Study Guide Thermodynamics (Physical Chemistry 1) (MOL135) 2021/2022

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Literature

- Book: Physical Chemistry; P.W. Atkins; edition 11, 10, 9 or 8, Oxford University Press
- Study guide: will be made available online during the course
- All information will be available via the link in Brightspace or directly at **http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html**

Aim

- Primary: Insight and skills
- Secondary: Knowledge

Organisation

- **Lectures.** During the lectures particularly the more difficult parts of the book will be emphasized. Furthermore, extra subjects that are not dealt with in the book will be treated. If necessary, these subjects will be incorporated in the study guide.
  NB., thus the study guide is NOT a summary of ALL subjects.
- **Tutorial Classes.** Every week there will be one-hour Turorial Classes (Q&A in the schedule) directly after the lunch break. The MS-tutors will then be present to answer questions and to help in solving exercises. This will involve extra exercises rather than exercises from the Exercise Classes (see next item).
  The division into Tutorial Classes will be the same as in previous quarters; others are free to join.

Tutor	Els Heijmen	Martin Waals	Ade Hoekstra	Yvette van Rijckevorsel	André Steenbergen
Location	HG00.622	HG00.308	HG00.062	HG00.616	HG00.071
Capacity	50	28	63	50	63
Language	Dutch	Dutch	English	English	English

- **Exercise Classes.** The exercises for both the Tutorial Classes and the Exercise Classes will be distributed in the lectures; answers will be available online after the Exercise Classes.
  The answers to the exercises do not have to be handed in. The level of the most difficult exercises is comparable to the most difficult exercises in the book and reflects the level of the problems in the exam. The five groups are the same as for the tutorials; others are free to join.

Location	HG00.622	HG00.308/310	HG00.062	HG00.616	HG00.071
Stud.Ass.	Niek Aarts	Shen van Hassel	Xiamei Klančnik	Sanne Kusters	Cas de Leeuw
Tutor	Els Heijmen	Martin Waals	Ade Hoekstra	Yvette van Rijckevorsel	André Steenbergen

- **Evaluation.** The final evaluation will solely be determined by the exam, which consists of 4 exercises with 4 questions each. All 16 parts have equal weight for the final mark. An example exam (without answers) will appear online at the end of the lectures series.
  A list of formulae (Appendix C), without further comments will be provided at the exam.
  Graphical calculators are NOT allowed during the exam (regular ones are).
- **Video recordings.** There will be no video recordings of the lectures (recordings of 2020/2021 will be put on Brightspace), primarily to promote the study efficiency and especially to promote studying of the book. During the course only subjects will be dealt with that are either in the book or in the study guide (see Table 1, 2 or 3).

Subjects that will be treated

The time schedule for the various topics of Thermodynamics will become clear from the tables below for the different editions of Atkins.

Day	Sections (**edition 11 Atkins**)	Subject
11/11	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3A + 3B + 3D1 + 3E2a-c + SG9-13	Entropy, Second Law of Thermodynamics
		Free energy, Irreversible processes
25/11	5A1b-c + SG14-16	Chemical Potential, Activity
	2C +3D2a + 6A	Thermochemistry, Chemical Equilibria
02/12	6B	T, P-dependence equilibria
	6C1-3 + 6D(p.224)	Electrochemistry, Standard Potential, Nernst-equation
09/12	5B + 5F1-2 + SG17-18	Mixtures, Colligative properties
16/12	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 1: Overview of the topics treated from **edition 11** of Atkins; SG*i*: page *i* of the study guide

Day	Sections (**edition 10 Atkins**)	Subject
11/11	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3A + 3C1 + 3D2a-c + SG9-13	Entropy, Second Law of Thermodynamics
		Free energy, Irreversible processes
25/11	5A1b-c + SG14-16	Chemical Potential, Activity
	2C +3C2a + 6A	Thermochemistry, Chemical Equilibria
02/12	6B	T, P-dependence equilibria
	6C1-3 + 6D(p.267)	Electrochemistry, Standard Potential, Nernst-equation
09/12	5B + 5E1-2 + SG17-18	Mixtures, Colligative properties
16/12	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 2: Overview of the topics treated from **edition 10** of Atkins; SG*i*: page *i* of the study guide

Day	Sections (**edition 9 Atkins**)	Subject
11/11	1.1 - 1.4 + 2.1 - 2.6 + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
18/11	3.1 - 3.3a + 3.5 + 3.9 + SG9-13	Entropy, Second Law of Thermodynamics
		Free energy, Irreversible processes
25/11	5.1b-c + SG14-16	Chemical Potential, Activity
	2.7 - 2.9 + 3.6 + 6.1-6.2	Thermochemistry, Chemical Equilibria
02/12	6.3 - 6.4	T, P-dependence equilibria
	6.5 - 6.8	Electrochemistry, Standard Potential, Nernst-equation
09/12	5.4-5.5 + 5.10-5.11 + SG17-18	Mixtures, Colligative properties
16/12	3.2 + SG19-22	Second Law of Thermodynamics, Efficiency
23/12	3.3 - 3.4 + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

Table 3: Overview of the topics treated from **edition 9** of Atkins; SG*i*: page *i* of study guide

Recommendations regarding study attitude

The aim of the course has already been summarized on page 1 of the study guide :
Primary: insight and skills   and secundary: knowledge
This means (some definitions will not be familiar yet):

- Insight is obtained by studying the material but particularly also by actively solving the problems in the tutorials.
  Insight into the backgrounds of the laws of Thermodynamics as well as the concepts that result from these laws is necessary.
  What do the symbols in a formula stand for?
  Under what circumstances can I apply a certain formula?
  How can I exploit a state function; is the process irreversible or reversible?
  When can I choose an alternative path for a certain process?

- Skills are obtained by actively solving exercises and problems and reflecting back on the insights gained:
  How do I solve a problem?
  Which paths are most suitable in a certain process?
  How do I compose a total differential?
  Can or should I calculate in moles?
  Can I replace an irreversible process by a reversible process?

- Knowledge is less important.
  The list of definitions from the beginning of the course containing concepts as system, bath, closed system, etc. are part of prepared knowledge, but also things like 'the work done *on* the system is positive' or 'adiabatic means $\mathrm{d}Q = 0$', or 'S is a state function'.
  Formulae are *not* part of prepared knowledge; do not spend any unnecessary energy in learning formulae by heart, you will have all relevant formulas available during the exam!

At the exam a list of formulae (Appendix C) without further comments will be provided. In principle this list will contain all relevant formulae necessary to complete the exercises. However, the list will also contain formulae that are not necessary. Insight and skills will allow you to choose and apply the right formulae.

The classic perfect gas

We determine the internal energy of a classic perfect atomic gas. We already know that a perfect gas obeys the (phenomenological) equation of state, or perfect gas law

$$PV = nRT = NkT \tag{1}$$

in which V represents the volume, P the pressure, T the temperature, N the number of atoms, R the gas constant, n the number of moles and k the Boltzmann constant.

The pressure of the gas is determined by collisions against the wall of the volume. Our perfect gas consists of atoms with mass m which have a certain velocity distribution due to collisions. The classic approach is that we assume the collisions are elastic as if the atoms were perfect billiard balls. The energy of such a gas then only consists of kinetic energy, which is determined by the average velocity of the atoms. The velocities of the individual atoms do change with every collision. However, the average velocity (of all atoms) does not change at constant T, P and V. We call this average velocity v. For this average velocity it holds that

$$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2 = 3v_y^2 = 3v_z^2 \quad \text{such that} \quad v_x^2 = v_y^2 = v_z^2 = \frac{1}{3}v^2, \tag{2}$$

because the average kinetic energy will be equal in all three directions. The components v_x, v_y, v_z of v are averages as well. During a collision with the wall (assume that the wall is perpendicular to $\hat{x}$) the average transfer of momentum is in the $\hat{x}$-direction according to figure 1

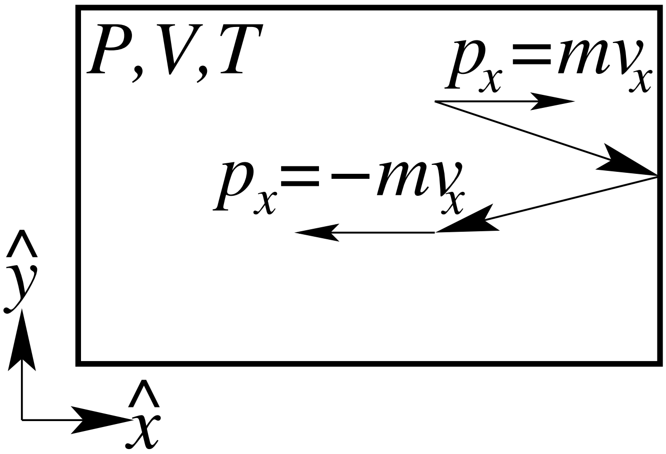

Figure 1: Transfer of momentum for a perfect gas of atoms.

$$\Delta p_x = 2mv_x \tag{3}$$

Via Newton this transfer of momentum can be related to the force on the wall and thereby to the pressure. For the pressure it holds that

$$P = \frac{F_x}{A} = \frac{ma_x}{A} = \frac{m}{A}\frac{\mathrm{d}v_x}{\mathrm{d}t} = \frac{1}{A}\frac{\mathrm{d}p_x}{\mathrm{d}t}, \tag{4}$$

in which F_x represents the average force on the wall, A the surface area of the wall, a_x the acceleration and p_x the momentum of the colliding particles.

The number of particles reaching the wall in a time interval $\mathrm{d}t$ is ($\rho = \frac{N}{V}$ is the density of the gas)

$$\frac{1}{2}\rho A v_x \mathrm{d}t = \frac{1}{2}\frac{N}{V}A v_x \mathrm{d}t. \tag{5}$$

The factor $\frac{1}{2}$ results from the fact that on average only half of the particles has an average velocity v_x in the direction of the wall; the other half has this velocity in opposite direction. So this is the average number of collisions with the wall in a time interval $\mathrm{d}t$. The average transfer of momentum per time interval $\mathrm{d}t$ for collisions with the wall is therefore, using equations (3) and (5):

$$\mathrm{d}p_x = \frac{1}{2}\frac{N}{V}Av_x\mathrm{d}t \cdot 2mv_x = m\frac{N}{V}Av_x^2\mathrm{d}t \quad \text{or} \quad \frac{\mathrm{d}p_x}{\mathrm{d}t} = m\frac{N}{V}Av_x^2. \tag{6}$$

The pressure on the wall then becomes (use equations (4) and (2))

$$P = \frac{1}{A}\frac{\mathrm{d}p_x}{\mathrm{d}t} = m\frac{N}{V}v_x^2 = m\frac{N}{V}\frac{1}{3}v^2. \tag{7}$$

This pressure is exactly the pressure of the gas we would measure with a pressure gauge attached to the wall of the volume.

