

# Study Guide Thermodynamics 2, 2023/2024

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## Literature

- Book: Physical Chemistry; P.W. Atkins.; edition 12, 11, 10 or 9, Oxford University Press
- Study guide: This study guide.
- All information will be available via the link in Brightspace or directly at <http://www.vsc.science.ru.nl/hugom/Thermo2/Thermo2.html>

## Aim

- Primary: Insight and skills
- Secondary: Knowledge

## Organisation

### • Introduction

Thermodynamics is built on two phenomenological perceptions, the first law and the second law describing the conditions for spontaneous processes. In the course Thermodynamics these laws were treated together with a few basic applications. In the course Thermodynamics 2 this basic perception is deepened and applied to more complex systems.

The following subjects will be treated:

- Stability of phases and phase diagrams - Phase transitions - Surface tension - Thermodynamics of mixtures - Thermodynamics of solutions - Activity - Electrolytes - The Boltzmann equation

### • Literature

- Physical Chemistry; P.W. Atkins.; edition 12, 11, 10 or 9, Oxford University Press
- Study guide: will be made available online during the course of the lectures and provides additional information to the book

### • Lectures, are on-campus and not recorded (earlier recordings are available).

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.**

A survey of subjects in Atkins which have been treated in the first year course Thermodynamics (2021/2022) can be found in Appendix E; See <https://dullenslab.com/teaching/> for the course of 2022/2023.

The present course Thermodynamics 2 will start with a concise recapitulation of the essential notions treated in Thermodynamics and will overall treat the following parts of the literature (SG is Study Guide, \* refers to add. info ternary phase diagrams on the home page)

Date	Atkins ed. 12 or 11	SG	ed. 10	ed. 9	Thermo 2: subjects
06/09	2D+3E	3-8,14-15	2D+3D	2.10-11+3.7-8	Exact diff., Molec. gasses
13/09	4	9-11	4	4	Phase diagr. of pure subst.
20/09	5A	9-13	5A	5.1-5	<i>P</i> , <i>x</i> -phase diagrams
27/09	5B-C	-	5B-C	5.5-8	<i>T</i> , <i>x</i> -phase diagrams
04/10	5D-E	-	5C-D	5.9+*	<i>s</i> – <i>l</i> , ternary phase diagr.
11/10	14C.2-4	16	16C.2-4	17.8-10+6	Interfaces, Chem. Eq.
18/10	6+5F	17-18	6+5F	6+5.13	Electrochem., Stat. Th.

- **Tutorials are on-campus and not recorded.**

The tutorial exercises will be available before, and the solutions after, each tutorial on the website: <http://www.vsc.science.ru.nl/hugom/Thermo2/Thermo2.html>.

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 exercises in the exam. There are three groups, for the Science, Chemistry and Premaster students, respectively. Students from other studies can choose freely which group to join.

Group	cohort	room	day	time	TA
1	Chemistry	HG00.514	Thursday	10:30-12:15	Tobias Dijkhuis & Jannes Peters
2	Premaster	Transitorium 00.005	Thursday	10:30-12:15	Hugo Meekes
3	Science	HG00.622	Thursday	13:30-15:15	t.b.a.

- **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 (with answers) will appear online at the end of the course.

Two lists of formulae (without further comments) will be provided at the exam. The first list is the same as was provided in the course Thermodynamics (Appendix C) and the second list adds the new formulae (Appendix D).

**Graphical calculators are NOT allowed during the exam (regular ones are).**

## 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 secondary: knowledge

- Insight is obtained by studying the material but particularly also by actively solving the problems in the exercise classes.  
Insight into the backgrounds of the laws of Thermodynamics as well as the definitions 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 mostly obtained by actively solving exercises and problems:  
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 Thermodynamics 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  $dQ = 0$ ', 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 receive all relevant formulas!

At the exam a list of formulae (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.

# Survey of the course Thermodynamics

## 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

$$PV = nRT = NkT \quad (1)$$

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

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

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

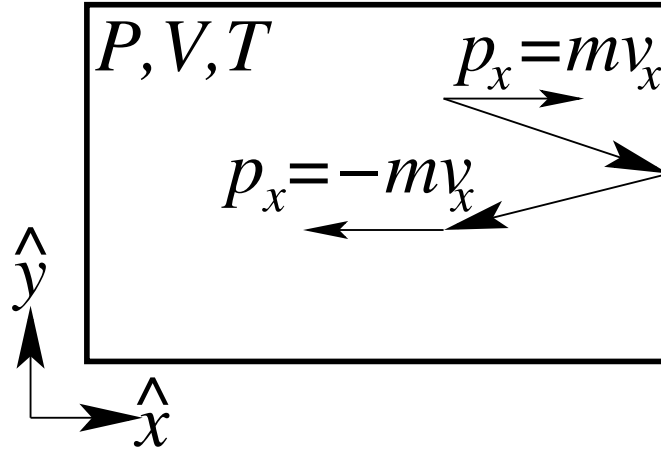


Figure 1: Transfer of momentum for a perfect gas of atoms.

average transfer of momentum is in the  $\hat{x}$ -direction according to figure 1

$$\Delta p_x = 2mv_x \quad (3)$$

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

$$P = \frac{F_x}{A} = \frac{ma_x}{A} = \frac{m}{A} \frac{dv_x}{dt} = \frac{1}{A} \frac{dp_x}{dt}, \quad (4)$$

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  $dt$  is ( $\rho = \frac{N}{V}$  is the density of the gas)

$$\frac{1}{2}\rho Av_x dt = \frac{1}{2} \frac{N}{V} Av_x dt. \quad (5)$$

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  $dt$ . The average transfer of momentum per time interval  $dt$  for collisions with the wall is therefore, using equations (3) and (5):

$$dp_x = \frac{1}{2} \frac{N}{V} Av_x dt \cdot 2mv_x = m \frac{N}{V} Av_x^2 dt \quad \text{or} \quad \frac{dp_x}{dt} = m \frac{N}{V} Av_x^2. \quad (6)$$

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

$$P = \frac{1}{A} \frac{dp_x}{dt} = m \frac{N}{V} v_x^2 = m \frac{N}{V} \frac{1}{3} v^2. \quad (7)$$

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

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

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))

