THERMODYNAMIC ANALYSIS IN THE DESIGN OF PROCESS NETWORKS

A thesis submitted for the degree of

Doctor of Philosophy

at

The University of Leeds

by

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April 1979

Abstract

This thesis discusses the use of thermodynamic Second Law analysis in the context of chemical process network design. It is divided into two parts. Part I is based on the study of entire processes while Part II concentrates on the problem of heat exchanger network design. This division into two parts facilitates a clear presentation of the results obtained.

Second Law analyses are frequently referred to in the academic literature as giving a more valid account of inefficiencies in engineering systems than simple heat balances, a view that would seem to be well founded in thermodynamic theory. On the other hand, process design engineers in industry do not seem to make much use of this type of analysis. They usually comment that the results obtained either state the obvious (e.g., "... do not degrade heat...", etc.) or lead to recommendations that are not practical (e.g., "... use fuel cells instead of thermal reactors...", etc.) Thus, there seems to be a conflict between theoretical claims and practical experience. The present thesis attempts to clarify this situation by giving a balanced view of both the potential value of Second Law analysis as well as its shortcomings.

In Part I, it is shown that Second Law analyses are both difficult to produce and difficult to interpret in the context of chemical process design. Consequently, an approach is developed to overcome these difficulties. However, the approach somewhat transforms the meaning of the words "thermodynamic analysis". Namely, it is no longer a strict application of Second Law textbook theory that is implied, but a rather more broad minded approach involving the use of carefully considered thermodynamic concepts. In other words, a somewhat "slackened" form of thermodynamic analysis is recommended. This slackened form is less well defined than the classical one but easier to produce and more meaningful to interpret. (A more detailed explanation of the concepts involved is given in the "Extended Abstract of Part I" on page iii). When applied to the case studies, the approach leads quickly to attractive design suggestions.

In Part II, the approach is applied to the rather specialised and recently well researched problem of heat exchanger network design. This leads to the development of several explicit design methods which consistently identify better solutions for identical problems than methods described previously in the literature. Also, an understanding of the subject matter is achieved that is quite unprecedented (see "Extended Abstract of Part II" on page v). These results seem to support the conclusions arrived at in Part I.

An interesting observation made in Part I and Part II is that some of the designs put forward would not only be cheap to run but also cheap to build. Thus, the thermodynamic approach developed here appears to be capable not only of identifying energy savings but capital savings, too. This gives rise to a very ambitious claim (compare pp. 270-271) : namely, that the approach may lead to designs that are "driving force conscious" in general. In other words, it may help the engineer to develop a better feel for the natural driving forces in his problem and may therefore stimulate him to create, in a quite general sense, more appropriate, simpler, and more elegant processes.

Extended Abstract of Part I

In Part I, a summary is given of the relevant thermodynamic theory in the context of Second Law analysis and case studies based on two general processes are described (sulphuric acid and nitric acid).

In the course of these studies, it is seen that a Second Law analysis of industrial chemical processes is quite cumbersome to produce, due to the data required and the computational effort necessary. Also, several reasons are recognised in the course of the studies why a Second Law analysis, once that it is produced, is almost certain to be difficult to interpret. Seven fundamental reasons emerge (see pp. 265-267), each of which points at a different cause why irreversibilities as identified in a Second Law study may not easily be avoided in practice. In summary, it is concluded that a Second Law analysis in the context of chemical process design is (1) difficult to produce and (2) difficult to interpret.

However, having identified these difficulties, suggestions are made to overcome them. With regard to the problem of producing an analysis, an approximation method is suggested (in Secion 2.4) that yields entropies and exergies of process flows as functions of enthalpies and operating conditions. In other words, a way is outlined of producing a Second Law analysis simply by using the information available from a heat balance and requiring no additional data whatsoever.

With regard to the problem of interpreting an analysis, several suggestions are made. Firstly, an idea outlined by Denbigh in 1956 is taken up. Denbigh pointed out that chemical reactions often account for much of the irreversibilities in a chemical process and that, in the absence of advanced reactor technology, little can be done about this in practice. Therefore, he suggested a procedure of accepting reaction-related irreversibilities as practically inevitable. In Section 2.6, an alternative procedure is developed that gives greater flexibility than the one suggested by Denbigh and leads to even more meaningful results.

Secondly in the context of interpretation, it is shown that to obtain insight into the constraints governing an integrated system, conclusions drawn from a Second Law study have to be checked against conclusions drawn from a First Law study. Based on a number of examples, it is argued that a Second Law study without reference to First Law concepts is just as incomplete an exercise as is the interpretation of a heat balance with no attention paid to Second Law concepts. A frequent iteration between First Law and Second Law study is recommended and the approximation method already referred to is naturally suited for this purpose.

Lastly in the context of interpretation, it is recommended that every irreversibility identified in a Second Law analysis be examined against the list of "seven fundamental reasons" referred to previously. If none of these reasons can explain why a given irreversibility should be practically inevitable, then the irreversibility in question is likely to be practically avoidable. Thus, a framework is obtained for a thorough energy conservation study which, starting from Second Law irreversibilities, discusses possible improvements from both Second and First Law points of view.

Extended Abstract of Part II

The design of heat exchanger networks as discussed in Part II has been a lively area of research over the last ten years or so. Thus, the work presented in Part II has two-fold implications. Firstly, it illustrates the scope for thermodynamic concepts in network design in general as discussed in Part I. Secondly, it offers specific results in the area of heat exchanger network design.

To begin with, a case is made in Part II for a thorough problem analysis prior to actual design. It is shown that such an analysis is possible with regard to (1) the thermodynamic limit to heat recovery, (2) the sensitivity of heat recovery to variations in approach temperatures, and (3) the minimum number of "units" (i.e. heaters, coolers and exchangers) in a heat recovery network. Analysis of a given problem from these three points of view yields performance bounds based on which a suggested network can be either accepted as near-optimal or be rejected.

This feature of a thorough problem analysis prior to design is shared with the work of Hohmann who made much the same recommendations in 1971. However, Hohmann's algorithms and procedures were restricted to the analysis. Also, some of his statements were fallible. The present thesis corrects these statements (see Section 6.3) and, with the better problem understanding so obtained, goes on to develop several explicit design aids. These are:

- A design method based on decomposition of the overall problem into temperature intervals (see Section 6.2). This method guarantees networks that perform at the thermodynamic limit to heat recovery.
- A technique for the evolutionary development of networks by intuition (see Section 6.2). This technique eliminates the consideration of temperatures when discussing network modifications, easing greatly the task of formulating strategies to achieve given design goals. In Appendix F, the technique is shown to be instrumental in improving a number of previous workers' optimum solutions to published example problems.

- A thermodynamic/combinatorial design method (i.e. the TC-Method, see Chapter Seven). This method guarantees an exhaustive list of solutions that achieve a requested degree of heat recovery with the minimum number of units.
- The so-called grid representation of heat exchanger networks (see Appendix F). This representation is used throughout Part II. It forms the basis of the technique for evolutionary development referred to above but can be used in connection with whatever design method the user happens to employ. It can represent any feasible network and greatly facilitates intuitive insight.

In addition to the development of these design aids, a number of conclusions are drawn in Part II that are significant in the field. They are based on fundamental problem understanding and on experience gained when solving ten problems from the literature. The six most important of these conclusions are as follows:

(1) The effect of approximate problem specification is profound. In other words, slight modifications of specified temperatures, heat loads, etc., are shown to enable superior solutions to be identified. Thus, it is concluded that a design method of any realism should not only solve a given problem satisfactorily but also tell the user whether there are superior approximate solutions. Further, the TC-Method as presented in Chapter Seven is shown to be probably the first programmable design method known that can identify such approximate solutions with no additional computational effort required.

(2) The so-called "stream termination heuristic" which is common to probably all previous work on heat exchanger network design (see page 195) is shown to be incompatible with an essential aspect of network design. Namely, the heuristic enforces the design of heat exchangers in isolation with no attention paid to effects on the overall network. This must lead to restricted options in design and to the non-intentional exclusion of possible solutions. As an example, the new optimum solution presented in

Appendix F for the most complex literature problem (i.e. 10 SP1) is easily seen to be incompatible with the heuristic. Lastly, the TC-Method as presented in Chapter Seven is, once more, shown to be probably the first programmable design method known not to incorporate this heuristic.

(3) Virtually all previous work in the field handles the problem of trade-off between energy and equipment costs by constraining the minimum allowable temperature difference in heat exchangers. The effect of so doing in the context of integrated networks is fully understood probably for the first time in Part II (see Section 8.2) and possible undesirable effects are clearly shown. Also, fallible conclusions drawn in previous work are corrected. Lastly, a procedure for the correct handling of this problem is outlined.

(4) Commonly, the well-known example problems from the literature are alleged to be heavily biased towards energy costs due to unrealistic cost data. In Part II, this bias is shown to be due not to the cost data used but to a somewhat more fundamental shortcoming in the description of these problems, namely the use of a single hot and a single cold utility. (See Section 8.3). This is important since design methods that solve the example problems successfully may break down when applied to industrial problems due to the added complexity introduced when multiple energy sources and sinks are considered.

(5) The problem of heat exchanger network design has always been described in the past as one of immense combinatorial complexity. Allegedly, the complete solution of, say, a six stream problem involves the generation and (mixed integer) optimisation of no less than $4.8 * 10^8$ alternative networks (compare Appendix H). In Part II, it is shown that such statements in the past were due to an insufficient understanding of the subject matter. The size of the combinatorial problem is in fact orders of magnitude smaller than commonly assumed and a need for mixed integer optimisation

does not exist in the case of the known example problems. In Chapter Seven, these conclusions are backed by the complete solution, with global optimality guaranteed, of a six stream problem by hand. However, a warning is given that the complexity of industrial problems might be somewhat larger than that of the literature problems due to the effect of multiple energy sources and sinks (see point (4) above).

(6) Industrial heat recovery problems often incorporate constraints (such as forbidden matches between process streams, etc.). The approach to solve such a problem which is commonly recommended in the literature involves solution of the unconstrained problem and the examination of solutions as to whether or not they are compatible with the constraints. In Part II, this approach is shown to be undesirable since constraints can be employed to reduce the complexity of a problem. The benefits to be obtained by considering constraints at an early stage during the generation of alternatives are shown to be profound and it is argued that the "size" of a problem should not, as is common practice, be expressed through the number of process streams involved but through the number of streams and the number of constraints.

All in all, it is probably fair to say that the work presented in Part II represents a significant advance in the field.

Acknowledgements

My sincere thanks are due to Dr J R Flower for his experienced and patient guidance in this research project. He provided the right mixture of criticism and encouragement, waiting patiently for the end result of what initially must have looked quite uncertain work. Also, I feel indebted to the British Council for providing three years' financial resources and to Professor G G Haselden as the head of the Department of Chemical Engineering for permission and encouragement to spend these years at Leeds University. The department in general provided the stimulus and background knowledge which for me as a mechanical engineering graduate was so important for tackling this project. External Professor G Sachs provided much help with his profound practical experience and initiated those industrial contacts that were to lead to actual case study data.

Outside the University, I am grateful for many discussions and for the constructive criticism that I obtained from people in industry. Especially, my thanks are due to Dr J S Gerrard from Sim-Chem Ltd. and to Mr S Whitefoot, Dr J Connolly, Mr J C F Cuss, Dr P Middleton, Mr C Davies, Mr T A Kantyka, Dr I Wardle and Mr R Maslin, all employees of ICI Ltd. Without the industrial case study data and the "practical touch" which came to bear in numerous discussions I do not think this work could have taken on its present shape.

More privately, I would like to thank Miss M M Woodier for her never ending patience in producing the typescript over a period of well over a year and even extending into her retirement. With similar patience and over much the same timespan, Miss R W Tough and her colleagues produced most of the diagrams. Further, thanks are due to my friends Ian and Nick for the trouble taken when proofreading the manuscript. And finally, I want to thank Elsbeth, my wife, who came with me to Leeds five years ago and has since tolerated much hardship to see this work completed. Now that it is, I promise that I want to be an altogether better husband and father again.

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INTRODUCTION

PART I

CHAPTER 1 Literature Survey

CHAPTER 2 Thermodynamic Analysis. - A Review and Suggestions

List of Symbols

(Unmisleadingly common symbols and superscripts or subscripts of obvious meaning are not necessarily listed.)

Symbols for Energy and Related Properties

cp	specific heat capacity (p = const)	(per unit mass or mole)
cv	specific heat capacity (v = const)	(")
ekin	kinetic energy	(")
epot	potential energy	(")
ex	exergy	(")
g	Gibbs free energy	(")
h	enthalpy	(")
q	heat	(")
s	entropy	(")
u	internal energy	(")
v	volume	(")
w	work	(")

(For the above, capital letters are used to indicate properties that are not mass (or mole) dependent : Ekin = m*ekin, etc.)

Latin Symbols

A	heat transfer surface area
a	general coefficient, factor, exponent, etc.
b	as "a" above
C	cost
c	velocity
D	outer pipe diameter
d	inner pipe diameter
f	fugacity
M	molecular weight
m	mass flow

Latin Symbols Cont'd.

n	number of units
n_{min}	minimum number of units
n_{poss}	possible number of units
$\underline{n}$	molar flow
p	pressure
R	individual gas constant
$\underline{R}$	universal gas constant
T	temperature
t	time
ut_c	number of cold utilities
ut_h	number of hot utilities
X	general symbol describing systems, species, functions, etc.
x	length, height
Y	as "X" above
Z	as "X" above
z	number of process streams
z_c	number of cold process streams
z_h	number of hot process streams

Italic Symbols

h	film heat transfer coefficient
k	thermal conductivity
U	overall heat transfer coefficient

Greek Symbols

α	additional steam raised, expressed as fraction of steam raised at present (See Appendix C)
β	cost of pipework and accessories as a fraction of heat transfer surface area cost (See Section 8.5)
γ	activity coefficient

Greek Symbols Cont'd.

ΔEx_{irr}	irreversible exergy loss
$\Delta H(T)$	= $m^*\Delta h(T)$, enthalpy change of reaction
$\Delta G(T)$	= $m^*\Delta g(T)$, Gibbs free energy change of reaction
$\Delta S(T)$	= $m^*\Delta S(T)$, entropy change of reaction
ΔT_{min}	minimum temperature difference in heat exchangers
ΔT_{LM}	log. mean temperature difference
$\Delta\overset{+}{T}$	temperature difference safely in excess of an experience based economic choice for ΔT_{min}
δ	useful lifetime of equipment
ε	steam quality (mass vapour/mass total)
η	efficiency
η_c	Carnot efficiency (compare Equation 2.34)
η_{ex}	exergetic efficiency (compare Equations 2.40)
κ	cp/cv
ν	molar fraction
ϕ	cost of annual maintenance of equipment, expressed as fraction of initial capital cost
σ	irreversible entropy increase
$\bar{\sigma}$	"avoidable" irreversible entropy increase (compare Section 2.6)

Superscripts

"*"	updated
"^"	solution property
"I.S."	ideal solution
"N.I.S."	non-ideal solution
"PR"	reaction products
"RE"	reactants

Subscripts

"o"	ambient
"inev"	inevitable
"irr"	irreversible
"R"	reaction
"rev"	reversible
"RS"	reference state
"STD"	standard state

Special Symbols

Non-Chemical Processes. For processes not involving reactions or non-ideal mixing, the following symbols have been adopted to express changes in enthalpy:

H_1^X enthalpy of system X at state (T_1,p_1),

and

$$H^X(T_1,p_1) = H_1^X - H_{RS}^X$$

Note:

> This notation makes it clear whether or not the enthalpy at any given state (T_1,p_1) is thought to include a chemical contribution. The equivalent notation has been used for entropy and exergy.

Chemical Reactions and Non-Ideal Mixing. For chemical processes, the following symbols have been adopted:

$\Delta HoR_{1,2}^{X,Z}$	enthalpy change of reaction from reactants X at state (1) to products Z at state (2)
$\Delta HoM_{1,2}$	enthalpy change of mixing (for transition from constituents at state (1) to solution at state (2))
ΔHoF_{STD}^{X}	$= \Delta HoR_{STD,STD}^{Elements,X}$, heat of formation of species X at standard state

Note:

(1) The above symbols make it possible to express Kirchhoff's law and Hess's law for reactants and reaction products at non-identical states. (Compare Equations 2.8 and 2.9).

(2) Analogous symbols are used for entropy and exergy changes, i.e. $\Delta SoM_{STD,STD}$, $\Delta ExoR_{1,1}^{X,Z}$, etc.

(3) For constant pressure and temperature chemical changes, the conventional notations $\Delta H(T)$, $\Delta S(T)$, and $\Delta Ex(T)$ have also been used. Thus:

$$\Delta H(T_{RS}) = \Delta HoR_{RS,RS}^{Reactants,Products}$$

etc., if $p = p_{RS}$.

(4) All symbols discussed here can also be expressed as mass (or mole) dependent:

$$\Delta HoF_{STD}^{X} = m \star \Delta hoF_{STD}^{X},$$

etc.

Mathematical Notation

$\oint$	integral over a cyclic path
C_b^a	$(b!)/((b-a)!*a!)$

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INTRODUCTION

A Thermodynamic Approach
to Practical Process Network Design

The efficient utilisation of resources and especially of energy has recently become a matter of priority in many aspects of industrial and social planning. The accepted reason is the rapid increase in the cost of key resources which has made a reappraisal of many adopted practices necessary. In addition, there seems to be a case for efficient resource utilisation even if it might not yet be economically justified: dwindling raw materials will tend to lead to further price increases - and scarcities - in the future and conservation in time will help to prepare for such a course of events. Perhaps it may even help to prevent it.

In the process industries, scope for energy conservation would appear to exist in the overall planning of business policies and in the operation and design of the production processes. In process design, energy conservation is commonly regarded as an optimisation problem: a suitable balance has to be struck between the consumption of energy and feedstocks on the one hand and whatever other aspects may be relevant on the other. An engineer selecting a compressor for a given process duty, for instance, will try to balance energy efficiency against capital expenditure and reliability.

However, one might argue that it may often not be sufficient to consider such a rather narrowly defined optimisation problem. Perhaps, an alternative flowsheet could be found in which the compression could be carried out in the liquid phase, or even one in which it might not be necessary at all. Thus, the challenge to develop improved processes may lie not so much in optimising the parameters of more or less defined network structures, but in "optimising" the structures themselves. For this latter task, however, formal techniques are rare and it cannot normally be said that an "optimum" is definite: in complex situations, there might always be yet a better solution to a given problem. It follows that many of our present day processes are perhaps not as good in terms of energy efficiency as they could be and to improve matters could require anything from finding original arrangements for a given set of separators and/or heat exchangers to developing novel reaction paths and/or processing technology.

When searching for new processes with enhanced technical performance along these lines, one may turn to thermodynamic Second Law analysis as a possible guide: it enables a projected process energy performance to be compared to the theoretical optimum and in cases where the energy supplied is inherent in the feed, an idea might be obtained regarding feedstock utilisation. This might lead to clues about major inefficiencies and about the effort worth investing into the development of novel processing equipment. Also, estimates might become possible of the benefits to be derived from using equipment that is known but not normally used (such as waste heat driven power recovery cycles, etc.).

In many practical design situations, however, the risks and costs associated with such technology are sooner or later found to be unreasonable and, at a certain stage of a project, all that is sought is the most appropriate way of sizing, matching, and sequencing streams which are to be processed by means of conventional technology and which are, by and large, defined through the definition of a reaction path. It is in this context, that it is often difficult to see how thermodynamic analysis could be of use: the discrepancies between the idealisations assumed for a reversible process (i.e. equilibrium conditions throughout, infinitely many pieces of equipment which are infinitely large in size, fuel cell technology, semipermeable membranes, etc.) on the one hand and practical requirements on the other are so fundamental that ways of improving a practical process might not necessarily be found by comparing it to an ideal one. As a result, cost analyses in connection with simple heat and mass balances are usually preferred as guidelines in design decisions. Together with suitable design experience, such analyses will frequently help the engineer to find practical improvements whereas the information obtained from a thermodynamic analysis will often appear to be somewhat esoteric and of no real use. Only in specialised applications, where the cost of energy is truly dominant and the unit operations used bear at least a qualitative resemblance to ideal operations, thermodynamic analysis seems to have proved practical. The obvious example is the field of cryogenic engineering. In other fields, thermodynamic analysis is apparently used only rarely.

The work presented in this thesis originated from the belief that even in the context of processes which involve, and have to involve, highly irreversible unit operations, some benefit might be gained from thermodynamic concepts. It was felt that clues which would lead to improved process design might be obtained in a more rigorous fashion when using a thermodynamic approach rather than conventional evaluation methods.

To gain evidence, a sulphuric acid plant and a nitric acid plant were considered as case studies in Part I. Second Law analyses were produced and were examined for the likely scope for enhanced energy efficiency. In doing so, improved process flowsheets were described in both cases but it would be difficult to decide to what extent these improvements resulted from the Second Law analyses as opposed to intuition. However, the impression was that the determination to use Second Law analyses and the consequent need to discuss why individual inefficiences were inconclusive, had furthered intuition: it had led to a thorough examination of the relevant feasibility constraints, of the types of equipment used, the levels of utilities connected, etc., and had thus drawn attention to perhaps all practical possibilities that would exist for improvement. Especially, it had led to a consistent discussion of the way in which energy was degraded in terms of temperatures and pressures and in the end, it had become quite clear that the extent to which improved energy utilisation is practical will often be determined by the relative levels of temperatures, pressures, and perhaps compositions: losses in terms of entropy or exergy were generally seen to be of less practical relevance. Thus, a "slackened" form of thermodynamic analysis emerged as useful in which irreversibilities, rather than being judged according to their magnitudes, are used as convenient starting points for the discussion of inefficiencies in First Law terms.

On first sight, this approach will seem similar to that implied by simple heuristic rules such as "maintain the highest levels when degrading material and heat" (see Wells and Hodgkinson (100)), and yet, the impression was gained that such commonly accepted rules are likely to be applied with increased circumspection if they are derived from an individual reasoning process rather than implemented without specific justification.

This impression was reinforced in Part II when the problem of systematic design of heat exchanger networks was tackled. The problem has recently attracted much attention in the literature and, in view of the enormous complexity involved, it is usually considered in isolation (i.e. separate from the design of the underlying process network) as well as highly idealised in other respects. Thus, a "solution" can only produce an initial network which may or may not be adopted for further examination. Nevertheless, the task of finding optimal initial networks is often difficult enough to present a serious challenge. In Part II, the problem is considered in the light of a "slackened" thermodynamic analysis as described above and three distinct design methods are developed which will not only prevent the unnecessary degradation of heat, but also allow the user to gain considerable insight into equipment related design aspects. The results obtained indicate that these methods add up to a considerably more powerful approach than others for the identification of networks with a high degree of energy recovery as well as low equipment costs. This is true although some previously published work has, also, been based on thermodynamic principles. The difference is that, in the previous cases, such principles have been implemented in ways which individual workers felt to be appropriate, but which were not rigorous. When derived from a consistent thermodynamic analysis, by contrast, a rigorous implementation of these principles could be guaranteed and superior results were quite easily obtained.

PART I

Design of General Process Networks

CHAPTER ONE

LITERATURE SURVEY

This survey is divided into four sections. The first section deals with the theory of thermodynamic analysis and with applications to process networks. In the second section, emphasis is laid on the question of how such analyses may be interpreted to help with the design of more efficient processes. It will become apparent that, while there is ample guidance in the literature on the task of establishing a Second Law analysis, relatively little is documented on the task of utilising the information obtained from it. In the third section, papers are discussed in which thermodynamic concepts have been used in process design fully systematically. When used in this way, shortcomings and limits of applicability can be expected to show up clearly. The last section represents a short summary.

1.1 THERMODYNAMIC ANALYSIS.- THEORY AND APPLICATIONS TO PROCESS NETWORKS

The theoretical foundations of the Second Law of thermodynamics and of the concept of entropy were laid in the work of mainly Carnot, Thomson (later Lord Kelvin), and Clausius in the last century, but it is probably valid to say that the notion of thermodynamic irreversibility has only gradually become important to the practising engineer. As late as 1938, Bošnjaković(30) argued that the difference between a heat loss in First Law terms and an irreversibility was still not clear enough to many. However, numerous publications have since been devoted to the evaluation of Second Law efficiencies, entropies, exergy losses, etc.(10 through 2 and although this list is no doubt incomplete, these references should, between them, offer all theoretical guidance likely to be required when drawing up a Second Law analysis of one sort or another. A selective review of the theory is given in Chapter Two.

There have been several publications in the last twenty years or so in which Second Law analyses were applied to industrial chemical processes. Ruhemann(64) in 1940 made extensive use of the entropy concept to guide the design of low temperature air separation processes. In 1956, Denbigh(31) made a study of the Second Law efficiency of an ammonia oxidation process, but considered, by and large, only the main reactions involved. In 1962, Szargut(36) analysed the heat processes in the steel and iron making industry in exergy terms and in 1967, Frankenberger(38) scrutinised a cement burning process. More recently, Riekert published two studies on an ammonia and an ammonia oxidation process(43,44), Fuge and Sohns(46) analysed the compression and separation sections of an ethylene plant, and Pinto and Rogerson(50) examined the methanol and ammonia processes. Again, this list is no doubt incomplete. With energy conservation becoming increasingly attractive economically, it seems reasonable to assume that various processes of sufficient interest to particular industries will have been analysed in recent years. The results may often not have been published at all or may have been presented in journals of limited circulation and/or on conferences. Examples are papers by Timmers(40), Spriggs(47), Middleton(48) and Fritsch(51). Further examples are referred to by Szargut(24), Rant(25) and Gaggioli(27).

1.2 THE INTERPRETATION OF THERMODYNAMIC ANALYSIS

Rögener(37) recalls an episode from the commissioning of a new 150 MW steam turbine installation. During the test for guaranteed performance, one of two feed water preheaters developed a leak and had to be taken off line. The operating company suggested to postpone the tests since results with only one preheater could not be conclusive. However, the engineer representing the contractor suggested to approximate the effect of by-passing the preheater by simply assuming that, with only one preheater on line, exergy losses associated with preheating would, roughly, be twice as high as in normal operation. The difference could be assumed to be available as additional power output in normal operation, compared with test results. The argumentation was accepted and the tests were continued. This episode reflects a considerable familiarity with the exergy concept on the part of the people concerned, and certainly some faith into the concept's conclusiveness*.

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* However, there is not enough detail given by Rögener (37) to allow checking the validity of the argument. - Some of the findings in the present thesis (compare, for example, Figure 4.10) would seem to justify scepticism.

Apart from the field of power generation, the exergy concept seems to be used by industry in the field of low temperature processes. Petrocarbon Developments Ltd., U.K., for example, have a "Loss Analysis Manual", in which guidance is given on how to establish the exergy analysis of a cryogenic process(39). However, when acting as rapporteur for a paper by Timmers(40) on the design of distillation units, R Sargent(41) suggested that adequate guidance in the design of low temperature processes could be obtained from simple heat balances coupled with an examination of temperature and composition differences. Further, he suggested that exergy studies may even lead to false conclusions unless some care is taken.

With regard to general chemical process networks, prejudices against the value of Second Law studies are perhaps even more common and little can indeed be ascertained of how thermodynamic analyses are utilised in design practice. As mentioned above, quite a few processes seem to have been analysed in recent years, but wherever results are published, the conclusions seem to be few and of a mostly general nature.

Szargut(36), for example, at the end of what is possibly the most detailed exergy study of industrial processes published to date, simply postulated that exergy balances must be useful to the engineer when trying to combat inefficiencies in processes, but offered no justification. Grassmann(17) recommended drawing up flowcharts of exergy but gave no explanation how, at a detailed level, these flowcharts are to be used when trying to design improved processes. Riekert(43,44) merely remarked that the compound efficiency of any network is easily evaluated in a consistent way using the exergy function and added that insight elucidating other than economic constraints could possibly be obtained. Fuge and Sohns(46) only said that, in an exergy study, the (ethylene) plant's character as an enormous heat sink becomes evident, and Pinto and Rogerson(50) said that a thermodynamic investigation can indicate to the designer the sections of a plant with the most potential for (energy) savings. Finally, Denbigh(31) simply summarised that processes would become more energy efficient if heat transfers were to take place at minimum temperature differences, if pressure drops were reduced, and if chemical reactions were carried out under "resisted" conditions (so as to yield useful work). In all these papers, there is a marked contrast between the analysis itself which is very detailed and the conclusions drawn which are very general.

However, Denbigh(31) recommended calculating practical efficiencies which would be unity when chemical reactions were carried out under prescribed conditions of irreversibility: this would help eliminating the effect of gross irreversibilities - common and inevitable in many reactions - from an analysis. (This idea is taken up in the present thesis). Further, he recommended computing not only the amount of useful work recoverable from a process but also the amount wasted. Although the results would be equivalent, the first method would show where to look for sources of recoverable energy whilst the second method would emphasise the causes of wastage . After more than twenty years, Denbigh's discussion and suggestions represent, perhaps, still the most comprehensive advice available in the literature on the problem of utilising information from a Second Law study. In other words, there is hardly any work published on this problem. The practical conclusiveness of Second Law studies in the light of problems such as minimum driving forces in unit operations, minimum size of equipment, network interactions etc., is discussed very little.

Perhaps, there are only two papers in the literature in which this question of conclusiveness of Second Law studies is given major attention. Even in these two papers, however, the results are warnings rather than constructive suggestions:

(1) A pragmatic approach was taken by Frankenberger(38) in 1967. Having evaluated sections of a process in First Law and in Second Law terms, he compared the results in the light of the known and likely scope for practical improvement and concluded that, while in some cases the exergy study seemed to pinpoint inefficiencies better than the First Law analysis, in other cases the opposite was true. He did not, however, offer explanations why and gave no guidance how to avoid deception in cases where the scope for improvement is less well known.

(2) Later in 1967, and in a more theoretical approach, Szargut(24) wrote about the "limits of applicability of the concept of exergy". He pointed out that exergy might be a more convenient parameter for optimisation studies than others (inefficiencies of all kinds can be expressed in a consistent way and properly scaled against each other) but also gave two fundamental reasons why, in the last resort, exergy could only be used to guide design decisions, but not to determine them: the first reason is that the costs of various forms of energy are only loosely related to associated exergies. The second reason is that, as Szargut says, "...no general method is yet known to evaluate the influence of the irreversibility of one part of a

process on the exergy losses in other parts...". In other words, network interactions have to be accounted for when trying to improve the efficiency of a particular unit operation.

Recently, Flower and Linnhoff(49) suggested that perhaps the best way to utilise Second Law analysis in network design is to keep iterating between Second Law study and heat and mass balance. In this way, the useful information to be obtained from Second Law figures is available while irregularities in the conclusiveness of these figures can be detected. To ease the computational task involved and to assist in developing a feel for the interaction of First and Second Law concepts, they described an approximation technique which enables Second Law information to be obtained from a heat and mass balance. In the present thesis, this approach is followed up further.

1.3 SYSTEMATIC USE OF ENTROPY AND EXERGY.- EXAMPLES

King et al.(86) used exergy losses as a main criterion governing the evolutionary improvement of a simplified methane liquefaction process. Starting from a simple feasible network, an automatic algorithm "flagged" that unit operation which showed the largest exergy loss and took action by resorting to a prepared list of possible remedies, formulated so as to reduce the loss within the unit operation in question. Initially, the algorithm evolved improved networks but, after four steps, performance was temporarily impaired and, after nine steps, performance reached its optimum. Nevertheless, further improvements were easily identified by inspection. In the discussion, the authors suggested that the algorithm had failed to continuously improve the process partly because it could not account for synergistic effects of two or more process changes (which would be different to the sum of the effects of each change individually). Also, they observed that the unit operation with the largest exergy loss was not always the one with the best scope for improvement.

It would appear that the problem of synergistic effects is identical to that of network interactions referred to above. Also, it seems that the other observation made by King et al. would justify Szargut's suggestion that exergy losses may guide design decisions but not determine them: exergy losses were used to form the basis of a heuristic rule but the rule was seen to be fallible. Admittedly, one could use the exergy concept in a more sophisticated way to identify scope for action* but the problem of finding a reliable way of transforming exergy information into process design suggestions would remain. This point seems worth noting since it follows that the user of a thermodynamic analysis has to resort to judgement, a requirement which is in marked contrast to the unambiguity and ultimate objectivity of the analysis itself.

Menzies and Johnson(87) described a program they used to systematically synthesise the low temperature gas separation section of an ethylene plant. The program (1) identified a suitable set of processing streams with yet to be satisfied temperature and pressure changes, (2) generated a large number of candidate equipment networks, and (3) selected a suitable low cost solution. When generating the candidate networks, the program used heuristic rules such as "adjust pressure before temperature", "observe

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* One might, e.g., refer to efficiencies as well as to losses: a low efficiency unit operation on a modest scale might show the same loss but a better scope for improvement than a high efficiency large scale operation.

minimum temperature difference in heat exchangers", and "observe maximum entropy increase in heat exchangers". In their discussion, Menzies and Johnson were able to justify especially this last rule since they could show that the cost of energy was well reflected by exergy (rather than enthalpy). Thus, this application of the concept of thermodynamic losses would appear to be more successful than that reported above (i.e. King(86)), but the fact remains that the concept had, again, to be implemented via a heuristic rule, and that no guarantee could be given as to the optimal definition of this rule.

Evans and Tribus(83) described a technique called "thermoeconomics" for the optimum design of saline water conversion systems. They claimed that, with this technique, the optimum value of design parameters may be determined with respect to given cost correlations. Reistad(13) developed a similar technique and applied it to a total energy system, and Kafarov et al.(85) recommended the use of the approach when planning general chemical engineering systems. Further discussions on thermoeconomics are given by Tribus and Evans(82) and by El-Sayed and Evans(84). With this technique, an initial network is split into subsystems, and in each subsystem, the cost of exergy losses is balanced against equipment costs. Evidently, the unit costs of exergy within the subsystems have to be determined such that they best reflect the effect of losses on the overall system's performance.

A basic limitation of the technique seems to lie in the fact that one cannot have sufficient knowledge to define the various unit costs of exergy unless the initial network, with its division into subsystems, already resembles the final system reasonably well. Indeed, the technique has only been demonstrated in applications which might more fittingly be described as optimisation studies, rather than problems of process design. However, in this narrower context, the technique appears to perform well, thereby justifying Szargut's suggestion that exergy might prove to be a convenient parameter for optimisation studies (see above).

1.4 SUMMARY

As argued by Szargut(24) and as evident from published studies(83,86,87) the use of the entropy/exergy concepts when making practical decisions in design must necessarily be somewhat subjective, and this is in clear contrast to the concepts of entropy/exergy themselves, which are strictly objective. Nevertheless, there is a marked lack of comments in the literature on the problem of making the least subjective use of a thermodynamic analysis. Valuable suggestions are given by Denbigh(31), but they remain general, and recommendations as to how precisely thermodynamic analysis can be employed when trying to invent flowsheets for a given process at a level of any detail simply cannot be found.

CHAPTER TWO

THERMODYNAMIC ANALYSIS. - A REVIEW AND SUGGESTIONS

2.1 HEAT AND MASS BALANCE OF A STEADY STATE PROCESS

Complete and consistent heat and mass balances represent convenient starting points for thermodynamic analyses of industrial processes. The following is a brief review of the concepts underlying a satisfactory heat balance. The theory is well established and references to the literature are only given where conventions might not be commonly accepted.

The First Law.- Internal Energy, Heat, and Work

For a "closed system" (i.e. a system which does not exchange matter with its surroundings), the First Law can be written as follows with respect to any change that might occur between two states, (1) and (2):

$$\int_1^2 dQ + \int_1^2 dW = (Ekin_2 + Epot_2 + U_2) - (Ekin_1 + Epot_1 + U_1) \qquad (2.1)$$

In this equation, $\int_1^2 dQ$ represents all heat given to the system during the transition from state (1) to state (2), $\int_1^2 dW$ represents all work done on the system*, Ekin and Epot denote the system's kinetic and potential energies, and U its internal energy.

Kinetic, potential and internal energy are intrinsic properties of a system whereas heat and work are not: heat and work are forms in which energy is exchanged between systems whereas kinetic, potential and internal energy are forms in which it is stored. When storing kinetic or potential energy, a system may change its mechanical state (velocity, position) and when storing internal energy, its thermodynamic state (T,p,composition).

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* Sign convention as proposed by the I.U.P.A.C. in 1970 (see Denbigh (2), p.14).

Like potential energy, internal energy must be defined with reference to some datum level. The datum is normally referred to as "reference state" (T_{RS},p_{RS}).

Steady State Processes. - Enthalpy

Consider now an "open system" (i.e. a system which exchanges matter with its surroundings) at the steady state. During any interval in time, Δt, heat dQ and work dW may be supplied across its boundaries and material flows i (i = 1,2,...,n) be exchanged. Counting inputs as positive and outputs as negative, the system's mass balance is given by:

$$\sum_{i=1}^{n} (m_i)_{\Delta t} = 0 \qquad (2.2)$$

To establish the system's energy balance, a closed system may be identified which represents the open system, see Figure (2.1), page 21. At the beginning of the time internal Δt, the closed system consists of the original open system and all masses that will enter the open system during Δt. At the end, it consists of the open system and all masses that have left the open system during Δt. Thus, the closed system is brought from state (1) to state (2) during Δt.

The volume of the closed system decreases by $\sum_{i=1}^{n} (V_i)_{\Delta t}$ from state (1) to state (2) and since these volume changes are brought about against pressures in the flows, the corresponding work done on the system amounts to:

$$W_{Flow,\Delta t} = \sum_{i=1}^{n} (p_i * V_i)_{\Delta t}$$

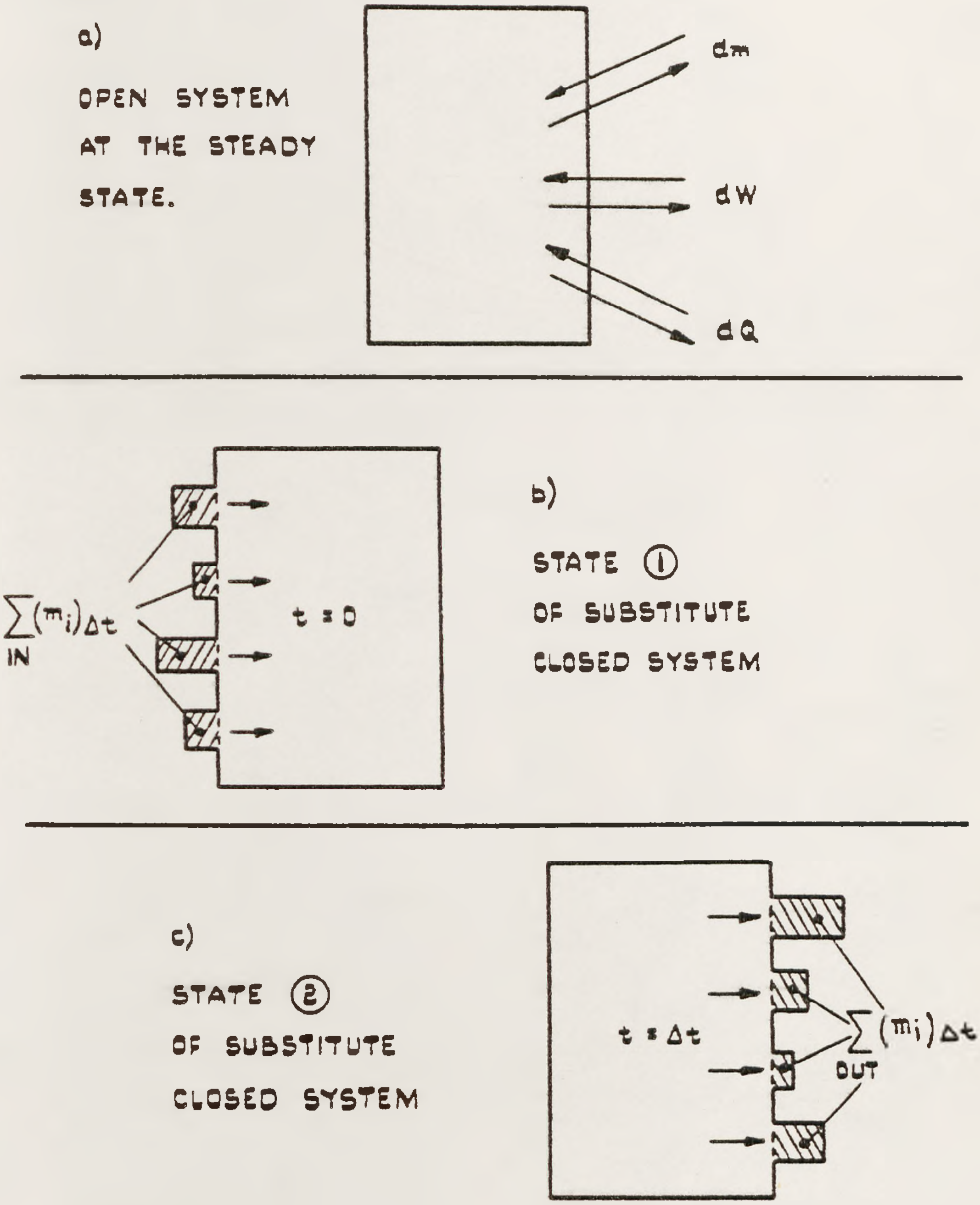

Figure (2.1) Replacing an open system by a closed one.

This is normally referred to as "flow-work" and has to be accounted for in addition to other work supplied to the system. Further, changes in the potential, kinetic, and internal energy of the closed system are restricted to the masses $(m_i)_{\Delta t}$ $(i=1,2,\ldots,n)$ and with Equation (2.1):

$$\int_{t=0}^{\Delta t} dQ + \int_{t=0}^{\Delta t} dW + \sum_{i=1}^{n} (p_i * V_i)_{\Delta t} + \sum_{i=1}^{n} (Ekin_i + Epot_i + U_i)_{\Delta t} = 0 \qquad (2.3)$$

The definition of enthalpy

$$H = U + p*V \qquad (2.4)$$

is convenient for open systems. Introducing enthalpy into Equation (2.3), the term describing the flow-work disappears:

$$\int_{t=0}^{\Delta t} dQ + \int_{t=0}^{\Delta t} dW + \sum_{i=1}^{n} (Ekin_i + Epot_i + H_i)_{\Delta t} = 0 \qquad (2.5)$$

Reference States for Simple Systems

Like internal energy, enthalpy has to be suitably referenced to some datum level:

For a single substance, the enthalpy of a given mass may be called H_{RS} at a chosen reference state and the total enthalpy at any other state (T_1,p_1) may be expressed as

$$H_1 = H_{RS} + H(T_1,p_1) \qquad (2.6)$$

so that $H(T_1,p_1)$ represents the enthalpy at the state (T_1,p_1) as measured against the reference state*. In systems not involving chemical changes, H_{RS} may be assigned any value for any substance since inputs and outputs of all substances must cancel each other.

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* For the calculation of terms $H(T,p)$ from physical property data see Section 2.4.

Also, the reference states for different substances can be chosen independently. In more general systems, the situation is more constrained (see below).

Heat of Reaction

Changes in internal energy which accompany a chemical reaction can be determined experimentally and the corresponding changes in enthalpy can be obtained with Equation (2.4). An enthalpy change so evaluated is usually - though somewhat misleadingly - referred to as "heat of reaction" and can be expressed as

$$\Delta HoR_{1,2}^{X,Y} = H_2^Y - H_1^X \tag{2.7}$$

if the state of the reactants "X" is (T_1, p_1) and the state of the products "Y" is (T_2, p_2).

Heats of reaction vary with the states in which products and reactants are considered. Combining Equations (2.7) and (2.6) leads to

$$\Delta HoR_{1,2}^{X,Y} = \Delta HoR_{3,4}^{X,Y} + \left[H^Y(T_2, p_2) - H^Y(T_4, p_4)\right] - \left[H^X(T_1, p_1) - H^X(T_3, p_3)\right] \tag{2.8}$$

i.e. a relationship often referred to as "Kirchhoff's law" if (1) = (2) and (3) = (4).

Heats of reaction do not vary with different reaction paths: any sequence of reactions, as long as it leads to the same products from the same reactants, can be assigned with the same overall heat of reaction:

$$\Delta HoR_{1,2}^{X,Y} = \Delta HoR_{1,3}^{X,Z} + \Delta HoR_{3,2}^{Z,Y} \tag{2.9}$$

This relationship is known as "Hess's law" if (1) = (2) = (3).

Heat of Formation

The physical significance of a substance's heat of formation can be described as the heat of reaction of the hypothetical reaction which would produce the substance in question from the elements. Heats of formation are usually found in the literature in tabulated form with the substance in question, as well as the elements, assumed at some standard state (T_{STD}, p_{STD}):

$$\Delta HoF^{X}_{STD} = \Delta HoR^{Elemts., X}_{STD,STD} \tag{2.10}$$

Thus, the heat of reaction of any real reaction can be equated to the difference between the heats of formation of the products and of the reactants

$$\Delta HoR^{X,Y}_{STD,STD} = \Delta HoF^{Y}_{STD} - \Delta HoF^{X}_{STD} \tag{2.11}$$

i.e. it is equated to the overall heat of reaction of hypothetical reactions which would, firstly, produce pure elements from the reactants and, secondly, produce the products from the elements (Hess's law is applied).

Reference States for General System

In a system involving chemical changes, the reference state of each substance for which the system acts as a source or a sink is conveniently chosen to equal the standard state, and the enthalpy at this state to equal the substance's heat of formation. By this procedure, enthalpies at reference states are easily assigned and a common datum level is obtained for the enthalpies of all species involved. (The enthalpies of the elements at standard state are used as a basis of comparison, see Equations 2.10 and 2.11). In cases where it is not convenient to equate standard and reference states, heats of formation at chosen reference states can be evaluated by means of Equation (2.12):

$$\Delta HoF_{RS} = \Delta HoF_{STD} - H(T_{STD}, p_{STD}) \qquad (2.12)$$

This procedure preserves the common data level for all species*.

Ideal Solutions

An "ideal solution" is usually defined as a mixture of substances for which the equation

$$\hat{f}_k = \nu_k * f_k \qquad (2.13)$$

is valid for any given temperature, pressure, and composition. In this equation, ν_k denotes the molar fraction of constituent k in the mixture, f_k may denote the fugacity of pure constituent k at the temperature and pressure of the mixture** and $\hat{f}_k$ is the fugacity of constituent k as present in the solution.

In the present context, the point of main interest is that there is no enthalpy change if an ideal solution is formed from its constituents, i.e. that the enthalpy of the solution at (T,p) is equal to the sum of the enthalpies of the pure constituents:

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* However, the procedure is not applicable in cases where heats of formation are to be used from different tables with different standard states. If such is the aim, heats of formation must be interpreted as heats of reaction (see Equation 2.10) and be corrected with Equation (2.8) - i.e. physical property data of the elements will be required.

** As pointed out by Van Ness (8), p.70, this definition of f_k may give rise to difficulties since pure constituents may not be stable in the same aggregate state as in the solution at (T,p). Often, this becomes important when vapour-liquid equilibria are considered. There are, however, ways to overcome this problem by defining f_k more flexibly (see, e.g., Perry V (52b), p.4-53).

$$H_1^{I.S.} = \sum_{k=1}^{z} (H_1^k) \qquad (2.14)$$

Mixtures of ideal gases qualify as ideal solutions: for an ideal gas, f_k equals p_k and Equation (2.13) is identical to Dalton's law. Also, quite a number of real gas mixtures and a few liquid solutions are known to approximate Equation (2.13) very closely. Provided this applies over the whole range of compositions, the enthalpy change of mixing for such a solution is ∿zero and Equation (2.14) applies .

Non-Ideal Solutions

A mixture of substances which does not obey Equation (2.13) is usually called a "non-ideal solution". Its enthalpy at any given state will be different from that of the sum of its pure constituents and the difference is usually referred to as the "heat of mixing". It must be exchanged if the solution is formed from its constituents and it can be defined analogous to the heat of reaction (see Equation 2.7), i.e. the following expression

$$\Delta HoM_{1,1} = H_1^{N.I.S.} - \sum_{k=1}^{z} (H_1^k) \qquad (2.15)$$

is valid for the transition from constituents at (T_1,p_1) to solution at (T_1,p_1). In most practical cases, heats of mixing will be obtained from charts and tables, applicable for ranges of compositions at sometimes peculiar temperatures. To convert readings to required reference or standard temperatures, Equation (2.8) may be used.

Kinetic and Potential Energy. - Usual Magnitudes

A figure of c = 50 m/s is perhaps on the high side of realistic gas and steam velocities in pipes and one of Δx = 50 m on the high side of normal in-plant height differences. When expressed as kinetic and potential energy, these figures yield

$$\underline{e_{kin}\ (c = 50\ m/s) = 1.25\ kJ/kg}$$

and

$$\underline{\Delta e_{pot}\ (\Delta x = 50\ m) = 0.50\ kJ/kg}$$

respectively, and are easily compared to energy transferred, e.g., in heat exchangers; the following table shows to what extent nitrogen and water, both at ambient conditions, could be heated up by equivalent amounts of heat:

	Water	Nitrogen
$\Delta T(0.5\ kJ/kg)$	$\sim 0.1^{\circ}C$	$\sim 2^{\circ}C$
$\Delta T(1.25\ kJ/kg)$	$\sim 0.3^{\circ}C$	$\sim 5^{\circ}C$

Thus, changes in kinetic and potential energy (in the simple mechanical forms considered here) will normally be negligible when compared to enthalpy changes in industrial processes.

Summary

The energy balance of most open systems at the steady state is given by Equation (2.16):

$$\int_{t=o}^{\Delta t} dQ + \int_{t=o}^{\Delta t} dW + \sum_{i=1}^{n} (H_i)_{\Delta t} = 0 \qquad (2.16)$$

In this equation, kinetic and potential energies have been neglected due to the findings just described and the enthalpy of the i-th flow, i.e. H_i, is computed by means of Equation (2.17a)

$$H_i = \sum_{k=1}^{z} \left[H^k (T_i, p_i) \right] + \sum_{k=1}^{z} \left[\Delta HoF^k_{RS} \right] \qquad (2.17a)$$

if the flow consists of an ideal solution. If the flow is a non-ideal solution, its enthalpy is computed by means of Equation (2.17b):

$$H_i = H^{N.I.S.}(T_i, p_i) + \Delta HoM_{RS,RS} + \sum_{k=1}^{z} (\Delta HoF^{k}_{RS}) \qquad (2.17b)$$

The terms describing the heats of formation in Equations (2.17) may be summarised over all inputs and outputs to give an overall heat of reaction, see Equation (2.18):

$$\Delta HoR^{overall}_{RS,RS} = \sum_{i=1}^{n} \left\{ \sum_{k=1}^{z} (\Delta HoF^{k}_{RS}) \right\} \qquad (2.18)$$

Thereby, the contributions of all species not involved in chemical reactions will cancel out.

2.2 THERMODYNAMIC IRREVERSIBILITY. - THE ENTROPY CONCEPT

Consider any process which leads a system from state (1) to state (2). In thermodynamic terms, the process is called reversible if it is possible not only to restore the system to its initial state, but also the surroundings, leaving no sign of the fact that the process has ever happened.

For thermodynamic processes, reversibility is given if two conditions are fulfilled: there must be no friction and all changes must be quasi-static*.

The commonly used method, however, to decide whether or not a process is reversible is by reference to entropy: if the process is reversible, the entropy of the universe remains constant and if the process is irreversible, the entropy of the universe increases. Also, the extent to which entropy increases may express the degree of irreversibility.

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* Mechanical processes, by contrast, can be reversible at finite speed. Think of the conversion of potential energy into kinetic energy and vice versa in a frictionless pendulum. (For a discussion of the difference between thermodynamic and mechanical processes, see e.g. Planck (3), Part III).

The following is a brief review of this fundamental concept in the context of steady state processes.

Entropy and Lost Work

The perhaps best known formulation of the Second Law states that heat cannot by itself pass from a cooler body to a hotter body. The following expression, which is usually referred to as "Clausius' inequality", relies on this simple observation:

$$\oint \frac{dQ}{T} \leq 0 \qquad (2.19a)$$

Thereby, dQ denotes the heat given to a material body from outside during a cyclic process and T denotes the temperature (absolute scale) at which the heat is supplied. The expression is valid for any real process. For an irreversible process, the inequality applies

$$\oint \frac{dQ}{T} < 0 \qquad (2.19b)$$

and for the limiting case of a reversible cycle, the equality holds:

$$\oint \frac{dQ_{rev}}{T} = 0 \qquad (2.19c)$$

The definition of entropy is given with

$$dS = \frac{dQ_{rev}}{T} \qquad (2.20)$$

whereby dQ_{rev} denotes the heat given to a material body* during a reversible process, T the absolute temperature at which the heat is transferred, and dS the increase in the body's entropy. Integrating Equation (2.20) for a cyclic process

$$\oint dS = \oint \frac{dQ_{rev}}{T}$$

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* The definition specifically applies to "bodies", i.e. closed systems and not to open systems. (See e.g. Denbigh (2), p.33).

and comparing the result to Equation (2.19c) shows that a body's entropy depends on its state only

$$\oint dS = 0$$

similar to its internal energy.

To appreciate the physical significance of the entropy concept, the following example, sketched in Figure (2.2), may be suitable. A closed system situated in specified surroundings undergoes cyclic changes. For each cyclic change of the system, the surroundings undergo a change from initial state (α) to final state (ω).

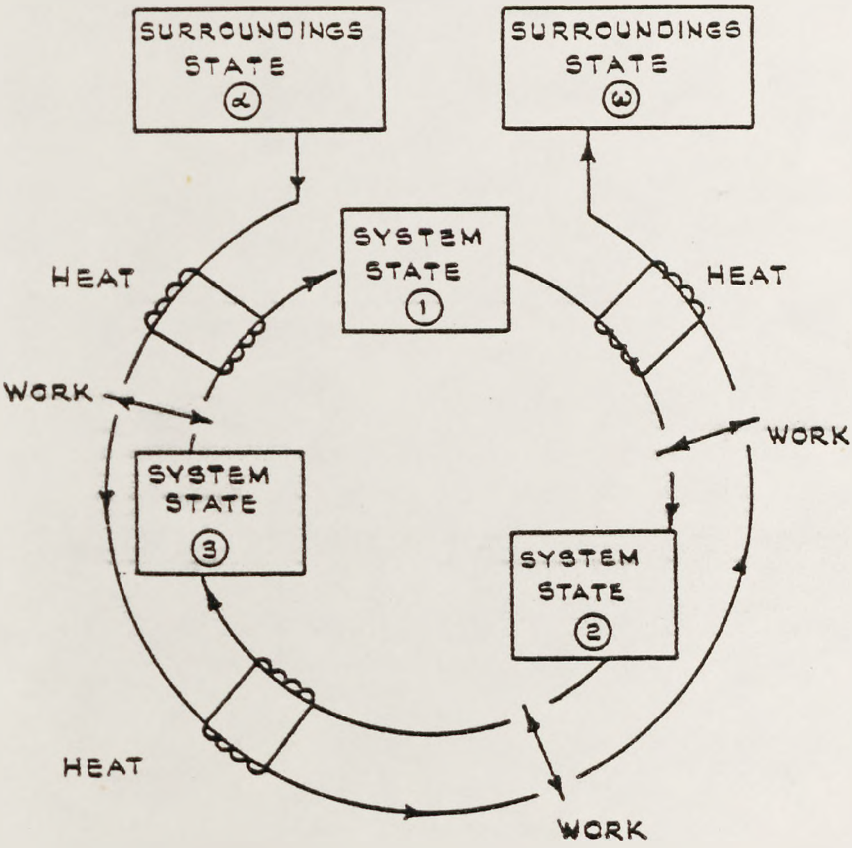

Figure (2.2) Closed system in specified surroundings.

The system and the surroundings exchange heat and work. The exchange of heat between system and surroundings is accomplished without temperature drops

$$\underset{\text{System}}{\oint \frac{dQ}{T}} = \underset{\text{Surroundings}}{-\int_{\alpha}^{\omega} \frac{dQ}{T}}$$

and similarly, all changes within the surroundings are reversible. Within the system, however, the changes might sometimes be reversible and sometimes irreversible.

Consider first the reversible case. If S_α and S_ω denote the initial and final entropies of the surroundings, then

$$0 = \underset{\text{System}}{\oint \frac{dQ_{rev}}{T}} = \underset{\text{Surroundings}}{-\int_{\alpha}^{\omega} \frac{dQ_{rev}}{T}} = S_\alpha - S_\omega$$

(see Equations 2.19c and 2.20) and there remains no change in entropy in either the system or the surroundings; as expected with a reversible process, the overall entropy change is zero.

Consider now the case where the changes in the system are irreversible. With Equations (2.19b) and (2.20)

$$0 > \underset{\text{System}}{\oint \frac{dQ}{T}} = \underset{\text{Surroundings}}{-\int_{\alpha}^{\omega} \frac{dQ_{rev}}{T}} = S_\alpha - S_\omega$$

and it follows that $S_\omega > S_\alpha$, i.e. the entropy in the surroundings has increased. With zero entropy change in the system (cyclic changes) the overall entropy has increased.

This example underlines the two main features of the concept of entropy, namely (1) that entropy must increase if irreversibilities take place and (2) that it is usually the entropy of the "universe", i.e. system plus surroundings, which must be monitored to evaluate irreversibilities: in the example, the irreversibilities occur in the system, but the entropy increase is manifest in the surroundings.

As remarked previously, the extent to which entropy is increased during irreversible processes may be used to express degrees of irreversibility Introducing a parameter σ

$$\sigma = (S_{final} - S_{initial})_{Universe} \tag{2.21}$$

irreversibilities due to different processes may be compared on a common scale. In addition, the magnitude of σ gives information especially interesting in engineering contexts:

Consider once more the example in Figure (2.2). The surroundings may be described as our natural surroundings, i.e. as consisting of a heat reservoir at $T = T_o$ and of several sources and sinks of work. For the case where the system undergoes an irreversible cyclic change,

$$\sigma = S_\omega - S_\alpha$$

and with Equation (2.20)

$$\sigma = \frac{Q_{add.}}{T_o}$$

whereby $Q_{add.}$ denotes the heat added ($\sigma > 0$) to the ambient heat reservoir. Since the system has undergone a cyclic change, the energy required to supply this extra heat to the reservoir must have come from within the surroundings (First Law), i.e. from sources of work. It follows that W_{lost}

$$W_{lost} = Q_{add.} = \sigma * T_o \tag{2.22}$$

is the amount of useful work that has been irretrievably lost in the process. Since each irreversible process in nature that leads a system from state (1) to state (2) can be followed by a reversible process (2) → (1) to complete an irreversible cyclic process, Equation (2.22) is of perfectly general validity for any natural change (1) → (2) a closed system can undergo. It lends a physical significance of obvious practical implications to the quantity of irreversible entropy changes, σ.

In addition to Equation (2.22), there are other contexts in which the entropy function is of significance in physics and perhaps in the whole of science. Firstly, entropy may be related to thermodynamic probability and thus be used as a pointer to indicate the direction of natural changes. (Every uncontrolled system will change towards a state of maximum probability, i.e. maximum entropy). Secondly, entropy may be used as a measure of order and disorder. (Systems which are completely unstructured, i.e. cannot invoke changes by reducing differences in potential, feature maximum entropy).* Lastly, entropy changes have been quantitatively related to the rates of certain non-equilibrium processes in the field of "irreversible thermodynamics" (see Denbigh(9)). Summaries of these different implications of the entropy function are given by Zemansky(5). However, none of these implications is of obvious relevance when studying the energy utilisation in industrial process networks and for this reason, the thermodynamic analyses presented in this thesis are mainly based on the implications of Equation (2.22).

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* In these two contexts (i.e. of probability and of order/disorder), entropy is increasingly used outside thermodynamics. An example is communication theory, see Tribus and McIrvine (45).

Reference States for Entropy

As noted previously, entropy is similar to internal energy in that it depends on a system's state only. Also, the definition of entropy (see Equation 2.20) may remind one of the definition of internal energy, and of enthalpy, since it is based on differences rather than absolute values. However, a common datum level for entropies of different substances need not be defined by reference to the elements since, according to "Nernst's theorem", the entropy of a pure substance approaches zero as its temperature approaches absolute zero. Thus, entropy changes of reactions simply correspond to the entropies of the species formed minus the entropies of the species consumed, all measured against zero absolute temperature. Nevertheless entropies of pure substances are tabulated at standard states, rather than absolute zero, in much the same way as heats of formation.

For convenience, the entropy of a given mass of a single substance at any reference state may be called S_{RS} and its entropy at any other state (T_1,p_1) may be expressed as

$$S_1 = S_{RS} + S(T_1,p_1) \tag{2.23}$$

whereby $S(T_1,p_1)$ denotes the entropy at the state (T_1,p_1) as measured against the reference state*. (Compare Equation 2.6). In cases where chosen reference states and standard states do not coincide, Equation (2.24) may be used for correction:

$$S_{RS} = S_{STD} - S(T_{STD},p_{STD}) \tag{2.24}$$

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* For the calculation of terms $S(T,p)$ from physical property data, see Section 2.4.

Ideal and Non-Ideal Solutions

Different to enthalpy, the entropy of an ideal solution is not identical to that of its constituents. It is larger by

$$\Delta SoM = \underline{R} * \sum_{k=1}^{z} (\underline{n}_k * \ln \frac{1}{\nu_k}) \qquad (2.25a)$$

with $\underline{R}$ = universal gas constant,

$\underline{n}_k$ = mole number of constituent k,

and ν_k = molar fraction of constitutent k.

As is evident from the equation, ΔSoM does not depend upon the state a solution is at but upon its composition only. For non-ideal solutions, however, the entropy change varies with the solution's state and this may be accounted for by introducing the activity coefficient γ_k* into Equation (2.25a) :

$$\Delta SoM = \underline{R} * \sum_{k=1}^{z} (\underline{n}_k * \ln \frac{1}{\gamma_k \nu_k}) \qquad (2.25b)$$

The activity coefficient will usually depend upon temperature, pressure and composition, and is determined experimentally.

While the study of entropies and of activity coefficients is of considerable interest in chemical thermodynamics to predict the behaviour of mixtures, the significance of Equations (2.25) in the context of studying the energy efficiency of industrial process networks is somewhat questionable. This will be discussed in detail in Section 2.5.

Entropy Balance of a Steady State Process

As remarked previously, the definition of entropy applies specifically to closed systems. Thus, the entropy balance of an open system has to be

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* See, e.g., Denbigh (2), p.270.

based on a suitable closed system, similar to the energy balance. Consider once more the system described in Figure (2.1) :

During the time interval Δt, the entropy of the closed system increases by

$$\Delta S_{\text{cl.system}} = - \sum_{i=1}^{n} (S_i)_{\Delta t}$$

and the entropy of the surroundings by

$$\Delta S_{\text{surr.}} = - \int_{t=o}^{\Delta t} \frac{dQ}{T}$$

(if all heat dQ is exchanged reversibly at the boundaries between system and surroundings). Thus, Equation (2.26)

$$\sigma_{\Delta t} = - \sum_{i=1}^{n} (S_i)_{\Delta t} \quad - \int_{t=0}^{\Delta t} \frac{dQ}{T} \tag{2.26}$$

determines the entropy increase of the universe during Δt due to the operation of the open process under scrutiny. Thereby, dQ denotes all heat given to the system from outside at the temperature T and S_i denotes the entropy associated with material flow i entering the system. S_i may be evaluated by means of the following expression which is based on Equations (2.23) and (2.25b):

$$S_i = \sum_{k=1}^{z} \left[S^k (T_i, p_i) \right] + \sum_{k=1}^{z} \left[S^k_{RS} \right] + \underline{R}^* \sum_{k=1}^{z} \left[\underline{n}_k^* \, \ln \frac{1}{\gamma_k \nu_k} \right] \tag{2.27}$$

Thereby, the index k denotes the k-th substance as present in the i-th flow. For ideal solutions, $\gamma_k = 1$ and for single component flows, $\nu_k = 1$.

As in the overall energy balance, the terms describing the entropies at reference states may be summarised as an overall entropy change of reaction, see Equation (2.28),

$$\Delta SoR^{\text{overall}}_{RS,RS} = \sum_{i=1}^{n} \left\{ \sum_{k=1}^{z} (S^{k}_{RS}) \right\} \qquad (2.28)$$

with the contributions of all species not involved in chemical reactions cancelling out.

2.3 THE CONCEPT OF EXERGY

Consider a material flow at the state (T_1, p_1). From the flow, as much work is to be recovered as is feasible in natural surroundings at (T_o, p_o). As shown in Figure (2.3), the flow may be passed through

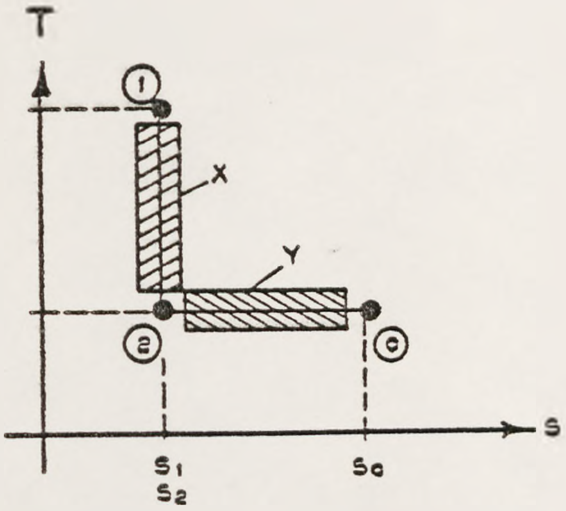


Figure (2.3) Bringing a material flow to equilibrium with its surroundings.

two open systems, X and Y, in which it may undergo reversible processes so as to lose its relative potential against ambient conditions. In the first system, X, it may undergo the adiabatic isentropic change (1) → (2) and in the second, Y, the isothermal change (2) → (0). The second system, Y, must exchange heat with the ambient reservoir at $T = T_o$. It follows from Equation (2.16) for any interval in time during steady state operation:

$$\int_{t=0}^{\Delta t} dQ_x + \int_{t=0}^{\Delta t} dW_x + (H_1 - H_2)_{\Delta t} = 0 \qquad (2.29a)$$

and $$\int_{t=0}^{\Delta t} dQ_y + \int_{t=0}^{\Delta t} dW_y + (H_2 - H_o)_{\Delta t} = 0 \qquad (2.29b)$$

Since $\int_{t=0}^{\Delta t} dQ_x = 0$ (adiabatic),

$\int_{t=0}^{\Delta t} dQ_y = -T_o*(S_o-S_2)_{\Delta t}$ (reversible),

and $S_2 = S_1$ (isentropic),

Equations (2.29) may be summarised as follows:

$$-\int_{t=0}^{\Delta t} dW_{(x+y)} = (H_1 - H_o)_{\Delta t} - T_o*(S_1 - S_o)_{\Delta t} \qquad (2.30)$$

Thereby, $-\int_{t=0}^{\Delta t} dW_{(x+y)}$ represents the total amount of work obtained in the reversible process, i.e. the maximum work that can be gained from the flow in natural surroundings. It is commonly referred to as the flow's exergy at the state (T_1,p_1) and expressed in comparison with its exergy at ambient conditions, which is nil:

$$(Ex_1 - Ex_o)_{\Delta t} = (H_1 - H_o)_{\Delta t} - T_o * (S_1 - S_o)_{\Delta t} \qquad (2.31)$$

Applying Equation (2.31) for any two states, (T_1,p_1) and (T_2,p_2), one may compute the maximum work available from a steady state flow when brought from state (1) to state (2) in natural surroundings at (T_o,p_o):

$$(Ex_2 - Ex_1)_{\Delta t} = (H_2 - H_1)_{\Delta t} - T_o * (S_2 - S_1)_{\Delta t} \qquad (2.32)$$

The History of Exergy

According to Grassmann(18), Gouy(28) in 1889 was probably the first to describe Equation (2.31) in his essay "Sur l' énergie utilisable", and according to Perry IV(52a), p.4-38, Bryan in 1907 was presumably the first to present a complete and precise treatment of the subject. However, it was more than twenty years later that J H Keenan(29) in America and F Bošnjaković(1) in Germany introduced the terms "availability" and "Technische Arbeitsfähigkeit", respectively, and tried to make the concept known. About another twenty years later, Z Rant(32) suggested the word "Exergie" at a conference in Germany and the German VDI issued a number of publications exclusively designated to the subject. Examples are the booklet "Energie and Exergie"(12) and a special issue of Brennstoff-Wärme-Kraft(11) in 1961. It is probably fair to say that the concept is widely known today and that Rant's suggestion has become accepted, also in the English speaking literature (→"exergy"). In chemical engineering contexts, there is a special advantage in the word "exergy" (when compared to Keenan's "availability"), in that no confusion is possible with "availability" as commonly used in reliability studies.

In 1963, Rant(33) suggested to generalise the concept further by interpreting exergy as all energy which is theoretically convertible into <u>any other form</u> of energy and introduced the term "anergy" for all energy that is not convertible into other forms. Thus, any given energy may be considered as consisting of a certain amount (sometimes zero) of exergy, with the remainder being anergy. When interpreted in this way, Equation (2.31) merely applies for the special case of a material flow at the steady state. However, Evans(34) in 1969 suggested "essergy" as the.."only consistent measure of potential work".. by including a species' chemical potential in its essergy. Whether or not Evans' formulation is preferable to that suggested by Rant will not be discussed here since, for the scope of this thesis, it is sufficient to refer to the concept of exergy as expressed in Equation (2.31), i.e. in the sense originally proposed by Gouy, Keenan, and Bošnjaković.

Exergy and Heat

Consider now the special case of heat being exchanged, but no work, with a medium flowing at the steady state at a constant temperature T (see Figure 2.4).

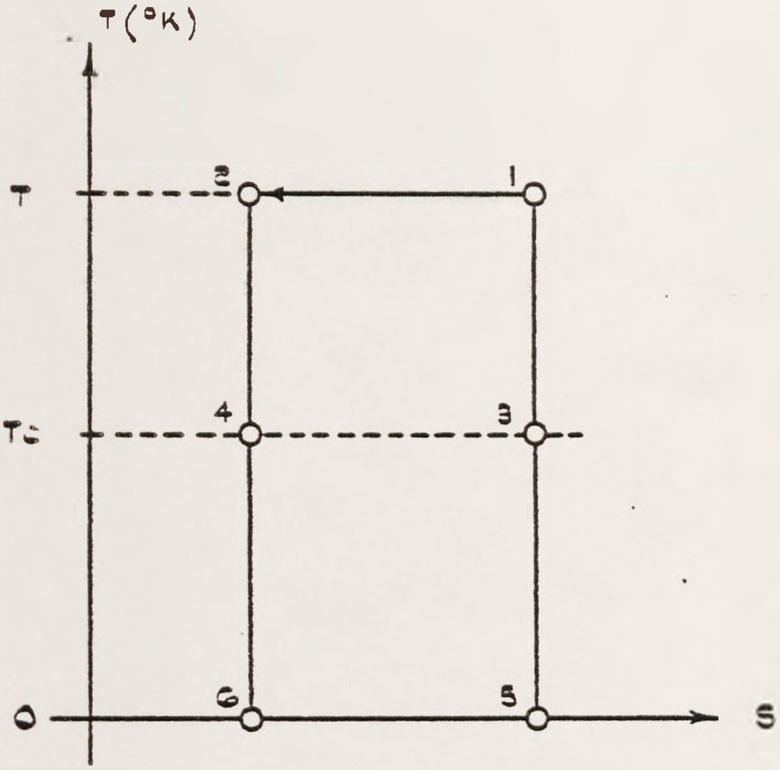


Figure (2.4) Isothermal release of heat in T,S-diagram.

With Equation (2.16)

$$\int_{t=0}^{\Delta t} dQ = (H_2 - H_1)_{\Delta t}$$

and with Equation (2.20) :

$$\int_{t=0}^{\Delta t} dQ = T^*(S_2 - S_1)_{\Delta t}$$

The reversible work equivalent exchanged with the medium is

$$(Ex_2 - Ex_1)_{\Delta t} = (H_2 - H_1)_{\Delta t} - T_o * (S_2 - S_1)_{\Delta t} \;,$$

i.e.

$$(Ex_2 - Ex_1)_{\Delta t} = (1 - \frac{T_o}{T}) * \int_{t=0}^{\Delta t} dQ \qquad (2.33)$$

This result is well-known in the context of the "Carnot factor": to obtain as much work as possible from the heat (1) - (2) - (6) - (5) - (see Figure 2.4), a Carnot engine is required which rejects the heat (3) - (4) - (6) - (5) - (3) at T_o and delivers the work (1) - (2) - (4) - (3) - (1).

Thus, the Carnot factor

$$\eta_c = (1 - \frac{T_o}{T}) \qquad (2.34)$$

gives the ratio of maximum work obtainable to heat consumed. In the case of a heat pump (which delivers heat at T by consuming work and absorbing heat at $T = T_o$), it gives the ratio of minimum work required to heat obtained.

Chemical Reactions.- Exergy and Gibbs Free Energy

When deriving Equations (2.31) and (2.32), no qualifying assumptions were made regarding the processes (1) → (2) and (2) → (0) in Figure (2.3) other than that they be reversible. Consequently, these equations are valid also if chemical reactions occur during the processes. Namely, Equation (2.32) may be applied for a reaction leading from reactants at (T_{STD}, p_{STD}) to products at (T_{STD}, p_{STD}) :

$$(\Delta ExoR)_{\Delta t} = (H_{STD}^{PR} - H_{STD}^{RE})_{\Delta t} - T_o * (S_{STD}^{PR} - S_{STD}^{RE})_{\Delta t} \qquad (2.35)$$

where "PR" denotes products and "RE" reactants.

When applying Equation (2.35) to exothermic reactions, the resulting exergy change (i.e. the maximum work available) is sometimes found to exceed the enthalpy change (i.e. amount of energy available), which may at first seem surprising. However, this is easily explained by Figure (2.5) : when carried out reversibly, such a reaction will (1) require a certain heat input at ambient temperature and (2) supply work. The resulting net energy output is smaller than the amount of work supplied.

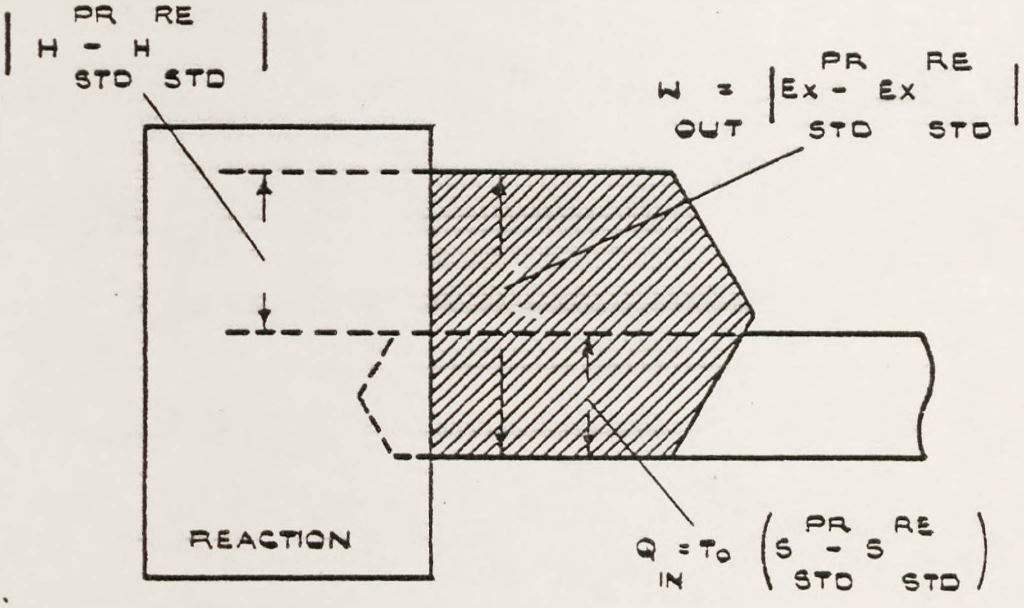


Figure (2.5) Maximum work available exceeds heat of reaction.

Lastly, a comparison between the exergy change and the Gibbs free energy change of reactions is interesting. The Gibbs free energy is defined by Equation (2.36)

$$\Delta G_{\Delta t} = (H^{PR} - H^{RE})_{\Delta t} - T * (S^{PR} - S^{RE})_{\Delta t} \tag{2.36}$$

and is explained as the maximum work available from a reaction which reservoir at the same temperature T. - In Figure (2.6), the

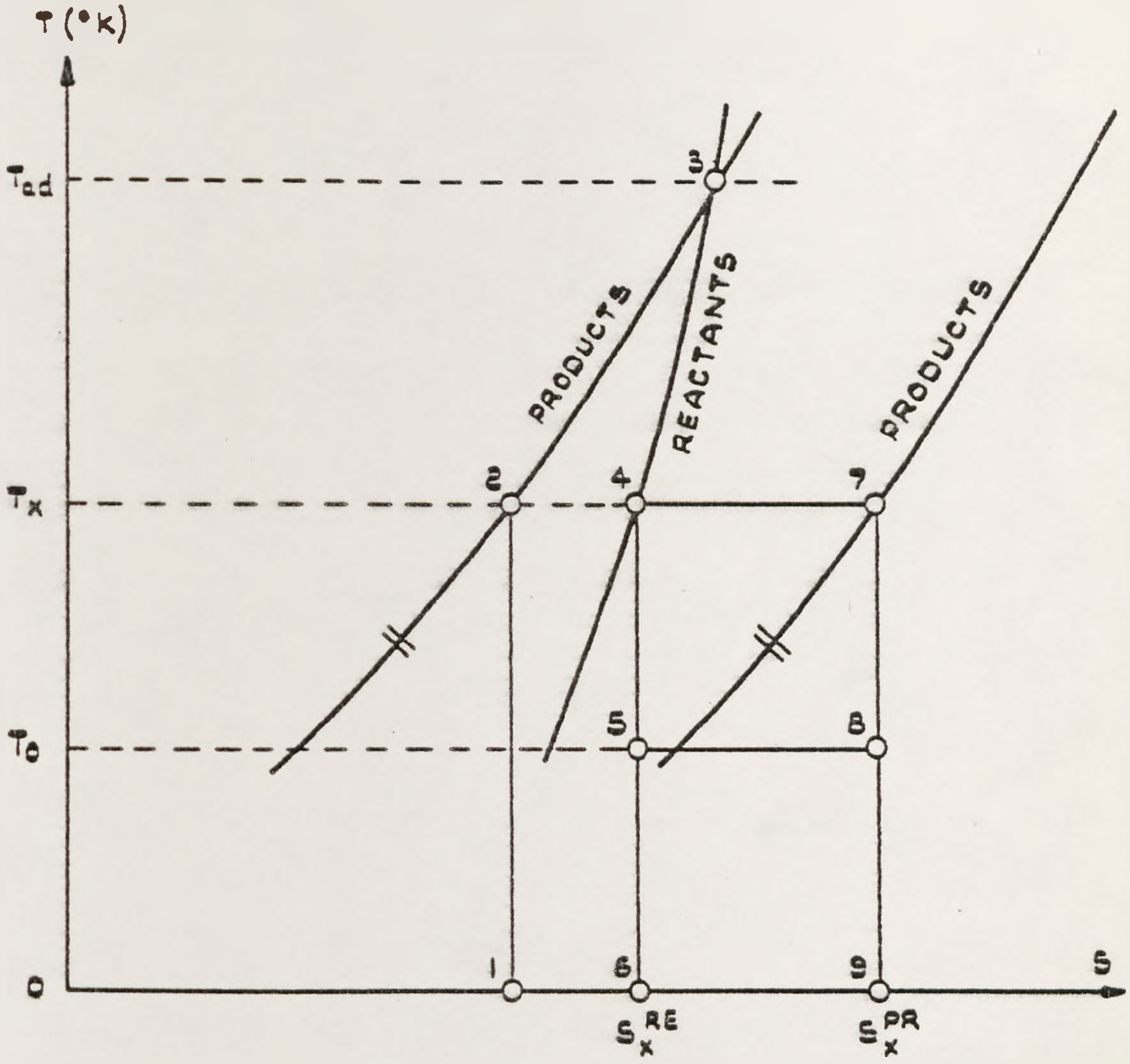


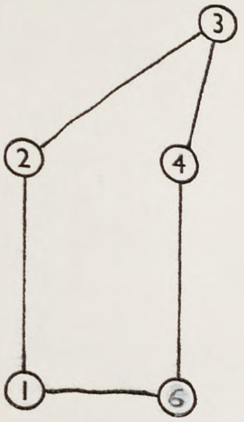
Figure (2.6) Diagram for the graphical interpretation of ΔHoR, ΔG, and ΔExoR.

isobars of reactants and products of an exothermic reaction with

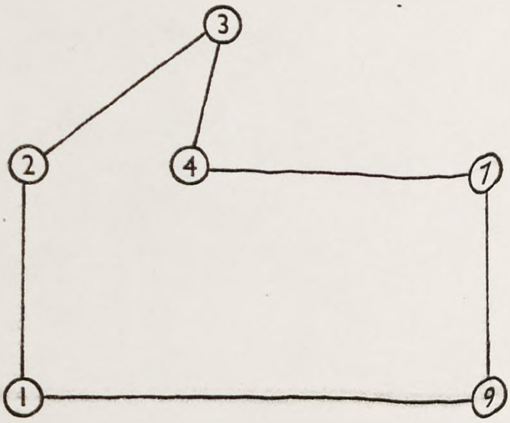
$$Cp^{PR}(T) > Cp^{RE}(T)$$

are superimposed in a common T,S-diagram in such a way that they meet at the adiabatic temperature T_{ad} where the heat of reaction is zero.

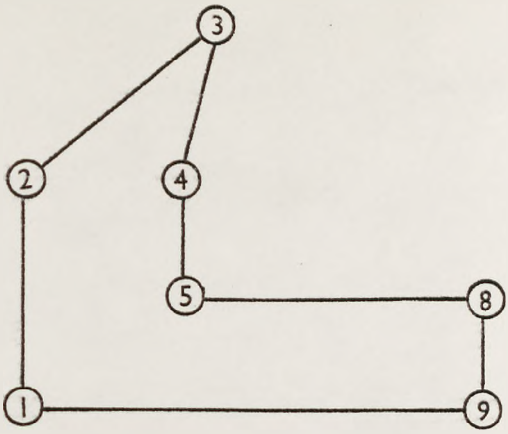
As a corollary, the area



represents the heat of reaction for any temperature T_x (Kirchhoff's law is applied). Further, a second isobar representing the products is added to the diagram in such a way that it would meet the isobar of the reactants at $T = 0^{o}K$ if both were extended. This ensures that, between these two isobars, the entropy difference $S_x^{PR} - S_x^{RE}$ can be read off for any temperature T_x. Thus, with Equation (2.36), the area



represents the Gibbs free energy change of the reaction. However, since $S_7 > S_4$, the reaction has to be supplied with the heat (4) - (7) - (9) - (6) - (4) at T_x, necessitating the use of a heat pump which absorbs heat (i.e. (8) - (5) - (6) - (9) - (8)) from the ambient reservoir at T_o and consumes work (i.e. (5) - (4) - (7) (8) - (5)). Subtracting this work from the Gibbs free energy change yields the net work surplus



i.e. the exergy change. (Compare Equation 2.35).

Thus, based on the definition of the Gibbs free energy as given above, the exergy change has been confirmed as the maximum work available from the reaction when heat is exchanged with the ambient reservoir only. The type of diagram shown in Figure (2.6) was probably first described by Linnhoff$^{(42)}$.

Exergy Balance of a Steady State Process

When producing the exergy balance of a general open system, it is convenient to define the parameter ΔEx_{irr}

$$\Delta Ex_{irr} = Ex_{in} - Ex_{out} \qquad (2.37)$$

which represents all potential work that is irretrievably lost in the system. For the system sketched in Figure (2.1), $(\Delta Ex_{irr})_{\Delta t}$ is consequently given by

$$(\Delta Ex_{irr})_{\Delta t} = \sum_{i} (Ex_i)_{\Delta t} + \int_{t=0}^{\Delta t} dW + \int_{t=0}^{\Delta t} (1 - \frac{T_o}{T}) * dQ \qquad (2.38)$$

whereby Ex_i denotes the exergy of the i-th flow as defined in Equation (2.31). Substituting Equation (2.31) leads to

$$(\Delta Ex_{irr})_{\Delta t} =$$

$$\underbrace{\sum_{i=1}^{n} (H_i)_{\Delta t} + \int_{t=0}^{\Delta t} dW + \int_{t=0}^{\Delta t} dQ}_{\substack{= 0 \\ \text{see Equation (2.16)}}} \underbrace{- T_o * \sum_{i=1}^{n} (S_i)_{\Delta t} - T_o * \int_{t=0}^{\Delta t} \frac{dQ}{T}}_{\substack{= T_o * \sigma_{\Delta t} \\ \text{see Equation (2.26)}}}$$

and it follows that:

$$(\Delta Ex_{irr})_{\Delta t} = T_o * \sigma_{\Delta t} \tag{2.39}$$

Thus, the result obtained in Equation (2.22) (i.e. "potential work lost equals σ times ambient temperature") has been found valid for the general open system, too.

Exergetic Efficiency

From a First Law point of view, energy is always conserved and efficiencies in First Law terms can only be based on subjective definitions of what energy is regarded as lost in a process. From a Second Law point of view, energy conversions are accompanied by objective losses (i.e. ΔEx_{irr}) and efficiencies in exergy terms may thus relate to an objective basis. If

$$Ex_{in} = Ex_{out} + \Delta Ex_{irr}$$

is the balancing equation of a general system, the ratio

$$(Ex_{out}/Ex_{in})$$

may, for instance, be quoted as exergetic efficiency. See, e.g., Gaggioli(27) and Riekert(44). However, as pointed out by Fratzscher(19), numerator and denominator of an efficiency should result from differences and the above ratio can indeed be "improved" by, say, a large flow of exergy which simply passes through the system, thereby increasing Ex_{in} and Ex_{out} by equal amounts. To overcome this difficulty, the balancing equation of a general system may be written as in Equation (2.40a)

$$\Delta Ex_{consumed} = \Delta Ex_{required} + \Delta Ex_{irr} \tag{2.40a}$$

and the exergetic efficiency be defined as in Equation (2.40b):

$$\eta_{ex} = (\Delta Ex_{required}/\Delta Ex_{consumed}) \tag{2.40b}$$

In the case of a simple heat exchanger, for example, "$\Delta Ex_{consumed}$" would be the exergy change of the hot fluid and "$\Delta Ex_{required}$" the one of the cold fluid. The definition of η_{ex} as in Equations (2.40) is compatible with suggestions made by Grassmann(16), Fratzscher(19), and Rant(25) for a generalised Second Law efficiency and is used in Chapters Three and Four. Usual magnitudes of η_{ex} for most unit operations lie in the region of forty to seventy percent.

Exergy versus Entropy. - A Comparison

The concept of availability/exergy appears to have become increasingly popular in the engineering literature. The reason for this might lie in the fact that numerical figures for entropy are rather difficult to appreciate intuitively: as heat is transferred to a cooler body, its entropy increases*, but as a process flow is cooled, its entropy decreases. To make matters worse, as a process flow is compressed, its entropy decreases, too. Thus, a process flow that is hot and compressed (i.e. is at a state of high potential) might have the same entropy as when cold and expanded.

In exergy terms, a drop of potential (i.e. degradation of heat, cooling of a flow, expansion of a flow) always leads to a decrease. The so-called "availability diagrams", "exergy flowcharts"**, etc., are closely connected with this rather useful characteristic of the exergy concept.

It would appear, therefore, that exergy might be more convenient to use than entropy in the particular task of analysing industrial processes. However, it should be born in mind that both concepts

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* This observation led Thring(35) in 1944 to define what he called the "virtue of energy". Essentially, Thring's virtue represents exergy as used in Equation (2.33).

** As pointed out by Grassmann(17), it is possible to draw Sankey type diagrams of processes with the width of the bars representing the exergies of flows. In such diagrams, unit operations represent exergy sinks with overall flows out being narrower than overall flows in, corresponding to Equation (2.37). This type of diagram has often been described as useful for intuitive appreciation of the ways in which energy is degraded in processes.

yield essentially the same information. A comparison is perhaps valid between exergy and entropy on the one hand and enthalpy and internal energy on the other : while internal energy and entropy represent fundamental thermodynamic concepts, enthalpy and exergy are only secondary concepts, based on the fundamental ones and defined merely for convenience; enthalpy is based on internal energy and exergy is based on entropy.

2.4 A NUMERICAL APPROXIMATION METHOD FOR THE CALCULATION OF ENTROPIES AND EXERGIES OF PROCESS FLOWS

For a homogeneous flow at constant composition, enthalpy changes (per unit mass) are given as a function of temperature and pressure by

$$dh = \left.\frac{\partial h}{\partial T}\right|_p dT + \left.\frac{\partial h}{\partial p}\right|_T dp$$

and entropy changes may be expressed by reference to the First Law

$$T*ds = dh - v*dp$$

(see e.g. Perry V$^{(52b)}$). With the definition of the specific heat capacity

$$cp = \left.\frac{\partial h}{\partial T}\right|_p$$

one obtains

$$dh = cp*dT + \left.\frac{\partial h}{\partial p}\right|_T dp \qquad (2.41)$$

and:

$$ds = cp*\frac{dT}{T} + \frac{1}{T}*\left.\frac{\partial h}{\partial p}\right|_T dp - \frac{v*dp}{T} \qquad (2.42)$$

For real gases, $\left.\frac{\partial h}{\partial p}\right|_T \neq 0$ and $pv = z(RT)$ and suitable information must be gathered to solve Equations (2.41) and (2.42). - For liquids, $\left.\frac{\partial h}{\partial p}\right|_T \approx 0$ and $v \ll 1$ and one obtains after integration:

$$\underset{\text{liquid}}{h_2 - h_1} \approx \int_1^2 cp*dT \qquad (2.43)$$

$$\underset{\text{liquid}}{s_2 - s_1} \approx \int_1^2 \frac{cp^* dT}{T} \qquad (2.44)$$

For ideal gases, $\left.\frac{\partial h}{\partial p}\right|_T = 0$ and pv=RT and, after integration:

$$\underset{\text{ideal gas}}{h_2 - h_1} = \int_1^2 cp^* dT \qquad (2.45)$$

$$\underset{\text{ideal gas}}{s_2 - s_1} = \int_1^2 cp^* \frac{dT}{T} - R^* \ell n \frac{p_2}{p_1} \qquad (2.46)$$

The term for the pressure dependence of entropy in Equation (2.46) may be calculated without reference to physical property data other than the appropriate gas constant. The integrals expressing the temperature dependence of enthalpy and entropy in Equations (2.43) through (2.46) may be solved based on polynomials for cp obtained from the literature.

In many practical circumstances, a heat and mass balance will be available when a Second Law analysis is to be produced. The following is a suggestion of how to base the calculation of the temperature integral for entropy changes, as encountered in Equations (2.44) and (2.46), on known enthalpy figures. One may write

$$\frac{s_2 - s_1}{h_2 - h_1} = \frac{\int_1^2 cp \frac{dT}{T}}{\int_1^2 cp^* dT}$$

and assume cp = const , so that:

$$\frac{s_2 - s_1}{h_2 - h_1} = \frac{\int_1^2 \frac{1}{T} dT}{\int_1^2 dT}$$

Thus,

$$s_2 - s_1 = (h_2 - h_1) * \left(\frac{1}{T_2 - T_1} \ell n \frac{T_2}{T_1}\right) \qquad (2.47)$$

and, with Equation (2.32):

$$ex_2 - ex_1 = (h_2 - h_1) * \left\{1 - \frac{T_o}{T_2 - T_1} \ell n \left(\frac{T_2}{T_1}\right)\right\} \qquad (2.48)$$

Equation (2.48) is closely related to the integral over the function

$$dex = cp(1-T_o/T)\,dT \qquad (2.49)$$

(which follows from Equation 2.33). In this form, it has presumably been used and referred to by many authors to compute approximate exergies based on the assumption cp = const .Examples are Bruges$^{(10)}$, Frankenberger$^{(38)}$ and Linnhoff$^{(42)}$.

However, when used as suggested in Equations (2.47) and (2.48), the results should be considerably more accurate than any results obtained by means of Equation (2.49). With this latter equation, constant cp is used to represent a physical property whereas, with the former equations, constant cp is used to establish a ratio. This ratio, in turn, is applied to enthalpy differences which were formerly computed by means of physical property data of any required degree of accuracy. Equations (2.47) and (2.48) have been tested with various polynomials for gases, and especially with data from steam tables (near saturated conditions) and the divergence between the true ratio

$$(s_2 - s_1)/(h_2 - h_1)$$

and the function

$$\frac{1}{T_2 - T_1} \ \ln \frac{T_2}{T1}$$

has usually been found to be below one percent. It follows that entropy changes computed by means of Equation (2.47) and based on correctly calculated enthalpy changes are accurate within about one percent. For exergy, the same degree of accuracy was observed. Both equations were used extensively in the case studies reported in Chapters Three and Four. Apart from easing computational tasks, the equations were seen to make explicit knowledge of heat capacities unnecessary.

With regard to exergy, the problem will often arise that the exergy change between a temperature T_1 and the ambient temperature is required.

When using Equation (2.48), however, the enthalpy change would have to be computed specially unless $T_o = T_{RS}$. For cases where $T_o \neq T_{RS}$, the following formula is suggested:

$$ex(T_1) = h(T_1) * \frac{T_1 - T_o}{T_1 - T_{RS}} * \left\{ 1 - \frac{T_o}{T_1 - T_o} \ln \frac{T_1}{T_o} \right\} \qquad (2.50)$$

Equation (2.50) is based on a linear interpolation (or extrapolation) of the enthalpy change between T_1 and T_{RS}, i.e. $h(T_1)$. It has been tested in Chapter Four and has been found not to impair the accuracy of the approximation procedure to any noticeable extent. The reason is presumably that, for low temperatures T_1, the linearisation is highly accurate and for high temperatures T_1, the error introduced by the linearisation is insignificant compared to the magnitude of $h(T_1)$, see Figure (2.7).

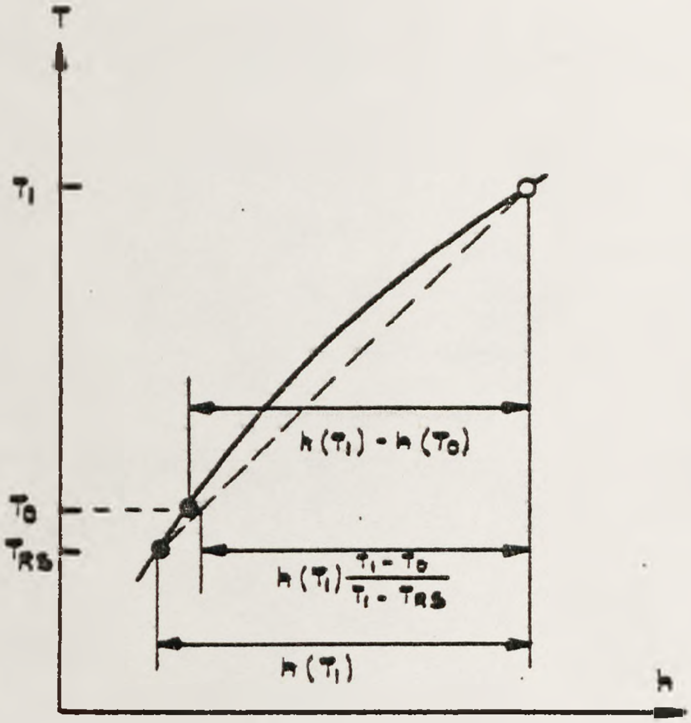


Figure (2.7) Linear interpolation of enthalpy change with temperature.

Instead of assuming cp = const , the approximation formulae might easily be based on the assumption of linear variation of cp with temperature and corresponding formulae were derived showing enhanced accuracy still. However, since the assumption of a linear variation of cp requires some explicit knowledge of heat capacities, the main advantage of the procedure (i.e. the fact that no physical property data is required) would be lost. For this reason and because the results obtained with the simpler formulae were considered to be perfectly satisfactory, the formulae based on linear variation were not used in the case studies. The formula for entropy, however, is documented in Appendix A and that for exergy follows with Equation (2.32).

2.5 PRACTICAL IMPLICATIONS OF REVERSIBLE MIXING

As stated in Section 2.2, the entropy of a mixture is larger than the sum of the entropies of its pure components by:

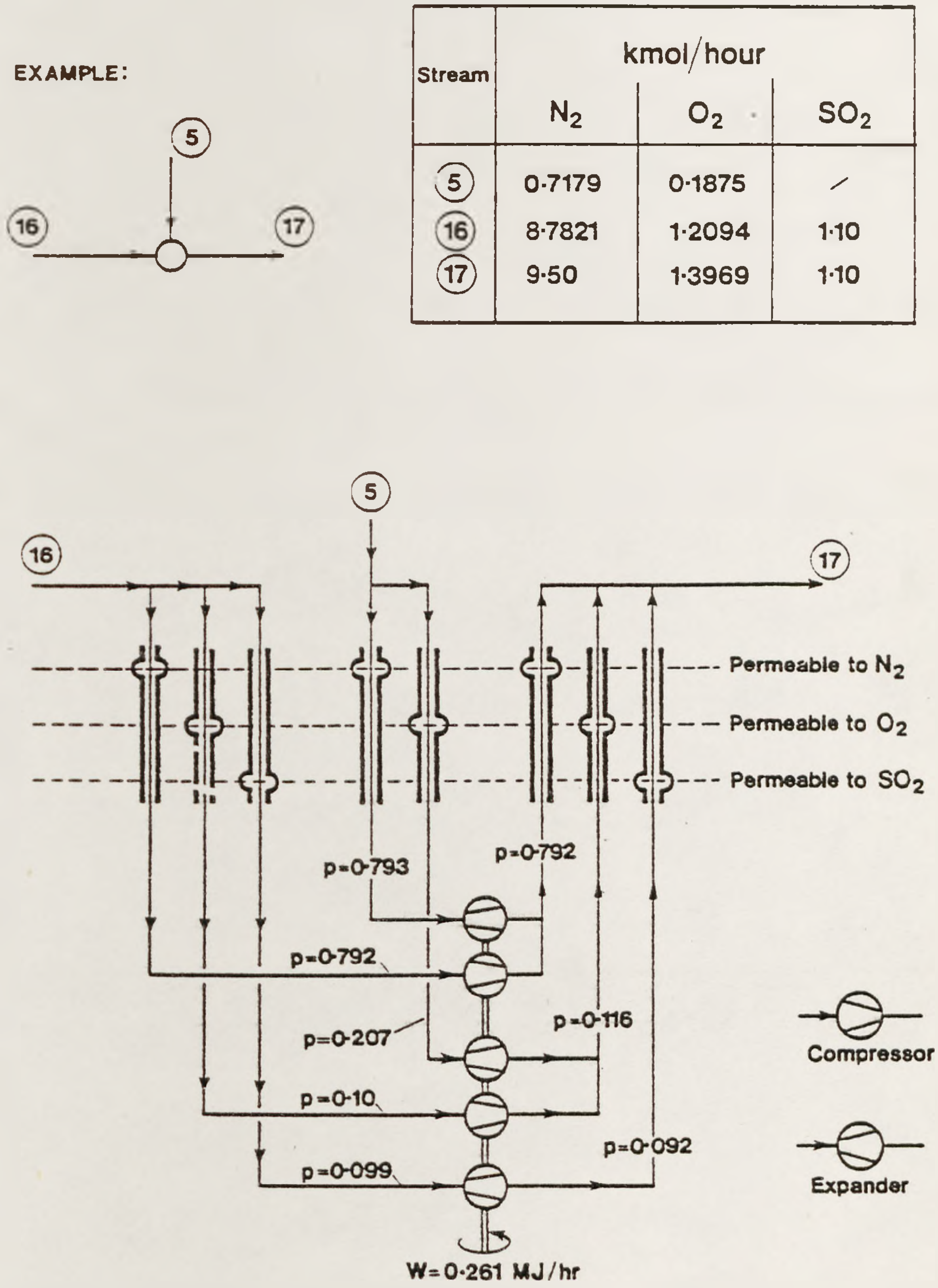
$$\Delta SoM = \underline{R} * \sum_{k=1}^{Z} (\underline{n}_k * \ell n \frac{1}{\gamma_k * \nu_k}) \qquad (2.25b) \text{ Repeat}$$

Correspondingly, work could be gained when a mixture is formed amounting to

$$\Delta ExoM = \Delta HoM - T_o * \Delta SoM$$

(see Equation 2.32). To obtain this work, semipermeable membranes could be used to exploit differences in partial pressures. In living organisms, the migration of certain fluids through membranes that are permeable to them but not to other fluids is known as osmosis and the pressure head which may be maintained - and exploited - due to osmosis is referred to as osmotic pressure. In technical applications, however, suitable membranes are known only for few solutions and constituents in the liquid phase (and even fewer in the gas phase), and industrial scale applications do not seem to be practical with most of these known membranes.

However, even if suitable membranes did exist, schemes aimed at the recovery of "mixing work" would often have to be unduly complex. In Figure (2.8), a scheme is shown as required for the reversible mixing



Stream	kmol/hour		
	N_2	O_2	SO_2
⑤	0·7179	0·1875	/
⑯	8·7821	1·2094	1·10
⑰	9·50	1·3969	1·10

Figure (2.8) Arrangement for reversible mixing.

of two gas flows. The mass flowrates and compositions are taken from the case study in Chapter Three, but temperatures are assumed to be constant. (Only the necessary expansion and compression equipment is shown). Quite clearly, the complexity of the arrangement is prohibitive, be semipermeable membranes available or not.

In the course of a Second Law analysis, terms for ΔS_{oM} appear with each process flow consisting of more than a single component. However, in unit operations not involving mixing or chemical reactions, input and output terms cancel. In the remaining unit operations, arrangements such as described in Figure (2.8) might be required to realise the scope for energy conservation. Thus, it is suggested that these terms be left out from an analysis altogether. This reduces the computational effort* and prevents results from being obtained that are irrelevant practically. If, in particular circumstances, exploitation of osmotic pressures would appear feasible, this might be examined separately.

