Entropy production as a measure for resource use

Method development and application to metallurgical processes

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There are only two things in the world that grow
when you give them away: Love and Entropy

(Anonymous)

Abstract

In this thesis, entropy production is introduced as a measure for resource use based on the laws of thermodynamics. The main motivation for the development of this measure is given by two facts: resource use is an important parameter in the ecological assessment of human activity and there exists as yet no satisfactory measure for the resource use of industrial processes. Also, linking ecological and economical aspects of industrial processes, entropy production and entropy export play an important role for the development of living structures. On the grounds of the laws of thermodynamics, the mathematical framework for analysing the entropy production of arbitrary processes is developed, including a method to compensate for incomplete data. Several basic applications of the concept of entropy analysis are given, which verify the proposition that entropy production and resource use are equivalent. In order to prove the method's practicability, an industrial-scale case-study is performed on the production of copper from ore concentrates and secondary (recycled) material. Interpreting the results reveals starting points for process optimisation and enables the comparison of production from concentrates and secondary materials respectively. Other proposed measures for resource use are discussed and compared to entropy production. Finally, it is shown how the method of entropy analysis can be integrated into the existing framework of ecological process (or product) assessment, especially life-cycle analysis.

Kurzzusammenfassung

In dieser Arbeit wird Entropieproduktion als Maß für Ressourcenverbrauch eingeführt. Als hauptsächliche Motivation dienen dabei zwei Umstände: Ressourcenverbrauch ist ein wichtiger Parameter in der ökologischen Einschätzung von menschlichen Aktivitäten, und es gibt bisher noch kein befriedigendes Maß für den Ressourcenverbrauch von industriellen Prozessen. Außerdem spielt Entropieproduktion und -export eine wichtige Rolle für die Entwicklung von lebenden Strukturen, ein Tatbestand der somit ökologische und ökonomische Aspekte von industriellen Prozessen miteinander verbindet. Aufbauend auf den Gesetzen der Thermodynamik, wird der mathematische Rahmen für eine Analyse der Entropieproduktion von beliebigen Prozessen entwickelt, inklusive einer Methode zum Ausgleich von fehlenden Daten. Einige grundlegende Anwendungen werden präsentiert, mithilfe derer die Bedeutung von Entropieproduktion als Maß für Ressourcenverbrauch bestätigt wird. Die Praktikabilität der Methode wird bewiesen mittels ihrer Anwendung auf ein industrielles Fallbeispiel: der Herstellung von Kupfer aus Erzkonzentraten und sekundärem (rezykliertem) Material. Eine Interpretation der Resultate enthüllt Startpunkte für eine Prozessoptimierung und ermöglicht den Vergleich von Kupferproduktion aus Erzkonzentraten, beziehungsweise sekundärem Material. Von anderer Seite vorgeschlagene Maße für Ressourcenverbrauch werden diskutiert und mit der Entropieproduktion verglichen. Abschließend wird gezeigt, wie sich die Methode der Entropieanalyse in den Rahmen der ökologischen Bewertung von Prozessen (oder Produkten) einbauen lässt, insbesondere in die Methode der Lebenszyklusanalyse (LCA).

Contents

Chapter 1

Introduction

1.1 Motivation and scientific context

For many decades now, thinkers and scientists have dealt with the question of the survival of humankind on this planet. The consensus among many of them is that a further uncontrolled growth of the human population plus its technical extensions, the *technosphere*, will have devastating effects on the environment and thus endanger the human species itself. For this reason, concepts for development have to be found which ensure the continuity of the human race without destroying its sustaining basis: the environment. One such concept is that of *sustainable development*. In one of its earliest formulations [14] it demanded that humans living on this planet today should satisfy their needs in a way which does not limit the ability of future generations to satisfy their needs. Although this formulation is simple and elegant, it lacks the necessary substance for supplying the directions needed for today's decision- and policy-makers. Furthermore, the progress towards sustainable development as defined by this early formulation proves difficult to be assessed: *the ability of future generations to satisfy their needs* is a property much too complex for measurement or assessment. In the public discussion following the first formulation of sustainable development, the goal of sustainability was divided into three aspects: social, ecological and economical sustainability. For each aspect one can now hope to find a measure that describes the actual progress towards sustainability.

A great step towards the practical application of the concept of sustainable development was made by the formulation of three basic rules for the management of substances at the *United Nations Conference on Environment and Development* in Rio de Janeiro in 1992 [68]. These rules were supplemented with a fourth rule by the *Enquete Commission of the German Bundestag on 'Protection of Humanity and the Environment'* in 1994 [22]. The four rules specify how the use of natural resources and the input of substances to the environment should be managed in order to preserve the functionality of nature as a supplier of resources and an absorber of residuals from economic activities:

1. *The depletion rates of renewable resources should not exceed their renewal rates. This is tantamount to the demand to preserve the ecology's efficiency, i.e. (at least) to safeguard the ecological real capital as defined in term of its functions.*
2. *Consumption of non-renewable resources should be limited to levels at which they can either be replaced by physically or functionally equivalent renewable resources or at which consumption can be offset by increasing the productivity of renewable or non-renewable resources.*
3. *Inputs of substances to the environment should be orientated towards the maximum absorption capacity of environmental media, taking into consideration all their functions, not least their 'hidden' and more sensitive regulating functions.*
4. *There must be a balanced ratio of the time-scales of man-made inputs to, or interventions in, the environment and the time-scales of the natural processes which are relevant for the reaction capacity of the environment.*

These rules need to be further specified to derive concrete guidelines for the decision-makers on the global, regional and local level. Tools have to be developed that aid in the assessment of the progress towards sustainability on all these levels. Introducing the concept of sustainable development thus opens a wide range of questions addressed to all members of humanity as to how it can be put into practice. Some of these questions must be answered by natural scientists, since they require quantitative answers which have to be derived from measurements performed on the metabolism of the technosphere[1]. One of the research fields especially apt for the physical sciences is the measurement of the quantities mentioned in the four rules of sustainable development from above: depletion and renewal rates of resources, consumption (or use) of resources, inputs of substances to the environment, time scales of interventions in the environment, and time scales of reactions of the environment. It is within this field of research that this thesis is situated. The main open question to be addressed is: *How can the use of resources of industrial processes be measured?* When this question is answered, it is straightforward to quantify the resource use of whole industrial sectors, households, regions, nations, and the human population as a whole.

Several attempts have been made to quantify the resource use, or find an approximation. Each of the measures so far proposed singles out one physical property of the materials and energy flows that make up the metabolism of the technosphere and use it as an indicator for, or as an approximation to the overall resource use. Three of these measures are discussed in this thesis.

The *MIPS (Material Intensity per Service Unit)* concept [61] measures the mass of the flows of matter traversing the production system of an economic good or service. This

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[1] The term *technosphere* describes the part of the biosphere (the life-bearing part of our planet) which is directly influenced and changed by humans and their artificial extensions.

approach does not, however, consider the actual *use* of the material flows, since it does not quantify their transformation. It rather measures the *throughput* of resources through the respective production system. Therefore, it cannot serve as a valid measure for resource use.

The *Cumulative Energy Demand (CED)* [30] is defined as the cumulative sum of all energetic inputs (flows of matter that have a non-zero heat of combustion) to the production system of a good or service. As with the MIPS approach, it also fails to consider the transformation of material flows and can therefore not be considered a valid measure for resource use either. It merely measures the throughput of energetic resources through the production system.

The *Exergy Analysis* [54, 67, 34, 6] measures the loss of available work due to the transformation of matter and energy and therefore quantifies the actual use of these flows. This loss is very closely linked to entropy production, the measure for resource use proposed in this thesis, and reflects the fact that exergy analysis is based on the second law of thermodynamics. However, the definition of exergy is based on the postulation of a *reference environment* that approximately describes the equilibrium state of the natural environment. This definition is not only based on the questionable assumption of an environment in equilibrium, but also introduces an unnecessary complication to the quantification of resource use. The interesting quantity, lost exergy, can more easily be determined by computing the associated entropy production, thereby sidestepping the mentioned difficulties.

The limitations of the above-mentioned candidates as a measure for resource use make it necessary, in the author's opinion, to develop a new measure for resource use which does not suffer from these limitations and which correctly describes the devaluation of matter and energy flows associated with the production of goods and services. This measure should be based on the second law of thermodynamics, since this is the fundamental physical law that describes the irreversible nature of all processes and thus quantifies the mentioned devaluation of matter and energy flows.

Thus, the main proposition of this thesis is that the entropy produced by a process is an exact measure of the use of resources attributable to this process. Then the use of environmental resources by the human population would simply be the sum of all entropy produced by processes related to human living. This argument is based on the assumption that 'using' a resource is basically equivalent to transforming it.

From the first and second law of thermodynamics we know that energy is never destroyed or created, but merely transformed. From special relativity we know that matter is a form of energy. In physical or chemical processes, the state of the energy or matter is changed, not the quantity[2]. A valid physical measure for the extent of this transformation process is the thereby produced entropy, which makes it a well defined candidate for the sought measure for resource use. The rate of resource use is then equally well defined by the entropy production rate. If one could quantify the entropy production rate of the human population, one could compare this to the entropy production rate of the whole

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[2] In most industrial processes an even stronger restriction holds. Since in these processes the conversion of matter into energy and vice versa can safely be neglected, mass and energy are conserved independently.

planet, thereby obtaining a measure for one aspect of the overall impact of humans on Earth, namely their resource use[3]. The entropy export ability of the planet is mainly determined by the temperature of the upper atmosphere. Energy conservation dictates that this temperature is more or less fixed[4], setting a natural limit for Earth's entropy export. On the other hand, one of the necessary conditions for a preservation of the (dynamical) status quo of life on Earth is a constant entropy content of the Earth. In other words: all living organisms on Earth can only produce entropy at a certain rate so that the total rate does not exceed the natural limit given by the entropy export ability of the Earth. If one species increases its entropy production rate, other species have to decrease theirs in return so that the net result is balanced. Again, knowing the actual entropy production of the human population would allow to quantify its role in the dissipative system Earth and eventually give rise to establishing real 'limits to growth'.

Having calculated the entropy production associated with a process (or the human population), this should be compared to a common standard or an intrinsic quantity of the process. This is very much related to finding a measure for the *efficiency* of the process. The meaning of this is obvious when one considers entropy production as a measure for resource use. If two competitive processes with differing entropy production are considered the one with the lower value is the more efficient one (in this 'entropical' sense), since it uses (i.e. transforms) less resources. For processes that have the same product or function, the entropy production (per product unit) works fine as a measure of efficiency.

The entropy production of a system is found by balancing the entropy of incoming and outgoing flows of matter and energy, and by determining the internal entropy accumulation. This is referred to as the *entropy balance.* In many cases the internal accumulation can be neglected or is zero. The results can be further analysed to find the main causes of entropy production and thus locate the stages with the largest irreversibilities. This step is referred to as *entropy analysis.*
When analysing the entropy balance of a process one can distinguish between three sources of entropy production, namely: ,

- Heat transfer across temperature gradients (convection, conduction and radiation)
- Mixing of substances (diffusion and dissipation)
- Chemical and physical transformation of materials (phase transitions, chemical reactions etc.)

Knowing the main sources of entropy production along the material flow of a process means

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[3] There are many other factors that determine the impact of a species on the complex system Earth, like the production of toxic emissions, or use of land, that are not linked to entropy production. This measure can therefore only serve as a first approximation to the problem of quantifying our ecological impact.

[4] It is assumed that the energy content of the Earth is constant. However, variations could arise from an increased fixation of solar radiation, e.g. by increased photosynthesis, from an increased release of formerly stored energy, e.g. by burning fossil fuels, or from changes in the atmospheric processes governing the energy and entropy export into space.

knowing the major irreversibilities, and thus pinpoints the highest waste of resources. This evidently facilitates the determination of the starting points for process optimisation. In most industrial processes the main source of entropy production is the transformation of chemical (or electrical) energy into thermal energy, e.g. by burning fuel. This is of course no surprise, since energy is one of the main production factors in almost any industry. In standard energy analysis, however, there is no reference to the ‘quality’ of the energy, i.e. what part of it can be utilised and how much is simply wasted inside the process boundaries. However, the main advantage of the entropy balance approach to measuring resource use is that it takes into account *how* the energy was transformed and how much of it was wasted[5].

The open question at the beginning of this PhD project arose from very different contexts. The primary question targeted by this thesis was, *How can the resource use of industrial processes be measured.* The proposed answer is: by measuring the entropy production of the process. The validity of this hypothesis was shown by theoretically examining the meaning of entropy production (and export) for complex dissipative structures, and by finding basic examples that show the connection between entropy production and resource use. Additionally, a framework for the general application of the method of entropy analysis was developed by describing arbitrary processes in terms of their material and energy flows and deriving the formulae determining the associated entropy production.
The greatest challenge, however, was the application of the method of entropy analysis to a real-life industrial process, namely the production of copper from ores and secondary materials. The main tasks in the course of this analysis were to find a valid representation of the process and to gather the required data describing this process. The representation of the process was to have the right level of detail in order for the analysis to yield realistic results without focussing too much on negligible contributions and side-processes. The representation of the process of copper production was derived from the technical and engineering literature on this subject and modelled along the set-up of the *Norddeutsche Affinerie (NA)* copper plant in Hamburg. Specifics were discussed with various scientists and engineers from the field of metallurgy and from the metallurgical industry to work out the admissible simplifications to the model. A much harder problem was to gather the data describing the process in sufficient detail. The literature on this subject was to a large extent outdated, imprecise or even inconsistent. This problem was also solved by conferring with scientists and engineers, mainly from the NA and the *Institut für Metallwesen und Elektrometallurgie (IME)* at the RWTH Aachen. The multiple data sources yielded a description of the process which was partly imprecise and inconsistent. This problem had to be solved by an iterative data-reconciliation process until all material and energy flows of the process were consistent. The actual entropy production was then calculated from the physical and chemical properties of the material and energy flows by employing the well-known relations from thermodynamics. It has turned out that the data requirements for an entropy analysis are somewhat higher than for the usual inventory of a *life-cycle*

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[5] The exergy analysis approach actually tackles this problem in a way quite similar to the entropy analysis method.

analysis[6], but this does not limit the applicability of the method significantly.

Another proposition made at the beginning of this project was that *analysing the entropy production of a process would reveal the starting points for a process optimisation* in terms of minimised resource use. This was demonstrated by locating the main sources of entropy production within the analysed production system, and by identifying the physical causes.

The statement that *entropy analysis and exergy analysis are basically equivalent*, following from theoretical considerations, was investigated by calculating the entropy production from published exergy analyses of equivalent processes [4, 31, 1] and comparing these values to the results from the case study in this thesis.

Lastly, there was the question of *whether the method of entropy analysis could be integrated into the existing tools for ecological assessment of industrial processes*, as, for example, life-cycle analysis. This question is of special importance, since the current practice of assessing the ecological impact of processes does not take the resource use into account. Instead, only the throughput of matter and energy associated with these processes is considered. The question was answered positively by laying out the necessary steps and describing the requirements of an implementation of entropy analysis.

1.2 Disposition

The hypothesis of this thesis, ‘Entropy production is an exact measure for resource use’, is easily stated and demands only little further explanation. However, it needs to be shown how this hypothesis springs from the basic thermodynamic laws, which is done in chapter 2. This chapter also includes some examples for the meaning of entropy production for dissipative systems, which motivates the use of entropy production as a measure for resource use.

Although the term ‘resource’ is commonly used, it has to be specified more clearly, which is done in chapter 3. In this chapter, the proper introduction of entropy production as a measure for resource use is given, and a comparison with other candidates for such a measure is made. Finally, a few statements are made about efficiency and how it can be determined from entropy production.

Chapter 4 then presents the necessary steps in order to determine the entropy production of industrial production systems by analysing the entropy change. This is usually facilitated by setting up an entropy balance[7].

The next chapter gives a few basic examples of the calculation of entropy production, and shows how it is linked to resource use.

Chapter 6 then gives a detailed, industry-scale example of how entropy analysis can be applied to real-life processes. The case studied is the production of copper from primary

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[6] One of the standard tools for assessing the ecological impact associated with the production, use and disposal of an economic good or service.

[7] Since the *entropy balance* directly yields the *entropy production*, as excess entropy, the two terms are sometimes used as synonyms.

and secondary materials. The problems encountered were not so much related to thermodynamics, but are due to poor data quality and gaps in the process description. Numerous assumptions had to be made, which are explained and motivated. Interpreting the results gives hints for the starting point of a process optimisation, and yields a basis for comparison with alternative processes. The primary and secondary copper production can also be compared directly regarding their resource use by looking at their respective entropy production per product unit. Three process alternatives for the recycling of copper scrap in a primary copper plant are discussed.
Chapter 7 compares the results from the entropy analysis with results obtained by using other approaches to measure resource use, namely the *cumulative energy demand (CED)*, the *MIPS concept (material input per service unit)* and the *exergy analysis*. The comparison between entropy analysis and CED or MIPS can only be qualitative. The comparison with results from different exergy analyses, however, showed general agreement in the relation between different alternatives, but the absolute differences were still large. A detailed discussion is included in chapter 7.
Chapter 8 then addresses the question of how entropy analysis can be integrated into the framework of life-cycle analysis.

In summary, the task was to find a general measure for resource use, which is rooted in the framework of thermodynamics and which maps the degradation of material and energy streams to a physical quantity. The measure should also be applicable to arbitrary processes. The already existing measures that try to quantify resource use were found to be insufficient or unnecessarily complicated. The entropy production fulfils the requirements stated above and the tool of entropy analysis is readily applicable to arbitrary processes.

Chapter 2

Entropy and complex dissipative systems

This section establishes the theoretical foundation of the entropy analysis approach to measuring the resource use of processes. It gives an overview of the concept of entropy, and shows how it is applied to dissipative systems.

2.1 The second law of thermodynamics and irreversible processes

In 1769 James Watt obtained a patent for a modification of Thomas Newcomen's steam engine. The rapid spreading of this invention across the world brought about not only the economic and social changes of the industrial revolution, but also gave a boost to the rather new field of thermodynamics, or the theory of heat. One of the corner stones of thermodynamics is its second law, sometimes referred to as the entropy law. The first law of thermodynamics was in essence the extension of the well-known law of energy conservation from Newtonian mechanics to many-particle systems[1]. The second law, however, revealed a new property of macroscopic systems that could not be explained by the microscopic properties and laws alone: the irreversibility of processes and the implied breakdown of time-symmetry. This effect was mathematically formulated with the help of a new physical quantity: entropy. Matching the topic of this thesis, entropy found its origin in the considerations of the efficiency of industrial machines: Sadi Carnot's thoughts on the efficiency of Watt's steam engines, or more generally on the efficiency of heat engines. He concluded that there must be a universal limit to the efficiency which is solely dependent on the temperatures of the involved heat reservoirs. Though he could not yet quantify his findings, he had already distinguished between reversible cyclic engines and irreversible ones[2]. The

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[1] However, it took around 150 years to conceptualise this extension. One of the obstacles was the initial view of heat as a substance (calor).

[2] In general, a reversible process is a process in which the variables that define the state of the system can be made to change in such a way that they pass through the same values in the reverse order when

latter ones, he remarked, had a non-maximal efficiency. Many years later Émile Clapeyron reproduced Carnot's ideas and described Carnot's reversible heat engine in mathematical detail. He found the maximal efficiency η of this type of heat engine to be

$$\eta = 1 - \frac{T_2}{T_1}\,, \tag{2.1}$$

with T_2 and T_1 being the absolute temperatures of the two heat reservoirs[3]. Rudolf Clausius then generalised Carnot's and Clapeyron's ideas to arbitrary reversible cycles (not limited to isothermal and adiabatic transitions). For a system that goes through an arbitrary reversible cycle, he found that the quantity $\delta Q/T$, with δQ being the infinitesimal heat exchanged with the environment at temperature T, obeyed

$$\oint \frac{\delta Q}{T} = 0\,, \tag{2.2}$$

where the closed integration path corresponds to a closed path of system changes. This finding gave rise to Clausius' definition of the state function entropy (derived from the Greek word $\tau\rho o\pi\eta$ = transformation) S for *reversible processes* by

$$dS = \frac{\delta Q}{T} \quad \text{or} \quad S_B - S_A = \int_A^B \frac{\delta Q}{T}\,, \tag{2.3}$$

and for *irreversible processes* by

$$dS \geq \frac{\delta Q}{T} \quad \text{or} \quad S_B - S_A \geq \int_A^B \frac{\delta Q}{T}\,. \tag{2.4}$$

The infinitesimal change of entropy dS can be rewritten in terms of two contributions: one that is due to exchange of matter and energy with the exterior, d_eS, and one that is due to internal irreversible processes, d_iS:

$$dS = d_eS + d_iS \quad \text{with} \quad \oint dS = \oint d_eS + \oint d_iS = 0\,. \tag{2.5}$$

Carnot's observation of the limited convertibility of heat into work and the subsequent analysis of Clapeyron and Clausius can be summarised in a statement known as the second law of thermodynamics:

> *"It is impossible to construct an engine which will work in a complete cycle, and convert all the heat it absorbs from a reservoir into work."*

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the process is reversed. It is also a condition of a reversible process that any exchanges of energy, work, or matter with the surroundings should be reversed in direction and order when the process is reversed. Any process that does not comply with these conditions when it is reversed is said to be an irreversible process. All natural processes are irreversible, although some processes can be made to approach closely to a reversible process.

[3] Actually, the absolute temperature scale was introduced later, by Lord Kelvin, as a consequence of the universal efficiency of reversible heat engines.

This purely macroscopic statement can be rephrased in many ways which reflect the many possible applications of the concept of entropy and the second law of thermodynamics. Clausius originally formulated the second law as

> *"Heat cannot by itself pass from a colder to a hotter body."*

Applying the entropy concept to cyclic processes, another valid formulation of the second law can be derived as

> *"The sum of the entropy of a system and its exterior cannot decrease."*

Yet another, very popular summary of the first and the second law of thermodynamics was also given by Clausius himself:

> *"The energy of the universe is a constant."*
> *"The entropy of the universe approaches a maximum."*

Generalising the idea of reversibility to arbitrary cycles, irreversibilities can be identified with $d_i S > 0$. For systems only exchanging energy with the exterior (closed systems) we then have

$$\oint d_e S = \oint \frac{\delta Q}{T} \leq 0\,. \tag{2.6}$$

This implies two important things:

- A closed system returning to its initial state has to discard its internally produced entropy through the expulsion of heat to the exterior.
- The increase of entropy distinguishes the past from the future and this defines an arrow of time.

The first statement can be generalised to *open systems* (systems which are exchanging energy and matter with the exterior) as follows below. An open system, in general, is not in equilibrium, demanding a description of its thermodynamic state in terms of local variables and flows. Still, the first conclusion from above holds for open systems that maintain their thermodynamic state: the internally produced entropy has to be exported to the exterior in the form of matter or heat flows. The validity of the second law of thermodynamics is not restricted to purely physical systems, and applies to all scales of (material) systems, from microscopic particles over biological systems to the universe itself. The first conclusion above is especially relevant for living systems. The environment serves them thus two purposes: supply of free energy in the form of food and disposal of internally produced entropy.

Quite generally, every naturally occurring process is irreversible. Reversibility is only approached in the limit of infinite slowness of processes. This also implies that the efficiency of a process in terms of reversibility is, in essence, a function of the speed of the process in relation to the inherent relaxation times of the system. The derivation of the maximal efficiency of heat engines by Carnot and Clapeyron explicitly demanded quasi-static processes and infinitely small temperature gradients. Thus, the deviation from these conditions along the thermodynamic path of a process determines its irreversibility and is apparent in the production of entropy.

2.2 Irreversible processes in open systems

For open systems it is convenient to split up changes of energy E and entropy S into internal and external contributions, as mentioned above:

$$\begin{aligned} dE &= d_eE + d_iE \\ dS &= d_eS + d_iS\,. \end{aligned}$$

Since (in non-nuclear processes) energy cannot be created or destroyed, $d_iE = 0$. The exchanged energy of an open system, allowing for irreversible processes, is then [21]

$$d_eE = \sum_i l_i dL_i + \sum_k \mu_k d_eN_k + \delta Q + \delta W_{irr}\,, \tag{2.7}$$

with l_i and L_i being conjugated variables, e.g. $l = -p$ and $L = V$, μ_k being the chemical potential of the chemical species k, and δW_{irr} being the irreversible work performed on the system, e.g friction. Accordingly, one finds for the entropy

$$d_eS = \frac{\delta Q}{T} - \frac{1}{T}\sum_k \mu_k d_eN_k \tag{2.8}$$

$$d_iS = \frac{\delta W_{irr}}{T} - \frac{1}{T}\sum_k \mu_k d_iN_k\,. \tag{2.9}$$

The entropy of a system may decrease when the entropy export overcompensates the internal entropy production:

$$dS < 0 \quad \text{if} \quad -d_eS > d_iS \geq 0\,. \tag{2.10}$$

This is only achievable for systems far from equilibrium, since otherwise $d_iS > 0$ would always dominate the entropy balance and drive the system towards equilibrium. Being far from equilibrium means that some of the parameters of a system are beyond threshold values marking the beginning of a regime of the system where self-organisation is possible. Only such systems can have a decreasing entropy. Thus, the emergence of structure and self-organisation, which is coupled to a decrease of entropy, is an ‘overcritical’ phenomenon, meaning it only appears when certain system parameters exceed critical values [21].

According to Werner Ebeling [21], systems exhibiting the ability to export more entropy than is internally produced usually possess an entropy pump of some sort. This pump is fed with free energy from a source which is either inside or outside of the system. Self-organising systems that have this pump inside their system boundaries are called ‘active’ systems, while systems with their pump outside are called ‘passive’ accordingly. Most physical systems exhibiting self-organisation are passive systems: Bénard cells, laser, electronic devices, etc. Many biological systems are active: animals, plants, humans, etc. The Earth itself is a passive system, since its entropy pump is the sun plus the surrounding universe.

If the system is isothermal and isobaric, the entropy export can be expressed through the enthalpy H and the Gibbs free enthalpy of the system G:

$$d_eS = \frac{1}{T}(dH - d_eG) \quad \text{and thus} \quad d_eG > (dH + Td_iS)\,, \tag{2.11}$$

where we have used the condition for self-organisation $-d_eS > d_iS$. In other words, the system must import enough free enthalpy to compensate for the total enthalpy change *plus* the internal entropy production.

The thermodynamic variables of a system far from equilibrium will, in general, show non-linear interdependencies. This is an essential property of all natural self-organising systems. *In summary, self-organisation is a property of non-linear systems, which only emerges under specific internal and external conditions far from equilibrium. These systems must be supplied with a sufficient amount of free energy and/or matter and must possess the ability to passively or actively export entropy.* Comparing the properties of systems which are either close or far away from equilibrium, one can distinguish two types of irreversible processes in nature:

- structure destroying processes in systems close to equilibrium, and
- structure creating processes in systems far from equilibrium under specific conditions (non-linearity, overcritical parameters).

According to Ilya Prigogine [53, 23], the stable (spatial, temporal or spatial-temporal) structures far from equilibrium and in the non-linear, overcritical regime are called *dissipative structures.* Examples are the Bènard cells and living organisms. For *linear* irreversible processes, Prigogine showed that in the vicinity of thermodynamic equilibrium, the entropy production density tends towards a minimum. Such a system, if perturbed from its stationary state, will develop in time with decreasing entropy production, approaching a stationary state. This is known as the *Prigogine Theorem.* Formally, the entropy production rate density σ of a homogeneous system with volume V is defined by [21]

$$\sigma := \frac{1}{V}\frac{d_iS}{dt}\,, \tag{2.12}$$

and can be expressed through generalised thermodynamic forces $\boldsymbol{X}_\alpha$ and flows $\boldsymbol{J}_\alpha$ as

$$\sigma = \sum_\alpha \boldsymbol{X}_\alpha \boldsymbol{J}_\alpha \,. \tag{2.13}$$

A typical example of a generalised force is $\boldsymbol{X} = \boldsymbol{F}/T$, where $\boldsymbol{F}$ is an external force acting on a system, forcing particles to flow with a flow density $\boldsymbol{J}$. The dissipative work from (2.8) then takes the form $\delta W_{irr} = (\boldsymbol{X}\boldsymbol{J})VTdt$ leading to the above formula for σ. Near equilibrium the flows can be assumed to be functions of the forces and can be expanded around their equilibrium values. Keeping only linear terms, the expansion reads

$$\boldsymbol{J}_\alpha = \sum_\beta L_{\alpha\beta} \boldsymbol{X}_\alpha \quad \text{with} \quad L_{\alpha\beta} = \left(\frac{\partial \boldsymbol{J}_\alpha}{\partial \boldsymbol{X}_\beta} \right)^{(0)} , \tag{2.14}$$

where (0) denotes the equilibrium value.
These so called *linear Onsager relations* lead to a quadratic expression for the entropy production density

$$\sigma = \sum_{\alpha\beta} L_{\alpha\beta} \boldsymbol{X}_\alpha \boldsymbol{X}_\beta \geq 0 \,. \tag{2.15}$$

The positive definiteness of σ implies the same for the coupling matrix $L_{\alpha\beta}$. Onsager even concluded from symmetry consideration that

$$L_{\alpha\beta} = L_{\beta\alpha} \,. \tag{2.16}$$

Prigogine then could show that for flows and forces in the vicinity of their stationary values, the change in σ can be expressed as

$$\delta\sigma = \sum_{\alpha\beta} L_{\alpha\beta} \delta\boldsymbol{X}_\alpha \delta\boldsymbol{X}_\beta \geq 0 \tag{2.17}$$

$$\text{with} \quad \delta\sigma = 0 \quad \text{only if} \quad \delta\boldsymbol{X}_\alpha = 0 \,. \tag{2.18}$$

This led to the above-mentioned Prigogine theorem. Although the derivation of (2.17) was based on the assumption of a homogeneous system, it can readily be extended to inhomogeneous systems by introducing local densities, for example mass density $\rho(\boldsymbol{r}, t)$, entropy density $s(\boldsymbol{r}, t)$ with $\int \rho(\boldsymbol{r}, t) s(\boldsymbol{r}, t) dV = S(t)$ and the corresponding flow densities. Equation (2.17) then reads

$$\delta\sigma(\boldsymbol{r}, t) \geq 0 \quad \text{with} \quad \delta\sigma(\boldsymbol{r}, t) = 0 \quad \text{only if} \quad \boldsymbol{X}_\alpha(\boldsymbol{r}, t) = \boldsymbol{X}_\alpha^{(0)}(\boldsymbol{r}) \,, \tag{2.19}$$

with $\boldsymbol{X}_\alpha^{(0)}(\boldsymbol{r})$ being the stationary local forces.