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

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)

$$PV = nRT = NkT. \quad (10)$$

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

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

For a *molecular* perfect gas it holds that

$$PV = nRT \quad \text{and} \quad U = nc_V T \quad (\text{molecular perfect gas}). \quad (12)$$

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, the internal energy, work and heat capacity

The internal energy ( $E = U$ ) was defined as

$$dU \equiv dQ + dW. \quad (13)$$

Implicitly, this equation also describes the *first law of thermodynamics* for a closed system ( $n$  constant). It is a conservation law stating that any change of the internal energy  $U$  during a process in a closed

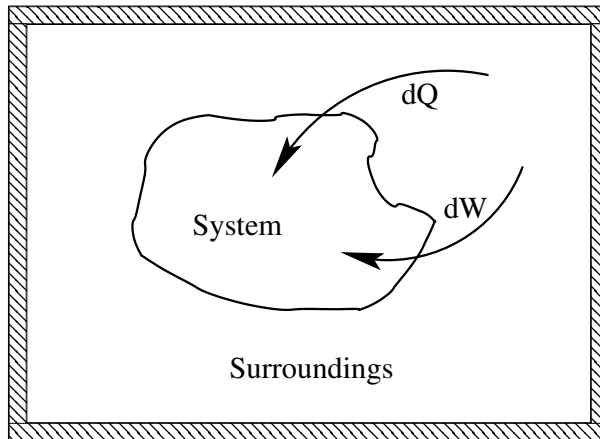


Figure 2: The total system of the system and its surroundings is isolated.

system is equal to the energy, flowing through the walls of the system, in the form of heat  $Q$  and work  $W$ , which is exchanged with the surroundings. An alternative expression of the first law of thermodynamics is

$$\oint dU = \oint (dQ + dW) = 0, \quad (14)$$

that is, the internal energy is a conserved quantity for any cyclic process in a closed system. This implies that in case we have any process running in a closed system, starting at a state given by the state variables  $(P_1, V_1, T_1)$  and ending the process in the same state  $(P_1, V_1, T_1)$ , the internal energy has the same value at the end. Such a quantity we call a *state function* of the variables  $P$ ,  $V$  and  $T$ . Note that the first law only holds when the initial and final states are thermodynamic equilibrium states, that is states for which the equation of state of the system holds. During the process, the system need not be in equilibrium. In other words a state function is unambiguously defined by the state variables, no matter, how the system has arrived in that (equilibrium) state; The first law of thermodynamics holds both for reversible as well as irreversible (spontaneous) processes.

The equation of state limits the number of independent variables for a state. In case of a perfect gas, for example, the perfect gas law,  $PV = nRT$ , allows for merely two independent variables for a closed system; Two of the state variables  $P$ ,  $V$ ,  $T$  can be chosen ( $n$  is constant for a closed system), and the third variable follows from the equation of state (the perfect gas law in this case).

If, for example, we choose  $T$  and  $V$  to describe the internal energy of any closed system, then the total differential of this state function is written as

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV. \quad (15)$$

In case of only volume work equation (13) becomes <sup>1</sup>

$$dU \equiv dQ + dW = dQ - PdV. \quad (16)$$

<sup>1</sup>For an irreversible process  $dW_{irr} = -P_{ext}dV$  and  $dQ = dQ_{irr}$ , but because  $U$  is a state function  $Q_{rev} + W_{rev} = Q_{irr} + W_{irr}$ , for any alternative reversible path.

Therefore we define the heat capacity at constant volume for any system as

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

The specific heat capacity is defined as ( $m$  is the mass of the molecules)

$$c_V = \frac{C_V}{Nm}. \quad (18)$$

with units J/gK.

De molar heat capacity at constant volume, with units J/molK, is defined as

$$c_V = \frac{C_V}{n}. \quad (19)$$

Note that  $c_V$  still is a function of  $T$  and  $P$ .

For a *perfect atomic gas* we have found that the internal energy only depends on the temperature:

$$U = \frac{3}{2}nRT. \quad (20)$$

The heat capacity of a perfect gas is therefore

$$C_V = \frac{3}{2}nR, \quad (21)$$

so independent of  $T$ ,  $P$  and  $V$ .

## The enthalpy and heat capacity

The extensive state function *enthalpy* was defined as

$$H \equiv U + PV, \quad (22)$$

so

$$dH = dU + d(PV) = dQ - PdV + PdV + VdP = dQ + VdP. \quad (23)$$

At constant pressure ( $dP = 0$ ) we obtain  $dH_P = dQ$ .

Therefore we defined the heat capacity at constant pressure as

$$C_P \equiv \left( \frac{\partial H}{\partial T} \right)_P. \quad (24)$$

Using equation (22) we find

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P + \left( \frac{\partial PV}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P. \quad (25)$$

Heating a general system at constant pressure will lead to a change in volume and therefore to additional volume work as compared to the case of heating at constant volume. This volume change depends on the system and can be very complicated.

For a *perfect atomic gas*, however, heating at constant pressure leads to a simple expression because the internal energy then only depends on  $T$ . Using equation (20) and the perfect gas law we find

$$C_P = \frac{3}{2}nR + P \left( \frac{\partial V}{\partial T} \right)_P = \frac{3}{2}nR + P \left( \frac{\partial \frac{nRT}{P}}{\partial T} \right)_P = \frac{3}{2}nR + nR = \frac{5}{2}nR \quad (26)$$

and the molar heat capacity becomes  $c_P = \frac{5}{2}R$  and is therefore constant for a perfect atomic gas.

For a perfect atomic gas we thus find the relation

$$C_P = C_V + nR \quad \text{en} \quad c_P = c_V + R. \quad (27)$$

This relation still holds for perfect molecular gases as we will see.

## The second law; entropy, free energy and spontaneous processes

The entropy was defined as

$$dS \equiv \frac{dQ^{rev}}{T}. \quad (28)$$

and is with this definition also a state function.

