ChemPlant Technology s.r.o.

Report CPT - 189-04

Issued: 10. 10. 2004

This report has 89 pages.

Balancing and Data Reconciliation

Minibook

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Ústí nad Labem October 2004

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1. INTRODUCTION

The intention of the present text is twofold. The main addressee is the potential user of a balancing software. He (or she, of course) is probably not so much interested in the mathematical theory and proofs, nor in the details of computation. Our aim is to show him what is required from his side, how the software works and what he can expect from it. Still, some insight into the principles on which it is based can be useful. This is done mainly by way of examples illustrating the basic ideas of balancing and reconciliation of measured data. The user is anyway supposed to participate in the construction of the balancing model, to a degree dependent on his professionality. Our aim is also to support his confidence in the principles of the theory, that the ideas are basically natural and sound. The requirements on his knowledge range from not very advanced algebra and analysis to elements of physical chemistry at a graduate, but not specialised level; in some examples, a little more chemical thermodynamics occurs just to show that the construction of a model will sometimes require a specialist.

The other addressee can be a (possibly future) specialist in balancing and reconciliation methods. In 1997, there appeared the book 'Material and Energy Balancing in the Process Industries' by Veverka and Madron. A considerable part of the book is concentrated on theory thus the mathematical and physical principles of the balancing and reconciliation of measured data. In a certain sense, the present text can also be regarded as an introduction to the book or some kind of 'guide' through it for a reader who decides to peruse it. The references to the book are mainly addressed to the latter reader. He will there find the formulae, proofs and other details. The references are numerous: for the sake of brevity, they are denoted by VE-MA .

2. BALANCING IN PROCESS INDUSTRIES

2.1.The subject and purpose of balancing

As an example, let us begin with a technological scheme according to Fig. 2-1.

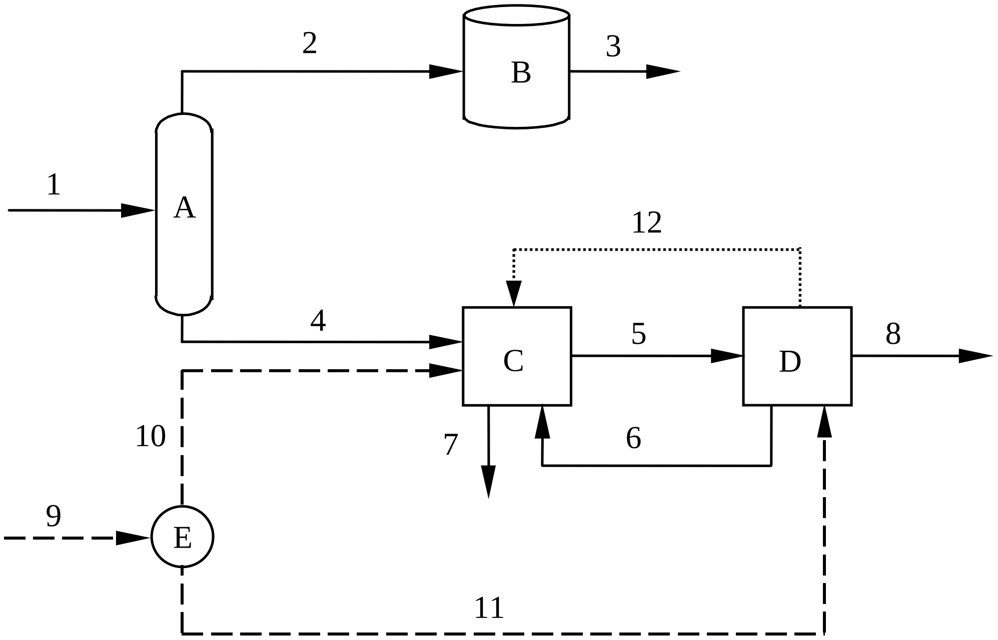

Fig. 2-1 A flowsheet for a single-component balance

The scheme is simplified as corresponds to the given task of balancing. Besides the distillation column A and distillate storage tank B, it comprises also more complex subsystems of apparatuses the individual balances of which are not required. Each of the subsystems is regarded as a (technological) unit or, more generally, a *node* of the flowsheet (A, B, ... , E included). They are balanced as 'black boxes' disregarding their detailed structure. Node E represents here a distributor of electric energy supply.

The nodes are connected among themselves and with the environment by *streams* (1, ... , 12 in the Figure). Streams are usually classified as process streams (1 to 8) and utilities, such as cooling water or electricity (9 to 11). The classification is useful because process streams usually don't mix with utilities; their balances are often independent and can be solved separately. The classification of the stream 12 is ambiguous: In the subsystem D arises a process off-gas, which is further led to subsystem C to be burned in a heating furnace (imagine pyrolysis of hydrocarbons as part of unit C); so stream 12 becomes here a utility. This means that it does not enter the material balance of node C. [If also energy is subject to balancing, the scheme has to be modified; see later in Section 3.3.]

Basically, the *balance* of a system in a certain time interval means the complete information about

- – exchange of balanced quantities (overall mass, chemical components, different forms of energy etc.) among separate elements (nodes) of the system or among nodes and the environment

- – inventories of balanced quantities in nodes at the beginning and end of the interval, or how the inventories have changed (accumulation).

More generally, the methods of balancing include also the solution of different associated problems (see Section 2.2) and they also yield other kinds of information as will be shown later.

In the simplest case, as corresponds to Fig. 2-1, we are interested in the overall mass flows in the case of material streams (for example in tons), and electric energy (for example in GWh). We are not interested in other characteristics of streams as chemical composition, because one can suppose that the quality of individual streams is guaranteed by the control system. This is the most widely used application of the balancing methods.

The equations for this (so-called) *single-component balance* are of the form

$$\textit{sum of inputs} = \textit{sum of outputs} + \textit{increase in inventory}\ ; \qquad (2.1.1)$$

for each node of the system we thus have just one equation. Involving a change in time, the balance can be classified as *dynamic*. The incentive for setting-up this kind of balance is the regular monitoring of yields of main products and that of specific consumption of utilities as part of 'good housekeeping' of the plant.

As the second example, let us consider the flowsheet according to Fig. 2-2.

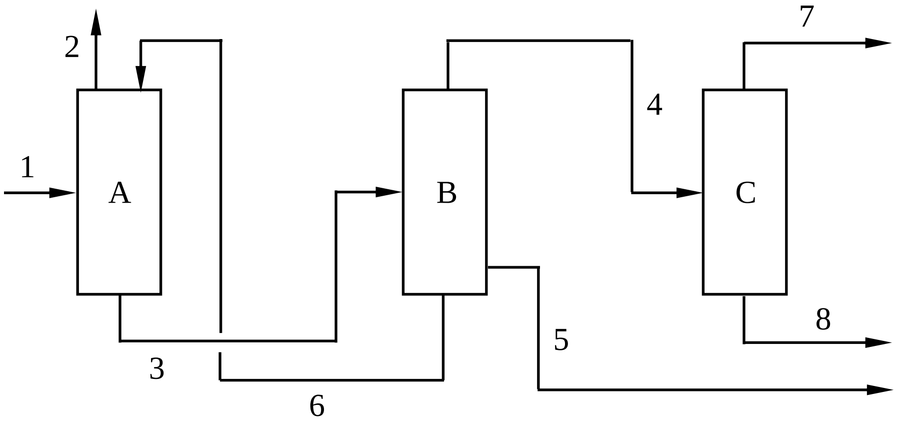

Fig. 2-2 Separation of light hydrocarbons

It represents the distillation / absorption train for processing of refinery off-gases. Refinery off-gas 1 consists of hydrocarbons C1 to C7, hydrogen, and inert gases (N_2 , Ar). The column A serves as absorber / desorber. Hydrogen, inerts, and C1 and C2 hydrocarbons are boiled up in the bottom part of the column and middle hydrocarbons (C3,C4) are absorbed in the upper part of the column by heavier hydrocarbons (C6 and C7). The lean gas 2 leaving the head of the column is later burned in a furnace. The second column serves for separation of C3 and C4 hydrocarbons from the absorbent 6 which circulates between columns A and B. The middle hydrocarbons consisting mainly of propane and butanes are separated from one another in the third column which produces commercial products propane 7 and butane 8.

In this case, we are interested in the (so-called) *multicomponent balance* when individual (chemical) components (inerts, hydrocarbons and hydrogen) are conserved. We have one component balance equation for each component and column (if the component is present in the column); it is again of the form (2.1.1) but the accumulation term (here: change in holdup) is commonly neglected. The result of the balance is the complete information not only about overall flows but also about the composition of individual streams.

Such multicomponent balance is important for tracing valuable components in the process. The value of commercial products (propane and butane) is much higher than the value of the lean gas. Significant economic losses can occur if the absorption in the first column does not operate properly and valuable hydrocarbons are lost in the lean gas.

There are also other incentives for setting up such a multicomponent balance. The balance in a multicomponent system can serve for the validation of sampling and analytical methods. The analysis of imbalances (inputs minus outputs) can reveal errors caused by improper sampling and erroneous methods of analysis. Still another incentive is tuning of the process simulator by comparison of computed results with the balance set up on the basis of process data.

The third example is that of a reactor; see Fig. 2-3.

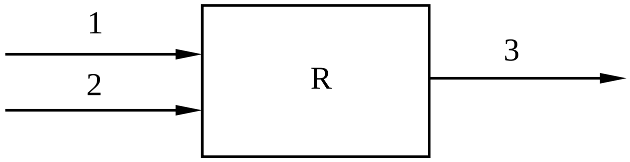

Fig. 2-3 Contact reactor in sulphuric acid plant

Gases from sulphur burning unit (stream 1 containing N_2 , Ar, O_2 , SO_2 , traces of SO_3) and additional dry air 2 (N_2 , Ar, O_2) are subject to the (catalysed) chemical reaction

$$SO_2 + 1/2\ O_2 = SO_3$$

producing sulphur trioxide; stream 3 further contains the inerts N_2 and Ar and nonreacted O_2 and SO_2 . In this case, the components O_2 , SO_2 , SO_3 are not conserved individually as they can be consumed or created by the reaction. More generally, several chemical reactions can take place in one reactor; see Fig. 2-4.

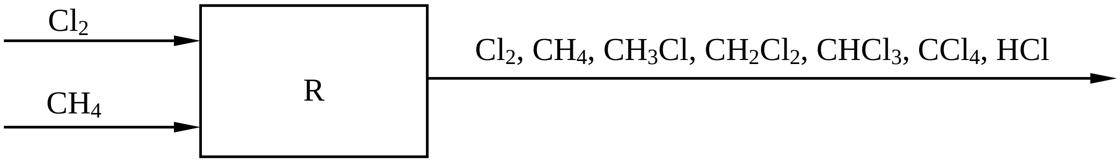

Fig. 2-4 Chlorination reactor

Here, methane is chlorinated in a complex reaction set which can be summarised as

$$
\begin{aligned}
CH_4 &+ Cl_2 = CH_3Cl + HCl \\
CH_3Cl &+ Cl_2 = CH_2Cl_2 + HCl \\
CH_2Cl_2 &+ Cl_2 = CHCl_3 + HCl \\
CHCl_3 &+ Cl_2 = CCl_4 + HCl\,.
\end{aligned}
$$

The balance of the reactor is governed by the reaction stoichiometry. In this case we speak of *multicomponent balance with chemical reaction(s)*. The result of balancing is the complete information about the amounts of individual components entering and leaving the reactor and possibly also about reaction characteristics such as *reaction rates* or *extents of reactions* ; in the case of Fig. 2-3, it is the (so-called) 'degree of conversion' of SO_2 to SO_3 . The balancing of reacting systems is important for detailed analysis of processes running in the reactor, either in the stage of laboratory or pilot plant studies, or as the regular monitoring of industrial reactors behaviour (yields, selectivity in the case of several reactions). In the industrial case, it is thus possible to reveal important changes as improper control, ageing of the catalyst etc., which can cause serious economic losses or even jeopardise the safety of the whole process.

Still another example is in Fig. 2-5.

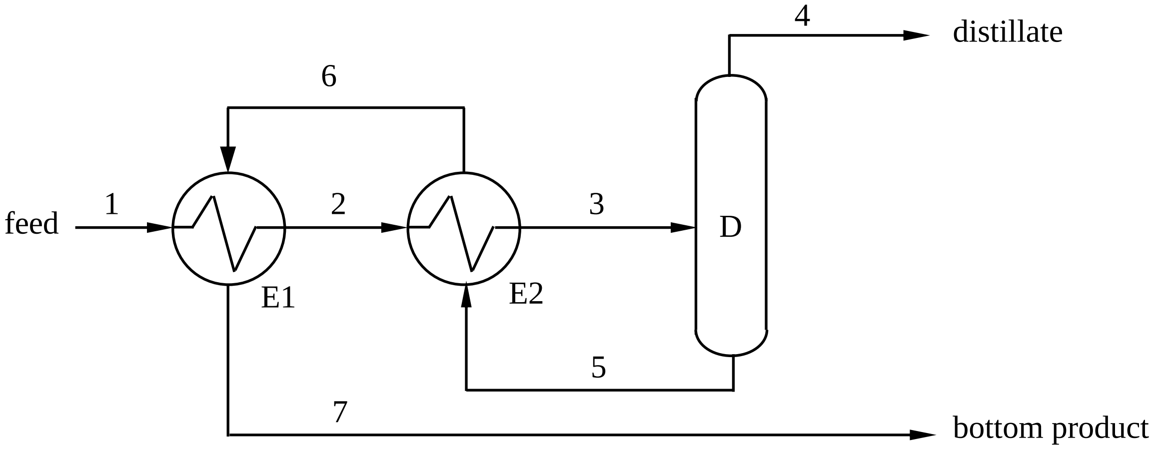

Fig. 2-5 Column feed preheat
(E1 and E2 are heat exchangers, D is distillation column)

To analyse such a system, the (so-called) *enthalpy* (heat) *balance* must be set up, which includes the complete information about enthalpies of streams and also heat fluxes occurring between some parts of the system. We can meet with this kind of balancing either when designing a new process, or during the monitoring or control of an existing process (evaluation of heat transfer coefficients, calculation of unmeasured temperatures, etc.). Such monitoring can reveal, for example a common quiet 'thief' in process plants – a heat transfer surface fouling.

Summarising, the balance of a system consists of individual node balances giving a set of equations to be solved. The general form of a node balance reads

$$\textit{quantity in} \; + \; \textit{source} \; = \; \textit{quantity out} \; + \; \textit{accumulation} \qquad (2.1.2)$$

where the source is null for a quantity that remains conserved (such as overall mass); in reactors, it equals the production of the quantity (component mass) by the chemical reaction(s) where negative production means consumption. The accumulation means generally the (positive or negative) increase in holdup (dynamic balancing); when (it can be) neglected, we speak of a *steady-state balance*. The purposes of the balancing can be manifold as indicated above. Here, we are in particular (though not exclusively) interested in *process analysis*. To this end, a number of associated problems have to be solved.

2.2.Associated problems

The quantities in the node balances (2.1.2) can be flowrates (e.g. mass per unit time) or their integrals over a given period of time. Thus, by definition, if $f(t)$ is the flowrate at time t then

$$f_{\mathrm{int}} = \int_{t_1}^{t_2} f(t)\,\mathrm{d}t \qquad (2.2.1)$$

is the integrated flowrate in the interval $[t_1 , t_2]$; in the same manner are integrated the source and accumulation terms. The node balance holds thus true in both cases. Written with the 'instantaneous' $f(t)$, it is more convenient in chemical engineering calculations such as when designing the apparatuses of a plant. In the process analysis, the balancing is usually carried out in certain intervals of time; this in particular in the case of overall mass (daily balancing). Even if a balance per unit time is written, we in fact consider the averages

$$<f> = \frac{1}{t_2 - t_1} f_{\mathrm{int}} \qquad (2.2.1a)$$

where the difference $t_2 - t_1$ can be of the order of magnitude of minutes at least, or more. Indeed, the instantaneous values are fluctuating for example due to the action of control devices. Then the response to the control action is 'delayed'; more precisely, the course of the response in time is described by the control theory, not to be dealt with here. So the balance equations are simplified by averaging to be solvable by algebraic methods. The balances (2.1.2) then hold true with the $<f>$ as well.

The individual node balances are dealt with in Chapter 3. They are written in terms of what we call 'balancing variables'. Thus for example the mass flowrate of a chemical component X equals my_X with balancing variables m (mass flowrate in the stream) and y_X (mass fraction of X in the stream). Let generally $f = mx$ be a flowrate. In the balancing interval, we have

$$\begin{aligned} m &= \langle m\rangle + \tilde{m}(t) \\ x &= \langle x\rangle + \tilde{x}(t) \end{aligned} \tag{2.2.2}$$

where $\tilde{m}$ and $\tilde{x}$ are the fluctuations. Let us further assume that, for a sufficiently large $t_2 - t_1$

$$<\tilde{m}> = 0 \qquad \text{and} \qquad <\tilde{x}> = 0 \tag{2.2.2a}$$

which corresponds to the idea that the fluctuations are random variables with zero mean. It is then easy to show that

$$<f> = <m><x> + <\tilde{m}\tilde{x}> . \tag{2.2.2b}$$

We can put $<\tilde{m}\tilde{x}> = 0$ if the fluctuations $\tilde{m}$ and $\tilde{x}$ are uncorrelated. The probabilistic interpretation is somewhat naive and the latter hypothesis does not generally follow from any exact theory ; but assuming small fluctuations, let us still *neglect* the latter term. We then approximate

$$<f> \cong <m><x> \tag{2.2.3}$$

thus also

$$f_{\text{int}} \cong m_{\text{int}} <x> \tag{2.2.3a}$$

with integral mass flowrate m_{int} and mean value $<x>$ of x .

In the case of energy ('enthalpy' or 'heat') balancing, the factor x (specific enthalpy) can generally be a complicated function of other balancing variables (composition, temperature, generally also pressure). We will not embarrass the reader by meticulous theoretical analysis. Let us simply state that assuming small fluctuations,

The balancing variables are averages over an interval of time.

When writing the balance equations, the variables must be *consistent* as concerns their physical dimensions. We prefer the *mass system* of variables because it is the (overall) mass that remains conserved (not generally the number of moles) and also the raw materials are bought and the products sold in tons. The consistency however requires using the SI system of units, thus kg for mass. The (possibly integrated) mass flowrate is denoted by m (with indices identifying the streams), its unit is kg s^{-1} (or kg if integrated). The corresponding composition variable in a mixture is then y_X (mass fraction) for component X. If also energy is being balanced, the streams can comprise 'net energy streams' such as in Fig. 2-1, or a 'heat flowrate' if the material is preheated or cooled; the unit is W (or Ws = J if integrated). The relevant part of the energy associated with material flow is its enthalpy ; it then equals $m\hat{H}$ where $\hat{H}$ is specific enthalpy (J kg^{-1}). The specific enthalpy is a function of (absolute) temperature T (unit K), composition and generally also pressure P (unit Pa). The thermodynamic data is part of the database. In particular for chemically reacting systems, care must be taken that the specific enthalpies be consistent with respect to the zero levels. This is generally a task for specialists in chemical thermodynamics.

The consistency requirements do not, of course, mean that the user is obliged to present his data and obtain the results in the above system of units. It is the task of the balancing software to re-calculate the quantities from and back into the units the user prefers, thus tons, MWh and the like.

In spite of the preference given to the mass system, the *molar system* is still worth mentioning. It is widely used in chemistry and chemical thermodynamics (for example instead of specific enthalpies, classical thermodynamical tables give molar enthalpies). The molar system is based on mole as unit quantity of matter (in fact a specified number of molecules). One kg-mole (10^3 moles) is denoted as kmol and is consistent with the mole mass (molecular weight) M_X of chemical species X in kg/kmol; to be precise, this M_X is related to the conventional chemical formula for X (not necessarily representing the actual configuration of a 'molecule' for example in solids). Then, if n_X is the number of kg-moles of species X, the mass is

$$m_X = M_X n_X \quad \text{(kg)}. \tag{2.2.4}$$

The composition of a mixture can also be expressed in mole fractions x_X of components X

$$x_X = \frac{n_X}{n} \tag{2.2.5}$$

where n is the total number of kg-moles, thus the sum of m_Y/M_Y over al species Y present in the mixture. Introducing the mean mole mass of the mixture

$$\overline{M} = \sum_Y x_Y M_Y = \frac{1}{\sum_Y \frac{y_Y}{M_Y}} \tag{2.2.6}$$

we have the formulae

$$y_X = \frac{M_X x_X}{\overline{M}} \quad \text{and} \quad x_X = \overline{M}\frac{y_X}{M_X} \tag{2.2.7}$$

with $(2.2.6)_1$ resp. $(2.2.6)_2$. The molar enthalpy $\overline{H}_X$ (J $kmol^{-1}$) of pure species X equals

$$\overline{H}_{\mathrm{X}} = M_{\mathrm{X}} \hat{H}_{\mathrm{X}} \tag{2.2.8}$$

where $\hat{H}_{\mathrm{X}}$ is the specific enthalpy of X. For a mixture, the molar enthalpy equals

$$\overline{H} = \overline{M}\hat{H}\,. \tag{2.2.9}$$

Using these simple formulae, the balancing software can recalculate the thermodynamic data from the molar to the mass system, and vice versa.

In the process analysis, the values of certain variables are measured. The primary (directly measured) quantities need not be just the balancing variables as introduced above. It is then the task of the *data pre-processing* to transform the measured values to those of the balancing variables. The transformation formulae (such as (2.2.7) for example), possibly with different simplifying assumptions, have also to be included in the software. We shall not go into further details of this routine.

The measured data are subject to unavoidable *measurement errors* (measured value minus true value). They always comprise some part that is of random character and can thus be treated by statistical methods. For more details, see for example Madron (1992), Chapter 3. Here, we shall restrict our attention mainly to the random errors that oscillate around zero (with zero mean) and are characterised by *standard deviation* σ. This is a theoretical value following from the (assumed) probability density function. Its estimate s can be obtained from repeated measurements as

$$s = \left(\frac{\sum_i (x_i - \overline{x})^2}{n - 1} \right)^{\frac{1}{2}} \tag{2.2.10}$$

where n is the number of measured values x_i and $\overline{x}$ their arithmetic average. The standard deviation characterises the precision of the measuring instrument ($\sigma = 0$ means absolute precision). For the statistical data processing by reconciliation, see Chapter 5.

It can happen that we only have information about maximum measurement errors provided by vendors of the instruments (sometimes as the *class of accuracy*). There then arises the question, what is the relation between the standard deviation σ and the maximum error $|e|_{\max}$ (absolute value). The rigorous answer probably does not exist. In practice, we can recommend to take

$$\sigma \cong \tfrac{1}{2} |e|_{\max}\,. \tag{2.2.11}$$

As a motivation, one can perhaps consider the fact that with probability 0.95, the absolute value of the error will not exceed the value (approximately) 2σ, for Gaussian distribution of the errors. On the other hand, also in practice an error whose probability is less than 0.05 is regarded as a *gross error* due to some failure.

3. INDIVIDUAL NODE BALANCES

We shall now specify different types of node balances (2.1.2), illustrated by examples. For the sake of unambiguosity and in order to make the formulae compatible with the book VE-MA we are constantly referring to, let us consider the quantities in (2.1.2) as *flowrates* per unit time; see the commentary in Section 2.2.

3.1.Single-component balance

The balance (2.1.2) takes here the form (2.1.1). It is almost trivial. Considering Fig. 2-1, for example for node B

$$m_2 = m_3 + a$$

where m_i is mass flowrate in stream i and a is the increase in inventory (positive or negative) per unit time. Other products are stored outside the units drawn in the flowsheet. The possible changes in holdups are neglected. Thus for node D we have

$$m_5 = m_6 + m_8 + m_{12}$$

but the node C-balance reads

$$m_4 + m_6 = m_5 + m_7$$

because the stream 12 does not enter the node C-mass balance. The integrated forms of the balances are the same.

3.2.Multicomponent balances

The quantities of individual chemical species (components) need not be conserved due to possible chemical reactions. We thus begin with the subsection

3.2.1. Chemical reactions and stoichiometry

As an example, consider the reaction

$$SO_2 + 1/2\ O_2 = SO_3 \qquad \text{(a)}$$

according to Fig. 2-3. It can also be written

$$2\ SO_2 + O_2 = 2\ SO_3\ . \qquad \text{(b)}$$

Disregarding the actual reaction mechanism (which can be more involved), from the viewpoint of balancing the effect is the same. The information contained in both of the reaction schemes reads

(i) The reaction participants are SO_2 , O_2 , SO_3
(ii) The reaction product is SO_3
(iii) The molecular ratios of the participants are 1 : 1/2 : 1 = 2 : 1 : 2.

Nitrogen and argon present in the mixture do not participate in the reaction (they are neither consumed nor produced by it); they are called *inert* components.

Whatever be the mechanism, the reaction schemes must obey the laws of *chemical stoichiometry*: the number of atoms of each element must remain conserved. Thus for oxygen we have 2+1 = 3 in (a).

Also disregarding the detailed mechanism, the (differential) rate of the reaction (a) can be introduced as the number of molecules of SO_3 arising by the reaction in unit volume per unit of time; or, in conventional units, as the corresponding number of kg-moles. This reaction rate will generally be different at different points of the reactor, due to the changes in composition and temperature in the direction of flow. Balancing the whole reactor R, we rather introduce the (volume-integrated) *reaction rate* W_a as the number of kg-moles of SO_3 produced by the reaction in R per unit of time. [Integrating further over an interval $[t_1 , t_2]$ of time, we have the *extent* of the reaction in the balancing interval.]

Note: The (integral or differential) reaction rate as introduced here is generally not a simple measure of the 'reactivity', which is the tendency to achieve reaction (thermodynamic) equilibrium. For example in the above case the reactivity increases with temperature but the equilibrium is then shifted towards a higher content of nonreacted SO_2 and limits the attainable W_a .

There can be several reaction products; for example in the oxidation of ammonia

$$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O \tag{c}$$

we have two. So as to make W_c independent of the choice of the product to which it is related, one defines W_c in the manner that $4\ W_c$ resp. $6\ W_c$ is the number of kg-moles of NO resp. H_2O arising by the reaction, and also $4\ W_c$ resp. $5\ W_c$ is the number of kg-moles of NH_3 resp. O_2 consumed by the reaction, again per unit time.

With this convention, considering the reaction (a) rewritten as (b), we have $W_a = 2W_b$ for the same amount of produced SO_3, thus $W_b = \frac{1}{2} W_a$ while the physical process is the same. So the *definition of the reaction rate depends on how the reaction is written* . Generally if, in the reaction

$$r: \quad a_1A_1 + ... + a_nA_n = b_1B_1 + ... + b_mB_m \tag{3.2.1.1}$$

P_i resp. Q_j is the number of kg-moles of B_i produced resp. A_j consumed (per unit time) then

$$W_r = \frac{P_1}{b_1} = ... = \frac{P_m}{b_m} = \frac{Q_1}{a_1} = ... = \frac{Q_n}{a_n} \tag{3.2.1.2}$$

is the reaction rate. Thus $P_{\mathrm{SO3}} \;=\; W_{\mathrm{a}} \;=\; 2W_{\mathrm{b}}$ in the first example. It can happen that the reaction runs in opposite direction (so-called 'reversible reaction', such as (a) where at high temperatures, SO_3 can conversely be decomposed); then $W_r < 0$. In algebraic operations that will follow later, it is convenient to write reaction (3.2.1.1) in the form

$$(-a_1)\mathrm{A}_1 \;+\; \dots \;+\; (-a_n)\mathrm{A}_n \;+\; b_1\mathrm{B}_1 \;+\; \dots \;+\; b_m\mathrm{B}_m \;=\; 0 \qquad (3.2.1.3)$$

thus with positive *stoichiometric coefficients* $(b_1 , \dots , b_m)$ for the reaction products, negative ones $(-a_1 , \dots , -a_n)$ for the chemical species consumed by the reaction.