The most important conclusion from the Prigogine theorem is that *linear* irreversible processes tend toward a stationary state with minimum entropy production. Thus, evolutionary processes, which consist of an endless chain of processes, cannot exist in the linear regime and must be sought in the area of *non-linear, non-equilibrium processes.* It seems that evolutionary processes are not bound by the minimum entropy production principle in general. The stable systems between evolutionary steps, however, obey Prigogine's theorem, and tend towards a state where the entropy production is minimised.

2.3 Entropy production in living and non-living dissipative structures

A living being can be described as an open thermodynamic system far from equilibrium in the above sense. Thus, the laws of self-organisation as outlined above also hold in this case, as is shown in the following. Assuming constant pressure and temperature, the amount of free enthalpy to be imported to maintain a stationary state d_eG is determined by

$$\frac{d_eG}{dt} = T\frac{d_iS}{dt} > 0\,. \tag{2.20}$$

The export of entropy is facilitated by exchange of heat and matter with the environment. It is assumed that the living being has a temperature of $T_L = T_0 + \Delta T$, with T_0 being the temperature of the environment. The rate of heat exchange with the environment through conduction is denoted by q_C. Additionally, it absorbs radiation q_A from the environment and emits radiation q_E. For photosynthetically-active beings, the radiation absorbed from the sun is an important factor for their functioning. Since the absorption is, in general, very selective, it is appropriate to assume several radiation components q_S^i of temperature T_S^i. The matter exchanged with the environment consists of chemical components k with molar entropy s_k and mole number N_k. The entropy export is then given by [21]

$$-\frac{d_eS}{dt} = q_C\left(\frac{1}{T_0} - \frac{1}{T_L}\right) + \frac{4}{3}\frac{q_E}{T_L} - \frac{4}{3}\frac{q_A}{T_0} - \sum_i \frac{4}{3}\frac{q_S^i}{T_S^i} - \sum_k s_k\frac{d_eN_k}{dt} \geq \frac{d_iS}{dt} > 0\,. \tag{2.21}$$

The entropy production will have the general form

$$P \equiv \frac{d_iS}{dt} = \frac{1}{T_L}\frac{\delta W_{irr}}{dt} - \frac{1}{T_L}\sum_k \mu_k\frac{d_iN_k}{dt}\,. \tag{2.22}$$

Equation (2.21) is sometimes called ‘the fourth law of thermodynamics for living systems’ [21] and determines the thermodynamically necessary conditions for life in general. The equality in (2.21) only holds for stationary states. For phases of growth, like embryogenesis, adolescence, recovery from injury and others, the stronger condition

$$-\frac{d_eS}{dt} > \frac{d_iS}{dt} > 0 \tag{2.23}$$

applies.

It is evident that the production of entropy and its export to the environment is an important factor for the stability of complex dissipative structures. If several such structures coexist in the same local environment, it is also evident that they will not only compete for the sources of free energy (the ‘resources’), but also for the possibility to export entropy to environmental ‘sinks’. In general, the local environment itself will also have a limited ability to export entropy to a meta-environment. For a meta-environment with entropy

S, having sub-environments with entropy S'_j, which again have sub-sub-environments with entropy S''_{jk} and so forth, the stability condition (2.21) becomes

$$\frac{d_iS}{dt} + \sum_j \frac{d_iS'_j}{dt} + \sum_{jk} \frac{d_iS''_{jk}}{dt} + \cdots \leq -\frac{d_eS}{dt}\,. \tag{2.24}$$

Naturally, an increase in the entropy production of one of the sub-systems will reduce the available capacity for entropy export of the other sub-systems. The entropy export rate of the meta-environment will generally depend on internal and external parameters. The ability to export entropy might therefore very well be affected by the activity of one or more of the subsystems. As observed in many examples of dissipative structures, the system's answer to an overcritical change in internal or external flows and forces is to 'seek' new patterns of internal structure that enable an enhanced entropy export. This transition appears in a way that fluctuations in the internal material and energy flows begin to increase until a new configuration is found that corresponds to a stable state. Dissipative structures are always non-linear systems, which allows for small variations in one of the parameters to have large effects on the whole system. It is therefore easily conceivable that even a slight increase in the entropy production or metabolism of one of the sub-systems might have detrimental effects on the meta-environment and the other sub-systems. However, to exactly quantify the critical parameters of a complex dissipative system remains difficult, if not impossible in many cases.

A simple example for a dissipative structure is the emergence of *Bénard cells* in layers of liquids exposed to a temperature gradient (see figures 2.1 and 2.2). The entropy export

Figure 2.1: Numerical simulation of a convective pattern in a horizontal layer of a fluid subjected to a vertical temperature gradient. The pattern is known as Bénard cells. Taken from [38].

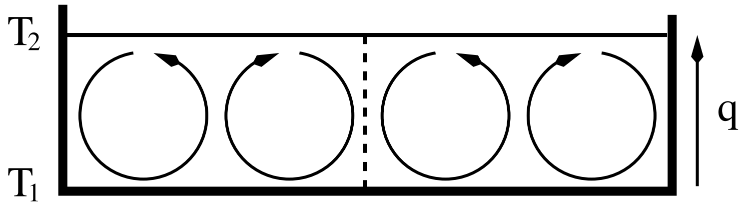

Figure 2.2: Schematics of the experimental set-up to observe Bénard cells. A horizontal liquid layer is subjected to a temperature gradient $T_2 - T_1$, causing a heat flow q. If the temperature difference exceeds a critical value, one observes the emergence of convective patterns as indicated.

rate of the liquid layer is given by

$$\frac{d_e S}{dt} = \frac{q}{T_1} - \frac{q}{T_2} = q\frac{T_2 - T_1}{T_1 T_2}\,. \tag{2.25}$$

The transfer of heat through the system is due to convection and conduction. For $\Delta T = T_2 - T_1$ below some critical value ΔT_c, the transport is mainly due to conduction. For $\Delta T > \Delta T_c$ the convection cells appear and heat transfer through the layer increases significantly (see figure 2.3). If the liquid layer is heated further, the cell pattern runs through a

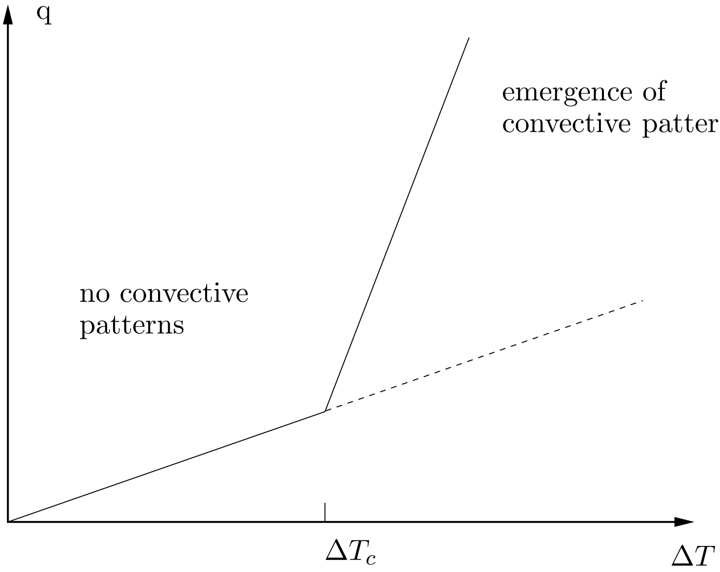

Figure 2.3: At the transition from conduction dominated to convection dominated heat transfer, the heat transfer rate shows a typical increase. This coincides with the emergence of convective patterns.

series of increasingly complex configurations until the convection eventually becomes turbulent. This transition into chaos is known from many non-linear systems and signals the breakdown of the conditions for self-organisation.

The findings from the Bénard cells can be generalised to arbitrary liquids, geometries and temperature differences by expressing the governing equations in terms of the dimensionless parameters *Reynolds number* and *Prandtl number*. If the liquid layer takes the form of a sphere and one allows for a more complex composition, including concentration gradients, the system can be used to model oceanic or atmospheric currents. Even the most trivial non-linear systems show almost unpredictable behaviour, which should remind us to use great caution when manipulating far more complex systems in our environment. The entropy export ability plays an important role in this process.

The role of entropy export for living systems shall be exemplified by the development of a *fertilised amphibian egg*. The entropy export is facilitated by two mechanisms: the exchange of heat and the exchange of gaseous flows with the environment, i.e.

$$d_e S = \frac{\delta Q}{T} + dS_{gas} \,. \tag{2.26}$$

The entropy production $d_i S$ will mainly take place in the developing embryo, since the build-up of biological structure is associated with highly irreversible processes [21], and thus $d_i S \approx d_i S_E$, with $d_i S_E$ being the entropy produced in the embryo. The gaseous exchange of the egg is usually small compared to the heat exchange and thus the internal entropy production of the embryo can be approximated by

$$d_i S_E \approx -\frac{\delta Q}{T} \,. \tag{2.27}$$

The heat exchange is easily accessible to measurement and has been investigated. A typical curve for the heat production of an amphibian egg and a human (male and female) as a function of time is given in figure 2.4. One notices that the entropy production rate is a function of the age of the system [21, 3, 2]. One can clearly distinguish the initial phase exhibiting an excessive growth of entropy production and the subsequent 'maturing' phase with slowly decreasing production. The first phase can be considered 'wasteful' in terms of material and energy consumption, but it probably just reflects the increased growth rate of the organism in terms of material build-up. The second phase is in agreement with the 'minimum-entropy-production' principle applicable to linear non-equilibrium systems [23, 43] and could be interpreted as the organisms tendency to optimise its processes and the associated decrease in material growth. The same two phases can be identified when investigating the entropy production as function of age in humans and eco-systems [3, 2].

One can conclude that nature seems not to avoid high costs of entropy production during the creation of new structures, while it is expending the least possible entropy production for established structures (E. Jantsch, cited in [21]). A rather bold application of these results to the human society as a whole could mean that currently the human race might be in the initial phase of a new development phase ('fertilised' by industrial innovations and

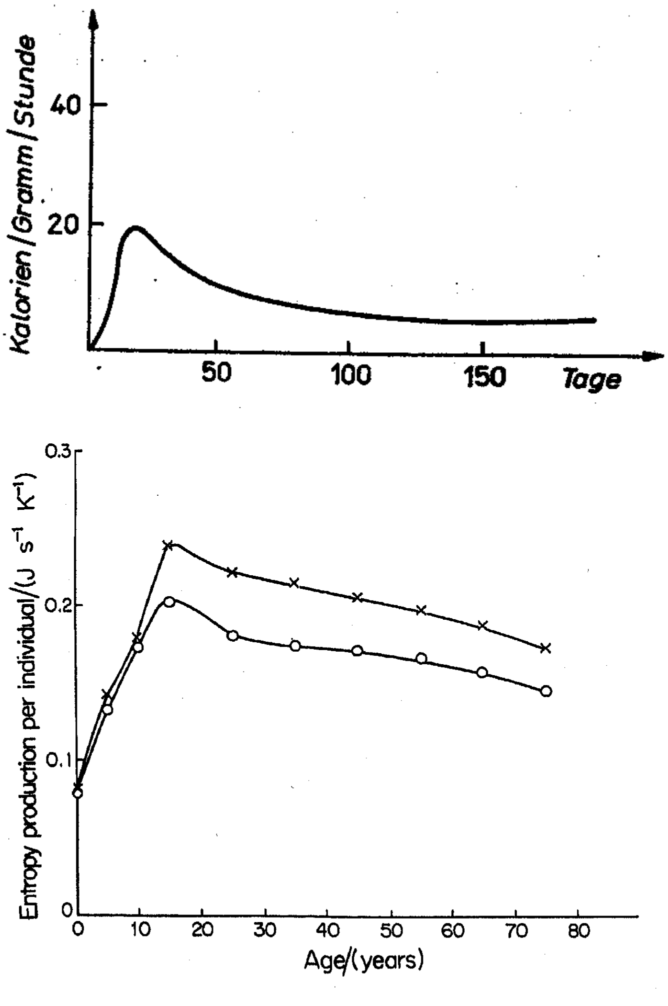

Figure 2.4: Upper plot: Heat generation rate of a fertilised amphibian egg as a function of time (x-axis: days) from [21]. Lower plot: Entropy production of a human being as a function of age (upper curve: male (x), lower curve: female (o)) from [2].

science) and might turn to optimising its processes and activities in a later phase of this development. As mentioned above, when the threshold of maximal entropy export to its environment is met, the human race has to find ways to limit its entropy production while maintaining its structural integrity, or it will inevitably suffer from more or less dramatic state transition. Until then, humans will probably supplant some of the weaker or sensitive eco-systems by enlarging their share of the Earth's limited entropy export rate.

2.3.1 The thermodynamic system Earth

The only source of free energy available to the 'living system' Earth is the radiation field of the sun. It supplies the Earth with necessary free energy to keep its distance from thermodynamic equilibrium, a necessary prerequisite for the development of life. The sun's radiation deposits some of its exergy on Earth and the Earth itself discards its internally produced entropy to space via heat radiation, see figure 2.5. If we imagined the Earth suddenly enclosed in an impenetrable sphere, it would start evolving into thermodynamical equilibrium with its surrounding until all physical, chemical and biological processes had come to a halt. Even if we made the sphere out of glass and let the sun shine through, most of the life on Earth would soon cease to exist, since the entropy produced within the sphere could not be properly disposed of. The long-wave radiation would be kept back by

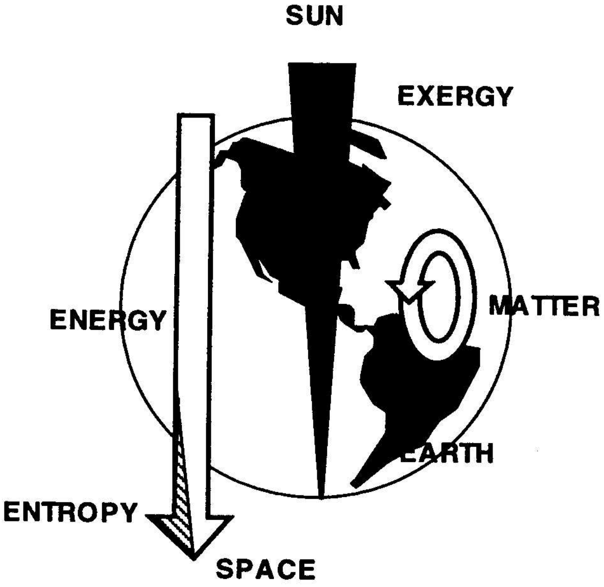

Figure 2.5: The sun delivers exergy (or free energy) to the Earth. The Earth's entropy production is discarded into space via heat radiation. Illustration taken from [47].

the glass, which lead to a heating of the inside until a new equilibrium at a higher thermal level had been reached.
This prompts the question, what makes life on Earth possible? From the theory on dissipative structures, as outlined above, we can identify at least three properties of the thermodynamic system 'Earth' that led to the development of living systems on its surface:

- The Earth is an open system
- It is supplied by a sufficient amount of free energy (by the sun)
- It is able to export the internally produced entropy into its surroundings

In view of the topic of this thesis, the last point is of particular importance. The importance lies in the fact that the ability to export entropy is limited. Thus, the meta-environment 'Earth' places some restrictions on the entropy production of its sub-environments. This has led Werner Ebeling to the formulation of the 'commandment' for humans to minimise their entropy production [20].

One way of determining the fitness of a living being would be to examine its entropy-export ability. The fitter (or better adapted) a system, the more it is able to convert the incoming free energy into internal structure and to export its internally produced entropy to the environment. Viewed from the Earth's perspective, there is practically no upper bound on how much entropy it *could* export into the universe, since it would not really matter to the universe. Viewed from the perspective of the human population on Earth (seen as a 'living system'), the picture looks different: in its current state, the Earth is only able to export a certain amount of entropy (as long as we do not want internal parameters such as temperature and climate to change drastically). Therefore, the amount of entropy that humans may contribute to the overall export is also limited. So, if we are concerned about the well-being of the human race, we should bear in mind that there is a limit to how wasteful we can be with the Earth's natural resources. It is rather difficult to support these statement with hard facts, since there are no calculations for how much entropy is actually produced by humankind. However, some approximations (see e.g. [64]) are in favour of the hypothesis that humans and their economic system have reached this upper limit already. The calculations and methods laid out in this thesis should help to support these statements with scientific evidence.

Earth, as a dissipative system, can only support life because it is able to export its internally-produced entropy into space, and is supplied with sufficient amounts of free energy. If this condition is violated, the system cannot keep away from thermodynamic equilibrium, which means 'death' [21]. This becomes evident when setting up the Gibbs' fundamental equation for an eco-system [21]:

$$\frac{dU}{dt} = T\frac{dS}{dt} - p\frac{dV}{dt} + \underbrace{\sum \mu_k \frac{dn_k}{dt}}_{\text{chemical components}} + \underbrace{\sum \bar{\mu}_i \frac{dN_i}{dt}}_{\text{biological species}} \quad . \tag{2.28}$$

This resembles the Gibbs' equation for an ordinary thermodynamic system with the addition of chemical potentials for biological species[4]. Analogously one can then define the free energy $F = U - TS$ of the eco-system. For isothermal and isochoric systems (a good approximation for many living systems) one then finds

$$\begin{aligned} \frac{dF}{dt} &= \frac{dU}{dt} - T\frac{dS}{dt} \equiv \frac{d_eF}{dt} + \frac{d_iF}{dt} && (2.29) \\ \Rightarrow \frac{d_iF}{dt} &= \frac{d_iU}{dt} - \frac{d_iS}{dt} = -T\frac{d_iS}{dt} \leq 0\,, && (2.30) \end{aligned}$$

because the internal entropy production is always positive or zero. This implies

$$\frac{d_eF}{dt} = -T\frac{d_eS}{dt} \geq T\frac{d_iS}{dt} =: TP\,, \qquad (2.31)$$

or for isobaric processes:

$$\frac{d_eG}{dt} = -T\frac{d_eS}{dt} \geq T\frac{d_iS}{dt}\,, \qquad (2.32)$$

with P being the entropy production. Thus, in order for the Earth to function as a dissipative system, the supply of free energy must at least compensate the internal destruction due to entropy production.

The entropy production density of the Earth can be derived from some simple considerations. Assuming a constant solar irradiation on Earth $\dot{Q}_S$ with temperature T_S and a constant mean temperature T_E of the Earth (the temperature as seen from outer space using the emitted radiation as a measure), the imported and exported entropy flows are

$$\dot{S}_{in} = \frac{4}{3}\frac{\dot{Q}_S(1-A)}{T_S}F_{abs} \quad \text{and} \quad \dot{S}_{out} = \frac{4}{3}\frac{\dot{Q}_S(1-A)}{T_E}F_{abs}\,, \qquad (2.33)$$

with F_{abs} being the absorbing area of the Earth's surface area F_E, as shown in figure 2.6, and A being the albedo of the Earth. It is also assumed that the Earth accumulates no energy, which is a good approximation for time scales of up to a decade or even longer. The total entropy export density can then be expressed as

$$-\frac{1}{F_E}\frac{d_eS}{dt} = \frac{4}{3}\dot{Q}_S(1-A)\frac{1}{4}\left(\frac{1}{T_E} - \frac{1}{T_S}\right) \approx 1.2\frac{\mathrm{W}}{\mathrm{K}\cdot\mathrm{m}^2}\,, \qquad (2.34)$$

where the commonly accepted values for $A \approx 0.3$, $\dot{Q}_S \approx 1367\mathrm{W/m}^2$, $T_E \approx 254\mathrm{K}$ and $T_S \approx 5700\mathrm{K}$ were used. Using equation (2.31), this sets a limit for the entropy production density:

$$\frac{1}{F_E}\frac{d_iS}{dt} \leq 1.2\frac{\mathrm{W}}{\mathrm{K}\cdot\mathrm{m}^2}\,. \qquad (2.35)$$

Since this value is determined by the Earth's temperature, it cannot easily be changed or controlled and therefore represents a real limit to growth on our planet, at least in the

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[4] The 'chemical potential' for biological species is much larger than the typical potential for chemical species, $\bar{\mu} \gg \mu \approx \mathcal{O}(kT)$.

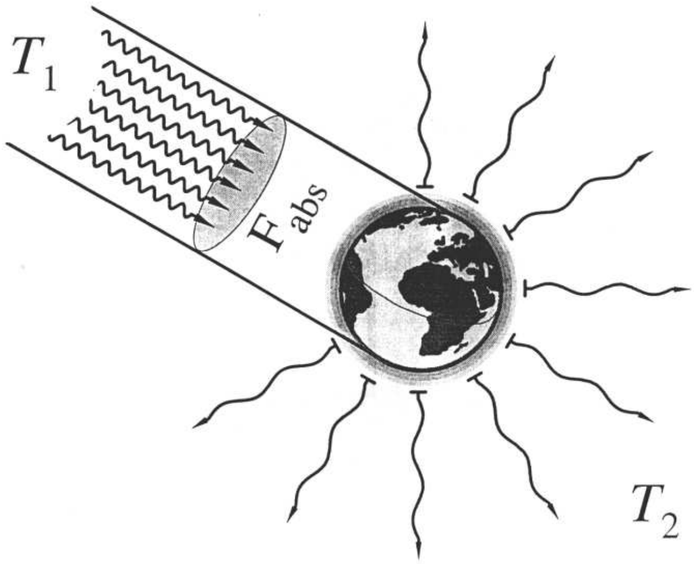

Figure 2.6: Earth's entropy export mechanism through radiation.

material and energetic sense. It should be noted though that it is not the overall amount of entropy production that is limited, but rather the *rate* of production[5]. Thus, a slower growth process is, in principle, not limited at all by equation (2.35).
The consequences for the system Earth of violating the above-mentioned necessary condition for living systems, reflected in equation (2.31), are not foreseeable. In view of the findings for simpler dissipative systems, it can only be assumed that drastic changes in the internal structure and turbulent intermediate states would be some of these consequences.

How does this limit for the entropy production density relate to human activities? The actual contribution to the overall entropy production rate from humans can only roughly be approximated by considering the energetic throughput of the human subsystem. The physiological activity of every human implicates an entropy production rate of about 0.5 W/K. The additional entropy production stemming from the associated economic activity varies largely with the level of industrialisation as is apparent from table 2.1 [64]. The total entropy production of 6 billion people is then $P_{tot} \approx 63$ GW/K. Compared to a total entropy production of the Earth of 600,000 GW/K, this means that human activity currently contributes at least 0.01% to the total entropy production. Related to the entropy export density, each human 'occupies' between 2 m^2 (India) and 25 m^2 (USA) of the Earth's surface area. Looking at some densely-populated regions, this is reflected in the necessity of these regions to export massive amounts of entropy into their surroundings.

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[5] The term 'entropy production' is used in both meanings throughout this thesis. It should always be clear from the context whether the *rate* of production or the *amount* of production is meant.

Entropy production rate		
Physiological		0.5 W/K
Economic	average	10 W/K
	USA	30 W/K
	Germany	20 W/K
	India	2 W/K

Table 2.1: Entropy production rate associated with physiological and economic activities of human beings, data taken from [64].

2.4 (Ab)uses of the concept of entropy

The inherent connection between the 'orderliness' or complexity of a structure and its entropy content has tempted many scientists to transfer the concept of entropy into their subject area – but not always successfully. One of the most famous errors in this context was Nicholas Georgescu-Roegen's postulation of a 'fourth law of thermodynamics' that forbids the complete recycling of matter, based on the assumption that the material entropy can only increase [57]. These conclusions have been disputed by many authors (see [62] for a detailed review) and are even in contradiction to the first law of thermodynamics. Nevertheless, Georgescu-Roegen's succeeded in incorporating thermodynamical considerations into the field of economics on a wider scale (see [19, 62]). Modern mainstream economics is still based on the ideas of Newton's mechanics and the first law of thermodynamics, and has not yet mastered the concept of entropy generation, energy devaluation or the finiteness of natural resources. This thesis cannot elaborate on this fact. However, there are a few misconceptions about entropy in this context that should be clarified.

One popular belief among non-physicists (and a few physicists) is that entropy equals *disorder*. This belief has its origin in the statistical interpretation of entropy by Ludwig Boltzmann, which relates the number of available microstates of a system, W, to its entropy via

$$S = k \ln W \,, \tag{2.36}$$

with k being the Boltzmann constant. The connection to 'order' becomes clear, when considering a many-particle system with only one available state, which is definitely more ordered than the same system with more available states. Think of a perfect crystal at a temperature of absolute zero compared to the same crystal at non-zero temperature, for example. The confusion arises from the fact that the colloquial meaning of order is not necessarily related to the microscopic order. A bookshelf with its books 'ordered' alphabetically has exactly the same entropy as the same bookshelf with the books in any other order. It is still appropriate to interpret lower entropy as higher order, as long as one refers to the physical meaning of order. Also, the absolute differences in entropy between macroscopically ordered and unordered systems is small compared to their total entropy.

Some economists have also argued that the low entropy of an object can serve as a measure for its economic value. This notion has to be dismissed, since the concept of value is intrinsically based on the human interpretation of usefulness and cannot be related to entropy. A mixture of cocoa, sugar, and dried milk has a higher economic value than the unmixed ingredients, yet its entropy is also higher.

There are many more uses of the term 'entropy' outside the context of physics that only have the word itself in common with the original concept. The subject areas range from information theory to social science and beyond. The concept of entropy indeed seems to have created the disorder in its interpretation, it is so often associated with [62]. Even when used in its original physical meaning, the concept of entropy generates some difficulties among scientists. At first there is the fact that entropy can be produced, but never be destroyed. If the supply of matter and energy to a system is finite, so is the potential amount of entropy that can be produced. For an isolated system, the state of maximum entropy is the state of thermodynamic equilibrium. In an open (or closed) system, however, it is not the amount of entropy that can be produced that is limited, rather the rate of entropy production itself. This rate is a function of the rates of matter and energy exchange of the system with its environment. As a physical quantity, entropy is not much different from other extensive quantities, like energy and mass, except that the entropy of a system *plus* its environment cannot decrease. Entropy is always the entropy of 'something', like the entropy of one litre of water, a kilogram of salt or a joule of electromagnetic radiation. Therefore, it makes perfect sense to speak of the entropy *content* of a material or energy reservoir.
Some authors have difficulties with the seemingly decreasing entropy in natural systems (during biological growth for example). They can be assured that a closer thermodynamical look will always reveal an entropy production somewhere else in the system, which at least compensates the seeming violation of the second law. The local decrease of entropy (of a sub-system) is a common feature of biological, geological and chemical systems, and is always coupled to a global entropy increase.

Finally, there is the relation between the use of the term entropy as defined by *Shannon's information theory* and the use in physics. Each exchange of information ΔI (as defined by Shannon's uncertainty relation $\Delta I = -\Delta H$) is coupled to an exchange of entropy $\Delta_{inf} S = k\Delta H$. The total entropy exchange ΔS of such a process is usually much greater than only the contribution from information exchange: $\Delta S \gg \Delta_{inf} S$. The exchange of entropy thus comes in different 'flavours'. Some are purely caloric, some are due to mixing and some represent information exchange. It is therefore not correct to identify every flow of entropy with a corresponding flow of information. It is appropriate to speak of 'information entropy', but it is not to be confused with the other forms of entropy. The exchange of information will increase (or decrease) the entropy of the exchanging systems. This change in entropy can be interpreted as the associated information entropy. After the exchange process has taken place, however, there is no way to distinguish the information entropy from the physical entropy of the system. It is all 'just' entropy. Therefore, it does not make sense to speak of the ‘information entropy content’ of a system or object. Information entropy is only defined in the context of exchanged information [21].

Chapter 3

Resources and use

There is a variety of meanings of the term *resource* throughout the literature, depending on the context and the scientific subject. Therefore, it has to be defined properly for the use within this thesis, which is done in this chapter. Additionally, it needs to be clarified what is to be understood by 'using' a resource and how to measure this usage. Another topic of this chapter is the description of other approaches to measuring resource use and how they are related (or not) to entropy production. Lastly, a few comments are made on the meaning of 'efficiency' and how to assess and, possibly, increase the efficiency of our technosphere.

3.1 Definition of the term *resource*

One common meaning of *resource* in economics is

> "Any means that enter into the production of goods and services"[59].

This definition includes *natural resources* like water, soil, air and others, as well as buildings, human beings, infrastructure and alike. Another definition of the term resource in the purely physical sense, as adopted by physical resource theory, is given as follows:

> "Energy, material and information will [...] be denoted by the term *physical resource*" [70].

Thirdly there is the notion of natural resources used in the field of ecology:

> "Any naturally occurring component of the environment that can sustain or benefit organisms, populations or communities within an eco-system" [52].

This definition includes soil, water, air, plants, animals, humans and more. In this thesis, the term *resource* is to be understood as the least common denominator of the three definitions above, namely:

> "Resources are the flows and reservoirs of matter and energy that can sustain or benefit living systems".

