

CHEMICAL AND ENERGY PROCESS ENGINEERING

SIGURD SKOGESTAD



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Preface

In everyday life we use and surround ourselves with products: cars, gasoline, plastic bags, glue, telephones, clothing, computers, lamps, airplanes, makeup, fishing rods and toilet paper. To produce these products we need raw materials. But this is not enough. We also need a “**process**”,¹ and in this book we concentrate on this process (or the path) from raw materials (feedstock) to products (including energy).

The development of a new process is demanding and exciting. Especially important are the choice of reaction conditions (pressure, temperature, degree of conversion) and the method for separation. The final process must be optimized to be competitive. Unfortunately, it is not often that an engineer gets a chance to participate in the development of a completely new process, but it is also very interesting to analyze and understand existing processes (which we focus on in this book).

This book uses three basic principles:

1. Mass is conserved (mass balance = material balance)
2. Energy is conserved (energy balance = the first law of thermodynamics),
3. Any system will proceed towards a more probable state (with more disorder) – and left to itself it will end up in a state of *equilibrium* (the second law of thermodynamics)

In this book, we will mainly apply these principles at the *macro scale*. This gives simple equations and the most essential information with relatively little effort. The same principles also apply if we look at the details on the micro scale, but rather than simple algebraic equations we then often end up with partial differential equations which are difficult to work with analytically.

The goal of this book is primarily to give a foundation for industrial process engineering calculations. But the principles are general and also apply for biological processes. I have attempted to write a book that is intellectually stimulating by deriving most of the formulas from the three basic principles mentioned above. This also promotes insight and understanding. Emphasis is placed on presenting analytical methods which give physical insight and which can be used for “calculations by hand.” Even though the calculations are often done with computers, it is imperative that one has the physical insight to be able to validate the results by performing simple calculations by hand.

To make analytical calculations possible and give insight, it is often necessary to simplify. Many industrially important processes take place in a gaseous phase. In

¹ In dictionaries, **process** has many definitions. One from Webster is the following: “Process. A continuous action, operation or series of changes taking place in a definite manner.”

addition to assuming ideal gas, we simplify our calculations significantly by assuming *perfect mixing*. This allows us to not look at the detailed flow pattern at micro scale.

This book has two main target audiences:

1. Students who need a basis in process engineering.
2. Practicing engineers and students at a more advanced level who need a reference book for practical calculations.

These targets are partly contradictory, but on the other hand a student who has invested time and money in a book should expect that it will prove useful later in his or her career. A suggestion to the students: Do not sell this book! The book contains many examples to illustrate the use of theory on actual problems. The emphasis is on obtaining numbers that can actually be used in the real world, so much of this book will be useful in your career as a process engineer!

A few words on using this book

Chapter 1 summarizes the most important notation, definitions and conversion factors. You should browse through this chapter, which is primarily meant to be used for later reference.

The reader is assumed to have some previous knowledge of physics, chemistry and thermodynamics. Most of this is summarized in Appendix A. I recommend you start by browsing through this material, possibly reading some parts carefully, since it forms the basis for later chapters.

The focus of this book is on the general principles of material and energy balance. This begins in Chapter 2 where we introduce the general balance principle and mass balances which are the most important tool for process engineers. This continues in Chapter 3 with chemical reaction systems and in Chapter 4 with energy balances and so on.

This book was originally written to be used in a process engineering course for second year chemical and petroleum engineering students at NTNU in Trondheim. The material has been taught in approximately the following order: We start with topics on basic thermodynamics from Appendix A (about two weeks) and then cover the following chapters: 2, 3, 4, 5, 6, 7, 8, and finally (if we have time) Chapter 9. The course has also included a field trip to a plant and an associated required project where the students utilize their knowledge on a specific chemical process.

This book is suitable also for students and engineers with other backgrounds, such as energy engineering, process engineering, mechanical engineering or control engineering. The book can also be used for courses in more advanced subjects, in particular the “bonus” Chapter 11 on process dynamics, and Chapters 7 and 8 on entropy and thermal power.

Use the index. To find specific information, such as conversion factors, definitions and data, you should use the index at the end of the book.

Further reading

Many books can be recommended for further reading. This applies in particular to thermodynamics where the following texts are recommended, depending on your

background:

J.M. Smith and H.C. van Ness, *Introduction to chemical engineering thermodynamics*, McGraw-Hill, 6th Edition, New York, 1996.