If we combine this expression with the perfect gas law (1) it follows that

$$nRT = PV = mN\frac{1}{3}v^2. \tag{8}$$

In order to determine the relationship between the internal energy and the temperature of a perfect gas we need to distinguish between the case of a perfect gas consisting of atoms or molecules.

In the case of atoms, the internal energy of our classic (read perfect) gas is only determined by the average kinetic energy of the N atoms, or (use equation (8))

$$U = N\frac{1}{2}mv^2 = \frac{3}{2}PV = \frac{3}{2}nRT. \tag{9}$$

Thus we see that U is an extensive quantity (scales with the size of the system) because of the factor n and that U only depends on the temperature (or the product PV).

This still holds for a perfect gas of molecules. However, the difference is that for molecules, apart from the kinetic energy of the molecules as a whole, there is also kinetic energy in the rotations of the molecules and kinetic as well as potential energy in the internal vibrations of the molecules. Depending on the number of atoms per molecule and the shape of the molecule, these extra contributions will increase the factor $\frac{3}{2}$ in equation (9). We will not further elaborate on this increase.

We define a **perfect gas of molecules** as a gas that obeys the perfect gas law (equation of state)

$$PV = nRT = NkT. \tag{10}$$

The fact that the internal energy for a given number of moles n only depends on T, or the product PV is unique for the perfect gas.

A special case is an *atomic* perfect gas for which we have derived

$$PV = nRT \quad \text{and} \quad U = \frac{3}{2}nRT = \frac{3}{2}PV \quad (\textit{atomic} \text{ perfect gas}). \tag{11}$$

For a *molecular* perfect gas it holds that

$$PV = nRT \quad \text{and} \quad U = nc_VT \quad (\textit{molecular} \text{ perfect gas}). \tag{12}$$

We will see that the factor $\frac{3}{2}R$, or c_V, is the molar heat capacity of a perfect gas of atoms, or molecules, at constant volume.

All other systems, like non-perfect gases, fluids and solids, will always have a more complicated equation of state and a more complicated expression for U, in which two of the three variables T, P and V play a role for a given n. We will come back to this in more detail.

In the following we will consider general systems and perfect gases will only be mentioned as a special case.

The first law of thermodynamics, conservation of energy

We consider a system together with its surroundings that is isolated from the rest of the universe, as is outlined in Figure 2. We define the heat Q that is absorbed by the system during a process, as well as the work W that is done on the system during that process as positive.

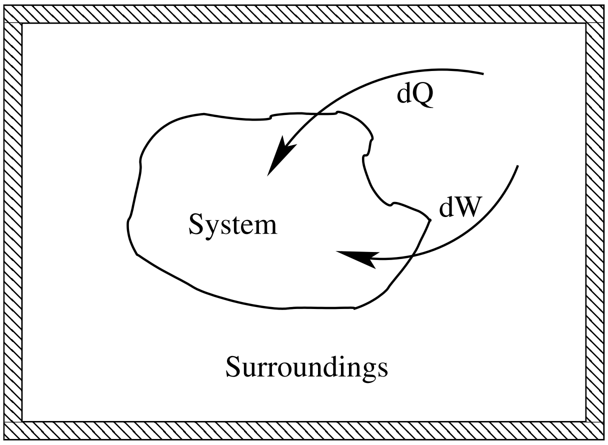

Figure 2: The total system of the system and its surroundings is isolated.

The (empirical) first law of thermodynamics tells us that for every process in an isolated total system (system plus surroundings) it holds that

$$\Delta U = Q + W, \tag{13}$$

in which U represents the internal energy of the system. This law turns out to hold for reversible processes as well as irreversible processes. Alternative formulations are

$$\oint \mathrm{d}U = 0 \tag{14}$$

and "U is a state function", meaning it is only determined by the state variables that unambiguously determine the state of the system and *not* by the path taken during a process to reach that state.

The internal energy and heat capacity

An infinitesimal change of the internal energy in the case of only volume work for a reversible process (possibly as alternative for an irreversible process) is given by

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P\mathrm{d}V. \tag{15}$$

We know that for an *arbitrary* system we can only choose two of the variables P, V, T as independent variables in the case of a closed system (n is constant); the third one is determined via the equation of state (the relationship between P, V, T and n for our system).
If we now consider the total differential of the internal energy for the independent variables T and V we find (see Appendix A for an explanation of total differentials)

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V. \tag{16}$$

We define the heat capacity at constant volume of an *arbitrary* system as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V . \tag{17}$$

Note that at constant volume the volume work $W = -\int P\mathrm{d}V = 0$ such that $U = Q$; hence the name *heat* capacity.
For a *perfect gas* of atoms it follows with equation (9) (N is the number of atoms)

$$C_V^{perfect,atoms} = \frac{3}{2}nR = \frac{3}{2}Nk, \tag{18}$$

whereas for a *perfect gas* of molecules $C_V^{perfect}$ will be larger. So in both cases the heat capacity is constant, which is unique to perfect gases.
We define the specific heat capacity or specific heat as (m is the mass of the molecules)

$$c_V = \frac{C_V}{Nm}. \tag{19}$$

This has as unit J/gK.
We define the molar heat capacity, with as unit J/molK, as

$$c_V = \frac{C_V}{n}. \tag{20}$$

The heat capacity of an *arbitrary* system remains dependent on the temperature T and the pressure P (or V). Often we can assume that C_V is constant within a certain range of T and P.

The enthalpy and heat capacity

An alternative energy function is the enthalpy which is defined by

$$H \equiv U + PV. \tag{21}$$

Since U and V are extensive state functions and P is an intensive state function, it automatically holds that H is an extensive state function. Naturally the unit is that of energy ($[H] = \mathrm{J}$). Analogously to the case of the internal energy it follows that (for the moment we only consider volume work)

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(PV) = \mathrm{d}Q - P\mathrm{d}V + P\mathrm{d}V + V\mathrm{d}P = \mathrm{d}Q + V\mathrm{d}P. \tag{22}$$

Notice that at constant pressure the term $V\mathrm{d}P = 0$, such that $\mathrm{d}H_P = \mathrm{d}Q$.
Therefore we define the heat capacity at constant pressure of an *arbitrary* system as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{23}$$

With equation (21) we find that

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial PV}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{24}$$

If we heat a real gas at constant pressure then the volume will increase such that, in contrast to heating at constant volume, apart from an increase in kinetic energy of the gas also volume work is being done. For a non-perfect gas this results in complicated expressions.
However, if we heat a *perfect* gas at constant pressure the above mentioned expression simplifies because, due to equation (9), the internal energy of a perfect gas only depends on the temperature. For a *perfect gas of atoms* using equations (9) and (1), we find that the heat capacity at constant pressure is given by

$$C_P^{perfect,atoms} = \frac{3}{2}nR + P\left(\frac{\partial V}{\partial T}\right)_P = \frac{3}{2}nR + P\left(\frac{\partial \frac{nRT}{P}}{\partial T}\right)_P = \frac{3}{2}nR + nR = \frac{5}{2}nR, \tag{25}$$

and $c_P^{perfect,atoms} = \frac{5}{2}R$. For a perfect gas, therefore also the heat capacity at constant pressure is independent of T.
So for a perfect gas it holds that

$$C_P^{perfect} = C_V^{perfect} + nR \quad \text{and} \quad c_P^{perfect} = c_V^{perfect} + R. \tag{26}$$

This relationship remains valid for a perfect gas of molecules, since the term nR results from the equation of state of a perfect gas (1), irrespective of whether this gas consists of atoms or molecules.

Choice of a suitable energy state function

For both the energy state functions, internal energy and enthalpy, we have seen that there are restrictions on certain state variables, depending on the actual process, that allow for a relatively simple expression for the changes in the energy, even for an arbitrary system. Which energy function is most suitable to describe a process thus depends on the circumstances of that process. At constant pressure the expression for the enthalpy simplifies according to equation (22); at constant volume the equation for the internal energy simplifies (equation (15)).

- If V is constant, so an isochoric process, we choose the internal energy U.
- If P is constant, so an isobaric process, we choose the enthalpy H.

These two energy state functions naturally have different values according to their definition.

The second law of thermodynamics, spontaneous processes and equilibria

In this chapter we will use the second law of thermodynamics to find the conditions necessary for processes to run spontaneously towards thermodynamic equilibrium.
This chapter is a very brief summary of and supplementary to the entire chapter 3 of Atkins, the order of the subjects deviating strongly from that in Atkins.

The entropy

The entropy of the system is defined as

$$\mathrm{d}S \equiv \frac{\mathrm{d}Q^{rev}}{T}. \tag{27}$$

With this definition S is a state function, in contrast to Q, so ΔS of a process is independent of the path taken from the initial state of the process to the final state.
The first law of thermodynamics, as mentioned before, holds for any process, so for both reversible as well as irreversible processes. In particular for irrversible processes the expression of volume work is defined in a different form, leading to the following more general expression for the first law

$$\mathrm{d}U \equiv \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P_{ext}\mathrm{d}V. \tag{28}$$

If we limit ourselves to a *reversible* process we find

$$\mathrm{d}U \equiv \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P_{ext}\mathrm{d}V = \mathrm{d}Q^{rev} - P\mathrm{d}V. \tag{29}$$

With the definition (27) of entropy this becomes

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V. \tag{30}$$

From the first law of thermodynamics we know that $\mathrm{d}U$ is independent of the path, such that for an *irreversible* process we can also write

$$\mathrm{d}U^{irr} = T\mathrm{d}S - P\mathrm{d}V, \tag{31}$$

in which we have to realize that the expressions on the right side describe the changes for an alternative *reversible* path, even though we want to determine $\mathrm{d}U$ for an *irreversible* path. If for example $\mathrm{d}Q^{irr} < T\mathrm{d}S$ then this difference in energy will have to be compensated by the difference due to $\mathrm{d}W^{irr} > -P\mathrm{d}V$. Naturally, a similar consideration holds for other forms of work, which we will treat furtheron, such as electrical work that is (ir)reversibly being done during a process.

