

PC1 PVK FS20

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# 1 Thermodynamic basics

## Systems: isolated, closed, open

We distinguish isolated, closed and open system. Note that closed systems allow energy flows (work or heat).

System type	can be transferred	cannot be transferred
Isolated	-	energy, mass
Closed	energy (work and/or heat)	mass
Open	energy, mass	-

## Equilibrium

A system is at equilibrium if its state does not change anymore over time.

**Exercise 1.** (2018-2, 1a) Describe equilibrium in words.

**Exercise 2.** How do two systems equilibrate that are connected via a moveable wall that is impermeable to heat?

## Transformations

**Types** We distinguish isothermal, isochoric, isobaric and adiabatic processes.

Condition	mathematically
Isothermal	$dT = 0$
Isochoric	$dV = 0$
Isobaric	$dp = 0$
Adiabatic	$q = 0$

**Reversibility & irreversibility** reversible processes are performed slowly and can be reversed in any step. Irreversible processes are the opposite of reversible processes.

## Sign convention for energies

I used to find sign conventions so confusing that it hindered me to properly understand things like the Carnot cycle, where energies seems to be arbitrarily negative/positive, sometimes they had a minus, sometimes they didn't. Let me try to make this clear for you.

The takeaway is:

*Energy is positive if the system receives energy. Energy is negative if the system loses energy.*

My experience is that this is easier said than understood. It is important to properly identify the system of interest since the signs of all energies depend on which system is of interest.

How to read or draw a diagram according to Barnes rules?

- a) Draw all parts of the setting: system, machines, heat reservoirs.
- b) Connect all parts of the settings where energy heat is transferred without an arrow. If any of the parts receives or loses energy in the form of work draw a line without arrow away from the respective part.
- c) Think about which direction the energy flows. Does the heat flow into the system or out of it? Does the system do work (energy flows away from the system) or is work done on the system (energy flows into the system)? Draw an arrow in the direction of the energy flow.
- d) Annotate the lines with the name of the heat or work. Use a minus if the heat or work is negative, i.e. if the energy flows out of the system.

**Exercise 3.** Draw a diagram for a machine that extracts heat from a warm reservoir and uses this heat to do work on the environment and put heat into a colder reservoir.

## 2 Work

- Work is useful energy (in contrast to heat that is energy that is not useful). Useful energy means that this energy can be used for things humans would want to use energy for, e.g. to drive a car, to power a fabric etc.
- In principle, there can be many types of work, see table. Our main focus will be volume/pressure and chemical work. Volume/pressure is the work that powers cars, chemical work powers chemical reactions.

Work name	force	coordinate	expression
Pressure/volume work	$-p$	$dV$	$-p dV$
Chemical work	$\mu$	$dn$	$\mu dn$
Magnetic work	$H$	$dM$	$H dM$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

- Barnes usually refers by work only to volume/pressure work. The expression is given by

$$\delta w = -p_{\text{ext}} dV.$$

- $p_{\text{ext}}$  is the pressure of the surrounding (draw sketch with system + surrounding and  $p_{\text{int}}, p_{\text{ext}}$ ). idea: system has to press against this pressure or is pressed by this pressure

- important:  $p_{\text{ext}} = p_{\text{int}}$  in reversible processes. useful because we often know how to compute  $p_{\text{int}}$ , e.g. ideal gas

$$\delta w_{\text{rev}} = -p_{\text{ext}} dV = -p_{\text{int}} dV$$

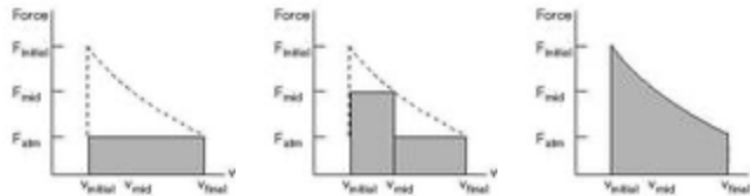
- in computation questions always finite quantities: infinitesimal  $\rightarrow$  finite

$$w = \int \delta w = - \int p_{\text{ext}} dV$$

if  $p_{\text{ext}}$  is not a function of  $V$ , then  $w = -p_{\text{ext}} \int dV = -p_{\text{ext}} \Delta V$ . if  $p_{\text{ext}}$  is a function of  $V$ , then  $w = - \int p_{\text{ext}}(V) dV$

draw two sketches: integral

- work are energies associated with processes, not with a system
- reversible processes extract the most work from the system



**Exercise 1.** Describe the concept of work in words and using a mathematical equation.

**Exercise 2.** Consider an (ideal) gas initially at pressure  $p_0$  and volume  $V_0$ . The gas now expands against its surrounding that is at constant pressure  $p$ .

- Draw a  $pV$ -plot and qualitatively indicate the process from the gas' initial to its final state.
- Indicate in your plot the work done by the system.
- How would you change the process so that the system can perform the most work? Indicate also the maximal work possible in your plot.

**Exercise 3.** (2017-1, 1n) A chemical reaction takes place in a container of cross-sectional area  $60.0 \text{ cm}^2$ . As a result of the reaction, a piston is pushed out through  $15.0 \text{ cm}$  against an external pressure of  $121 \text{ kPa}$ . Calculate the work done by the system.

**Exercise 4.** (2014-1, 1e) Derive the expression for the maximum work that can be extracted from an isothermal process (assume a monatomic ideal gas).

**Exercise 5.** (2015-1, 2e; 2016-1, 2d) Derive the equation for the maximum work extracted from an isothermal expansion of a van der Waals gas from  $V_1$  to  $V_2$ . The van der Waals equation of state is

$$\left( p + \frac{an^2}{V^2} \right) \left( \frac{V}{n} - b \right) = RT$$

### 3 Equations of states

$$pV = nRT \quad (\text{ideal gas})$$

$$\left(p + \frac{an^2}{V^2}\right) \left(\frac{V}{n} - b\right) = RT \quad (\text{van der Waals gas})$$

The van der Waals gas is a generalization of the ideal gas by the following corrections:

- Volume correction: Ideal gases assume gas molecules to be point particles that do not take up any volume. Real gases require a finite volume and thus the effective volume is reduced by a constant factor  $b$ , i.e.  $V/n \rightarrow V/n - b$ .
- Pressure correction: Ideal gas molecules are assumed to not interact. Molecules in real gases experience attractive or repulsive interactions among each other that lead to higher/lower pressure.

**Exercise 1.** Explain how to derive the van-der-Waal's equation of state from the ideal gas law.

### 4 Zeroth law of thermodynamics: temperature

If two systems A and B are at thermal equilibrium, i.e. have the same temperature, and systems B and C are at thermal equilibrium, then by the 0th law of thermodynamics, systems A and C are at thermal equilibrium.

**Exercise 1.** (2017-1, 1j; 2018-1, 1m; 2018-2, 1g) How can you experimentally determine the ideal gas constant,  $R$ ? Use a graphical plot of temperature to explain. (Hint, you may find the definition of Boyle's law on the equation sheet useful). In your experiment, what are the units of  $R$ ?

**Exercise 2.** (2014-1, 2f) Now, also show how you can derive the Ideal gas law from Boyle's law. Use a graphical plot of temperature to explain. (Hint, you may find the definition of Boyle's law on the equation sheet useful).

### 5 First law of thermodynamics: energy conversion

#### First law of thermodynamics

- The internal energy of a system,  $U$ , can change due to transferred heat,  $q$ , or by work,  $w$ , (volume work, chemical work, etc).
- The internal energy is an exact differential

$$\oint dU = 0.$$

For isolated, closed, open system, the first law can be stated as:

$$dU = 0 \quad (\text{Isolated})$$

$$dU = \delta q + \delta w \quad (\text{Closed})$$

$$dU = \delta q + \delta w + \sum_i \mu dn_i \quad (\text{Open})$$

Why is that a useful law? The first law forbids energy production. It says that energy can only be *converted*, not *produced*.

- a) The first part says that if the internal energy does change, then energy must have been transferred onto or away from the system. It further specifies that the two kinds of energies that could lead to a change in internal energy are heat and work.
- b) The internal energy  $U$  must be a state function, because otherwise we could design a perpetuum mobile. Imagine two thermodynamic states  $A, B$  are connected by two paths, 1 and 2, that change the internal energy differently,  $\Delta U_{A \rightarrow B,1} > \Delta U_{A \rightarrow B,2}$ . We could then first go from  $A$  to  $B$  using path 1 and then back from  $B$  to  $A$  using path 2. In total we would have gained the energy

$$\begin{aligned} \Delta U &= \Delta U_{A \rightarrow B,1} + \Delta U_{B \rightarrow A,2} \\ &= \Delta U_{A \rightarrow B,1} - \Delta U_{A \rightarrow B,2} > 0. \end{aligned}$$

If we continued to run this cycle we could be able to create infinite amounts of energy. This cannot be.

**Exercise 1.** (2018-1, 1a) State the first law of thermodynamics in words.

**Solution** The first law states that the change in internal energy of a system is equal to the sum of the work done on/by the system and the heat exchanged.

The first law states that the total energy of the system and its surroundings (the Universe), or an isolated system is constant.

**Exercise 2.** Formulate the first law of thermodynamics for isolated, closed and open systems.

**Exercise 3.** You and your friend are discussing a thermodynamic system. Your favorite transformation is from state  $A$  to state  $B$  with change in internal energy  $\Delta U_{A \rightarrow B}$ , but unfortunately this transformation is irreversible. Your friend claims it is advantageous to first change the state from  $A$  to  $C$  and only then to  $B$  such that the entire process can be done reversibly and thus  $\Delta U_{A \rightarrow C \rightarrow B} > \Delta U_{A \rightarrow B}$ . Discuss.

**Solution** It cannot be that  $\Delta U_{A \rightarrow C \rightarrow B} > \Delta U_{A \rightarrow B}$  since  $U$  is a state function.

**Exercise 4.** Why must the internal energy be a state function? Assuming internal energy not a state function, construct a perpetuum mobile.



**Solution** See construction above.

**Exercise 5.** At ETH Honggerberg we are 523 meters above sea level. Is the height above sea level with respect to coordinates a state function? Argue.

**Solution** Yes, height is a state function. For the height above sea level at a position, it does not matter which path you take to reach that position.

## 6 Heat & heat capacities

- definition of heat and heat capacities

Process		Heat	
Isochoric	$dV = 0$	$\delta q := C_V dT$	$q = C_V \Delta T$
Isobaric	$dp = 0$	$\delta q := C_p dT$	$q = C_p \Delta T$
Adiabatic	$\delta q = 0$	$\delta q := 0$	$q = 0$
Isothermal	$dT = 0$	no definition	

- connection between capacities for ideal gases

$$C_p - C_V = nR$$

- same heat  $q$  different  $\Delta T$

$$\Delta T = \frac{q}{C_V} \quad (\text{isochoric})$$

$$\Delta T = \frac{q}{C_p} = \frac{q}{C_V + R} < \frac{q}{C_V} \quad (\text{isobaric})$$

reason:  $dV = 0$ : no work done,  $dp = 0$ : work must be done

- monoatomic of freedom  $f$

$$C_V = \frac{f}{2}nR, \quad C_p = \left(1 + \frac{f}{2}\right)nR$$

- in terms of degrees of freedom  $f$

$$C_V = \frac{f}{2}nR, \quad C_p = \left(1 + \frac{f}{2}\right)nR$$

- degrees of freedom = translational + rotational + vibrational

$$f = 3 \quad (\text{monoatomic})$$

$$f = \begin{cases} 3 & 0 \text{ K} < T < \sim 100 \text{ K} \\ 3 + 2 & \sim 100 \text{ K} < T < \sim 1500 \text{ K} \\ 3 + 2 + 2 & \sim 1500 \text{ K} < T \end{cases} \quad (\text{diatomic})$$

**Exercise 1.** Define heat for isochoric, isobaric and adiabatic processes.

**Exercise 2.** (2015-1, 1d; 2016-1, 1d) Using words, mathematical notation, and a figure of a piston, explain why for gases  $C_p$  is always larger than  $C_V$ .

**Exercise 3.** (2017-1, 2d) Derive  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$  using the 1st law at constant pressure and an equation that relates heat transferred at constant pressure, heat capacity at constant pressure, and the temperature rise of a system.

