

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!

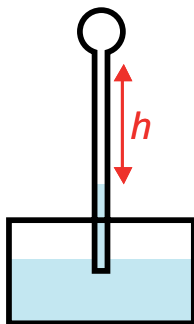


Figure 1.1 Principle of the thermoscope.

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

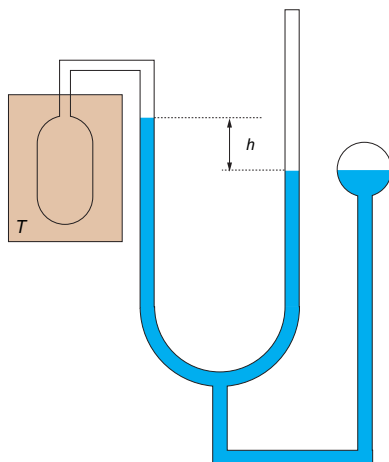


Figure 1.2 Principle of the constant volume thermometer.

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,

$$T = \lim_{V_m \rightarrow \infty} \frac{pV_m}{R} \quad (1.2)$$

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)

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

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 the gas of 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.

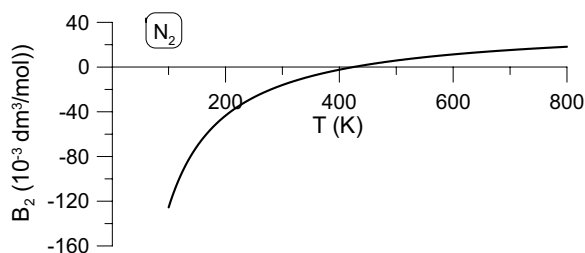


Figure 1.3 Temperature dependence of the second virial coefficient of nitrogen gas.

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

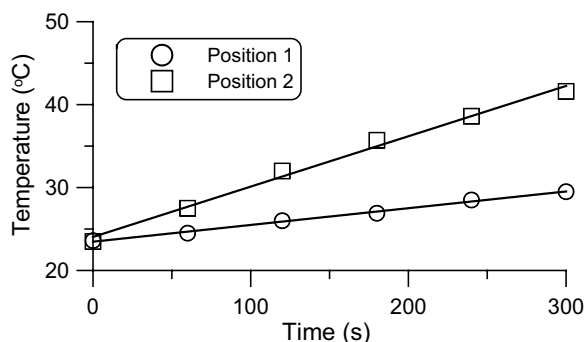


Figure 1.4 Microwave heating of a glass of water.

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

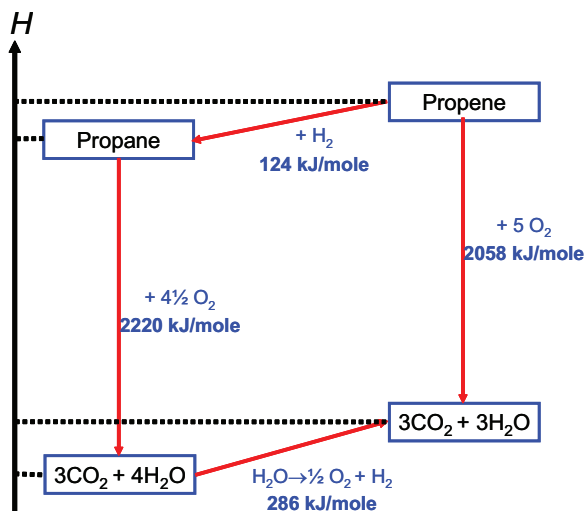


Figure 1.5 Hess' cycle involving the combustion of propane and propene.

direct combustion of propane, the propane is first dehydrogenated, then 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