Two alternative expressions for the second law of thermodynamics were based on this definition of entropy

- For any *spontaneous* process to run

$$dS_{tot} = dS + dS_{omg} \geq 0. \quad (29)$$

- The second expression is in the form of the so-called Clausius inequality, stating the for any *spontaneous* process

$$dS \geq \frac{dQ}{T_b} \quad (30)$$

In these expression  $S$  is the entropy of the system,  $S_{omg}$  the entropy of the surroundings (sometimes called the reservoir or thermal bath),  $Q$  the heat of the system and  $T_{(b)oundary}$  the temperature of the wall dividing the system from the surroundings.  $T_b$  can be set equal to the temperature  $T$  of the system in case of a homogeneous temperature distribution.

These two alternative expressions for the second law hold in general for a spontaneous process in a closed system.

In equilibrium, for which there is no net macroscopic change, therefore

$$dS_{tot} = dS + dS_{omg} = 0 \quad (31)$$

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

$$dW = -P_{ext}dV + dW', \quad (32)$$

in which  $W'$  represents electrical work, friction work, chemical work, etc., according to the system and the process in question.

### Consequences for the internal energy

$$\Delta U = Q + W \quad \text{or} \quad dU = dQ + dW = dQ - P_{ext}dV + dW'. \quad (33)$$

The Clausius inequality (30) gives

$$(dU)_{V,W'} = dQ \leq TdS. \quad (34)$$

So for an iso-entropic and isochoric, spontaneous process without non-volume work it holds that

$$(dU)_{S,V,W'} \leq 0, \quad (35)$$

or 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 (29). Since  $dS = 0$  according to (29) it must hold that  $dS_{sur} \geq 0$ , such that the surroundings must absorb heat from the system, and therefore for the system it holds that  $Q \leq 0$ . Because also  $dV = 0$  this implies  $U$  has to decrease, which is exactly what is stated by equation (35). In other words, equation (35) which *only* applies under the *restrictions* of constant  $S$ ,  $V$  and  $W'$  is a *consequence* of the second law according to (29).

Therefore in equilibrium it holds that

$$(dU)_{S,V,W'} = 0, \quad (36)$$

or,  $U$  is minimal in equilibrium at constant  $S$ ,  $V$  and  $W'$ .

## Consequences for the enthalpy

$$H \equiv U + PV. \quad (37)$$

Analogous to the case of the internal energy it follows that  $(d(PV) = PdV + VdP)$

$$dH = dQ - P_{ext}dV + dW' + PdV + VdP. \quad (38)$$

If  $P$  is constant it has to hold that  $P_{ext} = P$  and then we find for a spontaneous process

$$(dH)_{P,W'} = dQ \leq TdS, \quad (39)$$

such that for a spontaneous process it has to hold that

$$(dH)_{S,P,W'} \leq 0 \quad (40)$$

and in equilibrium

$$(dH)_{S,P,W'} = 0. \quad (41)$$

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 (29).

## The Helmholtz free energy

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

$$A \equiv U - TS. \quad (42)$$

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

$$dA = dQ - P_{ext}dV + dW' - TdS - SdT, \quad (43)$$

such that for a spontaneous process it holds that

$$(dA)_{V,W'} = dQ - TdS - SdT \leq TdS - TdS - SdT = -SdT. \quad (44)$$

So for a spontaneous process it holds that

$$(dA)_{V,T,W'} \leq 0, \quad (45)$$

and in equilibrium it holds that

$$(dA)_{V,T,W'} = 0. \quad (46)$$

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  $dU \leq TdS + dW$ , or  $dW \geq dU - TdS = (dA)_T$ . 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

$$dW_{max} = dU - TdS, \quad (47)$$

or

$$W_{max} = (\Delta A)_T. \quad (48)$$



## The Gibbs free energy

The second alternative energy function is the Gibbs free energy,

$$G \equiv H - TS. \quad (49)$$

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

$$dG = dH - TdS - SdT, \quad (50)$$

such that for a spontaneous process it holds that (use equation (39))

$$(dG)_{P,W'} = dQ - TdS - SdT \leq -SdT. \quad (51)$$

So for a spontaneous process it holds that

$$(dG)_{P,T,W'} \leq 0, \quad (52)$$

and in equilibrium it holds that

$$(dG)_{P,T,W'} = 0. \quad (53)$$

At constant  $P$  and  $T$  it holds that  $dG \leq dW'$ , such that  $G$  is the maximum non-volume work that can be done during an isothermal, isobaric process.

$$W'_{max} = (\Delta G)_{P,T}. \quad (54)$$

## 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 (29) or (30).

Therefore, 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 it holds that  $Q = 0$ , but only in the reversible case this means that also the entropy term  $TdS = dQ^{rev} = 0$ . 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 an 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 those usually determine the choice.

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

$$(dG)_{P,T,W'} = 0. \quad (55)$$

This equation tells us that in equilibrium the Gibbs free energy is constant and minimal (from equation (52)) 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, or  $dT = dP = 0$ . This appears to be a very strong restriction since the equation of state suggests that then also  $dV = 0$ , 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 (52) then gives

$$(dG)_{P,T,W'} = (dH)_{P,T,W'} - T(dS)_{P,T,W'} \leq 0. \quad (56)$$

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

$$\Delta H - T\Delta S \leq 0, \quad (57)$$

in which  $P$  and  $T$  are constant.

Now we can distinguish between exothermic (heat producing) and endothermic (heat absorbing) processes (use  $dH|_{P,W'} = dQ$ ):

$$\text{Exothermic } (\Delta H < 0) \quad \begin{cases} \Delta S > 0 & \text{spontaneous,} \\ \Delta S < 0 & \text{spontaneous if } T|\Delta S| \leq |\Delta H|, \end{cases} \quad (58)$$

$$\text{Endothermic } (\Delta H > 0) \quad \begin{cases} \Delta S > 0 & \text{spontaneous if } T\Delta S \geq \Delta H, \\ \Delta S < 0 & \text{never spontaneous.} \end{cases} \quad (59)$$

We find a special case for equilibrium situations, for which

$$\Delta G = \Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta H = T\Delta S. \quad (60)$$

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, it holds that ( $T = T_{fus}$ ):

$$\Delta_{fus}G = 0 \quad \text{such that} \quad \Delta H_{fus} - T_{fus}\Delta_{fus}S = 0 \quad \text{or} \quad \Delta_{fus}H = T_{fus}\Delta_{fus}S. \quad (61)$$