**Exercise 4.** (2015-1, 3c; 2018-1, 5b) What is the value of  $C_V$  in units of  $R$ ? Justify your answer with words, including “translational degrees of freedom”, “rotational degrees of freedom”, and “vibrational degrees of freedom”. (Recall: Take the gas to be  $N_2(g)$  between 100 and 200 Kelvin to make any appropriate approximations of the heat capacity.)

**Exercise 5.** (2017-1, 1k) What is  $C_V$  of diatomic Oxygen at 200 Kelvin (in units of  $R$ )?

**Exercise 6.** (2017-1, 1m) What is  $C_v$  of monatomic Helium at 200 Kelvin (in units of  $R$ )?

## 7 Enthalpy

Enthalpy: like internal energy, but more suitable for pressure, not volume

$$\delta q = dU + p dV = dU + p dV + V dp = d(U + pV) = dH$$

**Exercise 1.** (2015-2, 1d) Explain the difference between internal energy and enthalpy. Use at least one full sentence and one equation. Is enthalpy a state function?

**Exercise 2.** (2017-1, 2a; 2018-1, 2a) Derive Enthalpy using the 1st law at constant pressure and an equation that relates heat transferred at constant pressure, heat capacity at constant pressure, and the temperature rise of a system.

## 8 Thermodynamic processes

### 8.1 Typical assumptions

**Ideal gas** This is the single coolest assumption you can be given. It means that the ideal gas law holds

$$pV = nRT.$$

This has a cool list of consequences:

- $d(pV) = d(nRT) = nR dT$ . For example, in isothermal processes ( $dT = 0$ ) any  $pV$  correction like in the enthalpy will drop out.
- For monoatomic gases,  $C_V = \frac{3}{2}nR$  and  $C_p = \frac{5}{2}nR$

- $C_p - C_V = nR$ . This is useful to rewrite  $C_p$  and  $C_V$ . For example, enthalpy is defined as  $H = U + pV$ . In an isochoric ( $dV = 0$ ) process,  $U = q = C_V dT$  (see table below) and thus  $dH = d(U + pV) = C_V dT + d(pV)$ . Using  $d(pV) = d(nRT)$  from above, we get  $dH = (C_V + nR) dT$  and because  $C_V + nR = C_p$  we get  $dH = C_p dT$ .
- For ideal gases, the inner energy,  $U$ , is only a function of temperature,  $U = U(T)$ . This means that in isothermal processes ( $dT = 0$ ) the inner energy of an ideal gas never changes, i.e.  $dU = 0$ .
- For adiabatic processes, the adiabat equations holds

$$pV^\gamma = \text{const.} \quad TV^{\gamma-1} = \text{const.} \quad p^{1-\gamma}T^\gamma = \text{const.}$$

**Reversible**,  $p_{\text{ext}} = p_{\text{int}}$  Reversible processes also have some cool consequences:

- $p_{\text{ext}} = p_{\text{int}}$ . This allows us to compute work

$$w = \int \delta w = \int_{V_1}^{V_2} p_{\text{ext}} dV = \int_{V_1}^{V_2} p_{\text{int}} dV$$

at constant temperature and number of particles if we know the pressure of the interior. This is the case if we can additionally assume an ideal gas (see above) or a van der Waals gas,

$$p = \frac{nRT}{V}, \quad (\text{ideal gas})$$

$$p = \frac{R}{\bar{V} - b} - \frac{a}{\bar{V}^2}, \quad (\text{van der Waals gas})$$

with  $\bar{V} = V/n$ .

- It holds that  $dS = \frac{\delta q}{T}$ . In general this does not hold. In isolated systems even  $dS = 0$ .

**Constant external pressure**,  $p_{\text{ext}} = \text{const}$  This is useful in irreversible processes.

Using this assumption you can compute the work of the process

$$w = \int \delta w = - \int_{V_1}^{V_2} p_{\text{ext}} dV \stackrel{p_{\text{ext}} = \text{const}}{=} -p_{\text{ext}} \int_{V_1}^{V_2} dV = -p_{\text{ext}}(V_2 - V_1).$$

**$C_V, C_p$  independent of  $T$**  This assumption is often not stated explicitly, but most of the time you require this assumption to calculate heat. Using the definition of the heat capacities we can compute heat

$$q = \int_{T_1}^{T_2} C_V(T) dT \quad (\text{constant volume})$$

$$q = \int_{T_1}^{T_2} C_p(T) dT \quad (\text{constant pressure})$$

If the heat capacities are independent of temperature, these integrals simplify

$$q = \int_{T_1}^{T_2} C_V dT = C_V \Delta T \quad (\text{constant volume})$$

$$q = \int_{T_1}^{T_2} C_p dT = C_p \Delta T \quad (\text{constant pressure})$$

## 8.2 Adiabatic processes

In an adiabatic process, all three quantities  $V, T, p$  change. This makes it hard to compute energies in adiabatic processes. However, combinations of  $V, T, p$  can remain constant. For an ideal gas, the conditions are

$$pV^\gamma = \text{const.} \quad TV^{\gamma-1} = \text{const.} \quad p^{1-\gamma}T^\gamma = \text{const.}$$

The heat capacity ratio is defined as  $\gamma = \frac{C_p}{C_v}$ .

Adiabats are steeper than isotherms

$$\begin{aligned} \text{Isotherm :} & \quad p \propto \frac{1}{V} \\ \text{Adiabat :} & \quad p \propto \frac{1}{V^\gamma}, \gamma > 1 \end{aligned}$$

### 8.3 Overview ideal processes

<b>Isothermal</b>	$dT = 0$	ideal	
Energy	$dU = \delta q + \delta w$	$U = U(T) \Rightarrow dU = 0$	$\Delta U = 0$
Work	$\delta w = -p_{\text{ext}} dV$		$w = ?$
Heat	$\delta q = -\delta w$		$q = ?$
Enthalpy	$dH = d(U + pV)$	$d(pV) = d(nRT) = 0$	$\Delta H = 0$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = -\frac{\delta w_{\text{rev}}}{T}$	$dS = \frac{nR}{V} dV$	$\Delta S = nR \ln \frac{V_f}{V_i}$
<b>Isochoric</b>	$dV = 0$		
Work	$\delta w = -p_{\text{ext}} dV = 0$		$w = 0$
Heat	$\delta q = C_V dT$		$q = C_V \Delta T$
Energy	$dU = \delta q + \delta w$ $= \delta q = dq$		$\Delta U = C_V \Delta T$
Enthalpy	$dH = d(U + pV)$ $= C_V dT + d(pV)$	$d(pV) = d(nRT)$ $C_p = C_V + nR$	$\Delta H = C_p \Delta T$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{C_V}{T} dT$		$\Delta S = C_V \ln \frac{T_f}{T_i}$
<b>Isobaric</b>	$dp = 0$		
Work	$\delta w = -p dV$		$w = -p \Delta V$
Heat	$\delta q = C_p dT = dq$		$q = C_p \Delta T$
Enthalpy	$dH = \delta q + \delta w + p dV$ $= \delta q = dq$		$\Delta H = C_p \Delta T$
Energy	$dU = d(H - pV)$ $= C_p dT + d(pV)$	$d(pV) = d(nRT)$ $C_V = C_p - nR$	$\Delta U = C_V \Delta T$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{C_p}{T} dT$		$\Delta S = C_p \ln \frac{T_f}{T_i}$
<b>Adiabatic</b>	$\delta q = 0$		
Heat	$\delta q = 0$		$q = 0$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = -\frac{\delta w_{\text{rev}}}{T}$	$dS = \frac{nR}{V} dV$	$\Delta S = nR \ln \frac{V_f}{V_i}$
Work	$\delta w = -p_{\text{ext}} dV$		$w = ?$
Energy	$dU = \delta w = dw$		$\Delta U \stackrel{?}{=} C_V \Delta T$
Enthalpy	$dH = V dp$		$\Delta H \stackrel{?}{=} C_p \Delta T$

## 8.4 Overview reversible ideal processes

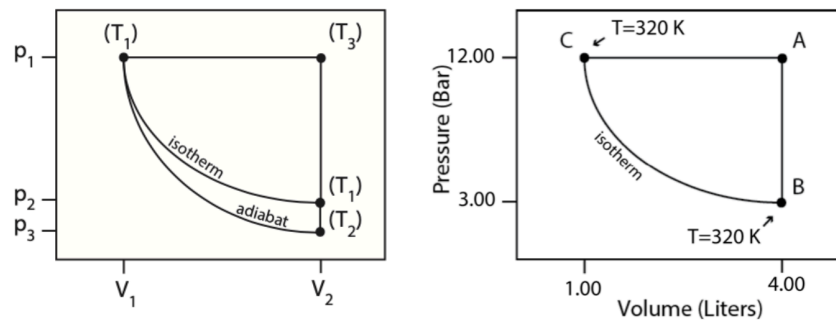
<b>Isothermal</b>	$d\mathbf{T} = \mathbf{0}$	ideal	
Energy	$dU = \delta q + \delta w$	$U = U(T) \Rightarrow dU = 0$	$\Delta U = 0$
Work	$\delta w = -p dV$	$\delta w = -\frac{nRT}{V} dV$	$w = -nRT \ln \frac{V_f}{V_i}$
Heat	$\delta q = -\delta w$		$q = nRT \ln \frac{V_f}{V_i}$
Enthalpy	$dH = d(U + pV)$	$d(pV) = d(nRT) = 0$	$\Delta H = 0$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = -\frac{\delta w}{T}$		$\Delta S = nR \ln \frac{V_f}{V_i}$
<hr/>			
<b>Isochoric</b>	$d\mathbf{V} = \mathbf{0}$		
Work	$\delta w = -p dV = 0$		$w = 0$
Heat	$\delta q = C_V dT$		$q = C_V \Delta T$
Energy	$dU = \delta q + \delta w$ $= \delta q = dq$		$\Delta U = C_V \Delta T$
Enthalpy	$dH = d(U + pV)$ $= C_V dT + d(pV)$	$d(pV) = d(nRT)$ $C_p = C_V + nR$	$\Delta H = C_p \Delta T$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{C_V}{T} dT$		$\Delta S = C_V \ln \frac{T_f}{T_i}$
<hr/>			
<b>Isobaric</b>	$d\mathbf{p} = \mathbf{0}$		
Work	$\delta w = -p dV$		$w = -p \Delta V$
Heat	$\delta q = C_p dT = dq$		$q = C_p \Delta T$
Enthalpy	$dH = \delta q + \delta w + p dV$ $= \delta q = dq$		$\Delta H = C_p \Delta T$
Energy	$dU = d(H - pV)$ $= C_p dT + d(pV)$	$d(pV) = d(nRT)$ $C_V = C_p - nR$	$\Delta U = C_V \Delta T$
Entropy	$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{C_p}{T} dT$		$\Delta S = C_p \ln \frac{T_f}{T_i}$
<hr/>			
<b>Adiabatic</b>	$\delta \mathbf{q} = \mathbf{0}$	$pV^\gamma = \text{const}$	
Heat	$\delta q = 0$		$q = 0$
Entropy	$dS = 0$		$\Delta S = 0$
Work	$\delta w = -p dV$	$\delta w = -p_i \left(\frac{V_i}{V}\right)^\gamma dV$ $\Delta(pV) = nR \Delta T$	$w = C_V \Delta T$
Energy	$dU = \delta w = dw$		$\Delta U = C_V \Delta T$
Enthalpy	$dH = V dp$	$V dp = V_0 \left(\frac{p_0}{p}\right)^{\frac{1}{\gamma}} dp$	$\Delta H = C_p \Delta T$

**Exercise 1.** (2017-1, 1e; 2018-1, 1j) How much heat is absorbed by an ideal gas expanding reversibly, and isothermally, from  $p_1, V_1$  to  $p_2, V_2$ ?

**Exercise 2.** (2017-1, 1d; 2018-1, 1i)

- What is the change in internal energy of an ideal gas after undergoing an isothermal reversible expansion from  $p_1, V_1$  to  $p_2, V_2$ ? What is the change in enthalpy of an ideal gas after undergoing an isothermal reversible expansion from  $p_1, V_1$  to  $p_2, V_2$ ?
- What is the change in internal energy and enthalpy of an ideal gas after undergoing an isothermal *irreversible* expansion from  $p_1, V_1$  to  $p_2, V_2$ ?

