085,−1)
distl         : 2(10,6,2,3,4×1,5,390,390,412,4×0,2,1)
print        :21(5, < 1 = 7 > s,1b,2b)
+
streams
mixture       : 1(−2,0,06,0,349,5,₁₀5,0,0,533,0,294,0.173)
+
```

Table P.10.5 (2)

Manufacure of acetic anhydride. Calculation results of flow-sheeting the [distilling block]

```
Distilling block  −     1
:          1s(     −2.0000          ,       60.000  ₁₀− 3,      −21.166   ₁₀+ 6,
                   349.50           ,      100.00   ₁₀+ 3,      106.88    ₁₀− 3,
                   533.00   ₁₀− 3,        294.00   ₁₀− 3,      173.00    ₁₀− 3)
:          2s(     −2.0000          ,       28.021  ₁₀− 3,      −14.479   ₁₀+ 6,
                   398.50           ,      100.00   ₁₀+ 3,        0.0000        ,
                    41.479  ₁₀− 6,        629.52   ₁₀− 3,      370.43    ₁₀− 3)
:          3s(     −2.0000          ,       31.979  ₁₀− 3,      −6.7608   ₁₀+ 6,
                   330.00           ,      100.00   ₁₀+ 3,        0.0000        ,
                     1.0000         ,        0.0000      ,        0.0000        )
:          4s(     −2.0000          ,        8.5000 ₁₀− 3,      −4.3921   ₁₀+ 6,
                   398.50           ,      100.00   ₁₀+ 3,        0,0000        ,
                    41.479  ₁₀− 6,        629.52   ₁₀− 3,      370.43    ₁₀− 3)
:          5s(     −2.0000          ,       19.521  ₁₀− 3,      −10.087   ₁₀+ 6,
                   398.50           ,      100.00   ₁₀+ 3,        0.0000        ,
                    41.479  ₁₀− 6,        629.52   ₁₀− 3,      370.43    ₁₀− 3)
:          6s(      0.0000          )
:          7s(      0.0000          )
:          1b(     16.000           ,        9.0000      ,        1.0000        ,
                     2.0000         ,        1.0000      ,        1.0000        ,
                     1.0000         ,        1.0000      ,        1.0000        ,
                   330.00           ,      330.00        ,      393.00          ,
                    99.996          ,      100.00        ,      −1.9159   ₁₀+ 6,
                     1.8424 ₁₀+ 6,          1.0000      ,        1.0000        )
:          2b(     10.000           ,        6.0000      ,        2.0000        ,
                     3.0000         ,        1.0000      ,        1.0000        ,
                     1.0000         ,        1.0000      ,        1.0000        ,
                   390.00           ,      390.00        ,      412.00          ,
                     0.0000         ,        0.0000      ,        0.0000        ,
                     0.0000         ,        2.0000      ,        1.0000        ),
+
end distilling block
```

Table P.10.5 (3)

Manufacture of acetic anhydride. Flow-sheet program and input data system of problem [Design of acetone distillation unit]

```
[Design of acetone distillation unit]
A 770311
stream type
still feed    : 2(117, 193, 194)
+
operations
print         : 2(5)
vary          : 6(1)
∧
dist1         :23(10,1, −2, −3)
print         : 2(4)
∨
stop          : 4(11)
+
data set no. :11
operating parameters of boxes
vary          : 1(0,12,3,2, 1e10b, 2e10b, 9e10b,
                 20,11,5
                 20,11,1
                 20,11,0.5,
                 16, 9,5,
                 16,9,2,
                 16,9,1
                 12, 7,5,
                 12, 7,2
                 12,7,1
                 8,5,5,
                 8,5,2,
                 8,5,1)
dist1         :10(20,11,1,2,1,1,1,1,5,330, 330,
                 393, 0,0,0,0,5,0)
print         : 4(5, < 2 = 3 > s, 10b)
print         : 5(5, 1s, 1b)
+
stream
still feed    : 1(−2, 60_{10}−3, 0, 349.5, 1_{10} 5,)
+
```

Table P.10.5 (4)

Manufacture of acetic anhydride. Calculation results of problem [Design of acetone distillation unit]

```
Design of acetone distillation unit  — 11
:          1s(     −2.0000          ,      60.000   10− 3,      −21.166   10+ 6,
                   349.50           ,     100.00    10+ 3,      106.88    10− 3,
                   533.00    10− 3,       294.00    10− 3,      173.00    10− 3)