2.6 PRESCRIBED DEGREE OF IRREVERSIBILITY FOR CHEMICAL REACTIONS

In 1956, Denbigh(31) pointed out that a major share of irreversibilities in industrial chemical processes occurs in chemical reactions and cannot be avoided in practice. Therefore, he suggested identification of practical efficiencies which would be unity when reactions were carried out under prescribed conditions of irreversibility and all other operations under ideal reversible conditions. Further, he showed that a ".... reaction taking place at constant temperature and pressure, the heat of reaction being transmitted to some other body (e.g. steam) which is at the same temperature...." will lead to an irreversibility of

---

* In an exergy analysis, it also helps to by-pass the problem of determining the ambient condition for materials not normally found in the natural surroundings. (Compare to this Szargut(36), Baehr(20) and Riekert(43)).

$$T_o * \sigma_{inev} = - \frac{T_o}{T} * \Delta G(T) \qquad (2.51)$$

with T = temperature of reaction

He recommended the use of Equation (2.51) in Second Law studies to identify the amount of work lost when the reaction proceeds under practically inevitable irreversible conditions.

In Figure (2.9) (see page 56), two sketches are shown which would apply to the ammonia oxidation reaction (used by Denbigh as an example) and which help to clarify why and where the irreversibilities computed by means of Equation (2.51) occur and what would have to be done to avoid them. In Figure (2.9a), the reversible case is shown with reactants and products at T_o, (i.e. the overall work gained amounts to $-\Delta G(T_o)$). The reaction is assumed to occur at constant temperature T, requires heat (i.e. $T*\Delta S(T)$), and delivers useful work (i.e. $-\Delta G(T)$). Some of this work drives a Carnot machine which provides the heat that is required. Further, the products are cooled down by means of an array of infinitesimal Carnot engines and the reactants are heated up by an equivalent array of heat pumps. The total surplus of work is equal to $-\Delta G(T_o)$, as mentioned before, and the total amount of heat exchanged with the ambient reservoir is

$$T_o*\Delta S(T) + T_o*S(T)^{RE} - T_o*S(T)^{PR} = T_o*\Delta S(T_o)$$

In Figure (2.9b), the irreversible case is shown which underlies Equation (2.51): the reaction occurs at the same temperature T but cannot exchange any work with its surroundings other than by displacing the atmosphere. In other words, fuel cell technology is considered unavailable and the reaction is carried out as an exothermic constant pressure process in which heat is released amounting to $-\Delta H(T)$. As far as possible, this heat is converted into work in the Carnot machine and the remainder of the arrangement is equivalent to the one in Figure (2.9a).

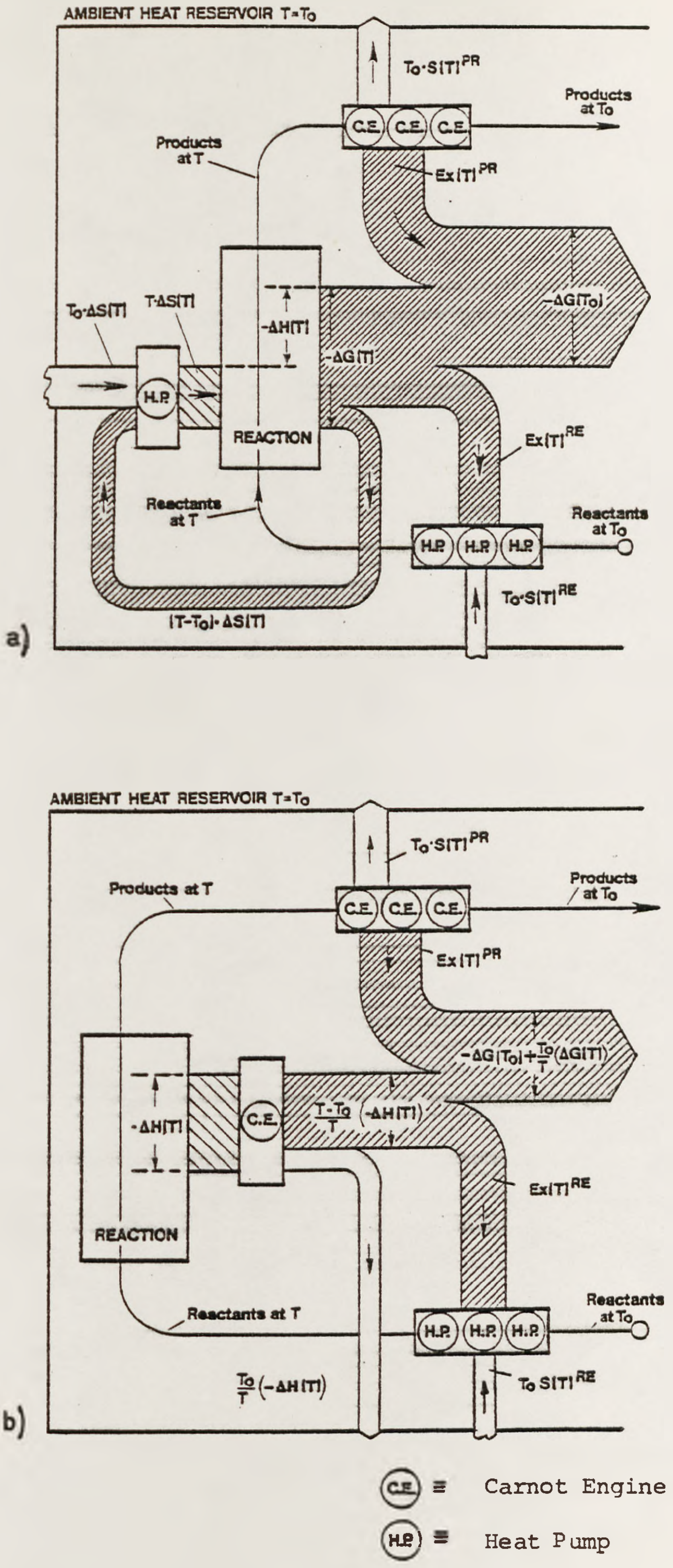


Figure (2.9) Exothermic reaction at $T > T_o$.

(a) Reversible case.

(b) Irreversible case as considered by Denbigh.

The decrease in work gained as compared to the reversible process must correspond to the increase in heat given to the surroundings, i.e. amount to

$$T_o*\Delta S(T)+\frac{T_o}{T}\left[-\Delta H(T)\right] = \frac{T_o}{T}\left[T*\Delta S(T) - \Delta H(T)\right] = -\frac{T_o}{T}*\Delta G(T) \ ,$$

as pointed out by Denbigh.

Apart from not avoiding those irreversibilities which would only be prevented by using novel reactor technology, arrangement (2.9b) is fully compatible with the usual idealisations of Second Law analyses. Since the difference between $-\Delta G(T_o)$ on the one hand and $-\Delta G(T_o)+(T_o/T)*\Delta G(T)$ on the other hand can be quite significant numerically (see Denbigh$^{(31)}$ and below), it would seem a great pity that Denbigh's suggestion, made more than twenty years ago, should have found hardly any response since. Possible reasons for this might include the fact that a fair amount of physical property data is required when solving Equation (2.51) and that the underlying thermodynamic theory which was discussed above, might intuitively not be very obvious.

An alternative approach to the definition of a prescribed degree of irreversibility will now be described which might prove to by-pass both these difficulties. Further, the alternative approach leads to results of greater practical significance than those from Equation (2.51).

A More General Model

In practice, reactions like ammonia oxidation start at temperatures lower than that of the products, so that:

(1) Some of the heat of reaction is consumed while the reaction proceeds by partly heating up products and by partly preheating reactants, and

(2) the remaining heat of reaction cannot be removed at the temperature of the products, T, but is only available at lower temperatures.

Thus, the true inevitable irreversibility is even greater than the one computed by means of Equation (2.51) and in Figure (2.10), a model is shown for discussing the consequences : the reaction occurs at various temperatures between T_{in} and T and the amount of heat removed from the reaction (i.e. Q_R) is smaller than $-\Delta H(T)$ and is available at $T=T_R$*. Thus, less work is extracted from this heat than in arrangement (2.9b). On the other hand, less work is required to

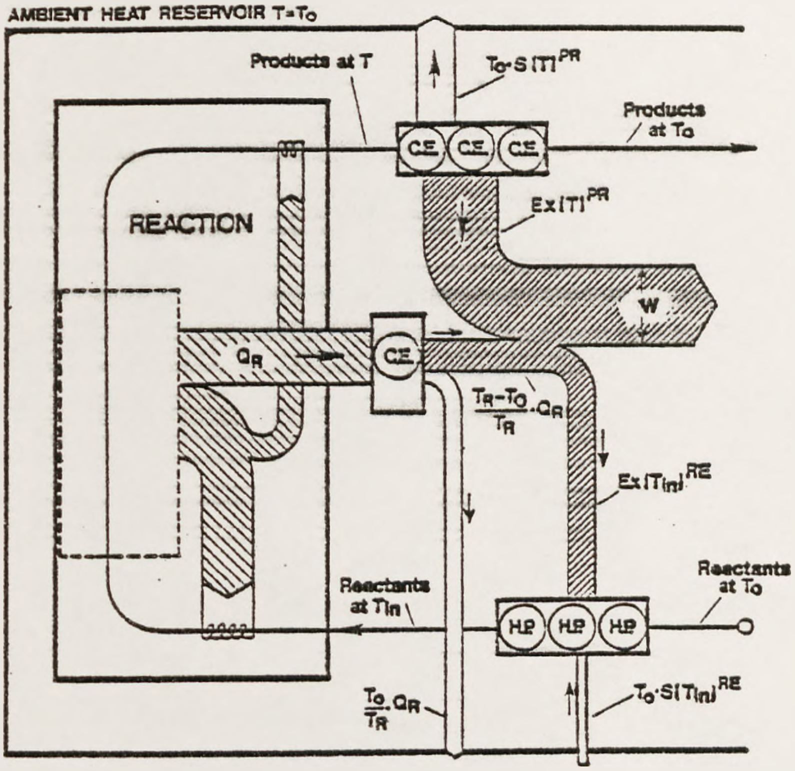


Figure (2.10) Exothermic reaction at $T > T_o$. Irreversible practical case.

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* Evidently, Q_R could be considered over a range of temperatures and arrays of Carnot machines could be assumed for avoiding losses due to heat transfer within the reaction chamber. Such a procedure would, however, make it necessary to know the precise temperature profile of the reaction and is not suggested here because Figure (2.10) is, eventually, to lead on to a practical formula for the prescribed degree

preheat the reactants, a fact which partly compensates for this. The useful work gained in Figure (2.10) may be evaluated by means of Equation (2.52):

$$W = \frac{T_R - T_o}{T_R} * Q_R + Ex(T)^{PR} - Ex(T_{in})^{RE} \qquad (2.52)$$

In the limiting case, where $T_{in} = T_R = T$ and $Q_R = -\Delta H(T)$ applies, this equation is compatible with Equation (2.51):

$$W_{\substack{\text{Figure}\\ (2.9b)}} = -\Delta G(T_o) + (T_o/T)\Delta G(T)$$

(see Equation 2.51)

$$\begin{aligned}
&= -\Delta H(T_o) + T_o * \Delta S(T_o) + \frac{T_o}{T} * \Delta H(T) - T_o * \Delta S(T) \\
&= -\Delta H(T) + H(T)^{PR} - H(T)^{RE} \\
&\quad + T_o * \Delta S(T_o) + \frac{T_o}{T} * \Delta H(T) \\
&\quad - T_o * \left[\Delta S(T_o) + S(T)^{PR} - S(T)^{RE}\right] \\
&= \underline{\underline{\frac{T - T_o}{T} * \left[-\Delta H(T)\right] + Ex(T)^{PR} - Ex(T)^{RE}}}
\end{aligned}$$

In practical cases, however, $T_{in} < T$ and the results obtained with Equation (2.52) may differ considerably from those obtained with Equation (2.51). The difference will depend upon the temperatures involved, upon the magnitude of Q_R, and upon the effect which variations in mass flowrates have in an arrangement such as shown in Figure (2.10):

In many instances, the mass flowrates of the reactant and product streams are considerably higher than those suggested by stoichiometric equations which do not show inert species. This might e.g. be necessary due to the presence of large recycle streams (as is the case in the absorption section of an H_2SO_4 plant, see Chapter Three) or be due to the presence of nitrogen if atmospheric air is used as a source of oxygen for combustion. The latter is the case in the ammonia oxidation reaction and in Figure (2.11), the effects of changes in the amount of air used on the amount of useful work that can be obtained from the reaction are shown*. The temperature of the products is assumed to be T = 850°C in all cases (as assumed by Denbigh):

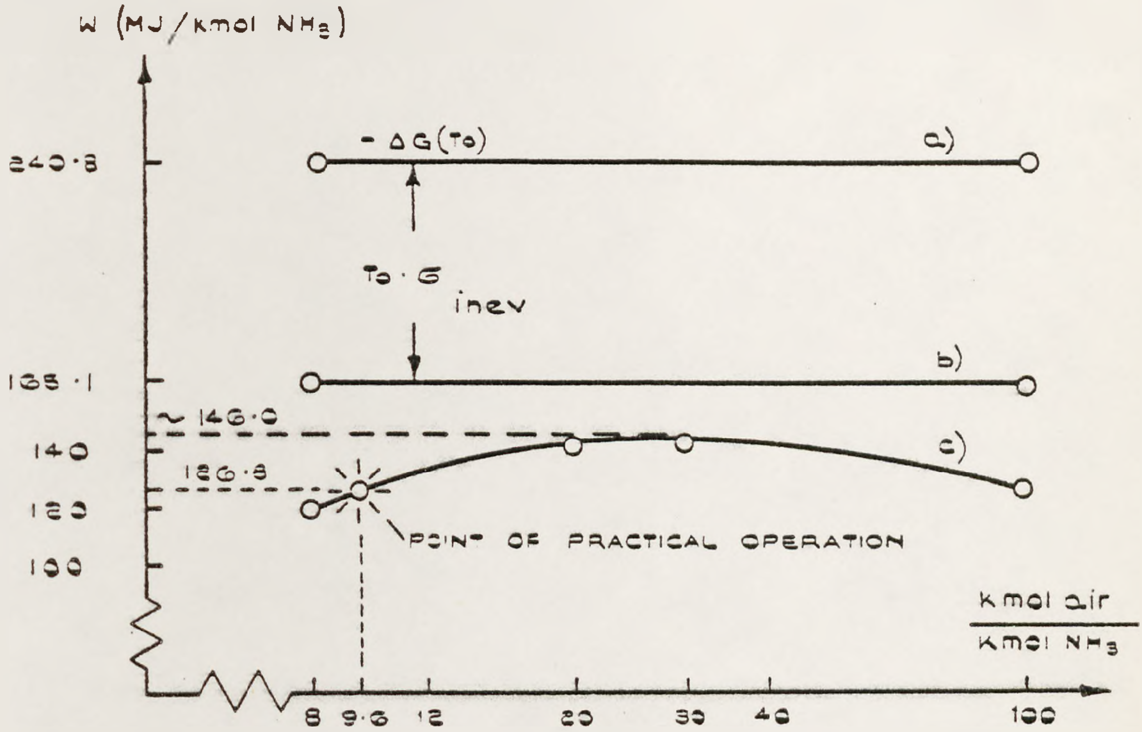

Figure (2.11) Effect of changes in mass flowrate on reversibility. (For explanations of graphs a), b), and c) see text.)

(a) <u>The reversible case (see Figure 2.9a)</u>. With increased mass flowrates, more work would have to be spent to preheat reactants but the work would be regained in full when cooling down products. The useful work obtained would, thus, be independent of the amount of excess

---

* The underlying data are those given by Aylward and Findlay(55), Chapter 6, with the figures for specific heat capacities assumed to be constant. Since it is the main purpose of Figure (2.11) to facilitate a <u>qualitative</u> discussion, this was felt to be adequate.

air used* and would amount to

$$-\Delta G(T_o) = 240.8 \text{ MJ/kmol NH}_3$$

(b) Case as shown in Figure (2.9b). The effect of increased mass flowrates would be entirely analogous to that in the reversible case. The amount of useful work obtained would thus be constant and equal to

$$165.1 \text{ MJ/kmol NH}_3.$$

(c) Case as shown in Figure (2.10) with $Q_R = 0$. Denbigh(31) gives the following equation for the ammonia oxidation reaction

$$NH_3 + 9.6 \text{ air} \rightarrow 1.5\ H_2O(g) + NO + 0.75\ O_2 + 7.6\ N_2$$

(i.e. he assumes a 60% excess of oxygen). Under these conditions, the enthalpy of the product stream at 850°C is large and to achieve an enthalpy balance, it is necessary to preheat the reactants even if no heat is removed from the reaction. With Equation (2.52), the useful work that could be obtained in this case is evaluated as

$$126.8 \text{ MJ/kmol NH}_3.$$

If the mass flowrates were increased further, the reactants would have to be preheated to a higher temperature but the exergy of the products would increase sufficiently for the overall amount of useful work that could be obtained to increase, too. Above a certain point, however, any further increase in mass flowrates would make it necessary to supply preheat at a temperature so high as not to make it worth while. At this point, which is given by $\approx$ 25 kmol of air supplied per kmol NH_3, graph c) in Figure (2.11) reaches its maximum with about

$$146 \text{ MJ/kmol NH}_3.$$

---

* As recommended in Section 2.5, the work to be gained by reversible mixing of gas flows is neglected.

Thus, only about (146/240.8 ≃) 61% of the useful work obtainable in the reversible case could be recovered, from a theoretical point of view, in case c), and only about (126.8/240.8 ≃) 53% if a practical mass flowrate was used. In case b), about (165.1/240.8 ≃) 69% would appear to be recoverable.

A Practical Suggestion

In the case of the ammonia oxidation reaction, the gas flow characteristics through the catalyst gauzes are of as much importance for a good conversion efficiency as the operating temperature (see Chapter Four). The positioning of heat exchangers in between the catalyst gauzes might, thus, be considered to be about equally impossible as a free choice of reaction temperature and the use of graph c) in Figure (2.11) rather than graph b) appears to be justified when determining the magnitude of inevitable irreversibilities. In the case of other reactions, however, heat removal directly from the reacting species - or, alternatively, in between reactor stages - might be possible or even necessary (e.g. to promote conversion). In such cases, the discrepancy between the results obtained by means of Equations (2.51) and (2.52) would be less marked (i.e. feasible points of operation would be somewhere in between graphs b) and c) in a diagram such as Figure 2.11). It follows that the scope available to the designer of a new plant for avoiding irreversibilities connected with exothermic reactions could be approximated by determining

- the highest practical temperature of the products,
- the largest amount of heat that could be removed directly from the reaction, as well as
- the highest, or lowest (see Figure 2.11), practical mass flowrate

and by comparing the corresponding "optimal" useful work that could be obtained to the "actual" in a proposed design:

$$W_{\text{optimal}} - W_{\text{actual}} = \left[Q_R \frac{(T_R - T_o)}{T_R} + Ex(T)^{PR} - Ex(T_{in})^{RE}\right]_{\text{optimal}} - \left[Q_R \frac{(T_R - T_o)}{T_R} + Ex(T)^{PR} - Ex(T_{in})^{RE}\right]_{\text{actual}}$$

(see Equation 2.52). Evidently, it would be legitimate to re-write this equation in the following form

$$(\Delta Ex_{irr})_{\text{avoidable}} = \left[Ex_{out} - Ex_{in}\right]_{\text{optimal}} - \left[Ex_{out} - Ex_{in}\right]_{\text{actual}} \qquad (2.53)$$

in which assumptions regarding insulation losses, etc., might be incorporated. Also, the equation might be applied to endothermic reactions, too. (It would, however, be necessary in the endothermic case to define the lowest practical temperature of the products and the smallest amount of heat that could be supplied to the reaction to identify the change in exergy for the "optimal" case). Equation (2.53) is compatible with Equation (1b) in Appendix A, which is expressed in entropy terms but based on the same considerations.

Summary

Denbigh(31) suggested the evaluation of Second Law efficiencies for industrial processes on the basis of prescribed degrees of irreversibility for the chemical reactions involved. Based on the assumption that reactions have to be carried out in conventional reactors at given temperatures, he derived Equation (2.51) for determining those irreversibilities which are inevitable. As is evident from Figure (2.11), these irreversibilities may account for more than half of the total to be associated with a chemical reaction. Thus, it would appear desirable that the concept of "inevitable irreversibilities" be used where Second Law analysis is employed in conventional process network design.

In addition, it would appear desirable to consider further constraints when evaluating inevitable irreversibilities: with Equation (2.53), the useful work equivalent may be evaluated that is lost in an actual case but could, perhaps, be recovered from a reaction even if allowances are made for constraints regarding (1) the feasibility of exchanging heat directly with the reacting species and (2) the feasibility of choosing mass flowrates. As is evident from Figure (2.11), the difference between results obtained from Equations (2.51) and (2.53) can, once again, be quite significant.

On first sight, assumptions concerned with practical aspects of heat transfer and mass flowrates might appear to be less rigid from a thermodynamic point of view than the assumptions on which Equation (2.51) is based. An assumption regarding the reaction temperature T, however, is necessary even in the case of Equation (2.51) and since, in many practical cases, the impossibility to keep the temperature of a reaction constant (and/or to choose mass flowrates) might be just as stringent as the impossibility to choose the temperature of the reaction, results obtained from Equation (2.53) could be considered to be no more subjective than those obtained from Equation (2.51). Generally, it is probably valid to say that, once a departure has been made from the rigid grounds of a "correct" Second Law analysis, the extent to which irreversibilities are considered to be inevitable must become a matter of judgement. The procedure suggested above allows one to use judgement by considering practical cases on individual grounds. In the limiting case where the assumptions which underlie Equation (2.51) are found to be appropriate, it will lead to the same results as the latter equation whereas, in other cases, the results will differ.

CHAPTER THREE

ENTROPY ANALYSIS OF A SULPHURIC ACID CONTACT PROCESS

In this chapter, an industrial process is analysed in entropy terms and the results are discussed in the light of practical scope for improved energy recovery. Conclusions are drawn regarding the usefulness of a Second Law analysis in such a context and schemes for improved energy recovery are identified. Also, the benefits are examined that may result from defining prescribed degrees of irreversibility and from using the numerical approximation method suggested in Chapter Two.

3.1 PROCESS DESCRIPTION

In the contact process, a mixture of oxygen and sulphur dioxide (which is, normally, obtained by burning sulphur) is reacted to form sulphur trioxide

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

in the presence of a catalyst (mostly platinum or vanadium oxides). The reaction is exothermic and low temperatures are required to favour equilibrium conversion to SO_3. On the other hand, the rate of reaction is considerably improved by increased temperature. Thus, cooling is usually effected gradually (i.e. in between stages). The sulphur trioxide is absorbed in 96-98% w/w acid to form the product by reaction with free water:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

There is no limit to the concentration that may be obtained and, in some instances, further trioxide is absorbed in pure acid to form fuming sulphuric acid:

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

The resulting mixture is called oleum. The absorption reactions are exothermic, too, but are carried out at low temperatures ($<100^oC$), so that extensive use of cooling water is made. The heat removed from the gas phase oxidation reaction, however, as well as the heat evolved when burning sulphur, is normally recovered.

Sulphuric acid plants used to constitute a major source of air pollution in the past, mainly due to incomplete conversion of the SO_2. For this reason, double absorption contact plants are built today. In these, some SO_3 is removed from the main gas flow in an intermediate absorber tower before the final conversion of the dioxide. With less SO_3 present, equilibrium conversion to SO_3 is favoured and less SO_2 reaches the stack.

The plant on which this case study is based is approximately ten years old and does not yet incorporate double absorption. (The overall conversion efficiency is approximately 98.3%). It is operated by ICI Ltd., Organics Division, and was designed by Sim-Chem Ltd. A rather unusual feature of the plant is the fact that only oleum is produced, while diluted acid is supplied to the plant. Nominal production capacity is 150 long tons/day of pure H_2SO_4 equivalent.

In Figure (3.1), a functional flowsheet is given showing the most important unit operations and material flows, see page 68 . A description of the flows is given in Table (3.1):

Table (3.1) Flow descriptions for contact process

Flow	Description	Flow	Description	Flow	Description
(1)	atm.air	(14)	sulphur (molten)	(29)	acid, 95.3% w/w
(2)	atm.air $p \sim 1.25$ atm.	(15)	SO_2-gas		
(3)	dry air $p \sim 1.25$ atm.	(16)	"	(30)	acid, 98.3% w/w
(4)	" "	(17)	"		
(5)	" "	(18)	"	(31)	acid, 98.1% w/w
(6)	" "	(19)	SO_2/SO_3-gas	(32)	"
		(20)	"	(33)	"
		(21)	SO_3-gas	(34)	"
		(22)	"	(35)	"
		(23)	"		
		(24)	stack gas	(36)	acid, 94.0% w/w
(9)	feed water 685 psia			(37)	"
(10)	water/steam "	(25)	oleum, 25% w/w	(38)	"
(11)	water "	(26)	"	(39)	"
(12)	saturated steam "	(27)	"		
(13)	superheated steam "	(28)	"	(40)	acid, 93.8% w/w

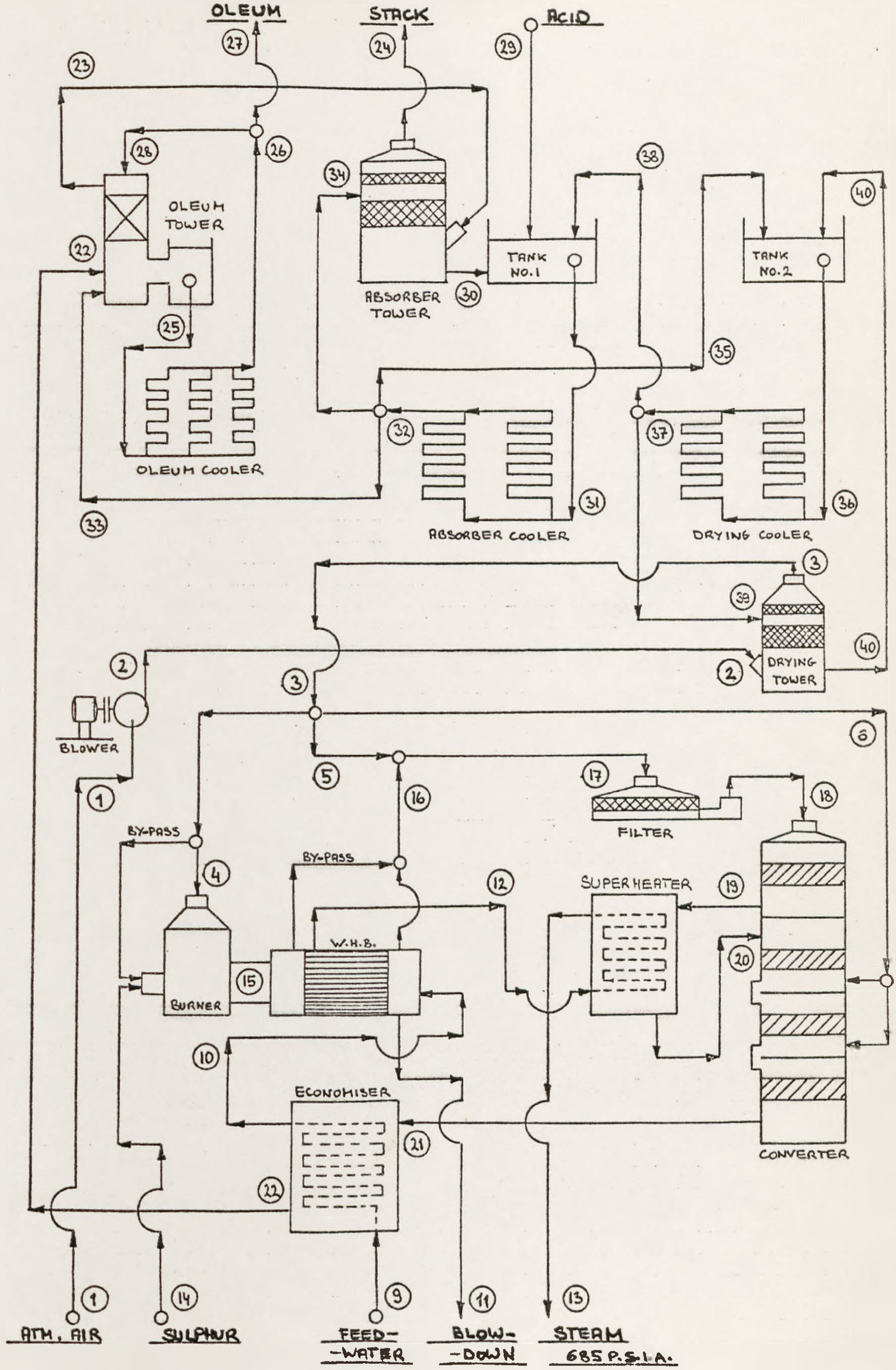

Figure (3.1) Functional flowsheet of contact process.

The following is a description of the process which has largely been taken from Sim-Chem Ltd's relevant information leaflet(66) but has been shortened and adapted in parts to match the particular plant shown in Figure (3.1) :

> Molten sulphur (14) is burnt in an air stream (4) which has been previously dried by contact with circulating sulphuric acid (39) and has also been boosted to sufficient pressure to drive the combustion gases through the plant.
>
> The SO_2-gases leaving the sulphur burner (15) are cooled in the waste heat boiler (W.H.B.), in which high pressure steam is raised, to the correct temperature for reaction of SO_2 and oxygen in the air, to produce SO_3 in the presence of the catalyst in the converter.
>
> The conversion is carried out in four stages with heat removal between the first two stages to control the temperature rise. The heat is used to superheat the steam raised (12). On the 2/3 stage and 3/4 stage cold air (6) is injected, having the double function of cooling the gases and supplying oxygen for the reaction.
>
> After the 4th stage of conversion, the SO_3 bearing gases (21) are cooled in an economiser, which preheats the boiler feed water (9) and pass,

in the particular case of the plant represented in Figure (3.1), into the oleum tower where some SO_3 is removed by contact with circulating oleum (28) and acid (33). From there, the gases (23) pass into the absorber tower where the remaining SO_3 is removed by contact with circulating acid (34).

The circulating acid (30) passes to a tank where it mixes with acid from the drying cycle (38) and with further acid (29) supplied from storage. From this tank, circulating acid (31) passes into a cooler and before it is passed back into the absorber tower, a make-up (35) is supplied to the drying cycle and the acid required for oleum formation (33) is supplied to the oleum tower.

3.2 HEAT AND MASS BALANCE

A design heat and mass balance was kindly made available by ICI Ltd. for the present study. The information contained in it, however, was incomplete and partly inconsistent. A consistent heat and mass balance is documented in Table (3.2) and Figure (3.2), see pages 71 and 72. All figures quoted refer to one minute of steady state operation at nominal production capacity and figures for enthalpy relate to a zero state of $p_{RS} \rightarrow 0$ and $T_{RS} = 0^{\circ}C$. In Figure (3.2), only enthalpy figures are shown (in MJ).

Results

Boxed entries in Figure (3.2) denote the total contribution of heats of reactions and/or mixing within the unit represented. (All these terms are exothermic). The non-boxed entries within unit operations denote loads on the acid and oleum coolers and insulation losses. All other entries represent enthalpies of flows (compare Table 3.2). The fact that all figures are given with two significant digits behind the decimal point bears no resemblance to the likely accuracy of the study; it is merely convenient for any checks to be carried out. Comments concerning the accuracy of the data used are given in Appendix B, where the physical property data for this study is documented. In Figures (3.3) and (3.4) on pages 73 and 74, two sketches are given which help to localise individual reactions and non-ideal mixing. These sketches correspond to Tables (3.3) and (3.4) which in turn, are based on data derived in Appendix B.

Table (3.2) Heat and mass balance of H_2SO_4/oleum contact process

Flow	T	m	S(ℓ)	H_2O(ℓ)	H_2O(g)		N_2		O_2		H(T,p)
	(°C)	(kg)	(kg)	(kg)	(kg)	(kmol)	(kg)	(kmol)	(kg)	(kmol)	(MJ)
(1)	20	462.4	0	0	6.5	0.361	350.6	12.52	105.3	3.29	9.43
(2)	39	"	0	0	"	"	"	"	"	"	18.44
(3)	50	455.9	0	0	0	0	"	"	"	"	23.04
(4)	"	319.8	0	0	0	0	245.9	8.78	73.9	2.31	16.16
(5)	"	26.1	0	0	0	0	20.1	0.72	6.0	0.19	1.32
(6)	"	110.0	0	0	0	0	84.6	3.02	25.4	0.79	5.56
(9)	92	136.1	0	136.1	0	0	0	0	0	0	52.43
(10)	260	"	0	118.8	17.3	0.961	0	0	0	0	183.46
(11)	260	12.3	0	12.3	0	0	0	0	0	0	13.99
(12)	260	123.8	0	0	123.8	6.876	0	0	0	0	346.27
(13)	400	"	0	0	"	"	0	0	0	0	396.28
(14)	140	35.2	35.2	0	0	0	0	0	0	0	6.20
			SO_2(g)		SO_3(g)						
			(kg)	(kmol)	(kg	(kmol)					
(15)	930	355.0	70.4	1.10	0	0	245.9	8.78	38.7	1.21	342.16
(16)	464	"	"	"	0	0	"	"	"	"	162.75
(17)	∿435	381.1	"	"	0	0	266.0	9.50	44.7	1.40	164.07
(18)	430	"	"	"	0	0	"	"	"	"	161.96
(19)	588	"	26.9	0.42	54.4	0.68	"	"	33.8	1.06	226.91
(20)	463	"	"	"	"	"	"	"	"	"	175.92
(21)	440	491.1	1.2	0.02	86.5	1.08	350.6	12.52	52.8	1.65	217.69
(22)	180	"	"	"	"	"	"	"	"	"	85.91
(23)	45	439.4	"	"	34.8	0.44	"	"	"	"	19.58
(24)	65	404.6	"	"	0	0	"	"	"	"	26.86
			H_2O(ℓ)	H_2SO_4(ℓ)	SO_3(ℓ)						
			(kg)	(kg)	(kg)						
(25)	∿56.9	4113.7	0	3085.2	1028.5						311.67
(26)	35	"	0	"	"						191.71
(27)	35	167.4	0	125.5	41.9						7.80
(28)	35	3946.3	0	2959.7	986.6						183.91
(29)	90	74.4	3.5	70.9	0						10.26
(30)	∿75.5	4140.7	71.1	4069.6	0						453.40
(31)	∿75.4	4372.6	84.0	4288.6	0						478.34
(32)	70	"	"	"	0						442.90
(33)	70	115.7	2.2	113.5	0						11.72
(34)	70	4105.9	78.9	4027.0	0						415.89
(35)	70	151.0	2.9	148.1	0						15.29
(36)	∿64.2	3379.3	202.3	3177.0	0						334.83
(37)	60	"	"	"	0						311.84
(38)	60	157.5	9.4	148.1	0						14.53
(39)	60	3221.8	192.9	3028.9	0						297.31
(40)	∿63.9	3228.3	199.4	"	0						319.52

All Figures are Based on One Minute Steady State Operation

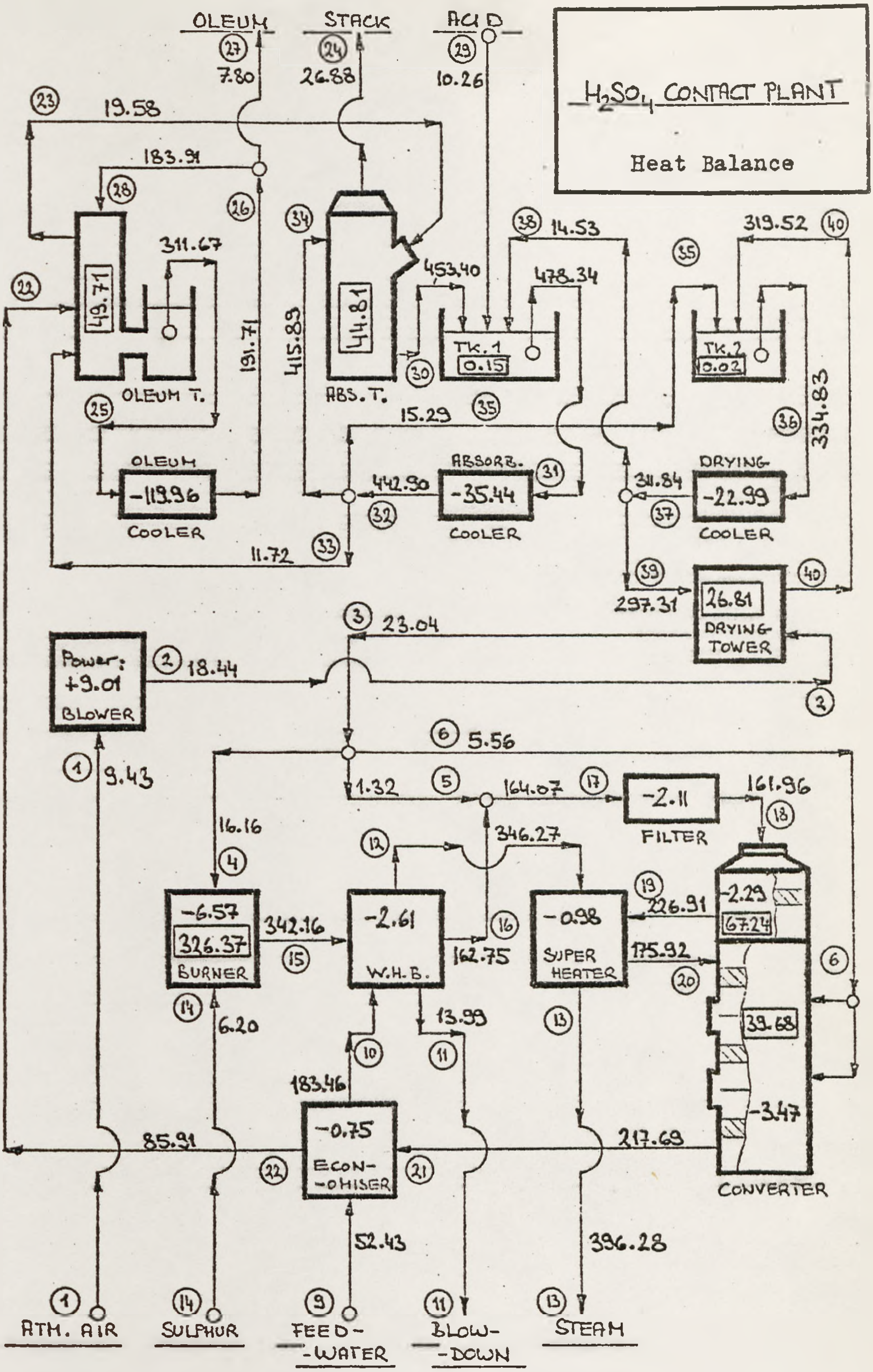

Figure (3.2) Heat balance for contact process.

(For explanation of figures shown see text.)

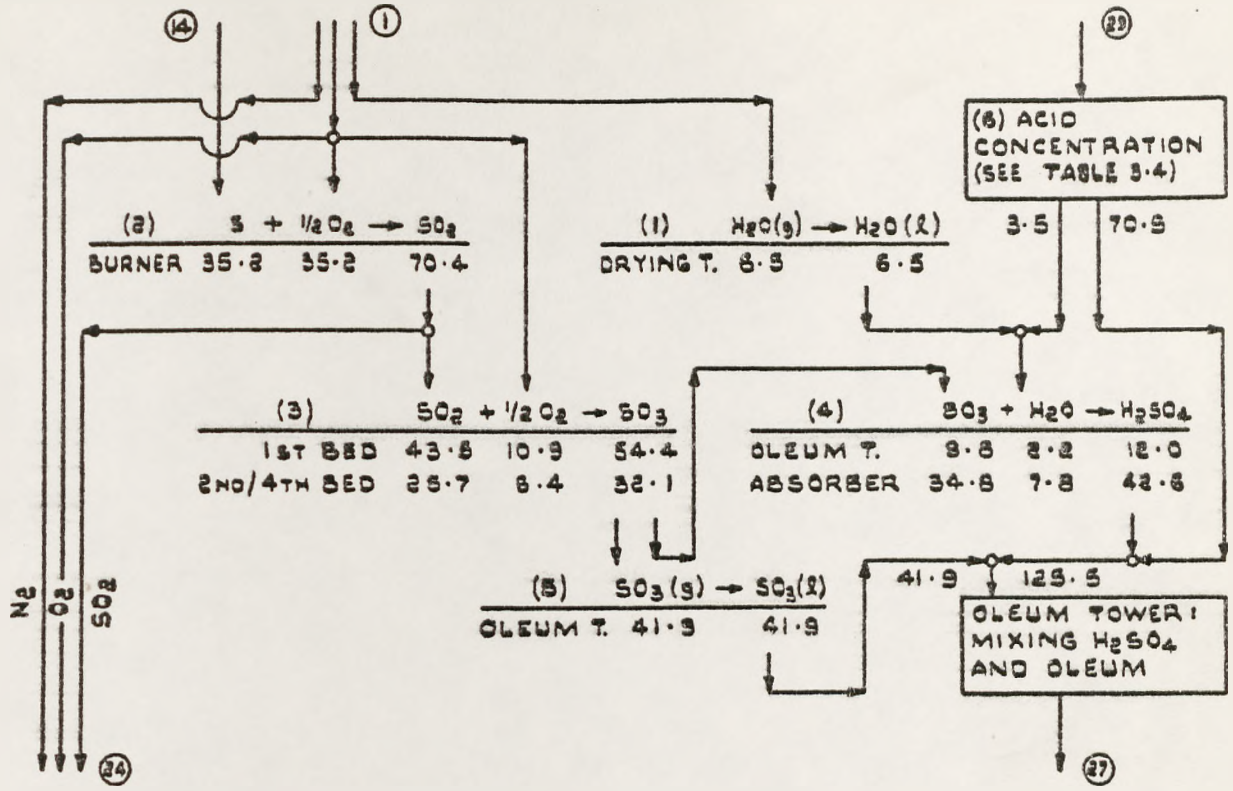

Figure (3.3) Reaction path in contact process. (Compare below.)

Table (3.3) Localisation of reactions for contact process

	Reactions		$\Delta hoR_{RS,RS}$	$\Delta soR_{RS,RS}$
Unit	Type	Extent	(MJ)	(kJ/^oK)
Drying Tower	(1)	6.5 kg	-15.90	-44.27
Burner	(2)	70.4 kg SO_2	-326.37	+13.38
1st Bed	(3)	54.4 kg SO_3	-67.24	-4.79
2nd/4th Bed	(3)	32.1 kg SO_3	-39.68	-2.82
Oleum Tower	(4) (5)	9.8 kg SO_3 41.9 kg SO_3	-16.34 -26.27	-20.96 -83.84
Absorber Tower	(4)	34.8 kg SO_3	-58.01	-74.44
Mixing of SO_3 (ℓ) and H_2SO_4 (ℓ) in Oleum Tower : $\Delta hoM_{RS,RS}$ = (-3.5 kJ/kg/%) * 125.5kg * 25% = -10.98 MJ				

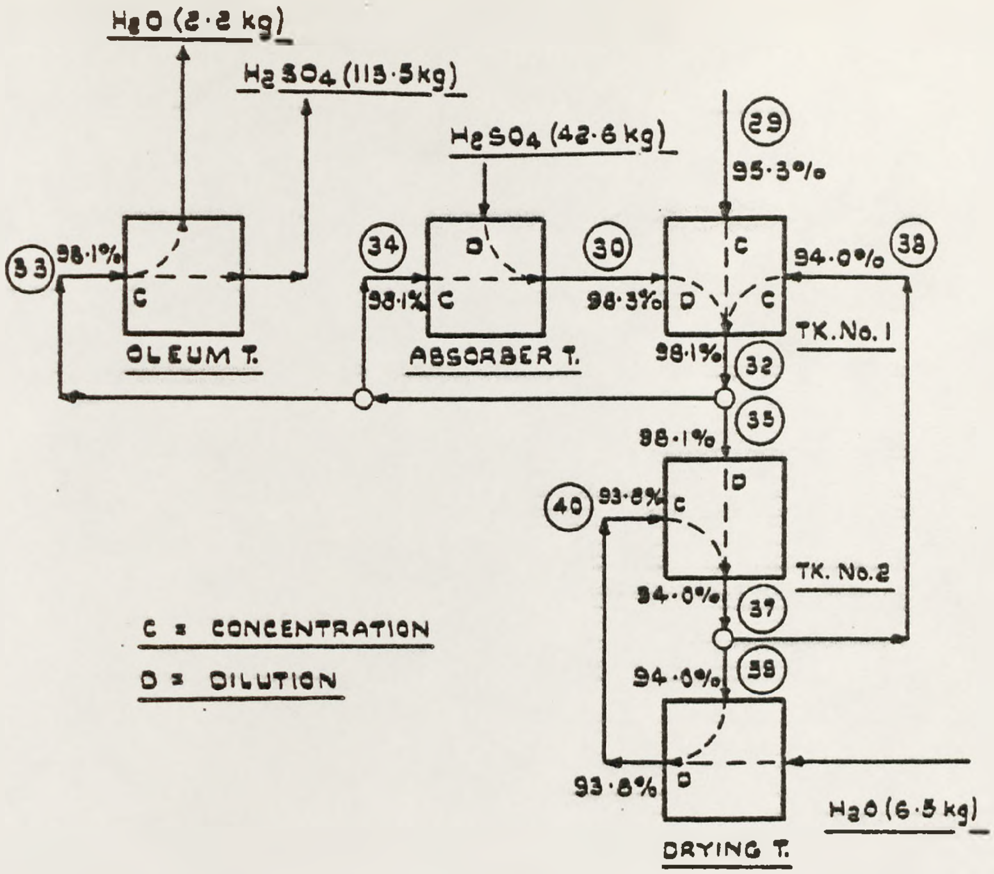

Figure (3.4) Non-ideal mixing in contact process. (Compare below.)

Table (3.4) Heats of acid mixing in contact process

	CODE	$m_{H_2SO_4}$ (kg)	CONC.$_{in}$ (%)	CONC.$_{out}$ (%)	Δ CONC. (%)	$\Delta HoM_{RS,RS}$ (MJ)
Oleum Tower	C	113.5	98.1	100.0	+1.9	+3.88
Absorber Tower	C D	4027.0 42.6	98.1 100.0	98.3 98.3	+0.2 -1.7	+14.51 -1.31
Tank No.1	C D C	70.9 4069.6 148.1	95.3 98.3 94.0	98.1 98.1 98.1	+2.8 -0.2 +4.1	+3.57 -14.65 +10.93
Tank No.2	D C	148.1 3028.9	98.1 93.8	94.0 94.0	-4.1 +0.2	-10.93 +10.91
Drying Tower	D	3028.9	94.0	93.8	-0.2	-10.91
Check :						Σ = + 6.00
Overall	C	70.9	95.3	100.0	+4.7	+ 6.00

Main Assumptions

When establishing this heat and mass balance, care was taken that

- overall conversion efficiency,
- compositions and temperatures of the gas flows in and out of the converter, and
- acid and oleum concentrations

assumed values as specified in the design heat and mass balance. The temperatures of input and output streams were assumed as observed on the plant and when their total enthalpy was compared to the overall heat of reaction and non-ideal mixing, a not-accounted-for loss of ∿18 MJ/min was identified. Although this figure could be explained by an error in the overall heat of reaction of only 3%, it was considered to be, probably, a realistic representation of insulation losses and was therefore "spread" over the seven unit operations in which insulation losses could be assumed (see Figure 3.2). Since a similar standard of insulation is used throughout the plant, the magnitudes of these losses relative to each other were based on the exposed surface areas and on the approximate process temperatures. The temperatures eventually obtained for the various process streams resemble the figures monitored on the plant very closely.

Power for Blower

Since the plant operates at substantially atmospheric pressure throughout, no account was taken of flow-individual pressure terms. To establish the power consumption of the blower, however, the (oral) information was used that the pressure increase across the blower amounts to about 60 to 70 inches H_2O (i.e. ∿0.165 bar) : if the compression was adiabatic and reversible, the temperature of the compressed air (2) would be given by the following equation

$$T_{2\,\text{reversible}} = T_1 * \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}}$$

with T in $^{\circ}K$

and $\kappa = cp/cv$ (~ 1.4 for air)

(see any textbook). This would give a figure of $T_2 \sim 33^{\circ}C$. Assuming however, an "isentropic efficiency"* of 0.7, i.e.

$$\frac{W_{\text{reversible}}}{W_{\text{actual}}} \sim 0.7$$

the actual temperature rise will be approx. 1/0.7 times greater and one obtains

$$T_2 = 39^{\circ}C.$$

The enthalpy change which corresponds to these assumptions is 9.01 MJ/min, or approx.

$$W_{\text{Blower}} \sim 200 \text{ BHP}$$

which appears to be a realistic figure. Compared to the heat recovered in the steam, this is less than 3%.

Energy for Start-ups

Although this is not of direct relevance for steady state design, it was thought worthwhile to examine the approx. energy consumption for start-ups. According to oral information, there are 40 start-ups a year, during each of which about 750 therms of natural gas are required for the converter and about half as much again for the burner. Assuming that the plant operates 320 days/year at nominal capacity, this is equivalent to a steady state consumption of about

8.2 MJ/min

Thus, one may state that the energy consumption for start-ups is about equal, per unit product, to the power requirement for the blower.

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* For definition and practical figures see e.g. Baehr(7).

Brief Evaluation

In Figure (3.5), a "typical example" of a single absorption sulphur-burning contact plant is shown as given by Duecker and West$^{(69)}$. In Table (3.5), the corresponding energy inputs and outputs are listed indicating that ∿56% of the energy turnover is recovered in steam.

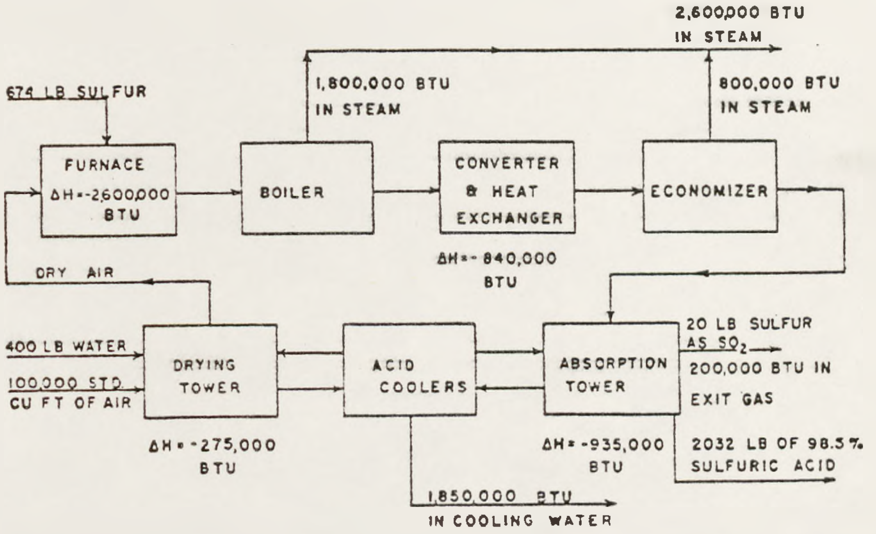

Figure 14.9. Typical heat and materials balance for a sulfur-burning contact sulfuric acid plant. (*Courtesy of Titlestad Corporation.*)

Figure (3.5) Heat and mass balance for a typical sulphur burning contact plant. (Source: Duecker and West$^{(69)}$.)

Table (3.5) Overall heat balance of typical contact plant

Inputs		Outputs	
Chemical Reactions	100%	Stack	4.3%
		Cooling Water	39.8%
		Steam	55.9%

Table (3.6) Overall heat balance for contact plant case study

Inputs	H (MJ/min)	%	Outputs	H (MJ/min)	%
Boiler Feed W. (9)	52.43	8.1	Blowdown (11)	13.99	2.2
Sulphur (14)	6.20	1.0	Stack (24)	26.88	4.2
Acid (29)	10.26	1.6	Product (27)	7.80	1.2
Air (1)	9.43	1.5	Σ (Cooling)	178.39	27.8
Power	9.01	1.4	Σ (Insulation)	18.78	2.9
Chemical Reactions and Mixing	554.79	84.6	Steam (13)	396.28	61.7
	Σ_{IN} = 642.12	100.0		Σ_{OUT} = 642.12	100.0

In Table (3.6), a similar list has been made up for the present case study. There is a clear similarity between the patterns emerging from Tables (3.5) and (3.6), with the energy recovery in steam appearing to be slightly more successful in the present case study.

An allowance should be made, however, for the fact that the plant shown in Figure (3.5) produces diluted acid whereas the plant studied here produces oleum. A significant amount of heat which will evolve when mixing the oleum with water to produce pure or diluted acid does not appear in the energy balance of the case study process itself. Assuming that no acid was imported and pure H_2SO_4 was produced, the inputs in Table (3.6) due to "Chemical Reactions and Mixing" would increase by as much as 38.6 MJ/min and, accordingly, the need for cooling would rise by about the same margin, whereas the usefully recovered energy (in steam (13)) would remain unaffected. As a result, the energy i steam would only amount to approx. 58% of the turnover. Thus, the energy utilisation of the process under study would appear to be "typical" (see above) once an allowance has been made for the rather unusual feature of exclusive oleum production.

When considered in more detail, the process could be seen as consisting of two separate sub-processes, namely a "high temperature" section in which SO_3 bearing gases are produced, and a "low temperature" section in which the absorption takes place (see Figure 3.6). There are only two energy transfers between these two sections, effected by the exchange of matter (stream (22) and water in the drying tower) and heat (in the drying tower). In the high temperature section, ∿77% of all energy inputs are diverted into the useful output (i.e. steam (13)) and in the low temperature section, practically no useful output is obtained. Obvious possibilities to

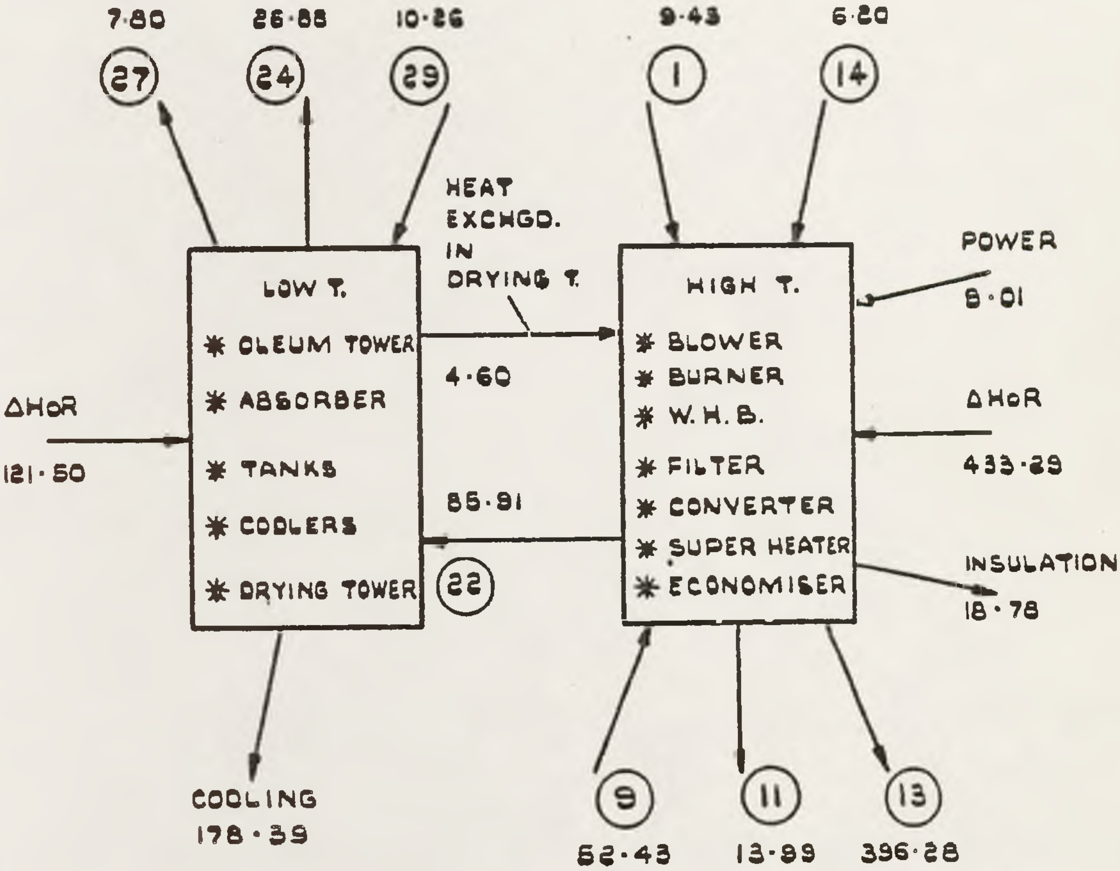

Figure (3.6) Dividing the contact process in two sections.

improve the overall energy performance would, thus, be to try and

- decrease the enthalpy of stream (22)
- decrease insulation losses and/or mass flowrate of blowdown
- recover some independent useful output (i.e. low temperature heat) from the low temperature section, or
- increase the amount of heat given from the low temperature section to the high temperature section.

The extent to which any of these policies is feasible and, may be, worthwhile will be discussed further below.

3.3 ENTROPY ANALYSIS

In a heat balance, the extent to which energy is directed into desirable and undesirable directions is examined and the term "loss" is usually applied to energy which leaves a process along an undesirable path. As a corollary, "losses" in a heat balance occur only at the boundary of the system under examination. In a Second Law analysis, the term "loss" is applied to quantities which are destroyed rather than misdirected (i.e. the potential for effecting energy transfers and transformations). Such "losses" occur at the boundaries of systems as well as inside : if a particular unit operation is carried out in a highly irreversible fashion, a corresponding "loss" will be identified in the same spot. From this, the basic assumption originates which is usually made in the literature, and which is mentioned in Appendix A, that each piece of equipment in a process can - in first approximation - be held responsible for the non-ideal energy performance of the whole process to a degree which is measured by the irreversible entropy change σ occuring in it.

In Table (3.7), the entropies of the process streams are listed, see page 82. The necessary calculations were based on the physical property data given in Appendix B. In the case of the gas phase streams

(No.1 through No.6 and No.15 through No.24), Equation (2.46) was used

$$\underset{\text{ideal gas}}{s_2 - s_1} = \int_1^2 cp * \frac{dT}{T} - R * \ell n \frac{p_2}{p_1} \qquad (2.46)\ \text{Repeat}$$

and the entropy changes due to the diffusion of gases were neglected (see in 2.5). For the calculation of the entropy integral, the polynomials given in Appendix B were used. In the case of the water/or steam streams (No.9 through No.13) and the sulphur stream (No.14), the values tabulated in Appendix B for entropy were used, and for the oleum and acid streams (No. 25 through No. 40), the calculations were based on specific heat capacities as given in Appendix B (i.e. constant value for oleum and first order polynomials for acid). Since the computations based on polynomials are quite cumbersome, a short computer program was written for the evaluation of the polynomials.

In Table (3.8), the entropy balance is shown for each unit operation according to Equations (2.26) through (2.28). The terms for the overall entropy change of reaction within each unit operation are readily calculated from the information given in Table (3.3). The terms concerned with the ambient heat production are computed from the information given in Figure (3.2) and based on the assumption $T_o = 20^oC$. When considering the terms for the "created entropy", σ, a small negative figure for "tank No.2" will be noticed. This is, of course, infeasible. However, it is explained by the fact that the entropies of streams in minus out constitute a difference of large numbers, so that even the rounding of temperatures to $1/10^oC$ can lead to sufficient numerical inaccuracies to suggest a decrease in entropy where only a small increase exists.

Table (3.7) Entropies of streams for contact process

Stream No.	S(T,p) kJ/°K	Stream No.	S(T,p) kJ/°K	Stream No.	S(T,p) kJ/°K
(1)	33.30	(15)	533.29	(29)	32.38
(2)	62.85	(16)	345.31	(30)	1462.81
(3)	77.22	(17)	356.42	(31)	1544.96
(4)	54.17	(18)	353.56	(32)	1441.56
(5)	4.42	(19)	436.82	(33)	38.14
(6)	18.63	(20)	372.75	(34)	1353.64
		(21)	470.16	(35)	49.78
		(22)	241.22	(36)	1099.53
(9)	165.50	(23)	66.24	(37)	1031.21
(10)	446.78	(24)	88.40	(38)	48.06
(11)	35.51			(39)	983.15
(12)	742.80	(25)	1036.98	(40)	1049.83
(13)	826.24	(26)	660.73	(One minute steady state operation)	
		(27)	26.88		
(14)	17.37	(28)	633.85		

Table (3.8) Entropy balances for unit operations in contact process

Unit operation	$\sum_{i=n}^{n} S_i(T,p)$	$\Delta SoR^{overall}_{RS,RS}$	Q/T_o	σ	%
	(kJ/°K)				(-)
Blower	29.55	/	/	29.55	2.5
Drying Tower	81.05	-44.27	/	36.78	3.1
Burner	461.75	13.38	22.42	497.55	42.0
W.H.B.	143.55	/	8.91	152.46	12.9
Junction	6.69	/	/	6.69	0.6
Filter	-2.86	/	7.20	4.34	0.4
1st Bed	83.26	-4.79	7.82	86.29	7.3
Superheater	19.37	/	3.34	22.71	1.9
2nd/4th Bed	78.78	-2.82	11.84	87.80	7.4
Economiser	52.34	/	2.56	54.90	4.6
Oleum Tower	190.01	-104.80	/	85.21	7.2
Oleum Cooler	-376.25	/	409.42	33.17	2.8
Absorber	131.33	-74.44	/	56.89	4.8
Tank No.1	1.71	/	/	1.71	0.1
Absorber Cooler	-103.40	/	120.96	17.56	1.5
Tank No.2	-0.08	/	/	-0.08*	0.0
Drying Cooler	-68.32	/	78.46	10.14	0.9
Overall	728.48	-217.74	672.93	1183.67	100.0
(One minute steady state operation)			* see text for explanation		

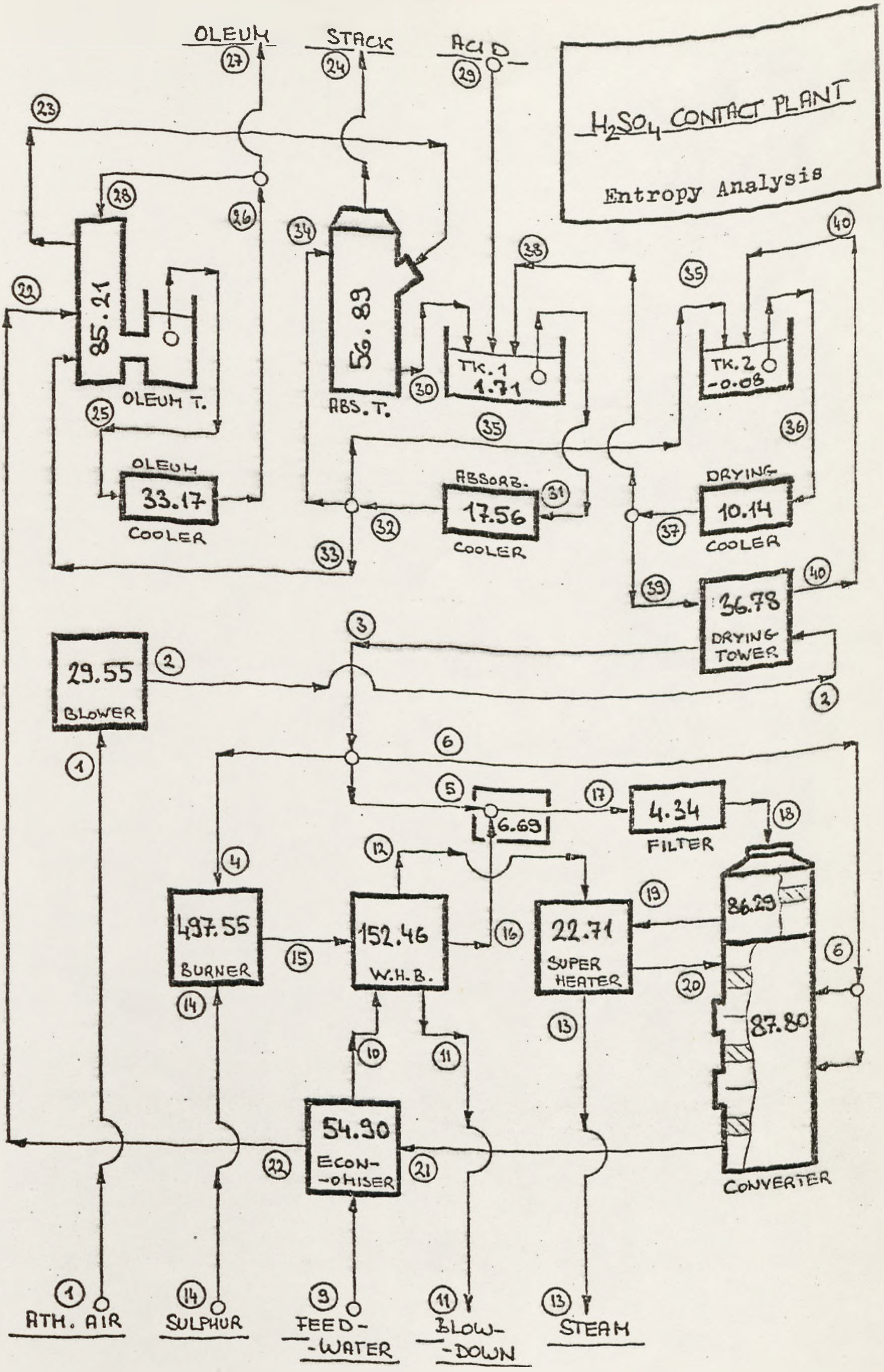

Figure (3.7) Irreversible entropy changes σ for unit operations in contact process.

Finally, the percentage to which each unit operation may be considered to contribute to the overall irreversible entropy increase is also given in Table (3.8). In Figure (3.7), the results listed in Table (3.8) are shown in the flowsheet context.

3.4 NUMERICAL APPROXIMATION METHOD

To provide some evidence regarding the computational accuracy of an analysis based on the formulae presented in Section 2.4, another entropy analysis for the present case study has been evaluated, independent of the first one.

In Table (3.9), the entropies of the process streams are listed as evaluated by means of Equation (2.47), based on the information contained in the heat and mass balance (i.e. Table 3.2). As an example, the enthalpy of stream No.18 is given in Table (3.2) with

$$H(T) = 161.96 \text{ MJ/min}$$

and its temperature with 430°C. Thus, its entropy can, with Equation (2.47), be approximated as

$$S(T) = 161.96 * \frac{\ln((430 + 273)/273)}{430} \quad \text{MJ/}^{\circ}\text{K/min}$$

$$= \underline{\underline{356.27 \text{ kJ/}^{\circ}\text{K/min}}}$$

(see Table 3.9). This particular figure is about 0.8% different from the equivalent one listed in Table (3.7) which was obtained by integration of third order polynomials for all components.

When approximating the entropies of streams where a phase change occurs between the reference temperature ($T = 0^{\circ}C$) and the process stream temperature, information about the latent heat and the phase change temperature is required. For streams No.10, No.12 and No.13, (i.e. where steam is involved), this information is found in Table (B.2) and for stream No.14 (i.e. the molten sulphur), figures are given in Table (B.3) which describe the specific

Table (3.9) Entropies of streams for contact process (Approximated calculations) (One minute steady state operation)

Stream No.	S(T,p) (kJ/°K)	% error *	Stream No.	S(T,p) (kJ/°K)	% error *	Stream No.	S(T,p) (kJ/°K)	% error *
(1)	33.34	0.1	(15)	545.65	2.3	(29)	32.48	0.3
(2)	63.14	0.5	(16)	348.34	0.9	(30)	1466.29	0.2
(3)	77.50	0.4	(17)	359.43	0.8	(31)	1547.18	0.1
(4)	54.36	0.4	(18)	356.27	0.8	(32)	1444.23	0.2
(5)	4.44	0.5	(19)	443.26	1.5	(33)	38.22	0.2
(6)	18.70	0.4	(20)	376.83	1.1	(34)	1356.15	0.2
			(21)	474.96	1.0	(35)	49.86	0.2
			(22)	241.70	0.2	(36)	1101.52	0.2
(9)	165.51	0.0	(23)	66.39	0.2	(37)	1032.56	0.1
(10)	452.08	1.2**	(24)	88.32	0.1	(38)	48.11	0.1
(11)	36.00	1.4				(39)	984.45	0.1
(12)	747.78	0.7**				(40)	1051.64	0.2
(13)	831.10	0.6**	(25)	1036.98	/			
			(26)	660.73	/			
			(27)	26.88	/			
(14)	17.54	1.0**	(28)	633.85	/			

* See Table (3.7) for comparison

** incl.phase change

Table (3.10) Entropy balances for unit operations in contact process (Approximated calculations)

Column:	1	2	3	4	5	6	7
Unit operation	$\sum_{i=1}^{n} S_i(T,p)$	$\Delta SoR^{\text{overall}}_{RS,RS}$	Q/T_o	σ	% error	%	%*
	(kJ/°K /min)				(-)		
Blower	29.80	/	/	29.8	0.8	2.5	2.5
Drying Tower	81.55	-44.27	/	37.28	1.4	3.1	3.1
Burner	473.75	13.38	22.42	509.55	2.4	42.9	42.0
W.H.B.	134.39	/	8.91	143.30	6.0	12.1	12.9
Junction	6.65	/	/	6.65	0.6	0.6	0.6
Filter	-3.16	/	7.20	4.04	6.9	0.3	0.4
1st Bed	86.99	-4.79	7.82	90.02	4.3	7.6	7.3
Superheater	16.89	/	3.34	20.23	10.9	1.7	1.9
2nd/4th Bed	79.43	-2.82	11.84	88.45	0.7	7.4	7.4
Economiser	53.31	/	2.56	55.87	1.8	4.7	4.6
Oleum Tower	189.60	-104.80	/	84.80	0.5	7.2	7.2
Oleum Cooler	-376.25	/	409.42	33.17	/	2.8	2.8
Absorber	132.07	-74.44	/	57.63	1.3	4.8	4.8
Tank No.1	0.3	/	/	0.3	82.0	0.0	0.1
Absorber Cooler	-102.95	/	120.96	18.01	2.6	1.5	1.5
Tank No.2	0.02	/	/	0.02	125.0	0.0	0.0
Drying Cooler	-68.96	/	78.46	9.50	6.3	0.8	0.9
*See Table (3.8)				Σ = 1188.62		100.0	

enthalpy of sulphur as a function of temperature in the relevant interval. Based on this table, Figure (3.8) has been drawn.

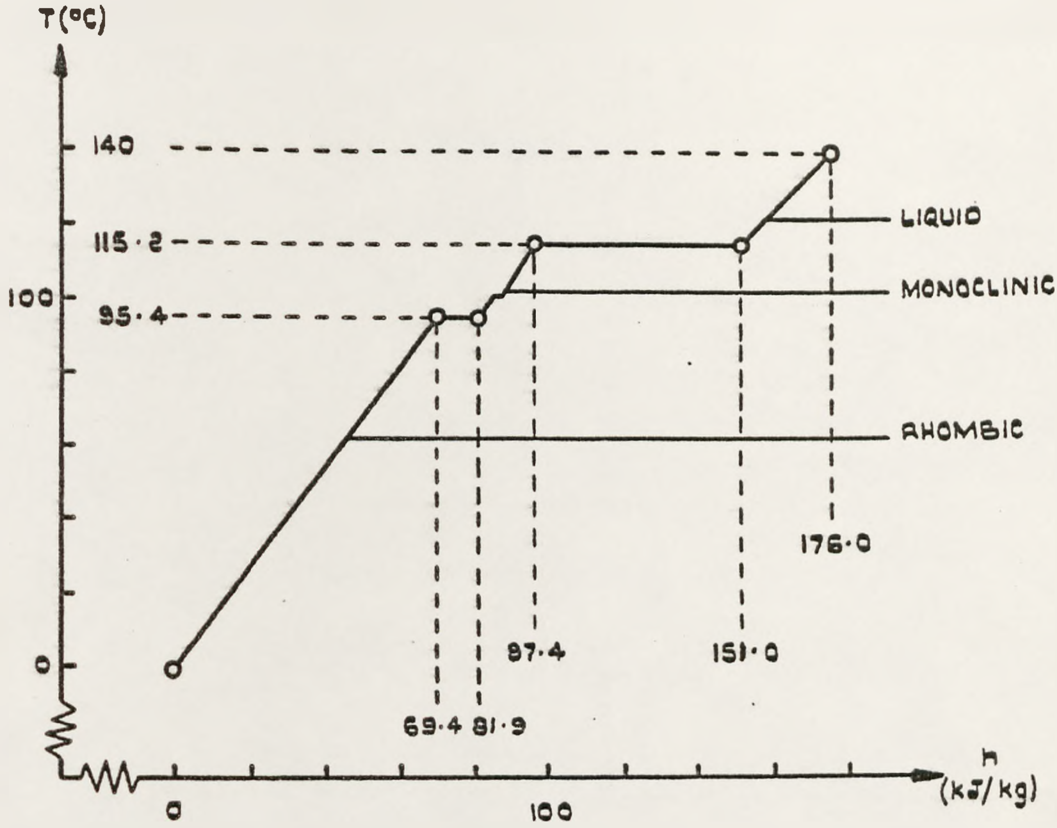

Figure (3.8) T,h-diagram for sulphur. (Source: Duecker and West(69).)

A seemingly crude approximation for the specific entropy, based on Figure (3.8), would be:

$$
\begin{aligned}
s(140^{\circ}\mathrm{C}) - s(0^{\circ}\mathrm{C}) = {} & 97.4 * \frac{\ell n((115+273)/273)}{115} && \text{(heating up solid)} \\
& + (151-97.4) * (1/(115+273)) && \text{(solid}\rightarrow\text{liquid)} \\
& + (176-151) * \frac{\ell n((140+273)/(115+273))}{(140-115)} && \text{(heating up liquid)} \\
= {} & \underline{\underline{0.4983\ \mathrm{kJ}/^{\circ}\mathrm{K}/\mathrm{kg}}}
\end{aligned}
$$

(Note the rounding of temperatures and the fact that the transition from rhombic to monoclinic sulphur has been ignored).

It is on this value that the entropy of stream No.14 has been based in Table (3.9) and the error as against the "correct" figure taken from Duecker and West(69) is about 1.0%. - This as well as all other deviations of the approximated figures from the equivalent "correct" ones are given in Table (3.9) in percentage terms.

As was to be expected, no deviations are found in the case of the oleum streams (No.25 through No.28), since constant specific heat was assumed, anyway, for oleum (see Appendix B). Also, only very minor deviations are found for the acid streams:

the "correct" calculations had been based on first order polynomials, see Table (B.3). As for the remaining streams, there are only five cases where the deviation exceeds one percent and only one case where it exceeds two percent (i.e. 2.3% for stream No.15). Bearing in mind, however, the temperature involved in this case ($T_{15} = 930^{\circ}C$), even this result can be considered to be quite good. Surely, this kind of accuracy could not be expected from an approximation which is based on the assumption cp = const unless the arguments put forward in Section 2.4 are considered.

In Table (3.10), the entropy balance for each unit operation is shown, again, in the same way as in Table (3.8), but based on the approximated figures for the entropies of the process streams. In column 5 of Table (3.10), the deviations in entropy changes σ of the individual unit operations when compared to the equivalent figures in Table (3.8) are given in percent. In column 6, the magnitude of each individual entropy change σ is, as it was done in Table (3.8), expressed as a percentage of the total, and in column 7, the equivalent figures are given once more as they were evaluated in Table (3.8). Evidently, a practically identical picture emerges from the approximate calculations as it did from the "correct" ones.

The reasons why the eventual results are so little affected by the approximations are easily understood : a figure for σ as obtained in column 4 of Table (3.10) constitutes the arithmetic sum of entropy inputs and outputs which, by themselves, may be many times larger than σ. Thus, small deviations in the entropies of input and output streams may result in sizeable ones for σ. (See, e.g., the deviations obtained in the case of the superheater and, especially, of the two tanks). On the other hand, this effect is bound to become especially marked in the context of the smaller figures for σ rather than the larger ones and, as a result, the importance of the individually identified figures for σ relative to each other is practically not affected. (A deviation of 11% for the σ of the superheater leads to a relative assessment of 1.7% instead of 1.9%, and so on.)

Coming to the question, then, whether or not an approximate entropy analysis such as the one derived here would be generally acceptable as a substitute for a "correct" one, both analyses, the one given in Table (3.8) and the one given in Table (3.10), ought to be considered in the light of the uncertainties which are already inherent in a usual heat and mass balance such as shown in Table (3.2). Uncertainties in the polynomials (with regard to fitting the original physical property data), uncertainties in the original physical property data themselves (incl. heats of reaction), and, most important, uncertainties with regard to the true compositions, mass flowrates, temperatures, and heat losses in the process should amount to at least ±3% overall uncertainty in the entropies of process streams even when the most careful of computational procedures were employed. From this point of view, the deviations noted in Table (3.9) would appear to be quite irrelevant and the differences between Table (3.10) and Table (3.8) could be considered to express no more than the sensitivity of the results of an entropy analysis to perfectly normal uncertainties in the original process description. It must even be regarded as a matter of chance whether results obtained in a "correct" analysis would be closer to the truth than the results of an equivalent approximate analysis: the fact that the small negative figure for σ which was evaluated in Table (3.8) for tank No.2 has turned into a small positive figure in Table (3.10) illustrates this point.

3.5 PRESCRIBING IRREVERSIBILITIES

Measured on grounds of relative magnitudes of the individual entropy increases listed in Table (3.10), the combustion of sulphur would deserve prime attention in the present case study: more than 40% of the overall entropy increase occurs in the burner. Next, there are sizeable contributions in the converter (∿15%), in the waste heat boiler (∿12%), and in the oleum tower (∿7%). The remainder of the overall entropy increase (∿23%) is spread over the remaining twelve unit operations. Thus, the major share of the irreversibilities appears to be due to chemical reactions and, in this situation, it seems appropriate to examine which irreversibilities are "inevitable" with present day technology (see in Section 2.6) :

The Burner. The temperature at which the products of the reaction

$$S + O_2 \rightarrow SO_2$$

are available is limited by practical considerations concerned with materials of construction. One might assume that, specific advantages shown, a temperature $T_{15} = 1100^\circ C$ might be acceptable for the product gases. The possibility, however, to install a heat exchanger directly in the burner (see in Section 2.6) shall not be considered : the technological difficulties would appear to be prohibitive. Thus, a situation exists for which graph c) in Figure (2.11) is applicable : the highest thermodynamic efficiency that can realistically be obtained in the burner is defined by the highest[*] practical mass flowrate with a corresponding amount of preheating for the input streams so that the highest product temperature defined above is reached. A practical limit for the mass flowrate of the process gases, however, is rather difficult to define. The conversion efficiency of the $SO_2 \rightarrow SO_3$ equilibrium reaction would not be adversely affected by an additional excess of oxygen and the obvious factor that would define a limit would be the capital costs per unit product. In the present context (of establishing thermodynamic limits), however, capital cost considerations should not be conclusive : first, it is necessary to examine what an improved thermodynamic efficiency would be worth. Thus, it was assumed that the mass flowrate of combustion air (4) might be increased by 20%[**]. This would be sufficient to clarify whether or not improvements could result that would, overall, be worthwhile:

$$\underline{m_4 = 319.8 \text{ kg/min}}$$

$$\rightarrow$$

$$\underline{\overset{*}{m}_4 = 383.6 \text{ kg/min}}$$

with the superscript "*" indicating a modification as compared to the original case study.

Assuming, further, that no heat is lost through the walls in an "optimal" arrangement,

$$\overset{*}{Q} = 0$$

one obtains:

---

[*] The conclusion that the mass flowrates must be increased (rather than decreased) is easily drawn when considering that, in the present case, the reactants exist at relatively low temperatures. (Compare text to Figure 2.11, case c) in Section 2.6).

[**] Some of the increase could, evidently, be provided by diverting flow (5) - partly or in whole - through the burner and the waste heat boiler.

$$\overset{*}{m}_{15} = m_{15} + (\overset{*}{m}_4 - m_4)$$

$$\overset{*}{H}_{15} = H_{15} * \frac{\overset{*}{m}_{15}}{m_{15}} * \frac{\overset{*}{T}_{15}}{T_{15}}$$

$$\overset{*}{H}_4 = H_4 * \frac{\overset{*}{m}_4}{m_4} * \frac{\overset{*}{T}_4}{T_4}$$

$$(\overset{*}{H}_4 + \overset{*}{H}_{14}) = (H_4 + H_{14}) + (\overset{*}{H}_{15} - H_{15}) - Q$$

$$\overset{*}{H}_{14} = H_{14} + (\overset{*}{T}_{14} - T_{14}) * Cp_{14}$$

$$\overset{*}{T}_{14} = \overset{*}{T}_4$$

The last two equations follow from initial checks which have made it clear that considerably more preheat is required than could be accommodated by flow (4) alone at temperatures below 140°C (i.e. the original temperature of the sulphur (14)). The equations are easily solved one by one and the results are listed in Table (3.11). Also in this table, the new values for the entropies of the three streams in question are listed (they were evaluated by means of Equation 2.47).

Table (3.11) Parameters describing "optimal" arrangement for burner

	$\overset{*}{m}$ (kg/min)	$\overset{*}{T}$ (°C)	$\overset{*}{H}(T,p)$ (MJ/min)	$\overset{*}{S}(T,p)$ (kJ/°K/min)
(4)	383.6	354	137.27	322.42
(14)	35.2	354	13.80	32.41
(15)	418.8	1100	477.44	701.09

With these results, the term

$$(S_{out} - S_{in})_{\text{optimal}} = \overset{*}{S}(T)_{15} - \overset{*}{S}(T)_{14} - \overset{*}{S}(T)_4$$

$$= 342.26 \text{ kJ/°K/min}$$

can be computed. Based on Table (3.10) and Figure (3.2),

$$(S_{out} - S_{in})_{\text{actual}} = S(T)_{15} - S(T)_{14} - S(T)_4 + Q/T_o$$

$$= 496.17 \text{ kJ/°K/min}$$

and the "avoidable" entropy rise $\bar{\sigma}$ is, thus, found to be:

$$\bar{\sigma}_{\text{Burner}} = (S_{\text{out}} - S_{\text{in}})_{\text{actual}} - (S_{\text{out}} - S_{\text{in}})_{\text{optimal}}$$

$$= \underline{\underline{153.91\ \text{kJ}/^{\circ}\text{K/min}}}$$

The Converter. The standard entropies of the products of the reaction

$$(Y)\text{AIR} + SO_2 \rightarrow SO_3 + (0.21Y - 0.5)O_2 + (0.79Y)N_2$$

are smaller than the ones of the reactants (see Table 3.10). This indicates that, with rising temperature T, the Free energy change approaches zero, i.e. equilibrium conditions are approached. Also, for high conversions of SO_2 to SO_3, the temperatures which define equilibrium are smaller than for low conversions : above $T = 700^{\circ}C$, equilibrium conversions are below 50% and only for $T < 500^{\circ}C$, conversions of over 90% are theoretically possible (see Duecker and West$^{(69)}$). Thus, heat has to be removed from the reaction at temperatures low enough to guarantee satisfactory conversion. In the present case study, this is done by means of

- the superheater (between first and second stage of conversion), and
- two "cold shots" (i.e. air injected between 2nd and 3rd and between 3rd and 4th stage).

Assuming that the temperatures of the reacting species as found in the case study represent upper limits from the conversion efficiency point of view, there is only one way worth considering to increase the thermodynamic efficiency of the converter: the injected air(6) could be preheated and the additional energy so introduced into the converter could be removed at reaction temperature by means of another interstage heat exchanger, such as the superheater. A corresponding arrangement, which should enable a similar conversion to be reached as in the original case study, is shown in Figure (3.9).

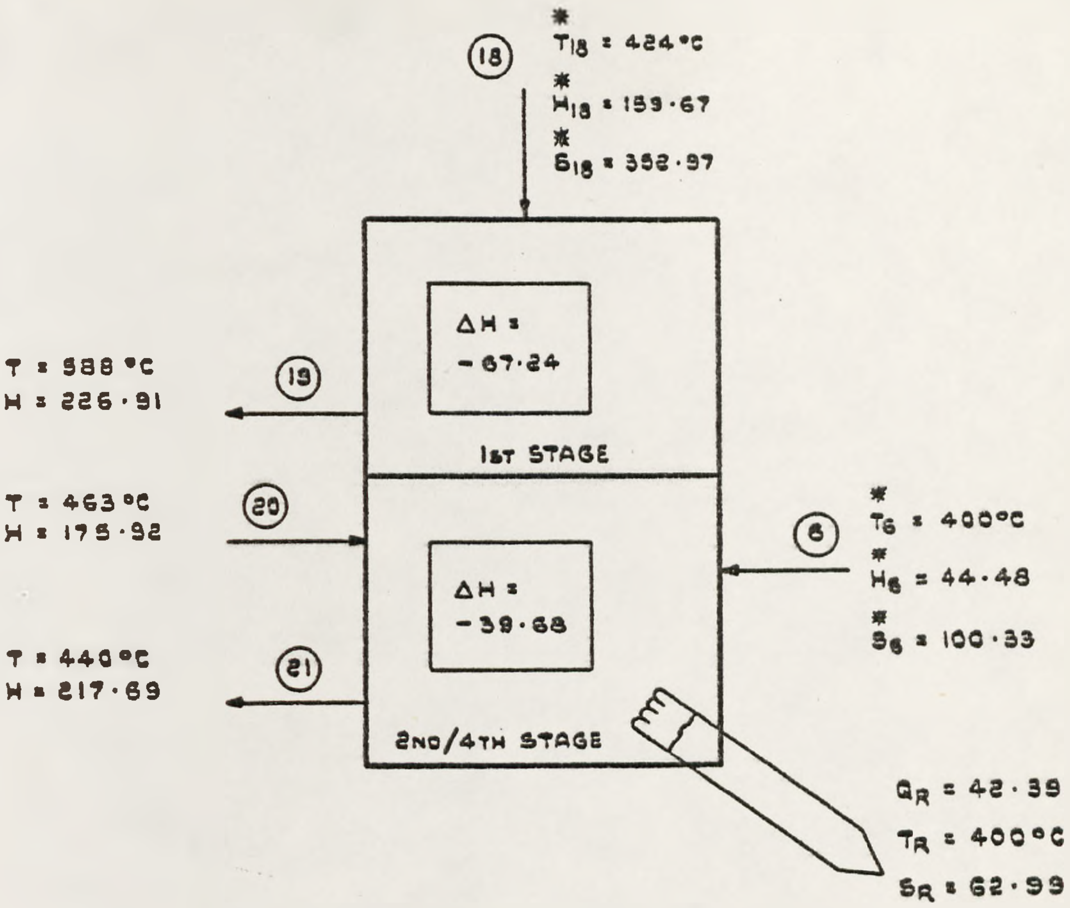

Figure (3.9) "Optimal" arrangement for SO_2 - SO_3 conversion.

Since the arrangement is to represent an "optimal" one, no insulation losses have been assumed. Further, no changes to the mass flowrates have been assumed. The reason is that, with input streams that are considerably "preheated" in the terms of Figure (2.11), the mass-flowrates would have to be <u>de</u>creased to improve thermodynamic efficiency and this would adversely affect conversion efficiency.

The figures for temperatures, enthalpies and entropies shown in Figure (3.9) have been evaluated in an equivalent way as in the case of the burner, compare Table (3.11). With the entropies $\overset{*}{S}_{18}$, $\overset{*}{S}_{6}$ and

S_R, and with the information given in Table (3.9), it is possible to evaluate the terms

$$(S_{out} - S_{in})_{optimal} = 90.29 \text{ kJ}/^{o}\text{K/min}$$

for the first stage of conversion and

$$(S_{out} - S_{in})_{optimal} = 60.79 \text{ kJ}/^{o}\text{K/min}$$

for the remaining stages. This leads, after comparison with the figures listed in Table (3.10), to the following figures for the "avoidable" entropy rises:

$$\underline{\underline{\bar{\sigma}_{1st\ Stage} = 4.52 \text{ kJ}/^{o}\text{K/min}}}$$

and

$$\underline{\underline{\bar{\sigma}_{2nd-4th\ Stage} = 30.48 \text{ kJ}/^{o}\text{K/min}}}$$

<u>The Oleum Tower</u>. The overall heat of reactions and of non-ideal mixing in the oleum tower is exothermic and this would indicate that one should try and raise input temperatures. However, there is a large recycle stream (i.e. the oleum cycle) which causes all output temperatures to be considerably lower than input temperature T_{22}. Thus, additional enthalpy in stream No.22 would be degraded and one has to try and lower T_{22} by as much as possible. A temperature of $T_{22} = 80^{o}$C would, probably, not impair the absorption efficiency and the figures listed in Table (3.12) are based on this assumption. To maintain the heat balance, a corresponding decrease for T_{25} was assumed:

Table (3.12) "Optimal" arrangement for oleum tower

	$\overset{*}{T}$ (^{o}C)	$\overset{*}{H}$(T,p) (MJ/min)	$\overset{*}{S}$(T,p) (kJ/^{o}K/min)
(22)	80	38.18	122.65
(25)	48.2	263.94	890.34

Based on these figures and on Tables (3.9) and (3.10), the "avoidable" entropy increase in the oleum tower is obtained:

$$\underline{\underline{\bar{\sigma}_{\text{Oleum Tower}} = 27.59 \text{ kJ}/^{\circ}\text{K/min}}}$$

To check the likely effects which changes in mass flowrates could have, the flowrate of oleum stream No.28 was considered reducible to 90% of its present value. With a corresponding rise in output temperature T_{25}, this was found to lead to a figure of

$$\bar{\sigma} = 28.09 \text{ kJ}/^{\circ}\text{K/min}$$

i.e. the effect is negligible. This is understandable since the heat released in the oleum tower is quite small compared to the turnover. Thus, even significant changes in mass flowrates effect only minor changes in temperature.

The Absorber Tower. The situation in the absorber tower is similar to the one in the oleum tower with the exception that the temperatures of the gas flows already assume values which are low as well as similar to each other. Thus, only marginal improvements could be achieved when modifying temperature and/or mass flowrate specifications. In a practical sense, there are not many irreversibilities in the absorber tower that could be avoided:

$$\underline{\underline{\bar{\sigma}_{\text{Absorber}} \simeq 0}}$$

The Drying Tower. In the drying tower, condensation of water and dilution of acid lead to an increase in temperature of both the acid and the air. If both input temperatures were increased, the accompanying entropy increase would become smaller. Also, the mass flowrate of the acid might be decreased but, similarly as in the oleum and in the absorber tower, the effect would be negligible. Based on the assumption that acid could be fed into the drying tower with $\overset{*}{T}_{39} = 70^{\circ}\text{C}$ and air with $\overset{*}{T}_2 = 50^{\circ}\text{C}$, and that the changes in temperature remained unaltered, the "avoidable" entropy increase in the drying tower is:

$$\underline{\underline{\bar{\sigma}_{\text{Drying Tower}} = 2.33 \text{ kJ}/^{\circ}\text{K/min}}}$$

Summary and Comment

Some of the irreversibilities termed "avoidable" above might not be completely avoidable in realistic circumstances. Further, some "avoidable" irreversibilities would - even though their prevention might be practical - better not be avoided if the consequences for the process as a whole were examined : a high burner gas temperature, e.g., will increase the thermodynamic efficiency of the burner but might decrease that of the waste heat boiler. Thus, it might be argued that such points of view ought to be considered when irreversibilities are prescribed. However, irreversibilities which are not examined on grounds of "inevitability" feature the same drawbacks and, consequently, it was felt premature to try and take a detailed account of practicality or network considerations when prescribing irreversibilities.

On the other hand, there is an important difference between "avoidable" entropy changes such as have emerged from calculations above and other entropy increases that have not been interfered with: the latter type can never be completely avoided in practice (because equilibrium conditions would have to be reached) whereas the former could, perhaps, be avoided in full. Depending upon how drastic the limits chosen for operating conditions are, they might be reached if advantages in doing so are shown. This leads on to the question whether irreversibilities might not preferably be prescribed in <u>all</u> unit operations so as to make allowance for the fact that equilibrium conditions are unobtainable. The concept of "inevitable" losses could be carried further by assuming, e.g., a finite minimum temperature difference within each heat exchanger and by comparing actual irreversibility to that which would result if minimum temperature difference was achieved. However, by assuming a minimum irreversibility for a given operation, the operation is implicitly accepted as necessary and, as pointed out in the

Introduction, one ought to examine whether a particular process step is at all necessary before trying to improve it. Thus, no practical "optimum" conditions were defined in this case study for unit operations not involving reactions. This strategy would appear to suit the situation where a reaction path is given and the designer's freedom of choice is restricted to selecting from alternative physical processing operations.

In Table (3.13), the entropy analysis of the process is presented as it finally emerges after the entropy increases found to be "inevitable" have been eliminated. In column 3, all entropy increases that would deserve attention are listed and in column 4, their relative magnitudes are expressed in percentage terms. When interpreting these figures, one can work on the assumption that something could be done about any of these irreversibilities by means of conventional technology. To facilitate comparison with the previous analysis, in which no difference

Table (3.13) "Avoidable" entropy changes $\bar{\sigma}$ for contact process

Column :	1	2	3	4	5
Unit Operation	$(S_{out}-S_{in})$ actual	$(S_{out}-S_{in})$ optimal	$\bar{\sigma}$	%	%
Blower	29.80	0	29.80	5.5	5.5
Drying Tower	81.55	79.22	2.33	0.4	$\boxed{6.9}$
Burner	496.17	342.26	153.91	28.5	$\boxed{94.4}$
W.H.B.	143.3	0	143.30	26.6	26.6
Junction	6.65	0	6.65	1.2	1.2
Filter	4.04	0	4.04	0.7	0.7
1st Bed	94.81	90.29	4.52	0.8	$\boxed{16.6}$
Superheater	20.23	0	20.23	3.7	3.7
2nd/4th Bed	91.27	60.79	30.48	5.7	$\boxed{16.4}$
Economiser	55.87	0	55.87	10.4	10.4
Oleum Tower	189.60	162.01	27.59	5.1	$\boxed{15.7}$
Oleum Cooler	33.17	0	33.17	6.2	6.2
Absorber	132.07	132.07	0.0	0.0	$\boxed{10.7}$
Tank No.1	+0.30	0	0.30	0.1	0.1
Absorber Cooler	18.01	0	18.01	3.3	3.3
Tank No.2	0.02	0	0.02	0.0	0.0
Drying Cooler	9.5	0	9.50	1.8	1.8
Note: Units as in Table (3.10)			$\Sigma = 539.72$	100.0	220.2

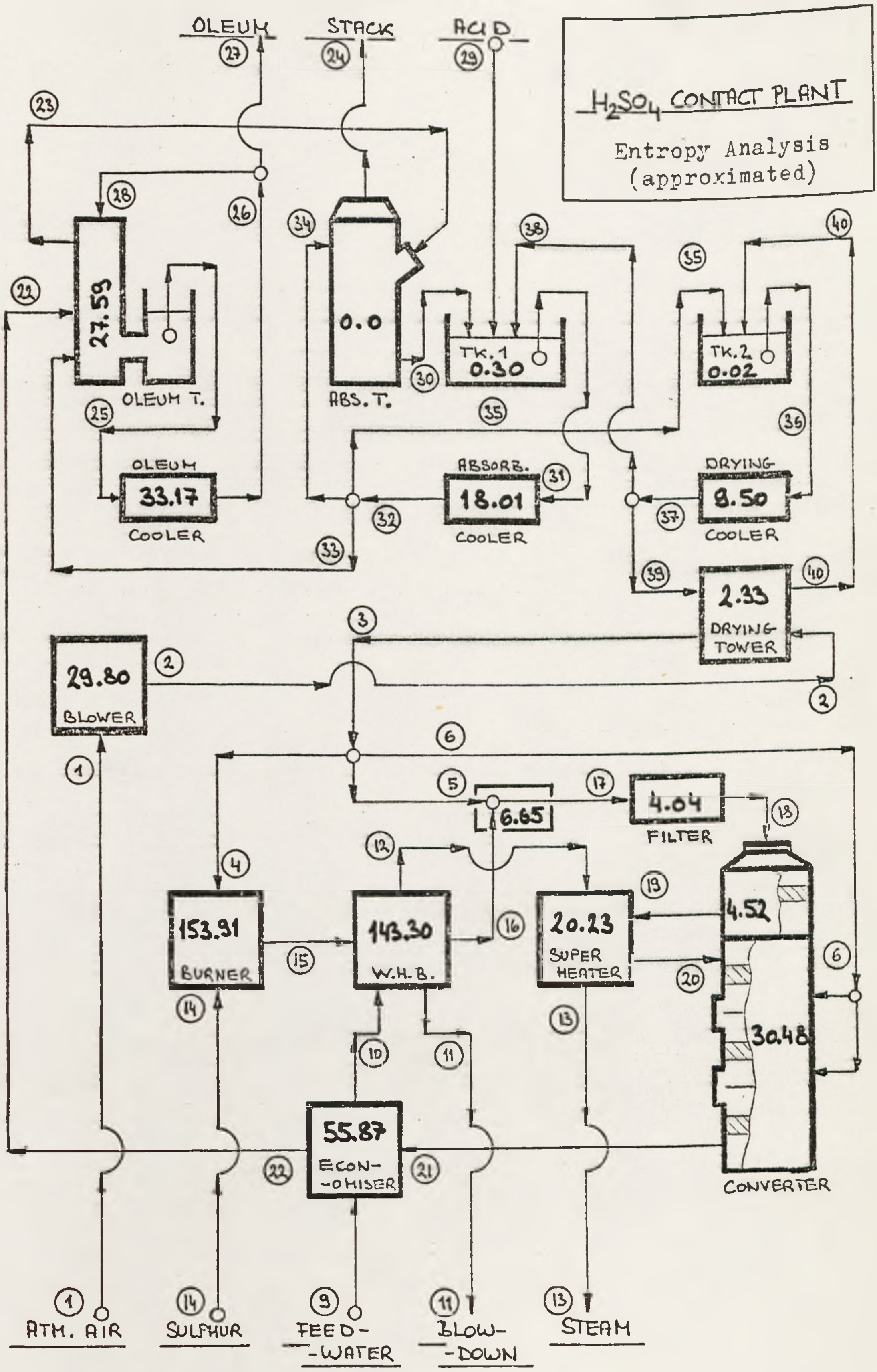

Figure (3.10) "Avoidable" entropy changes $\overline{\sigma}$ for unit operations in contact process.

was made between "avoidable" and "inevitable" entropy increases, the figures for σ evaluated in Table (3.8) have also been expressed in percentage terms, on the same basis, and have been listed in column 5. If these figures are compared to the ones in column 4, differences arise only in the cases of those unit operations which involve chemical changes (the relevant figures are shown boxed in column 5). The differences are, however, big enough to suggest relative priorities for the individual unit operations which are decidedly dissimilar. Also the overall entropy increase turns out different by more than one in two : less than half of the overall entropy increase listed in Table (3.8) can, realistically, be avoided. In Figure (3.10), the "avoidable" entropy changes are shown in the flowsheet context.

3.6 INTERPRETATION : GENERATION OF WORK

Due to the fact that the process is operated more or less at atmospheric pressure, the "avoidable" irreversibilities finally listed in Table (3.13) and shown in Figure (3.10) are all of a similar kind: they are connected with the degradation of heat.* In the burner, in the converter, and in the absorption section, heat is not sufficiently upgraded in the course of reactions and in the heat exchangers, the coolers, and in the mixing junction, heat is degraded due to heat transfer at finite temperature differences. Thus, all these irreversibilities could be avoided if the products of reactions were obtained at the highest practical temperatures and if ideal Carnot engines were employed in every case of heat transfer. The overall work gained in these Carnot engines would amount to

$$T_o * \bar{\sigma}_{overall} \quad \simeq 160 \text{ MJ/min}$$

i.e. would constitute approximately as much work equivalent again as

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*With the exception of the irreversibility in the blower, see Section 3.2.

is already found in the steam raised (13):

$$Ex(T,p)_{13} = H(T,p)_{13} - T_o * S(T,p)_{13} \simeq 150 \text{ MJ/min}$$

Thus, the process can be said to be roughly 50% efficient in Second Law terms with inevitable irreversibilities excepted.

In practice, however, work generating equipment could not be spread over the whole plant and one would have to try and avoid as large a share of the overall irreversibilities as possible with as few installations as possible. In the present case study, 55% of the total "avoidable" losses are concentrated in the burner and the waste heat boiler and the remaining 45% are spread over the rest of the process. Since an improvement in the burner will lead to hotter burner gases, the chance seems to exist of fighting about half of the overall losses in one single installation which would replace, or partly replace, the waste heat boiler. The function of this installation would be to exploit, in the thermodynamic sense, the large temperature difference between the hot burner gases* and the steam raised (or an ambient heat sink if no steam was raised). Assuming that the installation would operate with an exergetic efficiency of about 70%, which would be a good practical value, the useful work gained would amount to approximately

$$W_{gained} \simeq \eta_{ex} * T_o * (\bar{\sigma}_{Burner} + \sigma_{W.H.B.}) \tag{3.1}$$

$$\simeq 62 \text{ MJ/min}$$

i.e. the energy recovery of the process would, in Second Law terms, be improved by roughly (62/150≃) 41%.

Having identified that direct exploitation of the potential of high gas temperatures is required, an arrangement such as sketched in Figure (3.11a) might be appropriate:

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* at about 1100°C, once the performance of the burner has been improved.