The second law of thermodynamics

The second law of thermodynamics, which is an empirical law just like the first law, states that for a *spontaneous* process in an isolated total system the total entropy increases (or is constant)

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{sur} \geq 0, \tag{32}$$

where S_{sur} represents the entropy of the surroundings (the reservoir, bath) and S the entropy of the system. This total system is drawn schematically in Figure 2. Since the heat delivered by the surroundings to the system has to be equal to the heat absorbed by the system we conclude that

$$\mathrm{d}Q = -\mathrm{d}Q_{sur}. \tag{33}$$

Since we can choose the surroundings to behave as we like, for an irreversible process in the system we choose the surroundings to absorb or release heat reversibly, so

$$\mathrm{d}Q = -\mathrm{d}Q_{sur} = -\mathrm{d}Q_{sur}^{rev} = -T_{sur}\mathrm{d}S_{sur}. \tag{34}$$

If we now let the surroundings maintain the same temperature as the system, $T_{sur} = T$ -after all the surroundings is an idealized system- we find

$$\mathrm{d}S_{sur} = -\frac{\mathrm{d}Q}{T}, \tag{35}$$

which when substituted in the second law of thermodynamics (32) results in

$$\mathrm{d}S - \frac{\mathrm{d}Q}{T} \geq 0 \tag{36}$$

With this expression we have found an alternative formulation of the second law of thermodynamics:
For a *spontaneous* process in an isolated total system

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T} \quad \text{or} \quad \mathrm{d}Q \leq T\mathrm{d}S \quad \text{or} \quad \mathrm{d}Q \leq \mathrm{d}Q^{rev}. \tag{37}$$

Equation (37) is known as the Clausius inequality.
Both formulations of the second law of thermodynamics generally hold for a spontaneous process in an isolated total system. The Clausius inequality (37) as an alternative formulation of the second law of thermodynamics has the benefit that it only contains quantities of the system.
The first formulation shows that the total entropy never decreases during a spontaneous process. This means that in equilibrium, a situation in which no net spontaneous processes occur, it must hold that:

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{env} = 0 \tag{38}$$

This means that in equilibrium S_{tot} *always* has reached its *maximum value.* We will show that a *consequence* of this law is that different energy state functions have a *minimum value*, but only under certain conditions of the state variables (P, T, etc.). We will describe the most general case for which the work W consists of volume work and any other form of work W', such that

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W', \tag{39}$$

in which W' represents electrical work, friction work, chemical work, etc., depending on the system and the process in question. We will still limit the discussion to a *closed* system.

Consequences for the internal energy

$$\Delta U = Q + W \quad \text{or} \quad \mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P_{ext}\mathrm{d}V + \mathrm{d}W'. \tag{40}$$

The Clausius inequality (37) gives

$$(\mathrm{d}U)_{V,W'} = \mathrm{d}Q \leq T\mathrm{d}S. \tag{41}$$

So for an iso-entropic and isochoric, spontaneous process without non-volume work we find

$$(\mathrm{d}U)_{S,V,W'} \leq 0. \tag{42}$$

So for a spontaneous process under those circumstances the internal energy always decreases. This is actually a consequence of the second law of thermodynamics according to (32). Since $\mathrm{d}S = 0$ according to (32) we find $\mathrm{d}S_{sur} \geq 0$, such that the surroundings must absorb heat from the system, and therefore for the system $Q \leq 0$. Because also $\mathrm{d}V = 0$ this implies U has to decrease, which is exactly what is stated by equation (42). In other words, equation (42) which *only* applies under the *restrictions* of constant S, V and W' is a *consequence* of the second law according to (32).
The spontaneous process continues untill

$$(\mathrm{d}U)_{S,V,W'} = 0 \tag{43}$$

and thermodynamic equilibrium is reached, where U is minimal, still at constant S, V and W'.

Consequences for the enthalpy

$$H \equiv U + PV. \tag{44}$$

Analogous to the case of the internal energy it follows that ($\mathrm{d}(PV) = P\mathrm{d}V + V\mathrm{d}P$)

$$\mathrm{d}H = \mathrm{d}Q - P_{ext}\mathrm{d}V + \mathrm{d}W' + P\mathrm{d}V + V\mathrm{d}P. \tag{45}$$

The condition P is constant implies $P_{ext} = P$ and in that case we find for a spontaneous process

$$(\mathrm{d}H)_{P,W'} = \mathrm{d}Q \leq T\mathrm{d}S, \tag{46}$$

such that for a spontaneous process it has to hold that

$$(\mathrm{d}H)_{S,P,W'} \leq 0 \tag{47}$$

and in equilibrium

$$(\mathrm{d}H)_{S,P,W'} = 0. \tag{48}$$

Again there are restrictions for the state variables (now S, P and W') and these conditions for H are a *consequence* of the second law according to (32).

The Helmholtz free energy

Since the prerequisite of $\mathrm{d}S = 0$ is not always simple to realize, we introduce two alternative energy functions, that avoid this problem; first the Helmholtz free energy.

$$A \equiv U - TS. \tag{49}$$

A is an extensive state function again with $[A] = \mathrm{J}$. Alternative names for A are Helmholtz function, free energy and work function. Physicists often use the symbol F of *F(ree energy)*.

$$\mathrm{d}A = \mathrm{d}Q - P_{ext}\mathrm{d}V + \mathrm{d}W' - T\mathrm{d}S - S\mathrm{d}T, \tag{50}$$

such that for a spontaneous process, using the Clausius inequality, we find

$$(\mathrm{d}A)_{V,W'} = \mathrm{d}Q - T\mathrm{d}S - S\mathrm{d}T \leq T\mathrm{d}S - T\mathrm{d}S - S\mathrm{d}T = -S\mathrm{d}T. \tag{51}$$

So for a spontaneous process

$$(\mathrm{d}A)_{V,T,W'} \leq 0, \tag{52}$$

and in equilibrium it holds that

$$(\mathrm{d}A)_{V,T,W'} = 0. \tag{53}$$

The symbol A is derived from the German word *Arbeit*. A is the maximum (*free*) work that can be done by the system during an isothermal process. Indeed, with the Clausius inequality it follows that $\mathrm{d}U \leq T\mathrm{d}S + \mathrm{d}W$, so $\mathrm{d}W \geq \mathrm{d}U - T\mathrm{d}S = (\mathrm{d}A)_T$. The work done by the system is negative according to the definition of work, so the maximum work done by the system during an isothermal process is

$$\mathrm{d}W_{max} = \mathrm{d}U - T\mathrm{d}S, \tag{54}$$

or

$$W_{max} = (\Delta A)_T\,. \tag{55}$$

The Gibbs free energy

The second alternative energy function is the Gibbs free energy,

$$G \equiv H - TS. \tag{56}$$

G is an extensive state function again with $[G] = \mathrm{J}$. Alternative names for G are Gibbs function and free enthalpy.

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T, \tag{57}$$

such that for a spontaneous process (use equation (46))

$$(\mathrm{d}G)_{P,W'} = \mathrm{d}Q - T\mathrm{d}S - S\mathrm{d}T \leq -S\mathrm{d}T. \tag{58}$$

So for a spontaneous process

$$(\mathrm{d}G)_{P,T,W'} \leq 0, \tag{59}$$

and in equilibrium we find

$$(\mathrm{d}G)_{P,T,W'} = 0. \tag{60}$$

At constant P and T, $\mathrm{d}G \leq \mathrm{d}W'$, such that G is the maximum non-volume work that can be done during an isothermal, isobaric process.

$$W'_{max} = (\Delta G)_{P,T}\,. \tag{61}$$

Choice of a suitable energy state function

So for all four energy state functions there are restrictions for a number of state variables necessary to use the second law for determining changes of the corresponding energy during a process in or out of equilibrium. All these statements are a *consequence* of the formulation of the second law in terms of entropy (32) or (37).

Therfore, the most suitable energy function to describe a process depends on the circumstances of that process.

- If S and V are constant, so for an iso-entropic, isochoric process, we choose U.
- If S and P are constant, so for an iso-entropic, isobaric process, we choose H.
- If T and V are constant, so for an isothermal, isochoric process, we choose A.
- If T and P are constant, so for an isothermal, isobaric process, we choose G.

The four energy state functions naturally have different values according to their definition.

For an adiabatic process running in a thermally isolated system we have $Q = 0$, but only in the reversible case this implies that also the entropy term $T\mathrm{d}S = T\mathrm{d}Q^{rev} = 0$. Iso-entropic processes are thus (practically) difficult to realize. This means that for processes in practice the internal energy U and the enthalpy H often are not the best option.

During a chemical reaction in an open vessel it is often possible to keep the pressure $P_{ext.}$ and the temperature T constant. Then G is the most appropriate state function.

For processes in constant volumes at constant temperature A is often the most suitable state function.

Of course, for every arbitrary process all four energy functions remain state functions. However, 'easy' statements about changes of the corresponding energy during a process in or out of equilibrium are limited by the abovementioned restrictions and these usually determine the choice.

The equilibrium criteria should be interpreted as follows. As an example we consider

$$(\mathrm{d}G)_{P,T,W'} = 0. \tag{62}$$

This equation tells us that in equilibrium the Gibbs free energy is constant and minimal (from equation (59)) during an isobaric, isothermal process without non-volume work. So for such a process G will not change if during that process the other variables, V and S, change. The value of G, however, remains a function of T and P. In other words, for every other couple of values of T and P, G will take on a different equilibrium value that does not change as a function of V and S.

Spontaneous processes

When does a process proceed spontaneously? We will consider this for situations in which the pressure and the temperature are constant, so $\mathrm{d}T = \mathrm{d}P = 0$. This appears to be a very strong restriction since the equation of state suggests that then also $\mathrm{d}V = 0$, but out of equilibrium the system does not obey the equation of state.
For constant P and T the Gibbs free energy is the most suitable choice and equation (59) then gives

$$(\mathrm{d}G)_{P,T,W'} = (\mathrm{d}H)_{P,T,W'} - T\,(\mathrm{d}S)_{P,T,W'} \leq 0. \tag{63}$$

In terms of the enthalpy and entropy change as a consequence of the process this becomes

$$\Delta H - T\Delta S \leq 0, \tag{64}$$

in which P and T are constant.
Now we can distinguish between exothermic (heat producing) and endothermic (heat absorbing) processes (use $\mathrm{d}H|_{P,W'} = \mathrm{d}Q$):

$$\text{Exothermic} \quad (\Delta H < 0) \quad \begin{cases} \Delta S > 0 & \text{spontaneous,} \\ \Delta S < 0 & \text{spontaneous if} \quad T|\Delta S| \leq |\Delta H|, \end{cases} \tag{65}$$

$$\text{Endothermic} \quad (\Delta H > 0) \quad \begin{cases} \Delta S > 0 & \text{spontaneous if} \quad T\Delta S \geq \Delta H, \\ \Delta S < 0 & \text{never spontaneous.} \end{cases} \tag{66}$$

We find a special case for equilibrium situations, for which

$$\Delta G = \Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta H = T\Delta S. \tag{67}$$

This is a situation that occurs for example at the melting or boiling point of substances. For instance at the melting point of a solid, where the solid phase and the melt are in equilibrium, we find ($T = T_{fus}$):

$$\Delta_{fus}G = 0 \quad \text{such that} \quad \Delta H_{fus} - T_{fus}\Delta_{fus}S = 0 \quad \text{or} \quad \Delta_{fus}H = T_{fus}\Delta_{fus}S. \tag{68}$$

Similarly at the boiling point of the liquid we find

$$\Delta_{vap}G = 0 \quad \text{such that} \quad \Delta H_{vap} - T_{vap}\Delta_{vap}S = 0 \quad \text{or} \quad \Delta_{vap}H = T_{vap}\Delta_{vap}S. \tag{69}$$

The chemical potential

As final thermodynamic quantity we introduce the chemical potential μ. In principle the chemical potential is meant to describe a change in the free energy of an *open system*, i.e. a system in which the amount of matter is not constant. So in open systems particles can leave or enter the system. Examples are inhomogeneous systems that are composed of two or more systems, such as a solid in contact with its liquid or gas, or two systems separated by a semi-permeable membrane. Also closed systems in which chemical reactions proceed can be interpreted as open systems because the amounts of the reactants and products change during the reaction process.