:          1b(      0.0000          ,      12.000         ,       3.0000        ,
                    2.0000          ,      20.000         ,      11.000         ,
                    5.0000          ,      20.000         ,      11.000         ,
                    5.0000          ,      20.000         ,      11.000         ,
                    1.0000          ,      20.000         ,      11.000         ,
                   500.00    10− 3,        16.000         ,       9.0000        ,
                    5.0000          ,      16.000         ,       9.0000        ,
                    2.0000          ,      16.000         ,       9.0000        ,
                    1.0000          ,      12.000         ,       7.0000        ,
                    5.0000          ,      12.000         ,       7.0000        ,
                    2.0000          ,      12.000         ,       7.0000        ,
                    1.0000          ,       8.0000        ,       5.0000        ,
                    5.0000          ,       8.0000        ,       5.0000        ,
                    2.0000          ,       8.0000        ,       5.0000        ,
                    1.0000          )
+
:          2s(     −2.0000          ,      31.970   10− 3,       −6.7595  10+ 6,
                   330.00           ,     100.00    10+ 3,        0.0000        ,
                   999.95    10− 3,        51.762   10− 6,        0.0000        )
:          3s(     −2.0000          ,      28.030   10− 3,      −14.481   10+ 6,
                   398.43           ,     100.00    10+ 3,        0.0000        ,
                   406.53    10− 6,       629.27    10− 3,      370.32    10− 3)
:         10b(     20.000           ,      11.000         ,       1.0000        ,
                    2.0000          ,       1.0000        ,       1.0000        ,
                    1.0000          ,       1.0000        ,       5.0000        ,
                   330.00           ,     330.00          ,     393.00          ,
                    99.964          ,      99.991         ,      −5.7465  10+ 6,
                     5.6727  10+ 6,         5.0000        ,     410.04    10− 3)
+
:          2s(     −2.0000          ,      31.933   10− 3,       −6.7555  10+ 6,
                   330.00           ,     100.00    10+ 3,        0.0000        ,
                   999.49    10− 3,       509.65    10− 6,        0.0000        )
:          3s(     −2.0000          ,      28.067   10− 3,      −14.486   10+ 6,
                   398.11           ,     100.00    10+ 3,        0.0000        ,
                     2.2499  10− 3,       627.92    10− 3,      369.83    10− 3)
:         10b(     20.000           ,      11.000         ,       1.0000        ,
                    2.0000          ,       1.0000        ,       1.0000        ,
                    1.0000          ,       1.0000        ,       1.0000        ,
                   330.00           ,     330.00          ,     393.00          ,
                    99.803          ,      99.908         ,      −1.9144  10+ 6,
                     1.8395  10+ 6,         1.0000        ,     410.04    10− 3)
+
:          2s(     −2.0000          ,      31.814   10− 3,       −6.7620  10+ 6,
                   330.00           ,     100.00    10+ 3,        0.0000        ,
                   995.72    10− 3,         4.2700  10− 3,       11.890   10− 6)
:          3s(     −2.0000          ,      28.186   10− 3,      −14.485   10+ 6,
                   396.67           ,     100.00    10+ 3,        0.0000        ,
                    10.709   10− 3,       621.03    10− 3,      368.26    10− 3)
:         10b(     20.000           ,      11.000         ,       1.0000        ,
                    2.0000          ,       1.0000        ,       1.0000        ,
                    1.0000          ,       1.0000        ,     500.00    10− 3,
                   330.00           ,     330.00          ,     393.00
```

Table P.10.5 (4) (cont.)

