Chapter 4

Fundamental relations

4.1 Introduction

The state postulate of thermodynamics says: *the state of a thermodynamic system can be completely described by merely two independent thermodynamic quantities*. For the bag of crisps, these are pressure and temperature. Through the total differential, the volume can be expressed in P and T. However, it turns out that it is now not only possible to determine the volume, but also the other thermodynamic quantities like energy, enthalpy and entropy. This chapter explains how all thermodynamic quantities can be found from only a small set of measured data. Partial derivatives play an important part in this. A number of partial derivatives will also be issued meaning.

It is meaningful to stop and think about which thermodynamic quantities there are and which can and cannot be measured. Pressure, temperature and volume are thermodynamic quantities that can be measured with some effort. Whereas energy, enthalpy and entropy cannot be measured, or are very difficult to measure. There are two more energies that cannot be measured, the Helmholtz energy and the Gibbs energy. These two energies are discussed at the end of this chapter (4.4 en 4.5).

4.2 Internal energy

First, the internal energy, u is examined. There is a relation in thermodynamics in which the internal energy is a function of the quantities entropy, s, and volume, v (Thermodynamics book, *Çengel & Boles*, chapter 7.7, equation 7.23 or *Schmidt et al*, chapter 6.1, equation 6.13). The differential expression for the internal energy is

$$du = Tds - Pdv. \tag{4.1}$$

This equation relates the differentials of the internal energy, the entropy and the volume to each other. It indicates how the internal energy changes for changes in the volume and entropy. Such equations in a differential form are very important in thermodynamics because interest mainly lies in **changes** of energies and in a transition from one state to the other.

Now look at the general form of this relation, so u as a function of the quantities s and v, $u(s, v)$ and take the total differential of the internal energy. Meaning the derivative of u to its two variables. This is provided by

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv. \tag{4.2}$$

This equation also relates changes in the volume and entropy to changes in the internal energy and, in principle, equals equation 4.1. When comparing equation 4.1 and 4.2, it turns out that

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad \text{and} \quad -P = \left(\frac{\partial u}{\partial v}\right)_s. \tag{4.3}$$

The left of these two relations is the definition of temperature This is an important definition that forms the foundation of other equations and, as such, has major consequences for thermodynamics.

This derivative states that the change of the internal energy as a result of an isochoric (consistent volume) change in the entropy equals the absolute temperature (in Kelvin). Note that the absolute temperature is always positive. That is why the internal energy u must be a continuous ascending function of the entropy, s. The differential also states that in the absolute zero, a change of the internal energy is impossible, because $\left(\frac{\partial u}{\partial s}\right)_v = T = 0 \rightarrow du = 0$. This corresponds to the observations in which everything is standing still at absolute zero. There is no movement of molecules that are responsible for the internal energy, the entropy is at a minimum. In thermodynamics, the definition of temperature is important in the properties of the term entropy, which is where it is made plausible.

The right-hand partial derivative is also used in thermodynamics. This derivative states that the change of the internal energy as a result of an isentropic change of the volume equals minus the pressure. This means that the internal energy is a continuous descending function of the volume. This is also in line with the observations; when the volume is really small, the pressure will increase and when the volume becomes infinite, the pressure will decrease.

The graphs in figure 4.1 show the behaviour of the internal energy as a function of the entropy and the volume. In the left-hand graph, you can clearly see that the tangent in point $s = 0$ has a value of zero, meaning $(\frac{\partial u}{\partial s})_v = T = 0$. On the other points, the value of the derivative (the tangent) is always positive. This corresponds to the observation that the temperature is always positive and is zero in absolute zero. The right-hand graph shows that for $v \rightarrow \infty$ the tangent has a value of zero, meaning $(\frac{\partial u}{\partial v})_s = -P = 0$. This means that the pressure will be zero for an infinitely large volume. This is in accordance with nature; if a volume becomes big enough, the pressure will eventually become zero. For the other points of the line, the tangent is always negative, which means that the value is negative. This corresponds to the fact that the value is the negative pressure. Pressure is always positive, which means that -P is always negative.