**Exercise 3.** (2016-1, 4; 2014-1, 4; 2015-1, 3; 2018-1, 5) The figure below shows reversible thermodynamic processes in  $pV$  space. Assume the gas is diatomic nitrogen, with a constant molar heat capacity at points A, B & C. Make any appropriate approximations of the heat capacity. However, assume this is a “perfect” gas, in that there are no intermolecular interactions and the gas behaves the ideal equation of state.



First, consider the left figure.

- From the paths shown on the left figure, indicate the thermodynamic cycle (with arrows) that would yield the most work output of the system. At which point would you start your cycle to output the most work?

Now consider the system depicted in the right figure.

- Calculate the amount of gas molecules (in moles) in the system of the right figure.
- Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for each of the three paths, and the total work around the closed path.
- How many cycles per minute of this heat engine would be required to power a 200 Watt propeller?
- Explain in words how you could physically implement each of the thermodynamic pathways of your engine.

- f) Explain in words how you could make your engine more efficient (increase your work output by decreasing your work input). Assume extra heating or cooling does not cost you anything. Also draw your new thermodynamic cycle on the PV diagram above. You can use new pathways for your new engine.

**Exercise 4.** (2017-1, 1c) Do ideal gases cool in adiabatic reversible expansions? Why or why not?

**Exercise 5.** (2015-2, 1e) An ideal gas at 298 K expands irreversibly against a vacuum and isothermally from an internal pressure of 10 bar to 1 bar. What are the values of  $w$  per mole,  $q$  per mole,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ?

**Exercise 6.** (2018-2, 4)

- a) Starting with  $dG = V dp - S dT$ , derive an expression for the change in Gibbs free energy of an ideal gas from changing the pressure from  $p = p^\circ$ , to  $p = p^*$  (while keeping temperature constant).
- b) Use your result to calculate the change in free energy when 0.75 moles of a ideal gas is reduced in pressure to 0.50 bar from 1.0 bar, while maintaining a temperature of 298 Kelvin.

## 9 Joule-Thompson and Joule free expansion

$$\eta_J := \left( \frac{\partial T}{\partial V} \right)_U \stackrel{\text{id gas}}{=} 0 \quad (\text{Joule coefficient})$$

$$\eta_{JT} := \left( \frac{\partial T}{\partial p} \right)_H = \frac{V}{C_p} (T\alpha - 1) \stackrel{\text{id gas}}{=} 0 \quad (\text{Joule-Thompson coefficient})$$

$$\left( \frac{\partial U}{\partial V} \right)_T = -C_V \left( \frac{\partial T}{\partial V} \right)_U = -C_V \eta_J,$$

$$\left( \frac{\partial H}{\partial p} \right)_T = -C_p \left( \frac{\partial T}{\partial p} \right)_H = -C_p \eta_{JT}$$

$$dU = C_V dT - C_V \eta_J dV$$

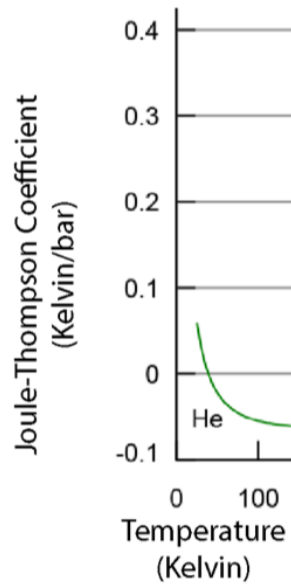
$$dH = C_p dT - C_p \eta_{JT} dp$$

**Exercise 1.** (2017-1, 1i) Explain the Joule-Thompson experiment using at least one figure. Calculate the change in enthalpy in the experiment by also calculating the total work done.

**Exercise 2.** (2017-1, 1b) Do gases always cool when they expand? Give examples to justify your answer.

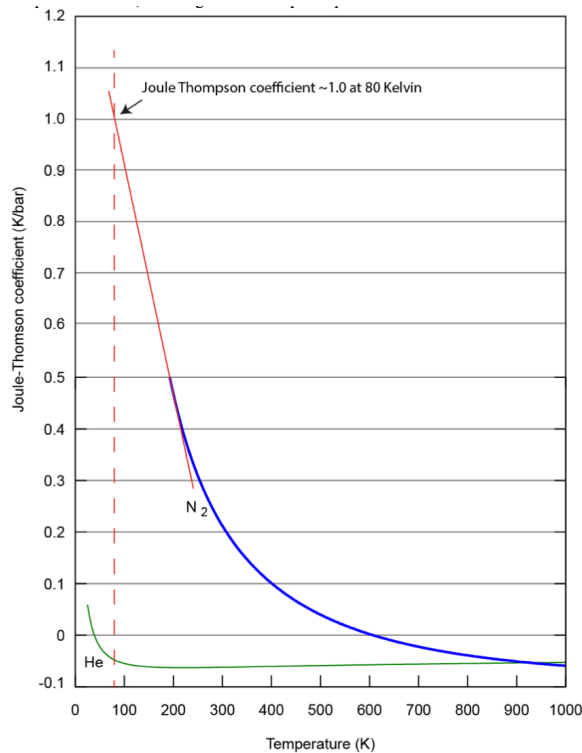
**Exercise 3.** (2016-1, 1h)





For the Joule-Thompson expansion shown above, calculate the temperature after expansion through a throttling nozzle (i.e. porous plug) for the following three initial temperatures of helium gas: 99 Kelvin, 47 Kelvin, and 9.0 Kelvin. The initial pressure was 17.9 bar, the final pressure 4.8 bar. Estimate whatever values you need to the best of your ability.

**Exercise 4.** The graph on the following page shows the Joule-Thompson coefficients of  $N_2(g)$  and  $He(g)$  as a function of temperature.



- a) If  $N_2(g)$  enters the bearing at 79.4 Kelvin and 3.0 bar, what is the temperature of the  $N_2(g)$  after it has expanded to 1.0 bar? Why might this lead to unstable

spinning and crashing of the rotor? Use a first order approximation to estimate the Joule-Thompson coefficient of N<sub>2</sub>(g) at 79.4 Kelvin (hint: notecards have straight edges that can be used to extrapolate curves). Show your work on the graph and the space provided below.

- b) Use  $\frac{a}{RT} - b = \mu_{JT}$  and the mathematical definition of the Joule Thompson coefficient to explain why Helium gas cools upon expansion < 43 Kelvin, but heats upon expansion > 43 Kelvin. Use words and equations in your answer and discuss intermolecular interactions.

**Exercise 5.** (2018-1, 4a)

- a) Calculate the change in enthalpy for one mole of a real gas expanding in a Joule-Thompson experiment by also calculating the work done on the first and the second piston. Take  $p_1 = 51$  bar,  $V_1 = 51$  L and  $p_2 = 12.8$  bar,  $V_2 = 204$  L. Although this is real gas, assume  $pV = ZnRT$  is valid, with  $Z = 1.002$ . Calculate the Joule-Thompson coefficient of the gas.
- b) Explain why we can calculate the enthalpy change, even though the Joule-Thompson experiment is an irreversible process. In your explanation use a diagram (figure) of the experiment.

## 10 Thermodynamic potentials

### 10.1 Fundamental equations

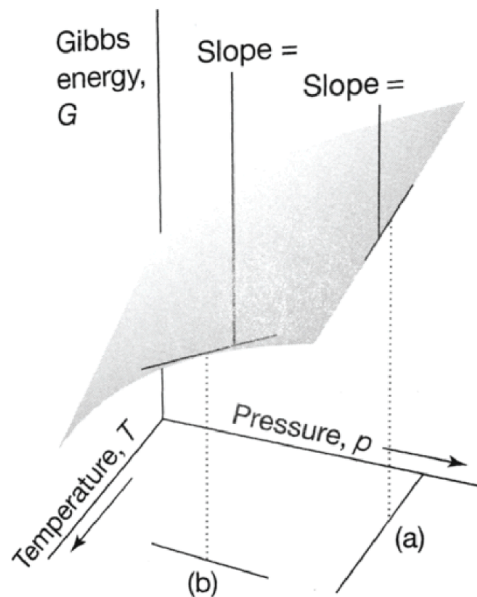
$$\begin{aligned}
 S &= S(U, V, n) = \frac{1}{T}(U + pV - \sum_i \mu_i n_i), & dS &= \frac{1}{T} dU + \frac{p}{T} dV - \frac{1}{T} \sum_i \mu_i dn_i \\
 U &= U(S, V, n) = TS - pV + \sum_i \mu_i n_i, & dU &= T dS - p dV + \sum_i \mu_i dn_i \\
 H &= H(S, p, n) = U + pV = TS + \sum_i \mu_i n_i, & dH &= T dS + V dp + \sum_i \mu_i dn_i \\
 A &= A(T, V, n) = U - TS = -pV + \sum_i \mu_i n_i, & dA &= -S dT - p dV + \sum_i \mu_i dn_i \\
 G &= G(T, p, n) = A + pV = \sum_i \mu_i n_i, & dG &= -S dT + V dp + \sum_i \mu_i dn_i
 \end{aligned}$$

Statement	condition	in words
$dU = \delta q = T dS$	$dV = 0, dn_i = 0$	internal energy = heat
$dH = \delta q = T dS$	$dp = 0, dn_i = 0$	Enthalpy = heat
$dU = \delta w = -p dV$	$dS = 0, dn_i = 0$	internal energy = work = useful energy
$dA = \delta w = -p dV$	$dT = 0, dn_i = 0$	Free energy = work ("free" energy)
$dG = \sum_i \mu_i dn_i$	$dT = 0, dp = 0$	Gibbs free energy = chemical work
$dA = \sum_i \mu_i dn_i$	$dT = 0, dV = 0$	Free energy = chemical work

**Exercise 1.** (2015-2, 2d) Assume a closed system ( $dn = 0$  for all components). Given the mathematical expressions for the 1st and 2nd law, derive the fundamental equation for  $dU$ . What is the fundamental equation for  $dU$  in open systems?

**Exercise 2.** (2015-2, 2e) Using the fundamental equation for  $dU$  and  $A = U - TS$  derive the fundamental equation for  $dA$  without chemical potentials.

**Exercise 3.** (2018-2, 1f) What are the slopes indicated below in terms of a single macroscopic thermodynamic variable (no derivatives) in the plot of Gibbs Free Energy below? Macroscopic thermodynamic variables are  $T, V, p, C_p, C_V, U, S, H, A, G$ .



**Exercise 4.** (2015-2, 4)

- In the recent study, “B2-Adrenergic Receptor Activation by Agonists Studied with 19F NMR Spectroscopy”, the authors find two molecular conformations with the same value of Gibbs Free Energy. If a sample of  $10 \cdot 10^{17}$  of these proteins is initially ALL in one of the two conformations was allowed to equilibrate at constant pressure and temperature, what would be the number of molecules in each state at equilibrium.
- Would this process be reversible or irreversible? Justify your answer using a mathematical statement of the 2nd law and full sentences.

## 10.2 Maxwell relations

General idea for  $dU = T dS - p dV$ : choose either T or p (intensive quantity), take derivative with respect to another extensive variable (not its conjugated one), do the same with the other intensive variable

The four most important Maxwell relations and shortcut using Guggenheim schema:

Maxwell's relations (common)		
$+\left(\frac{\partial T}{\partial V}\right)_S =$	$-\left(\frac{\partial P}{\partial S}\right)_V =$	$\frac{\partial^2 U}{\partial S \partial V}$
$+\left(\frac{\partial T}{\partial P}\right)_S =$	$+\left(\frac{\partial V}{\partial S}\right)_P =$	$\frac{\partial^2 H}{\partial S \partial P}$
$+\left(\frac{\partial S}{\partial V}\right)_T =$	$+\left(\frac{\partial P}{\partial T}\right)_V =$	$-\frac{\partial^2 F}{\partial T \partial V}$
$-\left(\frac{\partial S}{\partial P}\right)_T =$	$+\left(\frac{\partial V}{\partial T}\right)_P =$	$\frac{\partial^2 G}{\partial T \partial P}$

- S	U	V
H		F
- p	G	T

**Exercise 5.** Derive the Maxwell relation(s) from the fundamental relation of inner energy,  $dU$ , for

- closed systems,
- open systems.

