Thermodynamics

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1 Fundamental terms

Thermal physics, generally speaking, is the study of the statistical nature of physical systems from an energetic perspective, it is typically divided into thermodynamics and statistical mechanics. It deals with the *macroscopic* properties (and their mutual relations) of *macroscopic* systems, containing typically around 10^{23} particles.

Macr. systems
↓
Thermal physics
↙ ↘

Thermodynamics

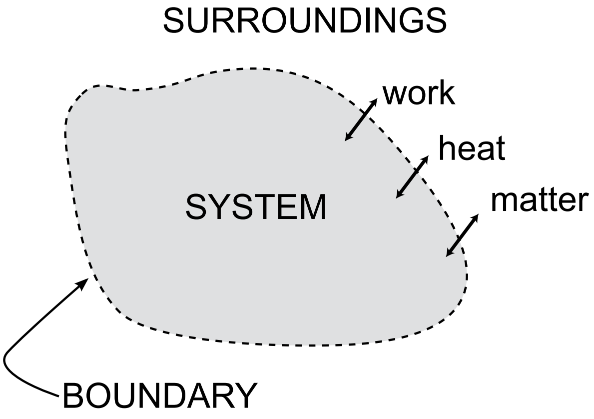
- phenomenological parameters
- independent of microscopic model
- very general conclusions and relations

Statistical mechanics

- microscopic derivations of materials parameters
- statistical interpretation of system properties

Thermodynamic system:

Above we have used the term *system.* The system is a very important concept in thermodynamics. Everything in the universe except the system is known as surroundings. A system is the region of the universe under study. A system is separated from the remainder of the universe by a boundary which may be imaginary or not, but which by convention delimits a finite volume. The possible exchanges of work, heat, or matter between the system and the surroundings take place across this boundary and are used to classify the specific system under study.



exchange of	system classified as
heat, work, and matter	open
heat and work	closed
heat	diathermic
work	adiabatic
–	isolated

Thermodynamic state:
A *thermodynamic state* is the macroscopic condition of a thermodynamic system as described by its particular *thermodynamic parameters* at a specific time. The state of any thermodynamic system can be described by a set of thermodynamic parameters, such as temperature, pressure, density, composition, independently of its surroundings or history.

Thermodynamic parameters:
The parameters required to unambiguously specify the state of the system. They depend on the characteristics of the system and need to be measurably.

Examples:

1. determined by surroundings:
   - volume
   - electric or magnetic fields
2. determined by internal interactions:
   - pressure, density, temperature
   - internal energy, polarization, magnetization

There is a *minimal ensemble of parameters* that uniquely specify the state, and all other parameters can be derived from these. The parameters of this minimal ensemble are independent.

The number of independent parameters equals the number of macroscopic degrees of freedom of the system.

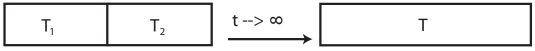
Intensive/extensive thermodynamic parameters:
An intensive property (also called a bulk property), is a physical property of a system that does not depend on the system size or the amount of material in the system. By contrast, an extensive property of a system does depend on the system size or the amount of material in the system.

Examples for intensive parameters:
- temperature (T)
- pressure (p)
- chemical potential (μ)

Examples for extensive parameters:
- mass
- volume (V)
- internal energy (U)

Basic postulate of thermodynamics (based on experience):
As time passes in an isolated system, internal differences in the system tend to even out (e.g., pressures and temperatures tend to equalize, as do density differences). A system in which all equalizing processes have gone practically to completion, is considered to be in a state of thermodynamic equilibrium. A system that is in equilibrium experiences no changes when it is isolated from its surroundings.

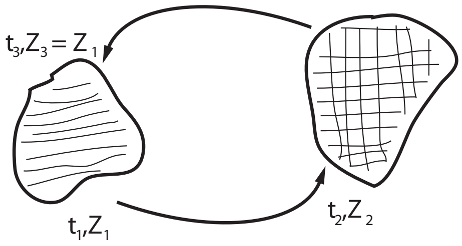
Systems in thermodynamic equilibrium are unambiguously characterized by a smaller number of thermodynamic parameters than systems that are not equilibrated.
Example:



The thermodynamic state changes by *reversible or irreversible processes.*

Reversible/irreversible processes:
A reversible process is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings. In thermodynamic terms, a process "taking place" would refer to its transition from its initial state to its final state. A process that is not reversible is termed irreversible. At the same point in an irreversible cycle, the system will be in the same state, but the surroundings are permanently changed after each cycle.

Example:
The process $z_1 \rightarrow z_2$ is called irreversible, if the process $z_2 \rightarrow z_3 = z_1$ leads to changes in the surroundings, otherwise it is reversible.



A reversible process, or reversible cycle if the process is cyclic, is a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy. Due to these infinitesimal changes, the system is at rest throughout the entire process. Since it would

take an infinite amount of time for the process to finish, *perfectly reversible processes are impossible.* However, if the system undergoing the changes responds much faster than the applied change, the deviation from reversibility may be negligible.
In some cases, it is important to distinguish between reversible and *quasistatic* processes.

Quasistatic processes:
Quasistatic processes happen infinitely slowly. In practice, such processes can be approximated by performing them "very slowly". The criterion for very slowly is that the change of the macroscopic state is much slower than the microscopic time scale, e.g., speed of piston movement vs. velocity of gas particles. The insures that the microscopic objects can adapt adiabatically, i.e., instantaneously.

Reversible processes are always quasistatic, but the converse is not always true. For example, an infinitesimal compression of a gas in a cylinder where there exists friction between the piston and the cylinder is a quasistatic, but not reversible process. Although the system has been driven from its equilibrium state by only an infinitesimal amount, heat has been irreversibly lost due to friction, and cannot be recovered by simply moving the piston infinitesimally in the opposite direction.

Thermodynamic phase:
A thermodynamic phase is an open, connected region in the space of thermodynamic states that is physically and chemically homogenous where the thermodynamical parameters are constant.
Example:
Constant pressure and temperature in the liquid and gaseous phase of water.

2 Zeroth law of thermodynamics

In many ways, this law is more fundamental than any of the other laws of thermodynamics. However, the need to state it explicitly as a law was not perceived until the first third of the 20th century, long after the first three laws were already widely in use and named as such, hence the zero numbering.

Zeroth law of thermodynamics $\triangleq$ introduce temperature axiomatically, proves that we can define a temperature function, or more informally, that we can 'construct a thermometer'.

For any thermodynamic system there exists an intensive parameter, called temperature. Its equality is necessary and sufficient for the thermodynamical equilibrium between two systems or two parts of the same system.

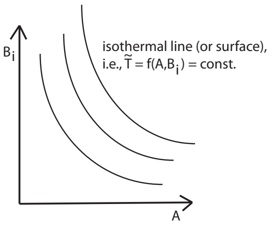
$\Longrightarrow$ If two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

$\Longrightarrow$ defines a measuring specification for the temperature:

2 systems S, S' characterized by parameters A, B_i with i=1,2,...

temperature itself is a thermodynamic parameter, i.e.,:

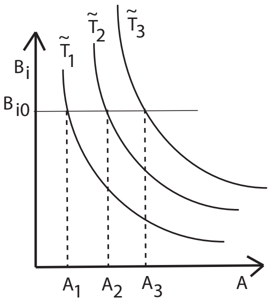
$\tilde{T} = f(A, B_i)$



thermodynamic equilibrium between S and S' $\Rightarrow \tilde{T'} = \tilde{T} = f(A, B_i)$

S≪S' (i.e., S' doesn't change upon measurement, equilibrium is soon established)

keep B_i fixed (=B_{0i}) $\rightarrow \tilde{T}(A)$



A represents a thermometric parameter

- define arbitrarily linear scale, i.e., $\tilde{T}(A) = cA$.
- by convention the tripel point of water is used as a temperature-fixed point, assign arbitrarily temperature of 273.16 K

$$\tilde{T}_{\text{tripel}} = 273.16K = cA_{\text{tripel}} \quad \Longrightarrow \quad \tilde{T} = 273.16K\frac{A}{A_{\text{tripel}}}$$

Examples:

A	thermometer
V	constant-pressure gas thermometer
p	constant-volume gas thermometer
length	mercury thermometer
electric resistance	electrical resistance thermometer
voltage	thermocouple

Data measured with different thermometers differ. The smallest differences occur with gas thermometers operated at low pressure. This is based on the fact that all gases become *ideal* in the limit of zero pressure. Therefore, we can define the *ideal gas temperature scale*:

$\mathrm{T}{=}273.16\ \mathrm{K} \cdot \lim_{p_{\mathrm{tripel}} \to 0} (\frac{p}{p_{\mathrm{tripel}}})|_{V=\mathrm{constant}}$

(later: equals the *absolute (or thermodynamic) temperature*)

3 First law of thermodynamics

3.1 Conservation of energy

The first law of thermodynamics is an expression of the more universal physical law of the conservation of energy. Succinctly, the first law of thermodynamics states:

Every thermodynamic system is characterized by an extensive property called internal energy U. Its increase is equal to the amount of energy added by heating the system (δQ), plus the amount gained as a result of the work (δW) done by the surroundings on the system.

$$\mathrm{dU} = \delta Q + \delta W$$

Isolated systems: $\delta Q = \delta W = 0 \Rightarrow U\,\text{is constant}, \mathrm{dU} = 0$

Work and heat are processes which add or subtract energy rather than thermodynamic parameters as the internal energy U. The latter is a particular form of energy associated with the system. The infinitesimal heat and work are denoted by δQ and δW rather than dQ and dW because, in mathematical terms, they are not exact differentials. The integral of an inexact differential depends upon the particular "path", i.e., thermodynamic process, taken through the space of thermodynamic parameters while the integral of an exact differential depends only upon the initial and final states. If the initial and final states are the same, then the integral of an inexact differential may or may not be zero, but the integral of an exact differential will always be zero.

$\delta Q > 0 \Rightarrow$ the system heat is heated

$\delta W > 0 \Rightarrow$ work is done on the system

Formulation equivalent to the 1st law of thermodynamics:
It is impossible to construct a *perpetual motion machine of the first kind*. By this we mean a device whose parts are not only in permanent motion, but provides work without input of external energy (e.g. heat) and without change of the physical or chemical status of its parts.

Examples for work term:

mechanical work: $\delta W = -p\,\mathrm{dV}$
magnetic work: $\delta W = \vec{H} d\vec{M}$
electric work: $\delta W = \vec{E} d\vec{P}$

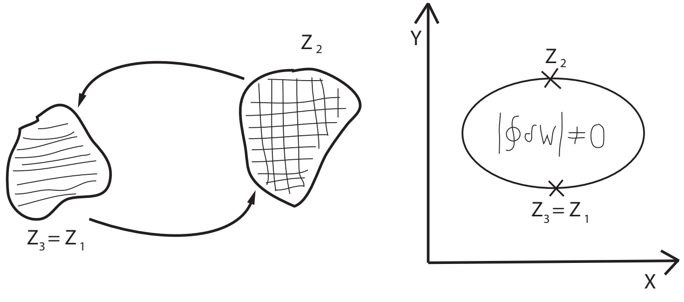
generally it holds:

$$\delta W = -\sum_i y_i \, \mathrm{dX}_i$$

where X_i=extensive and y_i=intensive properties.

Besides the X_i at least the temperature belongs to the minimal ensemble of thermodynamic parameters $\Rightarrow \delta W$ no exact differential, since it does not contain a temperature differential.

Cyclic processes:



3.2 pVT systems

Systems that are completely determined by pressure (p), volume (V) and temperature (T) are called pVT systems.

Experience tells us that only two of these parameters are needed to form a minimal ensemble of thermodynamic parameters. The third parameter is determined via the *thermal equation of state (TEOS)*:

$$f(p, V, T) = 0.$$

Consequently, the internal energy must be given as a function of two thermodynamic parameters. If these are chosen to be V and T, this function is known as *caloric equation of state (CEOS)*:

$$U = U(V, T)$$

where $\delta W = -p\,\mathrm{dV} \Rightarrow^{\text{1st law}} \mathrm{dU} = \delta Q - p\,\mathrm{dV}$

heat capacity, defined via $\delta Q = C\,\mathrm{dT}$

C depends on the kind of process
$C_v \to \delta$Q the system is heated with its volume kept constant
$C_p \to \delta$Q the system is heated at constant pressure

Determination of C_v and C_p from TEOS and CEOS:

1st law:

$C\,\mathrm{dT} = \mathrm{dU} + p\,\mathrm{dV}$ and CEOS: U=U(V,T)

$C\,\mathrm{dT} = (\frac{\partial U}{\partial T})_V\,\mathrm{dT} + (\frac{\partial U}{\partial V})_T\,\mathrm{dV} + p\,\mathrm{dV} = (\frac{\partial U}{\partial T})_V\,\mathrm{dT} + \left[(\frac{\partial U}{\partial V})_T + p\right]\mathrm{dV}$ **(*)**

now consider: dV=0

$$\Rightarrow C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

TEOS given as: V=V(p,T)

$\mathrm{dV} = (\frac{\partial V}{\partial p})_T\,\mathrm{dp} + (\frac{\partial V}{\partial T})_p\,\mathrm{dT}$

inserted in *(*)* yields:

$C\,\mathrm{dT} = (\frac{\partial U}{\partial T})_V\,\mathrm{dT} + \left[(\frac{\partial U}{\partial V})_T + p\right]\left[(\frac{\partial V}{\partial P})_T\,\mathrm{dp} + (\frac{\partial V}{\partial T})_p\,\mathrm{dT}\right] =$
$\left\{(\frac{\partial U}{\partial T})_V + \left[(\frac{\partial U}{\partial V})_T + p\right](\frac{\partial V}{\partial T})_p\right\}\mathrm{dT} + \left[(\frac{\partial U}{\partial V})_T + p\right](\frac{\partial V}{\partial p})\,\mathrm{dp}$

now consider: dp=0 $\Rightarrow C_p = \underbrace{(\frac{\partial U}{\partial T})_V}_{C_v} + \left[(\frac{\partial U}{\partial V}) + p\right](\frac{\partial V}{\partial T})_p$

$$C_p = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

difference $C_p - C_v$ completely determined by CEOS & TEOS!