The chemical potential describes how the Gibbs free energy of the system changes if the number of (mol of) particles changes and all other variables remain constant, or in formula

$$\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{P,T}. \tag{70}$$

Since we now have more variables the total differential (see Appendix A and especially (A-5)) becomes somewhat more complicated. It still holds that for every system there is a relationship between the state variables of that system, namely the equation of state. For G we usually take P, T as free variables, and for an open system also n. The total differential for the Gibbs free energy then becomes

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_{T,n} \mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n} \mathrm{d}T + \left(\frac{\partial G}{\partial n}\right)_{T,P} \mathrm{d}n, \tag{71}$$

and the fourth variable V is again determined by the equation of state and the values for P, T and n.

This expression describes G for a homogeneous system with one type of particles (e.g. pure water). For such a pure substance G increases linearly with the number of moles n, such that $G = nG_m$, in which G_m is the molar Gibbs free energy. Equation (70) then implies that $\mu = G_m$.

For impure substances, in other words systems with multiple types of particles that mix to a certain extent, we need an index to label these types. If the (molar) quantities of those species n_i are variable then also the Gibbs free energy of the entire system becomes a function of these quantities

$$G = G(n_1, n_2, n_3, \cdots, V, T, P). \tag{72}$$

If we choose again P, T and all n_i as variables, in which V is determined by the equation of state, we find as total differential for G

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} \mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} \mathrm{d}T + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \mathrm{d}n_i, \tag{73}$$

where the sum is over all types of particles.

Meanwhile we are also able to identify the partial derivatives. For closed systems we already know the expression $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$, so we can identify these derivatives with state variables or other thermodynamical functions. For open systems (with multiple types of particles) we define the chemical potential of species i as

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}. \tag{74}$$

We can identify the two other partial derivatives as

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i}, \tag{75}$$

or

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i. \tag{76}$$

Thus the chemical potential of species i describes the change of the Gibbs free energy of the entire system if we change the (molar) amount n_i of species i. The fact that this is a *potential* we can understand by making a comparison with the concept potential from electrochemistry. The electrical potential on an electrode describes the amount of work it takes to change the (molar) amount of charge on that electrode. Similarly, the chemical potential μ_i describes the amount of work that has to be done on the system (increase of G) to increase the (molar) amount of particles (of species i) in the system.
We have already seen earlier that we use the Gibbs free energy preferably for processes in which P and T are constant. Equation (76) then gives

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}n_i \quad (P, T \text{ constant}). \tag{77}$$

We have also seen that the Gibbs free energy at constant temperature and pressure describes the maximum non-volume work (see equation (61)). With (77) it then follows that

$$\mathrm{d}W'_{max} = \sum_i \mu_i \mathrm{d}n_i \quad (P, T \text{ constant}). \tag{78}$$

This maximum value is reached for a reversible process. As an example we consider an electrochemical cell. In that case the $\mathrm{d}n_i$ describe the changes of the (molar) amounts of particles (whether charged or not) and $\sum_i \mu_i \mathrm{d}n_i$ is the maximum electrochemical (electrical) work. We will come back to this issue when dealing with (electro)chemical equilibria.

Chemical potential in an arbitrary system; activity

For a mixture of gases the total pressure is equal to the sum of the partial pressures P_i according to

$$P = \sum_i P_i \quad \text{with} \quad \frac{P_i}{P} \equiv \frac{n_i}{n} = x_i, \text{ the mole fraction of component } i \quad \text{(Dalton's law).} \tag{79}$$

For a mixture of perfect gases we can consider every component C_i as independent and thus pure, with as chemical potential at given T (pure so $\mathrm{d}\mu = \mathrm{d}G_m = V_m \mathrm{d}P - S_m \mathrm{d}T$):

$$\mu_i(P_i) = \frac{G_i(P_i)}{n_i} = G_{m,i}(P_i) = G^{\ominus}_{m,i} + \int_{P^{\ominus}}^{P_i} V_m \mathrm{d}P = \mu_i^{\ominus} + RT \int_{P^{\ominus}}^{P_i} \frac{\mathrm{d}P}{P} = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}, \tag{80}$$

in which the so-called standard state, with $P^{\ominus} = 1$ bar, is chosen as a reference.
To keep an analogous expression for an arbitrary mixture of substances, in any phase, the concepts activity a_i and activity coefficient γ_i of component C_i are introduced according to

$$\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i \equiv \mu_i^{\ominus} + RT \ln \gamma_i x_i \quad \text{with} \quad x_i \equiv \frac{n_i}{n}, \text{ the mole fraction of component } i. \tag{81}$$

With this the standard state of the components C_i is determined by the, in many cases fictive, pure state of those components at $P = P^{\ominus}$ and $a_i = 1$. The same conditions hold for the biological standard state ($^{\oplus}$; or $^{\circ'}$) with the only difference that for the hydrogen ions $\mathrm{pH}^{\oplus} = -\log a^{\oplus}_{\mathrm{H^+(aq)}} = 7$ is chosen as standard state, instead of $\mathrm{pH}^{\ominus} = -\log a^{\ominus}_{\mathrm{H^+(aq)}} = 0$, for the thermodynamic standard state.
In summary, the standard state $\ominus$ of component i is given by

$$\ominus \quad \begin{cases} i \text{ is a pure component; a sometimes fictive situation} \\ a_i = 1 \\ P = P^{\ominus} = 1 \text{ bar; for the (fictively) pure component,} \end{cases} \tag{82}$$

while the activity a_i of component i in the mixture is defined as (see also exercise classes 3)

$$a_i = \begin{cases} P_i/P^{\ominus} \text{ for a perfect gas in the mixture} \\ \approx 1 \text{ for a pure liquid or the solvent in a very diluted solution} \\ \approx 1 \text{ for a pure solid or the solid in a very diluted solid solution} \\ \mu_i \equiv \mu_i^{\ominus} + RT \ln a_i \equiv \mu_i^{\ominus} + RT \ln \gamma_i x_i \text{ for all other situations.} \end{cases} \tag{83}$$

Importance of the chemical potential and equilibrium

If we now consider the Gibbs free energy of an arbitrary mixture then we can easily find this energy by choosing a clever path at constant T and P. If we prepare the mixture starting from the unmixed state to the mixed state, while keeping the composition (mixing ratio) equal to that of the final state at all times, then we have to find the same change for G as for an arbitrary way of mixing, since G is a state function, so is independent of the path taken.

$$G|_{P,T} = \int_0^{n_A} \mu_A \mathrm{d}n_A + \int_0^{n_B} \mu_B \mathrm{d}n_B = \mu_A \int_0^{n_A} \mathrm{d}n_A + \mu_B \int_0^{n_B} \mathrm{d}n_B = n_A\mu_A + n_B\mu_B, \tag{84}$$

where for the second set of integrals we used that μ_A and μ_B do not change if the mixing ratio in the system remains constant and only the total amount of mixture increases.
Thus equation (84) holds for an arbitrary mixture.

An important application of the concept chemical potential is found for equilibrium situations between two phases α and β; for example a liquid (mixture) phase and solid (mixture) phase, which are in mutual equilibrium. In equilibrium, at constant pressure and temperature, for each species (component) the total number of particles has to be constant for the total system, such that the net flux between the two phases is zero for each species, so $\mathrm{d}n_i^\alpha = -\mathrm{d}n_i^\beta$.
Using equation (60) and realizing that if there is no additional work ($\mathrm{d}W' = 0$)

$$0 = \mathrm{d}G|_{P,T,W'} = \mu_i^\alpha \mathrm{d}n_i^\alpha + \mu_i^\beta \mathrm{d}n_i^\beta = \mu_i^\alpha \mathrm{d}n_i^\alpha + \mu_i^\beta(-\mathrm{d}n_i^\alpha) = (\mu_i^\alpha - \mu_i^\beta)\mathrm{d}n_i^\alpha, \tag{85}$$

and therefore in equilibrium between two (or more) phases α and β at given T and P, we find

$$\mu_i^\alpha = \mu_i^\beta \quad \text{for all components } i \text{ in the phase mixtures.} \tag{86}$$

Mixtures of gases, liquids and solutions

The following can be considered as an alternative approach of the material discussed in the paragraphs 5A.2 and 5B.1 in Atkins (edition 10 or 11); applications such as osmosis, freezing-point depression and boiling-point elevation can be found in paragraph 5B.2.
We use the equilibrium equation (86) in terms of the chemical potentials of the components to describe the process of dissolution and mixing. We consider a binary mixture of components A and B, at temperature T and initially both at constant pressure P.

The general case

In the initial (unmixed case) we have pure phases for A and B with total Gibbs free energy G. We use * as superscript to denote pure substances while $\mu_i^\ominus$ by definition, equation (82), refers to the pure component. Using equation (84) we find

$$G_{no\ mix} = n_A\mu_A + n_B\mu_B = n_A\left(\mu_A^\ominus + RT\ln a_A^*\right) + n_B\left(\mu_B^\ominus + RT\ln a_B^*\right). \tag{87}$$

After mixing we obtain

$$G_{mix} = n_A\mu_A + n_B\mu_B = n_A\left(\mu_A^\ominus + RT\ln a_A\right) + n_B\left(\mu_B^\ominus + RT\ln a_B\right). \tag{88}$$

So for the Gibbs free energy of mixing, $\Delta_{mix}G$, we find (use $x_i = n_i/n$)

$$\Delta_{mix}G = G_{mix} - G_{no\ mix} = n_ART\ln\frac{a_A}{a_A^*} + n_BRT\ln\frac{a_B}{a_B^*} = nRT\left(x_A\ln\frac{a_A}{a_A^*} + x_B\ln\frac{a_B}{a_B^*}\right). \tag{89}$$

A mixture of perfect gases

For a mixture of perfect gases we can substitute $a_i^* = P/P^\ominus$ initially and $a_i = P_i/P^\ominus$ finally, resulting in

$$\Delta_{mix}G = nRT\left(x_A\ln\frac{P_A}{P} + x_B\ln\frac{P_B}{P}\right) = nRT\left(x_A\ln x_A + x_B\ln x_B\right), \tag{90}$$

where we used Dalton's law, equation (79).