This definition excludes the information resources used in physical resource theory, since these are difficult to quantify. The term *living system* has to be understood in the broader sense, including our economic system as a whole, since it is composed of humans and their technological 'extensions'. This definition also includes purely energetic components, like the radiation field of the sun, and distinguishes between the living system and its environment. The living system is thereby thought to be able to maintain its non-equilibrium state (possibly including reproduction) by entertaining a metabolism fuelled by one or more of the resources it finds in the environment. It also implicates that the question of whether a physical object or component can be viewed as a resource is dependent upon whether it can be utilised by a living system or not. Therefore, natural deposits not yet recognised as resources in this sense might fit this description with the emergence of new technologies or differently adapted life-forms. Another consequence of this rather functional definition is that so-called wastes of a system might be considered a resource, if only the necessary means to utilise it are given or developed. Thus, every component of the natural environment that is not in thermodynamic equilibrium with the wastes of a given system can potentially become a resource for that particular system.

The ultimate resource for all activity on Earth is the sun, which means that all processes on the planet ultimately receive their energy from solar radiation[1]. This resource is available in quasi unchanging quantities and will be abundant for a long time. The flow of solar energy incident on Earth has partly been stored over time in many different natural resources, like fossil fuels, elevated water reservoirs, oceanic currents, or winds in the atmosphere. It is also hidden in the chemical binding energy of natural substances that have been built by plants and animals and which are now at our disposal. These resources, however, *are* limited in the sense that they are only regenerated at a limited rate. This rate is very often much lower than the rate of consumption. Using these resources, whether direct solar radiation or stored solar energy, means transforming all or some part of the embodied energy and structural information into a form which is less available to further processing. The degrading, or *using*, of these resources then builds or maintains the structure of the resource-using system itself.

3.2 What is resource use?

The ways in which resources are used are rather diverse, depending on the resource and the system that is using it. In general, there will be a gradient of some sort involved that facilitates running a process within the system. As an example, look at the use of water

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[1] Apart from geological and some geomorphological processes, driven by the magmatic currents within the Earth's core and mantle, which in turn are fuelled by radioactive decays.

for cleaning purposes: the used water will in general be 'dirtier' than the unused one, allowing the 'washing off' of unwanted material from a surface. The dirtier the water, the less it is suited for further cleaning processes. Of course, now it might become valuable to another system, like a bacterial colony, and the dirt concentration now serves as a resource for these bacteria. This cascade system of resource use is often seen in natural systems, where one resource (e.g. sunlight) is only used partly by one system and another system specialises on using the partly degraded resource, such that the whole cascade makes the most efficient use of the primary resource.

An illustrative example of such systems with cascading resource use is a *forest*. Each layer of leaves in its canopy and below uses some portion of the incident solar radiation for photosynthesis, while the rest is either reflected, transmitted or absorbed in the organic material. The actual energy efficiency of photosynthetic plants alone is rather small. Only about 5% of the radiation energy incident on a single plant is used for the actual photosynthetic process. The transmitted and reflected portions can further be used by layers below and above which will in general be adapted to the lower intensity and changed spectral composition of the transmitted and reflected radiation. The absorbed portion on the other hand heats up the organic material, which in turn is balanced by concurrent evaporation of water from the stomata of the leaves. Thus, the use of the resource 'solar radiation' by a forest facilitates at least two services to the overall eco-system: the build-up of organic material which can be further utilised by other organisms, and the evaporation of water that leads to a distribution of the same to other areas, and represents an important link in the local and regional water cycle. The portion of the incident radiation seemingly wasted, namely the part reflected to the atmosphere, will (in parts) be absorbed by the atmosphere and thus be utilised to drive the regional and global climate system [41].

Another example which can help to clarify the term 'resource use' is space heating by burning fossil fuels: the temperature gradient between the inside and the outside of a house is maintained by utilising another gradient, namely the *enthalpy gradient* between fuel and its combustion products. The degraded resources, namely carbon dioxide and water, can also, in principle, be further used by another process, namely photosynthesis, to bring back the primary resource: carbohydrates. In this case, however, it is advisable not to view carbon dioxide and water as resources, since for chemical reactions they are already in their most stable state and can therefore not 'fuel' another process. In photosynthesis they are rather upgraded and the real resource is sunlight.

The definition of the term 'resource use' should therefore include a reference to its ability to supply a gradient of some form that can be utilised by appropriately designed processes. The gradient can generally be obtained by comparing the thermodynamic state of the resource with that of the environment of the system that uses this resource.

All the different forms of resource use have one feature in common: the production of *entropy*. Being a consequence of the second law of thermodynamics, the production of entropy is inevitable in any naturally occurring process. Even in the above example of photosynthesis, although carbon dioxide and water are upgraded (entropically and energetically), the whole process will produce a rather large amount of entropy. The main entropy producing process in this case is the evaporation of water and the subsequent mixing of the vapour with ambient air [29].

3.3 Entropy production as a measure for resource use

As was detailed in chapter 2, every dissipative structure lives on a gradient between incoming and outgoing flows of matter and energy. The incoming flows can be regarded as the resources of that system. The available gradient is decreased by the system's activity and simultaneously restored by an internal or external entropy pump. Decreasing the gradient is thus equivalent to using the resource. On the other hand, this decrease is exactly measured by the associated entropy production.
Hence, *entropy* production is the one common feature of all processes and it is directly linked to the accompanying degradation of resources. Therefore, it is straightforward to use it as a measure for resource use.

To really understand why entropy production is an excellent candidate for such a measure, one must identify the different forms of resource use and see how they are all linked to entropy production. Some basic examples are worked out in chapter 5. As an illustrative example, take the *combustion of fuels*. When the fuel reacts with air, the internally stored chemical binding energy is transferred to the combustion products as heat. It is assumed that fuel is burned with pure oxygen and the heat generated, ΔQ, is used to heat water from T_1 to T_2. If the reactants enter the system at T_0 and the products leave the system at T_2, the enthalpy balance yields a reaction heat of $\Delta H_r(T_0, T_2) = \Delta Q$. This heat is transferred to an appropriate amount of water to be heated to the above-mentioned temperature. This transfer changes the entropy of the system by

$$\Delta S_{trans} = \frac{\Delta Q}{T_2 - T_1} \ln\left(\frac{T_2}{T_1}\right).$$

The total entropy change of the system is then made up of the reaction part and the heat transfer part:

$$\Delta S_{sys} = \Delta S_{reac} + \Delta S_{trans}\,. \tag{3.1}$$

This entropy production exactly describes the associated resource use. Loosely speaking, the 'ordered' form of energy stored within the chemical structure has been 'set free' and has thereby become 'disordered'. More physically speaking, the system after the combustion processes has more available microstates than the system before the combustion took place, but its energy has not changed. This is nothing else but a rephrasing of the second law of thermodynamics. The increase in available microstates is measured by the amount of produced entropy. But what was really 'used up'? The use of the resources fuel and air cannot really be linked to the number of atoms, the total energy or the mass of the substances, since these quantities have not changed from the initial to the final state. What has changed, however, is the ability of the system to perform work on the environment. The partial loss of this ability is what we really mean when we say a resource was 'used'.

The ability to perform work is also called the *exergy* of a system [67, 34]. The definition of exergy is based on the assumption that the maximum amount of work extractable from any system is defined by the process of bringing it to physical and chemical equilibrium with 'the environment' (for more details see chapter 3.4). For this simple system, the exergy E can be expressed as

$$E = H - T_0 S \,,$$

with H being the enthalpy of the systems, S its entropy and T_0 the temperature of the environment. Then the change in the system's exergy is

$$\Delta E_{sys} = \Delta H_{sys} - T_0 \Delta S_{sys} = -T_0 \Delta S_{sys} \,. \tag{3.2}$$

Note that the system enthalpy has not changed, since the enthalpy loss of the reaction partners was absorbed by the water. Still, the ability to perform work on the environment has decreased, since the reaction enthalpy is now stored as heat, which can only partly be transformed to work. The extent of this decrease is equivalent to the decrease in exergy which in turn is proportional to the entropy produced within the system. Equation (3.2) is valid in general, and thus one could argue that exergy loss is really the correct measure for resource use and not entropy production. However, the calculation of the exergy loss by first obtaining the entropy production is much more straightforward and saves one from the difficulties associated with the definition of exergy (see chapter 3.4 for a discussion). Furthermore, exergy loss and entropy production are connected by the simple Gouy-Stodola relation,

$$\Delta E = -T_0 \Delta S \,,$$

where only the temperature of the environment has to be known. Consequently, it seems most plausible, from a physicist's point of view, to adopt entropy production as the right measure for resource use as understood in this context.

3.4 Other measures

There have been several other measures developed that try to quantify the use of resources. Most of them have been developed in the framework or *life-cycle analysis*, a method of assessing the overall ecological impact of products, goods and services (see chapter 8). These measures usually build upon the inventory analysis of a life-cycle analysis and aggregate the data of this inventory in some way. Only some of these measures, however, are derived from actual physical properties of the material and energy streams, like mass, energy content or entropy. Three such physically motivated measures are presented here.

3.4.1 MIPS

One of these measures is called *MIPS (material input per service unit)* and was developed at the Wuppertal Institute, Germany [61]. This approach cumulates the masses of the material flows along the production-, usage- and recycling-chain of goods, services or products. The flows are further subdivided into biotic and abiotic flows, water, air and soil. The electrical energy used along the production stage of a product or service is also accounted for and given as an additional contribution to the total resource use. The material input of a product (the MI in MIPS) is defined as the sum of the masses of all natural resources that are moved during the production, use and disposal (i.e from cradle to grave) of one unit of product or service.

The idea behind this approach is that the resource use and the ecological impact of a process or product is assumed to be directly proportional to the mass of the resources extracted from the environment[2]. The subdivision into the five categories has its background in the goal of the *Factor 10 Club* to reduce the material intensity of the industrialised nations by a factor of 10 (hence the name). If only one category existed, this reduction could be achieved by simply reducing the one resource input which is most easily reducible. For many industrial processes this would be water. By providing different categories, the resource use reduction will be better partitioned among the different resources.

The beauty of this concept evidently lies in its simplicity. But this is also its weakest point. Having only the mass of the extracted resources yields no insight into the actual *use* of the resources as understood in this thesis. There is no reference to the transformation of matter and energy along the life-cycle. Based only upon the mass throughput, no statement about the degradation of the matter and energy flows can be made. The MIPS concept serves as a rough approximation to the ecological impact of production, use, and disposal, but is too simplistic to distinguish between product alternatives according to their resource use. The MIPS concept measures the material throughput, while the entropy production measures the associated devaluation of the matter and energy streams. Thus, both approaches highlight different aspects of the production of a good, service or product. There might be cases where the entropy production might not give any hints as to the ecological impact: If there was a process that extracted a material stream from the environment and sent it back in exactly the same state, the entropy analysis would fail to detect the extraction at all. It would, however, measure the energy requirements of the extraction of the stream, but there would be no reference to the mass of the resource stream as it is moved through the production system[3]. In this sense, the MIPS concept can augment the entropy analysis in cases of no-transformation processes.

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[2] This includes any relocation of masses related to the process, like movement of excavation residues (gangue) in mining or soil erosion induced by farming.

[3] One could argue that this information is irrelevant, since the material flow was not transformed at all and therefore the resource use and its associated ecological impact was zero. However, this discussion is beyond the scope of this thesis.

3.4.2 Cumulative energy demand (CED)

A measure that quantifies the total input of primary energy resources is the *cumulative energy demand (CED)*. It is defined as

> *"the cumulative sum of all energy demands, valued as primary energy, which arise in connection with the production, use and disposal of an economic good, product or service or which may be attributed to it in a causal relationship"* [30].

This includes the energy demanded by the processes of production, use and disposal, as well as the energy demanded to supply the different materials and services needed to run these processes. The primary energy value of the final energy as derived from power plants is based on the *overall efficiency of supply* (from the extraction of the energetic resource to the supply of final energy to the end-user). Energy carriers not used for energetic purposes are included in the CED according to their energy content and their respective overall efficiency of supply. Other materials with a non-zero heat of combustion are treated similarly. Materials with no net heating value enter the CED through the energy demand for their supply to the process as mentioned above.

As an illustrative example, the CED of a residential house heating system based on an electrically driven heat pump, assuming a 20 year period, lies between 558 GJ and 1126 GJ (depending on the insulation of the house) [60]. This has to be compared to the CED of a heating system based on a modern natural gas burner, which lies between 764 GJ and 1549 GJ. Thus, the CED analysis reveals the energy related advantage of the heat pump system quiet clearly.

The CED analysis has been applied to a wide variety of processes, mainly to serve as one of the characteristic parameters of an ecological assessment. This is justified by the fact that the ecological impact of many industrial processes is dominated by their energy demand and the associated emissions. The CED approximately quantifies the resource use by measuring the total energy demand. The aspect of devaluation of the energetic resources, however, is not touched upon. There is no distinction made between energy carriers that are used as such and materials that possess a net heating value but are used as production or auxiliary materials or as consumables. Also, some important resources, like water and air for example, are not included in the CED. Thus, the CED gives a valid approximation to the throughput of energetic resources associated with the chain of processes leading from the raw materials to the economic good, but it fails to quantify the transformations to which these resources are subjected.

3.4.3 Exergy

The other measure of resource use mentioned above is the loss of exergy in a system. The method used is often called *exergy analysis* and was developed by Rant and others [54]. The exergy of a flow of matter can be defined as follows (taken from [13], slightly modified):

> *The exergy of a flow of matter is the quantity of work which can be extracted from it by reversible interactions with the environment until complete equilibrium (with the environment) is reached.*

Exergy analysis is not only a method to determine the resource use of processes, but is also intended to yield a measure for the efficiency of processes. In recent years, there has been a lot of work done in the field of exergy analysis and a large list of applications has been worked out [6, 5], but a still widely discussed issue of this method remains the definition of what is to be understood by ‘the environment’ [13, 24]. Since there is no such thing as a uniquely defined environment for an arbitrary process at an arbitrary location, the definition of exergy also includes a definition of a so-called *reference environment*. In this reference environment the chemical and physical state of each chemical element is defined. This includes the chemical compound in which it appears (e.g. carbon as CO_2), as well as its concentration and the temperature and pressure of the reference environment. The total exergy flow ϵ associated with a flow of matter is then the sum of a potential, a kinetic, a thermal, a mechanical and a chemical contribution. Each contribution reflects a single aspect of the equilibration process [58]:

$$\epsilon = \epsilon_{pot} + \epsilon_{kin} + \epsilon_{th} + \epsilon_{mech} + \epsilon_{chem} \, .$$

The potential and the kinetic exergy of a stream are equal to its potential and kinetic energy. The thermal contribution ϵ_{th} is the amount of work extractable by reversible processes when bringing the material flow to thermal equilibrium with the reference environment without changing either its composition or its other thermodynamic parameters[4]. The mechanical contribution ϵ_{mech} is defined similarly for the work obtainable from reversible equilibration of pressure differences. The sum of ϵ_{th} and ϵ_{mech} is also called *physical exergy* and denoted ϵ_{ph}. It can be derived from the specific enthalpy h and the specific entropy s of the stream:

$$\epsilon_{ph} \equiv \epsilon_{th} + \epsilon_{mech} = \dot{m}[h - h_0 - T_0(s - s_0)] \, ,$$

where the subscript 0 denotes the values in the reference state and $\dot{m}$ is the mass flow of the stream.

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[4] Note that the heat flow involved in this transition does not necessarily flow from the material flow to the reference environment, but might also flow the other way. The assumption of constant chemical composition over the whole temperature range of the thermal equilibration process is not always valid. Then the exergy associated with a flow of matter cannot easily be partitioned into the above-mentioned contributions.

The chemical contribution can be obtained from considering the necessary chemical reactions leading from the component mixture of the material flow to the component mixture of the reference state, including their concentration in the reference environment. Using the chemical potential μ_{k0} of component k in the matter flow at temperature T_0 and pressure p_0, and the chemical potential μ_{k00} of the same component in the reference environment, the chemical exergy of a flow of matter can be expressed via

$$\epsilon_{ch} = \dot{m} \sum_k (\mu_{k0} - \mu_{k00}) x_k \,,$$

where x_k is the mass fraction of component k and $\dot{m}$ is the total mass flow.
The exergy ϵ_s^q of a heat flow q across a surface region s on the boundary of the analysed system is given by

$$\epsilon_s^q = \left(1 - \frac{T_0}{T_s}\right) q \,,$$

where T_s is the (constant) temperature of the surface region.
The exergy balance of a steady-state system with incoming exergy flows ϵ_i, exiting exergy flows ϵ_e, heat exergy flows ϵ_s^q and mechanical work rate $\dot{W}$ performed on the system then reads

$$\sum_i \epsilon_i - \sum_e \epsilon_e + \sum_s \epsilon_s^q - \dot{W} - \dot{I} = 0 \,,$$

where $\dot{I}$ denotes the *exergy consumption rate*. The *Gouy-Stodola* relation relates exergy consumption rate and entropy production rate $\dot{S}$ via

$$\dot{I} = T_0 \dot{S} \,. \tag{3.3}$$

Despite all the efforts made, the correct definition of a reference environment remains a controversial subject. As long as only the differences in exergy are computed, this problem is not relevant, since the reference state cancels out in the equations. On the other hand, for determining the exergy consumption within a system, the exergy content of the streams is not really needed, since the exergy consumption can be derived from the entropy production via the Gouy-Stodola relation. It is thus sufficient to know the internally produced entropy, which can be calculated from basic thermodynamic properties without the need for a speculative reference environment.
It has to be noted though, that the exergy analysis gives a new view on the efficiency of processes since it can compare absolute values of the above-mentioned available work. For a wide range of applications, especially in the chemical process industries and in the field of power conversion, this method is widely applied and delivers valuable information to the designing engineer.

Each measure of resource use has its own advantages and range of applicability. Depending on the questions asked, each measure will either supply a valid answer or not. The entropy analysis combines several aspects of the other three mentioned approaches: it includes energetic and non-energetic resources, it describes the resource use of processes based on the laws of thermodynamics and it quantifies the devaluation of matter and energy flows within a production system. The latter property includes the devaluation of natural resources. In addition, the entropy production as gained from an entropy balance is directly linked to an eco-systemic view of the human population, and can easily be incorporated into more complex theories of the interaction between humanity and the environment.

3.5 Efficiency and the use of resources in natural systems

One of the key concepts of sustainable development is efficiency. But what *is* efficiency? The general notion of efficiency is

$$\mathit{Efficiency} = \frac{\mathit{Effect}}{\mathit{Expenditure}} \,. \tag{3.4}$$

In physics, effect and expenditure will most often be of the same dimension so that the efficiency will be dimensionless. Furthermore, it is most intuitive to expect the expenditure to always be greater than the effect, such that the efficiency will always be smaller or equal to one. This also reflects the dissipative nature of every physical process. In other fields, like economics for example, efficiency might be defined in a different way, leading to a range of values different from the one above.
In the framework of this thesis, however, expenditure will be interpreted as resource use and be measured as entropy production (per product or service unit). Can one also measure the effect in terms of entropy? This was one of the basic ideas (by Arne Stahl [64, 63]) that led to the development of the method of entropy balancing. Still, it cannot be answered in general. For processes that only purify (or dilute) one or more substances, like metal production from ores or sea-water desalination, the 'value added' of the process can indeed be measured as decreased partial entropy of a substance. The service of the process is then basically the decrease in mixing entropy of one of the material flows. In general, the best one can do is to find the minimal entropy production of a process and compare all other processes to this standard. Theoretically, the 'useful' entropy production of any process is zero, since it could, in principle, run reversibly. However, if certain parameters of the process are fixed, like production rate or design parameters, then the minimal entropy production will be non-zero and the comparison to a minimum value could be made.

In most cases, however, the definition of efficiency will be based on the characteristics of the process and cannot be defined in terms of entropy alone. To include the entropy generation in the definition of efficiency one could, for example, relate it to the production of one unit of the product or the service. The efficiency would then have the units of 'J/K per unit'. This *entropic efficiency* η_S, with

$$\eta_S = \frac{\mathit{entropy\ produced}}{\mathit{unit\ of\ product\ or\ service}} \,,$$

would directly relate the resource use to the production of goods and services. The usefulness of the concept of entropic efficiency lies in the fact that it aggregates all associated uses of resources into one number, and thereby aids in the quantification of the progress towards sustainable development. In the application of entropy analysis to the production of copper (chapter 6), the entropic efficiency has been defined in the above way, as 'specific entropy production'.

The general definition of efficiency (3.4) implies another pathway to increased sustainability. Parallel to decreasing the *expenditure*, one can increase the *effect* of a process. In essence, this means to copy nature's approach to sustainability. In the course of evolution, almost every 'waste' stream of the organisms or eco-systems on Earth has been transformed into a 'resource' stream for another organism or eco-system. This has created a global network of material and energy streams, driven by the free energy from the sun, that guarantees complete recycling of matter. The concept of recycling in nature was not born out of necessity, but was a consequence of the laws of physics, namely the second law of thermodynamics and the laws governing dissipative systems. For each waste stream appearing in the course of evolution, it was only a matter of time until another species or eco-system emerged that could make use of it. In the meantime, the waste stream was potentially harmful to the environment (think of the early oxygen-rich atmosphere for example), but life gradually adapted to the new conditions. Apart from saving the rest of the environment from the potentially harmful waste stream, the emergence of a new species or eco-system enhanced the efficiency of nature as a whole. This becomes evident when measuring the *effect* of nature by the total number of organisms and eco-systems, and their complexity. Of course, this mechanism can only function when the time scales of increasing waste streams and evolutionary adaptation are nearly equal. Rates of change beyond a critical level cannot be absorbed by evolution, and thus might have devastating consequences.

A good example for a well-adapted eco-system is a forest. The symbiosis of trees, shrubs, mosses, algae, microorganisms and forest animals, which has developed in the course of evolution, facilitates the efficient use of the resources sunlight, water and air. Most of the other material streams are recycled by the well-adapted network, such that there is almost no import of other matter necessary. As long as the internal and external changes are slow enough, the forest can adapt to these changes within limits. It has been found that a forest, in the course of succession, increases its ability to extract exergy from the incident sunlight, and thus increases its resource use efficiency (see [66] and references therein[5]). It is conceivable to measure a forests efficiency by relating its exergy consumption, or entropy production, to the produced biomass. However, the data necessary for such an analysis is not yet available.

The human population, like any population of organisms, also generates waste streams,

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[5] The exergy balance was calculated on the basis of the radiation household only, thus giving an incomplete result for the overall efficiency of the analysed forest. A complete analysis would have to include the material flows as well.

that are exported to the environment. During the last one hundred years, the amount of wastes from the human population has increased drastically. The rate of increase is at least proportional to the growth rate of the population, but generally much higher. Also, the composition of our waste streams has changed significantly since the onset of industrialisation. We emit substances which were previously unknown to the environment at a significant flow rate. The consequences of this are partly unforeseeable, but bear the risk of destroying vital parts of the environment. The approach to avoid further destruction of the environment should include two factors:

- the decrease of the emissions of potentially harmful wastes into the environment, and
- the increase of the efficiencies of human processes.

The latter can be achieved by the above-mentioned two pathways: decreasing the input and increasing the output of processes. Again, increasing the output can have many facets. Learning from nature, humans should think about finding new uses for seemingly waste-like output streams of industrial processes. Taking the symbiotic life-forms of eco-systems like forest and lakes as an example, humans should try to produce more wealth from the already existing structures by turning wastes into products, instead of constantly creating new structures, products, and consequently, waste streams. Increasing industrial efficiency in this sense also implies a higher recycling rate. Actually, recycling is just one possibility of turning wastes into products and thus forms one of the strategies for increasing efficiency as outlined above. But recycling is not a goal by itself. It is rather a consequence of the required decrease of resource use and waste export. Using entropy production as a measure for resource use enables the calculation of the entropic efficiency of the human population in terms of entropy production per capita and thus quantifies an important aspect of sustainability.

Chapter 4

The method of entropy analysis

When trying to assess the resource use of a process by analysing its entropy production, there are a few prerequisites. These include fixing the boundary of the system to be analysed, obtaining and reconciling the data for the network of material and energy flows, setting up the actual entropy balance, and allocating the entropy production of sub-processes to the products. This chapter discusses how the network formulation of an industrial production system leads to a system of elementary mass balance equations which, when solved, delivers the unknown parameters for the entropy balance. An expression is developed that allows the calculation of the entropy production for arbitrary steady-state processes. Different methods of allocating the entropy production of processes to their respective products are discussed.

4.1 Completing the material and energy balance

A first step on the way to an entropy balance, and usually a rather time-consuming one, is the completion of the above-mentioned material and energy balance. Most process descriptions from technical literature or eco-inventories only focus on those material or energy streams considered relevant in the respective context. A textbook on flash-furnace technology in the copper-making industries, for example, will list all of the metal bearing flows in detail, but will most probably neglect the combustion products from the furnace heating. An eco-inventory, on the other hand, will most likely take little notice of the noble metal contents of metallurgical wastes. A further complication arises from the fact that the given data is very often only known imprecisely. Thus, one is faced with an underdetermined system of flows of matter and energy that has to be completed in order to give a closed balance.

In general, the process at hand will be made up of several sub-processes that are linked by the respective material flows to form a network of J flows and I nodes (see for example figure 4.1). Each flow j is composed of a set of chemical components $k \in \{1..K\}$ which again are composed of the basic chemical elements $l \in \{1..L\}$. The conservation of mass

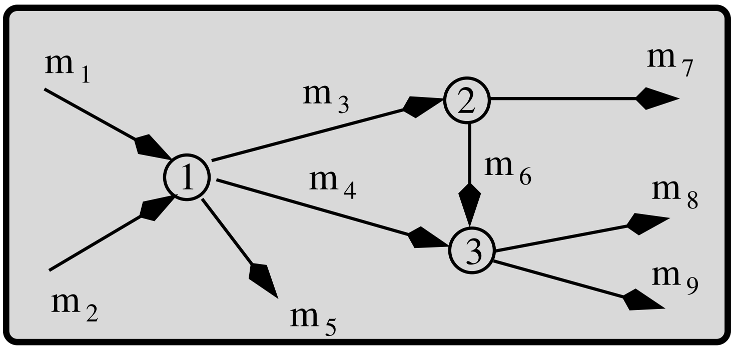

Figure 4.1: Example for a network of processes with $J = 9$ flows and $I = 3$ nodes.

dictates that for each sub-process the mole number of each element has to be conserved. It is to be noted that this is not necessarily true for the substances, since they might undergo chemical transformation. Denoting the mass[1] of a component k in flow j by m_j^k, the respective mass fraction is then given by $x_j^k = m_j^k / m_j$, where m_j is the total mass of flow j. With n_l^k denoting the mole fraction of element l in component k, and M_l and M_k denoting the molar mass of element l and component k respectively, the mass balance for each node i reads:

$$\sum_j \left\{ \sum_k x_j^k \frac{n_l^k M_l}{M_k} \right\} C_{ij} m_j = 0 \,, \tag{4.1}$$

where C_{ij} is +1 for flow j entering node i, -1 for flow j leaving node i and 0 else. In graph theory, C_{ij} is called the *incidence matrix* of the graph consisting of the links j and the nodes i.

Since there are I nodes and L different chemical elements in the system, equation (4.1) represents a system with $I \cdot L$ single equations in $J \cdot (K + 1)$ variables that have to be solved simultaneously. The variables are the mass flows m_j and the mass fractions x_j^k, which represent the composition of the different flows. This equation system is in general non-linear, prohibiting the solution by simple matrix inversion. Instead, an iterative method, like the *Newton-Raphson* method, has to be applied (see e.g. [7]). Alternatively, one can solve the unbalanced system of flows by applying methods from network theory, for example with the help of Petri Nets [49]. Nevertheless, the system will only have a unique solution if the number of variables does not exceed the number of equations. In order to assure this, one has to fix some of the variables (then called parameters of the system) and, if needed, introduce more equations that describe the physical and chemical nature of the system[2].

Let $z = (x_1^1, x_1^2, .., x_J^K, m_1, m_2, .., m_J)$ be the vector of variables. All equations making up the equation system, i.e. the mass balance equations (4.1) and the above-mentioned

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[1] The term ‘mass’ here is short hand for ‘mass flow’ (i.e. mass per time).

[2] These additional equations could be based on transfer rates, chemical reaction rates or other intrinsic limitations.

additional parameterisation equations, can then be expressed as

$$F(z) = 0\,, \tag{4.2}$$

with $F(z)$ being the vector of all $J \cdot (K+1)$ equations. The variables that were not fixed during the set-up of the equation system have to be given an appropriate starting value such that the starting point z^0 for the iteration is properly defined. Then, iterating the Newton-Raphson method $n+1$ times will yield an approximate solution

$$z^{n+1} = z^n - \left[(D_z F)\,(z^n)\right]^{-1} F(z^n)\,. \tag{4.3}$$

Here $(D_z F)\,(z^n)$ denotes the *Jacobi* matrix of F evaluated at z^n. Obviously this method only converges when the Jacobi matrix is invertible for all values z^n between the starting point z^0 and the exact solution. If this is not the case, then either the starting point has to be adjusted, or a different set of equations has to be found. Also, if the equation system has more than one solution, it is necessary to check the consistency of the result since the method will converge towards the nearest solution to the starting value[3]. Setting up the equation system (4.1) and finding a good starting point for the iteration already demands specific insight into the process design and the underlying physical and chemical processes. Usually this level of knowledge is readily available to the systems engineer or can be found in the engineering literature on the process at hand. It should be noted at this place that the difficulties associated with setting up the material and energy balance are not specific to the entropy analysis, but are rather quite common among all methods that try to quantify the resource use or ecological impact of industrial systems.