```
              99.056         ,     99.230          ,     -1.4370  10+ 6,
               1.3567 10+ 6,      500.00    10- 3,      410.04   10- 3)
+
:   2s(      -2.0000         ,     31.939    10- 3,     -6.7547  10+ 6,
             330.00          ,    100.00     10+ 3,      0.0000       ,
             999.72   10- 3,      276.42    10- 6,      0.0000       )
:   3s(      -2.0000         ,     28.061    10- 3,    -14.486   10+ 6,
             398.19          ,    100.00     10+ 3,      0.0000       ,
               1.7780 10- 3,      628.31    10- 3,    369.91    10- 3)
:  10b(       16.000         ,      9.0000         ,      1.0000       ,
               2.0000        ,      1.0000         ,      1.0000       ,
               1.0000        ,      1.0000         ,      5.0000       ,
             330.00          ,    330.00           ,    393.00         ,
              99.844         ,     99.950          ,     -5.7424  10+ 6,
               5.6679 10+ 6,        5.0000         ,    410.04    10- 3)
+
:   2s(      -2.0000         ,     31.934    10- 3,     -6.7560  10+ 6,
             330.00          ,    100.00     10+ 3,      0.0000       ,
             999.44   10- 3,      563.65    10- 6,      0.0000       )
:   3s(      -2.0000         ,     28.061    10- 3,    -14.486   10+ 6,
             398.10          ,    100.00     10+ 3,      0.0000       ,
               2.2972 10- 3,      627.87    10- 3,    369.84    10- 3)
:  10b(       16.000         ,      9.0000         ,      1.0000       ,
               2.0000        ,      1.0000         ,      1.0000       ,
               1.0000        ,      1.0000         ,      2.0000       ,
             330.00          ,    330.00           ,    393.00         ,
              99.798         ,     99.898          ,     -2.8716  10+ 6,
               2.7969 10+ 6,        2.0000         ,    410.04    10- 3)
+
:   2s(      -2.0000         ,     31.882    10- 3,     -6.7570  10+ 6,
             330.00          ,    100.00     10+ 3,      0.0000       ,
             998.03   10- 3,        1.9632  10- 3,      2.4373  10- 6)
:   3s(      -2.0000         ,     28.118    10- 3,    -14.486   10+ 6,
             397.52          ,    100.00     10+ 3,      0.0000       ,
               5.6986 10- 3,      625.14    10- 3,    369.16    10- 3)
:  10b(       16.000         ,      9.0000         ,      1.0000       ,
               2.0000        ,      1.0000         ,      1.0000       ,
               1.0000        ,      1.0000         ,      1.0000       ,
             330.00          ,    330.00           ,    393.00         ,
              99.499         ,     99.645          ,     -1.9148  10+ 6,
               1.8377 10+ 6,        1.0000         ,    410.04    10- 3)
+
:   2s(      -2.0000         ,     31.868    10- 3,     -6.7508  10+ 6,
             330.00          ,    100.00     10+ 3,      0.0000       ,
             998.40   10- 3,        1.5972  10- 3,      1.7745  10- 6)
:   3s(      -2.0000         ,     28.132    10- 3,    -14.493   10+ 6,
             397.50          ,    100.00     10+ 3,      0.0000       ,
               5.7963 10- 3,      625.23    10- 3,    368.97    10- 3)
:  10b(       12.000         ,      7.0000         ,      1.0000       ,
               2.0000        ,      1.0000         ,      1.0000       ,
               1.0000        ,      1.0000         ,      5.0000       ,
             330.00          ,    330.00           ,    393.00         ,
              99.490         ,     99.711          ,     -5.7391  10+ 6,
               5.6620 10+ 6,        5.0000         ,    410.04    10- 3)
+
:   2s(      -2.0000         ,     31.841    10- 3,     -6.7553  10+ 6,
             330.00          ,    100.00     10+ 3,      0.0000       ,
             997.18   10- 3,        2.8135  10- 3,      5.2493  10- 6)
```

Table P.10.5 (4) (cont.)