Several reactions can take place in one reactor. For example in the sulphur burning unit preceding the reactor R (Fig. 2-3), we have the reaction

$$\mathrm{S} \;+\; \mathrm{O_2} \;=\; \mathrm{SO_2} \qquad \text{(r)}$$

and a small amount of SO_3 is produced by the reaction

$$\mathrm{SO_2} \;+\; 1/2\;\mathrm{O_2} \;=\; \mathrm{SO_3}\;\; . \qquad \text{(s)}$$

We can rewrite the reactions according to the convention (3.2.1.3) thus for example $\mathrm{SO_2} \;-\; \mathrm{S} \;-\; \mathrm{O_2} \;=\; 0$. Let us now consider all the chemical species present in the unit, thus the inerts N_2 and Ar in addition: their coefficients in the reactions equal zero. The matrix of the coefficients then reads

$$\mathbf{M} \;=\; \begin{array}{cc} \begin{array}{cccccc} \mathrm{S} & \mathrm{O_2} & \mathrm{SO_2} & \mathrm{SO_3} & \mathrm{N_2} & \mathrm{Ar} \end{array} & \\ \hline \left(\begin{array}{cccccc} -1 & -1 & 1 & 0 & 0 & 0 \\ 0 & -1/2 & -1 & 1 & 0 & 0 \end{array}\right) & \begin{array}{c} \mathrm{r} \\ \mathrm{s} \end{array} \end{array} \; .$$

In VE-MA, the transpose $\mathbf{S} = \mathbf{M}^{\mathrm{T}}$ is called *stoichiometric matrix* of the set of reactions; but some authors call 'stoichiometric matrix' the matrix **M**. Having the matrix **M**, we can write the *molar production rates* P_{X} of the chemical species X present in the sulphur burning unit; for example

$$P_{\mathrm{SO2}} \;=\; W_{\mathrm{r}} \;-\; W_{\mathrm{s}}$$

$$P_{\mathrm{O2}} \;=\; -\,W_{\mathrm{r}} \;-\; \frac{1}{2}\,W_{\mathrm{s}} \quad \text{(< 0; consumed)}$$

$$P_{\mathrm{Ar}} \;=\; 0 \qquad\qquad \text{(inert)}$$

thus with coefficients that are the respective columns of matrix **M**, as follows from (3.2.1.2) with $Q_{\mathrm{X}} \;=\; -\,P_{\mathrm{X}}$ for components $\mathrm{X} = \mathrm{A}_1 , \dots , \mathrm{A}_n$.

Summarising, having R reactions $r \;=\; 1,\dots,R$ in a reactor, they are written with the above convention

$$r = 1,\ldots,R: \qquad \sum_{\mathrm{X}} \nu_{\mathrm{X}r}\mathrm{X} = 0 \tag{3.2.1.4}$$

with sum over components present in the reaction; we have $\nu_{\mathrm{X}r} > 0$ for reaction products, $\nu_{\mathrm{X}r} < 0$ for components X consumed, $\nu_{\mathrm{X}r} = 0$ for component X not participating in reaction r. [*Inert* is component Y with *all* $\nu_{\mathrm{Y}r} = 0$.] The stoichiometric matrix **S** (= $\mathbf{M}^{\mathrm{T}}$) is that of coefficients $\nu_{\mathrm{X}r}$ (row X, column r). Then the *molar production rate* of component X equals

$$P_{\mathrm{X}} = \sum_{r=1}^{R} \nu_{\mathrm{X}r} W_r \tag{3.2.1.5}$$

(kmol s^{-1}) where W_r is the r-th reaction rate, and in mass units (kg s^{-1}) we have $M_{\mathrm{X}}P_{\mathrm{X}}$.

3.2.2. Steady-state multicomponent balance

Let us go back to the balance (2.1.2) with the immediately following commentary. The accumulation term can play a role in particular in single-component (mass) balancing, inventories (e.g. in storage tanks) included; see then what is said in the paragraph preceding Eq. (2.1.1). Otherwise, in the process analysis we are rather interested in units such as columns, reactors and the like. The *steady-state hypothesis* then simplifies the analysis. It can be interpreted in the manner that by the time-averaging (2.2.1) with (2.2.1a), the (possibly fluctuating) change in holdup vanishes. The balance (2.1.2) is then written without the last term thus

$$\text{quantity out} - \text{quantity in} = \text{source.} \tag{3.2.2.1}$$

Consider now again the example in Fig. 2-3. The LHS of (3.2.2.1) reads, e.g. for O_2

$$\text{(say)}\ m_{\mathrm{O2}} = m_3\, y_{\mathrm{O2}}^{3} - m_1\, y_{\mathrm{O2}}^{1} - m_2\, y_{\mathrm{O2}}^{2} \quad (\text{kg s}^{-1})$$

where m_i is mass flowrate in stream i and generally y_{X}^{i} is mass fraction of component X in stream i; the m_i and y_{X}^{i} are our *balancing variables*. The source term equals the production rate of O_2 by the chemical reaction (a) in Subsection 3.2.1, thus in mass units

$$M_{\mathrm{O2}}P_{\mathrm{O2}} \ \text{where}\ P_{\mathrm{O2}} = -\frac{1}{2}W_{\mathrm{a}} \ \text{(consumed)}$$

where (-1/2) is the stoichiometric coefficient at O_2 in the reaction written by convention as $-1/2\ O_2 - SO_2 + SO_3 = 0$; see (3.2.1.3) and (3.2.1.2) where $P_{\mathrm{O2}} = -Q_{\mathrm{O2}}$. It is convenient to introduce the molar quantity

$$n_{\mathrm{O2}} = \frac{1}{M_{\mathrm{O2}}} m_{\mathrm{O2}} \quad (\text{kmol s}^{-1})$$

where M_X is mole mass of chemical species X. Then the O_2-balance reads

$$n_{O2} \ = \ P_{O2} \quad (= -\frac{1}{2} W_a)$$

where W_a is the rate of reaction (a) written in the above conventional form. We'll have $P_{SO2} = -W_a$, $P_{SO3} = W_a$ and $P_X = 0$ for the inerts X = N_2 , Ar (molar production rates).

Generalising, for each of the components X present in the node we introduce the 'balance excess'

$$m_X \quad (= \text{output minus input}) = \sum_{i,\text{out}} m_i y_X{}^i - \sum_{i,\text{in}} m_i y_X{}^i \tag{3.2.2.2}$$

where we put $y_X{}^i = 0$ for component X absent from stream i (e.g. $y_{SO2}{}^2 = 0$ in Fig. 2-3), further

$$n_X \ = \ \frac{1}{M_X} m_X \tag{3.2.2.3}$$

and write the balances for each X

$$n_X \ = \ P_X \tag{3.2.2.4}$$

where P_X is the molar production rate of component X computed generally according to (3.2.1.5) in terms of reaction rates W_r . *In addition*, considering the m_i and $y_X{}^i$ as balancing variables, we have the conditions

$$\text{for each stream } i: \quad \sum_X y_X{}^i \ = \ 1 \tag{3.2.2.5}$$

with sum over all X present in the stream. The condition (sum of mass fractions = 1) is obvious, but it must be explicitly written when solving a set of component balance equations in the latter variables. Then, as can be shown (VE-MA, Chapter 4), the overall mass balance is a *consequence* of (3.2.2.4 and 5) and need not be written explicitly as a further condition. Also the atom species (elements) remain thus conserved each separately (while the components X generally not), of course with correctly written reaction stoichiometry.

3.2.3. Nonreaction nodes

They are characterised by the (assumed) absence of chemical reactions. Then the above production rates $P_X = 0$ and we have directly

$$m_X \ = \ 0 \tag{3.2.3.1}$$

for each of the components X, with (3.2.2.2). Thus according to Fig. 2-2 we have, for column A

$m_1 y_X^1 + m_6 y_X^6 = m_2 y_X^2 + m_3 y_X^3$ along with (3.2.2.5)

for components X = N_2 , Ar, H_2 and hydrocarbons C1 to C7. We can suppose that $y_X^3 = 0$ and $y_X^6 = 0$ for X = N_2 , Ar, H_2 , most likely also for methane CH_4 at least. Observe that we here can use the transformations (2.2.7).

A special case of nonreaction node is a *splitter*

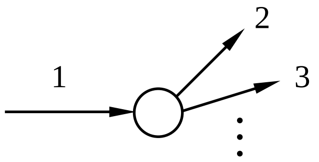

Fig. 3-1 Splitter

with one inlet and two or more outlet streams, characterised by the following property: The inlet stream is *only divided* (split) into several streams, *without undergoing any other change*. The balances (3.2.3.1) with (3.2.2.5) then don't provide the full information. Considering two outlet streams in Fig. 3-1, the component balances would be of the same form as those of a distillation column, thus admitting different composition in streams 2 and 3. The *splitter balance* reads more explicitly

$$m_1 = m_2 + m_3 + \ldots \tag{3.2.3.2}$$

and

$$\begin{aligned} y_X^2 &= y_X^1 \\ y_X^3 &= y_X^1 \\ &\ \vdots \end{aligned} \tag{3.2.3.3}$$

for each X, with

$$\sum_X y_X^1 = 1. \tag{3.2.3.4}$$

[The conditions (3.2.3.4) for the other y_X^i follow from (3.2.3.3) and need not be written.]

3.2.4. Reaction nodes (reactors)

Let us begin again with the simple example given in Subsections 3.2.1 and 3.2.2. The component balances (3.2.2.4) read

$$\begin{aligned} n_{O2} &= -\frac{1}{2} W_a \\ n_{SO2} &= -W_a \\ n_{SO3} &= W_a \end{aligned} \tag{3.2.4.1}$$

and $n_{N2} = 0$, $n_{Ar} = 0$, plus the definition of n_X by (3.2.2.2 and 3), plus the conditions (3.2.2.5). Along with the balancing variables m_i and y_X^i, we here have the parameter W_a, the reaction rate of the unique admissible reaction. This is the case of a standard technology. We know that oxidation of N_2 can be neglected under the given conditions and that, on the other hand, the oxidation $SO_2 \rightarrow SO_3$ does run in the contact reactor. Note that in the same plant, SO_3 with the nonreacted O_2 and SO_2 are cooled and led to an absorber where no such reaction takes place, although stoichiometrically possible and even thermodynamically preferred: it is here 'frozen' (negligibly slow) due to low temperature and the absence of catalyst. All these facts are known a priori and only then, the balance scheme with parameter W_a can be written.

The reaction rates are matter of interest of reactor experts; they can possibly be predicted or conversely computed: thus in our example when one of the LH-sides in (3.2.4.1) is known (e.g. measured). Otherwise, they can be eliminated. Indeed, from (3.2.4.1) we can obtain

$$\begin{aligned} & n_{SO2} + n_{SO3} = 0 \\ \text{and} \quad & \\ & n_{SO3} + 2\, n_{O2} = 0. \end{aligned} \tag{3.2.4.1a}$$

In the sequel, we shall be mainly interested in the auxiliary variables n_X (thus the production rates P_X expressed in terms of the balancing variables). Writing the balance equations explicitly using the substitutions (3.2.2.3) with (3.2.2.2) is then easy.

Note: Omitting the variables n_{N2} and n_{Ar} equal to zero, the equations (3.2.4.1) determine a straight line in the threedimensional space of coordinates n_{O2}, n_{SO2}, n_{SO3}, parametrised by W_a. The straight line is also the intersection of two planes (3.2.4.1a). It is the simplest example of a vector (sub)space, called here the *reaction space*, to which the variables n_X (thus P_X) must belong due to the reaction stoichiometry. In the same manner, the reaction space can be introduced for a general set of reactions and again, the reaction rates can be eliminated. The topic is dealt with in detail in VE-MA, Chapter 4.

Let us now give several less trivial examples. In order to simplify the numbering, the ad hoc formulae in the Examples are numbered as (Ex 1.1), ... , (Ex 2.1), ... , etc., formulae of more general character excepted.

Exemple 1. Burning of sulphur

The scheme is the same as in Fig. 2-3, but stream 1 is now liquid sulphur, stream 2 dry air and stream 3 the SO_2-gas. Consider now the two reactions (r) and (s) in a sulphur burning unit according to Subsection 3.2.1. Suppose we are no reactor experts and let us further admit the reaction

$$S + 3/2\ O_2 = SO_3 \tag{t}$$

thus also direct oxidation of sulphur to sulphur trioxide. The (transposed) stoichiometric matrix thus **M** now reads

$$\mathbf{M} = \begin{array}{c} \\ \\ \end{array} \begin{array}{cccccc|c} S & O_2 & SO_2 & SO_3 & N_2 & Ar & \\ \hline -1 & -1 & 1 & 0 & 0 & 0 & r \\ 0 & -1/2 & -1 & 1 & 0 & 0 & s \\ -1 & -3/2 & 0 & 1 & 0 & 0 & t \end{array} \tag{Ex 1.1}$$

and the production rates P_X thus n_X are

$$\begin{aligned} n_S &= -W_r \qquad\qquad - W_t \\ n_{O2} &= -W_r - \frac{1}{2} W_s - \frac{3}{2} W_t \\ n_{SO2} &= W_r - W_s \\ n_{SO3} &= \qquad W_s + W_t \end{aligned} \tag{Ex 1.2}$$

along with $n_{N2} = n_{Ar} = 0$. Let us have measured or otherwise fixed the balancing variables (mass flowrates and composition of streams). It turns out (and can be proved formally) that a solution in the reaction rates either does not exist at all (incompatible data), or it does but then, there is an infinite number of solutions. The incompatibility means that the n_X do not lie in the properly defined reaction space (see below). The nonuniqueness means generally that the reaction rates can perhaps be predicted by some model of reaction kinetics, but cannot be found by mere balancing. A reactor expert eliminates immediately the third reaction (t).

Let us now illustrate the general procedure leading to analogous conditions as (3.2.4.1a). The theoretical concept of reaction space stands again behind the operations (see VE-MA, Chapter 4), but we can avoid it in practice. In the first step, by Gauss-Jordan elimination in **M** we find the equivalent matrix

$$\begin{array}{cccccc|c} SO_2 & SO_3 & S & O_2 & N_2 & Ar & \\ \hline 1 & 0 & -1 & -1 & 0 & 0 & (1) \\ 0 & 1 & -1 & -3/2 & 0 & 0 & (2) \\ 0 & 0 & 0 & 0 & 0 & 0 & \end{array}$$

where we have changed the order of components to have unit submatrix in the left upper corner.

The matrix obtained by elimination is not unique, as is well known. Here, we have chosen certain 'key components' that constitute the columns of the unit submatrix (they are generally not arbitrary). The two nonnull rows represent some fictitious *independent* reaction schemes (1) and (2) with reaction rates W_1 and W_2 that are the new parameters (this means that the reaction space is of dimension 2). [In the given case, the independent reactions happen to be (r) and (t).] We thus can write

$$n_{SO2} = W_1$$

$$n_{SO3} = W_2$$

and from

$$n_S = -W_1 - W_2$$

$$n_{O2} = -W_1 - \frac{3}{2} W_2$$

by elimination of W_1 and W_2 we find the conditions

$$\begin{aligned} n_S + n_{SO2} + n_{SO3} &= 0 \\ n_{O2} + n_{SO2} + \frac{3}{2} n_{SO3} &= 0 \end{aligned} \qquad \text{(Ex 1.3a)}$$

(which can be rewritten in different other ways by combinations), and of course again

$$\begin{aligned} n_{N2} &= 0 \\ n_{Ar} &= 0\,. \end{aligned} \qquad \text{(Ex 1.3b)}$$

The balancing variables constituting the terms n_X by (3.2.2.3 and 2) must obey the conditions (Ex 1.3), and (3.2.2.5); the reaction rates are not needed. Observe also that denoting by 1 the stream of supplied (liquid) sulphur (with $y_S^1 = 1$), we have

$$n_S = -\frac{1}{M_S} m_1 \qquad \text{(Ex 1.4)}$$

assuming that sulphur is completely burnt thus absent from the outlet stream.

The procedure (transformation of matrix **M** and elimination of the fictitious reaction rates) can be formulated algorithmically (VE-MA, Chapter 4) and computer-coded.

Example 2. Oxidation of ammonia

In the production of nitric acid, ammonia is oxidised by air in a two-stage reactor with subsequent absorption (and further oxidation) to concentrated HNO_3 . Here, we'll limit ourselves to the first stage of the oxidation.

In the first stage of the reactor, mainly the following two reactions take place.

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O \qquad (1)$$

$$2\,NH_3 + \frac{3}{2}O_2 = N_2 + 3\,H_2O \qquad (2)$$

producing a large amount of water. The gas is then cooled and H_2O is condensed out. At the same time, by further oxidation of NO

$$NO + \frac{1}{2}O_2 = NO_2 \qquad (3)$$

in the gas phase and, after absorption in the liquid phase, by the summary reaction

$$2\,NO_2 + \frac{1}{2}O_2 + H_2O = 2\,HNO_3 \qquad (4)$$

diluted nitric acid is formed. The oxidation is then completed in the second stage after further addition of air.

The first stage, condensation of water included, is conceived as one node:

Fig. 3-2 Oxidation of ammonia

The matrix **M** of the four reactions with the conventions according to Subsection 3.2.1 reads

$$\mathbf{M} \;=\; \begin{array}{c} \\ \\ \end{array}\begin{array}{cccccccc|c} \mathrm{NO} & \mathrm{NO_2} & \mathrm{H_2O} & \mathrm{HNO_3} & \mathrm{NH_3} & \mathrm{O_2} & \mathrm{N_2} & \mathrm{Ar} & \\ \hline 4 & & 6 & & -4 & -5 & & & (1) \\ & & 3 & & -2 & -3/2 & 1 & & (2) \\ -1 & 1 & & & & -1/2 & & & (3) \\ & -2 & -1 & 2 & & -1/2 & & & (4) \end{array} \qquad \text{(Ex 2.1)}$$

where the void fields are zeros. Taking NO, NO_2 , H_2O, HNO_3 as key components and using the first four columns for the elimination, the equivalent matrix reads

$$\begin{array}{cccc|cccc|c} \mathrm{NO} & \mathrm{NO_2} & \mathrm{H_2O} & \mathrm{HNO_3} & \mathrm{NH_3} & \mathrm{O_2} & \mathrm{N_2} & \mathrm{Ar} & \\ \hline 1 & & & & & -1/2 & -1/2 & & (1') \\ & 1 & & & & -1 & -1/2 & & (2') \\ & & 1 & & -2/3 & -1/2 & 1/3 & & (3') \\ & & & 1 & -1/3 & -3/2 & -1/3 & & (4') \end{array} \qquad \text{(Ex 2.2)}$$

and after elimination of the fictitious reaction rates $W_{r'}$ ($W_{1'} = n_{\mathrm{NO}}$ etc.) we have the balance equations

$$\begin{aligned} \frac{2}{3}n_{\mathrm{H2O}} + \frac{1}{3}n_{\mathrm{HNO3}} + n_{\mathrm{NH3}} &= 0 \\ \frac{1}{2}n_{\mathrm{NO}} + n_{\mathrm{NO2}} + \frac{1}{2}n_{\mathrm{H2O}} + \frac{3}{2}n_{\mathrm{HNO3}} + n_{\mathrm{O2}} &= 0 \\ \frac{1}{2}n_{\mathrm{NO}} + \frac{1}{2}n_{\mathrm{NO2}} - \frac{1}{3}n_{\mathrm{H2O}} + \frac{1}{3}n_{\mathrm{HNO3}} + n_{\mathrm{N2}} &= 0 \\ n_{\mathrm{Ar}} &= 0 \end{aligned} \qquad \text{(Ex 2.3)}$$

where

$$n_{\mathrm{X}} = n_{\mathrm{X}}^{3} + n_{\mathrm{X}}^{4} - n_{\mathrm{X}}^{1} - n_{\mathrm{X}}^{2} \qquad \text{(Ex 2.3a)}$$

with

$$n_{\mathrm{X}}^{j} = \frac{1}{M_{\mathrm{X}}} y_{\mathrm{X}}^{j}\, m_j \qquad \text{(Ex 2.3b)}$$

and the conditions

$$\sum_{X} y_X^j = 1 . \qquad \text{(Ex 2.4)}$$

Again $y_X^j = 0$ if X is not present in stream j.

We complete the model by specifying the components X present in streams j.

stream 1: pure NH_3
2: O_2 , N_2 , Ar, H_2O (humidity)
3: O_2 , N_2 , Ar, NO, NO_2 (nonabsorbed), H_2O (noncondensed); we suppose complete burning of NH_3
4: H_2O, HNO_3 .

The balancing variables are thus m_1 , m_2 , m_3 , m_4 and $y_{NH3}{}^1$ (= 1 by (Ex 2.4)), $y_X{}^2$ for X = O_2 , N_2 , Ar, H_2O, $y_X{}^3$ for X = O_2, N_2 , Ar, NO, NO_2 , H_2O, $y_X{}^4$ for X = H_2O, HNO_3; in fact $y_{NH3}{}^1$ is not a variable, being uniquely determined a priori by the definition of stream 1.

The component balance of the node comprises 4 equations (Ex 2.3) and 4 (or only 3 with $y_{NH3}{}^1$ = 1 eliminated) conditions (Ex 2.4); with the substitutions (Ex 2.3a and b), it is written in terms of our balancing variables. Another variant is introducing as parameters the reaction rates W_r for the reactions (1) – (4) , using the matrix **M** (Ex 2.1). The reader can set up the balances, such as $n_{NO} = 4\, W_1 - W_3$. One obtains 8 equations plus again 4 (or 3) conditions
(Ex 2.4). In this case, the reactions are independent and no difficulty such as in Example 1 arises. [If the necessary data are compatible, the reaction rates are uniquely determined, as the theory shows.]

Note: In design or simulation problems, the equations such as (Ex 2.3 and 4) are part of the mathematical model of the plant. In the process analysis using measured data, it is not always a simple task to find, which balancing variables have to be measured in order to determine all of them. The above equations (constraints) represent certain conditions for the *compatibility* of the data. The measured data (usually more than needed) are then *reconciled* so as to make them compatible; see further Chapter 5.

Element balances

Let us first suppose that the conditions such as (Ex 2.3 and 4) in Example 2 are fulfilled. It can be shown (VE-MA, Chapter 4) that *then* also the individual chemical elements (atom species) remain conserved, which is a necessary condition for the compatibility of the data (nuclear reactions precluded). So the latter condition doesn't represent any further constraint. For example the oxygen atom balance $P_O = 0$ is fulfilled automatically.

In the example, we have

$$P_O = P_{NO} + 2P_{NO2} + P_{H2O} + 3P_{HNO3} + 2P_{O2}$$

because oxygen is present in the named chemical species and for example in NO_2 , we have two atoms O. Since $P_X = n_X$ (3.2.2.4), we thus have the result

$$n_{NO} + 2\, n_{NO2} + n_{H2O} + 3\, n_{HNO3} + 2\, n_{O2} = 0.$$

[By the way, we can see that this happens to be just 2 × the second equation (Ex 2.3); but generally, such a result need not be so simply obtained.]

Generally, we can introduce the *atom matrix* **A** whose rows correspond to the elements E and columns to the chemical species X present in the mixture (in the node). In row E and column X of the matrix, we have the number of atoms E in the chemical formula of X considered in the stoichiometry. Thus in the above example

$$\mathbf{A} = \begin{array}{cccccccc|l} NO & NO_2 & H_2O & HNO_3 & NH_3 & O_2 & N_2 & Ar & \\ \hline 1 & 1 & & 1 & 1 & & 2 & & N \\ 1 & 2 & 1 & 3 & & 2 & & & O \\ & & 2 & 1 & 3 & & & & H \\ & & & & & & & 1 & Ar \end{array}$$

[By another convention, atom matrix is called the transpose $\mathbf{A}^T$.] The conservation of elements in the node is expressed in algebraic form

$$\mathbf{A}\mathbf{n} = 0 \qquad (3.2.4.2)$$

where **n** is the column vector of components n_X (3.2.2.3 and 2) ordered according to the columns of **A**.

Frequently, the rows of the matrix **A** are linearly independent. Still, exceptions are possible. Considering the liquid solution (Na_2SO_3 , Na_2SO_4 , H_2O_2 , H_2O) corresponding to the oxidation of Na_2SO_3 by hydrogen peroxide, we have the atom matrix

$$\mathbf{A} = \begin{array}{cccc|ll} Na_2SO_3 & Na_2SO_4 & H_2O_2 & H_2O & & \\ \hline 2 & 2 & & & Na & \underline{\qquad} \\ 1 & 1 & & & S & \\ 3 & 4 & 2 & 1 & O & \mathbf{A}_0 \\ & & 2 & 2 & H & \end{array}$$

and the first row can be eliminated. The remaining submatrix (say) $\mathbf{A}_0$ has 3 independent rows. Thus generally, the equivalent formulation of (3.2.4.2) reads

$$\mathbf{A}_0\,\mathbf{n} \;=\; 0 \qquad (3.2.4.2a)$$

where $\mathbf{A}_0$ is the matrix obtained from **A** by the elimination of linearly dependent rows.

The rank of the matrix **A** thus the number of its linearly independent rows determines the *maximum number* $R_{\max}$ *of independent reactions* that are *stoichiometrically possible* in the given mixture. If there are K chemical species present in the reaction node, we have (VE-MA: 4.4)

$$R_{\max} \;=\; K \;-\; \mathrm{rank}\mathbf{A}. \qquad (3.2.4.3)$$

So with the last example of atom matrix, we have $R_{\max} \;=\; 4 - 3 \;=\; 1$ and indeed, the oxidation reaction $Na_2SO_3 + H_2O_2 \;=\; Na_2SO_4 + H_2O$ takes place. Also in the preceding example where $R_{\max} = 8 - 4 \;=\; 4$, we have just 4 independent reactions; see Example 2 , (1) – (4): *Then* the condition (3.2.4.2) is *equivalent* to the conditions (Ex 2.3).

Nevertheless, the *admissible* number of (independent) reactions in the node *can be lower*, or even zero. See the oxidation of SO_2 to SO_3 (3.2.4.1) with the commentary: in the absorber, the oxidation doesn't take place. Or imagine a mixture of hydrocarbons in a distillation column. The atom matrix has two rows (C and H) and the rank equals 2; for instance for 7 components we have $R_{\max} \;=\; 7 - 2 \;=\; 5$ but no chemical reaction runs in the column.