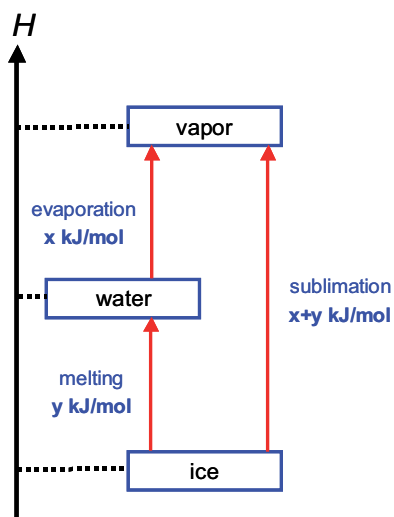


Figure 1.6 Hess' cycle involving the three aggregation states of water.

clear that the enthalpy of sublimation must be the sum of the enthalpies of melting and 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.

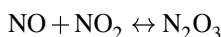
For the chemical experience, where ambient temperature and pressure can be considered to be practically constant, the Gibbs energy is the important quantity¹. The Second

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

Law of Thermodynamics 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.

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 monoxide with nitrogen dioxide according to the reaction



The Gibbs energy as a function of the extent of the reaction is given in figure 1.7. The

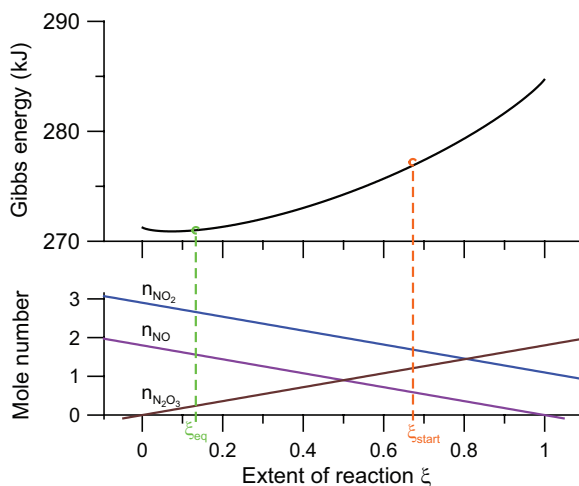


Figure 1.7 Gibbs energy as a function of extent for the reaction of nitrogen oxide and nitrogen dioxide to di-nitrogen trioxide.

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} .

confusion when the term Gibbs energy is used. The liberty has been taken here to use the simpler term.

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 $\Delta n_j = \nu_j \Delta\xi$. Here, ν_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.

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

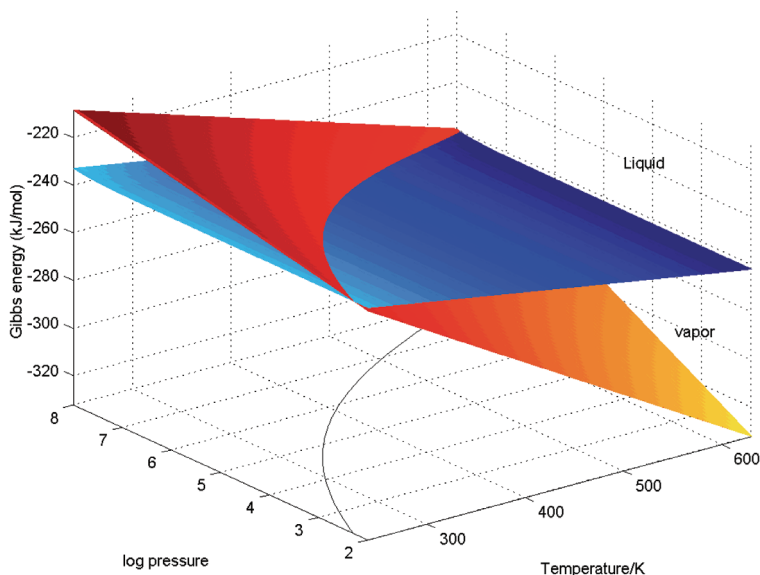


Figure 1.8 Gibbs energy of liquid benzene and its vapor versus temperature and pressure. Note the logarithmic pressure scale.