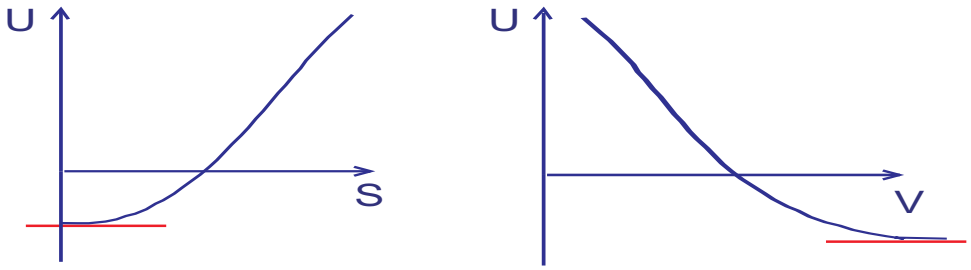

Figure 4.1: *The internal energy U as a function of S (left) and V (right). The red line is the tangent in $s = 0$ (left) and $v \rightarrow \infty$ (right)*

As it turns out, if data is known for the internal energy as a function of s and v the quantities P and T can be found from the partial derivatives from the data. A function like $u(s, v)$, that contains all thermodynamic data is called a **characteristic thermodynamic function** or a **fundamental relation**. Apart from $u(s, v)$ there are three more fundamental relations that are important to thermodynamics. The enthalpy, $h(s, P)$, is one, for example.

4.3 Enthalpy

The enthalpy, h, is defined as $h = u + Pv$. It is a thermodynamic energy that is used for the calculation of energies of flowing media. The term Pv represents the flow work, meaning the work required to let a medium flow over the system boundaries. The enthalpy is also more useful than the internal energy for processes in which the pressure remains constant (because the term vdP will not be included in the differential expression in this case). The differential expression for the enthalpy is (note that the product rule is applied to the term Pv)

$$dh = d(u + Pv) = du + d(Pv) = Tds - \cancel{Pdv} + (\cancel{Pdv} + vdP) = Tds + vdP. \tag{4.4}$$

It turns out a change in the enthalpy can be found by means of investigating the changes in the quantities s and P. The enthalpy is a function of the quantities s and P, so $h(s, P)$. For this function $h(s, P)$, you can do the same exercise as for the internal energy $u(s, v)$. The total differential of the enthalpy is

$$dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP. \tag{4.5}$$

Comparing equation 4.4 and 4.5 shows that

$$T = \left(\frac{\partial h}{\partial s}\right)_P \quad \text{and} \quad v = \left(\frac{\partial h}{\partial P}\right)_s. \tag{4.6}$$

Again, all other thermodynamic quantities can be found if the data for $h(s, P)$ is known. This means $h(s, P)$ is also a fundamental relation.

When the partial derivatives from the equations 4.3 end 4.6 are compared, it turns out that there are two relations for the temperature,

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad \text{and} \quad T = \left(\frac{\partial h}{\partial s}\right)_P. \tag{4.7}$$

Apart from the fact that two partial derivatives equal the temperature, one equals the pressure (negative) and one equals the volume. However, there are more partial derivatives that equal a quantity like $-P$, v or $-s$. For instance, there is a total of two partial derivative relations for the pressure, P, the volume, v, and the entropy, s. The other four partial derivative relations come from two other thermodynamic energies. Apart from the two quantities internal energy, u, and enthalpy, h, that are known from thermodynamics, there are two other energy quantities. These energies are called **free energies**. The **free energy** in thermodynamics is a quantity that tries to achieve a minimum under a constant temperature. In an equilibrium, the free energies are minimal contrary to the entropy that is at a maximum in equilibrium situations. Spontaneous processes will thus always lead to less free energy and more entropy.

There are two versions of free energy, the one of **Hermann von Helmholtz** and the one of **Josiah Willard Gibbs**; respectively, these are called the Helmholtz free energy, a, and the Gibbs free energy, g, or the **Helmholtz** and the **Gibbs energy** for short. The other partial derivatives follow by evaluating the total differentials of the Gibbs energy and Helmholtz energy in a way that is analogous to the enthalpy.

4.4 Helmholtz energy

Helmholtz's formulation for the free energy applies to constant volume, for example in a reactor. The Helmholtz free energy is indicated by the letter a or A from the German *Arbeit*. (In some literature, the letter F is also used for the Helmholtz energy.) It is defined as $a = u - Ts$ and has the quantities v and T as variables, so $a(v, T)$. Because the internal energy, the temperature and the entropy are state functions, the Helmholtz energy is also a state function.