M.M. Abbot and H.C. van Ness, *Thermodynamics with chemical applications*, Schaum's Outline Series, McGraw-Hill, New York, 1989.

M.J. Moran and H.N. Shapiro, *Fundamentals of engineering thermodynamics*, Wiley, 6th Edition, 2007.

K. Denbigh, *The principles of chemical equilibrium*, Cambridge Press, 4th Edition, 1981.

D.R. Gaskell, *Introduction to the thermodynamics of materials*, Taylor & Francis, 4th Edition, New York, 2003.

There are also several good textbooks that focus on material balance calculations for chemical process engineering, and these may be useful for gaining additional insight or finding additional problems:

R.W. Felder and R.W. Rousseau, *Elementary principles of chemical processes*, Wiley, 3rd Edition, 2000.

D.M. Himmelblau and J.B. Riggs, *Basic principles and calculations in chemical engineering*, Prentice Hall, 7th Edition, 2004.

T.M. Duncan and J.A. Reimer, *Chemical engineering design and analysis. An introduction*, Cambridge University Press, 1998.

It may also be interesting and rewarding to return to the classic:

Olaf A. Hougen and Kenneth M. Watson, *Chemical process principles.*, Wiley. Part 1: Material and energy balances (1943). Part 2: Thermodynamics (1947). Part 3: Kinetics and catalysis (1947).

Book home page

The book has its own web page: <http://www.nt.ntnu.no/users/skoge/>. Here you will find:

- Comments on and corrections to the book
- Complete solutions to starred exercises
- Additional exercises
- The MATLAB files used in the examples

Good luck with the reading of the book!

Thanks

There are many I would like to thank – for discussions, comments, corrections, inspiration, patience, translation, love, support The list is very long and if I listed them all I am afraid I would forget someone. Anyway, thank you all – you know who you are.

Epilogue

An epilogue belongs of course at the end of a text, but I'm placing it here because it is probably better to read it before you start.

The balance principle is the key to process engineering calculations. We start by considering a small part of the world (usually indicated by a dotted line in figures) which we call our “system.” The outside is the surroundings. Process streams may enter and exit our system, and energy can be provided in the form of heat or work. We can quite easily formulate mass balances based on “counting up” what goes in and out of our system.

Energy balances are usually more difficult to formulate, mainly because there are so many forms of energy, and because it makes use of *thermodynamics* with all its associated identities and variable transformations. The most important form of energy for us is *internal energy* (U). This is the energy of the molecules which includes chemical bonding energy, weaker forces between the molecules, as well as the thermal kinetic energy related to the movement of the molecules. In addition to its internal energy, a stream also contributes an associated flow (pV) work. By introducing the enthalpy $H = U + pV$ we no longer need to worry about this flow work (see also page 99):

Enthalpy is the sum of a stream's internal energy and flow work

The energy balance (the first law of thermodynamics) for a steady-state (stationary; static) open flow process (process with inlet and outlet streams) is

$$H_{\text{out}} - H_{\text{in}} = Q + W_n \quad [J/s] \quad (1)$$

where H is the stream enthalpy, Q is the heat supplied and W_n is the supplied non-flow work, (n stands for “non-flow”). That is, W_n is the overall work W minus the flow work (pV work) already included in H .

Note that H is the enthalpy of the *stream* and not of the system itself – the system is unchanged for a steady-state process. Also note that no assumption of constant pressure is made.²

The notion of the state of the system is also extremely important. If we consider a system (or a process stream) in internal equilibrium, then the state of the system is uniquely determined by specifying two variables in addition to the composition, for example enthalpy H and pressure p . The value of all other state variables, for example temperature T , entropy S are then given. Note that work W and heat Q deal with the transfer between systems and are not state variables.

An important consequence of the state notion is that one can evaluate changes in a real process by considering an imaginary process operating between the same start and end states. One can for example compute changes in enthalpy (which is a state variable) for an open system by considering an imaginary reversible process between the same conditions in a closed system.

² It is easy to confuse the energy balance for a steady-state *open* system in (1) with the energy balance for a *closed system* with constant pressure. Both are often written in the form $\Delta H = Q + W$, but ΔH has different meanings in the two cases – it is change in *stream* enthalpy for an open system and the change in *system* enthalpy for a closed system. You are now warned!

Of equal importance is the concept of entropy and the second law of thermodynamics. In short, the entropy (“degree of disorder”) of a system is a state function and the second law of thermodynamics says the total entropy of the universe (system plus its surroundings) must always increase. At the equilibrium state the total entropy reaches its maximum. This results in simple and practical results, including equilibrium constants for chemical reaction, phase equilibrium relationships, and the Carnot factor $\eta = 1 - T_C/T_H$ for the maximum fraction of heat that can be transferred to work.

