Panos Konstantin
Margarete Konstantin

# The Power Supply Industry

## Best Practice Manual for Power Generation and Transport, Economics and Trade

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# Preface

My first book of the series "Best Practice Manual" with the title "**Power & Energy Systems Engineering Economics**" was dedicated to provide a concise yet very comprehensive coverage of engineering economics required for techno-economic evaluation of investments in the energy supply business.

This book of the same series with the title "**The Power Supply Industry**" mainly deals with technologies used for power and energy supply and evaluates their economics by applying concepts and knowledge built in the first book.

Core aim of the books is to transfer know-how of power and energy systems in a practical way rather than pure theoretical knowledge, thereby avoiding the detail of voluminous reference texts as needed by experts in specific fields. This is also demonstrated in numerous application examples and case studies derived from experience of real world projects. The examples and case studies are also available as softcopies on my website to assist readers practicing the books' contents.

The books are neither scientific papers nor literature research. In writing these books, I have drawn on my cumulative knowledge gained from more than 35 years of experience as a consultant in engineering and power economics for energy business projects worldwide and also from delivering numerous training courses to junior utilities' staff in several countries. It is my ambition after retirement to make my knowledge and experience available through practically oriented books applicable to real world scenarios.

Target audience of the books are primarily international consultants, staff members of engineering companies, utility personnel, energy economists and lawyers, as well as employees of government agencies entrusted with regulating the energy and utility sector and, finally, students in related fields of engineering and economics.

Although being a non-native English speaker, I have written these books in English because this is the most suitable language in this field among others as most techno-economic terms are available in English only. I ask native English readers for their understanding for any linguistic shortcomings.

Comments and recommendations for improvements from readers are highly appreciated and will be thankfully considered in forthcoming editions.

Burgstetten, Germany, October 2017 Panos Konstantin

## Other practical books of the author:

Power and Energy Systems – **Engineering Economics**
**Springer**Vieweg, Germany, 2018

The book provides practical knowhow for appraisal and technical-economic evaluation of investments in the power and energy sector.

The book comprises eight chapters: Financial Mathematics, Inflation/Interest and Cost of Capital, Investment Appraisal, Financial and Economic Analysis, Introduction of Cost Allocation to Cogeneration Projects, Project Analysis under Uncertainties, Overview of Energy Markets and Price Mechanisms and finally case studies. The text part is supported by about 36 tables, 105 figures, 53 application examples and 13 case studies.

For German readers: **Praxisbuch Energiewirtschaft**[1], 4th Edition 2017, SpringerVieweg, Germany, ISBN 978-3-642-37264-4

Der Inhalt: Der Primärenergiemarkt, Beschaffung leitungsgebundener Energien, energierechtliche Rahmenbedingungen, Investitionsrechnung in der Energiewirtschaft, Physikalisch-technisches Grundwissen, Energieumwandlung und Emissionen, Kraftwerke – Technik & Kosten, Kraft-Wärme-Kopplung – Technik, Kostenaufteilung, Energietransport- und -verteilung, Abwicklung von Energieprojekten.

Der Textteil wird möglichst knapp gehalten und durch ca. 140 Tabellen und rund 160 Abbildungen ergänzt. Zum besseren Verständnis enthält das Buch auch ca. 80 praxisbezogene Beispiele.

For German readers: **Praxisbuch Fernwärmeversorgung.** In Bearbeitung, geplante Veröffentlichung Anfang 2018, SpringerVieweg.

Der Inhalt: Das Buch beginnt mit einem kurzen historischen Überblick und umfasst den Fernwärmenetzaufbau sowohl mit Heißwasser als auch mit Dampf als Wärmeträger, Leitungs-Verlegeverfahren, Fernwärme-Erzeugung durch Kraft-Wärme-Kopplung (KWK) in Kombination mit Spitzenlastkesseln, eine eingehende Behandlung der Kosten- und Aufwandaufteilung bei KWK, bis hin zur Fernwärme-Preisgestaltung für den Endkunden. Die Anwendungsbeispiele und Fallstudien im Buch stehen auch auf der Website des Autors als Softkopien in MS-Excel® zum Download zur Verfügung.

English Version „District Heating“ forthcoming in 2018.

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[1]) In English: “Practice Oriented Book on Energy Economy”

# Acknowledgments

First and foremost I am particularly thankful **to Fichtner GmbH & Co KG** in Stuttgart, Germany for their support and the opportunity to have access to their technical and human resources during my employment and beyond. The book mainly reflects the cumulative knowledge I have acquired and further developed from over 35 years' experience working for the Company as a consultant and trainer for energy business projects worldwide.

Many thanks are also due to the colleagues of **HelpDesk Görlitz GmbH**, Germany for their help in properly formatting the book.

I am grateful to Markus Groissböck, who has developed and maintains my Website and is always available for support.

I also acknowledge the support of many of my Fichtner colleagues, friends and clients for their advice and contribution to the development of this and previous books.

In particular, I wish to mention the following persons for reviewing chapters of the book: Adriana Mejia Gomez (Application examples and case studies), Dr. Ursula Haller (Modelling and development of KPRO®), Christian Mayr (Project development), Johannes Kretschmann and Christoph Scherer (Concentrated Solar Power), Ursula Mayr (Photovoltaics), Markus Schüller (Wind power), Dr. Liliana Oprea (Transmission & Distribution of Power), Till Aldinger (Electricity trading) and Arcady Greeshpoon (Nuclear power).

Many thanks also to Amy Gooderum and Maggie Konstantin for proofreading and linguistic revision of the book's text.

All my professional life as a consultant, I wrote hundreds of reports for projects and attained a certain routine in writing. I have furthermore greatly benefited from the experience in writing my first book "Praxisbuch Energiewirtschaft",[2] first published by Springer in 2006, and now available in its 4th edition in 2017 published by SpringerVieweg.