Similarly at the boiling point of the fluid it holds that

$$\Delta_{vap}G = 0 \quad \text{such that} \quad \Delta H_{vap} - T_{vap}\Delta_{vap}S = 0 \quad \text{or} \quad \Delta_{vap}H = T_{vap}\Delta_{vap}S. \quad (62)$$

## The third law of thermodynamics

The third law sets the entropy equal to zero at zero Kelvin.

$$S(T = 0) = 0. \quad (63)$$

## The chemical potential

As final thermodynamic quantity we introduce the chemical potential  $\mu$ . 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

$$\mu \equiv \left( \frac{\partial G}{\partial n} \right)_{P,T}. \quad (64)$$

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

$$dG = \left( \frac{\partial G}{\partial P} \right)_{T,n} dP + \left( \frac{\partial G}{\partial T} \right)_{P,n} dT + \left( \frac{\partial G}{\partial n} \right)_{T,P} dn, \quad (65)$$

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 (64) 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

$$G = G(n_1, n_2, n_3, \dots, V, T, P). \quad (66)$$

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  $G$

$$dG = \left( \frac{\partial G}{\partial P} \right)_{T,n_i} dP + \left( \frac{\partial G}{\partial T} \right)_{P,n_i} dT + \sum_i \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} dn_i, \quad (67)$$

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  $dG = VdP - SdT$ , 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

$$\mu_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}. \quad (68)$$

We can identify the two other partial derivatives as

$$V = \left( \frac{\partial G}{\partial P} \right)_{T,n_i} \quad \text{and} \quad S = - \left( \frac{\partial G}{\partial T} \right)_{P,n_i}, \quad (69)$$

or

$$dG = VdP - SdT + \sum_i \mu_i dn_i. \quad (70)$$

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  $\mu_i$  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 (70) then gives

$$dG = \sum_i \mu_i dn_i \quad (P, T \text{ constant}). \quad (71)$$

We have also seen that the Gibbs free energy at constant temperature and pressure describes the maximum non-volume work (see equation (54)). With (71) it then follows that

$$dW'_{max} = \sum_i \mu_i dn_i \quad (P, T \text{ constant}). \quad (72)$$

This maximum value is reached for a reversible process. As an example we consider an electrochemical cell. In that case the  $dn_i$  describe the changes of the (molar) amounts of particles (whether charged or not) and  $\sum_i \mu_i dn_i$  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

$$P = \sum_i P_i \quad \text{with} \quad \frac{P_i}{P} \equiv \frac{n_i}{n} = x_i, \text{ the mole fraction of component } i \quad (\text{Dalton's law}). \quad (73)$$

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  $d\mu = dG_m = V_m dP - S_m dT$ ):

$$\mu_i(P_i) = \frac{G_i(P_i)}{n_i} = G_{m,i}(P_i) = G_{m,i}^\ominus + \int_{P^\ominus}^{P_i} V_m dP = \mu_i^\ominus + RT \int_{P^\ominus}^{P_i} \frac{dP}{P} = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}, \quad (74)$$

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  $\gamma_i$  of component  $C_i$  are introduced according to

$$\mu_i \equiv \mu_i^\ominus + RT \ln a_i \equiv \mu_i^\ominus + RT \ln \gamma_i x_i \quad \text{with} \quad x_i \equiv \frac{n_i}{n}, \text{ the mole fraction of component } i. \quad (75)$$

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  $\text{pH}^\oplus = -\log a_{\text{H}^+(\text{aq})}^\oplus = 7$  is chosen as standard state, instead of  $\text{pH}^\ominus = -\log a_{\text{H}^+(\text{aq})}^\ominus = 0$ , for the thermodynamic standard state.

In summary, the standard state  $\ominus$  of component  $i$  is given by

$$\ominus \quad \begin{cases} i \text{ is a pure component; a sometimes fictive situation} \\ a_i = 1 \\ P = P^\ominus = 1 \text{ bar; for the (fictively) pure component,} \end{cases} \quad (76)$$

while the activity  $a_i$  of component  $i$  in the mixture is defined as

$$a_i = \begin{cases} P_i/P^\ominus \text{ for a perfect gas in the mixture} \\ \approx 1 \text{ for a pure liquid or the solvent in a very diluted solution} \\ \approx 1 \text{ for a pure solid or the solid in a very diluted solid solution} \\ \mu_i \equiv \mu_i^\ominus + RT \ln a_i \equiv \mu_i^\ominus + RT \ln \gamma_i x_i \text{ for all other situations.} \end{cases} \quad (77)$$

## 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.

$$G|_{P,T} = \int_0^{n_A} \mu_A dn_A + \int_0^{n_B} \mu_B dn_B = \mu_A \int_0^{n_A} dn_A + \mu_B \int_0^{n_B} dn_B = n_A \mu_A + n_B \mu_B, \quad (78)$$

where for the second set of integrals we used that  $\mu_A$  and  $\mu_B$  do not change if the mixing ratio in the system remains constant and only the total amount of mixture increases. Thus equation (78) holds for an arbitrary mixture.

An important application of the concept chemical potential is found for equilibrium situations between two phases  $\alpha$  and  $\beta$ ; 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  $dn_i^\alpha = -dn_i^\beta$ .

At constant pressure and temperature and is no additional work ( $dW' = 0$ )

$$0 = dG|_{P,T,W'} = \mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta = \mu_i^\alpha dn_i^\alpha + \mu_i^\beta (-dn_i^\alpha) = (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha, \quad (79)$$

and therefore in equilibrium between two (or more) phases  $\alpha$  and  $\beta$  at given  $T$  and  $P$ , we find

$$\mu_i^\alpha = \mu_i^\beta \quad \text{for all components } i \text{ in the phase mixtures.} \quad (80)$$

## 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 (80) 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  $T$ .