A mixture of liquids

For a mixture of liquids we can substitute $a_i^* \approx 1$ initially in equation (89), resulting in

$$\Delta_{mix}G = nRT\left(x_A\ln\frac{a_A}{a_A^*} + x_B\ln\frac{a_B}{a_B^*}\right) = nRT\left(x_A\ln a_A + x_B\ln a_B\right), \tag{91}$$

an equation describing the so-called non-ideal interaction between the molecules in a liquid mixture. It is convenient to describe this mixture in terms of a so-called ideal mixture of liquids, comparable to the situation of a perfect gases mixture, equation (90), by using the earlier mentioned activity coefficients γ_i, defined by $a_i \equiv \gamma_i x_i$, as

$$\Delta_{mix}G = nRT\left(x_A\ln\gamma_Ax_A + x_B\ln\gamma_Bx_B\right) = nRT\left(x_A\ln x_A + x_B\ln x_B\right) + nRT\left(x_A\ln\gamma_A + x_B\ln\gamma_B\right) \tag{92}$$

Ideal solutions

A special case of so-called idealy mixing liquids is described by Raoult's law, for which both acitvity coefficients are (nearly) equal to unity, or $\gamma_A \approx \gamma_B \approx 1$, resulting in

$$\Delta_{mix}G^{ideal} = nRT\left(x_A\ln x_A + x_B\ln x_B\right). \tag{93}$$

In other words, ideal solutions have the same mixing behaviour as perfect gases. Raoult's law boils dawn to the vapour pressure of both components for the liquid mixture being proportional to their mole fraction in the liquid, according to

$$P_i^g = x_i^l P_i^{g,*}, \text{ or } \frac{P_i}{P_i^*} = x_i, \tag{94}$$

where l and g represent the liquid and gas phase respectively.
For non-ideal solutions we can often still use such a relationship for (only) the solvent A in very diluted solutions of B in A ($n_B << n_A$).
For the general case, however, we will have to replace x_i by the activity a_i.

Ideal mixing liquids and gases

For ideal mixing gases and liquids (following Raoult's law) we therefore have

$$\Delta_{mix} G^{ideal} = nRT\left(x_A \ln x_A + x_B \ln x_B\right), \text{ with } x_i = \frac{n_i}{n_A + n_B}. \tag{95}$$

When we combine this with the definition of G, we find that at constant T

$$\Delta_{mix} G = \Delta_{mix} H - T\Delta_{mix} S, \tag{96}$$

such that

$$\Delta_{mix} H = 0, \tag{97}$$
$$\Delta_{mix} S = -nR\left(x_A \ln x_A + x_B \ln x_B\right). \tag{98}$$

Thus the mixing process of a system showing *ideal mixing* is completely determined by the change in entropy. For such an ideal mixing system the interactions between the components A and B is equal to (or at least comparable to) the mutual interactions between the components A and the mutual interactions between the components B.
Note that there is no heat of mixing, resulting in $dQ = 0$, such that $\Delta S^{sur} = 0$ and therefore

$$\Delta S^{tot} = \Delta S = \Delta_{mix} S = -nR\left(x_A \ln x_A + x_B \ln x_B\right) \geqq 0 \text{ for } 0 \leq x_A \leq 1. \tag{99}$$

in other words, ideal mixtures always mix spontaneously.
Also note that $\Delta_{mix} G$ is negative for all values of x_A (see figure 3). The second law of thermodynamics tells us once more that, at constant pressure and temperature, such a system will always mix spontaneously for any chosen molfraction, x_A.

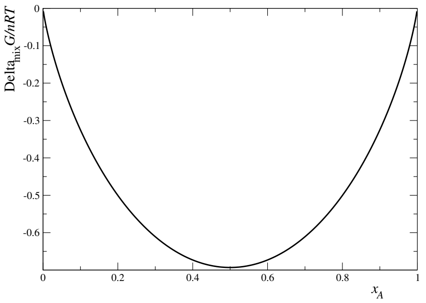

Figure 3: The change in Gibbs free energy resulting from the mixing of a binary system showing ideal solution behaviour is always negative.

Efficiency of thermodynamic processes

Historically, thermodynamics evolved from the need for a 'heat machine' as efficiently as possible, particularly the steam engine, in which the combustion heat of coal is transferred into mechanical work. Later other machines and processes were developed, such as power stations, jet engines, batteries, fuel cells, but also (bio)chemical processes.
As the *efficiency* of such processes is of great importance, we will take a closer look at efficiency for a couple of processes.

Heat engine

A 'heat engine' absorbs a certain amount of heat at a high temperature T_h, partially transfers this into some form of work W and conveys the rest of the heat to a low temperature reservoir at T_c. The process has to be cyclic so that we can use the machine in a continuous process. An idealized model of such a cyclic process is the Carnot cycle which models a reversible cyclic process consisting of two isotherms and two adiabates, as is outlined in figure 4. Since the internal energy is conserved in any cyclic process ($\Delta U = 0$) and heat exchange only occurs at the isotherms, the work is given by (we use absolute values because then the expressions are valid for both directions of the process)

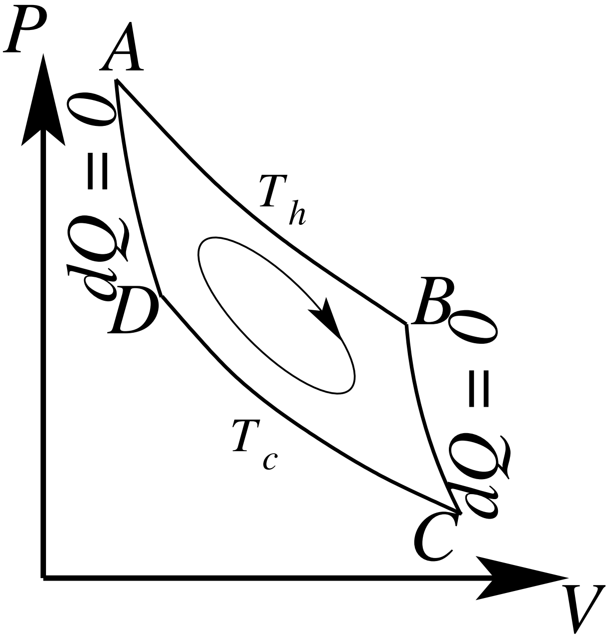

Figure 4: The Carnot-cycle in a *P*-*V* diagram. The Carnot cycle is a reversible process, which can run in either direction.

$$|W| = |Q_h| - |Q_c| \,. \tag{100}$$

We use the second law of thermodynamics to show that the heat engine runs as long as we withdraw an amount of heat Q_h from the high temperature resorvoir at T_h and dump a smaller amount of heat Q_c in the reservoir at a lower temperature T_c. For that we have to show that $\Delta S_{tot} = \Delta S + \Delta S_{sur} \geq 0$.
The system entropy, S, is a state function, so $\oint \mathrm{d}S = 0$ for any cyclic process (Note that Atkins uses the Carnot cycle to show that S is a state function; here we simply use this result).
The Carnot engine runs reversibly, so the change in entropy of the system in each cycle is given by

$$0 = \oint \mathrm{d}S = \Delta S = \frac{Q_h^{rev}}{T_h} + \frac{Q_c^{rev}}{T_c} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c}, \tag{101}$$

So, for any Carnot cycle the following expression is valid

$$\frac{Q_h}{Q_c} = -\frac{T_h}{T_c}. \tag{102}$$

Analogously, the change of entropy of the surroundings is

$$\oint \mathrm{d}S_{sur} = \Delta S_{sur} = -\frac{Q_h}{T_h} - \frac{Q_c}{T_c}. \tag{103}$$

Using equation (102), we find $\Delta S_{sur} = 0$, such that

$$\Delta S_{tot} = \Delta S + \Delta S_{sur} = 0. \tag{104}$$

So the total entropy change equals zero and the second law of thermodynamics tells us that the process is in equilibrium. This holds for any reversible process, so also for the Carnot cycle. If we would stop supplying heat from an external source to maintain the high temperature reservoir at T_h, the engine will slow down and finally stop.
The *thermodynamic efficiency* of such an engine is defined as the useful work divided by the heat that is absorbed (from the external energy source) at the high temperature,

$$\eta \equiv \frac{|W|}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}, \tag{105}$$

for a Carnot-cycle. If we combine equations (105) and (102) we find

$$\eta = 1 - \frac{T_c}{T_h}. \tag{106}$$

If we use this expression for the coal-fueled power station in Nijmegen (which was shut down in December 2015) that operated at a steam temperature of approximately 500 °C (at high pressure) and at a waste heat temperature of about 100 °C, we find an efficiency of 50 %. In reality such a power station does not operate reversibly and the actual *thermodynamic efficiency* is somewhere between 30 and 35 %. From (106) we conclude that the efficiency approaches 100 % if we let T_c approach 0 K or T_h approach ∞. However, there are practical limits to T_c and T_h, such that the efficiency will never be 100 %. Of course we can use the waste heat for useful purposes (other than dumping it in the river). Therefore the definition of efficiency depends on the point of view. Equation (105) only considers the thermodynamic cycle of the partial transformation of heat into work.