For standard technologies, the chemical species in the input and output streams and the admissible reactions are known a priori and there is then no reason for having recourse to analysis of the atom matrix. Still, there are cases of complicated systems and not well-known reaction mechanisms. It is then the task of a reaction expert to propose the possible reaction schemes. The topic lies beyond the scope of this text. Let us only illustrate the possible use of the atom matrix by simple examples.

Example 3. Stoichiometrically possible reactions

The maximal set of stoichiometrically possible reactions can be found by a method due to Schneider and Reklaitis (1975). Because then, the equation (3.2.4.2) represents in fact the balance equations where the parameters (reaction rates) have been eliminated, this is the inverse procedure: Given the above equation, we have to re-parametrise it.

To illustrate the procedure, let us consider Example 1. The atom matrix reads

$$\mathbf{A} \;=\; \begin{array}{cccccc|c} \mathrm{S} & \mathrm{O}_2 & \mathrm{SO}_2 & \mathrm{SO}_3 & \mathrm{N}_2 & \mathrm{Ar} & \\ \hline 1 & & 1 & 1 & & & \mathrm{S} \\ & 2 & 2 & 3 & & & \mathrm{O} \\ & & & & 2 & & \mathrm{N} \\ & & & & & 1 & \mathrm{Ar} \end{array}$$

and its rank equals 4, thus 6-4 = 2 independent reactions are possible. The formalism requires transforming **A** to an equivalent form, for example (imagine Gauss-Jordan elimination)

$$\begin{array}{cccc|cc} S & O_2 & N_2 & Ar & SO_2 & SO_3 \\ \hline 1 & & & & 1 & 1 \\ & 1 & & & 1 & 3/2 \\ & & 1 & & & \\ & & & 1 & & \end{array}$$

|> unit matrix <|

and Eq. (3.2.4.2) reads, transformed

$$\begin{aligned} n_S + n_{SO2} + n_{SO3} &= 0 \\ n_{O2} + n_{SO2} + \frac{3}{2} n_{SO3} &= 0 \\ n_{N2} &= 0 \\ n_{Ar} &= 0. \end{aligned} \tag{Ex 3.1}$$

Taking now the components SO_2 and SO_3 (whose columns do *not* form the LH-unit matrix) as 'key components', let us introduce two parameters

$$n_{SO2} = W_1$$

$$n_{SO3} = W_2$$

and we have in addition

$$n_S = -W_1 - W_2$$

$$n_{O2} = -W_1 - \frac{3}{2} W_2$$

along with $n_{N2} = 0$ and $n_{Ar} = 0$ (inerts). This corresponds precisely to the result of Example 1; the possible independent reaction schemes are $S + O_2 = SO_2$ and $S + 3/2\ O_2 = SO_3$. The reader can carry out the transformation (elimination) in different other manners. He will find different other possible reaction schemes, some of them quite strange. The only result that works is then the *parametrisation* of the balance equations by two (generally fictitious) reaction rates. It was possible to use directly the balances (Ex 3.1).

Example 4. Production of biomass

The example is taken over from Madron (1992): Example 2.2, and slightly modified. The biomass (yeast) is produced from ethanol in a fermentation reactor. The inlet streams are

ethanol (formula C_2H_6O), with H_2O
air (O_2, N_2 , Ar, humidity)
ammonia (NH_3)
mineral nutrients represented by a fictitious element Ah with relative atom mass 1.

In the liquid and gaseous outlet streams were found

gaseous: CO_2 and nonreacted O_2 , N_2 , Ar, humidity
liquid (suspension): biomass of empirical formula $C_{3.83}H_{7.00}O_{1.94}N_{0.64}Ah_{7.00}$ (which means that 1 kmol of biomass contains 7 kg of Ah), water, acetic acid ($C_2H_4O_2$) as undesirable product.

Based on the known input components and those found in the outlet streams, our reaction expert has proposed the following reaction schemes, rewritten according to the convention introduced above

production of biomass

$$- 1.915\ C_2H_5OH - 1.615\ O_2 - 0.64\ NH_3 - 7.00\ Ah + \text{biomass} + 3.205\ H_2O = 0 \qquad (1)$$

production of CO_2

$$- C_2H_5OH - 3\ O_2 + 2\ CO_2 + 3\ H_2O = 0 \qquad (2)$$

production of acetic acid

$$- C_2H_5OH - O_2 + CH_3COOH + H_2O = 0. \qquad (3)$$

The reader can easily set up the stoichiometric matrix and find that the three reactions are independent.

Our goal is now to check if the above reactions represent the stoichiometrically possible maximum. It is easy as well to set up the atom matrix **A**. The 6 rows are C, H, O, N, Ah, Ar (the atom species) and the columns represent the chemical components present in the streams, thus

ethanol (C_2H_6O), O_2 , NH_3 , Ah, biomass, acetic acid ($C_2H_4O_2$), CO_2, H_2O, and also N_2 , Ar (Ex 4.1)

in number 10. By the elimination, one finds that the rows are linearly independent hence the rank equals 6 and by virtue of (3.2.4.3) we have $R_{\max} = 10-6 = 4$: one independent reaction is stoichiometrically possible in addition.

The possible reaction schemes can theoretically be found by the procedure illustrated in Example 3 using the (Gauss-Jordan) elimination: As above, one finds the n_X (thus production rates P_X) as linear combinations of the parameters W_r ($r = 1,...,4$) with coefficients ν_{xr} in (3.2.1.5); then ν_{xr} is the stoichiometric coefficient at component X in the r-th reaction scheme (3.2.1.4). The problem is that the resulting form of the matrix depends on the elimination strategy and quite obscure 'reaction' schemes can be obtained. A hint is given by knowing already the three above reactions (1),(2),(3). It requires some skill, but by linear combinations of the obtained 'pseudoreaction' schemes or directly by guessing one can find, along with the reactions (1),(2),(3), the fourth possible independent reaction scheme as

$$- 2\ NH_3 - 3/2\ O_2 + 3\ H_2O + N_2 = 0\ . \tag{4}$$

Thus nitrogen can hypothetically (perhaps by catalytic oxidation in the liquid phase) arise by the reaction (4). Having precluded this possibility means *declaring* N_2 to be *nonreacting* (inert) component, neither consumed *nor* arising by any chemical reaction. Observe that one automatically obtains anyway (production rate) $n_{Ar} = 0$ because Ar is not present in any of the other components. There remains to add the condition

$$n_{N2} = 0 \tag{Ex 4.2}$$

to the condition (3.2.4.2). Or, being aware of it, consider only the reactions (1),(2),(3) in the balancing with three parameters (reaction rates) W_1 , W_2 , W_3 ; the condition (Ex 4.2) is then fulfilled automatically. This also corresponds to including (as in Madron 1992) only the first 8 components (Ex 4.1) in the balancing.

Example 5. Esterification reactions

The additional hypotheses such as (Ex 4.2) can be formulated more generally as 'conservation of certain groups of elements in certain chemical components'. As a simple example (cf. VE-MA: 4.4), consider the mixture of methanol (CH_3OH), ethanol (C_2H_5OH), acetic acid (CH_3COOH) and esterification products CH_3COOCH_3 , $CH_3COOC_2H_5$, H_2O, denoted briefly as met, et, ac, metest, etest, W repectively.

The original matrix **A** has 3 rows C, O, H and 6 columns met, et, ac, metest, etest, W. The reader can write it and find the rank equal to 3. So the number of stoichiometrically possible reactions is 6-3 = 3. Along with the two esterification reactions (which can be anticipated)

$$CH_3COOH + CH_3OH = CH_3COOCH_3 + H_2O \tag{1}$$

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O \tag{2}$$

one can find the third reaction for example as

$$\underset{\text{ac}}{C_2H_4O_2} + \underset{\text{etest}}{C_4H_8O_2} = 2\ \underset{\text{metest}}{C_3H_6O_2} \tag{3}$$

with structural regrouping of atoms. Having suggestively written the structural formulae, one is led to the assumption that the acetic group (CH_3COO) and alkyl groups (CH_3, C_2H_5) will remain conserved as certain (pseudo)atoms. Because element C is contained only in the named groups, one can write the (pseudo)atom matrix as

$$\begin{array}{r|cccccc|ll} & \text{met} & \text{et} & \text{ac} & \text{metest} & \text{etest} & \text{W} & & \\ \hline & & & 1 & 1 & 1 & & CH_3COO & \\ & 1 & & & 1 & & & CH_3 & \\ \mathbf{A} = & & 1 & & & 1 & & C_2H_5 & \mathbf{A}_0 \\ & 1 & 1 & & & & 1 & O & \\ & 1 & 1 & 1 & & & 2 & H & \end{array}$$

because met is composed of CH_3 , O, H; et of C_2H_5, O, H; ac of CH_3COO, H; metest of CH_3COO, CH_3 ; etest of CH_3COO, C_2H_5 ; H_2O of O, H.. One can eliminate row H by subtracting the sum of rows CH_3COO and O and adding the rows CH_3 and C_2H_5 giving row O instead of H, thus subtracting again row O one has zero row. The rank of the resulting matrix (say) $\mathbf{A}_0$ equals 4; we have the balance (3.2.4.2a). We have $R_{\max} = 6-4 = 2$ as corresponds to the two esterification reactions.

Such 'conservation of groups of atoms' (structural elements) is frequent in organic chemistry. One thus can restrict the number of admissible reactions. Or conversely, one can perhaps reveal the possibility of further reactions worthy of attention. Nonetheless, whether this formalistic approach is useful in practice remains questionable. By the way, one can have anyway omitted a possible presence of undesirable by-products not included in the list of the outlet chemical components due to lacking information.

Note: The admissible reactions create certain *reaction degrees of freedom* in the balancing. The more reactions are admitted, the less balance constraints are imposed and the easier are the given (e.g. measured) data adapted to obey them. But admitting reactions that don't take place can then only mask the incompatibility of given data. On the other hand omitting possible reactions and by-products gives rise to undesirable *model errors*.

Let us *summarise*.

The component balancing of chemical reactors requires the knowledge of chemical reactions that can run under the conditions prescribed by the technology. They are well-known for standard technologies but otherwise,it is the task of a *reactor expert* to propose the admissible reaction schemes. Then, either the corresponding reaction rates are introduced as parameters, or the latter can be eliminated; see the examples 1 and 2. The possible use of the atom matrix (element balance) is illustrated by examples 3,4,5. See then the beforelast two paragraphs.

3.3.Energy balance

With the same motivation as in Subsection 3.2.2, we shall not consider a general balance with accumulation of energy. It turns then out that the relevant part of energy associated with the material flow is its enthalpy. In addition, energy can be supplied/withdrawn to/from the node as 'heat' or 'work'; imagine heating/cooling or a compressor.

The topic is dealt with in detail in VE-MA, Chapter 5 with appendix C. Neglecting less relevant items such as kinetic or potential energy, the simplified (approximate) energy balance is obtained as the (steady-state) *enthalpy balance*. Its general form is quite simple:

$$\sum_{i,\text{in}} \hat{H}^i m_i \; + \; Q \;\; = \;\; \sum_{i,\text{out}} \hat{H}^i m_i \;\; + \;\; W \qquad (3.3.1)$$

where m_i is mass flowrate and $\hat{H}^i$ specific enthalpy of stream i, with summation over inlet resp. outlet streams. The supplied heat is Q (< 0 for cooling) and W is power (work per unit time) produced by the node (usually $W \leq 0$; consumed or null); the heat Q can be divided into several heat flows (streams). The accumulation, and also source terms in (2.1.2) equal zero: energy remains conserved.

Writing the balance in the form (3.3.1) corresponds to the rigorous thermodynamic definition of specific enthalpy, with a zero level taken by some convention. The most general convention takes specific enthalpies equal to zero for chemical elements at their standard states; then to any chemical species X is assigned its

$$\text{standard specific enthalpy:} \;\; \hat{H}_{\text{X}}^{(0)} \qquad (3.3.2)$$

again at its standard (reference) state. These values can be found in thermodynamical tables. But even then, the enthalpy of a multicomponent mixture is generally not a simple sum of component enthalpies: we here have increments due to mixing and phase transitions (such as evaporation). So setting up an exact energy balance requires generally good knowledge of *chemical thermodynamics*; this is a task for specialists.

For a given mixture at given state of aggregation (liquid, gaseous, ...), the specific enthalpy $\hat{H}$ can be expressed as function of the balancing variables: absolute temperature T, composition, and pressure P. For condensed phases (solid, liquid), the pressure dependence of $\hat{H}$ can usually be neglected; also for gases, if the pressure does not vary considerably, we can take P as a mean pressure in the stream given a priori and not regarded as a variable in the balancing. In the sequel, we shall limit ourselves to several simple examples of energy (enthalpy) balances. Let us begin with two special types of nodes.

3.3.1. Splitter

See Fig. 3-1. To the balance equations (3.2.3.2 – 4), we add the conditions

$$T^2 = T^1$$

$$T^3 = T^1$$

$$\vdots \qquad (3.3.3)$$

(and also $P^2 = P^1$, ...).

3.3.2. Heat exchanger

Generally, we can consider an arbitrary node C divided by a wall where only heat transfer takes place, for example

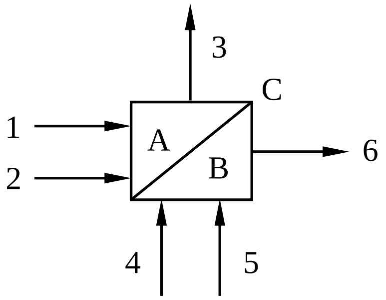

Fig. 3-3 General heat exchanger C

The part A can be a heating furnace (1:air, 2: combustible, 3: combustion products) followed by a heat exchanger in the proper sense; B is the other part of the node balanced as a whole. The streams 1,2,3 are not mixed with streams 4,5,6. We can modify the scheme

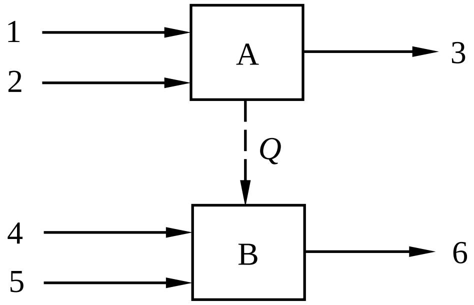

Fig. 3-3a Divided node C

where Q is the energy (heat) stream from A to B. We then write the mass (or component mass) balances *separately for* nodes A and B; this is more information than balancing both nodes together. The enthalpy balances of nodes A and B read

$$m_1 \hat{H}^1 + m_2 \hat{H}^2 - Q = m_3 \hat{H}^3$$

$$m_4 \hat{H}^4 + m_5 \hat{H}^5 + Q = m_6 \hat{H}^6$$

and by summation we have the node C enthalpy balance

$$m_1 \hat{H}^1 + m_2 \hat{H}^2 + m_4 \hat{H}^4 + m_5 \hat{H}^5 = m_3 \hat{H}^3 + m_6 \hat{H}^6 \qquad (3.3.4)$$

where the (possibly unknown) item Q has been eliminated. Compare with node C in Fig. 2-1 and its interpretation. Simple heat exchangers are for example E1 and E2 in Fig. 2-5. Then with node E1 the mass flowrates in streams 1 and 2 are balanced separately ($m_1 = m_2$), as well as those in streams 6 and 7. The heat (enthalpy) balance of E1 is one:

$$m_1 \hat{H}^1 + m_6 \hat{H}^6 = m_2 \hat{H}^2 + m_7 \hat{H}^7 \qquad (3.3.4a)$$

where we have eliminated the item $Q = m_6 \hat{H}^6 - m_7 \hat{H}^7$, which is heat flow from the hot stream 6 to the cold stream 1.

Let us further consider

3.3.3. Nonreaction nodes

It can be shown that in the absence of chemical reactions, the standard specific enthalpies (3.3.2) are not needed and can be put equal to zero at some given reference temperature T_0 (e.g. 273 K) and pressure P_0 (e.g. 10^5 Pa). As a simple example, let us consider the mixing of two (for example liquid) streams

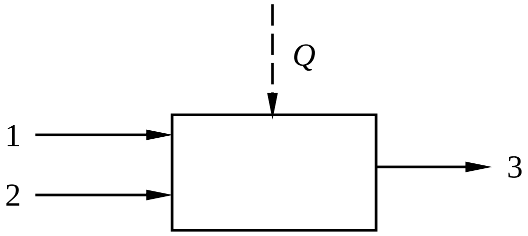

Fig. 3-4 Mixing of streams

Let first $T^1 = T^2 = T$ (say) and let the supplied heat Q (> 0 or < 0) be controlled in the manner that also $T^3 = T$, although the composition of the streams can be different. Then the difference

$$Q_{\text{mix}} = m_3\hat{H}^3 - m_1\hat{H}^1 - m_2\hat{H}^2 \qquad (T^1 = T^2 = T^3) \tag{3.3.5}$$

is the *heat of mixing*. For a number of liquids (and the more of gases), this Q_{mix} is negligible whatever be the ratio m_1/m_2 and the mass fractions of given components in the streams; imagine hydrocarbons. It can then be shown that the general enthalpy balance of the node in Fig. 3-4 reads

$$\text{for } Q_{\text{mix}} = 0: \quad m_1\bar{c}_p^{\,1}(T^1 - T_0) + m_2\,\bar{c}_p^{\,2}(T^2 - T_0) + Q = m_3\bar{c}_p^{\,3}(T^3 - T_0) \tag{3.3.6}$$

where $\bar{c}_p^{\,i}$ is (integral mean) isobaric specific heat of stream i (in the interval between T_0 and T^i). This holds true as well if the streams are in opposite direction and the node is a distillation column with boiler and condenser included; then Q in (3.3.6) equals $Q'' - Q'$ where Q' is heat supplied in the boiler and Q'' that withdrawn in the condenser. [One here assumes, however, that none of the components leaves the column in gas phase.]

Let us now give several examples just as an illustration of how thermodynamics works in less trivial situations. For the numbering of formulae, see the convention introduced before Example 1 of Subsection 3.2.4.

Example 1. Drying of air by sulphuric acid

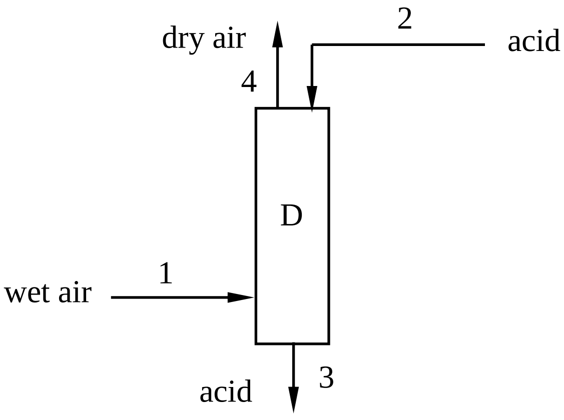

Fig. 3-5 Drying of air

Wet air (stream 1) is led into the column D and leaves it dry as stream 4. The countercurrently introduced acid (stream 2) leaves the bottom of column D as stream 3. The composition of dry air is standard; the composition of wet air can be defined by the humidity thus mass fraction y_W of H_2O; at the outlet, we suppose $y_W^4 = 0$. The composition of the acid can be expressed as mass fraction y_S of H_2SO_4 . The temperature is T^i in stream i.

The reader will easily set up the component balances. The enthalpy balance reads

$$m_4\hat{H}^4 - m_1\hat{H}^1 + m_3\hat{H}^3 - m_2\hat{H}^2 = 0 \tag{Ex 1.1}$$

where clearly

$$m_1 \;=\; m_4 + m_W \quad \text{with} \quad m_W \;=\; y_W{}^1 m_1 \tag{Ex 1.1a}$$

$$m_3 \;=\; m_2 + m_W \quad \text{and} \quad m_2 y_S{}^2 \;=\; m_3 y_S{}^3 \,. \tag{Ex 1.1b}$$

In sulphuric acid technology, it is sometimes convenient to define the acid composition as mass fraction y *of* SO_3, easily recalculated stoichiometrically from y_S ; indeed, the stoichiometric scheme $H_2O + SO_3 = H_2SO_4$ need not be thermodynamically regarded as a chemical reaction, but simply as a process of mixing with heat effects. [The acid is thus considered as mixture (H_2O,SO_3).] Then the specific enthalpy function can be expressed as $h(T, y)$ with $h(T_0\,, 0) \;=\; h(T_0\,, 1) \;=\; 0$ thus with zero levels for pure liquid components H_2O and SO_3 at reference temperature T_0 . This function can be found in tables as well as the enthalpy function $\hat{H}_A(T\,, y_W)$ for wet air. We can also approximate

$$\hat{H}_A(T\,, y_W) \;=\; (1 - y_W)\,\hat{H}_{A0}(T\,) \;+\; y_W\,\hat{H}_{Wg}(T\,) \tag{Ex 1.2}$$

where $\hat{H}_{A0}$ is specific enthalpy of dry air, $\hat{H}_{Wg}$ that of H_2O vapour; we can put $\hat{H}_{A0}(T_0) = 0$ *but* then $\hat{H}_{Wg}(T_0) \;=\; \hat{L}_W{}^{(0)}$: evaporation heat of liquid H_2O at T_0 (the standard state for H_2O is *liquid*). The pressure is assumed 'normal' (approximately that of the atmosphere).

The reader now easily writes the balance (Ex 1.1) on substituting $\hat{H}_A(T^1, y_W{}^1)$ for $\hat{H}^1$, $\hat{H}_{A0}(T^4)$ for $\hat{H}^4$, $h(T^2, y^2)$ for $\hat{H}^2$ and $h(T^3, y^3)$ for $\hat{H}^3$; in (Ex 1.1b) we have as well $m_2 y^2 \;=\; m_3 y^3$ (conservation of SO_3). We thus have the balances in balancing variables m_i , T^i , $y_W{}^1$ and y^2, y^3. The enthalpy functions are part of the database.

Note: We are perhaps interested in an a priori estimate of the temperature rise of acid in the column. Observe that the acid concentration must be held in narrow limits to make the partial pressure of H_2O negligible and to prevent the formation of acid mist at too high concentrations and temperatures. Using the formula (Ex 1.2) we *approximate*

$$\hat{H}^4 \;=\; \hat{H}_{A0}(T^4) \;=\; \hat{H}_{A0}(T^1) \;+\; c_{pA}(T^4 - T^1)$$

$$\hat{H}_{Wg}(T^1) \;=\; \hat{H}_{Wg}(T^2) \;+\; c_{pWg}(T^1 - T^2)$$

and further, using the Taylor formula with $\partial\hat{H}/\partial T \;=\; c_p$

$$\hat{H}^3 \;=\; \hat{H}(T^3, y_S{}^3) \;=\; \hat{H}^2 \;+\; c_p(T^3 - T^2) \;+\; (y_S{}^3 - y_S{}^2)\frac{\partial\hat{H}}{\partial y_S} \tag{Ex 1.3}$$

where $\hat{H}(T\,, y_S)$ is specific enthalpy function for the acid and $\partial\hat{H}/\partial y_S$ is taken at $(T^2, y_S{}^2)$. The specific heats c_{pA} (dry air), c_{pWg} (H_2O vapour) and c_p (acid) are approximated by constants. We further use the thermodynamic identity for a two-component mixture (see e.g.VE-MA: (C.10))

$$\hat{H} \; = \; \hat{H}_{\mathrm{W}} \; + \; y_{\mathrm{S}} \frac{\partial \hat{H}}{\partial y_{\mathrm{S}}} \qquad \text{(Ex 1.4)}$$

where $\hat{H}_{\mathrm{W}}$ is partial specific enthalpy of H_2O in the mixture. Using also (Ex 1.1a,b) we obtain the balance

$$m_4\, c_{p\mathrm{A}}(T^{\,4} - T^{\,1}) \; + \; m_{\mathrm{W}}\, c_{p\mathrm{Wg}}(T^{\,2} - T^{\,1}) \; + \; m_3\, c_p(T^{\,3} - T^{\,2}) \; + \; m_{\mathrm{W}}\, \delta_{\mathrm{Wg}} \; = \; 0 \qquad \text{(Ex 1.5)}$$

where

$$\delta_{\mathrm{Wg}} \; = \; \hat{H}_{\mathrm{W}}(T^{\,2}, y_{\mathrm{S}}^{\,2}) \; - \; \hat{H}_{\mathrm{Wg}}(T^{\,2}) \qquad (< 0) \qquad \text{(Ex 1.5a)}$$

is *differential heat of solution* of water *vapour* in sulphuric acid at $(T^{\,2}, y_{\mathrm{S}}^{\,2})$; it can also be found in thermodynamical tables. The interpretation is straightforward: The heat (approximately: $-\, m_{\mathrm{W}}\, \delta_{\mathrm{Wg}}$) evolved by the absorption of water vapour is consumed by the temperature changes $(T^{\,4} - T^{\,1})$ for dry air, $(T^{\,2} - T^{\,1})$ for the vapour, and the temperature rise $(T^{\,3} - T^{\,2})$ of the acid (*as if* the whole absorption proceeded at acid inlet conditions). Taking for simplicity $T^{\,1} \; = \; T^{\,2}$ and also $T^{\,4} \; = \; T^{\,2}$ at gas outlet, with $y_{\mathrm{S}}^{\,2} = 0.95$ and $y_{\mathrm{S}}^{\,3} = 0.93$ we obtain some 50 K for the temperature rise of acid; the condensation heat of H_2O represents some 60%, the rest is due to the mixing of liquid H_2O with the acid.

Example 2. Conversion of SO_2 to SO_3

We already know the scheme; see Fig. 2-3 and (3.2.4.1) – (3. 2. 4.1a). The cold dry air (stream 2) is in fact divided into several streams and controls the inlet temperatures to the stages of the contact reactor. So we can as well regard the balance as that of a single stage (usually with supply of air $m_2 = 0$ into the first stage). The enthalpy balance reads generally

$$m_1 \hat{H}^{\,1} \; + \; m_2 \hat{H}^{\,2} - m_3 \hat{H}^{\,3} \; = \; 0 \qquad \text{(Ex 2.1)}$$

with standard enthalpies $\hat{H}_{\mathrm{X}}^{(0)}$ (3.3.2). By convention, they equal zero for X = N_2 , Ar, O_2 (elements in the gas phase). Let us further adopt the convention that also the components X = SO_2 , SO_3 are *gaseous* in their standard states; we write SO_2(g) and SO_3(g) in the reaction scheme. The reactor works at approximately atmospheric pressure and we neglect the pressure dependence in the enthalpy functions. Then, for each of the X we have the specific enthalpy

$$\hat{H}_{\mathrm{X}}(T\,) \; = \; \hat{H}_{\mathrm{X}}^{(0)} \; + \; \bar{c}_{p\mathrm{X}}(T\,)(T - T_0) \qquad \text{(Ex 2.2)}$$

where $\bar{c}_{p\mathrm{X}}(T\,)$ is the integral mean specific heat of X for the interval between T_0 and T ; the values can be found in tables. Neglecting the heat of mixing, for each of the streams *i* we have

$$\hat{H}^{i} = \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{i}\ \hat{H}_{\mathrm{X}}(T^{i}) \qquad \text{(Ex 2.3)}$$

with sum over X present in the stream, or also over all X with $y_{\mathrm{X}}{}^{i} = 0$ if X is absent. Along with the component balances, with (Ex 2.1) the balance is complete; the $\bar{c}_{p\mathrm{X}}$ functions and $\hat{H}_{\mathrm{X}}{}^{(0)}$ are in the database.