### 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 (76), refers to the pure component. Using equation (78) we find at temperature  $T$

$$G_{no\ mix} = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\ominus + RT \ln a_A^*) + n_B (\mu_B^\ominus + RT \ln a_B^*). \quad (81)$$

After mixing we obtain

$$G_{mix} = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\ominus + RT \ln a_A) + n_B (\mu_B^\ominus + RT \ln a_B). \quad (82)$$

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

$$\Delta_{mix}G = G_{mix} - G_{no\ mix} = n_A RT \ln \frac{a_A}{a_A^*} + n_B RT \ln \frac{a_B}{a_B^*} = nRT \left( x_A \ln \frac{a_A}{a_A^*} + x_B \ln \frac{a_B}{a_B^*} \right). \quad (83)$$

### A mixture of perfect gases

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

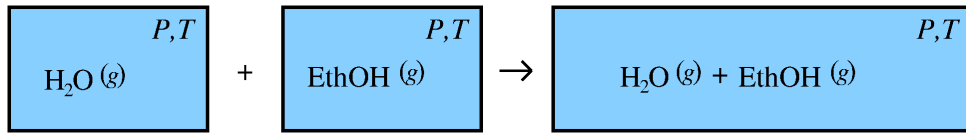


Figure 3: The mixing process of perfect gases at constant pressure  $P$  and temperature  $T$ .

$$\Delta_{mix}G = nRT \left( x_A \ln \frac{P_A}{P} + x_B \ln \frac{P_B}{P} \right) = nRT (x_A \ln x_A + x_B \ln x_B), \quad (84)$$

where we used Dalton's law and the definition of partial pressure, equation (73).

### A mixture of liquids

For a mixture of liquids we could substitute  $a_i^* \approx 1$  in equation (83) because the liquids are pure, initially, leading to

$$\Delta_{mix}G \approx nRT (x_A \ln a_A + x_B \ln a_B). \quad (85)$$

Alternatively, we consider the mixing process for an  $l$ - $g$  equilibrium of a binary system at constant temperature  $T$ , as shown in figure 4. Initially we have the liquids in equilibrium with their (pure phase) vapor pressures  $P_i^*$ , while after the mixing we have a vapor pressure of the liquid mixture equal to  $P = P_A + P_B$ . Following the same reasoning as for the gas phase mixing process, leading to equation (84), we now find for the gas phase

$$\Delta_{mix}G_g = n_g RT \left( x_{A,g} \ln \frac{P_A}{P_A^*} + x_{B,g} \ln \frac{P_B}{P_B^*} \right). \quad (86)$$

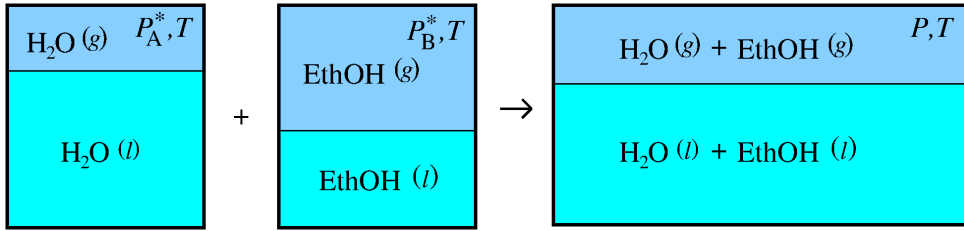


Figure 4: The mixing process of a liquid-gas equilibrium at temperature  $T$ .

For the liquid phase we would still write

$$\Delta_{mix}G_l \approx n_l RT (x_{A,l} \ln a_{A,l} + x_{B,l} \ln a_{B,l}), \quad (87)$$

where the activities as well as the partial pressures mainly depend on the interactions A-A, B-B and A-B in the liquid and cover with that the so-called non-ideal interactions between the molecules in a liquid mixture.

It is convenient to describe the liquid mixture in terms of a so-called ideal solution (see below), comparable to the situation of a perfect gases mixture, equation (84) and deviations from ideal behaviour, by using the earlier mentioned activity coefficients  $\gamma_i$ , defined by  $a_i \equiv \gamma_i x_i$ :

$$\Delta_{mix}G_l = n_l RT (x_{A,l} \ln \gamma_{A,l} x_{A,l} + x_{B,l} \ln \gamma_{B,l} x_{B,l}) = n RT (x_A \ln x_A + x_B \ln x_B) + n RT (x_A \ln \gamma_A + x_B \ln \gamma_B), \quad (88)$$

where the activity coefficients cover the non-ideal behaviour and the subscript  $l$  has been dropped in the right hand expression for clarity.

### Ideal solutions

A special case of so-called ideal solutions is described by Raoult's empirical law, for which both activity coefficients are (nearly) equal to unity, or  $\gamma_A \approx \gamma_B \approx 1$ , simplifying equation (88) to

$$\Delta_{mix}G^{ideal} = n RT (x_A \ln x_A + x_B \ln x_B). \quad (89)$$

In other words, ideal solutions have similar mixing behaviour as perfect gases (cf. equation (84)). Raoult's law boils down to the vapour pressures of both components for the liquid mixture being proportional to their mole fractions in the liquid, according to

$$P_i^g = x_i^l P_i^{g,*}, \text{ or } \frac{P_i^g}{P_i^*} = x_i, \quad (90)$$

where  $l$  and  $g$  represent the liquid and gas phase respectively. In other words, for ideal solutions, we can rewrite equation (86) to

$$\Delta_{mix}G_g = n_g RT (x_{A,g} \ln x_{A,l} + x_{B,g} \ln x_{B,l}), \quad (91)$$

where the subscripts  $g$  and  $l$  are explicitly left to show the mutual dependence of the two phases.

For non-ideal solutions we can often still use such a relationship for (only) the solvent  $A$  in very diluted solutions of  $B$  in  $A$  ( $n_B \ll n_A$ ), covered by the Henry constant as described in Atkins.

For the general case, however, we will have to replace  $\ln x_i$  by the activity  $\ln a_i$ .

### Ideal mixing liquids and gases

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

$$\Delta_{mix}G^{ideal} = n RT (x_A \ln x_A + x_B \ln x_B), \text{ with } x_i = \frac{n_i}{n_A + n_B}. \quad (92)$$

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

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S, \quad (93)$$

such that

$$\Delta_{mix}H^{ideal} = 0, \quad (94)$$

$$\Delta_{mix}S^{ideal} = -nR(x_A \ln x_A + x_B \ln x_B). \quad (95)$$

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

$$\Delta S^{tot} = \Delta S = \Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B) \geq 0 \text{ for } 0 \leq x_A \leq 1. \quad (96)$$

in other words, ideal mixtures always mix spontaneously.