**Exercise 6.** Derive a Maxwell relation for the following hypothetical thermodynamic state function  $\Psi$

$$d\Psi = \phi dH + \mu dG.$$

**Solution**

$$\left(\frac{\partial \phi}{\partial G}\right)_H = \frac{\partial^2 \Psi}{\partial G \partial H} = \frac{\partial^2 \Psi}{\partial H \partial G} = \left(\frac{\partial \mu}{\partial H}\right)_G$$

**Exercise 7.** (2015-2, 2b, c)

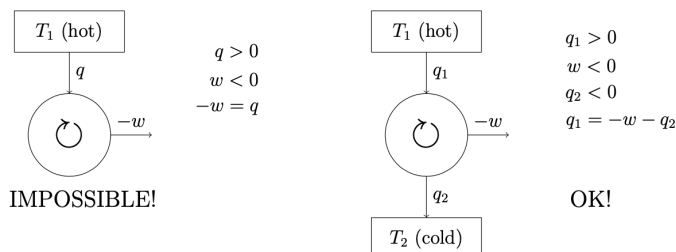
- Using a Maxwell Relation and starting with  $dU = T dS - p dV$ , prove that for an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

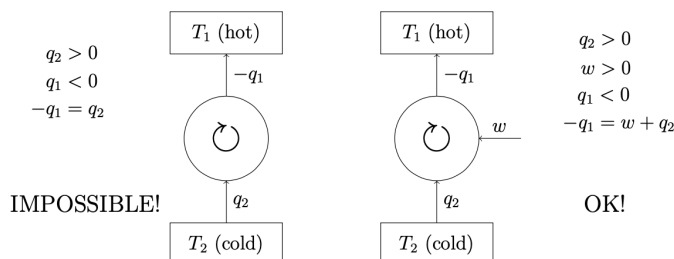
- Starting with the mixed partial derivatives of Free Energy, and a fundamental equation describing an infinitesimal change in Free Energy, derive the Maxwell Relation you used in 2b.

## 11 Second law of thermodynamics: entropy maximization

- Kelvin: "It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without at the same time transferring some heat to a colder reservoir."



- Clausius: "It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without at the same time converting some work to heat."



- Clausius: "All spontaneous processes are always irreversible."

**Exercise 1.** Explain Kelvin's and Clausius' statements of the second law of thermodynamics.

**Exercise 2.** Argue microscopically why only machines considered in Kelvin's statement of the second law of thermodynamics can exist, i.e. no machines that extract heat from one reservoir and convert it to work.

## 12 Heat engines & Carnot cycle

First step: we would like to build a heat engine that

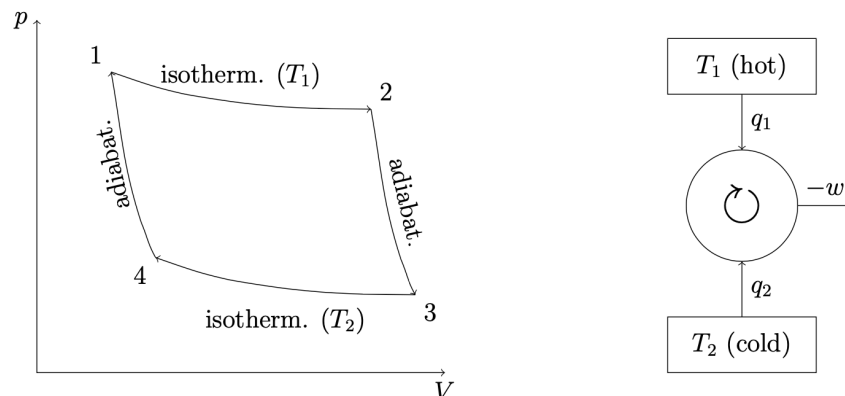
- can extract work from a heat reservoir. Why? We know how to create heat (e.g. burning coal, splitting atoms etc), but the only useful application of heat is to heat our houses, cars etc. We want to do more with energy, e.g. powering a elevator, and this usually requires directed energy. Work is exactly this kind of directed energy. We usually associate with work only volume expansion, but we could easily use work also as electrical work.

- runs in cycles such that after one cycle the machine is in the same state as initially. Why? Simply because only this way we can use the machine over and over again to extract work. If the state would change each cycle, it would be hard to predict how much energy can be extracted after many runs.

So, how to construct such a process?

- We need at least one hot thing, we call it heat reservoir, from which we can steal heat (phrased fancily "extract heat"). This should be intuitive. In practice we always use hot things to extract energy from.
- The second law now says that we cannot extract extract work from one heat reservoir alone and thus we need a second heat reservoir which the machine can put some heat into.
- So we need one process during which the machine takes up heat from the hot reservoir, and one process during which the machine releases heat into the cold reservoir. We also need a process that does work on the surrounding – the form of energy we aim for with the machine.
- A good choice for a process to take up heat and do work are isothermal expansions. Remember that ideal gases in isothermal expansions convert any heat that the gas takes up into work (i.e. the volume expansion).
- By symmetry, we can use an isothermal compression to release heat into the cold reservoir.
- We have to make our machine cyclic. It turns out that adiabats are a good choice to connect the initial and final states of the hot/ cold isothermal processes.

Voila, this is a Carnot machine. The two classic visualizations, a pV-diagram and a system diagram, look like this:



The work and heat for each process are listed in the table below.

$i \rightarrow j$	$\Delta U_{i \rightarrow j}$	$w_{i \rightarrow j}$	$q_{i \rightarrow j}$
$1 \rightarrow 2$	0	$w_1 < 0$	$q_1 = -w_1 > 0$
$2 \rightarrow 3$	$w'_1$	$w'_1 < 0$	0
$3 \rightarrow 4$	0	$w_2 > 0$	$q_2 = -w_2 < 0$
$4 \rightarrow 1$	$w'_2$	$w'_2 > 0$	0

The total work and change of inner energy are then sum of those

$$\begin{aligned}
 w_{\text{tot}} &:= w_1 + w'_1 + w_2 + w'_2, \\
 \Delta U_{\text{tot}} &= \Delta U_{1 \rightarrow 2} + \Delta U_{2 \rightarrow 3} + \Delta U_{3 \rightarrow 4} + \Delta U_{4 \rightarrow 1} \\
 &= q_1 + w_1 + w'_1 + q_2 + w_2 + w'_2 \\
 &= q_1 + q_2 + w_{\text{tot}}.
 \end{aligned}$$

Recall that the inner energy is a state function, thus  $\Delta U = 0$  or

$$-w_{\text{tot}} = q_1 + q_2.$$

The Carnot machine's efficiency is defined as the ratio of the work the machine can output and the heat it takes up from the hot reservoir

$$\epsilon = \frac{|w_{\text{tot}}|}{|q_1|} = \frac{-w_{\text{tot}}}{q_1}.$$

Note that this coefficient is denoted by an epsilon,  $\epsilon$ , and is distinct from the adiabatic coefficient,  $\gamma$ . Using above's result we can relate the ratio with the extracted heat

$$\epsilon = \frac{-w_{\text{tot}}}{q_1} = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}.$$

**Exercise 1.** (2015-2, 3b) Explain the second law of thermodynamics. In your explanation, include two reservoir/engine diagrams; one that follows the 2nd law, and another that violates the 2nd law. Using graphical plots of the occupation of energy levels, and the equation on Boltzmann's tomb, give a microscopic interpretation of why one of your engines follows the 2nd law, and the other violates it.

**Exercise 2.** (2015-2, 3; 2018-2, 3)

- Describe a reversible Carnot Cycle. Include a  $p$  vs.  $V$  diagram and  $S$  vs.  $T$  diagram in which you label and describe the four processes involved. Indicate the entropy change along each process and the total entropy change along the closed path. Also include a figure showing the heat, work, cycle, and temperature reservoirs. Include arrows on your reservoir diagram that indicate the flow of heat and work. Indicate if the heat is positive or negative (with respect to engine).
- Assume the hot reservoir is 350 Kelvin, and the cold reservoir is 105 Kelvin. If 250 Watts are extracted from the hot reservoir of your Carnot engine reversibly and in a cycle, how much work can be done on the surroundings per cycle?
- For the isothermal expansion in the Carnot cycle indicated in a), calculate or give expressions for  $w$  per mole,  $q$  per mole,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  (of the system) in terms of  $R$ ,  $T$ ,  $V_2$ ,  $V_1$ ?
- What is the entropy change of the surroundings after the reversible isothermal expansion in the Carnot cycle in terms of  $R$ ,  $T$ ,  $V_2$ ,  $V_1$ .
- Now take the isothermal expansion to be an irreversible process. Give an expression for the entropy change of the system in terms of  $R, T, V_2$  and  $V_1$ . Also give an expression for the entropy change of the surroundings in terms of  $R, T, V_2$  and  $V_1$ .
- Given for the Carnot cycle that  $\epsilon = 1 + \frac{q_2}{q_1}$  and

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1}, \quad \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

show that the maximum efficiency of a heat engine depends on the temperature of the two reservoirs as

$$\epsilon = 1 - \frac{T_2}{T_1}.$$

- Why can the Carnot cycle (or any other heat engine) not convert 100% of heat to work? Use a diagram of the occupation of quantized energy levels, and  $S = k \ln W$  in your answer.



## 13 Entropy

### 13.1 Entropy microscopically and macroscopically

You have learned about three definitions of entropy:

$$S = k_B \ln \Omega \quad (\text{Microscopic, Boltzmann})$$

$$S = -k_B \sum_i P_i \ln P_i \quad (\text{Microscopic, Gibbs})$$

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T} \quad (\text{Macroscopic})$$

**Exercise 1.** (2018-2, 1b) What are the units of entropy?

**Exercise 2.** (2015-1, 1h) Is it possible to have a negative entropy? Why or why not? Use the equation on Boltzmann's tomb to clarify.

**Exercise 3.** (ps3, ex1) Describe entropy by including the words/phrases: microstates, distribution, energy levels, occupation, configurations. You may use equations to clarify, but your explanation must be in complete sentences.

**Solution** Entropie ist eine statistische Entität, die den Zugriff eines Systems auf verschiedene Konfigurationen quantifiziert (Entartung mehrerer Konfigurationen). Für eine gegebene makroskopische Energie eines Systems können die möglichen Mikrozustände, die von seinen Teilchen besetzt sind, verwendet werden, um die Entropie mithilfe der folgenden Gleichung zu berechnen

$$S = - \sum_i P_i \ln P_i$$

wobei S die Entropie,  $k_B$  die Boltzmann-Konstante und  $P_i$  die Wahrscheinlichkeit ist, dass sich das System in einem bestimmten Mikrozustand  $i$  befindet. Laut der Boltzmann-Gleichung

$$S = k_B \ln \Omega$$

ist die Entropie eine Funktion der Entartung  $\Omega$  für ein isoliertes System, wobei die Entartung der Anzahl an Mikrozuständen mit der gleichen mittleren Energie entspricht. Ein Mikrozustand ist eine mögliche Verteilung der Teilchen des System auf die Energieniveaus, oder - mit anderen Worten - eine mögliche Konfiguration der Besetzung der Energieniveaus. Makroskopisch betrachtet ist die Entropie eine extensive Größe (sie variiert mit der Größe des Systems), die an die Temperatur konjugiert ist:

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$$

**Exercise 4.** When is Boltzmann's description of entropy,  $S = k_B \ln \Omega$ , valid?

**Solution** This description Of entropy is valid either when the system is isolated, thus the probability is equivalent to  $1/\Omega$  ( $1/Q$ ), or when the system is comprised

Of enough particles such that any fluctuations in the energy of the system are negligible. The crux of both cases is the fact that the energy of the system,  $E_i$ , is constant. We can then set it to zero, which takes all of our Boltzmann factors to 1, and thus the system's partition function (the sum of all those factors) now just becomes the sum of the number of degenerate states (states at our constant energy  $E_i$ ).

**Exercise 5.** (2015-2, 1a) Why does a human cell burst when it is placed in pure distilled water? Use the phrase, "distinguishable microscopic configurations" and the equation on Boltzmann's tomb in your answer.