In thermodynamics, the Helmholtz energy is the thermodynamic energy that indicates how big the usable amount of work is that can be extracted from a closed thermodynamic system at a constant temperature and constant volume. The Helmholtz energy in this case is decreasing or constant at a constant volume. A (negative) difference Δa gives the maximum amount of work that a thermodynamic process in which temperature and volume are constant can provide under reversible (ideal, reversible) conditions. This work can be volume work in part. The Helmholtz energy is minimally in equilibrium. The Helmholtz energy is thus that part of the energy that can be turned into work at constant temperature and volume and is minimally in equilibrium.

For the Helmholtz energy, you can now do the same exercise as for the enthalpy. The differential expression for the Helmholtz energy is

$$da = d(u - Ts) = du - d(Ts) = \cancel{Tds} - Pdv - (\cancel{TdS} + sdT) = -sdT - Pdv. \tag{4.8}$$

A change in the Helmholtz energy can be found by investigating the changes in the quantities T and v, the variables of the Helmholtz energy, $a(v,T)$. The function $a(v,T)$ can also be expressed as a total differential

$$da = \left(\frac{\partial a}{\partial T}\right)_v dT + \left(\frac{\partial a}{\partial v}\right)_T dv. \tag{4.9}$$

Comparing equation 4.8 and 4.9 shows that

$$-s = \left(\frac{\partial a}{\partial T}\right)_v \quad \text{and} \quad -P = \left(\frac{\partial a}{\partial v}\right)_T. \tag{4.10}$$

The right-hand term is the second partial derivative that equals minus the pressure. The left-hand term gives a partial derivative that equals minus the entropy. The Helmholtz energy $a(v,T)$ can also be used to find all other thermodynamic quantities from only two quantities (volume and temperature). This makes the Helmholtz energy $a(v,T)$ the third fundamental relation.

4.4.1 Hermann von Helmholtz

Hermann Ludwig Ferdinand von Helmholtz (figuur 4.2a) was a German physician and physicist. Helmholtz was born on 31 August 1821 in Potsdam as the eldest of four children of teacher Ferdinand Helmholtz and Caroline Penn, daughter of an artillery officer. His father studied philology (a linguistics field that focuses on dead languages) and philosophy was a good friend of philosopher Immanuel Hermann von Fichte.

Helmholtz's work is influenced by the philosophies of Fichte and Kant. He attempted to prove their theories in physiology. In his youth, Helmholtz got interested in exact sciences, but his father wanted him to study medicine, because he could get a scholarship for it.

He wrote his first major scientific achievement, a physics discourse from 1847 on the conservation of energy on the basis of his medicine studies and philosophical background. Helmholtz discovered the principle when he was studying the metabolism in muscles. He tried to prove that no energy is lost in muscle movement, because it would also prove that no *life force* was required to make a muscle move. With it, he would be able to reject the speculative tradition of natural philosophy that was the guiding principle in German physiology at that time.

In 1851, he invented the ophthalmoscope, an instrument used to look inside the human eye. By that time, Helmholtz was increasingly interested in the physiology of the senses. His primary publication was the *Handbuch der Physiologischen Optik (Handbook of Physiological Optics)*. During the second half of the nineteenth century, this was the standard work for this field. The handbook described theories substantiated by research on the observation of space and colours.

In 1863, Helmholtz published a book entitled *Die Lehre von den Tonempfindungen als physiologische Grundlage für die Theorie der Musik (On the Sensations of Tone as a Physiological Basis for the Theory of Music)* which once again showed his interests in the physics of perception. This book influenced musicologists into the twentieth century. Helmholtz invented the *Helmholtz resonator* to display the height of the different frequencies (figuur 4.2b).

In 1871, Helmholtz moved from Bonn to Berlin to become professor of physics. He became interested in electromagnetism. He himself did not make an important contribution, but his student Heinrich Rudolf Hertz amassed fame when he was the first to demonstrate the existence of electromagnetic radiation. Helmholtz predicted the existence of electromagnetic radiation based on Maxwell's laws (see chapter 6), and the wave equation now bears his name.