C_v, C_p are completely determined by thermodynamic parameters and therefore themselves thermodynamic parameters

Important processes:

1. isothermal process: T = const.
2. isochoric process: V = const.
3. isobaric process: p = const.
4. polytropic proess: C = constant (in particular: C = 0 → thermally isolated process, adiabatic process, $\delta Q = 0$).

discuss now <u>polytropic process:</u>

$C\,\mathrm{dT} = (\frac{\partial U}{\partial T})_V\,\mathrm{dT} + \left[(\frac{\partial U}{\partial V})_T + p\right]\mathrm{dV}$ **(*)**

$C_v = (\frac{\partial U}{\partial T})_V$ **(**)**

$C_p - C_v = \left[(\frac{\partial U}{\partial V})_T + p\right](\frac{\partial V}{\partial T})_p$ **(***)**

(/**)*: $(C - C_v)\,\mathrm{dT} = \underbrace{\left[(\frac{\partial U}{\partial V})_T + p\right]}_{(C_p - C_v)(\frac{\partial V}{\partial T})_p^{-1}}\mathrm{dV}$*(***)*

$\Rightarrow (C - C_v)\,\mathrm{dT} = (C_p - C_v)(\frac{\partial T}{\partial V})_p\,\mathrm{dV}$

Polytropic equation for T(V):

$$\frac{\mathrm{dT}}{\mathrm{dV}} = \frac{C_p - C_v}{C - C_v}\left(\frac{\partial T}{\partial V}\right)_p$$

(differential equation that allows for determining T(V), if $(\frac{\partial T}{\partial V})_p$ is expressed via TEOS)

the differential equations for p(V) and p(T) can be obtained as well:

start from TEOS that ensures $\mathrm{dT} = (\frac{\partial T}{\partial V})_p\,\mathrm{dV} + (\frac{\partial T}{\partial p})_V\,\mathrm{dp}$

insert in polytropic equation for T(V):

$$(C - C_v)\left[(\tfrac{\partial T}{\partial V})_p\,\mathrm{dV} + (\tfrac{\partial T}{\partial p})_V\,\mathrm{dp}\right] = (C_p - C_v)(\tfrac{\partial T}{\partial V})_p\,\mathrm{dV}$$

$$(C - C_v)(\tfrac{\partial T}{\partial p})_V\,\mathrm{dp} = (C_p - C_v + C_v - C)(\tfrac{\partial T}{\partial V})_p\,\mathrm{dV}$$

$$(\tfrac{\partial T}{\partial p})_V\,\tfrac{\mathrm{dp}}{\mathrm{dV}} = -\underbrace{\frac{C_p - C}{C_v - C}}_{\delta}(\tfrac{\partial T}{\partial V})_p$$

introduce here the polytropic index δ

so that polytropic equation for p(V):

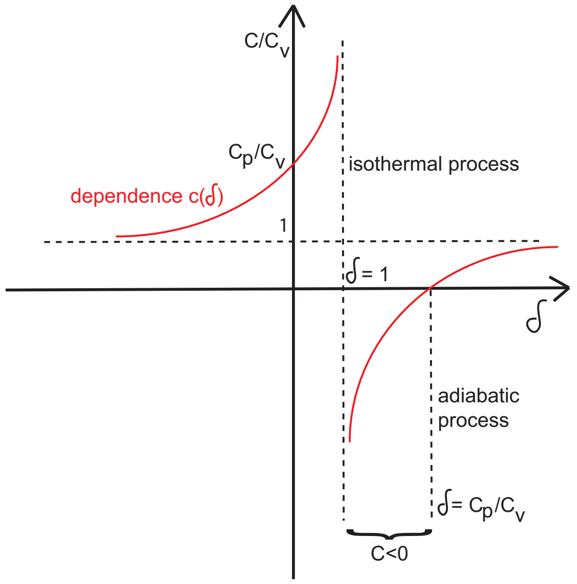
$$\left(\frac{\partial T}{\partial p}\right)_V \frac{\mathrm{dp}}{\mathrm{dV}} = -\delta\left(\frac{\partial T}{\partial V}\right)_p$$

eliminate partial derivatives using TEOS

in particular: adiabatic (thermally isolated) process $\delta = \frac{C_p}{C_v}$

now analyze the dependence $C = C(\delta) = \frac{\delta C_v - C_p}{\delta - 1}$ $\quad (C_p > C_v)$

in case $\delta = 1 \Rightarrow C = \frac{\delta Q}{dT} \to \infty$ (isothermal process , dT=0)



C negative between the isothermal and adiabatic processes, i.e., heating the system results in lowering its temperature! This does not violate the 1st law (system does work on the surroundings), but, as we will prove later, is no stable regime.

3.3 Ideal gas as example for a pVT system

TEOS: $pV = NkT$ **ideal gas law, Boyle-Mariotte law**

CEOS: $U = C_v T + \text{const.}$ $C_v = \text{const.}$**;** **Gay-Lussac law**

Earlier *(3.2)* $C_p - C_v = [\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=\,0\ \ CEOS} + p] \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{=\,\frac{Nk}{p}\ \ TEOS}$

$$\Rightarrow C_p - C_v = Nk$$

i.e, not only C_v but also C_p constant

specific heat capacity:

$\bar{c}_v = \frac{C_v}{N}$; $\bar{c}_p = \frac{C_p}{N}$

$\bar{c}_p - \bar{c}_v = k \rightarrow$ Boltzmann's constant

mikroscopic interpretation:

$\bar{c}_v = \frac{1}{2} f k$; f = number of microscopic degrees of freedom

f=3: monatomic gas

f=5: diatomic gas (+2 rotation included)

f=7: diatomic gas (+kinetic and potential energy of vibrations)

C_v, C_p are const., i.e., for C = const. (polytropic process) is δ constant as well

$\Longrightarrow$ this allows for integrating the polytropic equation for p(V):

$\underbrace{(\frac{\partial T}{\partial p})_V}_{=\frac{V}{Nk}\ TEOS}\ \mathrm{dp} = -\delta\ \underbrace{(\frac{\partial T}{\partial V})_p}_{=\frac{p}{Nk}\ TEOS}\ \mathrm{dV}$

$\Rightarrow V\,\mathrm{dp} = -\delta p\,\mathrm{dV}$

$\frac{\mathrm{dp}}{p} = -\delta \frac{\mathrm{dV}}{V}$

$\mathrm{lnp} = -\delta\,\mathrm{lnV} + \text{const.}$

$$\Rightarrow pV^\delta = \text{const.} = p_0 V_0^\delta$$

from $pV \sim T$ (TEOS) it follows $pVV^{\delta-1} \sim TV^{\delta-1} = \text{const.}$

and $pV^\delta \sim p(\frac{T}{p})^\delta$ =const., respectively

3.4 Work done by an ideal gas during polytropic process

$\underbrace{W_{12} = -\int_1^2 p\,\mathrm{dV} = -\,\text{const.}\int_{V_1}^{V_2}\frac{\mathrm{dV}}{V^\delta} =}_{\text{because}\, pV^\delta=\text{const.}=p_1V_1^\delta=p_2V_2^\delta\,(*)}$

$= -\,\text{const.}\ \frac{1}{1-\delta}(V_2^{1-\delta} - V_1^{1-\delta}) =^{(*)}= -\frac{1}{1-\delta}(p_2V_2^\delta V_2^{1-\delta} - p_1V_1^\delta V_1^{1-\delta}) =$

$\underbrace{-\frac{1}{1-\delta}}_{-\frac{1}{1-\frac{C_p-C}{C_v-C}}}\,(\underbrace{p_2V_2}_{NkT_2} - \underbrace{p_1V_1}_{NkT_1}) = (C_v - C)(T_2 - T_1)$

using above that $(1 - \frac{C_p-C}{C_v-C})^{-1} = \frac{C_v-C}{C_p-C_v} = \frac{C_v-C}{Nk}$

$$W_{12} = (C_v - C)(T_2 - T_1)$$

in particular for adiabatic process, i.e., C=0: $W_{12} = C_v(T_2 - T_1) = U_2 - U_1$

$\Rightarrow$ adiabatic compression increases temperature: $W_{12} > 0 \rightarrow T_2 > T_1$

compare with isothermal process:

$W_{12} = -\int_1^2 p\,\mathrm{dV} = -NkT\int_1^2\frac{\mathrm{dV}}{V} = NkT\ln(\frac{V_1}{V_2}) = (C_p - C_v)T\ln(\frac{V_1}{V_2})$

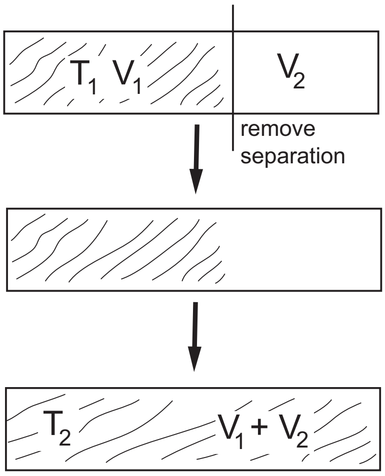
isothermal compression ($V_1 > V_2$) requires to do work on the system ($W_{12} > 0$), for isothermal process of pVT system it holds (1st law):

$\delta Q = -\delta W + \mathrm{dU} = -\delta W + (\frac{\partial U}{\partial V})_T\,\mathrm{dV}$
ideal gas CEOS: $(\frac{\partial U}{\partial V})_T = 0$

$\delta Q = -\delta W$

That mean the work done on the system during the isothermal compression (expansion) is converted into heat that is transferred to (gained from) the surroundings.

3.5 Gay-Lussac's experiment



no work done, not heat transferred, i.e., $\delta Q = \delta W = 0 \Rightarrow \mathrm{dU} = 0$

$U(T_1, V_1) = U(T_2, V_1 + V_2)$

exp. finding: $T_1 = T_2 = T$; $U(T, V_1) = U(T, V_1 + V_2)$
holds for any volums V_1, V_2.

$\Longrightarrow$ The internal energy does not depend on the volume; $(\frac{\partial U}{\partial V})_T = 0$ (CEOS)

4 Second law of thermodynamics

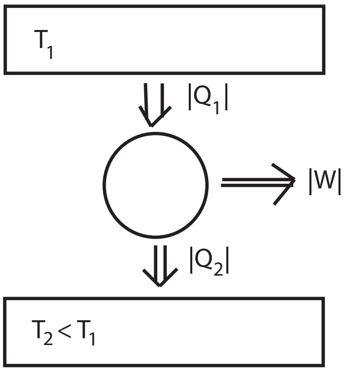
4.1 Carnot cycle

Every thermodynamic system exists in a particular state. A *thermodynamic cycle* occurs when a system is taken through a series of different states, and finally returned to its initial state. In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine.

A *heat engine* acts by transferring energy from a warm region to a cool region of space and, in the process, converting some of that energy to mechanical work. The cycle may also be reversed. The system may be worked upon by an external force, and in the process, it can transfer thermal energy from a cooler system to a warmer one, thereby acting as a *heat pump* rather than a heat engine.

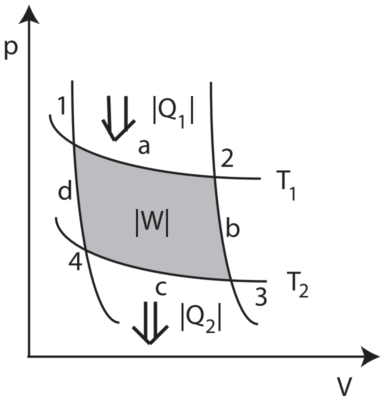
In thermodynamics a *heat reservoir* is considered as a constant temperature source. The temperature of the reservoir does not change irrespective of whether heat is added or extracted to or from it.

The Carnot cycle operates between two heat reservoirs of different temperatures ($T_1 > T_2$) and consists of four steps.



- a – Reversible isothermal expansion at $T=T_1$
- b – Reversible adiabatic expansion $T_1 \rightarrow T_2$
- c – Reversible isothermal compression at $T=T_2$
- d – Reversible adiabatic compression $T_2 \rightarrow T_1$

reversible cyle; Choice of substance: (to begin with) ideal gas



- a – $W_1 = -NkT_1 \ln(\frac{V_2}{V_1})$ (cf. 3.4)
  $U = U(T) \Rightarrow \mathrm{dU} = 0 \Rightarrow Q_1 + W_1 = 0$
- b – $W_2 = -C_v(T_1 - T_2)$ (cf. 3.4)

- c – $W_3 = NkT_2 \ln(\frac{V_3}{V_4})$
  $Q_2 + W_3 = 0$
- d – $W_4 = C_v(T_1 - T_2)$

total work:

$W = W_1 + W_2 + W_3 + W_4 = W_1 + W_3 = -NkT_1 \ln(\frac{V_2}{V_1}) + NkT_2 \ln(\frac{V_3}{V_4})$

using polytropic equation from *(3.3)* it holds

$T_1V_1^{\delta-1} = T_2V_4^{\delta-1}$; 4→1

$T_1V_2^{\delta-1} = T_2V_3^{\delta-1}$; $2 \rightarrow 3$

that leads to

$\frac{V_2}{V_1} = \frac{V_3}{V_4} \Rightarrow W = -Nk(T_1 - T_2)\ln(\frac{V_2}{V_1})$

that is for $T_1 > T_2$ it holds W< 0, i.e, during Carnot cycle system does work -W=|W|
$Q_1 = -W_1 = NkT_1 \ln(\frac{V_2}{V_1})$

$$\text{efficiency}\, \eta_c = -\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

remarks:

- the smaller $\frac{T_2}{T_1}$ the larger is η_c, i.e., η_c increases with temperature difference
- $T_1 = T_2 \Rightarrow \eta_c = 0$, no work done
- no complete conversion of heat in work
- Carnot cycle reversible, heat pump rather than heat engine

4.2 Nonexistence of perpetual motion machine of the second kind

1st law of thermodynamics states that any energy conversion is possibe, e.g., complete conversion of heat in work during cyclic process

$\Delta U = \oint \mathrm{dU} = 0 = \Delta Q + \Delta W \Rightarrow \Delta Q = \Delta W$.