```
:    3s(   −2.0000         ,    28.159   10− 3,    −14.490   10+ 6,
           397.10          ,    100.00   10+ 3,      0.0000       ,
             8.1225  10− 3,    623.26   10− 3,    368.62    10− 3)
:   10b(   12.000          ,     7.0000       ,      1.0000       ,
             2.0000        ,     1.0000       ,      1.0000       ,
             1.0000        ,     1.0000       ,      2.0000       ,
           330.00          ,   330.00         ,    393.00         ,
            99.285         ,    99.492        ,    −2.8714   10+ 6,
             2.7928  10+ 6,      2.0000       ,    410.04    10− 3)
+
:    2s(   −2.0000         ,    31.723   10− 3,     −6.7691  10+ 6,
           330.00          ,   100.00    10+ 3,      0.0000       ,
           992.55    10− 3,      7.4164  10− 3,     37.785   10− 6)
:    3s(   −2.0000         ,    28.277   10− 3,    −14.482   10+ 6,
           395.54          ,   100.00    10+ 3,      0.0000       ,
            17.461   10− 3,    615.50    10− 3,    367.04    10− 3)
:   10b(   12.000          ,     7.0000       ,      1.0000       ,
             2.0000        ,     1.0000       ,      1.0000       ,
             1.0000        ,     1.0000       ,      1.0000       ,
           330.00          ,   330.00         ,    393.00         ,
            98.456         ,    98.666        ,     −1.9178  10+ 6,
             1.8330  10+ 6,      1.0000       ,    410.04    10− 3)
+
:    2s(   −2.0000         ,    31.681   10− 3,     −6.7760  10+ 6,
           330.00          ,   100.00    10+ 3,      0.0000       ,
           990.65    10− 3,      9.2877  10− 3,     60.266   10− 6)
:    3s(   −2.0000         ,    28.319   10− 3,    −14.477   10+ 6,
           394.95          ,   100.00    10+ 3,      0.0000       ,
            21.033   10− 3,    612.50    10− 3,    366.46    10− 3)
:   10b(     8.0000        ,     5.0000       ,      1.0000       ,
             2.0000        ,     1.0000       ,      1.0000
             1.0000        ,     1.0000       ,      5.0000       ,
           330.00          ,   330.00         ,    393.00         ,
            98.137         ,    98.332        ,     −5.7583  10+ 6,
             5.6713  10+ 6,      5.0000       ,    410.04    10− 3)
+
:    2s(   −2.0000         ,    31.594   10− 3,     −6.7975  10+ 6,
           330.00          ,   100.00    10+ 3,      0.0000       ,
           985.88    10− 3,     13.980   10− 3,    141.11    10− 6)
:    3s(   −2.0000         ,    28.406   10− 3,    −14.461   10+ 6,
           393.60          ,   100.00    10+ 3,      0.0000       ,
            29.302   10− 3,    605.44    10− 3,    365.26    10− 3)
:   10b(     8.0000        ,     5.0000       ,      1.0000       ,
             2.0000        ,     1.0000       ,      1.0000       ,
             1.0000        ,     1.0000       ,      2.0000       ,
           330.00          ,   330.00         ,    393.00         ,
            97.397         ,    97.496        ,     −2.8869  10+ 6,
             2.7945  10+ 6,      2.0000       ,    410.04    10− 3)
+
:    2s(   −2.0000         ,    31.460   10− 3,     −6.8771  10+ 6,
           330.00          ,   100.00    10+ 3,      0.0000       ,
           972.99    10− 3,     26.472   10− 3,    537.26    10− 6)
:    3s(   −2.0000         ,    28.540   10− 3,    −14.394   10+ 6,
           390.67          ,   100.00    10+ 3,      0.0000       ,
            48.007   10− 3,    588.89    10− 3,    363.10    10− 3)
:   10b(     8.0000        ,     5.0000       ,      1.0000       ,
```

```
        2.0000      ,     1.0000      ,       1.0000
        1.0000      ,     1.0000      ,       1.0000
      330.00        ,   330.00        ,     393.00        ,
       95.716       ,    95.279       ,      -1.9433  10+ 6,
        1.8386 10+ 6,     1.0000      ,     410.04    10- 3)
+
end Design of acetone distillation unit
```

Table P.10.5 (5)

Manufacture of acetic anhydride. Design of acetone distillation unit. Summary

Number of cycles 1elb	Number of plates 1e10b	Reflux ratio 3e10b	Acetone mole fraction 7e2s	Acetone yield, % 13e10b	Acetic acid yield, % 14e10b	Heat load 16e10b