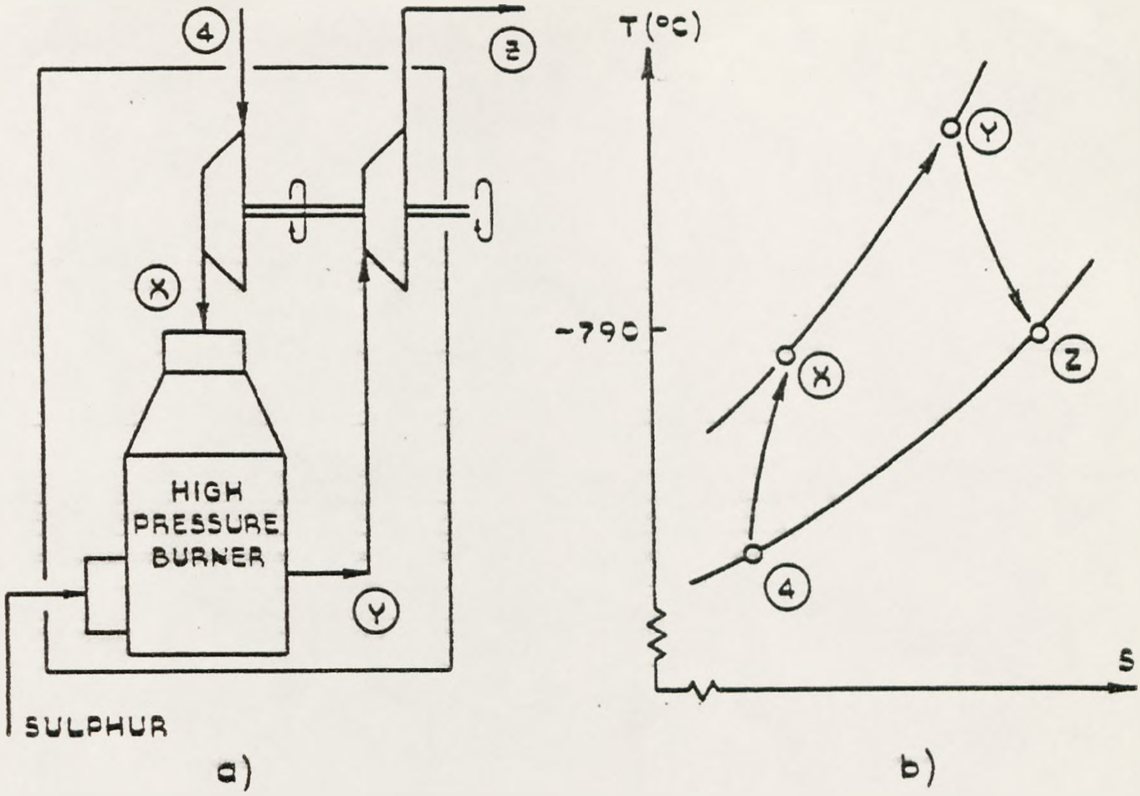

Figure (3.11) Arrangement for reduced losses in sulphur burner and waste heat boiler.

a) Functional flowsheet.

b) T,S-diagram representation.

The combustion of sulphur might be carried out under pressure and the combustion gases could drive a turbine which would provide the power necessary for compression, as well as some surplus power. Essentially, the arrangement represents an ordinary open gas turbine installation. In Figure (3.11b), the process is, qualitatively, sketched in a T,S - diagram. Based on the assumption that 20% of the heat of reaction could be won as surplus work*,

$$W_{surplus} = 65 \text{ MJ/min}$$

a heat balance can be made up for the system boxed in Figure (3.11a) to evaluate the temperature of the turbine exhaust gases:

$$T_Z \simeq 790^{o}C$$

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* see e.g. Baehr(7) for practical values.

Thus, steam could still be raised and, based on Table (3.2), the production of steam would only have to be decreased by about 18%. In Table (3.14), a crude comparison is given of the amount of work gained with and without gas turbine, as well as of other criteria of interest. The table is based on the assumption that the expansion equipment used to generate work from the HP steam would have an exergetic efficiency of $\eta_{ex} = 0.7$:

Table (3.14) Comparison between conventional steam raising process and process with gas turbine scheme

	Conventional Arrangement	Gas Turbine Scheme
Surplus work from gas turbine scheme	None	65 MJ/min
Process steam raised	123.8 kg/min	101.5 kg/min
Work from steam turbine	105 MJ/min	86 MJ/min
Total work gained	105 MJ/min	151 MJ/min
OTHER CONSIDERATIONS :		
Turbine, compr.,etc.	No	Yes
Steam raising plant	Larger	Smaller
Blower	Yes	No
Acid mist filter after drying tower	No	Yes

In thermodynamic terms, the adoption of the gas turbine would improve the process considerably but whether or not the scheme could ultimately be attractive, would depend upon capital cost considerations and problems of reliability and operability. Also, the HP steam raised might in some cases be used for process heating rather than for the generation of work and the marginal price of electricity might vary. However, with rising costs of fuels the scheme might become increasingly attractive. In Section 3.9, it will be discussed further.

When comparing the amount of extra work gained (i.e. 46 MJ/min, see Table 3.14) to the scope for improvement estimated before (i.e. 62 MJ/min, see Equation 3.1), the agreement is only approximate. However, it ought to be emphasised that Equation (3.1) and Table (3.14) are based on different as well as very crude assumptions. Generally, the rationale behind Equation (3.1) is obvious and there seems to be a case for recommending the procedure used above for crude estimations of the scope that might exist for improved energy efficiency in terms of generating work:

1) Make up Second Law analysis which lists "avoidable" irreversibilities.
2) Concentrate on single large irreversibilities, assume practical efficiencies for equipment to be used, and estimate scope for improvement as in Equation (3.1).
3) Define function which equipment has to fulfil to reduce irreversibilities and specify equipment accordingly in more detail.
4) Examine specified modification.

However, having made these recommendations, two snags ought to be pointed out. The first is the fact that there seems to be no general way of predicting practical efficiencies other than by specifying equipment. (This point is discussed in Appendix E where examples are shown of seemingly similar irreversibilities which are of different practical significance). Thus, estimates made under point 2 above can only be subject to revision under point 3 or point 4. The second snag is the fact that network interactions could be deliberately employed so as to create single large irreversibilities. In other words, one might shift several inefficiencies and concentrate them in a suitable unit operation only to introduce work generating equipment afterwards in that unit operation. Thus, it is necessary to consider not just those single large irreversibilities that emerge from an analysis but also those that could, perhaps, be created. This of course is a difficult task and success will largely depend upon experience and intuition.

3.7 INTERPRETATION : NETWORK INTERACTIONS

There is a fundamental difference between the substitution of equipment for improved energy recovery (e.g. the use of Carnot engines and heat pumps instead of a heat exchanger) and the modification of equipment for improved energy recovery (e.g. the increase of transfer area in a heat exchanger): substitute equipment will normally enable identical process stream outputs to be obtained from identical inputs (i.e. only utility streams are altered) whereas modified equipment will lead to different process outputs for changed inputs and vice versa. Thus, substitution of equipment does not necessarily lead to changes elsewhere in a network but modification does.

The type of improvements discussed in the last section relied largely on the substitution of existing plant by work generating equipment with consequently small effects in terms of network interactions. However, as was pointed out above, only large and isolated irreversibilities will normally justify the use of this approach. Smaller irreversibilities, by contrast, have to be dealt with by modifying existing equipment with sometimes marked and usually quite unpredictable changes caused elsewhere in the network. In the present section, some of the smaller irreversibilities listed in Table (3.13) are discussed in the light of their impact on the process as a whole. This will lead to conclusions which are not only compatible with, but usefully complement the ones drawn from the last section.

The Coolers. When trying to prevent the losses in the coolers, two strategies might be adopted : the first could be called the "First Law strategy" and would attempt to increase the useful outputs from the process elsewhere so as to reduce the need for cooling. The amount of additional enthalpy directed into useful outputs would thus, in First Law terms, correspond to the reduction in cooling requirements. The second could be called the "Second Law strategy" and would try to replace the coolers by work generating equipment.* This strategy would be based on the ideas outlined in Section 3.6.

A thorough assessment of the scope that would exist for improved energy performance of the process as a whole would have to carefully balance the "First Law strategy" against the "Second Law strategy". Even if work generating equipment was introduced, it might still be worthwhile to reduce the heat loads on the acid streams by increasing useful outputs elsewhere in the process. Alternatively, it might be advisable to increase the heat loads on the acid streams once that the alternative equipment is used. (This is in line with the idea put forward above of concentrating irreversibilities before introducing work generating equipment). Clearly, one would require simulations in heat and mass balance terms to obtain clarity. Thus, the role of a Second Law loss analysis seems, in this case, to be restricted to "flagging" a possibility for improved energy performance that may either be adopted or not, but the extent to which an overall improvement could be achieved if the possibility was adopted has to be examined by means of a conventional simulation.

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* It is clear that acid and oleum are not ideally suited for such a scheme, but the example is used only to discuss a general point.

Insulation Losses. In a heat balance, "losses" through the surface of plant are measured by reference to the quantity of heat involved and in a Second Law analysis, the source temperature of that heat is also important. Practically, however, the most important aspect of a loss might be where it occurs : poor insulation in the burner, e.g., would lead to lower burner gas temperature and, thus, to less steam raised. Poor insulation in the economiser, by contrast, would lead to a lower temperature T_{22} and thus to lower cooling requirements in the oleum cycle. In other words, the effect of poor insulation would be detrimental in one case but beneficial in the other.

To what extent, in either case, the effect would correspond to the quantity of heat lost, or to the entropy change σ, would have to be determined by means of a detailed simulation. However, it seems evident that straight-forward quantities of heat lost would often be of a better intuitive significance than corresponding entropy increases . To justify this point of view, it may suffice to repeat the following three simple facts:

(1) the significance of entropy changes σ is related to the generation of work (see Equation 3.1),

(2) insulation losses are normally small, and

(3) small losses do not normally justify the use of work generating equipment.

Thus, the conclusion reached is similar to that obtained in connection with the coolers : the role of entropy changes σ seems to be restricted to that of "flagging" an inefficiency but whether or not a realistic improvement could indeed be achieved, and how large it would be, has to be established by means of simulation.

The Superheater. Prevention of the loss in the superheater might be considered by way of changing input parameters (e.g. superheat steam at higher pressure) and/or by way of changing output parameters (e.g. superheat steam to higher temperature). The heat transfer area would have to be increased in either case. Also, the amount of heat removed from the process gases might have to be increased with consequent reduction in the reaction rate in a second catalyst bed of a given size. Whether or not the corresponding capital outlay could be justified, would depend upon the merit that could be derived from the increased pressure and temperature of the steam. In the present case study, the steam is passed into a mains at 685 psia and extra potential in terms of pressure or temperature would be destroyed almost completely by irreversible mixing and diffusion on entry into the mains, see Figure (3.12). Any benefit

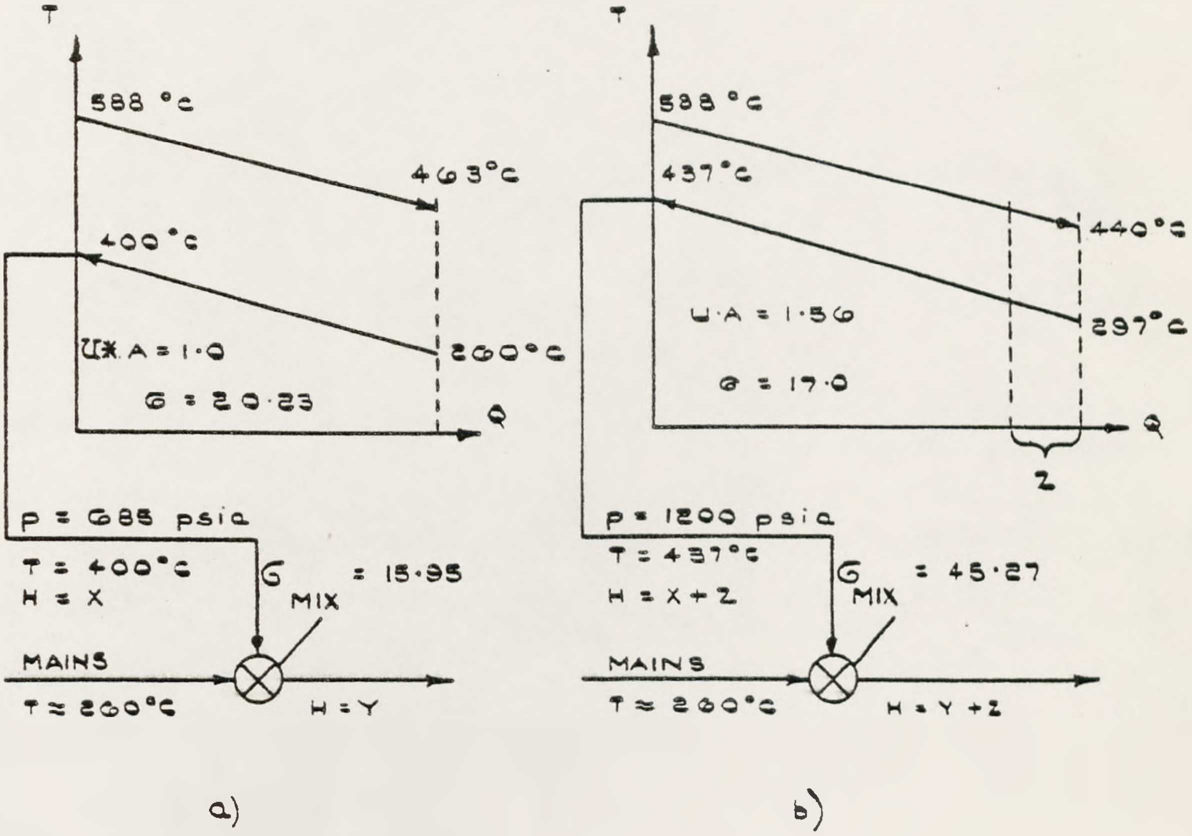

Figure (3.12) Reducing the irreversible entropy change σ in the superheater.

a) Present arrangement.

b) "Improved" superheater.

to be derived from increased steam temperature or pressure would therefore be measured in terms of enthalpy, which would only be available at the mains pressure*. The task of relating the magnitude of changes in $\sigma_{\text{superheater}}$ to the additional enthalpy that is available in the mains requires a complicated calculation. Consequently, alterations to the superheater are probably more sensibly discussed in terms of additional enthalpy passed on to the steam rather than in terms of irreversibilities avoided in the superheater. Once more the role of entropy can be seen to be one of "flagging" a possibility for maintaining higher levels of energy potential but not of quantifying corresponding benefits. Whether or not benefits would arise at all, and how large they would be, depends upon the consequences of a modification elsewhere and can only be evaluated by means of a heat and mass balance simulation in which entropy figures would no longer be required.

On the other hand, if entropy figures were monitored in the course of the simulation (as was done in Figure 3.12), changes of magnitudes might be observed which would be large enough to justify direct generation of work. In Figure (3.12), e.g., the rapid increase in the magnitude of σ_{mix} might suggest increasing the ex-superheater steam pressure and temperature even further and then employing a small turbine for expansion into the mains. This is, again, in line with the idea of concentrating inefficiencies before using work generating equipment referred to twice before. Thus, improvement in the thermodynamic efficiency of the superheater could, ultimately, lead to some extra work gained. The amount of this work would, however, be indicated by the magnitude of σ_{mix} and not by the change in $\sigma_{\text{superheater}}$.

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* This does in no way imply that such additional enthalpy would be of little value. Small amounts of superheat could be quite valuable for the mains in preventing condensation.

All these considerations seem to reinforce conclusions reached before and a brief summary of these conclusions (drawn in the present and the last section) follows:

1) A large irreversibility may suggest direct generation of work by means of suitable equipment placed where the irreversibility occurs. Roughly, the magnitude of the entropy increase may be taken as a guideline for the amount of work to be gained but detailed examination is required to obtain clarity.
2) An irreversibility which is not large enough to justify direct generation of work indicates nothing else than the fact that higher levels of potential might, possibly, be maintained where the irreversibility occurs. However, whether or not it would be advisable from an overall point of view to really maintain these higher levels, can only be clarified by means of simulation to examine effects on an overall process.
3) When studying these effects, constant monitoring of changes in irreversibilities is recommended since some might increase sufficiently to suggest direct generation of work.

From point 2) above, it is clear that suggestions to reduce irreversibilities in a practical flowsheet do not only have to be cross-examined against possible drawbacks in capital expenditure, safety, etc. (a commonly accepted truism) but also against overall benefit in purely thermodynamic terms : the overall improvement that could be realised following the improvement of a single unit operation might not at all resemble the improvement in that unit operation. Thus, it seems questionable whether the approach is justified of holding - even in a first approximation - each unit operation responsible for the non-ideal energy performance of the overall process to a degree which is measured by the irreversibility occurring in it. This more or less commonly accepted "rule of thumb" (see above in Chapter One, in Section 3.3, and in Appendix A) would now appear to require qualification to the extent that the approach is valid only if the irreversibility in question is large enough to justify the implementation of work generating equipment.

3.8 INTERPRETATION : RECOVERY OF LOW GRADE ENERGY

Some forms of energy might be more convenient to handle than others on a given industrial site and, at a certain stage in the design of a particular process, an energy recovery policy will, by and large, have been adopted. In the present case study, this policy was, apparently, to raise HP steam for the mains but not to generate any work on the H_2SO_4 plant. Reasons for this decision might have lain in the relative costs of energy and equipment ten years ago, in the marginal costs for steam and power that were applicable on the site, and in considerations concerning reliability, operability, etc. To avoid criticising past work after modifying important assumptions, this policy of not generating work will be observed here and all that will be examined is the question whether more steam could have been raised.

Thereby, the maximum amount of steam that could possibly be obtained will be considered determined by the maximum amount of heat that would be available <u>within</u> the process. In other words, an arrangement such as shown in Figure (3.13) on page 111 will not be considered : it would involve work generating equipment within the contact process and would therefore not be compatible with the policy not to use such equipment.

To clarify which sources and sinks of heat exist in the process, a sketch such as shown in Figure (3.14) on page 112 might be drawn. It shows the temperature profiles - over heat exchanged - of the process gases and of the boiler feed water and steam in the three heat

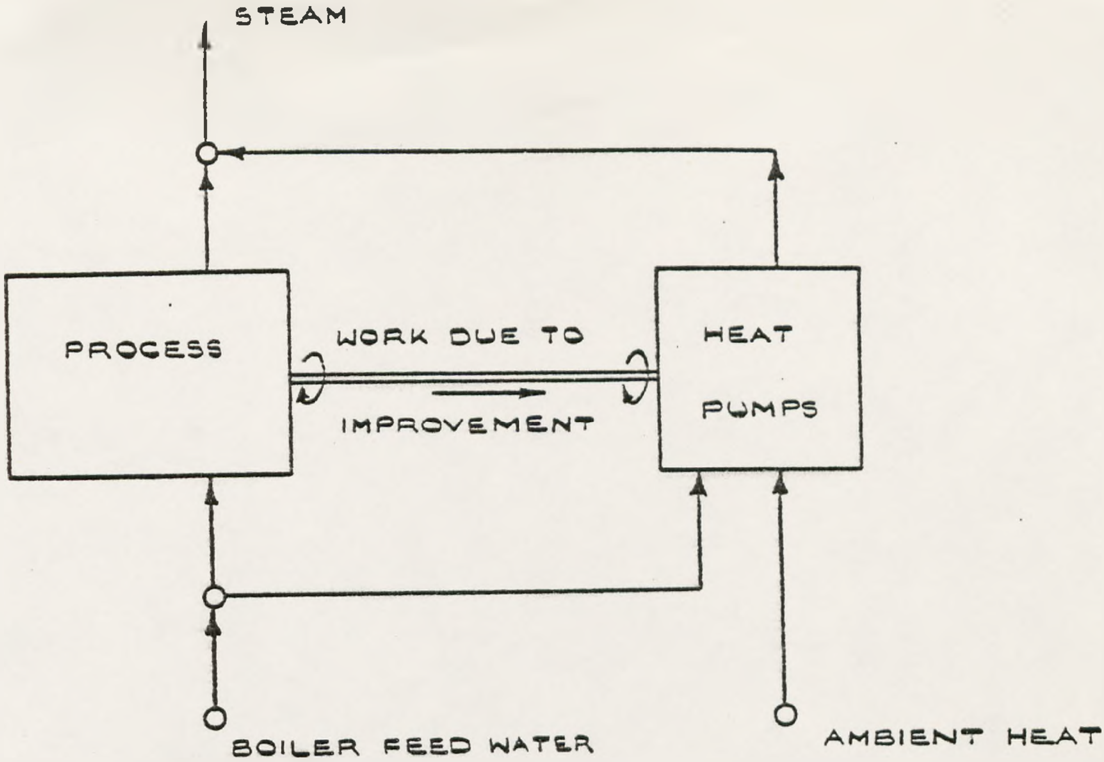

Figure (3.13) Unrealistic arrangement for additional steam raising.

exchangers. From this sketch, it appears that all heat available in the process above 260°C (i.e. the evaporation temperature) is, in fact, accommodated in steam. Thus, the amount of steam raised would appear to be about optimal : it could only be increased by reducing the temperature difference in the economiser. This impression is hardened when Figure (3.15) on page 112 is considered. The same temperature profiles are shown, now connected, and the effect of increasing the amount of steam raised by 10% is indicated by means of a dashed line : the temperature difference in the economiser would become rather small.

The dotted line in Figure (3.15) shows the effect of increased pressure. This would appear possible but, as discussed before, it would only be worthwhile if either the mains was likely to require some boost in terms of superheat or if a small turbine installation between superheater

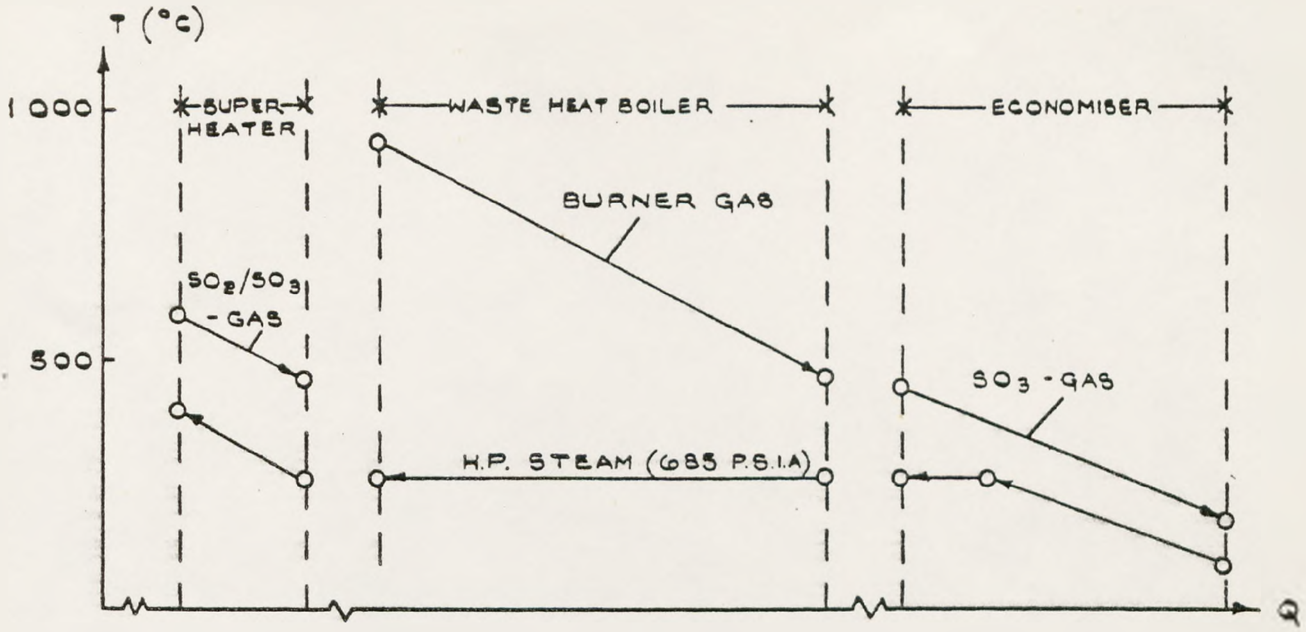

Figure (3.14) Heat sources and sinks in contact process.

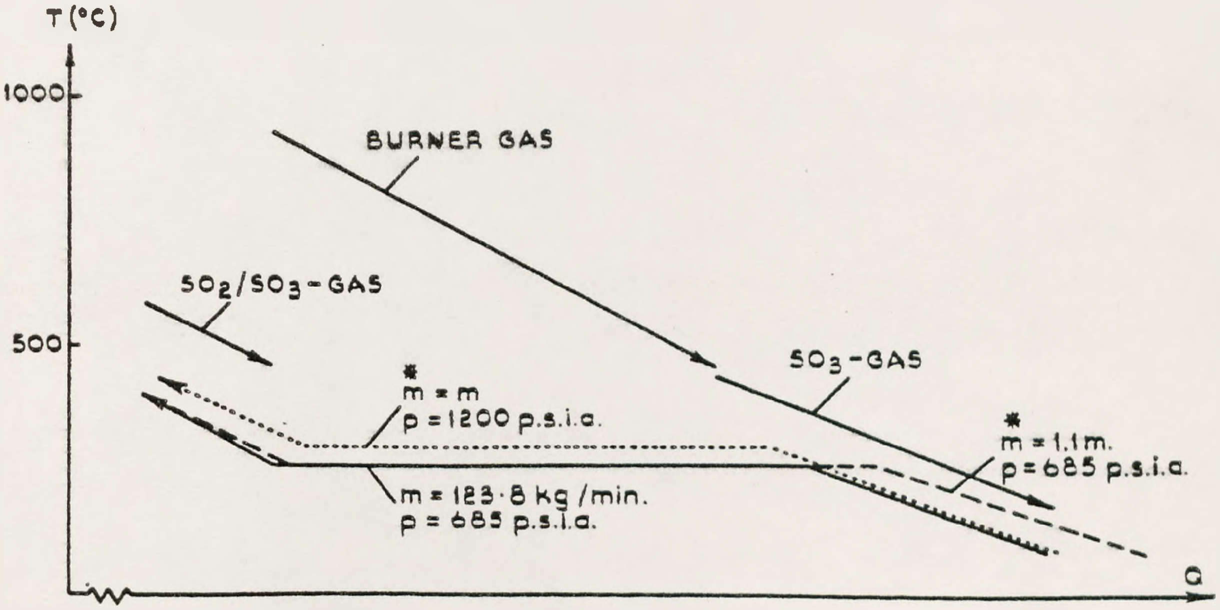

Figure (3.15) Effect of increased steam pressure or mass flowrate.

and mains could prove economical. Assuming that neither is the case, little benefit could be derived from raising steam at higher pressure.

Comparing the above argument with the entropy increases listed in Table (3.13) for the three heat exchangers, one might conclude that these irreversibilities are inevitable due to the decision not to generate work : the heat to be exchanged might be said to have a "source-entropy", defined by the temperature profiles of the process gases, and a "sink-entropy", defined by the temperature profiles of boiler feed water and steam. The increase from "source-entropy" to "sink-entropy" is inevitable and constitutes the irreversibilities in the heat exchangers. There is no possibility to avoid these irreversibilities and one cannot, e.g., criticise the "intuitively wrong" sequencing of waste heat boiler first and superheater second : from an overall point of view, a countercurrent arrangement is not necessary*.

In short, an entropy analysis of the three heat exchangers reveals no obvious chances to increase the amount of steam raised. However, when considering the rest of the process, and especially the meaning of the entropy increases $\bar{\sigma}_{\text{Burner}}$ and $\bar{\sigma}_{\text{2nd/4th Bed}}$ listed in Table (3.13), a possibility to raise additional steam becomes apparent : in the burner and in the converter, irreversibilities are due to the fact that "....heat is not sufficiently upgraded in the course of reactions..." (see above). In other words, if a certain amount of heat was given to the air (4) and/or the air (6) at low temperatures, this heat would become available at temperatures sufficiently high to allow further

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* Also, the arrangement chosen is a very convenient one : the quantities of heat that are available from the burner gases and from the SO_2/SO_3-gases are roughly defined by the temperature requirements of the equilibrium reaction and the chosen arrangement facilitates the practically desirable division between boiler and superheater.

steam to be raised. A corresponding arrangement is sketched in Figure (3.16) :

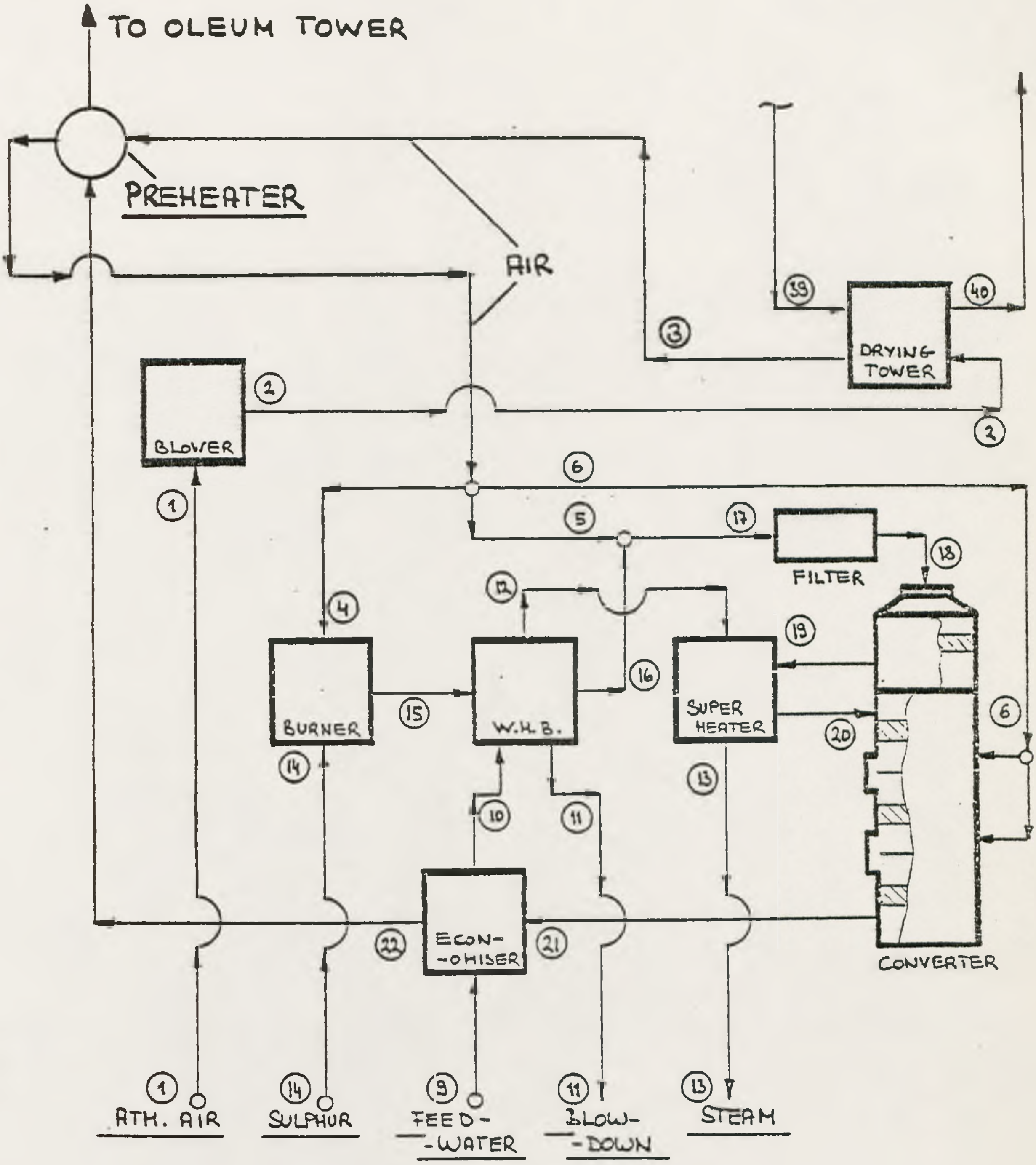

Figure (3.16) Basic arrangement for air preheating in contact process.

Heat from stream No.22 (that would otherwise be passed on to the acid/ oleum section) is used to preheat the dried air (3) and the additional enthalpy thus present in the air is channelled (via the burner, the mixing junction, and the converter) into the hot process gases. Once there, it can be usefully employed in raising additional steam by means of a larger waste heat boiler and superheater. The heat load of the economiser ought, perhaps, not to be increased since the temperature at the end of the last catalyst bed, i.e. T_{21}, ought to be kept constant to maintain conversion efficiency.

When evaluating this scheme it is, again, found that the extent to which irreversibilities could be reduced bears no intuitive resemblance to actual improvements : in spite of only small reductions in irreversibilities, a considerable improvement in the amount of HP steam raised is possible. (In Section 3.9, schemes which are based on the present scheme are outlined in some detail.) Thus, a summary can now be given that clarifies the use to which Second Law analysis can be put when maximising recovery of low grade energy:

Once the decision has been taken to recover low grade energy rather than work and not to use a heat pump arrangement such as sketched in Figure (3.13), a certain overall entropy increase σ becomes implicitly accepted. In such a situation, large and small entropy increases alike might or might not be part of this implicitly accepted total. If they are part of it, they are of no significance whatsoever from the energy recovery point of view (see e.g. $\sigma_{W.H.B.}$ above).

Nevertheless, a systematic discussion of all irreversibilities in a process is likely to help finding those entropy increases that are significant from the energy recovery point of view. The extent to which improvement is possible, however, must be clarified by means of simulation.

3.9 SCHEMES FOR IMPROVED ENERGY RECOVERY

In Figure (3.17), a scheme is shown which is based on the suggestion made above : a preheater connects the SO_3 bearing gases with the dry air.

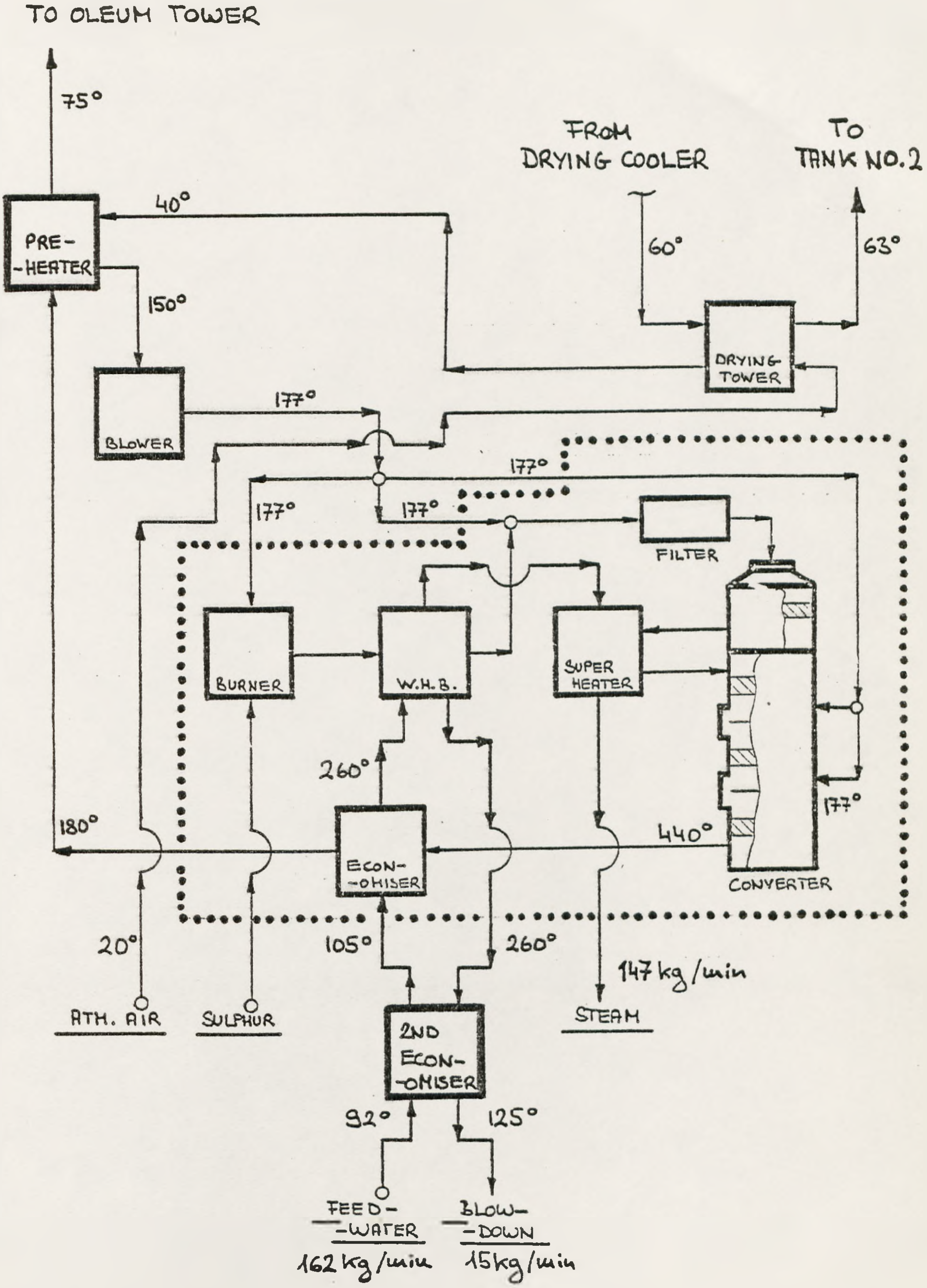

Figure (3.17) Complex scheme for improved energy recovery in contact process.

Also, some of the enthalpy of the blowdown is recovered and, lastly, the blower has been placed downstream of the preheater. This latter alteration leads to an increase of ∿40% in the power required to achieve the same pressure rise, but it also allows to increase the temperature of the air considerably beyond what could be achieved in the preheater. Consequently, with parameters as shown in Figure (3.17), about 4 MJ/min in HP steam are recovered for each additional MJ/min of power spent to drive the blower. However, in different circumstances such an arrangement could prove considerably more favourable. Whether or not it would be advantageous in the context presented in Figure (3.17) would depend on cost comparisons and, of course, on the difficulties which acid mist carried over from the drying tower could cause in the blower.

In total, approx. 77 MJ/min additional enthalpy are introduced into the subsystem defined by means of the dotted line in Figure (3.17), allowing ∿19% more steam to be raised than in the original case study. At a marginal cost of HP steam of about 4.00 £/ton and with 320 working days/year, this would lead to savings of about £40,000/year. The necessary capital outlay would be rather difficult to estimate. Due to the larger superheater required, some temperatures in the converter would be decreased. Thus, reaction could be slowed down, an effect that might have to be compensated for by increased catalyst mass. Also, there would be two additional heat exchangers and increases in the size of three existing ones. Whether or not the savings could justify the necessary complications would have to be examined in some detail.

However, these questions have not been studied any further and, instead, the scheme presented in Figure (3.18) was developed.

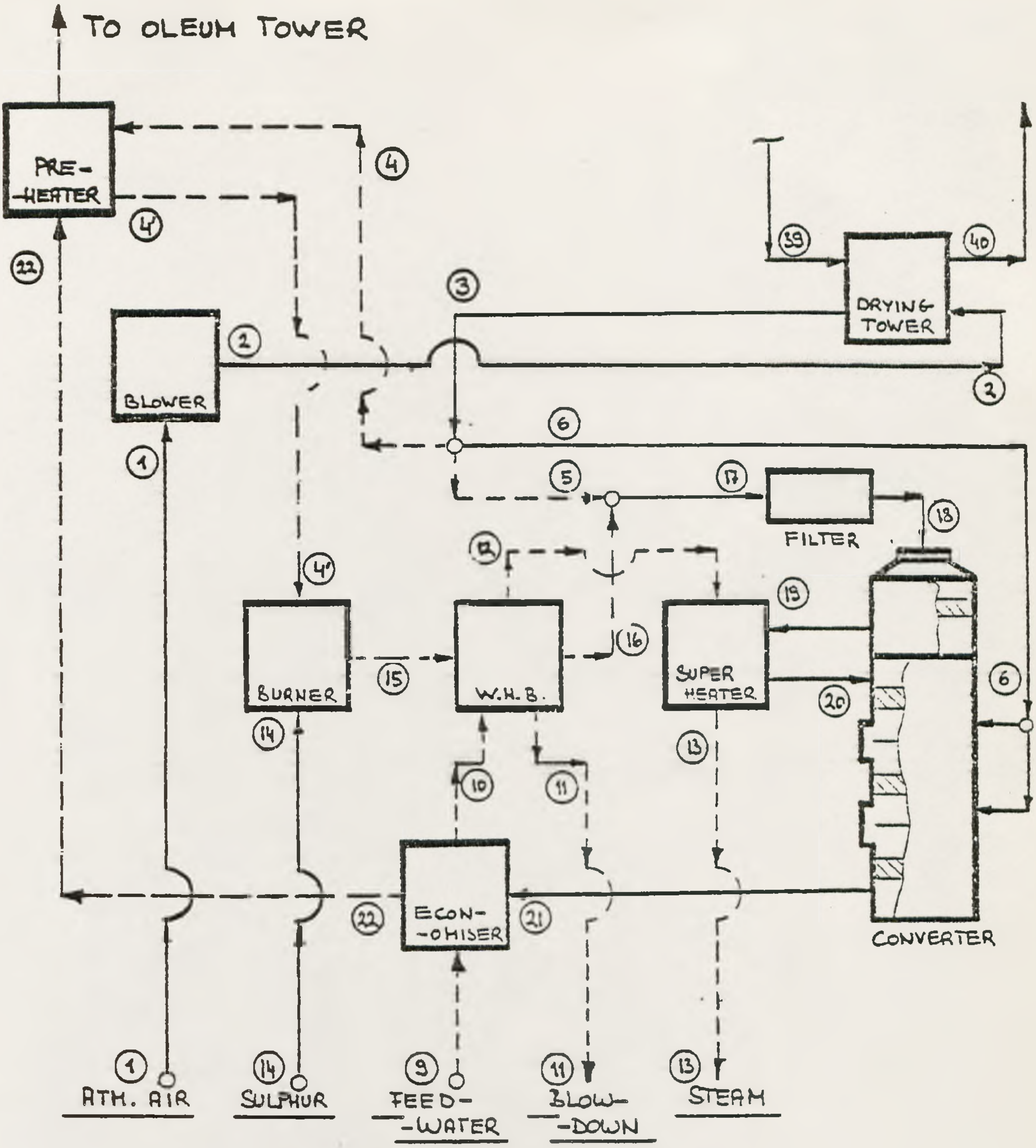

Figure (3.18) Recommended scheme for improved energy recovery in case study process.

Apart from being less adventurous, this scheme has the particular attraction that it would be integrated into the existing plant without any alteration to existing equipment (other than control equipment and pipework): all that would be required would be the installation of an additional heat exchanger - the preheater - between streams No.22 and No.4.

By choosing stream No.4 rather than stream No.3 for preheating, the operating conditions for the converter may remain unchanged. Also, the blower has to be left in its original place and the attempt to try and leave all other equipment unmodified followed in due course : changes in heat load can be accommodated in the existing heat exchangers by means of varying the respective mass flowrates of streams No.4 and No.5 so as to create such temperature differences in the waste heat boiler as are necessary to transfer the required amount of heat : if slight superheating is effected in the waste heat boiler, and if the steam exit temperature T_{13} is reduced by a small margin, more steam can be handled in the superheater with a given heat load, a given surface area, and given process gas temperatures T_{19} and T_{20}. Similarly, the heat load in the economiser can be evaluated from given input conditions and the load of the waste heat boiler can be adjusted accordingly. The streams drawn fully in Figure (3.18) represent those streams which may remain completely unaffected whereas the dashed lines represent streams which are subject to alteration.

A detailed description of the scheme comprising both a technical as well as an economic evaluation was given to ICI,Huddersfield, in Summer 1976 (see H_2SO_4 Report(70)). Extracts from this document are presented in Appendix C. As shown there, the need to increase T_{15} for increased amounts of steam raised (so that more heat is transferred in the waste heat boiler), makes it necessary to decrease m_4. This leads to temperature crossover in the preheater if steam is raised in excess of, say, 111% of the figure achieved in the existing plant. A moderate and attractive proposition would be to raise 8% more steam than in the existing plant and some parameters of interest which would describe this particular case are given in Table (3.15).

Table(3.15) Parameters of interest for scheme with 8% improved steam recovery

$\overset{*}{m}_9/m_9 = \overset{*}{m}_{11}/m_{11} = \overset{*}{m}_{13}/m_{13}$	$= 1.08$
additional steam raised	14.26 tons/day
credit for steam at £4/ton	£18,255/year
superheated steam temperature $\overset{*}{T}_{13}$	395°C
burner gas peak temperature $\overset{*}{T}_{15}$	1055°C
excess air in burner	∿ 103%
steam quality when entering W.H.B.	$\varepsilon = 9.2\%$
steam exit temperature in W.H.B.	265°C
smallest temperature difference in preheater	43°C
ratio of heat capacity flowrates in preheater	1.51
SO_3-gas exit temperature in preheater	121°C
heat transferred in preheater	25.25 MJ/min
U*A for preheater	27.65 MJ/hr/°C
heat transfer surface area of preheater	$U = 50$ KJ/m²/hr./°C (= 2.45 Btu/ft²/hr./°F) : 553 m² $U = 80$ KJ/m²/hr./°C (= 3.91 Btu/ft²/hr./°F) : 346 m²
cost of preheater (stainless steel * & incl.30% overheads)	A = 553 m² : £39,400 A = 346 m² : £30,000

The assumptions used when determining these parameters are described in Appendix C together with some of the findings discussed in the report(70) regarding time discounting, sensitivity analyses, etc. From an economic point of view, the results appear to be encouraging.

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* stainless steel construction was assumed to allow for possible corrosion problems, see below.

From an operability point of view, the scheme would appear to be realistic, too:

(1) Starting-up capability should not be impaired. During start-ups, natural gas is burned directly in the converter and in the burner, so that the plant would not depend upon the heat given to the air in the preheater.

(2) Steady state controllability should remain possible, too. If disturbances were "fed back" into stream No.4 through the preheater, they could be cancelled by employing the by-pass around the waste heat boiler as well as the "short cut" stream No.5.

(3) Lastly, the possibility to operate under turn-down conditions would be maintained and credits for steam would, relative to production rate, be increased : smaller mass flowrates m_{22} and m_4 would lead to closer temperature approach in the preheater. While conditions would remain operable, more heat would, relatively, be given to the air. Also, this effect could still be increased : with less heat to be transferred in the waste heat boiler, m_4 could, relative to other mass flowrates, be increased and more heat would, once more, be transferred in the preheater.

From the reliability point of view, the possibility of corrosion in the preheater must be considered. The preheater would cool the SO_3 bearing gases considerably below their acid dewpoint : part of the SO_3 would form sulphuric acid by reacting with the moisture content of the gases (mainly due to organic matter in the sulphur). However, according to the plant operating manual (68), the existing economiser already cools the gases below their dewpoint so that oleum has to be drained from the bottom of the economiser once every shift. Further, corrosion problems are likely to be most serious just below the dewpoint temperature and to become less severe if cooling is continued, see Ryland and Jenkinson (65). Consequently, corrosion in the preheater might present no worse a problem than in the existing economiser. On the other hand, temperature gradients across the gas flow in a heat exchanger are rather marked and flow conditions themselves are far from homogeneous so that local areas might exist with worse than average conditions. For this reason, nothing definite can be said about corrosion problems unless specific designs of preheaters are analysed. To allow for eventualities, the preheater was assumed to have stainless steel tubes. (The existing economiser has mild steel tubes). This assumption, together with the rather conservative figures used for the cost of steam, and the heat transfer coefficient, should ensure that the scheme has not been assessed over-optimistically.

Finally in this section, the prospects should be discussed of integrating some of the design suggestions made in this chapter into other contact plants. In Figure (3.19) the basic flowsheet is given of a modern plant

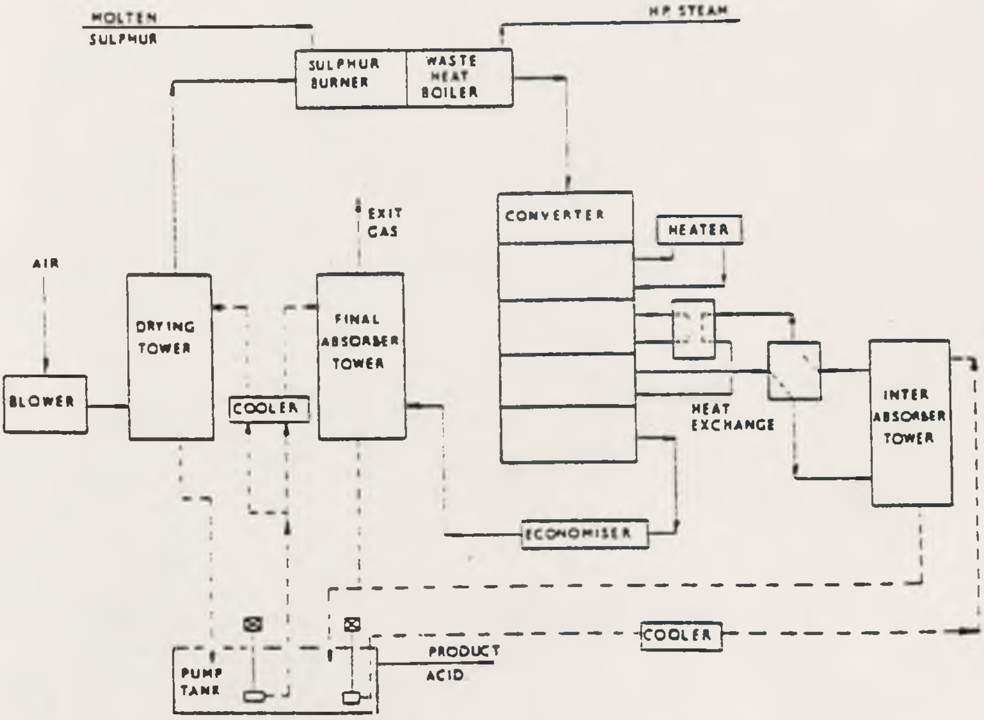

Figure (3.19) Simplified flowsheet of a double absorption contact plant. (Source: SIM-CHEM information leaflet$^{(67)}$.)

incorporating double absorption. (Source : a Sim-Chem information leaflet$^{(67)}$).

Clearly, the gases entering the inter absorber tower in Figure (3.19) must have a higher mass flowrate than the ones leaving it, as well as a higher temperature. Thus, heat must be passed from the converter into the inter absorption system and the chance to obtain more heat from the equilibrium reaction at ∿400°C, as suggested in Figure (3.9) and assumed in Figure (3.17), may not exist. On the other hand, the gases entering the economiser will have a lower mass flowrate than the equivalent flow in a single absorption process and it can be concluded from Figures (3.14) and (3.15), that this might tend to cause a narrow temperature approach in the economiser. Thus, depending upon the temperature at which boiler feed water is supplied, the installation of a preheater as suggested in Figure (3.18) might prove especially attractive in a double absorption plant.

Coming to the gas turbine scheme sketched in Figure (3.11), there is no reason why this should not be applicable to double absorption plants as well : the process streams in question in Figure (3.19) appear to be of a very similar description as those in the case study process.

Also, there has been a development reported by Ugine Kuhlmann in 1972 in which a double absorption process was pressurised (see Vidon$^{(71)}$).

In this development, compressor and burner were arranged as in Figure (3.11).

However, the turbine was situated at the end of the process (where less work can be recovered than that required for compression) and the reasons given for pressurising the process were given as:

(1) reduction of equipment size with increased production capacity, and

(2) better SO_3-yield in the equilibrium reaction.

The energy performance of the process was described with "full independence", i.e. there is, apparently, little export.

If compared to this development, a scheme to pressurise combustion for the sake of energy efficiency would appear to fail meeting practical requirements. On the other hand, the cost of energy has risen sharply since 1972 and today, there is a clear trend towards improved energy recovery. In this situation, processes might become attractive that achieve high energy efficiency in technologically tried and reliable equipment, even though the equipment may be costly. Maybe, the suggestion shown in Figure (3.11) fits into this category.

3.10 DISCUSSION

In this case study, an entropy analysis was used to localise and quantify thermodynamic inefficiencies in an existing industrial process. Quantification of these inefficiencies is recommended in thermodynamic textbooks because, theoretically, work could be gained corresponding to their magnitude if unit operations were carried out under resisted conditions. With reference to this basic significance of thermodynamic losses, the suggestion to integrate a gas turbine into a sulphuric acid plant (see Figure 3.11) was derived in a quite straight-forward manner.
However, different irreversibilities, if sought to be reduced by means of work generating equipment, were seen to offer different scope for improvement. Depending on operating conditions, practical efficiencies of suitable equipment might vary* and clarification of true scope for improvement was seen to require discussion in First Law terms.

Further, only single large irreversibilities can realistically justify the installation of work generating equipment and more than half of the overall loss encountered in the case study is made up of individual losses which are too small to justify such installations. Instead, these smaller irreversibilities can be opposed by modifying existing equipment. Often in this context, however, benefits achieved in one part of a process

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* See also Appendix E.

may be offset by drawbacks in another as a result of network interactions.

In cases where low grade energy (such as steam) is recovered from high grade inputs (such as fuel), a fundamental reason exists why network interactions may lead to exact cancellation of attempted improvements : a certain overall irreversibility is implicitly accepted in such cases, due to the choice of energy sources and sinks, and all a designer may do is shift losses from one part of a process to another.

In summary, individual entropy increases do not offer conclusive evidence that energy performance can be improved and clarification is required in heat and mass balance terms : in the improved flowsheets suggested in this chapter, entropy increases were not reduced in an indiscriminate fashion but only when they were found to be relevant to the performance of the overall process. To decide whether such relevance was given, the degradation of heat in simple temperature terms was seen to be the most important and most useful single concept.

On the other hand, the fact remains that the sum of all entropy increases distinguishes a real process from the ideal. Thus, if each entropy increase is thoroughly discussed in terms of what could be done to avoid it, no possibility for improvement that exists would be overlooked. Such thorough discussions were made in the case study and improvements were identified. This is not to say, however, that these improvements could not have been found otherwise : the fact that the temperature of the SO_3 bearing gases between economiser and oleum tower should be reduced was already recognised in the brief First Law analysis in Section 3.2 and the ideas of coupling a combustion with a gas turbine and of preheating combustion air are simple and straight-forward. Thus, the maximum claim for Second Law analysis in the present case study might be that it has produced a convenient framework for a thorough energy utilisation study at the end of which a fair degree of confidence was achieved that no substantial possibility for improvement had been overlooked. Whether or not such a result would justify the effort involved in producing Second Law analyses in industrial design situations must be left to individual judgement.

Once the decision has been made to produce a Second Law analysis, the approximation method used in this chapter will be found useful. Firstly, the accuracy of the method would appear to satisfy even more stringent requirements than those normally encountered in industrial practice and secondly, compositions need only be detailed with respect to species which experience phase transition between reference state and process state. This latter fact should greatly reduce efforts in the context of hand as well as computerised calculations. Apart from the approximation method, the concept of prescribed irreversibilities would appear to be useful. Firstly, it eliminates the need to identify free energy data of the species involved in a reaction. Secondly, part of the task of discussing "... each entropy increase in terms of what could be done to avoid it..." (see above) is automatically tackled when optimal conditions for the reactions in a process are identified. Lastly, a reduction of the irreversibilities associated with reactions down to about one half of the original size is significant (even given the fact that the magnitudes of entropy increases may be inconclusive): it could help to avoid misapprehensions about the scope that might exist for practical improvement.

CHAPTER FOUR

EXERGY ANALYSIS OF AN AMMONIA OXIDATION PROCESS

In this chapter, another industrial process is considered and a Second Law analysis is carried out in exergy terms. This will enable comparisons to be made regarding the use of the two functions entropy and exergy in the context of process evaluation. Also, it will help to generalise the conclusions drawn from Chapter Three regarding the usefulness of Second Law analysis in general.

4.1 PROCESS DESCRIPTION

Today, almost all commercially produced nitric acid is manufactured by the ammonia oxidation process. Ammonia is oxidised with air in the presence of a catalyst (gauzes of platinum/rhodium wires) to form nitric oxide

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (4.1)$$

and the oxide uses excess oxygen to form nitrogen dioxide

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad (4.2)$$

and nitrogen tetroxide:

$$2NO_2 \rightarrow N_2O_4 \qquad (4.3)$$

The tetroxide is absorbed in water to produce nitric acid. According to Miles(72), the following equation can be used to describe this absorption in an overall sense,

$$3N_2O_4 + 2H_2O \rightarrow 4HNO_3 + 2NO \qquad (4.4)$$

although the changes that actually happen are far more complex. It is obvious even from this simple equation, however, that there is need for some re-oxidation according to Equations (4.2) and (4.3) after the absorption has proceeded a certain way.

The absorption section in today's plants is invariably designed for operation at pressures higher than atmospheric. This is necessitated by the slowness of some of the changes covered in Equation (4.4) if acid at concentrations above, say, 50% w/w is to be produced without the use of refrigeration (See Lerolle(76)). Also, the size of the absorption system can be reduced with increased pressure. On the other hand, power requirements for compression can offset these advantages. There appear to be two main groups of designs for the absorption section, namely those operating at "medium pressure" (i.e. approx. 3 bar abs. to 5 bar abs.) and those operating at "high pressure" (i.e. approx. 6 bar abs. to 10 bar abs.), see Oosterwijk(75).

Promotion of the ammonia oxidation reaction (4.1) is achieved by means of a catalyst and undesired side reactions (which mainly lead to the decomposition of ammonia and/or the newly formed NO into nitrogen and water) must be kept to a minimum by optimum adjustment of a number of design and operating parameters. The two most important are probably the gauze temperature and the gas flowrate per unit area of catalyst mesh, see Drake(73). Increased pressure is known to influence the yield unfavourably. Thus, more layers of catalyst gauzes become necessary with increased pressure and losses of catalyst in operation - which might amount to a substantial part of operating costs - are increased. On the other hand, higher pressure allows construction of smaller converters and, thus, of plants with higher capacities. Also the extra power requirements for compression of the reacting gases are low since the gases are compressed for absorption anyway. Designs exist in which ammonia is converted at substantially atmospheric (i.e. "low") pressure, as well as others for "medium" or "high" pressure (same ranges as for the absorption). Which design would be preferable in a given situation will depend mainly on economics : low pressure conversion is cheaper in operating costs (higher chemical yield, smaller loss of catalyst), higher pressures allow lower initial investment and greater plant capacities.

Detailed discussions of existing processes as offered by various contractors as well as of the basic differences which exist due to alternative operating pressures are given e.g. by Drake(73), Bahari(74), Oosterwijk(75) and Lerolle(76).

During the last five or ten years, growing public concern about atmospheric pollution has led to the introduction of tail gas treatment units which, however, were usually designed to achieve decolouration rather than deacidification. In other words, the stack gases were diluted with air or NO_2 was reduced - by means of catalytic combustion or other techniques - to NO. This helped to make the yellow stack plume less visible but did not substantially improve the total amount of atmospheric pollution : as argued by Newman(77), the hazard from nitric oxide emission was not yet sufficiently recognised when decolourising equipment became more or less standard and it was only later that the almost total destruction of <u>any</u> oxide of nitrogen, including NO, has become considered desirable.

For a substantial improvement in this respect, however, tail gas treatment appears to be of a less proven suitability than for mere decolouration and, consequently, high absorption efficiency might become desirable beyond the point justified by the economic value of the recovered oxide. As is suggested by Newman(77), concentrations of approx. 700 ppm NO_x in the tail gases and less could be obtained at not too high an equipment cost by improving the absorbers and, especially, by increasing operating pressure. This indicates that high pressure absorption might become the usual choice, rather independent of marginal economic arguments. The recent report about the development of a process featuring high pressure absorption (8 bar abs.), as well as refrigeration and scrubbing, with a claimed NO_x-concentration of 200 ppm(!) appears to substantiate this point (see Adrian(78)).

The Kuhlmann Process

A process for which detailed data suitable for a case study could be obtained is the conventional Kuhlmann process which incorporates atmospheric pressure ammonia conversion and medium pressure (4 bar abs.) absorption. The plant in question is run by ICI Organics Division in their Huddersfield factory and produces acid of a high strength (69% w/w) at a nominal capacity of 170 metric tons of pure HNO_3 equivalent per day. NO_x figures lie around 2000 ppm but the tail gas is not treated except by dilution with air. The high strength of acid is made possible by Kuhlmann's unusual absorption system in which nitric oxide is re-oxidised in the liquid as well as in the gas phase (see Drake(73)). According to comments in the literature, the process features a high ammonia efficiency and low platinum losses but high capital costs. The energy economy is considered to be good; a net export of steam is possible and the latent heat of vaporisation of ammonia is used for cooling.

In Figure (4.1), a functional flowsheet of the process is given as shown

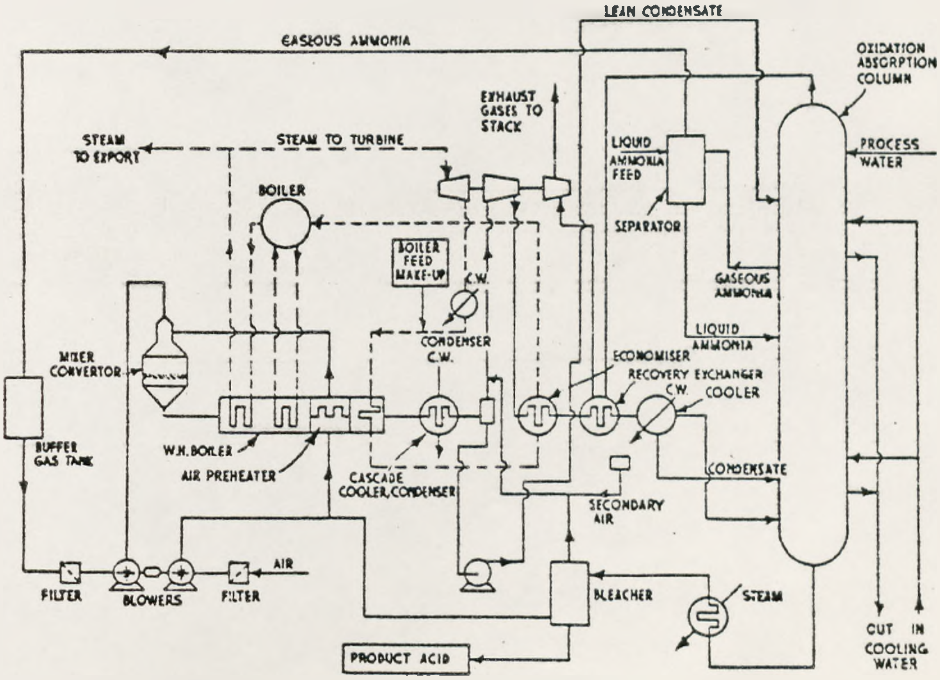

Figure (4.1) Functional flowsheet for Kuhlmann HNO_3 process.
(Source: Bahari(74).)

by Bahari(74). In the same source, the process is described in some detail and the following text is based on this description, with adaptations to the present case study where required:

> Air is preheated by means of nitrous gases and is then mixed with ammonia. One or more converters are employed, depending on the size of the plant. The converted hot nitrous gases are passed through the waste heat recovery system which includes a superheater, a waste heat boiler, an economiser, and the air preheater in one compact unit. The gases leaving the waste heat recovery system are further cooled in a cascade-type water cooler which also condenses out most of the reaction water which is collected in an integral sump with a concentration of 2 to 5% acid. This weak condensate is pumped to the absorption section.
>
> The cold gases leaving this cooler, together with some secondary air, are sucked into the turbo compressor which is powered by a recovery turbine and a steam turbine.
>
> The hot gases leaving the compressor pass through a steaming economiser and recovery exchanger and are finally cooled in a film-type water cooler of special design. The strong condensate formed in this cooler is passed into the appropriate part of the absorption section. One or more columns are employed depending on the capacity of the plant and acid concentration required.
>
> The nitrous gases flow upward counter-current to the water/acid mixture flowing down the columns.
>
> Strong acid from the sump of the last column is conveyed to a bleacher. The dissolved nitrous gases in the acid are removed from the air blower. The colourless

product acid is then sent to storage and the desorbed gases with the bleaching air are fed into the secondary air intake of the compressor.

The depleted gas from the top of the column is first preheated in a recovery exchanger and is then expanded in a recovery turbine coupled to the compressor. The gases leaving the turbine are passed to the stack.

A natural circulation waste heat boiler is employed. The condensate from the turbine, together with boiler feed make-up, is pumped through the feed water heater and pressure economiser before entering the boiler drum. The water from the boiler drum then circulates through the boiler and the steam from the top of the boiler drum is passed through the superheater. Most of this product steam is utilised in the steam turbine, with some available for export.

There are a few aspects in which the case study process differs from the one shown in Figure (4.1). Firstly, two converters are employed, with two waste heat recovery systems integrated into common housings with the converters. Secondly, two absorption columns are employed which are connected in series, according to the counter-current principle. In Figure (4.2), a block diagram is shown with the unit operations on which the simulation of the case study process was based. (See page 134.) The flows are numbered and a detailed key is given in Table (4.1), see page 135. Cooling cycle and ammonia supply have been modelled separately.

Also different to Figure (4.1), the nitrous gases (12) in Figure (4.2) enter the boiler feed water heater first and the air preheater afterwards. Thereby, the air preheater consists of a single large unit whereas the boiler feed water heater has been split into two parts

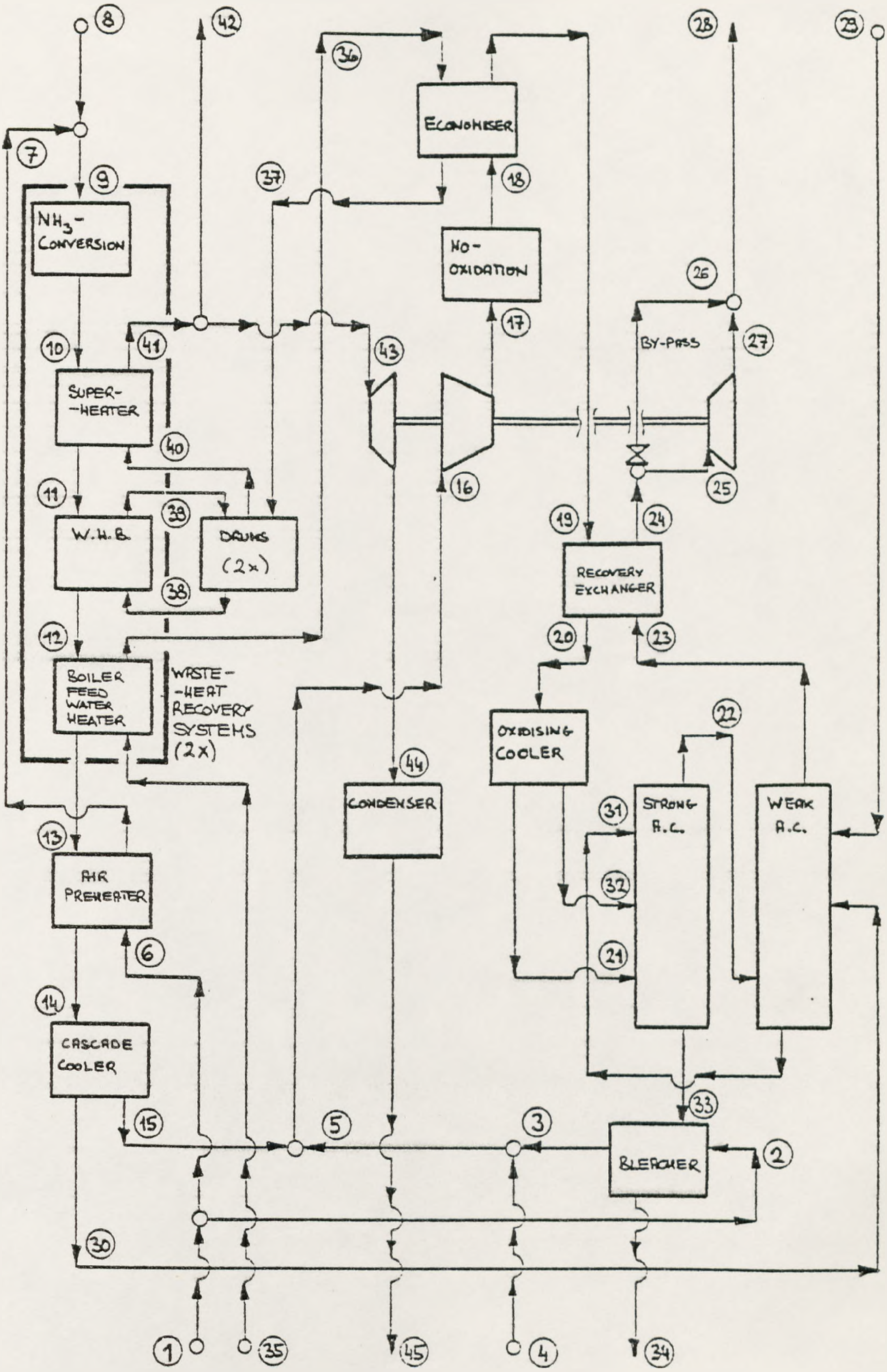

Figure (4.2) Block diagram for HNO_3 case study process.

Table (4.1) Description of flows in ammonia oxidation process

Flow	Description	Flow	Description
(1)	Primary air from blower	(29)	Absorption water
(2)	Air from bleacher	(30)	Weak condensate acid
(4)	Secondary air	(31)	~40% w/w acid
(8)	Ammonia from blower	(32)	Strong condensate acid
(9)	Air/ammonia mixture	(33)	Brown acid
(10)	Hot converted gases	(34)	Product acid
(11)-(17)	NO-gases		
(18)-(22)	$NO/NO_2/N_2O_4$ - gases	(35,(36)	Boiler feed water
(23)-(25)	Depleted gases	(42)	Export steam
(26)	Control by-pass	(43)	Turbine inlet steam
(27),(28)	Gases to stack	(44)	Turbine exhaust steam
		(45)	Condensate

which are integrated into the converter housings. The reason for this arrangement lies, presumably, in deaeration arrangements which are particular to the factory. Also, mention should be made of the method by which control of the absorption pressure is affected : the tail gas expander features different gas inlets, behind two of which the gases are simply throttled. By manually adjusting the massflow through these inlets (represented by means of by-pass (26) in Figure 4.2) , the absorption pressure can be controlled. More massflow results in less shaft power delivered and in a lower absorption pressure. Under normal operating conditions, a certain massflow must constantly be bled through these inlets to provide control movement in both directions. As will be seen below, the corresponding exergy loss is quite considerable.

4.2 HEAT AND MASS BALANCE

ICI Ltd. were very helpful in making available a simplified flow diagram of their plant, drawn by Kuhlmann. The information given in this diagram, however, was incomplete and had to be supplemented by measuring temperatures on the plant and by studying measured consumption of ammonia and absorption water, production of acid, and composition of tail gases. Then, a heat and mass balance was made up based on this information and on physical property data collected from the literature (see Appendix D).

Care was taken that the following figures would correspond to the values either specified or observed:

- overall conversion efficiency
- absorption efficiency
- tail gas composition
- amount of absorption water consumed
- acid strength (intermediate and product)
- air/ammonia mixture ratio
- temperatures and pressures in and out of compressor and turbines
- heat load on cooling water cycle

Also, vapour pressures of H_2O above diluted acid, as given by Miles(72), were compared to temperatures, pressures and compositions in gas flows.

Results

In Table (4.2) on page 137 and Figure (4.3) on page 138, the main results are shown. All figures quoted refer to the steady state production of one metric ton of pure HNO_3. The ambient temperature assumed is $20^{\circ}C$, but enthalpy figures are based on a reference state of $T_{RS} = 25^{\circ}C$ and $p_{RS} \rightarrow 0$. The figures shown in Figure (4.3) all represent enthalpies in $MJ/10^3*kg\ HNO_3$. The heats of reaction and/or of non-ideal mixing are shown by means of boxed figures inside the symbols for the relevant unit operations, and in Table (4.3) on page 139 and Table (4.4) on page 140, the chemical changes are listed in detail which are assumed to occur in the individual units. These tables are based on information collected in Appendix D concerning heats of reaction as well as the heat of mixing nitric acid. Also in Table (4.4), the free energy changes are listed for each unit operation. These will be referred to in Section 4.3.

Table (4.2) Heat and mass balance of ammonia oxidation process

Flow	T	p	m	m (kg)						H(T,p)
	(°C)	(psia)	(kg)	N_2	O_2	H_2O	NH_3	NO	NO_2	(MJ)
(1)	22	atm.	4185.9	3197.8	963.1	25.0	0	0	0	-12.8
(2)	22	"	349.4	266.9	80.4	2.1	0	0	0	-1.1
(3)	25	"	467.3	"	"	0	0	40.0	80.0	0.0
(4)	20	"	761.9	582.1	175.3	4.5	0	0	0	-3.9
(5)	22	"	1229.2	849.0	255.7	"	0	40.0	80.0	-3.9
(6)	22	"	3836.5	2930.9	822.7	22.9	0	0	0	-11.7
(7)	105	"	"	"	"	"	0	0	0	315.2
(8)	22	"	283.5	0	0	0	283.5	0	0	-1.8
(9)	94	"	4120.0	2930.9	822.7	22.9	"	0	0	313.4
(10)	854	"	"	2937.9	224.8	472.8	0	484.5	0	4137.1
(11)	771	"	"	"	"	"	0	"	0	3679.7
(12)	297	"	"	"	"	"	0	"	0	1281.7
(13)	219	"	"	"	"	"	0	"	0	907.4
(14)	150	"	"	"	"	"	0	"	0	580.5
(15)	40	"	3773.6	"	159.4	131.8	0	363.4	181.1	59.4
(16)	36	14.1	5002.8	3786.9	415.1	136.3	0	403.4	261.1	55.5
(17)	255	65.9	"	"	"	"	0	"	"	1214.1
(18)	292	65.9	"	"	359.9	"	0	299.9	419.8	1410.6
(19)	228	65.1	"	"	"	"	0	"	"	1064.3
(20)	127	64.3	"	"	"	"	0	"	"	530.0
(21)	25	63.5	4763.7	"	193.9	7.8	0	19.3	755.8	0.0
(22)	25	61.5	4147.4	"	175.3	13.1	0	83.9	88.2	0.0
(23)	30	59.5	3920.3	"	98.2	25.4	0	5.9	3.9	20.4
(24)	160	58.7	"	"	"	"	0	"	"	554.7
(25)	160	58.7	3331.3	3218.0	83.4	21.6	0	5.0	3.3	471.4
(26)	160	15.4	589.0	568.9	14.8	3.8	0	0.9	0.6	83.3
(27)	57	15.4	3331.3	3218.0	83.4	21.6	0	5.0	3.3	111.1
(28)	73	15.4	3920.3	3786.9	98.2	25.4	0	5.9	3.9	194.4
				m(kg)				Description		
				H_2O	HNO_3	NO	NO_2			
(29)	20	liquid streams	138.3	138.3	0	0	0	Absptn.Water		-2.9
(30)	40		346.4	340.1	6.3	0	0	1.8% Acid		21.8
(31)	25		711.8	426.4	285.6	0	0	40% Acid		0.0
(32)	25		239.1	110.0	129.1	0	0	54% Acid		0.0
(33)	20		1567.2	447.2	1,000	40.0	80.0	Brown Acid		-19.6
(34)	21		1449.3	449.3	"	0	0	69% Acid		-14.7
				m(kg)						
				$H_2O(\ell)$	$H_2O(g)$					
(35)	90	215	1294	1294	0	All Figures Based on Production of 10^3 Kg HNO_3				359.7
(36)	158	215	"	"	0					734.0
(37)	198	215	"	1229.3	64.7					1080.3
(38)	198	215	1229.3	"	0					906.4
(39)	198	215	"	0	1229.3					3304.4
(40)	198	215	1294	0	1294					3478.3
(41)	350	215	"	0	"					3935.7
(42)	350	215	102	0	102					310.2
(43)	350	215	1192	0	1192					3625.5
(44)	41.4	1.15	"	56	1136					2812.2
(45)	41.4	1.15	"	1192	0					81.9

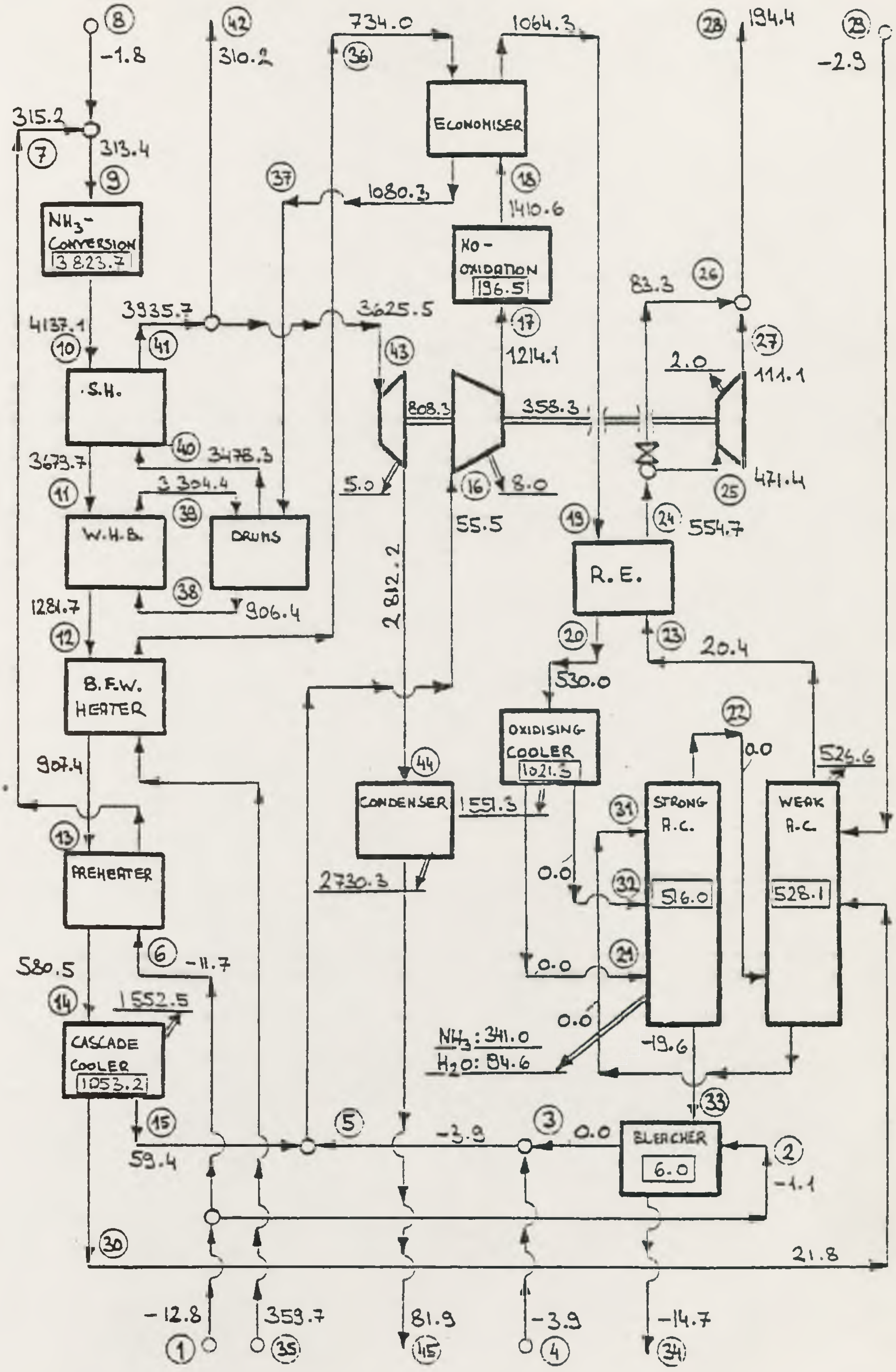

Figure (4.3) Heat balance for HNO_3 case study process. (For explanation of values shown see text.)

Table (4.3) Heat of diluting and concentrating nitric acid in unit operations (per 10^3 kg HNO_3)

	CASCADE COOLER	OXIDISING COOLER	STRONG ABSORPTION C	WEAK ABSORPTION C	BLEACHER
DIL.	6.3 kg 100% → 1.8% -3.16 MJ	129.1 kg 100% → 54% -49.7 MJ	585.3 kg 100% → 69.1% -178.52 MJ	279.3 kg 100% → 40% -124.01 MJ	1000 kg 69.1% → 69% -1.00 MJ
CONC.			129.1 kg 54% → 49.1% +10.33 MJ	6.3 kg 1.8% → 40% +0.36 MJ	
CONC.			285.6 kg 40% → 69.1% +39.70 MJ		
SUM	-3.2 MJ	-49.7 MJ	-128.5 MJ	-123.6 MJ	-1.0 MJ

The need for cooling is detailed in Figure (4.3) by means of underlined figures outside the blocks representing the relevant unit operations and in Figure (4.4) on page 141, a corresponding sketch is given of the cooling water cycle. In this sketch, an oil cooler is shown in which the energy dissipated in the compressor and the turbines but not given to the working media is discharged. - As mentioned before, cooling in the strong absorption column is effected partly by means of evaporating ammonia. In Figure (4.5) on page 142, this part of the cooling arrangement is described in two sketches. The underlying physical property data are also documented in Appendix D.

Compression and Expansion

The pressures of streams No.1 through No.15 are substantially atmospheric, with pressures becoming lower than atmospheric after the conversion. (This is a desired safety feature in case a leak develops.) However, the magnitudes of pressure drops in question do not warrant concern from an energy recovery point of view. Also, the small blowers through which air and ammonia are sucked in effect a temperature rise

Table (4.4) Chemical changes in unit operations in HNO_3 process

Unit Operation	Reaction *	Extent	$\Delta HoR_{RS,RS}$	ΔG_{RS}
CONVERTER	(1)	275.0 kg NH_3	-3,665.5	-3,879.7
	(2)	8.5 kg NH_3	-158.2	-163.4
		Σ =	-3823.7	-4,043.1
CASCADE COOLER	(3)	121.1 kg NO	-230.0	-146.7
	(4)	341.0 kg H_2O	-813.6	-162.3
	(5)	6.3 kg HNO_3	-6.4	-1.4
	Acid dilution		-3.2	-3.2
		Σ =	-1053.2	-313.6
NO-OXIDATION	(3)	103.5 kg NO	-196.5	-125.3
		Σ =	-196.5	-125.3
OXIDISING COOLER	(3)	280.6 kg NO	-532.9	-339.8
	(4)	128.5 kg H_2O	-306.6	-61.2
	(5)	129.1 kg HNO_3	-132.1	-29.4
	Acid dilution		-49.7	-49.7
		Σ =	-1021.3	-480.1
STRONG ABSORPTION COLUMN	(3)	-104.6 kg NO	198.6	126.6
	(4)	- 5.3 kg H_2O	12.7	2.5
	(5)	585.3 kg HNO_3	-598.8	-133.5
	Acid mixing		-128.5	-128.5
		Σ =	-516.0	-132.9
WEAK ABSORPTION COLUMN	(3)	78.0 kg NO	-148.1	-94.4
	(4)	-12.3 kg	29.3	5.8
	(5)	279.3 kg HNO_3	-285.7	-63.7
	Acid mixing		-123.6	-123.6
		Σ =	-528.1	-275.9
BLEACHER	(4)	2.1 kg H_2O	-5.0	-1.0
	Acid dilution		-1.0	-1.0
		Σ =	-6.0	-2.0
OVERALL SUM FOR PLANT :			-7144.8	-5372.9

* Compare Appendix D, Section D.2

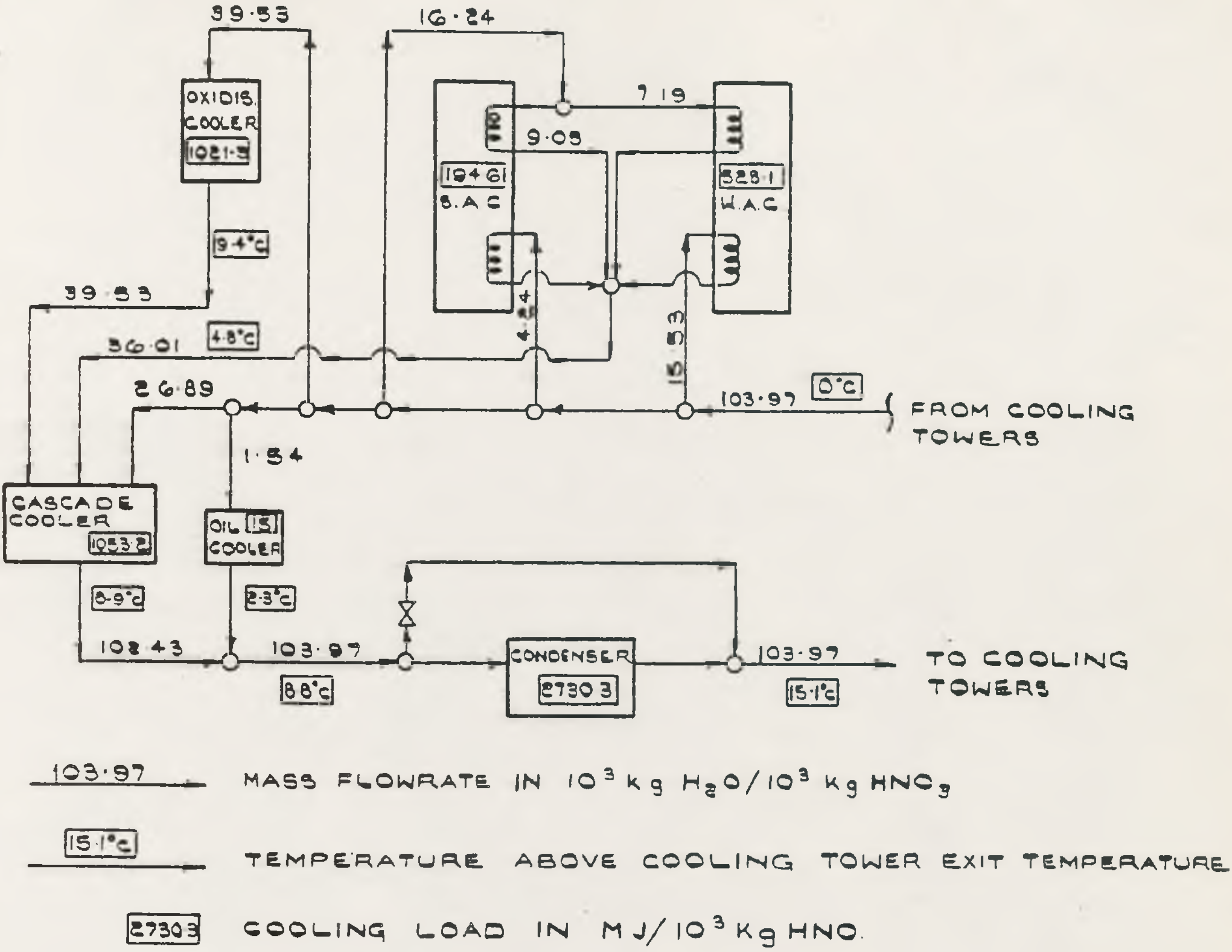

Figure (4.4) Cooling water cycle in HNO_3 process.

of only about $2^{\circ}C$, i.e. the corresponding power consumption amounts to less than 20 KW. This was felt to be negligible. For streams No.18 through No.23, however, pressures are of obvious interest and figures are given in Table (4.2). They were obtained by assuming a pressure drop of 0.8 p.s.i. for each pass through a heat exchanger and one of 2.0 p.s.i. for each absorption column. This adds up to the total pressure drop between compressor and recovery turbine (which is known).

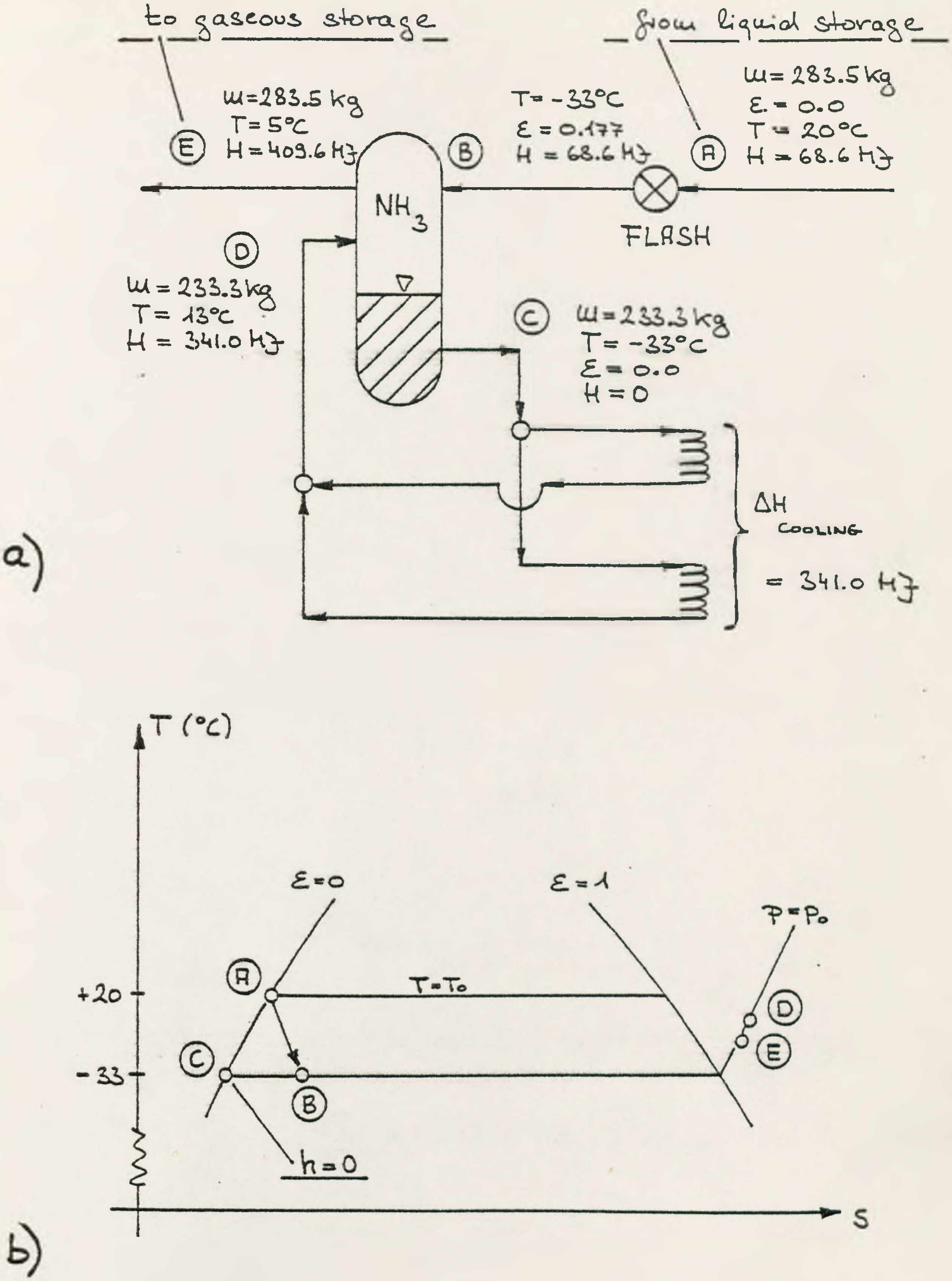

Figure (4.5) Process cooling by ammonia evaporation.

a) Flowsheet description.

b) Qualitative description in T,S-diagram.

The compressor consists of six stages and has a shaft power requirement of approx. 2.3 MW. No intercooling is carried out since the benefits to be gained would be more than offset by loss of recoverable heat in the economiser and the recovery exchanger. When comparing actual compressor performance to "ideal performance", characterised by isentropic adiabatic compression, the isentropic efficiency of the compressor is obtained as:

$$\eta_{\substack{is \\ \text{Compressor}}} \approx 0.76$$

Given the size of the unit, this efficiency is on the low side (see e.g. Baehr(7) for practical efficiencies). However, the gases are nitrous and emphasis will have been laid on reliability in the design of this compressor. Probably there would only be little scope for improving the process energy performance by providing a more efficient compressor.

Similarly, the efficiencies of the two turbines (i.e. steam and recovery turbine) suggest little scope for improvement : the recovery turbine has an isentropic efficiency of

$$\eta_{\substack{is \\ \text{Recovery Turbine}}} \approx 0.75$$

at an output of ~0.7 MW and the steam turbine has one of

$$\eta_{\substack{is \\ \text{Steam Turbine}}} \approx 0.73$$

at an output of ~1.6 MW. Considering the sizes of the units and especially the quite moderate steam conditions (~15 bar, 350°C), these efficiencies are very good (see Baehr(7) for practical values).

Uncertainty

The inherent numerical uncertainty of this case study is probably similar to that in Chapter Three as far as temperatures and enthalpies are concerned. However, considerably greater uncertainty exists with regard to compositions. Due to lack of information concerning residence times, the extent to which oxidation occurs according to Equations (4.2) and (4.3) in the gas flows can only vaguely be estimated and the simplifying assumptions were made that

- some oxidation to NO_2 occurs between compressor and oxidising cooler, and that
- no oxidation to N_2O_4 occurs outside the absorption section.

The extent to which oxidation to NO_2 was assumed after compression was chosen so as to match measured gas flow temperatures. The overall figures for molar flowrates and densities of gas flows, as well as of heat capacity flowrates, turned out to be hardly affected by these assumptions, due to the balancing effect of the large amount of nitrogen in each flow. Thus, only compositions could be regarded as inaccurate but not those parameters that are of importance for the discussion of energy recovery.

It is in the light of these considerations that no account was taken of insulation losses: apart from the recovery exchanger and the economiser, all relevant units in the process are either well insulated (i.e. indoors) or cooled by cooling water anyway. The introduction of insulation losses in the recovery exchanger and in the economiser would therefore - for given measured gas flow temperatures - only produce a slight shift from oxidation in the absorption section to oxidation after compression with no significant changes to mass flowrates and densities.

Finally, assumptions regarding the relative humidity of the ambient air were, also, seen to have little influence on mass flows, enthalpies, and temperatures, due to the balancing effect of nitrogen. A strong influence, however, was detected of ambient humidity on product acid strength : at $T_o = 20^{\circ}C$, an increase in relative humidity by $\sim$30% would cause a decrease in product acid strength of one per cent.* In the case study, a relative air humidity

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* The sensitivity of product acid strength to various operating parameters has been discussed at length in a document submitted to ICI, Huddersfield, in September 1976. Also in this document, the inherent uncertainty of the present heat and mass balance has been discussed in detail.

of 40% has been assumed, resulting in the specified product acid strength of 69% w/w.

Brief Evaluation

In Figure (4.6), a crude overall heat balance is sketched. This balance shows that of the imported energy, only about 20% is usefully recovered (∿16% to raise work needed in the process itself and ∿4% as export steam) and the rest is given to the cooling media. However, these figures include the inefficiencies involved in the work generating process and if an electric motor was to replace the steam turbine so that all steam could be exported, they would be somewhat improved : ∿53% of all energy imported would then be won in steam and 4% in work (in the recovery turbine). This would be about comparable with the performance of the H_2SO_4-plant in Chapter Three. On the other hand, the

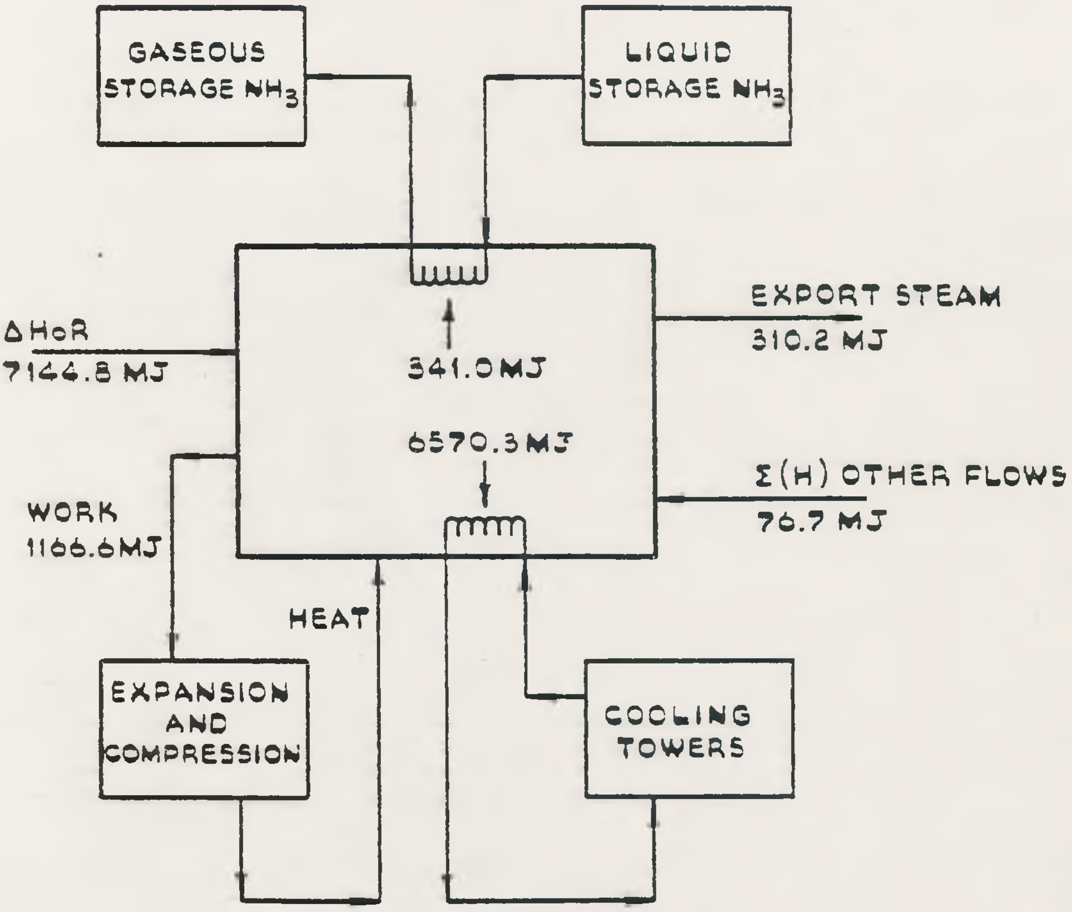

Figure (4.6) Crude identification of energy flows.

steam raised would only be IP steam and some of the energy imported would be electric power, so that one might expect a correspondingly better performance than in the case of the H_2SO_4-plant where HP steam is raised and the energy imported is inherent in the feed.

In Figure (4.7), the process is shown in four major sections with the most relevant interconnections (in heat balance terms).

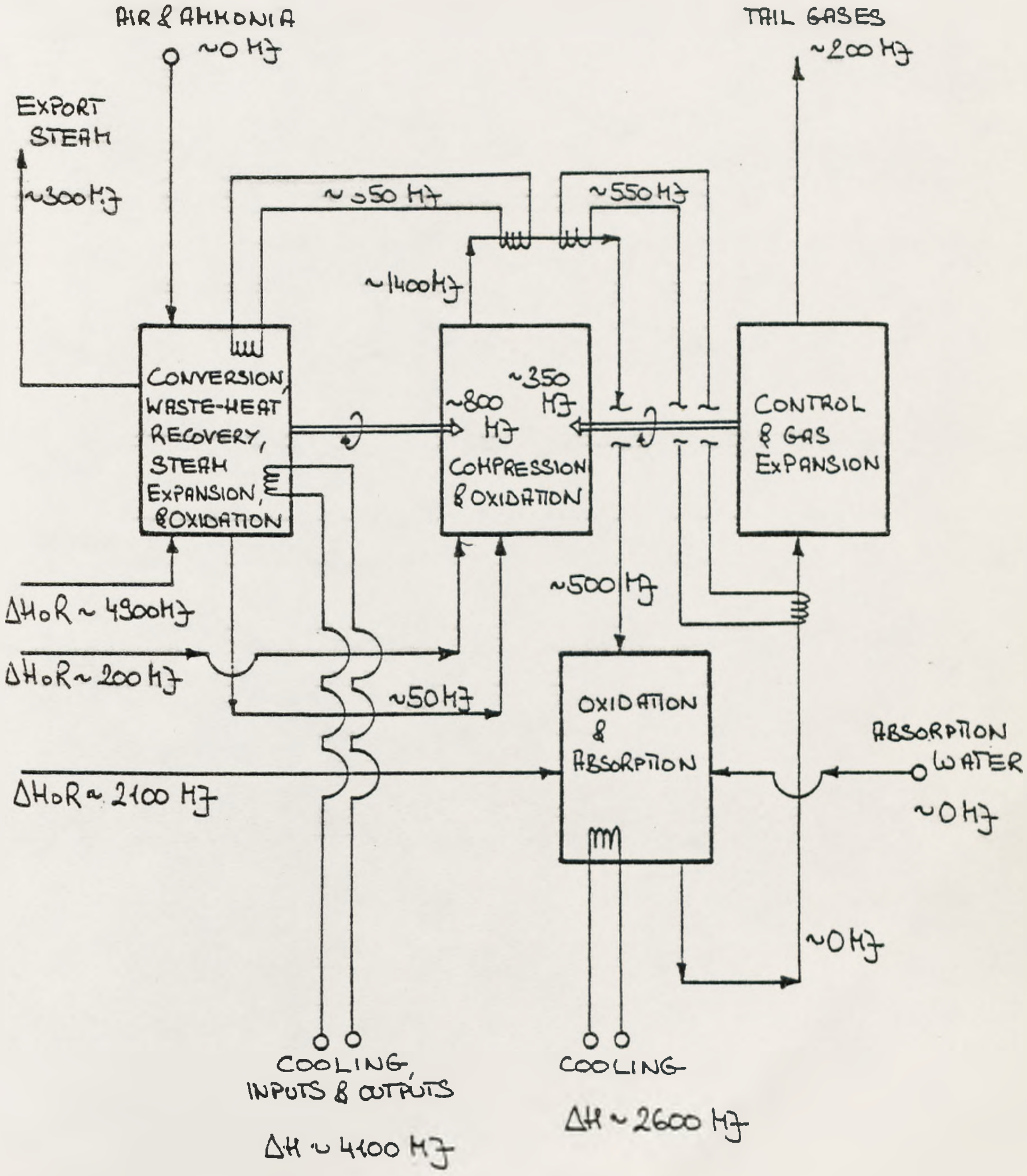

Figure (4.7) More detailed identification of energy flows.