Also note that  $\Delta_{mix}G$  is negative for all values of  $x_A$  (see figure 5). The second law of thermodynamics tells us once more that, at constant pressure and temperature, such ideal mixtures will always mix spontaneously for any chosen molfraction,  $x_A$ .

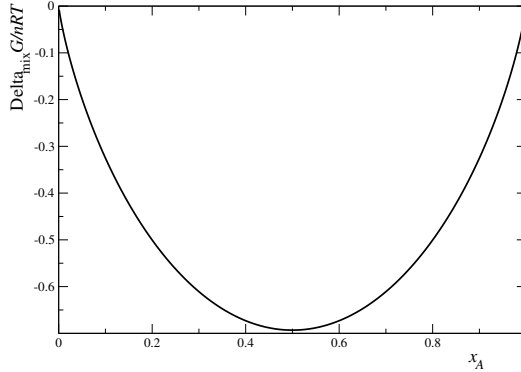


Figure 5: The change in Gibbs free energy resulting from the mixing of a binary system showing ideal solution behaviour is always negative.

Another consequence of equation (78) is that, given the fact that in equilibrium we have  $dG|_{P,T} = 0$ :

$$dG|_{P,T} = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B = 0. \quad (97)$$

If we now substitute equation (71), we find

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{or more generally } \sum_i n_i d\mu_i = 0, \quad (98)$$

an equation known as the Gibbs-Duhem equation.



# Extension of the course Thermodynamics

## Perfect gases of atoms

We already know that perfect gases in thermodynamic equilibrium obey the equation of state

$$PV = nRT = NkT, \tag{99}$$

which is often referred to as the perfect gas law.  $V$  is 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  $v$  (of all atoms) does not change at constant  $T$ ,  $P$  and  $V$ .

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, i.e. by the temperature

$$U = N \frac{1}{2} m v^2 = \frac{3}{2} N k T = \frac{3}{2} n R T, \tag{100}$$

as we found earlier in equation (11). Thus we see that  $U$  is an extensive quantity (scales with the size of the system) because of the factor  $n$  and that  $U$  further only depends on the temperature  $T$  (or the product  $PV$ ).

## Perfect gases of molecules; degrees of freedom, equipartition theorem

For perfect gases of molecules instead of atoms the situation changes. In case of molecules not only the kinetic energy of the molecules contributes to the average energy. One way to categorise all relevant energy contributions is to make a distinction between the translational energy of the molecule as a whole, the rotational energy of the molecule as a whole and the vibrational energy of the atoms and groups of atoms within each molecule. In the exchange of energy at every collision between molecules all three categories contribute. The contributions of the translations, rotations and vibrations to the average total energy of the system is of course complicated, but statistical thermodynamics, in principle, is able to accurately describe those contributions.

For now it is sufficient to summarize the results of statistical thermodynamics for the case of very high temperatures, where both the perfect gas law is the appropriate equation of state and the so-called equipartition theorem holds. The equipartition theorem states that for sufficiently high temperatures each degree of freedom for the motion of atoms in the molecules contributes  $\frac{1}{2}kT$  to the average internal energy of the system. For a system of  $N$  atoms we have  $3N$  degrees of freedom;  $N$  moving atoms and for each atom movements in 3 directions ( $x, y, z$ ). If we consider the molecular case for which  $N$  atoms, make up  $M$  identical molecules, then each molecule as a whole has 3 translational degrees of freedom ( $3M$  in total), leaving  $(3N - 3M)$  degrees of freedom for the rotations and the internal vibrations of the molecules. The division of these  $(3N - 3M)$  degrees of freedom depends on the number of atoms per molecule  $N_m = (\frac{N}{M})$  as well as the shape of the molecule. For the latter we again have three categories: atoms, linear and non-linear molecules having 0, 2 en 3 rotational degrees of freedom, respectively. Using the notation  $N_T, N_R$  en  $N_V$  for the number of degrees of freedom for translations, rotations and vibrations, respectively, we obtain the following results per molecule Using the equipartition theorem, we find for

	atom	linear molecule	non-linear molecule
$N_T$	3	3	3
$N_R$	0	2	3
$N_V$	0	$3N_m - 3 - 2$	$3N_m - 3 - 3$

the translations of the molecule a contribution to the internal energy of the system equal to  $3 \cdot \frac{1}{2}kT$ .

For the rotations it depends on the shape of the molecule. A  $\text{H}_2$ -molecule has two rotational degrees of freedom (two rotation axes perpendicular to the molecular axis) resulting in an energy contribution of  $2 \cdot \frac{1}{2}kT$ . An  $\text{NH}_3$  molecule has three rotational axes, contributing  $3 \cdot \frac{1}{2}kT$  to the internal energy. For the vibrations the situation is more complicated. For each vibrational degree of freedom (often referred to as vibrational mode) there are two contributions to the energy, the kinetic energy and the potential energy (cf. the case of a vibrating spring). So for the  $\text{H}_2$ -molecule we have only one vibrational mode, but it contributes  $2 \cdot \frac{1}{2}kT$  to the average internal energy.

Consider as another example a perfect gas of  $M$  CO-molecules at sufficiently high temperature, such that the equipartition theorem holds. Then we find the following contributions of translations, rotations and vibrations to the average internal energy of the gas:

$$U = U^T + U^R + U^V = 3 \cdot \frac{1}{2}MkT + 2 \cdot \frac{1}{2}MkT + 2 \cdot \frac{1}{2}MkT = \frac{7}{2}MkT = \frac{7}{2}nRT. \quad (101)$$

According to the equipartition theorem a perfect gas of  $M$  CO-molecules therefore has  $\frac{7}{3}$  times as large an internal energy as compared to a perfect gas of  $M$  Ar-atomen at the same temperature. For the heat capacity we find  $C_V = \frac{7}{2}nR$ . One needs, therefore,  $\frac{7}{3}$  as much energy to raise the temperature of the CO-gas as compared to an atomic perfect gas of Kr.

**In the following we will consider a perfect gas to be a gas of atoms or molecules, which obeys the equipartition theorem.**

## Surfaces and interfaces

In addition to Atkins (ed.11: 14C.2 to 14C.4; ed.10: 16C.2 to 16C.4; ed.9: 17.8 to 17.10; ed.8: 18.7 to 18.8) an explanation of the concept contact angle  $\Theta_c$  is given.