Carnot cycle shows that work can only be done if at least two heat reservoirs of different temperatures are involved. The experience shows that this does not only hold for the Carnot cycle.

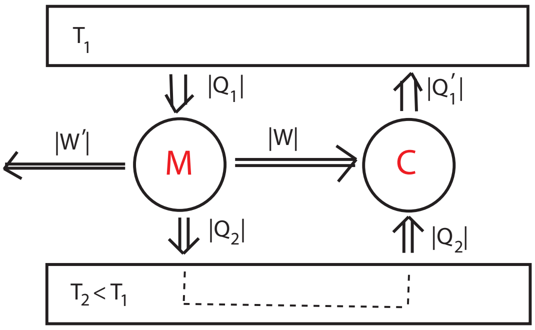
2nd law of thermodynamics (Planck's version):

It is impossible to construct a perpetual motion machine of the second kind, i.e., a machine that does nothing else than converting thermal energy into mechanical work.

two important conclusions:

1. All reversible cycles that operate between 2 heat reservoirs which do work by extracting heat from one reservoir at $T_1 > T_2$ and (partially) transfer this heat to the reservoir at $T_2 < T_1$ have the efficiency: $\eta = \eta_c = 1 - \frac{T_2}{T_1}$.

   proof: indirect, i.e., assume $\exists$ machine with $\eta_M > \eta_c$



M ... fictious machine
C ... Carnot cycle acting as heat pump

obvious from the figure: taken together both machines do work W' by extracting heat from reservoir 1, i.e., contradiction to the 2nd law of thermodynamics, i.e, $\eta = \eta_M = \eta_c$

2. Any irreversible cycle between two heat reservoirs has the efficiency $\eta < \eta_c = 1 - \frac{T_2}{T_1}$

   proof: indirect

   a) assume $\eta > \eta_c \Rightarrow$ see above, contradiction to 2nd law

   b) assume $\eta = \eta_c$

   combination with Carnot cycle results in a machine that does not lead to any changes in the surroundings, contradiction to the statement of irreversibility

conclusion: $\eta \leqslant \eta_c = 1 - \frac{T_2}{T_1}$

$$\eta = -\frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$
$$\frac{Q_2}{Q_1} \leqslant -\frac{T_2}{T_1} \Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leqslant 0$$

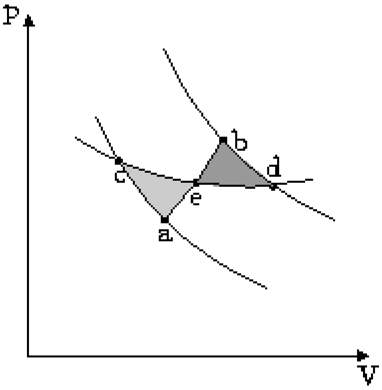
in particular cycle reversible:

$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$ (Clausius equality)

Generalization:
For any reversible thermodynamic cycle it holds $\oint \frac{\delta Q}{T} = 0$
(Clausius theorem)

proof:

First we have to prove the lemma: "any reversible process can be replaced by a combination of reversible isothermal and adiabatic processes".



Consider a reversible process a-b. A series of isothermal and adiabatic processes can replace this process if the heat and work interaction in those processes is the same as that in the process a-b. Let this process be replaced by the process a-c-d-b, where a-c and d-b are reversible adiabatic processes, while c-d is a reversible isothermal process.

The isothermal line is chosen such that the area a-e-c is the same as the area b-e-d. Now, since the area under the p-V diagram is the work done for a reversible process, we have, the total work done in the cycle a-c-d-b-a is zero.

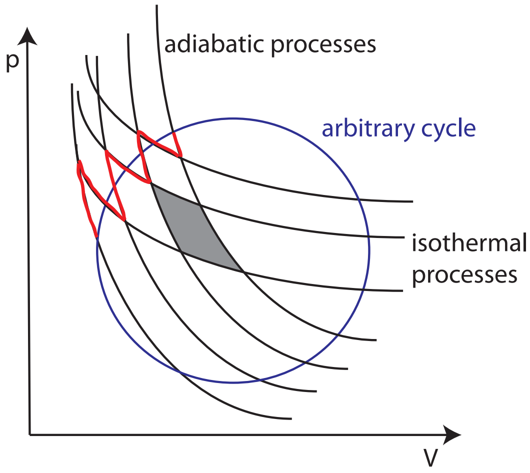
Applying the first law, we have, the total heat transferred is also zero as the process is a cycle.

Since a-c and d-b are adiabatic processes, the heat transferred in process c-d is the same as that in the process a-b.

Now applying first law between the states a and b along a-b and a-c-d-b, we have, the work done is the same.

Thus the heat and work in the process a-b and a-c-d-b are the same and any reversible process a-b can be replaced with a combination of isothermal and adiabatic processes. *A corollary of this theorem is that any reversible cycle can be replaced by a series of Carnot cycles.*

This lemma is now applied to the arbitrary reversible cycle below.



Every small segment (such as shown in gray) corresponds to a Carnot cycle

For Carnot cycle the Clausius equality holds; the heats transferred within the cycle cancel because the heat delivered by one cycle is captured by the cycle below.

What remains are the contributions from the isothermal processes at the boundary of the cycle.

$\sum_n \frac{\delta Q_n}{T_n} = 0 \rightarrow_{n\rightarrow\infty} \oint \frac{\delta Q}{T} = 0$

4.3 Entropy

$\oint \frac{\delta Q}{T} = 0 \rightarrow \frac{\delta Q}{T}$ exact differential

There exists a thermodynamic parameter called entropy (S) the exact differential of which is given by $\mathrm{dS} = \frac{\delta Q_{rev}}{T}$**, where** δQ_{rev} **corresponds to the reversibly transferred heat at the temperature T.**

consider cycle between 2 states with the same temperature T

$Z_1 \rightarrow Z_2$: extraction of δQ from heat reservoir (not necessarily reversible)

$Z_2 \rightarrow Z_1$: transfer of δQ_{rev} to the heat reservoir with $T_1 = T_2 = T$ and $Q_1 = \delta Q > 0$ and $Q_2 = -\delta Q_{\text{rev}} < 0$

it holds $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \frac{\delta Q}{T} - \underbrace{\frac{\delta Q_{rev}}{T}}_{=\text{dS}} \leqslant 0$

$$\text{dS} \geqslant \frac{\delta Q}{T}$$

with :=reversible heat exchange and >: irreversible heat exchange

in particular for closed systems: $\delta Q = 0 \rightarrow \text{dS} \geqslant 0$
i.e., the entropy of an isolated system cannot decrease

2nd law of thermodynamics (Sommerfeld's version):
Any thermodynamic system is characterized by an extensive property S, called entropy. Its change during reversible processes is given by the heat exchange δQ divided by T (ideal gas temperature). Irreversible processes lead to an entropy production within the system.

in short: $\text{dS} = \text{dS}_e + \text{dS}_i$
$\text{dS}_e = \frac{\delta Q}{T}$; $\text{dS}_i \geqslant 0$

isolated systems: $\text{dS}_e = \frac{\delta Q}{T} = 0 \rightarrow \text{dS} = \text{dS}_i \geqslant 0$

As long as processes occur spontaneously within the isolated systems, entropy is being produced. The entropy production stops if the equilibrium is reached. Then the entropy has reached its maximum.

2nd law characterizes the direction of spontaneous (natural) processes!

Application to heat engines:

consider cycle between 2 heat reservoirs:

1st law $\Rightarrow 0 = \oint \text{dU} = \oint \delta W + \oint \delta Q$
$\Rightarrow Q_1 + Q_2 + W = 0 \Rightarrow -W = Q_1 + Q_2$

$Q_1 > 0$ heat transfer to the system; $Q_2 < 0$ heat transfer from the system; $W < 0$ work done

2nd law $0 = \oint \text{dS} \geqslant \oint \frac{\delta Q}{T}$, i.e.,

$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leqslant 0$

$\frac{T_2}{T_1} + \frac{Q_2}{Q_1} \leqslant 0$, i.e.,

$$\eta = -\frac{W}{Q_1} = \frac{Q_1+Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} = \underbrace{1 - \frac{T_2}{T_1}}_{\eta_c} + \underbrace{\frac{T_2}{T_1} + \frac{Q_2}{Q_1}}_{\leqslant 0}$$

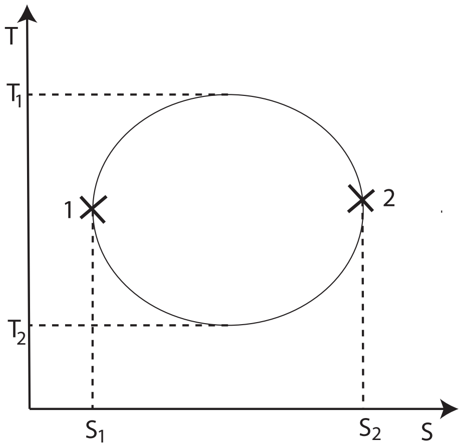
$\Rightarrow \eta \leqslant \eta_c$

No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs, efficiency cannot exceed η_c

What about more than 2 reservoirs? Consider reversible cycle operating at temperatures that are not constant

$1 \to 2$: Q_1reversibly transferred to the system at $T \leqslant T_1$

$2 \to 1$: Q_2 reversibly extracted from the system at $T \geqslant T_2$



$Q_{rev_1} = \int_1^2 \delta Q_{rev} = \int T \, \mathrm{dS} = \bar{T}_1(S_2 - S_1)$

$Q_{rev_2} = \int_2^1 \delta Q_{rev} = \int_2^1 T \, \mathrm{dS} = \bar{T}_2(S_1 - S_2)$

$\bar{T}_{1,2}$: mean temperature

$\frac{T_1}{\bar{T}_1} \geqslant 1$; $\frac{T_2}{\bar{T}_2} \leqslant 1; \Rightarrow \frac{T_2}{\bar{T}_2} - \frac{T_1}{\bar{T}_1} \leqslant 0 \Rightarrow \frac{T_2}{T_1} - \frac{\bar{T}_2}{\bar{T}_1} \leqslant 0$

$\frac{Q_{rev_1}}{\bar{T}_1} + \frac{Q_{rev_2}}{\bar{T}_2} = 0 \to \frac{Q_{rev_2}}{Q_{rev_1}} = -\frac{\bar{T}_2}{\bar{T}_1}$,
that means $\eta_{rev} = \frac{Q_{rev_1}+Q_{rev_2}}{Q_{rev_1}} = 1 + \frac{Q_{rev_2}}{Q_{rev_1}} = 1 - \frac{\bar{T}_2}{\bar{T}_1} =$

$$= \underbrace{1 - \frac{T_2}{T_1}}_{\eta_c} + \underbrace{\frac{T_2}{T_1} - \frac{\bar{T}2}{\bar{T}_1}}_{\leqslant 0,\text{see above}}$$
$$\Rightarrow \eta_{rev} \leqslant \eta_c$$

That is, the variation of the temperature reduces the efficiency of the reversible cycle with respect a reversible cycle operating between the respective minimum and maximum temperatures.

4.4 Thermodynamic and empirical temperature

For Carnot cycle it holds: $\frac{T_1}{T_2} = \frac{|Q_1|}{|Q_2|}$ with T_1,T_2 ideal gas temperature

$\eta_c = 1 - \frac{T_2}{T_1} \leqslant 1 \Rightarrow T_2 \geqslant 0$

That is, the cooler one of the two heat reservoirs cannot have a negative temperature, i.e, there exists an *absolute null or zero point* at 0 K of the empirical ideal gas temperatur.

Temperatures can be measured via heat transfer using the Carnot cycle:

$T = \frac{|Q|}{|Q_{ref}|} T_{ref}$; $T_{ref} = 273.16$ K (water tripel point)

Measurement specification independent of materials properties, (in fact measure energies, can be done using well established procedures) therefore we speak of **absolute or thermodynamical temperature**!

Usage of Carnot cycle for temperature measurement not really convenient $\Rightarrow$ use empirical temperature scale that is gauged with respect to the thermodynamic temperature.

4.5 Reversible ersatz processes

Entropy is thermodynamical parameter, i.e, entropy change $\Delta S = S_2 - S_1$ during a process between two states Z_1 and Z_2 does not depend on the particular "path", i.e., thermodynamic process leading from Z_1 to Z_2.