The enthalpy balance can be rearranged. We have

$$\hat{H}^{i} = \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{i}\ \hat{H}_{\mathrm{X}}{}^{(0)} + \bar{c}_{p}(T^{i})(T^{i} - T_0) \qquad \text{(Ex 2.4)}$$

where

$$\bar{c}_{p}(T^{i}) = \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{i}\ \bar{c}_{p\mathrm{X}}(T^{i})\ ; \qquad \text{(Ex 2.5)}$$

in (Ex 2.1) we have, with $y_{\mathrm{X}}{}^{i} = 0$ if X is not in stream i

$$\text{(say)}\ S = m_1 \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{1} \hat{H}_{\mathrm{X}}{}^{(0)} + m_2 \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{2} \hat{H}_{\mathrm{X}}{}^{(0)} - m_3 \sum_{\mathrm{X}} y_{\mathrm{X}}{}^{3} \hat{H}_{\mathrm{X}}{}^{(0)}$$

$$= \sum_{\mathrm{X}} \frac{1}{M_{\mathrm{X}}} (m_1 y_{\mathrm{X}}{}^{1} + m_2 y_{\mathrm{X}}{}^{2} - m_3 y_{\mathrm{X}}{}^{3})\, \overline{H}_{\mathrm{X}}^{(0)}$$

$$= -\sum_{\mathrm{X}} n_{\mathrm{X}}\ \overline{H}_{\mathrm{X}}^{(0)}$$

where $\overline{H}_{\mathrm{X}}^{(0)}$ is the standard molar enthalpy (2.2.8) and n_{X} is defined by (3.2.2.3 and 2). Using the parametrisation (3.2.4.1) we find (with $n_{\mathrm{N2}} = n_{\mathrm{Ar}} = 0$)

$$-S = (-\tfrac{1}{2}\, \overline{H}_{\mathrm{O2}}{}^{(0)} - \overline{H}_{\mathrm{SO2}}{}^{(0)} + \overline{H}_{\mathrm{SO3}}{}^{(0)})W_{\mathrm{a}}$$

thus

$$-S = Q_{\mathrm{a}}{}^{(0)} W_{\mathrm{a}} \qquad \text{(Ex 2.6)}$$

where

$$Q_{\mathrm{a}}{}^{(0)} = \nu_{\mathrm{O2}} \overline{H}_{\mathrm{O2}}{}^{(0)} + \nu_{\mathrm{SO2}} \overline{H}_{\mathrm{SO2}}{}^{(0)} + \nu_{\mathrm{SO3}} \overline{H}_{\mathrm{SO3}}{}^{(0)} \qquad \text{(Ex 2.6a)}$$

with stoichiometric coefficients of the reaction conventionally written as

$$-\tfrac{1}{2}\, O_2(g) - SO_2(g) + SO_3(g) = 0. \qquad \text{(a)}$$

The balance (Ex 2.1) with (Ex 2.4) thus reads

$$m_1 \bar{c}_p^{\,1}(T^1 - T_0) + m_2 \bar{c}_p^{\,2}(T^2 - T_0) - m_3 \bar{c}_p^{\,3}(T^3 - T_0) - Q_a^{(0)} W_a = 0 \qquad \text{(Ex 2.7)}$$

where $\bar{c}_p^{\,i}$ is the mean specific heat (Ex 2.5) of stream *i*. The equation (Ex 2.7) is considered along with the parametrised balances (3.2.4.1). W_a is the reaction rate and $Q_a^{(0)}$ is called the *standard* (molar) *heat of reaction* (a); we here have $Q_a^{(0)} < 0$ (exothermic reaction). Generally, we can have several reactions (r) in one node giving the sum $\sum_r Q_r^{(0)} W_r$ in the balance. The standard reaction heats (traditionally denoted by $\Delta H^{(0)}$) are known for a number of technological processes and using the above form of balance can mean better precision of the thermodynamic database.

Example 3. Synthesis of ammonia

The reaction is written as

$$\tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2 = NH_3 \ \text{(gases).} \qquad \text{(b)}$$

The catalytic reactor can be multistage, for example with compression and preheating before the first stage, cooling, condensation of NH_3 and re-preheating before each next stage. Let us consider one stage with inlet stream 1 (N_2 , H_2 , NH_3) and outlet 2 before the cooling and condensation. The mass flowrates are $m_1 = m_2 = m$ thus the general form of the enthalpy balance is trivial: $m\hat{H}^2 - m\hat{H}^1 = 0$ thus

$$\hat{H}^2 - \hat{H}^1 = 0. \qquad \text{(Ex 3.1)}$$

The standard heat of the reaction (b) thus $Q_b^{(0)}$ is known, so the balance will be rewritten using the parameter (reaction rate) W_b in the component balances (written per unit mass flowrate *m)*

$$y_{N2}^{\,2} - y_{N2}^{\,1} = -\tfrac{1}{2} M_{N2}\, w_b \qquad \text{(where } w_b = W_b/m\text{)}$$

$$y_{H2}^{\,2} - y_{H2}^{\,1} = -\tfrac{3}{2} M_{H2}\, w_b$$

$$y_{NH3}^{\,2} - y_{NH3}^{\,1} = M_{NH3}\, w_b\,. \qquad \text{(Ex 3.2)}$$

The equations can be written as

$$y_X^{\,2} = y_X^{\,1} + M_X\, \nu_X\, w_b \quad \text{where} \quad \nu_{N2} = -\tfrac{1}{2},\ \nu_{H2} = -\tfrac{3}{2},\ \nu_{NH3} = 1 \qquad \text{(Ex 3.2a)}$$

are the stoichiometric coefficients in (b) written in conventional form ($\nu_X > 0$ for reaction products).

Here, however, the pressure P_R (taken as mean pressure in the reactor) is several tens to 100 MPa and the gas mixture is no longer ideal. As an approximation, let us still assume that the heat of mixing can be neglected even at pressure P_R . Thus for the streams $i = 1$ and 2

$$\hat{H}^{i} = \sum_{X} y_X{}^{i} \, \hat{H}_X{}^{i} \tag{Ex 3.3}$$

where $\hat{H}_X{}^{i}$ is specific enthalpy of pure component X at stream i conditions. With the substitutions (Ex 3.2a), Eq (Ex 3.1) reads

$$\sum_{X} y_X{}^{1} (\hat{H}_X{}^{2} - \hat{H}_X{}^{1}) + (\sum_{X} \nu_X M_X \hat{H}_X{}^{2}) \, w_b = 0. \tag{Ex 3.4}$$

The pressure is P_R and the first term corresponds to temperature rise from T^1 to T^2 thus

$$\hat{H}_X{}^{2} - \hat{H}_X{}^{1} = c_{pX}^{R} (T^2 - T^1) \tag{Ex 3.4a}$$

where c_{pX}^{R} is mean specific heat of component X in the reactor, thus between temperatures T^1 and T^2. In the second term, we can substitute $\overline{H}_X{}^{2} = M_X \hat{H}_X{}^{2}$ where $\overline{H}_X{}^{2} = \overline{H}_X (T^2, P_R)$ is the value of the molar enthalpy function $\overline{H}_X$ at (T^2, P_R) . Thus

$$\sum_{X} \nu_X M_X \hat{H}_X{}^{2} = Q_b(T^2, P_R) \quad \text{where} \quad Q_b = \sum_{X} \nu_X \overline{H}_X \tag{E 3.4b}$$

is the (molar) *heat of reaction* (b) as function of temperature and pressure. If not known a priori, it can be computed. We have the thermodynamic relations

$$\frac{\partial \overline{H}_X}{\partial T} = C_{pX} \quad \text{(molar heat of X)} \quad \text{and} \quad \frac{\partial \overline{H}_X}{\partial P} = \overline{V}_X - T \frac{\partial \overline{V}_X}{\partial T} \tag{Ex 3.5}$$

where $\overline{V}_X$ is molar volume ($\mathrm{m^3\,kmol^{-1}}$) of X, regarded as function of temperature T *and* pressure P. This function and its derivative have to be found by numeric solution (inversion) of the *state equation* for gaseous species X, usually giving conversely P as function of $\overline{V}_X$ and T . Then denoting

$$\varphi_X = \overline{V}_X - T \frac{\partial \overline{V}_X}{\partial T} \tag{Ex 3.5a}$$

($\varphi_X = 0$ for *ideal* gas X) we have

$$\overline{H}_X (T^2, P_R) = \overline{H}_X^{(0)} + \int_{T_0}^{T^2} C_{pX} (T, P_0) \, dT + \int_{P_0}^{P_R} \varphi_X (T^2, P) \, dP \tag{Ex 3.6}$$

where $\overline{H}_X^{(0)}$ is standard molar enthalpy of (gaseous) species X. We suppose that the *standard reaction heat*

$$Q_b^{(0)} = \sum_X \nu_X \overline{H}_X^{(0)} \tag{Ex 3.7}$$

is known. [In fact, in our special case it equals just the standard enthalpy of NH_3 if taking $\overline{H}_X^{(0)}$ = 0 for gaseous X = N_2 , O_2 , with $\nu_{NH3} = 1$.] Then

$$Q_b(T^2, P_R) = Q_b^{(0)} + \sum_X \nu_X \left(\int_{T_0}^{T^2} C_{pX} (T, P_0)\, dT + \int_{P_0}^{P_R} \varphi_X (T^2, P)\, dP \right) \tag{Ex 3.8}$$

in the enthalpy balance (Ex 3.4)

$$\sum_X y_X^1 c_{pX}^R (T^2 - T^1) + Q_b(T^2, P_R)\, w_b = 0. \tag{Ex 3.9}$$

Note that if the reaction heat Q_b is known at certain 'normal' operating conditions ($\overline{T}^2$, $\overline{P}_R$), the correction for temperature $T^2 = \overline{T}^2 + \Delta T$ and pressure $P_R = \overline{P}_R + \Delta P$ can be approximated as

$$\Delta Q_b = \sum_X \nu_X (C_{pX}\, \Delta T + \varphi_X\, \Delta P) \tag{Ex 3.9a}$$

where C_{pX} and φ_X are taken at $\overline{T}^2$, $\overline{P}_R$.

The role of more advanced thermodynamics can be illustrated by

Example 4. Vapour-liquid feed into a distillation column

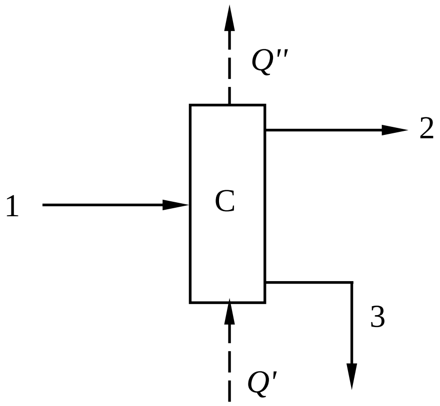

Fig. 3-6 Distillation column

Stream 1 (feed) enters the column C and is divided into liquid distillate 2 and bottom product 3. The heat supplied to the boiler is Q' and that withdrawn in the condenser is Q''; both the boiler and condenser are included as part of node C. The general form of the energy (enthalpy) balance reads, according to (3.3.1)

$$\hat{H}^1 m_1 + Q' - Q'' = \hat{H}^2 m_2 + \hat{H}^3 m_3 . \qquad \text{(Ex 4.1)}$$

The node is nonreaction thus in (3.3.2), we can put $\hat{H}_X^{(0)} = 0$ for each of the components X, at reference temperature T_0 and pressure P regarded as constant in C, in the *liquid* state of aggregation.

If the heat of mixing is neglected *and if* also stream 1 is in liquid state, we can use the remark to formula (3.3.6) thus put

$$\text{with } \textit{all streams liquid}\text{: } \hat{H}^i = \bar{c}_p^{\,i} (T^i - T_0). \qquad \text{(Ex 4.2)}$$

It can however, happen (and also happens, as experience shows) that the feed is a *vapour-liquid mixture*. Its specific enthalpy then equals

$$\hat{H} = (1-p)\hat{H}_L + p\hat{H}_V = \hat{H}_L + p(\hat{H}_V - \hat{H}_L) \qquad \text{(Ex 4.3)}$$

where $\hat{H}_L$ resp. $\hat{H}_V$ is specific enthalpy of liquid resp. vapour and p is mass fraction of the gas phase in the two-phase mixture.

In order to find the enthalpy function $\hat{H}$, one assumes that the two phases are in *thermodynamic equilibrium*. The computation of the equilibrium conditions is based, by definition, on the equality of the chemical potentials μ_X in liquid and vapour phases for each of the components X. The formulae are commonly written in molar units; see (2.2.4) to (2.2.9). If there are K components X, one has K equations; in addition the temperature T and pressure P are the same for both phases. We shall not describe the procedure, but only outline its idea; the procedure need not go just through the steps as indicated below.

Modifying our notation convention, let us designate x_k resp. y_k the mole fractions of the k-th component in liquid resp. vapour phase. Because $\sum_k x_k = \sum_k y_k = 1$, we have $2(K-1)$ independent composition variables plus variable T, while P is considered fixed. It can then be shown that the K equations determine uniquely the temperature T and $(K-1)$ variables y_k as functions of the $(K-1)$ (independent) liquid composition variables. Thus, say

$$T = T^*(x) \quad \text{and} \quad y_k = y_k^*(x) \quad (k = 2,\dots, K) \qquad \text{(Ex 4.4)}$$

where x represents $(x_2, \dots, x_K)$; $T^*(x)$ is the boiling point (at pressure P) and $y_k^*(x)$ the k-th equilibrium mole fraction in the vapour phase (imagine Raoult's law for an ideal gas mixture).

Let us now suppose that the overall composition of the two-phase mixture entering the column is given by mole fractions z_k ; again $\sum_k z_k = 1$. These variables are fixed and we have

$$k = 2,..., K: \quad (1 - q)x_k + qy_k = z_k \qquad \text{(Ex 4.5)}$$

where q is the mole fraction of the vapour phase. Putting $y_k = y_k^*(x)$ by (Ex 4.4), we have $(K - 1)$ equations in variables x_k . For simplicity, we shall *not* consider *azeotropic* mixtures. One can then assume that the latter equations determine (given the z_k) all x_k as functions of the parameter q. Then also $T = T^*(x)$ is function of q, thus finally the *molar enthalpy*

$$\overline{H} = (1 - q)\overline{H}_{\mathrm{L}} + q\overline{H}_{\mathrm{V}} = \overline{H}_{\mathrm{L}} + q(\overline{H}_{\mathrm{V}} - \overline{H}_{\mathrm{L}}) \qquad \text{(Ex 4.6)}$$

is *function of* q *, given* P *and* $z = (z_2 ,..., z_k)$; indeed, temperature T, x in liquid thus $\overline{H}_{\mathrm{L}}$, and also y in vapour thus $\overline{H}_{\mathrm{V}}$ are functions of q . One can see immediately that the parameter q ($0 \leq q \leq 1$) will cause a steep increase in $\overline{H}$ because $(\overline{H}_{\mathrm{V}} - \overline{H}_{\mathrm{L}})$ is of the order of magnitude of an evaporation heat.

One can also assume that the temperature T increases with q ; increasing q makes the concentrations of the more volatile components in the liquid phase smaller, thus the boiling point increases. At $q = 1$, the temperature will represent the dew point of the mixture with composition z. One can, instead of q, take also temperature T as parameter. The function $\overline{H}$ or also $\hat{H}$ (Ex 4.3) will then (quite schematically) look like

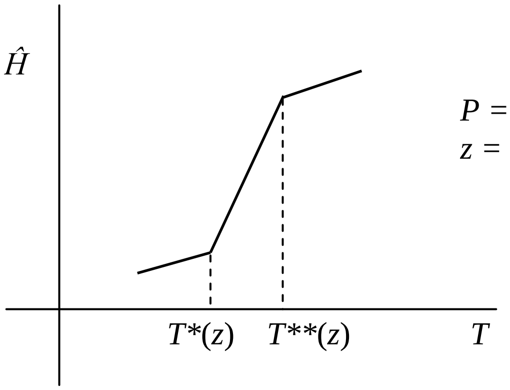

Fig. 3-7 Enthalpy of vapour-liquid mixture

where $T^*(z)$ resp. $T^{**}(z)$ is boiling resp. dew point of the mixture with overall composition z. The fraction p of the gas phase can be small; still, given the temperature and extrapolating the enthalpy $\hat{H}^1$ according to (Ex 4.2) *for* $T > T^*(z)$ one can commit a serious *model error*.

* * *

Let us *summarise*.

The balance of energy is usually formulated in simplified form as the (steady-state) *enthalpy balance* (3.3.1). Quite frequent is the case when no phase transition takes place and the heat of mixing can be neglected; as a simple example, see (3.3.6). The specific heats are given and we then have a 'heat balance' in combination with the (overall) mass balance. This is for example the case of a heat exchanger network. In a heat exchanger, the mass balances are written separately for the 'hot' and 'cold' sides, while the heat balance is common on eliminating the transferred heat term; see (3.3.4) for a slightly more general case, or (3.3.4a).

In less trivial situations, it is the task of a *specialist in chemical thermodynamics* to set up the balance and create the necessary *database*. The Examples 1 to 4 only illustrate what kind of problems can be encountered. It is to be noted that errors in the thermodynamic description and/or database can be source of *model errors* making the process data (even if exact) *incompatible with respect to* the *assumed* balance constraints.

3.4.Momentum balance

The momentum (mass$\times$velocity) is a vector quantity and its change is compensated by the action of force(s). In a streaming medium with local velocity **v** (m s^{-1}) and mass density ρ (kg m^{-3}), the momentum density (vector) is $\rho\mathbf{v}$. The differential balance of momentum takes then the form of the Equation of motion (Bird et al. 1960, § 3.2). By the methods described in the cited book and applied also in VE-MA: App.C, the equation can be integrated over a limited region in space (imagine a pipeline segment) and becomes the balance of inlet/outlet momentum and forces acting upon the boundary.

In standard industrial balancing, this kind of balance is rarely used. Observe that we here have in fact three (scalar) balances for the three vector components of momentum. The forces are mainly gravity (vector in perpendicular direction), pressure gradient and viscous friction. The information drawn from the momentum balance is generally quite poor because of complicated geometry of the boundary (walls) and irregular flow pattern; imagine a distillation column or catalytic reactor.

Let us thus consider directly the special case of a *gas pipeline network*. It is composed of cylindrical pipeline segments connecting nodes *n* of the type

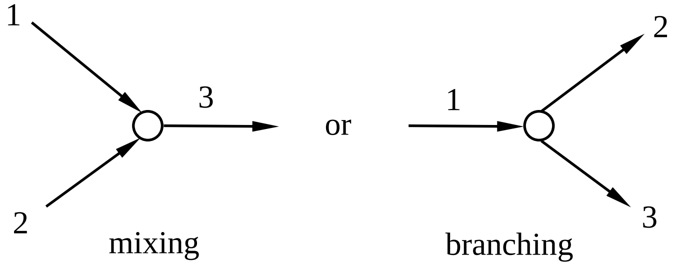

Fig. 3-8 Nodes of a gas pipeline network

The mass balances are trivial. Although not theoretically precise, we add the condition

$$P_1 = P_2 = P_3 = P(n) \tag{3.4.1}$$

for the pressures and no momentum balance is formulated. Here, P_1 etc. are pressures at the common point n where the streams meet and are mixed or split; they all equal $P(n)$, the pressure in node n.

Now the length of a segment can be several kilometers and more. The pressure difference between both ends can be considerable, thus also the density of the gas changes and in addition, at pressures of the order of megapascals the gas is no longer ideal. The segments need not be straight; imagine hills and valleys. We then can set up the momentum balance in the local direction of flow, in differential form as follows.

We suppose again *steady-state flow*; thus the change in holdup is neglected and

$$m \ (\text{kg s}^{-1}) \ \text{is} \ \textit{constant} \ \text{mass flowrate in the segment.} \tag{3.4.2}$$

The pipeline can be slightly curved, but of constant

$$\text{diameter } D \ (\text{m}) \ \text{and cross section area} \ S = \frac{\pi D^2}{4} \ (\text{m}^2). \tag{3.4.3}$$

The gas is of given (constant) composition (imagine natural gas), with (variable) density ρ and pressure P. The length coordinate in the pipeline is x in the direction of flow

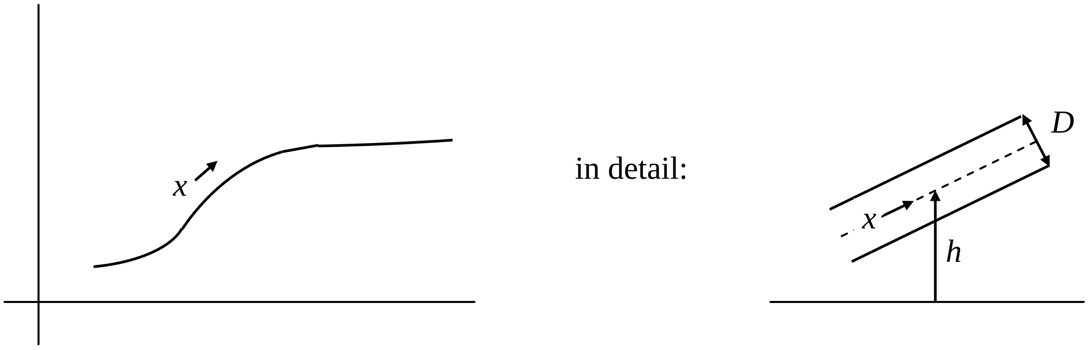

Fig. 3-9 A pipeline segment

where h (m) is height above a conventional ground level. The gravitational acceleration (scalar value) is g (m s^{-2}).

Recall now the standard formula for pressure drop due to friction in pipes

$$\Delta P_{\mathrm{f}} = \frac{1}{2}\lambda\frac{l}{d}\rho v^{2} \tag{3.4.4}$$

where l is length, d diameter, v velocity (scalar value), ρ density; the formula relates the pressure drop to a loss of kinetic energy by viscous forces (dissipation), to be precise for isothermal flow of incompressible fluid. We shall need this formula just for the *definition* of the *friction factor* λ. In the literature, the coefficient is given as function of the Reynolds number and roughness of the wall. We assume the roughness known and express the Reynolds number as

$$\mathrm{Re} = \frac{mD}{S\mu} \; ; \tag{3.4.5}$$

taking some mean value of dynamic viscosity μ (kg m^{-1} s^{-1}), the Reynolds number is function of m, thus also λ is (given D, S and the roughness) function of m. We then have the following equation (momentum balance)

$$\frac{\mathrm{d}P}{\mathrm{d}x} + \frac{1}{2}\frac{\lambda}{DS^{2}}m^{2}\frac{1}{\rho} + \rho g\frac{\mathrm{d}h}{\mathrm{d}x} + \frac{m^{2}}{S^{2}}\frac{\mathrm{d}(1/\rho)}{\mathrm{d}x} = 0 \tag{3.4.6a}$$

where P is (decreasing) function of length coordinate x; dh/dx is the slope of the pipeline in Fig 3-9 (≥ 0 or <0). The density ρ can be considered function of temperature (T) and pressure but usually, the *thermodynamic state equation* for a nonideal gas, of general form

$$F(T\,,\ \rho\,, P) = 0 \tag{3.4.6b}$$

gives rather pressure P as function of T and of molar volume

$$V_{\mathrm{mol}} = \frac{\overline{M}}{\rho} \tag{3.4.7}$$

with mean mole mass $\overline{M}$. The equation (3.4.6a with b) is then integrated numerically between $x = 0$ and $x = L$ (length of the whole segment). The temperature profile is commonly unknown in details; one then considers a mean temperature $\overline{T}$ in the segment.

There are different formulae that approximate the integral. We shall not go into further details. In the end, one can obtain the balance as a *nonlinear algebraic equation* in variables P_1 (inlet pressure), P_2 (outlet pressure) and m (having assessed $\overline{T}$) regarded as balancing variables.

Note: Other nodes of the network can be for example compressors or throttling elements. Their *empirical models* are of the form

$$f(m,\, T_{\mathrm{in}}\,,\, P_{\mathrm{in}}\,,\, P_{\mathrm{out}}\,;\ \alpha) = 0 \tag{3.4.8}$$

where T_{in} resp. P_{in} are inlet temperature resp. pressure, P_{out} is outlet pressure, and α represents certain construction and operation parameters (number of revolutions of a turbocompressor and the like); $m = m_{\text{in}} = m_{\text{out}}$ is inlet = outlet mass flowrate.

3.5.Special energy balances

The cited book (VE-MA) as well as the earlier Madron (1992) are largely concerned with industrial chemical processes. Although the (material and) energy balances hold as well in the power engineering, there are certain peculiarities that require special attention, in particular when applied to nuclear power plants; this even if (as we shall do) the processes in the nuclear reactor itself are not included.

Consider the steam production in a nuclear power plant. A simplified scheme is drawn in Fig. 3-10.

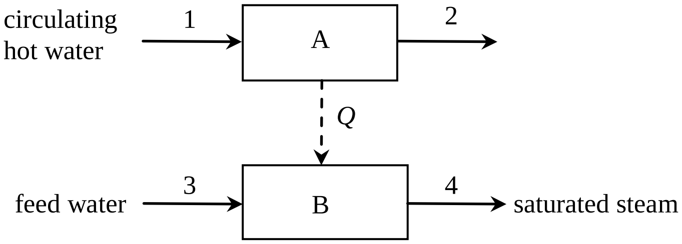

Fig. 3-10 Steam generation in a nuclear power plant

Hot (high-pressure) cooling water from the nuclear reactor enters the heat exchange system and heat Q (representing, at steady state and if energy losses are neglected, the energy generated by the nuclear reactions) is transferred into boiler B where feed water is evaporated. The enthalpy balance must here take account of the fact that the outlet steam is (not superheated but) *saturated* (and may even contain droplets of liquid phase). This peculiarity characterises standard nuclear power plants and requires, in addition to the balance, including the *two-phase equilibrium condition*. The plant is equipped with a number of measuring instruments and the balancing is part of the monitoring and control system where safety aspects are highlighted.

According to Fig. 3-10, the energy (enthalpy) balance (3.3.1) of boiler B reads

$$\hat{H}^3 m_3 + Q = \hat{H}^4 m_4 \tag{3.5.1}$$

and as such is quite trivial. We have

$$\hat{H}^3 = \hat{H}_{\mathrm{L}}(T^3, P^3) \tag{3.5.2}$$

where generally T^i resp. P^i is temperature resp. pressure of stream i; Z = L resp. G means liquid resp. gaseous (vapour) phase, $\hat{H}_Z$ is specific enthalpy function for phase Z of water H_2O. In stream 4, we however have generally admitted the presence of liquid droplets, say with mass fraction $y_L^4 = 1 - y_G^4$ in the two-phase mixture. Hence

$$\hat{H}^4 = (1 - y_G^4)\hat{H}_L(T^4, P^4) + y_G^4\hat{H}_G(T^4, P^4) \tag{3.5.3}$$

where we generally designate

$$y_G = 1 - y_L \quad \text{(so-called quality of the steam)} \tag{3.5.3a}$$

and where we *add* the *condition*

$$P^4 = P^*(T^4) \tag{3.5.4}$$

representing the two-phase equilibrium. $P^*(T)$ is the *equilibrium pressure*, a function of temperature T. Basically, we can eliminate the latter condition on introducing the functions

$$Z = \text{L or G:} \; H_Z^*(T) = \hat{H}_Z(T, P^*(T)) \tag{3.5.5}$$

considered also known as well as $P^*(T)$ itself. The values of these functions can be found in classical thermodynamical tables. Instead of $P^*(T)$, we can also consider the inverse function $T^*(P)$ giving the equilibrium temperature as function of pressure. Knowing T or P, the specific enthalpies such as (3.5.3) with (3.5.4) can be computed as functions of the mass fraction y_G and either T, or P only.