Students and fellow researchers of Helmholtz in Berlin included Max Planck, Heinrich Kayser, Eugen Goldstein, Wilhelm Wien, Arthur König, Henry Rowland, A.A. Michelson and Michael Pupin. Helmholtz wrote about a number of subjects varying from the age of the Earth to the origin of the solar system. He also made important contributions to the field theory, which was vital for Maxwell's work and to (classical) thermodynamics.

In 1883, he was lifted to nobility by Wilhelm I of Germany. A major German community of fifteen research institutes, the Helmholtz Association, was named after him. Hermann von Helmholtz passed

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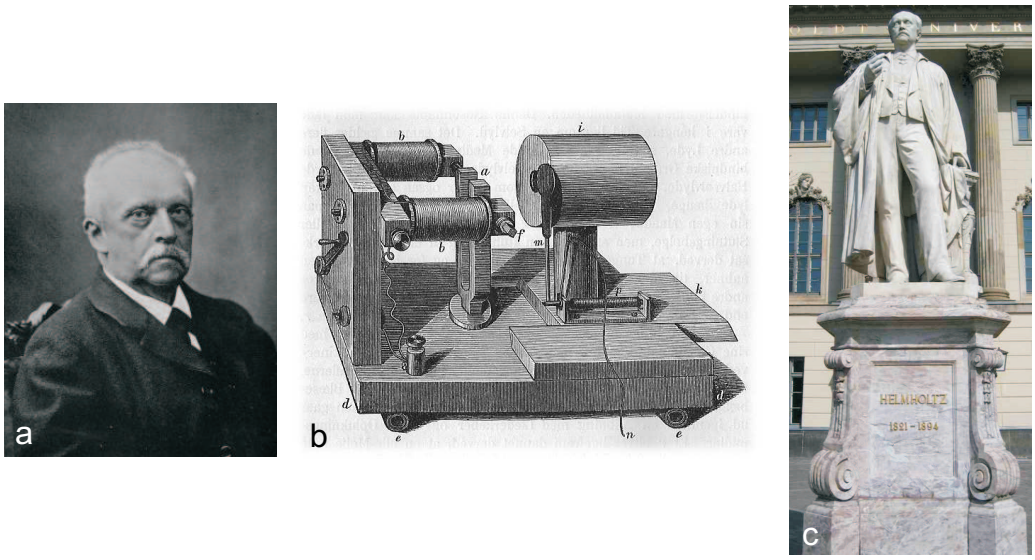


Figure 4.2: *a) The German physician and physicist Hermann von Helmholtz. b) The Helmholtz resonator invented to display the height of the different frequencies. c) Statue of Helmholtz in front of the Humbolt university in Berlin, Germany.*

away on 8 September 1894 in Berlin at age 73. There is a statue honoring this great scientist in front of the Humbolt university in Berlin (figure 4.2c).

4.5 Gibbs energy

The free energy as formulated by Josiah Willard Gibbs applies under constant pressure, e.g. for an experiment under atmospheric pressure. The Gibbs free energy, g, defined as $g = h - Ts = u + Pv - Ts$ has the quantities P and T as variables, so $g(P, T)$. The Gibbs energy is another state function.

In thermodynamics, the Gibbs energy is the thermodynamic energy that indicates how big the usable amount of work is that can be extracted from an isothermal (constant temperature), isobaric (constant pressure) thermodynamic system. The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system and, in this case, like Helmholtz energy, is descending or constant under constant pressure. This maximum can only be achieved in a fully reversible process. When a system undergoes a process of a well-defined initial state to a well-defined final state, the change of the Gibbs energy, Δg equals the work exchanged between the system and the environment minus the work of the pressure forces during a reversible transition of the system from the initial to the final state.

The Gibbs energy is also the energy that is minimal when a system enters into an equilibrium with the environment at a constant temperature and pressure. As a result, the Gibbs energy is also a measure for the direction in which a process will spontaneously develop at a constant temperature and pressure.