Refridgerator

A refridgerator is actually a reversed heat engine. We will have a look into this engine, again using the Carnot-cycle as a model. There is a difference, however, in the choice of the system. We withdraw an amount of heat Q_c from the system to be cooled at a temperature T_c. If this withdrawal process proceeds reversibly the entropy of the system will decrease according to

$$\Delta S = \frac{Q_c^{rev}}{T_c} = \frac{Q_c}{T_c} < 0. \tag{107}$$

Since for a refridgerator we dump an amount of heat Q_h at a higher temperature T_h in the surroundings the entropy of the surroundings increases, so

$$\Delta S_{sur} = \frac{Q_h^{sur}}{T_h} = -\frac{Q_h}{T_h} > 0. \tag{108}$$

Therefore, the total entropy change is (we use absolute values again)

$$\Delta S_{tot} = \Delta S + \Delta S_{sur} = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}. \tag{109}$$

Even if the Carnot-engine does not do any work, in which case $Q_h = -Q_c$ since $\Delta U_{cycle} = \oint \mathrm{d}U = 0$ for any cyclic process, and therefore $\Delta S_{tot} < 0$, since $T_c < T_h$. Thus the refridgerator will not run spontaneously (second law of thermodynamics). We have to put energy into the refridgerator in the form of work to force the process to run. The energy involved in this work is dumped in the surroundings as extra heat; in other words $|Q_h| = |Q_c| + |W|$. The efficiency of the refridgerator is then given by

$$\eta = \frac{|Q_c|}{|W|} = \frac{|Q_c|}{|Q_h| - |Q_c|}. \tag{110}$$

Equation (110) represents the maximum efficiency (the minimal work) achievable for this process as it is performed reversibly. Using equation (102) for a Carnot cycle again, we find for the maximum efficiency

$$\eta = \frac{T_c}{T_h - T_c}. \tag{111}$$

If we would keep the cycle running like this, assuming no leakage of heat into the system (cold chamber), its temperature T_c, and with that the efficiency, would keep on decreasing, demanding an increasing amount of work for the same withdrawal of heat Q_2.

The concept efficiency is a bit strange here since according to equation (111) the efficiency $\eta_{rev} > 1$ as long as $T_h - T_c < T_c$, so as long as $T_h < 2T_c$. The efficiency of a common refridgerator, if it were run reversibly, would be approximately 900 %.

Also here the definition of efficiency depends on the point of view. Q_c is a reasonable parameter in all cooling processes. In contrast, W is doubtful. Apart from losses that occur while doing work as a consequence of heat dissipation in the engine and the pump, one could use the heat that is dumped in the surroundings for other useful processes. Using the waste heat for other purposes generally also lowers T_h and therefore increases the efficiency. For refridgerators the efficiency η is often called the *performance.*

Batteries

Battery technology has developed in recent years very fast due to the need for efficient rechargeable batteries with high energy density, that is, small batteries with a large capacity and long life even after many (say 1000) repeated recharging cycles. Their use is in mobile electrical equipment and electric vehicles as well as in energy storage for renewable energy sources like solar panels and wind mills, which cannot provide a constant electrical power.

We will have a look at the efficiency of such rechargeable batteries. In figure 5 the situation is drawn schematically. The electromotive force, E_{EMF} is the maximum cell voltage the battery can deliver in case there is no load resistance R_L connected to its terminals. The electromotive force can be determined using the Nernst equation

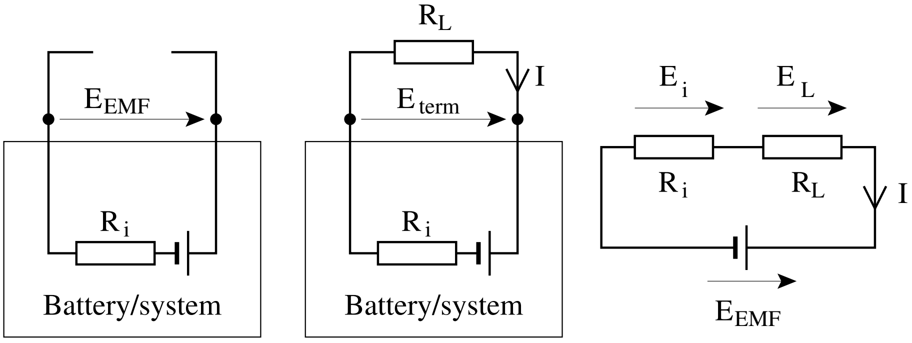

Figure 5: The battery is the system; if there is no external load resistance R_L, then the terminal voltage is equal to the maximum voltage of the battery E_{EMF}; if a resistance R_L is connected the terminal voltage drops with an amount of IR_i to a value of $E_{term} = E_{EMF} - E_i$.

$$-\frac{\Delta_r G}{\nu F} = E_{EMF} = E_{cell} = E^{\ominus} - \frac{RT}{\nu F} \ln Q, \tag{112}$$

where $\Delta_r G$ is the reaction gibbs free energy of the chemical reaction driving the battery. A fully charged cell will have the maximum E_{cell}, while a fully discharged (empty) battery will have $E_{cell} = 0$. If a load resistance is connected the current I is determined by

$$I = \frac{E_{cell}}{R_{tot}} = \frac{E_{cell}}{R_i + R_L}. \tag{113}$$

In such a situation electrical work, W^e, will be done on both the resistances R_L and R_i. If we assume these resistances to be pure ohmic resistances, Ohm's law will apply, leading to (use equation (113))

$$E_i = IR_i = E_{cell}\frac{R_i}{R_i + R_L} \quad \text{and} \quad E_L = IR_L = E_{cell}\frac{R_L}{R_i + R_L}. \tag{114}$$

The electrical work done on these resistances will be fully converted to a heat Q dissipated in the resistances (so-called Joule heating) according to

$$W^e = Q = \int P^e(t)\mathrm{d}t, \tag{115}$$

where the time dependence of the electrical power $P^e(t)$ is explicitly mentioned. This time dependence will be in $E_{cell}(t)$, because the the cell voltage will decrease in time as well as in the internal resistance $R_i(t)$ because R_i will depend on the current $I(t)$. $R_i(t)$ will be time dependent due to the charges that will accumulate across the membrane separating the electrolytes in the two half cells of the battery. This accumulation is a result of the limited flow capacity of ions through it.

The heat Q_i dissipated in R_i can be considered as a loss of energy, while the heat Q_L dissipated in R_L is useful energy. Their values follow from (use Ohm's law)

$$Q_i = \int P_i^e(t)\mathrm{d}t = \int I(t)E_i(t)\mathrm{d}t = \int \frac{E_i^2(t)}{R_i(t)}\mathrm{d}t \quad \text{and} \quad Q_L = \int P_L^e(t)\mathrm{d}t = \int \frac{E_L^2(t)}{R_L}\mathrm{d}t \tag{116}$$

The time dependence will be a subject in exercise 31 of exercise class 8. For the time being we will consider the case that the load of the cell will be shortly enough to assume that $E_{EMF} = E_{cell}$ can be considered as being constant in a time Δt, leading to

$$Q_i = \int \frac{E_i^2}{R_i}\mathrm{d}t = \frac{E_i^2}{R_i}\Delta t \quad \text{and} \quad Q_L = \int \frac{E_L^2}{R_L}\mathrm{d}t = \frac{E_L^2}{R_L}\Delta t. \tag{117}$$

If we put the time Δt equal to the time elapse per mol of the electrochemical reaction progression, that is $\Delta t = \frac{\nu F}{I}$, we can determine the efficiency of the loaded battery as (the useful electrical work is only done on the load resistance and $\Delta_r G$ is a molar quantity)

$$\eta = \frac{|W^e_{useful}|}{|\Delta_r G|} = \frac{|Q_L|}{|\Delta_r G|} = \frac{\frac{E_L^2}{R_L}\frac{\nu F}{|I|}}{\nu F|E_{cell}|} = \frac{E_L^2}{R_L|I||E_{cell}|}. \tag{118}$$

Using equation (114) this result becomes

$$\eta = \frac{\left(|E_{cell}|\frac{R_L}{R_i+R_L}\right)^2}{|E_{cell}|\frac{R_L}{R_i+R_L}|E_{cell}|} = \frac{R_L}{R_i + R_L}. \tag{119}$$

This result shows that even if we load the electrochemical cell reversibly the efficiency will be less than 100 %. The internal resistance, however, will be considerably smaller when the current is very small due to the smaller build-up of charges across the membrane separating the two half cells.

Statistical thermodynamics

One of the shortcomings of (classical) thermodynamics is that it can only describe macroscopic systems of many particles without the details of the microscopic properties of the particles coming into the picture. This makes thermodynamics a very powerful but also an abstract and in some sense an unsatisfactory construction. Statistical thermodynamics takes away this dissatisfaction by providing a foundation for thermodynamics based on the microscopic properties of the particles. We will briefly describe the essentials of statistical thermodynamics without giving a solid derivation. Such a fundamental construction is given in the optional course Statistical Thermodynamics.

Boltzmann distribution

Statistical thermodynamics assumes a system of particles of which all energy levels are known. These levels describe all the states of the particles in the system, such as translational, rotational and vibrational states with corresponding energies ϵ_i, where i labels a state. These energies are found by quantum mechanical calculations or by experimental spectroscopic measurements. Statistical thermodynamics then assumes that the chance of finding the particles (molecules) of the system in a certain energy state is only determined by the value of that energy and the temperature of the entire system. Eventually the temperature of the system is determined by the average occupation of all particles over the entire spectrum, i.e. over all energy states. This probability distribution is called the Boltzmann distribution and in formula is given by (we choose $\epsilon_0 = 0$, by shifting all energy levels accordingly)

$$\frac{n_i}{N} = \frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)}, \tag{120}$$

where N is the number of molecules in the system and $\frac{n_i}{N}$ is the fraction of molecules that, averaged over all particles and time, are in a quantum state with energy ϵ_i. Thus for low temperatures with $kT << \epsilon_i$ the number of particles in the state with energy ϵ_i is very small, whereas for higher temperatures the fraction relatively increases. The denominator in this equation, for which the sum runs over all possible energy states, ensures that the probability distribution is normalized; if we sum the fraction over all energy states we find

$$\sum_i \frac{n_i}{N} = \sum_i \frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)} = \frac{\sum_i \exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)} = 1, \tag{121}$$

which means nothing else than that all particles are in a state. This can be compared to rolling dice; the chance of an arbitrary number of eyes (1-6) is always equal to 1. That normalization of the Boltzmann distribution has a special name, the *partition function* q.

$$q \equiv \sum_i \exp\left(-\frac{\epsilon_i}{kT}\right). \tag{122}$$

The term kT can be interpreted as the thermal energy of the system. This is usually denoted by the symbol $\beta = \frac{1}{kT}$. The Boltzmann distribution plays an important role in statistical thermodynamics. For example the average value $< X >$ of an arbitrary quantity X of the entire system at a certain temperature can be determined from this probability distribution using

$$< X > = N < x > = N \sum_i x_i \frac{n_i}{N} = N \frac{\sum_i x_i \exp\left(-\beta\epsilon_i\right)}{q}, \tag{123}$$

where x_i is the value of that quantity for a (molecular) state i with energy ϵ_i. As an example consider the average total energy $< U >$ of the system:

$$< U > = N \frac{\sum_i \epsilon_i \exp\left(-\beta\epsilon_i\right)}{q} = -\frac{N}{q}\left(\frac{\mathrm{d}q}{\mathrm{d}\beta}\right). \tag{124}$$

The partition function q can be calculated if all energy levels ϵ_i are known. In a similar way we can calculate all thermodynamic functions such as G, A, H, etc. if we know the microscopic energy levels.