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 $\Delta_{\text{vap}}H$ 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 dif-

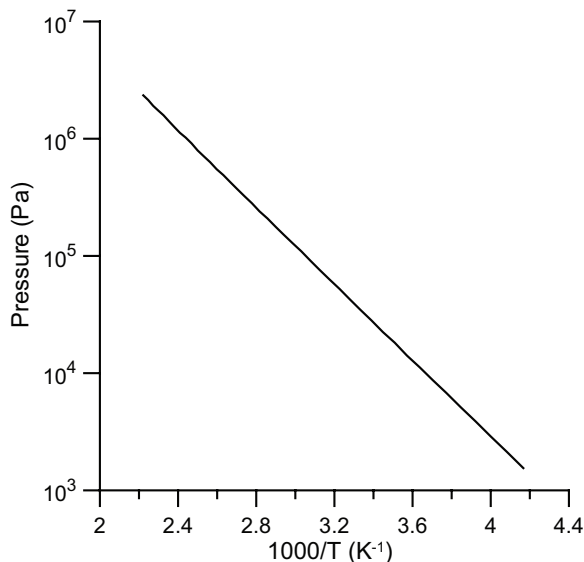


Figure 1.9 Liquid-vapor equilibrium line for water from figure 1.8.

ference 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 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

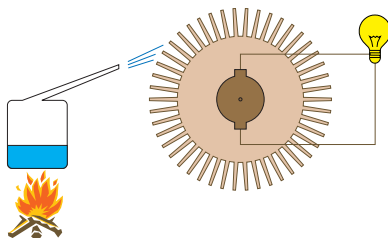


Figure 1.10 Sketch of a steam driven electricity generator.

a wheel which in turn drives a 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



Figure 1.11 Sketch of a fuel cell.

one electrode. The protons pass through the membrane whereas the electrons pass through the external 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

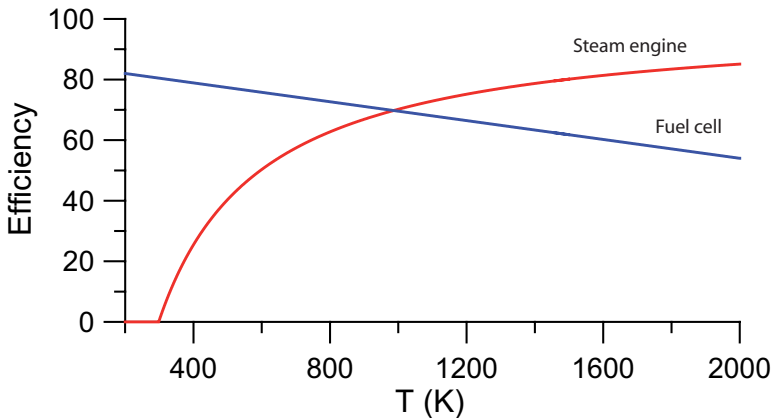


Figure 1.12 Maximum efficiencies of a steam engine and a hydrogen fuel cell.

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

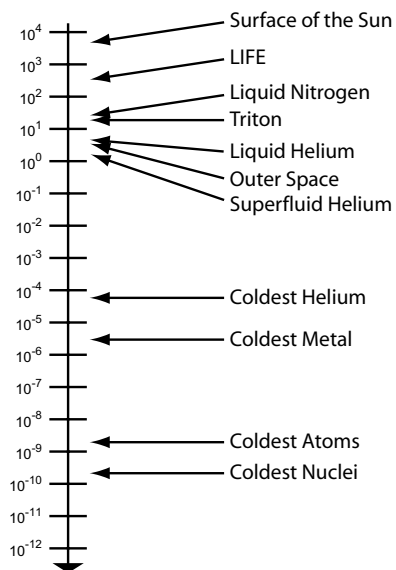


Figure 1.13 Logarithmic temperature scale.

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.