$\Longrightarrow$ May consider any reversible process (so-called ersatz process) instead of the real process in order to calculate the entropy change.

entropy change of the reversible ersatz process may be calculated by combining 1st and 2nd law of thermodynamics:

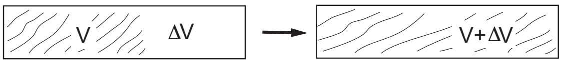
Example: pVT system

$\mathrm{dU} = \mathrm{TdS} - \mathrm{pdV} \rightarrow \mathrm{dS} = \frac{1}{T}\,\mathrm{dU} + \frac{p}{T}\,\mathrm{dV}$

i.e., S=S(U,V) using CEOS →U=U(T,V) it follows
S=S(T,V) using TEOS →T=T(p,V) one obtains
S=S(p,V)

Exercises:

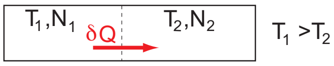
- Irreversible gas expansion (cf. Gay-Lussac's experiment, Chapt. 3.5)

  $\Delta S = Nk \ln[1 + \frac{\Delta V}{V}] \geqslant 0$

  increase of entropy → irreversible, potential work has been wasted; work is required to restore the initial state (e. g. isothermal compression)

- heat exchange between diathermic systems

  $T_1 > T_2$

  $\Delta S = C_v \ln \left[(n_1 + n_2 \frac{T_2}{T_1})^{n_1} (n_1 \frac{T_1}{T_2} + n_2)^{n_2} \right] \geqslant 0$ with $n_1 = \frac{N_1}{N_1 + N_2}$

  temperature equalization always accompanied by entropy increase

5 Thermodynamic potentials

5.1 Fundamental thermodynamic relation

1st law: $\delta Q + \delta W = \mathrm{dU} \Rightarrow \frac{\delta Q}{T} = \frac{1}{T}\,\mathrm{dU} - \frac{1}{T}\delta W$

2nd law: $\mathrm{dS} = \mathrm{dS}_i + \frac{\delta Q}{T}; \mathrm{dS} \geqslant 0$

1st & 2nd law: $\mathrm{dS} = \mathrm{dS}_i + \frac{1}{T}\,\mathrm{dU} - \frac{1}{T}\delta W; \mathrm{dS}_i \geqslant 0$

in particular reversible process, i.e., $\mathrm{dS}_i = 0$

Fundamental thermodynamic relation (FTR):

$$\mathrm{dS} = \frac{1}{T}\,\mathrm{dU} + \frac{1}{T}\sum_i y_i\,\mathrm{dX}_i$$

FTR: relation between exact differentials yields entropy as function of U and the thermodynamic parameters X_i

$\mathrm{S}=\mathrm{S}(\mathrm{U},\{\mathrm{X}_i\})$.

comparison with $\mathrm{dS}=(\frac{\partial S}{\partial U})_{\{X_i\}}\,\mathrm{dU} + \sum_i(\frac{\partial S}{\partial X_i})_{U,X_j,j\neq i}\,\mathrm{dX}_i$

results in $(\frac{\partial S}{\partial U})_{\{X_i\}} = \frac{1}{T}$ und $(\frac{\partial S}{\partial X_i})_{U,X_j} = \frac{y_i}{T}$

$\Rightarrow T = T(U,\{X_i\})$
$\Rightarrow y_i = y_i(U,\{X_i\})$

i.e., S,T, and all y_i are functions of (U,$\{X_i\}$)
$\Longrightarrow$ (U,$\{X_i\}$) form a special minimal ensemble of thermodynamic parameters

when S is given as a function of (U,$\{\mathrm{X}_i\}$), we know CEOS and TEOS as well, since

$\frac{1}{T} = (\frac{\partial S}{\partial U})_{\{X_i\}} \Rightarrow T = T(U,\{X_i\}) \Rightarrow U = U(T,\{X_i\})$ (CEOS)

$\frac{y_i}{T} = (\frac{\partial S}{\partial X_i})_{U,\{X_i\}} \Rightarrow y_i = Tf_i(U,\{X_j\})$ with U=U(T,$\{X_i\}$) (CEOS from above)

$\Rightarrow y_i = y_i(T,\{X_j\})$ (TEOS)

(number of TEOS' = number of work terms in FTR)

that is S=S(U,$\{\mathrm{X}_i\}$) determines TEOS and CEOS, i.e, all thermodynamic information about system contained in that function

therefore $S(U,\{X_i\})$ known as *thermodynamic potential*

A *thermodynamic potential* is a scalar potential function used to represent the thermodynamic state of a system. As we will see below, $S(U,\{X_i\})$ is neither the only thermodynamic potential nor the most convenient one.

Are TEOS&CEOS independent relations?

CEOS $\Rightarrow \mathrm{dU} = (\frac{\partial U}{\partial T})_{\{X_i\}}\,\mathrm{dT} + \sum_i(\frac{\partial U}{\partial X_i})_{T,\{X_j\}}\,\mathrm{dX}_i$ with $j \neq i$

insert in FTR:

$\mathrm{dS} = \frac{1}{T}\left\{(\frac{\partial U}{\partial T})_{\{X_i\}}\,\mathrm{dT} + \sum_i\left[(\frac{\partial U}{\partial X_i})_{\{X_j\},T} + y_i\right]\mathrm{dX}_i\right\}$

that is S=S(T,{X$_j$})

dS=$(\frac{\partial S}{\partial T})_{\{X_i\}}\,\mathrm{dT} + \sum_i (\frac{\partial S}{\partial X_i)})_{T,\{X_j\}}\,\mathrm{dX}_i$

compare coefficients: $(\frac{\partial S}{\partial T})_{\{X_i\}} = \frac{1}{T}(\frac{\partial U}{\partial T})_{\{X_i\}} \Rightarrow \frac{\partial^2 S}{\partial X_i \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial X_i \partial T}$ **(*)**

$(\frac{\partial S}{\partial X_i})_{T,\{X_j\}} = \frac{1}{T}\left[(\frac{\partial U}{\partial X_i})_{T,\{X_i\}} + y_i\right]$
$\Rightarrow \frac{\partial^2 S}{\partial T \partial X_i} = -\frac{1}{T^2}\left[(\frac{\partial U}{\partial X_i})_{T,\{X_j\}} + y_i\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial X_i} + \frac{\partial y_i}{\partial T}\right]$ **(**)**

(*)/(**) $\Rightarrow T(\frac{\partial y_i}{\partial T})_{\{X_i\}} = (\frac{\partial U}{\partial X_i})_{T,\{X_j\}} + y_i$; **Maxwell's Relation**

CEOS&TEOS related to each other!

Maxwell's relations are a set of equations in thermodynamics which are derivable from the definitions of the thermodynamic potentials. The Maxwell relations are statements of equality among the second derivatives of the thermodynamic potentials that follow directly from the fact that the order of differentiation of an analytic function of two variables is irrelevant.

5.2 Thermodynamic energy potentials

S(U,$\{X_i\}$ is thermodynamic potential provided it depends on the parameters (U,$\{X_i\}$), the parameters are known as *natural variables of that potential*

If a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables and this is true for no other combination of variables. Remember the last chapter, where TEOS and CEOS were obtained from $S(U,\{X_i\})$

FTR: dS=$\frac{1}{T}\,\mathrm{dU} + \frac{1}{T}\sum_i y_i\,\mathrm{dX}_i$

$\Rightarrow U = U(S,\{X_i\})$ thermodynamic potential with natural variables (S,{X$_i$})

dU=TdS$-\sum_i y_i\,\mathrm{dX}_i$

further Maxwell's relations from $\frac{\partial^2 U}{\partial X_i \partial S} = \frac{\partial^2 U}{\partial S \partial X_i}$

that is $(\frac{\partial T}{\partial X_i})_{S,\{X_j\}} = -(\frac{\partial y_i}{\partial S})_{\{X_j\}}$

analogously $\frac{\partial^2 U}{\partial X_i \partial X_j} = \frac{\partial^2 U}{\partial X_j \partial X_i} \Rightarrow (\frac{\partial y_j}{\partial X_i})_{S,\{X_j\}} = (\frac{\partial y_i}{\partial X_j})_{S,\{X_i\}}$

Problem: thermodynamic parameter S difficult to measure, difficult to control

→ $U = U(S, \{X_i\})$ as thermodynamic potential often not very useful
→ eliminate S by Legendre transform
→ introduce **free energy** F = U - TS

$\mathrm{dF} = \mathrm{dU} - \mathrm{TdS} - \mathrm{SdT} = -\,\mathrm{SdT} - \sum_i y_i\,\mathrm{dX}_i$; (FTR exploited: $\Rightarrow \mathrm{dU} = \mathrm{TdS} - \sum_i y_i\,\mathrm{dX}_i$)

$$\Rightarrow F = F(T, \{X_i\})$$

that is, F is thermodynamic potential with natural variables (T,{X$_i$})
Interpretation?

assume T=const. $\Rightarrow \mathrm{dT} = 0 \Rightarrow \mathrm{dF} = -\sum_i y_i\,\mathrm{dX}_i$; $\sum_i y_i\,\mathrm{dX}_i = \delta W$

That is, at constant temperature corresponds the difference of the free energy exactly the work done on the system.

Remark: The *free energy* was developed by Hermann von Helmholtz and is usually denoted by the letter A (from the German Arbeit or work), or the letter F. The IUPAC recommends the letter A as well as the use of name Helmholtz energy. In physics, A is somtimes referred to as the Helmholtz function or simply free energy (although not in other disciplines).

5.3 pVT systems

Maxwell's relation from S(U,{X$_i$}) (cf. 5.1)

$T(\frac{\partial y_i}{\partial T})_{\{X_i\}} = (\frac{\partial U}{\partial X_i})_{T,\{X_j\}} + y_i$

simplifies to
$T(\frac{\partial p}{\partial T})_V = (\frac{\partial U}{\partial V})_T + p \Leftrightarrow (\frac{\partial U}{\partial V})_T = T^2(\frac{\partial}{\partial T}(\frac{p}{T}))_V$

for pVT systems. Thus relation between TEOS&CEOS for pVT systems

Example ideal gas:
TEOS: $pV = NkT$
$\Rightarrow (\frac{\partial U}{\partial V})_T = T^2(\frac{\partial}{\partial T}(\frac{p}{T})) = T^2(\frac{\partial}{\partial T}(\frac{Nk}{V})) = 0$
⇒ internal energy cannot depend on the volume!

Compressibility:

$\kappa = -\frac{1}{V}\frac{\mathrm{dV}}{\mathrm{dp}}$ depends obviously on the conditions for the compression

- Isothermal: $\kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial p})_T$
- Adiabatic (isentropic): $\kappa_S = -\frac{1}{V}(\frac{\partial V}{\partial p})_S$

$\frac{\kappa_T}{\kappa_S} = \frac{(\frac{\partial V}{\partial p})_T}{(\frac{\partial V}{\partial p})_S}$

remember polytropic equation for p(V) in *(3.2)*

$(\frac{\partial T}{\partial p})_V \frac{\mathrm{dp}}{\mathrm{dV}} = -\frac{C_p - C}{C_v - C} (\frac{\partial T}{\partial V})_p$

now adiabatic process (C=0):

$\Rightarrow (\frac{\partial T}{\partial p})_V (\frac{\partial p}{\partial V})_S = -\frac{C_p}{C_v} (\frac{\partial T}{\partial V})_p$

$\Rightarrow (\frac{\partial V}{\partial p})_S^{-1} = -\frac{C_p}{C_v} (\frac{\partial T}{\partial V})_p / (\frac{\partial T}{\partial p})_V$ thus

$\frac{\kappa_T}{\kappa_S} = -\frac{C_p}{C_v} \underbrace{(\frac{\partial T}{\partial V})_p (\frac{\partial V}{\partial p})_T / (\frac{\partial T}{\partial p})_V}_{=-1,\ \ proof\ \ below}$

thus eventually

$$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_v}$$

addendum: missing proof
TEOS $f(p,T,V) = 0$
$\Rightarrow$ df $= \frac{\partial f}{\partial P}$ dp $+ \frac{\partial f}{\partial V}$ dV $+ \frac{\partial f}{\partial T}$ dT $= 0$

$\Rightarrow$ in particular:
$(\frac{\partial V}{\partial p})_T = -\frac{(\frac{\partial f}{\partial p})}{(\frac{\partial f}{\partial V})}$
$(\frac{\partial p}{\partial T})_V = -\frac{(\frac{\partial f}{\partial T})}{(\frac{\partial f}{\partial p})}$
$(\frac{\partial V}{\partial T})_p = -\frac{(\frac{\partial f}{\partial T})}{(\frac{\partial f}{\partial V})}$

$\Rightarrow (\frac{\partial V}{\partial T})_p (\frac{\partial T}{\partial p})_V (\frac{\partial p}{\partial V})_T = -1$

<u>further important thermodynamic potentials:</u>

hitherto: **internal energy** U=U(S,V); dU=T dS $-p$ dV

$T = (\frac{\partial U}{\partial S})_V; -p = (\frac{\partial U}{\partial V})_S$

equate 2nd derivatives $\triangleq$ Maxwell's relation $\Rightarrow (\frac{\partial T}{\partial V})_S = -(\frac{\partial p}{\partial S})_V$

free energy

F=U$-TS$; dF = dU $-T$ dS $-S$ dT = T dS $-p$ dV $-T$ dS $-S$ dT = $-S$ dT $-p$ dV

$\Rightarrow F = F(T,V) \Rightarrow -S = (\frac{\partial F}{\partial T})_V; -p = (\frac{\partial F}{\partial V})_T$

Maxwell's relation: $(\frac{\partial S}{\partial V})_T = (\frac{\partial p}{\partial T})_V$

Variation in the free energy corresponds to the work done on the system isothermally.

Chemical reactions often occur at const. pressure, e.g., atmospheric pressure, while the volume varies.