Last but not least I wish to thank Maggie Konstantin, my wife, for her support in editorial design and proofreading, and for her understanding for the long hours and evenings we have been spending in front of the computer.

[2] In English: "Practice Oriented Book on Energy Industry"

# Downloads

Readers of the book can access the author's website under the addresses

www.PK-Energy-Practical-Knowhow.com or

www.PK-Energie-Praxiswissen.com

and download the following items and software tools[1]:

Softcopies in Excel® of all **Application Examples** and **Case Studies** included in the book

Software tool **FluidEXL,** for calculations of water/steam properties.
The developer, University for Applied Sciences – Zittau/Goerlitz/Germany, Department of Thermodynamics, Prof. Hans-Joachim Kretzschmar and his co-worker Matthias Kunick, make available the software tool exclusively for readers of this book, free of charge.

You will find a link for download on the example page on the author's website, along with the installation instruction and read me file. A license code is automatically sent by email after registration.

Use of the software for purposes other than for the book or commercial use requires a special license from the developer.

Software tool **KPRO®**, for modelling and performance simulation of power generation thermodynamic cycles and power & steam supply systems. The German Consulting Company Fichtner, Stuttgart, announced that they will make available the software tool for registered readers of the book for a period of six months, upon direct request. Note, however, that this is a highly professional tool and requires a strong background on thermodynamics of cycle calculations and in information technology. Again, commercial use requires a special license from Fichtner.

**Note:** Purchasers of the book are highly advised to register in the author's website in order to be kept informed about updates and changes in the software

[1]) Brief instructions of the tools are available in the toolbox chapter of the book. Detailed instructions are available for download on the author's website.

Downloads

## Important notes on the chapters

**Examples:** All chapters contain numerous practical application examples. The examples as well as the case studies are intended to practice the contents of the book only and are not applicable for commercial use.

**Download examples:** Website www.pk-energy-practical-knowhow.com

Almost all examples and case studies are developed in MS-Excel® spreadsheets and inserted into the text as pictures. We tried to keep them relatively simple; nevertheless, it is not always easy to retrace the calculation steps because they often include complex calculation formulas. However, it is not possible to include these in the examples depicted in the chapters due to limited space. Readers have the opportunity to download softcopies of the examples from my website above.

**Currencies:** The book is written for an international audience in countries with different currencies. In formulas which are generally applicable, the term "CU" (currency unit) is used. In application examples, which are mainly derived from projects, either € (Euro) or US$ are used, depending on the origin of the projects. The real origin of the projects, however, is not disclosed.

**Unit system:** Throughout the book, the Standard International Unit System is used (based on MKS system: meter, kilogram, second). This system is based on physics, includes only a few basic units, and all the other units are derived from the basic units. The units are easy to handle in calculations without the need for conversions. In the European Union, its use is obligatory for public projects and in most countries it is the standard unit system.

**Heating values:** For energy balances, price references etc. the lower heating values LHV are used (also referred to in literature as net calorific values NCV or inferior heating value Hi). Worth mentioning is that natural gas is commonly traded based on its HHV and is to be converted in LHV.

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# 1 Basics of Technical Thermodynamics

## 1.1 Key Thermodynamic Concepts and Definitions

### 1.1.1 Energy, work and power

Technical thermodynamics deals with the processes of interconversion of energy forms into each other. It includes the behavior of related properties of substances involved in the process flow, e.g., pressure and temperature.

*Energy E* is defined as the ability to produce work; *Work W* is performed by moving a body with a force *F* at a distance *l* in the direction of the force *(W = F×l). Power P* is work divided by the time the work has been performed *(P=W/t).*

Based on these definitions several forms of energy are distinguished:

- Mechanical energy may occur as kinetic energy (movement energy) or potential energy (energy of the height)
- Thermal energy is contained in energy carriers as steam, hot water, thermooil etc.
- Chemical energy is contained, e.g., in fossil fuels
- Nuclear energy is contained in the nucleus of atoms
- Radiation energy such as solar irradiation

A different classification is done according to the state of energy conversion and usage chain. There are following forms:

- Primary Energy
- Secondary energy including the sub forms
  - Final energy
  - Useful energy

*Primary energy* is extracted from stocks of natural resources through mining or exploration such as coal, uranium, crude oil and natural gas, or captured from natural energy flows such as solar radiation or wind. Primary energy has not undergone any conversion other than separation and cleaning.

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*Final energy* is produced from primary energy through a conversion process. The conversion process may take place in a refinery, power generation plant or a different type of energy converter. Examples include oil products as light and heavy fuel oil or gasoline, natural gas, electricity. Other forms of final energy are blast furnace gas, converter gas, district heat or chilled water.

Final energy is converted in end-use appliances into *useful energy* such as electrical light, space heating or cooling, movement or rotation of tools.

### 1.1.2 Thermodynamic systems

A thermodynamic system is an imaginary confined volume of matter that is separated from the surrounding by its *system boundaries*. The boundaries may be fixed or movable. The system may have some exchange of mass or energy or both with its surroundings or neither of them – Figure 1-1.

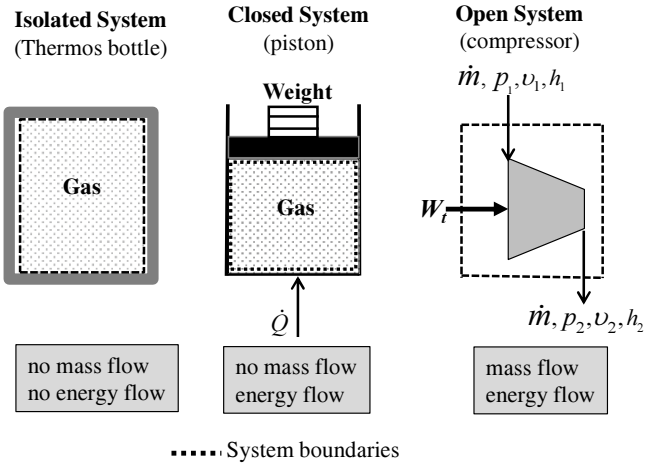


**Figure 1-1:** Examples of thermodynamic systems

The boundaries of thermodynamic systems are fixed in such a way that an analysis of mass and energy-exchange with the surroundings is feasible. In an open system, the space within the system boundaries is the control volume.