1.		5	.99995	99.964	99.991	5.6727×10^6
2.	20	1	.99949	99.803	99.908	1.8395×10^6
3.		0.5	.99512	99.056	99.230	1.3767×10^6
4.		5	.99972	99.844	99.950	5.6679×10^6
5.	16	2	.99944	99.798	99.898	2.7969×10^6
6.		1	.99803	99.499	99.645	1.8377×10^6
7.		5	.99840	99.490	99.711	5.6620×10^6
8.	12	2	.99718	99.285	99.492	2.7928×10^6
9.		1	.99255	98.456	98.666	1.8330×10^6
10.		5	.99065	98.137	98.332	5.6713×10^6
11.	8	2	.98588	97.397	97.496	2.7945×10^6
12.		1	.97299	95.716	95.279	1.8386×10^6

CHAPTER 11

THE STATE-OF-THE-ART

We intend to summarize the main aspects of evolving flow-sheeting programs and the mode of their solution.

One of the most important characteristics of programs or program packages calculating complex systems is the way they ensure that the result of the calculation of a unit operation is the input of the next. From this aspect, *fixed-structured* and *free-structured* methods may be distinguished. Most known programs belong to the fixed-structured group. One free-structured method, for example, is a former variant of the SPEED-UP system, which was essentially a frame program, evaluating the solution of sets of equations. The elasticity of such a system is undoubtedly an advantage, but it does not provide enough aid in solving practical tasks. The fixed-structured methods standardize the description of streams between unit operations. The data describing these are fairly obvious: one stream data for each component, the enthalpy and the pressure. The generally specified data are nevertheless a somewhat redundant — for practical reasons they may contain the total stream, the temperature and the state (in some cases, the vapour-liquid ratio). Different methods may interpret the components differently. Most methods define the components in the preparatory stage of the calculation (with a code which has to be interpreted accordig to some order). It is advantageous if more than one stream types can be terpreted. In a program system, a description of mixtures consisting of discrete components, and one of "continuous" mixtures (crude oil and its fractions), are barely compatible. These continuous mixtures have to be described by the overall stream and some true property function (e.g., true boiling point function). Calculation of the properties must thus be carried out in a different way.

The calculation order of the unit models is set up in fixed-structured programs by a permanent master program covering all necessary functions such that the input data of the unit models, besides the unit's operating parameters, are the characteristics of the entering streams, whereas the output data characterize the exit streams. This concept has the advantage that, if the models of the units used are available, it is not necessary to rewrite the program for each problem arising. Only the process system and the task need to be defined. It is conceivable to have a language easily used by chemical engineers lacking computing knowledge which may describe process flow-sheets, unit operations and associated task. The disadvantage of such a system is, however, that it would be more sophisticated and more computer time consuming than simpler systems. Another problem arises during simulation-mode calculations, namely the possible appearance of results (e.g., data relating to the load of the equipment, etc.) which do not comply with the strictly defined form of the stream vector. A possible solution in this case is to reserve space for these results among the parameters of the equipment, and to store the results there. The problem still remains that these are not directly accessible when calculating other units. Another solution is to reserve a common data field accessible during the calculation of all unit models. However, in both cases a reference facility would be necessary to ensure access to these data when formulating the task, without prior knowledge of which data are to be required. The best way is to indicate in the data system that the searched value at a given place is not a numerical value — this may be found elsewhere.