From this sketch, a way to improve the energy performance could be seen in improving the waste heat recovery/steam raising section (so that more export steam is yielded with less cooling required). However, as commented above, the efficiencies of the individual unit operations in the compressor/turbine set appear to be satisfactory and improvements would, mainly, have to be sought by specifying different operating parameters and/or different interconnections. Another way to improvement could be seen in diverting more preheat to the tail gases before expansion (so that less work would be required from the steam turbine and, again, more steam would be exported). However, a more detailed discussion will be necessary (see in Sections 4.4 and 4.5) to clarify whether or not these alterations would be feasible and worth while.

4.3 EXERGY ANALYSIS

In Table (4.5) (see page 148) the exergies of the process flows are listed. For streams No.1 through No.28, the results are documented in columns 1 and 2 as obtained by means of Equation (2.31)

$$(Ex_1 - Ex_o)_{\Delta t} = (H_1 - H_o)_{\Delta t} - T_o * (S_1 - S_o)_{\Delta t} \qquad (2.31)$$

Repeat

i.e. exergy changes due to irreversible diffusion of gases have, as in Chapter Three, been neglected. For the water and/or steam streams (i.e. No.35 through No.45), the results listed in column 1 are based on the figures documented in Table (D.2).

Numerical Approximation Method

In column 3 of Table (4.5), the temperature dependent terms in the exergies of the process flows are given once more, this time as obtained by means of the numerical approximation method suggested in Chapter Two. For the gas phase flows No.1 through No.28, and for the liquid phase flows No.29 through No.34, they were calculated by means

Table (4.5) Exergies of process flows in HNO_3 process

COLUMN:			1	2	3	4	5
Flow	T (^{o}C)	p (p.s.i.a.)	Ex(T)	Ex(p)	Ex(T) (approx.) (MJ)	% error (-)	Ex(T,p) (approx.) (MJ)
			(MJ)				
(1)	22	∿atm	∿0	∿0	∿0	-	∿0
(2)	22	"	∿0	∿0	∿0	-	∿0
(3)	25	"	∿0	∿0	∿0	-	∿0
(4)	20	"	0.0	∿0	0.0	-	∿0
(5)	22	"	∿0	∿0	∿0	-	∿0
(6)	22	"	∿0	∿0	∿0	-	∿0
(7)	105	"	40.7	∿0	40.9	0.5	40.9
(8)	22	"	∿0	∿0	∿0	-	∿0
(9)	94	"	36.5	∿0	36.4	0.3	36.4
(10)	854	"	2225.5	∿0	2192.2	1.5	2192.2
(11)	771	"	1899.7	∿0	1868.1	1.7	1868.1
(12)	297	"	389.0	∿0	386.5	0.6	386.5
(13)	219	"	221.8	∿0	220.5	0.6	220.5
(14)	150	"	104.6	∿0	104.1	0.5	104.1
(15)	40	"	2.6	∿0	2.6	0.0	2.6
(16)	36	14.1	2.1	∿0	2.1	0.0	2.1
(17)	255	65.9	331.5	638.9	329.6	0.6	968.5
(18)	292	65.9	423.1	632.7	420.5	0.6	1053.2
(19)	228	65.1	268.2	627.5	266.5	0.6	894.0
(20)	127	64.3	82.3	622.3	82.1	0.2	704.4
(21)	25	63.5	∿0	565.7	∿0	-	565.7
(22)	25	61.5	∿0	509.4	∿0	-	509.4
(23)	30	59.5	0.7	476.5	0.7	0.0	477.2
(24)	160	58.7	105.3	471.9	105.0	0.3	576.9
(25)	160	58.7	89.5	401.1	89.2	0.0	490.3
(26)	160	15.4	15.8	2.4	15.8	0.3	18.2
(27)	57	15.4	7.4	13.5	7.5	1.4	21.0
(28)	73	15.4	17.4	15.9	17.3	0.6	33.2
(29)	20	liquid streams			0.0		0.0
(30)	40				0.7		0.7
(31)	25				∿0		∿0
(32)	25				∿0		∿0
(33)	20				0.0		0.0
(34)	21				∿0		∿0
(35)	90	215	39.9		40.0	0.3	40.0
(36)	158	"	137.2		136.8	0.3	136.8
(37)	198	"	262.0		261.5*	0.2	261.5
(38)	198	"	203.6		203.1	0.2	203.1
(39)	198	"	1109.9		1109.3*	0.1	1109.3
(40)	198	"	1168.4		1167.7*	0.1	1167.7
(41)	350	"	1379.1		1378.5*	0.0	1378.5
(42)	350	"	108.7		108.7*	0.0	108.7
(43)	350	"	1270.4		1269.8*	0.0	1269.8
(44)	41.4	1.15	189.8		189.6*	0.1	189.6
(45)	41.4	"	3.8		3.8	0.0	3.8

* calculated as in example on page 86

of Equation (2.50):

$$ex(T_1) = h(T_1) * \frac{T_1 - T_o}{T_1 - T_{RS}} * \left\{ 1 - \frac{T_o}{T_1 - T_o} \ln \frac{T_1}{T_o} \right\} \qquad \begin{matrix}(2.50)\\ \text{Repeat}\end{matrix}$$

In column 4, the deviations in percent are shown as against the "accurately" computed results (where the latter are given) and from the magnitudes of errors observed, a similar picture emerges as in Chapter Three : the numerical accuracy achieved by using the approximation method is such that the results shown in column 3 might be considered to be of equal value as those in column 1. Similarly, the results obtained in column 3 for the water and/or steam flows No.35 through No.45 are practically identical to the ones in column 1. Consequently, it was thought unnecessary to follow up the effects of the approximation through the complete analysis, as was done in Chapter Three, but the conclusion arrived at in Chapter Three was considered confirmed:

> In view of the uncertainty inherent in the case study anyway, it could be regarded as a matter of chance whether an analysis based on "correct" calculations would be closer to the truth than the "approximate" analysis.

In column 5 in Table (4.5), the total exergy of each flow (i.e. including pressure dependent terms) is shown as the sum of the results given in columns 2 and 3.

In Table (4.6) (see page 150), the exergy balance is given for each individual unit operation. When evaluating the lost work $\sigma * T_o$ (see column 4, Table 4.6), the exergy given to the cooling media was considered to be irreversibly lost (i.e. account was taken of the fact that heat transferred to the cooling media ultimately takes on ambient temperature). In column 5 in Table (4.6), Table (4.6) Exergy balances for unit operations in HNO_3 process

COLUMN :	1	2	3	4	5
Unit Operation	$\sum_{i=1}^{n} Ex_i(T,p)$ (MJ)	overall $\Delta ExoR_{RS,RS}$ (MJ)	ΔW_{shaft} (MJ)	$\sigma * T_o$ (MJ)	% (-)
PREHEATER	75.5	%	%	75.5	1.4
JUNCTION (7)/(8)	4.5	%	%	4.5	0.1
NH_3 - CONVERSION	-2155.8	4043.1	%	1887.3	35.8
SUPERHEATERS	113.3	%	%	113.3	2.2
STEAM DRUMS	0.0	%	%	0.0	0.0
W.H.BOILERS	575.4	%	%	575.4	10.9
B.F.W.HEATERS	69.2	%	%	69.2	1.3
STEAM TURBINE	1080.2	%	-808.3	271.9	5.2
CONDENSER	185.8	%	%	185.8	3.5
CASCADE COOLER	100.8	313.6	%	414.4	7.9
JUNCTION (3)/(4)	∿0	%	%	∿0	0.0
JUNCTION (5)/(15)	0.5	%	%	0.5	0.0
COMPRESSOR	-966.4	%	1166.6	200.2	3.8
NO-OXIDATION	-84.7	125.8	%	40.6	0.8
ECONOMISER	34.5	%	%	34.5	0.7
RECOVERY EXCH.	89.9	%	%	89.9	1.7
OXIDISING COOLER	138.7	480.1	%	618.8	11.7
STRONG A.C.	56.3	132.9	%	189.2	3.6
BLEACHER	∿0	2.0	%	2.0	0.0
WEAK A.C.	32.9	275.9	%	308.8	5.9
CONTROL BY-PASS	68.4	%	%	68.4	1.3
RECOVERY TURBINE	469.3	%	-358.3	111.0	2.1
JUNCTION (26)/(27)	6.0	%	%	6.0	0.1
OVERALL PLANT :				$\sum$ = 5267.2	100.0

the percentage is given to which each unit operation would appear to be responsible for the overall irreversibility of the process.

Prescribing Irreversibilities

Just as in Chapter Three, chemical reactions account for the major share of irreversibilities ($\sim$65.7%, of which 35.8% stem from the NH_3-conversion alone) and the losses due to heat transfer and imperfect compression and expansion are comparatively small. In this situation, it seems again appropriate to examine which irreversibilities are "inevitable" with present day technology.

NH_3-Conversion

This reaction has been discussed at length in Chapter Two and the possibilities that might be thought of to avoid irreversibilities are similar to the ones that apply to the sulphur combustion (see in Section 3.5), i.e. increased mass flow and/or higher reaction temperature. However, an increase in mass flowrate would, perhaps, be less realistic in the present case: the dimensions of ammonia converters in conventional plants are already considerable and, as mentioned above, higher operating costs are often tolerated (in pressurised conversion) to reduce size. Similarly, rather definitive limits exist for the conversion temperature : depending on the design of the burner, temperatures may vary between 800°C and 960°C (see Bahari$^{(74)}$ and Drake$^{(73)}$). However, temperatures in atmospheric pressure converters usually reach lower peak values than those in pressurised converters (see Oosterwijk$^{(75)}$) and a figure of

$$\overset{*}{T}_{10} = 900^\circ C$$

was used for determining the "avoidable" exergy losses in the NH_3-conversion in the present case study. Based on this figure, modified values were obtained as listed in Table (4.7)

Table (4.7) Parameters describing "optimal" arrangement for ammonia converter

	$\overset{*}{T}$ (^{o}C)	$\overset{*}{H}(T,p)$ (MJ)	$\overset{*}{Ex}(T,p)$ (MJ)
(9)	145	543.0	94.5
(10)	900	4366.7	2363.3

and the "avoidable" exergy loss was obtained with Equation (2.53):

$$(\Delta Ex_{irr})_{avoidable} = (Ex_{out} - Ex_{in})_{optimal} - (Ex_{out} - Ex_{in})_{actual} \qquad (2.53)\ \text{Repeat}$$

$$= \underline{\underline{113.0\ \text{MJ}}}$$

NO-Oxidation

Improvement of the exergy balance of the oxidation of NO would be achieved by increasing temperatures of the reacting gases, i.e. by following the same line of thought as in the case of the NH_3-conversion. Since the NO-oxidation is spread over more than one unit operation, however, the average temperature might not only be increased by preheating reactants but also by effecting some further oxidation at the relatively high temperature of $T_{18} \approx 300^{o}C$ with a corresponding decrease of oxidation in the absorption section : according to data given by Miles$^{(72)}$, the concentration of NO_2 in gas flow No.18 is still far below equilibrium concentration, and further oxidation would take place in the pipes if the residence time of the gases was increased.

Assuming that the amount of reacting species between compressor and economiser could, e.g., be doubled, the following figures would be obtained for gas flow No.18

T^{*}_{18} (°C)	H^{*}_{18} (MJ)	Ex^{*}_{18} (MJ)
329	1607.1	1150.9

and the irreversibility thus avoided can be evaluated with Equation (2.53) as before:

$$\underline{\underline{\overline{\sigma} * T_{o}}}\ _{\text{NO-Oxidation}} \qquad \underline{\underline{= \quad 97.7 \text{ MJ}}}$$

The exergy balance of the absorption section, when considered in terms of Equation (2.53), will not change significantly with the amount of oxidation since inputs and outputs exist at substantially ambient temperature. Thus, the total benefit to be derived from the proposed shift of some oxidation would become apparent in the high temperature region and no benefit would become apparent in the absorption section. It is, perhaps, interesting to contrast this with the information that would emerge from a conventional Second Law analysis, see Table (4.8):

Table (4.8) Effect of increased oxidation in high temperature region as assessed in a conventional Second Law analysis

	After Compression	Absorption Columns	Sum
$\sigma * T_{o}$ (in MJ) in existing plant	40.6	498.0	538.6
$\sigma * T_{o}$ (in MJ) with proposed shift of oxidation	68.2	372.7	440.9
Improvement (in MJ)	-27.6	125.3	97.7

The overall benefit to be derived would, also, appear to be 97.7 MJ but improvement would only be shown in the absorption section while losses would be increased rather than decreased in the high temperature region. The reason lies in the fact that the reaction is always an irreversible phenomenon so that an increase in the amount of reacting species leads to an increase in irreversibility. Thus, losses are registered in the high temperature region to an extent that more than offsets the improvement due to the increased gas flow temperature. This seems to be a good example of a case where "inevitable" and "avoidable" losses do require distinction if "inevitable" losses are to be prevented from distorting and even completely burying the significance of the "avoidable" ones.

The Cascade Cooler

Some of the irreversibilities in the cascade cooler are related to the reactions taking place and some to the heat transfer from the process gases to the cooling water. As a crude approximation, the former irreversibilities amount to

$$\sim 313.6 \text{ MJ}$$

(see column 2 in Table 4.6) and the latter ones to

$$\sim 100.8 \text{ MJ}$$

(see column 1).

Practically, little can be done about these reaction related losses since reaction temperatures cannot be chosen. The heat transfer losses, by contrast, could partly be avoided by increasing heat transfer area to effect a higher rise in cooling water temperature and by usefully exploiting the potential thus given to the cooling water. On the other hand, the cascade cooler is a large - and expensive - piece of equipment and is particularly prone to corrosion. An alteration would thus be costly and perhaps be unreliable. Also, only about 50 MJ

$$0.5 * 100.8 \text{ MJ} \sim 50 \text{ MJ} *$$

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*Compare Equation (3.1)

(or 3% of the energy recovered at present) could be gained if the equipment used was 50% efficient. This would, clearly, not justify the installation and the assumption was made that the irreversibilities as observed in the cascade cooler at present are, by and large, inevitable:

$$\underline{\underline{\overline{\sigma} * T_o}}_{\text{Cascade Cooler}} \approx \underline{\underline{0}}$$

The Bleacher

On a smaller scale, similar arguments apply for the bleacher as for the cascade cooler. The temperatures involved cannot, really, be chosen and prospects of usefully exploiting the potential that is wasted in temperature drops do not exist realistically:

$$\underline{\underline{\overline{\sigma} * T_o}}_{\text{Bleacher}} \approx \underline{\underline{0}}$$

The Oxidising Cooler

Once more, similar arguments apply for the oxidising cooler as for the cascade cooler but there is the interesting difference that the gases in the oxidising cooler are pressurised : this contributes to the loss observed in Table (4.6) by as much as 56.6 MJ, see Figure (4.8) on page 156. Further, it is evident from Figure (4.8) that there are two independent phenomena which cause this pressure related loss, namely

- a reduction in molar flowrate at elevated pressure, and
- the pressure drop.

Thereby, the reduction in molar flowrate is by far the more significant factor and would become even more significant with further increased pressure. This seems important since, in the present case study, the pressure at which the oxidising cooler is operated is relatively low compared to other nitric acid processes

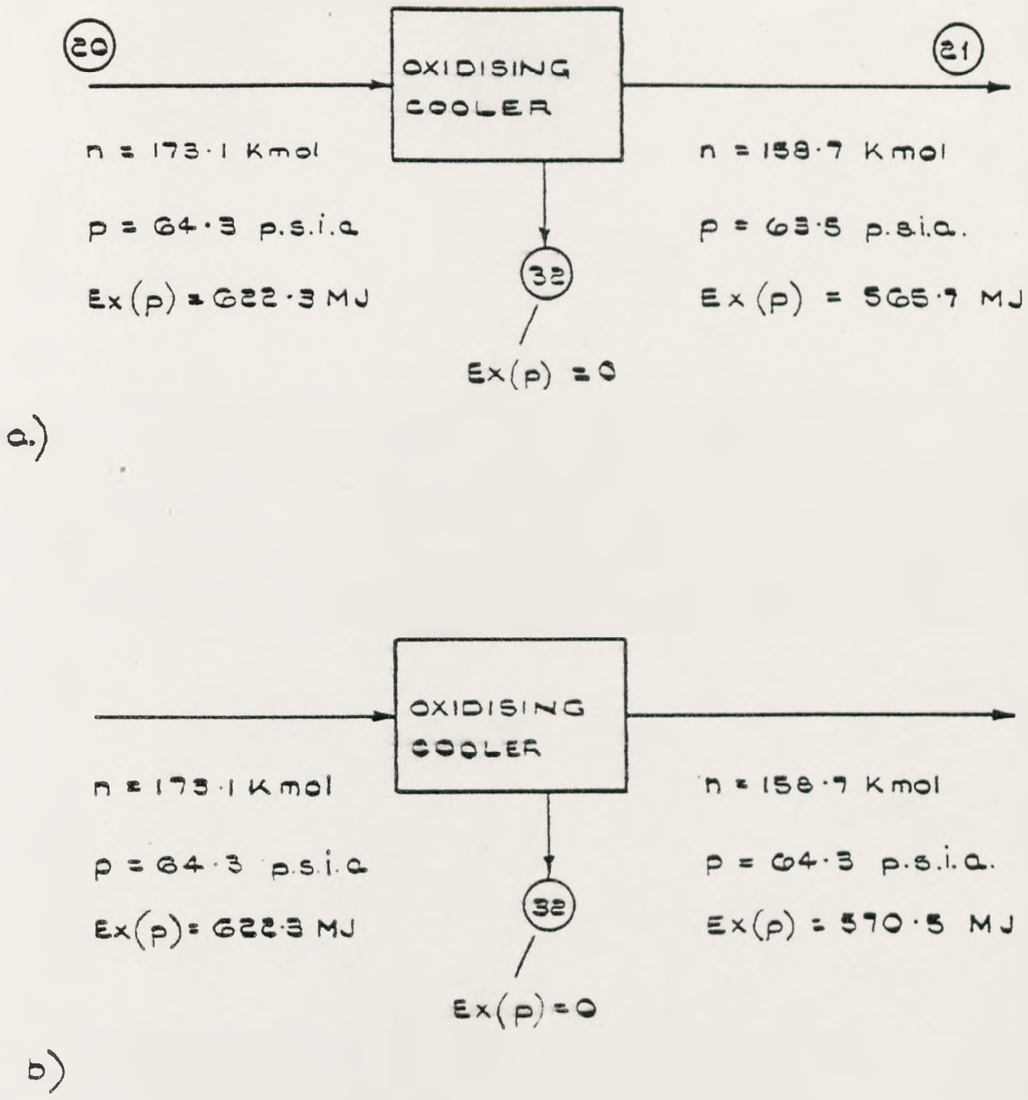

Figure (4.8) Molar flowrate and pressure drop in oxidising cooler.
a) Actual arrangement.
b) "Optimal" arrangement.

and it has been assumed that an even lower pressure would not be practical: pressure is necessary to promote the reaction, just as low temperatures are often necessary to promote certain exothermic reactions (such as $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$, see Chapter Three). Thus, the losses due to reduction in molar flowrate can be considered "inevitable" and the "optimal" arrangement for the oxidising cooler is shown in Figure (4.8b). It follows that the "avoidable" exergy loss $\bar{\sigma}*T_o$ is evaluated as :

$$\underline{\underline{\bar{\sigma}*T}}_{o\,\text{Oxidising Cooler}} = (56.6 \text{ MJ} - 51.8 \text{ MJ}) = \underline{\underline{4.8 \text{ MJ}}}$$

The Absorption Columns

For both absorption columns, similar considerations apply as for the oxidising cooler : there are losses related to reactions occurring at given temperatures, to heat transfer, to the reduction of mole numbers at elevated pressure level, and to pressure drop. In line with the assumptions used for the oxidising cooler, only the losses due to pressure drop were considered to be avoidable. This led to the following results:

$$\underline{\underline{\bar{\sigma} * T}}_{o\,\text{Strong A.C.}} \quad \underline{\underline{= \quad 11.4 \text{ MJ}}}$$

and

$$\underline{\underline{\bar{\sigma} * T}}_{o\,\text{Weak A.C.}} \quad \underline{\underline{= \quad 11.3 \text{ MJ}}}$$

Summary

In Table (4.9) (see page 158), the "avoidable" irreversibilities as evaluated above are listed in the context of the whole process. In column 4, the relative magnitudes of all "avoidable" irreversibilities are expressed in percentage terms and in column 5, the respective figures are given as based on the results obtained in the conventional analysis (listed in Table 4.6) . For the seven unit operations involving chemical reactions, markedly different figures emerge (shown boxed in column 5) and, as in the case of the sulphuric acid contact plant, the differences are big enough to suggest relative priorities for the individual losses which are decidedly dissimilar. Also, the figure for the overall loss in Table (4.9) is less than half of that obtained in the conventional analysis. In Figure (4.9) (see page 159), the "avoidable" irreversibilities are shown in the flowsheet context.

Table (4.9) "Avoidable" exergy losses $\bar{\sigma} * T_o$ for HNO_3 process

COLUMNS :	1	2	3	4	5
Unit Operation	$(Ex_{in}-Ex_{out})$ actual (MJ)	$(Ex_{in}-Ex_{out})$ optimal (MJ)	$T_o * \bar{\sigma}$ (MJ)	% (-)	%* (-)
PREHEATER	75.5	0	75.5	3.7	3.7
JUNCTION (7)/(8)	4.5	0	4.5	0.2	0.2
NH_3-CONVERSION	-2155.8	-2268.8	113.0	5.5	$\boxed{92.3}$
SUPERHEATERS	113.3	0	113.3	5.5	5.5
STEAM DRUMS	0	0	0	0.0	0.0
W.H.BOILERS	575.4	0	575.4	28.2	28.2
B.F.W.HEATERS	69.2	0	69.2	3.4	3.4
STEAM TURBINE	271.9	0	271.9	13.3	13.3
CONDENSER	185.8	0	185.8	9.1	9.1
CASCADE COOLER	100.8	~100.8	0	0.0	$\boxed{20.3}$
JUNCTION (3)/(4)	0	0	0	0.0	0.0
JUNCTION (5)/(15)	0.5	0	0.5	0.0	0.0
COMPRESSOR	200.2	0	200.2	9.8	9.8
NO-OXIDATION	-84.7	-182.4	97.7	4.8	$\boxed{2.0}$
ECONOMISER	34.5	0	34.5	1.7	1.7
RECOVERY EXCH.	89.9	0	89.9	4.4	4.4
OXIDISING COOLER	138.7	133.9	4.8	0.2	$\boxed{30.3}$
STRONG A.C.	56.3	44.9	11.4	0.6	$\boxed{9.3}$
BLEACHER	0	0	0	0.0	$\boxed{0.1}$
WEAK A.C.	32.9	21.6	11.3	0.6	$\boxed{15.1}$
CONTROL BY-PASS	68.4	0	68.4	3.3	3.3
RECOVERY TURBINE	111.0	0	111.0	5.4	5.4
JUNCTION (26)/(27)	6.0	0	6.0	0.3	0.3
* See Table (4.6)		$\sum$ =	2044.3	100.0	257.7

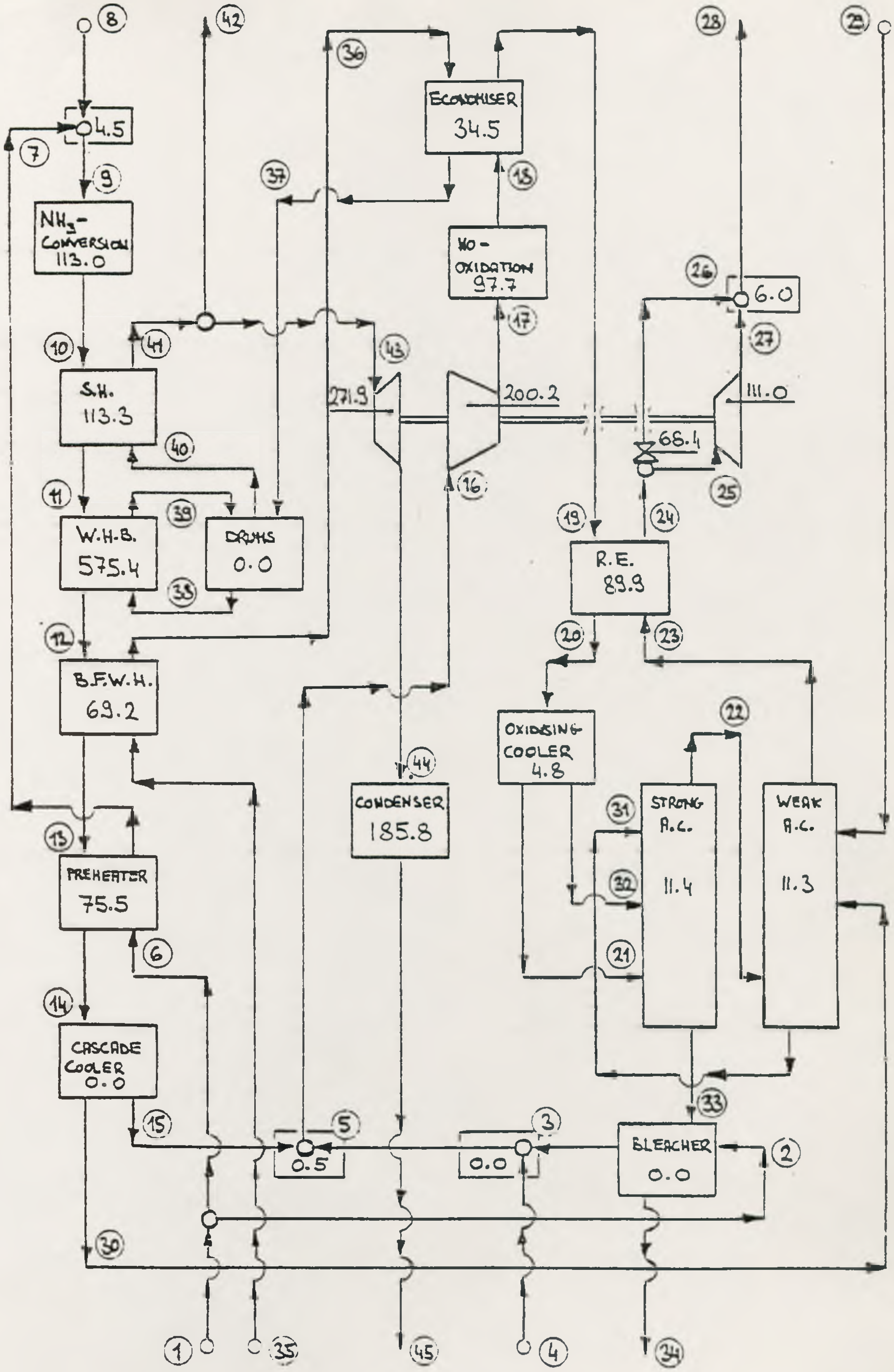

Figure (4.9) "Avoidable" exergy losses in HNO_3 process.

4.4 INTERPRETATION

In contrast to the sulphuric acid plant, the irreversibilities finally identified as "avoidable" in the present case study are due not only to the degradation of heat but also of work : heat is degraded in heat exchangers and not sufficiently upgraded in reactions, and work is degraded in non-isentropic compression and expansions, and dissipated due to pressure drops. If all these "avoidable" exergy losses were avoided indeed, extra work would be gained amounting to

$$T_o * \bar{\sigma}_{overall} \approx 2000 \text{ MJ}$$

(see Table 4.9). This is almost twice as much as the 1200 MJ of work (or work equivalent) harnessed at present and indicates that the energy recovery in the process is, roughly, 38% efficient

$$\frac{1200}{2000 + 1200} \approx 0.38$$

once that inevitable irreversibilities have been excepted.

Direct Generation of Work

As is evident from Figure (4.9), the avoidable irreversibilities are quite evenly spread over the plant with losses in excess of 5% of the total only occurring in the NH_3-converters, the superheaters, the waste heat boilers, the compressor, the turbines, and the condenser. The chances to implement work generating equipment so as to avoid part of these more relevant losses are now discussed one by one :

In the condenser, a temperature drop exists of only about 20°C and, practically, not much of the 185.8 MJ loss listed in Table (4.9) can be avoided by means of work generating equipment : the magnitude of this loss is, mainly, due to the large amount of heat that is degraded and not to the degree of degradation (which is quite insignificant).

(Compare to this Appendix E.) Similarly, the losses in the compressor and in the two turbines - although quite significant relative to other losses in the process - have already been seen to be perfectly acceptable given the amount of work consumed/produced in these units. In the waste heat boilers, however, an improvement might be possible : the losses amount to 575.4 MJ (or 28.2% of the "avoidable" total) and are due to excessive temperature drop. The losses in the superheaters are due to excessive temperature drop as well, and the possibility might exist to identify an installation which would not only help to partly prevent these losses but those in the converters, too: if converters were designed so as to allow the hot NO-gases to reach ∿900°C and the potential of these gases was exploited more efficiently than in the present superheater and waste heat boiler, about 560 MJ of work equivalent could be gained if the installation was approx. 70% efficient

$$0.7 * (113.0 + 113.3 + 575.4) \text{ MJ} \approx 560 \text{ MJ}$$

(compare Equation 3.1). This would seem a worthwhile improvement.

However, the type of installation needed would by and large be the same as the one suggested in Figure (3.11) for the contact process and, in the present context, such a gas turbine scheme would not be very promising : as pointed out in Section 4.1, high pressure in the ammonia converters has an adverse effect on ammonia efficiency, as well as on catalyst losses, and an increase of conversion pressure above absorption pressure would appear to be unrealistic. Also, the efficiency of the gas turbine scheme would be quite low with a peak gas temperature of only ∿900°C. Thus, the only obvious way to decrease exergy losses in the conversion/waste heat recovery section of the process would be by raising steam at a higher pressure level. This suggestion will be followed up further below.

Network Interactions

With regard to network interactions, the conclusions drawn in Chapter Three are confirmed by the present case study : individual unit operations might well be improved in their thermodynamic efficiency but the overall effect can only be clarified by means of a heat and mass balance simulation. Perhaps a little surprisingly, this holds true even in a context where network interactions are most straight-forward and the prospects of generating extra work are directly assessed in terms of exergy, i.e. work equivalent : trying to assess how much additional shaft work could be gained if the control by-pass around the recovery turbine was shut completely, one might examine the exergy analysis of the status quo, see Figure (4.9), and find that $\sigma^* T_o = 68.4$ MJ are lost in the by-pass and $\sigma^* T_o = 6.0$ MJ are lost in the junction of streams No.26 and No.27. Thus, 74.4 MJ of useful work equivalent would appear to be recoverable if the by-pass was shut. Assuming that the efficiency of the recovery turbine would not be affected by variations in load, this should lead to 56.8 MJ of additional shaft work:

$$\left(\frac{358.2}{490.3 - 21.0}\right) * 74.4 \text{ MJ} = \underline{\underline{56.8 \text{ MJ}}}$$

In Figure (4.10) on page 163, however, the heat and mass balance is given for the case of no mass flow through the by-pass and the amount of extra shaft work gained is seen to be

$$421.5 \text{ MJ} - 358.2 \text{ MJ} = \underline{\underline{63.3 \text{ MJ}}}$$

i.e. 11% more than predicted. The discrepancy is mainly due to the fact that the tail gas temperature T_{28}, and with it the exergy of stream No.28, changes when the by-pass is shut. This effect cannot be quantified by merely interpreting exergy figures which refer to a status quo but has to be examined by simulating the contemplated modification in heat and mass balance terms. One might conclude that,

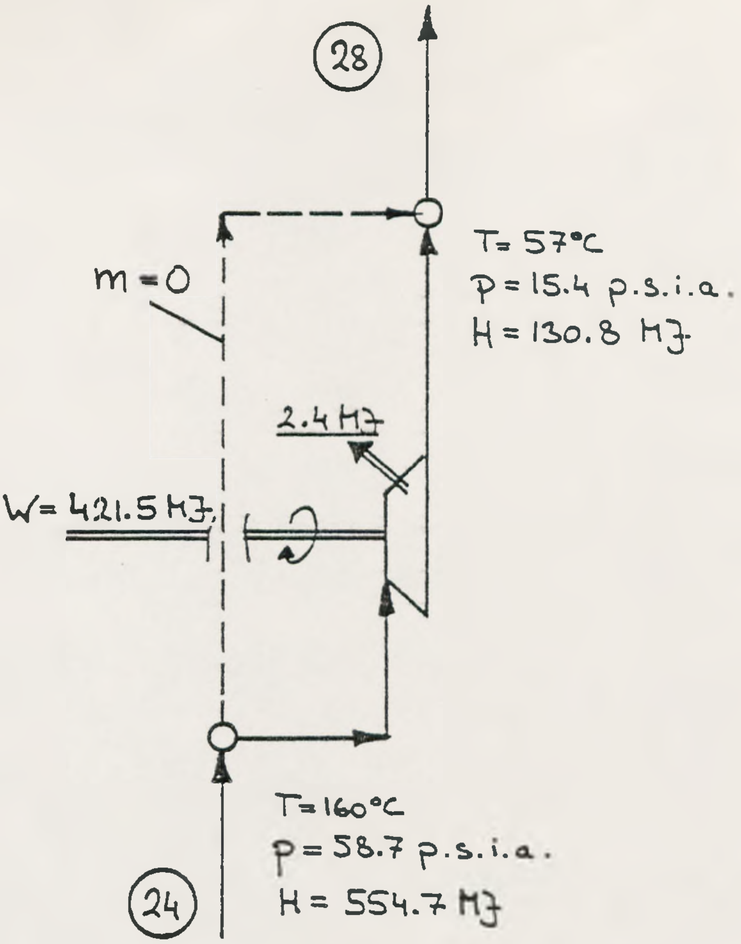

Figure (4.10) Simulation for shut control by-pass.

even in the context of very simple networks, cases will be few and far between in which exergy losses, or entropy changes, bear a direct numerical relevance to the amount of work that could be gained realistically.

Recovery of Low Grade Energy

In Chapter Three, irreversibilities of individual unit operations have been seen to be considerably different in their significance for potential improvement if low grade energy rather than work is to be recovered. If steam is to be raised, e.g., the temperatures at which heat is given to the steam need only be high enough to be compatible with the chosen pressure level and irreversibilities occurring at still higher temperatures do not adversely affect the amount of steam that can be raised. To obtain clarity, a T,Q-diagram of the process flows was seen to be of use. In Figure (4.11), such a diagram is given for the ammonia oxidation plant. From this diagram,

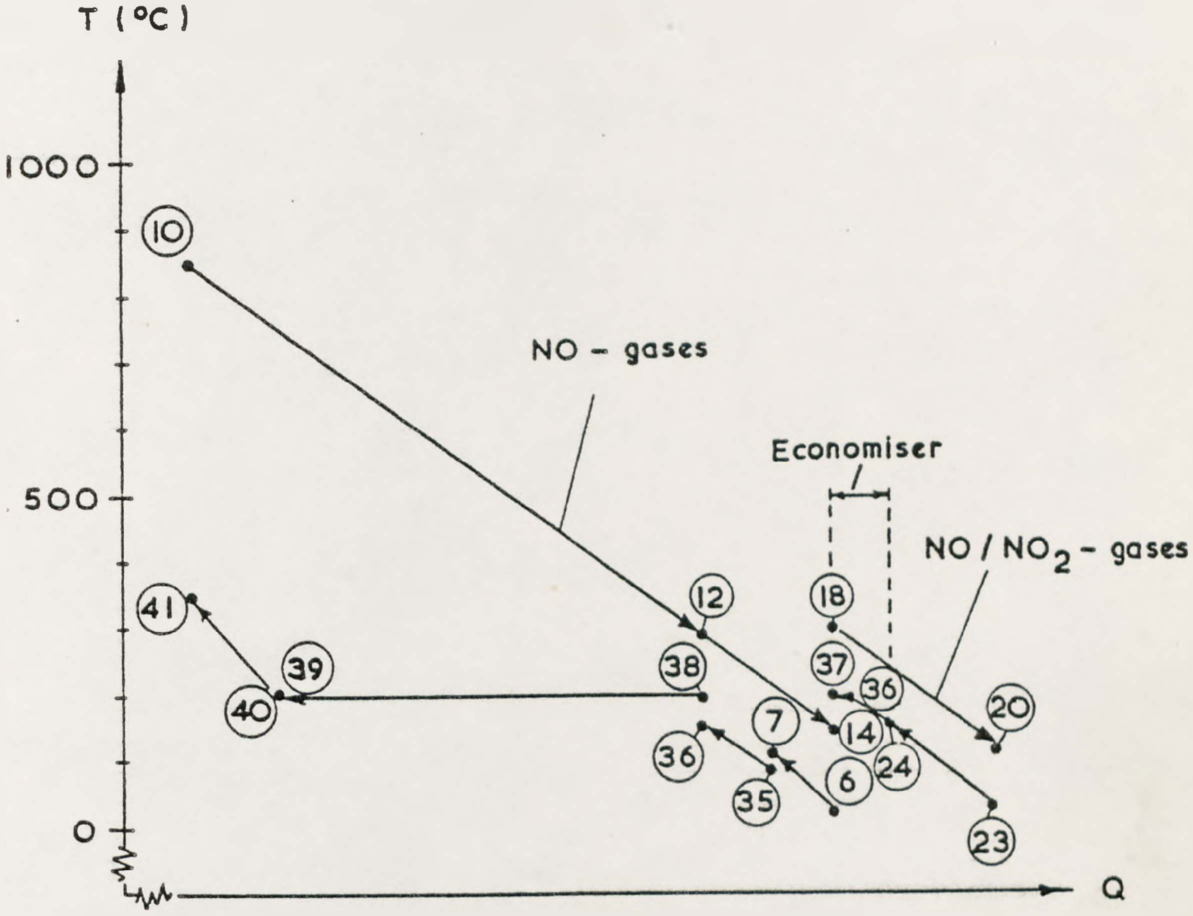

Figure (4.11) T,H-diagram for heat sources and sinks in HNO_3 process.

it would appear that practically all heat that is available from the NO-gases and the NO/NO_2-gases is usefully employed in preheating the air, heating the tail gases, and raising steam. Accepting the need for certain minimum approach temperatures in heat exchangers, additional heat is not available in the process at relevant temperatures unless - rather like in the case of the sulphuric acid plant - more heat was upgraded in reactions, i.e. in the NH_3-conversion and/or the NO-oxidation. In the NH_3-conversion, however, further preheat would have to be given to the air (7) at temperatures above 105°C and since all heat of sufficiently high temperatures is already usefully employed, no advantages could be gained. The NO-oxidation, by contrast, would appear to offer a genuine chance for improvement : by increasing the residence time of gas flow (17) in the pipes (as already discussed above), additional heat might become available to raise more steam and/or to preheat the tail gases further before they enter the recovery turbine. A detailed examination has shown that, if the temperature T_{18} was raised by 10°C, additional steam could be exported amounting to

$$\sim 19 \text{ kg}/10^3 \text{ kg } HNO_3$$

Thereby, it does not matter whether the additional heat is passed through the economiser or given to the tail gases, with a higher output resulting from the recovery turbine and less steam required in the steam turbine. The existing design appears to be well balanced insofar as both work generating processes - tail gas expansion and steam expansion - would utilise a marginal increase in heat supplied with practically identical efficiency.

It would be difficult, however, to quantify the alterations in terms of equipment sizing which would be necessary to achieve a given rise in temperature T_{18} and the suggestion to provide the oxidation of NO in the high temperature region has, thus, not been developed any further. Instead, the proposition to raise steam at higher pressure (see above) was followed up.

There is an HP steam mains in the factory with p = 685 p.s.i.a. and it would appear from Figure (4.11) that the temperature drops in the existing heat exchangers show sufficient reserves to enable steam to be raised at this higher level. (The evaporation temperature for HP steam at p = 685 p.s.i.a. is $\sim 260^{\circ}$C, compared to $\sim 198^{\circ}$C for the IP steam). Also, there is certainly no difficulty in superheating the steam to a higher turbine inlet temperature. Thus, a higher drop of potential across the turbine per unit mass of steam should be possible so that less steam is used in the turbine and more is exported. As further benefit, the exported steam would be HP rather than IP. In the next paragraph, two schemes are outlined which are based on this idea. Again, the benefits to be gained in these schemes were found not to be easily related to the corresponding improvements in Second Law terms : the second scheme (see later, Figure 4.13) exhibits considerable savings when compared to the first one (see Figure 4.12) but is only marginally more efficient in Second Law terms.

4.5 SCHEMES FOR IMPROVED ENERGY RECOVERY

In Figure (4.12) (see page 167) a design is detailed in which steam is raised at HP level and is superheated to 460°C - rather than 350°C as in the existing process - before it is passed into the condensing turbine. According to Valentine(62), this degree of superheat is still within the normal range. When specifying this design it became apparent that, with increased specific enthalpy of the steam at turbine inlet conditions but unaltered specific enthalpy of the boiler feed water, the amount of steam raised had to be decreased as compared to the existing process : the overall amount of enthalpy available is $\sim$constant*. With a decreased flowrate for boiler feed

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*This applies although the gas temperatures on entry into the cascade- and into the oxidising cooler have been re-defined. These latter changes were convenient to achieve heat load compatibility in the boiler feed water heater and in the recovery exchanger, but they do not lead to a significant improvement in terms of overall enthalpy available.

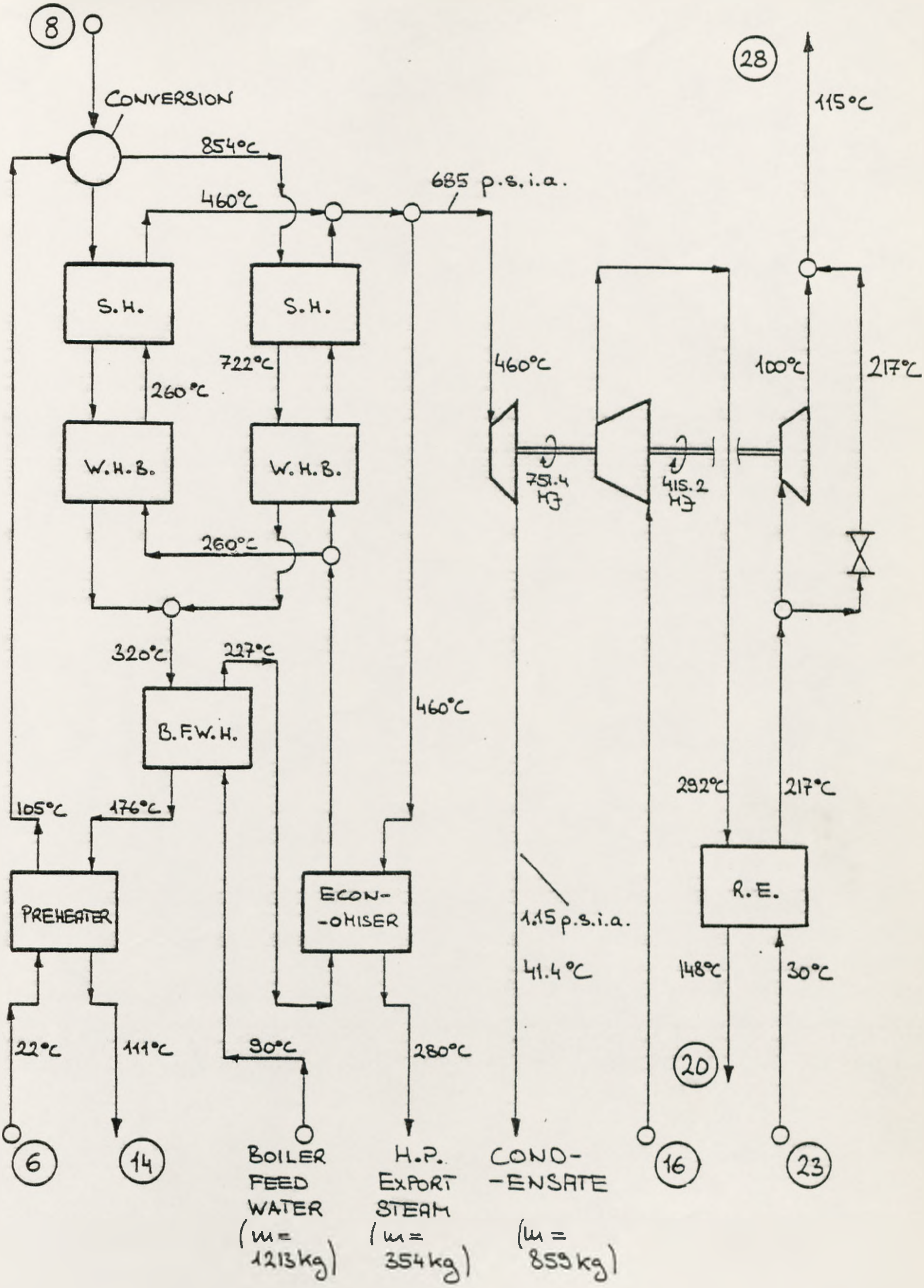

Figure (4.12) Possible scheme for improved energy recovery in HNO_3 process.

water, however, a rather close temperature approach would result in the economiser (see the temperature profile in the economiser in Figure 4.11). For this reason, the economiser in Figure (4.12) makes use of the superheat of the exported steam rather than of the heat from the NO/NO_2-gases. This ensures higher temperature differences in the economiser and, beyond this, it allows to increase the load on the recovery exchanger and the recovery turbine so that an additional advantage has been derived from the increased temperature and pressure of the steam at turbine inlet conditions. The figures quoted in Figure (4.12) are based on turbine efficiencies equal to the ones in the original case study and the smallest temperature difference in the heat exchangers is $\Delta T = 53^{\circ}C$ (compared to $68^{\circ}C$ in the original design). The number of heat exchangers employed is one less but the two boiler feed water heaters in the original design could, apparently, also be replaced by a single unit, making the numbers equal. By and large, equipment cost for the design shown in Figure (4.12) should be roughly similar to that for the original design. In terms of steam exported, however, 354 kg of HP steam are gained compared to 102 kg of IP steam . With credits for steam as estimated in Table (4.10), this is equivalent to a benefit of

60000 £/yr.

if the plant is on stream for 8000 hrs/year (at nominal capacity).

Table (4.10) Average and marginal cost of steam for three pressure levels

Steam pressure	Average Cost (£/10^3 kg)	Marginal Cost (£/10^3 kg) *
H.P. (685 p.s.i.a.)	5.00	4.00
I.P. (215 p.s.i.a.)	4.50	3.60
L.P. (40 p.s.i.a.)	4.00	3.20

* Marginal cost is used for savings and assessed as 80% of average cost.

However, in relation to total costs the savings are, probably, only marginal and the design shown in Figure (4.12) could certainly not be called a breakthrough when compared to the existing process.

A more significant improvement of energy costs could, possibly, only be achieved if a back-pressure turbine was used rather than a condensing turbine : with a back-pressure turbine, the exhaust steam could be exported into the existing L.P. steam mains (instead of being condensed) allowing an interesting credit to be earned (see Table 4.10) as well as reducing the load on the cooling water cycle by about half (see Figure 4.4). In equipment terms, the condenser would become unnecessary and one cooling tower (instead of the existing two) would, probably, suffice. However there is one difficulty : bearing in mind that, for start-up reasons, the turbine inlet pressure should be compatible with the pressure in the existing HP steam mains, the specific drop of potential across the turbine would be rather more limited than in the case of a condensing turbine and the amount of steam required to produce the same shaft power would be considerably increased. As can be shown with some brief calculations, there is not enough potential in the process gases to allow raising steam in sufficient quantity.

In Figure (4.13)(see page 170), a design is shown in which the installation of a back-pressure turbine has, nevertheless, been made possible. The decisive feature of this design lies in the fact that the steam coming from the waste heat boiler is, before it enters the superheater, supplemented with imported steam (from the HP mains). Thus, the quantity of steam reaching the turbine is adequate for producing the required amount of shaft work. - As in Figure (4.12), the superheat of the exported steam is given to the boiler feed water, but the sequence of economiser and boiler feed water heater had to be altered, due to the lower temperature at which the LP superheat

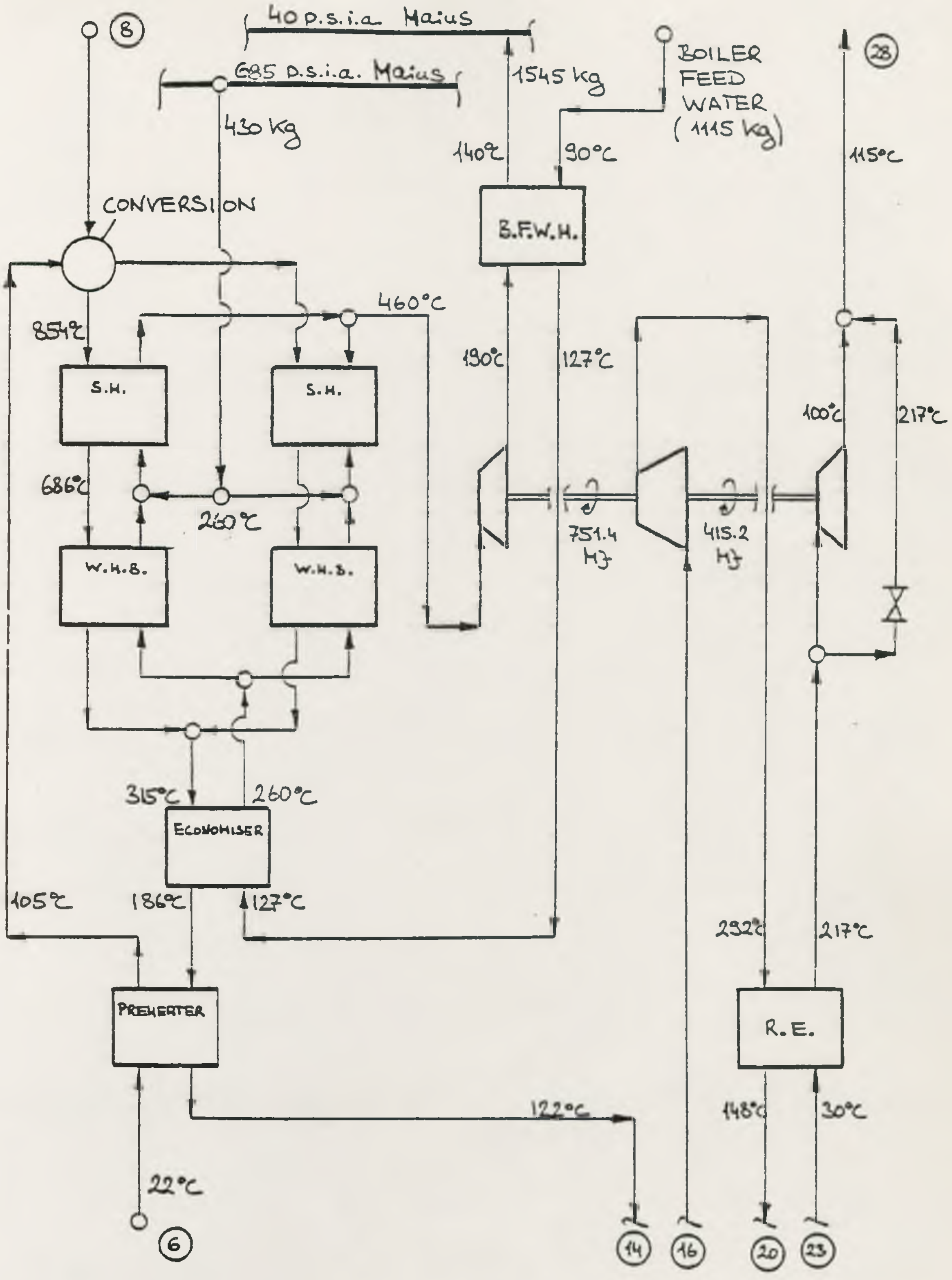

Figure (4.13) Recommended scheme for improved energy recovery and for capital savings in HNO_3 process.

is available. As far as recovery exchanger and recovery turbine are concerned, the design is identical to the one shown in Figure (4.12).

Based on Table (4.10), a benefit of about

160000 £/yr.

would be achieved in Figure (4.13) - as compared to the existing process -, if the plant was operated for 8000 hrs/year at nominal capacity. Also, there would be benefits in reduced cooling water consumption and cheaper equipment costs (no condenser and only one cooling tower, and the number of heat exchangers unchanged). From a financial point of view, the design shown in Figure (4.13) does seem to be attractive.

From an operability point of view there are no obvious difficulties. Basically, the design should be very similar in its control characteristics to the original case study with, perhaps, the added advantage that some crude control might be achieved by varying the amount of HP steam imported. (This would enable the mass flowrate in the by-pass (26) to be somewhat reduced). On the other hand, the dependence on a constant HP steam supply introduces an additional possibility for system failure and provision might have to be made for the event of a sudden drop of pressure in the mains. Larger steam drums might suffice to avoid sudden temperature changes in the plant, but a stand-by electrical motor (with an output of ∿0.4 MW) might be desirable if the possibility of full capacity operation was to be maintained independent of the HP steam supply. As far as starting-up capability is concerned, the compatibility between steam condition at turbine inlet and mains presure, which is a feature of the original process, has been preserved.

Turning to equipment reliability, the design should, again, be quite similar to the original case study : according to Oosterwijk (75), perhaps the most serious corrosion problem in nitric acid plants is encountered at the cold end of the recovery exchanger and no alterations have been suggested there. The other two pieces of equipment that are liable to corrosion are the cascade cooler and the oxidising cooler and, although the gas flow temperatures T_{14} and T_{18} have been slightly altered, this should not have a great impact on corrosion problems. If it had, the sizes of the economiser and of the recovery exchanger in Figure (4.13) could be adapted to approximate desired temperatures T_{14} and T_{18} .

Finally, the prospects should be discussed of integrating a scheme such as presented in Figure (4.13) into other nitric acid processes, especially future designs. Important in this context is the obvious flexibility of the scheme : more or less HP steam could be imported, depending upon individual power requirements for processes operated at various pressure levels. Also, the HP steam required might be raised in the process itself in cases where tail gas combustion is employed. Thus, the scheme would become independent of steam mains. It would appear that, with the cost of fuels likely to rise further, the scheme might turn out to be highly attractive in all cases where an appropriate demand for LP steam exists.

4.6 DISCUSSION

In this second case study, an exergy analysis was used for much the same task as the entropy analysis in Chapter Three and, as far as the relevance of Second Law analysis to practical process design is concerned, much the same conclusions were reached : (1) Few losses might be large enough to justify the installation of additional work generating equipment and smaller losses have to be dealt with by modifying existing equipment. (2) When doing so, however, network interactions make it difficult to predict results of changes without First Law simulation. (3) A certain minimum irreversibility might be impossible to combat because it has been implicitly accepted by choosing energy sources and sinks.

With regard to network interactions, a particularly striking example was encountered in Figure (4.10) : although the form of energy examined is shaft work and the concept used is exergy (i.e. potential for shaft work), and although the configuration in question looks exceedingly simple, the straight-forward interpretation of "shaft work lost equals exergy loss" leads to wrong results.

Another good example encountered in this case study is documented in Table (4.8) : in a conventional Second Law analysis, a proposed shift of some NO-oxidation from the absorption section to the high temperature section after compressor (so that the heat released would become available at useful temperatures) would lead to increased losses in the high temperature region and decreased losses in the absorption section. This might not be intuitively sensible since it is in the high temperature region where useful recovery is to be accomplished. With the concept of prescribed irreversibilities, the change in the high temperature region is assessed as beneficial. This results from the elimination of inevitable irreversibilities from the study which would thus appear to facilitate interpretation.

Coming to the numerical approximation method suggested in Chapter Two, this was seen to be equally successful in the context of exergy as of entropy. Even the correction necessary to allow for a choice of ambient temperature different from the reference temperature for enthalpy was seen not to impair the accuracy unduly. The fact that exergy analyses based on various assumptions regarding ambient temperatures may speedily be produced from enthalpy figures based on any other normal reference temperature could be a further important attraction of the method.

Lastly, a final assessment can now be made of the relative merits of the two concepts, entropy and exergy, in analysis work. Using entropy, heat rejected to the environment at ambient temperature has to be considered (compare 3rd column in Table 3.8). Using exergy, considerations may be limited to the process*. Thus, exergy might be more convenient to use. On the other hand, the computation of exergy figures is more involved than that of entropy figures (compare Equation 2.31) unless the approximation method is used (in which case the differences in computational effort are reduced: compare Equations 2.47 and 2.48).

Further, as pointed out previously (see Section 2.3), a process stream's exergy has a physical significance which is perhaps more easily appreciated than that of its entropy : a compressed gas has a higher potential for yielding useful work (and thus a higher exergy) than an uncompressed gas and a hot flow has a higher potential (and thus a higher exergy) than a cold flow. With entropy, rises in temperature lead to increases in entropy but rises in pressure lead to decreases. Thus, changes in the entropies of process flows are not very easily appreciated and it is not before the irreversible entropy increases within unit operations are evaluated that interpretation of an entropy analysis is intuitively easy. An exergy analysis, by contrast, offers intuitive relevance in the figures associated with streams as well as with losses in unit operations. This argument apart, however, both concepts yield essentially identical information. Thus, the choice between the two may often, and quite legitimately so, be made on grounds of greater familiarity on the part of the user.

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*This follows from the fact that heat exchange with the environment demands changes in the process enthalpy, which in turn enter exergy calculations.

PART II

Systematic Design of Heat Exchanger Networks

Note:

The work presented in Part II is based on Imperial Units to ensure compatibility with previous work in the field. An exception to this is Appendix F which consists of two published papers that had to be re-written in SI Units following the request of the editor.

CHAPTER FIVE

INTRODUCTION TO HEAT EXCHANGER NETWORKS

As noted on the previous page, some of the work to be presented in Part II has been the subject of two publications, copies of which are found in Appendix F. Since both papers have an introduction and a literature survey, the introductory remarks given below are not exhaustive but complementary to the information given in Appendix F.

5.1 HEAT EXCHANGER NETWORKS AS A PROBLEM OF PROCESS SYNTHESIS

The design of a heat exchanger network which is to be integrated into an otherwise defined process network is a sub-problem of process design in general. Typical examples of this type of problem were discussed in Chapters Three and Four when schemes with improved energy recovery for the case study processes were identified.

When discussed in the literature, however, the problem is often interpreted in the context of the somewhat special field of "process synthesis", implying that the problem may be tackled by means of a systematic approach rather than by engineering intuition (see references (79) through (101)). Simultaneously, the problem description is usually simplified, using a number of assumptions:

(1) There are no "forbidden matches". In other words, any "hot" process stream (i.e. a stream that is to be cooled) can be matched against any "cold" stream (i.e. a stream that is to be heated).

(2) Ancillary heating, if required, can only be provided with steam at one pressure level (i.e. there are no furnaces, no hot oil circuits, etc.).

(3) If there is process surplus heat, this can only be rejected into cooling water (i.e. there are no air coolers, no steam is raised, etc.).

(4) The process streams (all of known mass flowrates and of constant thermal properties) have to be brought from fixed supply to fixed target temperatures.

(5) The design goal is to find a network of single stream counter-current heaters, coolers, and exchangers ★ which is optimum with

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★ "Heater" : a match between a process stream and steam.
"Cooler" : a match between a process stream and cooling water.
"Exchanger" : a match between process streams.

respect to some objective function, such as the annual operating cost (due to consumption of steam and cooling water) plus capital charges. Usually, the solution must observe a design constraint given in form of a minimum approach temperature for heat transfer.

In Figure (5.1), a simple sketch is given which represents this type of problem.

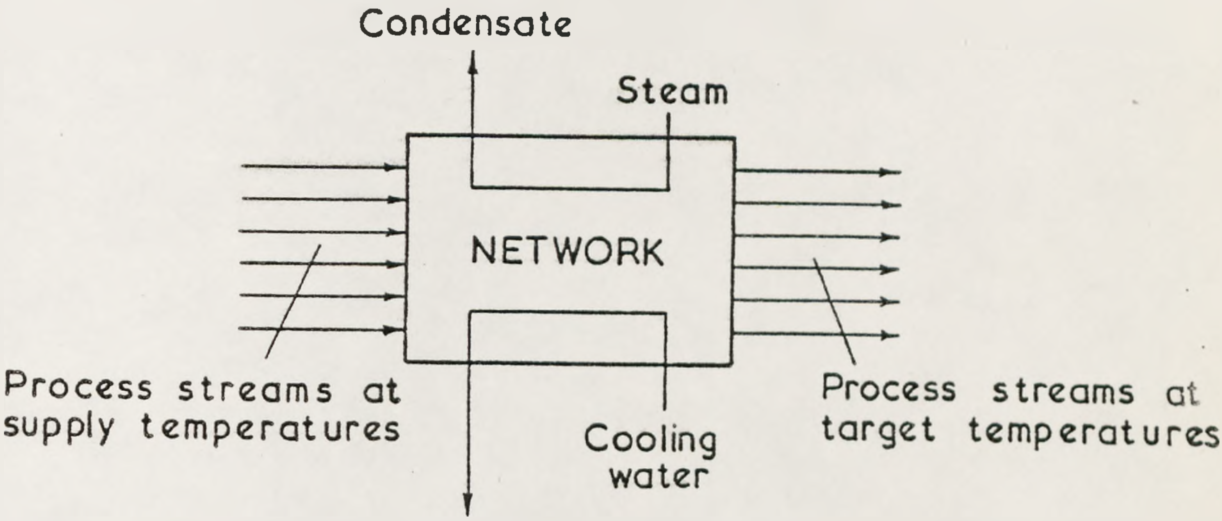

Figure (5.1) Heat exchanger network synthesis problem as usually posed in the literature.

There are at least seven different problems known from the literature which comply with this description. They are proposed by various authors in the field and have all been solved by different workers later. In Appendix K, the data for these problems are listed (as well as for three other ones, tackled below).

In a review paper in 1973, Hendry et al.(80) called the synthesis of heat exchanger networks a "....complex combinatorial problem involving pairing and sequencing of the exchanging streams.....". If the possibilities of introducing matches between streams are discussed on mainly combinatorial grounds - as was the case in most work published prior to Hendry et al. - the complexity of the problem is indeed immense. As stated by Ponton and Donaldson(95) and explained by way of a sketch such as Figure (5.2), the number of different networks X

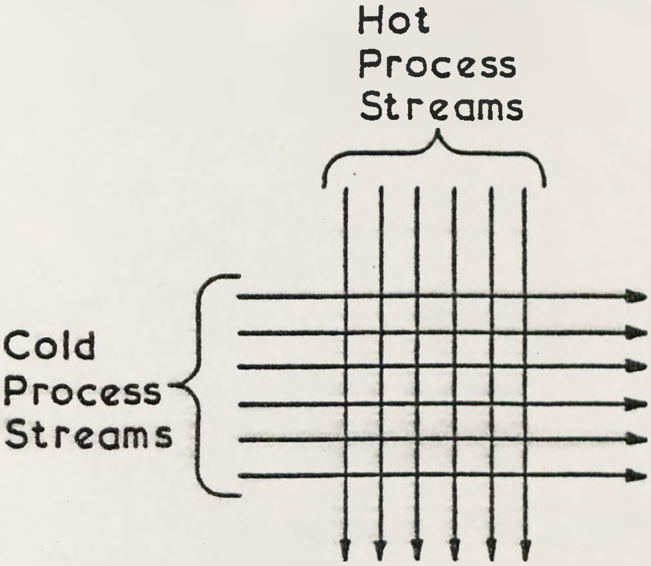

Figure (5.2) Combinatorial approach to heat exchanger networks.

that would have to be examined in an exhaustive combinatorial search would be

$$X = (z_h * z_c)! \qquad (5.1)$$

with z_h = number of hot streams

and z_c = number of cold streams

(There are $(z_h * z_c)$ possibilities of choosing a first match, $(z_h * z_c - 1)$ possibilities of choosing a second match, etc.) For a problem involving no more than five hot and five cold streams, e.g., this results in approx.

$$1.5 * 10^{25}$$

different topologies that have to be identified, simulated, and evaluated. It is this aspect of combinatorial size which is normally put forward as justification for treating the heat exchanger network problem in the idealised form outlined above.

However, there is an obvious danger that methods formulated to solve an idealised problem may either solve an irrelevant problem or not find as good a solution for the real problem as they should do. In other words, it should be the concern of anybody devising methods for the solution of such idealised problems to ensure that the promoted networks do not become unattractive once they are applied to real problems in the final evaluation. This aspect was observed throughout the present thesis and further discussions are given in Chapter Six and in Chapter Eight.

5.2 COMBINATORIAL VERSUS THERMODYNAMIC METHODS

In view of the argument surrounding Equation (5.1), most of the work published before, say, 1974 concentrated on reducing the combinatorial problem. Branch and bound and tree searching techniques, normally combined with heuristic decision making, were the usual methods employed, see Siirola(88). However, due to the still inordinate demand for computer store and time, optimality of results could not be guaranteed with these methods for problems with more than, say, six streams. Also, the difficulties tended to increase if cyclic matches (i.e. the same two streams matched more than once) or parallel splitting of streams was to be considered. Thus, it seemed doubtful whether synthesis methods for the design of heat exchanger networks would ever enter the industrial design practice in earnest.

In 1974, Ponton and Donaldson(95) published a "fast method for the synthesis of optimal heat exchanger networks" which allowed them to tackle the problem by using simple thermodynamic heuristics, thereby by-passing the combinatorial problem. This work is described in full by Donaldson(96). The results of the method can be seen to be somewhat unpredictable, depending on the particular problem specifications encountered, but the method does seem to be useful especially when the small computational effort that is required is born in mind.

In 1977, Nishida et al.(99) published "a simple and practical approach to the optimal synthesis of heat exchanger networks" which enabled the authors to synthesise by hand a new optimum solution for the then largest problem from the literature (i.e. 10SP1, see Appendix K). The approach is graphical and is based on the "horizontal" or "vertical" division of streams in T,Cp-diagrams. (One diagram for hot streams and one for cold streams). Horizontal divisions result in streams being matched more than once and vertical divisions in the parallel splitting of streams. So divided, pairs of streams are matched according to temperature compatibility. The method seems to be more cumbersome to use than that of Ponton and Donaldson but achieves superior results. However, there was still no claim for optimality. (See below, Table 6.2).

The synthesis methods to be described in the following chapters were developed because the apparent success of two approaches based on simple thermodynamic criteria was found stimulating. It was thought worth trying to find further thermodynamic criteria and to continue the trend set by Ponton and Donaldson and Nishida et al.

CHAPTER SIX

A THERMODYNAMIC/EVOLUTIONARY APPROACH

In this chapter, the heat exchanger network problem as described below is scrutinised in thermodynamic terms. Thereby, solution methods are developed which are based on an analysis of design objectives (i.e. of the problem data) instead of suggested designs. This is made possible by the high degree of idealisation applicable and provides an interesting contrast to the case studies in Chapters Three and Four where given equipment networks were analysed rather than the processing objectives.

6.1 ANALYSIS OF STREAM DATA

The enthalpy balance for any network which solves the problem described in Figure (5.1) can be based on a sketch such as shown in Figure (6.1). The width of the enthalpy flowbars is based on Equation (6.1)

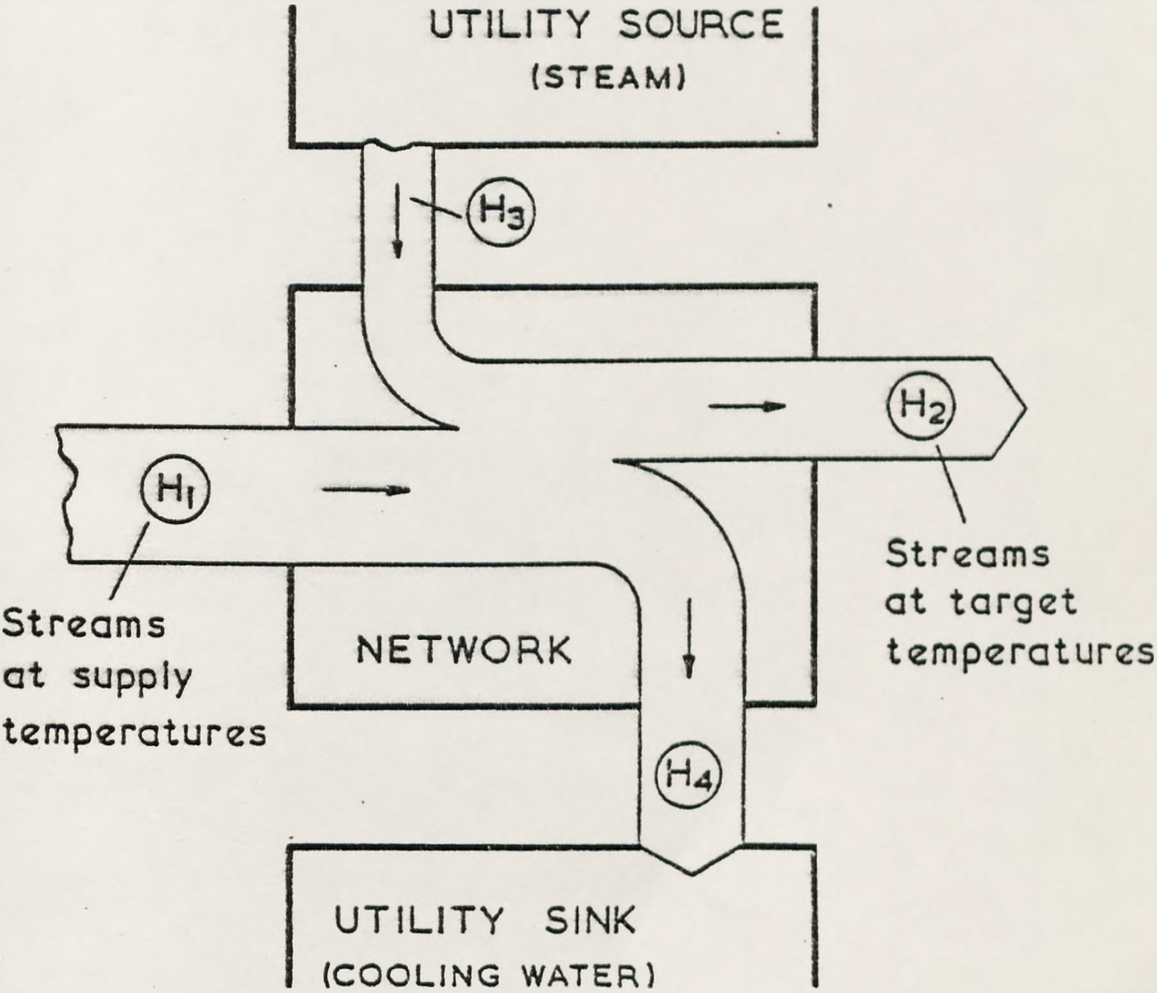

Figure (6.1) Enthalpy balance of a heat exchanger network.

$$(H_1 - H_2) = (H_4 - H_3) \quad (6.1)$$

which must always apply. In this equation, the magnitude of the term $(H_1 - H_2)$, and thus of $(H_4 - H_3)$, is uniquely determined by the data describing the process streams. As a corollary, a network design for a given synthesis problem cannot influence the magnitude of the term $(H_4 - H_3)$ but only that of H_4 and, consequently, that of H_3.

The question whether H_4 and H_3 are as small as possible in a particular design can be answered once a network has been identified for which either

$$H_4 = 0 \quad (6.2a)$$

$$\text{and} \quad H_3 = (H_2 - H_1) \quad (6.2b)$$

applies (i.e. no cooling water is required) or

$$H_3 = 0 \quad (6.3a)$$

$$\text{and} \quad H_4 = (H_1 - H_2) \quad (6.3b)$$

(i.e. no steam is required). If either of these two cases is encountered, one may rest assured that the degree of energy recovery that is achieved by the design under consideration is maximal.

Problems are conceivable, however, in which the process stream data are such that steam as well as cooling water is required

$$H_3 = a \quad (6.4a)$$

$$\text{and} \quad H_4 = (H_1 - H_2) + a \quad (6.4b)$$

and although a minimum figure for "a" must evidently exist, the problem of identifying this minimum figure would appear to be non-trivial if complex data are encountered. As a result, one cannot firmly answer the question whether or not a seemingly good network which solves a complex synthesis problem but requires steam as well as cooling water is optimal in the sense of energy recovery or not. It is this task of finding a general way of predicting the upper bound on energy recovery for a given problem that was first hoped in the present work to be amenable for solution by thermodynamic analysis.

Second Law Analysis of Stream Data

When trying to establish the theoretical limit of energy transfer performance, based on a given set of data, one might begin by carrying out a Second Law analysis of that data. Consider the simple problem described in Table (6.1) in which one stream is to be heated and one is to be cooled:

Table (6.1) A simple two stream problem

Streams	Heat Capacity Flowrate (10^4 * Btu/hr/°F)	T_{in} (°F)	T_{out} (°F)	Heat Load (10^4 * Btu/hr)
No.1 (cold)	1.0	100	300	200
No.2 (hot)	2.0	280	180	200

Assuming that the ambient temperature is 70°F, the exergy changes which correspond to the required changes in temperature are easily evaluated:

$$\Delta Ex_1 = 200 * \left(1 - \frac{530}{200} \ln \frac{760}{560}\right) * 10^4 \text{ Btu/hr}$$

$$= \underline{\underline{38 * 10^4 \text{ Btu/hr}}} \qquad (6.5a)$$

and

$$\Delta Ex_2 = -200 * \left(1 - \frac{530}{100} \ln \frac{740}{640}\right) * 10^4 \text{ Btu/hr}$$

$$= \underline{\underline{-46 * 10^4 \text{ Btu/hr}}} \qquad (6.5b)$$

(Compare Equation 2.48). The result indicates that an irreversible exergy loss of about 8 * 10^4 Btu/hr would occur if both streams were brought from their specified supply to their target states. In other words, the operation would be feasible. A conceivable arrangement which would fulfil the task is shown in Figure (6.2) on page 186.

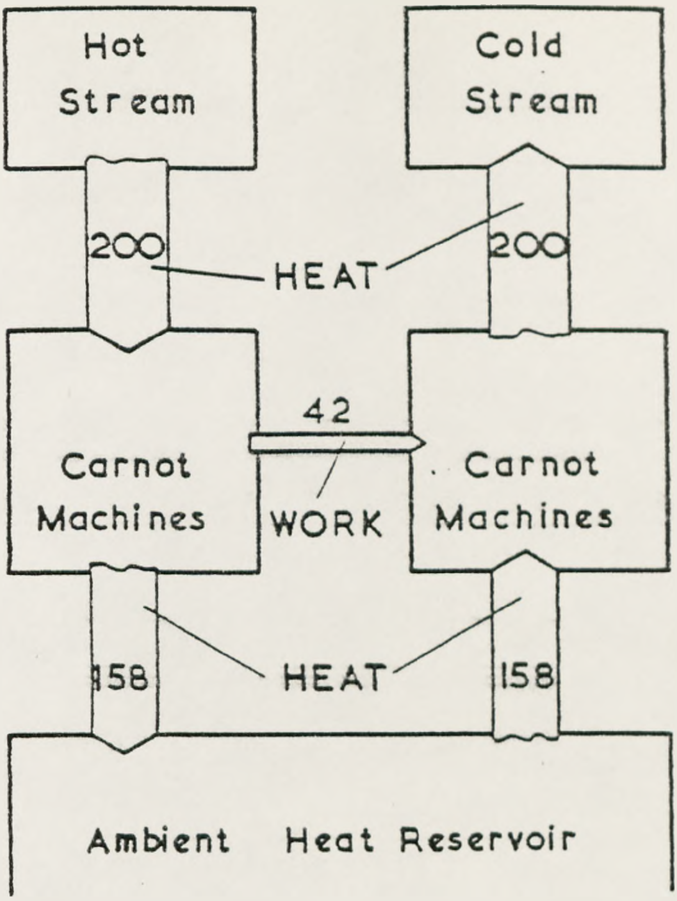

Figure (6.2) Feasible arrangement for the heat transfer problem given in Table (6.1).

In this arrangement, two sets of periodically working Carnot machines, one running as engines and the other as heat pumps, are mounted on a common shaft and exchange heat with the process streams and the ambient reservoir. Finite temperature differences and friction occur corresponding to the exergy loss of about $8 * 10^4$ Btu/hr predicted by Equations (6.5).

However, in a design environment where only heat exchangers are to be considered and no compressors or expanders, an arrangement such as shown in Figure (6.2) is irrelevant and a glance at the data in Table (6.1) is sufficient to establish that it is impossible, by means of mere heat transfer, to bring cold stream No.1 to its target temperature without using ancillary heat : the supply temperature of hot stream No.2 is too low. Clearly, it is temperature rather than exergy which has to be examined if the feasibility of mere heat transfer is to be discussed. As seen in Equations (6.5) and in Figure (6.2), a straight-forward exergy analysis of a heat recovery problem will intermingle the physical significance of temperatures with that of heat capacity flowrates : lower temperatures can be compensated for by higher heat capacity flowrates. Thus, in a context where heat exchange is the only unit operation to be considered, the exergy function - and the same applies to entropy - is of little use.

Having identified, however, that the shortcoming of exergy analysis in the given context is the lack of distinction between high temperature/low heat capacity flowrate on the one hand and low temperature/high heat capacity flowrate on the other hand, one might go on by discussing the importance of temperatures and of heat capacity flowrates independently. Clearly, temperature is the more important parameter. As shown in Figure (6.3) (see page 188), initial heat exchange is always feasible if the initial temperature difference is sufficient. Heat capacity flowrates can only indirectly, i.e. via temperature, influence feasibility : they may or may not adversely affect the temperature difference as heat transfer proceeds.

Thus, when trying to predict how much heat could optimally be recovered in the case of a given synthesis problem, some sort of approach would appear promising which would take a clear account of

(a) the absolute importance of temperatures,

and

(b) the influence of heat capacity flowrates on temperatures.

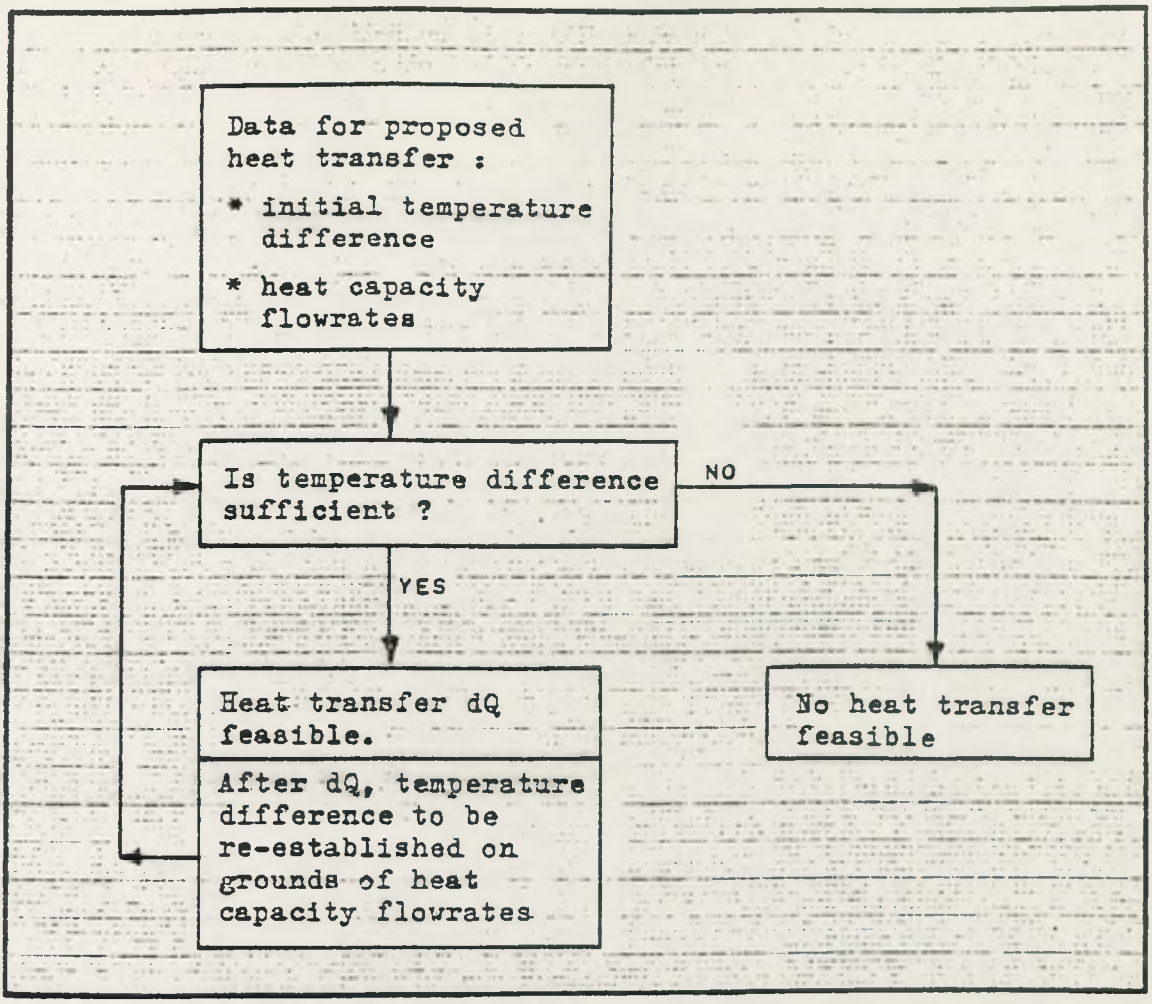

Figure (6.3) Relative importance of temperatures and heat capacity flowrates in heat exchange.

The "T,Cp - Tree"

Having established the last argument, diagrams such as shown in Figure (6.4) (see page 189) in which heat capacity flowrates are plotted against temperature were naturally considered. In Figure (6.4a), the data given in Table (6.1) has been used again. On the left, the "required" heat capacity flowrate (i.e. that of the cold stream) is shown, and on the right, the "available" one (i.e. that of the hot stream). Assuming that some minimum temperature difference (say $\Delta T_{min} = 20^{\circ}F$) is to be maintained, the "available" heat capacity flowrate may be represented 10°F below its actual source temperature and the "required" one 10°F above

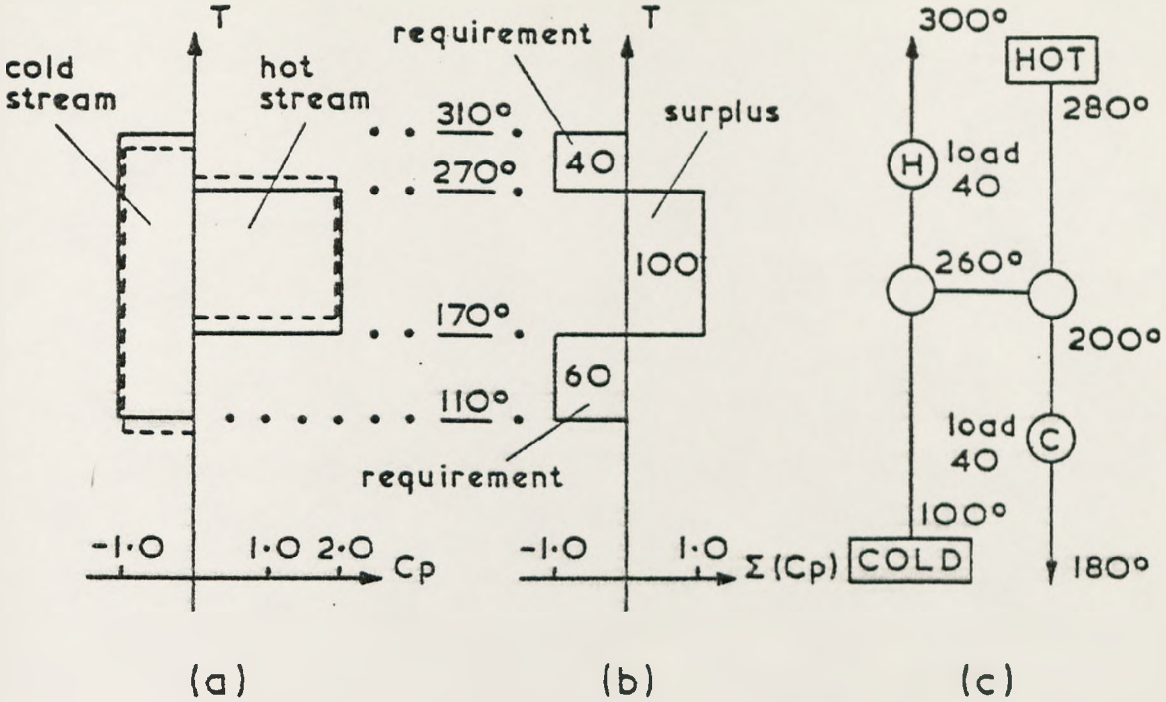

Figure (6.4) Synthesis based on "T,Cp-tree".
a) Individual stream heat contents.
b) Merged stream heat contents.
c) Heat recovery network.

its actual destination. These shifts are indicated in Figure (6.4a) by means of dashed lines for the actual stream temperatures and fully drawn lines for the temperatures at which heat exchange can be contemplated, once the allowance has been made for ΔT_{min}. In Figure (6.4b), the available and the required heat capacity flowrates are added up at any temperature. Thus, either an overall surplus of heat capacities or a deficit, or a balance, can be established. In the case of a balance, there would be just enough heat capacity available at the temperature in question to satisfy the requirements. (Isothermal heat transfer can be assumed since an allowance for ΔT_{min} has been made beforehand.) In the case of a deficit, some surplus would have to be found from higher temperatures to allow heat recovery, and in the case of a surplus, deficits may be satisfied at lower temperatures.

With the particular data used in Figure (6.4), a deficit exists in the upper temperature range, a surplus in the intermediate temperature range and a deficit in the lower temperature range. Clearly, the deficit in the upper temperature range cannot be satisfied other than by using process utility. Thus, a heater becomes necessary (load : 40 * 10^4 Btu/hr). The second deficit, however, can be satisfied by the surplus : an exchanger is possible with a load of 60 * 10^4 Btu/hr. The remainder of the surplus from diagram (6.4b) (i.e. 40 * 10^4 Btu/hr) has to be taken on by cooling water.

It is obvious that the degree of energy recovery which is achieved by the network shown in Figure (6.4c) is maximal and in general terms, two statements can firmly be made with regard to a "temperature, Cp-tree" such as shown in Figure (6.4b) :

1) Any surplus heat found above a certain temperature T can be used to satisfy any deficit either at or below that temperature T.
2) Any deficit for which no surplus can be found has to be satisfied by means of ancillary heat supply.

Thus, the "temperature, Cp-tree" allows one to identify the minimum requirement for ancillary heat for any given set of streams. By simply comparing surpluses to deficits with decreasing temperature, this problem can be solved.

6.2 THE "PROBLEM TABLE", THE "TI-METHOD", AND THE "ED-METHOD"

In Appendix F (first paper), a way is outlined by which heat surpluses and deficits in the T,Cp-tree can be compared systematically. The so-called "Problem Table" is introduced which will always predict the minimum requirement for ancillary heat supply for a given problem and the corresponding requirement for cooling. Further, the "Problem Table" gives valuable information with regard to bounds on the amount of heat to be transferred within identified intervals of temperature. Based on the information regarding these bounds, a systematic design method is described (called the "Temperature Interval" or TI-Method) which guarantees finding such networks.

In the second paper in Appendix F, techniques are presented which make it particularly easy for the engineer to discuss evolutionary changes to existing network structures. In summary, these techniques are called the "Evolutionary Development" or ED-Method. When used for the further manipulation of any given network, they allow the user to obtain a high degree of insight into the particular constraints and possibilities which exist in a given design situation. As a result, new optimum cost solutions are found for five of the seven literature problems dealt with*, as well as solutions with other desirable features (such as observation of a safety constraint, avoidance of excessively small exchangers, provision for step changes in available standard sizes of equipment, etc.). Further, guidance is given in Appendix F as to the minimum number of exchangers, heaters and coolers that will be required for the solution of a given synthesis problem and finally, guidance is given as to the potential benefits of parallel stream splitting and of cyclic topologies. <u>The text below assumes a knowledge of the contents of Appendix F on the part of the reader.</u>

In Appendix G, three computer programs are described which are complementary to Appendix F. The first of these programs allows the user to make up "Problem-Tables", based on the principles outlined in Appendix F. The second program has been used for the evaluation of all networks discussed in this thesis, and the third program is a subroutine which is required by both other programs.

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* In the remaining two cases, optimum solutions found by previous workers are confirmed.

When the papers in Appendix F were first submitted for publication, the most important comment made by a reviewer referred to the work of Hohmann(92) and later Hohmann and Lockhart(98):

As the (anonymous) reviewer pointed out, Hohmann's work contained some of the material claimed to be novel in the original version of the papers in Appendix F. This was indeed found to be the case and as an explanation it may be pointed out that the work of Hohmann was extremely little publicised.*

This latter fact is surprising because quite clearly, Hohmann's findings were much advanced of most subsequently published work. Essentially, Hohmann had presented an algorithm for the prediction of minimum energy requirements and had also established the formula for the minimum number of units. Further, he had pointed out that networks with more than the minimum number of units contain "heat load loops", i.e. have degrees of flexibility. However, he had drawn two fallible conclusions, too, which warrant discussion. This discussion is given below.

6.3 COMMENTS ON THE WORK OF HOHMANN

Hohmann(92) ascertained probably as the first in the literature that there is a "juxta optimum region" for heat exchanger networks, and that networks in that region can all be expected to be of very similar cost. He also established that this juxta optimum region is largely determined by lower bounds on

- the total area in a network
- the number of units, and
- the supplemental heat required.

He presented ways to predict these lower bounds and postulated that networks which would either approach or reach them would fall within the

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* To give examples, Nishida et al.(99) proposed a "new" optimum solution for 6SP1 in 1977 which was also given by Hohmann(92) in 1971. Also, Rathore and Powers(97) credited Siirola(88) with the optimum solution for 4SP1 which was also given by Hohmann(92) in 1971.

juxta optimum region. For the actual synthesis task, he used the T,H-diagram.

The minimum area algorithm is based on similar principles as that outlined by Nishida et al.(89) and comments about its scope for application will be made in Chapter Eight. The two other bounds (i.e. minimum number of units and minimum heat required) are based on the same insight as, and clearly establish prior claim to, the relevant findings in Appendix F. However, the present work has gone beyond this.

Minimum Utility Requirements

In his thesis, Hohmann presented a computerised algorithm (called "Feasibility Table") for the prediction of supplemental source heat required. This algorithm is identical to the "Problem Table" with the exceptions that

1) the ΔT_{min}-constraint is introduced globally for a problem (i.e. there is no facility of using different values for different streams), and
2) the algorithm does not predict "maximum permissible inputs and outputs" within temperature intervals.

The latter point seems important : Hohmann identifies enthalpy balances within temperature intervals of the same description as used in the Problem Table. He then compares surpluses and deficits with decreasing temperature, thereby establishing whether or not deficits can be cancelled by surpluses. If they can, full energy recovery is possible. If they cannot, the amount of surplus missing is calculated and set equal to the necessary supplemental heat. Thus, overall energy requirements are predicted but bounds within temperature intervals are not.

For this reason, the only use Hohmann's feasibility table can be put to when designing a network is that of target setting. Having got the target, one must somehow attempt to achieve it. In other words, an explicit synthesis method does not follow from the Feasibility Table. There is no equivalent in Hohmann's work to the last two columns of the Problem Table (see Figure 7 on page 637 in Appendix F) on which the TI-Method is based.

Minimum Number of Units

With regard to the minimum number of units, Hohmann(92) and later Hohmann and Lockhart(98) made in essence the following five statements:

1) The minimum number of units for any system of streams (this may include utility streams) is one less than the number of streams. (Compare Appendix F).
2) In special cases, networks may be feasible with less than the minimum number of units. (Compare Appendix F).
3) Networks with more than the minimum number of units have degrees of flexibility. (Compare Appendix F).
4) In a minimum number of units network, at least one stream must be terminated in each exchanger.
5) When parallel splitting of streams is permitted, it is always feasible to design a minimum number of units network.

There is no explanation given for the first four of these statements and the impression is that they are based on observation. For the fifth point, Hohmann attempts a theoretical justification. However, this justification is fallible and so is the point. Also, point 4) is fallible.

Consider first point 4). In Appendix F, an explanation is given for the formula describing the minimum number of units (see Figure 13 on page 649 in Appendix F). From this explanation, it is quite clear that a topology might exist for, say, an eleven stream system such as shown in Figure (6.5) (see page 195) where

(a) there is a match between hot stream No.10 and cold stream No.4 (see dashed box in Figure 6.5) and

(b) both these streams are involved in other matches, too.

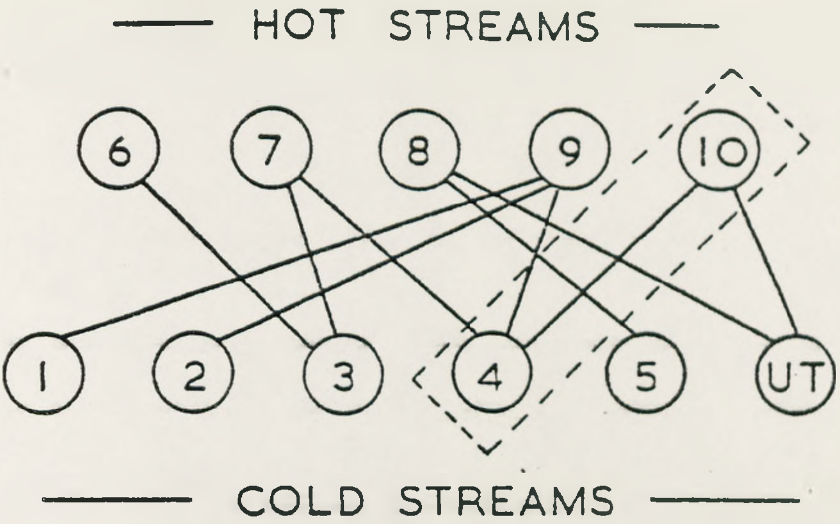
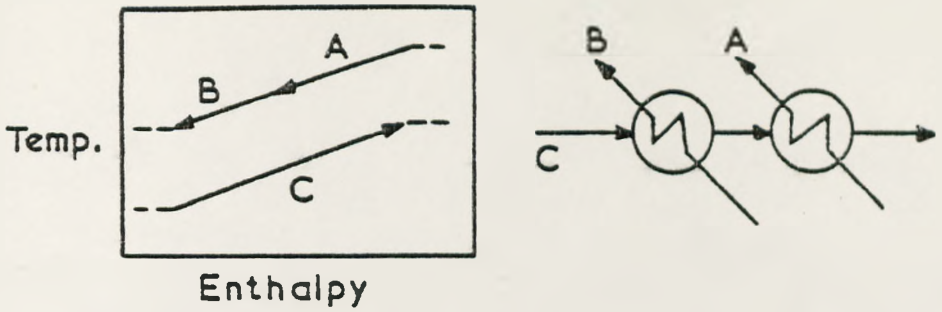


Figure (6.5) Minimum number of units topology with a match that might terminate no stream.

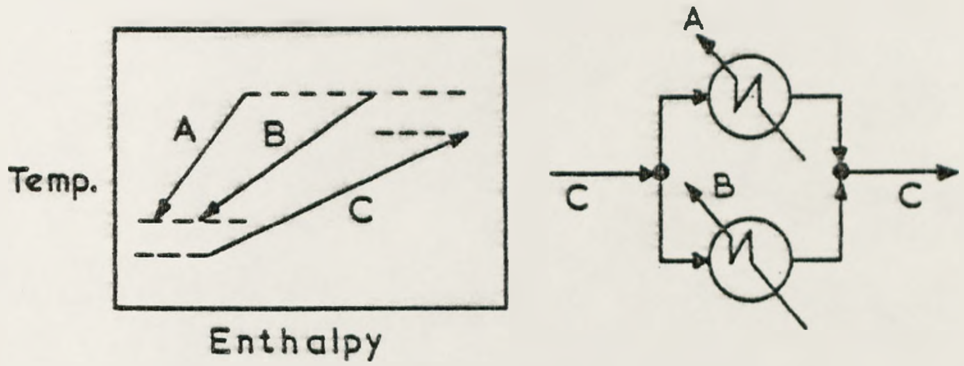
Evidently, a network might exist where the match emphasised in Figure (6.5) terminates neither of the two streams : such a network is the cost optimum for problem 10SP1 shown in Figure 16b on page 651 in Appendix F. (Figure 6.5 is based on this network).

The observation that networks such as the cost optimum for 10SP1 do exist is an important one. Most synthesis work on heat exchanger networks to date is based on the premise of making every exchanger as large as possible, given the two streams matched. (See, e.g., Ponton and Donaldson (95) and the "stream termination heuristic" referred to by Kelahan and Gaddy (101).) This premise ignores the fact that reasons might exist elsewhere in a problem (i.e. outside the two streams matched) for keeping an exchanger below maximum possible size. After all, the recognition of such reasons is the very essence of network design as opposed to the design of single exchangers.

Consider now point 5) above. In his thesis, Hohmann attempted a "worst case analysis" to justify this point. He produced the sketches shown in Figure (6.6) (see page 196) and postulated that every feasible stream system must fall in between these two "worst cases". Hence, he concluded,



a) A Stream System Which Requires Heat Exchangers in Series.



b) A Stream System Which Requires Heat Exchangers in Parallel.

Figure (6.6) Fallible "worst case analysis". (Source: Hohmann[92].)

it is always possible to design a network with the minimum number of units.

In Figure(6.7) (see page 197), a counterexample is given. The data is evident from Figure (6.7a) and so is the fact that an arrangement with the minimum number of units (i.e. two) in series is not feasible. In Figure (6.7b), the only feasible position for two units in a split stream arrangement is shown: there are minimum values for the heat capacity

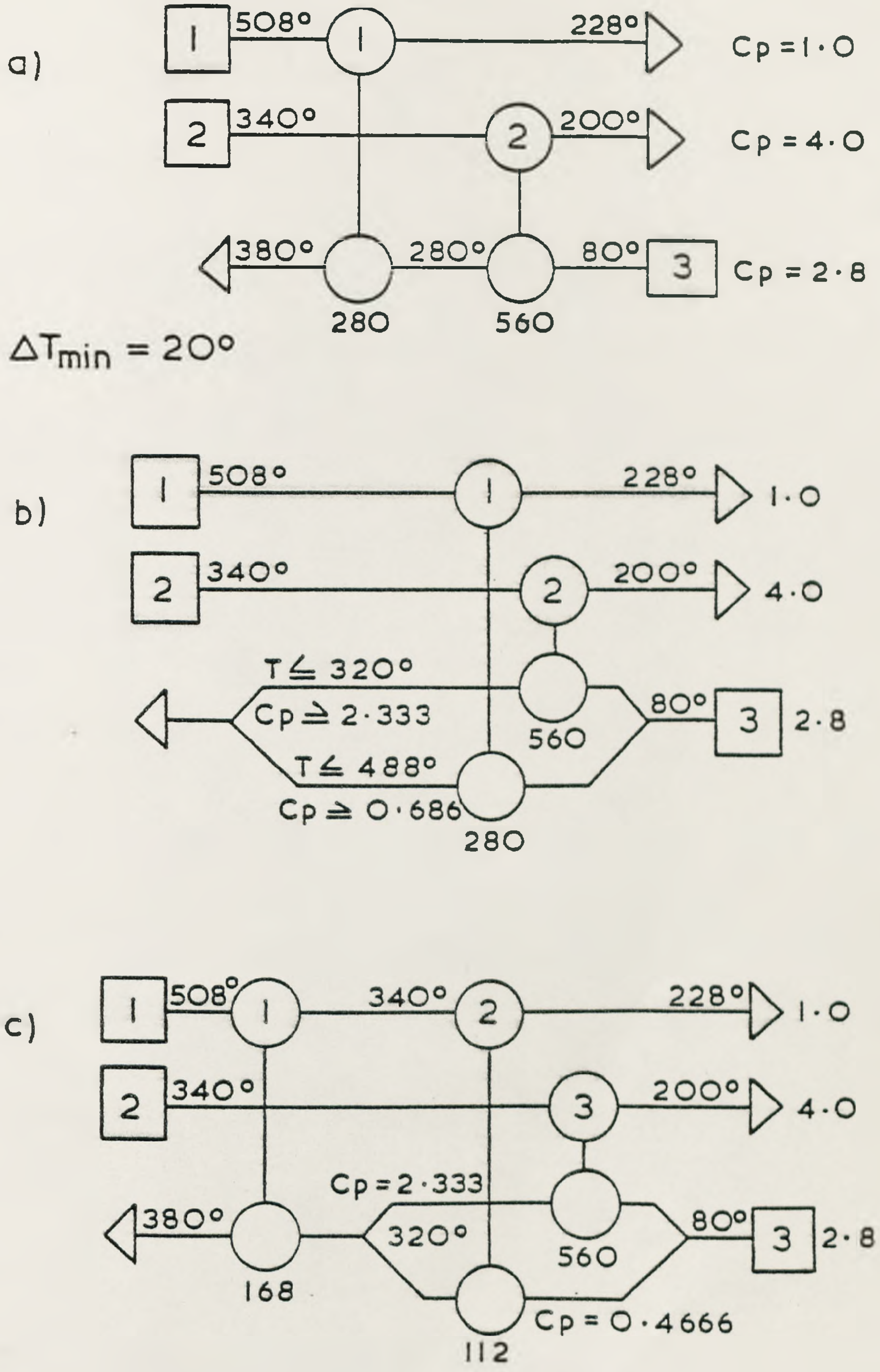


Figure (6.7) Problem which cannot be solved using the minimum number of units.

a), b) Infeasible networks with two units.

c) Feasible network with three units.

flowrates of each branch of the split stream No.3 and the sum of these minimum values exceeds the actual figure for the stream. Thus, this topology is infeasible, too. The conclusion is that there is no feasible network with only two units that would solve the problem.