### 1.1.3 The Standard International Unit System

The Standard International (SI) Unit System comprises seven quantities and their *base units* are shown in Table 1-1. All the other units are derived from these base units by applying laws and principles of the physics – Table 1-2.

**Table 1-1:** SI base units

| Quantity | | Base Unit | |
|---|---|---|---|
| **Name** | **Symbol** (*in italics*) | **Name** | **Unit** (in standard) |
| Length | *l* | Meter | m |
| Mass | *m* | Kilogram | kg |
| Time | *t* | Second | s |
| Thermodynamic temperature | *T* | Kelvin | K |
| Amount of substance | *n* | Mole | mol |
| Electric current | *I* | Ampere | A |
| Luminous intensity | *L* | Candela | Cd |

**Table 1-2:** SI Selected derived units used in thermodynamics

| **Quantity** | **Symbol**<br>**Unit** | **Definition** |
|---|---|---|
| Speed<br>Velocity | $\upsilon$, $w$, $c$<br>*m/s* | Displacement of a body in a distance l m in a time t in seconds.<br>$\boldsymbol{\upsilon = l/t}$ |
| Acceleration | $\boldsymbol{a}$<br>$m/s^2$ | The change of velocity in m/s per s<br>$\boldsymbol{a = \upsilon / t}$ |
| Force | $\boldsymbol{F}$<br>N - Newton<br>( $1N = 1\ kg \cdot m/s^2$) | 1 N is the force which, when applied to a body having a mass of 1 kg, gives it an acceleration s of 1 $m/s^2$<br>$\boldsymbol{F=m \cdot a}$ |
| Work,<br>Energy | $\boldsymbol{W}$<br>J - Joule<br>$J=N \cdot m=W \cdot s$<br>($1\ J = 1\ kg \cdot m^2/s^2$) | Work is force multiplied by the displacement in the direction of the force.<br>$\boldsymbol{W=F \cdot l}$ |
| Power | $\boldsymbol{P}$<br>W - Watt<br>W = J/s<br>($1\ W = 1\ kg \cdot m^2/s^3$) | Power is the rate of work divided by the time it is done.<br>$\boldsymbol{P = W / t}$ |
| Pressure | $\boldsymbol{p}$<br>Pa - Pascal<br>$Pa = N/m^2$<br>($1\ Pa = kg \cdot / (m\ s^2)$) | Force divided by the area of its application: $\boldsymbol{p = F/A}$<br>Gravity pressure: $\boldsymbol{p = \rho \cdot g \cdot h}$ |

**Note:** A more detailed list of SI derived units, their prefixes, decimals and multiples as well as conversion tables are shown in **Annex 1** and **Annex 2**.

### 1.1.4 Definitions and rules

**Rules for writing** quantities and units (see Table 1-1 and Table 1-2):

- Symbols of quantities are written in italics, e.g.: *l, m, T, F, P, υ*
- Units are written in standard characters, e.g.: m, kg, K, N, kW, m/s
- Quantities are denoted as a product of their symbol, equal sign, value and unit with a space in between e.g.: *P*=100 kW, *p*=200 Pa
- Compound units are denoted as a product or quotient, e.g.: N⋅m or Nm, m/s, kg⋅m/s$^2$
- Subscripts might be used to distinguish quantities which have the same unit, e.g.: electrical power $P_e$, thermal power $P_t$

**Mass, molar mass and amount of substance:** Mass and amount of substance are related quantities. The symbol for mass is "*m*" and its base unit "kg". The symbol of amount of substance is "*n*" and its base unit "mol" where $n = m/M$ [mol]. *M* is the symbol for *molar mass* with the unit kg/kmol. This is a specific physical property of substance referred to chemical elements or compounds **Annex 4.** The molar mass of compounds is calculated from that of their elements (the unit kmol instead of mol is common):

*M* kg/kmol: Carbon C=12; Oxygen O=16; Hydrogen H=1
*M* kg/kmol: Oxygen $O_2$= 32; Carbon dioxide $CO_2$=44; Water $H_2O$=18

**Temperature:** SI base unit for *thermodynamic temperature* and for temperature difference is Kelvin "K" denoted with the symbol "*T*" and "*ΔT*" respectively. In practice temperature is metered in degrees Celsius °C, the symbol is the small *t* (or *θ*). Where:

$$T = t\ °C + 273.15\ K; \quad 0\ °C = 237.15\ K; \quad \text{or} \quad 0\ K = -237.5\ °C$$

The temperature *T* = 0 K (respectively -237.5 °C) is the lowest feasible temperature and is characterized in physics as the absolute zero temperature.

In the USA and some other countries the customary unit degrees Fahrenheit °*F* is used for temperature (non-SI unit).

$$°F = 9/5 \times °C + 32; \quad °C = 5/9 \times (°F - 32)$$

**Pressure:** SI base unit for *pressure p* is Pascal [N/m$^2$]. In practice the unit [bar] is used.

$$1\ bar = 10^5\ Pa = 100\ kPa = 0.1\ MPa$$

Pressure is always measured as *over pressure* or *gauge pressure* "$p_o$, *or* $p_g$" on top of the atmospheric or barometric pressure $p_b$. For thermodynamic calculations the *absolute pressure* is used: $p = p_b + p_o$.