In summary, thermodynamics is a very useful tool – it is amazing how much practical knowledge can be obtained from the first and second laws of thermodynamics and the idea that internal energy and entropy are state variables.

To sum up: The basic theory of mass and energy balances is quite simple and, together with the phase and chemical equilibrium theory and some knowledge about rates, it constitutes the basis for what a process engineer needs to know.

A word of caution: even though the basic theory is simple, a fair amount of experience and insight is needed to put it to use. The best method of achieving this is by solving exercises, which is highly recommended!

About the author

Sigurd Skogestad was born in Norway in 1955 and is a professor of chemical engineering at the Norwegian University of Science and Technology (NTNU) in Trondheim. After obtaining his M.Sc. degree in chemical engineering at NTNU in 1978, he worked for four years in the industry at Norsk Hydro's Research Center in Porsgrunn, gaining valuable experience in the areas of process design and simulation. Moving to the US in 1983, he received a Ph.D. degree from the California Institute of Technology in 1987. Since his return to Norway in 1987, he has been a professor at NTNU, except for visiting Professorships at the University of California at Berkeley in 1994/95, and at the University of California at Santa Barbara in 2001/02.

The author of more than 140 international journal publications and 200 conference publications, he is the principal author with Ian Postlethwaite of a widely used textbook on *Multivariable Feedback Control* (Wiley, 1996, 2005). The goal of his research is to develop simple yet rigorous methods to solve problems of engineering significance. Research interests include the use of feedback as a tool to reduce uncertainty, change the system dynamics, and generally make the system more robust and well-behaved (including self-optimizing control). Other interests include plantwide control, interactions between process design and control, and distillation column design, control and dynamics.

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1

Notation, concepts and numbers

Collected here is a bit of everything that could have been placed in an Appendix, but I find them so important that I chose to place them first. The chapter starts with an overview of the notation and a discussion on the choice of basis. Engineers need numbers for practical calculations, and we provide an overview of conversion factors and some important numbers. After defining some important concepts, we next provide an overview of some important unit operations. We look at the difference between batch and continuous processes and give an introduction to economic analysis. Finally, you find some fun energy exercises which will make you familiar with the use of numbers and conversion between units.

1.1 Notation

Symbol	Name	SI unit
C_p	heat capacity, constant pressure	[J/K]
C_V	heat capacity, constant volume	[J/K]
c_p, c_V	specific heat capacity	[J/K kg]
c	concentration	[mol/m ³]
E	(total) energy	[J]
H	enthalpy	[J]
M	molar mass	[kg/mol]
m	mass	[kg]
n	number of mols	[mol]
Q	supplied heat	[J]
p	pressure	[N/m ²] = [Pa]
S	entropy	[J/K]
T	temperature	[K]
t	time	[s]
U	internal energy	[J]
V	volume	[m ³]
v	velocity	[m/s]
W	supplied work	[J]
x_i	mole fraction of component i	[mol i /mol total]
ρ	(mass) density	[kg/m ³]

The most important symbols are given in the table. They follow the international conventions (IUPAC and ISO). The following applies:

- Units are in the SI system which has seven basic units: m (meter), kg (kilogram), s (second), K (Kelvin), mol, A (ampere) and cd (candela). This book uses the first five of these. In addition, we use the derived SI units Newton (N), Pascal (Pa), Joule (J) and Watt (W):

$$N = \text{kg} \cdot \text{m} \cdot \text{s}^{-2}$$

$$\text{Pa} = N \cdot \text{m}^{-2} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

$$J = N \cdot \text{m} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$$

$$W = J/s = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3}$$

Conversion factors to some non-SI units are given on page 8.

