

An Introduction to Chemical Thermodynamics

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G.J.M. Koper

VSSD

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tel. +31 15 27 82124, telefax +31 15 27 87585, e-mail: hlf@vssd.nl

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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 ↔ 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. These do 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

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.

thermodynamics 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.

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