When choosing some of the variables to be fixed by assigning constant values (parameters) to them, it is interesting to know how the solution of the Newton-Raphson method depends on variations on these parameters. This is equivalent to analysing the propagation of errors [7]. Given the vector $z = (z_1, .., z_m)$ of all variables, some of the variables are fixed via

$$z_k = p_k \quad \text{for some } k \in \{1..J(K+1)\}\,. \tag{4.4}$$

The p_k are called the *parameters* of the system. The solution z of the equation system (4.2) can then be considered an implicit function of these parameters, i.e. $z = z(p)$. If the parameters p_k have a variance σ_k and an absolute error Δp_k, then the variance and absolute error of z_j is given by [7]

$$\begin{aligned} \Delta z_j &= \sum_k \frac{\partial z_j}{\partial p_k} \Delta p_k && (4.5) \\ \sigma_{z_j}^2 &= \sum_k \left(\frac{\partial z_j}{\partial p_k}\right)^2 \sigma_{p_k}^2\,, && (4.6) \end{aligned}$$

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[3] Since programming the Newton-Raphson method is a rather cumbersome task, a free software package (ASCEND IV) was used to solve the systems in this thesis.

where the matrix elements $\partial z_j / \partial p_k$ are given by

$$\left(\frac{\partial z_j}{\partial p_k} \right) =: (D_p z)_{jk} \quad \text{with} \quad D_p z = -(D_z F)^{-1} D_p F\,.$$

Equation (4.5) is also known as Gauss' law of error analysis and is the linear approximation to a Taylor expansion of the full error. The linear approximation is sufficient for almost all cases.

Another measure for the variations in z with varying parameters is the *sensitivity matrix* Σ, defined by

$$\Sigma_{jk} = \frac{\Delta z_j}{\Delta p_k} = \sum_l \frac{\partial z_j}{\partial p_l} \frac{\partial p_l}{\partial p_k}\,.$$

The absolute error of a given function $f(z)$ can often be approximated by Gauss' linearisation

$$\Delta f = \sum_j \left| \frac{\partial f}{\partial z_j} \right| \Delta z_j\,.$$

4.2 Setting up the entropy balance

The basis for an entropy balance is the material and energy balance of the process under investigation. Usually these balances are given as a rather large number of tabulated values for different input and output streams. In order to compute the entropy balance from this data, one has to gain detailed knowledge of the composition and thermodynamic state of the material and energy streams. For each material flow this information comprises composition, temperature, and pressure. From this, the enthalpy content of the flows and the heat balance of the process can be derived. The entropy content of energy flows (heat and radiation) depends solely on their temperature (when we treat radiation as black-body radiation). If this level of detail is not given ab initio, it has to be deduced from secondary sources of information and/or theoretical considerations based on the known physical and chemical nature of the process at hand. In essence, this means that those parts of the system that are unknown or known to a lesser degree have to be modelled according to the underlying process design.

The first thing to do when setting up an entropy balance is to define the system's boundaries. It is desirable to find boundaries that are meaningful in the framework of life-cycle analysis. The ideal case would be to analyse the full life-cycle. However, for pragmatical reasons, the choice for the system boundaries will mostly depend on the data available and its inherent system boundaries. As an example, see figure 4.2 for a 'black-box-process'. Note that for convenience, the boundary (dashed line) was shifted away from the physical boundary of the system such that all heat flows enter and leave the system at ambient temperature T_0, while the temperature of the material flows is assumed to remain unchanged by this choice. Physically this means the irreversible process of heat transfer between the system and the environment is fully included in the entropy balance. In figure 4.2 the material flows m have been subdivided into incoming ones (m_i) and outgoing ones (m_o) for clarity. Mathematically they are distinguished by their sign, i.e. incoming flows are positive and outgoing ones are negative[4]. The energy flowing into and out of the system is denoted by e and subdivided into flows of radiation e_s, heat e_q, and enthalpy of the mass flows h (not shown in figure 4.2). To reduce the number of variables in the entropy balance,

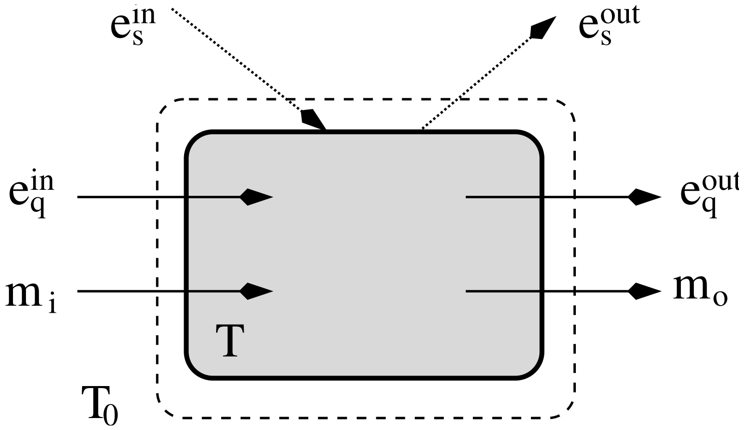

Figure 4.2: Typical set-up of system boundary for a single process.

it is appropriate to assume a unique temperature T_s^{in} for all radiation entering the system, but different temperatures $T_{s,n}^{out}$ for radiation leaving the system (due to non-uniform temperature levels along the physical boundary of the system). Then the total entropy change of the system dS during an infinitesimal time interval dt can be expressed as

$$dS = \underbrace{\left(\sum_j m_j s_j - \frac{e_q^{out}}{T_0} + \frac{e_q^{in}}{T_0} - \sum_n \frac{4}{3} \frac{e_{s,n}^{out}}{T_{s,n}^{out}} + \frac{4}{3} \frac{e_s^{in}}{T_s^{in}} \right) dt}_{d_e S} + d_i S \, . \tag{4.7}$$

As usual, the total entropy change is divided into an external part d_eS and an internal part d_iS. The only part generally accessible to measurement is the externally exchanged entropy d_eS. On the other hand, the actually interesting quantity, regarding the system's efficiency, is d_iS, the entropy produced within the system due to irreversible processes. For a steady-state system ($dS = 0$), the two contributions have to cancel each other and the entropy production is found to be:

$$d_i S = \left(\frac{e_q^{out}}{T_0} - \frac{e_q^{in}}{T_0} + \sum_j \frac{4}{3} \frac{e_{s,n}^{out}}{T_{s,n}^{out}} - \frac{4}{3} \frac{e_s^{in}}{T_s^{in}} - \sum_j m_j s_j \right) dt \, , \tag{4.8}$$

---

[4] Note that this notation is different from the network description in chapter 4.1, where all flows were assumed positive.

such that the internal entropy production can be obtained from measuring the 'metabolism' of the system. In general, the industrial processes under investigation will not be steady-state processes. However, if for non-steady-state processes one chooses a time interval $\Delta t = t_1 - t_0$ such that the system runs through a complete cycle and initial and final state are equal (typically true for batch processes), then (using equation 4.7) $\Delta S = \int_0^1 dS$ vanishes and the internal entropy production $\Delta_i S$ can again be calculated from the matter and energy flows exchanged with the environment. In many cases one of the leaving material flows m_p can be defined as the main product flow. If then ΔM_p denotes the amount of m_p produced in the time interval Δt, the ratio $\Delta_i S/\Delta M_p$ defines the *specific entropy production* of the process.

4.3 The heat and radiation balance of a single node

After having completed the material balance of the process (or process network), one can then determine the heat exchange of every node with the environment by setting up an energy balance. For this task one needs knowledge about the specific enthalpy h of every flow incident on the node at hand, and an account of all other energy forms entering and leaving the node. For most real-life processes it is appropriate to assume that no physical work is performed on or by the system. If one knows the electrical energy e_q^{el} dissipated (i.e. transformed into heat) within the system, the net heat exchanged with the environment in a node e_q can be obtained from

$$e_q \equiv e_q^{in} - e_q^{out} + e_s^{in} - e_s^{out} = e_q^{el} + \sum_j m_j h_j \,. \tag{4.9}$$

The unknown variables in equation (4.9), which are needed to determine the entropy production via equation (4.8), are the (conduction) heat flows $e_q^{in,out}$. These are then given by

$$e_q^{in} - e_q^{out} = e_q^{el} - e_s^{in} + e_s^{out} + \sum_j m_j h_j \,. \tag{4.10}$$

The heat flows can be calculated once the radiation heat flows have been determined. The radiation heat flows $e_s^{in,out}$ can be calculated from the Stefan-Boltzmann law, when the temperatures of both the outer physical boundary of the process and of the environment are known. Assuming the process vessels to be perfect black bodies of temperature T and surface area A, the heat flow given off in the form of radiation e_s^{out} is [32]

$$e_s^{out} = A\sigma T^4 \,, \tag{4.11}$$

where σ is the Stefan-Boltzmann constant. When the boundary does not have a uniform temperature, one has to sum over the partial areas A_n with well-defined temperature T_n:

$$e_s^{out} = \sum_n A_n \sigma T_n^4 \,. \tag{4.12}$$

Similarly, the process vessel is absorbing heat radiation from the surrounding. Assuming this radiation to be of temperature T_0, the absorbed heat due to radiation e_s^{in} is

$$e_s^{in} = A\sigma T_0^4\,, \tag{4.13}$$

and thus the net radiation heat emitted is

$$e_s = e_s^{out} - e_s^{in} = \sum_n A_n\sigma(T_n^4 - T_0^4)\,. \tag{4.14}$$

The heat exchanged with the environment $e_q^{in,out}$ is composed of two distinctive parts: conduction and radiation. The convective part is already included in the enthalpy content of the material flows leaving and entering the system. The entropy content of the energy flows is determined by their temperature. The entropy content of heat flow q absorbed at temperature T is $S_q = \frac{q}{T}$. The entropy of a flow of black-body radiation q_s of temperature T_s is $S_s = \frac{4}{3}\frac{q_s}{T_s}$. Heat and radiation flows that leave the system will be absorbed by some part of the environment, e.g. the layer of ambient air surrounding the furnace will absorb the heat flow and the walls of the nearby machinery and the building will absorb the radiation. These parts will then heat up and re-emit heat and radiation until an equilibrium with the primary heat and radiation flow is reached. The heat flow will rapidly be decreased in temperature down to the ambient level and thus lose all its available energy (meaning energy that could in principle be transformed into useful work or electrical energy). Already a few metres away from the physical boundaries of the process the heat flow will be dissipated to the ambient atmosphere. Therefore, it seems appropriate to accommodate for this additional entropy producing mechanism by adjusting the balance boundaries such that all heat flows leave the system with ambient temperature T_0. In principle, the same assumptions could be made for the radiation flow, since it is also absorbed by the near environment and re-emitted until its temperature reaches T_0. However, the radiation travels a much longer way before it is absorbed by the atmosphere and other items in the environment, and it can thus be treated as leaving the system without change at the temperature(s) of the outer physical boundary of the process. The surface area of the process vessels in the metallurgical industries is typically of the order of of 100 - 200 m^2 and the temperature between 323 K and 473 K. Therefore, the radiation emitted is typically of the order 3 to 40 GJ per day. The total heat loss to the environment on the other hand is between 350 and 800 GJ per day so that the heat radiation loss has been neglected in cases where the vessel shell temperature was below 373 K. Neglecting the heat radiation practically means treating the associated energy loss as a normal heat flow since now the radiation part in (4.9) is zero, and the heat flows $e_q^{in,out}$ are determined only from the electrical energy dissipation and the enthalpy balance. Thus, the energy balance is still satisfied.

The specific enthalpy h_j of material flow m_j appearing in (4.9) can be approximated when assuming an ideal mixture. It can then be calculated by summing over all components of the flow:

$$h_j = \sum_k x_k^j \frac{\bar{h}_k}{M_k}\,, \tag{4.15}$$

where $\bar{h}_k$ is the molar enthalpy and M_k is the molar weight of component k. The assumption of an ideal mixture may not always be justified. Then the enthalpy of mixing has to be taken into account. The thermodynamic data sources (like [16, 9, 42] do not always list the enthalpy of a substance for every temperature, but rather the values for the heat molar capacity at constant pressure c_p. Then the molar enthalpy of component k at temperature T has to be derived from [32]

$$\bar{h}_k(p,T) = \bar{h}_k(p,T_0) + \int_{T_0}^{T} c_p^k(T')dT' \,. \tag{4.16}$$

4.4 The specific entropy of material flows

Similarly to the enthalpy, the specific entropy of the j-th flow, s_j, can be obtained from the molar entropy of the components, $\bar{s}_k$ (derived from the tabulated values of the molar heat capacity), plus a mixing term which is dependent on the mole fraction y_k^j of component k in flow j and the total mole number n_j of all components in j:

$$s_j = \frac{1}{m_j}\left\{\sum_k n_j y_k^j \bar{s}_k - R\sum_k n_j y_k^j \ln y_k^j\right\} \text{, } with \tag{4.17}$$

$$\bar{s}_k(p,T) = \bar{s}_k(p,T_0) + \int_{T_0}^{T} \frac{c_p^k(T')}{T'}dT' \,. \tag{4.18}$$

Since x_k^j and m_j are the variables of our material balance, equation (4.17) should also be expressed in these variables:

$$n_j = \sum_k n_k^j \quad , \quad n_k^j = \frac{x_k^j m_j}{M_k} \quad \text{and} \quad y_k^j = \frac{x_k^j}{M_k \sum_{k'} x_{k'}^j / M_{k'}}$$

$$\Rightarrow s_j = \sum_k x_k^j \frac{\bar{s}_k}{M_k} - R\sum_k \frac{x_k^j}{M_k} \ln\left(\frac{x_k^j}{M_k \sum_{k'} x_{k'}^j / M_{k'}}\right) . \tag{4.19}$$

Having calculated all material and energetic entropy flows for a network of processes via equations (4.9), (4.14), (4.15) and (4.19), one can set up the balance equation (4.8) for each node of the network and for the whole network itself. Comparing the single node values for d_iS, one can identify the basic process with the largest entropy production, and thus the greatest resource use. The entropy production of the whole process network can be compared with alternative ways of producing the same product.

4.5 Allocating entropy production

When trying to assess the resource use associated with a certain product, one will generally have to take into account all stages of its manufacture, use and disposal or reuse.

This approach is called ‘cradle-to-grave’ or ‘cradle-to-cradle’ respectively. Even when only considering a simple product, like a roll of copper wire for example, this assessment will include a vast network of processes. In some cases, as in the example of the copper wire, one can identify a chain of processes inside this network that serves as something like a ‘backbone’ and includes those processes that transform and work on the main ingredient, i.e. copper in our case. The chain of processes can then be thought of as composed of basic processes which are defined by their property that they cannot be decomposed into simpler processes. The converting of copper matte to blister copper in the Peirce-Smith converter might serve as an example for a basic process[5]. The process is confined to a single process vessel, and for the purpose of resource use accounting cannot be broken down into smaller units. The total resource use associated with a certain product can then be obtained by ‘intelligently’ adding the resource use of the basic processes along the network of production, usage, and disposal/re-usage. ‘Intelligently’ means that one has to take care of how much of the resource use of a basic process is really to be allocated to the product under investigation. As long as a basic process has only one relevant output flow, which might be called the *product* of the basic process, the solution is simple: the whole resource use can be allocated to this one output flow. For processes with more than one product one has to think of more sophisticated ways of allocating the resource use to the different product flows. In the example of the copper wire the resource use can simple be allocated to the main copper bearing material flow of each basic process. For any basic process along the main production chain of copper wire, the output flow with the highest copper content will generally be the main product of the basic process, and the remaining flows can be thought of as by-products. Taking the flash smelter as an illustration, where the copper ore concentrate is partly oxidised to copper matte and the impurities transferred to the slag, all of the resource use can be allocated to the copper matte, since it is bearing the main copper throughput.

The production stage of a product shall serve as an example to clarify the allocation problem a little more. For simplicity, it is assumed that each basic process has only one product and possibly several by-products. The most simple case is a chain of say J basic processes with product m_j that form a production line which produces a final product flow p (see figure 4.3). The entropy production in node j, denoted by S_j, can either be expressed in terms of specific entropy production, i.e. entropy production per unit product flow m_j, or in terms of entropy production per unit final product p. In the latter case all intermediate product flows m_j would be scaled to the production of one unit of p. In either case, the total entropy production[6] S, as a measure for the associated resource use, is then given by

$$S = \sum_{j=1}^{J} a_j S_j \, , \tag{4.20}$$

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[5] For an explanation of the metallurgical terms refer to chapter 6.

[6] When considering a flow network, as in this case, the entropy production is really a rate. Nevertheless, it is still referred to by the term entropy production since no confusion should be expected.

where the a_j are factors that represent the fraction of S_j, the entropy production of basic process j, attributable to the final product p. When S_j is given in terms of entropy production per unit final product p, all the a_j are of value one, since all flows in node j are scaled to the production of one unit of p. If the S_j were given in terms of specific entropy production, the a_j would reflect the amount of product m_j needed to satisfy the input requirements of process $j + 1$. Thus, the factors are won by back-casting from the production of one unit of p. If one wants to incorporate entropy analysis into tools for life-cycle assessment or eco-balancing, one would probably define a set of general processes along with their specific entropy production so as to facilitate the modelling of a production network by connecting several of these unit processes. Then the allocation factors a_j could be calculated in the above mentioned fashion. In this case, usually only the mass relations output and input are known, i.e the values for $\gamma_j := m_{j-1}/m_j$. The allocation factors are then simply given by $a_j = \prod_{i=j+1}^{J} \gamma_i$ and $a_J = 1$. Then $S = \sum a_j S_j$ would be the entropy production for the production of one unit of p.

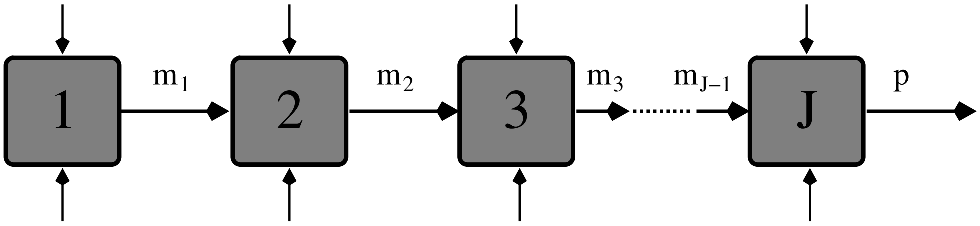

Figure 4.3: A simple production chain, where every production node j has only one product m_j. The final product is denoted by p.

When considering basic processes and process networks with more than one product, the allocation of produced entropy to the different products can be based on a variety of factors (see [48]). Consider a network of J basic processes and I flows between them, as exemplified in figure 4.1. The material flows $m_{1..9}$ can be categorised as inputs ($m_{1,2}$), intermediates ($m_{3,4,6}$) and outputs ($m_{5,7,8,9}$) of the process network. Once the flows have been computed and the entropy balance has been set up, the total entropy production of all nodes can be allocated to the four output flows in a variety of manners. The most simple case is the allocation of all entropy production to only one flow, the main product flow. Alternatively each output flow could be allocated a fraction of the total entropy production according to a common and quantifiable property of all outputs, e.g. their mass. Referring to the example in figure 4.1, for output m_7 only the entropy produced in node 2 and node 1 is relevant, since node 3 is not upstream of m_7. In this case, one could again allocate fractions of the entropy production of each node to the flows that leave the node according to their mass. In this way, each intermediate flow m_j is carrying some part of the entropy production of the node from which it originates. The process worked out in more detail in chapter 6, namely the production of copper cathodes from copper ore concentrate, is fortunately of the simple backbone type mentioned earlier. There is really only one product, namely cathode copper, so that the allocation problem does not arise in this case. Once the material and energy flows of all basic processes is known, and thus the total entropy production of the network is determined, it can simply be allocated to the produced cathodes. Dividing the entropy production by the mass of the produced cathodes yields the specific entropy production for copper produced using this specific technology.

4.6 Summary of the methodology

A mathematical framework for entropy analysis has been developed, which enables the calculation of entropy production for arbitrary steady-state processes. The methodology includes the reconciliation of incomplete data and the calculation of the entropy flows associated with the processes. All relations are based on standard thermodynamic properties of the involved substances and basic expressions describing the entropy production due to the exchange of radiation and heat. The problem of allocating the produced entropy to multiple outputs has been discussed and the allocation factor for production systems with one product per sub-process has been found to be the mass of the product (or the number of units respectively).

Chapter 5

Basic examples of entropy analysis

The entropy balance approach, or better still, entropy analysis, can be used to determine the losses of available work, or exergy in arbitrary systems, without the need to define a reference environment. This is equivalent to determining the resource use of the system, as understood in this thesis.
In the following, a number of mainly energetic transformation processes are discussed, that exemplify the application of entropy production as a measure for resource use. Though entropy analysis is not limited to energetic transformations, these are the most instructive examples to demonstrate the connection between entropy production and resource use.
In any process, a few basic thermodynamic processes can be identified which are the main sources for entropy production: mixing of substances, chemical reactions (especially combustion processes) and heat transfer. The general outline of entropy analysis of complex processes was given in the previous chapter. The basic entropy generating mechanisms analysed in this chapter can aid in the localisation of irreversibilities of more complex processes.

5.1 Mixing of substances

Even though the loss of exergy, and thus the production of entropy, seems to be a purely energetic quantity, it is really also a material property. This is probably most apparent when looking at the entropy of material flows. The entropy change of material flows can be due to a variety of reasons, not all of which are of energetic nature. Whenever the entropy increases the flows of matter are in one sense or another less available to further processing. As an example, the mixing of several pure gas flows increases the total entropy of the flows by

$$\Delta S_{mix} = -R \sum n_i \ln y_i \,,$$

with R being the gas constant, n_i being the mole number of substance i and y_i being the respective mole fractions in the mixture. It is not quite evident in how far the ‘availability’ of the flows has changed, especially not if only thinking in energetic terms; but one can think of the potential uses of the unmixed flows and compare these to the uses of the mixture. It is then immediately apparent that there are more potential processes that could make use of the unmixed flows, than there are processes that could use the mixture. Actually, the set of the latter processes is a subset of the former ones. In this sense, every increase in the entropy of a set of flows will decrease the number of potential uses of those flows. The entropy production is the most convenient measure for this decrease. However, there is nothing said about the actual 'usefulness' of the material flows in terms of their entropy. The 'usefulness' of a material flow involves the existence of a *real* process, as opposed to a *potential* process that could use this material flow. It can only be guessed that the number of real processes grows linear with the number of potential processes.

5.2 Combustion

The heat released by a combustion reaction, with the products returning to the standard state (T_0, p_0), is usually denoted by ΔH_r^0 and called the *heat of combustion.* In the same way, ΔS_r^0 refers to the accompanying entropy change. What is usually neglected in this description is a reference to the 'whereabouts' of the heat of combustion. Heat in general is only defined as a transition quantity, i.e. it is transferred from one object to another. When assessing the entropy production of combustion this is a very important issue. In the most simple case, the heat of combustion, ΔH_r^0, will stay with the products and heat them to the final temperature T_f (also known as the *adiabatic flame temperature*). The resulting entropy change ΔS is then

$$\Delta S = \Delta S_r^0 + \int_{T_0}^{T_f} \frac{C_p(T)dT}{T} \,,$$

with $C_p(T)$ being the heat capacity of the reaction products, which can be found as tabulated values or empirical expressions in the standard thermodynamic literature. The adiabatic flame temperature can then be numerically derived from

$$\int_{T_0}^{T_f} C_p(T)dT = \Delta H_r^0 \,.$$

Taking the combustion of methane (CH_4) with stoichiometric air[1] as an example, ΔS amounts to approximately 720 $\frac{\mathrm{J}}{\mathrm{K\,mol}}$. The corresponding loss of exergy, $T_0 \Delta S$, amounts to about 214 $\frac{\mathrm{kJ}}{\mathrm{mol}}$, which is 26% of the heat of combustion. In other words, the maximal efficiency of methane combustion (with air), based on the second law of thermodynamics, is only 74%. The unavailable portion of the initially available energy has been 'bound' by the produced entropy and has to be discarded to the environment in the form of heat.

The change of available energy can be expressed in more general terms, revealing the connection between loss of obtainable work and entropy production. Initially, the maximum

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[1] The amount of air necessary for complete combustion.

amount of work obtainable from the combustion reaction W^i_{max} is given by the Gibbs free enthalpy G:

$$-\Delta G^0_r = -\Delta H^0_r + T_0 \Delta S^0_r = W^i_{max}\,.$$

After the combustion process is complete, one is left with a reservoir of heat, which could be transformed into work W^f_{max} with the maximal efficiency defined by Carnot's factor:

$$W^f_{max} = -\Delta H^0_r \left(1 - \frac{T_0}{T_f}\right)\,.$$

The loss in the obtainable work $\Delta W = W^i_{max} - W^f_{max}$ is then

$$\Delta W = -\Delta H^0_r \frac{T_0}{T_f} + T_0 \Delta S^0_r = T_0 \Delta S\,.$$

This loss, on the other hand, exactly constitutes the use of the resource.

5.3 Chemical reactions

For arbitrary chemical reactions at constant pressure, the entropy change of the reaction system can be found to be [32]

$$dS = \underbrace{\frac{dH}{T} - \frac{\sum \mu_k d_e N_k}{T}}_{d_e S} \underbrace{- \frac{\sum \mu_k d_i N_k}{T}}_{d_i S}\,,$$

where μ_k denotes the chemical potential of species k and $d_e N_k$ and $d_i N_k$ denote the change in mole number of species k due to exchange with the environment and internal reactions respectively. In the simple case of a steady-state and steady-flow (SSSF) reactor, one finds the entropy production to be $d_i S = -dH/T$. In general, the entropy production is given by

$$d_i S = \frac{\sum \mu_k d_i N_k}{T} = \frac{\sum \mu_k \nu_k d\xi}{T} = \frac{A d\xi}{T}\,,$$

where the ν_k are the stoichiometric coefficients of the reaction, ξ is the extent of reaction and A is the affinity of the reaction. For $A = 0$ the system has reached its equilibrium state. For steady-state reactions, $A\,, d\xi/dt$ and T are constant and $d_i S/dt$ can easily be calculated from these basic parameters, without knowing (or measuring) the external flows.

5.4 Phase transitions

When a first-order phase transition takes place, the molar entropy of a substance undergoing that transition behaves discontinuously. The associated change in entropy ΔS_{pt} is given by

$$\Delta S_{pt} = \frac{\Delta Q_{pt}}{T_{pt}}\,,$$

where ΔQ_{pt} denotes the heat taken up/given off by the substance during that transition, and T_{pt} denotes the respective temperature. In the case of liquid-solid phase transitions, the relation between structure and entropy is quite evident. When a liquid turns into a solid, its internal structure is increasing, and thus its entropy is decreasing. In general, phase transitions are an effect of long-range correlations in many-particle systems, and thus constitute a special case of self-organisation. The entropy production of the heat transfer in this case can be made arbitrarily small, since there is no temperature gradient required to facilitate the flow of heat. The heat flow is initiated by adjusting the parameters of the system to critical values, thus generating a (finite) heat flow even for vanishing temperature gradients. In real processes, however, there will generally be a finite temperature gradient involved leading to the production of entropy. This entropy production is then due to the heat transfer across non-zero temperature gradients and not be due to the phase transition itself. Since the loss of heat at a given temperature can be made arbitrarily small (in principle), phase transitions are an excellent storage medium for heat.

5.5 Space heating

The main entropy generating mechanism of space heating is the transfer of heat across temperature gradients. Some of this entropy can be avoided by using more reversible processes than simply burning fuel. To give a simple example of how entropy analysis can be used to find the right target for optimisation, a simple space heating model is considered and a comparison between traditional 'combustion heating' and heat pumps is made. The entropy production for both alternatives is calculated and compared to the minimal entropy production, thus allowing the definition of an entropic efficiency for heating systems.

As a reference, a traditional gas-driven space heating system is considered. For simplicity, it is assumed that it is fed with pure methane (CH_4), with a upper heating value H[2]. The system is assumed to deliver 100% of H to the heated object in the form of a heat flow q. Since the heated object can be thought to be in a steady state, the entropy production $\Delta_i S$ can be derived from the entropy balance:

$$\begin{aligned} \Delta S &= 0 \quad \Rightarrow \quad \Delta_i S = -\Delta_e S \\ \Delta_e S &= \Delta_e S_q + \Delta_e S_m\,, \end{aligned}$$

where $\Delta_e S_q$ is the entropy exchange due to heat flows and $\Delta_e S_m$ is the entropy exchanged due to material flows. $\Delta_e S_m$, in our simplified model, is the entropy difference between the

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[2] This is the heat released when a complete combustion takes place and the products leave the combustion process in their standard state, which includes the H_2O to be in liquid form.

incoming flow of methane and the outgoing flow of combustion products. For a complete combustion process and all heat given off to the heated object, this contribution is negligible[3]. Thus, the entropy production of the system (heating system plus heated object) is

$$\Delta_i S = \frac{q}{T_0}\,. \tag{5.1}$$

This is the most simple example for the entropy production of a production system as described by equation 4.8, where only heat flows have been considered and both sides have been integrated over an appropriate time interval.

On the other hand, the actually necessary or 'useful' entropy production, ΔS_n, is given by the transfer of heat q from the inside of the heated object (e.g. a room) at temperature T to the exterior at temperature T_0:

$$\Delta S_n = q\left(\frac{1}{T_0} - \frac{1}{T}\right)\,.$$

Thus, the *entropic efficiency* η is derived to be

$$\eta = \frac{\Delta S_n}{\Delta_i S} = \frac{T - T_0}{T}\,. \tag{5.2}$$

For a typical winter day, with $T_0 = 273K$ and $T = 293K$ the efficiency is thus $\eta \approx 6.8\%$. It has to be added that a traditional heating system that uses 100% of the upper heating value of its fuel is already at the theoretical limit of the heat transfer efficiency. Still, about 93.2% of the available energy is wasted in such a device, according to the second law of thermodynamics.

