An introduction to Chemical Thermodynamics G.J.M. Koper

Second edition

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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.

Preface

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.

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*

$$pV_m = RT \tag{1.1}$$

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 m³/mol. The proportionality constant R = 8.314 J/(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



Figure 1.2 Principle of the constant volume thermometer.

remains the same. Another advantage is that the difference in liquid levels in the two arms is directly proportional to the temperature inside the measuring bulb. According to the ideal gas law, there would be a direct proportionality $T \propto h$ where h is the distance between the liquid levels.

Unfortunately, gases always deviate from ideality but luckily in the limit of low gas density or, equivalently, large molar volume this deviation vanishes,

$$T = \lim_{V_m \to \infty} \frac{pV_m}{R} \tag{1.2}$$

Using gas thermometers, scientists have used this technique for instance to make very accurate measurements of temperatures where various gases liquify. Advanced gas thermometers are still being used because they can be employed to measure absolute temperature as will be discussed later in this chapter.

The deviation from ideality is for gases not too close to the gas-liquid transition described by the *Virial Expansion* due to the Dutch Nobel laureate Heike Kamerlingh Onnes (1853-1926)

$$p = \frac{RT}{V_m} \left[1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \cdots \right]$$
(1.3)

in which B_n is the *n*-th *virial coefficient*. These virial coefficient obviously do not depend on pressure or molar volume but do depend on temperature as is graphically depicted in figure 1.3 for nitrogen gas. From the values in this graph one observes that the deviations from ideality are small: for not too low temperatures, the second virial coefficient and the molar volume differ by two or more orders of magnitude. The nonidealities described by the virial coefficients are due to the interactions between the gas molecules. For high temperatures only repulsions play a role but for low temperatures attractions, usually due to Van der Waals forces, become important.



Figure 1.3 Temperature dependence of the second virial coefficient of nitrogen gas.



Figure 1.4 Microwave heating of a glass of water.

Therefore, for high temperatures the second virial coefficient is positive and for low temperatures it is negative. At a certain temperature, the *Boyle temperature*, the attractive and repulsive molecular interactions balance and the second virial coefficient vanishes.

Apart from gas thermometers, liquid and metal thermometers have been developed but these are now all superseded by electronic devices that are no longer based on expansion but on the temperature dependence of electric potentials or currents.

1.2 First law: energy conservation

There are many forms in which energy can be found, the mechanical forms of kinetic and potential energy are well known as is thermal energy. Other forms are electrical energy, magnetic energy, radiation energy such as in light or X-rays, nuclear energy, and chemical energy. One important finding has been that all these energy forms can be converted into one another. That being a fact opens the way to a common measure for energy which is standardized as the Joule. The energies can vary enormously in magnitude, chemical energies may exceed megajoules whereas radiation energy may be microjoules or less.

A simple example is the conversion of radiation energy into heat which takes place in microwave ovens such as there are in many kitchens. In figure 1.4 a graph is shown of the temperature of the water in a glass as a function of exposure time to the radiation of a microwave oven. The linearity of the graph reflects the fact that the amount of heat transferred to the water is proportional to the power emitted by the microwave device.

As energy can be exchanged, it cannot be created or destroyed. This is the statement of the First Law of Thermodynamics. The far reaching consequences of this statement will be discussed in chapter 4. For chemists, the most important consequence is summarized in *Hess' Law* which states that the enthalpy difference between two states of matter is the same irrespective of the chemical reaction pathway between these two states.

Most chemical reactions take place in open connection to the direct environment which implies that the pressure in the system is equal to the ambient pressure and the temperature is the ambient temperature. Chemical energy is therefore expressed as *enthalpy*. Many physical experiments are taking place at constant volume in which case the *internal energy* would be the appropriate term. The difference between the two is the mechanical work associated with the expansion or compression of the system under varying conditions such as temperature changes. Using the enthalpy means that this expansion work does not need to be considered separately.