$\Rightarrow$ eliminate dependence on volume in the internal energy by Legendre transform;
that leads us to the **enthalpy**: $H = U + pV$

$\mathrm{dH} = \mathrm{dU} + p\,\mathrm{dV} + V\,\mathrm{dp} = T\,\mathrm{dS} - p\,\mathrm{dV} + p\,\mathrm{dV} + V\,\mathrm{dp} = T\,\mathrm{dS} + V\,\mathrm{dp}$

$\Rightarrow H = H(S,p) \Rightarrow T = (\frac{\partial H}{\partial S})_p; V = (\frac{\partial H}{\partial p})_S$

Maxwell's relation: $(\frac{\partial T}{\partial p})_S = (\frac{\partial V}{\partial S})_p$

Variation in the enthalpy corresponds to the change of energy during isobaric processes → Example: enthalpy of formation in chemistry

Problem: entropy is not really convenient as a natural variable

→ eliminate dependence on entropy by Legendre transform

Gibbs free energy: $G = H - TS = U + pV - TS \Rightarrow \mathrm{dG} = \mathrm{dU} + p\,\mathrm{dV} + V\,\mathrm{dp} - T\,\mathrm{dS} - S\,\mathrm{dT}$

$\Rightarrow \mathrm{dG} = T\,\mathrm{dS} - p\,\mathrm{dV} + p\,\mathrm{dV} + V\,\mathrm{dp} - T\,\mathrm{dS} - S\,\mathrm{dT} = V\,\mathrm{dp} - S\,\mathrm{dT} \Rightarrow G = G(p,T)$

For many practical purposes ideal, since (p,T) is constant for all homogenous parts of a system in equilibrium

$(\frac{\partial G}{\partial T})_p = -S$; $(\frac{\partial G}{\partial p})_T = V$

Maxwell's relation: $(\frac{\partial S}{\partial p})_T = -(\frac{\partial V}{\partial T})_p$

crib: Guggenheim scheme
(**SUV** **H**ift **F**ysikern **p**ei **G**roßen **T**aten)
(**G** ood **p**hysicists **h**ave **s**tudied **u** nder **v**ery **f**ine **t**eachers.
$\longrightarrow +$
S U V
H F
p G T
$\longleftarrow -$

contains thermodynamic potentials (centre) in dependence on its natural variables (corners), result of partial derivative in respective opposite corner, sign according to direction
(Examples: $(\frac{\partial U}{\partial S})_V = T$ and $(\frac{\partial F}{\partial V})_T = -p$)

Examples for thermodynamic poterntials: U and F for ideal gas
(proof: exercise)

$$U = U(S, V) = U_0 + C_v T_0 \left[(\tfrac{V}{V_0})^{-Nk/C_v} exp[\tfrac{S-S_0}{C_v}] - 1 \right]$$

$$F = F(V, T) = C_v(T - T_0) + U_0 - T \ln \left[(\tfrac{T}{T_0})^{C_v} (\tfrac{V}{V_0})^{Nk} \right] - TS_0$$

6 Third law of thermodynamics

1st/2nd law ⇒ ∃ absolute null point, absolute temperature (defined via Carnot cycle)

Nernst's postulate $\triangleq$ 3rd law of thermodynamics:
As a system approaches absolute zero (T→ 0) its entropy approaches a minimum value and tends to a constant independently of the other thermodynamic parameters.

That is $\lim_{T\to 0} S = S_0$ =const.

with $\Delta S = S - S_0$ it follows $\lim_{T\to 0} \Delta S = 0$

$\lim_{T\to 0}(\frac{\partial S}{\partial Z_k})_{T,\{Z_i\},i\neq k} = 0$

S_0 =const., independent of thermodynamic parameters ⇒ WLOG $S_0 = 0$

conclusion derived from the third law: **It is impossible by any procedure, no matter how idealised, to reduce any system to the absolute zero of temperature in a finite number of operations.**

proof that this statement follows from Nernst's postulate:

assume: T=0 can be achieved

operate Carnot cycle between two heat reservoirs at $T_1 > 0$ and T_2=0

$\oint \mathrm{dS} = 0 \Rightarrow \Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0$

$1 \rightarrow 2$: isothermal expansion $\Delta S_{12} = \frac{Q}{T}; Q \neq 0$

$2 \rightarrow 3$: adiabatic expansion $\Delta S_{23} = 0$

$3 \rightarrow 4$: isothermal compression $\Delta S_{34} = 0$ (3rd law S=const)

$4 \rightarrow 1$: adiabatic compresseion $\Delta S_{41} = 0$

D.h. $\Delta S_{12} = 0 \Rightarrow$ contradicts Q $\neq 0$

q.e.d.

Remark

- Carnot cycle between $T_1 = T > 0$ and T_2=0 were a perpetual motion machine of the second kind
- may postulate the unattainability of absolute zero of temperature as third law of thermodynamics
- thermodynamic coefficients for $T \rightarrow 0$:
  free energy $F = F(T, \{X_i\}); \mathrm{dF} = -S\,\mathrm{dT} - \sum_i y_i\,\mathrm{dX}_i$

  Maxwell's relations hold: $(\frac{\partial S}{\partial X_i})_{T,\{X_j\}} = (\frac{\partial y_i}{\partial T})_{\{X_j\}}$ with i$\neq j$

  $T \rightarrow 0 \Rightarrow (\frac{\partial S}{\partial X_i})_{T,\{X_j\}} = 0 \Rightarrow \lim_{T\rightarrow 0}(\frac{\partial y_i}{\partial T})_{\{X_j\}} = 0$
  (because of 3rd law)
  That means thermodynamic coefficients $\frac{\partial y_i}{\partial T}$ approach constant value with zero slop for T=0.

7 Systems with varying numbers of particles

Examples:

- liquid in equilibrium with its saturated vapor; number of particles in both phases depends on temperature and pressure
- chemical reactions

7.1 Chemical potential

Thermodynamic system with N_α particles in different phases or different particle species internal energy depends on respective numbers of particles N_α

$U = U(S, \{X_i\}, \{N_\alpha\})$: thermodynamic potential, i.e, has exact differential

$$\mathrm{dU} = T\,\mathrm{dS} - \sum_i y_i\,\mathrm{dX}_i + \sum_\alpha \mu_\alpha\,\mathrm{dN}_\alpha$$

$$\text{with}\,\mu_\alpha := (\frac{\partial U}{\partial N_\alpha})_{S,\{X_i\},\{N_\beta\}\beta\neq\alpha}$$

μ_α is called *chemical potential*

may use Legendre transform to obtain thermodynamic potentials that do not depend on the chemical potentials rather than on number of particles

earlier: $F = U - TS$; $\mathrm{dF} = -S\,\mathrm{dT} - \sum_i y_i\,\mathrm{dX}_i + \sum_\alpha \mu_\alpha\,\mathrm{dN}_\alpha$

Legendre transformation to derive *grand (or Landau) potential* Ω

$\Omega = F - \sum_\alpha \mu_\alpha N_\alpha$

$d\Omega = \mathrm{dF} - \sum_\alpha \mu_\alpha\,\mathrm{dN}_\alpha - \sum_\alpha N_\alpha d\mu_\alpha\,\text{with}\,\mathrm{dF} = -S\,\mathrm{dT} - \sum_i y_i\,\mathrm{dX}_i + \sum_\alpha \mu_\alpha\,\mathrm{dN}_\alpha$

it follows

$$d\Omega = -S\,\mathrm{dT} - \sum_i y_i\,\mathrm{dX}_i - \sum_\alpha N_\alpha d\mu_\alpha$$

i.e., $\Omega = \Omega(T, \{X_i\}, \{\mu_\alpha\})$

obviously $N_\alpha = -(\frac{\partial\Omega}{\partial\mu_\alpha})_{T,\{X_i\},\{\mu_\beta\}\beta\neq\alpha}$

internal energy and entropy are thermodynamic parameters, i.e.,

$U(\lambda S, \{\lambda X_i\}, \{\lambda N_\alpha\}) = \lambda U(S, \{X_i\}, \{N_\alpha\})$

apply *Euler's homogeneous function theorem*:
$f(\lambda X_k) = \lambda^n f(X_k) \Rightarrow \sum_k X_k \frac{\partial f}{\partial X_k} = n f(X_k)$

here n=1, i.e.,

$S\,\underbrace{(\frac{\partial U}{\partial S})_{\{X_i\},\{N_\alpha\}}}_{T} + \sum_i X_i\,\underbrace{(\frac{\partial U}{\partial X_i})_{S,\{X_j\},\{N_\alpha\}}}_{-y_i} + \sum_\alpha N_\alpha\,\underbrace{(\frac{\partial U}{\partial N_\alpha})_{S,\{X_i\},\{N_\beta\}}}_{\mu_\alpha} = U$
with $\beta \neq \alpha, i \neq j$

$$\Longrightarrow U = TS - \sum_i y_i X_i + \sum_\alpha \mu_\alpha N_\alpha$$

Gibb's free energy given by $G = F + \sum_i y_i X_i$

$$G = U - TS + \sum_i y_i X_i = G(T, \{y_i\}, \{N_\alpha\}) = \sum_\alpha \mu_\alpha N_\alpha$$

consider system with one phase

$G = \mu N \Rightarrow \mu = \frac{G(T,\{y_i\},N)}{N} = \mu(T, \{y_i\})$

$\Longrightarrow$ *chemical potential corresponds to Gibb's free energy per particle!*

chemical potentials are differential quotients of two extensive properties

$(\mu_\alpha := \frac{\partial U}{\partial N_\alpha}) \Rightarrow$ chemical potentiala are intensive properties!

that is $\mu_\alpha(T, \{y_i\}, \{\lambda N_\beta\}) = \mu_\alpha(T, \{y_i\}, \{N_\beta\})$

Euler's homogeneous function theorem for n=0

$\sum_\beta N_\beta (\frac{\partial \mu_\alpha}{\partial N_\beta})_{T,\{y_i\},\{N_\alpha\}} = 0$ with $\alpha \neq \beta$

That means variations of the chemical potentials are not independent from each other, they interact.

7.2 pVT systems

U = U (S, V, $\{N_\beta\}$) $\Rightarrow$ dU = T dS $-p$ dV $+ \sum_\alpha \mu_\alpha$ dN$_\alpha$

F = U - TS $\Rightarrow$ dF = $-S$ dT $-p$ dV $+ \sum_\alpha \mu_\alpha$ dN$_\alpha$

H = U + pV $\Rightarrow$ dH = T dS $+V$ dp $+ \sum_\alpha \mu_\alpha$ dN$_\alpha$

G = H - TS $\Rightarrow$ dG = $-S$ dT $+V$ dp $+ \sum \mu_\alpha$ dN$_\alpha$

obvious

$\mu_\alpha = (\frac{\partial U}{\partial N_\alpha})_{S,V,\{N_\beta\}} = (\frac{\partial F}{\partial N_\alpha})_{T,V,\{N_\beta\}} = (\frac{\partial H}{\partial N_\alpha})_{S,p,\{N_\beta\}} = (\frac{\partial G}{\partial N_\alpha})_{T,p,\{N_\beta\}}$
$(\beta \neq \alpha)$

thermodynamic potentials are extensive properties, i.e,

$U = U(S, V, N) = U(N\frac{S}{N}, N\frac{V}{N}, N) = NU(\frac{S}{N}, \frac{V}{N}, 1)$

introduce specific quantities :
$\bar{s} = S/N$ ... entropy per particle
$\bar{v} = V/N$ ... volume per particle
$\bar{u} = U/N$ ... internal energy per particle

now

$U = N\bar{u}(\bar{s}, \bar{v})$, analogous $F = N\bar{f}(T, \bar{v})$ and $H = N\bar{h}(\bar{s}, p)$ and $G = N\bar{g}(T, p)$

on the other hand we saw earlier $\mu = (\frac{\partial G}{\partial N})_{p,T} \Rightarrow \mu = \bar{g}$

thus $N\mu = G = U + pV - TS \Rightarrow U = TS - pV + \mu N$ (**)

for U, F, H, and G the particle number is the natural variable
Legendre transform to grand potential

$\Omega = U - TS - \mu N$ (*)

$d\Omega = -S\,\mathrm{dT} - p\,\mathrm{dV} - Nd\mu$ (7.1)
$N = -(\frac{\partial \Omega}{\partial \mu})_{T,V}$
(*) & (**) $\Rightarrow \Omega = -pV$ thus $N = V(\frac{\partial p}{\partial \mu})_{T,V}$

comment to (**): generalizable to several species:

$$G(T, p, \{N_\alpha\}) = \sum_\beta \mu_\beta N_\beta$$

7.3 Homogenous Mixtures

7.3.1 Ideal gas mixtures

altogether N particles in volume V

TEOS: $p\bar{v} = kT$ with $\bar{v} = \frac{V}{N}$

N_α particles of species α obey $p_\alpha \bar{v}_\alpha = kT$ with $\bar{v}_\alpha = \frac{V}{N_\alpha}$
(*real mixture*), i.e,

$$p_\alpha V = N_\alpha kT$$

comparison with $pV = NkT \Rightarrow p_\alpha = \frac{N_\alpha}{N} p = \bar{n}_\alpha p$
i.e, partial pressure ~ concentration

sum up $\Longrightarrow$ *Dalton's law of partial pressures*:

$$\sum_\alpha p_\alpha = p$$

total pressure $\triangleq$ sum of partial pressures

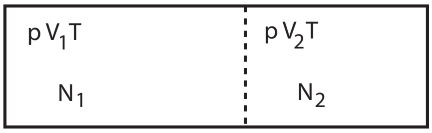
no real mixture: components occupy partial volumes, experience the same pressure: $p_\alpha = p$

TEOS: $pV_\alpha = N_\alpha kT$

comparison with $pV = NkT \Rightarrow V_\alpha = \frac{N_\alpha}{N} V$

$$\sum_\alpha V_\alpha = V$$

consider <u>transition to real mixture</u>



diffusion
-> irreversible mixing

entropy is additive

$\Delta S = S_1(T, V, N_1) + S_2(T, V, N_2) - S_1(T, V_1, N_1) - S_2(T, V_2, N_2)$

need ideal gas entropy, is holds (FTR+CEOS+TEOS):