The consequence of the temperature contribution in $g = h - Ts$ is that for higher temperatures, a system in equilibrium will have a stronger preference for disorder (s will increase, in equilibrium, the entropy is at maximum). This is expressed in many physical processes around us. An example is the existence of a *melting temperature* for a solid substance. Melting the substance requires an amount of energy, the enthalpy, h, of the substance will increase. The disorder will also increase during the melting process; there is a positive change of the entropy, s. At a specific critical temperature ($T = T_s$), $\Delta h = T_s \Delta s$; in other words melting is possible without a change in the free energy of the system. This temperature, T_s, is the melting temperature of the substance. Above of the melting temperature, the free energy of the fluid is lower than the free energy of the solid substance (the result is that the substance prefers the liquid phase). Below the melting temperature, the free energy of the solid substance is lower than that of the liquid (which means there is a thermodynamic preference for the solid phase).

The Gibbs energy is commonly used to determine thermodynamic energy in processes in the chemistry field and that have a constant pressure, e.g. atmospheric incineration (chemical reactions progress spontaneously in a specific direction because the Gibbs energy decreases in that direction). However, for products with a pressure that is not constant, such as explosions or incineration in a closed vessel, the Helmholtz energy is used because this is where the volume is constant instead of the pressure.

Before the formulation of the second law of thermodynamics (entropy always increases in spontaneous processes) was a fact, it was assumed that all systems strive towards an energy content that is as low as possible (chemically). One measure to express this was the enthalpy. It seems like a logical idea and it was supported by many experiments. Nearly all chemical reactions were exothermic reactions that released heat. Releasing heat seemed to be a natural process to get and keep the energy of the product as low as possible. However, the problem was that there were also spontaneous endothermic reactions in which heat was absorbed. It turned out that the logic that had been accepted for so long was incorrect. There was a second goal for a system: striving for a level of disorder that was as high as possible (entropy). These two goals find an equilibrium in the formula of the Gibbs energy as expressed above.

By evaluating the Gibbs energy in the same way as the internal energy, the enthalpy and the Helmholtz energy, the final two of the eight partial derivatives follow. The differential expression for the Gibbs energy is

$$dg = d(h - Ts) = dh - d(Ts) = \cancel{Tds} + vdP - (\cancel{Tds} + sdT) = -sdT + vdP. \tag{4.11}$$

A change in the Gibbs energy is found by investigating the changes in the quantities T and P, the variables of the Gibbs energy, $g(P,T)$. The function $g(P,T)$ as a total differential is

$$dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP. \tag{4.12}$$

Comparing equation 4.11 and 4.12 shows that

$$v = \left(\frac{\partial g}{\partial P}\right)_T \quad \text{and} \quad -s = \left(\frac{\partial g}{\partial T}\right)_P. \tag{4.13}$$

The left-hand term is the second partial derivative that equals volume. The right-hand term gives the second partial derivative equalling minus the entropy. In total, there are now eight partial derivatives, two that equal T, two that equal $-P$, two that equal v and two that equal $-s$. The quartet of fundamental relations is completed with the Gibbs energy, $g(P,T)$.

4.5.1 Graphical representation of the Gibbs energy

The partial derivatives of the Gibbs energy will be used here to again see what partial derivatives represent in a graph and how they can be interpreted (also see 2.4). In figure 4.3a, the Gibbs energy, g is displayed in a three-dimensional plane as a function of the temperature, T and the pressure, P. The graph shows that the incline of a random line that gives the change of g with T is negative. This incline equals $-s$, the negative entropy. The incline of a random line that gives the change of g with P is positive and equals the volume, v.

Figure 4.3b shows the connection between the Gibbs energy and the temperature at a constant pressure for the different phases in which a substance can exist. The incline of these lines equals the partial derivative of g to T at a fixed P and that equals the negative entropy (see equation 4.13). Because of the negative incline, all lines descend. The entropy of a substance in the gas phase is higher than the entropy of that substance in the liquid phase and the entropy of the solid phase is the smallest. The Gibbs energy of a substance in the gas phase will thus undergo a bigger change than in the liquid phase at an equal change of T. The incline of the substance in the gas phase is steeper than that of the substance in the liquid phase. The incline is least steep in the solid phase as the Gibbs energy will change the least, the entropy of the solid phase is the smallest.