An example of the use of Hess' law is illustrated in figure 1.5 where the combustion heat of propene is determined from that of propane. In order to create another pathway than



Figure 1.5 Hess' cycle involving the combustion of propane and propene.

direct combustion of propane, the propane is first dehydrogenated, than combusted and finally the water is oxidized. Once the enthalpies associated with the hydrogenation and of dissociation of water are known, the combustion enthalpy of propene follows.

Another example of the application of Hess' Law that does not involve a chemical reaction but a physical transformation is illustrated in figure 1.6. From this figure it is clear that the enthalpy of sublimation must be the sum of the enthalpies of melting and



Figure 1.6 Hess' cycle involving the three aggregation states of water.

vaporization. Such relations are extremely useful to determine the enthalpy of a transition that does not easily take place in practice such as the conversion of graphite into diamond. Other pathways may be available, often involving temperature and pressure changes.

1.3 Second law: Gibbs energy

An important result of chemical thermodynamics is that one may predict the direction of processes. Given a system, as defined above, that is in a particular state that may be characterized by *state variables* such as environmental temperature, pressure, and composition. The question then arises whether it would be possible for the system to spontaneously achieve another state which could for instance be the result of a chemical reaction running to completion: chemical thermodynamics provides the answer. Whether the process will actually take place depends on circumstances that are beyond chemical thermodynamics.

An example of such a question asked within the realm of physics would be whether a stone on a height of one meter over the ground would be able to fall down or not. In such a case, the answer is given in terms of the potential energy of the stone: it would lower its potential energy and hence the stone will fall. However, if this stone is lying on a table, it cannot fall out of itself: it is restricted in its kinetics by the table.

For the chemical experience, where ambient temperature and pressure can be considered to be practically constant, the Gibbs energy is the important quantity¹. The Second

¹In most textbooks this quantity is called the Gibbs free energy which is indeed an appropriate name. However, there is no other energy than the Gibbs free energy that carries the name Gibbs and so there can be no confusion when the term Gibbs energy is used. The liberty has been taken here to use the simpler term.

Law of Thermodyanamics states, that if the Gibbs energy difference between the final state and the initial state is negative, a process may run spontaneously between these two states. If the difference is positive, the process will not run without external help. The special case where the two states are at the same Gibbs energy level is called *equilibrium*.

As such, the Gibbs energy has much in common with the potential energy in mechanics. It has been suggested in the past that enthalpy, as discussed above, would be the measure to predict the spontaneity of processes. It turned out not to be the case and it is now generally accepted that two energy measures are necessary: one to keep track of the energy conservation and one to predict spontaneity. All chapters in this book will deal with Gibbs energy differences and the many possible ways these can be used. As shall be demonstrated, Gibbs energy differences can be measured. In fact the commonly used pH, or proton activity, in a solution is a Gibbs energy difference. Furthermore, Gibbs energy differences are tabulated for very many substances. Techniques exist by which the tabulated values can be applied to practical situations.



Figure 1.7 Gibbs energy as a function of extent for the reaction of nitrogen oxide and nitrogen dioxide to di-nitrogen trioxide in a helium background at 320 K and 3 bar.

Two illustrations of the application of the Second Law of Thermodynamics using the Gibbs energy will be given below. The first example concerns the reaction of nitrogen monooxide with nitrogen dioxide according to the reaction

$$NO + NO_2 \rightleftharpoons N_2O_3$$

The Gibbs energy as a function of the extent of the reaction is given in figure 1.7. The initial composition of the system is indicated by ξ_{start} which has a relatively high Gibbs energy. Spontaneously, this mixture will react until it reaches the equilibrium composition indicated by ξ_{eq} .

1. Overview

The extent of the reaction is defined such that when the reaction proceeds by an amount $\Delta\xi$ the mole numbers of the various components vary by an amount $\Delta n_j = v_j \Delta \xi$. Here, v_j is the stoichiometric coefficient of component *j*; it is negative for a reactant and positive for a reaction product. The value $\xi = 1$ is defined by the first reactant being depleted and likewise $\xi = 0$ is defined by the product being exhausted by the reverse reaction, see the bottom part of figure 1.7.