In the USA and some other countries the customary unit "psi" is used (pound per square inch – psia, psig). This is a non-SI unit.

$$1\text{bar} \approx 14.5 \text{ psi}; \quad 1 \text{ psi} \approx 0.069 \text{ bar}$$

**Conversion tables** for SI-units to imperial units are listed in **Annex 3**.

### 1.1.5 Properties and quantities, definitions, symbols and units

A *pure substance* is a matter[4] that has a defined composition, and its physical and chemical properties are uniform and constant. *Mixtures* can consist of two or more pure substances. In thermodynamics, pure substances or mixtures are characterized by their thermal and energetic properties. They are constituents of thermodynamic systems.

*Properties* are intrinsic characteristics for the actual state of the substance or a system and can be observed, metered and quantified. *Quantities* express the magnitude of properties and have a number and a unit.

*Thermal properties* are: temperature $T$ [K], pressure $p$ [Pa, bar], mass $m$ [kg], Volume $V$ [$m^3$] and density $\rho$ [$kg/m^3$] or specific volume $\upsilon$ [$m^3/kg$]. For solid matter and for liquids usually the density $\rho$ in $kg/m^3$ is used, while for gases the specific volume $\upsilon$ in $m^3/kg$ is more common. Thermal properties are independent from the mass; they are also known as *intensive properties*.

*Energetic properties* are: internal energy, enthalpy, entropy and exergy. In absolute terms their symbols are specified with capitals, while mass related symbols are specified with small characters: internal energy $U$ [kJ] or $u$ [J/kg], enthalpy $H$ [kJ] or $h$ [kJ/kg], entropy $S$ [kJ/K] *or* $s$ [kJ/kg K] and exergy $E$ [kJ] or e [J/kg]. The value of energetic properties depends on the mass included in a system. They are also known as *extensive properties*.

*Process properties* are heat $Q$ [kJ] and mechanical work W [kW]

*Time rated properties* (flows) are denoted with a dot on top of the symbol:

$$\dot{m}\left[\frac{kg}{s}\right], \quad \dot{V}\left[\frac{m^3}{s}\right], \quad \dot{Q}\left[\frac{\text{kJ}}{\text{s}}\right], \quad \dot{H}\left[\frac{\text{kJ}}{\text{s}}\right]$$

Equations describing the correlations between system properties are called *equations of state*. Thermal and energetic properties of different substances are shown in **Annex 4.**

[4] Matter is everything that has a mass and occupies space. It can occur in solid, liquid and gaseous state.

### 1.1.6 Mass, weight and acceleration of gravity

Mass and weight are different properties. The *mass* of matter is equal at any place on earth (or even on the moon), its unit is kg: In contrary, *weight* is the force of gravity; it is defined as mass multiplied with the acceleration of gravity; it has the unit of a force 1 N.

$$\text{Weight: } F_G = m[\text{kg}] \times g\left[\text{m/s}^2\right] \quad [N]$$

The *acceleration of gravity* depends on the latitude and altitude of a certain place. At the equator at sea level (altitude 0) it is 9.78 m/s$^2$, while in the poles it is 9.932 m/s$^2$. For technical calculations the value of 9.81 m/s$^2$ is used. This corresponds to the acceleration of gravity at latitude of 45° and sea level.

### 1.1.7 Normal reference conditions

Ambient temperature, atmospheric pressure and humidity are different in different places on earth and change also during the time of the day and elevation. Therefore it is necessary to define standard reference conditions in order to enable testing and comparison of the performance of machinery and to define amounts of matter and of commodities (e.g. natural gas). There are different definitions of normal conditions. The most common is the definition according DIN 1343 commonly used in Continental Europe and most other countries:

**Table 1-3:** Reference normal conditions, DIN 1343

| Quantity | Symbol | State |
|---|---|---|
| Temperature | $T_n$ | 273.15 K (or 0 °C) |
| Pressure | $p_n$ | 1.01325 bar (1 atm) |
| Relative humidity | $\varphi_n$ | 0% |
| Normal volume *) | $V_{mn}$ | 22.41383 m$^3$/kmol |

*) referred to ideal gas

In *Imperial and US customary* system, normal conditions are defined:
Temperature: 60 °F (15.6°C), pressure 14.969 psia (1atm). The reference temperature is different compared to the DIN definition. Hence, also the normal conditions are not identical.

**ISO conditions of gas turbines**: The performance parameters of gas turbines are defined according to ISO for the following reference conditions:

- Ambient temperature: 15°C
- Ambient pressure: 1.013 bar
- Relative humidity: 60%

## 1.2 The Principal Laws of Thermodynamics

### 1.2.1 The First Law of thermodynamics

The First Law of thermodynamics states that energy can neither be created nor be destroyed, but one form of energy can be converted into another form. The total energy associated with an energy conversion remains constant. The First Law is also known as the law of energy conservation. It is applied differently for closed and open systems.

The energy balance for a **closed system** that undergoes a change of state from its initial state 1 to the final state 2 is according to First Law:

$$Q_{12} + W_{12} = U_2 - U_1 \qquad (1.1)$$

The heat $Q_{12}$ and work $W_{12}$, transferred into a system, are utilized to increase its internal energy $U_2$-$U_1$. *Internal energy U* [kJ] *or u* [kJ/kg] *is* the total energy contained in a closed system after the state of equilibrium is reached. Thereby the following conventions apply:

- Heat transfer into the system (Q> 0, +), out of the system (Q< 0, -)
- Work transfer into the system (W> 0, +), out of the system (W< 0, -)

The work is defined $\boldsymbol{W_{12} = -p \cdot (V_1 - V_2) = W_{V12}}$ as the *volume expansion work* (note: subscript v) also known as *pressure-volume (PV)* work; it is utilized in a closed system with movable boundaries to increase its volume (see Figure 1-1). The equation (1.1) transformed becomes:

$$Q_{V12} = U_2 - U_1 + p \cdot (V_1 - V_2) \quad \text{or} \quad dQ_V = dU + p \cdot dV \qquad (1.2)$$

For *V* constant is $dV$=0, and the above equation becomes:

$$Q_{V12} = U_2 - U_1 = m \cdot c_\upsilon \cdot (T_2 - T_1) \qquad (1.3)$$

Where: $\boldsymbol{c_\upsilon}$ [J/(kg K)] is *the specific heat capacity* at a constant volume. This is the amount of heat required to raise the temperature of one kg of a substance by 1 K (values of $c_\upsilon$ see **Annex 5**).