Statistical thermodynamic entropy

The Boltzmann distribution (equation (120)) can also be used to find an expression for the entropy. The Boltzmann definition of entropy is:

$$S \equiv k \ln W. \tag{125}$$

In this expression W is the number of micro states of the system, or in other words, the number of possibilities to divide the particles (molecules) of the system over all energy states ϵ_i at temperature T, given the Boltzmann distribution at that temperature.

From this definition of entropy it directly follows that the entropy increases with increasing temperature since then, according to the Boltzmann distribution, more energy levels can be occupied by the particles and therefore there are more possibilities to divide the particles over the levels.

In the limit $T \to 0$ the number of micro states for the system approaches $W = 1$ since then the system will be in a crystalline state in which all atoms are motionless and thus there will only be a single micro state left. With the Boltzmann definition of the entropy (equation (125)) it follows that

$$S(T = 0) = k \ln 1 = 0, \tag{126}$$

which is in agreement with the third law of classical thermodynamics (section 3B.2 of Atkins).

We can also understand the specific mathematical form of the Boltzmann entropy, the logarithm of W. To this end, consider a system consisting of two subsystems with numbers of micro states W_1 and W_2, respectively. The total system will then have many more micro states, namely

$$W = W_1 W_2, \tag{127}$$

as long as W_1 and W_2 are independent. The entropy is an extensive parameter (according to the classical thermodynamics definition), so that we expect this to hold also for the statistical definition, or $S = S_1 + S_2$. This expectation is fulfilled, since

$$S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln W_1 W_2 = k \ln W = S. \tag{128}$$

The Boltzmann constant k takes care of the units and numerical value of S. Equation (127) only holds in the case that there is no interaction between the subsystems that changes the occupation chances of the subsystems as a consequence of the combination of these subsystems into one system. The simplest example of two subsystems that are independent in that way, consists of two volumes filled with perfect gases.

Is entropy a measure for disorder?

Although it appears attractive to associate the concept entropy with disorder, we will show that this is not entirely correct. In the end statistical thermodynamics will provide the correct basis for the interpretation of entropy.

As a counter example for the association of entropy with disorder we start again where we left off, i.e. in classical thermodynamics. We limit ourselves to the simplest system we know, the perfect gas. We consider equal amounts of two gases A and B. For mixtures of two perfect gases and for ideal solutions in general we have derived that the entropy of mixing is given by equation (97)

$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B). \tag{129}$$

We compare two processes for these gases and a third process for a pure perfect gas A.

First we mix A and B reversibly, more precisely isothermally and isochorically. We will do this with a very clever experiment, but which is also difficult to realize, a so-called Gedankenexperiment, as is clarified in Figure 6. Initially A and B are separated in two volumes V. The left semipermeable membrane is mechanically coupled to the piston, such that for both gases at every moment the volume is constant and equal to V. As a consequence of this the mechanical work during the process is equal to zero, because $\mathrm{d}W = -P_{ext} dV = 0$ for both gases. Since the process proceeds isothermally and since for perfect gases

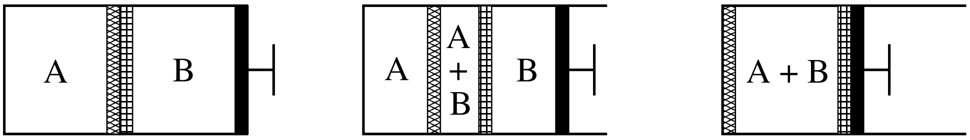

Figure 6: Isothermal reversible mixing of two perfect gases A and B. The process is done isochorically because the left membrane is permeable to A only, whereas the right membrane is only permeable to B.

the internal energy only depends on the temperature, it also holds that $\mathrm{d}U = 0$ for both gases. With the first law of thermodynamics it then follows that $\mathrm{d}Q_A = \mathrm{d}Q_B = 0$ and, since we conduct the process reversibly, it follows that $\mathrm{d}S_A = \mathrm{d}S_B = 0$. Thus we have found a process in which mixing of two gases, which we can associate with an increase in disorder, does not result in an entropy change.
For the second process we mix A and B, again isothermally and reversibly, but now no longer isochorically (see Figure 7). The volume will eventually become twice as large for both gases. The process is isothermal, so $Q_A = -\int \mathrm{d}W_A = \int P_A \mathrm{d}V_A = n_A RT \ln \frac{V_A^f}{V_A^i} = n_A RT \ln 2$ and analogously for B. Thus the entropy

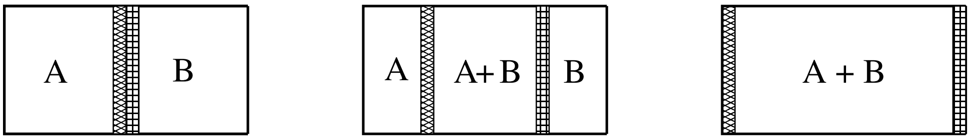

Figure 7: Isothermal mixing of two perfect gases A and B. The left membrane is again semipermeable to A, whereas the right membrane is only permeable to B. The process is conducted reversibly.

change is $\Delta S = (n_A + n_B) R \ln 2$. [1]
If we compare the two experiments, we see that the entropy does not increase as a consequence of solely mixing the gases A and B, but does increase if the mixture of gases occupies a larger volume.
This volume dependence of entropy is also found in the third experiment in which we irreversibly and isothermally expand a gas to a twice as large a volume in vacuum ($P_{ext} = 0$), so without mixing, as outlined in Figure 8. Isothermally, so $\mathrm{d}T = 0$, such that for a perfect gas it follows again that $\mathrm{d}U = 0$

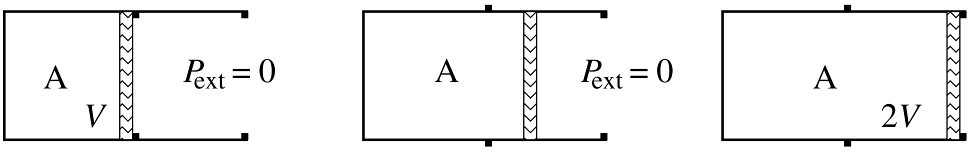

Figure 8: Isothermal, irreversible expansion of a perfect gas A in vacuum, in which the volume is doubled. Initially the process cannot proceed due to the middle ridges.

Hence $\mathrm{d}Q = -\mathrm{d}W = P_{ext}\mathrm{d}V = 0$. To determine the entropy change we need, however, a reversible alternative process, which results in $\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln 2$, so, again, an increase in entropy for a larger volume.
We can interpret the above mentioned results in terms of statistical thermodynamics. The distribution of particles over the different energy levels according to the Boltzmann distribution depends on the energies of all available states. And accordingly, a certain distribution is associated with a certain temperature. All three experiments were run isothermally, so the temperature can be chosen the same for all three. However, the energies of the available states do change. For a perfect gas of atoms the only relevant

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[1] We find the same result with equation (129), that was derived at constant (total) pressure and temperature; using $x_A = x_B = 0.5$ we obtain $\Delta_{mix} S = -nR \ln \frac{1}{2} = nR \ln 2$, with $n = n_A + n_B$. However, in that case it concerned spontaneous (irreversible) mixing, in which $P_{ext} = 0$, such that $0 = W = -Q = Q_{env}$ (see also table 4).

energies are the ones correponding to the translational motions of the atoms (compare Figure 1). There is no interaction between the atoms of perfect gases, not even for mixtures, other than elastic collisions. From a quantum mechanical point of view the energies are determined by the size of the volume of the system (and the mass of the atoms) according to (X is the size of the volume in one dimension; $V = XYZ$)

$$\epsilon_i = \left(i^2 - 1\right) \frac{h^2}{8mX^2} \quad \text{with partition function} \quad q = \frac{V}{\Lambda^3} \quad \text{and} \quad \Lambda = \frac{h}{\sqrt{2\pi mkT}}. \tag{130}$$

So only a volume change results in a change of the energy levels. An increase in V leads to a smaller distance between the energy levels, therefore an increase in the number of thermally available levels at a given temperature and thus an increase in entropy. This explains the absence of an entropy change in the first experiment, despite the increase of disorder in that experiment.
In table 4 all the entropy changes for the three processes are listed again.

exp.	ΔS	ΔS_{env}	ΔS_{tot}	rev./irr.
1	0	0	0	reversible
2	$(n_A + n_B)R\ln 2$	$-(n_A + n_B)R\ln 2$	0	reversible
3	$nR\ln 2$	0	$nR\ln 2$	irreversible

Table 4: An overview of the entropy changes for the three processes.

Thermodynamic entropy as a function of temperature

The third law of thermodynamics, which is in agreement with the Boltzmann definition of entropy thus sets the absolute value of the entropy according to equation (126). This is in contrast to all forms of energy that we have encountered, for which no absolute value is set. We chose that zero point by setting the standard enthalpy of formation and the standard Gibbs free energy of formation of the elements in their reference state to zero (Atkins paragraph 2C.2 and 3C.2a).
For entropy we can proceed one step further. The temperature dependence of the entropy follows from

$$S(T) = S(T=0) + \int_0^T \frac{\mathrm{d}Q^{rev}}{T} = S(0) + \int_0^T \frac{C_{P,V}}{T}\mathrm{d}T, \tag{131}$$

where C_P or C_V can be used for an isobaric or isochoric process, respectively. In all other cases we have to choose an alternative reversible path. In general $Q^{rev} = Q^{rev}(T)$ and $C_{P,V} = C_{P,V}(T)$, so these are dependent on T. At $T = 0$ the state of aggregation of nearly all substances is the crystalline state. For increasing temperature, in general, two phase transitions will be encountered, namely from solid to fluid at $T = T_{fus}$ and from the fluid phase to the gas phase at the boiling point, $T = T_b$. At these phase transition temperatures a jump in the entropy occurs. Since at any phase transition temperature, $T = T_{trs}$, two phases are in equilibrium with each other the Gibbs free energy at that temperature (and corresponding pressure) equals zero (cf. equations (68) and (69)).

$$\Delta_{trs}G\left(T_{trs}\right) = 0 \quad \text{such that} \quad \Delta_{trs}H - T_{trs}\Delta_{trs}S = 0 \quad \text{or} \quad \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}. \tag{132}$$

This results in a general expression for the (absolute) entropy of a pure compound, in the case of an isobaric process, according to

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_P(s)}{T}\mathrm{d}T + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_b} \frac{C_P(l)}{T}\mathrm{d}T + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_P(g)}{T}\mathrm{d}T, \tag{133}$$

in which we set $S(T = 0) = 0$ according to the third law of thermodynamics and we should not forget that the heat capacity remains a function of temperature in every state of aggregation.