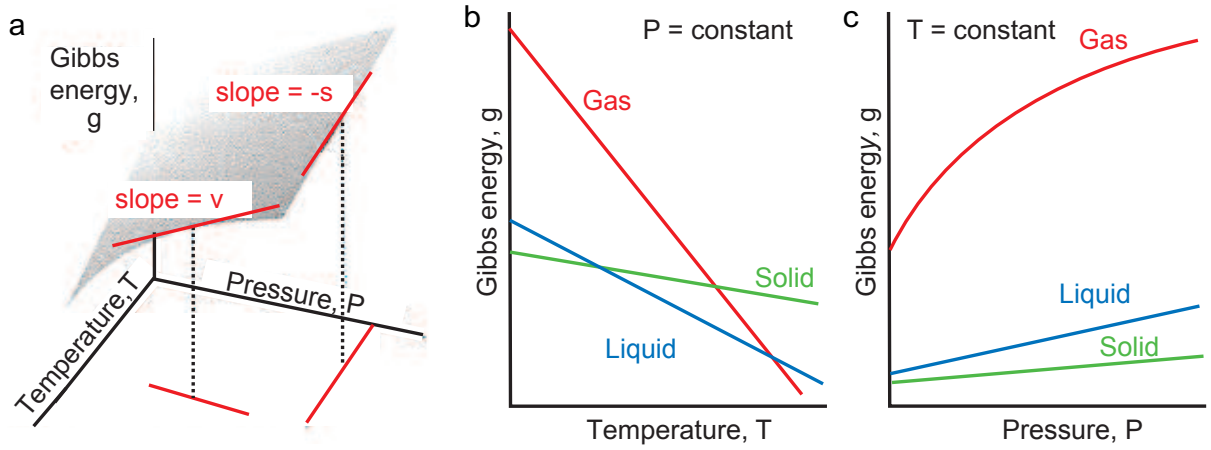


Figure 4.3: *a) The Gibbs energy as function of the temperature and pressure expressed in a three-dimensional plane. b) The change of the Gibbs energy as a function of the temperature c) and as a function of the pressure for the solid, liquid and gas phases of a substance.*

Figure 4.3c finally shows the connection between the Gibbs energy and the pressure at a constant temperature for the different phases in which a substance can exist. The incline of these lines equals the partial derivative of g to P at a fixed T and that equals the volume (see equation 4.13). Because of the positive incline, all lines ascend in this case. The line of the substance in the gas phase is steepest, followed by the lines in the fluid phase and solid phase. The difference in the inclines can be explained by looking at the volume of the phases in relation to the pressure. In the gas phase, the volume of a substance at the same temperature will be much bigger than in the liquid phase. The volume in the gas phase will also change much faster when the pressure changes; after all, gas can be compressed and a liquid or solid substance can barely be compressed. When a fluid or solid substance are considered to be fully uncompressible, the partial derivative will go to zero and the line will become a straight line; the volume is constant in that case.

4.5.2 Josiah Willard Gibbs

Josiah Willard Gibbs (New Haven (Connecticut), 11 February 1839 - 28 April 1903) was an American physicist and chemist who made an important contribution to chemical thermodynamics and physical chemistry (figuur 4.4). Moreover, he was also important to mathematics as one of the inventors of vector analysis. He was the first PhD student in Engineering in the US (Yale University) with his thesis entitled *'On the Form of the Teeth of Wheels in Spur Gearing'*.

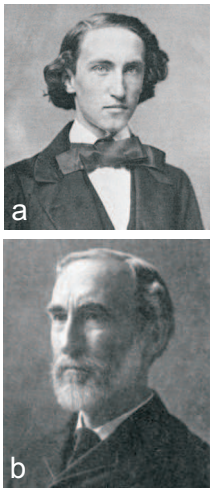
His career can be divided into four phases. Until 1879, he worked on the theory of thermodynamics. In 1876, Gibbs expressed his ideas on the Gibbs free energy in his work *On the Equilibrium of Heterogeneous Substances, a graphical analysis of multi-phase chemical systems* . This graphical interpretation is shown in figure 4.4c.

From 1880 to 1884, he worked on vector analysis. From 1882 to 1889, he worked on optics and theory of light. After 1889, he worked on course books on statistical mechanics and thought about entropy.

