

An Introduction to Chemical Thermodynamics

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Preface

After being asked to teach the first year Chemical Thermodynamics course for the newly developed *Molecular Science and Technology* education at the Delft University of Technology, I first conducted a small survey of what was being taught at other Dutch universities and what the experiences were. The answers were surprising: many of my colleagues responded that Chemical Thermodynamics was not very popular amongst the students, the results were usually not very good and many universities were contemplating whether the course should be removed from the curriculum.

Consulting the text books being used, it occurred to me that chemistry was not at the forefront. All start with the behavior of gases, then proceed to introduce work and heat transfer after which the First and Second Law are discussed, basically from a mechanical point of view. Only in later chapters, chemical topics are discussed. At that point, one may imagine, chemistry students will have lost interest!

After this the idea was born to develop a completely new course in Chemical Thermodynamics where chemistry would be the central issue. This was frequently discussed with colleagues and one brought a paper to my attention that dealt with the primary role of the Gibbs energy¹. This was a good starting point as it put what I consider the most important aspect of Chemical Thermodynamics up front: the prediction whether processes can run spontaneously or not².

The second issue was to proceed to Work and Efficiency without an emphasis on mechanics or heat engines. Both topics do not belong to the scope of chemistry students. The obvious alternative is the fuel cell. As a device, it contains all aspects of Chemical Thermodynamics that are necessary without the need to discuss in detail what is done with the delivered work. Unfortunately, there is some confusion in the literature about the efficiency of fuel cells: some claim it can be over 100% and others find it remarkable that the efficiency is higher than the Carnot efficiency. Both issues are discussed in detail by Lutz and coworkers³.

As always, an idea is not really new! At some point I found a booklet by Guggen-

¹G. Job and F. Herrmann, *Chemical potential – a quantity in search of recognition*, Eur J Phys 27 (2006) 353-371

²F.J. Gerhartl, *The $A + B \rightleftharpoons C$ of Chemical Thermodynamics*, J Chem Ed 71 (1994) 539 - 548

³A.E. Lutz, R.S. Larson, and J.O. Keller, *Thermodynamic comparison of fuel cells to the Carnot cycle*, Int J Hyd Energy 27 (2002) 1103 - 1111.

heim⁴. Guggenheim is relatively outspoken on the way Chemical Thermodynamics is to be taught. He starts the preface with

Anyone thoroughly familiar with thermodynamics can write an advanced treatise on the subject. It seems to be immeasurably more difficult to write an elementary introduction to chemical thermodynamics. Attempts at this differ only in the degree of their failure. The greatest difficulty is self-imposed by the authors. They have not troubled to ask themselves what they mean by 'elementary', still less what they ought to mean. In the worst type of exposition, 'elementary' means telling the reader untruths on the plea that an untruth is easier to understand than the truth. This is a blatant fallacy (Guggenheim, *Education in Chemistry*, 1966, **3** (2) 105). The more intelligent the student the sooner he will discover that something is wrong and the more severe will be the mental shock.

I know exactly what I mean by an elementary introduction to chemical thermodynamics. The one and only object to teach the student how the direction of chemical reactions and how the equilibrium condition for balanced reactions can be determined from calorimetry and related measurements. . . .

He then continues to explain how the topic should be worked out and he claims that at no place it is necessary to introduce "untruths". The booklet is no longer for sale, except at second hand bookshops.

The first part of the book is therefore wholly devoted to processes, mostly chemical. It discusses how to predict spontaneity using tabulated information, how to evaluate the maximum work from a process and what efficiency is achievable. For this, only the Gibbs energy and the enthalpy are needed. In the last chapter of this part, the concept of entropy is introduced as the difference between the Gibbs energy, that predicts the maximum work, and the enthalpy, that manages the entropy balance.

The second part of the book is devoted to chemical and physical equilibria. An attempt is made to expose the universality of the various relations that exist for equilibria and their relation with the Gibbs energy. Ideal mixing relations and ideal solution relations are constantly being used as a simplified approach to the real situation. In the last chapter of this part, the deviations from ideality are assessed and the magnitude of the fugacity and activity coefficients is critically discussed.