**Solution** Outside the cell, only one species is present (H<sub>2</sub>O), but inside the cell, a wide variety of would increase the number of microstates less drastically. By putting a molecule of water inside the cell, one could vastly the cell - because of the wide variety of chemicals, more permutations are available. Compare this to putting a molecule mixing outside of the cell, where only one type of molecule is present - the added molecule would increase the number of microstates less drastically. So by transferring water into the cell (through a semipermeable membrane), the number of available microstates for the universe will go up, thus increasing entropy  $S = k_B \ln \Omega$ . The S increase is the entropy of mixing (this neglects the electrostatic, enthalpic contributions from water solvating salts or proteins, which also would lower  $\mu_{H_2O}$  within the cell).

**Exercise 6.** (2018-2, 1d) Starting with the 1st law and  $dU = C_V dT$ , prove mathematically (using cross derivatives) that reversible heat is not a state function, but entropy is.

## 13.2 Entropy and Clausius theorem

Clausius theorem can be confusing because of some subtleties. It states that for general processes

$$\oint \frac{\delta q}{T} \leq 0 \quad (\text{Clausius inequality})$$

and for reversible processes

$$\oint \frac{\delta q}{T} = 0. \quad (\text{Clausius for reversible})$$

In general, *the Clausius integral is not entropy*, i.e.

$$\Delta S \neq \oint \frac{\delta q}{T}.$$

Let me expand on this by explaining the major confusions with Clausius theorem.

- The heat  $\delta q$  could be due to an irreversible heat transfer. Recall that the definition of entropy,  $S = \int \delta q_{\text{rev}}/T$ , only applies to reversible heat flows. Only if  $\delta q = \delta q_{\text{rev}}$  the integral equals entropy.

- Note the difference between  $\oint$  and  $\int$ . An integral with  $\oint$  is closed, i.e. the integral begins and ends in the same state. Applied to our setting this means Clausius inequality only considers such processes which end in the same state they started with.
- Often, we split the closed integral  $\oint$  into two or more subprocesses. For example, we could begin in state 1, transfer the system to state 2 and then back to 1. In this case  $\oint = \int_1^2 + \int_2^1$ , i.e.

$$0 \geq \oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^1 \frac{\delta q}{T}.$$

A special case of Clausius' inequality states that

$$dS \geq \frac{\delta q_{\text{rev}}}{T}.$$

This equation can be derived from the above Clausius inequality (see the exercises below). This special case Clausius inequality is probably the most useful way to think about the second law of thermodynamics outside the realm of heat engines. The following table summarizes the second law expressed through the special case Clausius inequality.

Process / System	Isolated	Closed, open
Reversible	$dS = 0$	$dS = \frac{\delta q_{\text{rev}}}{T}$
Irreversible, spontaneous	$dS \geq 0$	$dS > \frac{\delta q_{\text{irrev}}}{T}$

This table allows us to determine if a process is reversible or spontaneous = irreversible.

**Exercise 7.** Explain Clausius' inequality using full sentences and at last one mathematical equation.

**Exercise 8.** Starting from the general Clausius inequality, show that

$$dS \geq \frac{\delta q_{\text{rev}}}{T}$$

by choosing reversible/ irreversible paths between two states.

**Exercise 9.** Using Clausius' inequality, state the second law of thermodynamics for isolated systems, closed and open systems.

**Solution** Combining the second with the first law of thermodynamics isolated, closed, open system, the second law can be stated as:

$$dS \geq 0 \quad (\text{Isolated})$$

$$dS \geq \frac{\delta q}{T} \implies 0 \geq dU - T dS + p dV \quad (\text{Closed})$$

$$dS \geq \frac{\delta q}{T} \implies 0 \geq dU - T dS + p dV - \sum_i \mu dn_i \quad (\text{Open})$$

**Exercise 10.** (ps6, ex7) A system undergoes a process in which the entropy change is  $+2.41 \text{ JK}^{-1}$ . During the process,  $1.00 \text{ kJ}$  of heat is added to the system at  $500 \text{ K}$ . Is the process thermodynamically reversible?

### 13.3 Computing entropy for system and surrounding

**Exercise 11.** (2018-2, 2f) Given that  $dS = \frac{\delta q_{\text{rev}}}{T}$  and  $dU = \delta q + \delta w$ , derive (and calculate) the entropy change of an ideal gas that undergoes an irreversible Joule free expansion from  $1$  to  $5$  liters at  $298 \text{ Kelvin}$ . Also calculate (do not derive)  $\Delta G$  for this expansion.

**Exercise 12.** (ps7, ex4) Consider an isolated system consisting of an ideal gas at  $298 \text{ K}$  and its surroundings. The ideal gas expands isothermally from a pressure of  $10 \text{ bar}$  to  $1 \text{ bar}$ . Compute associated changes enthalpy  $\Delta H$  and entropy  $\Delta S$  of the ideal gas. What will be the corresponding changes of these thermodynamic quantities in the surrounding, if you relate them to one mole of gas in the system? What will be the corresponding thermodynamic quantities for the whole isolated system ideal gas + its surrounding? Make your computations for the following three scenarios:

- The reversible expansion of an ideal gas.
- The irreversible expansion of an ideal gas against a constant external pressure of  $1 \text{ bar}$ .
- The irreversible expansion of an ideal gas against vacuum, which is blocked by a fixed wall at the new total volume that exceeds the initial volume of the ideal gas ten times (i.e. the gas pressure again changes from  $10 \text{ bar}$  to  $1 \text{ bar}$ ).

**Exercise 13.** (fs17, ps4, ex2) Bestimmen Sie für die folgenden Prozesse die ausgetauschte Arbeit und Wärmemenge zwischen System und Umgebung sowie die Entropieänderung des Systems und der Umgebung. Sie dürfen annehmen, dass sich die Gase ideal verhalten. Die molaren Wärmekapazitäten für ein einatomiges ideales Gas bei konstantem Volumen bzw. konstantem Druck sind

$$C_V = \frac{3}{2}R, \quad C_p = C_V + R = \frac{5}{2}R$$

- $1 \text{ mol Ne (g)}$  wird durch diathermanen Kontakt mit einem idealen Wärmereservoir mit  $T = 380 \text{ K}$  von  $350 \text{ K}$  auf  $T = 380 \text{ K}$  erhitzt. Während des Prozesses bleibt das Gasvolumen konstant.
- $1 \text{ mol Kr (g)}$  wird durch diathermanen Kontakt mit einem idealen Wärmereservoir mit  $T = 380 \text{ K}$  von  $350 \text{ K}$  auf  $T = 380 \text{ K}$  erhitzt. Während des Prozesses bleibt das Gasdruck konstant.

- c) 1 mol He (g) expandiert isotherm und reversibel zum vierfachen Volumen. Der Anfangsdruck beträgt 2 bar und das System ist in diathermanem Kontakt mit einem idealen Wärmereservoir mit  $T = 380$  K.
- d) 1 mol Kr (g) expandiert adiabatisch und reversibel zum vierfachen Volumen. Die Anfangstemperatur beträgt  $T = 380$  K.
- e) 1 mol Ne (g) expandiert isotherm zum vierfachen Volumen gegen einen Aussendruck von 0.5 bar. Der Anfangsdruck beträgt 2 bar und das System ist in diathermanem Kontakt mit einem idealen Wärmereservoir mit  $T = 380$  K.
- f) 1 mol He (g) expandiert adiabatisch ins Vakuum (Aussendruck  $p_a = 0$  bar) zum vierfachen Volumen.

**Exercise 14.** (hs16, exam, ex2) Wir betrachten das Gefrieren von 100 g unterkühltem Wasser bei der Temperatur  $T = 269$  K und dem konstanten Druck von  $p^\ominus = 1$  bar. Dabei gilt im Temperaturbereich zwischen  $-10^\circ\text{C}$  und  $0^\circ\text{C}$  für die Wärmekapazitäten von Wasser und Eis

$$C_p(\text{Eis}) = 38 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p(\text{Wasser}) = 75 \text{ J mol}^{-1} \text{ K}^{-1}$$

Die molare Schmelzenthalpie von Eis bei 273 K und 1 bar beträgt  $\Delta_m H^\ominus = 6026$  J/mol. Die Umgebung kann als ideales Wärmebad bei  $T = 269$  K betrachtet werden.

- a) Bestimmen Sie die Wärmemenge, die es braucht, um 100 g Eis und 100 g unterkühltes Wasser von 269 K auf 273 K zu erwärmen.
- b) Bestimmen Sie die entsprechenden Entropieänderungen.
- c) Wie gross ist die Entropieänderung des Wasser beim Gefrieren bei 269 K?
- d) Welche Wärmemenge wird beim Gefrieren des unterkühlten Wassers bei 269 K zwischen Wasser und Umgebung transferiert? Wird dabei die Wärme dem Wasser entzogen oder beigesteuert?
- e) Wie gross ist die Entropieänderung der Umgebung?
- f) Durch das Gefrieren des Wassers nimmt seine Entropie ab. Wieso läuft dieser Prozess trotzdem spontan ab?

### 13.4 Entropy of mixing

**Exercise 15.** Consider a system with two subsystems A and B separated by a wall. When you release the wall, the subsystems mix. Compute the entropy for the mixing.

**Exercise 16.** (2018-2, 5abc; 2015-2, 4)

- a) Using statistical thermodynamics (the translational partition function), calculate the entropy of mixing when  $n_a$  moles of gas starting in volume  $V_a$  mixes with  $n_b$  moles of gas in a volume  $V_b$ . Take  $N = N_a + N_b$  and  $V = V_a + V_b$ .
- b) Using classical thermodynamics (the 1st and 2nd laws), calculate the entropy of mixing when  $N_a$  moles of gas starting in volume  $V_a$  mixes with  $N_b$  moles of gas in a volume  $V_b$ . Take  $N = N_a + N_b$  and  $V = V_a + V_b$ .
- c) Describe the difference in the entropy of mixing if the calculation is performed from statistical thermodynamics (question a), or macroscopic thermodynamics (question b).

## 14 Third law of thermodynamics

- "Temperature of 0 K can never be reached"
- At hypothetical absolute zero Kelvin,  $S = 0$ .
- As  $T \rightarrow 0$ ,  $S \rightarrow 0$  for every chemically homogeneous substance in a perfect crystalline state.
- Infinite work is required to reach 0 Kelvin.

**Exercise 1.** (2018-2, 1e) Describe why is it impossible reach 0 Kelvin.

**Solution** As 0 Kelvin is approached asymptotically, the specific heat capacity approaches zero asymptotically as well, which prevents the expression:  $\Delta S = \int_{T_0}^{T_2} C_P dT$  from diverging. As  $C_p$  gets increasing small (which is observed experimentally), even a single photon from radiative heat transfer will then result in a substantial increase in temperature.

**Exercise 2.** (2014-1, 1c) Calculate the entropy for an atomically perfect crystalline lattice at 0 Kelvin.

## 15 Spontaneity of a process for various conditions

We have learned that at constant energy and volume the entropy of the universe always increases. The universe is an isolated system, i.e. has constant energy. Normally, we do not have conditions in which energy remains constant. For example, a chemical reaction in the lab is usually done at constant pressure and temperature. It turns out that our helper functions,  $U, H, A, G$ , help us to express a conditions for spontaneity at other conditions (i.e. other constant variables).

Combining the first law and the condition for spontaneity,  $dS > \delta q_{\text{irrev}}/T$ , we find the general condition for spontaneity

$$dU = \delta q_{\text{irrev}} - p dV < T dS - p dV.$$

At constant energy and volume, i.e.  $dU = 0, dV = 0$ , this general condition reduces to the known condition of positive entropy change  $dS > 0$ .

However, at  $dp = 0, dT = 0$  we can reformulate the condition

$$0 > dU - T dS + p dV = d(U - TS + pV) = dG.$$

At constant pressure and temperature the Gibbs free energy  $G$  is minimized.

The table below lists criteria of spontaneity for other conditions.

Constant	Criterion	Equation	At equilibrium...
$U, V$	$(dS)_{U,V} > 0$	$S = k_B \ln \Omega$	$S_{\text{sys}}$ is maximized
$S, V$	$(dU)_{S,V} < 0$	$dU = \delta q + \delta w$	$U_{\text{sys}}$ is maximized
$S, p$	$(dH)_{S,p} < 0$	$H = U + pV$	$H_{\text{sys}}$ is maximized
$T, V$	$(dA)_{T,V} < 0$	$A = U - TS$	$A_{\text{sys}}$ is maximized
$T, p$	$(dG)_{T,p} < 0$	$G = H - TS$	$G_{\text{sys}}$ is maximized

**Exercise 1.** (2018-2, 2a) From mathematical statements of the 1st and 2nd laws, derive the general criterion for a spontaneous process.