The Gibbs phenomenon was named after him, as was the Gibbs free energy. The Gibbs-Helmholtz equations and the Gibbs-Duhem equation are named after him. In 1901, he received the Copley Medal from the Royal Society of London, because he was the first to apply the second law of thermodynamics to chemical, electrical and thermal energy for external work.

4.6 Overview of the thermodynamic energies

In total, there are four thermodynamic energies that are all a function of two independent variables from the set of thermodynamic quantities v, T, P and s. The four energies are all state functions (they



C On the equilibrium of Heterogeneous Substances, a graphical analysis of multi-phase chemical systems(1876)

Willard Gibbs' 1873 free energy graph, which shows a plane perpendicular to the axis of *v* (volume) and passing through point A, which represents the initial state of the body. MN is the section of the surface of dissipated. Qε and Qη are sections of the planes $\eta = 0$ and $\varepsilon = 0$, and therefore parallel to the axes of ε (internal energy) and η (entropy) respectively. AD and AE are the energy and entropy of the body in its initial state, AB and AC its available energy, the Gibbs energy and its capacity for entropy (the amount by which the entropy of the body can be increased without changing the energy of the body or increasing its volume) respectively.

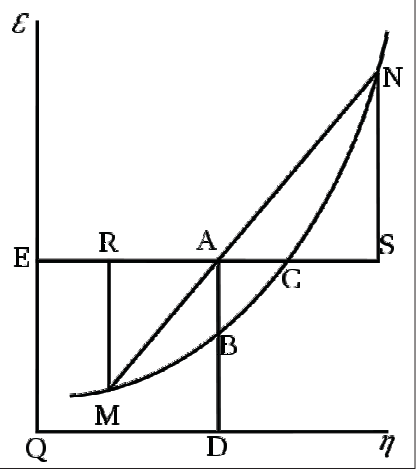


Figure 4.4: *a) The American physicist and chemist Josiah Willard Gibbs at younger and b) at older age. c) Graphical interpretation of a multiphase chemical system from 1873.*

have exact differentials, see chapter 3). This means that their value in a specific state only depends on the value of the quantities in that state. Their value has not changed when they return to the same state in a circle process. The four energies are four **fundamental relations**, which means relations from which all other thermodynamic quantities can be found if only two are known. By rewriting the relations, other quantities can be found. However, it is necessary to know what the value or physical meaning of the partial derivatives is.

It has been found that eight partial derivatives equal a quantity that can be measured (or looked up in a table). However, many more partial derivatives can be thought of. With the eight quantities, T, P, v, s, u, h, a and g, you can make $8^3 = 512$ partial derivatives. A number of them have value zero (e.g. $(\partial x/\partial y)_x$) or value one (e.g. $(\partial x/\partial x)_y$). However, it is much less easy to relate most derivatives to a quantity or value. However, it is possible to rewrite such partial derivatives to a combination of known partial derivatives and, as such, it is possible to find expressions that contain quantities that can only be measured or looked up. This will be discussed in chapter 8. Chapter 5 en 6 will first discuss a number of mathematical tools to perform this rewriting.

An overview of the four thermodynamic energies, their differentials and the partial derivatives that follow is provided in table 4.1.

Energy	**Symbol, variables**	**Differential**	**Partial derivatives**
Internal energy	$u(s,v)$	$du = Tds - Pdv$	$T = \left(\frac{\partial u}{\partial s}\right)_v$ *and* $-P = \left(\frac{\partial u}{\partial v}\right)_s$
Enthalpy	$h(s,P) = u + Pv$	$dh = Tds + vdP$	$T = \left(\frac{\partial h}{\partial s}\right)_P$ *and* $v = \left(\frac{\partial h}{\partial P}\right)_s$
Helmholtz energy	$a(T,v) = u - Ts$	$da = -sdT - Pdv$	$-s = \left(\frac{\partial a}{\partial T}\right)_v$ *and* $-P = \left(\frac{\partial a}{\partial v}\right)_T$
Gibbs energy	$g(T,P) = u - Ts + Pv$	$dg = -sdT + vdP$	$-s = \left(\frac{\partial g}{\partial T}\right)_P$ *and* $v = \left(\frac{\partial g}{\partial P}\right)_T$

Table 4.1: *Overview of the four thermodynamic energies.*