Generally, the values of thermodynamic functions stemming from different sources may become sources of model errors due to their not-full consistency. The case of the one-component liquid water-steam system is, to some extent, an exception. Recent water/steam properties computation routines (such as Harvey (1997) and ASME (1998)) can be regarded, due to their derivation, as intrinsically *consistent*. In particular we can compute the specific enthalpies $\hat{H}_Z(T, P)$ for phases Z = L and G.

On the other hand, the great number of measuring instruments yields a great number of measured values providing a chance for their *reconciliation* due to their *redundancy*; for the latter concepts, see further Section 4.3 and Chapter 5. So in one stream, possibly both temperature T and pressure P are measured even if they are assumed to be at equilibrium. In contrast to what has been adopted in the simple examples of Section 3.3, we here can consider *both* T *and* P as *balancing variables* and in particular subject their measured values to reconciliation making them compatible with the balance equations.

Thus *generally*, if the technology qualifies a stream j as that of *saturated* steam, its specific enthalpy in (3.3.1) equals

$$\hat{H}^j = (1 - y_G^j)\hat{H}_L(T^j, P^j) + y_G^j\hat{H}_G(T^j, P^j) \tag{3.5.6}$$

and we *add the condition*

$$P^j = P^*(T^j) \qquad (\text{or} \quad T^j = T^*(P^j)\,) \tag{3.5.7}$$

with the same interpretation as in (3.5.3 and 4) for $j = 4$. In this manner, both *variables* (T and P) occur in the balance of the system and a new *equation* (3.5.7) is written *in addition*. More precisely: The definition of $\hat{H}^j$ occurs in the set of the node balance equations generally twice (the stream goes from one node to another). However, the equations (3.5.7) are each written *just once*, viz. for the stream j where saturated steam is assumed. New balancing variables are also $y_G{}^j$ (*quality* of steam in stream j).

The additional equations such as (3.5.7) are in fact not node balances but rather of the same type as (3.2.2.5), also associated with given stream i. Further, speaking about redundancy, we can also consider the case where one variable associated with given stream j is measured by more than one instrument (some authors call it 'measurement reduncancy'). It is possible to introduce fictitious nodes between the two (or more) measurement places. But *if no* pressure drop and/or heat loss between them are admitted, it is simpler to consider for example one physical variable T^j occurring in the node balance(s) and *add the equations*

$$T^j = T^{j\,'}\,,\ T^j = T^{j\,''}, \ldots \tag{3.5.8}$$

where $T^{j\,'}$, $T^{j\,''}$, ... represent the measurements.

On the other hand, if a pressure drop is admitted one has to introduce a (fictitious or real) throttling element

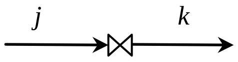

Fig. 3-11 Throttling element

separating the outlet from the first node and inlet to the other, and the node balances read

$$m_j = m_k \tag{3.5.9a}$$

$$\hat{H}^j = \hat{H}^k \tag{3.5.9b}$$

possibly with (3.5.6) and (3.5.7) for j and k . In the same manner, admitting a heat loss we have the scheme

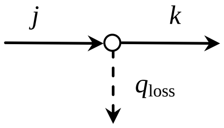

Fig. 3-12 Fictitious node representing loss of heat

with the balances of the *fictitious node*

$$m_j = m_k \tag{3.5.10a}$$

$$m_j \hat{H}^j = m_k \hat{H}^k + q_{\mathrm{loss}} \, . \tag{3.5.10b}$$

Other types of balances

Classical (thermal) power plants use fossil fuel as the source of ('chemical') energy. We here preclude the case of a gas turbine where the scheme is different. Then in Fig. 3-10, A is combustion chamber with two inlets (fuel and air) and two outlets (combustion gases and ash if the fuel is coal). The material and energy balances of node A will not be written and our scheme thus begins with energy input Q, given or computed. With the combustion of fuel (or also in certain new types of nuclear plants with other cooling medium than water), the stream 4 is superheated steam. Then

$$\text{for superheated steam:} \quad \hat{H}^4 = \hat{H}_{\mathrm{G}}(T^4, P^4) \tag{3.5.11}$$

in the balance (3.5.1).

A special type of energy balance is again the *splitter* balance; see (3.3.3) with Fig. 3-1; stream 1 is the inlet stream. The complete information ('balance') reads again

$$\begin{aligned} T^2 &= T^1 \\ T^3 &= T^1 \\ &\cdot \\ &\cdot \\ &\cdot \end{aligned}$$

and

$$\begin{aligned} P^2 &= P^1 \\ P^3 &= P^1 \\ &\cdot \\ &\cdot \\ &\cdot \qquad ; \end{aligned} \tag{3.5.12}$$

in addition, *if* the inlet stream is *saturated steam* (3.5.6) we put

$$\begin{aligned} y_{\mathrm{G}}^2 &= y_{\mathrm{G}}^1 \\ y_{\mathrm{G}}^3 &= y_{\mathrm{G}}^1 \\ &\cdot \\ &\cdot \\ &\cdot \end{aligned} \tag{3.5.12a}$$

and write *just one condition*

$$P^1 = P^*(T^1) \qquad (\text{or } T^1 = T^*(P^1)\,) \tag{3.5.12b}$$

for the stream 1. Then the equilibrium conditions for the outlet streams follow automatically from (3.5.12).

The material streams are one-component (H_2O) thus steam and condensate recovered as feed water; the latter enters the system as fresh feed water and the (chemical) making-up process is not included in the balancing. The material (mass) balances are thus trivial. Cooling (e.g. river) water is not mixed with feed water and only heat exchange takes place.

It is convenient to write the general energy balance (3.3.1) of a node in the form

$$\sum_{j,\text{in}} \hat{H}^j m_j + \sum_{i,\text{in}} e_i = \sum_{j,\text{out}} \hat{H}^j m_j + \sum_{i,\text{out}} e_i \tag{3.5.13}$$

where the $\hat{H}^j$ are either $\hat{H}_L(T^j, P^j)$ as in (3.5.2) (feed water, condensate), or $\hat{H}_G(T^j, P^j)$ as in (3.5.11) (superheated steam), *or* of the form (3.5.6), *in which case* the *condition* (equation) (3.5.7) is *added* for any such j. The *net energy flowrates* e_i are those due to *heat transfer*, further those representing the transport of *mechanic* and *electric* energies. The mechanic energy is transported and transformed mainly in engines driving alternators, possibly also supplied to/from the environment. A stream i of *electric* energy is *not* current but

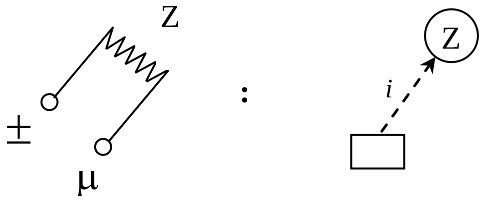

Fig. 3-13 Transport of electric energy

where the arrow represents the stream of energy consumed in node Z (segment of electrical network). All the three types of energy transport are illustrated by a simplified scheme of a turbine driving an alternator

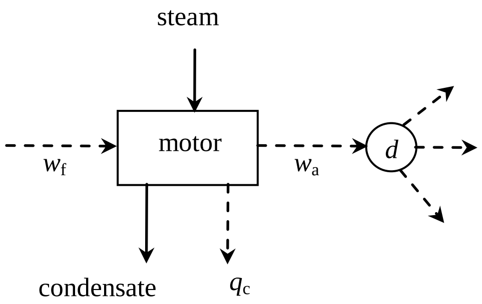

Fig. 3-14 Turbine and alternator.

Here, the (macro)node 'motor' represents a complex system with droplet separation and internal heat exchange; the condensate then means (partially) preheated feed water. The $e_{i,\mathrm{in}} = w_\mathrm{f}$ means mechanic power supply to feed water pump(s) (a relatively small item), the $e_{i,\mathrm{out}}$ are q_c (heat withdrawn in the condenser) and w_a (mechanic power supplied to the alternator). The node d (alternator) then produces and distributes electric energy.

As is seen, the *energy transforming plant* includes nodes such as d in Fig. 3-14 representing production and distribution of electric energy. In the balance of such a node d , the set of incident material streams is empty and the balance (3.5.13) is reduced to

$$\sum_{i,\,\mathrm{in}} e_i \quad = \quad \sum_{i,\,\mathrm{out}} e_i \qquad (3.5.14)$$

where the $e_{i,\mathrm{out}}$ may also represent energy losses.

4. TECHNOLOGICAL SYSTEMS

4.1.Equations of the system

The balance of a technological system (a plant or a smaller group of units) is the set of its node balances. They are written as equations in the balancing variables and as the *balancing model*, they are generally part of the mathematical model of the system used in design and simulation problems. In the latter case, the partition of the system into nodes can be quite detailed; thus a distillation column can be divided into the column itself, condenser, splitter of the distillate with reflux stream, boiler etc. For the purpose of balancing as dealt with in this text, one merges certain groups of apparatuses to units taken as a whole, thus to some kind of 'black boxes' as illustrated in Fig. 2-1. One is not interested in physical details of the process inside, but only in inputs and outputs. Thus a distillation unit, schematically drawn as

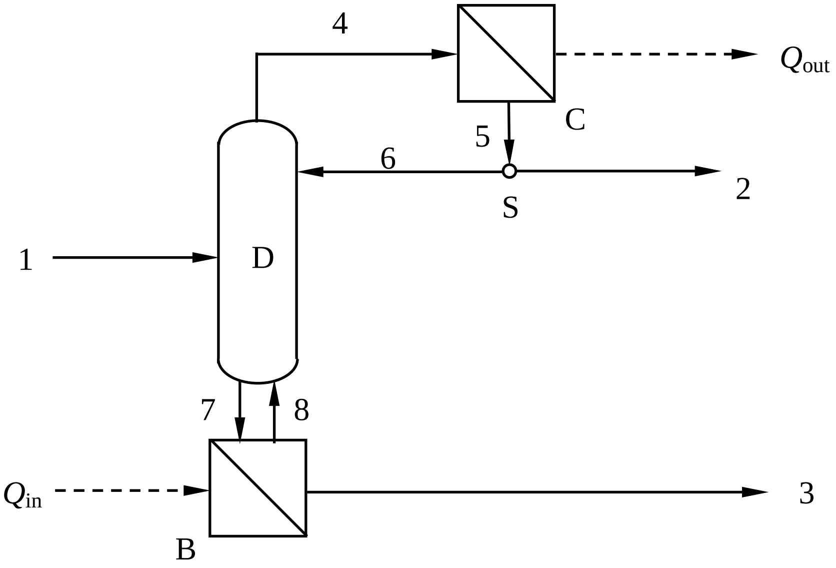

Fig. 4-1a Distillation column D with condenser C, splitter S and boiler B

is regarded as one node D (cf. Fig 3-6)

.

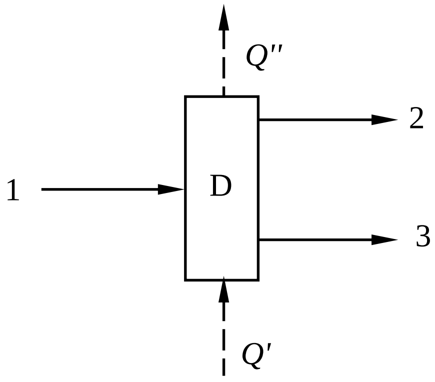

Fig. 4-1b Distillation unit as one node D

with inlet stream (feed) 1 and outlet streams 2 (distillate) and 3 (bottom product); the heats *Q*' supplied in the boiler and *Q*" withdrawn in the condenser represent balancing variables if also the energy (enthalpy) balance is considered. The streams 4-8 have been deleted by the merging.

The set of nodes connected by streams (possibly with 'net energy streams' such as in Fig.4-1b) can be drawn as the (balancing) *flowsheet* of the system; see again Fig. 2-1, and other examples below. Certain streams (such as 1 and 8 in Fig. 2-1) do not have both 'endpoints' in the drawing; they represent inputs (as stream 1) or outputs (stream 8) into/from the whole system. Physically, they certainly do have some origin / point of destination thus again some 'nodes' whose *balance* is, however, *not included*. [This convention is necessary; otherwise the flowsheet could become infinite or not well-defined.] We thus regard the totality of these 'nodes' as the *environment*. Formally, this concept makes sense in the graph theory (see, e.g., VE-MA). But the graph operations are task of the balancing software; for the user, it is sufficient to know that the *balancing flowsheet* does not comprise the nodes included in the environment (not subject to balancing). They can also be drawn as information for the user, but *with the latter specification*. By the way, imagine a subsystem of a larger plant; it is common practice to set up individual subsystem balances.

The set of balance equations can involve tens or even hundreds of nodes and streams, and the more equations and balancing variables in case of multicomponent and/or energy balancing. The task of the balancing software is primarily to give the solution of the equations based on given data on the balancing variables, plus possibly additional resulting information. In this and the following chapters, our aim is only to illustrate, by way of simple examples, how and on which conceptual basis the balancing software works and what kind of information can be drawn from the results.

Let us begin with a steady-state mass balance.

Example 1. Steady-state mass balance

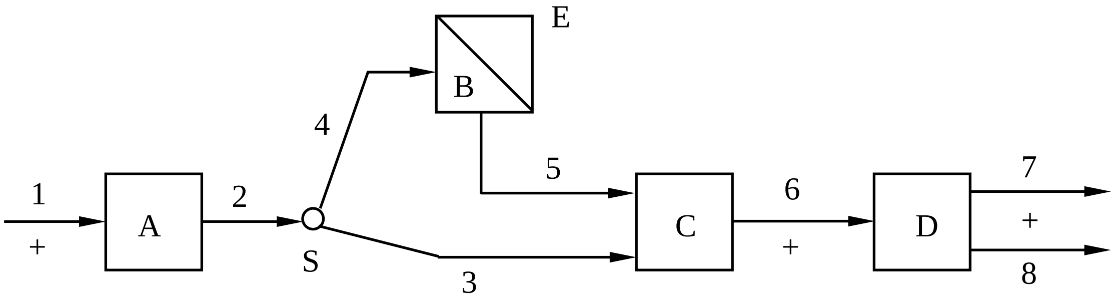

Fig. 4-2 Mass balance flowsheet

The system consists of pump A, splitter S, heat exchanger E by-passed by stream 3, node C where the streams 5 and 3 are re-mixed, and distillation column D with outlet streams 7 (distillate) and 8 (bottom product). The energy balance is not considered so only part B of the exchanger E is included in the mass balancing. The equations read, with mass flowrates m_i

$$\begin{aligned}
&\text{A:} && m_1 - m_2 &&= 0\\
&\text{S:} && m_2 - m_3 - m_4 &&= 0\\
&\text{B:} && m_4 - m_5 &&= 0\\
&\text{C:} && m_3 + m_5 - m_6 &&= 0\\
&\text{D:} && m_6 - m_7 - m_8 &&= 0.
\end{aligned} \tag{4.1}$$

Having such a simple system, we can analyse it without using any computer. We have 5 linearly independent equations in 8 variables, so it is sufficient to give 3 values of the latter in order to determine uniquely the solution: for example giving the values of m_1, m_4 and m_7 as the reader readily verifies. The selection is, however, *not arbitrary*. Instead, let us choose the variables marked by + in the flowsheet, thus the values (say) $\hat{m}_1$, $\hat{m}_6$ and $\hat{m}_7$. Adding up Eqs. A,S,B,C we have the *condition*

$$\hat{m}_1 - \hat{m}_6 = 0. \tag{4.2}$$

The remaining 4 equations can be rearranged to give

$$\begin{aligned}
m_2 &= \hat{m}_1\\
m_8 &= \hat{m}_6 - \hat{m}_7\\
m_3 + m_4 &= \hat{m}_1\\
m_4 - m_5 &= 0
\end{aligned} \tag{4.3}$$

(rewrite A, then D, then add up A+S, finally re-write B). The condition (4.2) is the *compatibility condition* for the two values, and also the *necessary and sufficient condition of solvability* with the a priori fixed variables $\hat{m}_i$. It concerns only two of them, $\hat{m}_1$ and $\hat{m}_6$: they are called *redundant*, while the value $\hat{m}_7$ is not subject to any condition: it is called *nonredundant*. ['Redundant' means that even if not fixed, it remains determined by the condition; 'nonredundant' means that if not fixed, it remains unknown.] Now *having satisfied* the condition (4.2) (thus having adjusted the values $\hat{m}_1$ and $\hat{m}_6$ when necessary), the values of m_2 and m_8 are *uniquely determined*: they are called *observable*; on the other hand, there is an infinity of solutions in m_3, m_4, m_5 obeying the condition: the latter variables are called *unobservable* (for example one can pick *arbitrary* m_3 and only then, m_4 and m_5 are uniquely determined).

Observe that for example the condition (4.2) is the balance of nodes (A,S,B,C) merged to one node (which is a graph operation). Generally, the balancing software analyses the flowsheet by graph methods and can also classify the variables as above. If the a priori given values have been measured, they are then *adjusted by reconciliation*; see Chapter 5, Example 1.

The next example is that of a (steady-state) heat and mass balance.

Example 2. Heat and mass balance

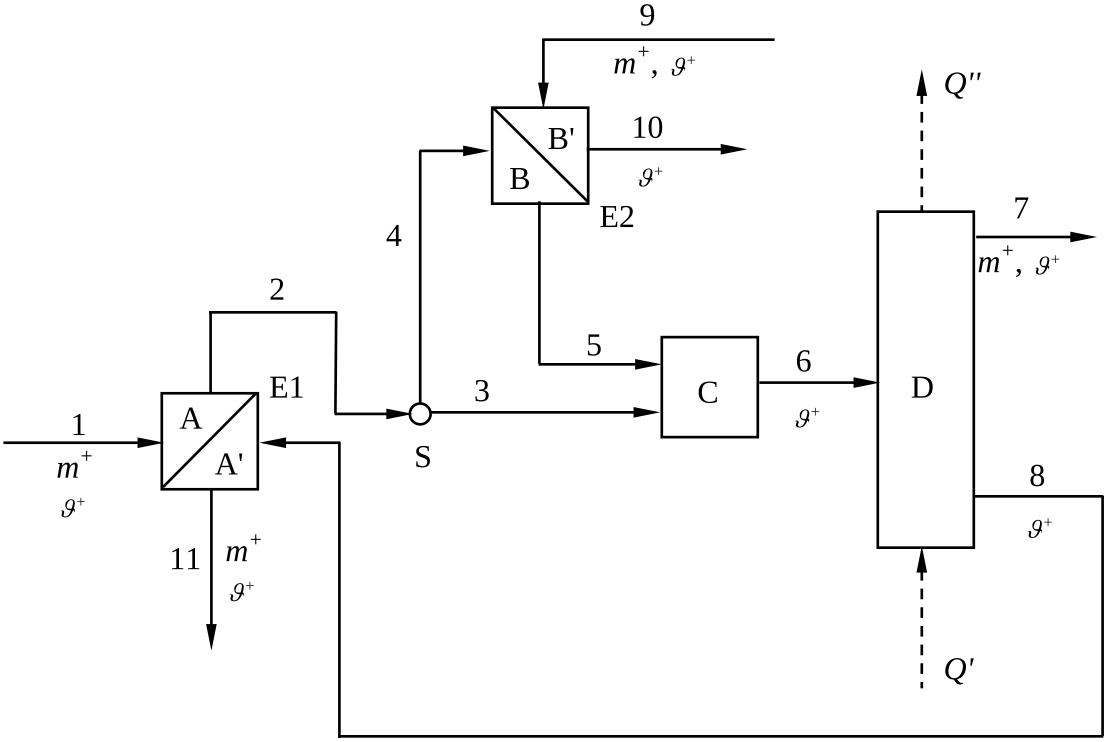

Fig. 4-3 Heat and mass balance flowsheet

Stream 1 is preheated in heat exchanger E1 and as stream 2 is split in node S into by-pass 3 and stream 4, further preheated in heat exchanger E2; the outgoing stream 5 is re-mixed in node C with stream 3 and as stream 6 enters the distillation column D with the interpretation according to Fig. 4-1b. Stream 7 is distillate; the hot bottom product (stream 8) preheats stream 1 in exchanger E1 and leaves it as stream 11. The hot stream 9, of the same nature, comes from another subsystem of the plant into exchanger E2 and leaves it as stream 10.

In the mass balance, the exchangers E1 and E2 are divided into cool and hot sides (A,A') and (B,B'), respectively. The heat (enthalpy) balances are written for the whole E1 resp. E2. We further *assume* that the *heat of mixing* can be *neglected*; then in particular the enthalpy balance of column D takes the form (3.3.6) with the interpretation following after the formula; see also (Ex 4.1) with (Ex 4.2) in Section 3.3. In addition, we approximate the specific heats by constant (a priori known) values

$c_p{}^{\mathrm{A}}$ for streams 1,2,3,4,5,6

$c_p{}^{\mathrm{t}}$ for stream 7 from the top of the column

$c_p{}^{\mathrm{b}}$ (bottom) for streams 8 and 11

c_p' for streams 9 and 10

(4.4)

and we introduce the temperature variable

$$\vartheta = T - T_0 \qquad (T_0 \text{ : reference temperature ; } \vartheta_i \text{ for stream } i). \tag{4.5}$$

Then the balance reads

$$
\begin{aligned}
&\text{E1, mass A:} && m_1 - m_2 = 0\\
&\text{A':} && m_8 - m_{11} = 0\\
&\text{enthalpy:} && m_1 c_p{}^{\mathrm{A}} \vartheta_1 + m_8 c_p{}^{\mathrm{b}} \vartheta_8 - m_2 c_p{}^{\mathrm{A}} \vartheta_2 - m_{11} c_p{}^{\mathrm{b}} \vartheta_{11} = 0\\
&\text{splitter S:} && m_2 - m_3 - m_4 = 0\\
& && \vartheta_3 - \vartheta_2 = 0\\
& && \vartheta_4 - \vartheta_2 = 0\\
&\text{E2, mass B:} && m_4 - m_5 = 0\\
&\text{B':} && m_9 - m_{10} = 0\\
&\text{enthalpy:} && m_4 c_p{}^{\mathrm{A}} \vartheta_4 + m_9 c_p' \vartheta_9 - m_5 c_p{}^{\mathrm{A}} \vartheta_5 - m_{10} c_p' \vartheta_{10} = 0\\
&\text{C:} && m_3 + m_5 - m_6 = 0\\
& && m_3 c_p{}^{\mathrm{A}} \vartheta_3 + m_5 c_p{}^{\mathrm{A}} \vartheta_5 - m_6 c_p{}^{\mathrm{A}} \vartheta_6 = 0\\
&\text{D:} && m_6 - m_7 - m_8 = 0\\
& && m_6 c_p{}^{\mathrm{A}} \vartheta_6 - m_7 c_p{}^{\mathrm{t}} \vartheta_7 - m_8 c_p{}^{\mathrm{b}} \vartheta_8 + Q' - Q'' = 0
\end{aligned}
\tag{4.6}
$$

thus 13 equations in 2×11(streams) + 2 = 24 balancing variables m_i, ϑ_i (streams i), Q', Q''.

A 'rule of thumb' says that the set of equations has 24-13 = 11 'degrees of freedom' thus number of variables necessary and sufficient to be fixed in order to obtain a unique solution. Rigorously, this assertion has to be precised by additional formal conditions (such as the 'independence' of the equations in a rigorous mathematical sense). Nevertheless, it can be shown (VE-MA, Chapter 8) that with the above set of equations, the conditions are fulfilled. The choice is, however, not arbitrary. Let us fix the values of the variables marked by + in the flowsheet thus

$$\hat{m}_1,\ \hat{\vartheta}_1,\ \hat{m}_{11},\ \hat{\vartheta}_{11},\ \hat{m}_9, \hat{\vartheta}_9,\ \hat{\vartheta}_{10},\ \hat{\vartheta}_6,\ \hat{m}_7, \hat{\vartheta}_7, \hat{\vartheta}_8 \tag{4.7}$$

in number 11.

Let us now rearrange the equations. It requires some skill, but an experienced engineer can do it without difficulty. The trick consists in formulating combinations of balances.

(1) The node A' mass balance is replaced by the balance of subsystem (A,S,B,C,D,A')

$$\hat{m}_1 = \hat{m}_7 + \hat{m}_{11} \tag{α}$$

(2) The node E1 enthalpy balance is rewritten using $m_2 = \hat{m}_1$ and $m_8 = \hat{m}_{11}$

$$\hat{m}_1 c_p^{\mathrm{A}} \vartheta_2 = \hat{m}_1 c_p^{\mathrm{A}} \hat{\vartheta}_1 + \hat{m}_{11} c_p^{\mathrm{b}} (\hat{\vartheta}_8 - \hat{\vartheta}_{11}) \tag{β}$$

(3) The node E2 enthalpy balance is first replaced by the overall enthalpy balance of subsystem (S,E2,C) with $m_2 = \hat{m}_1$, $m_6 = \hat{m}_1$ (balance of A,S,B,C)

$$\hat{m}_1 c_p^{\mathrm{A}} \vartheta_2 + \hat{m}_9 c_p' (\hat{\vartheta}_9 - \hat{\vartheta}_{10}) = \hat{m}_1 c_p^{\mathrm{A}} \hat{\vartheta}_6$$

and then, substituting from (β), the E2-balance is finally replaced by

$$\hat{m}_1 c_p^{\mathrm{A}} (\hat{\vartheta}_1 - \hat{\vartheta}_6) + \hat{m}_9 c_p' (\hat{\vartheta}_9 - \hat{\vartheta}_{10}) + \hat{m}_{11} c_p^{\mathrm{b}} (\hat{\vartheta}_8 - \hat{\vartheta}_{11}) = 0. \tag{γ}$$

So replacing the above three balances by (α),(β),(γ) in (4.6), the equivalent set of 13 equations reads

$$\hat{m}_1 - \hat{m}_7 - \hat{m}_{11} = 0$$

$$\hat{m}_1 (\hat{\vartheta}_1 - \hat{\vartheta}_6) + \hat{m}_9 \frac{c_p'}{c_p^{\mathrm{A}}} (\hat{\vartheta}_9 - \hat{\vartheta}_{10}) + \hat{m}_{11} \frac{c_p^{\mathrm{b}}}{c_p^{\mathrm{A}}} (\hat{\vartheta}_8 - \hat{\vartheta}_{11}) = 0$$

(4.8a)

further

$$m_2 = \hat{m}_1\,,\quad m_6 = \hat{m}_1\,,\quad m_8 = \hat{m}_{11}\,,\quad m_{10} = \hat{m}_9$$

$$\vartheta_2 = \hat{\vartheta}_1 + \frac{\hat{m}_{11}}{\hat{m}_1}\,\frac{c_p^{\,\mathrm{b}}}{c_p^{\,\mathrm{A}}}\,(\hat{\vartheta}_8 - \hat{\vartheta}_{11}),\quad \vartheta_3 = \vartheta_2\,,\quad \vartheta_4 = \vartheta_2 \tag{4.8b}$$

finally

$$\begin{aligned} m_3 + m_4 &= \hat{m}_1 \\ m_4 - m_5 &= 0 \\ m_4(\vartheta_5 - \vartheta_2) &= \hat{m}_1(\hat{\vartheta}_6 - \vartheta_2) \\ Q' - Q'' &= \hat{m}_7 c_p^{\,t}\hat{\vartheta}_7 + \hat{m}_{11} c_p^{\,\mathrm{b}}\hat{\vartheta}_8 - \hat{m}_1 c_p^{\,\mathrm{A}}\hat{\vartheta}_6 \end{aligned} \tag{4.8c}$$

where in the node C-enthalpy balance we have put $m_6 = \hat{m}_1$, $m_5 = m_4$, $m_3 = m_2 - m_4 = \hat{m}_1 - m_4$ and $\vartheta_3 = \vartheta_2$.