The course is not only to be given to chemistry students but also chemical engineering students. They need to know more about processes and their efficiencies. Most textbooks deal with efficiency in some way, but it remains unclear why the thermodynamic efficiencies are not realized in practice. There is usually a vague discussion of irreversibility but no connection is made to energy dissipation in relation to the efficiency of a process. An exception is the book by Kondepudi and Prigogine⁵ that does cover the thermodynamics

⁴E.A. Guggenheim, *Elements of Chemical Thermodynamics*, The Royal Institute of Chemistry, London, 1966.

⁵D. Kondepudi and I. Prigogine, *Modern Thermodynamics : From Heat Engines to Dissipative Structures*, John Wiley & Sons, 1998.

of irreversible processes. Therefore the last part of the book is devoted to distributed processes. In the first chapter some important aspects of formal thermodynamics are covered. In particular the role of entropy to identify equilibrium and stability is discussed. The second chapter of this part continues this discussion and introduces the concept of internal entropy production. To discuss these two issues, systems are subdivided into two parts that are not necessarily in equilibrium: the system is inhomogeneous. The final chapter of this part explains how fully inhomogeneous and flowing systems can be dealt with.

The development of this course was interesting and I hope that students appreciate it. There was one problem: no textbook is available that deals with Chemical Thermodynamics in this way. Also, many of the exercises are not suited for this treatment. This is the reason for writing this book. Exercises are being made available electronically.

Finally, I thank all who have helped me writing this book and the Technical University of Delft for their support. Last but not least I thank my wife and children for their patience: they had to suffer my absentmindedness while working to finish this book.

Ger Koper

Leiden, 4 June 2007.

Preface to the second edition

Many corrections have been made to the text of the first edition and I thank students and colleagues for pointing these out to me. In some places also some additional material has been inserted. I realize that a text as this will probably never be flawless and I therefore invite anyone to look for possible errors and make them known to me.

The book is now used by myself for a course in Chemical Thermodynamics for three courses: *Molecular Science and Technology*, *Life Science and Technology*, and *Applied Earth Sciences* of the Technical University in Delft. After being asked to give a more advanced course in chemical thermodynamics for the *Life Science and Technology* students, I decided to add three chapters dealing with macromolecular systems. The topics dealt with in these chapters are relatively modern. Appropriate references to the relevant literature are made. An effort has been made to present this material from a few unifying concepts in order to demonstrate the analogy between the various treatments in the current literature. Also, the relation to colloid science - even though dealing more with particles than with macromolecules - is being discussed.

Over time, more and more exercises are being made. It will take some more time though to have these neatly organized in an electronic format. Until that time, an old collection is all that is currently available upon request from the publisher.

Ger Koper

Leiden, 25 August 2008.

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Part I

**Processes in Chemistry and
Biochemistry**

Chapter 1

Overview

The core of chemical thermodynamics is captured in four *Laws of Thermodynamics* that in essence summarize the experimental findings in this field over the past hundreds of years. Most of the times only the First Law on energy conservation and the Second Law on the direction of processes are named. But the Zeroth Law is important as well as it tells us how to think about thermal equilibrium. The Third Law is often neglected because at first glance it appears to be only of theoretical importance. But it does provide our best definition of the absolute temperature scale and as such it is sufficiently important to be mentioned as well.

1.1 Zeroth law: thermal equilibrium

The object of study in thermodynamic analysis is called *system*. This could be a chemical reactor but also a beaker glass filled with a solution of various chemicals. Everything outside the system is called *surroundings*. To surroundings of the beaker glass is rather well defined, but it may prove to be more difficult to describe for the chemical reactor. The best way to proceed is to define the *boundaries* of the system that are necessarily also the boundaries of the surroundings. The system may exchange matter and energy through these boundaries with its surroundings in which case the boundaries are *open*. When it is possible for a system to exchange matter or energy with its environment, *thermal equilibrium* is achieved when the flows between the system and its environment have come to an end or, more exactly, when the flows balance so that there is no net transfer.

Consider now two systems that share their surroundings. The question whether the two are in thermal equilibrium with each other is one that is often important in thermodynamic analysis. When both system boundaries are open to the environment, one would expect this to be the case when the flows between the systems and the environment have ceased.