Such a system allowing these references or more generally reference chains, may be accomplished, but increases the time consumption of the calculations, because before starting the calculation of each unit model a test must be carried out. The aim is to find the references among the data. If a reference is found then it has to be searched — eventually in the background store. If a multiprogramming operating system is used, the search time presents a smaller problem. Whichever reference system is used, the program is rigid if the calculation of any arithmetic expression cannot be prescribed when formulating the task. This is necessary, e.g., when defining the objective function of optimization or when calculating the conversion from the input parameters in a general reactor program. This is not easy to solve whatever the language of the master program, and requires a different coding from the usual. Further, the interpreting mode is time-consuming. The absence of this possibility restricts the applicability of fixed-structured programs significantly.

The programs are generally written in high-levelled program language (most in FORTRAN). These languages have restrictions, however, which render the task specification more difficult or even impossible. Programming in assembler code is disadvantageous because it is cumbersome during programming itself, and even more so when additional modifications are necessary.

When using fixed-structured methods, the compilation of the unit models needed to solve the problem is always solved from the available assortment without manual programming, i.e., without additional error source.

When considering the simplest case in simulation, i.e., when all input and unit operation parameters are given and there are no loops in the system, then the task is directly solvable, i.e., the output of the units already calculated is in the input of the next. For other cases, a system of equations must be solved. As the models of the unit operations are non-linear almost without exception, systems of multivariable non-linear equations often need solving. Two basic questions are thus raised, which are answered in a different manner by various simulation programs. The first is the setting of the system of equations. The problem has to be suitably broken down in order to obtain many small systems of non-linear equations instead of one or a few larger ones, in other words in the graph symbolizing the process, the loops representing the recycles have to be found, then that stream has to be found for every loop, which enables the system of equations to be solved iteratively as fast as possible by cutting the loop and starting from a presumed initial value.

There are still unsolved problems in this field relating to simulation-mode calculations in the chemical industry. The aim itself is not specific, but defined more clearly, the quickest solution of the system of equations, taking the constraint of the required storage space into consideration is not useful practically. The computation effort cannot be estimated in advance. We can choose a cutting point where the assumed number of variables is minimal, but we still have no definite information about the convergence rate, i.e., about the required number of iteration steps. It would be practicable to find variables to which the solution is least sensitive.

According to the principles governing the solution of systems of equations, these methods may be classified according to two viewpoints: the algorithm of iteration and the simultaneous serial mode of solution. It is surprising that a large number of program systems still use primitive direct iteration to calculate the steady-state behaviour of recycle loops, probably for simplicity. In other programs, more sophisticated methods are available, such as the well-known Newton–Raphson method, the secant method (probably only in the case of one unknown) and the method of Broyden (1965). This method guarantees a second order convergence, similar to the Newton–Raphson method, but corrects the matrix of partial derivatives after each new iteration step on the basis of available information, thus saving time-consuming recalculation. For the most advanced methods, the so-called convergence-accelerating methods are available, e.g., the method of Crowe (1975), based on dominant eigenvalue. Although this method uses a more sophisticated iterating algorithm, compared with the Newton-type methods, it nevertheless seems to be favourable because of the significant decrease in the number of iteration steps expected, especially if the calculation of the models is time-consuming. This and similar algorithms ensure fairly quick convergence, especially, if the vicinity of the root is well behaved. These more advanced methods easily become divergent in unfavourable cases.

All generally known programs utilize the *serial method*. This means that if a non-linear system of equations has to be solved, one iteration step consists of calculating in series all the models in the loop, provided that the calculation results in a new value instead of the initial trial value. Using one of these methods to solve non-linear system of equations, a new initial value is calculated from the differences and the cycle is recalculated, provided the estimate and calculated value agree sufficiently.

The *simultaneous methods* are based upon a different principle. It is generally known that a linear system of equations can be solved practically in one step if the solution exists. Consequently, all the models were linear, no iteration would be necessary; the result would be reached in one step. The essence of the simultaneous method consists of the linear approximation of each model in the region of the actual initial state. This is followed by solving the linear system of equations resulting from the linearized models, thus arriving at a new state. This operation is continued until the required accuracy is obtained.