The equations (4.8a) involve only the fixed values (4.7), with the exception of $\hat{\vartheta}_7$. They are again the compatibility conditions for the choice of the values (4.7), or also the *conditions of solvability*. The variable (value) $\hat{\vartheta}_7$ can again be called *nonredundant* (not subject to any condition), while the other variables are *redundant*. Having fixed the values (4.7) and adjusted them to obey the conditions of solvability, one determines *uniquely* the values of the *observable* variables m_2, m_6, m_8, m_{10}, ϑ_2 thus also ϑ_3 and ϑ_4 by (4.8b). In the equations (4.8c), one can take *arbitrary* m_4; only then the values of m_3, m_5, ϑ_5 are also determined. Finally, for example the choice of Q'' is arbitrary and only then, also Q' is determined. So the variables m_4, m_3, m_5, ϑ_5, Q', Q'' are (can be called) *unobservable* (not uniquely determined).

It can happen that we have more information than needed for the determination of certain unknown variables (as ϑ_2 above}; still, the information need not be sufficient for the determination of all of them. Imagine the fixed variables as measured. Then, for example, measuring in addition ϑ_2 (thus fixing $\hat{\vartheta}_2$) we only replace ϑ_2 by $\hat{\vartheta}_2$ in (4.8b and c). As an exercise, the reader can verify that we then have one solvability condition in addition and one (which?) of the equations (4.b) is added to (4.8a). The value $\hat{\vartheta}_2$ becomes redundant, while the remaining classification is unaffected. As another example, leaving again ϑ_2 unmeasured, let us fix the value of Q'', thus $\hat{Q}''$. Then Q' becomes observable by (4.8c), leaving the remaining classification unaffected. Finally fixing also Q' as $\hat{Q}'$, the three values $\hat{Q}', \hat{Q}''$ and $\hat{\vartheta}_7$ become redundant thus subject to a new solvability condition.

The node balances (4.6) comprise a subset of *nonlinear* equations. Having *fixed* the variables (4.7), we have seen that it was still possible to rearrange the equations in the manner that the solvability (compatibility) conditions were formulated explicitly, and the (as we called them) observable variables could then be uniquely determined. In practice, the difficulty of carrying out such a rearrangement increases with increasing complexity of the system. Nevertheless, it can be shown that this rearrangement is, at least *theoretically* possible for a general set of nonlinear equations, if it obeys certain mathematically formal conditions; see again VE-MA, Chapter 8. It also turns out that the intuitive concepts of redundancy and observability are generally somewhat vague from the rigorous mathematical point of view. We will not, however, embarrass the reader with these mathematical details. Quite briefly, let us state that with possible *exceptions*, the set of balance equations behaves quite reasonably and can be treated by mathematical methods made use of in the balancing software. In principle, the methods are based on the theoretical possibility mentioned above, but employ it in a more sophisticated mathematical frame; it is then the procedure of *reconciliation* dealt with in the next Chapter.

Let us still give an example of difficulty that can arise. The example is rather naive, just a simple illustration.

Example 3. Blending of streams and preheating

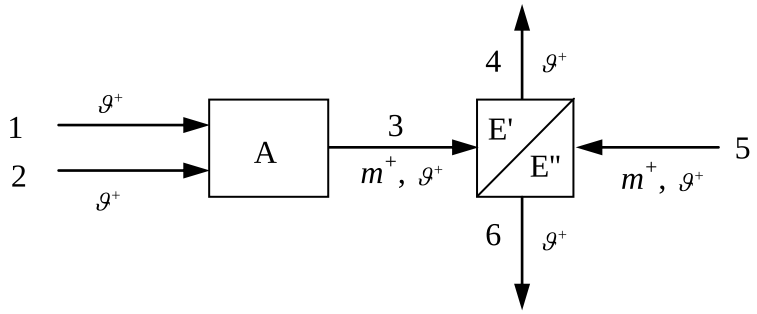

Fig. 4-4 Blending of streams and preheating

The scheme is obvious. Two streams are blended in node A and preheated in exchanger (E',E"). The temperature variable is ϑ (4.5). We neglect again the heat of mixing and in addition, for simplicity take all specific heats c_p of the streams equal; so the enthalpy balances are divided by c_p. We thus have

A, mass: $m_1 + m_2 - m_3 = 0$

enthalpy: $m_1 \vartheta_1 + m_2 \vartheta_2 - m_3 \vartheta_3 = 0$

E', mass: $m_3 - m_4 = 0$

E", mass: $m_5 - m_6 = 0$

(E',E"), enthalpy: $m_3\vartheta_3 + m_5\vartheta_5 - m_4\vartheta_4 - m_6\vartheta_6 = 0.$

$$\tag{4.9}$$

Let us fix the variables denoted by + in Fig. 4-4 thus the values

$$\hat{\vartheta}_1,\ \hat{\vartheta}_2,\ \hat{m}_3,\ \hat{\vartheta}_3,\ \hat{\vartheta}_4,\ \hat{m}_5,\ \hat{\vartheta}_5,\ \hat{\vartheta}_6\,. \tag{4.10}$$

The equations can be rearranged to obtain the solvability condition

$$\hat{m}_3\hat{\vartheta}_3 + \hat{m}_5\hat{\vartheta}_5 - \hat{m}_3\hat{\vartheta}_4 - \hat{m}_5\hat{\vartheta}_6 = 0 \tag{4.11a}$$

and the remaining equations

$$\begin{aligned} m_1 + m_2 - \hat{m}_3 &= 0 \\ m_1\hat{\vartheta}_1 + m_2\hat{\vartheta}_2 - \hat{m}_3\hat{\vartheta}_3 &= 0 \\ \hat{m}_3 - m_4 &= 0 \\ \hat{m}_5 - m_6 &= 0 \end{aligned} \tag{4.11b}$$

determine m_4, m_6 and also m_1 and m_2 by

$$m_1 = \hat{m}_3\frac{\hat{\vartheta}_3 - \hat{\vartheta}_2}{\hat{\vartheta}_1 - \hat{\vartheta}_2} \tag{4.12a}$$

$$m_2 = \hat{m}_3\frac{\hat{\vartheta}_1 - \hat{\vartheta}_3}{\hat{\vartheta}_1 - \hat{\vartheta}_2} \tag{4.12b}$$

assuming $\hat{\vartheta}_1 \neq \hat{\vartheta}_2$. We can directly imagine that the values (4.10) have been measured and adjusted to obey Eq. (4.11a). We also see that the values $\hat{\vartheta}_1$ and $\hat{\vartheta}_2$ are nonredundant, thus remain unadjusted being subject to no condition. The case that we have found $\hat{\vartheta}_1 = \hat{\vartheta}_2$ precisely can be regarded as unlikely, but let us admit the possibility that $|\hat{\vartheta}_1 - \hat{\vartheta}_2|$ is small. Precluding gross measurement errors, we can expect that the (adjusted) $\hat{\vartheta}_3$ will lie somewhere between $\hat{\vartheta}_1$ and $\hat{\vartheta}_2$, thus a fortiori $|\hat{\vartheta}_3 - \hat{\vartheta}_2|$ and $|\hat{\vartheta}_1 - \hat{\vartheta}_3|$ will be small. In (4.12), we then have ratios of small numbers thus the ('observable') values of m_1 and m_2 will be uncertain. We then can say that the balancing problem with fixed variables (4.10) is 'not well-posed' as concerns the determination of m_1 and m_2. [This is a theoretical concept introduced in VE-MA, Chapter 8 in a mathematically formal way and generally.] In the next Chapter, we'll show how this property can be characterised quantitatively.

4.2.Degrees of freedom

Given a set of equations, the *number of degrees of freedom* is the necessary and sufficient number of variables that have to be given a priori in order to uniquely determine a solution. So in the example illustrated by Fig. 4-2, in the equations (4.1) it is sufficient to give the values of m_1 , m_4 and m_7 , and as the reader readily verifies, the remaining variables are successively determined. It is also easy to show that this number (= 3) is necessary. We here have 3 = 8(number of variables) – 5(number of equations) . Thus the number of degrees of freedom

$$D = N - M \tag{4.13}$$

where N is the number of all variables and M that of equations. The example also shows that the choice of the D variables is not arbitrary, and is nor unique either.

Basically, the equality (4.13) holds true also for a set of nonlinear equations if they obey certain mathematically formal conditions; in particular they have to be *independent* in a sense precised by mathematical analysis. For the chemical component mass and energy balance equations, this analysis was performed in VE-MA: Chapter 8 and the equality (4.13) proved.

Let us consider Example 2 thus Fig. 4-3 with the equations (4.6), rearranged into (4.8). In the list (4.7) of a priori given variables, let us

delete $\hat{m}_{11}$ and $\hat{\vartheta}_{11}$
and add m_4 and Q' thus values $\hat{m}_4$ and $\hat{Q}'$

hence the number 11 remains unchanged; we have now given a priori

$$(\hat{m}_1, \hat{\vartheta}_1, \hat{m}_4, \hat{m}_9, \hat{\vartheta}_9, \hat{\vartheta}_{10}, \hat{\vartheta}_6, \hat{m}_7, \hat{\vartheta}_7, \hat{\vartheta}_8, \hat{Q}') . \tag{4.14}$$

Then by the first of the equations (4.8a), m_{11} is determined, by the second we then determine ϑ_{11}. By (4.8b), m_2 , m_6 , m_8 , m_{10} , ϑ_2 , ϑ_3 , ϑ_4 are again determined. Finally by (4.8c), we successively determine m_3 and m_5 , then also ϑ_5 (m_4 and ϑ_2 being known), and finally Q''. We have $N = 24$, $M = 13$ and correctly $D = 11 = N - M$ where the D variables (4.14) determine the complete solution. No solvability conditions such as (4.8b) are necessary.

Generally, the degrees of freedom needn't be represented just by our balancing variables thus mass flowrates and composition of streams in the case of multicomponent balancing. Let us consider Example 1 in Section 3.2. The equations (Ex 1.3) obtained by the elimination of parameters W_1 and W_2 suggest taking the molar production rates n_{SO2} and n_{SO3} (reaction degrees of freedom) as auxiliary variables. It is possible to consider the balance equations in molar units for simplicity. Denoting by $n_X{}^i$ the molar flowrate of species X in stream i we have

$$n_X{}^i = x_X{}^i n^i \tag{4.15}$$

where x_X^i is the mole fraction of X in stream i and n^i the overall molar flowrate. Let us give a priori the values of the following 5 auxiliary variables

$$n_{SO2}\,,\ n_{SO3}\,,\ n_{O2}^2,\ n_{N2}^2,\ n_{Ar}^2 \tag{4.16}$$

(stream 1 is liquid sulphur, stream 2 dry air, stream 3 outlet gas). By the definition of the 'molar excess' quantities n_X (molar output minus molar input of X) we find, according to (Ex 1.3)

$$n_S^1 = -n_S = n_{SO2} + n_{SO3}$$

$$n_{O2}^3 - n_{O2}^2 = n_{O2} = -n_{SO2} - \tfrac{3}{2}n_{SO3}$$

$$n_{N2}^3 - n_{N2}^2 = n_{N2} = 0$$

$$n_{Ar}^3 - n_{Ar}^2 = n_{Ar} = 0.$$

The 4 equations (Ex 1.3), given (4.16), determine all n_X^i for components X present in streams i because $n_X^3 = n_X$ for X = SO_2 , SO_3 (absent from streams 1 and 2).

The balancing variables are n^i (i = 1,2,3) where $n^1 = n_S^1$ ($x_S^1 = 1$ need not be regarded as variable), further x_X^2 for X = O_2, N_2 , Ar and x_X^3 for X = O_2 , N_2 , Ar, SO_2 , SO_3 , thus in number 3 + 3 + 5 = 11. We now add two equations corresponding to (3.2.2.5)

$$\sum_X x_X^2 = 1 \quad \text{where X} = O_2 , N_2 , \text{Ar}$$

$$\sum_X x_X^3 = 1 \quad \text{where X} = O_2 , N_2 , \text{Ar} , SO_2 , SO_3 .$$

We thus have $M = 4 + 2 = 6$ equations, $N = 11$ variables and $D = 5$ (auxiliary) variables (4.16). The variables are all determined because from the latter 2 equations with the definitions (4.15) follows

$$n^i = \sum_X n_x^i$$

where all n_X^i are known, and then by (4.15) $x_X^i = n_X^i / n^i$. So $D = N - M$ is the number of degrees of freedom , specified as the auxiliary variables (4.16). We then say that the set of solutions has been *parametrised*: Any solution is function of the D independent parameters.

It is not always this simple to specify the degrees of freedom. A general procedure (using a parametrisation) is described in VE-MA, Sections 8.2 and 8.3 with examples on pp. 238 and 254. The task is common in design practice and simulation. One then makes use of detailed models of the apparatuses and in the synthesis, one must take into account the fact that (considering possible losses in addition) any variable characterising a stream is common to two nodes connected by the stream, with the exception of streams going from or into the environment which is not subject to balancing. With recycling (streams going 'back' with respect to the succession of operations), the problem can meet with complications. Several decades ago, such (mainly design) problems were solved by experience, skill and intuition of the design engineers. Sophisticated computer programs nowadays available facilitate the task considerably.

4.3.Classification of variables

In the process analysis when the balancing is based on measured data, it is rarely the case that the measured variables just represent a complete set of certain degrees of freedom. Quite frequently, more variables are measured than is needed so as to determine the required values and conversely, certain values can remain undetermined, perhaps being not required. The Examples 1 and 2 in Section 4.1 suggest the following classification.

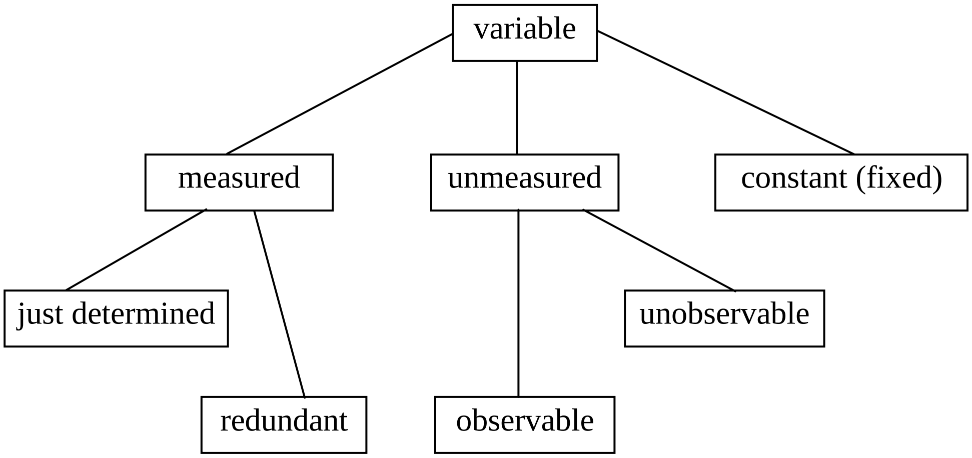

Fig. 4-5 Classification of variables

Here, we have added the entry 'constant'; it can include for example the specific heats in Example 2. The constants are *a priori fixed without* admitting any adjustment due to the conditions of solvability (compatibility of the data with the model equations). The values of the remaining variables can be given as *measured*, or not given but assumed to obey the model equations such as (4.1) or (4.6); the latter are called *unmeasured*.

With these nomenclature conventions, the classification is based on the following ideas illustrated by the above two Examples. A *redundant* measured variable is subject to certain conditions of solvability (compatibility) and if it were not measured, it would still remain determined by the conditions (so the measurement is 'redundant'). A measured variable not subject to the conditions is *nonredundant,* thus *just determined* by its given, in our case measured value; if not given (not measured), it remains undetermined. The value of an unmeasured variable is either determined by the given data thus *observable,* or remains undetermined thus *unobservable*.

Let us consider Example 1. We have the set of *linear* equations (4.1). The solvability problems are completely resolved by the methods of linear algebra and it can be shown that the above classification is *formally exact*. In particular for the mass (single-component) balance equations, the analysis can be performed by graph methods (see, e.g., VE-MA, Chapter 3). The balancing software is able to provide the complete information about redundant /just determined and observable /unobservable variables classification *if* the variables have been partitioned into measured/ unmeasured, this *irrespective* of the given (measured) values.

In Example 2, we have also succeeded in analysing the equations and obtained a plausible classification. Why 'a plausible'? Looking at the equations, the result appears unambiguous. Nevertheless, a mathematician could raise objections. Let us admit that $\hat{\vartheta}_9 = \hat{\vartheta}_{10}$ in (4.8a); then, as is easily shown, $\vartheta_2 = \hat{\vartheta}_6$ by (4.8b), in (4.8c) we have $m_4(\vartheta_5 - \vartheta_2) = 0$ and assuming $m_4 > 0$, we have $\vartheta_5 = \vartheta_2$ thus ϑ_5 becomes 'observable' as ϑ_2 is. Of course the case that $\hat{\vartheta}_9 = \hat{\vartheta}_{10}$ is technologically absurd, but the fictitious example shows at least that generally, the classification *can depend* on the measured (and adjusted) values. In VE-MA: Section 8.1 and Subsection 8.5.1, a number of examples are given illustrating cases where the classification of variables can become ambiguous or even fail.

However, let us abandon the rigorous theory. Pragmatically, the above classification still makes sense unless the measurement system is chosen inadequately, or with rather unlikely exceptions. The classification is obtained as a result of the reconciliation procedure; see Chapter 5. An inadequate choice of the measurement system ('not well-posed problem') is illustrated by Example 3 of Section 4.1 and later also analysed in Chapter 5.

For a reader interested in more technical details of the classification, the idea is schematically presented in the enclosed *Appendix*.

5. BALANCING WITH RECONCILIATION OF MEASURED DATA

Let us begin with the example according to Fig. 4-2. Let us have measured certain values of m_1, m_6 and m_7 (denoted by + in the Figure), say m_1^+, m_2^+, m_7^+. Due to unavoidable measurement errors, they most likely will not (as fixed values) obey the condition (4.2). We thus have to find some *adjustments* v_1 and v_6 such that, setting

$$\begin{aligned} \hat{m}_1 &= m_1^+ + v_1 \\ \hat{m}_6 &= m_6^+ + v_6 \end{aligned} \qquad (5.1)$$

the condition is satisfied. The adjusted values have to lie in the straight line, say L

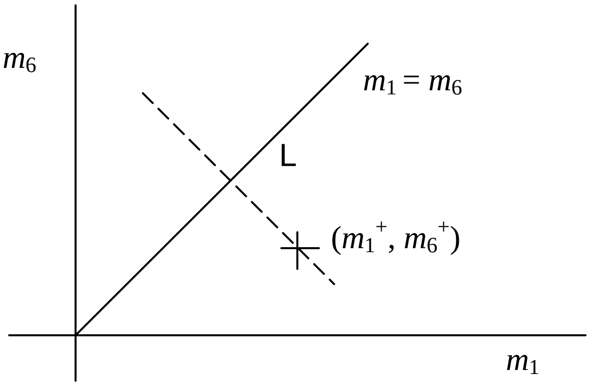

Fig. 5-1 Compatibility condition for adjusted values

while the measured point (m_1^+, m_6^+) doesn't. The actual mass flowrates m_1 and m_6 are unknown; we can only try to *estimate* their values as the adjusted ones.

Intuitively, one would expect that the actual values thus point (m_1, m_6) would lie in the nearest possible neighbourhood of the measured ones. If we have no information on the possible measurement errors, we thus draw a line perpendicular to L in Fig. 5-1 and passing through the measured point; the intersection will be the estimated $(\hat{m}_1, \hat{m}_6)$ whose distance from (m_1^+, m_6^+) is smallest. We have thus resolved the problem (4.2) with the condition

$$(\hat{m}_1 - m_1^+)^2 + (\hat{m}_6 - m_6^+)^2 = \text{minimum.} \qquad (5.2)$$

In addition we put $\hat{m}_7 = m_7^+$ (unadjusted): we can imagine the third coordinate (m_7) as perpendicular to the coordinates m_1 and m_6 and the equation (4.2) as determining a plane perpendicular to the (m_1, m_6) plane and passing through L; then the distance between (m_1^+, m_6^+, m_7^+) and $(\hat{m}_1, \hat{m}_6, \hat{m}_7)$ is again minimum.

Suppose we know the standard deviations of random errors in measuring the flowrates, say σ_i for m_i ; see Chapter 2, the last two paragraphs. We here assume that the errors are uncorrelated and with zero statistical means. Then the larger is σ_i , the larger is the error that can be expected. It is thus natural to 'normalise' (re-scale) the adjustments as v_i / σ_i : the larger is σ_i , the larger adjustment is admitted. Our problem thus reads: Find $\hat{m}_1$ and $\hat{m}_6$ obeying Eq.(4.2) and such that

$$\left(\frac{\hat{m}_1 - m_1^+}{\sigma_1}\right)^2 + \left(\frac{\hat{m}_6 - m_6^+}{\sigma_6}\right)^2 = \text{ minimum.} \tag{5.3}$$

We can also imagine different scales for m_1 and m_6 in Fig. 5-1. With the normalised scales, the straight line passing through (m_1^+, m_6^+) is again perpendicular to L (the latter forming now a different angle) and the distance is again smallest. It is also smallest between the measured and adjusted points in the 3-dimensional space (with the third coordinate m_7 / σ_7) when setting $\hat{m}_7 = m_7^+$. We thus can write the minimum condition as

$$\sum_{i=1,6,7}\left(\frac{\hat{m}_i - m_i^+}{\sigma_i}\right)^2 = \text{ minimum} \tag{5.4}$$

along with (4.2); the sum is over all measured variables.

The generalisation is obvious. The minimum condition requires that the sum of weighted squares of the adjustments is minimum; the weighted square is $(v_i / \sigma_i)^2$. This condition is imposed upon the adjustments $v_i = \hat{x}_i - x_i^+$ (x_i^+: measured, $\hat{x}_i$: adjusted) that are added to x_i^+ in order to make the set of equations *solvable*.

In the examples in Chapter 4, we have succeeded in formulating the solvability conditions explicitly. Generally, it is the task of the balancing (reconciliation) software to include this requirement in the mathematical procedure. The methods nowadays available can do it even if certain variables are not only unmeasured, but even unobservable. They thus solve the following *reconciliation problem*:

Given measured values x_i^+, *find*

(1) the adjusted values $\hat{x}_i = x_i^+ + v_i$(adjustment) such that

(1a) the (balance) equations are solvable with fixed values $\hat{x}_i$

(1b) the adjustments obey the condition

$$\sum_{x_i \text{measured}}\left(\frac{v_i}{\sigma_i}\right)^2 = \text{ minimum} \tag{5.5}$$

where σ_i is standard deviation of measurement error in x_i^+ , and

(2) the values $\hat{y}_j$ of observable unmeasured variables y_j , uniquely determined by the equations with fixed $\hat{x}_i$.

[The condition (1a) can further restrict the values; see below.]

In the condition (5.5), we *assume* that the *measurement errors* are

(A) uncorrelated (see below)

(B) of zero statistical mean.

The condition (B) is quite delicate. Basically, it is a problem of maintenance of the instruments; see Madron (1992), Chapter 3 (systematic errors), or also VE-MA: 9.5 concerning the consequences for the reconciled values. The assumption (A) is in fact not necessary, only the condition (5.5) is then generalised for an arbitrary covariance matrix (that of variances σ_i^2 and covariances representing the correlations); the reconciliation can work as well with general covariance matrix (see, e.g., the formulae in VE-MA). But in practice, when using directly measured values in the reconciliation the assumption (A) is quite plausible.

Remarks

(i) The condition (5.5) has been motivated by the simple concepts of 'minimum distance' or 'minimum weighted sum of squares'. In the statistical theory of errors, it is pronounced as the 'maximum likelihood principle' and as written above, holds then true only if the statistical distribution of errors is Gaussian. In practice, the result is the same because one rarely knows more than the standard deviations. Concerning the Gaussian distribution, it is sometimes postulated as a prerequisite but the reconciliation works as well as an 'optimisation' of the adjustments if the errors are Gaussian or not (which we usually cannot decide).

(ii) The correlatedness of measurement errors can arise if we use other than the balancing variables as introduced. Let for example m be an overall flowrate, y and z two concentrations in a ternary mixture thus $u = my$ and $v = mz$ are the flowrates of the respective components regarded as measured if m, y, and z have all been measured. The balance equations are then of simpler form and were used as such in the earlier stages of the reconciliation techniques. We then have for example, using approximation by Taylor formula with $\mathrm{d}u = m\mathrm{d}y + y\mathrm{d}m$

$$-e_u = u - u^+ \cong m^+(y - y^+) + y^+(m - m^+) = -m^+e_y - y^+e_m$$

for the error e_u in u and small primary errors e_y and e_m with standard deviations σ_y and σ_m. Assuming the latter uncorrelated and denoting by < > the statistical mean value, we have

$u = my$
$v = mz$:

$$\sigma_u^2 = \langle e_u^2 \rangle \cong (m^+)^2 \langle e_y^2 \rangle + (y^+)^2 \langle e_m^2 \rangle = (m^+)^2 \sigma_y^2 + (y^+)^2 \sigma_m^2 \tag{5.6a}$$

$$\sigma_v^2 \cong (m^+)^2 \sigma_z^2 + (z^+)^2 \sigma_m^2 \tag{5.6b}$$

but also

$$\sigma_{uv} = \langle e_u e_v \rangle \cong y^+ z^+ \langle e_m^2 \rangle = y^+ z^+ \sigma_m^2 \neq 0 \tag{5.6c}$$

thus e_u and e_v are correlated. The nonlinear methods don't need introducing this kind of variables and in addition they don't require that for example both m and y be measured, when there are other redundant data.

Let us now give several simple examples, just to show how the reconciliation works. The first example is that of

5.1.Mass balance

This is the most elementary, mathematically most exact and most widely used form of balancing.