Appendix A

State functions and total differentials

A *state function* is a function that only depends on the state of the system and is independent of how that state was reached. With that, a state function only depends on the *state variables.* The state variables of a system are P, T, V and n. The relation between the state variables is given by the *equation of state.* For a *perfect gas* (irrespective of whether it is an atomic or a molecular gas) the equation of state is given by

$$PV = nRT \tag{A-1}$$

For an arbitrary system, for example a Van der Waals gas, this relation is of course more complicated. We have already seen the internal energy U or E as examples of a state function. It does not matter how we reached a certain state given by P, T, V and n, the internal energy is only determined by those state variables. The same holds for the enthalpy, simply because of the definition $H \equiv U + PV$.

For a perfect gas, both the internal energy U and the enthalpy H turned out to depend only on the temperature T and the number of moles n via $U = \frac{3}{2}nRT$ and $H = \frac{5}{2}nRT$, respectively (we disregard the energy of molecular vibrations and rotations in this appendix; in other words, we consider a perfect gas to be a perfect atomic gas here). Via the equation of state (A-1) we also could have written $U = \frac{3}{2}PV$ and $H = \frac{5}{2}PV$. These expressions show how the state functions energy and enthalpy change as a function of the state variables.

More general, the *total differential* of a state function shows how that function changes when we change the state variables. Therefore it is important which variables can be changed. In fact, the equation of state poses limitations on this.

For a *closed* system there is no exchange of matter with the *surroundings* such that n is constant. This leaves three variables P, T and V. However, according to the equation of state only two of these variables are free. For example if we give P and T a certain value, then V is fixed. If we set P and V, then T is fixed, whereas a choice of T and V fixes the value P via the equation of state. In other words, for a closed system we only have two variables that we can choose independently. Then we can write the *total differential* of a state function as a general change of that function determined by the change of the two independent state variables that we can choose freely.

For example if we choose P and T as variables, then the total differential of for example the total energy for a *closed* system ($\mathrm{d}n = 0$) is given by

$$\mathrm{d}U = \left(\frac{\partial U}{\partial P}\right)_{T,n} \mathrm{d}P + \left(\frac{\partial U}{\partial T}\right)_{P,n} \mathrm{d}T. \tag{A-2}$$

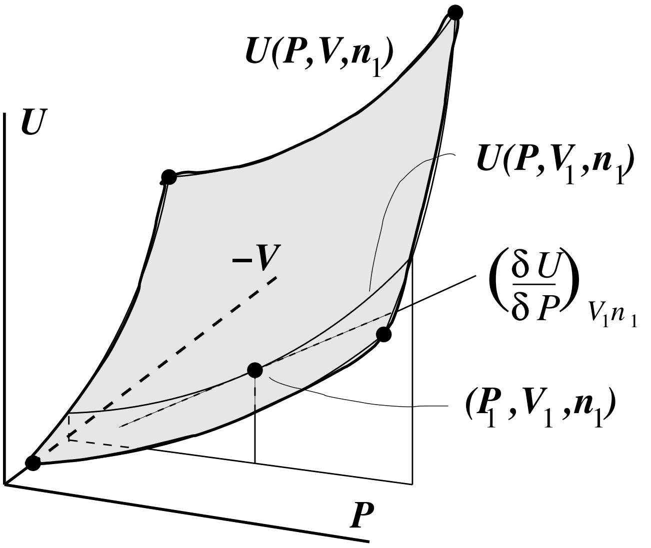
In case it is clear that one is considering a closed system and therefore $\mathrm{d}n = 0$, the last subscript is usually omitted, which results in

$$\mathrm{d}U = \left(\frac{\partial U}{\partial P}\right)_{T} \mathrm{d}P + \left(\frac{\partial U}{\partial T}\right)_{P} \mathrm{d}T. \tag{A-3}$$

If we choose P and V as independent variables, then the total differential thus becomes

$$\mathrm{d}U = \left(\frac{\partial U}{\partial P}\right)_{V} \mathrm{d}P + \left(\frac{\partial U}{\partial V}\right)_{P} \mathrm{d}V. \tag{A-4}$$

Let us consider the last expression (A-4) in somewhat more detail. This expression describes the change of U at constant n. Say we consider the behaviour of U at $n = n_1$. The first term describes how U changes as function of P if we also take V constant (say $V = V_1$). To that end, T has to 'follow' to still obey the equation of state. That term thus represents how U changes as a function of P in a state given by (V_1, n_1). That change will still be a function of P and thus depend on the value of P for which we consider the change (say for $P = P_1$). Then the term $\left(\frac{\partial U}{\partial P}\right)$ is nothing more than the derivative of U with respect to P in the point (P_1, V_1, n_1). That derivative is a measure for the steepness of U in that point if we only change P infinitesimally with $\mathrm{d}P$. The second term represents the analogous change of U in the point (P_1, V_1, n_1) if we change V infinitesimally with $\mathrm{d}V$. The total change of U is the sum of the two and is difficult to plot since for the independent variables P and V together with the change of the function (U) this results in a three-dimensional plot. An attempt to plot this in given in the figure below. In this figure a 'landscape' of U has been plot as a function of P and V at a chosen value $n = n_1$. Due to the sign of the term $-P\mathrm{d}V$ in $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ the V-axis is plotted as $-V$. The partial derivative of that landscape at constant volume $(V = V_1)$ is indicated for the point (P_1, V_1, n_1). The displayed state function can never be that of a perfect gas, because then due to the state function the internal energy would be given by $U = \frac{3}{2}PV$, such that at constant V the internal energy would be a linear function of P. If we would now consider another state, for example in a point (P_2, V_1, n_1), then both derivatives from (A-4) would have a different value, since in general the derivative of a function depends on where you determine that derivative, which is also the case in the figure (only for a perfect gas the derivative is independent of the point along the P-axis or the point along the V-axis, respectively, due to the linear dependency mentioned earlier). We find different values again in the point (P_1, V_2, n_1). Moreover, we also find different values for those derivatives in a point (P_1, V_1, n_2). However, due to the equation of state we can only choose two independent variables for a closed system. If we would change P, V and T arbitrarily, we would likely end up in states (P, V, T) that are impossible (in equilibrium) for our system. The fact that, for example, U is a state function, and thus has a value independent of the path taken to reach that state, also means that also infinitesimally it does not matter whether we first change P and then V or the other way around to go from the point (P_1, V_1) to the point (P_2, V_2) at constant n. The final value T_2 automatically is the same for both paths. This holds for any state function. A state function is also called a *conserved quantity.*



If we would have chosen P and T as independent variables, then we could have explained equation (A-3) analogously. Which variables we choose as independent is usually determined by the process we want to describe. For example, for an isothermal process in a closed system we could choose P and T or V and T , because for both choices the term $\mathrm{d}T$ in equation (A-3) would vanish.

For an *open* system we have three independent variables. Choosing for example T, V and n as independent variables, this results in the total differential

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{V,n} \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{T,n} \mathrm{d}V + \left(\frac{\partial U}{\partial n}\right)_{T,V} \mathrm{d}n. \tag{A-5}$$

We will return to open systems later on in the course.

Appendix B

Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from an helicopter view, in such a way that we can forget about microscopic processes (averaging).

System That part of the universe in which we are interested; we only consider macroscopic systems with many particles in thermodynamics.

Surroundings The rest of the universe we need to allow exchange of matter or energy with the system; is also a system, but not *the* system.

Thermal bath A heat reservoir (usually as surroundings), from which you can extract heat or to which you can deliver heat, without changing the temperature of the reservoir.

State variables Macroscopic quantities $(P, V, T, n, \cdots)$ that describe the thermodynamic state of a system. For a complete description a minimal amount of (independent) state variables is required.

Equation of state Relation between state variables that determines the possible states of the system in thermodynamic equilibrium.

Thermodynamic equilibrium A system is in thermodynamic equilibrium if the state variables of the system do not change spontaneously.

State function A (thermodynamic) single valued function of the (independent) state variables; The value of a state function is independent of the way the system has reached a certain state.

Reversible process A process during which the system is in thermodynamic equilibrium at every moment; with that a reversible process is also reversible.

Irreversible process A process that is not necessarily reversible.

Isothermal process A process that proceeds at constant temperature ($\mathrm{d}T = 0$ for the system).

Isobaric process A process that proceeds at constant pressure ($\mathrm{d}P = 0$ for the system).

Isochoric process A process that proceeds at constant volume ($\mathrm{d}V = 0$ for the system).

Adiabatic process A process that proceeds without heat exchange with the environment ($\mathrm{d}Q = 0$).

Isolated system No exchange between system and surroundings ($\mathrm{d}W = \mathrm{d}Q = \mathrm{d}n = 0$).

Closed system No exchange of matter between system and surroundings ($\mathrm{d}n = 0$); there can be exchange of work ($\mathrm{d}W \neq 0$) or heat ($\mathrm{d}Q \neq 0$).

Open system A non-closed system ($\mathrm{d}n \neq 0$).

Homogeneous system A system in which every (macroscopic) subsystem has the same properties.

Isotropic system A system that has the same properties in all directions, such as an homogeneous fluid. A crystal is not isotropic.

Intensive quantity Does not change if we enlarge the system; e.g. T and P.

Extensive quantity Doubles if we make the system twice as large; e.g. V and n.

Statistical thermodynamics Relates microscopic processes and (macroscopic) thermodynamics.

Appendix C

Formulae

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W' \quad \text{and} \quad \mathrm{d}W'_{max} = (\mathrm{d}G)_{P,T}$$

$$\mathrm{d}Q|_P = C_P\mathrm{d}T \quad \text{and} \quad \mathrm{d}Q|_V = C_V\mathrm{d}T$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{env} \geq 0$$

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$H = U + PV$$

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT\ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT\ln K = -\Delta_r G^{\ominus}$$

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^{\ominus} + RT\ln a_i = \mu_i^{\ominus} + RT\ln\frac{P_i}{P^{\ominus}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}}H}\right)x_B$$

$$\Delta S = -nR\left(x_A\ln x_A + x_B\ln x_B\right)$$

$$\Pi = [B]RT = \frac{n_B}{V}RT$$

$$S = k\ln W$$

$$\frac{n_i}{N} = \frac{\exp\frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp\frac{-\epsilon_i}{kT} \quad \text{and} \quad < X >= N < x >= N\sum_i x_i\frac{n_i}{N}$$