It is difficult to compare methods for solving non-linear systems of equations for efficiency. It is obvious that in particular cases one is more favourable, but this is obvious only when both methods have been tried. In a system containing only a few recycles, the serial method is preferable whilst in complex networks the simultaneous method is preferred. It should be remembered that the calculation of a series-connected recycle-free system could only be effected with iterations using the simultaneous method. The time-consumption of the simultaneous solution probably depends less on the intricacy of the network than that of the Newton-type methods.

In addition to the solution of non-linear systems of equations, most flow-sheeting programs use other mathematical procedures. The most important are: the *optimizing algorithms* considering constraints; the *algorithms integrating differential equations;* the *algorithms producing approximating functions*. We do not intend here to enter into a detailed discussion only to mention a few important aspects.

Since the aim of flow-sheeting is the optimization of the object in some way, it is essential to be able to optimize in the program. The user may use this facility for the whole task or one or more parts of it, according to the characteristics of the task. It should therefore be possible to formulate the task so that the optimizing procedure calculates some free parameters of certain sub-systems during simulation. If the optimizing procedure can be called in a recursive manner, then decompositional, multi-level optimization becomes possible in principle. We have no knowledge on the practical application of such a method.

It is an obvious requirement that the optimizing algorithm should operate effectively. Nevertheless the point is emphasized because the more time is used to calculate the objective function, the more time may be economized by looking for a search algorithm which may be more sophisticated but is more effective. The priority is to reduce the number of calculations leading to the objective function! The problem of evaluating the efficiency occurs here just as it did when solving systems of equations. In this field, efforts should not be concentrated primarily on developing the available methods, but in formulating the task itself. It is not sufficient to compare efficiencies of optimizing methods considering a few examples, which may be characteristic but are nevertheless chosen arbitrarily. It is necessary to interpret the efficiencies of the methods for different function groups more precisely than has so far been done. Without this kind of interpretation, new and better methods of optimizing objective functions appear which become more and more difficult to evaluate and select from, when solving practical problems.

There is a significant difference between procedures solving and optimizing systems of equations and the integrating procedure. The latter is not generally listed among the procedures to be specified when formulating the task, because the relation between the elements of the system is always described by algebraic equations. With the exception of dynamic simulation of complex operations, integration of differential equations is needed within the unit models, and activation of this procedure is this effected on an other level. Thus the integrating procedure is not necessarily the main part of the program system, but its availability facilitates development of the unit models and keeps the program length short avoiding the need to build such a procedure in every model.

Opinions about integrating algorithms seem to be in a closer agreement than about problems of optimization. The predictor-corrector methods are considered to be most suitable, although the disadvantage of this method lies in the need for another algorithm at the beginning, and therefore the size of the program increases significantly compared with the size of Runge–Kutta-type programs. The required accuracy of the integration and the aim to shorten time consumption jointly motivate automatic selection of step length.

Algorithms producing approximating functions may be required either on the level of task formulation, or at lower levels. In the first case they may be used, e.g., to simplify the model of a complex operation; in the second case, on a lower level, when some physical properties are supplied by the user with which knowledge the approximation has to be made.

Some aspects of the unit-operation models have already been discussed. It is important, that they should be flexible according to needs, the addition of a new element should be carried out easily, and also that no problem should arise if elements unnecessary for solving the task are omitted.

It may be considered as a general experience that more than one model of the same unit operation are needed, according to the characteristics of the task. We may need some kind of approximating model, more exact, and in some cases a design model, which selects some of its own parameters. It is possible to realize the last two functioning modes in the same program, but more effective programs may generally be developed from two separated algorithms.

Models of different reactors are generally developed individually, without combination. The *stoichiometric* model — based on the prescribed conversion — is a useful tool, worthy of development such that it provides the final product of complex reactions between any components, any stoichiometry and any conversion as output stream.

A comprehensive procedure, suitable for prescribing any modification of the input stream is a useful and extensively used part of the model assortment. From experience gained by ourselves and others, common utilizations and good results may be stated. Instead of the model of the heat exchanger, for example, two units of this kind may be used if the outlet temperature alone is prescribed. The first sets the outlet temperature and calculates the enthalpy change on one side, the second modifies the enthalpy and calculates the outlet temperature on the other side. This procedure may be used similarly as a simplified compressor model and in many other cases.