For **open systems** that also include mass flow, the enthalpy is preferred instead of internal energy. *Enthalpy* denoted with *H* or *h* is defined:

$$H = U + p \cdot V \left[\text{kJ}\right] \text{ or in specific form: } h = u + p \cdot \upsilon \left[\frac{\text{kJ}}{\text{kg}}\right] \qquad (1.4)$$

The energy balance for an open system that undergoes a change of state from its initial state 1 to the final state 2 is according to First Law:

$$Q_{12} + W_{S12} = H_2 - H_1 \left[\text{kJ}\right] \quad \text{or} \quad q_{12} + w_{S12} = h_2 - h_1 \left[\frac{\text{kJ}}{\text{kg}}\right] \tag{1.5}$$

Where $W_{S12} = \int_1^2 V \cdot dp$ is *the shaft work*. This is the work transferred into or out of a system by a shaft. It is also known as *technical work*. Thereby equation (1.5) becomes:

$$dH = dQ + V \cdot dp \tag{1.6}$$

For constant pressure is $dp = 0$, $W_{S12} = 0$ and equation (1.5) becomes:

$$Q_{12} = H_2 - H_1 = m \cdot c_p \cdot (T_2 - T_1) \tag{1.7}$$

where $c_p$ is the *specific heat capacity at constant pressure*. The following conventions and relations exist:

- Specific capacity for solids and liquids is practically constant $c_p = c_v = c$
- Specific capacities of gases depend on the temperature
- Relation $c_p = c_v + R$

Specific heat capacities for different substances see **Annex** 5.
For an open system mostly *time rates* are used. Equation (1.5) expressed in time rates, becomes:

$$\dot{Q}_{12} \left[\frac{\text{kJ}}{\text{s}}\right] + P\left[\text{kW}\right] = \dot{m} \cdot \left(h_2 - h_1\right) \left[\frac{\text{kJ}}{\text{s}}\right] \tag{1.8}$$

**Note:** kJ/s = kW the former unit is used for heat, the latter for power. Instead, it can also be written $\text{kW}_m$ ($_m$ for mechanical) and $\text{kW}_t$ ($_t$ for thermal). Time rates of quantities are denoted with a dot on the symbol, e.g.:

$$\dot{Q}\left[\text{kJ/s}\right], \quad \dot{H}\left[\text{kJ/s}\right], \quad \dot{m}\left[\text{kg/s}\right], \quad \dot{V}\left[\text{m}^3/\text{s}\right]$$

### 1.2.2 The Second Law of thermodynamics

The First Law of thermodynamics is known as the law of the conservation of energy; it states that all forms of energy are equivalent and can be mutually converted one into another as long as energy is not created or destroyed.
We know from experience, however, that mutual conversion of different energies is limited and that real processes follow a distinct direction, namely:

- While mechanical energy can be fully converted to thermal energy, heat can never be fully converted to mechanical energy
- Heat cannot be transferred by itself from a lower (heat sink) to a higher temperature level (heat source)
- Mass cannot be transferred by itself from a lower to a higher pressure level
- Work cannot be created solely from internal energy of a system

The Second Law of thermodynamics, in contrary to the First Law, restricts the convertibility of energy forms by introducing the *privileged process direction* and the irreversibility of processes.

The Second Law distinguishes between reversible and irreversible processes. For *reversible* processes it is deemed that the initial state of the system can be fully restored solely by changing the direction without any energy expense. In contrary, *irreversible* processes occur in one direction only, and the initial state can only be restored by expense of energy. The Second Law is also known as the *law of the preferential process direction.*

The Second Law further states that there is a property of state known as *entropy,* denoted with the symbol $S$ [kJ/K] or $s$ [kJ/kg K], that in a closed system undergoing a change of state never decreases. All natural processes are irreversible; they are characterized by entropy increase. Entropy is mathematically defined as the ratio of heat transfer to the thermodynamic temperature of a system.

$$dS = \frac{dQ}{T} \geq 0 \quad \left[\frac{\text{kJ}}{\text{K}}\right] \tag{1.9}$$

The following conventions apply for thermodynamic systems undergoing a process:

- dS < this is a technically not feasible process
- dS = this is an ideal, reversible process
- dS> = this is a technically feasible, real, irreversible process

Under consideration of equation (1.9) the main equations of thermodynamics (1.2) and (1.6) become:

$$dU = T \cdot dS - p \cdot dV \quad \text{and} \quad dH = T \cdot dS + V \cdot dp \tag{1.10}$$

The entropy is an essential parameter for cycle calculations with Mollier h-s diagrams.

## 1.3 Gas Thermodynamics

### 1.3.1 The equation of state of the ideal gas

The state of a gas is defined by the properties of state pressure $p$, volume $V$ and thermodynamic temperature $T$. The equation of state of the ideal gas is:

Specific form: $p \cdot \upsilon = R_i \cdot T$ or $p \cdot V = m \cdot R_i \cdot T$ (1.11)

Molar form: $p \cdot V = n \cdot \overline{R} \cdot T$ or $p \cdot \overline{\upsilon} = \overline{R} \cdot T$ (1.12)

Where:

$P$ : Pressure [N/m$^2$]

$V$ : $\upsilon$[m$^3$/kg]: Gas volume, specific volume [m$^3$]

$T$ : Thermodynamic temperature [K]

$R_i$ : Specific gas constant of the gas $i$ [kJ/kg$\cdot$ K]:

$\overline{R}$: Universal gas constant [KJ/kmol$\cdot$ K]

$m$ : Mass of the gas $i$ [kg]

$n=m/M_i$ Amount of substance [kmol], $M_i$ Molar mass of the gas $i$ [kg/kmol]

$\overline{\upsilon}$ Molar volume [m$^3$/kmol]

*Ideal gases* are gases which satisfy the above equations (1.11) and (1.12) !whereas r*eal gases* satisfy the above equations only approximately. For technical applications, however, with atmospheric air or flue gases and some other technical gases the margin of accuracy is sufficient.