Figure 1.8 Gibbs energy of liquid benzene and its vapor versus temperature and pressure. Note the logarithmic pressure scale.

The second example deals with the physical transformation between liquid and its vapor, see figure 1.8. The Gibbs energy of liquid water and its vapor as a function of temperature and pressure is depicted. For low pressures and high temperatures the vapor plane is below the liquid plane and for high pressures and low temperatures the liquid plane is below the vapor plane. According to the Second Law of Thermodynamics, the water will try to attain the lowest Gibbs energy state which is on the lower plane of the two. The demarcation line, that is copied on the ground plane of the graph, is where the Gibbs energies of liquid and vapor are equal. This is where liquid and vapor are in equilibrium with one another and liquid-vapor coexistence may occur.

The liquid-vapor equilibrium line obeys the *Clausius Clapeyron equation* that allows one to obtain the vaporization enthalpy $\Delta_{vap}H$ from a semilogarithmic graph of pressure versus inverse temperature, see figure 1.9.

1.3.1 Available work

The two above examples demonstrate the predictive power of the Second Law of Thermodynamics through the Gibbs energy. But there is more. In fact, the Gibbs energy difference between two states is equal to the maximal available work that can be delivered by a process running from the one state to the other. This property of the Gibbs



Figure 1.9 Liquid-vapor equilibrium line for water from figure 1.8.

function is mostly used for processes that are made to run continuously. The classical example is a steam driven electricity generator as sketched in figure 1.10.

The heated steam drives a wheel which in turn drives an electrical generator. The heating is provided by wood in the sketch in figure 1.10 which is not commonly done nowadays. The present electricity plants utilize efficient combustion of coal, natural gas or oil. It should be noted, that the modern nuclear power plants are not much more sophisticated. Indeed, the nuclear reaction merely serves to heat up the water!

Processes where chemical energy is converted directly, rather than through heat, to electrical energy involve fuel cells, see the sketch in figure 1.11. The principle of operation is relatively simple. Hydrogen molecules are dissociated into protons and electrons at one electrode. The protons pass through the membrane whereas the electrons pass through the exteral circuit. At the other electrode the two meet again in the presence of oxygen thus forming water. Many variations on the theme exist, but the principle remains the same. The continuous supply of oxygen and hydrogen makes this process a continuous one. Water is also constantly released.

As the Gibbs energy is the maximum work that a process can deliver and the enthalpy measures the consumed amount of energy, the ratio between the two yields the maximum efficiency of a process. In figure 1.12 the efficiencies of the above two examples is plotted versus operation temperature. Clearly, fuel cells perform optimally at low temperatures



Figure 1.10 Sketch of a steam driven electricity generator.



Figure 1.11 Sketch of a fuel cell.



Figure 1.12 Maximum efficiencies of a steam engine and a hydrogen fuel cell.

whereas steam engines perform better at higher temperatures.

1.4 Third law: absolute zero

Temperatures range over enormous scales. The surface of the sun has a temperature of 5785 K whereas Helium becomes superfluid at about 5 K at ambient pressures. The coldest Helium ever observed was at a few hundred microKelvin. By cooling individual molecules and atoms, lower and lower temperatures are attainable. The lowest record is a few hundred picoKelvin. Absolute zero is impossible to attain, one may only get closer and closer as is depicted on the logarithmic scale in figure 1.13. It is exactly this experimental fact that the Third Law of Thermodynamics implies: no process can run to absolute zero temperature.

The classical way to obtain a reliable value for the absolute zero temperature used the gas thermometer introduced earlier. By measuring a series of temperatures during cooling experiments a regression line may be drawn to extrapolate to zero temperature. The inherent error involved in extrapolation, however, limits the reliability of the obtained values.



Figure 1.13 Logarithmic temperature scale.