The most problematic part of flow-sheeting chemical-process systems is probably the unified method of the physical-property calculation. The aim is to calculate all the physical properties in question of all the components, with acceptable accuracy, using programs and computer runs as short as possible, with the aid of a data base whose size is acceptable and handling is simple. It seems, however, that nature is not kind enough to present this chance, because the correlations allowing the same property to be calculated differ according to the type of compound not only in the parameters but in their form; this is because to calculate one certain property, it often becomes necessary to calculate a number of other properties; and also because to calculate the properties of a mixture, individual data of the components are not sufficient, etc. A lot of research efforts has been directed towards this field, and considerable results have been achieved. Nevertheless, the situation cannot be assessed with optimism, because it is principally impossible to attain fair accuracy when using relatively simple algorithms. Calculation of physical properties is still the most time-consuming and uncertain part of flow-sheeting.

In addition to research work aimed at finding and checking approximating algorithms, it is possible to adopt a sophisticated program management to calculate various stream properties in such a sequence that calculation of the same property more than once can be avoided. Efforts should be made somehow to enable the calculation of all necessary properties of a stream to be prescribed simultaneously with a defined composition. Another possibility of acceleration, attainable with adequate organization, may be not to recalculate the physical properties after each iteration step, but to use values interpolated in some way, for calculation purposes.

There is no significant difference with respect to the input between several fixed structured programs. Generally, when starting the calculation, they need the "processes" defining the topology of the flow-sheet, the equipment parameters, the input streams and the initial values of the iterations. Most of the programs leave the output of the results to the sub-programs such that after the calculation they are recalled successively, and activating their output duty instead of the calculation, the output of all parameters is effected. Other programs contain procedures to print the results so that the variables to be printed have to be specified when formulating the task. The advantage of this solution is in the compactness of the output, but there is a disadvantage that data, not specified as output, cannot be retrieved later. In this case, the printing of the output texts raises difficulties, although this problem can be overcome.

There is a significant difference between *conversational* and *interactive* techniques: the difference is not distinct but their senses differ. The conversational solution enables information (primarily on display) to be entered in the form of questions and answers. The interactive solution allows for intervention during the running of the program, for example to include a statement to print intermediate results, or to enter new initial values for the iteration if the number of iteration steps is too high.

The CONCEPT program, for example, is fundamentally conversational, the task itself being defined by questions and answers. This can really only be utilized economically on big computers with terminals, since a small computer is hardly suitable for solving the task and big computers should not be exploited for conversation — apart from using their terminals. Besides formulating the task conversationally, input of the task must also be possible on an information carrier. Herewith, repeated input of the task as a circumstantial dialogue is avoided. The input of a data system previously drawn up is also more practicable in that case if these are final design data. Their preparation is very time-consuming and they need to be checked in advance from every point of view – including not only the contents but also the typing errors. It is advantageous if the type of input and output peripheral equipment can be easily selected according to the need, for example, the input as display, card reader, paper tape or magnetic tape instead of typewriter; the output as typewriter display, printer, card punch or magnetic tape.

The first chemical-process flow-sheeting programs appeared in the early sixties. Their basic principles resembled ours today. It is a matter of course that if possible, the input stream of the one unit operation should be the output stream of the previous one. The rapid development of computers increased the size and scope of soluble problems. The new program systems contain a broader assortment of unit operations and greater power for calculating physical properties.

This is only natural. Nevertheless, if we ask how the principles and solution modes of chemical-process flow-sheeting programs have developed, we find that there are no essential new features.

The ability of any chemical-process flow-sheeting program is restricted and it should not be expected that a plant containing many units and recycles could be described entirely, with sufficient accuracy or even optimized, within a short period. Any of these programs has to be considered as an auxiliary tool in chemical-engineering practice. In order to obtain useful results, we have to balance the demands and requirements with accuracy.

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SUBJECT INDEX

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