Example 1. Steady-state mass balance

Let us consider Fig. 4-2. The balancing software takes over the flowsheet with specification of measured flowrates and transforms it by graph methods. Let the measured values (in tons per hour) be

$m_1^+ = 1.1,\ m_6^+ = 1.13,\ m_7^+ = 0.5$

with the corresponding standard deviations of measurement errors (also in t/h)

$\sigma_1 = 0.02,\ \sigma_6 = 0.03,\ \sigma_7 = 0.02.$

We then obtain the reconciled values

$\hat{m}_1 = 1.1092,\ \hat{m}_6 = 1.1092,\ \hat{m}_7 = 0.5$

and the estimates of the observable unmeasured variables

$\hat{m}_2 = 1.1092,\ \hat{m}_8 = 0.6092$

along with the information that m_3, m_4 and m_5 are unobservable, and also that m_7 is nonredundant.

We perhaps don't need to know the values of m_3, m_4 and m_5 thus we have the complete result. We know that the adjusted measured values are *compatible* with the node balances and that the observable unmeasured values are then *uniquely* determined. In addition, the adjustments were found in an optimal way with respect to our additional information (the standard deviations); adopting the hypothesis that the probability distribution is Gaussian, we have the *maximum* *likelihood estimates*. Observe that the measured value of m_7 has remained unadjusted. This is a *general* property: With *uncorrelated* measurement errors

Any *nonredundant* measured variable is *nonadjustable*.

The precision of the results can be expressed quantitatively by the *standard deviations of the estimates*; the smaller the standard deviation is, the more precise is the estimate. The reader can imagine the Gaussian distribution. Then, if σ_x is the standard deviation, the error in the estimate $\hat{x}$ will be smaller in absolute value than (approximately) $2\sigma_x$ with 95% probability; the error means the difference between the estimate and the (otherwise unknown) true value.

The necessary information for computing the latter standard deviations can be gained in the course of the transformations the computer performs. If making use of it, we can find the values

measured	unmeasured observable
$\sigma_{m1} = 0.0167$	$\sigma_{m2} = 0.0167$
$\sigma_{m6} = 0.0167$	$\sigma_{m8} = 0.0260$.
$\sigma_{m7} = 0.02$	

We can see that $\sigma_{m1} < \sigma_1$ and $\sigma_{m6} < \sigma_6$. The result is again *general*:

For the *redundant* measured variables, the *precision increases* by reconciliation

if compared with the result of the measurement itself. The nonredundant variable is unadjusted and the precision remains the same.

We can also examine what happens if we add some measurement. Let us measure the value of m_8 in addition, with

$\sigma_8 = 0.03$.

We can obtain other estimates, but anyway

measured	unmeasured observable
$\sigma_{m1} = 0.0151$	$\sigma_{m2} = 0.0151$.
$\sigma_{m6} = 0.0151$	
$\sigma_{m7} = 0.0173$	
$\sigma_{m8} = 0.0197$	

All measured variables are now redundant and the precision has increased for all estimates. The result is again *general*:

Increasing the *redundancy increases* the *precision* of the estimates.

'Increasing the redundancy' means here adding the measurement of a variable that was unmeasured but observable; if an unobservable variable becomes measured, it becomes nonredundant and the precision does not increase.

This is also one of the merits of reconciliation. The measured data are compatible, and also more precise if adjusted. But *attention*: The precision is to be interpreted *statistically*. Individual results can be spoiled, in particular if a gross measurement error is present.

Example 2. Dynamic mass balance

Let us now add a *storage tank* to Fig. 4-2. The product (stream 7) is conveyed into node T according to the scheme

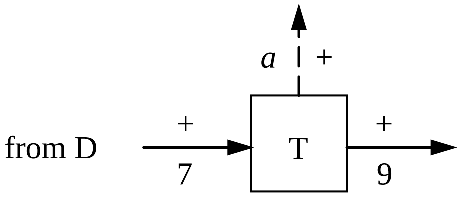

Fig. 5-2 Storage tank added to Fig. 4-2

and as stream 9, taken over by the client(s); the fictitious stream *a* represents the accumulation thus increase in the inventory. According to Section 3.1, the node balance

$$m_7 - m_9 - a = 0 \tag{5.7}$$

is added to the balances (4.1).

We now consider the case of *daily balancing*. At discrete times t_k (t_k - t_{k-1} = 24 h), the integrated mass flowrates m_i are measured between t_{k-1} and t_k in the streams marked by + in Figs. 4-2 and 5-2, and also the state *s* of the inventory is measured. Then, adding subscripts *k* to the m_i and *a* (at t_k) in (4.1) and (5.7), we have in particular

$$a_k = s_k - s_{k-1} \; ; \tag{5.8}$$

s_0 is the initial state of the inventory.

Our goal is to make the measured *states* s_k *compatible with* the *measured flowrates*. Because, by (5.8), the balances at times *k* = 1,2,... are interrelated we obtain, for large *k*, a huge set of linear equations thus constraints used in the reconciliation; imagine more generally a system with many streams and several nodes with accumulation. The reconciliation can be made simpler as will be shown.

We consider average daily production 25 t of the distillate; let the storage tank have the capacity of 10 days' production, thus 250 t. We assume that the random measurement errors are uncorrelated also for the same variable but measured at different times; let their constant standard deviations be (in tons)

$$\sigma_1 = 0.5, \quad \sigma_6 = 0.6, \quad \sigma_7 = 0.25, \text{ and } \quad \sigma_s = 1$$

for the inventory. The measured flowrate of stream 9 is considered *errorless*. It is the so-called custody measurement agreed by the client: What has been measured, that counts. So

m_9^+ is a fixed value at each t_k or, which is the same, we put

$$\sigma_9 = 0.$$

Apparently simplest is regarding the difference a (5.8) as a (measured) balancing variable and reconcile as such; then the t_k-balances are separated from each other (independent). We can compute the estimate at time K

$$\hat{s}_K = s_0^+ + \sum_{k=1}^{K} \hat{a}_k \tag{5.9}$$

using the estimates $\hat{a}_k$. However, it has turned out in practice that for large K, nonsensic values can be obtained (e.g. $\hat{s}_k$ exceeds the storage capacity). This can be explained as the cumulation of (even small) systematic errors in some of the flowrates. As an illustration, let us hypothetically assume the primary systematic errors

$$e_{7\,0} = +0.02 \text{ and } e_{s\,0} = +0.5$$

in m_7^+ and s^+, respectively. According to VE-MA, Chapter 11, we can compute the systematic error E_K in the estimate (5.9) after 100 days

$$E_{100} = 2.44$$

and the standard deviation Σ_K from E_K (which is the mean)

$$\Sigma_{100} = 2.46.$$

These values are perhaps not alarming (due to the special structure considered). But it can be shown that generally, $|E_K|$ increases linearly with K and Σ_K increases linearly with $\sqrt{K}$; the result (see again VE-MA, ibid.) holds true for an arbitrary number of streams and accumulation nodes.

Another possibility is regarding, at each k, the measured s_k as balancing variable while the previous estimate $\hat{s}_{k-1}$ as constant. Thus in the balance (5.7) with (5.8), we put

$$a_k = s_k - \hat{s}_{k-1} \tag{5.10}$$

only with measured value s_k^+ subject to reconciliation; the equations for each t_k are again separated. It can again be shown generally that the $|E_K|$ and Σ_K also increase but *remain bounded* by limit values $|E_\infty|$ and Σ_∞. In our simple example, we can even compute

$$0 < E_K \leq 0.821, \quad \Sigma_K \leq 4.123$$

for any K. The value Σ_K is independent of the systematic errors. Experience has shown that indeed, the mentioned nonsensic values can thus be avoided.

Note: Although irrelevant for the above general conclusions, we have introduced the custody measurement to signal the possibility of *errorless measured variables*. They can be several in a large system. It then *can happen* that the reconciliation problem becomes *not solvable*. Consider the case

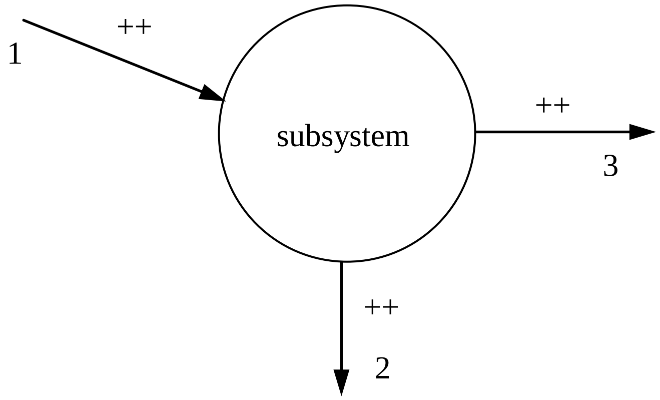

Fig. 5-3 Non-solvable reconciliation problem

where all the three in/outgoing streams represent errorless (++) measured variables. The equality among constants $m_1^{++} = m_2^{++} + m_3^{++}$ becomes *contradictory* because in reality, no measurement is absolutely accurate. The Figure is suggestively drawn in the manner that this model error is immediately detected. In a complex flowsheet, the arrangement need not be this suggestive and the error has to (and can) be found by graph analysis or another algebraic treatment of the model equations with specified measured streams. If detected, the issue must be solved by some agreement.

The mass balancing, more generally single-component balancing (see Section 2.1) belongs to the class of *linear* problems. They can be solved using graph or also other algebraic methods and from the mathematical viewpoint of solvability, no difficulties can arise. The case of

5.2.Nonlinear reconciliation

is not that simple; see VE-MA, Chapters 8 and 10 for the theoretical analysis. Still, a number of methods are nowadays available; see Narasimhan and Jordache (2000) for a good survey. Let us characterise the methods quite briefly.

The historical development of the reconciliation routines has led to nonlinear methods *tailored for the special use* in reconciliation. One of them is due to Crowe, with modification by Pai and Fisher (1988) as presented in Plácido and Loureiro (1998) ; see also Narasimhan and Jordache (2000), pp. 127, 134 and 66. Two other such methods are presented in VE-MA, Chapter 10. Basically, the three methods are equivalent and solve the problem as formulated above (points (1) and (2) with (5.5)) by different strategies.

The reconciliation problem can also be regarded as that of *optimisation* thus minimisation of an objective function with certain constraints; the objective function is here the LHS in (5.5). Such problems arise in many branches of technology and economy and were solved by mathematicians to these general purposes, first as linear, then extended as *nonlinear programming* (NLP). The position of the optimum is a priori quite unknown and the *region* where it has to be found is *restricted by* certain *inequalities* (such as a production capacity that cannot be exceeded and the like). Quite often, the optimum is then found just at the boundary (as is always the case in linear programming). Going back to the reconciliation, this means adding certain *inequality constraints* (such as nonnegative mass flowrates) to the solvability conditions (1a) above. Mainly in the last decade, the NLP techniques were recommended also for the latter purpose, as reported at conferences, in articles and also (though not exclusively) in Narasimhan and Jordache (2000). The software is elaborated in technical details, available on the market even with possible modifications, and it works.

It is difficult to make a comparison; different (teams of) authors clearly recommend the methods they have used. The NLP-methods are probably more robust and can facilitate the convergence of the successive approximations in certain cases; if the successively approximated point (solution) tends to escape from the admitted region, they can let it slide on or even reflect from the boundary. [This can be the case of 'bad' measured data.] Still, the conclusion is not unambiguous. If the final solution is found just at some point of the boundary, its interpretation is dubious; something is probably wrong with the model or measured values. Anyway, the 'tailored' methods (Crowe, VE-MA) appear to be more suitable for the *statistical analysis* of the data; see VE-MA, Chapter 10. [In fact, they can also be regarded as NLP methods, but without the boundary conditions.]

Example 3. Heat and mass balance

Let us now consider the example according to Fig. 4-3. The balancing software does not know our detailed analysis that follows after (4.7); nor the user is obliged to perform it. The model is given by the original node balances (4.6) with specification (4.7) of measured variables to be reconciled; in addition, the specific heats are in the database. For simplicity, let us take the same specific heat

$c_p = 2.2 \text{ kJ kg}^{-1} \text{K}^{-1}$

for all streams (hydrocarbons). Observe that the user can give the input values and require the output ones in physical units he prefers; the software itself performs the necessary transformations. Let the mass flowrates be in t/h, temperatures ϑ (4.5) in deg C and heat flows in kW. Let the measured values be

$m_1^+ = 1.01$ $\qquad$ $\vartheta_1^+ = 21$ $\qquad$ $\theta_9^+ = 137$

$m_7^+ = 0.32$ $\qquad$ $\vartheta_6^+ = 100$ $\qquad$ $\vartheta_{10}^+ = 105$

$m_9^+ = 0.79$ $\qquad$ $\vartheta_7^+ = 81$ $\qquad$ $\vartheta_{11}^+ = 39.5$.

$m_{11}^+ = 0.68$ $\qquad$ $\vartheta_8^+ = 119$

Again for simplicity, let us consider the standard deviations

for all measured flowrates $\qquad \sigma_m = 0.01$ (t/h)

temperatures $\quad \sigma_\vartheta = 0.5$ (K).

The nonlinear procedure requires, however, also *initial guesses* for the *unmeasured* variables. The user has probably some idea of what they can be. So let the latter guesses equal

$m_2^* = 1.01$ $\qquad$ $\vartheta_2^* = 50$ $\qquad$ $Q'^* = 120$ (kW)

$m_3^* = 0.202$ $\qquad$ $\vartheta_3^* = 50$ $\qquad$ $Q''^* = 100$ (kW).

$m_4^* = 0.808$ $\qquad$ $\vartheta_4^* = 50$

$m_5^* = 0.808$ $\qquad$ $\vartheta_5^* = 105.5$

$m_6^* = 1.01$

$m_8^* = 0.68$

$m_{10}^* = 0.79$

The more qualified guesses we have, the faster is the convergence of the procedure. [By the way, with a superstandard equipment of the software, the guesses can be improved before reconciliation; see VE-MA: 10.4.1.] Nonsensic guesses (and also very 'bad' measured values) can, alas, make the procedure fail. For a simple system as ours this is, however, unlikely. The result is obtained in no time. It reads (rounded-off) for reconciled measured values: $\hat{m}_1 = 1.0068$ $\hat{\vartheta}_1 = 20.99$ $\hat{\theta}_9 = 136.99$

$\hat{m}_7 = 0.3236$ $\hat{\vartheta}_6 = 100.01$ $\hat{\vartheta}_{10} = 105.01$

$\hat{m}_9 = 0.7898$ $\hat{\vartheta}_7 = 81$ $\hat{\vartheta}_{11} = 39.51$

$\hat{m}_{11} = 0.6832$ $\hat{\vartheta}_8 = 118.99$

where the variable ϑ_7 is classified as nonredundant; indeed, $\hat{\vartheta}_7 = \vartheta_7^+$ precisely. Further are obtained the estimates of unmeasured variables classified as *observable*

$\hat{m}_2 = 1.0068$ $\hat{\vartheta}_2 = 74.92$

$\hat{m}_6 = 1.0068$ $\hat{\vartheta}_3 = 74.92$

$\hat{m}_8 = 0.6832$ $\hat{\vartheta}_4 = 74.92$

$\hat{m}_{10} = 0.7898$

while the variables m_3 , m_4 , m_5 , ϑ_5 and Q', Q'' are classified as *unobservable*. [In fact their *pseudoestimates*

$m_3 = 0.1837$, $m_4 = 0.8231$, $m_5 = 0.8231$, $\vartheta_5 = 105.51$

$Q' = 112.09$, $Q'' = 107.92$

obeying the balance along with the preceding values are also computed, but they *depend on* the initial guesses and generally also on the chosen strategy. From the viewpoint of probability (statistical reliability), the result is meaningless.]

Note: Observe that the sum of the temperature adjustments ($\hat{\vartheta} - \vartheta^+$) equals zero; this is due to the special structure considered. Also due to the special structure is the fact that all these adjustments are of the same order of magnitude; having rounded-off the adjustments to two decimals, they are all equal to ± 0.01 K. This small order of magnitude is mere coincidence. Changing for example θ_6^+ from 100 to 101 the order of magnitude will equal some 0.15 K. Only the nonredundant $\hat{\vartheta}_7 = \vartheta_7^+$ will subsist.

We suppose that the nonlinear reconciliation has been carried out by one of the 'tailored' methods (modified Crowe, VE-MA). In addition to the classification of variables, we can also obtain information on the *degree of redundancy* (say) H of the system of measurement. It can generally be interpreted as the number of (possibly only hypothetical, explicitly unknown) conditions of solvability (compatibility). In our example, we find $H = 2$ in accord with our detailed analysis leading to Eqs. (4.8a).

Remark

Let us suppose that the source of the hot stream 9 is distant from our subsystem and some heat is lost on the way to E2. Let the temperature be measured at the source. Then a model error arises in the equations (4.6). In fact, with (say) ϑ_{12} (measured as ϑ_{12}^{+}) we have

$$\vartheta_9 = \vartheta_{12} - \frac{Q_{\mathrm{loss}}}{c_p{}' m_9}; \tag{5.11}$$

the equation is to be *added to* (4.6) and ϑ_{12} instead of ϑ_9 is then the measured variable. It can be shown that our set of data has sufficient redundancy to compute this Q_{loss} as an observable unmeasured variable; but one degree of redundancy is lost and the precision of the results is lowered (see below). Instead, we can estimate the Q_{loss} using the measured ϑ_{12}^{+} and a semiempirical chemical engineering formula; we thus have some value (say) Q_{loss}^{+} considered also *measured* and assigned some 'sufficiently large' standard deviation, for example using (2.2.11) where $|e|_{\max}$ is the assessed error in the computation. [This is an idea due to F. Madron: an 'automatically generated stream', see VE-MA, pp. 464 and 471.] The adjusted value $\hat{Q}_{\mathrm{loss}}$ is then obtained along with $\hat{\vartheta}_{12}$; $\hat{\vartheta}_9$ is computed as unmeasured observable.

As a *superstandard equipment*, the software *can* (although commonly doesn't) contain the evaluation of other characteristics of the system with measured variables. As already indicated in Example 1, the underlying information can be gained in the course of the mathematical transformations. We didn't describe them in detail, but the reader is perhaps still interested in how this is possible in principle. Well, at the end (after the last iteration), we have the final point (in the vector space of variables) which is our solution. At this point, the Jacobi(an) matrix (that of partial derivatives of the functions constituting the model thus e.g. the LH-sides in (4.6)) is evaluated. An intelligent engineer can perhaps draw some information from the matrix directly (Dempf and List, 1998). The 'tailored' methods transform the matrix to a 'canonical format' (arrangement) from where also the classification of variables results, and the degree of redundancy. [Basically, the arrangement then corresponds to our rearrangement (4.8.a,b,c) in the special case.] We then can also compute, for example using the formulae in VE-MA 9.6 with 9.3 and 10.7 with 10.3, different *statistical characteristics* of the solution. To be precise (and not to offend statisticians:theorists), the characteristics are only 'pseudostatistical', thus for example (pseudo)standard deviations.They *approximate* the intuitive (theoretically not precisely defined) notion of probability for the computed values. Omitting the meticulous 'pseudo', the *standard deviation* σ_x of estimate $\hat{x}$ informs us again that (with a Gaussian distribution) the error in the estimate will be, in absolute value smaller than $2\sigma_x$ *with* 95% probability. It is to be noted immediately that this σ_x generally *depends* on the final point where it has been evaluated; see below for an example of strong dependency.

Going back to the above Example 3, one can for instance compute the standard deviations for $\hat{\vartheta}_1$ and $\hat{\vartheta}_6$: $\sigma_{\vartheta 1} = \sigma_{\vartheta 6} = 0.458 = 0.916\sigma_{\vartheta}$

where σ_{ϑ} is standard deviation for the temperature measurement

for $\hat{m}_7$: $\sigma_{m7} = 0.007 = 0.7\sigma_m$

where σ_m is standard deviation for the mass flowrate measurement, while

for $\hat{\vartheta}_7$: $\sigma_{\vartheta 7} = \sigma_{\vartheta}$

(nonredundant variable). It can be shown that the conclusion is of general character:

> *With the exception of variables classified as nonredundant, the reconciliation improves the precision.*

Also the σ_x for unmeasured observable variables can be found; for example

for $\hat{\vartheta}_2$: $\sigma_{\vartheta 2} = 0.611$.

Higher precision can be obtained *when increasing the degree of redundancy*. For simplicity and so as to have a comparison, let the final point (solution) be the same as above, but let us have measured ϑ_2 in addition, again with the same standard deviation σ_{ϑ} of measurement errors. We then obtain

for (now measured) $\hat{\vartheta}_2$: $\sigma_{\vartheta 2} = 0.387$ instead of 0.611 (of course $\sigma_{\vartheta 2} < \sigma_{\vartheta} = 0.5$)

for ϑ_6: $\sigma_{\vartheta 6} = 0.426$ instead of 0.458

etc.

This kind of information can be gained more generally. The final point (solution) includes certain values of the unobservable variables as pseudoestimates satisfying the balance (and as close to the initial guesses as possible). [It can be shown formally that the (pseudo)statistical characteristics are independent of the latter values *if* they obey the balance.] Having once the transformed Jacobi matrix (and having completed the superstandard equipment), we can make different *computer experiments* as increasing (or also decreasing) the number of measured variables and examine also what happens with the observability and redundancy (and the standard deviations). To be precise, the information thus gained concerns only the given point, but one usually can expect that it will not alter very much at least for points not very distant from the given one. So in particular, in our example we'll find that (compare with the analysis that follows after (4.8c)) measuring *Q*'' in addition, *Q*' becomes observable, and when measuring both *Q*' and *Q*'' they become redundant along with ϑ_7 and the degree of redundancy increases by one thus precision is improved. This information (reclassification, change in standard deviations) can be important for upgrading the system of measurement.

Example 4. A not well-posed problem

In certain cases regarded rather as exceptions, the classification of variables can become ambiguous. Without going into detailed theoretical analysis, let us consider one example; viz. that illustrated in Fig. 4-4. Having already assumed that all specific heats are equal, the equations are (4.9) and the measured values to be adjusted are (4.10). The computer again does not know our rearrangements (4.11) etc. We again consider the standard deviations

$\sigma_\vartheta = 0.5$ for all measured temperatures

$\sigma_m = 0.01$ for all measured flowrates.

(a) Let us suppose that starting from certain measured values, we have found the estimates

$\hat{m}_3 = 1 \qquad \hat{\vartheta}_1 = 60 \qquad \hat{\vartheta}_4 = 80$

$\hat{m}_5 = 1 \qquad \hat{\vartheta}_2 = 40 \qquad \hat{\vartheta}_5 = 100$

$\hat{\vartheta}_3 = 50 \qquad \hat{\vartheta}_6 = 70$

thus adjusted measured values, and for observable unmeasured variables

$\hat{m}_1 = 0.5 \qquad \hat{m}_4 = 1$

$\hat{m}_2 = 0.5 \qquad \hat{m}_6 = 1$.

We can also compute the standard deviations of the estimates. We find for example

$\sigma_{m1} = 0.0293$ thus $\sigma_{m1} / \hat{m}_1 = 0.0586$

which we will consider a sufficient precision.

(b) Let us suppose that the estimates $\hat{m}_3$ (= $\hat{m}_4$), $\hat{m}_5$ (= $\hat{m}_6$), $\hat{\vartheta}_3$, $\hat{\vartheta}_4$, $\hat{\vartheta}_5$, $\hat{\vartheta}_6$ are as above, but that we have found

$\hat{\vartheta}_1 = 50.3 \qquad \hat{m}_1 = 0.7$

and (observable)

$\hat{\vartheta}_2 = 49.3 \qquad \hat{m}_2 = 0.3$

obeying again the balance. We then find the standard deviations

$$\sigma_{m1} = 0.586 \quad \text{thus} \quad \sigma_{m1} / \hat{m}_1 = 0.837$$

$$\sigma_{m2} = 0.585 \quad \text{thus} \quad \sigma_{m2} / \hat{m}_2 = 1.86 > 1 \ \ !!$$

Let us first consider the case (a). If the technology doesn't admit the difference $(\vartheta_1 - \vartheta_2)$ to be smaller than some 20 K, the variables m_1 and m_2 can be estimated as observable with sufficient precision. In the case (b) however, the technology admits that ϑ_1 and ϑ_2 can only slightly differ from one another (1 K in our example). Our analysis following after (4.12b) has already come to the conclusion that the estimates of m_1 and m_2 will be uncertain. This is expressed quantitatively by the values of σ_{m1} and σ_{m2} ; for m_2 , the standard deviation is even larger than the estimated value. The (theoretical concept of) 'not-well-posedness' means here that the m_1 and m_2 are *practically unobservable*. In VE-MA: 10.4.5 (iii), this property has been predicted generally by theory. It also follows from the theory that if we have, using certain data, detected such an effect then with other, perhaps 'worse' data the reconciliation may even fail.

Of course the example was trivial. In complexer situations, the result need not be a priori evident. The important fact is that it can be *detected by the statistical analysis* as shown. Compare with Plácido and Loureiro (1998); in their case study, large standard deviations of an unmeasured observable variable were also found and attributed "to the structure of matrices used" thus in fact to the model of the system and its measurement. The authors used modified Crowe's method and stress the importance of statistical analysis of the estimates.

Let us now, by way of a *computer experiment*, regard the *value of* m_1 as *measured*. So the estimates are the same as above; but the standard deviations are different. For the (now measured and reconciled) value $\hat{m}_1$ we find

$$m_1 \text{ measured:} \quad \sigma_{m1} = 0.9998 \times 10^{-4} \cong 0.01 = \sigma_m$$

thus m_1 is *almost nonredundant* (nonadjustable); the estimate error variance is practically equal to the measurement error variance (σ_m^2). Also such cases can occur generally; they cause no problem in the reconciliation, but disqualify the detection of a gross measurement error in the variable (see, e.g., VE-MA: 10.5).

Note: Observe that a small value of the adjustment itself doesn't necessarily mean that the variable is almost nonadjustable. Thus in Example 3, the ϑ-adjustments are all ± 0.01 K (see the *Note* ibid.), but for example $\sigma_{\vartheta 1} = 0.916\,\sigma_\vartheta$ is though not dramatically, still sensibly different from the standard deviation of measurement errors.

Also the estimate error standard deviation for the unmeasured variable m_2 in the above computer experiment changes dramatically. We now have

$$\sigma_{m2} = 1.51 \times 10^{-2}$$

instead of the above 0.585. Finally let us measure both m_1 and m_2. We find

m_1 and m_2 measured: $\sigma_{m1} = 0.8346 \times 10^{-2}$ $(< \sigma_m = 10^{-2})$

$\sigma_{m2} = 0.8337 \times 10^{-2}$ $(< \sigma_m)$

thus both m_1 and m_2 become *redundant*, with a well-pronounced effect on the precision.

The superstandard equipment (which is easily installed in particular with the 'tailored' reconciliation methods) thus can yield useful additional information. It makes possible the *statistical analysis* (estimate error variances calculation) detecting 'practically unobservable' unmeasured and 'almost nonadjustable' measured variables. It further enables one to carry out *computer experiments*: what happens if some measurement is added (or also deleted). Theoretically, this is a way to an optimisation of measurement: *an* optimisation because it depends on the criteria adopted. There is a number of articles in journals dealing with this topic. Information about a successful optimisation of this kind installed in industrial practice is, however, lacking. Optimisation is, of course, rather a theoretical (mathematical) concept. But it is important to know that at least some *improvement* is possible.