$\mathrm{dS} = \frac{C_v}{T}\,\mathrm{dT} + \frac{Nk}{V}\,\mathrm{dV}$

$\Rightarrow S - S_0 = C_v \ln\frac{T}{T_0} + Nk\ln\frac{V}{V_0}$

apply to both parts of the system:

variation of entropy $\Delta S = N_1 k \ln\frac{V}{V_1} + N_2 k \ln\frac{V}{V_2}$
it holds $\frac{V}{V_1} = \frac{N}{N_1}$ and $\frac{V}{V_2} = \frac{N}{N_2} \Rightarrow \Delta S = N\left\{\frac{N_1}{N}k\ln\frac{N}{N_1} + \frac{N_2}{N}k\ln\frac{N}{N_2}\right\}$
thus $\Delta S = -Nk\left\{\bar{n}_1 \ln\bar{n}_1 + \bar{n}_2\ln\bar{n}_2\right\}$

generalize to more components : <u>entropy of mixing ideal gases:</u>

$$\Delta S = -Nk\sum_\alpha \bar{n}_\alpha \ln\bar{n}_\alpha$$

Obviously $\Delta S > 0$, thus mixing irreversible

Remarkably $\bar{n}_\alpha = N_\alpha/N$ corresponds to the probability P_α to pick a particle of species α from the mixture. The specific entropy of mixing is thus $-k\sum_\alpha P_\alpha \ln P_\alpha = -k\overline{\ln P}$. This is one of the very few parts of thermodynamics that give a hint for the statistic interpretation of the entropy!

consider variations of specific quantities upon mixing:

$\frac{S}{N} = \bar{s}(T,p,\{\bar{n}_\alpha\}) = \sum_\alpha \bar{n}_\alpha \underbrace{\bar{s}_\alpha(T,p)}_{A1} - k\sum_\alpha \bar{n}_\alpha \ln \bar{n}_\alpha =$

$= \sum_\alpha \bar{n}_\alpha \underbrace{\tilde{s}_\alpha(T,p,\{\bar{n}_\alpha)}_{\underbrace{\bar{s}_\alpha - k\ln\bar{n}_\alpha}_{A2}}$

where A1 = specific entropy of component α before the mixing
and A2 = partial specific entropy after the mixing

derive specific Gibb's free energy of mixing:

$\bar{g}(T,p,\bar{n}_\alpha) = \bar{u} - T\bar{s} + p\bar{v} = \sum_\alpha \left\{ \frac{N_\alpha}{N}\frac{U}{N_\alpha} - T\bar{n}_\alpha\tilde{s}_\alpha + p\frac{N_\alpha}{N}\frac{V_\alpha}{N_\alpha} \right\}$
(here it holds $\bar{v} = V/N; V = \sum_\alpha V_\alpha$)
$= \sum_\alpha \{\bar{n}_\alpha\bar{u}_\alpha - T\bar{n}_\alpha\tilde{s}_\alpha + p\bar{n}_\alpha\bar{v}_\alpha\}$
$=: \sum_\alpha \bar{n}_\alpha\tilde{g}_\alpha$

with $\tilde{g}_\alpha(T,P,\bar{n}_\alpha) = \bar{u}_\alpha + p\bar{v}_\alpha - T\tilde{s}_\alpha = \underbrace{\bar{u}_\alpha + p\bar{v}_\alpha - T\bar{s}_\alpha}_{\bar{g}_\alpha(T,P)\ldots\text{spec. Gibb'sfreeEn. before mix.}} + kT\ln\bar{n}_\alpha$

Earlier (7.2): $G = \sum_\alpha \mu_\alpha N_\alpha$

Here: $\bar{g} = \sum_\alpha \mu_\alpha \frac{N_\alpha}{N} = \sum_\alpha \mu_\alpha \bar{n}_\alpha$
thus

$$\mu_\alpha(T,P,\bar{n}_\alpha) = \bar{g}_\alpha(T,P) + kT\ln\bar{n}_\alpha$$

That means the chemical potentials depend on the contration!

if the species are the same, it holds in particular

$\Delta S = S(T,V,N) - S(T,V_1,N_1) - S(T,V_2,N_2)$
$= N\bar{s}(\bar{v},T) - N_1\bar{s}(\frac{V_1}{N_1},T) - N_2\bar{s}(\frac{V_2}{N_2},T)$

TEOS for “equal” pVT systems: $p = f(\frac{V}{N},T) = f(\frac{V_1}{N_1},T) = f(\frac{V_2}{N_2},T)$

$\Rightarrow \frac{V}{N} = \frac{V_1}{N_1} = \frac{V_2}{N_2} \Rightarrow \Delta S = 0$

7.3.2 Mixtures of real gases

particles interact ⇒ partial specific parameters $\tilde{z}_\alpha$ do not only depend on $\bar{n}_\alpha$, but depend also on the concentration of the other species. In particular, the internal energy does not simply correspond to the sum of the specific energies of the respective components, but consists generally on deviating quantities $\tilde{u}_\alpha$ multiplied with the respective concentration

tangent rule to determine $\tilde{u}_\alpha$:

consider binary mixture (α=1,2)

$U(T, P, N_1, N_2) = N_1\tilde{u}_1 + N_2\tilde{u}_2$
$\bar{u}(T, P, N_1, N_2) = \bar{n}_1\tilde{u}_1 + \bar{n}_2\tilde{u}_2$

How to determine $\tilde{u}_1$ und $\tilde{u}_2$?

earlier *(7.1)*: $\sum_\beta N_\beta \frac{\partial \tilde{z}_\beta}{\partial N_\alpha} = 0$ (Euler's homogeneous function theorem for partial specific parameter)

yields here
$\Rightarrow N_1(\frac{\partial \tilde{u}_1}{\partial N_1})_{T,P,N_2} + N_2(\frac{\partial \tilde{u}_2}{\partial N_1})_{T,P,N_1} = 0$
$\Leftrightarrow \bar{n}_1\frac{\partial \tilde{u}_1}{\partial \bar{n}_1} + \bar{n}_2\frac{\partial \tilde{u}_2}{\partial \bar{n}_1} = 0$

calculate by exploiting $\bar{n}_2 = 1 - \bar{n}_1$
$\frac{\partial}{\partial \bar{n}_1}\bar{u}(T, P, N_1, N_2) = \frac{\partial}{\partial \bar{n}_1}(\bar{n}_1\tilde{u}_1 + \bar{n}_2\tilde{u}_2) =$
$$= \tilde{u}_1 + \underbrace{\bar{n}_1\frac{\partial \tilde{u}_1}{\partial \bar{n}_1} + \bar{n}_2\frac{\partial \tilde{u}_2}{\bar{n}_1}}_{=\ 0\ (see\ \ above)} - \tilde{u}_2$$
$\Rightarrow \frac{\partial \bar{u}}{\partial \bar{n}_1} = \tilde{u}_1 - \tilde{u}_2$, as well as $\bar{u} = \bar{n}_1\tilde{u}_1 + \bar{n}_2\tilde{u}_2$

⇒ measure dependence $\bar{u}$ on concentration → obtain $\tilde{u}_1$ and $\tilde{u}_2$!

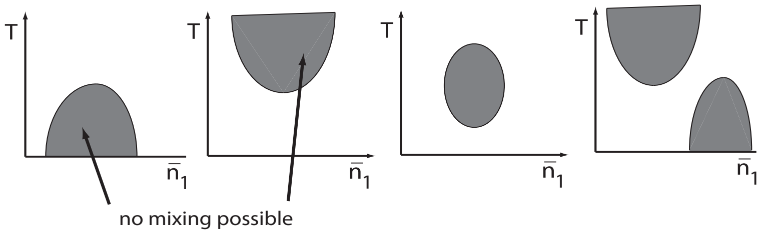
heat of mixture

before mixing: $H_0(T, p, \{N_\alpha\}) = \sum_\alpha N_\alpha \bar{h}_\alpha(T, p)$
after mixing: $H(T, p, \{N_\alpha\}) = \sum_\alpha N_\alpha \tilde{h}_\alpha(T, p)$

$\Rightarrow \Delta H = H - H_0 = \sum_\alpha N_\alpha(\tilde{h}_\alpha - \bar{h}_\alpha)$
$\Rightarrow q_m = \frac{\Delta H}{N} = \sum_\alpha \bar{n}_\alpha(\tilde{h}_\alpha - \bar{h}_\alpha)$

- mixtures of ideal gases always stable
- liquids may or may not be mixable, depends on temperature and concen-

tration



8 Conditions of stable equilibrium

the entropy of an isolated system cannot decrease, dS $\geqslant 0$

in equilibrium dS $= 0; S = S_{\max}$

that means equilibrium corresponds to the solution of an extremal problem with the side condition of isolation

Example: pVT system with mass M

side conditions: U=const.; V=const. and M=const.

condition of equilibrium
$\delta S = \sum_i \frac{\partial S}{\partial y_i} \delta y_i = 0$
where δy_i is a virtual change of the parameter y_i that is compatible with $\delta U = \delta V = \delta M = 0$

in short, the condition of equilibrium is

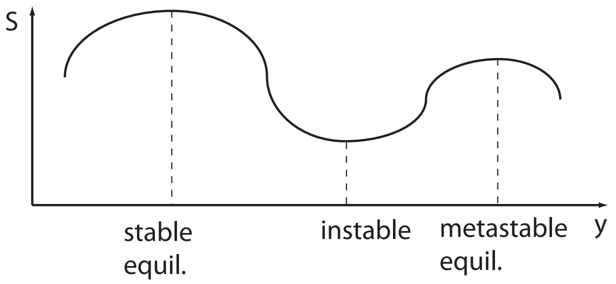
$$(\delta S)_{U,V,M} = 0$$

condition of equilibrium → entropy assumes extreme value; in particular maximum for

$$(\delta^2 S)_{U,V,M} = \frac{1}{2} \sum_{i,j} \frac{\partial^2 S}{\partial y_i \partial Y_j} \delta y_i \delta Y_j < 0$$

that is the condition for *stable* equilibrium

ensure stability or at least meta stability (Example: overheated liquid)



Often system in equilibrium with their surroundings are more interesting than isolated systems. In those cases the equilibrium conditions are different. They can be determined by combining 1st and 2nd law. In particular for pVT systems it holds

$T\,\mathrm{dS} \geqslant \delta Q = \mathrm{dU} + p\,\mathrm{dV}$

1. system isolated, i.e., $\mathrm{dU} = 0, \mathrm{dV} = 0 \Rightarrow \mathrm{dS} \geqslant 0$ (see above)
2. processes occur at const. entropy and const. volume, i.e,

   $\mathrm{dS} = 0, \mathrm{dV} = 0 \Rightarrow \mathrm{dU} \leqslant 0$
   condition for stable equilibrium
   $(\delta U)_{S,V,M} = 0; (\delta^2 U)_{S,V,M} > 0$
3. processes occur at const. temperature and const. volume, i.e,

   $\mathrm{dT} = 0, \mathrm{dV} = 0$
   $T\,\mathrm{dS} \geqslant \delta Q = \mathrm{dU} + p\,\mathrm{dV}$ = dF + TdS + SdT +pdV
   $\Rightarrow 0 \geqslant \mathrm{dF} + \underbrace{S\,\mathrm{dT}}_{=\,0} + \underbrace{p\,\mathrm{dV}}_{=\,0} \Rightarrow \mathrm{dF} \leqslant 0$
   condition for stable equilibrium
   $(\delta F)_{T,V,M} = 0; (\delta^2 F)_{T,V,M} > 0$
4. processes occur at const. entropy and const. pressure, i.e,

   d.h. $\mathrm{dS} = 0, \mathrm{dp} = 0$
   $\underbrace{T\,\mathrm{dS}}_{=\,0} \geqslant \delta Q = \mathrm{dU} + p\,\mathrm{dV}$ = dH -pdV - Vdp + pdV
   $\Rightarrow \mathrm{dH} \leqslant 0$
   condition for stable equilibrium
   $(\delta H)_{S,p,M} = 0; (\delta^2 H)_{S,p,M} > 0$
5. (particularly important!) processes occur at const. temperature and const. pressure, i.e.,

   d.h. dT=0, dp=0
   $T\,\mathrm{dS} \geqslant \delta Q = \mathrm{dU} + p\,\mathrm{dV} = dG + TdS + SdT - pdV - Vdp + pdV$

$\Rightarrow$ dG $\leqslant 0$
condition for stable equilibrium
$(\delta G)_{p,T,M} = 0; (\delta^2 G)_{p,T,M} > 0$

That means there are no universal conditions that ensure stable equlibrium! The experimental conditions define the appropriate thermodynamic potential that assumes in equilibrium a minimum (or maximum) value.