**Exercise 2.** (2018-2, 2b; 2015-2, 2a) From mathematical statements of the 1st and 2nd laws, derive the criterion for spontaneous change at constant pressure and temperature.

**Exercise 3.** (2018-2, 2c) Derive the criterion for spontaneity at constant entropy and volume. Does your result describe changes in the system or the surroundings? Explain why your result is a reflection of the change in entropy of the universe.

**Exercise 4.** (2015-2, 5a) Recent magic angle spinning NMR (MAS NMR) experiments performed in the chemistry department at WUSTL suggest activators of Protein Kinase C (PKC) could have multiple binding modes to PKC C1b regulatory domains. The MAS NMR data on a large ensemble of  $10 \times 10^{17}$  molecules show  $4.7 \times 10^{17}$  of the ligand molecules adopt a rigid conformation (left, in figure below), and  $5.3 \times 10^{17}$  are associated with the C1b domain, but are flexible (right, in figure below).

[A binding mode is defined as: The orientation of the ligand relative to the receptor as well as the conformation of the ligand and receptor when bound to each other.]

- Using the condition (equation) for a spontaneous process at constant volume and temperature, and the equation on Boltzmann's tombstone, describe how multiple bound conformations could contribute to tight binding (low value of  $K_d$ ).
- A hypothetical plot of the internal energy ( $U$ , not Free Energy) along the binding pathway is shown below. Indicate the rigid bound conformation with





## 16 States in statistical mechanics

Microstate: a distinguishable arrangement of the occupation of the quantized energy levels within the ensemble.

**Exercise 1.** Explain in complete sentences the concept of a state in statistical mechanics. What is the difference between micro- and macrostates? Provide an example for each.

## 17 Ergodic Hypothesis

*The time average of the energy or state for one molecule is equivalent to the ensemble average of many molecules at a given point in time.*

**Exercise 1.** (2017-1, 1f) State the Ergodic hypothesis in a complete sentence. Why is this postulate so fundamental to statistical mechanics?

**Exercise 2.** (2014-1, 1a) Describe why statistical mechanics is often referred to as the “bridge” between quantum mechanics and thermodynamics.

**Exercise 3.** (2018-1, 1h) Molecular dynamics simulations use classical equations of motion to describe molecular motion and structure. It is useful to describe the entropy determined from such calculations using Gibb’s equation of entropy in terms of microstate probabilities,

$$S = -k_B \sum_i P_i \ln P_i,$$

rather than Boltzmann’s equation in terms of system degeneracy. Using the words “ergodic hypothesis” and “sufficient sampling”, explain in words why very short molecular dynamics simulations can not fully describe molecular thermodynamics, but long simulations can.

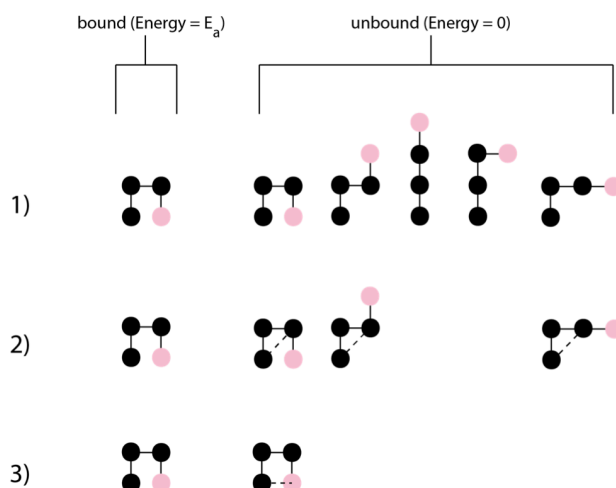
## 18 Boltzmann distribution

$$P_i(\epsilon_i) = \frac{\exp\left(-\frac{\epsilon_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)} = \frac{\exp\left(-\frac{\epsilon_i}{k_B T}\right)}{q}$$

**Exercise 1.** (2014-1, 2c ) Using the words, “degeneracy”, “configuration”, “microstates”, “occupation”, and “energy levels” explain the equation on Boltzmann’s tomb.

**Exercise 2.** (2014-1, 3) The figure below shows a simple model of how a drug (bryostatin, for example) could sample multiple configurations while it is not bound

to its protein target (Protein Kinase C, for example). Note, this is slightly different than what we covered in class, in that the drug can sample the “bound conformation = 3 dimensional structure”, while it is not bound. There is a favorable energy of interaction ( $E_{\text{int}}$ ) when the drug is in the bound conformation AND it is bound to the protein.



- Give an explicit expression for the probability of finding the drug bound to the protein in case 1) which has 5 unbound conformations.
- Now, assume we design a new drug with an additional covalent bond (dotted line) that restricts the conformational space, such as in case 2). Give an explicit expression for the probability of finding the drug bound to the protein in case 2).
- On the bottom right of the figure, draw the drug with a new covalent bond (dotted line) that would yield the highest fraction of bound drug.

**Exercise 3.** (2017-1, 3) Calculate the fractional occupations ( $N_i/N$ ) of the energy levels of a particle in a one-dimensional box at a temperature at which the population of the  $n=2$  level is 0.397 of the population of the  $n=1$  level. The energy levels of a particle in a one-dimensional box are nondegenerate. The relative energies of the levels can simply be taken as 1,4,9,16,25, .... (hint... you will want to first calculate the molecular partition function). (only first 5 energy levels).

**Exercise 4.** (2014-1, 1f) Calculate the relative population (i.e. relative probability  $P_{-1/2}/P_{1/2}$ ) of the  $1/2$  and  $-1/2$  NMR and EPR spin states at 10 K and 300 K to six significant digits. Take the frequency splitting to be 299.710 MHz for NMR and 197.574 GHz for EPR. Which of these four relative populations would yield the highest magnetic resonance sensitivity?

**Exercise 5.** (2015-1, 1e) The sensitivity of magnetic resonance is directly correlated to the relative difference in the population of spin states.

- a) Calculate the temperature at which the relative population of the 1/2 and -1/2 NMR spin states is 1.00093. Take the frequency splitting to be 125.286 MHz for NMR.
- b) Calculate the temperature at which the relative population of the 1/2 and -1/2 EPR spin states is 1.00093. Take the frequency splitting to be 198.457 GHz for EPR.

## 19 Partition functions

### 19.1 Molecular/ canonical partition function

$$q = \sum_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) \quad (\text{Molecular})$$

$$Q = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \quad (\text{Canonical})$$

Partition function is representative of number of accessible microstates if lowest energy is set to 0

From molecular to canonical partition function

$$Q = q^N \quad (\text{distinguishable})$$

$$Q = \frac{q^N}{N!} \approx \left(\frac{q\epsilon}{N}\right)^N \quad (\text{indistinguishable})$$

**Exercise 1.** (2016-1, 1g) For an isolated system, explain why the canonical partition function is the same as the system degeneracy if the zero of energy is taken to be equal to the system energy.

**Exercise 2.** (2016-1, 1e) If the zero of energy is chosen to be the ground electronic state, what is the value of the molecular electronic partition function of a hydrogen atom at room temperature? (calculation not required for full credit)

**Exercise 3.** (2016-1, 1f; 2018-1, 1b) What is the molecular partition function? What is the canonical partition function? Give your answers BOTH in complete sentences AND in mathematical notation (an equation). What is the difference between the molecular and canonical partition functions?

**Solution** The molecular partition function ( $q$ ) is the sum of all the non-normalized probabilities (Boltzman factors) for being in a given quantized energy state with an energy of  $\epsilon_i$ , and can be expressed as  $\sum_i \exp(-\epsilon_i/k_B T) = q$ . In general, assuming the same zero of energy, a larger molecular partition function indicates more available states or lower energy states, while a smaller molecular partition function indicates fewer available states or higher energy states. While the molecular partition function describes an individual particle, the canonical partition function ( $Q$ ) describes

how an assembly of particles is partitioned among its available energy states. The canonical partition function ( $Q$ ) is the sum of all the non-normalized probabilities (Boltzmann factors) for the assembly being in a given energy state with an energy of  $E_i$ , where  $E_i$  is the total energy for all particles in the assembly. It can be expressed as  $\sum_i \exp(-E_i/k_B T) = Q$ . All partition functions are unitless numbers. All partition functions normalize Boltzmann factors into probabilities. The canonical partition function is particularly crucial to understanding statistical mechanics, and can be used to derive many thermodynamic expressions and values.

**Exercise 4.** (2018-1, 1cd)

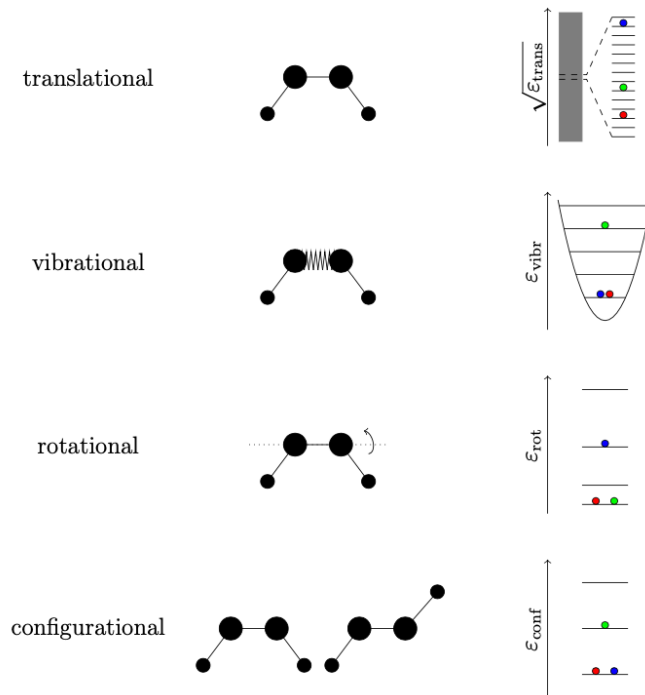
a) Describe the following quantities in words:

$$\frac{e^{-\epsilon_i/kT}}{q} \quad \text{and} \quad \frac{e^{-E_i/kT}}{Q}.$$

b) When are the two quantities from above equal?

$$\frac{e^{-\epsilon_i/kT}}{q} = \frac{e^{-E_i/kT}}{Q}.$$

**19.2 Degrees of freedom: trans, vib, rot, conf, electronic**



dof	energy $\epsilon_i$	$\epsilon_i/k_B T$	partition function $q$	energy $U$
trans. 1d	$\frac{\hbar^2 n^2}{8ma^2}$	$\ll 1$	$\left(\frac{2\pi mk_B T}{h^2}\right)^{1/2} a$	
trans. 3d	$\frac{\hbar^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$	$\ll 1$	$\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V$	$\frac{3}{2}nRT$
NMR	$\gamma\hbar B_0 \sim 300 \text{ MHz}$	$10^{-4}$	$1 + e^{\gamma\hbar B_0/k_B T}$	
EPR	$\gamma\hbar B_0 \sim 300 \text{ MHz}$	$0.1$	$1 + e^{\gamma\hbar B_0/k_B T}$	
Rotational	$\frac{\hbar^2 J(J+1)}{2I}$	$0.1$	$\frac{2Ik_B T}{\sigma\hbar^2}$	$nRT$
Vibrational	$h\nu \left(\frac{1}{2} + v\right)$	$5$	$\frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}}$	see below
Electronic	too complex	$10^4$	$g_e e^{D_e/k_B T}$	

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B}, \quad \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$$

$$U_{\text{vib}} = Nk_B \left( \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{\exp(\Theta_{\text{vib}}/T)} - 1 \right)$$

Total partition function

$$q = q_{\text{conf}} \cdot \underbrace{\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V}_{q_{\text{trans}}} \cdot \underbrace{\left(\frac{2Ik_B T}{\sigma\hbar^2}\right)}_{q_{\text{rot}}} \cdot \underbrace{\left(\frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}}\right)}_{q_{\text{vib}}} \cdot \underbrace{\left(g_e \exp\left(\frac{D_e}{k_B T}\right)\right)}_{q_{\text{elec}}}$$