Universal gas constant $\overline{R} = M \cdot R = 8.31451 \left[ \frac{\text{kJ}}{\text{kmol} \times \text{K}} \right]$

Molar volume: $\overline{\upsilon} = \frac{\overline{R} \cdot T}{p} = \frac{M \cdot R \cdot T}{p} = M \cdot \upsilon \quad \left[ \frac{\text{m}^3}{\text{kmol}} \right]$ (1.13)

The specific molar volume of all ideal gases at the same temperature and pressure is the same.

The molar volume $\overline{\upsilon}_n$ of all ideal gases for normal conditions (273 K, 1.01325 bar)[5] is 22.4141 m$^3$/kmol:

$$\overline{\upsilon}_n = \frac{\overline{R} \cdot T_n}{p_n} = \frac{8.314 \cdot 10^3 \cdot 273.15}{1.01325 \cdot 10^5} \left[ \frac{\text{kg} \cdot \text{m}^2 \cdot \text{K} \cdot \text{m} \cdot \text{s}^2}{\text{s}^2 \cdot \text{kmol} \cdot \text{K} \cdot \text{kg}} \right] = 22.4141 \left[ \frac{\text{m}^3}{\text{kmol}} \right] \quad (1.14)$$

The specific volume can be obtained from equations (1.11) or (1.14) and is:

[5] see Table 1-2 for unit control

$$\upsilon_i = \frac{V}{m} = \frac{R_i.T}{p_i} = \frac{\bar{\upsilon}}{M_i} \left[\frac{\mathrm{m}^3}{\mathrm{kg}}\right] \tag{1.15}$$

**Important Note:** Thermodynamic calculations include parameters with complex compound units. It is therefore highly recommended and necessary to conduct unit control as it is done in equation (1.14).

**Table 1-4:** Molar mass and gas constant of selected technical gases

| Gas | Exact Value | | Technical Applications | |
|---|---|---|---|---|
| | Molar mass | Gas constant | Molar mass | Gas constant |
| | kg / kmol | Nm / kg K | kg / kmol | Nm / kg K |
| Atmospheric air | 28.964 | 287.1 | 29.0 | 287.0 |
| Hydrogen $H_2$ | 2.016 | 4,124.4 | 2.0 | 4,124.4 |
| Nitrogen $N_2$ | 28.013 | 296.8 | 28.0 | 297.0 |
| Oxygen $O_2$ | 31.999 | 259.8 | 32.0 | 260.0 |
| Carbon dioxide $CO_2$ | 44.010 | 188.9 | 44.0 | 189.0 |
| Water vapor (super heated) | 18.015 | 461.5 | 18.0 | 461.5 |

**Example 1-1:** Specific volume ideal gases

Find the molar volume of ideal gases at a pressure of 5 bar and 120 °C (393 K) and the specific volume of Oxygen (32 kg/kmol).

$$\bar{\upsilon} = \frac{\bar{R} \cdot T}{p} = \frac{8{,}314 \left[\frac{\mathrm{N\,m}}{\mathrm{kmol \times K}}\right] \cdot 393.15\,[K]}{5 \cdot 10^5 \left[\frac{\mathrm{N}}{\mathrm{m}^2}\right]} = 6.54 \left[\frac{\mathrm{m}^3}{\mathrm{kmol}}\right]$$

$$\upsilon = \frac{\bar{\upsilon}}{M} = \frac{6.54 \left[\frac{\mathrm{m}^3}{\mathrm{kmol}}\right]}{32 \left[\frac{\mathrm{kg}}{\mathrm{kmol}}\right]} = 0.204 \quad \left[\frac{\mathrm{m}^3}{\mathrm{kg}}\right]$$

**Example 1-2:** Mass content of a gas tank

Two tanks of 3 $m^3$ each contain hydrogen and oxygen at a pressure of 25 $bar_a$. Find the mass content in the tanks. Conduct also unit control[6].

[6] see Table 1-2 for unit control

| Item | | Unit | Hydrogen | Oxygen |
|---|---|---|---|---|
| **Given:** | | | | |
| Tank content | | $m^3$ | 3.0 | 3.0 |
| Pressure | 25 bar | $N/m^2$ | 2.50E+06 | 2.50E+06 |
| Temperature | 20 °C | °C | 293.15 | 293.15 |
| Gas constant | | Nm/ (kg K) | 4124.4 | 259.83 |
| **Sought** | | | | |
| Mass $m = p \cdot V/R \cdot T$ | Tn=273.15 | kg | 6.20 | 98.47 |

$$m = \frac{p\left[\mathrm{N/m^2}\right] \cdot V\left[\mathrm{m^3}\right]}{R\left[\mathrm{Nm/kg\,K}\right] \cdot T\,[\mathrm{K}]}\ [\mathrm{kg}]$$

**Example 1-3:** Density of ideal gases at actual and at normal conditions

| Item | | Unit | Hydrogen | Oxygen | Air |
|---|---|---|---|---|---|
| **Given:** | | | | | |
| Temperature *t* | 150 °C | K | 423 °C | | |
| Pressure *p* | 25 bar | bar | 2.5.E+06 | | |
| Molar mass *M* | | kg / kmol | 2.016 | 31.999 | 28.964 |
| Gas constant *R* | | Nm / (kg K) | 4124.4 | 259.83 | 287.06 |
| Molar volume of ideal gas | | $m^3$ / kmol | 22.41 | | |
| **Results** | | | | | |
| Density at normal conditions | | kg / $m^3$ | 0.09 | 1.43 | 1.29 |
| Density at actual conditions | | kg / $m^3$ | 1.43 | 22.74 | 20.58 |

### 1.3.2 Mixtures of ideal gases

In technical thermodynamics usually working fluids are mixtures of gases such as combustion air or flue gas.