6. PROPAGATION OF ERRORS

In Chapter 5 (Examples 1 and 3), we have characterised the precision of the results of the reconciliation by *standard deviations of the estimates* (more precisely of the estimate errors), thus σ_{xi} for the *i*-th measured and adjusted variable, σ_{yj} for the *j*-th unmeasured observable estimate. In the analysis of errors and precision, it is convenient to introduce the *variances* thus σ_z^2 for variable z where σ_z is the standard deviation. In addition to the *statistical characteristics* such as the named variances, let us further introduce the *global criterion* $Q_{\min}$ obtained by (5.5)

$$Q_{\min} = \sum_{x_i \text{measured}} \left(\frac{v_i}{\sigma_i} \right)^2 \tag{6.1}$$

where σ_i is standard deviation of the *i*-th measurement error and v_i the *i*-th *adjustment* (added to the *i*-th measured value). Along with the σ_{xi}^2 and σ_{yj}^2, we can compute also the *i*-th *adjustment variance* σ_{vi}^2. All these characteristics (as well as $Q_{\min}$) can be computed for example by the formulae given in VE-MA: 9.3 and 10.3; in the latter (nonlinear) case, they are in fact certain 'pseudostatistical' characteristics due to the linearisation of the equations in the neighbourhood of the solution; see the commentary in Example 3 of Chapter 5, in the paragraph following after that with formula (5.11) and dealing with *superstandard equipment.* The characteristics depend on the model structure and in the nonlinear case, also on the point (solution) where they have been evaluated.

The adjustment variances obey the relation

$$\sigma_{xi}^2 + \sigma_{vi}^2 = \sigma_i^2 \tag{6.2}$$

and we have $\sigma_{vi}^2 > 0$ *with the exception of*

nonredundant variable x_n : $\quad \sigma_{vn}^2 = 0;$ (6.2a)

indeed, the adjustment is then identically zero. From $\sigma_{xi}^2 = \sigma_i^2 - \sigma_{vi}^2$ follows immediately the general result: With the exception of a nonredundant measured variable, the estimate error variance is smaller than the respective measurement error variance thus (in the statistical average) reconciliation improves precision of measured data.

With the reconciliation, the error in some measurement does not affect only the measured variable itself, but generally also the other estimates. The following analysis assumes, as in Chapter 5, that the *measurement errors* are of *zero mean* and *uncorrelated*. From the statistical point of view, the analysis is exact in the linear case and intuitively approximative as explained above when the model is nonlinear.

Let e_h be the *h*-th measurement error, e_{xi} resp. e_{yj} the estimate error in measured variable x_i resp. unmeasured observable variable y_j . For example using the formulae in VE-MA, pp. 321 and 315 or p.372 we have

$$e_{xi} = \sum_h a_{ih} e_h \tag{6.3a}$$

$$e_{yj} = \sum_h b_{jh} e_h \tag{6.3b}$$

with summation over all measurement errors e_h . *Each* of the coefficients a_{ih} resp. b_{jh} depends on the model structure and generally *all* the measurement error variances σ_k^2 , and in the nonlinear case, in addition on the point (solution) where they have been evaluated. They are generally nonnull and characterise the *propagation of errors* among the estimates; e.g. the error e_h contributes by the item $a_{ih}e_h$ to the error e_{xi} (of course the items can partially compensate). There is still an exception: Let x_n be a *nonredundant* variable; then

$$x_n \text{ nonredundant:} \quad \begin{array}{l} a_{in} = 0 \text{ for every } i \neq n \\ a_{nh} = 0 \text{ for every } h \neq n \end{array} \quad \text{and } a_{nn} = 1. \tag{6.3c}$$

The error e_n in a nonredundant measurement affects only the variable itself giving $e_{xn} = e_n$ (no adjustment) and *no other measured* variable estimate. But attention: *it can affect* the estimates of observable *unmeasured* variables (though not necessarily all; that depends on the structure).

The errors themselves are, however, unknown. So as to have an idea of how the precision of the results is affected, we can introduce the *matrices of shares* (Madron 1992: pp. 90 and 168). From (6.3) follows

$$\sigma_{xi}^2 = \sum_h (a_{ih})^2 \sigma_h^2 \tag{6.4a}$$

$$\sigma_{yj}^2 = \sum_h (b_{jh})^2 \sigma_h^2 \, . \tag{6.4b}$$

The matrices (say) $\mathbf{S}_x$ (for measured variables) and $\mathbf{S}_y$ (for observable unmeasured variables) are of elements

$$\mathbf{S}_x : \quad S_{x,ih} = \frac{a_{ih}^2 \sigma_h^2}{\sigma_{xi}^2} \quad \text{in row } i \text{ and column } h \tag{6.5a}$$

$$\mathbf{S}_y : \quad S_{y,jh} = \frac{b_{jh}^2 \sigma_h^2}{\sigma_{yj}^2} \quad \text{in row } j \text{ and column } h \, . \tag{6.5b}$$

We here have, by virtue of (6.4)

$$\text{for any } x_i : \quad \sum_h S_{x,ih} = 1 \tag{6.6a}$$

$$\text{for any } y_j : \quad \sum_h S_{y,jh} = 1 \; . \tag{6.6b}$$

So the element $S_{x,ih}$ resp. $S_{y,jh}$ represents the relative contribution (share) of the h-th measurement error variance to (in) the estimate error variance σ_{xi}^2 resp σ_{yj}^2 .

The matrices provide useful information when the estimate precision is to be improved by replacing some instrument with another. For example looking at matrix $\mathbf{S}_y$, the elements in the j-th row suggest the first candidate for the improvement of the estimate of y_j : it is the h-th measurement giving the largest $S_{y,jh}$; of course one must also consider the price etc. See again Madron (1992), pp. 169-170 for more details.

7. GROSS ERRORS

Intuitively, a gross error is due to some failure: of the instrument, personnel and the like. [We preclude the case of total failure of an instrument which doesn't work.] A model error is due to the failure of some model hypothesis: an omitted (possibly deliberately neglected) stream such as an energy flow representing heat loss, an unknown chemical reaction, or also more delicate errors in the thermodynamic description; some possibilities of model errors were indicated above (Chapter 3). Also model errors are usually detected as *gross errors*, thus errors whose occurrence is regarded as *unlikely*. We can then apply criteria derived from statistics to the results of the reconciliation. Of course also an absurd result (such as an estimated negative mass flowrate or mass fraction of some component) can signal the presence of a gross error.

The techniques for the detection and (if possible) also elimination of gross errors are numerous; see for instance Madron (1992): 4.5 and VE-MA: 13.4, a theoretical analysis in VE-MA: 9.4 and 10.5, or quite recently an extensive review in Narasimhan and Jordache (2000) where a substantial part of the book (Chapters 7,8,9, also 11) is devoted to this problem. We will here only illustrate how the *statistical analysis* can work.

Let us first remark that the statistical hypotheses on which the analysis is based hold true exactly for the linear recociliation only. Otherwise, the same remark applies as that concerning the standard deviations above. But having no other possibility, we shall regard the 'pseudostatistical' criteria as useful approximations; see VE-MA, pp. 372-373. The classical criterion for the gross error *detection* is the value (5.5) minimised by reconciliation (we constantly assume uncorrelated errors), thus $Q_{\min}$ (6.1). [Note that the statistical hypotheses are correctly approximated if the reconciliation problem (see again the paragraphs with (5.5)) is formulated as (1) and (2), without further restricting the condition (1a); this note concerns the nonlinear programming methods including inequality constraints.] Now by the approximation (precisely for linear problems and Gaussian distribution of errors), this $Q_{\min}$ is a random variable with (so called) χ^2-distribution. We then consider the value unlikely when it exceeds some conventionally adopted value. One commonly takes the value such that it can be exceeded with 5% probability; this is the *critical value*, say Q_{crit}. This value depends on the *degree of redundancy H* illustrated in Example 3 of Chapter 5 (number of hypothetically formulated conditions of solvability); the H is found by the reconciliation algorithm. We thus write $Q_{\text{crit}}(H)$ and if H is known, the value can be found in statistical tables or directly in the database (H represents here the 'number od degrees of freedom' for the distribution). If

$$Q_{\min} > Q_{\text{crit}}(H) \tag{7.1}$$

then we have *detected* the (possible) presence of some *gross error(s)*. The case ('event') (7.1) has probability 5% with the above convention.

Detecting the presence of a gross error is a *warning*: Due to the reconciliation mechanism, the error can propagate among all estimates (see Chapter 6) and more or less *corrupt* the whole result. Our aim is now to separate and (if possible) eliminate the error: thus, first, *identify* its source. It can be an error of measurement associated with some variable x_i, or also a model error in some equation (balance), say Eq(k). The elimination will then mean that the variable x_i is deleted as measured, i.e. not considered in the reconciliation and ranged among the unmeasured ones, or also the k-th equation is deleted as a constraint. The safest way seems to be deleting immediately, one by one, the measured variables or, again one by one, the constraints and see how the criterion $Q_{\min}$ has changed; it can be shown that (at least with a linear model), the criterion will not increase. We then identify the case where the new $Q_{\min}$ is smallest (i.e. the reduction is largest). We first go through the x_i ; the smallest $Q_{\min}$ indicates that a gross error can be present in the measurement of x_i, or also in a model equation where this x_i occurs. We can also go through the Eq(k): the largest reduction makes suspect the model equation (or also some measured variable occurring therein).

The repeated reconciliation may be time-consuming. The power of modern computers has weakened such arguments considerably. Nonetheless, the procedure can be speeded up by a simple assessment of the $Q_{\min}$-reduction. Let us consider the x_i-deletions. We have already mentioned that the software is able to compute the (pseudo)standard deviations σ_{xi} for the estimate errors, or also directly the (pseudo) standard deviations σ_{vi} for the adjustments v_i ; see (6.2). Then the *standardised adjustment* is introduced as

$$z_i = \frac{v_i}{\sigma_{vi}} . \tag{7.2}$$

It can be shown (VE-MA, pp. 339 and 399) that the square z_i^2 *equals* (in the linear case) *or at least approximates* (in the nonlinear case) the *reduction of* $Q_{\min}$ after deleting the measurement x_i . So we can directly look for the largest $|z_i|$ (or z_i^2) identifying the first suspect as source of a gross error; this way of searching can also be supported by other arguments. [An analogous assessment is possible for the Eq(k)- deletions.]

Finding a variable suspect of a gross measurement error is itself a useful result. It is a motivation for *checking the measurement device*, or also its placement, the method etc. It is then also information for the control engineers. Finding a model equation where a model error can have occurred means that the *model* is to be *re-examined*. Plácido and Loureiro (1998) report that in this way, an earlier unsuspected chemical reaction was revealed.

Let us remark that when deleting the measured variables, one immediately *precludes* the variables classified as *nonredundant* (nonadjustable). The adjustment v_i is then zero, the term does not occur in (6.1) and (see Chapter 6) an error in x_i does not influence the other measured variable estimates. Alas, it can still affect the estimates of observable unmeasured variables. The measurement system should, as far as possible, *avoid* the presence of *nonredundant* measurements. Difficulties can also arise when some of the x_i is almost nonadjustable thus $\sigma_{xi} \cong \sigma_i$; see Example 4 in Chapter 5, m_1 measured in addition: Then (6.2) $\sigma_{vi} \cong 0$ and it can be shown that also $v_i \cong 0$; hence the ratio (7.2) is that of small numbers thus uncertain. Then also the detection of a gross error in x_i is uncertain. In addition, recall that in the cited Example 4, if we delete again the m_1-measurement then the problem becomes not well-posed: m_1 and m_2 become practically unobservable. Such a case was also found by Plácido and Loureiro (1998) and can perhaps be explained in this manner.

Suppose we have specified one suspect variable (or equation). Having deleted it, we reconcile again and find the new $Q_{\min}$; we (as can also be shown) have now $H-1$ instead of H and if now $Q_{\min} < Q_{\mathrm{crit}}(H\text{-}1)$ then no further gross error is detected. [Of course if we had $H = 1$ then all measurements would now be nonredundant and no new reconciliation would take place.] Otherwise, we can continue by further deletion, etc. Finally, if the last reduction has been successful, we thus have (or rather can hope that we have) *eliminated* the gross errors. This is an ideal scheme. There are, however, different limitations to this procedure; see again an example in Plácido and Loureiro (1998), or of course a more detailed analysis in the literature cited above.

Among other statistical methods, let us mention the *nodal test* (Narasimhan and Jordache 2000; see also Madron 1992, p. 188 or VE-MA, p. 341). It is used mainly for single-component balancing where several nodes can be merged to one so as to eliminate the unmeasured variables; see for example Eq.(4.2) and the second paragraph following thereafter. The (linear) balance of one node can then be written as

$$\sum_i c_i x_i = 0 \tag{7.3}$$

with sum over all variables x_i occurring in the node balance; we here assume that all these variables are measured. The coefficients c_i are constants (± 1 in a mass balance) and Eq(7.3), if correctly written, is necessarily satisfied with true values x_i . Denoting by x_i^+ the measured values and (error) $e_i = x_i^+ - x_i$, we can compute the *residual*

$$r = \sum_i c_i x_i^{\,+} \quad \text{which equals} \quad \sum_i c_i e_i \ . \tag{7.4}$$

With the same hypotheses as above about the statistical distribution of errors, r is a random variable with variance

$$\sigma_r^{\,2} = \sum_i c_i^{\,2} \sigma_i^{\,2} \ . \tag{7.5}$$

Assuming in addition that the distribution is Gaussian, the *standardised residual*

$$z_r = \frac{r}{\sigma_r} \tag{7.6}$$

has standard normal distribution. In statistical tables, we can again find a critical value, say $z_{r,\mathrm{crit}}$ such that the case (event)

$$|z_r| > z_{r,\mathrm{crit}} \tag{7.7}$$

occurs with probability (say) 5%. If such a case is detected, the node balance is suspect of a gross error in the measurement of some variable occurring therein. It can also be a model error: perhaps some stream was omitted or wrongly oriented, in which case the balance (7.3) cannot be obeyed even with true values of x_i .

Notation

Only repeatedly occurring, not ad hoc introduced symbols are listed. See Section 2.2 for consistent physical units.

a	generic symbol for accumulation (increase in inventory)
$\mathbf{A}$	atom matrix, see (3.2.4.2) and the preceding text
$\mathbf{A}_0$	transformed atom matrix reduced to linearly independent rows, see (3.2.4.2a)
c_p	(isobaric) specific heat (J kg^{-1} K^{-1})
$\bar{c}_p$	integral mean specific heat
D	diameter (m) of pipeline segment in Section 3.4
D	number of degrees of freedom (4.13) in Section 4.2
g	gravitational acceleration (m s^{-2}) in Section 3.4
$\hat{H}$	specific enthalpy (J kg^{-1}), $\hat{H}^i$ in stream *i*
$\hat{H}_\mathrm{X}$	specific enthalpy of chemical species X
$\hat{H}_\mathrm{X}^{(0)}$	standard specific enthalpy of species X (3.3.2)
$\overline{H}$	molar enthalpy (J kmol^{-1} K^{-1}), see (2.2.9)
$\overline{H}_\mathrm{X}$	molar enthalpy of species X (2.2.8)
$\overline{H}_\mathrm{X}^{(0)}$	standard molar enthalpy of X
m	generic symbol for mass flowrate (kg s^{-1}), possibly time-inegrated (kg); m_i in stream *i*
m^+	measured value of m, in Chapter 5 only
$\hat{m}$	estimate of m after reconciliation, in Chapter 5 only
m_X	balance excess of component (species) X (3.2.2.2)
M_X	mole mass (molecular weight) of species X (kg kmol^{-1}); see Section 2.2
$\overline{M}$	mean mole mass of a mixture (2.2.6)
$\mathbf{M}$	(transpose of) stoichiometric matrix, see Subsection 3.2.1
n_X	$= m_\mathrm{X} / M_\mathrm{X}$ (3.2.2.3), auxiliary variable in multicomponent balancing
P	pressure (Pa), P^i in stream *i* (average)
P_X	production rate of species X (3.2.1.5)
Q	heat flowrate (J s^{-1} = W), see (3.3.1)
$Q_r^{(0)}$	standard heat of *r*-th reaction, see Example 2 in Section 3.3
Q_min	global criterion (6.1)
$Q_\mathrm{crit}(H)$	critical value of Q_min, dependent on degree of redundancy H; see (7.1)
R_max	maximum number of independent stoichiometrically possible reactions (3.2.4.3)
S	*only* in Section 3.4: cross section area (m^2) of pipeline segment
$\mathbf{S}$	stoichiometric matrix with elements $\nu_{\mathrm{X}r}$ (3.2.1.4) , rows X, columns r
t	time (s)
T	absolute temperature (K), T^i in stream *i*
T_0	reference temperature chosen by convention
v_i	$= \hat{x}_i - x_i^+$, adjustment in (5.5)
W_r	(volume integrated) molar rate of *r*-th reaction (kmol s^{-1}), see Subsection 3.2.1; a reactor balancing parameter

x	*only* in Section 3.4: length coordinate (m) in pipeline segment
x_{X}	mole fraction of species X (2.2.5), see also (2.2.7)
x_k	*only* in Example 4 of Section 3.3: mole fraction of *k*-th component in liquid phase
x_i^+ , $\hat{x}_i$	measured resp. reconciled value of variable x_i , only in Chapter 5
X	generic symbol for chemical species (component of mixture)
y_{X}	generic symbol for mass fraction of species X, see also (2.2.7); y_{X}^{i} in stream *i*
y_k	*only* in Example 4 of Section 3.3: mole fraction of *k*-th component in vapour phase
$\hat{y}_j$	estimated (computed) value of unmeasured observable variable y_j , only in Chapter 5
z_i	standardised adjustment (7.2)

Greek

ϑ	temperature variable (4.5), ϑ_i in stream *i*
ϑ^+	measured value of ϑ , in Chapter 5 only
$\hat{\vartheta}$	estimate of ϑ after reconciliation, in Chapter 5 only
λ	friction factor (3.4.4) in Section 3.4
$\nu_{\mathrm{X}r}$	stoichiometric coefficient in (3.2.1.4), element of matrix **S**
ρ	mass density (kg m^{-3}) in Section 3.4
σ	generic symbol for standard deviation of random variable, estimated by (2.2.10); σ^2 is variance
σ_i	standard deviation of measurement error in *i*-th measured value x_i^+
σ_x	standard deviation of error in estimate $\hat{x}$, specified ad hoc in the examples to Chapter 5; generally
σ_{xi}	standard deviation of estimate error in measured variable x_i , see Chapter 6
σ_{yj}	standard deviation of estimate error in unmeasured observable variable y_j , see Chapter 6
σ_{vi}	standard deviation of adjustment v_i ; see (6.2)

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Appendix

MORE ON THE CLASSIFICATION OF VARIABLES

See Section 4.3. As mentioned ibid. and in the paragraph following after that containing Formula (5.11), the classification results from a rearrangement of the Jacobi matrix (that of partial derivatives) obtained in the last step of the reconciliation; thus that evaluated at the final point (solution). In the linear case, this is simply the matrix of the linear system.

The idea is due to F. Madron; see Madron (1992): 4.2, in particular Fig. 4.2. Rearranging the matrix as

$$\mathbf{C} = (\mathbf{B}, \mathbf{A}) \tag{A.1}$$

where the columns of **B** correspond to the unmeasured, those of **A** to measured variables, it is subject to *Gauss-Jordan elimination*. The operations (linear combinations of rows) are carried out with *all* columns of the matrix. For simplicity, let us assume (as is the case of a correctly written set of balance equations) that the rows of matrix **C** are *linearly independent*. With a possible rearrangement of the columns of submatrix **B** and leaving the columns of **A** in their places, we then first eliminate certain rows of **B**; we obtain, schematically, a matrix of the form

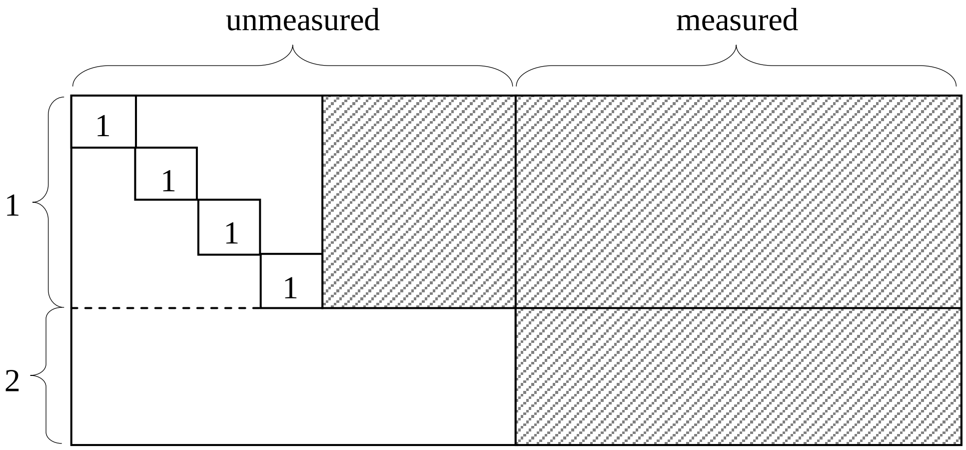

Fig. A-1.

If it happens that the horizontal band 2 is empty (absent), no reconciliation takes place. Precluding this case (of so-called null redundancy), we further carry out the elimination with the rows of band 2. We obtain, again schematically

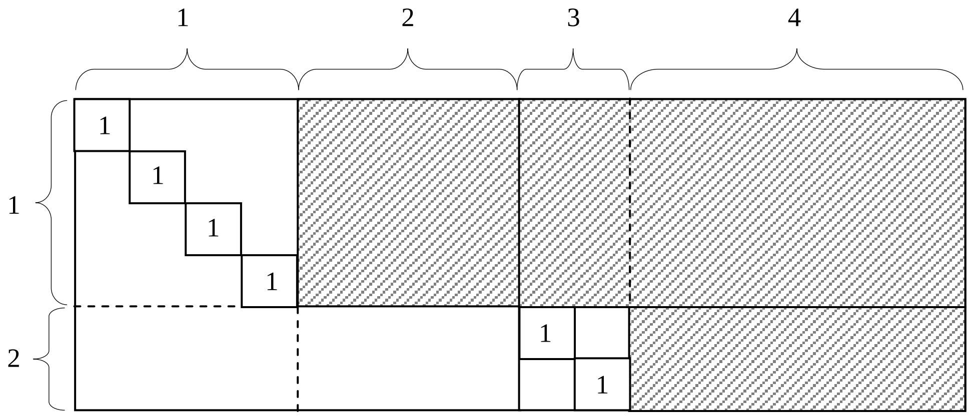

Fig. A-2

as corresponds to the linear independence of the rows of **C**. Finally, we rearrange separately the rows of horizontal band 1 and columns of vertical band 1, and then the columns of vertical band 4 to have the (so-called) *canonical format* of matrix **C**

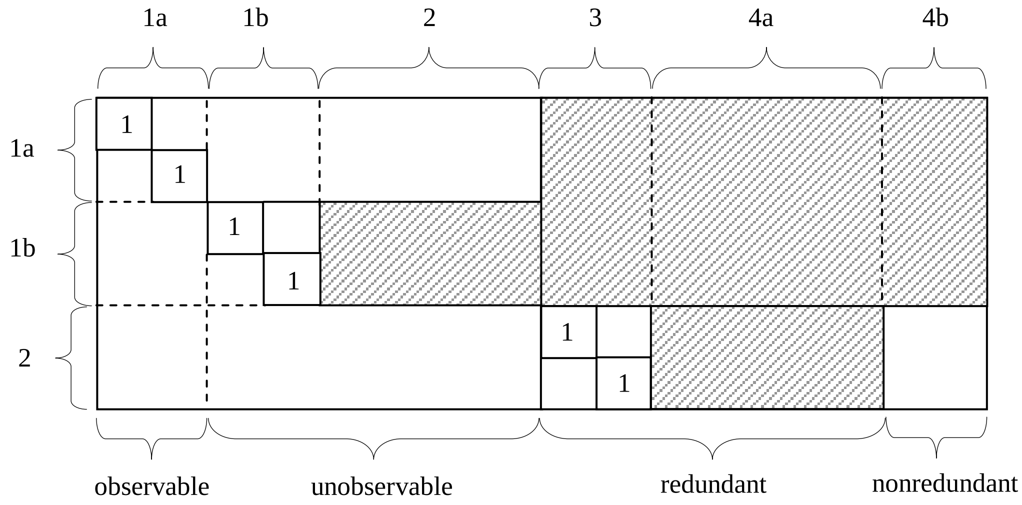

Fig. A-3.

[Observe that certain submatrices may be empty.] In the horizontal band 1a we have succeeded, by the rearrangement, in separating the submatrix 1a × 1a such that in the remaining vertical bands 1b and 2 we have zeros as drawn. Then the unmeasured variables corresponding (after the rearrangement) to columns 1a are classified as *observable*. The remaining unmeasured variables (columns 1b and 2) are classified as *unobservable.* Further, in the vertical bands 3 and 4a we have columns corresponding to measured variables classified as *redundant*; having separated the

zero columns of submatrix 2×4, the remaining variables (columns 4b) are classified as *nonredundant* (just determined in
Fig. 4-5).

If the system is *linear*, we see directly (see horizontal band 2) that the redundant variables are subject to a subset of equations (constraints) constituting the *conditions of solvability* and used for the *reconciliation*. Then (see horizontal band 1a) the unmeasured variables in columns 1a are uniquely determined by the (reconciled) measured ones. [It is sufficient to imagine the right-hand sides of the linear equations $\mathbf{By} + \mathbf{Ax} = \mathbf{c}$ subject as well to the elimination procedure.] In the *nonlinear* case, this represents in fact a classification based on the *linearisation* of the equations in a neighbourhood of the final point (solution). See then VE-MA: 10.4.5 (ii). [By the way, the idea of elimination can be (and is) applied in methods of solving the nonlinear reconciliation problem by successive approximations.]

Note

Concerning the classification of *measured* variables, recall the standard hypothesis that the covariance matrix (say) **F** of measurement errors is *diagonal* (uncorrelated errors). In the *opposite* case, the classification of a variable as *nonredundant* remains the same, as it is only given by the properties of matrix **C** (A.1), thus finally by the zero submatrix $2 \times 4b$ in Fig. A-3. It holds again true that the criterion $Q_{\min}$ thus (5.5) *generalised* for the case of *nondiagonal* **F** is *unaffected* by the measured values of the nonredundant variables. Still, as shown in VE-MA: 9.2(iii) (p.312), the measured value of a *nonredundant* variable can be subject to an *adjustment dependent just on* the *redundant measured* values. Due to the correlation, the nonredundant variable then generally shares a portion of the adjustment with the redundant ones, though its own measured value does not affect the result. In Fig. 4-5, the expression 'just determined' is then somewhat misleading. Anyway, it holds true generally that a nonredundant variable must remain measured; otherwise (if unmeasured), it becomes unobservable thus not determined..