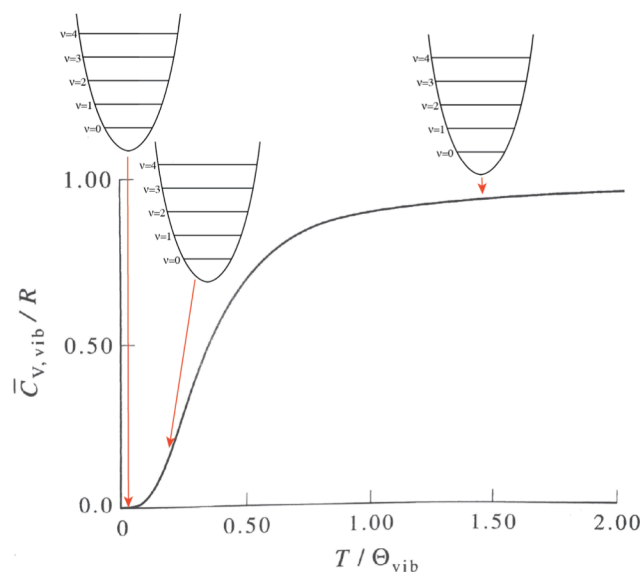
$$= q_{\text{conf}} \cdot \underbrace{\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V}_{q_{\text{trans}}} \cdot \underbrace{\left(\frac{T}{\sigma\Theta_{\text{rot}}}\right)}_{q_{\text{rot}}} \cdot \underbrace{\left(\frac{\exp\left(-\frac{\Theta_{\text{rot}}}{2T}\right)}{1 - \exp\left(-\frac{\Theta_{\text{rot}}}{T}\right)}\right)}_{q_{\text{vib}}} \cdot \underbrace{\left(g_e \exp\left(\frac{D_e}{k_B T}\right)\right)}_{q_{\text{elec}}}$$

**Exercise 5.** (2014-1, 1b) Using only words, define the molecular rotation partition function,  $q_{\text{rot}}$ .

**Exercise 6.** (2017-1, 1h) Draw an energy diagram showing the occupation of rotational energy levels of a typical polyatomic gas at room temperature. Also draw the fractional occupation of rotational energy levels with respect to the J quantum number from J=1 to J=12. Which rotational energy level is the most occupied? Why?

**Exercise 7.** (2015-1, 1b) Is the lowest energy state always the most populated? Why or why not? Clarify your answer using a mathematical expression for the probability of finding a molecule with energy  $\epsilon_i$  in state  $\epsilon_i$ . Also include qualitative plots of 1) the degeneracy of rotational energy levels versus J, 2) the probability of finding a molecule with rotational energy J (excluding degeneracy), and 3) the product of the two functions.

**Exercise 8.** (2015-1, 4) The figure below shows the vibrational contribution to the molar heat capacity of an ideal diatomic gas as a function of reduced vibrational temperature.



- For each of the three points on the curve above indicated with red arrows, draw ten balls to represent the population/occupation of energy levels. Also draw an arrow to represent the approximate magnitude of  $kT$  (thermal energy) on each vibrational energy diagram.
- Circle the vibrational energy diagram that most closely represents the occupation of vibrational levels of a typical diatomic molecule at room temperature.
- Calculate the relative population of the first excited state compared to the ground state vibrational state at 298.15 Kelvin if the energy splitting is  $1435 \text{ cm}^{-1}$ .

**Exercise 9.** (2016-1, 3) The normal mode vibrational frequencies of  $\text{H}_2\text{O}$  are  $3657, 1595, 3756 \text{ cm}^{-1}$ .

- Given 10 balls to represent population in each of the 3 figures below; draw the occupation of vibrational modes you would expect at a temperature of 10 Kelvin. Calculation is allowed, but not required for full credit. (Note, the figures below have different scales for energy on the y-axis)
- Given 10 balls to represent population in each of the 3 figures below; draw the occupation of the three vibrational modes you would expect at a temperature of 2,300 Kelvin. Calculation is allowed, but not required for full credit. (Note, the figures below have different scales for energy on the y-axis)
- Given 10 balls to represent population in each of the 3 figures below; draw the occupation of the three vibrational modes you would expect at a temperature of 10,000 Kelvin. Calculation is allowed, but not required for full credit. Assume the water molecules will not break apart, or otherwise decompose at this temperature. (Note, the figures below have different scales for energy on the y-axis)

### 19.3 Deriving thermodynamic quantities from partition functions

**Exercise 10.** (2014-1, 2a; 2018-1, 2b; 2018-2, 2e) Starting with  $A = U - TS$  and using  $A = -k_B T \ln Q$ , show that  $S = -k_B \sum_i P_i \ln P_i$ .

**Exercise 11.** (2014-1, 2b) Starting from your expression for Entropy  $S = -k_B \sum_i P_i \ln P_i$ , derive the inscription on Boltzmann's tomb.

**Exercise 12.** (2014-1, 2e) Derive the ideal gas law using the molecular partition function of a monatomic ideal gas and

$$p = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,n}.$$

Include an explanation in words of how it makes sense physically, that each of the terms besides  $N, k_B, T, V$  dropped out of the right hand side. (for full credit, you must explicitly discuss EACH term that drops out, not all of them together)

**Exercise 13.** (2015-1, 2a) Starting with  $U = \sum_i P_i E_i$  derive

$$U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,n}.$$

## 20 Chemical potential and partial pressure

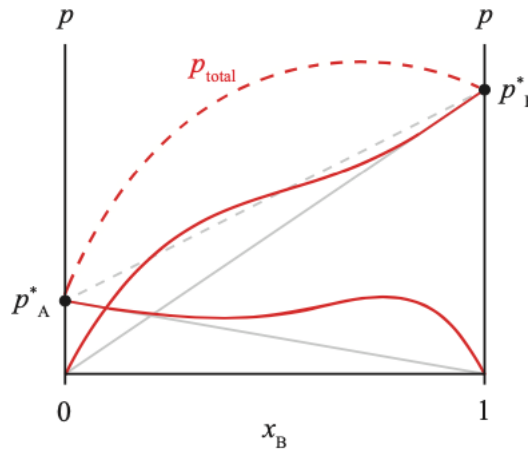
Chemical potential  $\mu$  "is like" the molar Gibbs free energy  $G$  at constant  $p, T$ . Same conditions for spontaneity apply.

Partial pressure for ideal mixtures of gases and liquids. In liquids, partial pressure refers to a partial vapor pressure.

$$p_A = x_A p \quad (\text{Dalton, gas})$$

$$p_A = x_A p_A^* \quad (\text{Raoult, liquid})$$

$$p_A = x_A K_{H,A} \quad (\text{Henry, liquid})$$



Chemical potential of ideal mixtures

$$\mu_X(\text{pure}, T, p) = \mu_X^\ominus(T) + RT \log \left( \frac{p}{p^\ominus} \right)$$

$$\mu_X(\text{mixed}, T, p_X) = \mu_X(\text{pure}, T, p) + RT \log x_X$$

$$= \mu_X^\ominus(T) + RT \log \left( \frac{p_X}{p^\ominus} \right)$$

Equilibrium condition

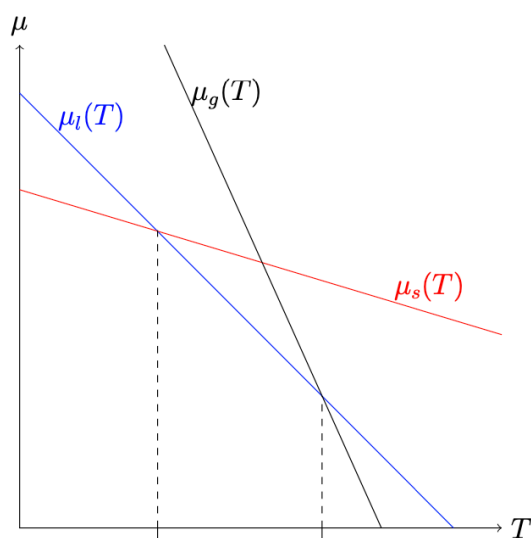
$$0 = \sum_i \nu_i \mu_i(\text{mixed}, T, p_i)$$



**Exercise 1.** Write down the equilibrium condition for a system that contains molecules A, B, C, of which only A can cross the system's boundaries. The surrounding contains only molecules A.

**Solution** Denote the left container by 1, the right by 2. The equilibrium condition states that the chemical potential of A on both sides equilibrates, i.e.  $\mu_{1,A} = \mu_{2,A}$ . The chemical potential of B and C does not matter as they are not free to move across the membrane.

**Exercise 2.** Using the criterion for spontaneity for processes at constant pressure and temperature, determine the stable phases in the following diagram. What is the meaning of the marked temperatures?



**Solution** The criterion for spontaneity states that the Gibbs free energy is minimized. The molar Gibbs free energy is the chemical potential. Thus, in the picture above the stable phase is always the one with minimal chemical potential. The marked temperatures represent the temperatures of phase transition.

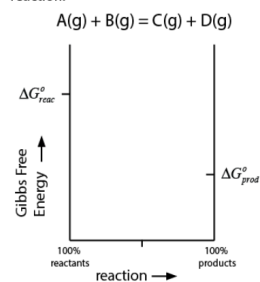
## 21 Gibbs free energy of mixing, $\Delta G_{\text{mix}}$

**Exercise 1.** (2015-2, 1f) Using plots of Gibbs free energy versus progress of a reaction, describe how entropy of mixing prevents chemical reactions from proceeding 100% to products.

**Exercise 2.** (2018-1, 5d) On the diagrams on the following page, draw a curve representing the Gibbs Free Energy as a function of reaction progress from 0% to 100%. Use an arrow to indicate the position of equilibrium. Note,  $\Delta G^\circ$  is the summation of the Gibbs free energy of formation of the products or reactions (that you would look up in tables).

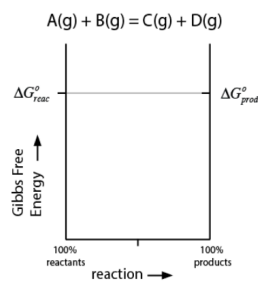
**part a (10 pts)**

reaction:



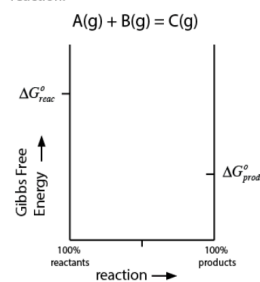
**part b (10 pts)**

reaction:



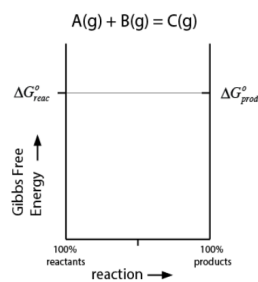
**part c (10 pts)**

reaction:



**part d (10 pts)**

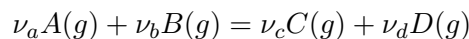
reaction:



## 22 Equilibrium constants

$$K_p = \prod_i \left( \frac{p_i}{p^\ominus} \right)^{\nu_i} = \exp \left( -\frac{\Delta_{\text{rxn}} G^\ominus}{RT} \right)$$
$$K_x = \left( \frac{p}{p^\ominus} \right)^{\Delta\nu} K_p, \quad \Delta\nu = \sum_i \nu_i$$

**Exercise 1.** (2018-2, 4c) Derive the expression for the equilibrium constant,  $K_p$ , for the following reaction in terms of partial pressures  $p_a$ ,  $p_b$ ,  $p_c$ ,  $p_d$ , reference pressures, stoichiometric coefficients,  $\nu_a$ ,  $\nu_b$ ,  $\nu_c$ ,  $\nu_d$ ,  $R$  (gas constant),  $T$  (temperature) and  $\Delta G_{\text{rxn}}^\ominus$ .



**Exercise 2.** (2018-2, 4d) Describe how  $K_p$  changes with pressure.

**Exercise 3.** (2018-2, 4e,f) What are the units of  $K_p$ ? What are the units of a solution equilibrium constant,  $K$ , for a reaction which converts two moles of reactants into 1 mole of products?