One alternative, with much lower entropy production and fuel consumption, is to use the methane to generate electricity and heat in a power plant. The electricity W is then delivered to a heat pump and the heat Q is delivered directly to the heated object. It is still assumed that the heat requirement of the heated object may be q. The heat pump will extract a heat flow q_0 from the environment at temperature T_0 and deliver the heat flow $q - Q$ to the object at temperature T, thereby using the electrical power W

$$q - Q = q_0 + W\,.$$

The *coefficient of performance (COP)* α of a heat pump relates the pumped heat to the electrical energy input via

$$\alpha = \frac{q - Q}{W} \leq \frac{T}{T - T_0} = \alpha_{id}\,,$$

where α_{id} is the COP of an ideal (reversible) heat pump. A non-ideal heat pump can be thought of as being composed of an ideal heat pump plus a simple resistor, dissipating the unused electrical energy to the exterior as a heat flow q_{off}, with

$$q_{off} = \left(\frac{1}{\alpha} - \frac{1}{\alpha_{id}}\right)(q - Q)\,.$$

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[3] $\Delta_e S_m / \Delta_e S_q \approx 0.1\%$

The electricity W is generated in a power plant (cogeneration unit) with electrical efficiency[4] η_{el} and thermal efficiency η_{th}:

$$W = \eta_{el} H \quad , \quad Q = \eta_{th} H \, .$$

The unused portion of H is dissipated to the environment at temperature T_0 as a heat flow $Q_{\mathit{off}} = (1 - \eta_{el} - \eta_{th})H$. The total entropy balance (as given by integrating 4.8) then reads

$$\Delta_e S = \underbrace{-\frac{Q}{T} - \frac{Q_{\mathit{off}}}{T_0}}_{power\ \ plant} \underbrace{-\frac{q_{\mathit{off}}}{T_0} + \frac{q_0}{T_0} - \frac{q}{T} + \frac{Q}{T}}_{object} \, . \tag{5.3}$$

The required heat flow q is the sum of the contributions from the heat pump and the power plant,

$$q = \alpha W + \eta_{th} H = \alpha \eta_{el} H + \eta_{th} H \, ,$$

and thus

$$\begin{aligned} H &= \frac{q}{\alpha \eta_{el} + \eta_{th}} \quad \text{and} \\ q_{\mathit{off}} &= \left(\frac{1}{\alpha} - \frac{1}{\alpha_{id}} \right) \alpha \eta_{el} \frac{q}{\alpha \eta_{el} + \eta_{th}} \\ &= \frac{q}{\alpha_{id}} \left(\frac{\eta_{el}(\alpha_{id} - \alpha)}{\alpha \eta_{el} + \eta_{th}} \right) . \end{aligned}$$

Plugging in all terms and rearranging, yields

$$\Delta_e S = -\frac{q}{T_0} \left\{ \frac{1 + \eta_{el} \left(1 - \frac{\alpha}{\alpha_{id}} \right)}{\alpha \eta_{el} + \eta_{th}} \right\} ,$$

and thus the entropic efficiency becomes

$$\eta = \frac{\Delta S_n}{\Delta_i S} = \frac{T - T_0}{T} \left\{ \frac{\alpha \eta_{el} + \eta_{th}}{1 + \eta_{el} \left(1 - \frac{\alpha}{\alpha_{id}} \right)} \right\} . \tag{5.4}$$

Typical values for the parameters are $\alpha = 4$, $\eta_{el} = 0.4$, and $\eta_{th} = 0.5$ leading to an efficiency of $\eta = 11.1\%$, which means an increase of more than 62% compared to the traditional system. Also, the fuel requirement drops by more than 52%. While the efficiency calculated for the traditional system already marked the end of technological improvements, the result for the combined power plant - heat pump system can still be improved. Entropical efficiencies well above 20% are technically already feasible, albeit not yet economical.

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[4] 'Degree of utilisation' is correct here, but 'efficiency' is widely used.

5.6 Application to more complex processes

These analyses have shown that the resource use of basic processes can readily be calculated from the respective entropy balances using the general relations from chapter 4. In the case of space heating systems, the entropy change due to material flows was not considered, but would have to be included to give a complete and realistic result. In principle, the efficiencies of the processes analysed can be fully determined from the complete and detailed entropy balance, without further assumptions. All of the above processes were steady-state processes. If there were non-steady-state processes to be analysed, the entropy accumulation inside the system would also have to be considered in order to derive the total resource use. Apart from that, the method of entropy balancing can easily be extended to these cases. Since in the application of entropy analysis to space heating no multiple-product processes were considered, the allocation problem as outlined in chapter 4 did not arise. All entropy production was attributed to one service only: the heating of an object.

Chapter 6

Application to copper production

As a detailed example of how the method of entropy balancing can be applied to industrial processes, the production of copper cathodes from sulphide ore concentrates has been chosen. The processes analysed constitute only a part of the whole process network that leads from the copper ore in the Earth's crust to the final copper wire or rod available to the processing industries. Nevertheless, these processes are typical examples of the metallurgical and basic material industries and the transfer of the method to other examples of the production or service industries should be straightforward.

6.1 Production path and system boundaries

There are several possible pathways for copper production from sulphide ore concentrates. Though they all follow a common scheme (oxidation of ore concentrates, converting of matte, refining of blister copper), there are significant variations in the actual technique used. In this analysis, the production is modelled on the actual set-up at the Norddeutsche Affinerie (NA) in Hamburg, Germany. However, it is just a model and should be understood as such. The numbers given for input and output of materials and energy are typical for the processes at the NA, but not necessarily a one-to-one representation. The real data can deviate from the model by about 10 to 20%.

The complete production path assumed for this analysis is given in figure 6.1. The parts analysed are: Outokumpu flash smelter, Peirce-Smith converter, rotary anode furnace and electrolytic refinement (ISA technology). The other parts (air liquification plant, sulphuric acid plant, slag treatment processes and others) are processes not directly involved in the purification of the copper content of the raw materials, but rather side processes and as such are neglected in this work. Once the entropy production associated with the four core processes is determined, this number can serve as a lower bound for comparison with other production paths, for example the production from secondary materials (scrap, electronic waste etc.).

The system boundary of each process is taken to be the actual physical boundary of the process itself with the exception for heat flows noted in chapter 4. This means only the entropy produced within the process and at its surface is taken into account. When there are any subsequent processes which further utilise output streams of the process under investigation these are neglected. This is typically the case for utilising the heat incorporated in the offgas flows of the various furnaces. This can be justified by noting that these secondary processes cannot decrease the total entropy production but only increase it. As an example, consider the converter process: the matte is transferred from the flash smelter to the converter in batches and then blown with air to remove the sulphur in the form of SO_2. The entropy produced within this process can be computed by subtracting the entropy contents of the in-going flows (matte, air, flux, fuel, scrap, anode slag) from the outgoing flows (blister copper, offgas, slag) and adding the entropy produced by heat transfer across the boundary of the furnace. The entropy of the outgoing flows is taken directly at the outlets of the converter before they are further processed. This especially applies to the offgas flow. Although a great part of the incorporated heat is recovered after leaving the furnace and the SO_2 content is used to produce sulphuric acid, the entropy produced during the converting process cannot be destroyed anymore. The benefits of waste heat recovery and sulphuric acid production do appear as additional useful products, but not as decreased entropy production[1]. This is important to keep in mind when comparing alternative pathways.

6.2 Data acquisition

In order to establish an entropy analysis for the full production path of figure 6.1 appropriate data had to be acquired. This turned out to be much more difficult and time consuming than initially anticipated. Difficulties had to be solved on three levels:

1. Access to data
2. Inaccurate data and process variations
3. Incomplete data

ad 1) Copper producers like the Norddeutsche Affinerie tend to keep actual operation data confidential. This is done for safeguarding their competitive advantage on the market. In addition, the extraction of noble metals from the cathode slime is very profitable and hence kept under strict confidentiality. As a consequence it was impossible to get a full data set from the producer. Instead, this thesis had to rely mostly on data from the standard literature on metallurgy [10, 18, 46, 11], published articles with partial process descriptions

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[1] This raises the question of what is to be understood by the term *product*. Economically, only items that can be sold count as products. When viewing the economy from an ecological perspective, taking nature as a role model, one should also consider waste streams as products, since these might become economically valuable under the right circumstances.

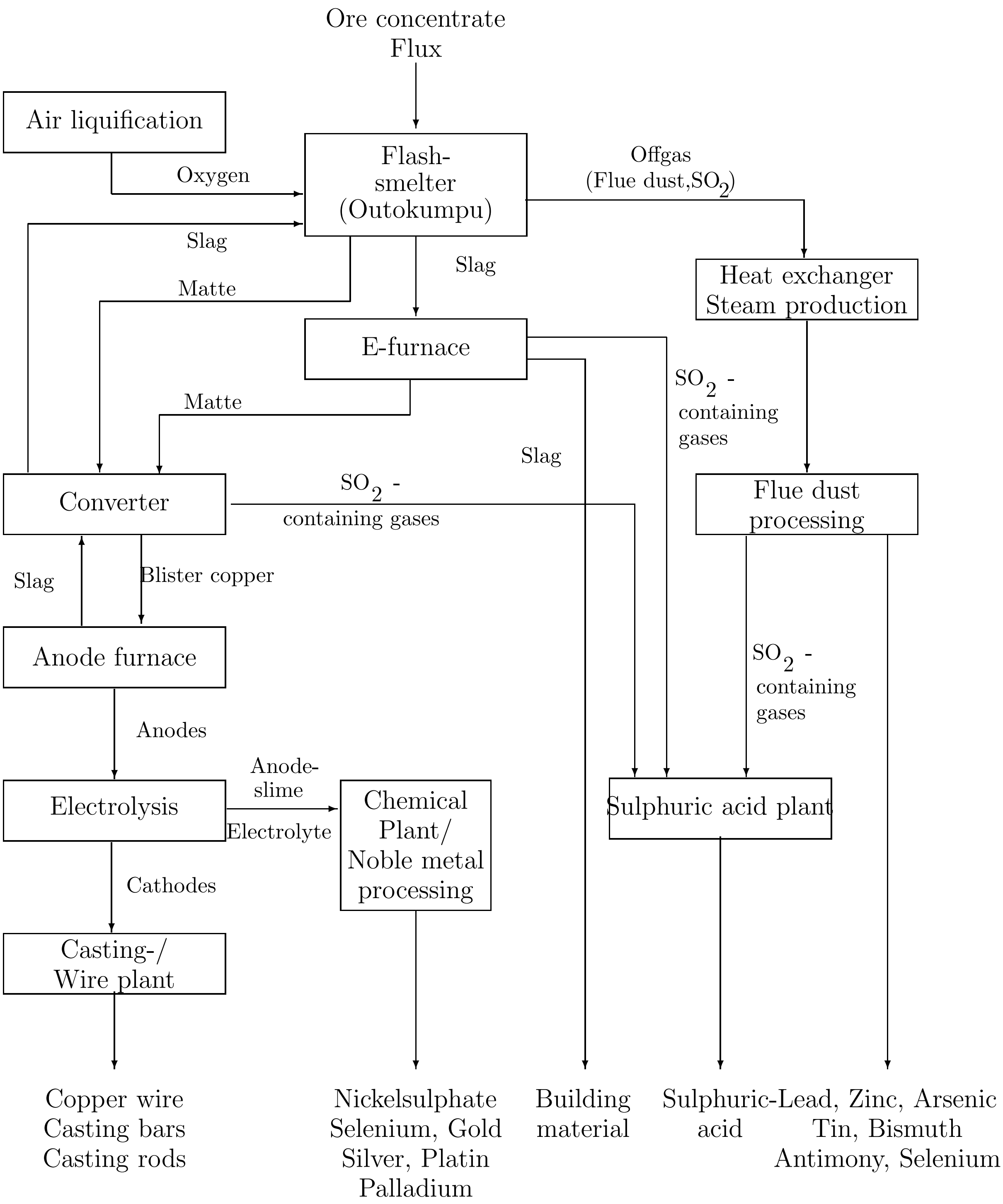

Figure 6.1: Schematic overview of copper production from ore concentrates. Sources: [10][35][44]

[17, 25, 71, 27, 28, 26], papers on the inventory of copper production [35, 36], and personal contacts to scientists and engineers from various institutions. Of valuable help were the discussions with G. Rombach and J. Krüger from the Institute for Metallurgy and Electro-Metallurgy (IME) at RWTH Aachen, and the insightful comments from H.-J. Velten and M. Kopke from the Norddeutsche Affinerie.

ad 2) As mentioned above, the processes within the production chain of copper vary significantly from site to site. But even within one site, the process description varies from day to day or maybe even from cycle to cycle. It is therefore hard, if not impossible, to exactly determine the inputs and outputs of a process. The solution to this problem was to find the typical range for the data describing each process, and to *construct* a process that fits within these margins and can be considered *typical*. The standard literature presents data of mass flows in copper production usually without error margins. According to G. Rombach, one of the authors of the inventory of copper production [35, 36], the error margins are not known at all and some of the mass flows and compositions had even to be guessed 'intuitively'. According to W. Marnette, chief executive officer of the NA, internally, mass flows are known with error margins much below 10%. In this thesis, however, 10% is used as a conservative estimate of the uncertainty of the published data. This also takes account of the differences between different publications.

ad 3) In order to be able to compute an entropy balance, it is necessary to know the composition and thermodynamic state of the in- and outgoing flows. This often implies a level of detail not available in the standard literature and sometimes even unknown to the engineer at the plant. Therefore, the empirical data and that found in the literature has to be completed by filling in the gaps with 'reasonable' assumptions, based on the knowledge of the chemical and physical nature of the processes, and subsequently completing the material balance by means of an iterative process such as that described in chapter 4.

6.3 Process description

Acquired in the above-mentioned way, the detailed process descriptions as used for the entropy balance are given below (sections 6.3.1 to 6.3.4) along with the assumptions necessary for a complete description. Initially, the material and energy balance of each process is given for the main output flow having a magnitude of one ton[2]. Later, the different nodes will be linked together and the flows scaled in magnitude, such that the overall output of the network is again one ton of cathodes. In this fashion, it is possible to first compare the

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[2] Again it should be noted that neglecting the temporal dimension is irrelevant in a steady-state-steady-flow network as this one. One can still determine the entropy production *rate* at a later time by dividing all terms by the time necessary to produce the amount of the respective product.

specific entropy production of the four processes to find the one with the greatest resource use per product unit, and later determine its contribution to the whole network.

In order to make the discussion of the network and its flows more comprehensible, a few notations and abbreviations shall be defined. The process network consists of four nodes (basic processes): **flash smelter**, **converter**, **anode furnace** and **electrolysis**, which are referred to by the letters F, C, A and E respectively. When later evaluating the process network in terms of its recycling capabilities, and calculating the associated entropy production (see chapter 6.8), some of the flows are of specific importance, since they will change in magnitude and composition when recycling material (scrap) enters the network. These flows are:

- ore concentrate entering F (m_{co})
- converter slag from C to F (m_{csf})
- converter slag transferred from C to A (m_{csa})
- matte (m_{mt})
- blister copper (m_{bc})
- anode copper (m_{ac})
- anode slag (m_{as})
- cathode copper (m_{cc})
- anode reverts from E (m_{ar})
- scrap copper entering A (m_{sca})

The total entropy production of a node X (for a given set of flows entering and leaving the node) is denoted by S_X and the specific entropy production associated with the production of one of the flows m_y is denoted by $\bar{S}_y$. Take the production of anode copper in the anode furnace as an example. Below we calculate the entropy production of the anode furnace S_A (in the case that the flow of anode copper leaving the furnace $|m_{ac}|$ is exactly one ton) to be $1.7{\cdot}10^7$J/K. When one allocates all of the produced entropy to the anode copper, as is quite natural, since there are no other products of this process, the specific entropy production associated with the production of anode copper, only using the anode furnace, is then $\bar{S}_{ac} = S_A/|m_{ac}| = 1.7 \cdot 10^7(\mathrm{J/K\,t})$.

6.3.1 Flash smelting

The flash smelter under consideration in this thesis is of the Outokumpu type, as described for example in [18], see also figure 6.3. The reference basis for the material, energy and entropy balance is the production of one ton of matte (the main output of a flash smelter). The flash smelter is charged with sulphide ore concentrate, flux material (mainly sand) and oxygen-enriched air, plus slag from the converter process (see section 6.3.2). The oxidation of the concentrate delivers enough surplus heat to melt the reaction products (matte and slag), which are collected in the settler below the reaction shaft. The hot offgas is collected, cooled, de-dusted and then sent to the sulphuric acid plant for further processing. The dust is recycled to the flash smelter. The material and energy balance is given in table 6.1.

As an example for the assumptions that have to be made in the course of setting up the entropy balance, consider the composition of the ore **concentrate** used at the NA. The

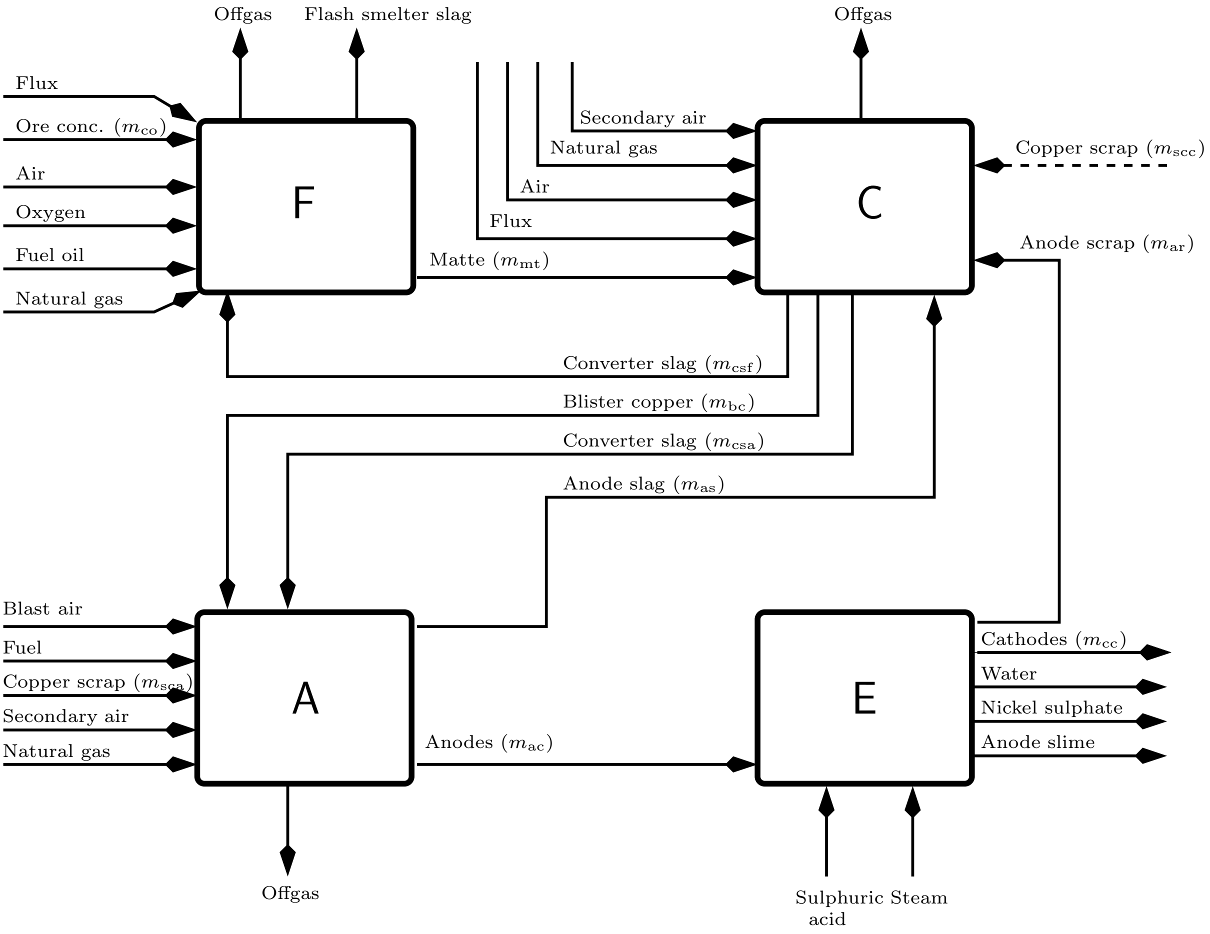

Figure 6.2: The material flows of the four main processes: flash smelter (F), converter (C), anode furnace (A) and electrolysis (E). Some flows have been named for easier reference.

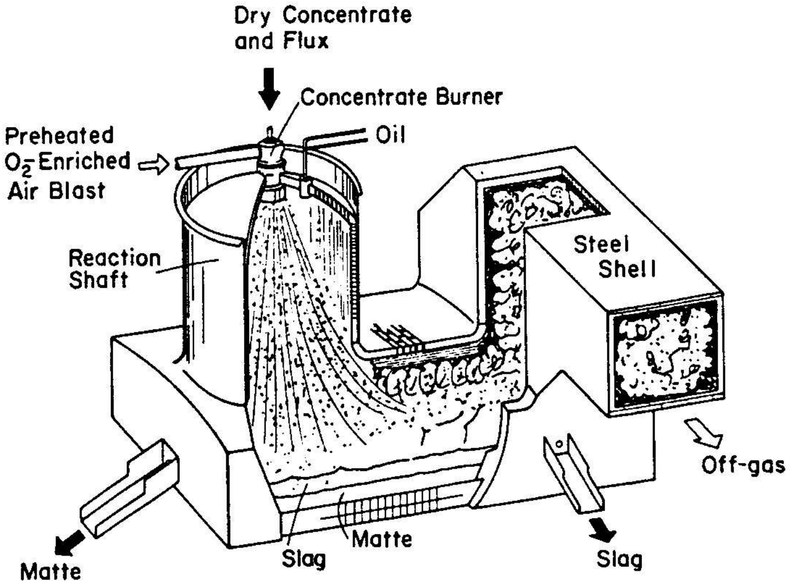

Figure 6.3: Schematic view of an Outokumpu flash furnace. Source: [11].

Input			**Output**		
Ore concentrate	2.14	t	Matte (1460 K)	1.00	t
Flux material	0.14	t	Slag (1500 K)	1.18	t
Dust	0.10	t	Dust (1500 K)	0.10	t
Converter slag (1500 K)	0.27	t	Offgas (1570 K)	1592	Nm^3
Air	1275	Nm^3	Heat	1085	MJ
Oxygen	293	kg	Radiation	15	MJ
Fuel oil	38	kg			
Natural gas	5.4	Nm^3			
Electrical energy	14	kWh			

Table 6.1: Mass and energy balance of the flash smelter (Outokumpu process). Temperature of material flow given in parenthesis if differing from T_0=298.15 K. Original data from [11, 18, 71, 35, 36, 69, 33, 17, 55] was modified to create a consistent network of material flows by using the iterative process described in chapter 4.1.

composition[3] according to [18] is given in table 6.2. But this is only half the truth: the chemical compounds formed by these components are not mentioned and there are 7% of the composition undefined. A detailed knowledge, however, is necessary in order to com-

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[3] All compositions are given in mass fractions (Mass-%), except for the compositions of gaseous flows which are given in terms of volume fractions (Vol.-%).

Component	Cu	Fe	S	SiO_2	C	Al_2O_3	Zn	Pb	H_2O	As	undef.
Fraction [%]	29	23	28	7	2	2	1	0.3	0.3	0.24	7

Table 6.2: Composition of the ore concentrate according to [18].

pute the complete entropy balance. The most abundant form in nature for copper, iron and sulphur in sulphidic ores is chalcopyrite ($CuFeS_2$). The actual mass ratios confirm this, thus it is assumed that all the copper appears as this compound. The chemical form of appearance for zinc, lead and arsenic is most likely as sulphides [11]. According to table 6.2, 7% of the mass of the concentrate remained unexplained by [18]. Looking at the composition of products and intermediates further downstream of the process, the missing components have to include calcium oxide and nickel. The sulphur content has to be raised in order to balance the sulphur content of the outputs. The resulting composition of the concentrate is given in table 6.3. The **flux material** consists mainly of sand so that its main component is SiO_2 (95%). Other components are Al_2O_3(3%) and Fe_3O_4(2%). The **flue dust** is recycled to the flash smelter and could therefore be neglected (it cancels out in the mass balance) if it had the same temperature at input and output. According to [18], the main components of the dust are copper (29%), iron (17%) and sulphur (12%). The mass ratio of Fe_3O_4 and Fe is approximately 1 and the remaining Fe (which is not present as Fe_3O_4) is assumed to be present as $CuFeS_2$ [69]. The sulphur fraction which cannot be explained by chalcopyrite has probably been transformed by a roasting reaction to $CuSO_4$. The copper fraction that now remains is assumed to be oxidised to CuO. The same is assumed for lead and zinc, which would then be present as PbO and ZnO. Applying all this to the literature data and neglecting minor components as arsenic and nickel, the dust composition can be calculated as given in table 6.4.

Component	$CuFeS_2$	SiO_2	C	Al_2O_3	ZnS	PbS	H_2O	As_2S_3	Ni	CaO
Fraction [%]	84.42	7.40	2.30	2.24	2.12	0.35	0.30	0.30	0.05	0.52

Table 6.3: Calculated composition of ore concentrate

Component	$CuFeS_2$	$CuSO_4$	CuO	SiO_2	Fe_3O_4	ZnO	PbO
Fraction [%]	13.93	35.76	17.72	4.37	18.57	6.12	3.53

Table 6.4: Composition of dust from flash smelter.

The composition of the **converter slag** is given in table 6.10 and explained in section 6.3.2. The **oxygen** requirement can be calculated from the reactions and compared with data found in the literature. The main reactions are:

$$\begin{array}{rcl} 2\,\mathrm{CuFeS_2} + \frac{13}{4}\,\mathrm{O_2} & \rightarrow & (\mathrm{Cu_2S}\cdot\frac{1}{2}\,\mathrm{FeS}) + \frac{3}{2}\,\mathrm{FeO} + \frac{5}{2}\,\mathrm{SO_2} \\ \mathrm{FeO} + \mathrm{SiO_2} & \rightarrow & (\mathrm{FeO}\cdot\mathrm{SiO_2}) \\ \hline 2\,\mathrm{CuFeS_2} + \frac{13}{4}\,\mathrm{O_2} + \frac{3}{2}\,\mathrm{SiO_2} & \rightarrow & (\mathrm{Cu_2S}\cdot\frac{1}{2}\,\mathrm{FeS}) + \frac{3}{2}\,(\mathrm{FeO}\cdot\mathrm{SiO_2}) + \frac{5}{2}\,\mathrm{SO_2}\,. \end{array}$$

These reactions imply an oxygen use of approximately 488 kg per ton of produced matte (62% copper). The blast air has an oxygen content of 40 Vol-%, so that approximately 293.4 kg oxygen have to be added to 730.2 Nm^3 ambient air in order to balance the above reactions. This is in good agreement with the literature data, e.g. [11] where a value of 300 kg O_2 is given. In addition to the oxygen requirements of the above reactions, there needs to be air supplied to the oil and gas burners inside the furnace amounting to 545.34 Nm^3. These burners run on **fuel oil and natural gas** and compensate the heat losses due to convection, conduction and radiation. For simplicity, we assume the natural gas to consist of 97.8 Vol-% methane (CH_4) and 2.2 Vol-% ethane (C_2H_6), which corresponds to an average North-Sea gas (cf. [12]). The composition of the fuel oil is difficult to determine and is usually only given in terms of distillation fractions. For simplicity, it is assumed that it can be treated as octane[4] (C_8H_{18}).

Following the same line of thought as in the example of the concentrate, one can also determine the composition of the **matte** from the elemental composition as given in [18]. Copper, iron and sulphur mainly appear as $Cu_2S\cdot\frac{1}{2}FeS$, which is confirmed by the mass ratios of the elements in the elemental matte composition (Cu:Fe:S = 61:14:22.5). The remaining copper and iron fractions, which are not in the form of $Cu_2S\cdot\frac{1}{2}FeS$, are assumed to be oxidised to CuO and FeO. The same applies to the zinc and lead fractions, which appear as ZnO and PbO. The total composition of the matte is then computed as given in table 6.5.

Component	$Cu_2S\cdot\frac{1}{2}FeS$	CuO	FeO	ZnO	PbO	Ni
Fraction [%]	95.05	1.85	1.21	1.25	0.54	0.10

Table 6.5: Composition of matte as a product of the Outokumpu process.

The **slag** is basically an iron-silicate which can also be found in nature as *olivine* ($(FeO,MgO)_2[SiO_2]$) or *fayalite* ($(FeO)_2[SiO_2]$). According to [18], the total iron content is 43%, where 4% are present as Fe^{+++} and the rest as Fe^{++}. This leads to the total FeO and Fe_3O_4 content, which in turn enables the calculation of the fayalite content. The composition of the Outokumpu slag is then determined as in table 6.6.

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[4] This rather crude approximation is only used for the entropy balance. The energy balance treats the fuel oil as a standard industrial mixture with a net heating value of 38.9 MJ/kg.

Component	Cu_2S	SiO_2	$(FeO)_2[SiO_2]$	As_2S_3	Fe_3O_4	Al_2O_3	CaO	ZnO
Fraction [%]	2.51	9.40	71.32	0.44	8.17	4.08	1.02	3.06

Table 6.6: Composition of Outokumpu process slag

The **offgas** consists mainly of N_2 (62.1%) and SO_2 (22%) plus the dust load (5%), which is recycled to the flash smelter. Further components are the combustion products from the burners (which are operating inside the reaction shaft and the settler), and transiting argon from the ambient air. Calculating the offgas amount from the reaction data of the furnace, the combustion processes and the sulphur balance (fixing the SO_2 content at 22%) yields a result of 1592.77 Nm^3 per ton of matte, which is in quite good agreement with the literature data of approximately 1650 Nm^3 [11].