A feasible network which consists of three exchangers (i.e. one more than the minimum number) is shown in Figure (6.7c).

The observation that minimum number of units solutions may not be feasible is also an important one. In the course of this research, a number of stream systems* were identified which would not be amenable to such solutions. Two of these were encountered when solving the test cases introduced in Appendix F. A solution for Test Case No.2 which employs the "smallest possible" (as opposed to the "minimum") number of units is shown in Figure (6.8). The best general criterion found which

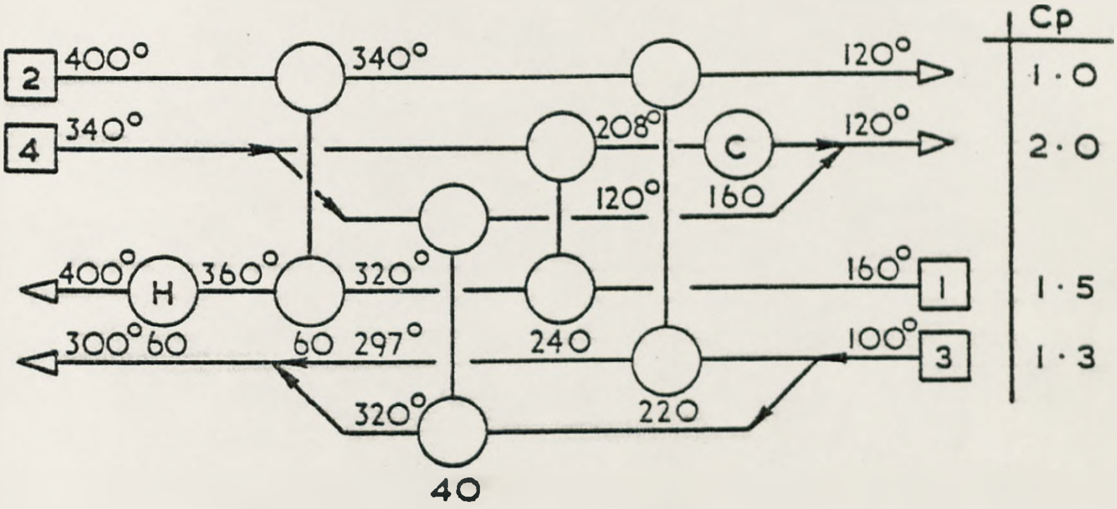


Figure (6.8) Solution for Test Case No. 2 with the "smallest possible" number of units for full heat recovery (at $\Delta T_{min} = 20^{\circ}F$).

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*It is important to distinguish between a "stream system" and a synthesis problem. For a synthesis problem, utility streams are solution-dependent and there is always a solution with two units less than the number of streams: a cooler on every hot stream and a heater on every cold stream. A "stream system", by contrast, includes specified utility streams (which may or may not represent minimum requirements) and cannot necessarily be solved with the minimum number of units. Thus, the term "stream system" (as used by Hohmann) is more to the point than the word "problem" (as used in Appendix F) when discussing the minimum number of units.

would characterise all these systems is the fact that, for reasons of temperature constraint, at least one match cannot be made as large as would be necessary to obtain the minimum number of units. However, this criterion is not very explicit and there is clearly a challenge for future work in identifying an algorithm which, based on stream data, will predict the smallest possible number of units. By similar reasoning, networks must exist for some problems that achieve a "best" (as opposed to maximum) energy recovery with the minimum number of units.* The systematic identification of such networks would present another challenge.

6.4 RAISING STEAM (PROBLEM 10SP2)

In 1977, Wells and Hodgkinson(100) modified the design constraints for Problem 10SP1 so as to allow raising steam instead of exporting all surplus heat to cooling water. Based on the heat content diagram as described by Nishida et al.(99), they presented the solution shown in Figure (6.9) on page 200. Bearing in mind that, according to the original problem definition for 10SP1 as presented by Pho and Lapidus(94), the surplus heat amounts to ~31% of the heat available from the hot streams and that, accordingly, the entry temperatures of the process streams to the coolers are quite high (259°F and 252°F, e.g., in structure 16b on page 651 in Appendix F), the suggestion to consider steam raising appears to be one which would be made in many practical environments, too. Wells and Hodgkinson quote a cost of 6000 $/year for their solution which compares favourably with the cost of ~44000 $/year for solutions of the original problem and appears to prove the point. It was thought that the initiative taken by Wells and Hodgkinson was worth following up further and that, by doing so, a good opportunity would arise to test the synthesis methods presented in Appendix F by tackling a type of

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* Test Case No.1 is such a problem : compare structure 6c on page 637 in Appendix F.

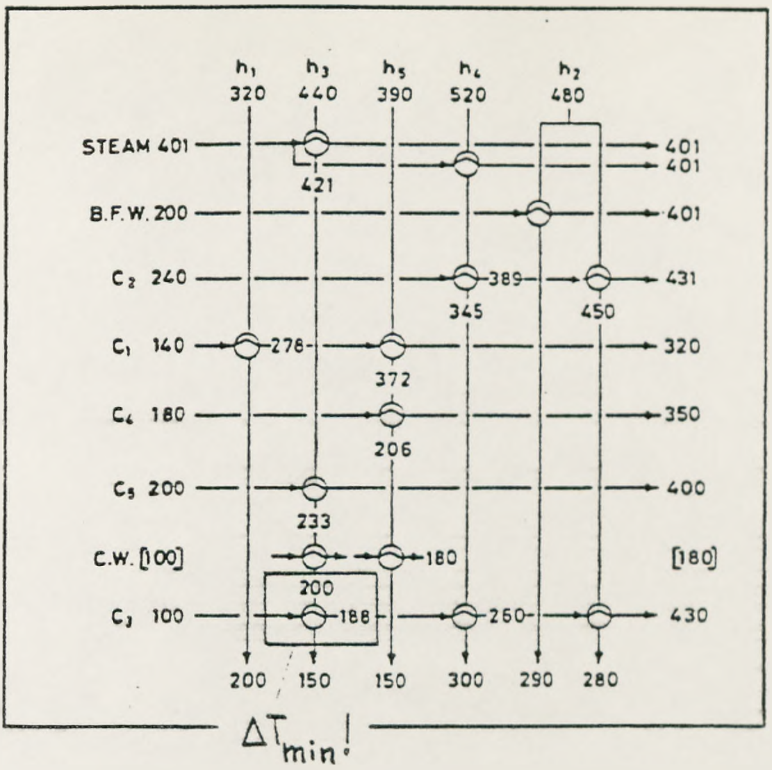

Figure (6.9) Solution for 10SP2. (Source: Wells and Hodgkinson[(100)].)

problem which would be more realistic than, and different from, the type of problem for which the methods were originally formulated. For simplicity, the problem is called 10SP2 in this work.

<u>Problem Description</u>

The design and costing data used are the same as suggested by Wells and Hodgkinson and are given in Appendix K, Tables (K.2), (K.3) and (K.4). Worth noting is that

- no blowdown is to be considered,
- the steam raised is to be saturated but not to be superheated, and that
- economiser and boiler are to be designed separately (i.e. at least two units are required). The former may, however, be designed as a steaming economiser, i.e. partial evaporation may occur in it.

Maximum Energy Recovery

In the form as formulated in Appendix F and programmed in Appendix G, the Problem Table could be used for calculation of the maximum degree of energy recovery by introducing the boiler feed water stream and the phase change stream as two additional cold streams and by varying their mass flowrates so as to determine the maximum values at which no utility heaters would be needed. Based on the original concept of the T,Cp-tree, however, there appears to be a quicker way by hand. In Figure (6.10) (see page 202), the relevant (i.e. upper temperature) part of the problem is shown in T,Cp-coordinates and the latent heat required is represented by a circle at 401°F (i.e. the evaporation temperature) on the cold stream side. The problem of identifying how much heat would, in the limiting case, be available for phase change can now be solved by means of comparing the heat which is available in this diagram above 401°F to that which is required. (The necessary allowance for $\Delta T_{min} = 20^{\circ}F$ has been introduced by means of shifting the hot streams). Adding up all heat that is available, one obtains

$$(500^{\circ}F - 401^{\circ}F) * 2.38 * 10^4 \text{ Btu/hr/}^{\circ}F$$

$$= 235.62 * 10^4 \text{ Btu/hr}$$

from stream No.9,

.... $118 * 10^4$ Btu/hr

from stream No.7, and

.... $53.2 * 10^4$ Btu/hr

from stream No.8. Similarly, the heat required is found to be

.... $34.59 * 10^4$ Btu/hr

for stream No.2, and

.... $46.4 * 10^4$ Btu/hr

for stream No.3. In total, there is a net surplus of

$$\underline{\underline{\sim 325.8 * 10^4 \text{ Btu/hr}}}$$

With a latent heat of 826.5 Btu/lb (see Appendix K), this allows no

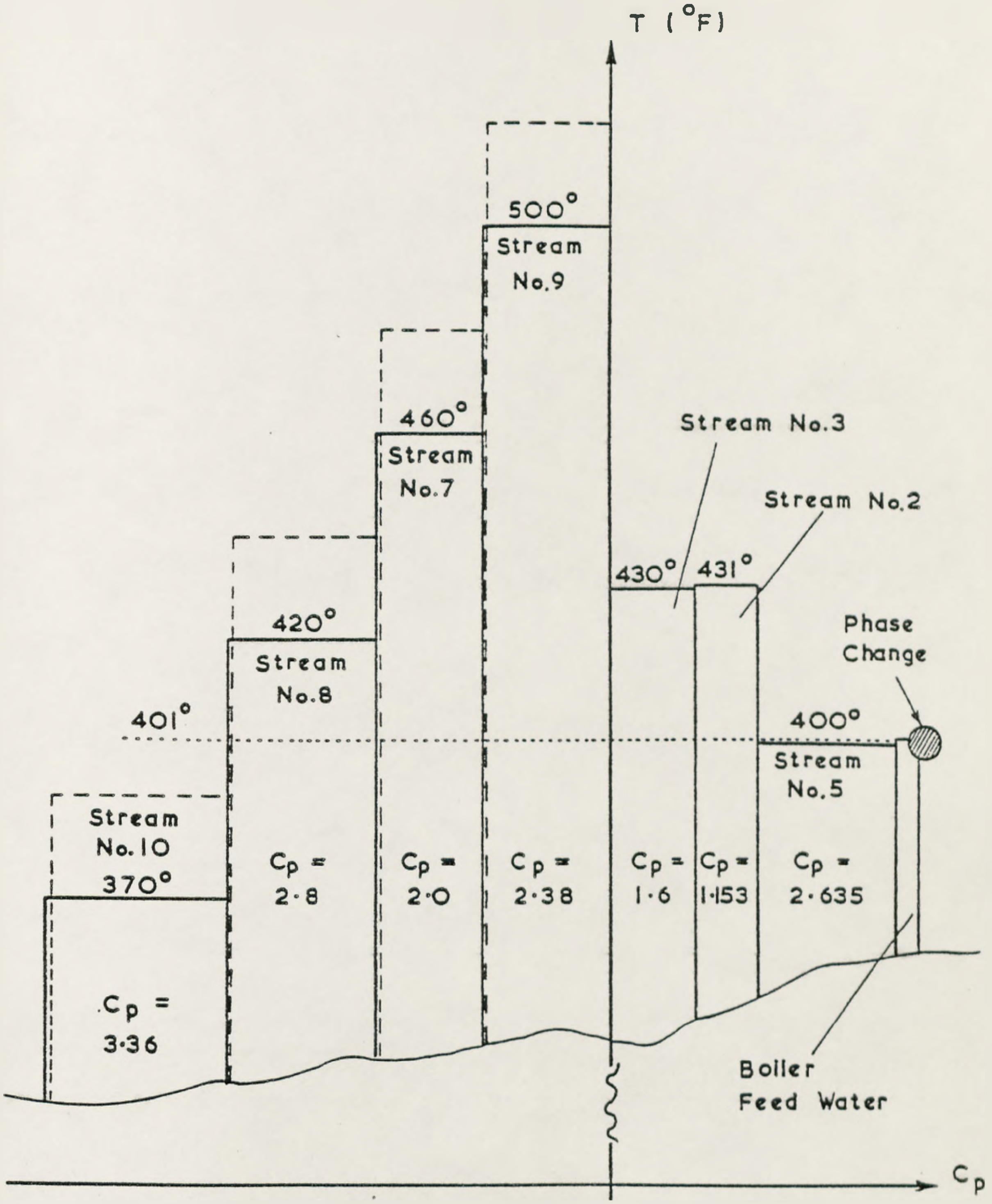

Figure (6.10) Heat contents of streams in upper temperature range in 10SP2.

more than

$$\underline{\sim 3942 \text{ lbs/hr}}$$

of steam to be raised.

With this figure, the corresponding heat capacity flowrate of the boiler feed water stream is easily determined (i.e. $0.394 * 10^4$ Btu/hr/$^\circ$F) and the diagram in Figure (6.10) can be completed for temperatures below 401°F. Then, the heat capacity flowrates available and required below evaporation temperature may be compared. In the present example, a reassuring net surplus is observed

$$\underbrace{(2.8 + 2.0 + 2.38)}_{\text{hot streams}} > \underbrace{(1.6 + 1.153 + 2.635 + 0.394)}_{\text{cold streams}}$$

and a further check at still lower temperatures was thought to be probably unnecessary.

However, a quick way to determine whether there would, indeed, be no further problems at still lower temperatures would be to compute the Problem Table with the boiler feed water stream and the phase change stream fixed at 3942 lbs/hr. Thereby, the phase change stream could be simulated by a liquid stream with an excessively large heat capacity flowrate, e.g.:

$$Cp = 325.8 * 10^4 \text{ Btu/hr./}^\circ\text{F}$$

$$(T_{supply} = 401\ ^\circ\text{F};\ \ T_{target} = 402\,^\circ\text{F})$$

This has been done and the impression that full heat recovery would be feasible in the remaining temperature intervals was confirmed.

Simultaneously, the total heat load that would have to be given to cooling water in an optimum energy network was identified as:

$$\sim 244.8 * 10^4 \text{ Btu/hr}$$

Thus, the lowest possible cost for utilities can already be stated. It would be a credit of about:

13800 \$/yr

Further, for each $1 * 10^4$ Btu/hr of heat that would not be recovered, this credit would decrease by about

148 \$/yr*.

Considering that the cost of plant for alternative solutions for the original Problem 10SP1 may vary only between, say, 9400 \$/yr and 10200 \$/yr, a strong sensitivity can be predicted of overall costs to the degree of energy recovery.

Minimum Number of Units

With twelve different process streams and cooling water, the minimum number of units required to solve the problem is twelve.

Brief Evaluation of Wells and Hodgkinson's Solution

In the network presented by Wells and Hodgkinson (see Figure 6.9), steam is raised to the extent of

3562.2 lbs/hr**

and fourteen units are employed.

The three observations that

(a) optimum degree of energy recovery is not achieved,

(b) more than the minimum number of units are employed, and even so,

(c) stream splitting is used,

indicate that the heat recovery situation might be rather tight. However, the deviation from optimum energy performance is quite considerable. According to the considerations made above, the amount of steam raised is ∿10% less than what could at best be achieved and the corresponding increase in cooling water consumption is ∿16%. In terms of operating costs, a credit is accepted which lies about 4655 \$/yr (or ∿34%) below the best possible figure. Whether or not this performance could be improved without too adverse effects on capital costs is certainly worth examining.

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* This figure includes the effect that, with more steam raised, more boiler feed water must be preheated, too, which reduces the load on coolers beyond the equivalent of the additional steam raised.

** As presented in Figure (6.9), hot stream No.2 does not reach its specified target temperature. To amend this, more load has been given on the economiser, leading to some additional steam raised. Also, the ΔT_{min} - constraint is not observed in the match shown boxed in Figure (6.9). To amend this, hot stream No.3 can be split at the end.

Synthesis

It would be possible to carry out the synthesis by simply using the TI-Method but, alternatively, one may interpret Figure (6.10) in a more direct way. There are three hot streams above 401°F (cold stream temperature) and three cold streams (including the phase change stream), and since heat balance is given but no equal residuals may be produced, no less than five matches are required to achieve full heat exchange (see Figure 6.11). Although it would be feasible to use less than five matches, this would prejudice optimum energy recovery. If, e.g., four matches were arranged as shown in Figure (6.12), $6.8 * 10^4$ Btu/hr of heat

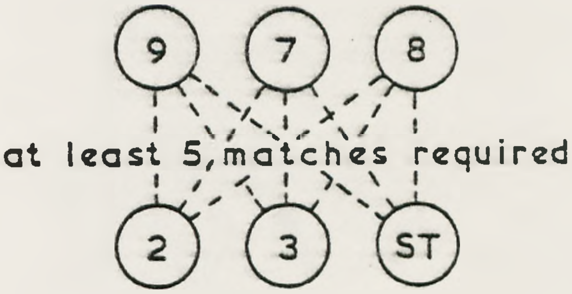


Figure (6.11) Six heat loads in 1OSP2 above steam raising temperature demand five matches for full heat recovery.

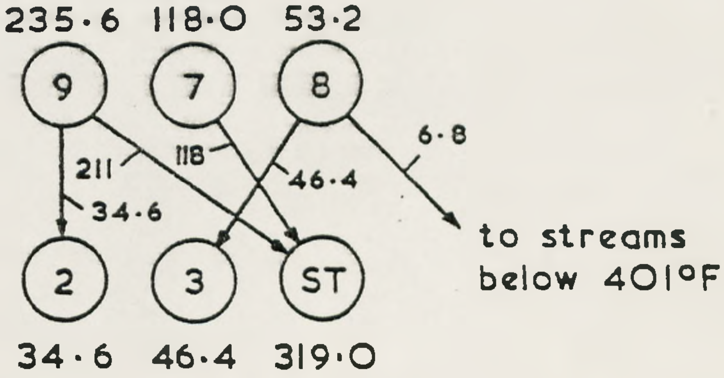


Figure (6.12) Four matches in 1OSP2 above steam raising temperature produce residual heat load.

would be lost below the 401°F limit. This would cost ~1006 $/yr in terms of utility costs (see above) and since it is unlikely that corresponding savings in capital could be made, five matches above 401°F shall be accepted. The consequences are clearly seen in Figure (6.13). Choosing

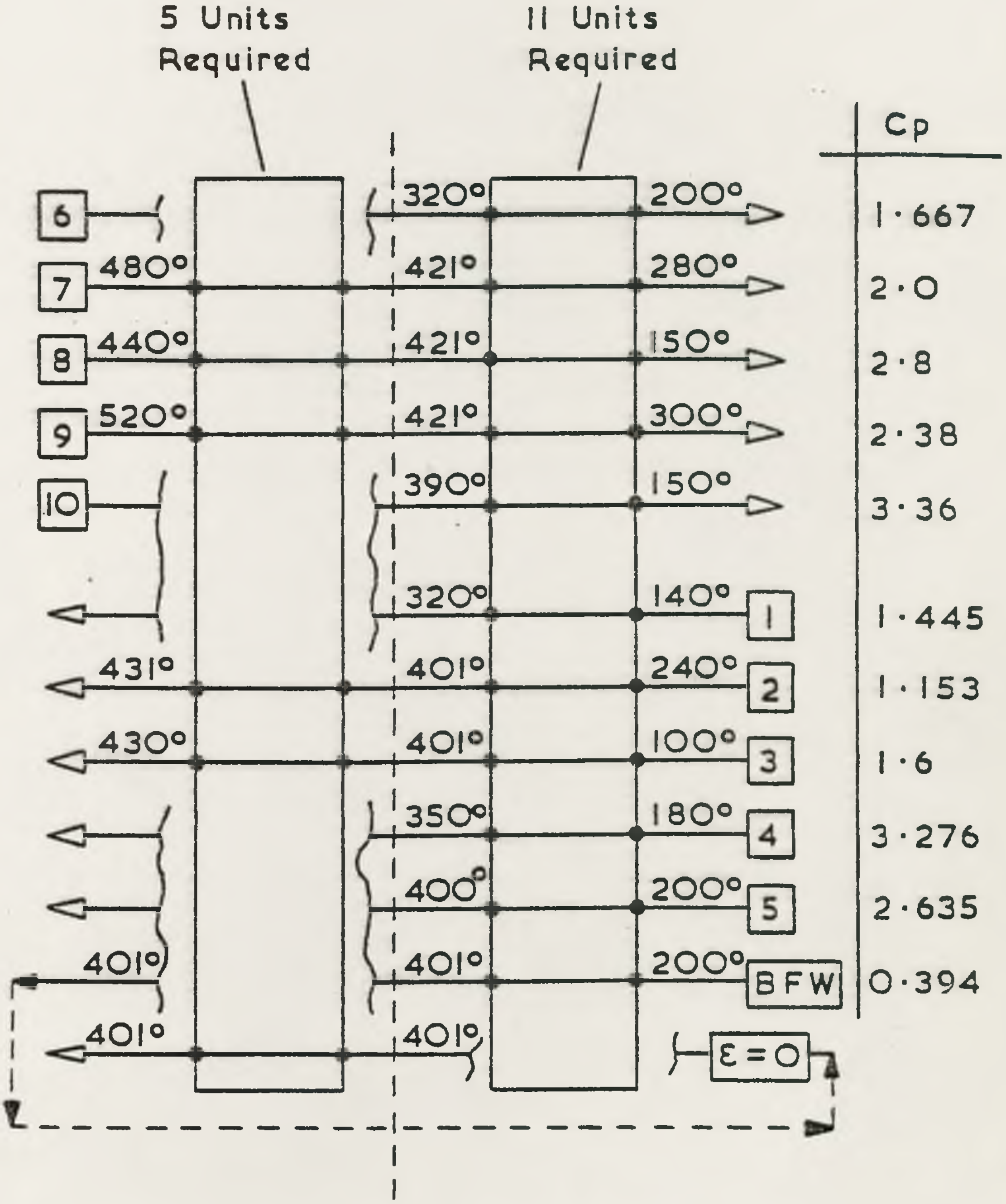


Figure (6.13) Appraisal of separate subproblems above and below steam raising temperature in 10SP2.

any set of five matches above 401°F, a synthesis problem remains which consists of eleven residuals and streams, with cooling required, so that at least another eleven matches are required. This would bring the total up to sixteen units. Also, it is quite evident from the temperatures involved, that stream splitting could not be avoided if energy recovery was to be kept maximal. There are four cold streams in the 11 stream problem with target temperatures of 401°F and 400°F, respectively, but only three hot streams at 421°F.

If stream splitting is inevitable, however, it might as well be already employed in the six stream problem above 401°F. Consider Figure (6.14a) on page 208. A simple and rather obvious solution for the six stream problem is given. In this solution, match No.5 could quite evidently be extended so as to form a steaming economiser with the effect that the boiler feed water stream would be eliminated from the remaining synthesis problem. Also, one might examine whether an equivalent extension would be possible with match No.4. In this case, a difficulty is encountered : match No.4 could only be extended if the heat capacity flowrate of the relevant branch of stream No.7 could be made at least equal to that of stream No.2. The only way in which this can be done without reducing the load of match No.5 is by introducing a by-pass round match No.3 as indicated by a dashed arrow in Figure (6.14a) : the by-pass increases the hot stream supply temperature for match No.5. The resulting network is shown in Figure (6.14b). Based on this particular configuration, the remaining problem is smaller by two streams and final networks might exist that would achieve maximum energy recovery with only fourteen units.

Due to the very constrained temperature situation, the synthesis of an acceptable network for the remaining problem is rapid. A match between streams No.8 and No.5 is necessary (consider the heat capacity flowrates shown in Figure 6.14b), as well as another match between streams No.9 and No.3. Making these first matches as large as possible, a match follows

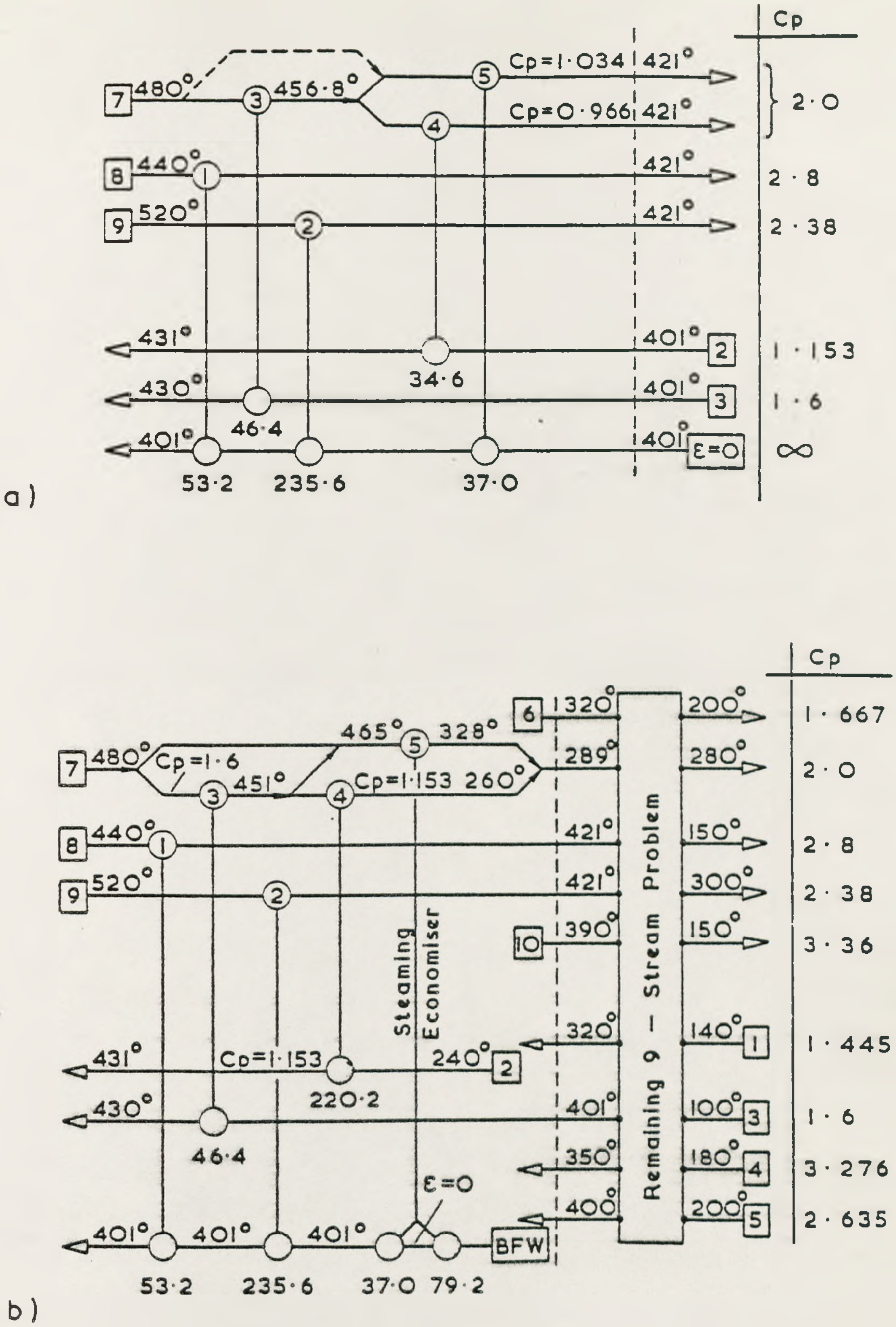


Figure (6.14) Split stream design with by-pass produces favourable remaining problem.

a) Basic topology above steam raising temperature.

b) Sizing the by-pass so as to extend matches No. 4 and No. 5 below steam raising temperature.

between streams No.10 and No.1 and another one between streams No.10. and No.4. This leaves five matches left to be found and each of these can be postulated like the first four from temperature considerations. The resulting structure is shown in Figure (6.15). The split of stream

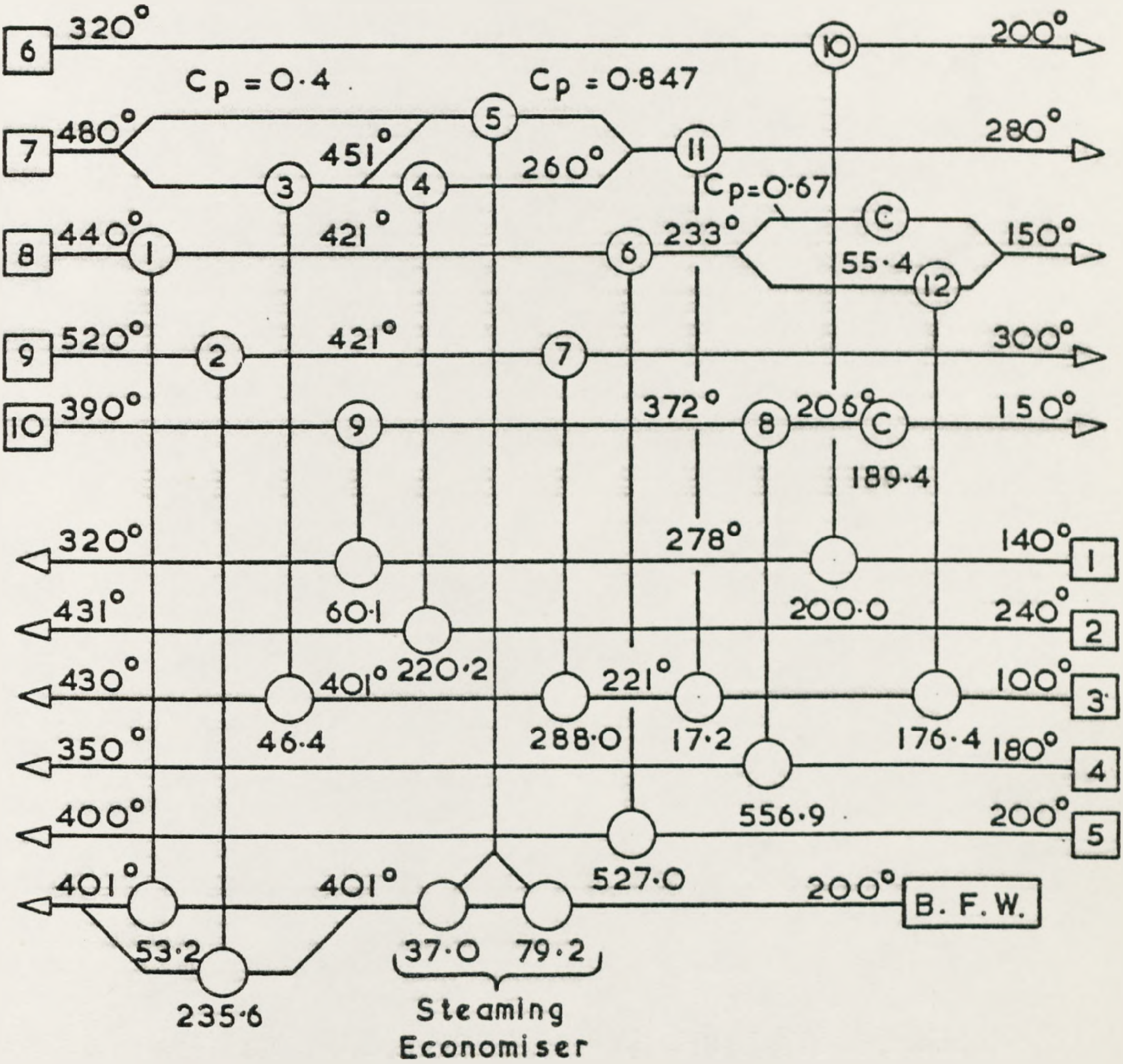


Figure (6.15) Final solution for 10SP2.

No.8 at the cold end was found appropriate for securing the maximum feasible cooling water exit temperature for the cooler situated there. (This reduces the amount of cooling water used.)

A comparison of the network so identified with the one proposed by Wells and Hodgkinson reveals a great deal of similarity. With the exception of the positions of matches No.3, No.4, No.5 and No.11 (as shown in Figure 6.15) and the corresponding differences in heat load distribution, the two topologies are identical. Referring to Figure (6.14b), it is precisely the arrangement of these matches which is crucial for the final network to achieve maximum energy recovery with no more than fourteen units. Thus, structure (6.15) saves about 4655 $/yr in utility costs when compared with Wells and Hodgkinson's solution, due to the replacement of no more than four units by four alternative ones, more appropriately arranged. The overall cost of

1986 $/yr

(compared to 6137 $/yr for Wells and Hodgkinson's solution based on the data in Appendix K) reflects this improvement well. More importantly, however, the cost of structure (6.15) can be relied on to be practically optimal: the degree of energy recovery is maximal and the number of units employed is no more than two above the theoretical minimum (which could, however, only be achieved if energy recovery was impaired).

Relaxation of Design Constraints

Having said initially that a problem definition which includes steam raising is more realistic than the original one, one might stress that there seems to be yet another point in the original definition of the literature problems where there is little realism:

If the heat recovery situation is tight, optimum energy recovery can sometimes only be achieved by accepting some relatively small matches. The small boiler in Figure 6.15 (i.e. match No.1) and match No.3 may serve as examples. Similarly, stream splitting and small matches may, if heat recovery is difficult, be inevitable if the aim is to minimise the number of units (see match No.11). In this situation, some incentive might be felt in an academic study to design networks with less than optimum energy recovery and/or more than the minimum number of units to avoid complicated topologies with excessive differences in exchanger size. In a practical environment, however, another cure would probably be examined first : a relaxation of the ΔT_{min}-constraint and, quite possibly, of the stream supply and target temperature specifications.

In order to gain some idea about the possible consequences of such constraint relaxation, Problem 10SP2 was looked at in these terms. A design was synthesised which is based on a reduced figure for the minimum approach temperature,

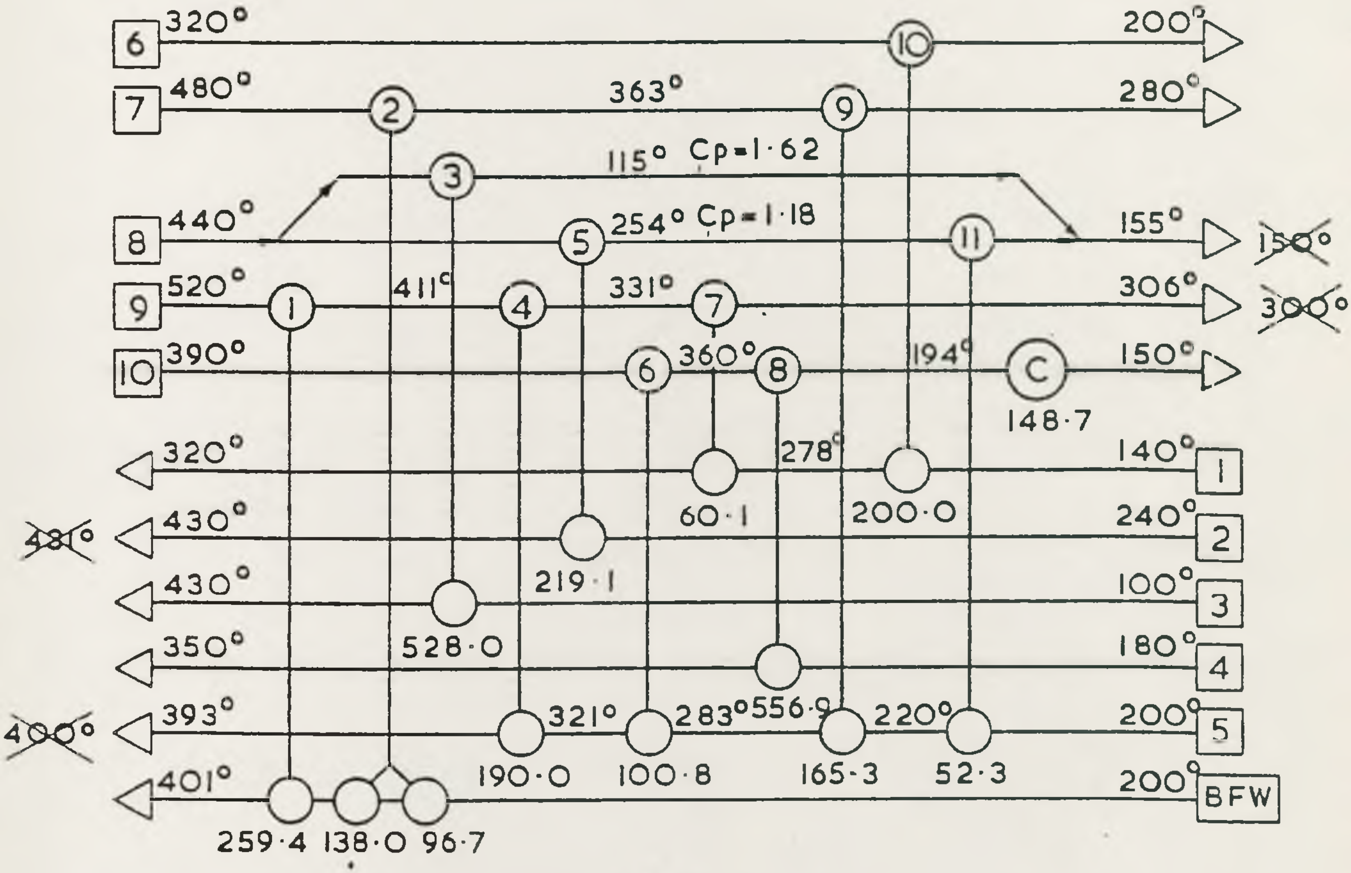
$$\Delta T_{min} = 10^{o}F$$

and on the assumption that the process streams may miss their target temperatures by as much as

$$\pm 10^{o}F.$$

Both these assumptions influence the degree to which energy recovery is possible but it was decided to alter target temperatures only if an explicit advantage in structural simplicity could be secured. By means of adjusting the total heat load of a stream, the heat loads of individual matches on this stream can be adjusted so that small matches can either be developed into reasonably sized ones or be eliminated altogether.

Starting from a diagram such as Figure (6.10) to allow for the reduced value of ΔT_{min}, the network shown in Figure (6.16) (see page 212) was quite readily found. This network raises the optimum amount of steam (based on $\Delta T_{min} = 10^{o}F$) and employs twelve units (i.e. the minimum number) without complicated stream splitting arrangements, excessive differences in exchanger sizes, or any other obvious inelegancies. To make this solution possible, no more than four target temperatures had to be altered (by as much as $-1^{o}F$, $+5^{o}F$, $+6^{o}F$, and $-7^{o}F$, respectively). To identify which temperatures would be most suitably adjusted and by how much, some time was spent at the final stage of the synthesis with the ED-Method. The "rules for shifting and merging" as given in



$\Delta T_{min} = 10°F$

Target temperatures: ±10°F

Figure (6.16) Approximate solution for 10SP2.

Appendix F were used to create heaters and coolers at the end of streams and, when small enough, these heaters and coolers were simply left out.

The total cost of this network is a credit of 4133 \$/yr which compares well with the cost of structure(6.15) (i.e. 1986 \$/yr costs, see above). However, solutions might well exist that would solve the problem with an even better credit. The objective in presenting structure (6.16) is not to demonstrate the implications of constraint relaxation on cost but on flexibility in design. These latter implications seem to be significant, a conclusion which adds further weight to a point already made in Appendix F : a synthesis method of any realism should allow the user to seize on advantages that might be possible through constraint relaxation.

6.5 DISCUSSION

In Table (6.2) (see page 214), a comparative survey is given of solutions by different workers for the eight synthesis problems discussed above which were taken from the literature. Results from eleven sources (including this work) are compared after explicit enumeration of the networks in question using consistent data*. The effort involved in drawing up this table was considerable but it was thought worthwhile. There is a great deal of confusion in the literature as to the relative ranking of most suggested networks due to differences in data used and, quite frequently, to computational errors. In some cases, errors have even led to the suggestion of infeasible networks or of networks which do not comply with the given design constraints. As a result, inferior solutions were often believed to be improvements on previous work and identical solutions were not readily recognised as such. In Table (6.2), identical costs signify identical networks (with one possible exception noted for 7SP1).

The Importance of Setting Targets

Judged by their results, three of the methods listed in Table (6.2) would appear to be more powerful than others : the method of Nishida et al(99) and especially that of Hohmann(92) and the present work.

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* As pointed out in Appendix K, such a comparison is valid since, as long as a set of data is used consistently, different data will not lead to changes in the relative ranking of alternative networks.

Table (6.2) Comparative survey of solutions from eleven different sources for eight problems from the literature

Source	4SP1	4SP2	4SP2 *)	5SP1	5SP1 *)	6SP1	7SP1	7SP2	10SP1	10SP2
Masso and Rudd$^{(90)}$				$\boxed{38268}^{2)}$			34447$^{1)}$	28624$^{1)}$		
Lee et al.$^{(91)}$	13685$^{1)}$			38268$^{1)}$		37331$^{3)}$	-	-		
Hohmann$^{(92)}$	$\boxed{13587}^{4)}$			-		$\boxed{35010}^{4)}$	-	-		
McGalliard & Westerberg$^{(93)}$	13685$^{4)}$			38268$^{4)}$		35780$^{5)}$	-	-		
Pho and Lapidus$^{(94)}$	13685			38268		35657$^{6)}$	$\boxed{31381}^{3)}$	7)	44160$^{1)}$	
Ponton & Donaldson$^{(95)}$	13685$^{9),1)}$	23724$^{6)}$		-		35407$^{5)}$	30172$^{5),10)}$	-	44160$^{5)}$	
Rathore & Powers$^{(97)}$	13587$^{1)}$	-		-		-	-	-	-	
Nishida et al$^{(99)}$	13587$^{1)}$	-	20353	-	38219$^{2)}$	35010	-	-	$\boxed{43984}$	
Wells & Hodgkinson$^{(100)}$	-	-	-	-	-	-	-	-	-	6137$^{1),3)}$
Kelahan & Gaddy$^{(101)}$	8)	-	-	38268$^{1)}$	-	8)	-	-	-	-
This work	13587	$\boxed{21654}$	$\boxed{19571}$	38268	$\boxed{38207}$	35010	$\boxed{30172}$	$\boxed{28260}$	$\boxed{43934}$	$\boxed{1986}$

Figures shown denote cost (in $/year) of optimum solution given. Unless indicated otherwise, computations are based on the data given in Tables (K.3) and (K.4). Boxed entries denote optima at the time of publication (unless first time tackled).

*) Solutions involve the parallel splitting of streams.

1) Cost quoted in source is slightly different, presumably due to different steam data and to round-offs in computation.

2) Cost quoted in source is different, mainly due to different assumptions re. equipment downtime. (Compare Table K.3).

3) Cost quoted in source is different, mainly due to an easily identified error.

4) Solution is presented in source without cost quotation.

5) This cost is quoted in source but solution is not shown.

6) This cost is quoted in source. It cannot be ascertained since solution shown is not sufficiently defined. Solution is however feasible.

7) The solution presented by Pho and Lapidus is infeasible and there is too little information to identify the error.

8) Kelahan and Gaddy did not observe the ΔT_{min}-constraint in their solution.

9) The solution is documented by Donaldson$^{(96)}$.

10) Quite surprisingly, the solution documented by Donaldson$^{(96)}$ is more expensive and <u>not</u> identical to the optimum shown in Appendix F, page 645, Figure (5b).

An interesting point is that all these three methods are based on hand calculation (or the use of simple programs such as listed in Appendix G) with thermodynamic criteria playing an important role in overcoming the alleged combinatorial problem. Further, all three methods rely on graphical aids to implement the "synthesis by hand" : Hohmann used the T,H-diagram, Nishida et al. relied on the "heat content diagram" and the present work uses the grid representation of networks in the TI- and the ED-Method. There seems to be some argument in support of perfectly conventional ways to improve one's creativity. Namely, the use of suitable diagrams and of thermodynamic insight to clarify the basic constraints on a system.

The importance of especially this latter point becomes even clearer when the main difference between the three methods just discussed is considered. The analysis of basic constraints is rather less developed in the work of Nishida et al. than in that of Hohmann or the present work*. In the latter two cases, this analysis leads to almost separate stages in the approach. Firstly, the identification of targets prior to design and secondly, the design itself. Thereby, the design is partly left to intuition but tightly controlled - and stimulated - by the targets known. It could be coincidental, but it is probably not, that apart from the present work that of Hohmann is perhaps most successful in Table (6.2) (based on the criterion that no solution was improved in subsequent work) and this might be a reminder of a well-known "human factor", namely that the stimulating effect which achievable targets might have on creativity is quite considerable.

In general terms of process design, it may often be useful to analyse a problem in fundamental physical terms prior to solution so as to identify suitable targets. Questions should be asked such as "What fundamental performance criteria might exist?", "How could these

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* Nishida et al. have neither a general algorithm to predict the upper bound on energy recovery, nor do they offer a concept of the minimum number of units.

criteria be met?", etc. - Quite clearly, the range of criteria to be considered will often be somewhat broader than that of mere Second Law efficiency but, as long as the criteria are of a tangible technological nature, thermodynamic analysis, in a broad sense, is probably the adequate tool for identifying them and thus for giving practical targets in design.

Problem Individual Insight Versus Heuristics

The discussion given above has shown that the work of Hohmann has been very similar to that reported here and the question arises to what extent the present work has brought an improvement on that of Hohmann. Quite clearly, very little can be claimed as far as setting targets is concerned. The correction of two of Hohmann's statements by way of counterexamples (see Figures 6.5 and 6.7) is relatively insignificant when compared to the rest of his findings in this respect. As far as actual synthesis is concerned, however, a considerable step forward has been made.

Firstly, the TI-Method was developed. This method is an almost natural extension of the Problem Table, i.e. the approach known already to Hohmann to predict the definite target for energy recovery has been extended into an explicit procedure to achieve it. The TI-Method is unique amongst synthesis methods in that it guarantees the generation of energy optimal networks in any situation. Secondly, the grid representation of networks with the concept of Freedom and the ED-Method was developed. If a synthesis method is described as giving the user a certain strategy for the solution of a problem without necessarily making the problem itself more transparent to him, then the ED-Method may be said to make the problem more transparent, thereby allowing the user to define his own strategy. Thus, it seems to present something of a link between a synthesis method and an intelligent user.

A speculation may be appropriate now why the work of Hohmann, so advanced with regard to target setting, remained so seemingly crude with regard to synthesis as is indicated by Hohmann's use of the T,H-diagram. As a possible reason, it is suggested that the T,H-diagram represented one of the few ways known at the time of obtaining insight into a design situation so as to formulate synthesis steps without the use of heuristics.

The disadvantages of heuristics are sufficiently known (they tend to reinforce one's prejudices) and their only justification seems to be that they might allow the user to tackle a problem otherwise too complex. However, if it is practicable to replace heuristics by problem individual insight, this must be preferable. Hohmann might have found that for problems of the size considered by him (i.e. up to seven streams), problem individual insight was obtainable from the T,H-diagram to an extent that made it unnecessary to resort to heuristics.

The basic reason for the clear - and especially consistent - success of the TI- and the ED-Method that is evident from Table (6.2) quite likely lies in the fact that these methods represent a design tool which combines a very high degree of insight with the virtual absence of heuristics. The TI-Method is based on a very thorough a priori analysis of temperature and heat recovery constraints, and the ED-Method facilitates individual problem analysis where this is necessary. Further, should a problem be too complex after all, the ED-Method facilitates the careful checking of the consequences of any heuristics used.

The Advantage of Fundamental Physical Criteria

As pointed out in Chapter Five, synthesis problems of the kind discussed here are highly idealised and the question arises whether methods designed for the optimal solution of these problems would necessarily be successful when solving a real problem. In this context, it is worth emphasising that the TI-Method and the ED-Method are both based on fundamental physical criteria so that none of the simplifying assumptions made (e.g., cp=const , uniform heat transfer coefficient, simplified cost equations, etc.) plays a role for the validity of these methods. Evidently, Problem Tables could be based on any set of T,H-correlations for process streams, the TI-Method could be used for exchangers with individual heat transfer coefficients and the ED-Method might be extended for multistream exchanger networks, to name but a few examples of modifications that might be required in a more realistic design context.

The solution of Problem 10SP2 somewhat supports this claim for flexibility. Despite changes in design objectives, a meaningful analysis was still possible of the bounds and constraints applicable and the degree of energy recovery could still be held in firm grasp during the synthesis, as could the number of units employed. Thereby, the T,Cp-tree was used to determine the maximum feasible mass flowrate of a cold stream and the concept of the minimum number of units was used in the context of two sub-problems, each defined by heat balance within a temperature range narrower than that of the original problem. Finally, the ED-Method was instrumental in finding an intricate split stream arrangement (see Figure 6.14) and, last but not least, in making use of relaxed design constraints. It seems that the approach developed in the present chapter to the design of heat exchanger networks is flexible enough to allow such unforeseen variations. Further, it seems that the main reason for this flexibility is the fact that the approach is based on criteria that are sufficiently fundamental.

CHAPTER SEVEN

A THERMODYNAMIC/COMBINATORIAL APPROACH

Having acknowledged in Chapter Six that optimality cannot always be guaranteed when complex heat exchanger networks are synthesised by means of the TI-Method and the ED-Method, an alternative synthesis method is presented in this chapter by means of which all solutions to a given problem can be obtained which feature

- a prescribed degree of energy recovery
- the minimum number of units, and
- no parallel stream splitting.

Specifying the prescribed degree of energy recovery as maximum (i.e. as that predicted by the Problem Table), the method might or might not produce solutions. If the latter is the case, maximum energy recovery networks with the minimum number of units and no split streams do not exist. If the former is the case, an exhaustive list of the most attractive solutions is obtained. As far as the literature problems are concerned, this list can be virtually guaranteed to contain the global optimum cost network.

The method is based on combinatorial principles (other than tree searching) and employs feasibility arguments of both thermodynamic and topological nature to reduce the problem size. The method is called "TC-Method" (for "Thermodynamic/Combinatorial") and appears to be equally well suited for automatic application as for intuitive implementation by hand. When applied by hand, thermodynamic and topological feasibility arguments are formulated ad hoc to avoid the combinatorial problem almost completely whereas, when applied automatically, generally applicable - and thus simpler - feasibility arguments are employed.

7.1 AUTOMATIC IMPLEMENTATION OF THE TC-METHOD

Consider Problem 6SP1. The data are given in Appendix K, Table (K.2). Assuming the usual minimum approach temperature of $\Delta T_{min} = 20^{o}F$, the Problem Table may be computed, predicting that no steam is required but cooling water to the extent of $530.0 * 10^{4}$ Btu/hr. (Compare Table K.2.) It is now possible to identify the minimum number of units, n_{min}. Based on the explanations given in Appendix F and on the formula given already by Hohmann(92) and by Hohmann and Lockhart(98) one obtains $n_{min} = 6$.

The Basic Idea of the TC-Method

Next, the number of different matches that could exist in the problem, n_{poss}, may be identified. With Equation (7.1) :

$$n_{poss} = z_h * (z_c + ut_c) + z_c * ut_h \tag{7.1}$$

with z_h = number of hot process streams

z_c = number of cold process streams

ut_h = number of hot utilities

ut_c = number of cold utilities

This equation may be derived from Figure (5.2). In the case of Problem 6SP1, n_{poss} is found to be twelve and with this information, the basic task of the TC-Method can be tackled. This task consists of solving the simple combinatorial problem of finding all possible sets of n_{min} matches that can be formed when selecting from n_{poss} different ones. With Equation (7.2) :

$$C^{n_{min}}_{n_{poss}} = \frac{n_{poss}!}{n_{min}! * (n_{poss} - n_{min})!} \tag{7.2}$$

(See, e.g. Bronstein(59)). In the case of 6SP1, Equation (7.2) indicates that there are 924 sets of n_{min} (i.e. six) matches each. Thus, an automatic algorithm might simply identify these 924 sets of six matches and proceed by computing the heat loads of the individual exchangers in each set. (The heat load of each match in a minimum number of units solution is uniquely determined by the problem data, see Figure 13 on page 649 in Appendix F).

Many of the sets so found will, however, be found to be infeasible because they will either leave streams entirely unconnected, or be incompatible with the problem data on numerical grounds. The latter situation is encountered, e.g., if the only connection to a stream with a larger heat load is to a stream with a smaller heat load, and is readily detected in an automatic algorithm due to the fact that the heat load of at least one match in the set will turn out negative. Although the number of different combinations of n_{min} matches that will be eliminated in this way is problem-dependent, experience suggests that less than ten percent of the original number as identified by means of Equation (7.2) will normally be found to be feasible on these grounds.

Next, an automatic algorithm could proceed by arranging, for any of the remaining sets, the individual matches in any feasible sequence. Consider Figure (7.1).

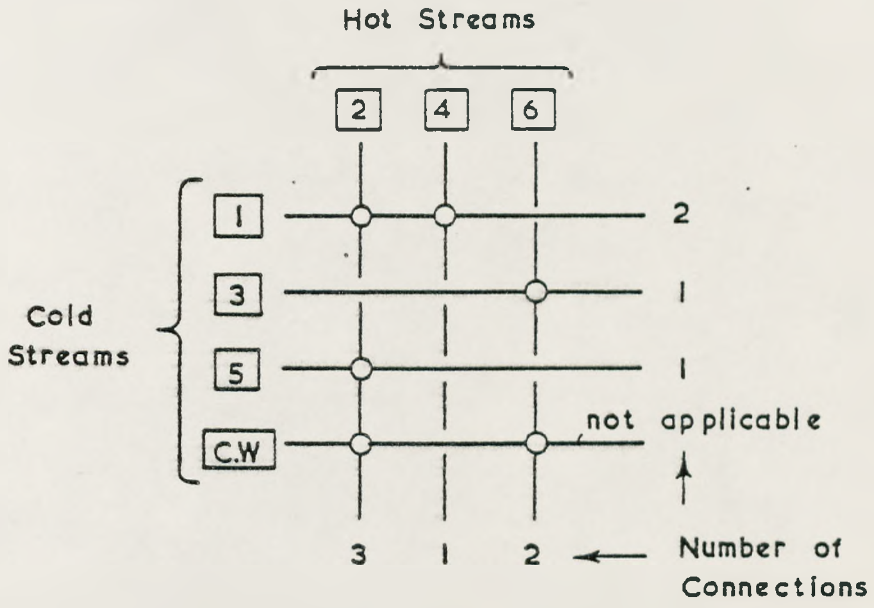

Figure (7.1) Set of six matches for 6SP1.

A set of six matches is shown which may represent a feasible selection for problem 6SP1. The task of identifying all feasible process networks represented by this particular set is carried out systematically by

(a) establishing all possible sequences of connections to each individual stream, and

(b) checking all possible combinations of the sequences so found on thermodynamic grounds (i.e. by checking temperatures).

The number of possible sequences of the connections to a particular stream is, according to simple mathematical theory, given by the number of permutations of the connections. Thus, there are 3! possible sequences for the connections to stream No.2 in Figure (7.1), 1! for stream No.4, 2! for stream No.6 and so on. By multiplying these figures, the number of combinations described under point (b) above is obtained as twenty-four:

$$(3!) * (1!) * (2!) * (2!) * (1!) * (1!) = 24^{*} \qquad (7.3)$$

Usually, other sets of matches found to be feasible on grounds of heat load compatibility would lead to similar results so that a simple automatic search algorithm of the kind described here would, in the case of 6SP1, have to evaluate a number of networks approximately equal to

$$924 * \frac{1}{10} * 24 \simeq 2220$$

to produce an <u>exhaustive</u> list of solutions that feature maximum energy recovery as well as the minimum number of units!

Reducing the Problem Size Further

The number of networks to be evaluated just identified may be reduced even further by means of topological and thermodynamic arguments when applied before, rather than after, the parameters n_{min} and n_{poss} are determined. One such possibility is by comparing all supply and target temperatures of hot and cold streams. Consider Figure (7.2) on page 224. In the case of 6SP1 where no hot utility usage is predicted, it is obvious that there must be a match between streams No.4 (hot) and No.1 (cold) since otherwise stream No.1 could not reach its target temperature.

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* Note: the number of connections made to a utility is not considered since, on the utility side, matches will normally be part of a larger utility network.

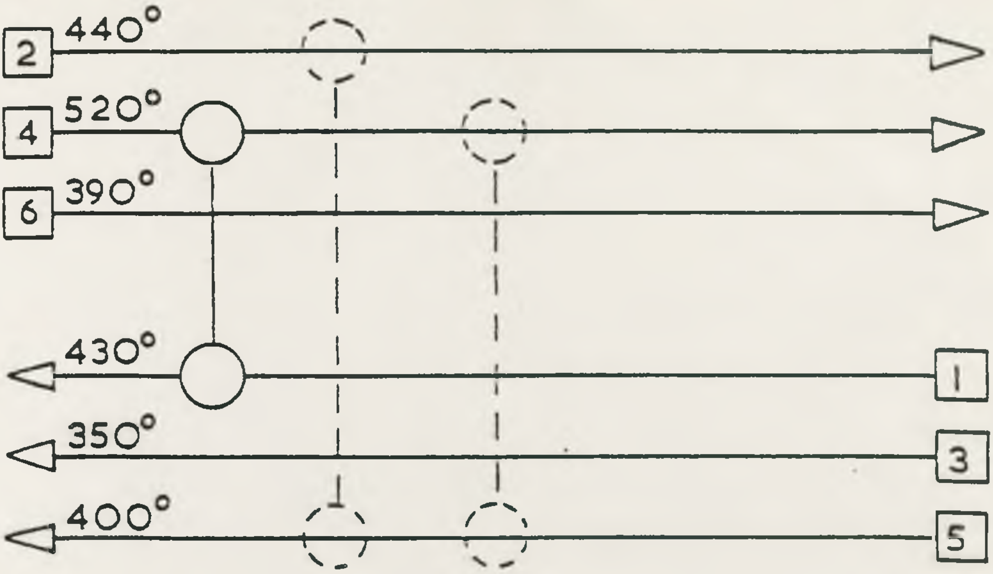

Figure (7.2) Compulsory matches in 6SP1.

Another way of reducing the combinatorial problem is by examining the ways in which heaters and coolers may be arranged. The total heat load to be exchanged between process and utility streams is known from predicted utility requirements and it is obvious that constraints exist as to where in the network the heaters and coolers in question may be placed. In the case of 6SP1, only cooling is required and it might be worth checking whether or not maximum energy recovery would be feasible with only one cooler. The answer may be that it is not since, with only one cooler, heat may have to be removed from the process at a higher average temperature than in the case of two coolers, so that less heat remains available for inter process stream heat exchange at intermediate temperature levels. To carry out this check, utility requirements can be examined by means of the problem table for the modified problem with the target temperatures of the hot streams adjusted in such a way as to allow for the existence of single coolers situated at the cold ends of individual process streams. Modified in this way, the problem will require zero utility usage if maximum energy recovery is still feasible but produce a need for additional heating and cooling (to equal extents) if maximum energy recovery is no longer feasible.

Based on the hot stream target temperatures and heat capacity flowrates in Problem 6SP1, it is easily predicted that the least severe effect on the overall heat recovery situation results when a single cooler is situated on stream No.6. However, even in this case maximum energy recovery was found to be no longer feasible, an additional utility load of $12.0 * 10^4$ Btu/hr being required. If follows that any solution featuring no more than one cooler can be ruled out. If the procedure is repeated assuming two coolers, maximum energy recovery is found possible with the coolers situated on streams No. 2 and No. 6. If they were situated on streams No. 4 and No. 6, however, energy recovery would be impaired and in the case of two coolers on streams No. 2 and No. 4, the deterioration in energy consumption would be even more severe. Finally, it is possible to assume three coolers, i.e. one for each hot stream, without affecting maximum energy recovery.

Using these simple findings, the combinatorial problem may be much reduced. There are only two possibilities of choosing two of the matches between process streams (see Figure 7.2) and only two possibilities for selecting coolers. Thus, there are no more than four basic combinations on which further choices of matches may be based. For two of these combinations, only one further match may be chosen to bring the total up to six (these are the sets involving three coolers), and for the other two combinations, two further matches may be chosen. With only seven possible matches to choose from in all cases, the number of different selections of six matches eventually obtained is fifty-six:

$$2 * C_7^1 + 2 * C_7^2 = 56$$

Thus, fifty-six sets of matches (instead of the original 924 sets) would initially be identified, and then checked on grounds of heat load compatibility, etc., in the course of the still rather simple search algorithm which includes these preliminary thermodynamic tests to be invoked prior to the definition of the overall combinatorial problem.

This number is quite dramatic when compared with the figure of approximately $3.6 * 10^5$ different networks that would be encountered in the context of a conventional tree searching algorithm if an exhaustive search was carried out for 6SP1 (estimated with Equation 5.1 as given by Ponton and Donaldson(95)). Perhaps even more surprising, however, is the ease with which an exhaustive search can be accomplished by hand when using the TC-Method. Examples of this are now presented.

7.2 EXHAUSTIVE SEARCH BY HAND

The calculation of a Problem Table for 6SP1 is a simple exercise, so it is assumed that the information is available that either three coolers are required or two coolers, one on stream No. 2 and one on stream No. 6. It is also evident that a match is required between streams No.4 and No.1 and another match either between streams No.2 and No.5, or between streams No.4 and No.5. Thus, the sketches shown in Figure (7.3) (see page 227) can be produced in which resulting initial selections of matches are presented: any maximum energy recovery/minimum number of units solution for 6SP1 must be based on one of these three arrangements.

The purpose of the sketches is to facilitate the formulation of topological arguments by which it can then be confirmed whether or not a solution may result if any of these three arrangements are completed. This approach helps to considerably reduce the combinatorial problem that has to be overcome when identifying the last matches.

Consider Figure (7.3a). In this arrangement, the need for a further match is easily seen for stream No.1, since the heat load of stream No.4 is not large enough to satisfy that of stream No. 1 in full. This situation, i.e. the fact that there is a connection yet to be provided for stream No.1, is indicated by means of a cross on stream No.1 in

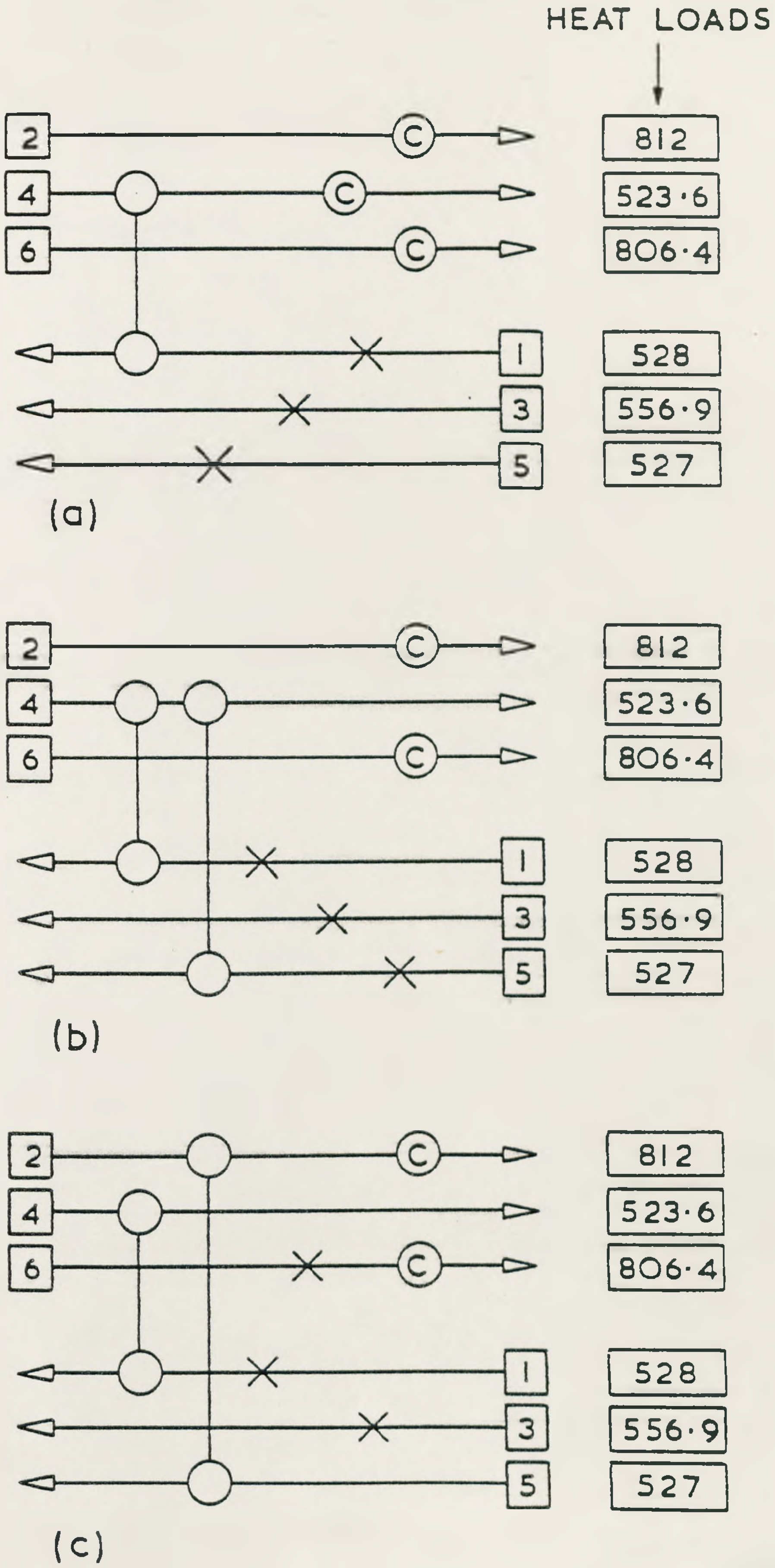

Figure (7.3) Three initial arrangements for 6SP1. (For discussion of structures a), b), and c) see text.)

Figure (7.3a). Also, it is evident that at least one connection must be made to stream No.3, and one to stream No.5. (Thus, crosses are shown on streams No. 3 and No. 5). With three connections still required to three different cold streams, however, and only two more matches to choose (to bring the total up to six matches), a solution is not feasible. Therefore, it can be concluded that no maximum energy recovery/minimum number of units solution exists for 6SP1 which would be based on the arrangement shown in Figure (7.3a).

Next, consider Figure (7.3b). In this arrangement, similar arguments to those used above lead to the conclusion that at least one further connection is required for stream No.1 and one for stream No.3. Also, another connection must be made to stream No.5 for the same reason as for stream No.1: the heat load of stream No.4 is too small. Thus, the same situation is encountered as before. With three cold connections still required but only two more matches to choose, a solution is not feasible.

Finally, consider Figure (7.3c). Since the cooler on stream No.6 cannot have a heat load larger than $530.0 \star 10^4$ Btu/hr (i.e. the total need for cooling), at least one further connection will be required for stream No.6. Also, at least one more connection must be specified for stream No.1 (on the same grounds as before) and one for stream No.3. The remaining streams do not appear to obviously require further connections. Thus, there are only one hot and two cold connections still to be made and, with two matches yet to be chosen, feasible solutions might exist.

The problem is by now small enough to suggest further examination by combinatorial search. There are only six possibilities of introducing the required last two matches. Either streams No.6 and No.1 are matched, leaving three possible matches for stream No.3, or streams No.6 and No.3 are matched, leaving three possible matches for stream No.1. In Table (7.1) these six possibilities are listed.

Table (7.1) Possibilities for the last two matches in Figure (7.3c)

Possibility No.	Match No.		Discussion
	(3)	(4)	
1	6/1	2/3	see Figure (7.4a)
2	6/1	4/3	see Figure (7.4b)
3	6/1	6/3	see Figure (7.4c)
4	2/1	6/3	see Figure (7.4d)
5	4/1	6/3	Cyclic
6	6/1	6/3	see Possibility No. 3.

Possibility No.5 in Table (7.1) is readily seen to lead to a cyclic topology (not feasible in a minimum number of units solution) and possibility No.6 is seen to be identical with No.3. Thus, only the first four possibilities listed in Table (7.1) have to be evaluated in any detail. This has been done in Figure (7.4) (see page 230), and two of the four sets were readily seen to be infeasible. The selection of matches shown in Figure (7.4a) is infeasible because the heat load of stream No.2 is not large enough to match both stream No.3 and stream No.5, while the possibility shown in Figure (7.4b) is infeasible because the heat load of stream No.4 is not large enough to match that of stream No.3. The remaining two possibilities, then, are the only ones that might lead to feasible networks on grounds of topology, target temperature constraints and heat load compatibility. The heat loads of the individual matches in these selections are shown in Figure (7.4c) and in Figure (7.4d).

Happily, both these selections do represent networks that are feasible on grounds of intermediate temperatures, too. In Figure (7.5) on page 231, two networks are shown (structures 7.5a and 7.5b) which are based on these selections and in both networks, match No.3 could be placed in three different positions (the alternative positions being indicated by dashed arrows). Thus, the following firm conclusion can now be drawn:

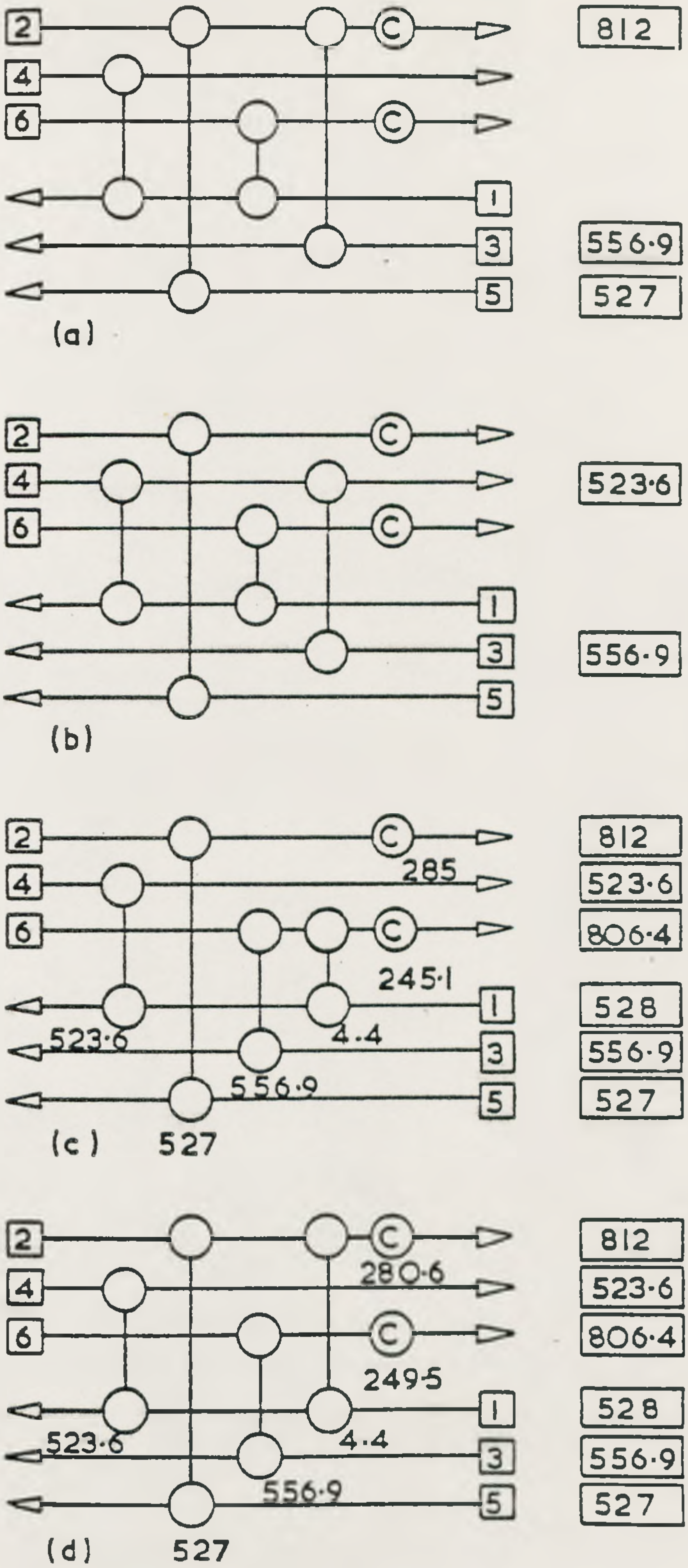

Figure (7.4) Finding two feasible sets of six matches each for 6SP1.

a), b) Infeasible sets. (For discussion see text.)

c), d) Feasible sets. (For discussion see text.)

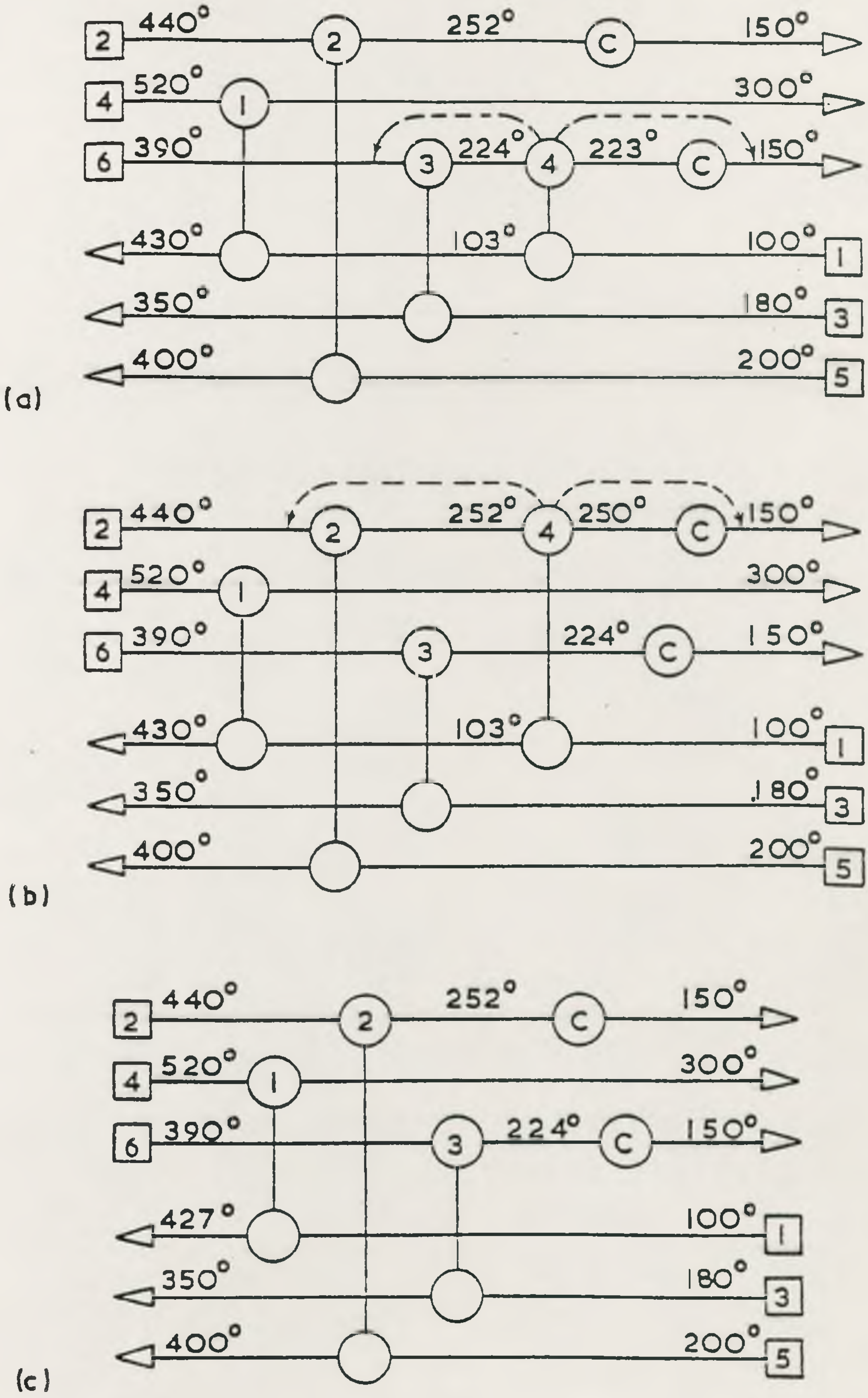

Figure (7.5) Solutions for 6SP1.

a) Three solutions based on Figure (7.4c).

b) Three solutions based on Figure (7.4d).

c) Approximate solution.

> There are no more and no less than six feasible networks that solve Problem 6SP1 by achieving maximum energy recovery with the minimum number of units, use no split streams and observe the desired design constraint of $\Delta T_{min} = 20^{o}F$.

Amongst these six solutions the two shown in Figure (7.5) are the two cheapest, costing 35017 $/yr (Figure 7.5a) and 35010 $/yr (Figure 7.5b). Thus, accepting the premise that optimum cost networks are to be found amongst maximum energy recovery/minimum number of units networks, one may rest assured that structure (7.5b) - which was first presented by Hohmann(92) - is the optimum cost solution, given the design constraints and cost parameters usually taken. In Figure (7.5c), however, a "practical" solution is shown which results from any of the six "exact" minimum number of units solutions if the - exceedingly small - match No.4 is simply left out. This solution would probably be considered to be the most promising design in a practical environment.*

Problem 5SP1

Apparently, there is scope for intelligent and ad hoc formulated thermodynamic and topological arguments when the TC-Method is employed by hand and a short description of the solution of Problem 5SP1 may shed some more light on the various kinds of situations that might be encountered. In contrast to the case of 6SP1, there is only one obvious temperature feasibility argument for 5SP1 that can be invoked before the combinatorial problem is tackled and the main effort has, therefore, to be devoted to finding suitable arguments for the rapid checks of heat load compatibilities.

The utility needs for 5SP1 are $302 * 10^{4}$ Btu/hr of heating and no cooling and the minimum number of units is, thus, five. With no coolers and the

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* This solution was shown by Hohmann(92), too.

"cold end" stream temperatures as given, a match between stream No.4 and No.1 must always exist, see Figure (7.6). Thus, the remaining problem is to examine the possibilities that exist for selecting four matches out of eight possible ones, see Figure (7.7).

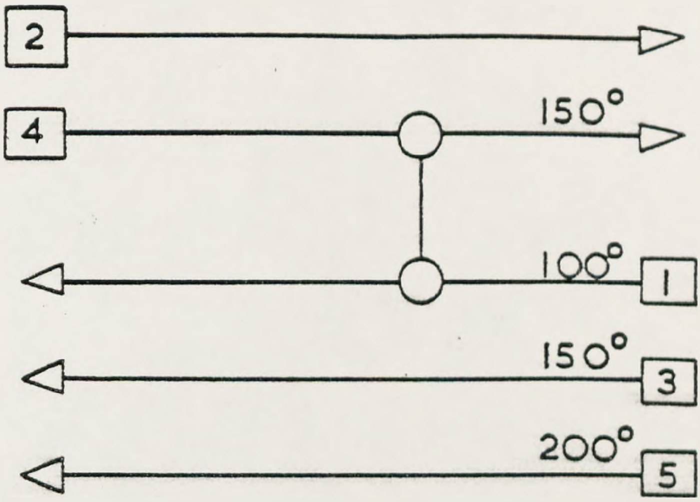


Figure (7.6) Compulsory match for 5SP1.

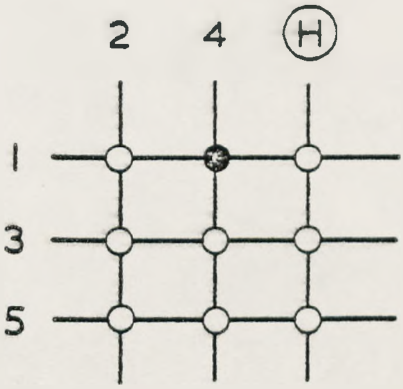


Figure (7.7) The compulsory and eight more possible matches for 5SP1.

The number of sets, i.e. $C_8^4 = 70$, is still quite large by the standards of hand calculation, but it is possible to reduce this figure by disregarding all those possibilities in which the utility or process streams remain unconnected. There must be

$$C_5^4 = 5$$

sets in which the utility would remain unconnected, five more in which stream No.2 would remain unconnected, and five, also, in which either stream No.3 or stream No.5 would not be connected. Thus, the total number of possibilities to be considered can be reduced to fifty:

$$70 - (4 \times 5) = 50$$

Next, the obvious argument may be employed that the stream with the largest head load requires at least two connections. In the case of 5SP1, this leads to the conclusion that possibilities with only one match for stream No.2 are not feasible. Amongst the first seventy possibilities thirty

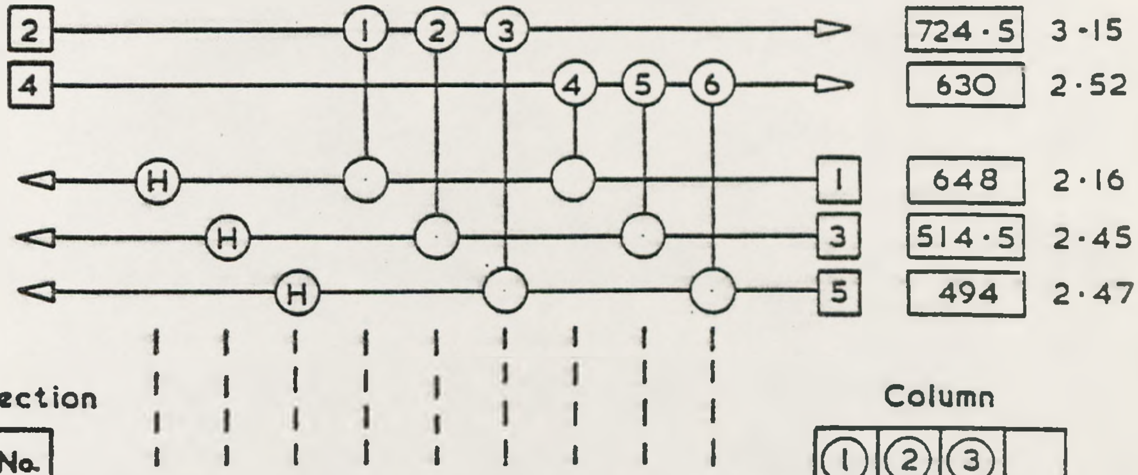
$$3 \times C_5^3 = 30$$

such cases were included and it can be seen readily that two such possibilities leave stream No.3 unconnected and two others leave stream No.5 unconnected. Thus, the total number of possibilities to be considered is finally reduced to twenty-four:

$$50 - (30 - 2 - 2) = 24$$

A combinatorial problem of this size can be tackled by hand and it has been found convenient to use a sketch such as shown in Figure (7.8) (see page 235). In this sketch, the nine possible matches evident from Figure (7.7) are shown in the network context while below the diagram, the twenty-four sets of five matches each are produced systematically by choosing the connections to stream No.2 first, and then selecting heaters. A cross under a match indicates its presence in a particular selection.

The first argument used to eliminate selections is based on temperature considerations. Since the heat capacity flowrate of stream No.1 is less than that of stream No.4, the temperature difference in match No.4 will decrease from its initial value at the cold end to a smaller value at the hot end. If the minimum acceptable value is taken at 20°F, simple



Selection										Column			
No.										①	②	③	
1	X			X	X	X	X			NO			
2		X		X	X	X	X			NO			
3			X	X	X	X	X			NO			
4	X		X	X	X		X			NO			
5		X	X	X	X		X			NO			
6			X	X	X		X	X				NO	
7			X	X	X		X		X				ⓥ
8	X			X	X		X		X				ⓥ
9		X		X	X		X		X				ⓥ
10	X	X		X		X	X			NO			
11		X	X	X		X	X			NO		NO	
12		X		X		X	X	X					ⓥ
13		X		X		X	X		X			NO	
14	X			X		X	X	X					ⓥ
15			X	X		X	X	X					ⓥ
16	X	X			X	X	X			NO			
17	X		X		X	X	X			NO			
18	X				X	X	X	X					ⓥ
19	X				X	X	X		X				ⓥ
20		X	X		X	X	X				NO		
21		X			X	X	X	X			NO		
22		X			X	X	X		X		NO		
23			X		X	X	X	X			NO		
24			X		X	X	X		X		NO		

Figure (7.8) Examining twenty-four possible sets of matches for 5SP1.

calculation shows that the maximum heat load of match No.4 is $453.6 * 10^4$ Btu/hr. Thus, match No.4 cannot on its own satisfy stream No.4. It follows that none of the sets need be considered further which feature match No.4 as the only connection for stream No.4. These sets are marked in column (1) in Figure (7.8).

The other two arguments used are based on further heat load comparisons and are very simple. Unless matched against stream No.2, stream No.1 must have at least two connections (see column (2)), and any of the cold streams, if connected to a heater, must have at least one further connection to a hot stream (see column (3)).*

At this stage, eight possible sets of five matches each are left. These have been examined and have all been found to be feasible from the point of view of heat loads. In only five cases, however, could networks be found in which the required minimum approach temperature would be observed. These networks are documented in Figure (7.9) on page 237. Set No.7 leads to the structure shown in Figure (7.9a), set No.14 to structure (7.9b), No.15 to structure (7.9c), No.18 to structure (7.9d) and No.19 to structure (7.9e). In all five cases, however, the approach temperatures in the individual matches would allow no alternative sequence of matches. Thus, one may conclude that

> there are no more and no less than five networks that solve Problem 5SP1, achieve maximum energy recovery, use the minimum number of units with no split streams, and observe the desired design constraint of $\Delta T_{min} = 20^{\circ}F$.

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*The argument based on the heat load of match No.4 would not only eliminate sets with match No.4 as the only connection to stream No.4 but also all sets with match No.4 as the only connection to stream No.1. This eliminates sets No.20 through No.24, i.e. duplicates the effect of the argument employed in column (2) in Figure (7.8). The latter argument has, however, been employed as well since it does not depend upon a value for ΔT_{min} and this will be of advantage when the relaxation of the ΔT_{min}-constraint is discussed. (See below).

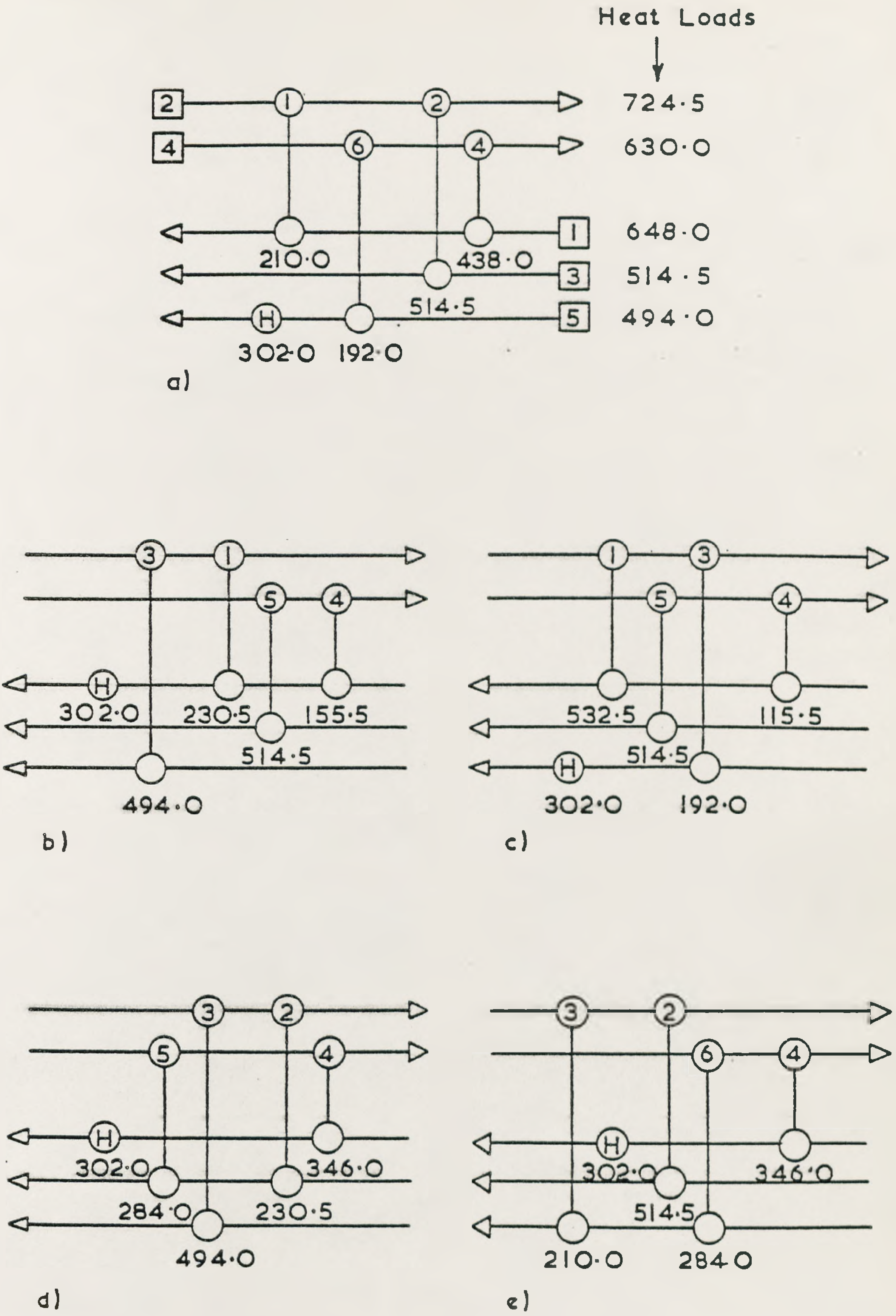

Figure (7.9) Solutions for 5SP1. (For discussion of structures a), b), c), d), and e) see text.)

In Table (7.2) the annual costs of these five networks are given. Solution (7.9b) is the same one as presented by many previous workers as the optimum cost network (without stream splitting). It can now be considered to be definitely confirmed as such.

Table (7.2) Annual costs for solutions for 5SP1

Structure	Annual Cost ($)
7.9a	38336
7.9b	38268
7.9c	38519
7.9d	38550
7.9e	38278

It is worth emphasising that more solutions could be found if the ΔT_{min}-constraint was relaxed. Assuming that this constraint was re-defined as

$$\Delta T_{min} = 0$$

the argument based on the approach temperature in match No.4 in Figure (7.8) would have to be re-formulated and one would then find that the selections of matches marked in column (1), Figure (7.8), are no longer to be rejected. Finally, feasible networks would emerge from as many as eleven different possibilities shown in Figure (7.8) (namely from No.2, No.3, No.7, No.9, No.12, No.14, No.15, No.16, No.17, No.18 and No.19) and the number of solutions found would be even greater than that since, in most cases, more than one feasible sequence would emerge. Conceivably, one or more of the networks so identified would be cheaper than solution (7.9b). Thus, it is evident that the design constraint of $\Delta T_{min} = 20^{\circ}F$ has no other effect in problem 5SP1 than to prevent some feasible and perhaps attractive structures from being identified. This is an important observation which will be taken up in Section 8.2.

7.3 DISCUSSION

Apart from the fact that a new synthesis method has been presented in the present chapter, this is probably the first time that lists of solutions with a valid claim for exhaustiveness have been obtained for any of the literature problems. Thus, while some of the conclusions drawn below are relevant to the TC-Method itself, others refer to synthesis work and network design in general and are based on observations made possible by complete solution.

The Merits of the New Method

Based on the limited evidence gained, it might be suggested that the TC-Method represents a more promising approach to heat exchanger network synthesis than any other combinatorial method presented to date. It is based on combinatorial principles quite different from tree searching methods or branch and bound algorithms and it appears to be the first method which enables exhaustive searches to be carried out with no more than a reasonable, if not small, computational effort. The number of enumerations required seems to be less than in conventional combinatorial methods where the problem size is reduced by heuristics* even though no claims for exhaustiveness can be made with these latter methods.

In the context of hand calculations, the merits of the TC-Method are more difficult to assess since the time required to solve a problem will depend on the individual characteristics of the problem tackled and on the skill and the experience of the user. The demands made on the user appear however to be reasonable. This could be important because the use of the method by hand will lead to practice in applying thermodynamic and topological arguments of the kind described here and will thus improve a user's general design skill.

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* Solving problem 6SP1, e.g., required tackling 132 network problems in the work by Lee, Masso and Rudd(91).

The Principle of Non-Independent Design of Unit Operations

As noted in Section 6.3, most synthesis work on heat exchanger networks to date is based on the heuristic of making every exchanger as large as possible, given the two streams matched. Further, this heuristic seemed to be theoretically justified by Hohmann's(92) statement that, in a minimum number of units network, each match would terminate at least one stream. However, Hohmann's statement was shown to be fallible and as an example of a network that could, by necessity, not be found using the heuristic in question the optimum cost solution for 10SP1 from Appendix F was quoted. A look at the way in which matches are terminated in the TC-Method allows one to understand this point even better.

In the TC-Method, each match is sized as dictated by the network topology so as to be compatible with all other matches in the network. Thus, matches may result that are terminated for no obvious reason as far as the two streams matched are concerned. In other words, each match is sized not just from the point of view of the two streams matched but with the overall network in mind. This interpretation would appear to somewhat expose conventional synthesis methods in that they solve network problems by sequential (and non-iterative!) design of unit operations with the remainder of a network being ignored while a unit operation is designed. The principle of what might be called the "non-independent design of unit operations" is nicely illustrated in this discussion and, quite likely, the implementation of this principle might be a major key for successful future work on systematic design of process networks.

Approximate Solutions

Even in the context of a fully automated algorithm, the TC-Method can help to overcome the unrealistic influence of rigidly fixed process stream temperatures (and heat loads). Any "practical" solution of the kind presented in Figure (7.5c) for 6SP1 (or in Figure 17, page 652, in Appendix F for 10SP1) has corresponding exact minimum number of units solutions with a very small match. These exact solutions must appear in the exhaustive list of solutions produced by the TC-Method and the chance of identifying the practical solution cannot pass unnoticed.*

This opens up a strategy of identifying preferred structures early in the synthesis. It would obviously be possible, once that sets of matches are identified, to further examine those sets first that feature the smallest matches. This must lead to considerable time savings due to early identification of preferred approximate solutions with less than the minimum number of units if such solutions exist. In an automated algorithm for industrial applications, such a facility might prove essential when large problems are tackled.

This discussion illustrates another general point. The principle of promoting solutions that are approximate but show some explicit advantage in return is highly desirable in the context of synthesis. Although it might seem unlikely that this principle can be applied easily in an automated algorithm, the above discussion demonstrates that there are instances where this is possible and where it actually may help to reduce the problem size. It would appear that the implementation of this principle is another main key for successful future work.

Problem Type and Size

If a problem has a difficult heat recovery situation so that maximum energy recovery solutions would only be possible with parallel stream splitting and/or more than the minimum number of units, the TC-Method as presented above would identify no solution. However, it is precisely in the case of such problems that synthesis by the TI-Method is rapid. Namely, the TI-Method leaves little choice in subnetwork design where

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* It would, however, be necessary to modify the whole procedure in such a way that the thermodynamic and topological arguments used to eliminate rudimentary structures at an early stage cannot be based on feasibility criteria that are only narrowly missed. (Compare to this the argument used to postulate a second connection for stream No.1 in Figure 7.3a).

heat recovery is difficult and offers many alternative designs in subnetworks only when heat recovery is easier. Thus, a general approach would seem to follow of synthesising partial networks which ensure maximum energy recovery by the TI-Method with suitably identified remaining problems. These remaining problems can then be tackled with the TC-Method. This is somewhat analogous to the solution of problem 10SP2 in Section 6.4 where the partial network shown in Figure (6.14) could be obtained by the TI-Method with the remaining problem amenable to solution by the TC-Method.

The size of problems that may be tackled by the TC-Method (be it original problems or remaining ones in the sense just outlined) is difficult to estimate without further experience. It seems, however, that practical problems with constraints (such as forbidden matches) would be less difficult to solve than unconstrained literature type problems, given the same number of streams. Also, it seems that the speed of an automated algorithm would largely depend upon how successfully thermodynamic and topological arguments of the type described above can be programmed. (Clearly, the right balance must be struck between the time saved with such arguments and the time spent when carrying out the necessary tests). One conclusion, however, is firm. Namely, that larger problems will be amenable to complete solution than is generally thought and that the synthesis of heat exchanger networks is, on reflection, not as complex an issue as is usually alleged.*

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* This point (i.e. problem complexity) is also affected by the role of continuous and discrete variables in a given network structure and is discussed in some detail in Section 8.4 and in Appendix H.

CHAPTER EIGHT

COMMENTS AND SPECULATIONS

8.1 THE CONCEPT OF MINIMUM TOTAL AREA

Hohmann(92) and Nishida et al(99) made use of a minimum overall area concept. Since any stream system represents heat sources and sinks at given temperatures, the minimum total area can be predicted based on the assumption of uniform heat transfer coefficient. However, in cases where streams are in "temperature contention", i.e. where more than one hot or more than one cold stream exist over identical intervals in temperature, minimum area networks require split stream arrangements and tend to be complex. Hohmann makes the interesting point that minimum area networks establish an "effective maximum number of units". While it is certainly possible to design networks with even more units, no further benefits in terms of reduced area would result. Thus, for networks with less than the effective maximum number of units, an optimisation problem might be expected between the number of units and the total area in a network.

However, it was found in the course of the present work that savings due to decreased area cannot normally offset increased costs resulting from additional units. This is explained by the degree of "concavity" of the equipment cost equation

$$\text{Cost} = \text{const} * (\text{Surface Area})^{b}$$

with its exponent $b = 0.6$ (which is perfectly typical in realistic contexts)*. Thus, it was decided in this work not to use the concept of minimum area but to concentrate on solutions with the minimum number of units. The decision was helped by the fact that the prediction of minimum area becomes approximate if the assumption of uniform heat transfer coefficient is no longer valid, see also Hohmann(92) and Nishida et al.(99).

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* Hohmann, too, states that minimum number of units networks have typically areas within 102.5% of the minimum.

8.2 THE ΔT_{min} - CONSTRAINT IN NETWORKS

It is often said that the magnitude of the figure chosen for ΔT_{min} is an economic consideration based on the relative costs of equipment and utilities (see e.g. Hohmann and Lockhart$^{(98)}$). However, different to the case of a single heat exchanger, the implications of a ΔT_{min} - constraint in the context of networks have probably not yet been fully understood. Donaldson$^{(96)}$, e.g., stated that "... the value of 20°F ..." (for the literature problems) "... was arrived at from design experience..." and examined the effect of different values for Problems 5SP1, 6SP1, 7SP1 and 7SP2. Each problem was solved several times by means of a branch and bound algorithm with various figures used for ΔT_{min}. For some problems, better solutions were obtained with increased values whereas for others the opposite effect was noticed. Since identical cost functions were used in all cases, Donaldson concluded that the effect was problem dependent.

However, it is well-known that utility costs are quite predominant in the literature problems and it was thought surprising in the present work that solutions should improve for any of these problems with figures for ΔT_{min} in excess of 20°F. Consequently, the implications of fixed values for ΔT_{min} in the context of networks were carefully studied.

As was briefly mentioned in Appendix F, the sensitivity of the upper bound on energy recovery for any problem to increased minimum approach temperature can be tested by computing the Problem Table several times with different figures underlying for ΔT_{min}. The results of six such runs for Problem 5SP1 are shown as a graph in Figure (8.1a) on page 246. Up to ΔT_{min} = 42°F, no sensitivity exists and the amount of heat to be imported from the utility source is given by the enthalpy balance of the problem data. For ΔT_{min} = 43°F and higher values, the amount of steam required increases (and, accordingly, cooling water must be used) Given the data of 5SP1, it is easily understood why sensitivity sets in

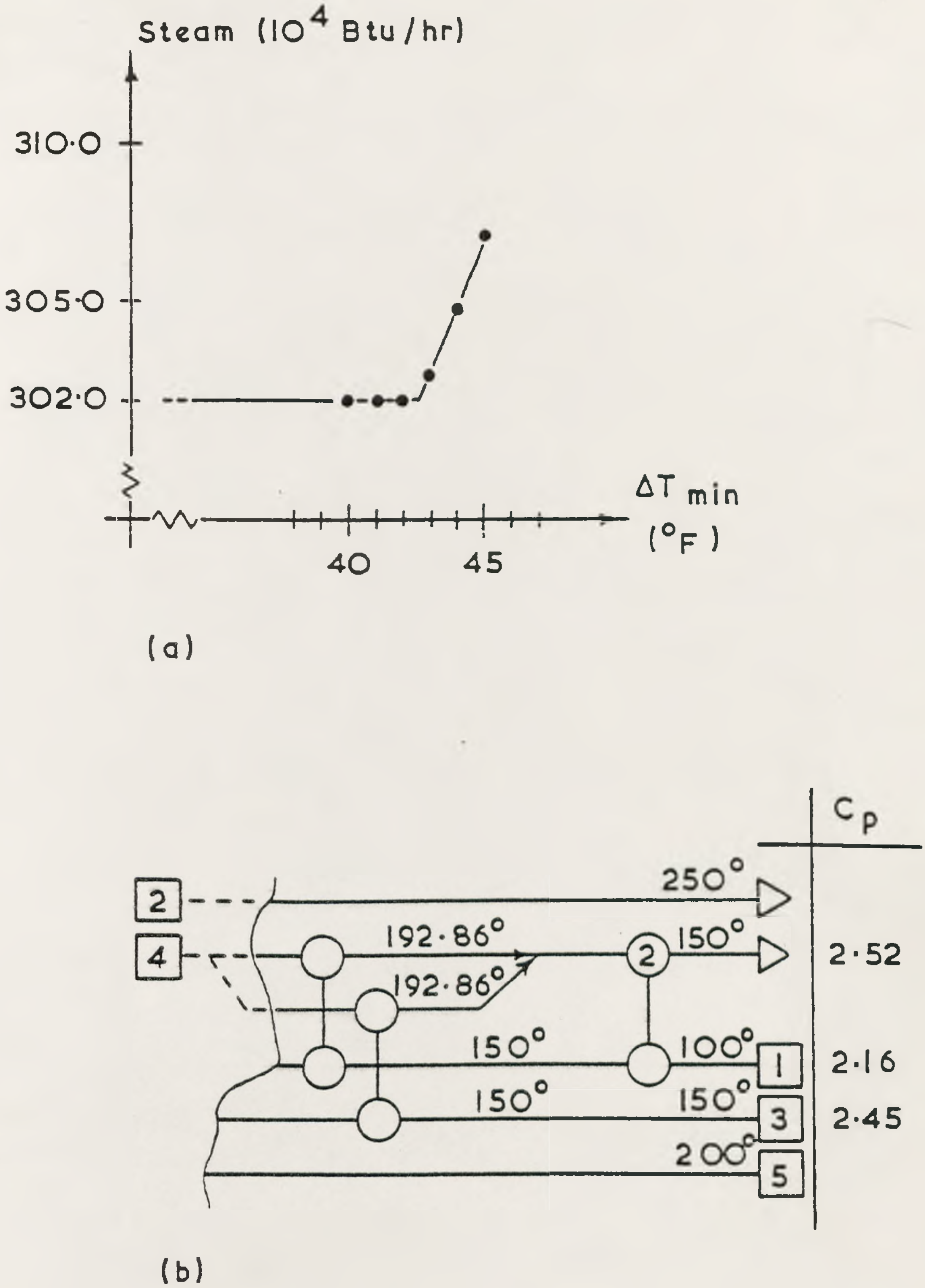

Figure (8.1) Sensitivity threshold for energy recovery in 5SP1.

a) Utility requirement as function of ΔT_{min}.

b) Understanding the threshold.