## 23 Computing equilibria

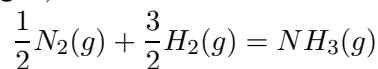
Express reaction in terms of  $\xi$ , the number of moles that have reacted until the reaction reaches equilibrium.

	reactant 1	reactant 2	product 1	...
initial	$n_1$	$n_2$	0	...
equilibrium	$n_1 - \xi$	$n_2 - \xi$	$\xi$	

Express  $n_{tot}$  in terms of  $\xi$

Equilibrium in gas phase  $p_{eq} = \frac{RT}{V} \cdot n_{tot}(\xi)$  solve for  $\xi$

**Exercise 1.** (2018-2, 4g,h)



- The Haber process shown below has a reaction enthalpy of  $-46.21$  kJ/mol, and a reaction free energy of  $-16.74$  kJ if carried out at 1 bar at 298 K. Calculate the reaction entropy at 1 bar and 298 K.
- The Haber process is crucial to maintaining a human population on earth above 1 billion because it yields a form of Nitrogen which can readily be incorporated into plant metabolism. Determine the fraction of Nitrogen atoms in Ammonia at thermodynamic equilibrium of the Haber process (1 bar and 298 K) if 1 mole of Nitrogen gas is added to 3 moles of hydrogen gas.

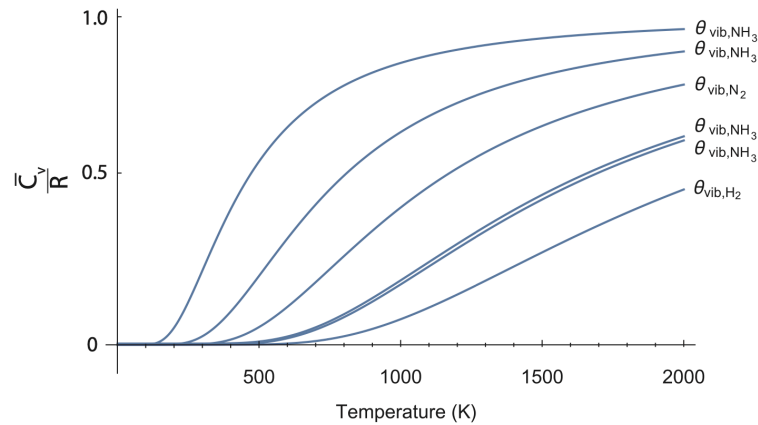
## 24 Van't Hoff equation

Models the temperature dependence of equilibrium constant

$$\log \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

**Exercise 1.** (2018-2, 4i,j,k)

- Derive the explicit Van't Hoff Equation (temperature dependence of equilibrium) using your result from before.
- The Haber process is more often carried out at 800 K to accelerate the kinetics. In lecture, we stated that  $K_p$  at 800 K is 0.007. Calculate the equilibrium constant at 800 K using an approximation to the Van't Hoff Equation (describes how equilibrium changes with respect to reaction enthalpy and temperature) which assumes that the heat capacities of the products and reactants are the same.
- Describe the diagram below. Draw a thermodynamic cycle which shows how you can determine the reaction enthalpy at  $T_2$ , if you already know the reaction enthalpy at  $T_1$ . Explain why your calculated  $K_p$  using an approximated Van't Hoff Equation differs from the experimental value of  $K_p = 0.007$  at 800 K.



f) Give an estimate of the reaction enthalpy of the Haber process at 800 K.

## 25 Phase rule

$$f = N - P + 2$$

**Exercise 1.** (fs17, ps12, ex1b) Wann liegt ein reiner Stoff gleichzeitig in allen drei Aggregatzuständen vor? Können Sie eine allgemeine Aussage über  $f$  an diesem Punkt treffen?

**Exercise 2.** (fs17, exam, ex3a,c) Ein evakuiertes Gefäß wird zur Hälfte mit reinem Benzol gefüllt und in ein Wärmebad der Temperatur  $T$  gebracht. Nach einer gewissen Zeit stellt sich ein Gleichgewichtsdruck  $p(T)$  ein.

a) Bestimmen Sie die Freiheitsgrade des Systems mit der Phasenregel

Das Gefäß wird nun mit einer Mischung von Benzol und Toluol befüllt und auf  $90^\circ\text{C}$  temperiert. Nehmen Sie an, dass sich die Mischungen sowohl in der Gasphase als auch in der flüssigen Phase ideal verhalten

b) Bestimmen Sie die Zahl der Freiheitsgrade mit der Phasenregel. Geben Sie Ausdrücke für die chemischen Potentiale beider Substanzen in beiden Phasen.

**Exercise 3.** (fs17, ps12, ex1a) Bestimmen Sie die Anzahl Freiheitsgrade  $f$  der folgenden Systeme.

- $\text{H}_2(\text{g})$  und  $\text{O}_2(\text{g})$  sind gleichzeitig aber nicht vollständig gelöst in Wasser bei Raumtemperatur.
- $\text{NaCl}$  gelöst in einem Gemisch aus Wasser und Diethylether bei Raumtemperatur, wobei die Lösung nicht gesättigt ist.
- $\text{CaCO}_3(\text{s})$  bei einer Temperatur, bei der die thermische Dissoziation in  $\text{CaO}(\text{s})$  und  $\text{CO}_2(\text{g})$  stattfindet, aber nicht vollständig ist.

- d) Eine flüssige Mischung aus Toluol, Dichlormethan und Aceton steht im thermodynamischen Gleichgewicht mit der Gasphase. Die Gasphase enthält nur die Dämpfe der drei flüssigen Substanzen und alle drei Flüssigkeiten sind vollständig miteinander mischbar. Wie würde die Situation aussehen, wenn die drei flüssigen Stoffe vollständig unmischbar wären?
- e) Eis, Wasser und Wasserdampf.

## 26 Clausius Clapeyron

General Clausius Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{1}{T} \frac{\Delta H}{\Delta V}$$

with  $\Delta$  the difference between the phases

Simplification: gas transitions (often  $p_1 = p^\ominus$ )

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**Exercise 1.** (fs17, exam, ex3b) Ein evakuiertes Gefäß wird zur Hälfte mit reinem Benzol gefüllt und in ein Wärmebad der Temperatur  $T$  gebracht. Nach einer gewissen Zeit stellt sich ein Gleichgewichtsdruck  $p(T)$  ein. Der Gleichgewichtsdampfdruck wird bei  $77^\circ\text{C}$  als 0.91891 bar und bei  $82^\circ\text{C}$  als 1.0730 bar gemessen. Bestimmen Sie aus den Daten die Verdampfungsenthalpie von Benzol.

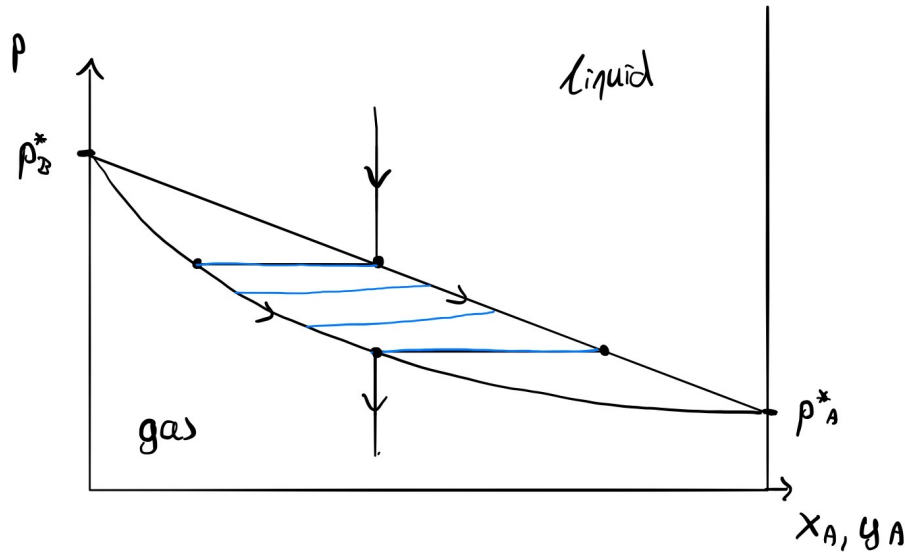
## 27 Two-component systems

If you choose the mole fraction on the dew line,  $x_A$ , then the component on the bubble line,  $y_A$ , is fixed. The other way round, if you choose the mole fraction on the bubble line,  $y_A$ , then the component on the dew line,  $x_A$ , is fixed. The following equation gives an overview over the formulas.

chosen freely	fixed other mole fraction	pressure
$x_A$	$y_A = \frac{x_A p_A^*}{p_B^* + x_A(p_A^* - p_B^*)}$	$p = p_B^* + x_A(p_A^* - p_B^*)$
$y_A$	$x_A = \frac{y_A p_B^*}{p_A^* - y_A(p_A^* - p_B^*)}$	$p = \frac{p_A^* p_B^*}{p_A^* - y_A(p_A^* - p_B^*)}$

**Exercise 1.** Sketch the vapor pressure for an ideal binary mixture of substances A and B as a function of the mole fraction  $x_A$ . The pure substance vapor pressures are  $p_A^* = 2 \text{ bar}$ ,  $p_B^* = 1 \text{ bar}$ . Sketch the mole fraction  $x_A$  for liquid and gaseous phases as a function of decreasing pressure until pressure  $p = 1 \text{ bar}$  is reached.

**Solution**



**Exercise 2.** (fs12, ps11, ex3) Bei 320 K sei eine ideale flüssige Mischung zweier Substanzen A und B mit molaren Anteilen 15% und 85% im thermodynamischen Gleichgewicht mit einer idealen Gasphase. Der Dampfdruck des reinen Stoffes A bei 300 K beträgt  $p_A^*(300K) = 10 \text{ kPa}$  und die näherungsweise temperaturunabhängige Verdampfungsenthalpie  $\Delta H = 40 \text{ kJ mol}^{-1}$ . Das chemische Potential des Stoffes A in der Gasphase ist  $\mu_A^\ominus(320K) = 8 \text{ kJ mol}^{-1}$ . Der Dampfdruck des reinen Stoffes B bei 320 K beträgt  $p_B^*(320K) = 5.24 \text{ kPa}$ .

- Berechnen Sie den Dampfdruck des reinen Stoffes A bei 320 K. Welche Annahmen haben Sie für die Berechnung getroffen?
- Berechnen Sie den Dampfdruck des Stoffes A über der Mischung und den Molenbruch von Stoff B in der Gasphase. Ist Stoff A oder Stoff B leichter flüchtig?
- Berechnen Sie die chemischen Potentiale des Stoffes A in der Gasphase der Mischung und in der flüssigen Phase. Vergleichen Sie die beiden Werte miteinander.

**Exercise 3.** (fs14, exam, ex2) Zwei Substanzen A und B sind miteinander in der flüssigen Phase unbegrenzt mischbar. Wir betrachten ein Phasengleichgewicht (flüssige Phase + Gas) der Mischung von A und B in einem geschlossenen Volumen bei der gegebenen Temperatur  $T_0$ . Nehmen Sie an, dass bei  $T_0$  der Dampfdruck von B kleiner als derjenige von A ist ( $p_B^*(T_0) < p_A^*(T_0)$ ). Es gibt keine chemische Reaktion zwischen A und B.

- Wie viele Freiheitsgrade hat ein solches System? Ist die Information, dass zwischen A und B keine Reaktion stattfindet, dafür wichtig?

- b) Ist es durch geeignete Wahl der Stoffmengen von A und B in der Mischung möglich, bei  $T = T_0$  einen Gesamtdruck von  $p_0$  zu erreichen, so dass  $p_B^*(T_0) < p_0 < p_A^*(T_0)$  gilt?
- c) Ist es durch geeignete Wahl der Stoffmengen von A und B in der Mischung möglich, bei  $T = T_0$  einen Gesamtdruck von  $p_0$  zu erreichen, so dass  $p_0 > p_A^*(T_0)$  gilt?
- d) Ist es durch geeignete Wahl der Stoffmengen von A und B in der Mischung möglich, bei  $T = T_0$  ein Gleichgewicht zu erreichen, in dem die Partialdrücke für A und B in der Gasphase gleich zwei zufällig gewählten Werten sind:  $p_A = p_1, p_B = p_2$ ?