The **heat** released into the environment has been estimated from the total energy balance and amounts to 1210.15 MJ per ton of matte. This is in fair agreement with the data given by the Norddeutsche Affinerie (approx. 1150 MJ [69, 33]) and found in the literature (approx 1070 MJ [11]). Knowing the physical dimensions of the flash smelter and the shell temperature, one can calculate how much of the heat is radiated into the surroundings. Assuming a shell temperature of 300 K for the walls and 373 K for the roof of the smelter [33], the total radiation amounts to 14.91 MJ per ton of matte. Since the amount of radiated energy depends on T^4 (black emitter), this result is heavily affected by the assumptions on the shell temperature. Nevertheless, the entropy production through radiation is only approximately one third larger ($S_{rad} = \frac{4}{3}\frac{E_{rad}}{T}$) than by conduction for temperatures T near T_0, so that the effect of this uncertainty on the entropy balance is only marginal. The rest of the heat loss is considered to happen by conduction as a heat flow from the smelter and the products to the ambient air.

6.3.2 Converting

The converter used at the NA is of the Peirce-Smith type, see figure 6.4. The matte transferred from the flash smelter is loaded into the furnace via ladles, together with flux material (mainly SiO_2 in the form of sand), copper scrap (anode scrap from the electrolytic refinery, rejected anodes from the anode furnace and others) and a small amount of copper-rich slag from the anode furnace. It is then blown with oxygen-enriched air in order to oxidise the sulphur content to SO_2. The process proceeds in two stages: the *slag blowing* stage in the beginning, when most of the slag is formed, and the *copper blowing* phase when most of the sulphur is removed from the system. The different stages of operation are shown in figure 6.5, which also shows how, during charging and skimming, large amounts of ambient (secondary) air can enter the process. The final products are blister copper, slag and offgas rich in SO_2. The detailed material balance for one ton of blister copper is

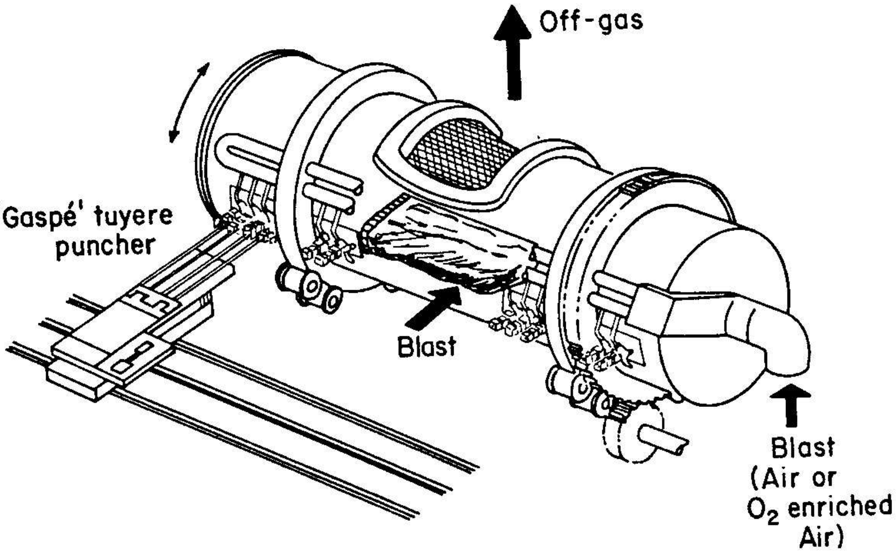

Figure 6.4: Schematic view of a Peirce-Smith converter. The puncher is used to keep the tuyeres free from magnetite build-up during blowing. The converter can be rolled in and out for charging and skimming of slag and blister copper respectively. Source: [11].

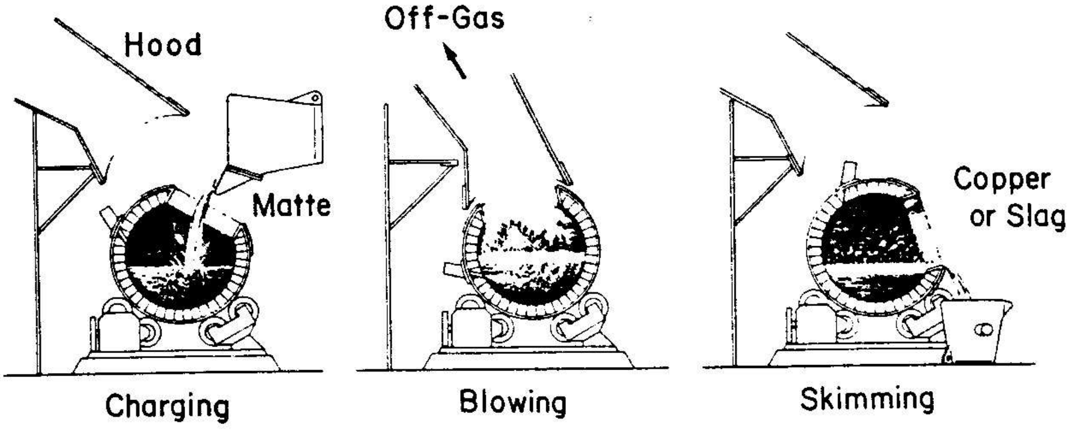

Figure 6.5: Stages of operation of a Peirce-Smith converter. During charging and skimming large amounts of ambient air can enter the process, which leads to additional entropy production. To prevent the risk of fugitive emissions into the environment, some copper plants, like the NA, use a secondary offgas-hood. Source: [11].

given in table 6.7.

Input			Output		
Matte (1460 K)	1.46	t	Blister copper (1470 K)	1	t
Air (23.5% O_2)	992	Nm^3	Offgas (1023 K)	3073	Nm^3
Flux	0.17	t	Offgas from start-up	591	Nm^3
Scrap copper	0.16	t	Slag (1470 K)	0.43	t
Secondary air	2626	Nm^3	Radiation	90	MJ
Natural gas	56.5	Nm^3	Heat	1635	MJ
Anode slag	0.06	t			
Electrical energy	20	kWh			

Table 6.7: Mass and energy balance of the converter process (Peirce-Smith converter). Temperature of material flow given in parenthesis if differing from T^0=298.15 K. Original data from [11, 71, 35, 36, 69, 33, 17, 28, 25, 55, 46] was modified to create a consistent network of material flows by using the iterative process described in chapter 4.1.

The composition of the **matte** was described in section 6.3.1. The temperature is assumed to be the same as when leaving the flash smelter (1460 K). The **air** used to oxidise the sulphur content of the matte is only slightly enriched and has an O_2 content of 23.5%. The **flux** consists of 95% SiO_2, 4.5% H_2O and 0.5% Al_2O_3. For simplicity and because of its small mass contribution, the **copper scrap** is considered to be pure copper. Since it is mainly composed of rejected anodes (99.99% Cu) and its copper content is at least above 90% [33], this assumption seems justified.

The **natural gas** used to preheat the furnace is taken to be a typical north-sea type gas (see section 6.3.1). The data sources vary greatly when specifying the actual amount of natural gas consumed by the converter process. The numbers range from 10 Nm^3[28] to 56 Nm^3[36]. Since the data from [36] presumably originates from the NA, which is the blueprint plant for the model used here, this data was used. The energy balance for this process (including the radiation part, which can be calculated from the known shell temperature of the furnace) leads to the heat loss given in table 6.7 which is dissipated into the environment. The shell temperature was assumed to be 473 K [25].

Using the sulphur balance as a reference, and assuming an average SO_2 content in the offgas of 8.375% (average of the two process stages), the numerically correct offgas amount was found to be 3073.49 Nm^3. According to metallurgists [55], the assumptions seem to be correct and this is a reasonable result. The composition is given in table 6.8. The combustion products from the natural gas burners have been included in the additional stream 'offgas from start-up', since they are only operated at start-up time to preheat the furnace, and are thus not mixed with the production phase offgas. Since this stream is lost to the environment, its temperature is assumed to be T_0. The amount of **secondary air** (ambient air) was derived from balancing the oxygen contents of inputs and outputs by assuming that air could enter the offgas stream through the hoods sucking off the process offgas. This amount is fairly large and one of the reasons for the converter's high entropy production.

Component	SO_2	O_2	N_2	Ar	
Slag blow	5	15	79	1	25% of offgas
Copper blow	9.5	11.5	78	1	75% of offgas

Table 6.8: Composition of converter offgas during slag blowing stage and copper blowing stage

The blister copper has a copper content of 99.1% and a sulphur content of 0.1%. Further elements present are oxygen, lead, nickel and arsenic. It is assumed that the lead content is present as PbO and the sulphur content as Cu_2S. Further assumptions are that the oxygen forms Cu_2O, arsenic is present as Cu_3As and nickel is dissolved in its elemental form. The resulting composition is given in table 6.9.

Component	Cu	Cu_2S	Cu_2O	PbO	Cu_3As	Ni
Fraction [%]	94.42	0.50	4.50	0.10	0.38	0.10

Table 6.9: Composition of blister copper.

The converter slag composition is based on [46], where it is given as in table 6.10 (the component Fe stands for total iron content). Most of the elements in the converter slag are either present as sulphides or oxides. According to [27], the iron content mainly binds to the SiO_2 and forms an iron-silicate known as *Fayalite* ($(FeO)_2[SiO_2]$) when solidifying. To further determine the chemical composition of the slag, it is assumed that the copper content is still mainly bound as matte ($Cu_2S\cdot\frac{1}{2}FeS$) and that the (Fe_2O_3) fraction is negligible. Zn and Pb are most likely in their oxide form, so that the complete composition can be calculated as given in table 6.11. Sb has been neglected since it does not appear in any of the other input or output streams, Ni has been neglected for its small fraction, and As has been neglected using the argument that most of the As transfers to the blister copper [11].

Component	SiO_2	Fe	Fe_3O_4	Cu	Sb	Zn	Pb	As	Ni	undef.
Fraction [%]	25	46	16	3	0.3	2	1	0.1	0.04	6.56

Table 6.10: Composition of converter slag as given in [46].

Component	SiO_2	$(FeO)_2[SiO_2]$	Fe_3O_4	Cu_2S	FeS	ZnO	PbO
Fraction [%]	6.8	65.7	16.7	5.56	1.54	2.6	1.1

Table 6.11: Calculated and normalised composition of converter slag.

6.3.3 Fire refining

The last pyrometallurgical stage of producing high grade copper, the fire refining stage, is usually performed in the anode furnace, which largely resembles a Peirce-Smith converter. The still liquid blister copper from the converter is transferred to the anode furnace via ladles, is then blown with oxygen to reduce the sulphur content to below 10 ppm[5] and subsequently with natural gas[6] to reduce the oxygen level to below 1000 ppm. The latter stage is also called *poling*. Additionally, the anode furnace is used in some locations to remelt some of the rejected anodes and anode scrap from the electrolysis. The refined copper is cast into moulds to produce anodes (see figure 6.6), which are then processed in the last refining stage, the electrolytic refinery. Some of the copper oxidises during the oxidation phase and settles in the slag layer, along with other impurities, mainly iron, which were transferred into the furnace due to imprecise skimming of the blister copper at the converter. The total mass and energy balance is given in table 6.12. The **blister copper** and **converter slag** have been described above (see section 6.3.2). The **blast**

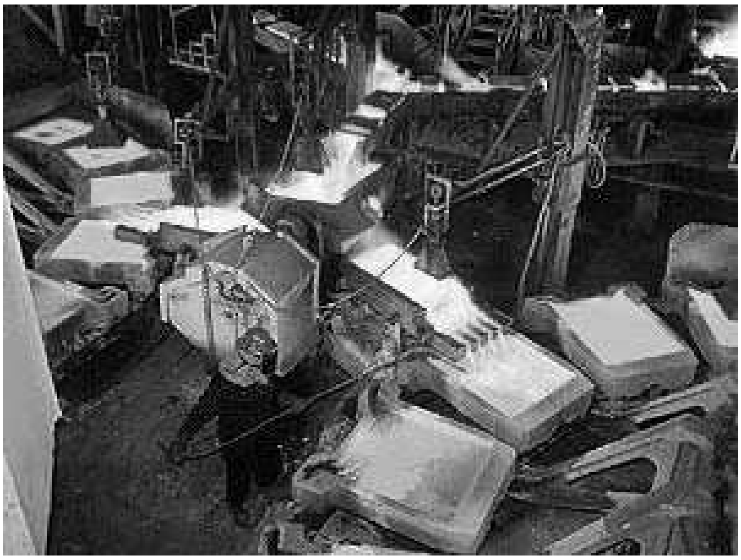

Figure 6.6: Copper from the anode furnace is cast into moulds to form anodes for the electrolysis. Source: [45].

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[5] (Mass-) parts per million.

[6] Different agents are used in different plants. Natural gas is the choice at the NA.

Input			**Output**		
Blister copper (1470 K)	1.01	t	Anodes (1470 K)	1	t
Converter slag (1500 K)	0.03	t	Slag (1470 K)	0.07	t
Blast air	1.3	Nm^3	Offgas (furnace, 860 K)	1168	Nm^3
Fuel oil	0.03	t	Radiation+Heat	1550	MJ
Scrap copper	0.01	t			
Secondary air	1127	Nm^3			
Natural gas	6.7	Nm^3			
Electrical energy	16	kWh			

Table 6.12: Mass and energy balance of the anode furnace. Temperature of material flow given in parenthesis if differing from T^0=298.15 K. Original data from [11, 71, 35, 36, 69, 33, 17, 28, 55, 46] was modified to create a consistent network of material flows by using the iterative process described in chapter 4.1.

air is just air taken from the environment. The **fuel** is used to preheat the furnace and compensate for heat losses during the process. The burners are inside the furnace and their combustion products therefore add to the offgas. The scrap copper consists of anode scrap from the electrolysis and other high-grade reverts (Cu content > 99%).

The anodes have a copper content of about 99.55 %. There are still some impurities present, which will mostly be removed in the last refining stage, the electrolysis. The main impurities for this calculation are taken to be lead (as PbO), arsenic (as Cu_3As), nickel and oxygen. The composition is given in table 6.13. The amount of **secondary air** can be derived from the nitrogen balance, once the offgas amount is fixed (as taken from the literature and current process data [11, 33]). The **slag** from the anode furnace is fairly high in copper (more than 40% Cu [33]) in the form of Cu_2O and is therefore decopperised in the converter (see above). Other components are Fe, SiO_2, Pb, Zn and O_2. Since the iron was imported from the converter (as slag), the chemical form should be the same as in the converter slag, namely Fe_3O_4 and $(FeO)_2[SiO_2]$. According to [51], the most likely chemical configurations of the other components are PbO, ZnO and dissolved O_2. This results in the composition given in table 6.14. The furnace **offgas** contains the reaction products of the oxidation phase (SO_2) and the poling phase (CH_4, C_2H_6 and CO), as well as combustion products from heating the furnace with fuel oil. The (calculated) composition, based on the consumption of the inputs from table 6.12, is given in table 6.15. The **heat** released into the environment also includes the radiation part and the heat given off due to the

Component	Cu	Cu_3As	PbO	Ni	O
Fraction [%]	99.27	0.39	0.15	0.15	0.04

Table 6.13: Composition of anodes.

Component	Cu_2O	$(FeO)_2[SiO_2]$	SiO_2	Fe_3O_4	PbO	ZnO	O_2
Fraction [%]	45.04	27.32	8.0	6.94	3.24	1.24	8.21

Table 6.14: Composition of anode slag.

Component	N_2	O_2	CH_4	C_2H_6	Ar	CO	CO_2	H_2O
Fraction [%]	75.26	12.24	0.31	0.01	0.97	0.25	5.22	5.72

Table 6.15: Composition of anode furnace offgas.

subsequent cooling of the anodes (approximately 731.34 MJ). It was calculated from the enthalpy balance of the process. Since there was no data on the furnace dimensions and shell temperature available, the radiative part could not further be specified.

6.3.4 Electrolytic refining

The anodes coming from the anode furnace (after being cooled down) are transferred to the tankhouse where they are installed in electrolysis tanks (divided into individual cells) for the last refinement stage, see figure 6.7.

The **electrolyte** mainly consists of water, $CuSO_4$ and H_2SO_4, plus small amounts of levelling and graining agents, which are neglected here. The starter cathodes are either made from high-grade copper (by electrolytic plating) or stainless steel. During the electrolytic dissolution of the anodes, the cathodes are replaced approximately three times. For one anode to be dissolved the process takes about 21 days. The bath is heated by steam in order to maintain a temperature of about 63° C. In order to control the composition of the electrolyte, a small bleed stream is taken from the tank to a cleaning unit, where it is decopperised and cleaned from other impurities and sent back to the tank. The amount of electric energy used for refinement depends on several factors. It is, in principle, bound by the finite conductivity of the electrolyte and the external circuitry. Further limitations arise from corroded contacts, contact between anodes and cathodes, spilled electrolyte which causes short circuits, and re-oxidation of cathode copper by O_2 and Fe^{+++} in the electrolyte.

Not all of the anodes dissolve during the electrolysis, since they extend above the electrolyte level. Approximately 16% of the anodes go directly back to the anode furnace or the converter for remelting. The impurities in the anodes partly dissolve in the electrolyte and partly form slime on the anode surface, which then collects at the bottom of the tank. The impurities collecting in the electrolyte are extracted from a small bleedstream. In the simplified model used here, $NiSO_4$ is the only impurity treated in this way. The H_2SO_4 usage is then computed by compensating for the sulphate loss in the anode slime and for

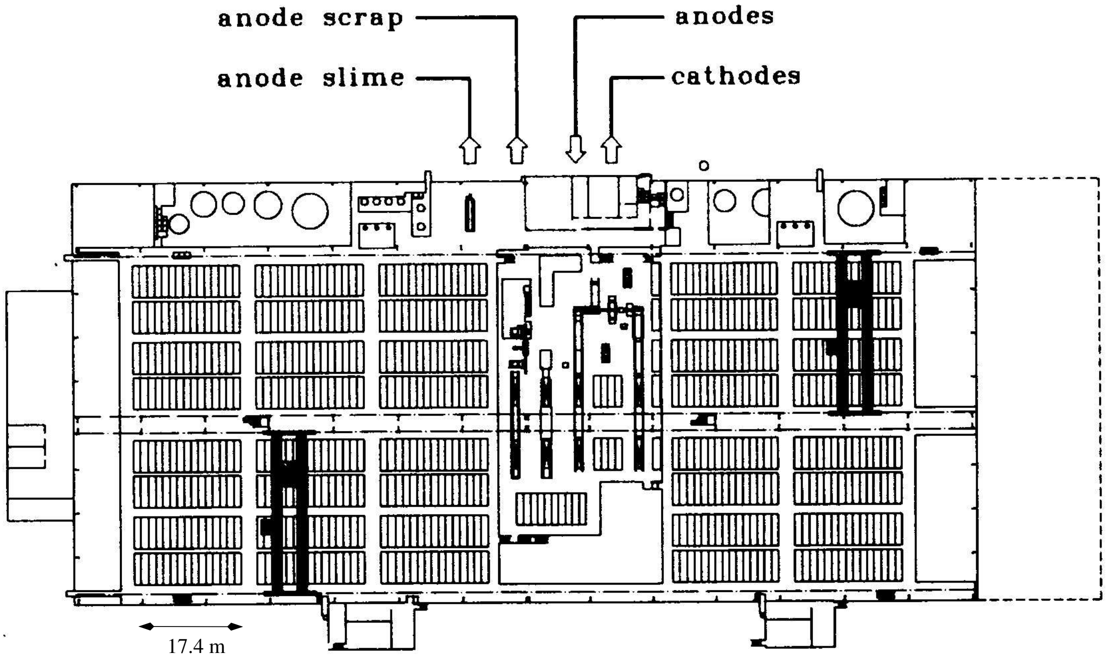

Figure 6.7: Schematic view of a tankhouse with 600 electrolysis cells, each containing 57 anodes and 56 cathodes. Loading and unloading is done via automatic cranes reaching across the tanks. Source: [39].

the extracted $NiSO_4$. The total input and output balance for the production of one ton of cathodes is given in table 6.16. The composition of the **anodes** was discussed in section 6.3.3. The **cathodes** have a copper content of at least 99.99% and are therefore considered to be of pure copper. The **anode slime** is thought to consist of only those impurities that appear in non-negligible amounts in the anodes[7]. These are sulphur (as Cu_2S), lead (as $PbSO_4$) and arsenic (as Cu_3As). The composition is given in table 6.17.

Input			**Output**		
Anodes	1.199	t	Cathodes	1.0	t
H_2SO_4	2.5	kg	Anode scrap	0.192	t
Steam (4bar, 150 ° C)	128	kg	Cond. water	128	kg
Electrical energy	300	kWh	Anode slime	6.0	kg
			$NiSO_4$	4.0	kg
			Heat+Radiation	1438	MJ

Table 6.16: Mass and energy balance of the electrolysis. Original data from [11, 71, 35, 36, 69, 33, 17, 28, 55] was modified to create a consistent network of material flows by using the iterative process described in chapter 4.1.

Component	Cu_2S	$PbSO_4$	Cu_3As
Fraction [%]	0.83	34.16	65.01

Table 6.17: Assumed composition of anode slime. The noble metals had to be neglected due to unavailable data. They were thus eliminated from the whole process network.

The heat released into the environment stems from the steam and the dissipated electrical energy. It is assumed that the temperature of the tank, including the solvent, remains constant at 63 ° C during the electrolysis[8]. At this temperature the heat radiation plays only a minor role, and has therefore been included in the overall heat surplus.

6.4 Entropy balance of the four processes

The detailed compositions and magnitudes of the material flows was derived in the previous section by using the mass balance equations (4.1) and by applying the iteration process described in chapter 4.1. The entropy balance of each of the four sub-processes (flash

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[7] The noble metals had to be neglected since there was no sufficient data available. Moreover, they only appear in small amounts in the anodes (contribution $\leq 0.1\%$), thus justifying their neglect.

[8] This applies to the mean temperature of the tank, although the local temperature of the solvent is different at the inlet and outlet of the tank.

smelting, converting, fire refining and electrolytic refining) is now derived from equation (4.8), integrated over an appropriate time interval[9]. The heat and radiation flows in (4.8) is deduced from the heat balance equation (4.10) and equations (4.12), (4.13), and (4.14). The specific entropy and enthalpy of the material flows was calculated from the molar entropy and enthalpy given in standard reference books [16, 9] via equations (4.15) and (4.19) respectively, or from parametric expressions for the molar heat capacity as given in [42] which were then plugged into equations (4.16) and (4.18). An example calculation of the specific entropy of blister copper is given in the appendix. The results are given in tables 6.18 to 6.22. The entropy production through heat transfer as given in the tables comprises heat conduction *and* heat radiation. All results are given without error margins, but an error analysis and an approximate error margin is presented in the next chapter.

Input	**Entropy [J/K]**	**Output**	**Entropy [J/K]**
Ore concentrate	$1.65 \cdot 10^6$	Matte	$1.90 \cdot 10^6$
Flux	$8.95 \cdot 10^4$	Slag	$2.85 \cdot 10^6$
Dust	$7.57 \cdot 10^4$	Offgas/Dust	$1.65 \cdot 10^7$
Converter slag	$6.36 \cdot 10^5$	Heat loss	$4.06 \cdot 10^6$
Air/Oxygen	$1.19 \cdot 10^7$		
Fuel oil	$1.17 \cdot 10^5$		
Natural gas	$3.99 \cdot 10^4$		
Sum	$1.45 \cdot 10^7$	**Sum**	$2.53 \cdot 10^7$

Table 6.18: Entropy balance of the flash smelter for the production of one ton of matte. The heat loss contribution comprises heat conduction and radiation. Values computed from thermodynamic data sources [16, 9, 42].

As mentioned above, the real measure for resource use is the produced entropy within a process. In this sense, it is not the absolute values of in- and outgoing entropy, as given in the above tables, that are of interest, but rather the difference between total input and total output of entropies. For the production of one ton of respective product, these values are given in table 6.22. In table 6.23 the overall entropy production for the production of one ton of copper cathodes is given.

6.5 Error analysis

As discussed in chapter 6.2, the error margins of the magnitude and composition of the material flows making up the production network analysed in this thesis are mostly unknown. The data given in the standard literature on extractive copper metallurgy is also

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[9] The time interval is intrinsically given by the time needed to produce one ton of the respective product of each sub-process. The magnitudes of the flows from the previous section have been derived accordingly.

Input	**Entropy [J/K]**	**Output**	**Entropy [J/K]**
Matte	$2.78 \cdot 10^6$	Blister copper	$1.40 \cdot 10^6$
Flux	$1.43 \cdot 10^5$	Slag	$1.02 \cdot 10^6$
Anode slag	$7.69 \cdot 10^4$	Offgas	$3.65 \cdot 10^7$
Copper scrap	$7.07 \cdot 10^4$	Offgas from start-up	$4.66 \cdot 10^6$
Air/Oxygen	$7.80 \cdot 10^6$	Heat loss	$5.72 \cdot 10^6$
Secondary air	$2.06 \cdot 10^7$		
Natural gas	$6.02 \cdot 10^4$		
Sum	$3.15 \cdot 10^7$	**Sum**	$4.92 \cdot 10^7$

Table 6.19: Entropy balance of the converter for the production of one ton of blister copper. The heat loss contribution comprises heat conduction and radiation. Values computed from thermodynamic data sources [16, 9, 42].

Input	**Entropy [J/K]**	**Output**	**Entropy [J/K]**
Blister copper	$1.51 \cdot 10^6$	Anodes	$1.37 \cdot 10^6$
Converter slag	$6.96 \cdot 10^4$	Slag	$1.87 \cdot 10^5$
Fuel oil	$1.07 \cdot 10^5$	Offgas	$1.08 \cdot 10^7$
Copper scrap	$6.96 \cdot 10^3$	Heat loss	$5.20 \cdot 10^6$
Air	$1.05 \cdot 10^4$		
Secondary air	$8.84 \cdot 10^6$		
Natural gas	$4.93 \cdot 10^4$		
Sum	$1.06 \cdot 10^7$	**Sum**	$1.75 \cdot 10^7$

Table 6.20: Entropy balance of the anode furnace for the production of one ton of anodes. The heat loss contribution comprises heat conduction and radiation. Values computed from thermodynamic data sources [16, 9, 42].

Input	**Entropy [J/K]**	**Output**	**Entropy [J/K]**
Anode copper	$6.33 \cdot 10^5$	Cathodes	$5.22 \cdot 10^5$
H_2SO_4	$5.18 \cdot 10^4$	Anode scrap	$1.01 \cdot 10^5$
Steam	$9.60 \cdot 10^5$	Anode slime	$2.83 \cdot 10^3$
		Heat loss	$4.82 \cdot 10^6$
		Water	$4.97 \cdot 10^5$
Sum	$1.59 \cdot 10^6$	**Sum**	$5.95 \cdot 10^6$

Table 6.21: Entropy balance of the electrolysis for the production of one ton of cathodes. The heat loss contribution comprises heat conduction and radiation. Values computed from thermodynamic data sources [16, 9, 42].

Process	**Entropy production**
Flash smelter	$1.08 \cdot 10^7$ J/K
Converter	$1.77 \cdot 10^7$ J/K
Anode furnace	$0.69 \cdot 10^7$ J/K
Electrolysis	$0.44 \cdot 10^7$ J/K

Table 6.22: Entropy production of all four processes for the production of **one ton of the respective main product**.

Process	**Entropy production**	**Entropy coefficient η_e**
Flash smelter	$(1.92 \cdot 10^7 \pm 10\%)$ J/K	0.069
Converter	$(2.14 \cdot 10^7 \pm 25\%)$ J/K	0.080
Anode furnace	$(0.83 \cdot 10^7 \pm 10\%)$ J/K	0.006
Electrolysis	$(0.44 \cdot 10^7 \pm 10\%)$ J/K	0.002
Sum	$(5.33 \cdot 10^7 \pm 16\%)$ J/K	

Table 6.23: Entropy production of all four processes for the production of **one ton of cathodes**. The error margins were derived a discussed in chapter 6.5. For the meaning of the entropy coefficient see chapter 6.6.

unsuitable to deduce the uncertainties, since it usually stems from single measurements performed under unknown conditions and is in all cases given without any reference to its accuracy. However, at every copper plant the magnitude and composition of flows is usually known with an error margin well below 10% (cf. chapter 6.2). Thus, the conservative guess for the error margins applying to the calculation in this thesis is 10%, except for the error of the flow of natural gas into the converter process, which is assumed to be 60% (cf. the discussion in chapter 6.3.2).

Then, using the linear approximation to the propagation of errors (cf. equation (4.5),

$$\Delta f(x) = \sum_j \left| \frac{\partial f}{\partial z_j} \right| \Delta z_j \,,$$

one can determine the overall error of the results. An exact error analysis can be performed by using the general equations from chapter 4 and the equation above, when expressing the entropy production ΔS as a function of the flows, compositions and temperatures

$$\Delta S = \Delta S(m_j, x_j^k, T_j, ...) \,.$$

The high uncertainty in the natural gas flow of the converter implicates the same uncertainty for the heat flow output of the converter, thus yielding a relative error of the entropy production of the converter of 25%. The entropy production of all other units has an error of approximately 10%. This results in an overall error of the total entropy production of all production stages (per ton of cathode copper) of 16%.

6.6 Interpretation of results

First it is to be noted that this entropy analysis only comprises four core processes of one possible copper production chain. Thus, generalisations for the whole copper industry are not possible. These four processes, however, are quite typical for many production sites around the world, and are among the most modern techniques in use.