But not all systems are arranged in such a way that they can exchange matter or energy either between themselves or through the surroundings. This is the case when they have boundaries that are effectively closed to flow of matter and energy. Still, two such *isolated* systems can be in thermal equilibrium with one another and in order to determine this we use a third system. The Zeroth Law effectively makes the relation *thermal equilibrium* an associative one as it states that two systems are in thermal equilibrium when they both are in thermal equilibrium with a third. The Zeroth Law hence provides for the legalization of the thermometer as a means to verify thermal equilibrium!

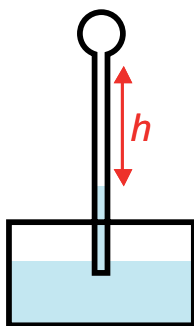


Figure 1.1 Principle of the thermoscope.

1.1.1 Thermometry

The oldest system with which temperatures were measured is the thermoscope, see figure 1.1. It consists of a glass bulb connected with a tube. To operate, the bulb is first heated up to the maximum temperature that needs to be measured. Subsequently, the tube is put in a vessel with liquid, such as water, and the bulb is allowed to equilibrate with the environment. The water will come up into the tube until a certain height. The thermoscope is ready to measure and can be brought into thermal contact with another system. The difference in height of the liquid column when equilibrated with the system and the height when equilibrated with the environment is a measure of the temperature difference between the system and the environment.

The above described phenomenon derives from what we now know as the *Ideal Gas Law*

$$pV_m = RT \quad (1.1)$$

which relates the pressure p measured in Pascal with the temperature T measured in Kelvin. The molar volume is the amount of volume one mole of the entrapped gas, air in this case, occupies and can be found by dividing the volume of the system by the amount of moles of gas in the volume, i.e. $V_m = V/n$. The dimension of molar volume is m^3/mol . The proportionality constant $R = 8.314 \text{ J}/(\text{K mol})$ is the gas constant.

The temperature difference between system and environment is then proportional to the pressure difference due to the hydrostatic pressure of the liquid column of length h as

$$\Delta T \propto h$$

A major drawback of the thermoscope is that the range of temperatures that can be measured with the instrument is rather limited. The *Constant Volume Gas Thermometer* does not have this drawback, see figure 1.2. It has a reservoir for the liquid of which the level can be adjusted such that under all circumstances the volume inside the measuring bulb

Chapter 2

Spontaneity of processes

Some substances have a natural tendency to change, such as the rusting of iron, the spreading of perfume in a room, or the melting of ice. Other processes only occur after a little initial push, such as the burning of natural gas. All these phenomena are termed “spontaneous processes” because they take place without continuous external help. One of the great achievements of thermodynamics is that it provides a method to predict this natural tendency for any process that might be conceived.

2.1 Gibbs energy predicts spontaneity

The method is based on a quantity called the *Gibbs energy*. The difference in Gibbs energy between one state, A, and another state, B, given by $\Delta G = G_B - G_A$, determines whether the process can go spontaneously from A to B or not. There are three possibilities:

- $G_A > G_B$: the process can go from state A to state B.
- $G_A = G_B$: no process can go, possibly equilibrium.
- $G_A < G_B$: the process can go from state B to state A but *not* in the opposite direction.

The Gibbs energy of a substance depends on its nature and state of aggregation and on conditions such as pressure, temperature and for solutes on concentration. The unit of the Gibbs energy is the Joule and since it is proportional to the amount of substance, it is frequently given in Joule/mol; it is then formally called the *molar* Gibbs energy, a term that often is assumed implicitly. As an illustration, consider figure 2.1 which is a plot¹ of the difference in Gibbs energy, as a function of pressure and temperature, between the native state and the unfolded state of the protein *Staphylococcal nuclease* (Snase) which is a small protein of about 17.5 kDa containing 149 amino acids. In the pressure-temperature regime where $\Delta G < 0$ the protein unfolds.

Whether a process will indeed go or not can not be determined by chemical thermodynamics as it depends on the *friction* that a process finds on its path. This friction can sometimes be very strong, in the sense that a process is actually blocked from occurrence. This is for instance the case when two vessels with liquid at different temperatures are isolated from one another. Even though the Gibbs energy difference between them would favor an equilibration process, it will never happen unless the vessels get thermally connected. At other times, the rate at which the process occurs is merely limited as is the case when two vessels containing gas at different pressures are connected by a very tiny

¹Picture adapted, with permission, from I. Daniel, P. Oger, and R Winter, Rev Chem Soc 35 (2006) 858 - 875.