(For discussion see text)

between $\Delta T_{min} = 42^{o}F$ and $\Delta T_{min} = 43^{o}F$: in Figure (8.1b), the cold end of the problem is shown. As discussed previously, the match between streams No.4 and No.1 is inevitable unless a cooler is introduced.

If the heat load of this match is such that the cold stream exit temperature is equal to the supply temperature of stream No.3, identical smallest temperature differences are observed (i.e. $\Delta T = 42.86^{o}F$) in all three matches shown in Figure (8.1b) and there is no alternative arrangement that would allow even greater temperature differences to be maintained throughout without the use of a cooler. In other words, there is no optimum energy solution for 5SP1 that could, throughout, maintain temperature differences above $42.86^{o}F$ and any figure fixed for ΔT_{min} below $42.86^{o}F$ would be without consequence for energy recovery.

In the light of $20^{o}F$ as the figure suggested by "design experience" (see above), $42.86^{o}F$ is large enough a figure to virtually guarantee that economic designs will maintain temperature differences smaller than $42.86^{o}F$ and achieve optimum energy recovery. In this situation, it might seem most appropriate not to introduce a ΔT_{min}-constraint at all. The only effect which a figure of ΔT_{min} below $42.86^{o}F$ would have would be to exclude feasible structures from consideration and figures for ΔT_{min} above $42.86^{o}F$ would make no sense economically.

Coming back to Donaldson's observations, it can now be explained why better solutions were found with <u>de</u>creased values for ΔT_{min} (more networks could be considered) but one still needs to explain the better network costs observed in two cases (6SP1, 7SP1) with <u>in</u>creased values for ΔT_{min}. This effect must be due to the fact that Donaldson used a heuristic synthesis algorithm : such algorithms often show preferences for particular - and non optimal - structures. By varying values for ΔT_{min}, situations can be created where such preferred structures are abandoned in favour of other - and perhaps better - structures. This has evidently happened in the cases in question and it would be a gross misinterpretation of the circumstances involved to relate the "sensitivity" observed in overall network cost to a balancing effect of utility versus equipment costs. The proper conclusion to draw is that heuristic algorithms might react to constraint relaxation in a quite unpredictable manner.

A General Recommendation

Based on the above discussion, a general recommendation can be given as to the use of the ΔT_{min}-constraint to arrive at correct economic balances of utility versus equipment costs in networks. Before any network is synthesised, an "economic" value for ΔT_{min} should be chosen based on past design experience. Secondly, a temperature difference $\Delta\overset{+}{T}$ should be determined that is safely larger than the economic choice of ΔT_{min}. Thirdly, the "sensitivity threshold" for energy recovery as a function of ΔT_{min} should be established in the way shown in Figure (8.1a). Three classes of synthesis problems can then be distinguished:

1) *There is no sensitivity for $\Delta T_{min} < \Delta\overset{+}{T}$.* In this case (resembled by Problem 5SP1 in Figure 8.1), an optimisation problem of utility versus equipment costs does not exist. The utility streams should therefore be fixed for maximum energy recovery and the synthesis should proceed without any constraint on ΔT_{min}.

2) *Sensitivity exists for $\Delta T_{min} = 0$.* In this case, an optimisation problem must exist. Often in practice, networks are designed in this situation subject to a uniform figure for ΔT_{min} (arrived at from past experience) but this approach would appear a bit crude. Hohmann(92) presented a method to predict a suitable problem individual uniform figure, but the method is approximate and might still be considered unsatisfactory. Perhaps, there is only one correct approach. This would involve identifying all solutions that exist with $\Delta T_{min} = 0$ (i.e. with infinite heat exchange surface area) and then individual optimisation

for reduced energy recovery. This optimisation would involve as many continuous variables as there are possible paths through the network from utility sources to sinks. In Figure (8.2) on page 250, an example is given for Problem 4SP1, involving two utilities, one path, and therefore one continuous variable (which describes the loads on heater and cooler and all exchangers situated on the "path").

3) The sensitivity threshold lies in the region $0 < \Delta T_{min} < \overset{+}{\Delta T}$.

In this case, an optimisation problem may or may not exist. The synthesis should proceed by identifying solutions with maximum energy recovery with subsequent attempts to optimise for reduced energy recovery (in the manner shown in Figure 8.2). This may or may not lead to improvements.

Quite clearly, the above approach must lead to the correct economic balance of utility versus equipment costs in each case and it is certainly practical for simple problems such as 4SP1 in Figure (8.2). Whether it is practical for complex problems will largely depend upon the complications encountered when new structures become feasible as energy recovery is decreased. If this happens, an optimisation problem with both continuous and discrete variables exists and no attempt shall be made here to predict the chances of complete solution.

It is interesting to note that the above recommendations must always lead to the definition of a fixed stream system for network generation prior to optimisation. This simplifies the actual synthesis task and preserves the applicability of known synthesis methods. Further, these recommendations completely eliminate the ΔT_{min}-constraint from the actual synthesis task. Instead, the constraint is used in the context of initial problem analysis and classification. Bearing in mind that the constraint is a heuristic one, this latter context is probably appropriate. As long as $\overset{+}{\Delta T}$ is chosen large enough to be on the safe side, optimality can be guaranteed in spite of the application of a heuristic.

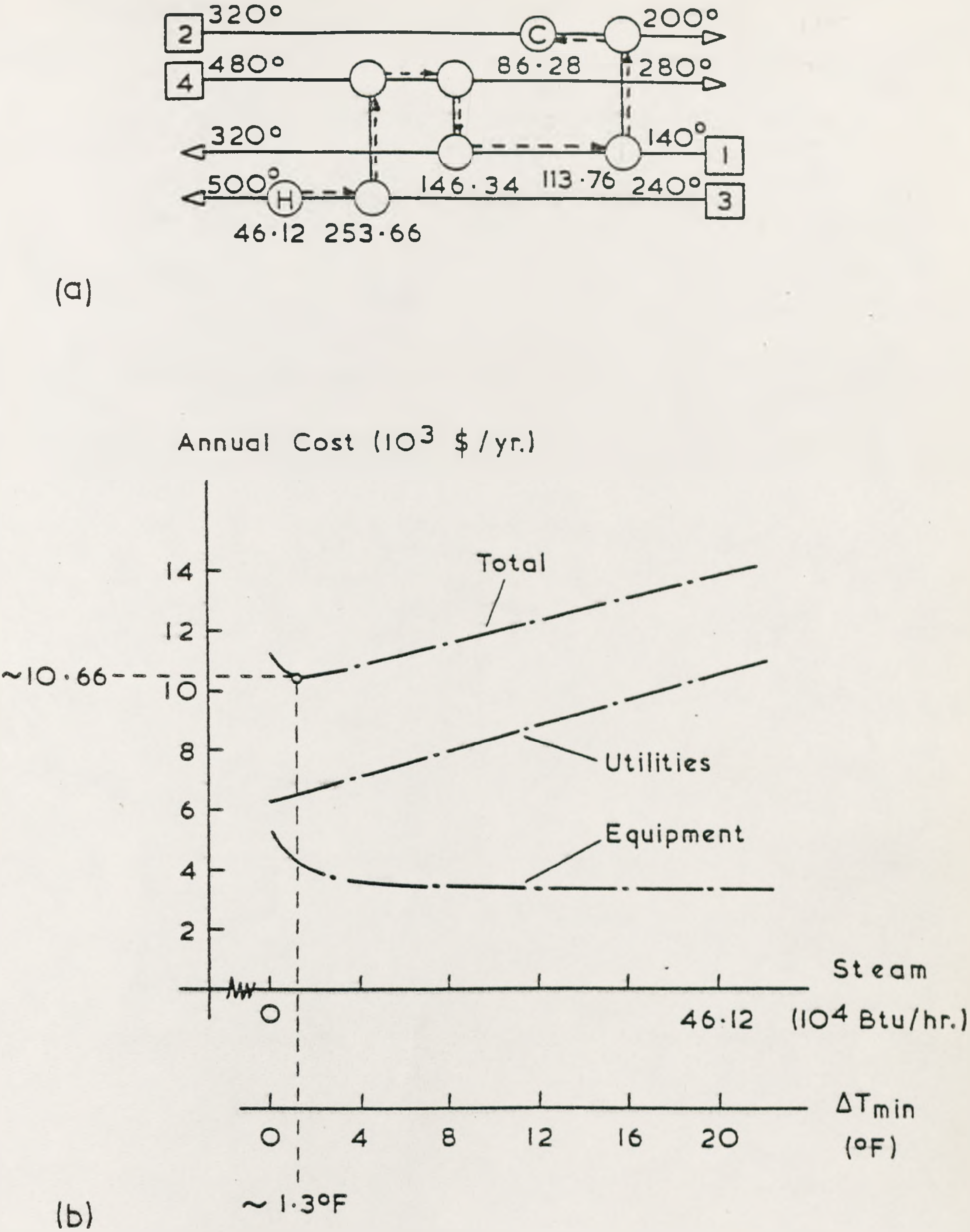

Figure (8.2) Energy versus capital trade-off for a given topology for 4SP1.

a) Network structure with one degree of freedom.

b) Costs as a function of ΔT_{min}.

In Table (8.1), the sensitivity thresholds are given for the ten problems solved in this thesis. They were obtained by appropriate runs of the Problem Table program listed in Appendix G.

Table(8.1) Maximum values for ΔT_{min} if energy recovery is to remain unimpaired

Problem	Sensitivity threshold lies at ΔT_{min} =
TC1	0
TC2	0
4SP1	0
4SP2	∿46 °F
5SP1	∿43 °F
6SP1	∿65 °F
7SP1	∿49 °F
7SP2	∿51 °F
10SP1	∿72 °F
10SP2	0

It is now evident that six of these problems can be grouped under class 1) above since the sensitivity threshold lies in no case anywhere near an economic choice for ΔT_{min} and it follows that these problems should perhaps be looked at again with the ΔT_{min}-constraint abandoned. This would preserve the solutions already known while enabling new and perhaps attractive solutions to be found. The remaining problems (i.e. TC1, TC2, 4SP1 and 10SP2) are seen to be of class 2) above. Their solution would therefore benefit from the approach outlined above with the ΔT_{min}-constraint eliminated and substituted by optimisation of individual structures.

Interestingly, there is no problem in Table (8.1) that would fall into class 3) above. For two reasons, this is not a great pity. Firstly, class 3) problems involve substantially the same principles for solution as the other two classes. Secondly, it will be shown in Section 8.3 that realistic problems with multiple utility sources and sinks will hardly ever be of class 3).

8.3 THE USE OF UTILITIES

The comment has often been made in the literature that the cost of utilities as originally proposed by Masso and Rudd(90) in 1969 (see Appendix K) is rather high. Also, the relative importance of utility costs as compared to equipment costs seems further exaggerated by the unrealistic payback time for equipment (i.e. ten years).
However, the importance of utility costs as against equipment costs has probably increased since 1969 and a comparison of the data given by Masso and Rudd with industrial data today might reveal a better similarity in the relative importance of equipment and operating costs than perhaps a few years ago. In addition, one can expect further increases in the cost of fuels as well as some learning in the design of heat exchange equipment (prompted by the recent increases in the cost of energy). Thus, the relative importance of utility versus equipment costs as proposed by Masso and Rudd might, with a grain of salt, be quite useful for present day practical design situations.
A far more fundamental criticism concerning the use of utilities in the literature problems would be based on a qualitative rather than a quantitative argument. Due to the fact that only one utility source and one sink is considered, the design task of balancing utility costs against equipment costs must always involve the comparison of benefits on the equipment side with double costs on the energy side (more steam used also means more cooling water used, compare Figure 8.2). This leads consistently to the recommendation to maintain maximum energy recovery

or, alternatively, "economic" temperatures of approach such as established in Figure (8.2). If the design data were to be modified so that more than one utility source and/or sink was to be considered, heat could e.g. be supplied from the HP steam mains instead of the IP mains at constant cooling requirements. Thus, the design task would involve the comparison of networks with substantially different equipment lay-out but only slight differences in energy costs.

The choices to be made in such a context would be subtler than could ever be encountered in problems with only one utility source and one sink: even with cost parameters similar to those listed in Appendix K savings on the equipment side might often warrant different utility requirements. Also, virtually any problem with multiple utilities will be a class 2) problem in the terms adopted in Section 8.2. Energy optimality would require minimum usage of high temperature sources and this would, in turn, require zero temperature approach between medium temperature utility heat sources and process streams. Thus, a situation would exist where a) an optimisation problem would definitely exist and b) the optimisation would involve a perhaps considerable number of independent variables.*

It follows that the assumption of single utilities is perhaps the main shortcoming of the literature problems. A synthesis method developed for the solution of these problems need not necessarily succeed in the context of multiple utilities, due to the substantially different dependency of overall network cost on utility requirements. As far as the methods presented in this thesis are concerned, they could still be used. The Problem Table could evidently be modified in such a way as to discriminate minimum heat requirements according to source temperatures.

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*As stated previously there could be at least as many continuous variables as there are paths through a network between matches to utilities (compare Figure 8.2). Thus, with N matches to utilities, there would be at least $\frac{N}{2}*(N-1)$ continuous variables.

(The evaluation of the maximum possible surplus that can be given to a "high temperature sink" has already been demonstrated when solving Problem 1OSP2.) Accordingly, optimum energy networks could still be designed by means of the TI-Method and, as from there, the ED-Method could be used to study possible shifts of heaters to different sources and coolers to different sinks. The concept of the minimum number of units could be used to identify services that could be wholly or partly abandoned (so as to reduce the number of streams in the system or to create heat load residuals equal to others) and the TC-Method could be used to synthesise networks for the alternative stream systems so identified. Quite clearly, optimality could probably be guaranteed in simple cases only but even in quite complex cases, good designs should be obtained with confidence. To a limited extent, the solution of Problem 1OSP2 might support this claim.

8.4 THE COMBINATORIAL PROBLEM

Discrete and Continuous Variables. As stated before, the number of alternative configurations for heat exchanger networks is usually thought to be immense, see e.g. Ponton and Donaldson(95). Further, it is often claimed that optimal synthesis requires consideration of a great number of continuous variables (such as exchanger size) as well as discrete ones (such as a topological connection), see e.g. Kelahan and Gaddy(101).

Based on the findings in Chapter Seven, these views may be questioned. After all, there are no more than five solutions for Problem 5SP1 and no more than six solutions for Problem 6SP1 (based on $\Delta T_{min} = 20^{o}F$) and none of these solutions incorporates a continuous variable. Evidently, one might argue that a solution with more than the minimum number of units (i.e. with continuous variables) might sometimes be desirable but, as pointed out in Chapter Seven, particular reasons would then exist and the same reasons would help to identify the additional (or alternative) units. Also, each additional unit would introduce no more than one continuous variable (which would determine the loads on the exchangers in the heat load loop caused by the additional unit).

It is probably fair to say that a distinction should be made between the combinatorial complexity of a problem and that of a solution method. The complexity of problems such as 5SP1 and 6SP1 would appear to be almost non-existent judged by the complete list of best solutions now known. If the combinatorial problem to be overcome in the course of finding these solutions is rather more complex, this would seem to be due to the solution method. The following statement can be made quite categorically:

> Methods which start off from topologies incorporating all possible matches have to work their way through a virtual jungle of discrete and continuous variables towards simpler topologies. These methods simply start off from the "wrong end" of the problem, thereby letting it appear far more complex than it is.

This insight is of great importance when assessing the potential scope for various techniques used previously in the synthesis literature. Branch and bound, tree searching, random search, all these methods - and others - might conceivably be applied to start off from the "right end" of the problem. Possibly, this would lead to viable competition for the TC-Method as described in Chapter Seven. Mainly for this reason a proper comparison has been worked out between the combinatorial problem as encountered (1) when initially considering networks with all possible matches and (2) when initially considering networks with the minimum number of units only (see Appendix H).

Constraints. Further in the context of complexity, it was seen in Chapter Seven that simple constraints such as "there must be a cooler on this stream", etc., can considerably reduce complexity. In a practical design environment, constraints will frequently exist such as that two particular streams must not be matched against each other for safety reasons or that a heater is required on a certain stream for start-ups, etc. It is quite clear that such constraints have the same welcome effect on overall complexity as the thermodynamic arguments frequently referred to in Chapter Seven. This leads one to suspect that realistic heat exchanger network problems might often be considerably less complex than unconstrained problems with the same number of streams.

To take advantage of this, one would have to give up the strategy so often recommended in the literature of

1) identify the unconstrained problem,
2) produce solutions, and
3) select those solutions that are compatible with practical constraints

and would have to replace it with a strategy such as

1) identify the constrained problem, and
2) produce only those solutions that observe constraints.

This strategy of selective generation would seem far more promising than that of indiscriminate generation and subsequent evaluation. The TC-Method as described in Chapter Seven could be said to employ such "selective generation".

Summary. All in all, the combinatorial complexity of problems such as discussed in this thesis is much lower than is commonly thought because desirable solutions will not normally contain continuous variables. Further, if practical constraints would be made use of in realistic problems the complexity would be reduced even more. Having said this, it was shown in Section 8.3 that the example problems are unrealistic in their use of utilities and that increased realism in this respect might increase complexity. Thus, realistic heat exchanger network problems may still be complex, albeit for different reasons than is commonly assumed.

8.5 SYNTHESIS PROBLEMS WITH INCREASED REALISM

Apart from the assumption of only one hot and one cold utility, which was discussed in Section 8.3, there are further shortcomings in the literature problems that make these problems more unrealistic than would perhaps be necessary.

The most obvious simplification is that of constant heat capacity flowrates. It appears that this assumption is not normally instrumental in the success of synthesis methods or, in other words, that most methods could be modified to allow for temperature dependency. On the other hand, it is quite clear from a few examples considered* that enthalpy correlations - and especially condensing curves - would lead to different networks proposed than would constant specific heats. This is especially true when thermal integration is tight. It follows that synthesis methods must ultimately be used with such correlations and since the computational complications involved are considerable, it might be desirable to have example problems with such correlations, too. If anything, this will give a realistic idea of the computational effort required when using synthesis methods in practical contexts.

Another important aspect in the context of problem realism is that of stream temperature specification. As found in Section 6.4, the degree of flexibility that can be introduced into the design task by slight adjustments of process stream temperatures is substantial. In a practical environment, this flexibility would certainly be exploited and a synthesis method which is designed to find optimum networks for a problem with fixed stream temperatures might simply tackle an irrelevant task. For future experience, synthesis problems should

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* not documented in this thesis

incorporate specified tolerances for the supply and target temperatures of some streams. This would encourage the development of methods that show the user where an advantage could be gained by making use of such tolerances.

Another important aspect is that of design constraints. As pointed out in Section 8.4, realistic designs are often subject to problem-individual constraints (such as forbidden matches) and the specification of one or two such constraints in synthesis problems would be desirable. Otherwise, it is difficult to see how well a method can exploit such constraints by selective generation with subsequent evaluation, see Section 8.4 .

Further, the cost of networks could be assessed much more realistically without unduly complicating the necessary computations. As stated in Appendix F, an important shortcoming of the equation used for the cost of single heat exchangers

$$C = a * A^b$$

with C = cost (e.g. in dollars)

and A = heat transfer area (e.g. in ft^2)

is the tendency to favour the creation of excessively small exchangers in a network optimisation. This tendency could be eliminated by defining a constant cost for exchangers below a certain size :

$$C = a * A^b \quad \text{for } A \geq A_{min} \tag{8.1a}$$

and

$$C = a * A_{min}^b \quad \text{for } A < A_{min} \tag{8.1b}$$

Also, the cost for pipework and pumps should be accounted for and in cases where streams are split in parallel branches, that for control valves. Unless this is done, stream splitting may lead to seemingly attractive - but quite unrealistic - improvements on paper. Based on some value β expressing the cost of pipework and accessories as a fraction of the cost of heat transfer area in a simple network, and on the observation that the number of pipe runs and junctions in a simple network is about four times the number of units, this additional equipment cost could be approximated by Equation (8.2)

$$C_{add} = \frac{n_{pipes} + n_{nodes}}{4 * n_{units}} * \beta * \sum_{i=1}^{n_{unit}} (C_i) \qquad (8.2)$$

where n_{nodes} represents the number of splitting and mixing junctions in a network involving split streams.

Lastly in the context of costs, an "operating cost of equipment" should be introduced. Complex networks cost more in maintenance than simple ones and the effect would be easily described by specifying the fraction of initial capital cost that is required for annual maintenance, ϕ. Altogether, these suggestions would lead to the following equation for capital related annual network cost:

$$\sum_{\text{Equipment}} (\text{Annual Cost}) = \left[1 + \beta\left(\frac{n_{pipes} + n_{nodes}}{4 \times n_{units}}\right)\right] * \left[\frac{1}{\delta} + \phi\right] * \sum_{i=1}^{n_{unit}} (C_i) \qquad (8.3)$$

(with δ = useful life of equipment in years). This equation is slightly more involved than that which follows from Masso and Rudd's design data but it would still permit speedy evaluation while at the same time assessing networks in a far more realistic way. The only additional data required would be figures for A_{min}, β, and for ϕ.

To summarise, the "next generation" of synthesis problems here suggested should feature

- multiple utilities (e.g. direct furnaces, hot oil circuits, steam used and raised at various levels, air and water cooling),
- enthalpy correlations and phase changes (incl. condensing curves),
- stream supply and target temperature tolerances,
- problem - individual constraints, and
- capital costs according to Equation (8.3).

Further, a minimum approach temperature should not be specified. Instead, the design task should involve finding the individual best balance between operating and fixed costs.

Evidently, further complications might be thought desirable to improve the realism of synthesis problems. To give but a few examples, one might want to introduce more than one material of construction, various heat transfer coefficients, design for construction, design for operating flexibility, etc. However, it is quite evident that some work might yet have to be done before even problems such as just outlined can be solved in a manner such that best solutions are obtained consistently and with reasonable effort. Thus, to complicate problems even further at the present stage could be wrong for two reasons. Firstly, it could weaken the incentive for workers in the field to understand a problem thoroughly. Secondly, people outside the field might be misled into believing that current solution methods are more powerful than they really are and this could damage the credibility of synthesis work in general. Perhaps, one should aim at "realistic" problems in this other sense, too.

8.6 APPLICATIONS IN INDUSTRIAL PRACTICE?

Donaldson (96), among others, described the situation in which systematic synthesis algorithms would be used in industrial practice. He outlined that a network synthesiser might form part of a library of computer programs, some of which could be used for further aspects of synthesis (such as the development of safety procedures) but most of which would be used for aspects of evaluation (such as steady state simulation, controllability, starting-up behaviour, performance under varying operating conditions, reliability, maintenance, and detailed cost). In this situation two main demands ought to be met by the synthesiser : it ought to be fast (because so much other work would also have to be done) and it ought to be flexible (so as to allow information to be fed back).

Whether or not the concepts and methods presented in Part II of this thesis could make a useful contribution in this context is perhaps best discussed by considering them separately.

The ED-Method. This method can be used in many contexts, ranging from intuitive design to conventional optimisation and evaluation. It offers a realistic chance to the engineer to increase his insight into design problems and to accordingly achieve improvements. Perhaps even more importantly, it enables him to gain a feel for patterns. In other words, the method might not only be suitable for applying process engineering expertise but also for developing it. As presented in Appendix F, the method relies on only one idealisation (namely $\mathcal{C}p$ = const.) and if required temperature dependent heat capacity flow-rates could be introduced. In this case, Freedoms would become temperature dependent and the method could be developed into an interactive program with the network appearing on screen. Whether in this form or in the context of hand calculation, it appears reasonable to assume that this method will find practical application.

The TC-Method and the TI-Method. The TC-Method seems set to establish something of a standard for solution power for problems to which it is applicable. Apart from the assumption that the minimum number of units is desirable (and this should apply nearly always), the method has no heuristic element it would depend on. Also, worthwhile adjustments of problem data (which could not normally be expected from a systematic method) can be identified. The question that remains is : how many realistic problems are there for which the method is suitable?

As far as the condition "predicted degree of energy recovery feasible with the minimum number of units and no split streams" is concerned, the remarks made in Section 7.3 hold valid. For problems where this condition is not met, the TI-Method as described in Appendix F is particularly suitable, with remaining problems to be solved by the TC-Method. As far as problem size is concerned, the computational effort in the TI-Method increases roughly pro rata with the number of streams, and the limit for a fully automatic algorithm for the TC-Method might, perhaps, be somewhere around the twelve stream mark for an unconstrained problem. In the case of larger problems, the user might define constraints so as to achieve a reduction in problem complexity at a given number of streams. Also, a realistic problem might be solved more speedily if approximate solutions are sought first. (Compare Section 7.3).

The Problem Table. Quite likely, the Problem Table will become accepted as a simple algorithm by means of which the upper bound on energy recovery for a given heat recovery problem can be determined. The use to which this information can be put has been demonstrated in many instances in the present thesis and since the underlying computations are easy, and are easily programmed, the application of the Problem Table in industrial design situations would appear certain.

Summarising, the systematic synthesis of heat exchanger networks has, perhaps, reached a stage of development now where the emphasis has shifted from the fast and convenient identification of many alternatives emphasised by Donaldson(96) (see above) to the identification of structures that might - subject to a final evaluation from practical points of view - simply be <u>better</u> than those identified without the use of synthesis methods. In other words, the possible benefits have shifted from convenience in design to superior process plants with improved network simplicity and reduced fuel consumption.

CONCLUSIONS

The Potential Value
of Thermodynamic Concepts
in the Design of
Inherently Irreversible Process Networks

Thermodynamic analyses of industrial chemical processes are normally interpreted as pointers to areas in which possibilities for improved energy performance might exist in rather broad and speculative terms: by establishing the magnitudes of the main irreversibilities in a process, it is possible to assess the benefits that could result from introducing alternative reaction paths and/or novel technology in unit operations. In the present thesis, however, thermodynamic analysis has been discussed in the narrower but perhaps more practical context of ordinary process network design, i.e. design along a given reaction path and employing conventional technology in unit operations.

As argued in the Introduction, the value of thermodynamic criteria would appear to be questionable in this context and examples where the applicability of Second Law analysis is indeed limited are discussed by Szargut(24), Denbigh(31), and Frankenberger(38). The main points that evolve from these sources could perhaps be summarised as follows:

(1) Network interactions often make it difficult to relate the thermodynamic performance of a particular unit operation to that of an overall process.

(2) The thermodynamic potential of various forms of energy may often not reflect their economic value.

(3) Some operations cannot be carried out other than under grossly irreversible conditions.

Apart from these rather obvious points, the following four have emerged from the present thesis:

(4) One of the main assumptions on which workers in the field base interpretations of Second Law analyses may be of limited validity. The assumption in question is that each piece of equipment in a

network may be held responsible for overall inefficiencies to a degree roughly measured by the losses occurring in it. As argued in Section 3.7, this assumption may be valid if a loss is large enough to justify the installation of work generating equipment but it need not be valid if a loss is too small to justify such equipment. In realistic chemical process flowsheets, most losses will normally be "too small".

(5) Even if a loss is "large enough" from the above point of view, seemingly similar irreversibilities in seemingly similar unit operations might offer substantially different scope for improvement, due to purely technical reasons. As discussed in Appendix E, irreversibilities are a function of (1) the degree of energy degradation and (2) the amount of energy degraded. The extent to which work could be recovered depends on the relative weight of both factors and on further aspects which will often be too intricate to be recognised other than by simulation.

(6) Like the thermodynamic losses themselves, entropies and exergies of process flows are a function of both flowrates and relative levels of energy potential: a small heat flow Q_H at a high temperature T_H might be exactly equivalent in Second Law terms to a large heat flow Q_L at a low temperature T_L. (Thus, Q_H at T_H and Q_L at T_L could be converted into one another by means of ideal Carnot cycles.) However, in a situation where Carnot cycles are impractical, Q_H can be brought from T_H to T_L (by simple heat transfer), but Q_L cannot be brought from T_L to T_H. Consequently, the objective to conserve convertibility of energy may focus attention on temperature rather than entropy. Similarly, cases exist where parameters such as composition or pressure are of prime interest.

(7) If energy sources (e.g. hot process gases) and sinks (e.g. steam mains) are given at fixed levels, a minimum overall irreversibility is inevitable for most practical processes transferring energy from sources to sinks. In such cases, it cannot often be easily decided whether a particular irreversibility is part of this inevitable total or not.

Together, these seven points (and possibly other ones not here identified) suggest that if an entropy increase is observed in a particular unit operation then this must not be regarded as sufficient evidence for improvements to be possible, or even desirable. Whether or not improved energy performance would be

- possible
- practical, and
- worthwhile

should be clarified by simulation. As stated in Appendix A, an interaction between heat and mass balance and Second Law analysis would appear to be required to ensure practical relevance when interpreting a Second Law analysis.

In this situation, the approximation method outlined in Chapter Two for the deduction of entropy and exergy figures from heat and mass balance data seems to be useful. In many instances, this method may encourage the designer to interact more than usual with the necessary calculations and this would help him to develop a feel for the process he is attempting to improve. Also, it would help him to understand the ways in which First Law and Second Law concepts complement each other. The method was used extensively in Chapters Three and Four and its accuracy was found to be compatible with that of normal industrial heat and mass balances.

Apart from the approximation method, the concept of prescribed irreversibilities which was applied in the case studies would appear to be useful. As mentioned in Chapter Two, this concept was probably first introduced by Denbigh(31), and equations were suggested by Denbigh for implementation. In the present thesis, an alternative procedure has been described which is compatible with that suggested by Denbigh in that it produces identical results if identical assumptions are used. In addition, however, it allows assumptions to be varied, so as to fit best individual circumstances with more meaningful results obtained. As it stands, the procedure is attractive for two reasons: firstly, it prevents practically inevitable irreversibilities from distorting the significance of other irreversibilities that are, perhaps, avoidable. Secondly, it allows discussion of chemical processes in Second Law terms without the need to use free energy data for the species involved. The search for such data often presents problems and the possibility of avoiding them altogether would seem attractive.

However, even with the approximation method and the concept of prescribed irreversibilities helping to establish a Second Law analysis more easily, the question remains whether it is worth the effort to produce Second Law analyses in practical situations: since the need for simulation cannot be eliminated, thermodynamic inefficiencies could perhaps be discussed in terms of temperature drops, pressure drops, etc., rather than in terms of a separate (i.e. Second Law) analysis. Such a more conventional approach might require less effort while possibly producing results of equal validity.

Based on the limited evidence that has been gathered in this thesis, it is suggested that the approach most likely to lead to positive results might well be a combination of a Second Law analysis with a conventional heat and mass balance. Sometimes, it will be difficult for a designer to ensure that he has considered every possibility that exists for improvement if he adopts the conventional approach since a clear target against which he could check thermodynamic inefficiencies might not always be easily identified. Thus, he should carry out a Second Law analysis to obtain definite targets. However, he should critically examine the analysis in the light of points (1) to (7) above, and should then modify his targets by expressing them in parameters of practical relevance (such as temperature, pressure, etc.). To carry out this latter step, he must take decisions with regard to the type of unit operations he will use, the minimum sizes of equipment, the services to be connected, etc. As demonstrated in Chapter Six, (i.e. when developing the "Problem-Table"), the final approach to a design problem may well be formulated in First Law terms, but when derived from a Second Law analysis, it might be more rigorous than if it were derived by intuition alone. And although it seems true that the heat recovery network problem with its high degree of idealisation is particularly suited to a clear-cut thermodynamic approach, it seems also true that in the more general and less idealised case studies in Chapters Three and Four the Second Law analyses have helped to achieve a fair degree of confidence that no basic possibilities for improvement have been overlooked.

To summarise, thermodynamic analyses will often need to be modified and expressed in parameters other than entropy or exergy to become relevant in the design of processes using conventional technology in unit operations. When modified, they might seem little different from ordinary heat and mass balances in which experience regarding energy saving techniques is brought to bear. However, the difference does seem to remain that studies based on an initial Second Law analysis are likely to be more thorough and, perhaps, to produce more consistent suggestions than studies based on the merely intuitive discussion of apparently inefficient unit operations. This suggests that the effort involved in drawing up Second Law analyses alongside heat and mass balances might often be justified, even in the design of flowsheets for inherently irreversible processes. The rewards might range from "fair confidence that nothing substantial has been overlooked" in a detailed study of a practical process to near certainty that "all best solutions" have been identified for problems in an early and simplified stage. However, some skill will usually be required to transform an original entropy - or exergy - analysis into First Law terms without losing some of its rigour, and only if this transformation is carried out successfully are valuable suggestions likely to be generated. It would appear that there is a great challenge for future work in trying to identify firm rules for such transformations for problems more general and less idealised than the synthesis of heat exchanger networks.

Finally, the range of contexts in which thermodynamic strategies may be of use in process design warrants discussion. As stated previously, thermodynamic analysis is normally referred to in the context of energy conservation and, perhaps, with regard to feedstock utilisation. In cases where concerns such as capital costs, operability, safety, etc. are more important than efficiency, thermodynamic analysis is usually thought to be irrelevant. However, there is evidence that the potential scope for thermodynamic analysis might be somewhat greater.

The concept of Freedom, as described in Appendix F, is based on exclusively thermodynamic principles. However, it has been developed not for the optimisation of energy costs, but for the evolutionary development of heat exchanger networks with low equipment costs, fewer heat exchangers, favourable control characteristics, suitably modified design constraints, etc. In particular, the concept was seen to be instrumental in finding minimum equipment costs at a fixed level of energy recovery. Trying to interpret the essential feature of the concept in general terms, one may say that it allows the designer to recognise more easily the full range of available design options. Consequently, policies to achieve whatever goal he has in mind become more easily formulated.

Similarly, the TC - Method as described in Chapter Seven represents a combinatorial (i.e. mathematically orientated) method for the synthesis of heat exchanger networks in which thermodynamic criteria are used to ensure that only the most promising structures are generated. This helps to ensure optimality in spite of considerably reduced computational effort.

In a way, such a use of thermodynamic principles might be more general and more fundamental than a mere attempt to improve energy efficiency: in an energy optimisation context, freedom of choice in design - signalled by irreversibilities - is reduced in exchange for one particular advantage, namely the conservation of energy. In the more general case, freedom of choice is traded against other and not a priori specified advantages. Perhaps there are further problems in systematic synthesis for which methods would exist which would describe the full range of feasible options in generalised terms. The development of such methods presents another great challenge for future work. In times of rapidly changing costs for many materials and services, such methods might be especially valuable. They might encourage the designer to clarify the physical constraints on a system and to explore as many feasible alternatives as possible that would comply with these constraints. Thus, his view would be restricted by limits of feasibility rather than by economic criteria which are subject to change.

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APPENDICES

Appendix A	"The Use of Entropy in Process Design" (Paper submitted to the Annual I.Chem.E. Research Meeting, 4-6 April 1977, Swansea, U.K.)
Appendix B	Physical Property Data for Contact Process Case Study.
Appendix C	Case Study : Integration of Preheater into Existing Sulphuric Acid Contact Plant.
Appendix D	Physical Property Data for Ammonia Oxidation Process.
Appendix E	The Influence of Minimum Driving Forces and of Flowrates on Practical Efficiencies.
Appendix F	Synthesis of Heat Exchanger Networks : I. Systematic Design of Energy Optimal Networks II. Evolutionary Generation of Networks with Various Criteria of Optimality. (Copies from the A.I.Ch.E. Journal, July 1978)
Appendix G	Computer Programs.
Appendix H	The Combinatorial Size of Generation Trees for Minimum Number of Units Networks.
Appendix K	Data for Synthesis Problems.
Appendix L	Two More Solutions for 4SP2.

APPENDIX A

"THE USE OF ENTROPY IN PROCESS DESIGN"

(Paper submitted to the Annual IChemE Research Meeting, 4-6 April 1977, Swansea, U.K.)

THE USE OF ENTROPY IN PROCESS DESIGN

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Thermodynamic "second-law" analyses of industrial processes allow comparison of actual process energy performance against the theoretical optimum (which would be achieved by a fictitious process incorporating devices such as fuel cells and semipermeable membranes and operating under equilibrium conditions throughout). Using this comparison, the potential benefits of effort devoted to the development of processes which operate closer to the fictitious ideal can be estimated. Such processes might follow unconventional chemical reaction paths, make use of novel equipment designs, or might simply be based on more efficient flowsheet designs.

CONVENTIONAL ENTROPY ANALYSIS

A possible way of establishing a Second-Law analysis of a process is by calculating the entropy of each process stream, e.g. by applying equation (1) provided that the usual simplifications, e.g. Cp is independent of p, are permissible.

$$S_{(T,p)} = \sum_{i=1}^{z} \left[m_i \left(\int_{T_{std}}^{T} cp_i \frac{dT}{T} - R_i \ln \frac{p_i}{p_{std}} + s_{i_{std}} \right) \right] \quad \ldots\ldots (1)$$

with z = number of components,
m_i = mass of component i,
$s_{i_{std}}$ = standard entropy of component i, and
p_i = partial pressure of component i

This equation is easily derived from principles discussed in many textbooks. A particularly thorough discussion is given, e.g., in (7), chapter 13. For each case of heat exchange/generation, equation (2)

$$\Delta S_{12} = \int_1^2 \frac{1}{T} dQ \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

has to be applied. This will, invariably, lead to a situation where

$$\sum_{OUT} (S) > \sum_{IN} (S)$$

for any piece of equipment. The differences constitute irreversible entropy increases, thus assigned to different sections of the process. The ideal process (see above) would be one where the overall entropy increase is zero; its energy performance would be correspondingly more favourable than that of any real process. Examples will be presented at the conference to this type of analysis.

PRESCRIBED DEGREE OF IRREVERSIBILITY

In the context of process design, where the objective is to devise improved flowsheets which follow specified overall reaction paths and where conventional technology is not to be abandoned without explicit advantage being shown, the figures evaluated in an entropy analysis require careful interpretation. One reason is that inefficiencies which cannot be avoided (e.g. burning NH_3 to obtain NO in an HNO_3-plant) tend to distort the relative significance of other inefficiencies which are, perhaps, not inevitable (e.g. mismatch of heat capacity flowrates in the heat recovery section of an HNO_3-plant). For this reason, two equations are given below which could be used instead of equation (1):

$$S_1 = m_1 \left(\int_{T_{STD}}^{T_1} c_p \frac{dT}{T} - R \ln \frac{p_1}{p_{STD}} \right) \quad \ldots\ldots\ldots\ldots (1a)$$

$$\Delta S_{\substack{irrev.\\ REACTION}} = \left(S_{PRODUCTS} - S_{REACTANTS} \right)_{ACTUAL} - \left(S_{PRODUCTS} - S_{REACTANTS} \right)_{OPTIMAL} \quad \ldots (1b)$$

Equation (1a) has to be solved for each process stream, and equation (1b) for each reaction and/or case of non-ideal mixing. In the latter equation, the entropies of products and reactions are, again, computed by means of Eqtn. (1a) and the index "optimal" implies a particular mode of operation which would result in the highest thermodynamic efficiency, given the chemical, metallurgical and other constraints which must be observed in operation. The entropy analysis based on these equations will, by and large, consider an ideal process as one in which the reactions proceed as irreversibly as is inevitable with the usual technology but in which temperature and pressure drops, as well as "friction", are non-existent. The proposal to assume such a "prescribed degree of irreversibility" when considering process networks in second-law terms was, probably, first made by Denbigh (1).

MAKING USE OF ENTROPY ANALYSIS

A proposal made from time to time in the literature is to use entropy analyses for evolutionary flowsheet development. The basic assumption is that each piece of equipment is - to a first approximation - responsible for the non-ideal energy performance of the process to a degree which is measured by the entropy increase occurring in that piece of equipment. Thus, one might concentrate attention on that piece of equipment which shows the largest entropy increase - see e.g. (2).

In many physical process engineering problems, low temperature gas separation processes, and power plants, this idea is more or less justified. In the case of chemical process networks, however, the design objectives are often not as clear cut as in the above mentioned examples and the operating constraints are much more varied. Furthermore, the influence of the network interactions are more marked: Seemingly similar process networks will show highly individual responses to seemingly similar modifications.

The three points listed below are an attempt to identify the main consequences which these characteristics of chemical processes appear to have with regard to the significance of second law analyses:

(1) Entropy increases do not necessarily bear a close correlation to the objective processing function. (The more rapid, e.g., a quench, the better the product specification but the lower the thermodynamic inefficiency.)

(2) Entropy increases are not necessarily caused where they are observed. (Bad design of a separator, e.g., might necessitate excessive mass flowrate in a recycle stream. This will increase the entropy change in any heat exchanger connected to that recycle stream.)

(3) A large entropy increase is not necessarily easier to "design out" than a small one. (A small compressor with a low efficiency is more easily improved than a large compressor with a high efficiency.)

Due to these and other less general points, the results may be somewhat unpredictable if one attempts to improve a process according to the principle "tackle the biggest entropy loss first"(3). The need to re-evaluate the whole process in terms of heat and mass balance calculations after each such step is clear and only after this has been done, can one see, in retrospect, the significance of a particular entropy increase.

On the other hand, the present authors have found that it is precisely this iteration between heat and mass balances and entropy analyses which helps to clarify the engineers' understanding of the way in which energy is utilized in a process network. It is this procedure which will help to avoid confusion where the points listed above make an interpretation difficult. Thus, entropy analysis is employed with benefit, in addition to heat and mass balances, when choosing policies of evolutionary process improvement but it is doubtful whether there are many cases in which the entropy function is of such a clear-cut significance that it would be a suitable parameter for the automatic definition of evolutionary improvement steps.

EFFICIENT USE OF HEAT AND MASS BALANCE DATA

When employing entropy analyses in the way just suggested, a numerical approximation technique to be described now was found to be useful:

The solution of equation (1a) requires integration of the function cp(T)/T for all components of a stream which can be a significant computational task. Since enthalpy changes of process streams at constant pressure are evaluated by integrating the function cp(T), one can write

$$\Delta S\Big|_{T_1}^{T_2} = (H_2 - H_1)\cdot\left[(\ln(T_2/T_1))/(T_2 - T_1)\right] \quad . \; . \; . \; . \quad (3)$$

This expression shows how the entropy change can be related to the enthalpy change under the assumption cp = const. The numerical error found when using equation (3) to evaluate entropy changes from known enthalpy changes is, however, much smaller than one would tend to expect from the simple assumption cp = const. The reason is that the errors due to this assumption in the entropy and the enthalpy terms tend to cancel each other.

If a linear variation of Cp with temperature is assumed, eqtn.(4) is derived

$$\Delta S \Big|_{T_1}^{T_2} = (H_2 - H_1) \ast \frac{\alpha / \Delta T_{LM}(T_1, T_2) + 1}{\alpha + 1/2\,(T_1 + T_2)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (4)$$

$$\text{with } \alpha = [T_2\,(Cp(T_1)) - T_1\,(Cp(T_2))]/[Cp(T_2) - Cp(T_1)]$$

which may be used instead of equation (3) to give results which differ from those obtained by accurate integration by factors much smaller than the assumed uncertainties in the Cp polynomials.

Equations (1a), (1b), (2), and either (3) or (4) make it possible to deduce, with great ease, an entropy analysis of surprising numerical accuracy from an existing heat and mass balance (temperatures and pressures known). No additional physical property data need be collected.

SYNTHESIS OF HEAT EXCHANGER NETWORKS

Having suggested above that entropy will not necessarily be the most suitable function on which to base process design calculations however valuable it may be as a guide in obtaining insight into a process problem, it seems appropriate to report a particular development which appears to substantiate this suggestion:

The problem of automatically synthesizing heat recovery networks (4, 5) has, so far, usually been interpreted as a combinatorial problem or one which ought to be solved by using heuristic decision making. In (6), however, the problem is identified as one in which a definite minimum for the overall entropy increase is inevitable (due to the given problem specification) and a systematic synthesis method is described which is based on the idea of always introducing that particular synthesis step which results in the lowest individual entropy rise. This policy leads, necessarily, to a situation where the sequence of synthesis steps is almost complete, but the accumulated entropy increase is still far below the figure known to be inevitable overall. As a result, there will be large entropy increases during the final few steps leading to great flexibility in the decisions made, i.e. many different possible designs with minimum entropy increase can be proposed. This "freedom of choice" is particularly valuable since the consequences of any adopted step with regard to, e.g., costs and controllability are - so close to the end of the synthesis - easily understood. When applied to the standard test problems described in the literature, this new technique identified new "optimum" networks which were improvements on those previously described in the more complex cases. In the remaining (simpler) cases, the previously reported optimum networks were confirmed and a number of competitors found.

The point to emphasise is that the actual synthesis algorithm is based on First Law considerations, i.e. temperature and heat loads are the main variables. The entropy function itself - although of key significance for the formulation of the approach - is not suitable for comparison with the particular design constraints which apply to heat exchanger networks.

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APPENDIX B

PHYSICAL PROPERTY DATA FOR CONTACT PROCESS CASE STUDY

B.1 SPECIFIC HEAT CAPACITIES

Specific Heat Capacities of Gases

In Table (B.1), five polynomials are given which were used to calculate enthalpies and entropies of gas flows. They were found in Myers and Seider(54).

Table (B.1) Polynomials used for gas flows in contact process

$$cp(T) = A + B*Z + C*Z^2 + D*Z^3$$

with $Z = T*10^{-3}$

and :

	N_2	O_2	H_2O	SO_2	SO_3
A =	+6.903	+6.085	+7.7	+6.157	+3.918
B =	-0.3753	+3.631	+0.4594	+13.84	+34.83
C =	+1.93	-1.709	+2.521	-9.103	-26.75
D =	-0.6861	+0.3133	-0.8587	+2.057	+7.744

(T in ^oK and cp(T) in kcal/kmol/^oK)

The maximum error for the O_2-polynomial is specified as 1.19%. The errors of the other polynomials are specified not to exceed 0.59% (N_2), 0.53% (H_2O), 0.45% (SO_2), and 0.29% (SO_3).

Enthalpy and Entropy of Steam and Water

The steam pressure is given as 685 p.s.i.a. The steam tables used (i.e. Callendar(56)) had to be interpolated for this figure and the units had to be converted. The results are listed in Table (B.2).

Table (B.2) Enthalpy and entropy for H_2O (contact process)

$T_{evap.}$ = 260.3°C

$\left[h(260.3^{\circ}C) - h(0^{\circ})\right]_{H_2O(\ell)}$ = 1.137 MJ/kg

$\left[s(260.3^{\circ}C) - s(0^{\circ})\right]_{H_2O(\ell)}$ = 2.887 kJ/kg/°K

Δh_{evap} = 1.660 MJ/kg

Δs_{evap} = 3.113 kJ/kg/°K

$\left[h(400^{\circ}C) - h(260.3^{\circ}C)\right]_{H_2O(g)}$ = 0.404 MJ/kg

$\left[s(400^{\circ}C) - s(260.3^{\circ}C)\right]_{H_2O(g)}$ = 0.674 kJ/kg/°K

All figures apply for 685 p.s.i.a.

For the boiler feed water, a figure of

$$cp_{H_2O} = 1.0 \text{ kcal/kg/}^{\circ}\text{C}$$

was assumed.

Enthalpy and Entropy of Sulphur

Sulphur is delivered to the plant at 140°C in the liquid state. Enthalpy as well as entropy changes between solid sulphur at 25°C and liquid sulphur at 140°C were obtained from Duecker and West(69) :

$h(140^{\circ}C) - h(25^{\circ}C)$	37.766 kcal/kg
$s(140^{\circ}C) - s(25^{\circ}C)$	0.1028 kcal/kg/°K *

---

*It was observed that the table for "ENTROPY OF SULFUR ABOVE 25°C" on page 456 in Duecker and West(69) showed inconsistencies as against the equivalent tables for cp(T) and for enthalpy for the monoclinic state between T=101°C and T=115.207°C. The value quoted above has been derived using the table for cp(T). (The original figure given by Duecker and West reads "0.1071".)

The specific heat of rhombic sulphur at T=25°C is given by Aylward and Findlay(55) as cp(25°C) = 23 J/mol/°K. Using this value to approximate the enthalpy as well as the entropy change between T=0°C and T=25°C, the two results shown below were obtained:

h(140°C) - h(0°C)	176.0 kJ/kg
s(140°C) - s(0°C)	0.4934 kJ/kg/°K

When basing approximate entropy figures on enthalpy figures, it is of interest to know at which temperatures the transitions from rhombic to monoclinic and from monoclinic to liquid sulphur occur and what the respective enthalpy changes are. In Table (B.3), the relevant information is collected. It is based, also, on data given by Duecker and West(69).

Table (B.3) Specific enthalpy of sulphur between T = 0°C and T = 140°C

T (°C)	State	h(T) - h(0°C) (kJ/kg)
0	rhombic	0
95.4	↓	69.4
95.4	↑	81.9
101	mono-	86.21
101	-clinic	86.22
115.2	↓	97.4
115.2	↑	151.0
140	liquid	176.0

Specific Heat Capacity of Diluted H_2SO_4

Figures which apply for 20°C were found in Perry (52b) for various concentrations. By means of linear interpolation :

Acid Strength	93.8%	94.0%	95.3%	98.1%	98.3%
cp (20°C)	1.521	1.515	1.477	1.420	1.418
(kJ/kg/°K)	total error probably < ± 0.2%				

Figures for various concentrations at four different temperatures are given, in chart form, by Duecker and West(69). By means of linear interpolation :

Acid Strength	93.8%	94.0%	95.3%	98.1%	98.3%
cp(50°C) - cp(20°C)	0.070	0.070	0.066	0.053	0.053
cp(60°C) - cp(20°C)	0.093	0.093	0.088	0.071	0.071
cp(70°C) - cp(20°C)	0.116	0.116	0.110	0.089	0.089
cp(80°C) - cp(20°C)	0.140	0.140	0.132	0.107	0.107
cp(90°C) - cp(20°C)	0.163	0.163	0.153	0.125	0.125
(kJ/kg/°K)	total error probably < ± 10%				

From the above two tables, first order polynomials

$$cp = A + BT$$

were derived, see Table (B.4) :

<u>Table (B.4) First order polynomials for specific heat capacity of diluted acid at various concentrations</u>

$cp(T)_{93.8\%}$	=	$1.4744 + 0.0023\,T$	cp in kJ/kg/°C and T in °C
$cp(T)_{94.0\%}$	=	$1.4684 + 0.0023\,T$	
$cp(T)_{95.3\%}$	=	$1.4331 + 0.0022\,T$	
$cp(T)_{98.1\%}$	=	$1.3844 + 0.0018\,T$	
$cp(T)_{98.3\%}$	=	$1.3824 + 0.0018\,T$	
Total error probably < ± 1%			

Specific Heat Capacity of Oleum

Duecker and West(69) give a graph which shows the specific heat capacity of oleum as a function of concentration at 30°C. From this graph:

% Oleum (Free SO_3)	25
cp(30°C)	1.3315 kJ/kg/°K

This figure is used in Chapter Three for streams No. 25 through No.28.

In order to correct the heat of formation of $H_2S_2O_7$ from T = 25°C to T = 0°C, the specific heat capacity of pure $H_2S_2O_7$ needs, approximately, to be known. According to the molecular weights of SO_3, H_2SO_4 and $H_2S_2O_7$, pure $H_2S_2O_7$ is equivalent to about 45% oleum. From the above mentioned graph in Duecker and West(69) :

% Oleum (Free SO_3)	45
cp(30°C)	248 kJ/kmol/°K

B.2 CHEMICAL DATA

In Table (B.5) (see page B6), the standard heats of formation, standard entropies, molecular weights and specific heat capacities are listed in consistent units for most of the substances of interest here. (Standard state : T = 25°C, p<<1). All these data were taken from Aylward and Findlay(55).

Table (B.5) Chemical data for relevant species (contact process)

Species	M (g/mol)	ΔhoF_{STD} (kJ/mol)	s_{STD} (J/mol/°K)	cp(25°C) (J/mol/°K)
S(s)	32	0	32	23
O_2	32	0	205	29
SO_2	64	-297	248	40
$SO_3(g)$	80	-396	257	51
$H_2O(g)$	18	-242	189	34
$H_2O(\ell)$	18	-285	70	75
$H_2SO_4(\ell)$	98	-814	157	139

Heats of Reaction

The following are the chemical changes for which heats of reaction had to be evaluated:

(1) $H_2O(g) \rightarrow H_2O(\ell)$

(2) $S + O_2 \rightarrow SO_2$

(3) $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

(4) $SO_3(g) + H_2O(\ell) \rightarrow H_2SO_4(\ell)$

(5) $SO_3(g) \rightarrow SO_3(\ell)$

Based on the figures given in Table (B.5) and with Equations (2.11) and (2.12), the enthalpy changes for the first four of these reactions at the reference state ($T = 0^\circ C$, $p = 1$ bar) were evaluated, see Table (B.6) on page B7 (bottom of page).

The heat of condensation of SO_3, which is also listed in Table (B.6), had to be evaluated by means of Equation (2.8), based on the following additional data:

$SO_3(g) \rightarrow SO_3(\ell)$	
$\Delta hoR_{STD,STD}$	- 45 kJ/mol

(Source: Aylward and Findlay(55)) , and

$cp_{SO_3(\ell)}$ (25°→ 35°C)	0.77 kcal/kg/°K

(Source : Duecker and West(69)).

Thereby, the specific heat capacities were, as given, used for the interval between 0°C and 25°C.

Heat of Non-Ideal Mixing

Duecker and West(69) give a chart showing the heat which evolves if 1 lb of pure H_2SO_4 is mixed with various amounts of water at 25°C. According to this chart, the heat of mixing is approximately constant in the range of acid concentrations which is of interest in Chapter Three :

$$\underline{\Delta HoM_{STD,STD} = -4.4 \text{ kcal}}$$

if 1 kg of pure acid is diluted one further percent in the range between ∿85% w/w and 100% concentration.

Table (B.6) Heats of reaction for contact process

Reaction	$\Delta hoR_{RS,RS}$ (MJ/kg as specified)
(1)	-2.446/kg H_2O
(2)	-4.636/kg SO_2
(3)	-1.236/kg SO_3
(4)	-1.667/kg SO_3
(5)	-0.627/kg SO_3

An equivalent figure for T = 0°C can be derived by means of Equation (2.8), when applied for various concentrations : pure acid and water are assumed to be heated up separately from T = 0°C to T = 25°C, to be mixed at T = 25°C, and to be cooled again, as diluted acid, to T = 0°C. (See Table B.7). The three concentrations chosen are the ones for which figures for cp (20°C) are given in Perry V(52b). These figures as well as cp_{H_2O} and $cp_{H_2SO_4}$ were assumed constant between T = 0°C and T = 25°C.

Table (B.7) Correcting the heat of acid mixing for T = 0°C as reference temperature

Acid Concentration (% w/w)	91.81	94.82	97.44
$m_{H_2SO_4}$ (kg)	1.0	1.0	1.0
m_{H_2} (kg)	0.08909	0.05463	0.02627
$m{*}cp_{H_2SO_4} + m{*}cp_{H_2O}$ (kcal/°C)*	0.42429	0.038983	0.36147
$\Delta H_{H_2SO_4 + H_2O}$ (0°C → 25°C) (kcal)	+10.607	+9.746	+9.037
ΔHoM (25°C) (kcal)	-36.036	-22.792	-11.264
$m{*}cp_{\text{diluted acid}}$ (kcal/°C)	0.3787	0.3554	0.3404
$\Delta H_{\text{diluted acid}}$ (25°C→0°C) (kcal)	-10.311	-9.370	-8.734
ΔHoM (0°C) (kcal)	-35.740	-22.416	-10.961
ΔHoM (0°C) (kcal/%)	-4.36	-4.33	-4.28

* cp_{H_2O} = 1.0 kcal/kg/°C; $cp_{H_2SO_4}$ = 0.3352 kcal/kg/°C

The variations found as against the original figure (i.e. for T = 25°C) are hardly significant. However, the following figure was used throughout:

$$\underline{\Delta HoM_{RS,RS} = -4.3 \text{ kcal} = -18.0 \text{ kJ}}$$

if 1 kg pure H_2SO_4 is diluted one further percent within the range of concentrations considered in Chapter Three.

For the heat of mixing SO_3 with H_2SO_4 to form oleum, no equivalent data was found. Aylward and Findlay (55), however, give the standard heat of formation of fuming sulphuric acid:

	$H_2S_2O_7(\ell)$
ΔhoF_{STD}	-1274 kJ/mol

With this data, the enthalpy change of the reaction $SO_3(\ell) + H_2SO_4(\ell) \rightarrow H_2S_2O_7(\ell)$ at T= 0°C is easily found. The required data for heats of formation and specific heat capacities have all been given previously in this Appendix. The result is :

	$SO_3(\ell) + H_2SO_4(\ell) \rightarrow H_2S_2O_7(\ell)$
$\Delta hoR_{RS,RS}$	-156.1 kJ/kg H_2SO_4

As mentioned in Section B.1, fuming sulphuric acid represents an oleum of approx. 45% strength ("free SO_3"). In order to obtain a figure for the heat of mixing SO_3 and H_2SO_4 when a 25% oleum is formed, an assumption has to be made about the dependence of the heat of mixing upon concentration. A simple assumption, based on an analogy with the mixing of H_2SO_4 and H_2O, would be to say that

$$\underline{\Delta HoM_{RS,RS} = -3.5 \text{ kJ}}$$

if oleum containing 1 kg of pure H_2SO_4 is increased in strength by 1%

due to the addition of further liquid SO_3.[*]

Entropy Changes

The entropy changes of reactions (1) to (4) are given in Table (B.8). They were evaluated by means of Equations (2.24) and (2.28), based on the data given in Table (B.5). For reaction (5), i.e. condensation of SO_3, the entropy change was evaluated by using Equation (2.36) at the boiling point (T = 45°C, see Aylward and Findlay[(55)]) where liquid and gas phases are in equilibrium, i.e. $\Delta g = 0$ applies :

$$\Delta s = \Delta h / T$$

The enthalpy change at 45°C was obtained by using Equation (2.8).

Also in Table (B.8), the free energy changes of reactions (1) through (5) are given. They were evaluated by means of Equation (2.36) and based on the figures listed in Table (B.6).

Table (B.8) Changes of entropy and Gibbs free energy for reactions in contact process

Reaction	$\Delta soR_{RS,RS}$ (kJ/°K/kg as specified)	$\Delta g_{RS,RS}$ (MJ/kg as specified)
(1)	-6.81 / kg H_2O	-0.587 / kg H_2O
(2)	+0.19 /kg SO_2	-4.688 / kg SO_2
(3)	-0.088 /kg SO_3	-1.212 / kg SO_3
(4)	-2.139 / kg SO_3	-1.083 / kg SO_3
(5)	-2.001 / kg SO_3	-0.081 / kg SO_3

For the entropy changes which accompany the non-ideal mixing of acid and the formation of oleum, no data could be found. However, both

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[*] The accuracy of this assumption is not at all critical since the only two parameters in the heat and mass balance which will - slightly depend on it are the temperature of stream No.25 and the heat load on the oleum cooler.

these changes are exothermic and are known to release heat rapidly, so that one may assume the change of free energy to be about equivalent to the change in enthalpy, if not greater :

$$\Delta G_{RS} \simeq \Delta HoM_{RS,RS}$$

The accuracy of this assumption will influence, to a minor extent, the irreversible losses identified in the oleum tower, the absorber, the drying tower and in the two tanks. As will be seen in Section 3.5, this will not be very important.

APPENDIX C

CASE STUDY : INTEGRATION OF PREHEATER INTO EXISTING SULPHURIC ACID CONTACT PLANT

(Excerpts from report(70).)

C.1 INTRODUCTION

In Figure (C.1), the preheater scheme described in Section 3.9 is shown once more. Process streams that remain unaltered are drawn fully and those that have to be altered are drawn dashed. When

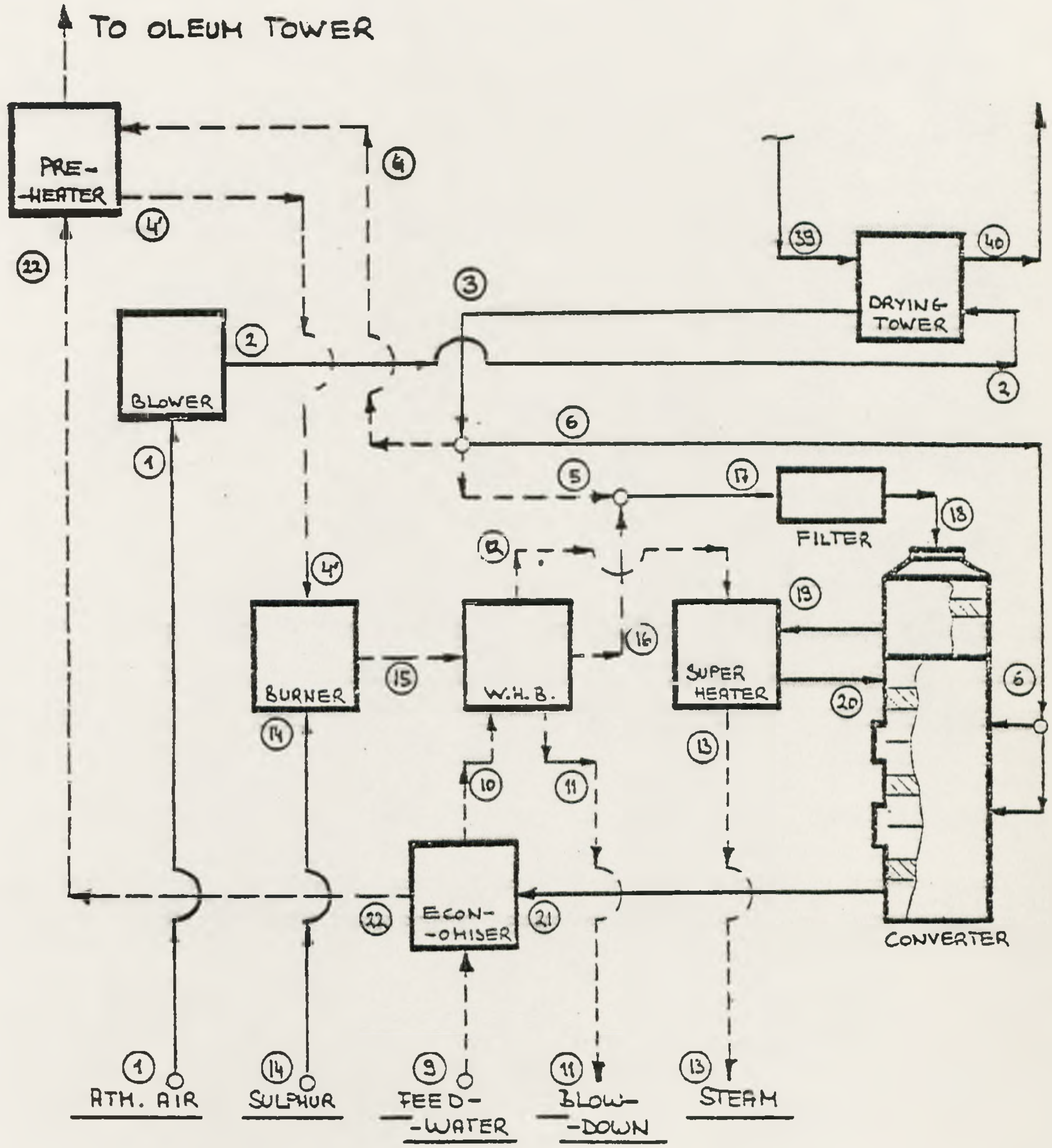

Figure (C.1) Recommended scheme for improved energy recovery in contact process. (Compare Figure 3.18.)

simulating the scheme, the expression

$$\alpha = \frac{\overset{*}{m}_{13} - m_{13}}{m_{13}} \tag{C.1}$$

with $\overset{*}{m}_{13}$ = new mass flowrate (13)

was chosen as a convenient parameter to describe the amount of additional steam gained. Further, as is evident from Table (3.15), the blowdown (11) as well as the boiler feed (9) were increased pro rata with m_{13}. This was done to avoid exaggerating savings.

In Figure (C.2) on page C3, a signal graph diagram is given which describes the calculation sequence adopted to evaluate the scheme for a chosen value of α. The calculation tended to converge rapidly. The reason was that most influences that necessitated iterations (such as changing surface losses with changing temperatures) were of little significance for final results. In Section C.2, a description is given of some of the modelling assumptions used. In Section C.3, costing assumptions are reported, and in Section C.4, results are presented.

C.2 MODELLING ASSUMPTIONS

Temperature Profiles

Within heat exchangers, Cp = const. was assumed for constant phase (see Figure C.3, page C4), so that Equation (C.2) could be used to describe heat transfer :

$$Q = U * A * \Delta T_{LM} \tag{C.2}$$

with Q = heat transferred

U = overall heat transfer coefficient

A = effective heat transfer surface area

ΔT_{LM} = log.mean temperature difference

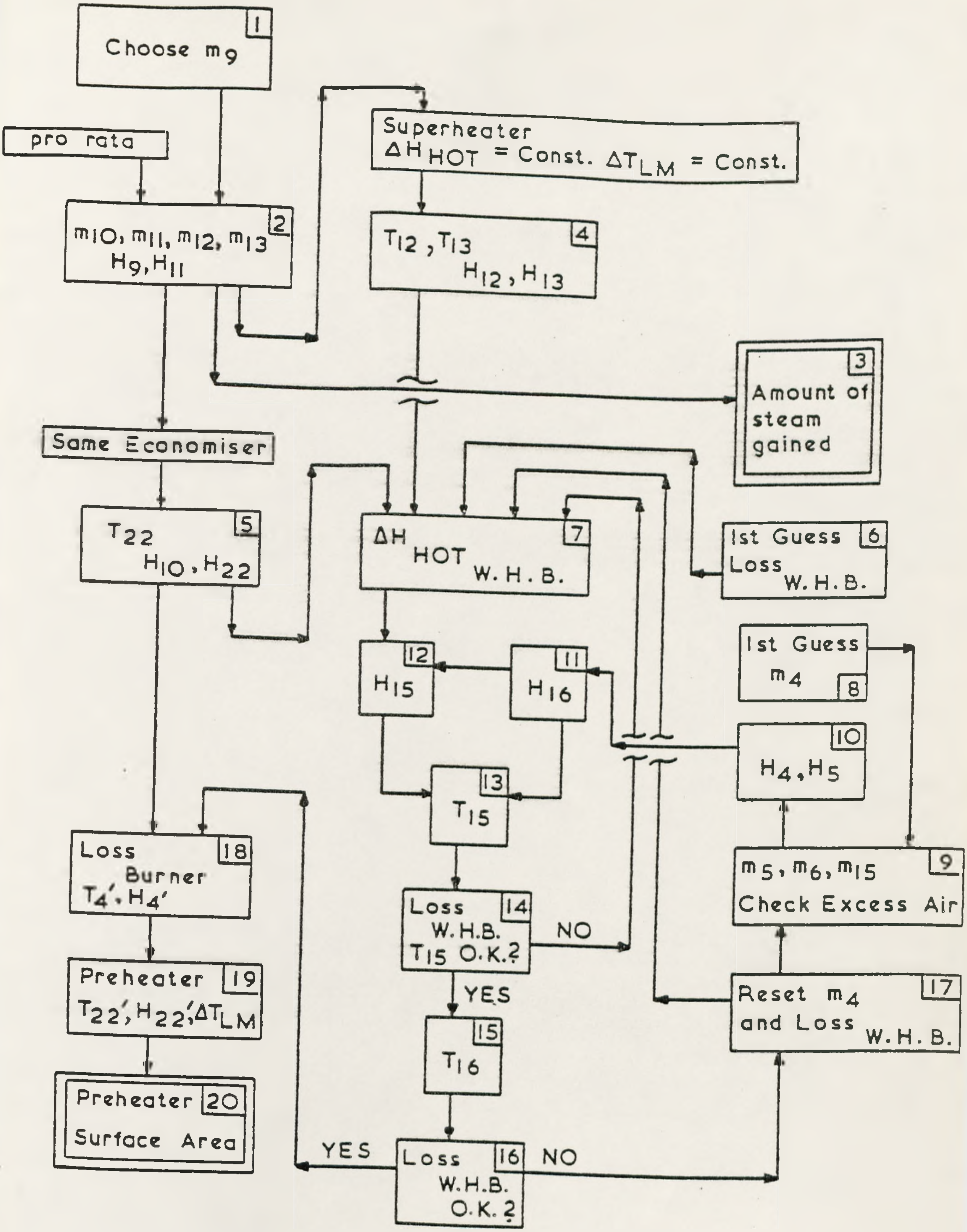

Figure (C.2) Sequence of calculations for evaluation of recommended scheme.

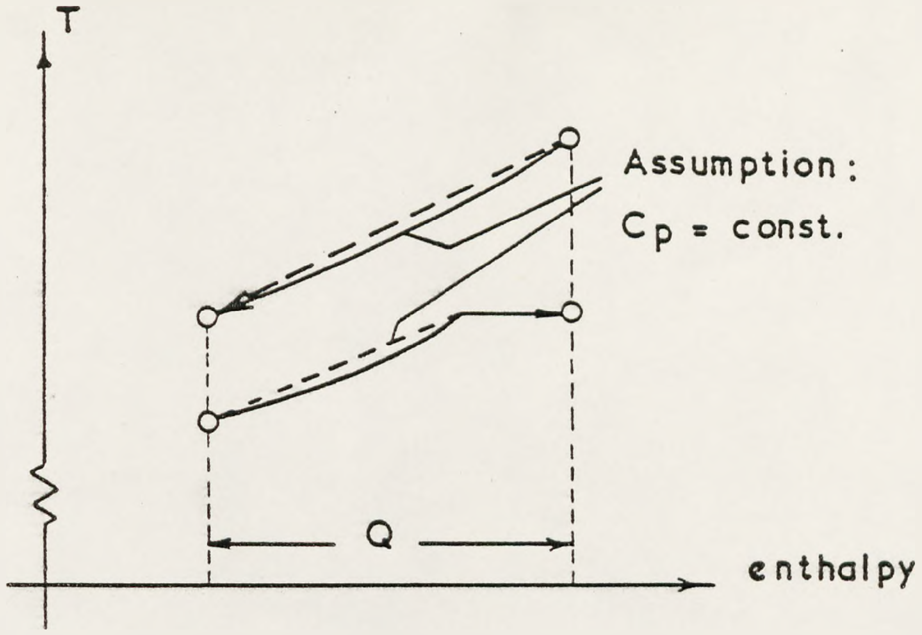

Figure (C.3) Assumption: constant specific heat for each phase.

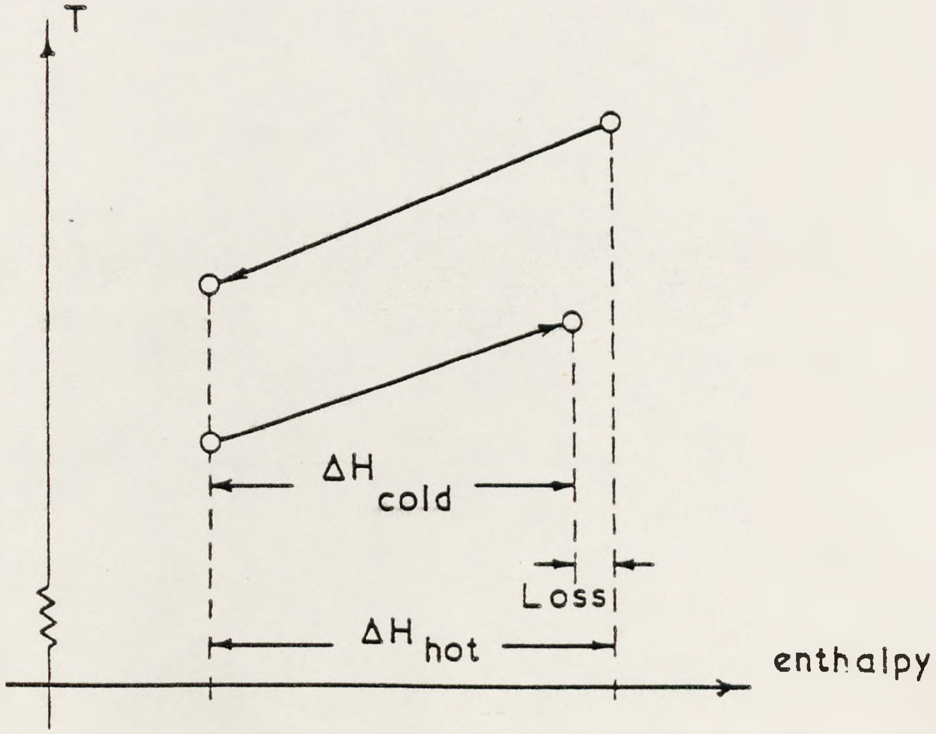

Figure (C.4) Assumption: heat losses covered by hottest phase.

The consequent numerical errors have been found to lie below uncertainty of data. Further, it was assumed that insulation losses are covered by the hottest phase present in a heat exchanger, see Figure (C.4), page C4. This corresponds to the following equations:

$$H_{\text{cold out}} - H_{\text{cold in}} = \Delta H_{\text{cold}}$$

$$H_{\text{hot in}} - H_{\text{hot out}} = \Delta H_{\text{hot}} = \Delta H_{\text{cold}} + \text{Loss}$$

Further, losses have been assumed to vary pro rata with the temperature difference ($T_{\text{hot in}} - T_o$).

Heat Transfer Coefficients

For any one region within a heat exchanger with either latent or sensible heat transferred, Equation (C.2) was used. Applying the equation to a heat exchanger of constant surface area once in the original operating mode and once in a different operating mode (indicated by the superscript " * ") leads to:

$$\overset{*}{Q} = Q * \frac{\overset{*}{U}}{U} * \frac{\overset{*}{\Delta T}_{LM}}{\Delta T_{LM}}$$

If the type of heat transferred is not subject to change, this reduces to Equation (C.3) :

$$\overset{*}{Q} = Q * (\overset{*}{\Delta T}_{LM}/\Delta T_{LM}) \tag{C.3}$$

However, if the type of heat transferred <u>is</u> subject to change, the change of U must also be considered. This is, fortunately, easy:

The overall heat transfer coefficient U across a pipe with the inner diameter d and the outer diameter D is given as:

$$U = \frac{2/(D+d)}{1/(d*h_{ins}) + (1/2k)*\ell n\ \frac{D}{d} + 1/(D*h_{outs})}$$

with h_{ins} = heat transfer coefficient inside

h_{outs} = heat transfer coefficient outside

and k = thermal conductivity of pipe material

(see any textbook). For a normal heat exchanger containing bundles of thin metal pipes, the term describing the thermal resistance of the pipe material can be neglected and the equation may be simplified to:

$$U = \text{const.} * \frac{h_{ins} * h_{outs}}{h_{ins} + h_{outs}} \qquad (C.4)$$

In this expression, h_{ins} and h_{outs} are interchangeable and by considering the approximate ranges that are applicable, insight can be gained concerning the dependence of U upon either value:

$$h_{gas \rightarrow metal} = (10 - 100) \frac{kcal}{m^2*hr*^oC}^{*}$$

$$\text{and} \quad h_{wet\ steam \rightarrow metal} = (8000 - 10000) \frac{kcal}{m^2*hr*^oC}^{*}$$

Further, according to Kreith(60), changes of heat transfer coefficients with quality of steam do not occur rapidly in the regions $\varepsilon \simeq 0$ and $\varepsilon \simeq 1.0$. For $0 < \varepsilon < 0.1$ and for $0.9 < \varepsilon < 1.0$, changes in the magnitude of h can be expected to remain below 30%. In Table (C.1), the effect of a 30% change in $h_{wet\ steam \rightarrow metal}$ on the magnitude of U is given as evaluated by means of Equation (C.4) :

---

* Source : Technische Formeln(58)

Table(C.1) Effect of changes in steam quality on overall heat transfer coefficient

$h_{outside} = 100 * const._1$	
$h_{inside} = 8000 * const._1$	$h_{inside} = 5600 * const._1$
$U = 98.8 * const._2$	$U = 98.2 * const._2$

Thus, Equation (C.3) was found to be applicable even if bubbly flow was replaced by liquid flow (→ economiser) and mist flow by vapour flow (→ waste heat boiler).

In the preheater, gas/gas heat transfer takes place. Practical values for the overall heat transfer coefficient in tubular heat exchangers were found in Technische Formeln(58) :

$$U = (5 - 30) \text{ kcal/m}^2\text{/hr/}^\circ\text{C}$$

This corresponds, approximately, to

$$U = (1 - 6) \text{ Btu/ft}^2\text{/hr/}^\circ\text{C}$$

or to

$$U = (20 - 125) \text{ kJ/m}^2\text{/hr/}^\circ\text{C}$$

i.e. the figures appear to be fairly conservative. Nevertheless, they were used. To estimate the effect of uncertainty on costing, two cases were considered:

$$U_1 = 50 \text{ kJ/m}^2\text{/hr/}^\circ\text{C}$$
$$U_2 = 80 \text{ kJ/m}^2\text{/hr/}^\circ\text{C}$$

C.3 COSTING ASSUMPTIONS

The credit available for HP steam was assumed to be £4/ton. This is probably too low a figure but it was chosen to avoid exaggerating savings. The cost of the preheater was assumed to be determined by

$$\text{Cost} = 2 * 10^{(2.59 + 0.58 * \log(\text{area}))}$$

with Cost in £

and area in m^2

This equation was derived from data given in Capital Cost Estimation(61), assuming an inflation of 100% between 1969 (when the data was published) and today. Also, stainless steel was assumed necessary in view of the possible corrosion problems with acid formed in the preheater (see Section 3.9). Further, overheads were added for piping, instrumentation, etc. (30% of cost of preheater). When comparing capital costs to credit for steam, time discounting was used.

C.4 RESULTS

In Figure (C.5), the feasibility limit is established which exists due to temperature crossover in the preheater : the amount of steam raised must remain somewhat below 111% of the amount that is raised in the existing plant. In Figure (C.6) (see page C9), three parameters of general interest are shown that are subject to change : the

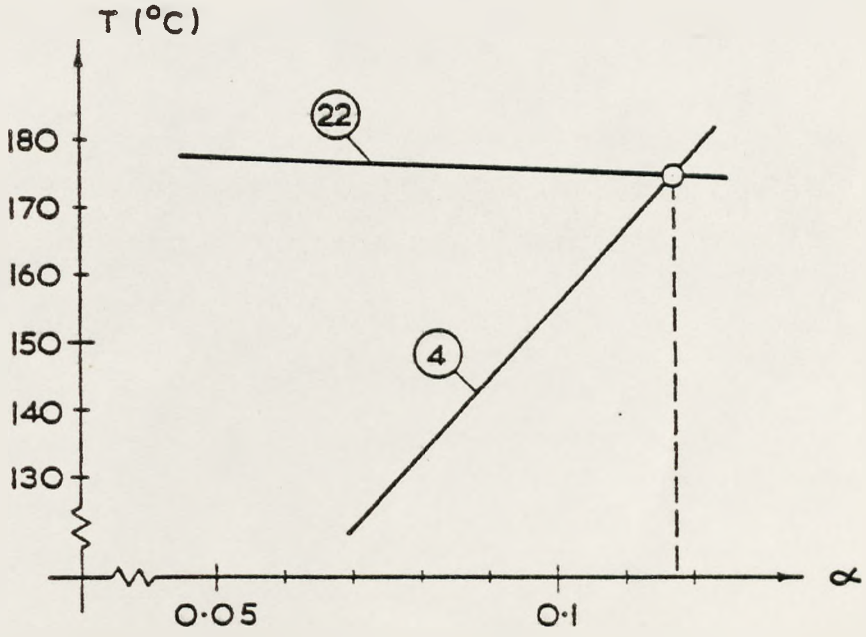

Figure (C.5) Feasibility limit due to temperature crossover.

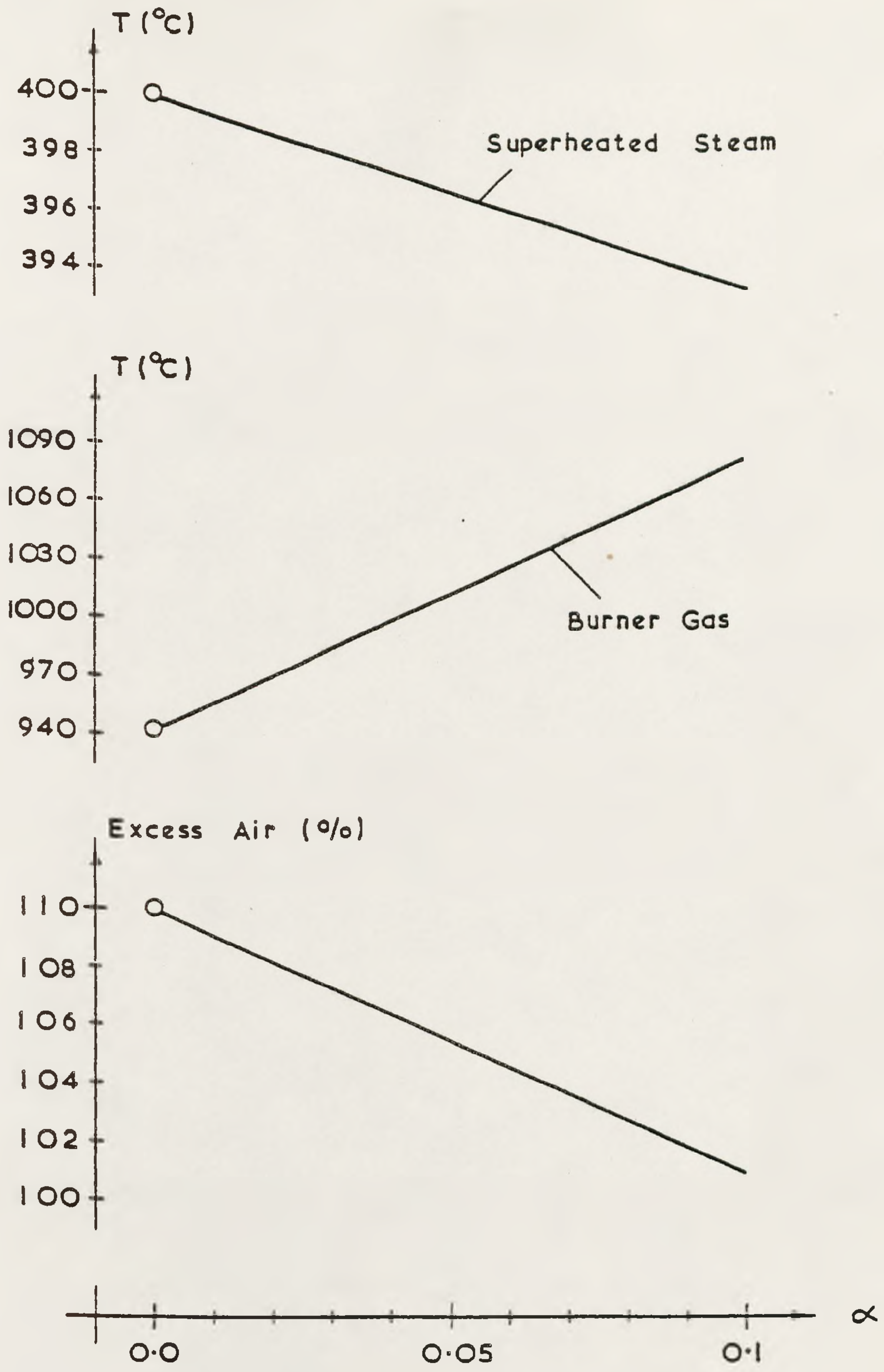

Figure (C.6) Parameters of interest as functions of additional steam raised.

a) Superheated steam temperature.

b) Burner gas temperature.

c) Excess air percentage.

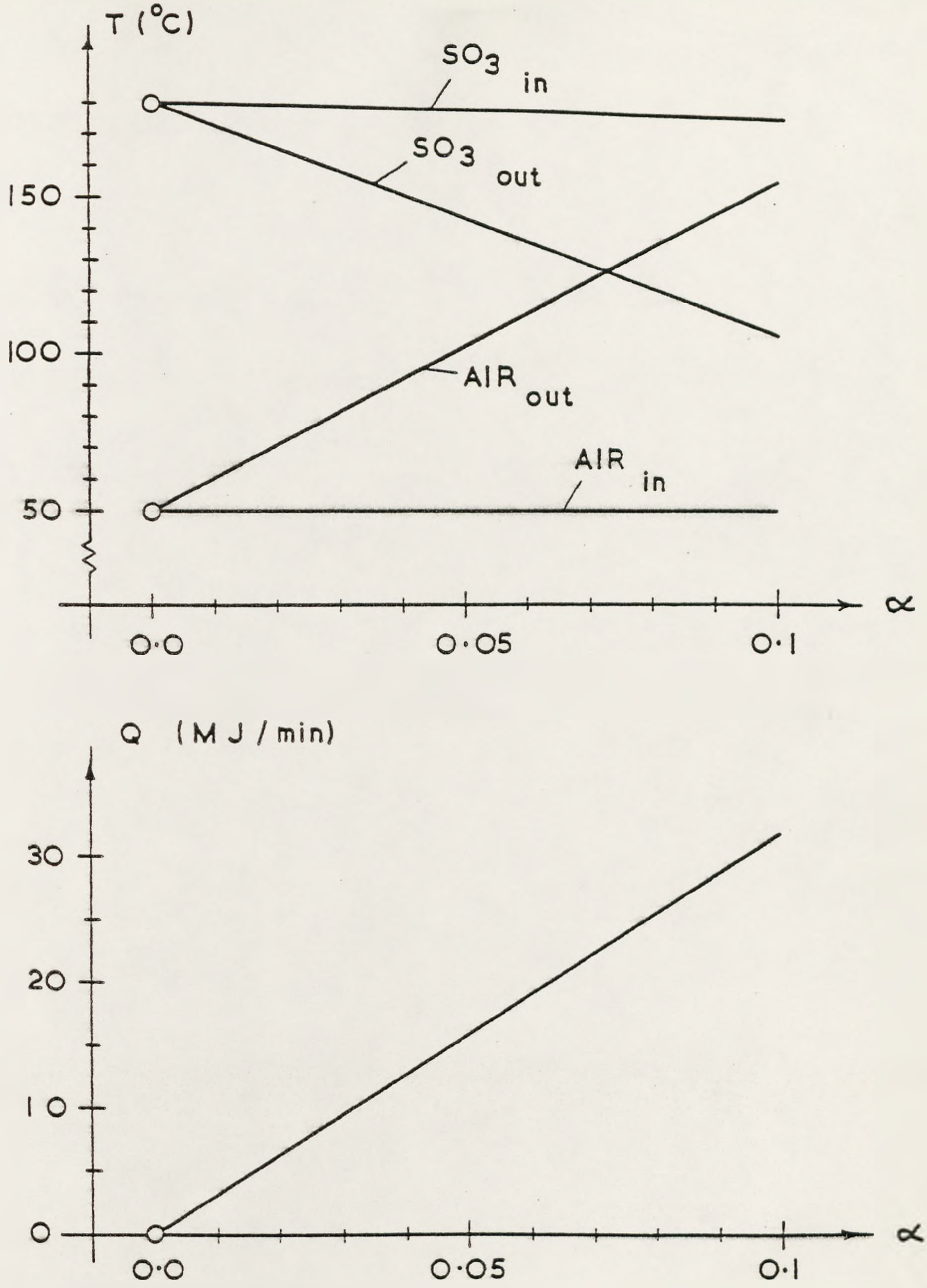

Figure (C.7) Temperatures and heat load in preheater as functions of additional steam raised.

superheated steam temperature T_{13}, the peak burner gas temperature T_{15}, and the percentage excess air present during the sulphur combustion. The changes observed appear to be within perfectly practical limits. In Figure (C.7) (see page C10), the temperatures in and out of the preheater are given, as well as the amount of heat exchanged. With these data, the magnitude of U*A was determined for the preheater and, based on the two different estimates mentioned above for the overall heat transfer coefficient, the necessary capital outlay was evaluated. In Figure (C.8), this outlay (including 30% overheads) is compared to the annual credit for steam. Evidently, the capital outlay could be expected to be recovered within the second year after installation. Further, the best financial return, in percentage terms, would appear to be somewhere around α = 0.055,

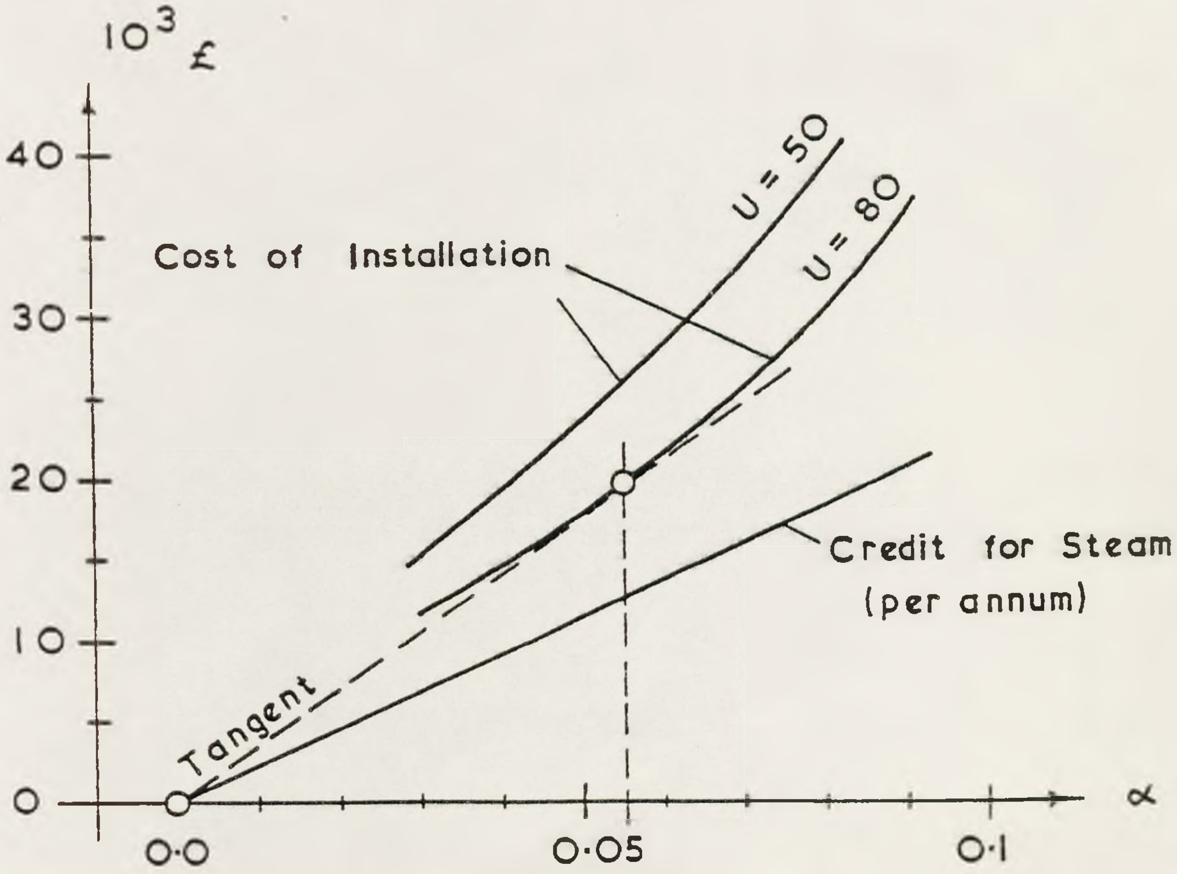

Figure (C.8) Cost and annual credit as function of additional steam raised.

see tangent drawn in Figure C.8 to indicate the minimum ratio of cost to credit. In the report (70), these findings have been elaborated, and results were time discounted allowing for future inflation in the cost of steam and for interest payable to service capital. Also, sensitivity analyses were made with regard to technical parameters, cost assumptions, and assumptions used in time discounting. The optimum ratio of cost to credit was found to be consistently in the neighbourhood of $\alpha = 0.06$ but the optimum would be quite flat if the preheater was in service for more than three years : with middle-of-the-road assumptions, the effective* gain per year would amount to ∿40% of the capital invested if $\alpha = 0.06$, and ∿38% if $\alpha = 0.08$. In the interest of energy conservation, it would appear appropriate to choose $\alpha = 0.08$. In Section 3.9, the corresponding case has been documented (see Table 3.15).

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* i.e. after time discounting

APPENDIX D

PHYSICAL PROPERTY DATA FOR AMMONIA OXIDATION PROCESS

D.1 SPECIFIC HEAT CAPACITIES

Gas Phase Streams

For the calculation of enthalpies and exergies of gas flows, the same polynomials were used as in Chapter Three for N_2, O_2 and H_2O (see Table B.1). For NO and NO_2, equivalent polynomials from the same source were used, see Table (D.1) :

Table (D.1) Polynomials used for gas flows in HNO_3 process

$$\left.\begin{array}{l} cp_{N_2}(T) \\ cp_{O_2}(T) \\ cp_{H_2O}(T) \end{array}\right\} \quad \text{see Table (B.1)}$$

$$cp_{NO}(T) = 7.008 - 0.2244\ Z + 2.328\ Z^2 - 1.00\ Z^3$$

$$cp_{NO_2}(T) = 5.48 + 13.65\ Z - 8.41\ Z^2 + 1.88\ Z^3$$

with $Z = T * 10^{-3}$

T in $^{\circ}K$,

and $cp(T)$ in kcal/kmol/$^{\circ}K$

Source : Myers and Seider(54)

The maximum error for the NO - polynomial is specified as 0.97% and the one for the NO_2 - polynomial as 0.46%.

Steam and Water

For absorption water and cooling water,

$$cp_{H_2O} = 1.0\ \text{kcal/kg/}^{\circ}C$$

was used. For boiler feed water, steam and condensate, however, figures for enthalpy and exergy were derived from steam tables (see Callendar(56)). They are listed in Table (D.2). The figures for enthalpy are based on the chosen reference state of $T_{RS} = 25^{\circ}C$, $p_{RS} \sim 1$ bar whereas the figures for exergy are based on the ambient

Table (D.2) Enthalpy and exergy for IP steam and for condensate

$\left[h(90^{\circ}C) - h(25^{\circ}C)\right]_{H_2O(\ell)} = 278.0$ kJ/kg $\left[h(158^{\circ}C) - h(25^{\circ}C)\right]_{H_2O(\ell)} = 567.2$ kJ/kg $\left[h(198^{\circ}C) - h(25^{\circ}C)\right]_{H_2O(\ell)} = 737.3$ kJ/kg $\Delta h_{evap} = 1950.7$ kJ/kg $\left[h(350^{\circ}C) - h(198^{\circ}C)\right]_{H_2O(g)} = 353.5$ kJ/kg	$p = 215$ p.s.i.a. $T_{evap} = 198^{\circ}C$
$\left[ex(90^{\circ}C) - ex(20^{\circ}C)\right]_{H_2O(\ell)} = 30.8$ kJ/kg $\left[ex(158^{\circ}C) - ex(20^{\circ}C)\right]_{H_2O(\ell)} = 106.0$ kJ/kg $\left[ex(198^{\circ}C) - ex(20^{\circ}C)\right]_{H_2O(\ell)} = 165.6$ kJ/kg $\Delta ex_{evap} = 737.3$ kJ/kg $\left[ex(350^{\circ}C) - ex(198^{\circ}C)\right]_{H_2O(g)} = 162.9$ kJ/kg	
$\left[h(41.4^{\circ}C) - h(25^{\circ}C)\right]_{H_2O(\ell)} = 68.7$ kJ/kg $\Delta h_{evap} = 2403.7$ kJ/kg	$p = 1.15$ p.s.i.a. $T_{evap} = 41.4^{\circ}C$
$\left[ex(41.4^{\circ}C) - ex(20^{\circ}C)\right]_{H_2O(\ell)} = 3.2$ kJ/kg $\Delta ex_{evap} = 163.7$ kJ/kg	

state. Since exergy figures are as such not given by Callendar, Equation (2.31) had to be used to establish exergy figures.

Nitric Acid

Since the acid streams in the case study (i.e. streams No.30 through No.34) exist either at or near $T = 25^{\circ}C$, accuracy is not critical regarding the specific heat capacities used at various concentrations. Consequently, the figures for cp_{HNO_3} and for cp_{H_2O}, as listed in Table (D.3) below, were used pro rata with concentration.

Ammonia

Part of the cooling in the strong absorption column is effected by means of evaporating ammonia. The corresponding calculations were based on the following three figures

(+) $cp_{NH_3(g)}$ $(0^{\circ}C)$ = 2.06 kJ/kg/°K

(++) $cp_{NH_3(\ell)}$ $(-10^{\circ}C)$ = 4.56 kJ/kg/°K

(+) Δh_{evap} $(-33^{\circ}C)$ = 1.367 MJ/kg

which were taken from "Hütte I"(57) (+) and from Vancini(63) (++), respectively.

D.2 CHEMICAL DATA

In Table (D.3), the standard heats of formation and free energies of formation, as well as molecular weights and specific heat capacities, are listed for the substances of interest. All these data were taken from Aylward and Findlay(55).

Table (D.3) Chemical data for substances of interest in HNO_3 process

Species	M (g/mol)	ΔhoF_{STD} (kJ/mol)	Δg_{STD} (kJ/mol)	cp (25°C) (J/°K/mol)
NH_3 (g)	17	-46	-16	35
N_2	28	0	0	29
O_2	32	0	0	29
NO	30	90	87	30
NO_2	46	33	51	37
$H_2O(g)$	18	-242	-229	34
$H_2O(\ell)$	18	-285	-237	75
$HNO_3(\ell)$	63	-174	-81	110

Reactions

The following five reactions were used to simulate chemical changes:

(1) $NH_3 + 5/4\ O_2 \rightarrow 3/2\ H_2O(g) + NO$

(2) $NH_3 + 3/4\ O_2 \rightarrow 3/2\ H_2O(g) + 1/2\ N_2$

(3) $NO + 1/2\ O_2 \rightarrow NO_2$

(4) $H_2O(g) \rightarrow H_2O(\ell)$

(5) $NO_2 + 1/4\ O_2 + H_2O(\ell) \rightarrow HNO_3(\ell)$

In Table (D.4), the enthalpy changes $\Delta hoR_{STD,STD}$ and the free energy changes Δg_o are listed as evaluated from the data given in Table (D.3). The figures for free energy were calculated for the assumed ambient state, i.e. 20°C, so as to correspond to the exergy change of reaction with products and reactants at ambient state. The calculations of the enthalpy changes were based on Equation (2.11) and the ones of the free energy changes on Equation (2.36).

Table (D.4) Enthalpy and free energy changes for reactions in HNO_3 process

Reaction	$\Delta hoR_{RS,RS}$ (kJ/mol)	Δg_o (kJ/mol)
(1)	-227	-240.5
(2)	-317	-327.5
(3)	-57	-36
(4)	-43	-8
(5)	-64.5	-13.5

Acid Mixing

Miles$^{(72)}$ gives a graph showing the heat of diluting nitric acid with water at various concentrations. The temperature is not quoted for which the graph is designed but, presumably, it applies at ~25°C since this is the usual operating temperature in the absorption section of a nitric acid plant. In Figure (D.1), five points of this graph have been interpolated which are of interest in the present case study:

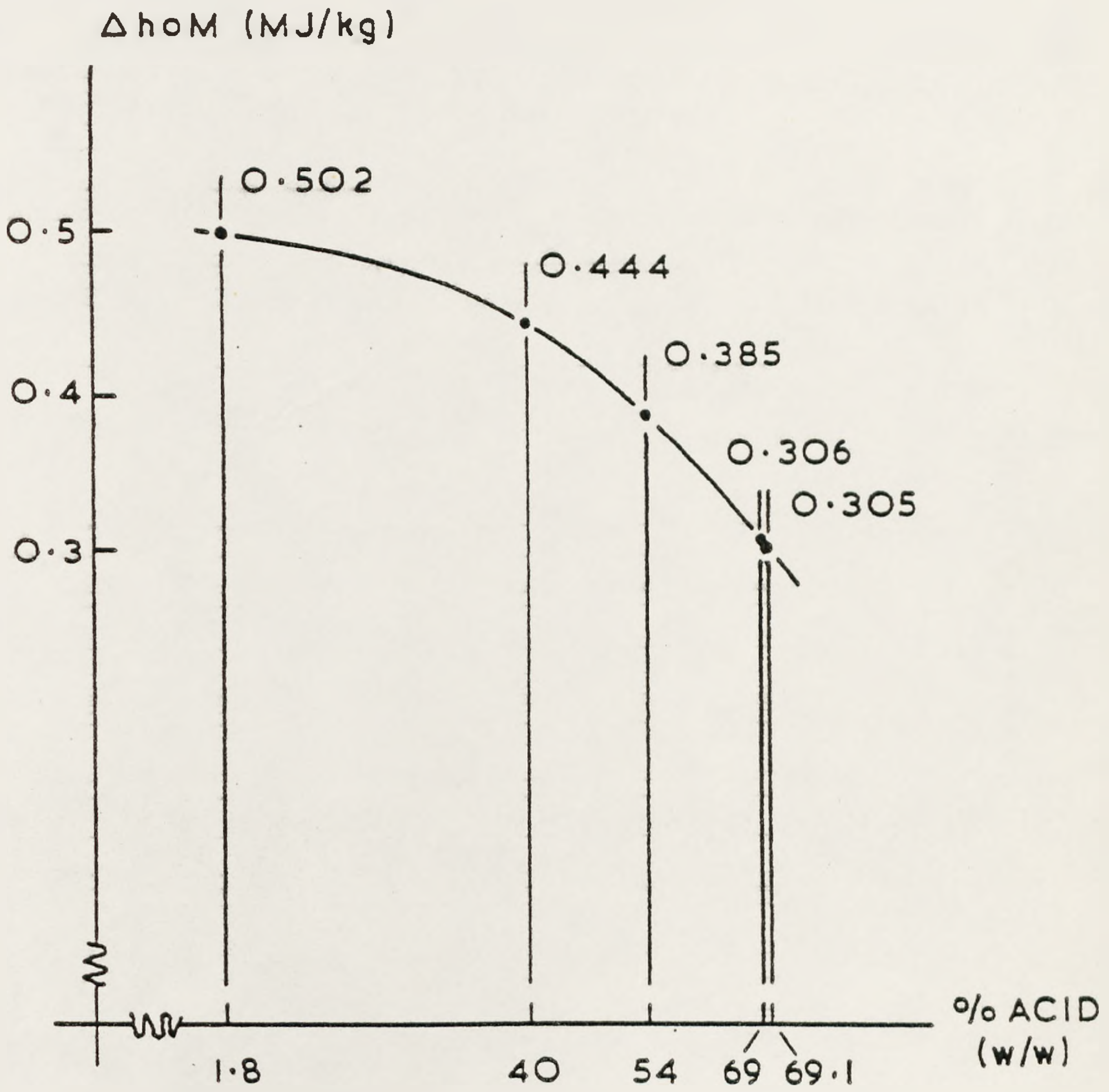

Figure (D.1) Heat of diluting nitric acid. (Source: Miles$^{(72)}$.)