The principal character of the copper production as a concentration and refining process can be seen when looking at the amount of entropy per mole of copper in the main copper bearing material flows, S_{Cu}:

$$S_{Cu} = \frac{S}{n_{Cu}} . \tag{6.1}$$

Here S is the respective entropy flow, and n_{Cu} is the molar flow of copper. While the value for S_{Cu} for the ore concentrate is approximately 167.6 J/K, it decreases to 33.2 J/K in the final copper cathodes, which demonstrates the concentration process quite well. The decrease of this quantity is the direct consequence of the increasing copper concentration but not just a re-parameterisation of the same, since it takes the mixing of the different components into account. Also, it has the same units as the entropy production, enabling the definition of a dimensionless parameter, the *entropy coefficient* η_e, which describes the entropical degree of perfection of the process. It is simply defined as the total copper entropy decrease in the process divided by the total entropy production of this process. For a process X (X = F, C, A or E) with main copper bearing input flow m^i and main copper bearing output flow m^o the definition for η_e is given by

$$\eta_e := \frac{\Delta S_{Cu} n^o_{Cu}}{S_X} \quad \text{with} \quad \Delta S_{Cu} = S^i_{Cu} - S^o_{Cu} , \tag{6.2}$$

where S_X denotes the entropy production rate of process X for the given magnitudes of m^i and m^o.

The values for η_e for all four analysed processes are given in table 6.23. It is most obvious that, although the converter has a large total entropy production, it also has a large entropy coefficient and is thus 'more perfect' than the other processes. Anode furnace and electrolysis are decreasing the copper entropy only slightly, but are producing a large amount of 'overhead' entropy, and have thus a lower entropy coefficient. Still, one has to bear in mind that the 'service' of the electrolysis is not only to make the copper purer, but by this to enhance its conductivity, which again saves entropy production when used as electrical cables or wires[10].

The large entropy production values for the flash smelter and the converter are easily explained by the conversion of chemical energy stored in the sulphides into thermal energy

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[10] The electrolysis produces 4.4 MJ/K per ton of cathodes. If these cathodes were manufactured into an electric cable with a cross-section of 1 mm^2, and a current of 1 A was run through it, it would take approximately one month before the same amount of entropy was saved due to the higher conductivity.

stored in the products, mainly the offgas. This is an intrinsic property of the process and can hardly be changed without changing the whole process set-up[11]. Actually, the excess heat is needed in order to melt the products so as to be able to process them in the following process steps.
Nevertheless, the entropy production is not only determined by the amount of energy transferred to the products, but also by the temperature level at which this transfer takes place. This comes into play when the entropy production due to dissipation of energy to the offgas is considered. In particular the converter process leaks in a large amount of secondary air, which is not needed for the conversion process itself. As a consequence, the final temperature of the offgas is lower than would be achieved by limiting the overall air intake. Thus, comparably more entropy is produced. This fact can also be proven analytically by analysing the mass dependence of heat transfer entropy production. *Thus, from an entropic standpoint, it is advisable to limit the influx of secondary air into the process.*
A different point of view clarifies this: imagine if only the minimum amount of air necessary to run the process were to enter the converter. The final offgas stream would then also be minimal. Its temperature would be determined by the overall enthalpy balance. If one now dilutes this ‘hot’ offgas with ambient air, one dissipates the stored heat energy to a larger volume, thereby decreasing the temperature of the offgas stream. The final offgas stream then has a higher entropy and is thus less available (or ‘valuable’) for further processing. Having an offgas stream with higher temperature would mean more of the internally stored heat energy could be transformed into useful energy, e.g. electricity or steam. The resource use associated with this dilution effect is not instantly visible from an energy balance, but rather obvious when looking at the entropy balance.

Another major contribution to the entropy production of all four processes is the combustion of fossil fuels. This is especially true for the converter and the anode furnace, and is unfortunately not visible for the electrolysis, since the combustion process (for producing the needed electricity) is outside the system. The Peirce-Smith converter process is, in principle, energetically self-sustaining, since the oxidation reactions are strongly exothermic. Still, since it is operated as a batch process, there are start-up procedures necessary that consume large amounts of fossil fuel. This also is an intrinsic property of the process and cannot be changed easily. Yet there are numerous efforts made to design a continuous process that does not have these disadvantages and should therefore have a lower entropy production. One should note that this use of fossil fuel would also be noticeable in an ordinary energy balance and is known well to most metallurgists.

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[11] One could, for example, dream up a process that runs at near ambient temperature using a technique similar to a fuel cell. The excess electrical energy could then be used to drive the subsequent processes.

6.7 Conclusions and recommendations for the primary production

The entropy analysis applied to the copper production from ore concentrates pinpoints the process stages with the highest resource use and indicates several possible optimisation approaches.

1) The major source of entropy production, and hence the process with the highest resource use, is the *converter* (Peirce-Smith type). The main contributions come from the exergetic oxidation reactions and the mixing of hot process gases with ambient air. While the basic design of this process, including the reactions with their intrinsic entropy production, cannot be changed easily, the influx of ambient air can, in principle, be decreased by appropriate engineering measures. Though the converter process is the one with the highest entropy production, it is also the major concentration process along the production path, making it a rather efficient process.

2) For the *flash smelter*, the process design is already minimising the influx of secondary air. Its main entropy source is the oxidation process and the subsequent dissipation to the reaction products. This could only be changed if it was possible to find an efficient reaction path at lower temperatures as, for example, via electrochemical reactions. Although this is currently not feasible, the expected entropy production for this alternative process is considerably smaller.

3) The *anode furnace's* main entropy source is the dissipation of heat to the ambient air, which could be depreciated by re-designing the offgas handling system and improving the insulation.

4) The *electrolysis'* main entropy production is through dissipation of electrical energy to the environment in form of heat. This is already visible from an energy analysis, but could be confirmed by this entropy approach. Increasing the efficiency of this process is probably only possible by further increasing the electrolyte conductivity and providing good electrical contacts within the circuitry. Enhancing the cathode current efficiency is probably not an option at the NA, since it is already at around 98%.

5) All process steps would benefit from increased insulation of furnaces and offgas systems, which would decrease the energy requirements for heat loss compensation.

There still seems to be enough room for process optimisation in the current practice of copper production. Though some inefficiencies cannot be eliminated without fundamentally changing the process chain, there are other enhancements which are achievable through better design of the already-installed techniques. The entropy analysis, combined with an energy analysis and economical considerations, can be of help in finding the most promising targets for optimisation approaches.

6.8 Secondary copper production

The recycling of copper plays an important role in the world's copper consumption. In the year 2000, worldwide production of refined copper was 14.9 million tons of which 2.0 million tons were produced from secondary materials (recycled material and internal reverts), representing a share of 14%. In some countries, this share was as high as 62% [26]. There is a great variety of materials available for copper recycling, ranging from low-grade materials like dusts and ashes with a copper content of 1-2%, to high grade scraps with a copper content of more than 99%. The diversity of the sources for secondary copper is reflected in the diverse list of processes employed for recycling. The primary copper smelters very often have the facilities to also process large amounts of secondary material. The NA, for example, produces around 30% of its refined copper output from secondary sources [45]. In the case of a process set-up as described in chapter 6.3, the secondary material can be fed into the primary production network at two places: the converter and the anode furnace. The large amount of excess heat in the primary converter facilitates two effects: the fuel-free melting of solid scraps and the complete breakdown of organic material, as is present in printed circuit boards and cable insulation. The latter effect combined with the reducing conditions in the offgas stream inhibits the production of dioxins, a rather unpleasant side-effect of the recycling of such material in purely secondary copper plants. The anode furnace is suited to melt and refine high-grade scraps with a copper content greater than 90%.

Within the framework of this thesis it was not feasible to calculate the entropy production for all possible recycling pathways. Not only are there simply too many, but also the required data for a detailed analysis was not available and could hardly be estimated from the principal knowledge of the physics and chemistry of those processes. Thus, for copper recycling in a primary copper smelter plant, three simple scenarios have been chosen for which the entropy balance could be calculated from the data available.

6.8.1 Recycling of pure copper scrap in the anode furnace

The most simple scenario for recycling in a primary production network is to feed high-grade copper scrap, such as copper granules from cable comminution, directly into the anode furnace. Actually, this is already included in the analysis in chapter 6.3.3, since one of the inputs to the anode furnace is pure copper scrap (Cu $> 99\%$). Thus, the only task left in this case is to calculate the fraction of the total entropy production attributable to the processing of this scrap. This leads us back to the allocation problem outlined in chapter 4. Here we have two different outputs from the process network: copper cathodes from primary production (i.e. from ore concentrate) and cathodes produced from secondary production (i.e. from scrap). Of course, the two products are physically indistinguishable and appear in the same form of copper cathodes at the end of the electrolysis process. But still, each copper atom took either of the two routes and should therefore be allocated a corresponding portion of the total entropy production. In fact, the problem is even more complicated, due to the several reflows inside the network, which theoretically could let some of the copper atoms cycle through the whole network more than once. However, these feedback effects will be rather small and are therefore neglected here.

So how can the entropy production calculated in chapter 6.4 be allocated to either primary or secondary cathode copper? All four processes purify the inputs, and the use of resources is directly linked to the quantity and quality of the main copper bearing flow entering the processes. Hence, the most intuitive choice for the allocation factor is the mass fraction of the copper bearing input streams. For the anode furnace as described in chapter 6.3.3, this factor would be $\frac{m_{sca}}{M_A}$, where M_A is the total input of copper bearing flows to the anode furnace: $M_A = m_{bc} + m_{csa} + m_{sca}$.

Using the values calculated in chapter 6.3, the entropy production in the *anode furnace* attributable to the processing of scrap is then 0.0133/1.052 ≈ 1.3% of the total entropy production S_{A}. As described above, some portion of the copper input is oxidised and finds its way into the anode furnace slag. This is also true for the scrap copper input. This slag is recycled to the converter and thus some portion of the converter's entropy production has to be allocated to the processing of copper scrap. To distinguish the material flow originating from scrap, the notation of a * superscript is introduced. The aforementioned fraction is then directly proportional to m^*_{as}/M_C, with m^*_{as} being the flow of anode furnace slag originating from scrap and M_C being the total mass of all copper bearing inputs to the converter. Plugging in all the values from chapter 6.3, one finds that approximately 0.02% of the *converter's* entropy production have to be attributed to the processing of scrap. A similar calculation yields 0.005% as the respective fraction of the *flash furnace's* entropy production.

Following the same line of thought, the *electrolytic refinery* contribution to the overall entropy production is then $\frac{m^*_{ac}}{M_E} S_E$, where $M_E = m_{ac}$, since the only copper bearing input to the electrolysis is anode copper. Since anode copper from scrap should behave no different from regular anode copper, the ratio of cathode copper from scrap to anode copper from scrap should equal the ratio of the total cathode and anode quantities r, i.e. $m^*_{cc}/m^*_{ac} = m_{cc}/m_{ac} \equiv r$. Adding the single contributions of the four processes, and relating the result to the output of cathodes produced from scrap m^*_{cc}, one finds the entropy production attributable to the processing of scrap S^*_{cc} and the specific entropy production for cathodes from scrap $\bar{S}^*_{cc}$ in this scenario to be:

$$S^*_{cc} = \frac{m^*_{csf}}{M_F} S_F + \frac{m^*_{as}}{M_C} S_C + \frac{m_{sca}}{M_A} S_A + \frac{m^*_{ac}}{M_E} S_E \tag{6.3}$$

$$\bar{S}^*_{cc} = \frac{m_{ac}}{m^*_{ac} m_{cc}} S^*_{cc} \, . \tag{6.4}$$

Plugging in the values from chapter 6.3 and 6.4, one finds the specific entropy production for cathodes produced from scrap input to the anode furnace to be $1.29 \cdot 10^7$ J/Kt. How much each process contributes is shown in table 6.24. It is noteworthy that the electrolysis now contributes roughly 34% to the overall entropy production, while it was only 9% in the primary case. The anode furnace in this example serves mainly as a melting furnace and thus its entropy production should be related to this service. For melting and solidifying the scrap copper, the minimal entropy production is determined by the heat transfer to the scrap and the final transfer to the environment in the cooling phase (assuming that this heat is not transferred to some other unit). The associated entropy production for melting and cooling is then approximately $2.94 \cdot 10^6$ J/K per ton of cathodes compared to the actual $8.1 \cdot 10^6$ J/K observed. This indicates that this scenario is a rather unsuitable choice for recycling high-grade scrap. When there is no fire-refining necessary, it is probably advisable to use a more specialised melting device, like the shaft furnace.

Process	**Entropy production**
Anode furnace	$(0.81 \cdot 10^7 \pm 10\%)$ J/K
Converter	$(0.03 \cdot 10^7 \pm 25\%)$ J/K
Flash smelter	$(0.01 \cdot 10^7 \pm 10\%)$ J/K
Electrolysis	$(0.44 \cdot 10^7 \pm 10\%)$ J/K
Sum	$(1.29 \cdot 10^7 \pm 16\%)$ J/K

Table 6.24: Entropy production for **cathode copper from scrap per one ton of cathodes**. The scrap was assumed to have a copper content of 100% and to be fed into the anode furnace. Since these results are won from the same data as the results for the production from ore concentrate, the same error margins as derived in chapter 6.5 apply.

6.8.2 Recycling of PVC-contaminated copper scrap in the anode furnace

The second scenario for copper recycling is the feed of copper scrap from cable comminution to the anode furnace. Here it is assumed that this scrap input has a variable PVC fraction x, where x typically lies in the range of 0.01 to 0.20. If the total mass is taken to be constant, then the specific entropy production for cathodes in this scenario depending on the PVC content of the scrap can be investigated. Again, it is assumed that all other processes are not affected by the composition of the scrap input, which is quite reasonable when looking at the mass ratio of copper scrap to total copper bearing input to the anode furnace: $m_{sca}/(m_{sca} + m_{bc} + m_{csa}) \approx 1.3\%$. The oxidation of PVC inside the furnace is taken to be complete, thus neglecting the possibility of dioxin formation. The heat of combustion of PVC will substitute some part of the fuel oil input needed for heating the furnace. Since the entropy production for combustion of PVC at standard conditions (neglecting all heat transfers) is slightly lower than for fuel oil with the same net heating value, the anode furnace's entropy production will also slightly decrease with increasing x:

$$\begin{aligned} S_A(x) &= S_A(0) + \Delta S_{PVC}(x) \text{ with} \quad (6.5) \\ \Delta S_{PVC}(x) &= -x \cdot 0.4 \cdot 10^3 \text{ J/K.} \quad (6.6) \end{aligned}$$

The anode copper output $m_{ac}(x)$ decreases with increasing x, since the copper fraction $(1-x)$ decreases. When r_A denotes the transfer ratio of total copper input to anode copper, the output is described by

$$m_{ac}(x) = m_{ac}(0) - m_{sca} x r_A \,. \tag{6.7}$$

Accordingly, the output of anode copper originating from scrap $m^*_{ac}(x)$ decreases with x:

$$m^*_{ac}(x) = (1-x) m_{sca} r_A \,. \tag{6.8}$$

Now the entropy production of the anode furnace attributable to the processing of scrap is proportional to m_{sca}/M_A, as was discussed above. The specific entropy production for anodes produced from scrap is then

$$\bar{S}^*_{ac}(x) = \frac{m_{sca}/M_A}{m_{sca}(1-x) r_A} (S_A(0) + \Delta S_{PVC}(x)) \,. \tag{6.9}$$

From chapter 6.3 we take the values for the production of one ton of anodes when $x = 0$: $m_{sca} \approx 13.33\ \mathrm{kg}, \mathrm{M_A} \approx 1052.0\ \mathrm{kg}, \mathrm{S}_A(0) \approx 0.69 \cdot 10^7 \mathrm{J/K}$ and $r_A \approx 0.97$ and then (neglecting $\Delta S_{PVC}(x)$) we find

$$\bar{S}^*_{ac}(x) \approx \frac{0.69 \cdot 10^7 \mathrm{J/K}}{1.02(1-x)} \,. \tag{6.10}$$

For $x = 0$ (no PVC in scrap), the specific entropy production in the anode furnace is $0.67 \cdot 10^7$ J/K – only slightly smaller than for the original case from chapter 6.4. This only reflects that the composition of scrap copper is not much different from the blister copper's composition. For small x, $\bar{S}^*_{ac}(x)$ is slowly increasing but diverges to infinity when x approaches 1. This is understandable when one notes that in the limiting case of $x = 1$ the anode furnace would mainly be used for combusting PVC with only a small output of anode copper from scrap. The reasoning that was applied to the case of pure copper scrap above can now be applied to this scenario to yield the contributions to the entropy production from the other processes (converter, flash smelter and electrolysis). When calculating $\bar{S}^*_{cc}(x)$ in this scenario, the contribution from the electrolysis remains constant, i.e. independent of x at $0.44 \cdot 10^7$ J/K per ton of cathodes. The contributions from the converter and the flash smelter are still relatively small, since the reflow of slags originating from scrap is small. The dependence of $\bar{S}^*_{cc}(x)$ and the contributions from the different units is shown in figure 6.8. It is evident that the anode furnace and the electrolysis make up most of the entropy production in this scenario and should therefore be the primary target for any optimisation approach.

6.8.3 Recycling of SiO_2- and PVC-contaminated copper scrap in the converter

A third possibility for copper scrap being recycled using the primary process network is feeding it into the converter. Again, the easiest way to obtain the entropy production for

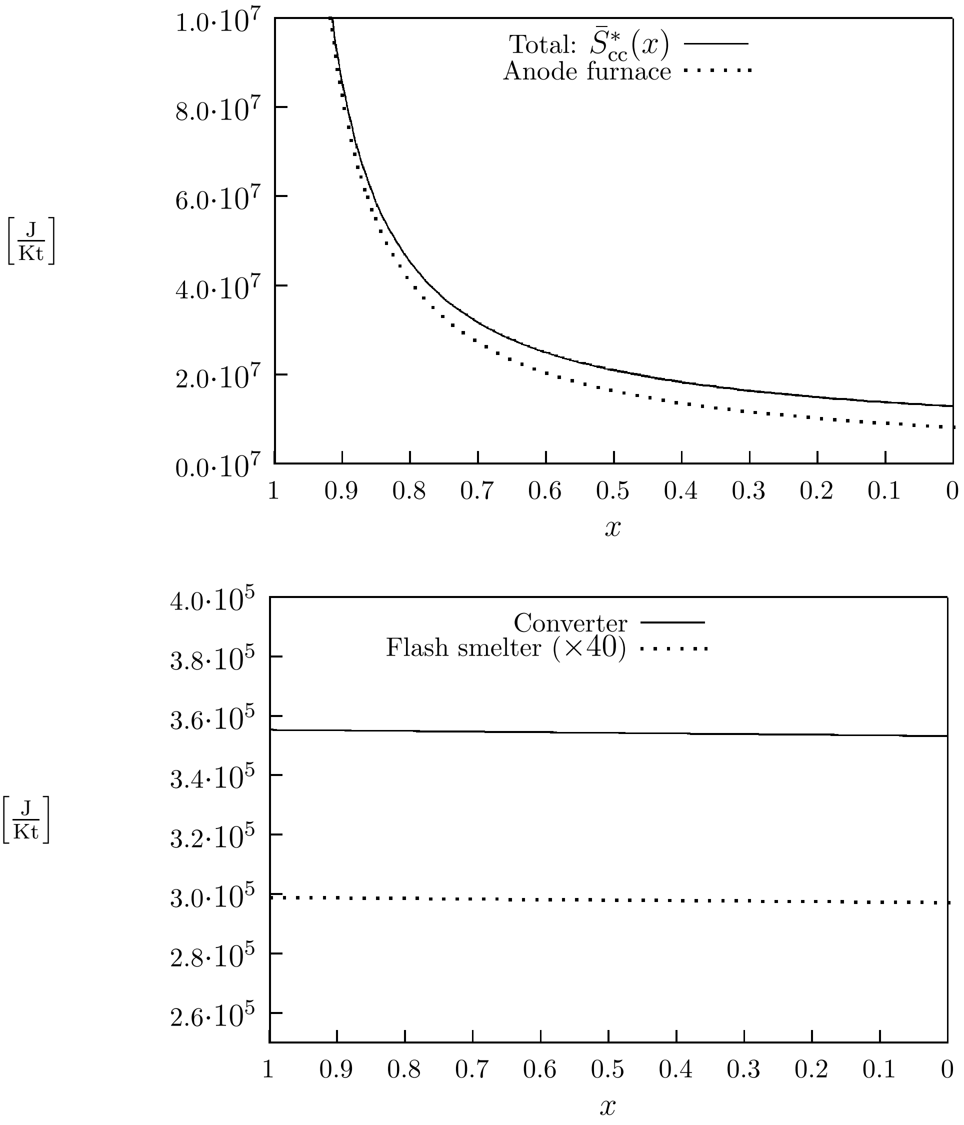

Figure 6.8: The solid line in the upper plot shows the specific entropy production for cathode copper produced from scrap input to the anode furnace, $\bar{S}^*_{cc}(x)$, with varying PVC content x. The dotted line is the contribution from the anode furnace alone. The lower plot shows the contribution from the converter (solid line), and the flash smelter (dotted line), which has been magnified by a factor of 40. The contribution from the electrolysis is constant ($0.44{\cdot}10^7$ J/K) for varying x and is not shown in the plots.

cathodes produced in this manner is to *perturb* the already solved system from chapter 6.3 by changing the mass flow of reverted anodes from the electrolytic refinery, m_{ar}. The model for the electrolysis in chapter 6.3 included that about 16% of the anodes entering the electrolysis are sent back to the converter due to limitations in the mechanical set-up of the electrolytic cells. An easy way to accommodate for another recycling route is then simply to assume a smaller percentage of anodes recycled to the converter and compensate for the input loss at the converter by feeding additional copper scrap into it. Keeping all other flows in the network fixed, this means an increased output of cathodes m_{cc}. When $r := m_{ac}/m_{cc}$ denotes the fraction of anodes refined into cathodes in the electrolysis, the fraction recycled to the converter is approximately[12] $(1-r)$. For the unperturbed network the fraction of refined anodes is denoted by r_0. The specific entropy production in the electrolysis is then also a function of r, since it is defined by $S_E/m_{cc} = S_E/m_{ac}r$. It is further assumed that the additional scrap input to the converter is composed of copper, silicon dioxide and PVC with mass fractions α (Cu), β (SiO_2) and $\gamma = 1-\alpha-\beta$ (PVC) respectively, which roughly reflects the components of wastes from printed circuit boards (cf. [40]). The entropy production in the converter attributable to the processing of scrap, S_C^*, is again proportional to the scrap mass, m_{sc}: $S_C^* = (m_{sc}/M_C)S_C$. The scrap copper mass is chosen as to compensate the copper input loss due to the decreased flow of reverted anodes m_{ar}, such that

$$\alpha m_{sc} = (r - r_0) m_{ac} \,. \tag{6.11}$$

Assuming that the copper fraction of the scrap will completely end up in the blister copper (and not be slagged), the fraction of blister copper originating from scrap, m_{bc}^*, is solely dependent on α and the copper concentration of the blister copper c:

$$m_{bc}^* = \frac{\alpha m_{sc}}{c} \,. \tag{6.12}$$

For the anode furnace the same allocation rule applies as for the converter, i.e. $S_A^* = (m_{bc}^*/M_A)S_A$ with m_{bc}^* determined by (6.12). The mass of anodes produced from scrap, m_{ac}^*, is given by

$$m_{ac}^* = \frac{m_{ac}}{m_{bc}} m_{bc}^* \,. \tag{6.13}$$

And thus S_E^* is given by

$$S_E^* = \frac{\alpha m_{ac} m_{sc}}{c m_{bc} M_E} S_E \,. \tag{6.14}$$

The cathode output from scrap is given by $m_{cc}^* = r m_{ac}^*$ yielding:

$$m_{cc}^* = \frac{\alpha r}{c} \frac{m_{ac} m_{sc}}{m_{bc}} \,. \tag{6.15}$$

The flash furnace also contributes to the entropy production for processing of copper scrap. Its share is determined by the amount of converter slag generated by the additional scrap feed. It is assumed that the only fraction generating slag in the converter is the SiO_2

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[12] Neglecting the copper loss in the anode slime which is about 0.3%.

content of the scrap, thus the entropy production in the flash furnace attributable to scrap processing, S_F^*, is proportional to β and determined by

$$S_F^* = \frac{\beta m_{sc}}{M_F} S_F \, . \tag{6.16}$$

Adding all the contributions from F,C,A and E, we obtain the total entropy production for cathode copper produced from scrap, S_{cc}^*, as

$$S_{cc}^* = \frac{\beta m_{sc}}{M_F} S_F + \frac{m_{sc}}{M_C} S_C + \frac{\alpha m_{sc}}{c M_A} S_A + \frac{\alpha m_{ac} m_{sc}}{c m_{bc} M_E} S_E \, . \tag{6.17}$$

Due to the additional scrap input, some of the mass flows are changing in magnitude and the entropy production of the converter S_C changes due to the input of PVC (similar to the case of the anode furnace discussed above). The new values can be given as deviations from the values for the undisturbed network (denoted by a 0 superscript).

$$\begin{aligned} M_C &= M_C^0 + (1-\alpha) m_{sc} \\ M_F &= M_F^0 + \beta m_{sc} \\ S_C &= S_C^0 + \gamma m_{sc} \Delta \bar{S}_C \, , \end{aligned}$$

where $\Delta \bar{S}_C \approx 17.8 \frac{\text{MJ}}{\text{Kt}}$, which can be derived from the reaction enthalpy and entropy of the PVC combustion.

Plugging these new values into equation (6.17) and dividing by m_{cc}^* yields the specific entropy production for cathode copper produced from scrap input to the converter:

$$\bar{S}_{cc}^* = \frac{1}{r} \frac{m_{bc}}{m_{ac}} \left(\frac{\beta c}{\alpha} \frac{S_F^0}{(M_F^0 + \beta \frac{r-r_0}{\alpha} m_{ac})} + \frac{c}{\alpha} \frac{(S_C^0 + (1-\beta-\alpha) \frac{r-r_0}{\alpha} m_{ac} \Delta \bar{S}_C)}{(M_C^0 + \frac{1-\alpha}{\alpha}(r-r_0) m_{ac})} + \frac{S_A^0}{M_A^0} + \frac{S_E^0}{m_{bc}} \right) . \tag{6.18}$$

It is interesting to see how $\bar{S}_{cc}^*$ behaves for different scrap compositions. One would intuitively expect that the specific entropy production should be smaller for a higher scrap quality, i.e a larger value for α. This is confirmed by looking at the plot in figure 6.9. With $\beta = 0$ in these plots, we have recreated the scrap quality from chapter 6.8.1, only that now the scrap is fed into the converter. For pure copper scrap ($\alpha = 1$) the converter path produces almost twice as much entropy per ton of cathodes as the anode furnace path (see table 6.25). *This makes the anode furnace the superior furnace for high-grade copper scrap*[13]. For low-grade scraps the difference is less pronounced, such that for $\alpha = 0.1$ and $\gamma = 0.9$ the ratio decreases to 1.5.

For $\alpha = 0.3$, $\beta = 0.4$, and $\gamma = 0.3$ we have a scrap composition comparable to the ore

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[13] The accuracy of this statement hinges very much on the accuracy of the entropy balance of the converter, which suffers from the inconsistent data on its fossil fuel consumption (see chapter 6.3.2). The entropy production for this recycling route could be up to 7 MJ/K lower than calculated above. Neverthelss, this would still leave it substantially higher than for the anode furnace route.

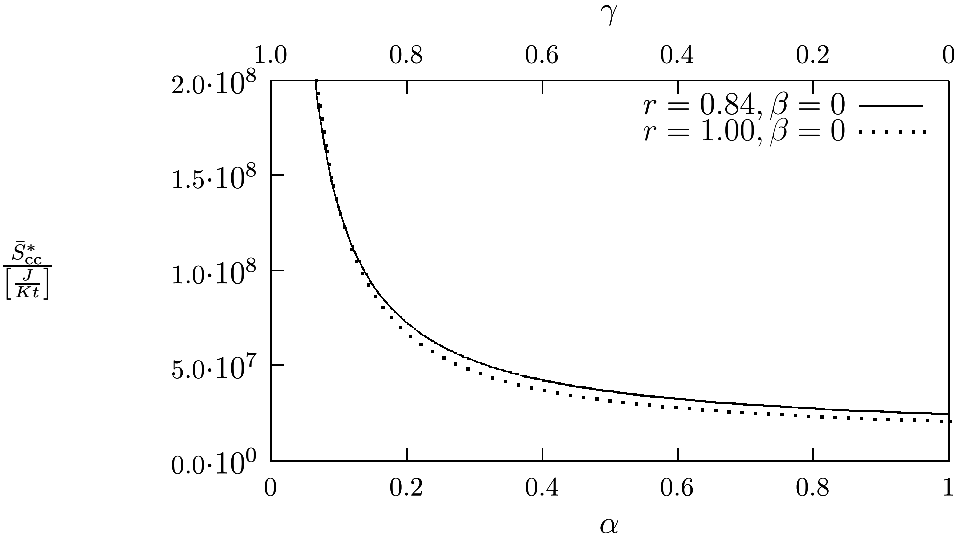

Figure 6.9: Specific entropy production for the production of cathode copper from scrap fed into the converter with varying compositions. The lower x-axis shows the copper content, the upper x-axis shows the corresponding PVC content. The SiO_2 content is zero in this case. The solid line represents an electrolysis transfer ratio of 0.84 (anode input to cathode output). The dotted line is the same plot for a ratio of 1.

Process step	**Scrap into A**	**Scrap into C**
Flash smelter	0.07 MJ/K	0.00 MJ/K
Converter	0.35 MJ/K	12.07 MJ/K
Anode furnace	8.13 MJ/K	7.99 MJ/K
Electrolysis	4.40 MJ/K	4.53 MJ/K
Sum	12.89 MJ/K	24.60 MJ/K

Table 6.25: Entropy production for the production of one ton of cathode copper from scrap, using two different recycling paths and pure copper scrap (100% Cu) as input. The first column refers to scrap input to the anode furnace (A) as calculated in the previous chapter, and the second column refers to scrap input to the converter (C).

concentrate input in the primary production. The specific entropy production for the converter path (with a realistic value of $r = 0.9$) is then 53.7 MJ/K, which is almost identical to the primary production with 53.3 MJ/K. Thus, the processing of low-grade copper scraps (Cu $\approx$ 30%) has the same resource use associated with it, as the production from ore concentrates. This finding confirms the result from an energy analysis done by Krüger et al [36, 35].