### Capillary action

The process of capillary action (rise or depression) is depicted in figure 6. If the contact angle  $\Theta_c = 0$ , the radius of the capillary is equal to the radius of the circular meniscus ( $R = r$ ), such that in the equation for the capillary rise  $h$  equals the radius  $R$  of the capillary, so

$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}. \quad (102)$$

In case  $\Theta_c \neq 0$  (figure 6b;  $\cos \Theta_c = R/r$ ; N.b., Atkins uses the symbol  $r$  instead of  $R$ )

$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R} \cos \Theta_c. \quad (103)$$

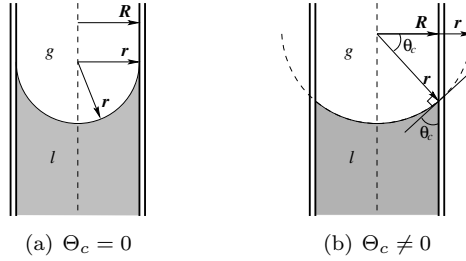


Figure 6: Capillary rise (concave meniscus) for  $\Theta_c = 0$  and  $\Theta_c \neq 0$ ;  $l$  = liquid,  $g$  is air or vapour

### Wetting

In case the surface tensions of all interfaces are relevant the situation becomes more complicated. To illustrate this situation we consider the case of the spreading (wetting) of a liquid droplet on a solid-vapour interface. In such a case all three surface tensions  $\gamma_{sg}$ ,  $\gamma_{sl}$  and  $\gamma_{lg}$  play a role. Such a situation is depicted in figure 7. If we assume that the surface tension between liquid and vapour,  $\gamma_{lg}$ , is isotropic and the surface of the droplet does not change as a result of the change of the shape of the droplet during the wetting process, we can conclude from the difference between figures 7b and 7a that the work per unit of surface of the wetting process (i.e. of the adhesion) is equal to ( $dW = \gamma d\sigma$ )

$$w_{ad} = -\frac{W}{\sigma} = -\frac{\gamma_{sl}\sigma - \gamma_{sg}\sigma - \gamma_{lg}\sigma}{\sigma} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}. \quad (104)$$

The balance of forces is shown in figure 7c and is given by

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \Theta_c. \quad (105)$$

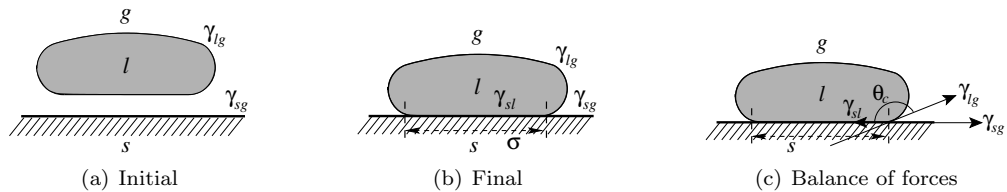


Figure 7: Wetting process

## 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 basis for thermodynamics based on the microscopic properties of the particles. We will briefly describe the foundations 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  $\epsilon_i$ , 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)

$$\frac{n_i}{N} = \frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)}, \quad (106)$$

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, that are in a quantum state with energy  $\epsilon_i$ . Thus for low temperatures with  $kT \ll \epsilon_i$  the number of particles in the state with energy  $\epsilon_i$  is very small, whereas for higher temperatures the fraction relatively increases. The denominator in this equation ensures that the probability distribution is normalized. Namely if we sum the fraction over all energy states we find

$$\sum_i \frac{n_i}{N} = \sum_i \frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)} = \frac{\sum_i \exp\left(-\frac{\epsilon_i}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)} = 1, \quad (107)$$

which means nothing more 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*  $q$ .

$$q \equiv \sum_i \exp\left(-\frac{\epsilon_i}{kT}\right). \quad (108)$$

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  $\langle X \rangle$  of an arbitrary quantity  $X$  of the entire system at a certain temperature can be determined from this probability distribution using

$$\langle X \rangle = N \langle x \rangle = N \sum_i x_i \frac{n_i}{N} = N \frac{\sum_i x_i \exp(-\beta\epsilon_i)}{q}, \quad (109)$$

where  $x_i$  is the value of that quantity for a (molecular) state  $i$  with energy  $\epsilon_i$ . As an example we can consider the average total energy  $\langle U \rangle$  of the system:

$$\langle U \rangle = N \frac{\sum_i \epsilon_i \exp(-\beta\epsilon_i)}{q} = -\frac{N}{q} \left( \frac{dq}{d\beta} \right). \quad (110)$$

The partition function  $q$  can be calculated if all energy levels  $\epsilon_i$  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 (106)) can also be used to find an expression for the entropy. The Boltzmann definition of entropy is very suitable for this:

$$S \equiv k \ln W. \quad (111)$$

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  $\epsilon_i$  at temperature  $T$ . 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.

In the limit  $T \rightarrow 0$  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 (111)) it follows that

$$S(T = 0) = k \ln 1 = 0, \quad (112)$$

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

$$W = W_1 W_2, \quad (113)$$

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

$$S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln W_1 W_2 = k \ln W = S. \quad (114)$$

Equation (113) 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.

## 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 ( $dn = 0$ ) is given by

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

In case it is clear that one is considering a closed system and therefore  $dn = 0$ , the last subscript is usually omitted, which results in

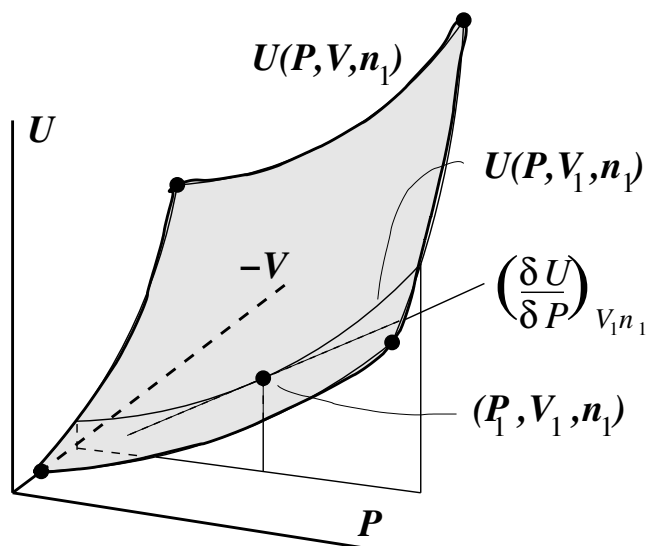
$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT. \tag{A-3}$$