- SI-notation is also used for prefixes:

$$E \text{ (exa)} = 10^{18}$$

$$P \text{ (peta)} = 10^{15}$$

$$T \text{ (tera)} = 10^{12}$$

$$G \text{ (giga)} = 10^9$$

$$M \text{ (mega)} = 10^6$$

$$k \text{ (kilo)} = 10^3$$

$$h \text{ (hecto)} = 10^2$$

$$c \text{ (centi)} = 10^{-2}$$

$$m \text{ (milli)} = 10^{-3}$$

$$\mu \text{ (micro)} = 10^{-6}$$

$$n \text{ (nano)} = 10^{-9}$$

$$p \text{ (pico)} = 10^{-12}$$

- In English (American) literature one finds some non-SI numbers and prefixes, including

$$\text{billion} = 10^9$$

$$\text{trillion} = 10^{12}$$

$$M = 10^3 \text{ (because M is the roman number 1000)}$$

$$MM = 10^6 \text{ (yes, this is really a strange one!)}$$

- To indicate small fractions, one often uses the non-SI terms

$$\text{ppm} = 10^{-6} \text{ (parts per million)}$$

$$\text{ppb} = 10^{-9} \text{ (parts per billion)}$$

- E or e is commonly used to indicate exponentials with base 10, e.g., $E-4 = 10^{-4}$.

- The **universal gas constant** is

$$R = 8.314510 \text{ J/K} \cdot \text{mol} \quad (\text{SI units})$$

The value of R in some other units is

$$R = 1.987 \text{ cal/mol} \cdot \text{K}$$

$$R = 1.987 \text{ Btu/lb} \cdot \text{R} \quad (\text{here, the latter R stands for degrees Rankine})^1$$

$$R = 82.06 \text{ cm}^3 \text{ atm/mol} \cdot \text{K}$$

$$R = 0.08206 \text{ l atm/mol} \cdot \text{K}$$

- The standard value for the acceleration of gravity is (IUPAC)

$$g = 9.80665 \text{ m/s}^2$$

However, we often set $g = 10 \text{ m/s}^2$ as it varies around the earth anyway.

¹ Unfortunately, the number of symbols and letters is limited, so the same letter is sometimes used in different meanings. For example, W is the symbol for work, but W is also the unit Watt for power ($1 \text{ W} = 1 \text{ J/s}$); R is the universal gas constant, but R is also the unit for degrees Rankine.

- **Standard temperature and pressure (STP).** According to IUPAC, the standard temperature is 273.15 K (0°C) and the standard pressure is

$$p^\ominus = 1 \text{ bar} = 10^5 \text{ N/m}^2.$$

However, most thermodynamic data are given at the **standard ambient temperature**

$$T_0 = 298.15 \text{ K}$$

and we actually rarely use the “standard temperature” 273.15 K in this book. Also, note that until 1982 the standard pressure was set as

$$1 \text{ atm} = 1.013250 \text{ bar}.$$

- Superscript $^\ominus$ (or $^\circ$) is used generally to indicate standard or reference states. For a gas at temperature T , the standard state is a (hypothetical) state as ideal gas at $p^\ominus = 1 \text{ bar}$ and temperature T .
- Standard enthalpy of formation $\Delta_f H^\ominus$ and other thermodynamic quantities are given at 1 bar and 298.15 K (25 °C), unless otherwise stated.
- Superscript * often indicates pure components.
- Superscript ' often indicates ideal gas.
- Subscript $_0$ often indicates initial state at time t_0 , or feed stream to a reactor, or standard temperature T_0 .
- Subscript $_f$ often indicates final state at time t_f .

Note

- We use lowercase letter for mass m [kg] and number of moles n [mol]. However, these are exceptions, because we use capital letters for most other **extensive** quantities (which are variables that depend on the size of the system), for example V , H , S , U , Q and W .
- The following are examples of **intensive** quantities (which are point variables that do not depend on the size of the system): c , M , p , T , x and ρ .
- We follow the IUPAC-convention and let Q indicate *supplied* heat and W indicate *supplied* work (to the system from the surroundings). For work, the opposite older convention, where W is work performed by the system (on the surroundings), is still commonly used, especially in mechanical engineering literature, i.e., W gets the opposite sign.
- In SI units, the **molar mass** M is in [kg/mol], for example, water has $M = 18.015 \cdot 10^{-3} \text{ kg/mol}$. Usually, we give molar mass in [g/mol], which is not a standard SI unit, for example $M = 18.015 \text{ g/mol}$ for water. A closely related quantity is the relative molar mass (**molecular weight**) M_r [dimensionless], which has the same numerical value as M [g/mol] but without the units. For example, water has $M=18.015 \text{ g/mol}$ and $M_r=18.015$.
- Exact relationship between mass, number of moles and molar mass:

$$m[\text{kg}] = n[\text{mol}] \cdot M[\text{kg/mol}] \quad (1.1)$$

(which may be viewed as the definition of molar mass M).

- We use brackets with the meaning “with unit,” for example [kg] means “with unit kg.” Brackets are used sometimes as “extra-information” in the equations. For