According to *Dalton's law* each gas of a mixture occupies the whole available volume as if there were no other gases. Each gas of the mixture exerts a *partial pressure*. The sum of the partial pressures is the total pressure. The following equations apply (subscripts: $i$ for gas, $m$ for mixture):

Volume fraction: $$\upsilon_i = \frac{V_i}{V_m} = \frac{p_i}{p_m} = \frac{M_i}{M_m} \quad \sum \upsilon_i = 1 \tag{1.16}$$

Mass fraction: $$\mu_i = \frac{m_i}{m_m} = \upsilon_i \cdot \frac{M_i}{M_m} \quad \sum \mu_i = 1 \tag{1.17}$$

Molar mass $$M_m = \sum \upsilon_i \cdot M_i \tag{1.18}$$

Gas constant $$R_m = \sum \mu_i \cdot R_i \tag{1.19}$$

**Example 1-4:** Properties of combustion air

Combustion air is assumed to be composed of 79% nitrogen ($N_2$) and 21% oxygen ($O_2$).
Where:
$N_2$: $M$=28 kg/kmol; $R$=297 J/(kg K)
$O_2$: $M$=32 kg/kmol; $R$=260 J/(kg K)
**Properties of mixture:**
Molar mass:
$M_m = \Sigma\, \upsilon_i \cdot M_i$ = 0.79⋅ 28+0.21⋅ 32=28.84 kg/kmol
Mass fractions:
$\mu_i = \upsilon_i \cdot M_i / M_m$: $\mu_{N2}$=0.79⋅ 28/28.84=0.767; $\mu_{O2}$=0.21x32/28,84=0.233
Gas constant: $R_m = \Sigma \mu_i \cdot R_i$: =0.767⋅ 297+0.233⋅ 260 = 288.4 J/(kg K)

### 1.3.3 Thermodynamic processes

A *thermodynamic process* is an operation in which a thermodynamic system changes its properties of state and passes from one equilibrium to another. A thermodynamic system is in equilibrium when all its properties of state remain constant. In the course of a thermodynamic process conversion of thermal energy and work takes place.

*Thermodynamic processes* are distinguished according to the property of the system that remains constant during the process (denoted with prefix "iso") namely: isochoric (constant volume), isobaric (constant pressure), isothermal (constant temperature), and isentropic (constant entropy). Based on the equation of state of the ideal gas the following equations apply [1] [2] [3]:

**Isochoric process**, $V$ constant: $$\frac{p_1}{T_1} = \frac{p_2}{T_2} \tag{1.20}$$

$$W_{V12}=0; \quad W_{S12} = V \cdot (p_2 - p_1) = m \cdot R \cdot T \cdot (T_2 - T_1) \tag{1.21}$$

$$Q_{12} = m \cdot c_\upsilon \cdot (T_2 - T_1) \tag{1.22}$$

Technical application: e.g. heat storage

**Isobaric process**, $p$ constant: $$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{1.23}$$

$$W_{V12} = -p \cdot (V_2 - V_1) = -m \cdot R \cdot (T_2 - T_1); \quad -W_{S12} = 0 \tag{1.24}$$

$$Q_{12} = m \cdot c_p \cdot (T_2 - T_1) \tag{1.25}$$

Technical application: Heat exchanger (friction loss)

**Isothermal process**, T constant: $p_1 \cdot V_1 = p_2 \cdot V_2$ (1.26)

$$W_{V12} = m \cdot R \cdot T \cdot \left( \frac{p_2}{p_1} \right) = -R \cdot T \cdot \ln \frac{V_2}{V_1} = W_{S12} = -Q \tag{1.27}$$

Technical application: ideally cooled compressor

**Adiabatic process**, heat Q=0: $p_1 \cdot V_1^{\kappa} = p_2 \cdot V_2^{\kappa}$ (1.28)

Approximately is: $\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = \left( \frac{V_1}{V_2} \right)^{k-1}$ and $\frac{p_2}{p_1} = \left( \frac{T_2}{T_1} \right)^{\frac{\kappa}{\kappa-1}}$ (1.29)

$$W_{V12} = m \cdot \frac{R}{\kappa - 1} \cdot (T_2 - T_1) = m \cdot c_{\upsilon} \cdot (T_2 - T_1); \quad W_{S12} = m \cdot c_p \cdot (T_2 - T_1) \tag{1.30}$$

Technical application: e.g. adiabatic process ($q$=0), pumps, compressors, turbines;

**Isentropic process** is a reversible adiabatic process at constant entropy (Q=0; S=constant).

**Table 1-5:** Isentropic exponent

| Type of gas | Gas examples | Isentropic exponent |
|---|---|---|
| Monoatomic | Inert gases, He, Ar, Ne | κ=1.67 |
| Diatomic | $N_2$, $O_2$, CO, atm., air | κ=1.4 |
| Triatomic | $CO_2$, $H_20$, $SO_2$ | κ=1.33 |