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

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV. \tag{A-4}$$

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  $dP$ . The second term represents the analogous change of  $U$  in the point  $(P_1, V_1, n_1)$  if we change  $V$  infinitesimally with  $dV$ . 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 is given in the figure below. In this figure a 'landscape' of  $U$  has been plotted as a function of  $P$  and  $V$  at a chosen value  $n = n_1$ . Due to



the sign of the term  $-PdV$  in  $dU = TdS - PdV$  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 the 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. Of course for an isothermal process in a closed system we choose  $P$  and  $V$  and for an isochoric process in a closed system we choose  $P$  and  $T$ .

So 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

$$dU = \left( \frac{\partial U}{\partial T} \right)_{V,n} dT + \left( \frac{\partial U}{\partial V} \right)_{T,n} dV + \left( \frac{\partial U}{\partial n} \right)_{T,V} dn. \quad (\text{A-5})$$

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

## Appendix B

### Glossary

**Microscopic** On an atomic or molecular scale.

**Macroscopic** Seen from a 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. 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 ( $P, V, T, n, \dots$ ) 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 ( $dT = 0$  for the system).

**Isobaric process** A process that proceeds at constant pressure ( $dP = 0$  for the system).

**Isochoric process** A process that proceeds at constant volume ( $dV = 0$  for the system).

**Adiabatic process** A process that proceeds without heat exchange with the environment ( $dQ = 0$ ).

**Isolated system** No exchange between system and surroundings ( $dW = dQ = dn = 0$ ).

**Closed system** No exchange of matter between system and surroundings ( $dn = 0$ ); there can be exchange of work ( $dW \neq 0$ ) or heat ( $dQ \neq 0$ ).

**Open system** A non-closed system ( $dn \neq 0$ ).

**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 a 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.



Formulae first year course Thermodynamics

$$PV = nRT = NkT$$

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

$$\Delta U = W + Q$$

$$dW = -P_{ext}dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

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

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{env} \geq 0$$

$$dU = -PdV + TdS + \sum_i \mu_i dn_i$$

$$H = U + PV$$

$$dH = VdP + TdS + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

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

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

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad dW' = Edq \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

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

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

$$\sum_j n_j d\mu_j = 0$$

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

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

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

$$S = k \ln W$$

## Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T}\right)_{P,W',n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_{j \neq i}}$$

$$\sum_j n_j d\mu_j = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \Delta_{\text{trs}} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -\Delta_{\text{trs}} S$$

$$P = P^* \exp\left(\frac{V_m \Delta P}{RT}\right)$$

$$\frac{dP}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}$$

$$\frac{d \ln P}{dT} \approx \frac{\Delta_{\text{trs}} H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{trs}} H}\right) x_B \quad \ln x_B = \frac{\Delta_{\text{fus}} H}{R} \left[\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right]$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln x + RT \ln \gamma$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln \frac{b}{b^\ominus} + RT \ln \gamma$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\Delta_{\text{solv}} G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{\frac{1}{p+q}}$$

$$\log \gamma_\pm = -|z_+ z_-| A \sqrt{I}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}$$

$$P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r} \quad P = \rho g h \quad w_{\text{ad}} = \gamma_{\text{sg}} + \gamma_{\text{lg}} - \gamma_{\text{sl}} \quad \gamma_{\text{sg}} = \gamma_{\text{sl}} + \gamma_{\text{lg}} \cos \Theta_c$$

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

## Appendix E

### Subjects treated in the first year course Thermodynamics.

In the course Thermodynamics (2022) parts from Part 1 (Equilibrium) of Atkins have been treated. In addition a few subjects treated can be found in the Study Guide to Thermodynamics

(<http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html>).

For the course of 2023 see <https://dullenslab.com/teaching/> .

Week	Sections ( <b>edition 11 Atkins</b> )	Subject
1	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
2	3A + 3B + 3D1 + 3E2a-c + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
3	SG14-18 + 5A1b-c + 5B + 5F1-2	Chemical Potential, Activity Mixtures, Colligative properties
4	2C + 3D2a + 6A + 6B	Thermochemistry, Chemical Equilibria $T, P$ -dependence equilibria
5	6C1-3 + 6D(p.224)	Electrochemistry, Standard Potential, Nernst-equation
6	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
7	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

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

Week	Sections ( <b>edition 10 Atkins</b> )	Subject
1	1A + 1C + 2A + 2B (+ 2E) + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
2	3A + 3C1 + 3D2a-c + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
3	SG14-18 + 5A1b-c + 5B + 5E1-2	Chemical Potential, Activity Mixtures, Colligative properties
4	2C + 3C2a + 6A + 6B	Thermochemistry, Chemical Equilibria $T, P$ -dependence equilibria
5	6C1-3 + 6D(p.267)	Electrochemistry, Standard Potential, Nernst-equation
6	3A3 + SG19-22	Second Law of Thermodynamics, Efficiency
7	3B + 3C + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

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

Week	Sections ( <b>edition 9 Atkins</b> )	Subject
1	1.1 - 1.4 + 2.1 - 2.6 + SG4-8	Gases, First Law of Thermodynamics, Reversible processes
2	3.1 - 3.3a + 3.5 + 3.9 + SG9-13	Entropy, Second Law of Thermodynamics Free energy, Irreversible processes
3	SG14-18 + 5.1b-c + 5.5 - 5.6	Chemical Potential, Activity Mixtures, Colligative properties
4	2.7 - 2.9 + 3.6 + 6.1 - 6.4	Thermochemistry, Chemical Equilibria $T, P$ -dependence equilibria
5	6.5 - 6.8	Electrochemistry, Standard Potential, Nernst-equation
6	3.2 + SG19-22	Second Law of Thermodynamics, Efficiency
7	3.3 - 3.4 + SG23-26	Statistical Thermodynamics, Boltzmann equation and entropy

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