The anode to cathode transfer ratio r in the electrolysis affects the entropy production only marginally. It becomes only relevant for very low-grade copper scraps, as can be seen from figure 6.10. As one would expect, the specific entropy production decreases slightly with increasing r, since the overall process is then more efficient (less internal reverts are produced). Figure 6.11 shows the dependency of $\bar{S}^*_{\mathrm{cc}}$ on the proportions of β and γ for a fixed $\alpha = 0.1$, i.e. a rather low grade scrap comparable to typical printed circuit board scraps. The graphs reflect the shift in entropy production from the converter to the flash furnace with increasing β. This behaviour becomes clear when one notes that the entropy production for PVC combustion is proportional to $(1-\alpha-\beta)/(\alpha r)$, and thus decreases with β. This is only visible for α sufficiently small and is otherwise compensated by the increasing entropy production in the flash furnace, since in this case $S^*_F \propto \beta/r$. For α *and* r small, S^*_F is almost constant for varying β.

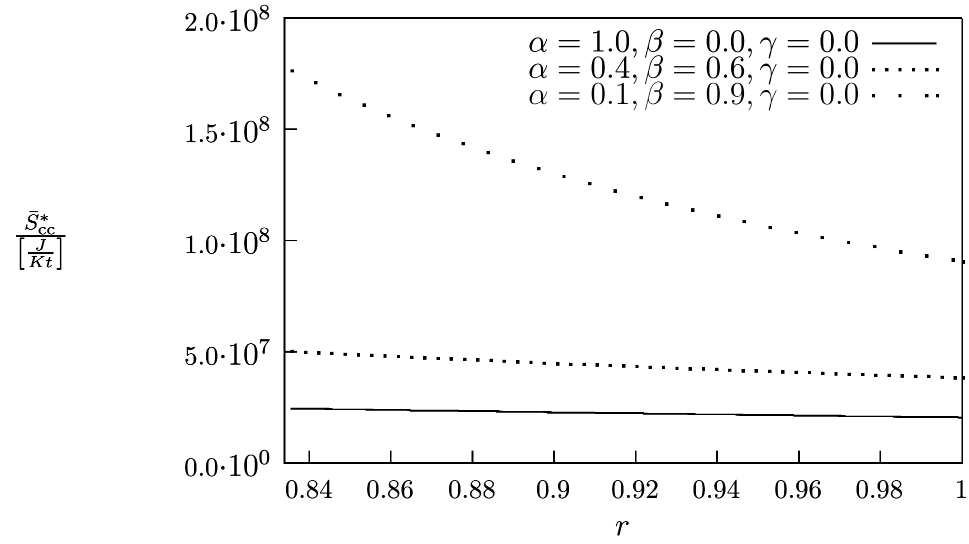

Figure 6.10: Variation of the specific entropy production of cathode copper from scrap fed into the converter with varying anode to copper transfer ratio r. The effect is only non-negligible for small α and large β, since then the entropy production of converter *and* flash furnace are decreasing significantly with r.

In conclusion, it can be stated that processing of medium- to high-grade copper scrap in

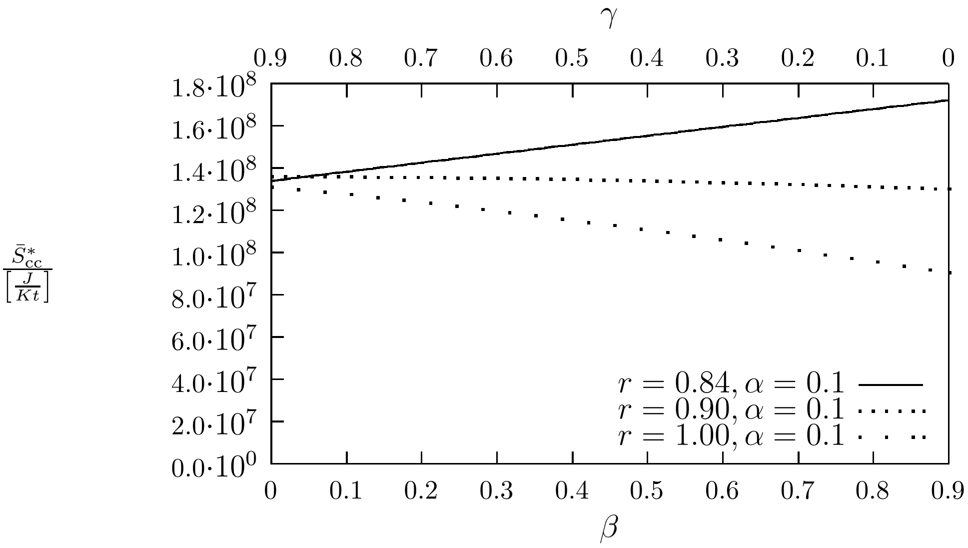

Figure 6.11: Specific entropy production of cathode copper from scrap fed into the converter with varying proportions of β and γ for a fixed α and different anode to copper transfer ratios r. See text for explanation.

either the anode furnace or the converter uses significantly less resources than the primary production from ore concentrates. The anode furnace is thereby the favourable choice for high-grade scraps, if no specialised melting device is available. The copper content of the scrap influences the result greatly, which has to be taken into account when evaluating recycling scenarios.

Chapter 7

Comparison with alternative approaches

The results from the entropy analysis can be compared with the results from other approaches only within limits, as mentioned in chapter 3.4. As discussed earlier, the only really related measure of resource use is the exergy destruction. The concepts of MIPS and CED measure a different quantity, and thus a comparison can only be done qualitatively. A further complication arises from the fact that the data on MIPS, CED and exergy analysis in the literature is given without error margins, with no exception. Thus, a scientifically sound comparison is impossible. In this thesis, error margins have been established for the entropy production of a specific industrial set-up for producing pure copper from ore concentrates, see chapter 6.5. Nothing is known, however, about the precision of the results from other approaches or about the underlying data leading to these results. This has to be borne in mind, when reading the following comparison.

7.1 MIPS

The **MIPS** associated with the production of *primary* and*secondary* copper[1], as calculated by the Wuppertal Institute (WI), is given in the first two columns of table 7.1. The exact set-up of the production system analysed by the WI is not known to the author, but will probably be a 'common average' of the different production systems available. As noted above, the error margins are also not known. The third column gives the values calculated by the author, based on the data from [28]. The production system described in this publication is a 'weighted average' [28] of the world-wide copper production and consists of the stages of mining and beneficiation, transportation, smelting, and refining. There were several technologically different smelting and refining stages analysed in [28].The set-up which most closely resembles the one at the NA was chosen as a basis for the calculation of the MIPS in this thesis. The metallurgical set-up chosen is thus given by the

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[1] Primary copper is produced from copper ore, while secondary copper is produced from recycled copper wastes and reverts.

processes of flash smelting (Outokumpu process), Peirce-Smith converter, anode furnace and electrolytic refining. Since no data was available for the production of secondary copper, the MIPS for this pathway was not computed.

MIPS category	primary (WI)	secondary (WI)	primary (SG)
abiotic mat.	500 t/t	4.04 t/t	330 t/t
water	260 t/t	6.31 t/t	121 t/t
air	2 t/t	0.00 t/t	12 t/t
electricity	3000 kWh/t	1195.7 kWh/t	3827 kWh/t

Table 7.1: MIPS for the primary and secondary production of cathode copper. The first two columns are taken from [61], while the values in the third column have been calculated from the data in [28].

For secondary copper production the numbers in 7.1 are significantly lower, reflecting the enormous material and energetic expenditures necessary to extract the low-grade ore from the Earth's crust and process it into a concentrate. The numbers calculated from the data in [28] deviate significantly from the values given by the WI. This is probably due to the fact that the data for primary copper production available to the WI was insufficient and thus the MIPS had partly to be guessed. The system boundary for this MIPS analysis includes the mining and beneficiation processes and is therefore not compatible with the entropy analysis as given in this thesis.

7.2 CED

The **CED** for primary and secondary copper production was analysed at the Institute for Metallurgy and Electro-Metallurgy (IME), RWTH Aachen, by Krüger et al [56, 35, 36], see table 7.2. As discussed earlier, there are no error margins given in this analysis either, which is also true for all the following references. The composition of scraps assumed for the secondary production pathway is also not known to the author, which makes a comparison with the results from chapter 6.8 difficult. Nevertheless, the huge differences between primary and secondary copper production regarding their energy use speak for themselves. As is evident from the analysis in chapter 6, the primary production always includes secondary production through the processing of copper scrap in the converter and anode furnace. Thus, a clear distinction of the two production types is not possible. Table 7.2 reveals again the large contribution of the mining and beneficiation stage to the overall energy demand. The metallurgical stage in table 7.2 largely corresponds to the system analysed in chapter 6. The secondary production as analysed in [35, 36, 56], however, does not correspond to the recycling considerations of chapter 6.8. It is noteworthy that in the IME's analysis the metallurgical stage of the primary production has almost the same CED as that of the secondary production. This reflects the high energy content of the ore

Production stage	**primary**	**secondary**
Mining and beneficiation	35.0 GJ/t	–
Metallurgy	21.8 GJ/t	20.55 GJ/t
Total	56.8 GJ/t	20.55 GJ/t

Table 7.2: Cumulative energy demand (CED) for primary and secondary production of cathode copper, taken from [56].

concentrates which enables an almost autogenous operation in some of the sub-processes of the primary production.
A comparison with the energy demand as part of the MIPS assessment (see table 7.1) is not possible, since the MIPS concept takes only electricity into account, whereas the CED approach considers all energetic inputs, as long as they have a non-zero heating value.

The CED for the metallurgical stage using two different set-ups is given in table 7.3. The values were calculated by Kolenda et al [31]. Set-Up A consists of a blast furnace as the main smelting aggregate producing copper matte, a converter producing blister copper and an anode furnace producing anode copper. The slag from the furnaces is not treated in this set-up. Set-Up B is comprised of a flash smelting furnace producing blister copper, an electric furnace processing the flash smelter's slag (thereby producing a small amount of a Cu-Fe-Pb alloy which is further treated in a converter), and an anode furnace producing anode copper. The values are significantly higher than those found by Krüger et al, see table 7.2. The analysis by Kolenda et al was (most probably) performed on a different smelter plant, operating with different techniques than those analysed by Krüger et al, which should explain most of the deviations.

Set-Up A	**Set-Up B**
33.1 GJ/t	47.1 GJ/t

Table 7.3: CED for two different set-ups of anode copper production taken from [31]. Set-Up A consists of a blast furnace, a converter and an anode furnace. Set-Up B consists of a flash smelter, an electric furnace, a converter and an anode furnace.

7.3 Exergy

The flash smelter mentioned in the analysis from Kolenda et al must be of a different type than the one analysed in this thesis, since it produces blister copper and not matte. In addition, the other devices are not directly comparable to the ones analysed in this thesis. Nevertheless, the principal inputs and outputs of the process chains are the same and thus it is interesting to compare the **exergy analysis** carried out in the same paper with the entropy balance from chapter 6, see table 7.4. Set-Up A is probably closer to the set-up used in this thesis, since the blast furnace produces matte from concentrates, and the converter and the anode furnace perform the same functions as the corresponding devices from chapter 6. For set-up A the entropy production was broken down into contributions from the different sub-processes, as given in table 7.4. For set-up B the data for the sub-processes in [31] was inconsistent with the aggregated results for the whole process chain, so only the sum of the four processes of set-up B is given in table 7.4. The first noteworthy fact is the fairly good agreement in the results, considering the large uncertainty in the data basis. As mentioned in chapter 6.3.2, the literature on the converter process yields greatly varying values for its consumption of natural gas. Taking the lowest value found in the literature, this alone could amount to a decrease of the converter's specific entropy production of about 6 MJ/Kt. Thus, the rough agreement of the results from [31] with the results from the entropy balance must be considered satisfactory. *A real comparison between processes can only be made if the data basis is sufficiently accurate, the system boundaries for the processes to be compared are equivalent, and the error margins of the analyses are known.*

Set-Up A		**Set-Up B**	**This thesis**	
Blast furnace	39.2 MJ/Kt		Flash smelter	(19.1 ± 10%) MJ/Kt
Converter	17.1 MJ/Kt		Converter	(21.4 ± 25%) MJ/Kt
Anode furnace	11.0 MJ/Kt		Anode furnace	(6.9 ± 10%) MJ/Kt
Total	67.3 MJ/Kt	38.2 MJ/Kt		(47.4 ± 17%) MJ/Kt

Table 7.4: **Specific entropy production** of two different set-ups for the production of anode copper compared to the analysis from this thesis. The results for the sub-processes of set-up B from [31] were inconsistent with the results for the whole process and thus only the grand total is given. For a scientifically sound comparison, the error margins of the analysis from [31] would have to be known. If the same error margin as for this thesis is assumed, the results are in agreement within one standard deviation.

The results as given in table 7.4 show the relation of exergy analysis and entropy balance insofar as they both yield a comparable value for the degradation of resources. The analysis by Kolenda et al even goes a step further. In an additional analysis (not referenced in table 7.4), they calculate the *cumulative entropy production* by including the contributions from the preliminary stages of production. These preliminary stages include the processes necessary to supply the different feeds and energy carriers (ore concentrate, fossil fuels, coke, electricity, etc.). This alters the comparative results between set-up A and set-up B significantly and makes A the favourable choice in terms of resource use. The higher resource use of set-up B is hidden in the non-cumulative analysis, behind the higher consumption of electrical energy with its large *entropy rucksack*. *This again proves the necessity for* *a cradle-to-grave analysis in order to arrive at valid statements about the resource use of processes.*

Another exergy analysis was performed by Ayres & Masini [4]. The production path analysed in this paper consists of three not further specified units: beneficiation (without mining!) of sulphidic ores, smelting and de-sulphurisation, and electrolytic refining. The latter two units correspond roughly to the process set-up used in the entropy balance undertaken in this thesis. Ayres & Masini found that the exergy destruction due to smelting, de-sulphurisation, and electrolytic refining is 8010.2 MJ per ton of cathodes, corresponding to an entropy production of 26.9 MJ/Kt (via equation 3.3). This has to be compared with 53.3 MJ/Kt from the entropy balance in chapter 6. The difference between these values cannot be explained without knowing the metallurgical set-up and the mass flows of the analysis used by Ayres&Masini in more detail. However, in view of the findings of Kolenda et al, and the results from the entropy balance, this value seems to be much too low. It is interesting to note that the ore beneficiation unit in [4] has an associated entropy production of 41.2 MJ/Kt – twice as much as the whole metallurgical part. A similar conclusion was drawn from the CED analysis above. This again calls for an inclusion of the pre-metallurgical phases of mining and beneficiation in any analysis of copper production.

Alvarado et al have compared the exergy destruction of two different smelting technologies [1]: the reverberatory furnace (RF) and the Teniente converter (TC). Both of the furnaces produce matte from sulphidic ore concentrates and are operated at the same copper smelting plant in Chile. This analysis is a good example of how an evaluation of industrial processes based on the second law of thermodynamics can point out the more efficient technology. The results were given in terms of exergy loss per ton of processed concentrate and have been rescaled to the production of one ton of matte in table 7.5. It is obvious that the outdated RF technology is significantly less efficient than the other two more modern techniques. It has to be noted that the matte quality of the three processes is not the same, making a direct comparison difficult. The RF matte has a copper content of about 40% to 60%, while the OO matte usually contains at least 60% copper and the TC matte reaches grades well above 70%. This even enhances the differences in the respective efficiencies apparent in table 7.5. Another disadvantage of the RF might also contribute to the high

Furnace type	**Specific entropy production**
Reverberatory furnace	22.3 MJ/Kt
Teniente Converter	6.0 MJ/Kt
Outokumpu flash smelter	(10.8 ± 10%) MJ/Kt

Table 7.5: Entropy production of reverberatory furnace (RF), Teniente converter (TC) and Outokumpu flash smelter (OO) for the production of matte. The values for RF and TC were derived from an exergy analysis performed by Alvarado et al [1]. the values for OO are from this thesis, chapter 6

entropy production: it produces large amounts of very dilute offgases, inappropriate for further processing in a sulphuric acid plant. The OO furnace produces the least amount of offgases with a medium SO_2 content followed by the TC furnace with a quite high SO_2 offgas concentration. Thus, the entropy production reflects very well the overall efficiency of the processes.

In summary, it can be concluded that exergy analysis and entropy balancing yield comparable results for the total resource use. The absolute differences, however, are still large and the reasons behind this should be investigated more closely. A large fraction of the disagreements can probably be explained by considering the generally poor data quality and the many different technologies found in the metallurgical sector.

It is recommended that authors of respective studies shall specify the *uncertainties* of their raw data and final results in a more systematic way. This will require cooperative contributions from the copper mining and producing companies, in particular more accurate *monitoring* of the mass and energy flows in the copper production chain. This especially applies to mass flows not directly affecting the economic performance of the production system, like secondary (infiltration) air and offgas amounts.

Chapter 8

Entropy balancing in life-cycle assessments

The assessment of ecological impact and resource use is one of the major concerns of society today. As recent surveys show, most people in countries like Germany are aware of the effects that human activities have on the environment (see e.g. [72]). People and institutions, even parts of the industry, are seeking advice on how to minimise their impact on nature. The answer to this question must consequently be as complex as the interactions between society and nature themselves. A tool to aid in this decision process is the *life-cycle assessment (LCA)*. The LCA tries to determine a measure for the ecological impact associated with a product or service. At the heart of every LCA lies an *inventory analysis*, which summarises all relevant matter and energy flows associated with the analysed product. Building on top of the inventory analysis, the *impact assessment* establishes more general statements on the actual ecological impact in terms of resource use, emissions, toxicity, eutrophication, and other categories. The real art of an LCA lies within the transition from the 'mountain' of data, which is delivered by the inventory analysis, to useful statements about the impact of the analysed object in the different categories. The statements then serve as the ground for ecological decision-making.

A necessary step in the transition from inventory analysis to impact assessment, is the aggregation of the data according to some set of categories. Many aggregated measures have been suggested in recent years, three of which (MIPS, CED, Exergy) have been discussed in chapters 3.4 and 7. In the same sense, the entropy balance is aggregating material and energy flow data with respect to the use of resources. The current practice of LCA does not really take resource use into account, it merely uses the throughput of matter and energy as a substitute measure for resource use. Nevertheless, resource use naturally is one of the main impact categories of human activity. Thus, entropy analysis can and should be a part of any LCA, independent of the actually chosen set of categories. The only prerequisite is a detailed material and energy inventory of the processes involved. As discussed earlier, this requirement is not always easy to fulfil and requires considerable time and manpower. Still, a detailed inventory analysis is the backbone of any ecological assessment and should therefore be carried out with due diligence.

The inclusion of entropy production as a measure for resource use would thus add a quantitative component to the methodology of life-cycle assessment. Furthermore, entropy production is also economically relevant, since it allows the definition of a *resource efficiency* by comparing resource use with product output. Hence, it links economic(al) considerations to ecological ones and allows a holistic view of industrial processes bridging the gap between ecology and economy.

There are many software tools available that aid in the establishment of an LCA. Most of them provide a database of unit processes and their associated matter and energy flows. Additionally, most of these tools also provide one or more sets of impact categories and algorithms that aid in the impact assessment according to the chosen set of categories. The implementation of entropy balancing into these tools mainly requires the addition of a database for the specific or molar entropies of substances and a few thermodynamic formulae, which describe entropy production due to heat transfer, radiation[1], and mixing. The temperature of the material flows has to be known, since the otherwise necessary calculation from basic properties of the processes is a task too complex for general LCA tools. However, one could imagine linking the LCA tool directly to engineering simulation software (e.g. FactSage or AspenPlus). This would facilitate the completion of the inventory analysis in terms of missing thermodynamic data by giving access to the thermodynamic database and equilibration algorithms.
If the inventory analysis is sufficiently detailed, it is not necessary to link a usually high-priced simulation software to the LCA tool. It is sufficient if the LCA tool contains or has access to a database with thermodynamic properties of substances. Usually the entropy and enthalpy of substances is given in terms of a polynomial, describing the temperature dependency of the heat capacity at constant pressure C_p. From this polynomial, and the reference value for enthalpy H_0, all other thermodynamic potentials can be calculated (cf. chapter 4). A database of the polynomial coefficients is usually small in size and comparably cheap. Thus, the implementation of entropy balancing into existing LCA tools seems straightforward. A discussion of this topic with the developers of UMBERTO, one of the leading LCA tools, has supported this assertion [50]. With C_p in polynomial form, differences in enthalpy can also be calculated, allowing the calculation of the heat balance in each sub-process – usually a rather cumbersome task if no measurement data is available.

In conclusion, it can be said that including the entropy analysis into the framework of LCA adds a valuable aggregate measure to the inventory analysis. This measure reflects well the general resource use of the processes under consideration and thus supports the ecological, i.e. long-term economical, decision-making process.

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[1] Only relevant for equipment with high shell temperatures.

Chapter 9

Conclusion and outlook

9.1 Summary

The goal of this thesis was to define and test a measure of resource use, based on the second law of thermodynamics. The underlying hypothesis is that the physical use of a matter or energy flow is best described by the associated entropy production. Evidence for this was found in the thermodynamic analysis of dissipative structures, from Bénard cells to living systems. All these systems live on the degradation of gradients, which can generally be identified with the resources. The degradation of these gradients is exactly quantified by the associated entropy production. Thus, the sought for measure of resource use was found to be just that: entropy production. For arbitrary systems, the entropy production can readily be derived from the entropy balance. This was shown for several basic examples (chapter 5) and then applied to an industry-scale process, the production of copper from ore concentrates and secondary material (chapter 6).

The main problems of the entropy balance approach were found to lie in the requirement of a detailed material and energy balance for the process under investigation. It was shown that poor and insufficient data can partly be compensated for by making appropriate assumptions pertaining to the thermodynamic state of the flows, and by iteratively solving a system of non-linear equations (chapter 4.1). The application of the method of entropy balancing to find the entropy production was then straightforward. Finally, a comparison was made between entropy production and other measures of general resource use.

9.2 Discussion of results

The results from the application of entropy analysis to basic examples, and the industry-scale case study, have shown that entropy production is indeed a valid measure for the general resource use. It aggregates all matter and energy transformations into one number, thereby giving a *complete picture of the associated degradation of flows of matter and energy.* This makes the entropy production an important parameter in the environmental assessment of industrial processes. Since entropy production is a highly aggregated measure, it has to be augmented by other impact categories, besides resource use, in order to yield insight into the overall ecological impact of a process.

The entropy production also serves as a measure for the *resource use efficiency* of processes, when it is related to the products or services of this process. An increase in this efficiency then signals a better adaptation of the production system to the available resource streams. For the primary copper production system, a few recommendations could be made as to how the resource use efficiency can be increased markedly. The two main recommendations are to decrease the amount of secondary (ambient) air infiltrating the pyrometallurgical process stages and to increase the thermal insulation of the devices in order to minimise the heat loss. It also saves resources, when the necessary cooling of systems is done in a way that enhances the re-usability of the captured heat, e.g. by water cooling. At present, most of the heat leaves the analysed system with the offgas stream.

Unfortunately, entropy production is not (yet) coupled to economic parameters, so that an increase in resource use efficiency (as defined by entropy production) is not necessarily related to an increase in economic efficiency, as presently defined. They share common parameters, like the use of fossil fuels, but are not linked in general. This might change, however, when the ecological impact of a process is included in the economic assessment of a process, as is demanded by many modern economists. Entropy production and the derived measure of resource use efficiency link ecological and economic aspects of industrial processes and thus help in finding an integral view on the technosphere. This eventually leads to a shift in the economic focus from short-term to long-term considerations.

The application to secondary copper production (from recycled materials) was an example of how the resources used, measured by entropy production, can be allocated to multiple products of the production system. It was shown (chapter 6.8), as expected, that the secondary production from high-grade scraps uses significantly less resources, than the production from ore concentrates. The favourable choice for the entry point of high-grade scraps into a primary copper plant, in the absence of special smelting devices like shaft furnaces, is the anode furnace[1]. The processing of low grade scraps (copper content below 30%), however, uses approximately the same amount of resources as the production from ore concentrates. For scraps of very low grade, the resource use increases greatly. Considering the vanishing natural deposits of copper ore, this clearly indicates the necessity of high-grade recycling, keeping the copper content of the scraps as high as possible[2].

The comparison with other aggregate measures of resource use has shown an overall agreement in the relations between primary and secondary copper production. Apart from that, the absolute values differ greatly between different measures. The only measure directly comparable is the exergy loss of a process. It was found (chapter 7) that the results from

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[1] This only applies to the resource use, as measured by entropy production. Including more categories in the description, e.g. toxicity, will probably yield a different result.

[2] This has to be achieved without introducing other sources of high entropy production, of course.

exergy and entropy analysis have the same order of magnitude, but differ by up to 100% and more. The reasons for this difference are probably the poor data quality for most of these analyses and the differences in the actual industrial set-up investigated. From theory, the two methods, exergy and entropy analysis, should yield the same results. In theory and in application it could be shown that the entropy analysis can be performed without further prerequisites, if only the detailed material and energy balance is given. Only a table with thermodynamic properties of the relevant substances is needed. In contrast to the exergy analysis, there is no need to decide on a specific reference environment. Only the temperature, and in some cases the pressure, of the environment have to be known.

All in all, the inclusion of the method of entropy analysis into the framework of life-cycle analysis, or any other tool for ecological impact assessment, is straightforward.

9.3 Remaining problems and further research tasks

The real problems arising in the course of an entropy analysis are actually problems outside of the thermodynamic context. It has to be stressed that a detailed material and energy balance (including the specification of uncertainties and error margins) is a crucial ingredient of *every* ecological assessment. This is especially true if the use of resources is to be analysed. Thus, most of the work spent on this thesis was devoted to gathering the necessary data and closing the gaps in the process description. Therefore, it seems to be desirable to investigate the possibility of how the entropy analysis can be included in the design stage of industrial processes. One necessary part surely is the inclusion of sufficiently accurate *monitoring* (on the percent level) of all relevant mass and energy flows of these processes..

The standard simulation and design tools for engineers mostly have the necessary thermodynamic databases and algorithms available to include an entropy analysis. Using the entropy production to optimise the process would then not only have ecological benefits, but also economic ones.

Another interesting question is how to include entropy production (and other ecological impact categories) into the framework of economics. It seems that entropy production is the only measure for physical resource use, and it should therefore find its way into an ecologically orientated description of the economy. A first approach could be to relate the entropy production of a given process or product to its value added in the economic sense. Thus, one would create a thermodynamics based relation between resource use and creation of value.

A common objection to a *closed loop economy* is the impossibility of complete recycling. Although this objection is not quite true[3] , it is correct that complete recycling (of a given material) would have prohibitively high financial and energetic costs and is thus *practically*

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[3] The recycling losses can, in principal, be made arbitrarily small.

impossible. Also, recycling most often means ‘downcycling’, meaning the recycled material has a lower purity or decreased usability. In order to find a level of recycling which is economically and ecologically justifiable, one could employ the entropy production as a measure for the associated costs. One could then evaluate scenarios for recycling, taking the loss of usability of recycled materials into account, and compare them on the basis of their *entropic costs.* This could lead to an optimisation of incentive systems and organisation structures for recycling. Additionally, if the assessment of entropy production as a measure for resource use would be an integral part of the whole production process, it would also influence the design phase, automatically leading to a product design which is well suited for recycling. These statements are worthwhile a more detailed investigation and should be backed up by appropriate case-studies.

Appendix A

Example calculation of specific entropy

The specific entropy of a material flow j can be calculated via expression (4.19):

$$s_j = \sum_k x_k^j \frac{\bar{s}_k}{M_k} - R \sum_k \frac{x_k^j}{M_k} \ln \left(\frac{x_k^j}{M_k \sum_{k'} x_{k'}^j / M_{k'}} \right)$$

The necessary 'ingredients' are the mass fractions x_k^j of component k, the molar mass M_k, and the molar entropy $\bar{s}_k$. The respective values for the flow of blister copper from the converter are given in table A together with the data source.

Component k	$\mathbf{x_k}$ [%]	$\mathbf{s_k}$ [J/(g K)]	$\mathbf{M_k}$ [g/mol]
Cu	94.42	86.575	63.55
Cu_2S	0.50	281.478	159.15
Cu_2O	4.50	255.701	143.09
PbO	0.10	177.064	223.20
Cu_3As	0.38	305.154	265.56
Ni	0.10	89.287	58.71

Table A.1: This table shows the mass fractions x_k for the components k of blister copper, their molar entropy s_k, and their molar mass M_k. The mass fractions have been computed from original data found in [46, 11, 10], which was averaged and adjusted to fit into the network of material flows as laid out in chapter 6. Since there are no error margins given in the original literature, they can only be assumed to be 10%, see the discussion in chapter 6.5. The values for the molar entropies (at a temperature of 1470 K) were taken from [15], where no error margins were given. The values for the molar masses were taken from [16] with error margins well below 0.1%.

With the assumptions on the error margins from above, the specific entropy of blister copper can then be computed to be (1.40 ±10%) $\mathrm{JK^{-1}g^{-1}}$. The contribution due to mixing is (0.0170 ±10%) $\mathrm{JK^{-1}g^{-1}}$, which accounts for 1.2% of the total specific entropy. For other flows, the mixing contribution ranges between 2 and 12%.

The entropy flow $\dot{S}_j$ associated with material flow j is given by $\dot{S}_j = m_j s_j$. Most data, however, is given in terms of fixed amounts of product output and not in terms of material flows. Thus, the entropy balances in section 6.4 have been computed on the basis of one ton of the respective main output. Using the above result, one ton of blister copper has an entropy content of ($1.40 \cdot 10^7$ ±10%) J/K.

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