8.1 Phase equilibrium in pVT systems

pVT system with 2 phases:

$U = U_1 + U_2$
$V = V_1 + V_2$
$N = N_1 + N_2$

$S = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2) = S(U_1, V_1, N_1, U_2, V_2, N_2)$

$$\underbrace{\delta S}_{=\ 0} = \tfrac{\partial S_1}{\partial U_1}\delta U_1 + \tfrac{\partial S_1}{\partial V_1}\delta V_1 + \tfrac{\partial S_1}{\partial N_1}\delta N_1 + \tfrac{\partial S_2}{\partial U_2}\delta U_2 + \tfrac{\partial S_2}{\partial V_2}\delta V_2 + \tfrac{\partial S_2}{\partial N_2}\delta N_2$$

side conditions $\delta U = \delta U_1 + \delta U_2 = 0$
$\delta V = \delta V_1 + \delta V_2 = 0$
$\delta N = \delta N_1 + \delta N_2 = 0$

$$\text{thus } (\underbrace{\frac{\partial S_1}{\partial U_1}}_{=\ \frac{1}{T_1}} - \underbrace{\frac{\partial S_2}{\partial U_2}}_{=\ \frac{1}{T_2}})\delta U_1 + (\underbrace{\frac{\partial S_1}{\partial V_1}}_{=\ \frac{p_1}{T_1}} - \underbrace{\frac{\partial S_2}{\partial V_2}}_{=\ \frac{p_2}{T_2}})\delta V_1 + (\underbrace{\frac{\partial S_1}{\partial N_1}}_{=\ -\frac{\mu_1}{T_1}} - \underbrace{\frac{\partial S_2}{\partial N_2}}_{=\ -\frac{\mu_2}{T_2}})\delta N_1 = 0$$

δU_1 arbitrary $\Rightarrow T_1 = T_2$ *thermal equlibrium*
δV_1 arbitrary $\Rightarrow p_1 = p_2$ *mechanical equilibrium*
δN_1 arbitrary $\Rightarrow \mu_1 = \mu_2$ *diffusive equilibrium*

alternatively start from $S = S_1 + S_2$;$V = V_1 + V_2$;$N = N_1 + N_2$
$U = U_1(S_1, V_1, N_1) + U_2(S_2, V_2, N_2)$

$$\underbrace{\delta U}_{=\ 0} = (\underbrace{\frac{\partial U_1}{\partial S_1}}_{=\ T_1} - \underbrace{\frac{\partial U_2}{\partial S_2}}_{=\ T_2})\delta S_1 + (\underbrace{\frac{\partial U_1}{\partial V_1}}_{=\ -p_1} - \underbrace{\frac{\partial U_2}{\partial V_2}}_{=\ -p_2})\delta V_1 + (\underbrace{\frac{\partial U_1}{\partial N_1}}_{=\ \mu_1} - \underbrace{\frac{\partial U_2}{\partial N_2}}_{=\ \mu_2})\delta N_1$$

and again if follows
$T_1 = T_2$
$p_1 = p_2$

$\mu_1 = \mu_2$

condition for stable equilibrium
$(\delta^2 U)_{S,V,N} = \frac{1}{2}\left(\frac{\partial^2 U_1}{\partial S_1^2} + \frac{\partial^2 U_2}{\partial S_2^2}\right)(\delta S_1)^2 +$
$\frac{1}{2}\left(\frac{\partial^2 U_1}{\partial V_1^2} + \frac{\partial^2 U_2}{\partial V_2^2}\right)(\delta V_1)^2 + \frac{1}{2}\left(\frac{\partial^2 U_1}{\partial N_1^2} + \frac{\partial^2 U_2}{\partial N_2^2}\right)(\delta N_1)^2 +$
$\left(\frac{\partial^2 U_1}{\partial S_1 \partial V_1} + \frac{\partial^2 U_2}{\partial S_2 \partial V_2}\right)(\delta S_1 \delta V_1) +$
$\left(\frac{\partial^2 U_1}{\partial S_1 \partial N_1} + \frac{\partial^2 U_2}{\partial S_2 \partial N_2}\right)(\delta S_1 \delta N_1) +$
$\left(\frac{\partial^2 U_1}{\partial V_1 \partial N_1} + \frac{\partial^2 U_2}{\partial V_2 \partial N_2}\right)(\delta V_1 \delta N_1) > 0.$

8.2 Conditions of stable equilibrium for pVT system

considerations in *(8.1)* hold as well for any 2 parts of a single-phase pVT system

$\Rightarrow T, p, \mu$ const. within the system in equilibrium

system is homogenous, therefore $\frac{\partial^2 U_1}{\partial V_1^2} = \frac{\partial^2 U_2}{\partial V_2^2}$ and so forth, i.e, may drop indices, stability conditions simplify to

$\frac{1}{2}\left(\frac{\partial^2 U}{\partial S^2}\right)(\delta S)^2 + \frac{1}{2}\left(\frac{\partial^2 U}{\partial V^2}\right)(\delta V)^2 + \frac{1}{2}\left(\frac{\partial^2 U}{\partial N^2}\right)(\delta N)^2 +$
$\left(\frac{\partial^2 U}{\partial S \partial V}\right)(\delta S \delta V) + \left(\frac{\partial^2 U}{\partial S \partial N}\right)(\delta S \delta N) + \left(\frac{\partial^2 U}{\partial V \partial N}\right)(\delta V \delta N) > 0$

obviously the partial derivatives represent a positive definite quadratic form

$\sum_{n,m} A_{nm} \lambda_n \lambda_m > 0$

which requires that

$A_{nn} > 0 \; \forall \; n$
$A_{nn} A_{mm} - A_{nm}^2 > 0 \; \forall \; n, m \; (n \neq m)$

in particular it follows in the present case that

- $(\frac{\partial^2 U}{\partial S^2})_{V,N} > 0$;
  with $(\frac{\partial^2 U}{\partial S^2})_{V,N} = (\frac{\partial T}{\partial S})_{V,N} = \frac{T}{C_v}$ follows (because T > 0) $C_v > 0$
  i.e., stable equilibrium requires positive C_V ⇒ heating the system results in temperature increase

- $(\frac{\partial^2 U}{\partial V^2})_{S,N} > 0$;
  with $(\frac{\partial^2 U}{\partial V^2}) = (-\frac{\partial p}{\partial V})_{S,N}$ follows $(\frac{\partial V}{\partial p})_{S,N} < 0$

i.e., increasing the pressure at const. entropy (i.e., adiabatically) reduces the volume of stable systems

8.3 Gibbs' phase rule

system consists of K components (i.e., species) that occur in P phases; exclude conversion of species

(8.1) equilibrium characterized by common temperature T and common pressure p

$\Rightarrow$ Gibb's free energy $G(T, p, \{N_\alpha\})$ appropriate thermodynamic potential

(7.2) $G = \sum_\alpha^K \sum_i^P \mu_\alpha^i N_\alpha^i$; K = number of components, P = number of phases and N_α^i= number of particles of species (component) α in phase i

search for minimum of G with side condition of particle number conservation

$N_\alpha = \sum_i N_\alpha^i$ with $\alpha = 1 \dots K$

method of Lagrange multipliers:

$\delta(G - \sum_\alpha \sum_i \lambda_\alpha N_\alpha^i) = 0$
$\Rightarrow \sum_\alpha \sum_i [\underbrace{(\frac{\partial G}{\partial N_\alpha^i})}_{\mu_\alpha^i}{}_{T,p,N_\beta^i} - \lambda_\alpha]\delta N_\alpha^i = 0$ with $\beta \neq \alpha$

$\Longrightarrow \sum_\alpha \sum_i (\mu_\alpha^i - \lambda_\alpha)\delta N_\alpha^i = 0 \Rightarrow \mu_\alpha^i - \lambda_\alpha = 0$

Thus **(*)** $\begin{matrix} \mu_1^1 = & \mu_1^2 = & \mu_1^3 = & \dots = & \mu_1^p \\ \vdots & & & & \vdots \\ \mu_k^1 = & & \dots & & = \mu_k^p \end{matrix}$

here it holds $\mu = \mu(p, T, \{n_\alpha^i\})$

only K-1 concentrations in a single phase i may be independent, i.e., each μ depends on $2+(K-1)$ independent variables, i.e., altogether there are $2+P(K-1)$ independent variables

system of equations *(*)* has $K(P-1)$ equations
can only be solved if $K(P-1) \leqslant 2 + P(K-1)$
$\Longrightarrow$ *Gibbs' phase rule*

$$P \leqslant K + 2$$

A system with K chemical components may not contain more than

K+2 phases in equilibrium.

Example: single-component system K=1 $\Rightarrow P \leqslant 3$
$\Rightarrow$at most 3 phases in equilibrium

$f := K + 2 - P \triangleq$ number of *thermodynamic degrees of freedom*

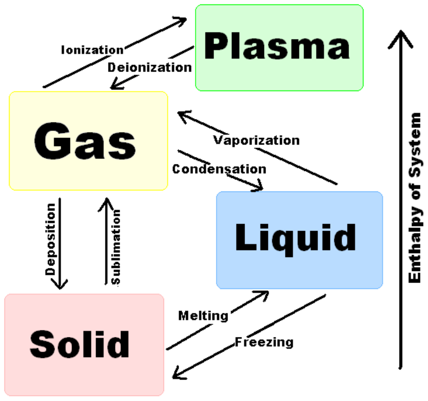
The number of *degrees of freedom* for a given thermodynamic condition are the number of thermodynamic parameters (pressure, temperature etc) that may be altered while maintaining this condition.

In the example K=1 that means

- K=1, P=1 (1 component, 1 phase) $\Rightarrow$ 2 degrees of freedom (f=2)
  may vary, e.g., p and T, V is then determined
- K=1, P=2 (1 component, 2 phases) $\Rightarrow$ f=1
  may vary, e.g., T, V and p are then determined
- K=1, P=3 (1 component, 3 phases) $\Rightarrow$ f=0
  V,T and p are fixed, no modifiation possible (Example: Tripel point of water)

9 Phase transitions

Phase transition or phase change is the transformation of a thermodynamic system from one phase to another. The distinguishing characteristic of a phase transition is an abrupt change in one or more physical properties, in particular the heat capacity, with a small change in a thermodynamic variable such as the temperature. The term is most commonly used to describe transitions between solid, liquid and gaseous states of matter, in rare cases including plasma.

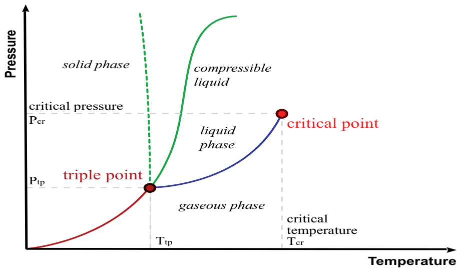


Earlier *(8.1)*: 2 phases of a (single-component) pVT system in equlibrium for

$T_1 = T_2 = T$; $p_1 = p_2 = p; \mu_1 = \mu_2 = \mu$

$\mu_1(T, p) = \mu_2(T, p)$
yields $p = p(T)$ or $T = T(p)$, respectively, that corresponds to the boundary between the two phases in the p-T phase diagram

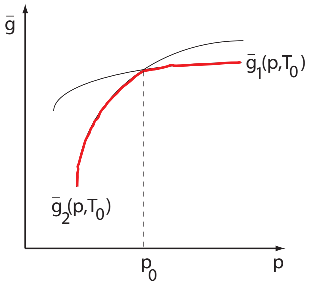
below a typical phase diagram is shown. The dotted line gives the anomalous behaviour of water



In any system containing liquid and gaseous phases, there exists a special combination of pressure and temperature, known as the *critical point*, at which the transition between liquid and gas becomes a *second-order transition.* Near the critical point, the fluid is sufficiently hot and compressed that the distinction between the liquid and gaseous phases is almost non-existent. Critical points only exist for phases that are distinct from each other quantitatively, such as by different strengths of the molecular interaction rather than for phases that exhibit qualitative differences, such as between liquids and crystalline solids.

9.1 First-order phase transitions

Assume: system with 2 phases: $\mu_1 = g_1(T, p)$ and $\mu_2 = g_2(T, p)$,
set $T = T_0 =$ const.



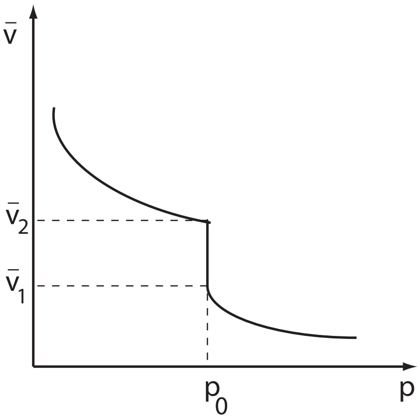
p_0 : at T $= T_0$ both phases are in equilibrium for $p = p_0$

$p < p_0$: phase 2 stable
$p > p_0$: phase 1 stable

(earlier, *(5.3)*):
$(\frac{\partial \bar{g}}{\partial p})_T = \bar{v}$

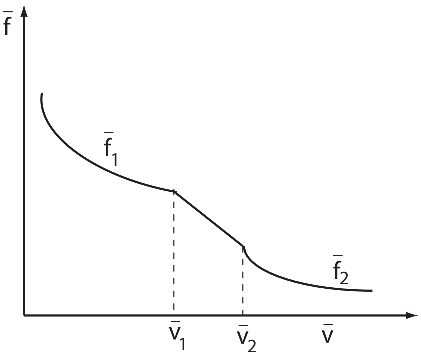
obviously there is a discontinuity in the derivative of $\bar{g}$ with p at $p = p_0$

$\bar{v} = (\frac{\partial \bar{g}}{\partial p})_T$ has a step at $p = p_0$

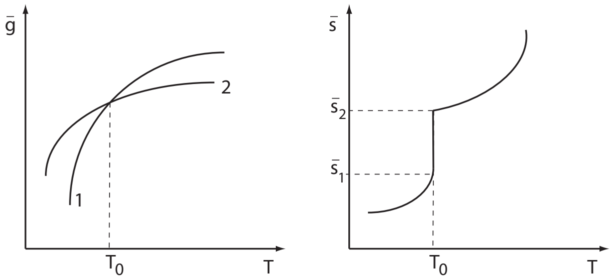


consider specific free energy $\bar{f} = \bar{g} - p\bar{v}$

it holds $p = p_0 =$ const. for the coexistence of the phases
$\bar{g}_1(p_0) = \bar{g}_2(p_0) \Rightarrow \bar{f}$ descents linearly



analogous consideration for specific entropy
$\bar{s} = -(\frac{\partial \bar{g}}{\partial T})_p$ has a discontinuity at the phase transition