For the free energy (or the entropy) changes that accompany the mixing of nitric acid no data was found and since the same situation applies as in the case of diluting sulphuric acid (i.e. dilution is exothermic with rapid release of heat), the equivalent assumption was used as in Appendix B:

$$\Delta g_{\text{mixing}} \simeq \Delta \text{hoM}$$

As in Chapter Three, the accuracy of this assumption will not be critical for the discussion of improved ways of energy recovery in the process.

APPENDIX E

THE INFLUENCE OF

MINIMUM DRIVING FORCES

AND OF FLOWRATES

ON PRACTICAL EFFICIENCIES

As mentioned previously, the magnitude of the expression

$$\sigma * T_o$$

in any part of a process may be taken as a guideline for the amount of additional work obtainable if work generating equipment was used. However, as pointed out in Section 3.6, practical efficiencies have to be accounted for and there does not seem to be a general way to predict practical efficiencies other than by specifying the equipment to be used. In this appendix a simple example is given which shows that the effect of practical efficiencies can be significant and some generalised comments are made.

The Example

There are three coolers in the contact process case study with the following values for σ (approximated calculations, see Chapter Three)

	σ (kJ/^{o}K/min)
Oleum Cooler	33.17
Absorber Cooler	18.01
Drying Cooler	9.50

(compare Table 3.10). Thus, the oleum cooler would appear the most promising target for inclusion of a power recovery scheme, with the absorber cooler second and the drying cooler last*.

Consider Figure (E.1) on page E2. Idealised Carnot cycle systems are shown (with reversible compression and expansion), two for the oleum stream and one for the absorber acid. In both cases, heat is rejected against some ambient medium (i.e. at $T_o = 20^{o}C$) and a minimum temperature difference of $5^{o}C$ is observed for heat transfer. Due to level and

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*As pointed out in Section 3.7, sulphuric acid and oleum are not ideally suited for such schemes but the example is used to discuss a general point.

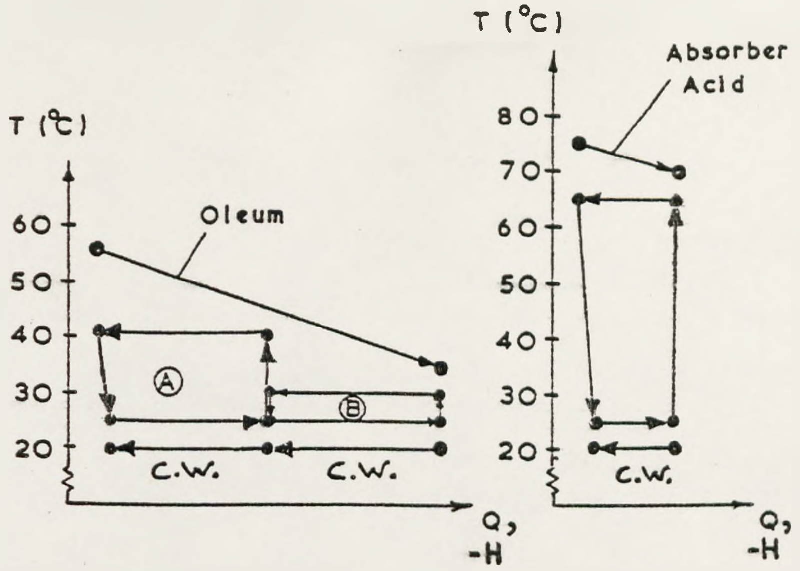

Figure (E.1) Carnot cycles for waste heat recovery (shown in T,Q-diagram).

Table (E.1) Crude data for power recovery schemes connected to oleum and absorber acid

	Oleum		Absorber Acid
$\sigma^* T_o$ (MJ/min)	9.06		4.92
T_{in}	56.9°C		75.4 °C
T_{out}	35°C		70°C
Q (MJ/min)	119.96		35.44
Carnot Cycles :	(A)	(B)	
T_{high}	41°C	30°C	65°C
T_{low}	25°C	25°C	25°C
$\eta_c = \frac{T_{high} - T_{low}}{T_{high}}$	0.0510	0.0165	0.1183
$Q^* \eta_c$	3.06	0.99	4.19
W_{gained}	4.05 MJ/min		4.19 MJ/min
$\eta = \frac{W_{gained}}{\sigma^* T_o}$	0.45		0.85

gradient of its temperature profile, the acid stream enables a good efficiency to be obtained in a single cycle. The oleum stream, by contrast, would necessitate two or more cycles for complete cooling with reasonable performance and would, nevertheless, permit efficiencies of only about half the value of that in the acid stream cycle. (See Table E.1). Thus, less work is obtained from the oleum stream in spite of considerably higher theoretical potential and more complicated equipment, too.

Comments

Trying to interpret this example in general terms, one might come to analyse an irreversibility (expressed in σ or $\sigma{*}T_o$) as dependent not only on the severity of, e.g., a temperature drop but also on the amount of energy degraded across this drop : a high degree of degradation with less energy degraded might lead to the same entropy rise σ as a low degree of degradation with more energy degraded. By and large, a high degree of degradation might be expected to offer more scope for the integration of realistic equipment with practical driving forces* but care is needed in this comment since further aspects (such as the steeper gradient of the T,Q - profile for the oleum stream) will often bring further complicating effects to bear.

This latter argument is the main reason for not recommending here an approach to Second Law analysis that would otherwise seem obvious : one might analyse a unit operation not only from the point of view of loss but also of efficiency, so that attention might be drawn to, say, a low efficiency/medium loss operation rather than a high efficiency/high loss operation. (The former could be expected to be more easily improved than the latter). This approach was tested but rather too many exceptions were observed. Thus, it is not recommended here. Ultimately, simulation

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* Due to the higher temperature of the acid stream, e.g., the relative influence of the minimum temperature difference of 5°C is smaller than in the case of the oleum stream.

would remain necessary for final evaluation of possible improvements and, given this fact, it was considered desirable to keep a preliminary evaluation tool (i.e. Second Law analysis) as simple as possible.

APPENDIX F

SYNTHESIS OF HEAT EXCHANGER NETWORKS

(Copies from the AIChE Journal, July 1978)

Synthesis of Heat Exchanger Networks:

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and
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I. Systematic Generation of Energy Optimal Networks

A thermodynamically orientated method is presented for the synthesis of heat exchanger networks. With this method, the problem is solved in two stages. In the first stage, preliminary networks are generated which give maximum heat recovery. In the second stage, the most satisfactory final networks are evolved using the preliminary networks as starting points. In this paper, emphasis is given to the synthesis of the preliminary networks. Two four-stream examples are solved. In Part II, emphasis will be given to the synthesis of final networks.

SCOPE

The problem of automatically synthesizing chemical process networks has recently attracted some attention in the chemical engineering literature. Relevant work has been reviewed by Hendry et al. (1973) and Hlavacek (1975). As an easily formulated and comparatively simple subproblem, the automatic synthesis of heat recovery networks has received a great share of this attention. For a survey covering this special field, see, for example, Siirola (1974).

Essentially, the synthesis task consists of finding a feasible sequence of heat exchangers in which pairs of streams are matched, such that the network is optimal as judged from overall cost viewpoint. The difficulties arise from the extremely large number of possible stream combinations. Even for small problems, all possible networks cannot normally be enumerated, due to the inordinate demand for computer store and time. Techniques like branch-and-bound (for example, Lee et al., 1970) and tree searching (for example, Pho and Lapidus, 1973) have helped to reduce the number of combinatorial possibilities to be enumerated, but the largest problem solved so far in the literature by means of such techniques involved no more than ten streams (Pho and Lapidus, 1973). Also, optimality could not be strictly guaranteed with these techniques, and cyclic network structures (that is, structures in which two streams are matched against each other more than once) could not be obtained unless the combinatorial problem was allowed to increase in size quite significantly (Rathore and Powers, 1975).

An alternative synthesis method, presented by Ponton and Donaldson (1974), is mainly based on the heuristic of always matching the hot stream of highest supply temperature with the cold stream of highest target temperature. This method can yield cyclic network structures without additional computational effort, and it has been applied to problems of realistic size (see Donaldson et al., 1976). Unfortunately, the method is somewhat unreliable in the sense that it may produce results which are quite far from optimum so that it tends to generate demand for additional heuristics in unexpected situations.

Rathore and Powers (1975), among others, pointed out that costs for steam and cooling water will normally be more important than the costs for plant to the extent where several quite dissimilar network topologies will all feature near optimal costs insofar as they feature near maximum energy recovery. Based on this observation, they recommended a procedure to identify the upper bound on energy recovery for a given problem, and to carry out a depth first tree search in order to rapidly identify some, but not all, networks with maximum or near maximum energy recovery. These networks, they argued, will feature similar and near optimal costs. They can then be compared on grounds of safety, control, starting-up procedures, etc. A strategy of this sort appears even more justified by reports about poor control behavior and other difficulties found with automatically synthesized networks (see, for example, Hlaváček, 1975).

Nishida et al. (1977) presented an algorithmic evolutionary synthesis method which appears to be suitable for the solution of realistic size problems. It employs three basic criteria: trying to ensure maximum energy recovery, trying to minimize total heat transfer area, and trying to minimize the total cost of the network. The total heat transfer area is minimized by a minimum area algorithm, while the total cost is minimized using evolutionary rules. Maximum energy recovery is sought by a theorem and corollaries using a heat content diagram adopted from previous work (see Siirola, 1974). Hohmann (1971) presents a method for synthesis of minimum area networks which also includes a technique for assessing the feasibility of a system of streams assuming a suitable approach temperature and given utility supplies. Hohmann and Lockhart (1976) describe developments which are aimed at assessing the feasibility of a network of exchangers by examination of the minimum approach temperature found in the network. Both techniques indirectly provide correct estimates

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of resource requirements by confirming the feasibility of a network for assumed utility supplies.

A new synthesis method (called temperature interval, or TI method) is proposed which also makes use of the fact that desirable network structures will normally feature high degrees of energy recovery. The method deals with the problem in two stages. In the first stage, preliminary networks are generated which exhibit the highest possible degree of energy recovery. In the second stage, these preliminary networks are used as convenient starting points when searching for the most satisfactory network from other points of view. Apart from costs, criteria like safety constraints, controllability, etc., are easily observed.

In this paper, the main emphasis is laid on the first stage (that is, generation of preliminary networks). The original synthesis problem is split into subproblems, each of which extends over a limited temperature interval only. Synthesis of subnetworks which solve these subproblems is trivial, even when carried out in a way which ensures maximum overall energy recovery. The approach is based on thermodynamic theory and is thoroughly systematic. Combinatorial problems are considerably reduced, since suitable networks can be methodically assembled from smaller units so that there is no need to carry out searches through the complete solution space. In cases where maximum energy recovery would require too complex or too expensive a network, this will be recognized during the synthesis, and the introduction of parallel stream splitting may be considered.

The second stage (that is, search for the most satisfactory final networks) is discussed in detail in Part II.

CONCLUSIONS AND SIGNIFICANCE

The temperature interval method as presented allows the user to identify the upper bound on energy recovery for a given heat exchanger network synthesis problem. This method is based on enthalpy balances which also form the basis of the methods of Hohmann (1971) and Nishida et al. (1977). It also allows the user to systematically generate a variety of networks which perform at this upper bound. The networks are produced by the TI method with very small computational effort. This has been made possible by interpreting the problem on thermodynamic rather than on combinatorial grounds; the physical constraints which govern the feasibility of heat transfer are kept as relaxed as possible by an entirely systematic procedure.

Since synthesis problems are normally based on cost optimization, the fact that optimality is sought with respect to heat recovery rather than costs might appear to be a disadvantage of the TI method. However, as noted previously (Siirola, 1974), the overall costs are heavily dominated by the cost of energy. So different networks which solve the same problem and feature maximum heat recovery are all suitable starting points when evolving the most satisfactory final networks. This has been demonstrated by means of two examples; the TI method was shown to identify with great ease a variety of energy optimal networks so that a choice of different solutions with, for example, different control characteristics (but similar and near optimum costs) could rapidly be identified.

PROBLEM STATEMENT

The way in which the synthesis task was defined has varied in the literature, but most of the recent work has concentrated on the solution of identical types of problems (for example, Masso and Rudd, 1969; Lee et al., 1970; Hohmann, 1971; McGalliard and Westerberg, 1972; Pho and Lapidus, 1973; Ponton and Donaldson, 1974; Rathore and Powers, 1975; Hohmann and Lockhart, 1976; Nishida et al., 1977). The following is a brief outline of this type of problem:

A set of z streams, of known mass flow rates and constant specific heat capacities, are to be brought from given supply temperatures T_S to given target temperatures T_T. For $T_S > T_T$, the stream in question is called a hot one and for $T_T > T_S$, a cold one. Apart from heat exchange between the streams, cooling with cooling water and heating with steam may be considered. The heat exchangers, heaters, and coolers are countercurrent, single-pass units operating with a given minimum approach temperature $\Delta T_{\min}$. The use of multistream exchangers and/or parallel stream splitting is not considered. The streams are all single phase. Change of phase can be accommodated using known ways of reformulating the problem (Donaldson et al., 1976). Given these constraints, that network is to be found which is optimal with respect to the annual cost of steam, cooling water, and plant. For a more detailed problem description as well as design data, see, for example, Nishida et al. (1977). Hohmann (1971), Hohmann and Lockart (1976), and Nishida et al. (1977) solved the same type of problem except for the fact that they included parallel stream splitting. While stream splitting will be discussed in detail in Part II, its implications will be briefly summarized at appropriate points in this paper.

THE TEMPERATURE INTERVAL METHOD

The temperature interval method will be illustrated by solving a four-stream example, called test case No. 1. The data for the problem are given in Figure 1.

Any network which will solve the problem may be thought of as an array of n subnetworks, see Figure 2. Each of these subnetworks includes all streams (or parts of streams) which fall within a defined temperature interval. The temperatures $T_1, T_2, \ldots . T_{n+1}$ are deduced from the problem data in the following way. Each stream's supply and target temperatures are listed after the temperatures of the hot streams have been reduced by the minimum temperature difference $\Delta T_{\min}$. The highest temperature in the list is called T_1, the second highest T_2, and so on. Generally, the following expression holds

$$n \leq 2z - 1 \quad (1)$$

with the equality applying in cases where no two temperatures coincide.

Each subnetwork represents a separate synthesis task. However, since all streams in a subnetwork run through the same temperature interval, the synthesis task is very easy. Consider, for example, $SN(1)$ in Figure 2. There is

Stream No. and Type	Heat Capacity Flowrate "Cp" [kW/°C]	T_S [°C]	T_T [°C]	Heat Load $Cp(T_S - T_T)$ [kW]
(1) COLD	3.0	60	180	−360
(2) HOT	2.0	180	40	280
(3) COLD	2.6	30	105	−195
(4) HOT	4.0	150	40	140
				Σ = 165

Fig. 1. Data for test case No. 1.

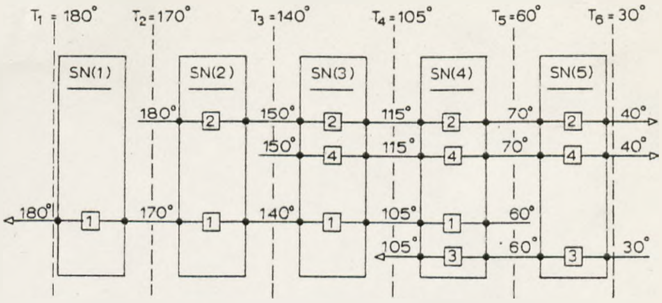


Fig. 2. Subnetworks defined through temperature intervals (for test case No. 1).

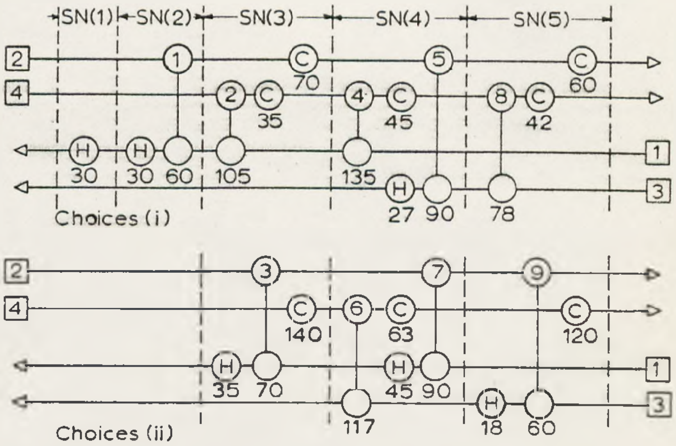


Fig. 3. Subnetwork designs for test case No. 1.

only one cold stream so that there is no alternative but to introduce a heater, see Figure 3*. In the case of $SN(2)$, there is only one hot and one cold stream to be matched, and a heater is required to deal with the residual of the cold stream (which has the higher heat capacity flow rate). Evidently, this heater must be placed on the hot side of the exchanger, since otherwise the $\Delta T_{\min}$ constraint would be violated.

For $SN(3)$, $SN(4)$, and $SN(5)$, two alternative designs can be identified in each case which require different amounts of heat to be supplied by the heaters.

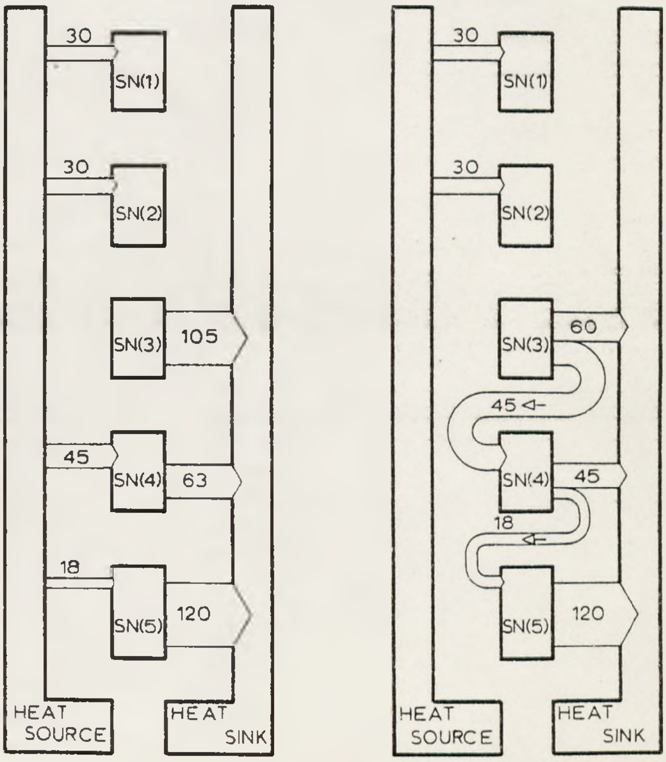
These designs can be proposed by simple inspection, but in more complex cases, a systematic method will be required:

1. Rank the hot and cold streams in order of decreasing heat capacity flow rates.
2. Specify matches between the first hot and first cold, second hot and second cold, etc., streams until the only original streams left are either all hot or all cold.
3. Match the largest remaining stream with the largest residual of the primary matches, the second largest remaining stream with the second largest residual, etc. (at this stage, temperature constraints must be considered).
4. Whatever remains after these steps, that is, original streams, primary residual, or secondary residuals, etc., the final step is to match these against utility heat and cold.

This method will produce a single design which may not be more convenient than others at a later stage in the synthesis but which will always produce a subnetwork structure in which the heater and cooler loads are not greater than those obtained by different rules. Even smaller heater and cooler loads may be found by either using parallel stream splitting within the subnetwork or by creating cyclic subnetwork structures using a structure such as one developed by the above method as a starting point. These possibilities will be discussed in detail when we deal with the second example, test case No. 2.

If the aim of the synthesis task were to design each subnetwork on its own to use the minimum process utility heat, choices (i) in Figure 3 would be adopted throughout when assembling the final network. It is, however, the overall requirement for process utility heat which is to be minimized, and the following considerations will show that choices (ii) for $SN(4)$ and $SN(5)$ should not necessarily be discarded.

In Figure 4*a*, a heat flow diagram is given showing all five subnetworks as well as a heat source (representing process utility heat) and a heat sink (that is, cooling water). Choice (i) has been adopted for $SN(3)$. This uses the lowest possible intake of process utility heat for $SN(3)$. For $SN(4)$ and $SN(5)$, however, choices (ii)



(a) (b)

Fig. 4. Introducing matches between subnetworks.

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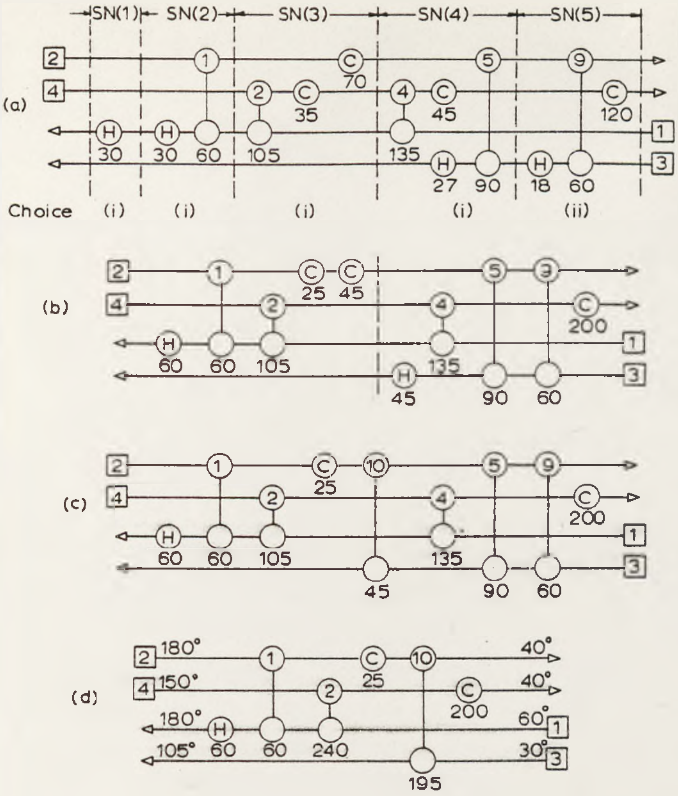
* The particular way of representing a heat exchanger network graphically which has been adopted in Figure 3 is used throughout this work. Hot streams run to the right at the top of the diagram, and cold streams run to the left at the bottom. Beneath each symbol for heaters Ⓗ, coolers Ⓒ, and exchangers ○―○, heat loads are noted in appropriate units (kilowatts throughout this work). The exchangers are numbered in their upper node.



Annual cost : 16560$

Fig. 5. Final synthesis for test case No. 1. The figures beneath the symbols for heaters, coolers, and exchangers represent heat loads in *kW*. The figures shown on the streams (in structure (d)) represent temperatures in °C.

have been adopted. This leads, in each case, to higher process heat intakes than would have been required if choices (i) had been adopted. These increases are seen to be irrelevant, however, if the arrangement shown in Figure 4*b* is realized. The coolers and heaters in Figure 4*a* have partly been converted into exchangers between streams from different subnetworks.

Such a conversion is possible because there is, for example, no hot stream in *SN*(3) with a temperature lower than $T_4 + \Delta T_{\min}$ (see Figure 2), and there is no cold stream in *SN*(4) and *SN*(5) with a temperature above T_4. The equivalent argument can be repeated for any of the subnetworks. Thus, transformations such as the one from Figure 4*a* to Figure 4*b* can be assumed regardless of the particular values of temperatures or heat capacity flow rates.

Whatever method is used for synthesizing a network, the maximum degree of energy recovery will never be realized if the method creates, at an early stage, a situation which later results in prohibitive constraints. One way of avoiding such a situation is by making sure, during each step of the synthesis, that the freedom of choice of design decisions at later steps is not prejudiced. This freedom of choice can be related to the source temperature of the next unit of heat which is to be exchanged; the higher this temperature is, the more flexibility there is as to where this unit of heat may be placed in the network. Accordingly, the freedom of choice can be maximized, throughout the synthesis, simply by matching a hot stream section to that particular cold stream section which has the highest temperature. This is the main function of the temperature partitions between the original subnetworks of the TI method; heat will be passed on from the K^{th} subnetwork to the next one of lower temperature only after all cold streams within the K^{th} subnetwork have been provided for.

In this way, the maximum variety of subnetwork design is available. The same principle, of course, appears in estimation of minimum resource requirements by the present method or as expressed in alternative forms by Hohmann (1971), Hohmann and Lockhart (1976), and Nishida (1977). In these cases, however, subnetworks are not used, so that freedom of choice is not an explicit consideration.

It should be noted that any arbitrarily selected temperatures would be suitable as partitions between subnetworks. The particular choice of temperatures recommended here is just very convenient from the point of view of minimizing the number and complexity of the subnetwork designs and the labor of assembly into a total network for the whole system.

Returning to Figure 3, it is now evident that choices (ii) may be considered for *SN*(4) and *SN*(5), even though they are not optimum solutions for these subnetworks in isolation. Their adoption would not prejudice an overall optimum, since the extra amount of heat is available from hot streams at higher temperatures, and no extra process utility heat is needed. For *SN*(3), however, choice (ii) cannot be adopted without introducing extra process utility heat; there is no excess heat available from *SN*(1) or *SN*(2). Consequently, choice (ii) for *SN*(3) need no longer be considered. Figure 5 shows the subsequent development of a network for the whole system. In Figure 5*a*, a set of selected subnetwork designs is presented. Choice (i) has adopted for *SN*(4), since this produces a first match which is identical to the last match in *SN*(3) (both matches connect streams 4 and 1). This might make it possible later to merge neighboring exchangers into single larger units. For *SN*(5), choice (ii) has been adopted, since this produces a first match which is identical to the last one in *SN*(4). As it stands, the whole network would require an input from process utility heat of 105 kW and an output (through coolers) of 270 kW. However, since all subnetworks designs are consistent with a minimum overall requirement for process utility heat, it is possible to replace pairs of coolers and heaters with equal loads by new exchangers until a network is obtained which shows the highest possible degree of energy recovery.

The only heaters that can be replaced by new exchangers are the two on stream 3 for which suitable coolers (that is, coolers operating at higher temperatures) can be identified. Coolers to match against the two heaters on stream 1 do not exist. In Figure 5*b*, coolers and heaters have been rearranged accordingly; the two heaters on stream 1 and the three coolers on stream 4 have been merged. It was necessary to shift one of the original coolers through exchanger No. 4. This can, evidently, be done without hesitation, since it must increase the temperature difference within the exchanger. Similarly, the two heaters on stream 3 were merged after one of them had been shifted through exchanger No. 5. This shift also increases the temperature difference within the exchanger. Finally, the cooler on stream 2 has been split into two parts. This has been done to provide a heater and a cooler with corresponding equal loads on the cold and the hot sides of the dividing line between the original subnetworks *SN*(3) and *SN*(4). According to the arguments put forward above, a new exchanger can be formed from such an arrangement without any need for checking temperature levels. This new exchanger is shown, as match No. 10, in Figure 5*c*. Evidently, parts of the coolers on stream 4 might have been used as well to form new exchangers, but this would have prejudiced the feasibility of the next, and last, step in the synthesis. Matches No. 2 and No. 4 can be merged, likewise matches No. 10, No. 5, and No. 9. A network results which consists of six units (that is, three exchangers, one heater, and two coolers), see Figure 5*d*. The annual cost is \$16 560/yr, using the data of Table 1.

It is easy to see that the network finally arrived at does indeed achieve the best possible degree of energy recovery. Although hot stream No. 2 would, potentially, be capable of heating cold streams up to 170°C, it cannot do so in the particular case of cold stream No. 1 because the heat capacity flow rate of stream No. 1 is too large. Therefore, stream No. 4 has to heat up stream No. 1 to as high a temperature as possible (that is, 140°C), and from this temperature upwards, stream No. 1 may absorb whatever heat is available from stream No. 2. The remainder of the heat which is required to bring stream No. 1 to its target temperature must be supplied through a heater from the process utility. Both matches, No. 1 and No. 2, operate at the minimum temperature difference at the adjacent ends of the exchangers. Any increase in the temperature differences of these exchangers would adversely affect the degree of energy recovery achieved by the whole network. This tight constraint on the energy recovery situation is reflected in the fact that there is no choice open in Figure 3 as to the design for *SN*(1), *SN*(2), and *SN*(3).

It is worth noting at this point that the juxtaposition of the cooler and exchanger 10 on stream 2 suggests that some improvement would result if these units were rearranged. If the positions are reversed, the temperature difference in exchanger 10 will be infeasible. If, however, steam 2 is split and the cooler and exchanger 10 placed on parallel branches, a network identical to that obtained by the method of Nishida et al. (1977) is obtained.* The cost will be \$16 481/yr. The relationship between networks not involving split streams and their splitting equivalents will be discussed in Part II.

A different initial combination of subnetwork designs to that selected in Figure 5*a* would have led to a different final network. Also, different choices of heaters and coolers for the formation of new exchangers would have led to different final networks. Figure 6*a* shows maximum heat recovery at a marginally lower overall cost than Figure 5*d* or its split stream modification. Figure 6*b* also shows maximum heat recovery, again, but at higher cost because it incorporates an additional exchanger. Note, however, that this structure allows the designer to choose the size of one match (other than match No. 1). Structure 6*b* may thus be called a more flexible design than the others. Also, its cost could still be improved by making use of this flexibility. Structure 6*c*, finally, consists of only five units (one heater, three exchangers, and one cooler) but does not feature maximum heat recovery so that the overall cost is higher.

All three networks in Figure 6 were obtained by means of a consistent variation of the initial designs chosen for *SN*(4) and *SN*(5) as well as of the way in which coolers and heaters were transformed into exchangers. In the context of this latter task (manipulation of heaters and coolers), however, more complicated changes had to be considered than the simple shifts through exchangers discussed above. The rules governing such changes will be given in the second paper, and the following remarks must suffice at this time. Each of the four final networks shown in Figure 5*d* and Figure 6, as well as any other topology which solves the problem, can be obtained from any initial

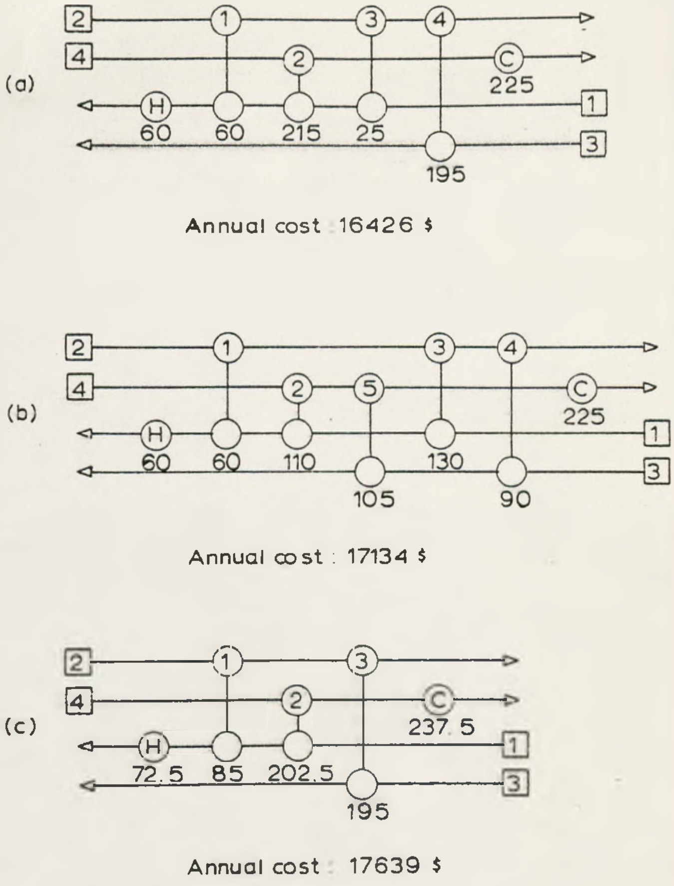
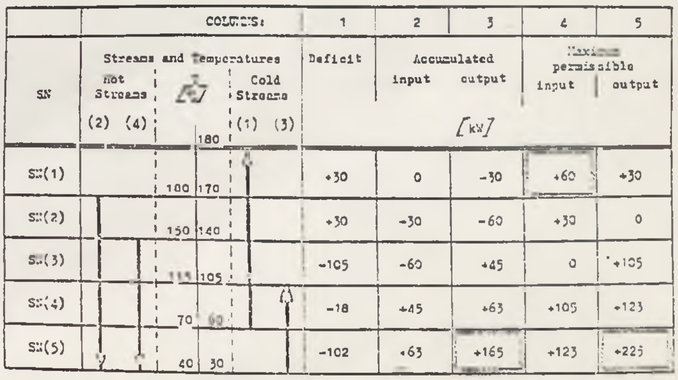


Fig. 6. Three more solutions for test case No. 1.

TABLE 1. DESIGN DATA

Steam Pressure	45 bars
Temperature	258°C
Latent heat	1 676 kJ/kg
Cooling water temperatures	$T_{\text{in}} = 30°\text{C}$; $30°\text{C} \leq T_{\text{out}} \leq 80°\text{C}$
$\Delta T_{\min}$	10°C
Overall heat transfer coefficient	1 000 W/m²K (heaters) 750 W/m²K (exchangers and coolers)
Cost of steam	0.006 \$/kg
Cost of cooling water	0.00015 \$/kg
Equipment availability	8 500 hr/yr
Cost of heat transfer area a	3 000 ($a^{0.5}$) \$ (a in m²)
Annual rate of return	0.1



	COLUMNS:			1	2	3	4	5
SN	Streams and Temperatures Hot Streams (2) (4)	[°C] 180	Cold Streams (1) (3)	Deficit	Accumulated input	 output	Maximum permissible input	 output
				[kW]				
SN(1)		180 170		+30	0	−30	+60	+30
SN(2)		150 140		+30	−30	−60	+30	0
SN(3)		115 105		−105	−60	+45	0	+105
SN(4)		70 60		−18	+45	+63	+105	+123
SN(5)		40 30		−102	+63	+165	+123	+225

Fig. 7. Problem table for test case No. 1.

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* The authors acknowledge the assistance of a reviewer in providing this example.

Stream No. and Type	Heat Capacity Flowrate "Cp" [kW/°C]	T_S [°C]	T_T [°C]	Heat Load Cp (T_S - T_T) [kW]
(1) COLD	3.0	60	180	−360
(2) HOT	2.0	180	40	280
(3) COLD	2.6	30	130	−260
(4) HOT	4.0	150	40	440
				Σ = 100

Fig. 8. Data for test case No. 2.

SN	Streams and Temperatures: Hot Streams (2) (4)	[°C]		Cold Streams (1) (3)	Deficit	Accumulated input	Accumulated output	Maximum permissible input	Maximum permissible output
			180						
SN(1)		180	170		+30	0	−30	+60	+30
SN(2)		150	140		+30	−30	−60	+30	0
SN(3)		140	130		−30	−60	−30	0	+30
SN(4)		70	60		−28	−30	−2	+30	+58
SN(5)		40	30		−102	− 2	+100	+58	+160
					[kW]				

Fig. 9. Problem table for test case No. 2.

combination of subnetwork designs. Equally well, the networks shown in Figure 6 can be deduced from the one shown in Figure 5*d* and vice versa. It is, thus, sufficient to identify only one suitable design for each subnetwork, even if a variety of final structures is to be investigated.

The Problem Table

For more complicated problems, it would be a lengthy procedure to evaluate possible designs for each subnetwork and discuss their suitability by means of sketches like Figure 4. Fortunately, a far more rapid procedure can be adopted.

In Figure 7, the search for the upper limits to the loads of heaters and coolers in the subnetworks is carried out in a systematic way. The data used refer to test case No. 1, and Figure 7 represents what will be referred to as a problem table. In column 1, the values are given of the net heat requirement for each subnetwork. This deficit D_K is the difference between the heat input I_K, which corresponds to the heat supplied by the heater(s), and the heat output O_K, that is, the heat removed by the cooler(s). For the K^{th} subnetwork, the term D_K may be calculated by means of Equation (2):

$$D_K = I_K - O_K = (T_K - T_{K+1})(\Sigma Cp_{\text{cold}} - \Sigma Cp_{\text{hot}}) \quad (2)$$

The summations only include the streams present in $SN(K)$. Since Equation (2) is just an enthalpy balance, the results will be independent of any subnetwork design subsequently adopted. D_K will be positive or negative, depending on whether the heat capacity flow rates of the hot streams are less or greater than those of the cold streams. If D_K is positive, more heating than cooling is required.

Consider, now, the principle shown in Figure 4 in which the output from $SN(K)$ is passed to $SN(K+1)$ to satisfy any requirements for heat in $SN(K+1)$. If there is no separate connection to a process utility heat source in $SN(K+1)$, Equation (3) can be used to calculate the maximum amount of heat made available to $SN(K+1)$:

$$I_{K+1} = O_K \quad (3)$$

Equation (4) may be used to calculate the heat output from $SN(K+1)$:

$$O_{K+1} = O_K - D_{K+1} \quad (4)$$

Thus, assuming no heat supply to $SN(1)$, the figures for the inputs and outputs for each subnetwork are found in columns 2 and 3.

The physical significance of these figures is as follows. If no process utility heat is supplied to any of the subnetworks, and all surplus heat from the matches between the streams in one subnetwork is passed to the next, the heat inputs to each subnetwork would be given as the values in column 2 and the heat outputs in column 3. If any of the values in column 3 are negative, as is the case here for $SN(1)$ and $SN(2)$, process utility heat must be introduced to these subnetworks to increase these outputs to zero. It follows that if one must use process utility heat anywhere in the system, it may as well be introduced at its highest available temperature, that is, into $SN(1)$ and then passed through the sequence of subnetworks. In this way, the amount of heat available in the intervening subnetworks is increased to maximize the choice of subnetwork designs. Accordingly, columns 4 and 5 in Figure 7 have been drawn up. They are based on exactly the same sequence of calculations as columns 2 and 3, with the single difference that the minimum heat requirement for the whole network (the most negative figure in column 3) is introduced as the input to $SN(1)$ from process utility heat sources. As a result, the figures in columns 4 and 5 represent the heat flows into and out of the subnetworks for the case where the necessary minimum process utility heat is received at the highest possible temperature.

The transfer of this heat from one subnetwork to the next creates the maximum degree of choice for subnetwork design without any adverse effect on consumption of resources. Any further increase of a subnetwork's heat input must be provided by additional heat from process utilities. Thus, the figures in columns 4 and 5 represent the upper limits for the heater and cooler loads in the subnetworks which must not be exceeded if subnetworks are to be designed which do not prevent maximum energy recovery. In this sense, they are maximum permissible values (see Figure 7). Comparing the limits obtained in Figure 7 for $SN(3)$, $SN(4)$, and $SN(5)$ with the alternative designs shown for these subnetworks in Figure 3, it is clear that choices (ii) could be adopted for $SN(4)$ and $SN(5)$, but not for $SN(3)$.

Owing to the logic on which the problem table is based, three values in columns 3, 4, and 5 will have a significance not just for the subnetwork to which they belong, but also for the whole problem. In Figure 7, these figures are shown boxed:

1. The bottom figure in column 3 denotes the net cooling requirement for the whole problem as found by an overall enthalpy balance (see Figure 1).
2. The top figure in column 4 is the minimum process utility heat requirement for the whole problem (see networks shown in Figure 5*d* and Figure 6).
3. The bottom figure in column 5 is the corresponding cooling requirement for the whole problem (see, again, networks shown in Figure 5*d* and Figure 6).

In summary, the following procedure is used:

1. The temperature $T_1, T_2 \ldots T_{n+1}$ are identified.
2. An enthalpy balance, that is, Equation (2), must be solved for each subnetwork, giving figures for net heat requirements, column 1.
3. Columns 2 and 3 are calculated by means of Equations (3) and (4), assuming $I_1 = 0$.
4. Columns 4 and 5 are produced by adding the value of the most negative entry in column 3 to each entry in

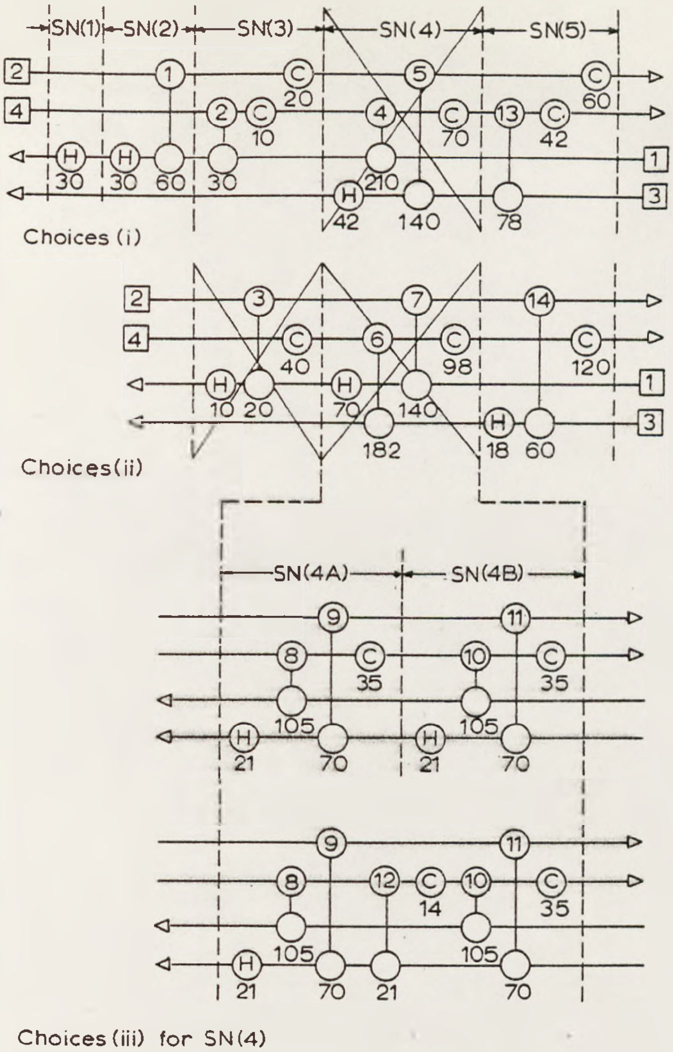


Fig. 10. Subnetwork designs for test case No. 2.

columns 2 and 3. If there is no negative entry in column 3, columns 4 and 5 are identical to columns 2 and 3.

The problem table will then show:

1. Values for the total process heat and cooling loads which will be required if maximum energy recovery is achieved.
2. Maximum permissible figures for the heater and cooler loads of each subnetwork which must not be exceeded if the final network is to be optimum from an energy recovery point of view.

These figures do not depend upon the particular way in which the subnetwork in question, or any other subnetwork, is constructed. Thus, it is possible to design individual subnetworks without reference to the others.

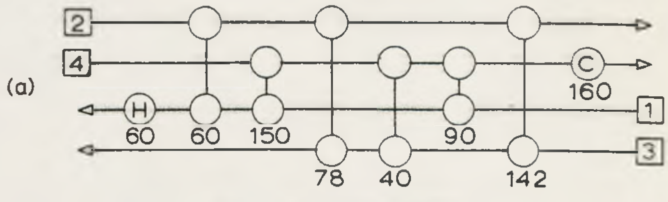
Energy Recovery vs. Network Complexity

In Figure 8, data are given for a second example, test case No. 2. The example is identical to test case No. 1 except that the target temperature of stream No. 3 has been raised to 130°C. The problem table is given in Figure 9. The minimum requirement for process utility heat is unchanged compared to Figure 7 (that is, 60 kW), but the figures for net cooling requirement (that is, 100 kW) and for actual cooling load (that is, 160 kW) are different owing to the change in heat load of stream No. 3. Also, the maximum permissible limits for input and output of $SN(3)$, $SN(4)$, and $SN(5)$ allow less variation in choice of subnetwork design than those in Figure 7. This latter fact indicates that topologies which would ensure maximum energy recovery might have to be more complex for test case No. 2 than they are for test case No. 1.

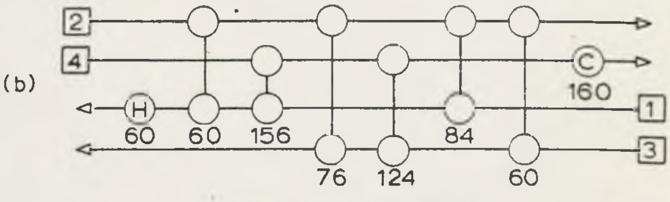
In Figure 10, subnetwork designs are shown for test case No. 2. Just as in Figure 3, choices (i) and (ii) include, for each subnetwork, all possible solutions with not more than one match per stream. A comparison, however, of these designs with the problem table in Figure 9 shows that choice (ii) for $SN(3)$ and also both possibilities for $SN(4)$ do not conform to the appropriate limits for input and output. Choice (i) for $SN(4)$ exceeds the limit by 12 kW and choice (ii) by 40 kW. So, a different design has to be sought for $SN(4)$ such that lower values for input and output will result.

As noted previously, it is possible to use parallel steam splitting within the subnetwork, and indeed it is always possible to design split stream subnetworks which require only one service, that is, either heaters or coolers, not both. In this case, if steams 3 and 4 are split into 3a (0.6), 3b (2.0), 4a (0.4), 4b (0.6), and 4c (3.0) (where the figures in brackets show the heat capacity flow rates), it is possible to specify three exchangers between the following pairs of streams, 1 and 4c, 2 and 3b, 3a and 4b, leaving a single cooler situated on stream 4a with a load of only 28 kW.

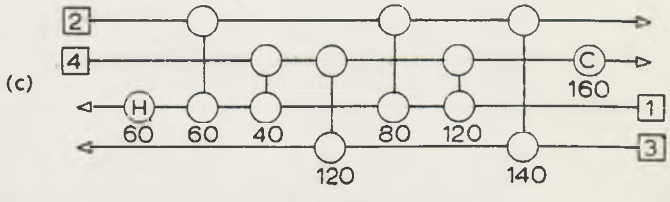
However, when the designer comes to merge the subnetworks to produce a final network for the whole problem, any shifting of heaters or coolers will be impeded by the splitting and merging of streams within subnetworks



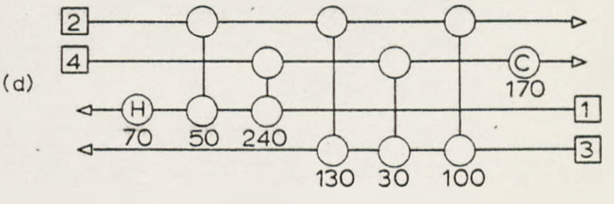
Annual cost : 17560 $



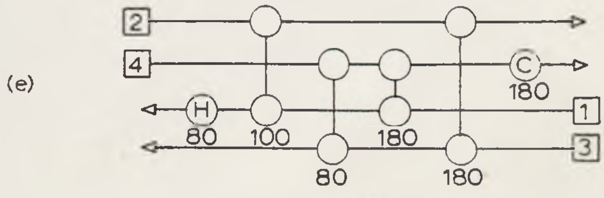
Annual cost : 17631 $



Annual cost : 17648 $



Annual cost : 17989 $



Annual cost : 18590 $

Fig. 11. Solutions for test case No. 2.

unless the same stream is split in exactly the same proportions in a number of adjoining subnetworks.

Thus, while parallel stream splitting within the subnetworks is often an easy solution to the problem of not prejudicing maximum heat recovery, the disadvantages in merging such subnetwork designs later often outweigh these benefits. This is not to say that stream splitting has not a place in design of the final optimal network, merely that steam splitting is not a convenient technique in the design of subnetwork structures.

If parallel stream splitting is not used, then a cyclic design with heater and cooler loads reduced to sufficiently low values can always be found to give maximum energy recovery.

In Figure 10, such a design has been found in a systematic way. Firstly, $SN(4)$ has been split into $SN(4A)$ and $SN(4B)$, and for both these subnetworks the same topology has been chosen as featured by choice (i) for $SN(4)$. (This choice results from matching the largest streams first as suggested earlier.) Secondly, the cooler in $SN(4A)$ has, according to the principle illustrated in Figure 4, been matched against the heater in $SN(4B)$ to form a new exchanger (match No. 12 in Figure 10). Consequently, the total heater load in $SN(4)$ is half that in choice (i), which brings it below the maximum permissible limit shown in Figure 9.

This method of finding a subnetwork design with sufficiently low figures for input and output will sometimes produce solutions with more exchangers than strictly necessary. [For $SN(4)$ in Figure 10, for example, a cyclic solution exists with an input of 30 kW and only four exchangers.] This method is, however, simple compared with evolutionary or exhaustive search methods, and experience has shown that it is very easy to eliminate superfluous exchangers during the final synthesis (as shown in Figure 5). If splitting a subnetwork into two parts does not sufficiently reduce the figures for input and output, the same procedure might be adopted after division into three parts, four parts, and so on. If choice (ii) had been used, division into three parts would be necessary. If the exchangers introduced in this way begin to seem unrealistically small, the increase in equipment cost can, based on the different designs for the subnetwork in question, be compared to the corresponding savings owing to the steam and cooling water economies for that subnetwork. It can be shown that this will give a fair indication of whether maximum energy recovery would be economical for the whole problem, even allowing for any subsequent merging of exchangers to give the final network. If exchanger costs turn out to be prohibitively large, it will be worthwhile to revert to the introduction of parallel stream splitting despite the known inconveniences for future merging of exchangers and shifting of heaters and coolers.

For test case No. 2, however, the annual cost of choice (iii) for $SN(4)$ is clearly below the one for choice (i), and, accordingly, choice (iii) has adopted for final synthesis. Together with choices (i) for $SN(1)$, $SN(2)$, $SN(3)$ and choice (ii) for $SN(5)$ (to obtain the neighboring matches No. 11 and No. 14), this guarantees that topologies can be found, after manipulation of heaters, coolers, and exchangers, which feature maximum energy recovery. In Figure 11, three such topologies are shown (structures *a*, *b*, and *c*). They are the only three which exist with eight pieces of equipment which do not use split streams. The cost of structure *a* could be further improved by surface optimization. Structures *d* and *e* in Figure 11 represent alternative solutions with simpler network structures, made possible by progressive movement away from maximum heat recovery. With pricing parameters given in Table 1, the solutions with maximum energy recovery are cheapest, but different relative weights of equipment vs. utility costs might make the other solutions more economic. This point, as well as the fact that questions concerning control, safety, starting-up procedure, reliability, maintenance,, etc., must, ultimately, be considered in synthesis work makes it evident that the identification of a great variety of near optimum cost structures is rather more desirable than the identification of a single optimum structure. In this context it is worth emphasizing that structures like *d* and *e*, as well as any other near optimum cost structure, are rapidly obtained from structures like *a*, *b*, or *c*, by means of the manipulation of heaters and coolers, the rules of which will be given in Part II (see Linnhoff and Flower, 1978). The design engineer remains in positive control over the balance he is prepared to strike between maximum energy recovery and simplicity or cheapness of network design. Stream splitting can be introduced at this final stage with fewer disadvantages than at the stage of subnetwork design.

CONCLUDING REMARKS

Comparison with Other Synthesis Methods

Nishida et al.'s method is based on a systematic ordering of all heat loads occurring in a problem according to their temperature. Thus, the basic strategy is thermodynamically orientated and based on similar enthalpy balances to those of the TI method. The ways in which matches between streams are introduced, however, are rather different in the two methods. Nishida et al. introduce matches in such a way that parallel stream splitting may appear necessary at an early stage in the synthesis. The TI method, by contrast, introduces matches in such a way that maximum energy recovery can always be obtained by alternative cyclic subnetwork structures. This by no means prevents the introduction of stream splitting at any stage but delays such a step until the definite need for doing so has been confirmed. (A detailed discussion of this will be given in Part II.) A further difference lies in the contrast between the evolutionary rules, cited by Nishida et al., and the thermodynamically based concepts developed in Part II of this paper to implement desirable design strategies. Lastly, minimum utility requirements cannot be predicted using Nishida's method unless explicit consideration is made of feasible networks (see below).

Ponton and Donaldson's method is based on the main heuristic of always matching the hottest hot stream with the cold stream of highest target temperature. This heuristic is thermodynamically sensible and will, in many cases, lead to thermally efficient networks. A systematic safeguard, however, against individual matches which would prejudice an overall optimum for the whole network is not provided. The TI method, by contrast, may introduce similar matches (the second subnetwork will normally consist of an exchanger between the hottest hot stream and the highest target cold stream, etc.), but by introducing coolers and heaters for the various residuals, different matches must result if these should be essential to ensure maximum heat recovery.

When compared to combinatorial methods such as suggested by Rathore and Powers (1975), the TI method exhibits the following advantages: maximum energy recovery and low computational effort in finding multiple solutions (including split stream structures, see Part II).

The Upper Bound on Energy Recovery

Rathore and Powers (1975) have recommended a simple rule to find the upper bound on energy recovery, but the feasibility of heat transfer is checked merely from a temperature point of view. If, as in the two test cases, the heat capacity flow rates are such that they adversely affect the extent to which heat transfer is feasible, this cannot be detected by their rule. When applied to the test cases, steam requirements of only 30 kW are wrongly predicted.

Nishida et al. (1977) determine the maximum amount of heat exchange among process streams in their corollary 2 using the same rule as suggested by Rathore and Powers with the consequent shortcomings. However, situations such as in the two test cases could be identified using their synthesis method if step 2 of their design procedure (p. 82 of their text) were repeatedly applied during the synthesis. (This has not been demonstrated by Nishida et al.) Consequently, networks utilizing minimum utilities may be found, but an algorithm to compute minimum utilities independently of the design of explicit network structures does not follow.

Hohmann (1971) used the conventional enthalpy/temperature diagram for synthesis but suggested a feasibility table for estimation of minimum resource requirements. This is based on an analogous type of enthalpy balance as the problem table, yielding identical results for utility requirements of an overall problem. However, it does not predict limits to inputs and outputs within temperature intervals and cannot therefore be used for the task of synthesizing networks which achieve maximum energy recovery.

The problem table and the TI method allow first identification of minimum utility requirements independent of network design and then synthesis of networks which necessarily achieve minimum requirements.

The Role of ΔT_{min}

Although part of the network specifications rather than the problem data, ΔT_{min} influences the results shown in the problem table. In this context it should be noted that allowances for minimum approach temperatures need not be introduced in as simple a way as used in this paper. Each stream may be assumed to contribute part of the overall value ΔT_{min} which thus becomes a function of the two streams being matched in an exchanger. Depending upon, for example, whether the fluid in question is corrosive or the flow rate is subject to excessive variations, values for the contributions could be chosen which differ among the various streams, etc. This would lead to different values for the maximum permissible limits as well as for the upper bound on energy recovery. A technique for carrying out sensitivity analysis which would establish the influence of assumptions regarding ΔT_{min} on the upper bound on energy recovery (and thus on utility costs) follows automatically (Linnhoff, 1978). The theoretical limit for the upper bound on energy recovery, which can only be approximated in practice, can be found by setting up a problem table based on the assumption $\Delta T_{min} = 0$ throughout.

Solution of More Complex Problems

The two examples chosen to illustrate the TI method are not chosen to be typical of many larger real problems, since their purpose is to aid explanation of the thermodynamic principles. The complexities of real problems necessitate further developments not discussed in this paper but which do not alter the basic method. One frequent criticism of the test examples used in the literature is the assumption of constant specific heat capacity. It is convenient to distinguish between minor nonlinearity of the enthalpy-temperature relation, for example, as in most liquid streams and the major effects of change of phase. In the calculation of the problem table, the net heat requirements are found from an enthalpy balance on the subnetworks; consequently, explicit calculation of specific heat capacities is not strictly necessary.

The variations in specific heat capacities are only important in the design of subnetwork structures. Minor variations in specific heat capacity may create situations where the smallest approach temperature is found in the interior of an exchanger, but it is thought unlikely that this would remain undetected in the final stages of a synthesis. In any case, allowance for this can be made in assigning the ΔT_{min} values for exchangers. Major variations such as those due to change in phase do not introduce radically different problems. Often, different phases and the transitions may be represented as separate streams. Indeed, for the final stages of the synthesis, the practical necessity of separating single phase units from vaporizers or condensers tends to prevent accidental specifications of internal crossovers.

An important aspect of the design of larger systems is that of specifying the choice of different sources of process heat and cold. From a thermodynamic point of view, sources of process heat or cold are only distinguished by their capacity and temperature. The procedure for setting up the problem table yields the total quantity of process utility heat and, by virtue of the overall enthalpy balance, the total quantity of process cold.

With reference to Figure 4*b*, it is important to recognize that the procedure adopted in the solution of test case No. 1 of introducing the total process heat requirement in $SN(1)$ has the advantage of maximizing the choice of subnetwork designs for $SN(1)$. However, in a hypothetical case, where for reasons of availability or cost the heat input was split between $SN(1)$ and $SN(2)$ as shown, the only change in the design procedure is to limit the available designs of $SN(1)$. The choice of subnetwork structures available for $SN(2)$ to $SN(5)$ is unaltered. The final network would be as shown in Figure 5*d*, except for the provision of two heaters on stream 1 each served by a separate process utility source. In the same way, if it is assumed that there is an additional source of process cold only capable of absorbing heat at temperatures above 60°C, it is clear that the single cooler on stream 4 in Figure 5*d* could be replaced by two coolers of loads 80 and 120 kW, respectively, each served by a different utility source.

While these examples of multiple resources are trivial in themselves, there is no doubt that very complicated systems can be analyzed and successful networks designed using subnetworks based on the problem table (Linnhoff, 1978).

ACKNOWLEDGMENT

Bodo Linnhoff gratefully acknowledges the financial support from The British Council which has made this work possible. The authors also wish to acknowledge the helpful and constructive comments of Dr. J. J. Siirola, Dr. J. W. Ponton, and the other referees.

NOTATION

C_p = heat capacity flow rate, kW/°C
D_K = deficit in enthalpy balance [Equation (2)], kW
I_K = heat input into K^{th} subnetwork, kW
n = number of subnetworks in a problem
O_K = heat output from K^{th} subnetwork, kW
$SN(K)$ = K^{th} subnetwork
T_S = supply temperatures, °C
T_T = target temperatures, °C
$T_1, T_2, \ldots T_{n+1}$ = temperatures of cold streams between subnetworks, °C

z = number of streams in a problem
$\Delta T_{\min}$ = minimum temperature difference within heat exchangers

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II. Evolutionary Generation of Networks with Various Criteria of Optimality

An evolutionary method is presented for the synthesis of heat exchanger networks. Starting from feasible solutions which preferably exhibit maximum energy recovery,[*] the method allows systematic promotion of desired design features such as low overall cost, suitability for starting-up procedures, observation of safety constraints, etc. Seven examples based on standard literature problems are used to illustrate the method.

SCOPE

In Part I, previous work on heat exchanger network synthesis was discussed and a new synthesis method proposed. It allows systematic generation of networks which achieve maximum energy recovery.

However, attempts to obtain useful interaction between the systematic approach of a formalized method and the imaginative, heuristic based intelligence of the experienced designer may not be automatically successful. As with other systematic methods, variations of design constraints such as $\Delta T_{\min}$ (that is, the minimum temperature difference to be permitted within an exchanger), or of costing parameters, are possible, but whether or not such variations will produce desired differences in the final networks cannot be easily predicted. Once the design constraints are defined and the criteria of optimality approximated in a feasible quantitative manner, an automatic algorithm will base decisions on marginal numerical differences which may not be very relevant from points of view such as safety, control, reliability, etc.

Until recently, the literature dealing with the synthesis of heat exchanger networks offered little advice in this matter. The identification of near optimum cost structures for a given problem was usually chosen as the objective. Rathore and Powers (1975), however, observed that the costs of networks showing a high degree of energy recovery are near optimal as well as quite insensitive to significant changes in network topology. They suggested the following strategy: identification of a number of networks featuring high degrees of energy recovery, and final selection of one of these networks using whatever combination of criteria seems relevant.

Apart from enabling the user to consider aspects other than costs, such an approach has the merit that not all feasible structures have to be enumerated. This helps to overcome the problem of dimensionality which is usually very large in the synthesis of heat exchanger networks.

There are, however, two basic disadvantages in the approach. Firstly, the computational effort required per final candidate structure identified may not be significantly reduced. Secondly, some suitable candidates might not be found because they narrowly fail to meet design constraints (such as $\Delta T_{\min}$) or the problem specifications (such as a target temperature for a stream).

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[*] The synthesis of such solutions has been discussed in Part I (see Linnhoff and Flower, 1978).

0001-1541-78-1232-0642-$01.55.

A synthesis technique of any realism should not only be capable of identifying optimal networks for a strictly defined problem but should also allow the user to recognize chances where they exist of slightly relaxing problem constraints to gain some advantage.

Shah and Westerberg (1975) and Nishida et al. (1977) suggested the use of evolutionary rules for the synthesis of low cost networks. This approach to the synthesis problem is attractive owing to the ease with which interactive computer-user participation is made possible. However, an approach based on heuristic rules will always require the user to make some decisions. This is especially true when the objectives include matters such as safety, operability, etc., which are less well interpreted in terms of network structures than overall cost.

In the present paper, a synthesis method is presented which is suitable for hand implementation or for use as an interactive computer program. It enables the user to use evolutionary rules such as suggested by previous workers with great ease as well as to gain considerable insight into the consequences of future synthesis steps. This allows heuristic rules to be replaced when necessary by other evolved strategies without increased effort. Thus, desired network features can be actively promoted during the synthesis, rather than passively emerging from a limited number of trial solutions.

The method uses a systematic representation of heat exchanger networks, in which exchangers and streams form a grid. In such a grid, each exchanger may be interpreted as consisting of a heater and a cooler. Heaters and coolers, however, may be shifted through the grid according to simple feasibility rules. These rules help to determine what the consequent effects of a shift on the network would be. Starting from a given structure, any other structure may be obtained. This includes cyclic networks (that is, networks in which the same two streams are matched against each other more than once) as well as topologies which incorporate parallel stream splitting.

CONCLUSIONS AND SIGNIFICANCE

The evolutionary development method (ED method) enables the user to obtain rapid insight into beneficial, or detrimental, effects of potential synthesis steps in the design of heat exchanger networks. Thus, the formulation of strategies aimed at achieving given design goals is greatly helped. This eliminates, by and large, the need to accumulate many different solutions to a given problem before checking whether any display a desired combination of features in aspects such as cost, operability, safety, etc. Instead, the desired features can be methodically introduced in a sequence of evolutionary steps, starting from any feasible structure. Preferably, but not necessarily, the structure from which one starts should exhibit maximum energy recovery. Such structures can always be found by means of the TI method described in Part I.

Design strategies which would help to develop networks of low overall cost have been found. Some of them are related to heuristic rules for evolutionary network development given by previous workers; others are new. When implemented by means of the ED method and applied to seven examples from the literature, they produce new optimum cost solutions which are improvements on those previously described in five cases. In the remaining two cases (that is, 4*SP*1 and 6*SP*1, see text), optimum solutions found by previous workers were confirmed. In some cases, the TI method was used to provide initial maximum energy recovery networks, while in other cases, the networks of previous workers were used as starting points.

Perhaps more important, though, solutions were synthesized for several problems which appear to be better candidates from a practical point of view than the respective optimum cost networks. Most of these solutions combine near optimum cost with a high degree of flexibility in terms of choice of certain design and/or operating parameters. One particular network proposed (for 10*SP*1, see text) narrowly fails to meet the problem specifications but compensates for this disadvantage by exhibiting an attractively simple structure.

Further, criteria were identified which are applicable to the design of heat exchanger networks in general and which seem to be of great importance. It has been previously noted that investment costs for plant are mainly influenced by the number of heaters, coolers and exchangers used (for example, Nishida et al., 1977), but, apart from the work of Hohmann (1971), there is little discussion of the minimum number of units required in a given problem. Apart from costs, points of concern such as flexibility of design and the potential benefits of parallel stream splitting are shown to be closely related to the number of pieces of equipment used. Three main points emerged: (1) stream splitting may be employed to reduce the number of exchangers where this cannot be done in any other way, (2) sizes of exchangers may be varied if more pieces of equipment are used than the minimum number strictly necessary, (3) stream splitting may allow variation of exchanger sizes without increasing the number of exchangers.

Intelligent choice of the number and sizes of those pieces of equipment which are not totally constrained and a flexible attitude towards design constraints, combined with the ability to direct the synthesis towards a desired topology, should make satisfactory solution of realistic design problems possible by the ED method.

PROBLEM STATEMENT

As stated in Part I, most of the recent work in heat exchanger design has concentrated on the solution of identical types of problems, and a brief description has been given there.

In the present paper, solutions will be sought to seven problems from the literature, but apart from annual costs, aspects will be considered such as the degree of interconnection of streams (which would influence controllability), flexibility in design, possible safety constraints, etc. The design and costing parameters to be used are those of Pho and Lapidus (1973) to ensure comparability with previous work.

THE CONCEPT OF FREEDOM AND THE ED METHOD

In Figure 1*a*, the optimum solution found by Masso and Rudd (1969) for problem 7*SP*1 is shown. The method of graphically presenting the network is the

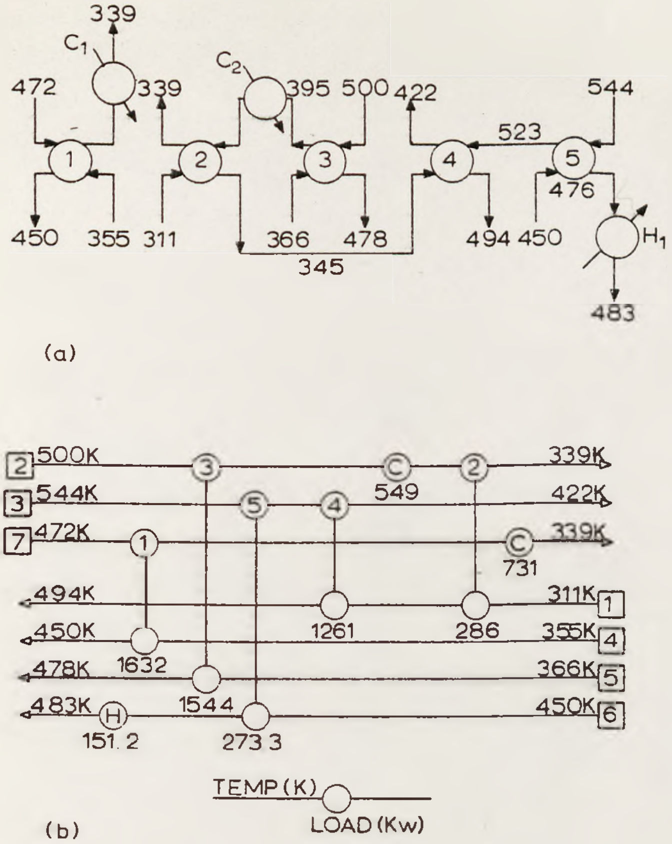


Fig. 1. 7SP1 as solved by Masso and Rudd. (a) Conventional drawing. (b) Grid representation.

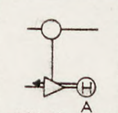
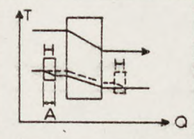
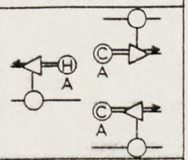
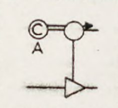
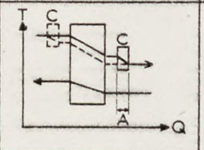
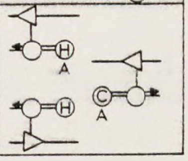
RULE NO.	BASE CASE	EFFECT ON FREEDOM	EXPLANATION (FOR BASE CASE)	EQUIVALENT OTHER CASES
①	 shift through node with CPL	+A		
②	 shift through node with CPS	$+A\left(\frac{CPL}{CPS}\right)$		

Fig. 2. Shifts along streams of heaters and coolers through exchangers.

same as adopted by Masso and Rudd themselves. In Figure 1*b*, the network is shown by means of a method introduced in Part I. The diagram represents a grid, made up of streams and exchangers. Hot streams run from the left to the right at the top, and cold streams run from the right to the left. Beneath the symbols for heaters, coolers, and exchangers, heat loads are noted in appropriate units (kilowatts for all examples introduced in this paper). Temperatures may be shown against each stream and so may heat capacity flow rates. The exchangers may be numbered at one of their nodes.

The explanation of the synthesis method is conveniently based on this diagram which can represent any feasible network. In turn, particular features of the diagram can be justified by an explanation of the method.

The Definition of Freedom

In Equation (1), a parameter is introduced which is called the "freedom" of a heat exchanger:

$$F = CPL(\Delta TS - \Delta T_{\min}) \qquad (1)$$

This parameter has the same physical dimension as a heat load. The purpose of introducing this parameter is to ease methodical investigation of the effects of changes in the positions of exchangers. The effects of such changes are normally discussed in terms of the changes in temperatures and temperature differences which occur in the exchanger, since these changes affect the feasibility of the revised network in a quite familiar and fundamental way. However, relating the size of shifting heat loads and the temperature differences in this way requires continual reference to the heat capacity flow rates of the individual streams. It is more convenient to describe the effects on the heaters and coolers in the network in terms of the temperature changes of the streams passing through the heaters and coolers. In this way, the effects of shifts are more easily understood by comparing temperature differences in exchangers with temperature drops across heater and cooler loads.

If the heat capacity flow rates are constant over reasonable ranges of temperature, then the temperature drop across a load will be independent of its position on the stream. Thus, shifting a load through an adjacent exchanger will alter the smallest temperature difference in the exchanger by the fixed value of the temperature drop across the load.

In a similar way, the temperature differences between the source of utility heat or cold and the process stream in a heater or cooler will change. In many applications, the temperatures of the utilities will be so different from those of any feasible process stream that the possibility of the heater or cooler showing infeasible temperature differences can be ignored. In other cases, the feasibility of the heater or cooler can be investigated in a way exactly similar to that described below for an exchanger.

Alternatively and preferably when more complex changes are considered, the scope for shifting can be interpreted in terms of the maximum load which can be shifted through the exchanger before the point of infeasibility is reached. The maximum load which can be shifted through an exchanger in a simple case is equal to the freedom as defined by Equation (1). Shifts of smaller loads will merely reduce the freedom of the exchanger by the size of the load.

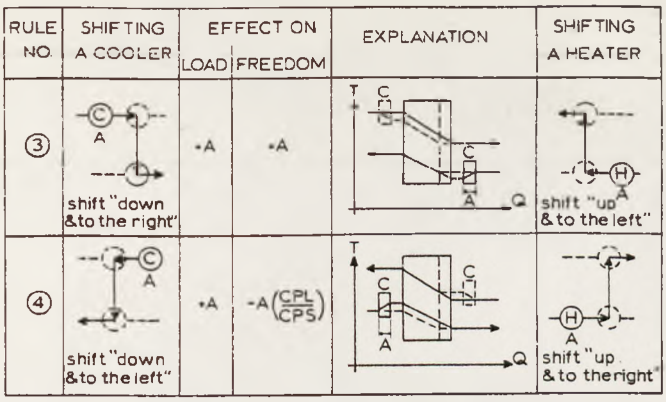
While the use of temperature differences has the advantage of familiarity, the concept of freedom has equally important advantages in complex situations, even when the enthalpy-temperature curve shows marked nonlinearity (Linnhoff, 1978).

Basic Elements of Synthesis Method

Figure 2 summarizes the effects that simple shifts of heaters and coolers have on an exchanger's freedom; shifts according to rule No. 1 (that is, along the stream with the larger Cp) will alter the exchanger's freedom by the heat load of the cooler (or heater) which is shifted. The effect of shifts according to rule No. 2 (that is, along the stream with the smaller Cp) is greater by the factor CPL/CPS (where CPS is the smaller of $Cp_{\text{hot stream}}$ and $Cp_{\text{cold stream}}$). To make it easily recognizable which one of the two streams matched in a particular exchanger has the larger Cp. the following conventions have been adopted:

1. To situate an exchanger's reference number in the node on the stream with the smaller Cp.

2. To replace the node on the stream with the larger Cp by a triangle as a qualitative indication of the temperature profile within the exchanger. Thus, it will always point, like an arrow, towards that side of the exchanger at which the smallest actual temperature difference is



RULE NO.	SHIFTING A COOLER	EFFECT ON LOAD	EFFECT ON FREEDOM	EXPLANATION	SHIFTING A HEATER
③	shift "down & to the right"	+A	+A		shift "up & to the left"
④	shift "down & to the left"	+A	$-A\left(\frac{CPL}{CPS}\right)$		shift "up & to the right"

Fig. 3. Shifts from one stream to another of heaters and coolers through exchangers.

found. In the case of equal *Cps* for both streams, two circles may be retained. For exchangers in which the freedom is zero (that is, $\Delta T_{\min}$ is reached), the triangle or one of the circles (in the case of equal *Cps*) may be blacked out.

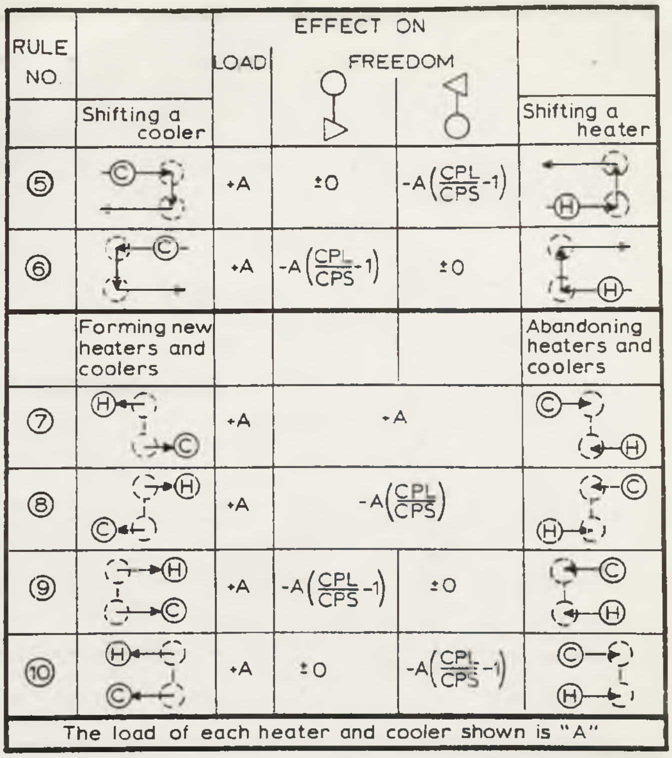
In Figure 3, two more rules are given. They are concerned with cases in which the heater (or cooler) in question is shifted from one stream to another. Such shifts not only affect the freedom of the exchanger but also affect its load. On the other hand, the effects are independent of the heat capacity flow rates so the exchangers are not shown in full detail in Figure 3.

It will be appreciated that the direction of each shift shown in Figures 2 and 3 may be reversed and that coolers may be shifted instead of heaters and vice versa. The effects on load and freedom of the exchanger concerned would be equal in magnitude to the effects shown in Figures 2 and 3 but opposite in sign. Furthermore, those combinations of rules No. 1 to No. 4 are shown in Figure 4 which have been found to be of practical value. Each of these combinations, again, could be applied with reversed direction and reversed sign.

Applying the Method to 7SP1

In Figure 5*a*, the network presented in Figure 1*b* is shown again with the new symbols. The freedoms of the exchangers are also shown (vertically, in the space between hot and cold streams). When choosing which evolutionary synthesis step would be most beneficial to the network, one should always question the necessity of a small heater being present as well as coolers. Unless there is a strict thermodynamic reason for such an arrangement (for example, a cold stream becoming hotter than any hot stream), utility resources are wasted on grounds of both steam consumption and a corresponding requirement for additional cooling water.

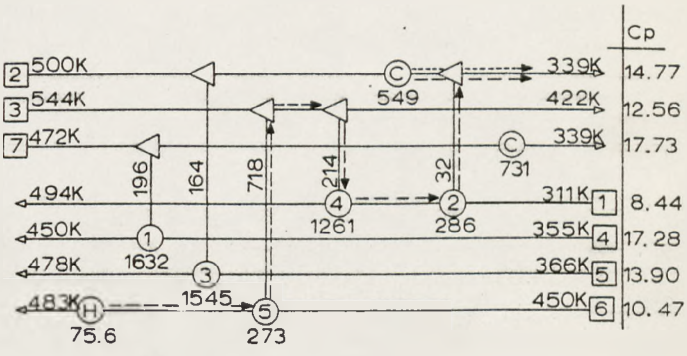
To eliminate the heater, however, would only be possible if it could be shifted to a point in the network next to a cooler (so that a fraction of the cooler could cancel the heater). Consequently, the mobility of the heater in the network has to be examined. This can be done by simply comparing its heat load (that is, 75.58 kW) with the freedoms of the exchangers in the network (if appropriate, after consideration of the relevant factor *CPL/CPS*). It quickly becomes clear that the heater could be shifted through any of the exchangers except No. 2. The freedom of exchanger No. 2 (that is, 32.24 kW) is too small. On the other hand, the cooler on stream No. 2 can be shifted through exchanger No. 2, thereby increasing the exchanger's freedom (see dotted line in Figure 5*a*). It is then possible to shift the heater through the network along the dashed line, and the structure shown in Figure 5*b* results. The shift through exchanger No. 5 took place according to rule No. 4, the one through exchanger No. 4 according to rule No. 3, and rule No. 4 was used, once again, for the shift through exchanger No. 2. The freedoms in structure 5*b* may either be calculated by means of these rules based on the values shown in structure 5*a* or they may be evaluated from temperatures and heat loads, as given in Figure 5*b*, by means of Equation (1).



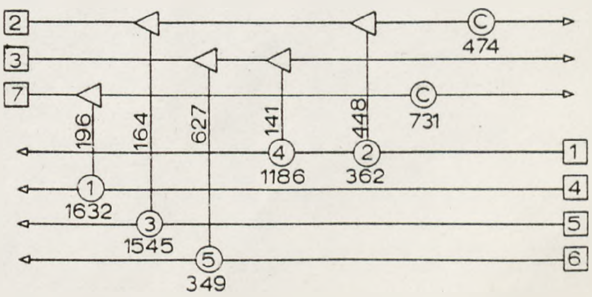
RULE NO.	Shifting a cooler	EFFECT ON LOAD	EFFECT ON FREEDOM ○–▷	EFFECT ON FREEDOM ◁–○	Shifting a heater
⑤		+A	±0	$-A\left(\frac{CPL}{CPS}-1\right)$	
⑥		+A	$-A\left(\frac{CPL}{CPS}-1\right)$	±0	
	Forming new heaters and coolers				Abandoning heaters and coolers
⑦		+A	+A		
⑧		+A	$-A\left(\frac{CPL}{CPS}\right)$		
⑨		+A	$-A\left(\frac{CPL}{CPS}-1\right)$	±0	
⑩		+A	±0	$-A\left(\frac{CPL}{CPS}-1\right)$	
The load of each heater and cooler shown is "A"					

Fig. 4. Further rules for shifting and merging.

With an annual cost of only $30 172, structure 5b is over 12% cheaper than structure 5*a*. It is, in fact, the cheapest solution presented so far to the problem. Apart from Masso and Rudd, only Pho and Lapidus



(a) Annual cost : 34, 447 $



(b) Annual cost : 30172 $

Fig. 5. Evolutionary improvement of solution for 7SP1. (a) Solution as shown in Fig. 1. (b) Optimum cost solution.

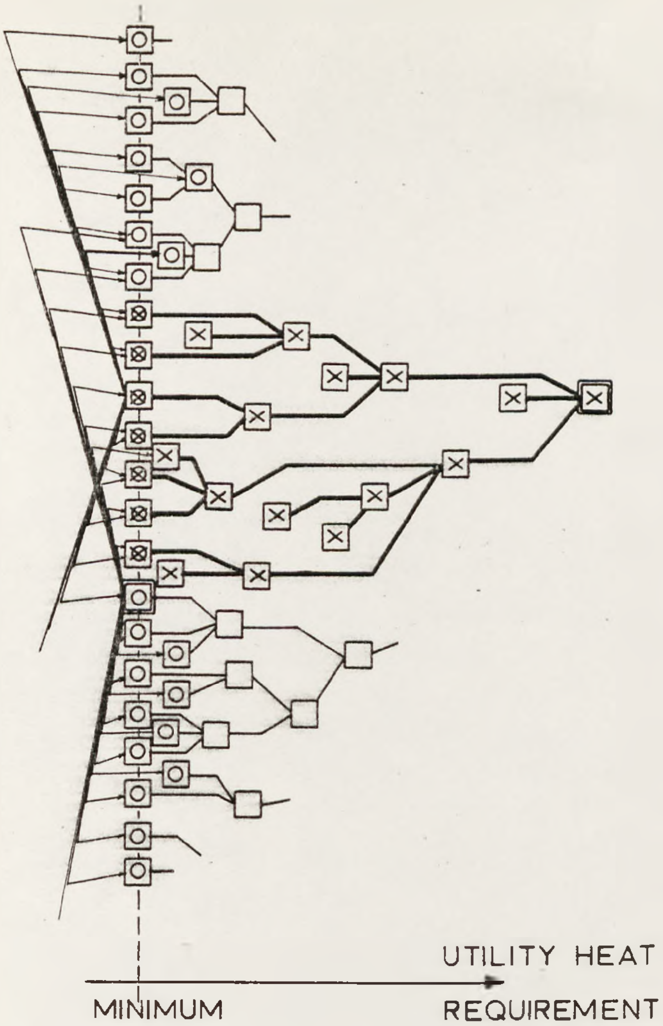


Fig. 6. Section of a simplified synthesis tree.

(1973) and Ponton and Donaldson (1974) have solved 7SP1. Pho and Lapidus claimed an annual cost of $30 433 for their solution owing to an error in cooling water costs, as noted by Nishida et al. (1977). The true cost for their solution is approx. $31 700/yr. Thus, the network shown in Figure 5*b* represents some worthwhile improvement. Ponton and Donaldson did not present a network but reported finding one (by means of their H/2H search algorithm) costing $30 172/yr, too. It seems quite certain that they found the same structure as presented in Figure 5. A short search with the rules as presented in Figures 2, 3, and 4 shows that there is no other solution for 7SP1 with such a low cost.

Evolutionary Development Instead of Depth First

In Figure 6, a conventional heat exchanger network synthesis tree is presented symbolically. Each square represents a particular structure. The position of a square in the diagram indicates the energy performance achieved by the structure which is represented. Networks operating with minimum requirement for process utility heat are situated on the far left. In branch and bound and in tree searching algorithms, such synthesis trees are evolved by consistently adding further matches to existing structures, so that new structures result from the existing ones. Thus, all feasible networks can, theoretically, be derived from primary matches. Practically, however, there are too many enumerations required even for small problems.

To overcome this problem, Rathore and Powers recommended giving emphasis to the rapid evaluation of several, but not all, structures with a high degree of energy recovery "For a large industrial problem . . . . developing any of the decision nodes containing a primary match will probably lead to a number of networks which are close to the cost of the optimal one." This approach (that is, depth first) is indicated in Figure 6 by means of crosses; starting off from primary match $\boxed{\times}$, a certain number of optimum and near optimum energy networks are found. Since overall costs are heavily dominated by utility costs, these networks will all be ". . . close to the cost of the optimal one" (see above).

The evolutionary approach to synthesis favored here is indicated in Figure 6 by means of circles; starting off from optimum energy structure $\boxed{\bigcirc}$, other structures situated either on or near the optimum energy line may rapidly be evolved, no matter how many steps back in the tree the common origin lies. From each structure found in this way, further structures may be evolved. (This is indicated for only one case in Figure 6.)

In recent studies, Shah and Westerberg (1975) and Nishida et al. (1977) suggested a similar approach. In both these studies, however, a limited number of evolutionary rules were given which would help to produce a limited number of neighboring structures starting from a feasible base. The feasibility rules presented in this work (see Figures 2, 3, and 4), by contrast, are based on generally applicable thermodynamic principles and allow the user to find any feasible solution starting from any other feasible structure. Thus, while rules such as those suggested by Shah and Westerberg and by Nishida et al. could be called strategic rules, the rules presented in this paper could be called tactical rules, enabling any strategic policy to be implemented. The identification of such tactical feasibility rules seems appropriate, since strategic policies might be more easily formulated if available tactical options are more clearly appreciated. The networks used as starting structures do not necessarily have to lie on the optimum energy line (see, for example, Figure 5), but experience has shown that it is very convenient if they do. The problem of identifying an optimum energy starting point in the first place can always be solved by means of the TI method introduced in Part I.

It is evident that the ED method may be capable of identifying a greater number of promising network structures with less computational effort than the depth first strategy. What may be an even more valuable asset of the new method, however, is the fact that particular network characteristics can, within certain limits, be deliberately developed or suppressed. Thus, it is not necessary to carry out an exhaustive search through a defined part of the solution space (in the hope that one of the solutions obtained would turn out suitable in the light of whatever combination of criteria seems relevant) since it is possible to concentrate one's effort on the development of only those structures which appear to lead to suitable final networks. The approach taken in Figure 5 may serve as an example. The goal was to eliminate the heater, if possible, and the strategy adopted was simply to shift the heater through the network along that particular path which would bring it next to a cooler. The ED method, based on the concept of freedom as presented here, makes it possible to consistently pursue suitable strategies in particular situations. To substantiate these claims, further examples will now be solved.

4SP2, CYCLIC NETWORKS AND STREAM SPLITTING

Ponton and Donaldson (1974) suggested that cyclic arrangements of heat exchangers had to be considered to solve this problem satisfactorily. They presented a

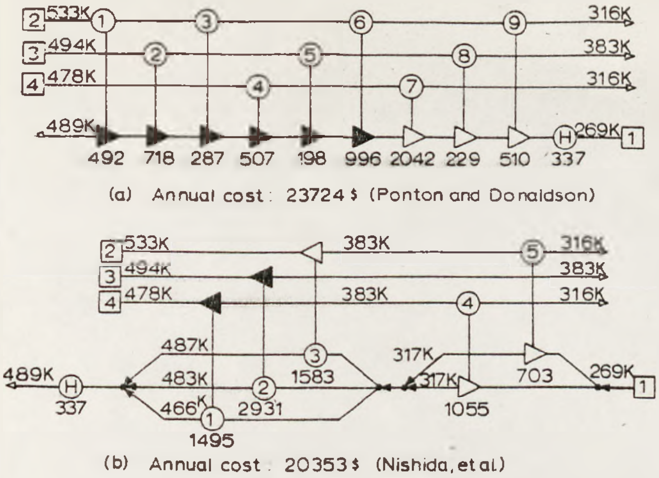


Fig. 7. Previous solutions for 4SP2. (a) Ponton's and Donaldson's solution. (b) Nishida, et al.'s solution.

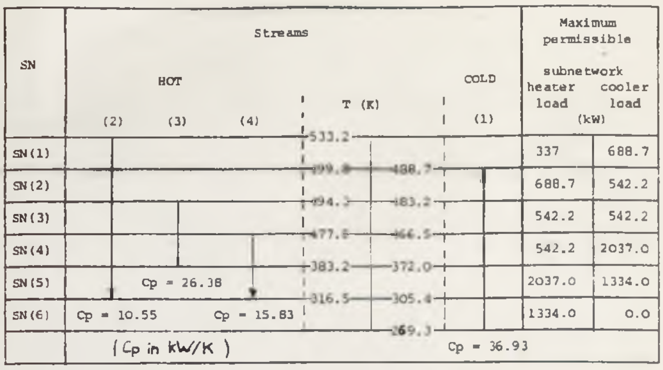
solution featuring four different matches between the same two streams and costing \$23 724/yr (see Figure 7*a*) and compared this to the annual cost of acyclic solutions which would be about three times as high. Nishida et al. (1977), however, showed that a further significant saving was possible if parallel splitting of stream No. 1 was considered and presented a solution costing \$20 353/yr (see Figure 7*b*). New solutions will now be sought by means of the TI method as described in Part I (to generate an optimal energy network) and the ED method (to produce satisfactory final solutions). First, solutions which do not incorporate stream splitting will be produced, and, afterwards, stream splitting will be considered.

A Cyclic Solution for 4SP2

In Figure 8, the problem table for 4SP2 is shown. (For a detailed explanation of the problem table, see Part I) From this table, the data for the problem are easily identified as well as the maximum permissible loads on heaters and coolers within each subnetwork. These loads must not be exceeded if the final network is to give maximum energy recovery. In Figure 9*a*, an array of subnetworks is shown which complies with this condition. In Figure 9*b*, four pairs of heaters and coolers have, according to the principles discussed in Part I, been arranged ready for the formation of new exchangers. In Figure 9*c*, these four matches have been formed, and neighboring units have been merged. Structure 9*c* is optimal from an energy recovery point of view.

At this point, the ED method can be employed to identify further solutions in the manner described in Figure 6. In the present case, an attempt was made to reduce the number of exchangers in the network as far as possible. This should lead to simpler topologies.

Looking for a chance to eliminate superfluous exchangers, one easily finds, by comparison of heat loads and freedoms, that exchanger No. 3 may be merged partly into exchanger No. 7 and partly into exchanger No. 10 (see dashed line in Figure 9*c*); match No. 3 may be visualized as consisting of heaters and coolers, and the freedoms of exchangers No. 4, 5, and 9 are big enough to allow a heater of the required size (for example, 128.95 kW) to be shifted on stream No. 1 towards the cold end (rule No 1). Also, the freedom of exchanger No. 7 is big enough to allow a merging of a heater and a cooler (loads: 35.17 kW) according to rule No. 9. The other two necessary operations (shift through match No. 8 according to rule No. 1 and merging into match No. 10 according to rule No. 10) do not decrease freedom, that is, must be possible.



SN	Streams HOT (2)	(3)	(4)	T (K)		COLD (1)	Maximum permissible subnetwork heater load (kW)	cooler load (kW)
				533.2				
SN(1)							337	688.7
				499.8	488.7			
SN(2)							688.7	542.2
				494.3	483.2			
SN(3)							542.2	542.2
				477.6	466.5			
SN(4)							542.2	2037.0
				383.2	372.0			
SN(5)		Cp = 26.38					2037.0	1334.0
				316.5	305.4			
SN(6)	Cp = 10.55		Cp = 15.83				1334.0	0.0
					269.3			
	(Cp in kW/K)					Cp = 36.93		

Fig. 8. Problem table for 4SP2.

Once match No. 3 has been eliminated, matches No. 8 and No. 4 become neighbors and can be merged. A network results which consists of six exchangers and one heater (Figure 9*d*). Its annual cost is \$21 654. This compares favorably with the cost of the solution found by Ponton and Donaldson which is \$23 724/yr.

Further reductions in the number of exchangers have not been found. Six exchangers appear to be the minimum number required if stream splitting is not considered. There are, however, two other topologies featuring six exchangers, and they, too, are easily identified by means of simple shifting operations such as demonstrated in Figure 9*c*. The structures in question are shown elsewhere (Linnhoff, 1978).

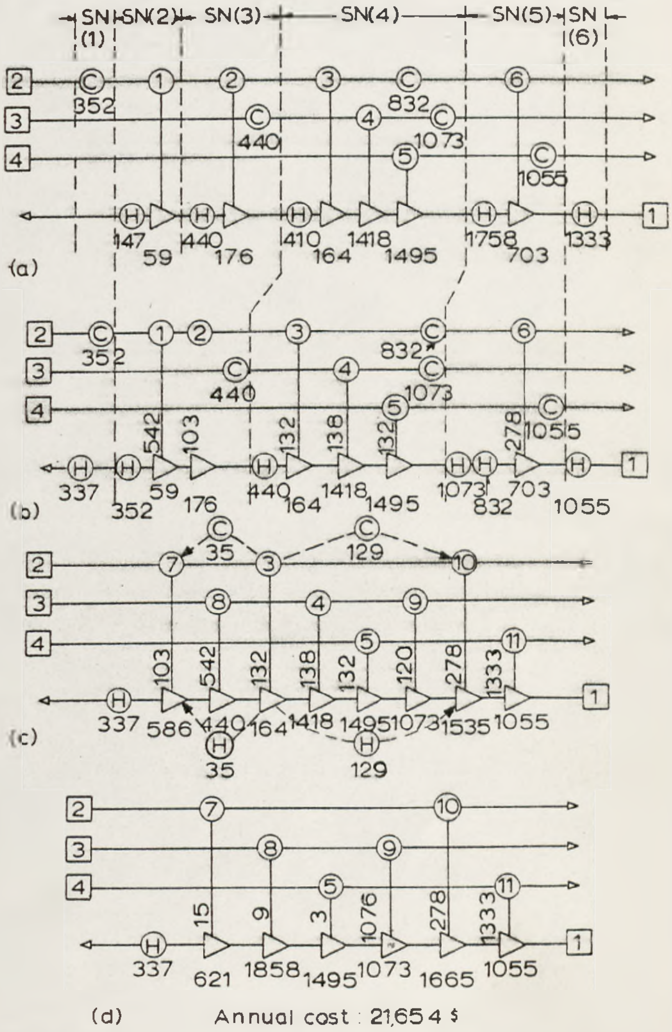
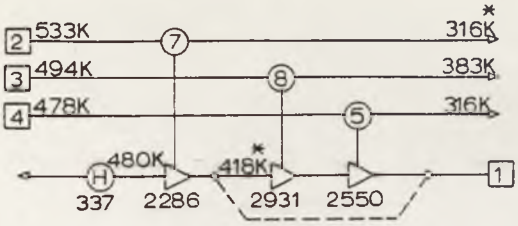
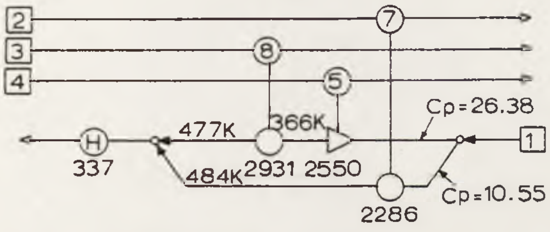


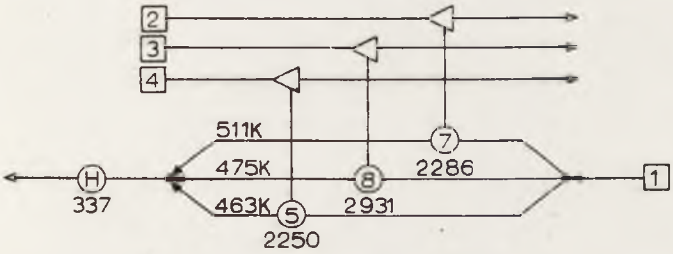
Fig. 9. Complete synthesis for 4SP2. (a) Array of subnetworks. (b) Heaters and coolers ready for formation of new exchangers. (c) Eliminating match No. 3. (d) Final solution without stream splitting.



(a) infeasible structure



(b) Annual cost: 19854 $



(c) Annual cost: 19571 $

Fig. 10. Split stream solutions for 4SP2.

Solutions for 4SP2 Incorporating Stream Splitting

As Nishida et al. (1977) pointed out, costs of networks are likely to decrease with decreasing number of exchangers, and since their solution for 4SP2 incorporates only five exchangers, as compared to the six exchangers required, for example, in structure 9*d*, it is significantly cheaper.

On the other hand, it is quite clear that with three hot streams and one cold stream, there need only be three distinct heat exchange tasks between the process streams. Attempts to find structures which use three exchangers proved successful.

In Figure 10*a*, an infeasible structure is shown which has been obtained from structure 9*d* by simply merging matches No. 10 into No. 7, No. 9 into No. 8, and No. 11 into No. 5. The resulting matches No. 8 and No. 5 are feasible, but in match No. 7, the temperature difference at the cold end has become infeasible, however, this problem can easily be solved by splitting stream No. 1 in the fashion indicated in Figure 10. If a bypass is introduced around matches No. 8 and No. 5 (see dashed line in Figure 10*a*), match No. 7 may be shifted into the bypass which will ensure that the temperature difference at its cold end becomes feasible. To ensure that its temperature difference at the hot end does not, in turn, become too small, the heat capacity flow rate chosen for the bypass must not be chosen below a certain threshold value. Since

$$Cp_{\text{bypass}} \geq \frac{\text{Head load in bypass}}{\text{Maximum temperature rise in bypass}} \qquad (2)$$

the minimum value is found to be 9.041 kW/°K. Similarly, any figure below Cp = 25.621 kW/°K for the remaining branch of stream No. 1 would lead to a violation of the $\Delta T_{\min}$ constraint in match No. 8. Thus, the total heat capacity flow rate of both branches of stream No. 1 in Figure 10*b* must not lie below 34.663 kW/°K. This condition is compatible with the actual heat capacity flow rate of stream No. 1 (that is, 36.926 kW/°K) and leaves some room for further refinement of exchanger areas.

The two values adopted in Figure 10*b* (that is, 10.55 and 26.375 kW/°K) have been chosen purely on grounds of computational convenience. The resulting network is, with $19 571/yr, about $500/yr cheaper than Nishida et al.'s (1977) solution.

To reduce the costs further, stream No. 1 can be split twice, which leads to yet another topology with only three exchangers, see Figure 10*c*. The way in which structure 10*c* may be found from either structure 10*a* or 10*b* is entirely analogous to the way in which structure 10*b* was evolved from 10*a*. The cost of structure 10*c* is $19 567/yr. A short search makes it clear that structures 10*b* and 10*c* are the only two topologies which exist for 4SP2 with only three exchangers. However, both topologies allow considerable variation of the heat capacity flow rates in the different branches of stream No. 1, and the cost for both solutions could still be slightly improved by optimizing the network with respect to these parameters.

According to the cost parameters as given by Pho and Lapidus (1973), structure 10*c* is about 4% cheaper than Nishida et al.'s solution. In practical terms, however, the costs of additional valve gear and pipe fittings would probably be quite sensitive to stream splitting. On these grounds, it is possible that structure 10*b* might be the most attractive solution for the problem.

4SP1, THE MINIMUM NUMBER OF UNITS AND FLEXIBILITY IN DESIGN

Problem 4SP1 was first presented by Lee et al. (1970) and has been solved several times in the literature. Siirola (1974) presented the optimum solution. The problem will now be solved by means of the TI and the ED methods. Firstly, this allows a good comparison of these methods with other methods. Secondly, it pro-

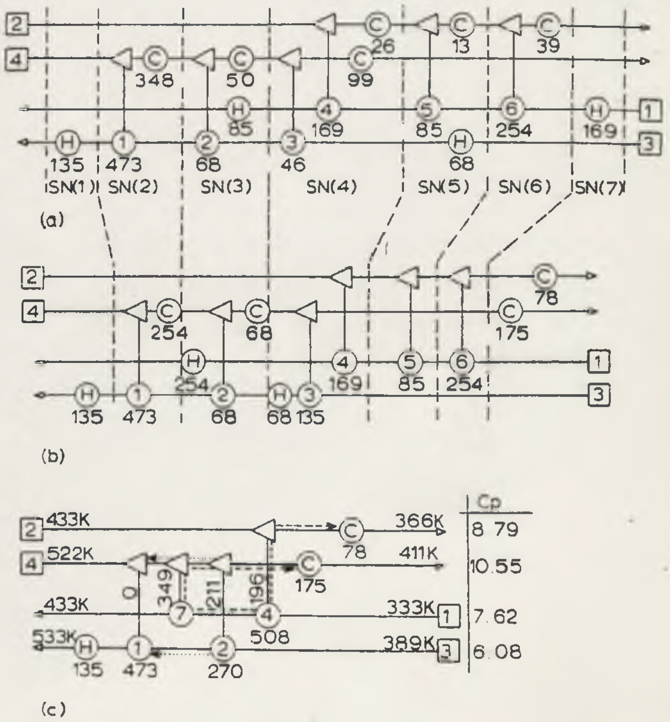
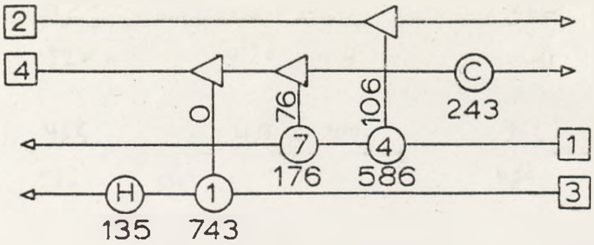
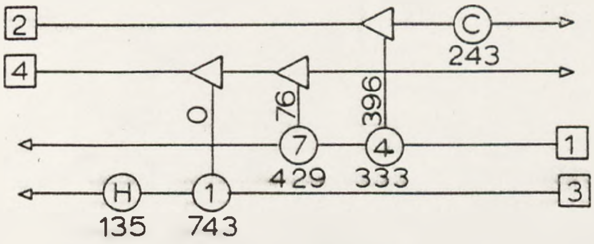


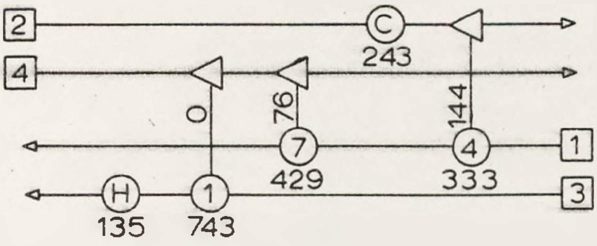
Fig. 11. Synthesis of energy optimal network for 4SP1. (a) Array of subnetworks. (b) Subnetworks after shifting of heaters and coolers. (c) Preliminary network (with optimum energy recovery).