Relation $\kappa = c_P/c_{\upsilon}$

**Polytropic process,** $p, V, T$ changing: $p_1 \cdot V_1^n = p_2 \cdot V_2^n$ (1.31)

$$\frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} = \left( \frac{V_1}{V_2} \right)^{n-1} \quad \text{and} \quad \frac{p_2}{p_1} = \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \tag{1.32}$$

$$W_{V12} = m \cdot \frac{R}{n-1} \cdot (T_2 - T_1) = m \cdot \frac{R \cdot T_1}{n-1} \cdot \left[ \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right]; \quad W_{S12} = n \cdot W_{V12} \tag{1.33}$$

$$Q_{12} = c_v \cdot \frac{n-\kappa}{n-1} \cdot (T_2 - T_1) \tag{1.34}$$

**Polytropic exponent: 1<n<κ**

Technical application: e.g., cooled compressor

**Isenthalpic process:** $H_2 = H_1 \quad W_{V12} = W_{S12} = 0$ (1.35)

Pressure reduction without generation of work, virtually destruction of work

Ideal gas: $H_2 - H_1 = m \cdot c_p \cdot (T_2 - T_1) = \text{constant} \quad \Rightarrow T_2 = T_1$ (1.36)

Technical application: Throttling of fluids to reduce pressure

**Example 1-5:** Isochoric process, tanks containing $O_2$ and $H_2$

Two tanks with the same volume contain oxygen and hydrogen respectively. Due to direct exposure to solar radiation their temperature increases. Calculate mass content, pressure, final pressure and the heat transfer. **Note:** Properties to be taken from **Annex 4**.

| Item | Symbol | Unit | Values | |
|---|---|---|---|---|
| **Given** | | | | |
| Substance | - | - | Oxygen | Hydrogen |
| Volume | $V$ | $m^3$ | 0.25 | 0.25 |
| Initial pressure | $p_1$ | bar | 5.0 | 5.0 |
| Initial temperature 25 °C | $T_1$ | K | 298.15 | 298.15 |
| Final temperature 60 °C | $T_2$ | K | 333.15 | 333.15 |
| **Properties** | | | | |
| Density (0°C) | $\rho$ | kg /$m^3$ | 1.43 | 0.09 |
| Gas constant | $R$ | J/kg K | 259.80 | 4,124.80 |
| Heat capacity | $c_p$ | kJ/kg K | 0.92 | 14.30 |
| Heat capacity | $c_v = c_p - R$ | kJ/kg K | 0.66 | 10.18 |
| **Results** | | | | |
| Mass | $m = pV/RT$ | kg | 1.61 | 0.10 |
| Pressure, isochoric process | $p_2 = T_2 \cdot p_1 / p_2$ | bar | 5.59 | 5.59 |
| Heat transfer | $Q = m \cdot c_v \cdot (T_2 - T_1)$ | kJ | 37.3 | 36.2 |

**Comments:** Although the properties of the two gases are completely different, the two gases absorb almost the same amount of heat.

**Example 1-6:** Isobaric process, preheating of combustion air

The combustion air of a small industrial boiler is preheated with some waste heat from an industrial process. Calculate the heat flow for the given temperature increase.

| Item | | Symbol | Unit | Values |
|---|---|---|---|---|
| **Given** | | | | |
| **Boiler capacity** | | $Q$ | kJ/s | 20,000 |
| Air | 20,000 m3/h | $V$ | $m^3$/s | 5.56 |
| Pressure, constant | 1 bar | $p$ | bar | 1.00E+05 |
| Temperature | 20 °C | $T_1$ | K | 293 °C |
| Temperature | 80 °C | $T_2$ | K | 353 °C |
| **Air Properties** | | | | |
| Gas constant | | $R$ | J/kg K | 287.1 |
| specific heat | | $c_p$ | kJ/kg K | 1.00 |
| **Results** | | | | |
| Mass flow of air | | $m=pV/RT$ | kg/s | 6.60 |
| Heat flow | | $Q=m \cdot c_p \cdot (T_2-T_1)$ | kJ/s | 396 |

**Note:** Temperature dependency of $c_p$ is neglected

**Example 1-7:** Expansion process of a fluid

Atmospheric air contained in a vessel of 20 liter and at a pressure of 12 bar expands to environmental pressure of 1 bar. Calculate the final volume, temperature, volume expansion work and heat transfer if the expansion is isothermal, adiabatic or polytropic.

| Item | | Symbol | Unit | Isothermal | Adiabatic | Polytropic |
|---|---|---|---|---|---|---|
| **Given** | | | | | | |
| Volume, air | 20 liter | $V_1$ | $m^3$ | 0.02 | | |
| Initial pressure | 12 | $p_1$ | $N/m^2$ | 1.2.E+06 | | |
| Final pressure | 1 | $p_2$ | | 1.E+05 | | |
| Temperature | 25 °C | $T_1$ | K | 298.15 | | |
| **Properties** | | | | | | |
| Gas constant | | $R$ | kJ/kg K | 0.287 | | |
| Specific heat | cp= 1.00 | $c_v=c_p-R$ | kJ/kg K | - | 0.713 | 0.71 |
| Exponent | | $\kappa$, $n$ | - | 1.00 | 1.40 | 1.30 |
| **Results** | | | | | | |
| Mass | | $m=p \cdot V/R \cdot T$ | kg | 0.280 | | |
| Final volume | | $V_2$ | $m^3$ | 0.240 | 0.122 | 0.142 |
| Final temperature in K | | $T_2$ | K | 298.2 | 144.4 | 165.6 |
| Final temperature in °C | | $t_2$ | °C | 25.0 | -128.7 | -107.6 |
| Volume expansion work | | $W_{V12}$ | kJ | -59.6 | -30.9 | -35.6 |
| Heat transfer | | $Q_{12}$ | kJ | 59.6 | 0.0 | 8.8 |

**Note:** Formulas are different in the columns

**Notes**: Properties to be taken from **Annex 4**, Equations for process calculations are available in section 1.3.3. Note: Formulas are different in the columns! Work leaving the system is negative, heat transferred into the system is positive. Carrying out unit control of all calculations is indispensable.