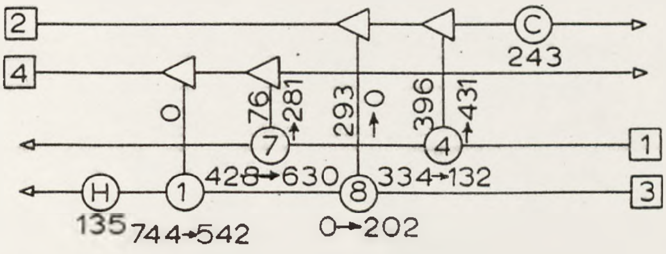
(a) Annual cost: 13685 $



(b) Annual cost: 13587 $



(c) Annual cost: 13679 $



(d) Annual cost: 13587 $ →13909 $

Fig. 12. Four final solutions for 4SP1.

vides a suitable basis for the discussion of the importance of the number of units on the flexibility of a network.

Solving 4SP1

In Figure 11*a*, an array of subnetworks is presented for 4SP1. In Figure 11*b*, two pairs of heaters and coolers are ready for merging, and in Figure 11*c*, the new exchangers have been formed, and neighboring units have been merged. The resulting network shows maximum energy recovery. The problem data for 4SP1 can easily be deduced from Figure 11*c*.

To reduce, again, the number of exchangers as far as possible, there are two obvious possibilities in Figure 11*c*. Firstly, exchanger No. 2 may be shifted through exchanger No. 7 (the freedom of match No. 7 is big enough) so that it can be merged with match No. 1. Secondly, the two coolers may be merged into one unit, either on stream No. 2 or on stream No. 4. These two changes are indicated in Figure 11*c* by means of dotted and dashed lines, respectively. Two networks emerge (see Figures 12*a* and 12*b*) with three exchangers, one cooler, and one heater, that is, five pieces of equipment. From the freedoms and heat loads in structure 12*b*, it is evident that the cooler on stream No. 2 may also be situated on the hot side of match No. 4. The third (and last) structure with no more than five pieces of equipment is found, see Figure 12*c*.

The Minimum Number of Units

Rathore and Powers (1975) concluded that the three structures *a*, *b*, and *c* in Figure 12 are the three cheapest solutions. This is understandable, since they are the only three structures found with no more than five units; as mentioned above, networks involving fewer but larger units tend to cost less. Thus, it would be a worthwhile approach, in general, to try and identify the minimum number of units required to solve a problem and to try and generate networks which use this number.

Hohmann (1971) proposed that a lower bound on the number of units be defined by the following rule:

> The minimum number of units is nearly always one less than the number of streams and services required in the problem (3).

Figure 13 illustrates for the case of 4SP1 that the minimum number is five. The reservation nearly always has to be made since it is not impossible that heat loads of a hot and a cold stream are equal to each other (or to the total load on coolers or heaters), or residuals turn out to be equal to each other or to original heat loads. In any one of these situations, the minimum number of units is one less than that suggested in expression (3).

However, all these considerations are just based on the compatibility of heat loads and ignore temperatures. Evidently, both temperatures and heat capacity flow rates define whether or not a problem can be solved with the minimum number of units. Particular combinations of data might make it necessary to resort to cyclic topologies or to parallel stream splitting, and, contrary to the comments made by Hohmann (1971), the minimum number of units may not always be achievable.

Flexible Designs

As is self-evident from Figure 13, solutions using the minimum number of units show fixed exchanger loads; exchanger sizes can only be varied, to a very limited

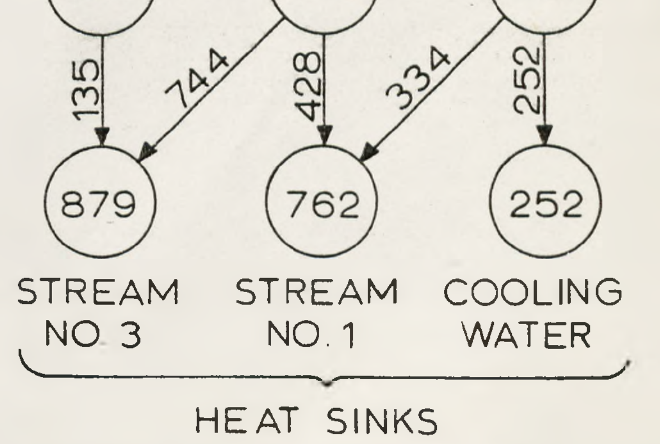
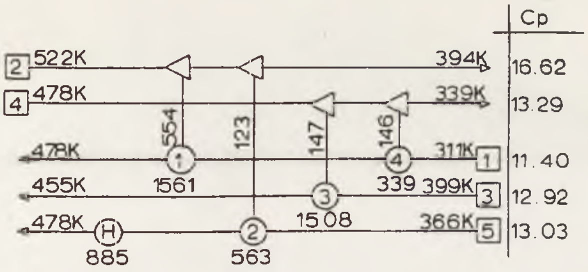
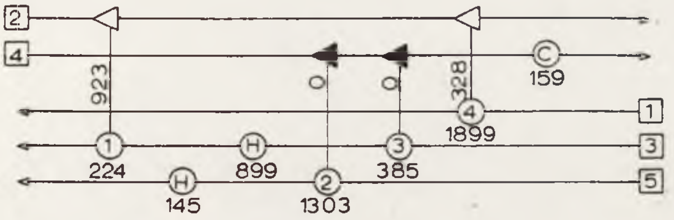


Fig. 13. Finding the minimum number of units. All figures apply for 4SP1. The figures for "utility steam" and "cooling water" are evaluated by means of the problem table and the assumption of maximum energy recovery.



(a) Annual cost : 38519 $



(b) Annual cost : 50341 $

Fig. 14. Two solutions for 5SP1. (a) Near-optimum-cost network. (b) Solution without a match between streams No. 4 and No. 1.

extent, by altering the sequence of the matches (compare, for example, structures 12*b* and 12*c*).

In Figure 12*d*, a solution is shown for 4SP1 with six pieces of equipment rather than five. Many such solutions can be made up by introducing additional matches, one at a time, into any of the three solutions with only five units. (Rathore and Powers, for example, have shown three other networks of this type.) The interesting common feature of all such networks is the fact that they allow variation of certain design and/or operating parameters within certain ranges. This has been indicated in Figure 12*d* by noting the full possible range for heat loads, as well as for freedoms. Rathore and Powers quote solutions of this type with fixed values found at one extreme end of the feasible range. Similarly, other previous workers have often presented potentially flexible solutions, without explicitly noting flexibility. Dealing with problems like control behavior, step changes in available size of equipment, etc., such flexibility will be a valuable asset of a design. With the rules for shifting and merging as introduced in Figures 2, 3, and 4, the range of flexibility is easily identified; in Figure 12*d*, for example, the range is limited by the heat load of match No. 8 at one end and by the freedom of match No. 8 at the other end. As far as costs are concerned, such flexible designs can be very attractive, too; structure 12*d* has been derived from the overall cheapest solution (that is, structure 12*b*), and it can be cheaper than either of the other two networks with the minimum number of units.

5SP1, AVOIDING UNDESIRABLE MATCHES

Optimum Cost Solutions

First presented by Masso and Rudd (1969), 5SP1 has been solved by many workers who all proposed the same best solution, costing $38 263/yr (see, for example, Pho and Lapidus, 1973). An application of the TI and ED methods to the problem confirmed this solution and revealed four others, costing between $38 278 and $38 550/yr (see Linnhoff, 1978). One of these networks is shown in Figure 14*a*. Each of these five solutions features the minimum number of units [that is, five, according to expression (3)], and a great variety of flexible solutions, featuring six pieces of equipment, may be made up in the way demonstrated in Figure 12*d*. All of these would, in practical terms, be considered optimal. Nishida et al. (1977), who considered stream splitting, presented a new optimum cost solution costing $38 219/yr.[*] This solution will be shown later to be closely related to the structure shown in Figure 14*a*, and an examination of this relationship will lead to an improvement on Nishida, et al.'s solution.

Assuming a Safety Constraint

In Figure 14*b*, however, a solution is shown to 5SP1 which costs $50 341/yr and consists of seven pieces of equipment. The interesting feature of this solution is the fact that it does not incorporate a match between the two streams No. 4 and No. 1. Considering the hot stream target temperatures in the problem as well as the cold stream supply temperatures, it becomes clear that the installation of a cooler cannot be avoided unless streams No. 4 and No. 1 are matched against each other at the cold end. Accordingly, all near optimum cost solutions mentioned above incorporate such a match. If, for safety reasons, this match cannot be allowed, the solution of the problem becomes somewhat more difficult. One possible approach would be to use the TI method, avoiding the use of the forbidden type of match already in the subnetworks. Another approach would be to take any of the original low cost solutions, replace the forbidden match by a cooler and a heater, and try to form new exchangers from this heater and cooler (after shifting and merging) to as large an extent as possible. A variety of solutions will be obtained. The one shown in Figure 14*b* is not proposed as the definite cost optimum, but it has been chosen because it does not feature exchangers of unrealistic size as do other solutions which are marginally cheaper.

Relevance of Costing Equations

Before we discuss solutions to the other problems, it is worth pointing out an important shortcoming of the usual 0.6 power of area costing equation for heat transfer area as given by Pho and Lapidus. It is well known that, according to this equation, total surface area costs least if it is distributed over as few separate exchangers as possible, see, for example, Hohmann (1971). Another consequence of this equation is the prediction that a given overall surface area will cost least if distributed as unevenly as possible over a given number of separate exchangers. Compare, for example, two exchangers, both of surface area a, with two exchangers having surface areas $a + b$ and $a - b$, respectively:

$$2a^{0.6} > (a + b)^{0.6} + (a - b)^{0.6} \tag{4}$$

This leads to a situation where optimum cost networks are proposed which will show maximum possible variation in exchanger size. In practice, the optimum variation of exchanger sizes will be less since the installed cost of small units tends to a constant value. In the present context, however, it was thought desirable to make strict comparisons between the results obtained here and those found by previous workers. For this reason, optimum cost solutions were synthesized according to the original equation.

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[*] Their own pricing is $38 713/yr for their own solution and $38 762/yr for the single stream optimum structure. Nishida et al. used 260 hr/yr equipment downtime and 1 785.11 kJ/kg (767.5 Btu/lb) as latent heat of steam, compared to 380 hr/yr and 1 786.27 kJ/kg (768 Btu/lb) used by Pho and Lapidus (1973), McGalliard and Westerberg (1972), and this paper.

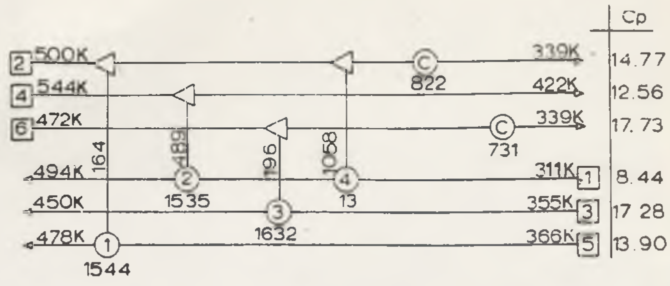
6SP1, 7SP2, AND 10SP1, FURTHER DEMONSTRATIONS OF THE ED METHOD

6SP1 was first presented by Lee et al. (1970). They found a solution which they claimed costs $35 110. However, as pointed out by Nishida et al. (1977), this figure is based on the same type of error as that of Pho and Lapidus in the case of 7SP1 (see above). The true cost of Lee et al.'s solution is $37 331/yr. Hohmann (1971) found a solution costing $35 010; McGalliard and Westerberg (1972) found one costing $35 780/yr, and Pho and Lapidus (1973) found one costing $35 657/yr. Nishida et al. showed the same solution as Hohmann. In this work, Hohmann's solution was confirmed as the optimum, see Figure 15*a*. With the TI and the ED methods, the network was found by deliberately creating a very small exchanger (that is, match No. 4) and, at the same time, by using the minimum number of units. In other words, a search through the solution space was found unnecessary to find this optimum cost network since the two features which would result in low cost (that is, minimum number of units together with extreme differences in exchanger size) were easily developed by means of the ED method. Another network, found by means of the same strategy, exhibits an annual cost of $35 017/yr (see Linnhoff, 1978).

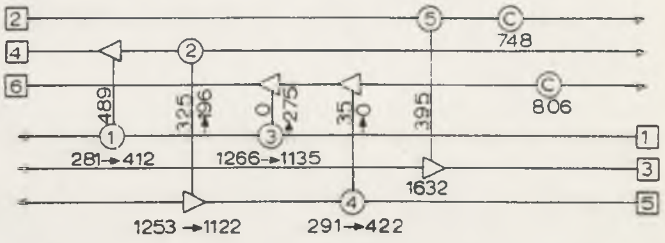
However, both these networks feature differences in exchanger sizes which may not be practical; for the optimum cost structure, the ratio of largest transfer area to smallest transfer area is about 440. For this reason, an alternative solution for 6SP1 is shown in Figure 15*b*. It is a flexible structure, incorporating one piece of equipment more than strictly necessary and exhibiting a ratio of largest to smallest transfer area of between 8.0 and 5.5. Over most of the range of variation, the cost is still within 2% of the optimum. For these reasons, structure 15*b* is considered to be quite an attractive solution for 6SP1. It has been found by shifting heaters and coolers in such a way as to create a certain amount of difference in exchanger sizes to reduce cost but with practical limits in mind.

Problem 7SP2 was presented by Masso and Rudd (1969) as one for which the combinatorial possibilities are overwhelming. The heat recovery situation is very easy, and there are many feasible structures which use the minimum number of units and achieve maximum energy recovery. Masso and Rudd presented a solution costing $28 628/yr. Pho and Lapidus claimed to have found a solution costing $28 518/yr, but the structure they presented is not feasible since at least two streams miss their target temperatures. In Figure 11*a*, a new optimum cost solution for 7SP2 is shown which costs $28 258/yr. It was found by means of the same strategy as described above.

The most complex example from the literature is 10SP1. It was presented by Pho and Lapidus as a problem which would make it necessary, when using conventional synthesis algorithms, to approach the practical limits which exist for computer store and time. They found a solution costing $44 158/yr. Nishida et al. (1977) found a solution costing $43 984/yr. Figure 16*b* shows a solution costing $43 934/yr. This new optimum was found by means of the same strategy as employed when finding the optimum cost solutions for 6SP1 and 7SP2. It can, incidentally, be evolved in only a few steps from Pho and Lapidus's solution.

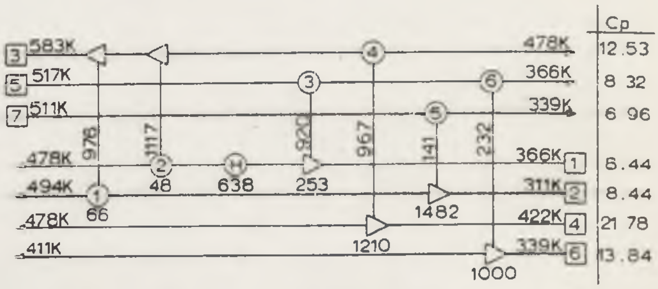


(a) Annual cost: 35010$ (Hohmann)

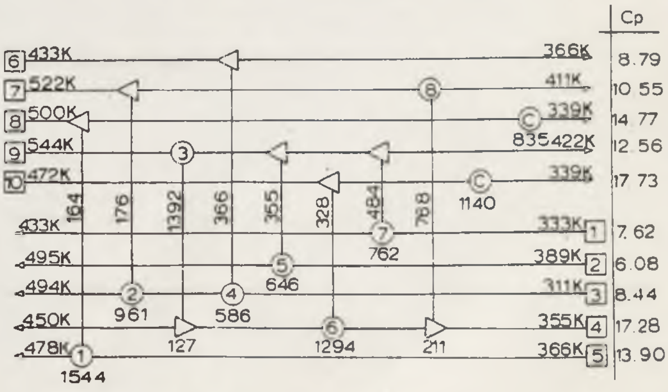


(b) Annual cost: 35468$→35672 $

Fig. 15. Two solutions for 6SP1. (a) Optimum cost solution. (b) Flexible structure of near optimum cost.



(a) 7SP2 Annual cost 28258 $



(b) 10SP1 Annual cost 43934 $

Fig. 16. Two new optimum cost solutions. (a) For 7SP2. (b) For 10SP1.

Practical Solution by Relaxing Problem Specifications

In Figure 17, a solution for 10SP1 is shown in which stream No. 3 misses its target temperature by 1.53°C. Owing to this slight relaxation of the problem data, it has been possible to design a network which consists of only nine pieces of equipment. (This is one less than the minimum number of units which would normally be necessary; the heat loads of streams No. 9 and No. 3 have, owing to the slight change in target temperature, become equal.) From a theoretical point of view, this solution is not of strictly optimal cost because the failure to recover 12.9 kW of heat results in an increase in the amount of cooling water required. However, the structure is less complex than any one of the correct solutions, and this will almost certainly mean lower costs for piping. In an industrial situation, structure 17 would probably warrant further investigation.

DISCUSSION

Cyclic Topologies and Parallel Stream Splitting

With the exception of 4SP2, all examples dealt with in this paper have been solved to give maximum energy recovery using the minimum number of units without the introduction of cyclic structures or parallel stream splitting. In the case of 4SP2, a cyclic topology was found necessary to achieve maximum energy recovery (see, for example, Figure 9*d*), while parallel stream splitting was found necessary to reduce the number of units to the minimum number (see, for example, Figure 10*c*). Both techniques, the use of more exchangers than suggested by expression (3) in an unsplit network, as well as parallel splitting of streams were seen to be powerful means of securing maximum energy recovery. Beyond this, the parallel splitting of streams sometimes also allows the use of the minimum number of units at the same time. There is no guarantee, however, that stream splitting solutions will always enable the minimum number of units to be realized (Linnhoff, 1978).

Stream Splitting and the Minimum Number of Units

As Ponton and Donaldson (1974) and Nishida et al. (1977) pointed out, the main difficulty in problem 4SP2 is the fact that the heat capacity flow rate of the cold stream is excessively large as compared to the three hot streams. This makes it impossible to recover all heat in a simple acyclic network. On the other hand, it is precisely the fact that stream No. 1 is excessively large, which makes such simple stream splitting solutions possible as shown in Figure 10. When evolving these structures, minimum figures were identified for the heat capacity flow rates of the different branches of stream No. 1 [see Equation (2)], and it is only due to the fact that the actual Cp of stream No. 1 exceeds the sum of these minimum figures that solutions 10*b* and 10*c* are feasible.

In the two test cases of Part I, a large and a small hot stream are to be exchanged with two cold streams of intermediate heat capacity flow rates. This situation may give rise to thermodynamic difficulties just as great as the rather obvious situation found in 4SP2, and, when coupled with unfavorable temperatures, simple structures will not allow maximum energy recovery (see solutions for test case No. 2 in Part I). As documented elsewhere (Linnhoff, 1978), the thermodynamic constraints in the two test cases are such that even stream splitting solutions have to consist of at least six pieces of equipment [that is, one more than the minimum according to expression (3)].

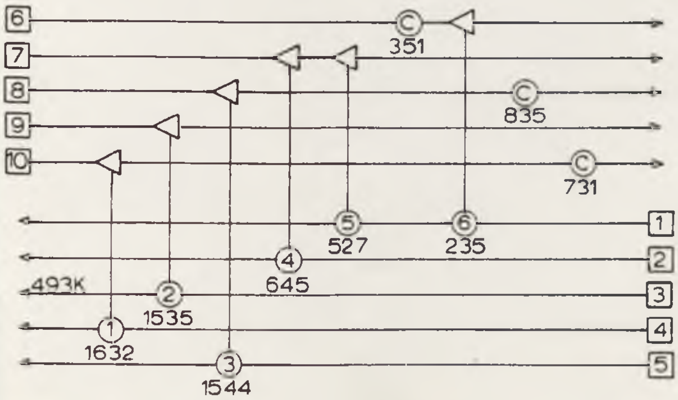


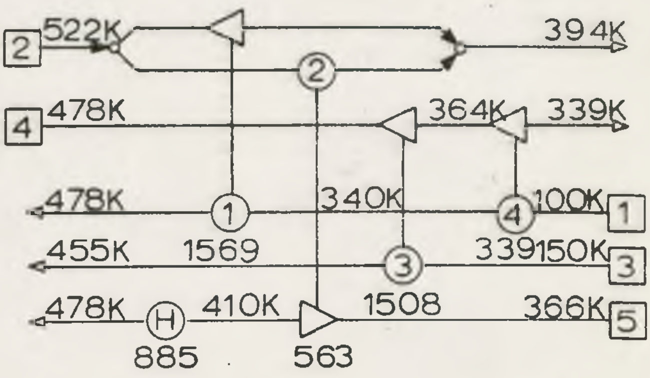
Fig. 17. Practical solution for 10SP1.

Stream Splitting and Flexibility

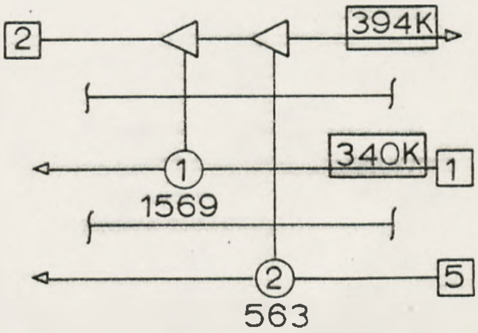
Last, but not least, the potential benefits of cyclic arrangements or stream splitting should be discussed even where maximum energy recovery can be obtained by simple unsplit solutions.

The introduction of stream splitting into any such structure can be considered by means of Figure 18. Nishida et al.'s optimum cost solution for 5SP1 is shown in Figure 18*a*. Figure 18*b*, taken from Figure 14*a*, shows that the only difference between the two structures is, in fact, the arrangement of exchangers. In Figure 18*b*, the two temperatures which will always show whether the introduction of stream splitting is possible are shown boxed; if the hot stream exit temperature of the second match is higher (by at least $\Delta T_{\min}$) than the cold stream entry temperature of the first match, the transition from the single stream to the split arrangement is definitely feasible. (An equivalent argument is easily formulated for the case of two matches which are connected in series to a cold stream.)

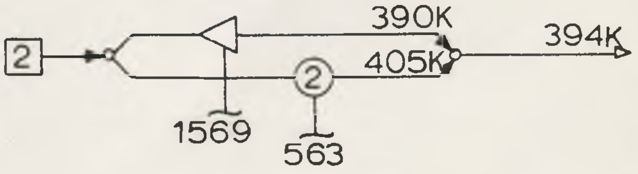
However, the transition may be feasible even if the two temperatures in question do not satisfy this test.



(a) Annual cost : 38219 $
(Nishida, et al)



(b) Matches No1 and No. 2 in sequence.
Annual cost : 38519 $



(c) Making use of flexibility
Annual cost : 38207 $

Fig. 18. Stream splitting for flexibility. (a) Nishida, et al.'s optimum cost solution for 5SP1. (b) Taken from Figure 14a. (c) Choice of heat capacity flowrates in the branches of stream No. 1 allows varying exchanger sizes.

After all, once one has introduced stream splitting, there is flexibility in the choice of one of the heat capacity flow rates of the newly produced branches of the split stream; the temperatures before the mixing point in Figure 18*a* can thus be adjusted appropriately. This extra degree of choice is not considered by Nishida et al. when proposing structure 18*a*. In Figure 18*c*, different values are given for the temperatures in question (arising from a different choice of heat capacity flow rates). The result is a marginal improvement in cost.

The important aspect of Figure 18*c*, however, is not the fact that a new optimum has been found but rather that an alternative way has been identified of introducing flexibility into network design. From a comparison of matches No. 1 and No. 2 in Figures 18*a* and 18*b*, it is clear that substantial differences in cost are unlikely to occur. The number of units remains unchanged and the changes in surface area will always be beneficial for one of the exchangers and detrimental for the other. However, in terms of flexibility, there is a distinct advantage. The surface areas of the two matches may be varied, within a certain range, just as in the case of flexible solutions produced by introducing additional items of equipment into a network. The interesting difference is the fact that the number of units need not be increased if flexibility is introduced by means of stream splitting. It appears that even in cases where stream splitting is not required to obtain maximum energy recovery, its main attraction might be in promoting flexibility. The feasible range over which parameters may be varied is easily established by an appropriate application of Equation (2).

The ED Method and Heuristic Based Evolutionary Rules

It is, perhaps, worth stressing once more that the ED method as introduced in this paper represents a means by which heuristic rules and strategies for the evolutionary improvement of heat exchanger networks may be implemented, but that it is itself based on elementary thermodynamics, that is, is of general validity. Although a number of apparently suitable heuristic strategies were formulated in the course of solving the various examples, the main contribution of this work is thought to be the fact that a theoretically based method has been found which greatly helps the rapid formulation of whatever strategy is suitable for a given type of synthesis task. In other words, the potential power which appears to be offered by the ED method to obtain increased insight into particular future problems might be more valuable an asset to the design engineer than heuristic rules based on limited past experience or on simplified cost equations.

Accordingly, no attempts have been made in this work to try, for example, to formulate detailed evolutionary rules which would invariably lead to a reduction of the number of units until the minimum number for any given network is reached. Such rules have been given by Nishida, et al. (1977), and it has been conceded that they might, sometimes, fail. With the ED method, it is easy to see why they will work in most cases, but it is just as easy to see when and why they will fail. What is more important is that if they fail, it is generally still easy to see by what other means the number of units may be reduced. (Compare Nishida et al.'s solution for 4SP2, that is, structure 7*b* to structure 10*c*.) Similarly, the same authors have given theoretical guidance as to where in a network utility heaters and coolers ought to be placed. With the ED method, such guidance is not required from a thermodynamic point of view.

On the other hand, the findings discussed in this work with regard to number of units, flexibility of design, stream splitting, and cyclic structures are probably of quite general relevance, and, based on these findings, the following recommendations are given.

General Recommendations

The following might be a promising approach to heat exchanger network design:

1. Identify the minimum number of units from expression (3), using utilities predicted by the problem table.
2. Synthesize a maximum energy recovery network by means of TI method and reduce number of units by means of ED method. (If thermodynamic constraints exist which make it difficult to approach the minimum number of units, stream splitting should be considered).
3. When the network is sufficiently close to a minimum number of units, promote features of individual interest and suppress unwanted characteristics.
4. With present pricing parameters or those used here for comparability with past work, maximum energy recovery is almost certain to be a feature of interest. However, different pricing parameters might make it worthwhile examining structures which offer lower capital costs with less than maximum energy recovery. In such a case, the strategy adopted should be to first examine those structures, if they exist, which feature fewer units than are found necessary to achieve optimum energy recovery. In other words, the guideline of the final stages of the synthesis should be the number of units rather than the degree of departure from maximum energy recovery. As an example of this strategy, see the solutions to test case No. 2 in Part I.

ACKNOWLEDGMENT

Bodo Linnhoff gratefully acknowledges the financial support from The British Council which has made this work possible. The authors also wish to acknowledge the helpful comments of Dr. J. J. Siirola.

NOTATION

All numerical values quoted are based on calculations using original data in Imperial units. Inevitable rounding on conversion to S.I. units may lead to small discrepancies. Original data can be supplied by the authors.

A = heat load of a cooler or a heater to be shifted or merged, kW
a, b = given sizes of heat transfer surface area, m^2
Cp = heat capacity flow rate, kW/°K
CPL = larger Cp of the two streams matched in an exchanger, kW/°K
CPS = smaller Cp of the two streams matched in an exchanger, kW/°K
F = freedom of a heat exchanger, kW
n = number of separate exchangers
$SN(K)$ = K^{th} subnetwork
T_S = supply temperature, °K
T_T = target temperature, °K
z = number of streams in a problem
$\Delta T_{\min}$ = minimum temperature difference within heat exchangers, °K
ΔTS = smallest actual temperature difference within heat exchangers, °K

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Manuscript received March 17, 1977; revision received February 21, and accepted February 23, 1978.

On-Line Gain Identification of Flow Processes with Application to Adaptive pH Control

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A simple and practical method is presented for the control of first-order flow processes with time varying gain and a pure delay in the measurement of the control variable. It involves on-line identification of the process gain and a subsequent adjustment of the controller parameter. The method is well suited for applications in the chemical process industries where high frequency fluctuations in the process gain are not generally expected. It is tested on a computer simulated process as well as experimentally by application to a continuous stirred-tank neutralization process involving *p*H control, where buffer concentration in the feed varies with time. There is a potential for the application of this method to an industrial process such as wastewater treatment.

SCOPE

Processes whose gains vary widely during operation cannot be controlled satisfactorily by conventional fixed-parameter controllers. A solution to such a problem is to identify the process gain on-line and adjust the controller parameter suitably. This paper presents a method of on-line gain identification and control that applies to first-order flow processes with time-varying gain. An identification system (also of first order) in series with the process being controlled is perturbed by a signal consisting of a variable frequency, constant amplitude, rectangular wave to generate discrete estimates of the process gain. The identification is based on the fact that for a constant input to the identification system, the time taken for the identification system output to go from one preselected value to another is inversely proportional to the gain. The gain identification is achieved without disturbing the normal operation of the plant. The method is simpler and more easily implemented than the sinusoidal perturbation method proposed by Mellichamp et al. (1966).

The control strategy is based on maintaining a constant loop gain so as to maintain the same degree of stability. Thus, employing a two-mode (PI) or three-mode (PID) controller, the controller gain is self-adjusted as the process gain varies such that their product remains constant. All on-line computation, data storage, and control are handled by a moderate size analog computer with patchable logic.

The proposed method of identification and control is first tested on a computer-simulated process and then applied experimentally to a *p*H control system involving continuous stirred-tank neutralization of an acidic stream containing monobasic phosphoric acid as the buffer species by potassium hydroxide. This system can be modeled as a first-order process with time-varying gain. The variation in the process gain is caused by a change in the concentration of the buffer species in the feed stream. The perturbation input to the identification system consists of alternate flow of an acid (nitric acid) and a base (potassium hydroxide) at constant flow rate.

Process gain changes as large as 10 to 1 are introduced.

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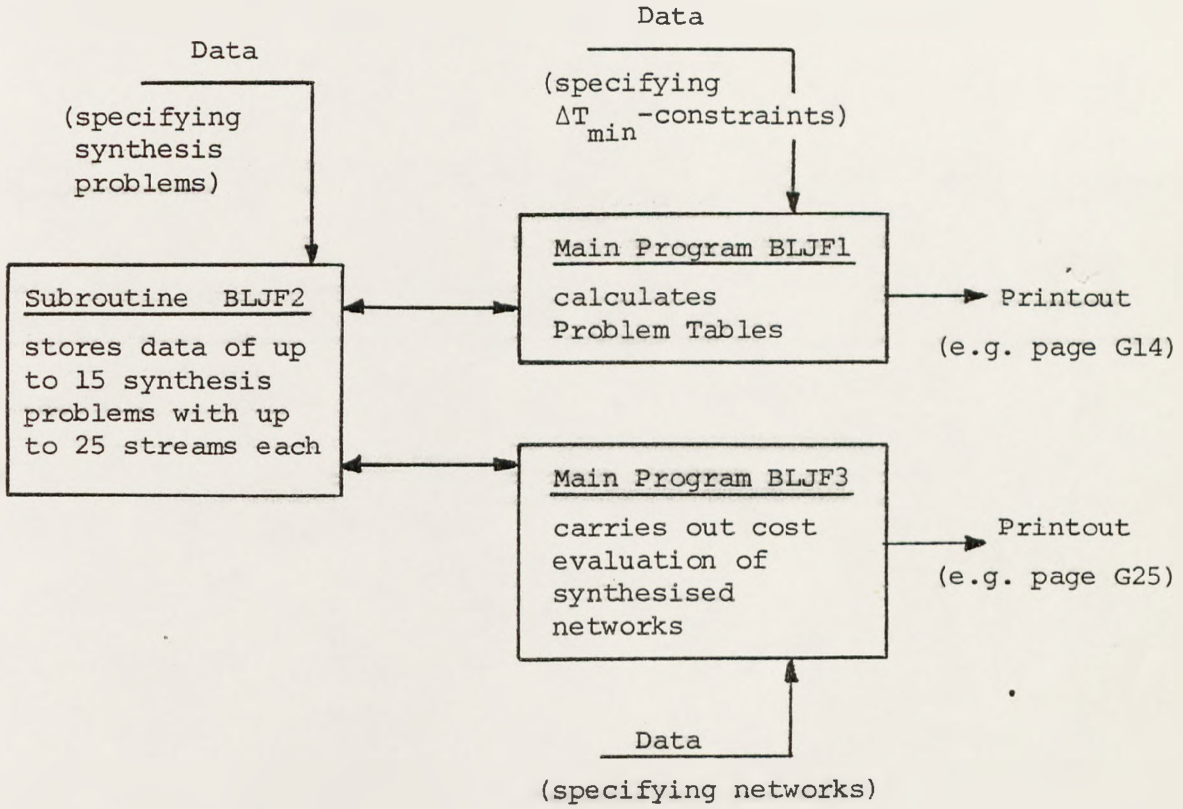
0001-1541-78-1133-0654-$01.35.

APPENDIX G

COMPUTER PROGRAMS

Three short computer programs are presented in this appendix which relate to the work on heat exchanger network synthesis. Two of these programs, BLJF1 and BLJF3, are independent main line programs whereas the third one, BLJF2, is a subroutine required by both main line programs, see sketch below:



By means of BLJF1, Problem Tables may be evaluated in accordance with the principles described in Appendix F. As outlined there, it is possible to base a Problem Table on ΔT_{min}-constraints which are individual for each stream and BLJF1 incorporates this facility.

By means of BLJF3, networks may be evaluated. The program has, however, been written with the option in mind of forming part of a future synthesis algorithm. Thus, the data input is adapted to the synthesis and, apart from costs, the program evaluates Freedoms. Also, the surface areas of heaters, coolers and exchangers are printed out to allow the user to judge whether or not exchanger sizes are realistic.

Short descriptions are given below of how these programs function, along with listings. Also, detailed descriptions are given of the data input and samples are presented of the printouts.

G.1 THE SUBROUTINE BLJF2

A listing is given on pages G3 and G4. As is evident from the listing, the two variables "KR" and "KP" (which are assigned values in the main line program) define whether the subroutine is used for storing data, or for printing a problem identification, or for both.

If "KR" is positive, BLJF2 reads up to 15 different sets of data, each of which contains the particulars of an individual synthesis problem. (The structure of these individual data sets is explained in detail on pages G5 and G6). Then, BLJF2 classifies each stream as either hot or cold and stores the total information thus collected in COMMON-arrays.

If "KP" is positive, BLJF2 produces one line of printout to identify a particular synthesis problem. This line appears in the printouts of BLJF1 and BLJF3 in the upper left hand corner. The numbers which were chosen as identification numbers for the synthesis problems dealt with in Appendix F are evident from the last part of the listing of BLJF2 : they are identical with the FORMAT-statement numbers used there.

Listing for BLJF2

```
// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS

      SUBROUTINE BLJF2(KR,KP)

      COMMON THOT(15,25),TCOLD(15,25),CP(15,25),NCOSR(15,25)
      COMMON STPR(15)
      COMMON NSTR(15),BTUST(15),TSTM(15),DUTY(15),CSTM(15),CWAT(15)
      COMMON UH(15),UEX(15),UC(15),COEF(15),EXP(15),TWIN(15),TWOUT(15)
      COMMON NYR(15)

C     THIS SUBROUTINE READS AND STORES DATA OF UP TO 15 SYNTHESIS
C     PROBLEMS WITH UP TO 25 STREAMS EACH.

      IF(KR) 199,199,200

  200 READ(2) NSET
      DO 199 LMN = 1,NSET
      READ(2) IDPR,NSTRM
      K = IDPR
      NSTR(K) = NSTRM
      READ(2) STPR(K),DUTY(K)
      IF(STPR(K)-962.5) 192,194,195
  192 IF(STPR(K)-450.) 195,193,195
  193 BTUST(K)=768.
      TSTM(K)=456.
      GO TO 196
  194 BTUST(K)=657.
      TSTM(K)=540.
      GO TO 196
  195 BTUST(K)=1.
      TSTM(K)=1.
  196 READ(2) CSTM(K),CWAT(K),UH(K),UEX(K),UC(K),COEF(K),EXP(K),TWIN(K),
     ITWOUT(K),NYR(K)
      DO 199 J = 1,NSTRM
      READ(2) IDSTR,SPH,TIN,TOUT
      M = IDSTR
      CP(K,M) = SPH
      IF(TIN-TOUT) 197,197,198
  197 NCOSR(K,M) = 1
C  THE STREAM IN QUESTION IS COLD
      THOT(K,M) = TOUT
      TCOLD(K,M) = TIN
      GO TO 199
  198 NCOSR(K,M) = -1
C  THE STREAM IN QUESTION IS HOT
      THOT(K,M) = TIN
      TCOLD(K,M) = TOUT
  199 CONTINUE

      IF(KP) 101,101,116

  116 IF(15-KP) 115,115,1150
  115 WRITE(3,15)
      GO TO 101
 1150 IF(14-KP) 114,114,1140
  114 WRITE(3,14)
      GO TO 101
```

Listing for BLJF2 (Cont'd)

```
1140 IF(13-KP) 113,113,1130
 113 WRITE(3,13)
     GO TO 101
1130 IF(12-KP) 112,112,1120
 112 WRITE(3,12)
     GO TO 101
1120 IF(11-KP) 111,111,1110
 111 WRITE(3,11)
     GO TO 101
1110 IF(10-KP) 110,110,1100
 110 WRITE(3,10)
     GO TO 101
1100 IF(9-KP) 109,109,1090
 109 WRITE(3,9)
     GO TO 101
1090 IF(8-KP) 108,108,1080
 108 WRITE(3,8)
     GO TO 101
1080 IF(7-KP) 107,107,1070
 107 WRITE(3,7)
     GO TO 101
1070 IF(6-KP) 106,106,1060
 106 WRITE(3,6)
     GO TO 101
1060 IF(5-KP) 105,105,1050
 105 WRITE(3,5)
     GO TO 101
1050 IF(4-KP) 104,104,1040
 104 WRITE(3,4)
     GO TO 101
1040 IF(3-KP) 103,103,1030
 103 WRITE(3,3)
     GO TO 101
1030 IF(2-KP) 102,102,1020
 102 WRITE(3,2)
     GO TO 101
1020 WRITE(3,1)
 101 CONTINUE

     RETURN

   1 FORMAT(5X,' PROBLEM ..... TEST CASE NO. 1',////)
   2 FORMAT(5X,' PROBLEM ..... TEST CASE NO. 2',////)
   3 FORMAT(5X,' PROBLEM ..... PONTON AND DONALDSON',////)
   4 FORMAT(5X,' PROBLEM ..... 4SP1',////)
   5 FORMAT(5X,' PROBLEM ..... 5SP1',////)
   6 FORMAT(5X,' PROBLEM ..... 6SP1',////)
   7 FORMAT(5X,' PROBLEM ..... 7SP1',////)
   8 FORMAT(5X,' PROBLEM ..... 7SP2',////)
   9 FORMAT(5X,' PROBLEM .....     ',////)
  10 FORMAT(5X,' PROBLEM ..... 10SP1',////)
  11 FORMAT(5X,' PROBLEM .....     ',////)
  12 FORMAT(5X,' PROBLEM .....     ',////)
  13 FORMAT(5X,' PROBLEM .....     ',////)
  14 FORMAT(5X,' PROBLEM .....     ',////)
  15 FORMAT(5X,' PROBLEM .....     ',////)

     END
```

Data input for BLJF2

1st card : NSET

2nd card : IDPR,NSTRM
3rd card : STPR,DUTY
4th card : CSTM,CWAT,UH,UEX,UC,COEF,EXP,
TWIN,TWOUT,NYR
5th card : IDSTR,SPH,TIN,TOUT
6th card : IDSTR,SPH,TIN,TOUT
.. ..
.. ..

one card per stream

set for the first problem

xth card : IDPR,NSTRM
(x+1) th card : STPR,DUTY
.. ..
.. ..

set for the second problem

etc.

Explanations :

NSET	number of problem sets read in
IDPR	identification number of a problem
NSTRM	number of streams in a problem
STPR	steam pressure (in p.s.i.a.)
DUTY	hours per year during which equipment is on duty
CSTM	cost of steam (in \$/lb.)
CWAT	cost of cooling water (in \$/lb.)
UH	overall heat transfer coefficient (heater)
UEX	overall heat transfer coefficient (exchanger)
UC	overall heat transfer coefficient (cooler)

(in $\frac{\text{Btu}}{\text{hr*ft}^2\text{*}^\circ\text{F}}$)

Data input for BLJF2 (Cont'd)

COEF	factor "A" in the equation $\underset{\text{in dollars}}{\text{COST}} = \underset{\text{in ft}^2}{\text{A*(SURFACE AREA)**B}}$ for the calculation of equipment costs
EXP	exponent "B" in the above equation
TWIN	cooling water supply temperature (in $^{\circ}$F)
TWOUT	maximum allowable cooling water temperature (in $^{\circ}$F)
NYR	useful lifetime of equipment in years
IDSTR	identification number of a stream
SPH	specific heat capacity flowrate of a stream (always measured positive (in 10^4*Btu/($^{\circ}$F*hr))
TIN	stream supply temperature (in $^{\circ}$F)
TOUT	stream target temperature (in $^{\circ}$F)

G.2 THE MAIN PROGRAM BLJF1

A listing is given on pages G9 through G12 and a detailed description of the input data structure is given on page G13. Since one of the purposes for which BLJF1 was written is to evaluate the influence which varying assumptions regarding ΔT_{min} might have on the energy recovery situation, the data specifying the ΔT_{min}-constraints are read in to BLJF1 itself rather than in to BLJF2.

The computational efficiency of BLJF1 could doubtlessly be improved on but the program appears to be sufficiently short for no such effort to be justified. The following is a brief explanation of the various computational steps, based on the program listing. BLJF1

- calls BLJF2 to load synthesis problem data,
- reads IDPR, DTMAX, NIT (see page G13 for explanation),
- calls BLJF2 to print problem identification,
- checks whether or not stream-individual figures for the minimum approach temperature are to be used (by checking DTMAX, see page G13) and reads, if necessary, the data which specify these individual figures.

As from statement 40 onwards, BLJF1 computes the heat load of each stream and prints out a data description for the problem dealt with. (This part of the printout is not documented).

As from statement 70 onwards, BLJF1 identifies the ΔT_{min}-constraints that are applicable to the particular run which is to follow. This is done on the basis of step by step reducing the figures specified in the data, until the assumption $\Delta T_{min} = 0$ throughout is reached. If, e.g., seven runs are made the second run will be based on figures for ΔT_{min} which are smaller by one sixth than the ones used in the first run, the third run will be based on figures smaller by two sixths, and so on, so that the last run is based on the assumption $\Delta T_{min} = 0$ throughout.

As from statement 130 onwards, BLJF1

- corrects the original stream supply and target temperatures by adding (cold streams) or subtracting (hot streams) the relevant partial contributions to ΔT_{min} (up to statement 150),

- establishes an array of all - so corrected - stream supply and target temperatures, ordered according to magnitude (up to statement 160),
- eliminates duplication in this array and thus identifies the number of subnetworks, i.e. the variable "NSN" (up to statement 180),
- establishes, for each subnetwork, which streams are present and which are not and calculates the term "deficit" (i.e. the enthalpy difference, variable : "EPAOP(I)") for each subnetwork (up to statement 190),
- calculates the "maximum permissible input" ("ACCIP(I)") and the "maximum permissible output" ("ACCOP(I)") for each subnetwork (up to statement 210),
- prints out the Problem Table (up to statement 230).

The sample printouts given on pages G14 through G16 show some results for Test Case No.1. First, a Problem Table which is based on the assumption $\Delta T_{min} = 20^{O}F$ throughout (page G14), then one which is based on $\Delta T_{min} = 0^{O}F$ throughout (page G15), and finally, one based on stream-individual figures for ΔT_{min} (page G16).

Listing for BLJF1

```
// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*IOCS(CARD,1132 PRINTER)

      INTEGER STRPR(50,25)
      DIMENSION HL(25),DTPAR(25)
      DIMENSION DTP(25)
      DIMENSION TM(50)
      DIMENSION T(50),TMAX(50),DTSN(50),EPAOP(50),ACCIP(50),ACCOP(50)
      COMMON THOT(15,25),TCOLD(15,25),CP(15,25),NCOSR(15,25)
      COMMON STPR(15)
      COMMON NSTR(15),BTUST(15),TSTM(15),DUTY(15),CSTM(15),CWAT(15)
      COMMON UH(15),UEX(15),UC(15),COEF(15),EXP(15),TWIN(15),TWOUT(15)

      COMMON NYR(15)
      KP=0
      KR=1
      WRITE (3,1000)
      CALL BLJF2(KR,KP)
      KR=0

  500 READ(2) IDPR,DTMAX,NIT
      K=IDPR
      KP=IDPR
      CALL BLJF2(KR,KP)

      M = NSTR(K)
      IF(DTMAX+.001) 38,40,40
   38 DO 39 I = 1,M
      READ(2) NID,DT
      DTPAR(NID) = DT
   39 DTP(I) = DTPAR(I)
   40 CONTINUE

      HLTOT = 0.
      DO 50 I = 1,M
      IF(NCOSR(K,I)) 48,48,49
   48 HL(I) = CP(K,I)*(TCOLD(K,I)-THOT(K,I))
      GO TO 50
   49 HL(I) = CP(K,I)*(THOT(K,I)-TCOLD(K,I))
   50 HLTOT = HLTOT + HL(I)

      WRITE(3,2000)
      WRITE(3,2001)
      DO 60 J = 1,M
      IF(NCOSR(K,J)) 58,58,59
   58 WRITE(3,3001) J,THOT(K,J),TCOLD(K,J),CP(K,J),HL(J)
      GO TO 60
   59 WRITE(3,3002) J,TCOLD(K,J),THOT(K,J),CP(K,J),HL(J)
   60 CONTINUE

      HT = ABS(HLTOT)
      WRITE(3,4000) HLTOT
      IF(HLTOT) 69,70,68
   68 WRITE(3,4001) HT
      GO TO 70
   69 WRITE(3,4002) HT
   70 CONTINUE
      WRITE(3,1000)
```

Listing for BLJF1 (Cont'd)

```
    MIT = NIT - 1
    DO 300 IJK = 1,NIT
    MIJK = NIT - IJK
    IF(IJK-1) 120,120,125
120 IF(DTMAX+.001) 130,123,123
123 DO 124 I = 1,M
124 DTPAR(I) = DTMAX/2.
    GO TO 130
125 IF(DTMAX+.001) 126,128,128
126 DO 127 I = 1,M
127 DTPAR(I) = DTP(I)*MIJK/MIT
    GO TO 130
128 DO 129 I = 1,M
129 DTPAR(I) = DTMAX*MIJK/MIT/2.
130 CONTINUE

    DO 150 I = 1,M
    IM = I + M
    IF(NCOSR(K,I)) 148,148,149
148 T(I) = THOT(K,I) - DTPAR(I)
    T(IM) = TCOLD(K,I) - DTPAR(I)
    GO TO 150
149 T(I) = THOT(K,I) + DTPAR(I)
    T(IM) = TCOLD(K,I) + DTPAR(I)
150 CONTINUE

    TT = .002
    MM = 2*NSTR(K)
    DO 160 L = 1,MM
    DO 155 I = 1,MM
    IF(TT-T(I)) 152,152,155
152 TT = T(I)
    IMEM = I
155 CONTINUE
    TMAX(L) = TT
    T(IMEM) = .001
    TT = .002
160 CONTINUE

    NCT = 1
    TM(1) = TMAX(1)
    DO 170 I = 2,MM
    IF(TMAX(I-1)-TMAX(I)) 170,170,165
165 NCT = NCT + 1
    TM(NCT) = TMAX(I)
170 CONTINUE
    NSN = NCT - 1
    DO 180 I = 1,NSN
180 DTSN(I) = TM(I) - TM(I+1)

    DO 190 I = 1,NSN
    SCP = 0.
    DO 189 J = 1,M
    IF(NCOSR(K,J)) 182,182,186
182 TTEST = THOT(K,J)-TM(I)-DTPAR(J) + .001
    IF(TTEST) 183,183,184
183 STRPR(I,J) = -1
    GO TO 189
184 TTEST = TM(I+1) + DTPAR(J) - TCOLD(K,J) + .001
    IF(TTEST) 183,183,185
185 SCP = SCP - DTSN(I)*CP(K,J)
    STRPR(I,J) = 1
    GO TO 189
```

Listing for BLJF1 (Cont'd)

```
186 TTEST = THOT(K,J) - TM(I) + DTPAR(J) + .001
    IF(TTEST) 183,183,187
187 TTEST = TM(I+1) - DTPAR(J) - TCOLD(K,J) + .001
    IF(TTEST) 183,183,188
188 SCP = SCP + DTSN(I)*CP(K,J)
    STRPR(I,J) = 1
189 CONTINUE
    EPAOP(I) = SCP
190 SCP = 0.

    OVIP = 0.
    ACCIP(1) = 0.
    DO 200 I = 1,NSN
    ACCOP(I) = EPAOP(I) - ACCIP(I)
    ACCIP(I+1) = -ACCOP(I)
    IF(ACCOP(I)-OVIP) 200,200,199
199 OVIP = ACCOP(I)
200 CONTINUE
    ACCIP(1) = OVIP
    DO 210 I = 1,NSN
    ACCOP(I) = EPAOP(I) - ACCIP(I)
210 ACCIP(I+1) = -ACCOP(I)

    XMIT = MIT
    XMIJK = MIJK
    DUMM = 100.*XMIJK/XMIT + .01
    NDUM = IFIX(DUMM)
    IF(NIT-1) 216,216,217
216 NDUM=100
217 TUMM = DTPAR(1)*2. + 0.01
    IF(DTMAX+.001) 218,219,219
218 WRITE(3,5001) NDUM
    GO TO 220
219 WRITE(3,5000) TUMM,NDUM
220 CONTINUE

    WRITE(3,5002) OVIP
    PRNT = -ACCOP(NSN)
    WRITE(3,5003) PRNT
    WRITE(3,5004) NSN
    WRITE(3,6000)

    DO 230 I = 1,NSN
    WRITE(3,7000) I,EPAOP(I),ACCIP(I),ACCOP(I)
    DO 230 J = 1,M
    IF(STRPR(I,J)) 230,230,226
226 IF(NCOSR(K,J)) 227,227,228
227 THIN = TM(I) + DTPAR(J)
    THOUT = TM(I+1) + DTPAR(J)
    WRITE(3,8000) J,DTPAR(J), THIN, THOUT
    GO TO 230
228 TCIN = TM(I+1) -DTPAR(J)
    TCOUT = TM(I) - DTPAR(J)
    WRITE(3,9000) J,DTPAR(J),TCIN,TCOUT
230 CONTINUE

    WRITE(3,1000)

300 CONTINUE

    GO TO 500
```

Listing for BLJF1 (Cont'd)

```
1000 FORMAT('1')
2000 FORMAT(//,32X,' T',6X,' T',16X,' SPEC. HEAT' ,14X,' HEAT LOAD',/,
    133X,' IN',5X,' OUT',//)
2001 FORMAT(30X,' ** DEGR. F. **',7X,' 10 000 BTU/HR./DEGR.F.',5X,
    1' 10 000 BTU/HR.',///)
3001 FORMAT(8X,'  HOT STREAM NO.',I3,5X,F5.1,3X,F5.1,15X,F8.6,15X,F8.2,
    1//)
3002 FORMAT(8X,' COLD STREAM NO.',I3,5X,F5.1,3X,F5.1,15X,F8.6,15X,F8.2,
    1//)
4000 FORMAT(////,30X,' TOTAL HEAT LOAD IS',F8.2,
    1' * 10 000 BTU/HR.',//)
4001 FORMAT(//,20X,' I.E. INPUT EXCEEDS OUTPUT BY',F8.2,
    * ' * 10 000 BTU/HR.',//)
4002 FORMAT(//,20X,' I.E. OUTPUT EXCEEDS INPUT BY',F8.2,
    * ' * 10 000 BTU/HR.',//)
5000 FORMAT(5X,' DTMIN IS',F5.1,' DEGR. F.',//,5X,' (THIS IS A',
    1I4,' - PERCENT FRACTION OF THE BIGGEST VALUE SPECIFIED.)',////)
5001 FORMAT(5X,' DTMIN IS FLEXIBLE (SEE BELOW).',//,5X,
    1 ' (THE FRACTIONS USED IN THIS RUN ARE',I4,' PERCENT FOR EACH STRE
    2AM.)',////)
5002 FORMAT(5X,' MINIMUM LOAD ON HEATERS IS',
    * 1X,F6.1,' * 10 000 BTU/HR.',///)
5003 FORMAT(5X,' MINIMUM LOAD ON COOLERS IS',
    * 1X,F6.1,' * 10 000 BTU/HR.',///)
5004 FORMAT (5X,' NO. OF SUBNETWORKS IS',I3,///)
6000 FORMAT(95X,' MAXIMUM  PERMISSIBLE',/,37X,' DT',9X,' T',6X,' T',
    *13X,' I/P + O/P',/,
    139X,' PART',6X,' IN',5X,' OUT',33X,' INPUT', 8X,' OUTPUT',/////,
    237X,' ******* DEGR, F, *******',10X,
    3 ' *************** 10 000 BTU/HR, **************',///)
7000 FORMAT(/,5X,' SN( ',I2,' )',
    * 59X,F8.2,13X,F8.2,6X,F8.2,/,
    15X,' *******************',/)
8000 FORMAT(9X,' STREAM NO.',I3,6X,' HOT',6X,
    1F4.1,6X,F5.1,3X,F5.1,/)
9000 FORMAT(9X,' STREAM NO.',I3,5X,' COLD',6X,
    1F4.1,6X,F5.1,3X,F5.1,/)


     END
```

Data input for BLJF1

First, a full data set for the subroutine BLJF2.
Thereafter, the following :

1st card : IDPR,DTMAX,NIT
2nd card : NID,DT
3rd card : NID,DT
4th card : NID,DT
.. ..
.. ..
only if DTMAX negative : one card per stream
set for the first problem

x-th card : IDPR,DTMAX,NIT
(x+1)th card : NID,DT
.. ..
only if ...
set for the second problem

etc., as many sets as required.

Explanations :

IDPR	identification number of problem
DTMAX	either : positive figure, specifying the minimum approach temperature which is to be assumed for each match in the first run (in °F) or : negative figure, indicating that individual figures for the approach temperatures of the various streams will be given
NIT	number of runs (The first run is carried out with the specified approach temperatures and the last run with the assumption $\Delta T_{min} = 0$ throughout. If more than two runs are required - i.e. NIT > 2 - the other runs will be based on fractionally reduced figures for the minimum approach temperatures, see text.)
NID	identification number of a stream
DT	partial contribution of an individual stream to minimum approach temperature (given as positive figure in °F).

Sample printout for BLJF1

```
DTMIN IS 20.0 DEGR. F.
(THIS IS A 100 - PERCENT FRACTION OF THE BIGGEST VALUE SPECIFIED.)

MINIMUM LOAD ON HEATERS IS    60.0 * 10 000 BTU/HR.

MINIMUM LOAD ON COOLERS IS   225.0 * 10 000 BTU/HR.

NO. OF SUBNETWORKS IS  5

                                DT          T        T                 I/P + O/P                MAXIMUM  PERMISSIBLE
                                  PART       IN       OUT                                        INPUT         OUTPUT

                                ******** DEGR. F. ********             ***************** 10 000 BTU/HR. ***************

SN(  1 )                                                                   30.00                 60.00         -30.00
*********************
     STREAM NO.  1      COLD      10.0        380.0    400.0

SN(  2 )                                                                   30.00                 30.00           0.00
*********************
     STREAM NO.  1      COLD      10.0        320.0    380.0
     STREAM NO.  2       HOT      10.0        400.0    340.0

SN(  3 )                                                                 -105.00                  0.00        -105.00
*********************
     STREAM NO.  1      COLD      10.0        250.0    320.0
     STREAM NO.  2       HOT      10.0        340.0    270.0
     STREAM NO.  4       HOT      10.0        340.0    270.0

SN(  4 )                                                                  -18.00                105.00        -123.00
*********************
     STREAM NO.  1      COLD      10.0        160.0    250.0
     STREAM NO.  2       HOT      10.0        270.0    180.0
     STREAM NO.  3      COLD      10.0        160.0    250.0
     STREAM NO.  4       HOT      10.0        270.0    180.0

SN(  5 )                                                                 -102.00                123.00        -225.00
*********************
     STREAM NO.  2       HOT      10.0        180.0    120.0
     STREAM NO.  3      COLD      10.0        100.0    160.0
     STREAM NO.  4       HOT      10.0        180.0    120.0
```

Sample printout for BLJF1 (Cont'd)

```
DTMIN IS  0.0 DEGR. F.
(THIS IS A   0 - PERCENT FRACTION OF THE BIGGEST VALUE SPECIFIED.)

MINIMUM LOAD ON HEATERS IS   30.0 * 10 000 BTU/HR.

MINIMUM LOAD ON COOLERS IS  195.0 * 10 000 BTU/HR.

NO. OF SUBNETWORKS IS  5

                              DT            T         T                                MAXIMUM  PERMISSIBLE
                                PART         IN        OUT           I/P + O/P            INPUT        OUTPUT

                              ******** DEGR. F. ********          **************** 10 000 BTU/HR. ***************


SN(  1 )                                                                 30.00             30.00          0.00
*********************
     STREAM NO.  1      COLD       0.0        340.0     400.0
     STREAM NO.  2       HOT       0.0        400.0     340.0

SN(  2 )                                                               -135.00              0.00       -135.00
*********************
     STREAM NO.  1      COLD       0.0        250.0     340.0
     STREAM NO.  2       HOT       0.0        340.0     250.0
     STREAM NO.  4       HOT       0.0        340.0     250.0

SN(  3 )                                                                -18.00            135.00       -153.00
*********************
     STREAM NO.  1      COLD       0.0        160.0     250.0
     STREAM NO.  2       HOT       0.0        250.0     160.0
     STREAM NO.  3      COLD       0.0        160.0     250.0
     STREAM NO.  4       HOT       0.0        250.0     160.0

SN(  4 )                                                                -68.00            153.00       -221.00
*********************
     STREAM NO.  2       HOT       0.0        160.0     120.0
     STREAM NO.  3      COLD       0.0        120.0     160.0
     STREAM NO.  4       HOT       0.0        160.0     120.0

SN(  5 )                                                                 26.00            221.00       -195.00
*********************
     STREAM NO.  3      COLD       0.0        100.0     120.0
```

Sample printout for BLJF1 (Cont'd)

```
DTMIN IS FLEXIBLE (SEE BELOW).
(THE FRACTIONS USED IN THIS RUN ARE 100 PERCENT FOR EACH STREAM.)

MINIMUM LOAD ON HEATERS IS   54.0 * 10 000 BTU/HR.

MINIMUM LOAD ON COOLERS IS  219.0 * 10 000 BTU/HR.

NO. OF SUBNETWORKS IS  6

                                                                            MAXIMUM  PERMISSIBLE
                                  DT          T         T        I/P + O/P
                                    PART       IN        OUT                  INPUT       OUTPUT

                                  ******** DEGR. F. ********     ****************** 10 000 BTU/HR. ***************


SN(  1 )                                                           22.50         54.00       -31.50
*********************
    STREAM NO.  1        COLD     10.0      385.0     400.0

SN(  2 )                                                           31.50         31.50         0.00
*********************
    STREAM NO.  1        COLD     10.0      322.0     385.0
    STREAM NO.  2         HOT      5.0      400.0     337.0

SN(  3 )                                                         -105.00          0.00      -105.00
*********************
    STREAM NO.  1        COLD     10.0      252.0     322.0
    STREAM NO.  2         HOT      5.0      337.0     267.0
    STREAM NO.  4         HOT      8.0      340.0     270.0

SN(  4 )                                                          -18.40        105.00      -123.40
*********************
    STREAM NO.  1        COLD     10.0      160.0     252.0
    STREAM NO.  2         HOT      5.0      267.0     175.0
    STREAM NO.  3        COLD     12.0      158.0     250.0
    STREAM NO.  4         HOT      8.0      270.0     178.0

SN(  5 )                                                          -93.50        123.40      -216.90
*********************
    STREAM NO.  2         HOT      5.0      175.0     120.0
    STREAM NO.  3        COLD     12.0      103.0     158.0
    STREAM NO.  4         HOT      8.0      178.0     123.0

SN(  6 )                                                           -2.10        216.90      -219.00
*********************
    STREAM NO.  3        COLD     12.0      100.0     103.0
    STREAM NO.  4         HOT      8.0      123.0     120.0
```

G.3 THE MAIN PROGRAM BLJF3

A listing is given on pages G19 through G22 and the input data structure is described on pages G23 and G24. As is evident from the listing, the program is specially adapted to the particular assumptions made in the literature with regard to costing networks (see Appendix K). The input data structure, however, is specially adapted to the way of graphically representing networks which was called "grid-representation" in Appendix F. A network is sufficiently described if

- each unit is specified as either a heater, an exchanger, or a cooler,
- the process streams are named which are involved in a unit as well as the amount of heat transferred, and
- the sequence with which the individual unit specifications are given corresponds to the sequence of these units in the grid-representation of the network (from the hot end to the cold end of the problem).

Also, the synthesis problem must be specified which is to be solved and the ΔT_{min}-constraints must be given which are applicable to heaters, coolers and exchangers. (The latter are required for the calculation of cooling water exit temperatures and for the evaluation of Freedoms).

The detailed programming structure of BLJF3 is quite straight-forward and does not appear to warrant a special explanation. The program is based on the idea of following up all stream temperatures from the hot end of the synthesis problem by computing the temperature changes which occur due to the proposed matches. Worth mentioning are, perhaps, the two details that the process streams involved in a unit can be specified in any sequence (the program will identify whether they are hot or cold) and that the program will produce error messages if either the chosen minimum approach temperature constraints are violated (see e.g. printout on page G26) or if the specified synthesis problem turns out not be solved by the proposed network (see e.g. page G27). A normal printout without error message is shown on page G25. It represents the network presented in Figure 14a, page 650 in Appendix F as a solution for 5SP1. As is evident from these printouts, networks are fully documented by the information given.

Listing for BLJF3

```
// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*IOCS(CARD,1132 PRINTER)

      DIMENSION ID1(40),ID2(40)
      DIMENSION TR(25)
      DIMENSION Q(40),NCOUN(40),DTPAR(25)
      COMMON THOT(15,25),TCOLD(15,25),CP(15,25),NCOSR(15,25)
      COMMON STPR(15)
      COMMON NSTR(15),BTUST(15),TSTM(15),DUTY(15),CSTM(15),CWAT(15)
      COMMON UH(15),UEX(15),UC(15),COEF(15),EXP(15),TWIN(15),TWOUT(15)
      COMMON NYR(15)

  500 FORMAT(70X,' VERSION ...................................',//)
  501 FORMAT(70X,' NO. OF UNITS IS',I3,//)
  502 FORMAT(70X,' TOTAL HEAT INPUT IS' 1X,F6.1,
     * ' * 10 000 BTU/HR.',)
  503 FORMAT(5X,
     *       ' EQUIPMENT IS ON DUTY FOR',IX,F6.1,' HRS./YEAR',//)
  504 FORMAT(5X,' STEAM PRESSURE IS',1X,F5.1,' P.S.I.A.',//)
  505 FORMAT(5X,
     *       ' COST OF STEAM IS',F6.3,' DOLLARS/LB.',//)
  506 FORMAT(5X,
     *       ' COST OF COOLING WATER IS',F8.5,' DOLLARS/LB.',//)
  507 FORMAT(5X,

     *       ' COST OF HEAT EXCHANGE SURFACE AREA IS EVALUATED',
     * ' BY MEANS OF THE EQUATION',//,
     *  15X,' COST IN DOLLARS = A*(SURFACE AREA)**B',
     * //,15X,' WITH A =',1X,F5.1,' AND B =',1X,F3.1,//)
  508 FORMAT(5X,
     *       ' USEFUL LIFETIME OF PLANT IS',I3,' YEARS',/////)
  509 FORMAT(17X,' STREAMS',4X,' **** HOT ****',4X,' *** COLD ****',
     1 5X,' CRIT.',3X,' HEAT',5X,' FREEDOM',4X,' AREA', 9X,' COST OF',
     2 //,18X,' H',3X,' C',5X,' T',6X,' T',8X,' T',6X,' T',9X,' DT',7X,
     3 ' LOAD',31X,' PLANT',/,31X,' IN',5X,' OUT',6X,' IN',5X,' OUT',//,
     4 29X,' *************** DEGR. F. ***************',5X,
     5 ' 10 000  BTU/HR. ',3X,' SQ.FT.',6X,' DOLLARS/YR.',///)
  510 FORMAT(5X,' COOLING WATER TEMPERATURE EXTREMES ARE',
     * F6.1,' AND',F6.1,' DEGR. F.',//)
  511 FORMAT(5X,' HEAT TRANSFER COEFFICIENTS ARE',//
     * 16X,F5.1,' BTU/(HR.*SQ.FT.*DEGR.F.)  FOR HEATERS.',//,
     * 16X,F5.1,' BTU/(HR.*SQ.FT.*DEGR.F.)  FOR EXCHANGERS.',//,
     * 11X,' AND',F6.1,' BTU/(HR.*SQ.FT.*DEGR.F.)  FOR COOLERS.',//)
 1000 FORMAT('1')
 1001 FORMAT(8X,' HEATER',8X,I2,
     * 5X,F5.1,3X,F5.1,5X,F5.1,3X,3(F5.1,5X),'   *)',5X,F6.1,10X,F6.1,
     * //)
 1002 FORMAT(5X,' EXCHANGER',3X,I2,3X,I2,
     * 5X,F5.1,3X,F5.1,5X,F5.1,3X,4(F5.1,5X),F6.1,10X,F6.1,//)
 1003 FORMAT(8X,' COOLER',3X,I2,5X,
     * 5X,F5.1,3X,F5.1,5X,F5.1,3X,3(F5.1,5X),'   *)',5X,F6.1,10X,F6.1,
     * //)
 1004 FORMAT(///,5X,' TOTAL COST OF PLANT IS',F10.1,
     *  ' DOLLARS PER YEAR',/)
 1005 FORMAT(5X,
     *       ' T0TAL UTILITY COST IS ',F10.1,
     *  ' DOLLARS PER YEAR',/)
```

Listing for BLJF3 (Cont'd)

```
1006 FORMAT(5X,
    *        '               TOTAL COST IS',F10.1,
    * ' DOLLARS PER YEAR',12X,' *)',/,70X,' FREEDOMS FOR',
    * ' HEATERS AND COOLERS ARE NOT EVALUATED')
1007 FORMAT(//,18X,' ATTENTION *** STREAM NO.',I3,' DOES NOT',
    * ' NOT EXCHANGE ITS FULL HEAT LOAD *** CHECK INPUT DATA',/)
1008 FORMAT(18X,' ATTENTION *** DTMIN-CONSTRAINT IS VIOLATED IN',
    * ' THIS UNIT *** CHECK INPUT DATA',///)

      KS=0
      KP=0
      KR=1
      WRITE (3,1000)
      CALL BLJF2(KR,KP)
      KR=0
 200  READ(2) IDPR,NUNIT,DTH,DTEX,DTC
      DTMAX=DTEX
      KP=IDPR
      CALL BLJF2(KR,KP)
      M=NSTR(IDPR)

      IF(DTMAX + .001) 20,22,22
  20  DO 21 I=1,M
      READ(2) NID,DT
  21  DTPAR(NID) = DT
      GO TO 24
  22  DO 23 I=1,M
  23  DTPAR(I) = DTMAX/2.
  24  CONTINUE

      DO 25 I=1,M
  25  TR(I)=THOT(IDPR,I)

      QTOT=0.
      CPL = 0.
      CUT = 0.

      DO 40 J=1,NUNIT
      READ(2) NCOUN(J),ID1(J),ID2(J),Q(J)
      IF(NCOUN(J)) 39,40,40
  39  QTOT = QTOT + Q(J)
  40  CONTINUE

      WRITE(3,500)
      WRITE(3,501) NUNIT
      WRITE(3,502) QTOT
      WRITE(3,503) DUTY(IDPR)
      WRITE(3,504) STPR(IDPR)
      WRITE(3,505) CSTM(IDPR)
      WRITE(3,510) TWIN(IDPR),TWOUT(IDPR)
      WRITE(3,506) CWAT(IDPR)
      WRITE(3,511) UH(IDPR),UEX(IDPR),UC(IDPR)
      WRITE(3,507) COEF(IDPR),EXP(IDPR)
      WRITE(3,508) NYR(IDPR)
      WRITE(3,509)

      DO 100 I=1,NUNIT
      IDA=ID1(I)
      IDB=ID2(I)
      IF(NCOUN(I)) 50,60,70
```

Listing for BLJF3 (Cont'd)

```
 50 U=UH(IDPR)
    UT=Q(I)*10000.*DUTY(IDPR)*CSTM(IDPR)/BTUST(IDPR)
    THIN=TSTM(IDPR)
    THOUT=THIN
    TCOUT=THOT(IDPR,IDB)
    TCIN=TCOUT-Q(I)/CP(IDPR,IDB)
    THOT(IDPR,IDB)=TCIN
    TEST = THIN-TCOUT
    IF (TEST-DTH) 59,80,80
 59 KS=1
    GO TO 80

 60 U=UEX(IDPR)
    UT=0.
    THIN=THOT(IDPR,IDA)
    TCOUT=THOT(IDPR,IDB)
    IF(NCOSR(IDPR,IDB)) 61,61,62
 61 TC=TCOUT
    TCOUT=THIN
    THIN=TC
    IDA=ID2(I)
    IDB=ID1(I)
 62 THOUT=THIN-Q(I)/CP(IDPR,IDA)
    TCIN=TCOUT-Q(I)/CP(IDPR,IDB)
    THOT(IDPR,IDA)=THOUT
    THOT(IDPR,IDB)=TCIN
    GO TO 80

 70 U=UC(IDPR)
    THIN=THOT(IDPR,IDA)
    THOUT=THIN-Q(I)/CP(IDPR,IDA)
    TCIN=TWIN(IDPR)
    TEST=(THOUT-TCIN)
    IF (TEST-DTC) 704,705,705
704 KS=1
705 TCOMP = THIN-DTC
    IF(TCOMP-TWOUT(IDPR)) 71,71,72
 71 TCOUT=TCOMP
    GO TO 73
 72 TCOUT=TWOUT(IDPR)
 73 UT=Q(I)*DUTY(IDPR)*CWAT(IDPR)*10000./(TCOUT-TCIN)
    THOT(IDPR,IDA)=THOUT

 80 DT1=THIN-TCOUT
    DT2=THOUT-TCIN
    IF(DT1-DT2) 81,82,82
 81 DTCR=DT1
    GO TO 820
 82 DTCR=DT2
820 IF(NCOUN(I)) 83,821,83
821 IF(CP(IDPR,IDB)-CP(IDPR,IDA)) 822,822,823
822 CPBIG=CP(IDPR,IDA)
    GO TO 824
823 CPBIG=CP(IDPR,IDB)
824 FR=CPBIG*(DTCR-DTPAR(IDA)-DTPAR(IDB))
    IF(FR) 825,83,83
825 KS=1
 83 TEST=ABS(DT1-DT2)
    IF(TEST-0.1) 84,84,85
 84 DTLM=(DT1+DT2)/2.
    GO TO 86
 85 DTLM=TEST/ABS(ALOG(DT1/DT2))
```

Listing for BLJF3 (Cont'd)

```
 86 A=(Q(I)*10000.)/(U*DTLM)
    CPLT=COEF(IDPR)*A**EXP(IDPR)
    RN=NYR(IDPR)
    CPLT=CPLT/RN

    IF(NCOUN(I)) 91,92,93
 91 WRITE(3,1001) IDB,THIN,THOUT,TCIN,TCOUT,DTCR,Q(I),A,CPLT
    GO TO 94
 92 WRITE(3,1002) IDA,IDB,THIN,THOUT,TCIN,TCOUT,DTCR,Q(I),FR,A,CPLT
    GO TO 94
 93 WRITE(3,1003) IDA,THIN,THOUT,TCIN,TCOUT,DTCR,Q(I),A,CPLT
 94 IF(KS) 96,96,95
 95 WRITE(3,1008)
 96 KS=0

    CPL=CPL+CPLT
    CUT=CUT+UT
100 C=CUT+CPL

    DO 101 I=1,M
    TEST=ABS(THOT(IDPR,I)-TCOLD(IDPR,I))
    TEST=TEST*5.
    IF (TEST-1.) 101,101,102
102 WRITE(3,1007) I
101 THOT(IDPR,I)=TR(I)

    WRITE(3,1004) CPL
    WRITE(3,1005) CUT
    WRITE(3,1006) C
    WRITE(3,1000)

    GO TO 200

    END
```

Data input for BLJF3

First, a full data set for the subroutine BLJF2.

Thereafter, the following:

```
       1st card : IDPR,NUNIT,DTH,DTEX,DTC       ┐
       2nd card : NID,DT  ┐                     │
       3rd card : NID,DT  │     only if         │
       4th card : NID,DT  │ DTEX negative :     │
          ..        ..    │    one card         │  set for the
          ..        ..    ┘   per stream        │  first network
       x-th card : NCOUN,ID1,ID2,Q ┐            │
    (x+1)th card : NCOUN,ID1,ID2,Q │ one card   │
    (x+2)th card : NCOUN,ID1,ID2,Q │ per unit   │
          ..        ..             │            │
          ..        ..             ┘            ┘
       y-th card : IDPR,NUNIT,DTH,DTEX,DTC      ┐
          ..        ..                          │  set for the
          ..        ..                          │  second network
                                                │
                                                :
               etc., as many sets as required
```

Explanations :

IDPR	identification number of problem
NUNIT	number of units in the network
DTH	minimum approach temperature in heaters (in ^{O}F)
DTEX	either : positive figure, specifying the minimum approach temperature applicable to exchangers (in ^{O}F) or : negative figure, indicating that minimum approach temperatures are individually specified.
DTC	minimum approach temperature in coolers (in ^{O}F)
NID	identification number of a stream

Data input for BLJF3 (Cont'd)

DT	partial contribution of an individual stream to minimum approach temperature (given as positive figure in $^{\circ}$F)
NCOUN	code number for a unit : "-1" for a heater, " 0" for an exchanger, "+1" for a cooler
ID1	identification number of one of the two streams matched in an exchanger. (Number of the process stream in the case of a heater or a cooler.)
ID2	identification number of the other stream matched in an exchanger. (Number of the process stream, again, in the case of a heater or a cooler.)
Q	heat load transferred in unit (in 10^4*Btu/hr).

Sample printout for BLJF3

```
PROBLEM ..... 55P1

                                                               VERSION ..............................

                                                               NO. OF UNITS IS  5

EQUIPMENT IS ON DUTY FOR 8380.0 HRS./YEAR                      TOTAL HEAT INPUT IS  302.0 * 10 000 BTU/HR.

STEAM PRESSURE IS 450.0 P.S.I.A.

COST OF STEAM IS 0.001 DOLLARS/LB.

COOLING WATER TEMPERATURE EXTREMES ARE 100.0 AND 180.0 DEGR. F.

COST OF COOLING WATER IS 0.00005 DOLLARS/LB.

HEAT TRANSFER COEFFICIENTS ARE
         200.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR HEATERS.
         150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR EXCHANGERS.
     AND 150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR COOLERS.

COST OF HEAT EXCHANGE SURFACE AREA IS EVALUATED BY MEANS OF THE EQUATION
         COST IN DOLLARS = A*(SURFACE AREA)**B
         WITH A = 350.0 AND B =   0.5

USEFUL LIFETIME OF PLANT IS 10 YEARS


           STREAMS     ***** HOT *****    **** COLD *****      CRIT.    HEAT      FREEDOM     AREA        COST OF
           H    C      T        T         T        T           DT       LOAD                               PLANT
                        IN       OUT       IN       OUT
                       ***************** DEGR. F. ****************     10 000    BTU/HR.     SQ.FT.      DOLLARS/YR.

  HEATER        5      456.0    456.0     277.7    400.0       56.0     302.0       *)        143.0         687.5
EXCHANGER  2    1      480.0    310.9     153.4    400.0       80.0     532.5     189.0       310.3        1094.3
EXCHANGER  2    5      310.9    249.9     199.9    277.7       33.2     192.0      41.6       311.0        1097.6
EXCHANGER  4    3      400.0    195.8     150.0    360.0       40.0     514.5      50.4       800.4        1932.2
EXCHANGER  4    1      195.8    150.0      99.9    153.4       42.3     115.5      56.3       167.1         754.8


TOTAL COST OF PLANT IS     5566.6 DOLLARS PER YEAR
TOTAL UTILITY COST IS     32952.6 DOLLARS PER YEAR
      TOTAL COST IS       38519.2 DOLLARS PER YEAR          *)  FREEDOMS FOR HEATERS AND COOLERS ARE NOT EVALUATED
```

Sample printout for BLJF3 (Cont'd)

```
PROBLEM ..... 5SP1

                                                        VERSION ..............................................

                                                        NO. OF UNITS IS  7

EQUIPMENT IS ON DUTY FOR 8380.0 HRS./YEAR               TOTAL HEAT INPUT IS  356.1 * 10 000 BTU/HR.

STEAM PRESSURE IS 450.0 P.S.I.A.

COST OF STEAM IS 0.001 DOLLARS/LB.

COOLING WATER TEMPERATURE EXTREMES ARE 100.0 AND 180.0 DEGR. F.

COST OF COOLING WATER IS 0.00005 DOLLARS/LB.

HEAT TRANSFER COEFFICIENTS ARE
        200.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR HEATERS.
        150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR EXCHANGERS.
    AND 150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR COOLERS.

COST OF HEAT EXCHANGE SURFACE AREA IS EVALUATED BY MEANS OF THE EQUATION
        COST IN DOLLARS = A*(SURFACE AREA)**B
        WITH A = 350.0 AND B = 0.6

USEFUL LIFETIME OF PLANT IS 10 YEARS


          STREAMS     **** HOT ****     *** COLD ****     CRIT.    HEAT      FREEDOM     AREA       COST OF
           H    C      T        T         T       T        DT      LOAD                               PLANT
                        IN       OUT       IN      OUT
                      ***************** DEGR. F. *****************  10 000   BTU/HR.    SQ.FT.     DOLLARS/YR.

   HEATER       3     456.0    456.0     214.6   360.0     96.0    356.1        *)      112.9         596.7
EXCHANGER  2    5     480.0    464.3     380.0   400.0     80.0     49.4    189.0        40.0         320.5
EXCHANGER  4    5     400.0    223.5     200.0   380.0     20.0    444.6      0.0      1363.5        2659.9
EXCHANGER  2    1     464.3    258.6      99.9   400.0     64.3    648.0    139.5       413.5        1300.1
EXCHANGER  4    3     223.5    171.4     161.0   214.6      8.9    131.2    -27.8       905.4        2080.5
          ATTENTION *** DTMIN-CONSTRAINT IS VIOLATED IN THIS UNIT *** CHECK INPUT DATA

EXCHANGER' 2    3     258.6    249.9     149.9   161.0     97.5     27.1    244.2        18.2         200.1
   COOLER  4          171.4    150.0     100.0   151.4     20.0     54.1       *)       110.2         588.1


TOTAL COST OF PLANT IS     7746.3 DOLLARS PER YEAR
TOTAL UTILITY COST IS     43267.7 DOLLARS PER YEAR
       TOTAL COST IS      51014.1 DOLLARS PER YEAR             *)  FREEDOMS FOR HEATERS AND COOLERS ARE NOT EVALUATED
```

Sample printout for BLJF3 (Cont'd)

```
PROBLEM ..... SSP1

                                                                VERSION ..................................

                                                                NO. OF UNITS IS  7

                                                                TOTAL HEAT INPUT IS  356.1 * 10 000 BTU/HR.
EQUIPMENT IS ON DUTY FOR 8380.0 HRS./YEAR

STEAM PRESSURE IS 450.0 P.S.I.A.

COST OF STEAM IS 0.001 DOLLARS/LB.

COOLING WATER TEMPERATURE EXTREMES ARE 100.0 AND 180.0 DEGR. F.

COST OF COOLING WATER IS 0.00005 DOLLARS/LB.

HEAT TRANSFER COEFFICIENTS ARE
        200.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR HEATERS.
        150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR EXCHANGERS.
    AND 150.0 BTU/(HR.*SQ.FT.*DEGR.F.)  FOR COOLERS.

COST OF HEAT EXCHANGE SURFACE AREA IS EVALUATED BY MEANS OF THE EQUATION
        COST IN DOLLARS = A*(SURFACE AREA)**B
        WITH A = 350.0 AND B = 0.6

USEFUL LIFETIME OF PLANT IS 10 YEARS


            STREAMS    **** HOT ****     *** COLD ****      CRIT.    HEAT     FREEDOM     AREA        COST OF
            H    C     T        T        T        T          DT       LOAD                               PLANT
                        IN       OUT      IN       OUT
                       ***************** DEGR. F. ***************    10 000   BTU/HR.     SQ.FT.      DOLLARS/YR.

   HEATER        3     456.0    456.0    214.6    360.0      96.0    356.1       *)      112.9          596.7

EXCHANGER   2    3     480.0    471.0    203.1    214.6     265.3     28.1     772.9       7.0          112.7

EXCHANGER   2    5     471.0    455.3    380.0    400.0      71.0     49.4     160.8      44.9          343.4

EXCHANGER   4    5     400.0    223.5    200.0    380.0      20.0    444.6       0.0    1363.5         2659.9

EXCHANGER   2    1     455.3    249.6     99.9    400.0      55.3    648.0     111.4     455.4         1377.5

EXCHANGER   4    3     223.5    171.4    149.5    203.1      20.4    131.2       1.0     413.8         1300.6

   COOLER   4          171.4    150.0    100.0    151.4      20.0     54.1       *)     110.2          588.1

          ATTENTION *** STREAM NO.  2 DOES NOT NOT EXCHANGE ITS FULL HEAT LOAD *** CHECK INPUT DATA

          ATTENTION *** STREAM NO.  3 DOES NOT NOT EXCHANGE ITS FULL HEAT LOAD *** CHECK INPUT DATA

TOTAL COST OF PLANT IS      6979.3 DOLLARS PER YEAR
TOTAL UTILITY COST IS      43267.7 DOLLARS PER YEAR
       TOTAL COST IS       50247.1 DOLLARS PER YEAR           *) FREEDOMS FOR HEATERS AND COOLERS ARE NOT EVALUATED
```

APPENDIX H

THE COMBINATORIAL SIZE
OF GENERATION TREES
FOR MINIMUM NUMBER OF UNITS NETWORKS

As discussed in Section 8.4, synthesis methods that consider networks containing all possible matches simply start off from the "wrong end" of the problem. When tackled from the "right end" (i.e. by considering only those networks that contain the minimum number of units), the problem is less complex since fewer networks exist. Also, heat loads of matches are not open to choice in such networks so that there is no need for continuous optimisation.

In a way, the TC-Method as described in Chapter Seven represents just one particular possibility of carrying out an exhaustive search starting from the "right end" of the problem. Conceivably, other methods and techniques such as branch and bound could be based on a generation tree allowing for minimum number of units networks only. For this reason, the approximate size of such a generation tree is established below and is related to the size of the commonly accepted generation tree.

As discussed in Chapter Seven, Equation (7.2)

$$C_{n_{poss}}^{n_{min}} = \frac{n_{poss}!}{n_{min}! * (n_{poss} - n_{min})!} \qquad (7.2) \text{ Repeat}$$

identifies the number of heat load sets that can exist giving minimum number of units networks. Further, only about ten percent of the sets identified in this equation can be expected to pass a test based on heat load feasibility.

Finally, all sets that are feasible on heat load grounds have to be examined for various match sequences on any one stream. Assuming that on average there are between two and three connections per process stream (this is rather on the safe side) and that only one utility is used, there are approximately

$$\frac{2! + 3!}{2} * n_{min} = 4 * n_{min}$$

(where n_{min} expresses the number of process streams)

sequences to be examined for each feasible heat load set.

Thus, the total number of networks to be evaluated becomes approximately

$$Y \approx \frac{4}{10} * \frac{n_{poss}!}{(n_{min}-1)! * (n_{poss} - n_{min})!} \qquad (H.1)$$

In Table (H.1), Equation (H.1) has been evaluated for sample problems with i hot and i cold streams (i = 3,4,...,8) and one utility. Also, the results so obtained are contrasted against the size of the conventional generation tree as described by Ponton and Donaldson$^{(95)*}$. Further, the ratio of the sizes of the two types of generation trees is documented.

Table (H.1) Comparing the size of a conventional generation tree to that of one defined by Equation (H.1)

i	n_{min}	n_{poss}	X^* $(n_{poss}!)$	Y (see Equation H.1)	$\frac{X}{Y}$
3	6	12	$\sim 4.8 * 10^{8}$	$\sim 2.2 * 10^{3}$	$2.2 * 10^{5}$
4	8	20	$\sim 2.4 * 10^{18}$	$\sim 4.0 * 10^{5}$	$6.0 * 10^{12}$
5	10	30	$\sim 2.7 * 10^{32}$	$\sim 1.2 * 10^{8}$	$2.3 * 10^{24}$
6	12	42	$\sim 1.4 * 10^{51}$	$\sim 5.3 * 10^{10}$	$2.6 * 10^{40}$
7	14	56	$\sim 7.1 * 10^{74}$	$\sim 3.2 * 10^{13}$	$2.2 * 10^{61}$
8	16	72	$\sim 6.1 * 10^{103}$	$\sim 2.6 * 10^{16}$	$2.3 * 10^{87}$

From Table (H.1), it is quite evident that the conventional generation tree increases in size with i in a manner faster than factorial, i.e. according to

$$\frac{X(i = a)}{X(i = a - 1)} \approx \text{const} \; * i^{(b*i)}$$

$$(\text{with} \quad b > 1.0)$$

whereas the generation tree according to Equation (H.1) increases in a manner little worse than geometrical :

$$\frac{Y(i = a)}{Y(i = a - 1)} \approx \text{const}$$

---

*Ponton and Donaldson (95) used a formula such as Equation (5.1). However, as is evident from the discussion of the physical significance of this formula in Chapter Five, matches to utility are neglected in it. This is corrected in Table (H.1) by using simply $n_{poss}!$ to describe the size of the conventional generation tree, X.

Based on the conventional generation tree, networks with up to, say, six streams are normally considered to be amenable to complete solution while non-exhaustive methods produce satisfactory solutions of problems with up to, say, ten streams. Taking the corresponding entries under "X" in Table (H.1) as a guideline, as well as the growth characteristics just discussed, exhaustive procedures based on a minimum number of units generation tree should be possible for problems with up to, say, ten streams while non-exhaustive procedures might be possible for problems with up to thirty and more streams!

APPENDIX K

DATA FOR SYNTHESIS PROBLEMS

In this appendix, the data is brought together which defines the heat exchanger network synthesis problems discussed in the present thesis. In Table (K.1), the source is given in which each problem was introduced. Thereby, the notation "4SP2" was adopted for the four stream problem presented by Ponton and Donaldson(95) - Nishida et. al.(99) have already used this notation - and Problem 10SP1 in the modification suggested by Wells and Hodgkinson(100) was termed "10SP2". The abbreviations "TC1" and "TC2" stand for Test Case No.1 and Test Case No.2, respectively.

Table (K.1) Origin of synthesis problems

Presented by :	TC1	TC2	4SP1	4SP2	5SP1	6SP1	7SP1	7SP2	10SP1	10SP2
Masso and Rudd(90)					X		X	X		
Lee et al(91)			X			X				
Pho and Lapidus(94)									X	
Ponton and Donaldson(95)				X						
Wells and Hodgkinson(100)										X
Linnhoff and Flower *	X	X								

In Table (K.2) on pages K2 through K6, the process data for each problem is listed. Heat loads for each stream, overall heat balance, upper bound on energy recovery (based on $\Delta T_{min} = 20^{o}F$), and the sensitivity threshold for energy recovery (as discussed in Section 8.2) are included.

In Table (K.3) on page K7, the design data is given. With reference to 10SP2, the term "boiler" is used for exchangers in which steam is raised. Although it would seem logical to use the same values for heat transfer coefficient and ΔT_{min} as in heaters, the values proposed by Wells and Hodgkinson(100) (i.e. the same as for exchangers) were retained.

please turn to page K8

---

* See Appendix F

Table (K.2) Process data for synthesis problems

PROBLEM ..... TEST CASE NO. 1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR/DEGR.F.	10 000 BTU/HR
COLD STREAM NO. 1	160.00	400.0	1.500000	360.00
HOT STREAM NO. 2	400.0	120.0	1.000000	-280.00
COLD STREAM NO. 3	100.0	250.0	1.300000	195.00
HOT STREAM NO. 4	340.0	120.0	2.000000	-440.00

$\sum$ = 165.00 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 60.00 (H) ; 225.00 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} = 0$

PROBLEM ..... TEST CASE NO. 2

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR/DEGR.F	10 000 BTU/HR
COLD STREAM NO. 1	160.0	400.0	1.500000	360.00
HOT STREAM NO. 2	400.0	120.0	1.000000	280.00
COLD STREAM NO. 3	100.0	300.0	1.300000	260.00
HOT STREAM NO. 4	340.0	120.0	2.000000	-440.00

$\sum$ = 100.00 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 60.00 (H) ; 160.00 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} = 0$

Table (K.2) Process data for synthesis problems (Cont'd)

PROBLEM 4SP1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	140.0	320.0	1.445000	260.10
HOT STREAM NO. 2	320.0	200.0	1.666680	-200.00
COLD STREAM NO. 3	240.0	500.0	1.153000	299.78
HOT STREAM NO. 4	480.0	280.0	2.000000	-400.00

$\sum$ = 40.12 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{\circ}F$) : 46.14 (H) ; 86.26 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} = 0$

PROBLEM 4SP2

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	25.0	420.0	7.000000	2765.00
HOT STREAM NO. 2	500.0	110.0	2.000000	-780.00
HOT STREAM NO. 3	430.0	230.0	5.000000	-1000.00
HOT STREAM NO. 4	400.0	110.0	3.000000	-870.00

$\sum$ = 115.00 (H)

Upper bound on energy recovery ($\Delta T_{min} = 20^{\circ}F$) : 115.00 (H)

Sensitivity threshold for energy recovery : $\Delta T_{min} \approx 46^{\circ}F$

Table (K.2) Process data for synthesis problems (Cont'd)

PROBLEM 5SP1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	100.0	400.0	2.160000	648.00
HOT STREAM NO. 2	480.0	250.0	3.150000	-724.50
COLD STREAM NO. 3	150.0	360.0	2.450000	514.50
HOT STREAM NO. 4	400.0	150.0	2.520000	-630.00
COLD STREAM NO. 5	200.0	400.0	2.470000	494.00

$\sum$ = 302.00 (H)

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 302.00 (H)

Sensitivity threshold for energy recovery : $\Delta T_{min} \simeq 43^{o}F$

PROBLEM 6SP1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	100.0	430.0	1.600000	528.00
HOT STREAM NO. 2	440.0	150.0	2.800000	-812.00
COLD STREAM NO. 3	180.0	350.0	3.276000	556.92
HOT STREAM NO. 4	520.0	300.0	2.380000	-523.60
COLD STREAM NO. 5	200.0	400.0	2.635000	527.00
HOT STREAM NO. 6	390.0	150.0	3.360000	-806.40

$\sum$ = 530.00 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 530.00 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} \simeq 65^{o}F$

Table (K.2) Process data for synthesis problems (Cont'd)

PROBLEM 7SP1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	100.0	430.0	1.600000	520.00
HOT STREAM NO. 2	440.0	150.0	2.800000	-812.00
HOT STREAM NO. 3	520.0	300.0	2.380000	-523.60
COLD STREAM NO. 4	180.0	350.0	3.276000	556.92
COLD STREAM NO. 5	200.0	400.0	2.635000	527.00
COLD STREAM NO. 6	350.0	410.0	1.984000	119.04
HOT STREAM NO. 7	390.0	150.0	3.360000	-806.40
			$\sum$ =	411.04 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{\circ}F$) : 411.04 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} \simeq 49^{\circ}F$

PROBLEM 7SP2

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	200.0	400.0	1.600000	320.00
COLD STREAM NO. 2	100.0	430.0	1.600000	528.00
HOT STREAM NO. 3	590.0	400.0	2.376000	-451.44
COLD STREAM NO. 4	300.0	400.0	4.128000	412.79
HOT STREAM NO. 5	471.0	200.0	1.577000	-427.36
COLD STREAM NO. 6	150.0	280.0	2.624000	341.11
HOT STREAM NO. 7	533.0	150.0	1.320000	-505.56
			$\sum$ =	217.55 (H)

Upper bound on energy recovery ($\Delta T_{min} = 20^{\circ}F$) : 217.55 (H)

Sensitivity threshold for energy recovery : $\Delta T_{min} \simeq 51^{\circ}F$

Table (K.2) Process data for synthesis problems (Cont'd)

PROBLEM 10SP1

	T_{IN}	T_{OUT}	SPEC. HEAT	HEAT LOAD
	** DEGR.	F. **	10 000 BTU/HR./DEGR.F.	10 000 BTU/HR.
COLD STREAM NO. 1	140.0	320.0	1.445000	260.10
COLD STREAM NO. 2	240.0	431.0	1.153000	220.22
COLD STREAM NO. 3	100.0	430.0	1.600000	528.00
COLD STREAM NO. 4	180.0	350.0	3.276000	556.92
COLD STREAM NO. 5	200.0	400.0	2.635000	527.00
HOT STREAM NO. 6	320.0	200.0	1.667000	-200.04
HOT STREAM NO. 7	480.0	280.0	2.000000	-400.00
HOT STREAM NO. 8	440.0	150.0	2.000000	-812.00
HOT STREAM NO. 9	520.0	300.0	2.380000	-523.60
HOT STREAM NO.10	390.0	150.0	3.360000	-806.40
				$\sum$ = 649.79 (C)

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 649.79 (C)

Sensitivity threshold for energy recovery : $\Delta T_{min} \simeq 72^{o}F$

PROBLEM 10SP2

Streams No. 1 through 10 identical to 10SP1.

Further, a boiler feed water stream ($T_{IN} = 200^{o}F$, $T_{OUT} = 401^{o}F$) and steam ($T_{IN} = T_{OUT} = 401^{o}F$) of unknown mass flowrates as additional cold streams.

Upper bound on energy recovery ($\Delta T_{min} = 20^{o}F$) : 244.8 (C)

(This corresponds to 3942 lbs/hr. steam raised).

Sensitivity threshold for energy recovery : $\Delta T_{min} = 0$

Table (K.3) Design Data

Steam Pressure in Heaters	450 p.s.i.a. (962.5 p.s.i.a. for 4SP1)
Cost of Steam in Heaters	0.001 $/lb.
Boiler Feed Water Pressure	250 p.s.i.a.
Boiler Feed Water Supply Temperature	$200^{\circ}F$
Credit for Steam Raised	0.0008 $/lb.
Cooling Water Temperatures	$T_{in} = 100^{\circ}F$ $100^{\circ}F \leq T_{out} \leq 180^{\circ}F$
Cost of Cooling Water	0.00005 $/lb.
Specific Heat Boiler Feed Water and Cooling Water	1.0 Btu/lb/$^{\circ}$F
Equipment Downtime	260 hrs./year * (380 hrs./year for 4SP1, 5SP1 and 6SP1)
ΔT_{min}	$25^{\circ}F$ (Heaters) $20^{\circ}F$ (Exchangers, Boilers, Coolers)
Overall Heat Transfer Coefficient	200 Btu/hr/ft^2/$^{\circ}$F (Heaters) 150 Btu/hr/ft^2/$^{\circ}$F (Exchangers) 150 Btu/hr/ft^2/$^{\circ}$F (Boilers) 150 Btu/hr/ft^2/$^{\circ}$F (Coolers)
Cost of Heat Transfer Area A	$350 * A^{0.6}$ \$ (A in ft^2)
Useful Lifetime of Equipment	10 years

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* Masso and Rudd(90) presented Problem 5SP1 with 260 hrs./year but apart from themselves only Nishida et al.(99) have used this figure.

With reference to the steam pressure specification, it was pointed out by Nishida et al(99) that exact figures should be given for the latent heat to avoid discrepancies in utility costing. This was thought to help avoiding confusion, when comparing different workers' results. (The confusion which arose in the literature due to different costs quoted for identical designs is indeed considerable). Accordingly, Table (K.4) was made up which shows the values used in this work. Values for phase change temperatures are also shown in this table. An exact definition is desirable here, too, since the cost of plant will slightly vary with temperature differences and, more importantly, the upper bound on energy recovery may be sensitive where heat recovery is constrained by ΔT_{min} (see e.g. 10SP2).

Table (K.4) Additional steam data

Steam Pressure (p.s.i.a.)	Latent Heat (Btu/lb.)	T_{evap} (°F)
250	826.5	401
450	768.0	456
962.5	657.0	540

It should be pointed out, however, that differences due to variations in steam data cannot become as large as suggested by Nishida et al.* Also, and more importantly, individual workers' relative assessments of alternative solutions for an "SP-problem" must be identical even if considerably different steam data are used : best networks for these problems are compared on grounds of equipment cost since they all feature optimum utility costs anyway. In other words, if a particular worker suggests a particular network as optimum, he would have suggested the same network even if he had used different steam data. This argument provides validity to the survey given in Table (6.2).

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* Nishida et al. stated that differences of up to 80 $/yr can be explained by variations of 0.5 Btu/lb. in the figure used for latent heat. Even in the case of problem 5SP1, however, which has the highest requirements for steam, the difference in question only amounts to 22 $/yr.

APPENDIX L

TWO MORE SOLUTIONS FOR 4SP2

The two papers bound in Appendix F contain many references to the present thesis. To my best knowledge, these references were all taken up above in appropriate passages. For one reference, however, (see page 647 in Appendix F where two more topologies for 4SP2 are mentioned with six exchangers each and no split streams) an appropriate passage was not found. Thus, the topologies in question are shown below. The numerical information is given in Imperial Units, i.e. it is consistent with the data given in Appendix K.

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April 1979

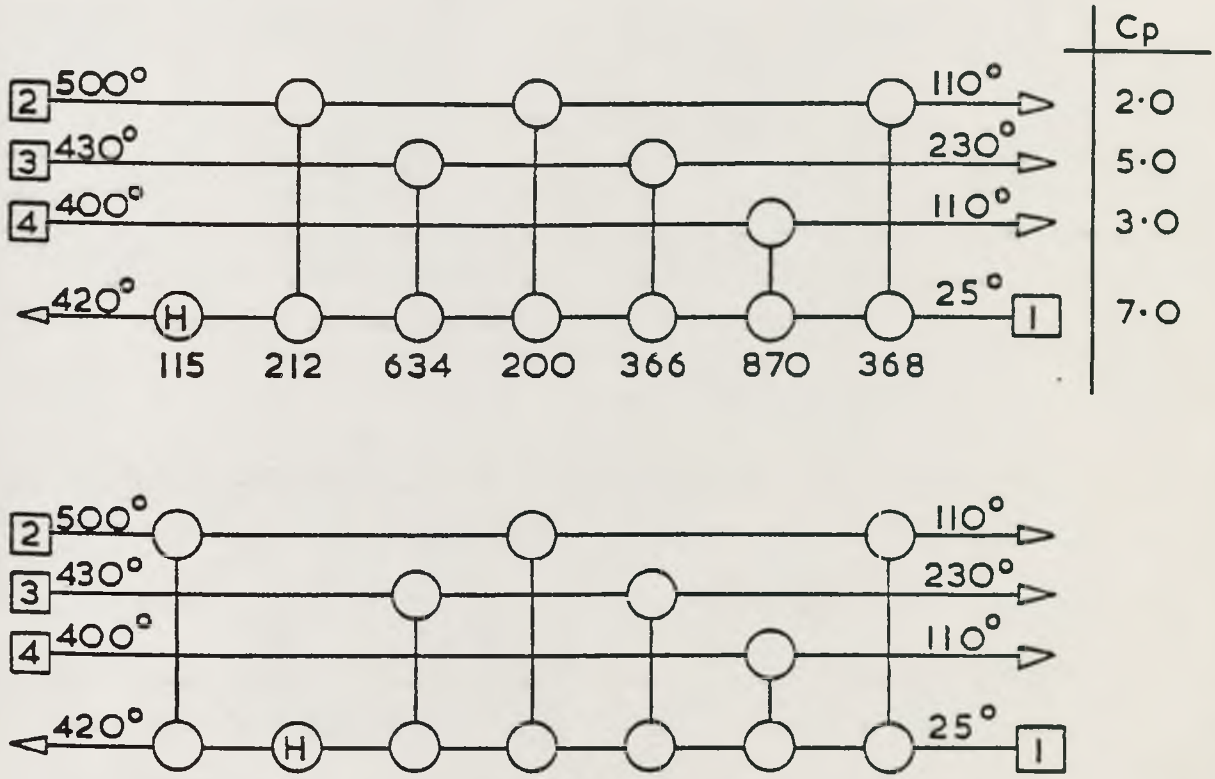

Figure (L.1) Two more solutions for 4SP2.