$\bar{h} = \bar{g} + T\bar{s} \Rightarrow \bar{q}_{12} = \bar{h}_2 - \bar{h}_1 = T_0(\bar{s}_2 - \bar{s}_1)$;
($\bar{g}$ is constant for the conditions of coexistence of the two phases);
$\bar{q}_{12}$ is the *latent heat*

coexistence of 2 phases $\Rightarrow \mu_1 = \bar{g}_1 = \bar{g}_2 = \mu_2$

$d\bar{g}_1(T,p) = -\bar{s}_1\,\mathrm{dT} + \bar{v}_1\,\mathrm{dp} = d\bar{g}_2(T,p) = -\bar{s}_2\,\mathrm{dT} + \bar{v}_2\,\mathrm{dp}$
$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\bar{s}_2 - \bar{s}_1}{\bar{v}_2 - \bar{v}_1}$

leads to the *Clausius-Clapeyron relation* (for $\mathrm{T} = \mathrm{T}_0$)

$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\Delta\bar{s}T}{\Delta\bar{v}T} = \frac{q_{12}}{T(\bar{v}_2 - \bar{v}_1)}$$

Example: transition liquid → gas, i.e., $\bar{v}_2 \gg \bar{v}_1; q_{12} > 0 \Rightarrow \frac{\mathrm{dT}}{\mathrm{dP}} > 0$
i.e., upon increasing pressure the boiling point shifts to higher temperatures

now quantitatively for the case liquid - gaseous:
$\bar{v}_2 \gg \bar{v}_1 \Rightarrow \frac{\mathrm{dp}}{\mathrm{dT}} \approx \frac{q_{12}}{T\bar{v}_2}$

approximation ideal gas: $p\bar{v} = kT$
$\frac{\mathrm{dp}}{\mathrm{dT}} \approx \frac{q_{12}p}{kT^2}$
$\Rightarrow \frac{\mathrm{dlnp}}{\mathrm{dT}} \approx \frac{q_{12}}{kT^2}$

need latent heat q_{12}

$\frac{\mathrm{dq}_{12}}{\mathrm{dT}} = \frac{d}{\mathrm{dT}}(\bar{h}_2 - \bar{h}_1) = (\frac{\partial\bar{h}_2}{\partial T})_p + (\frac{\partial\bar{h}_2}{\partial p})_T\frac{\mathrm{dp}}{\mathrm{dT}} - (\frac{\partial\bar{h}_1}{\partial T})_p - (\frac{\partial\bar{h}_1}{\partial p})_T\frac{\mathrm{dp}}{\mathrm{dT}}$

$d\bar{h} = Td\bar{s} + \bar{v}\,\mathrm{dp}$
$\mathrm{dp} = 0 \Rightarrow \bar{h} = \delta q \Rightarrow (\frac{\partial\bar{h}}{\partial T})_p = \bar{c}_p$
thus $\frac{\mathrm{dq}_{12}}{\mathrm{dT}} = \bar{c}_{p2} - \bar{c}_{p1} + \left[(\frac{\partial\bar{h}_2}{\partial p})_T - (\frac{\partial\bar{h}_1}{\partial p})_T\right]\frac{\mathrm{dp}}{\mathrm{dT}}$

consider $\bar{h}(T,p)$ as $\bar{h} = \bar{h}(p, \bar{s}(T,p))$
then $(\frac{\partial\bar{h}}{\partial p})_T = \underbrace{(\frac{\partial\bar{h}}{\partial p})_{\bar{s}}}_{=\,\bar{v}} + \underbrace{(\frac{\partial\bar{h}}{\partial\bar{s}})_p}_{=\,T}(\frac{\partial\bar{s}}{\partial p})_T =$

$\bar{v} + T(\underbrace{\frac{\partial \bar{s}}{\partial p}}_{= -(\frac{\partial \bar{v}}{\partial T})_p \text{ Maxwell's relation}})_T$

$= \bar{v} - T(\frac{\partial \bar{v}}{\partial T})_p$

thus

$\frac{\mathrm{dq_{12}}}{\mathrm{dT}} = \bar{c}_{p2} - \bar{c}_{p1} + \left[\bar{v}_2 - \bar{v}_1 - T(\frac{\partial(\bar{v}_2 - \bar{v}_1)}{\partial T})_p\right] \frac{\mathrm{dp}}{\mathrm{dT}}$

with $\bar{v}_2 \gg \bar{v}_1$

$\approx \bar{c}_{p2} - \bar{c}_{p1} + \underbrace{[\bar{v}_2 - T(\underbrace{\frac{\partial \bar{v}_2}{\partial T}}_{\frac{k}{p}\text{ (TEOS id. gas)}})_p]}_{\approx 0\text{ (TEOS id. gas)}} \frac{\mathrm{dp}}{\mathrm{dT}} \approx \Delta \bar{c}_p$

assume a weak temperature dependence of $\Delta \bar{c}_p$

$\Rightarrow \bar{q}_{12} = \Delta \bar{c}_p (T - T_0) + q_{12}^{(0)}$

thus

$\frac{d \ln p}{dT} = \frac{\Delta \bar{c}_p}{kT} + \frac{\bar{q}_{12}^{(0)} - \Delta \bar{c}_p T^{(0)}}{kT^2}$

solution of this differential equation given by

$$\frac{p}{p^{(0)}} = \left(\frac{T}{T^{(0)}}\right)^{(\Delta \bar{c}_p / k)} \exp\left[\frac{\bar{q}_{12}^{(0)} - \Delta \bar{c}_p T^{(0)}}{kT^{(0)} T}(T - T^{(0)})\right]$$

thus boiling point increase for higher pressures

9.2 Phase transitions of a higher order

hitherto: continuos transition of $\bar{g}$, discontinuities in the derivatives

$\bar{s} = -(\frac{\partial \bar{g}}{\partial T})_p ; \bar{v} = (\frac{\partial \bar{g}}{\partial p})_T$

there are phase transition where the derivatives of $\bar{g}$ are continuous upon phase change, e.g.,

- structural phase changes such as α-Quartz → β-Quartz
- ferromagnetic transition
- order-disorder transition in alloys
- normal → superconductor (here $\bar{g} = \bar{g}(T, H)$ with H mag. field)

Such phase transitions are known as *higher-order phase transitions* or *continuous phase transitions*

definition nth-order phase transition
$\left(\frac{\partial^k \bar{g}_1}{\partial T^k}\right)_p = \left(\frac{\partial^k \bar{g}_2}{\partial T^k}\right)_p ; \left(\frac{\partial^k \bar{g}_1}{\partial p^k}\right)_T = \left(\frac{\partial^k \bar{g}_2}{\partial p^k}\right)_T$ for k⩽n-1
and $\left(\frac{\partial^k \bar{g}_1}{\partial T^k}\right)_p \neq \left(\frac{\partial^k \bar{g}_2}{\partial T^k}\right)_p ; \left(\frac{\partial^k \bar{g}_1}{\partial p^k}\right)_T \neq \left(\frac{\partial^k \bar{g}_2}{\partial p^k}\right)_T$ for k=n

Example: 2nd-order phase transition

it holds $\bar{g}_1(T,p) = \bar{g}_2(T,p)$

$$(\underbrace{\frac{\partial \bar{g}_1}{\partial T}}_{-\bar{s}_1(T,p)})_p = (\underbrace{\frac{\partial \bar{g}_2}{\partial T}}_{-\bar{s}_2(T,p)})_p ; (\underbrace{\frac{\partial \bar{g}_1}{\partial p}}_{\bar{v}_1(T,p)})_T = (\underbrace{\frac{\partial \bar{g}_2}{\partial p}}_{\bar{v}_2(T,p)})_T$$

$\Rightarrow \bar{s}_1(T,p) = \bar{s}_2(T,p)$

$$\Rightarrow (\underbrace{\frac{\partial \bar{s}_1}{\partial T}}_{\frac{\bar{c}_{p1}}{T}})_p \,\mathrm{dT} + (\underbrace{\frac{\partial \bar{s}_1}{\partial p}}_{-(\frac{\partial \bar{v}_1}{\partial T})_P})_T \,\mathrm{dp} = (\underbrace{\frac{\partial \bar{s}_2}{\partial T}}_{\frac{\bar{c}_{p2}}{T}})_p \,\mathrm{dT} + (\underbrace{\frac{\partial \bar{s}_2}{\partial p}}_{-\frac{\partial \bar{v}_2}{\partial T}})_T \,\mathrm{dp}$$

with $\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_p$ =isobaric expansion coefficient
follows $\underbrace{\bar{c}_{p2} - \bar{c}_{p1}}_{\Delta \bar{c}_P} = T\frac{\mathrm{dp}}{\mathrm{dT}}[\underbrace{\bar{v}_2}_{=\bar{v}_1=\bar{v}} \alpha_2 - \bar{v}_1\alpha_1]$

1st Ehrenfest relation:

$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\Delta \bar{c}_p}{T\bar{v}\Delta\alpha}$$

(analogon to the Clausius-Clapeyron relation)
from $\bar{v}_2 = \bar{v}_1$ follows analogously

2nd Ehrenfest relation:

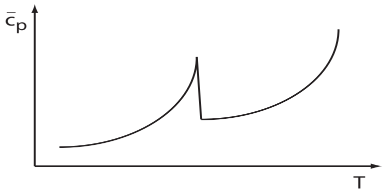
$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\Delta\alpha}{\Delta\kappa_T}$$

with κ_T =isothermal compressibility

eliminate $\frac{\mathrm{dp}}{\mathrm{dT}}$ in 1st and 2nd Ehrenfest relation

$$\Rightarrow \Delta\bar{c}_p = T\bar{v}\frac{(\Delta\alpha)^2}{\Delta\kappa_T}$$

typical discontinuities in the heat capacities for 2nd-order phase transitions:



Remark: often possible to define *order parameter*, e.g.,

- magnetization $M = \frac{S\uparrow - S\downarrow}{S\uparrow + S\downarrow}$ for a ferromagnetic system undergoing a phase transition
- structural order for solids
- density for solid/liquid or liquid/gas transitions

that characterize the phase transition. An *order parameter* is a measure of the degree of order in a system; the extreme values are 0 for total disorder and 1 for complete order. In a first-order transition, the order parameter would change discontinuously at the transition temperature (e.g., melting of a solid) while it changes continuously for higher-order phase transition (e.g., ferromagnetic transition)

10 Application to magnetism

$\vec{B} = \mu_0 \vec{H} + \vec{M}$
here is $\vec{B}$: magnetic field (historical magnetic induction) $\vec{H}$: auxiliary magnetic field or magnetizing field and $\vec{M}$: magnetization density

magnetic moment $\vec{M} = \int \vec{M}(\vec{r}) d^3\vec{r}$

for the sake of simplicity scalar variables in the following

work needed to change magnetic moment of a body in external field by dM:
$\delta \mathrm{W} = H \, \mathrm{dM}$

volume of the body remains constant
$\mathrm{dU} = \delta Q + H \, \mathrm{dM}$
$\mathrm{dF} = \mathrm{dU} - T \, \mathrm{dS} - S \, \mathrm{dT} = -S \, \mathrm{dT} + H \, \mathrm{dM}$

$H = (\frac{\partial F}{\partial M})_T$: TEOS for magnetic materials
cf. $p = -(\frac{\partial F}{\partial V})_T$: TEOS for pVT system

that means we apply all previously derived thermodynamic relations for pVT systems to magnetizable materials by means of simply replacing

$p \rightarrow -H$
$V \rightarrow M$

e.g., $C_M = (\frac{\partial U}{\partial T})_M; C_H - C_M = -T(\frac{\partial H}{\partial T})_M(\frac{\partial M}{\partial T})_H$

relation between TEOS&CEOS: $(\frac{\partial U}{\partial M})_T = H - T(\frac{\partial H}{\partial T})_M$ **(*)**

10.1 Diamagnetism

Diamagnetism is the property of an object which causes it to create a magnetic field in opposition of an externally applied magnetic field, thus causing a repulsive effect. It is a form of magnetism that is only exhibited by a substance in the presence of an externally applied magnetic field.

$M = \mu_0 \chi_M H$ with $\chi_M < 0$, magnetic susceptibility const, does not depend on temperature

$(\frac{\partial C_M}{\partial M})_T = \frac{\partial^2 U}{\partial T \partial M} = (*)$
$\frac{\partial}{\partial T}(H - T(\frac{\partial H}{\partial T})_M)_M = -T(\underbrace{\frac{\partial^2 H}{\partial T^2}}_{=\,0})_M = 0$
$\rightarrow C_M$ does not depend on M!

$\mathrm{dS} = \frac{\mathrm{dU} - H\,\mathrm{dM}}{T} = \frac{1}{T}\left\{(\frac{\partial U}{\partial T})_M\,\mathrm{dT} + (\frac{\partial U}{\partial M})_T\,\mathrm{dM} - H\,\mathrm{dM}\right\} = (*)$
$= \frac{1}{T}\{(\underbrace{\frac{\partial U}{\partial T}}_{C_M})_M\,\mathrm{dT} + H\,\mathrm{dM} - T(\underbrace{\frac{\partial H}{\partial T}}_{=\,0})_M - H\,\mathrm{dM}\}$
$\Rightarrow \mathrm{dS} = \frac{C_M}{T}\,\mathrm{dT} \Rightarrow$ entropy depends on the temperature only!

Thus the temperature does not change upon adiabatic reversible change of the magnetic moment of the body.

10.2 Paramagnetism

Paramagnetism is a form of magnetism which occurs only in the presence of an externally applied magnetic field. Paramagnetic materials contain atoms or molecules with an internal magnetic moment that aligns in the external field. The alignment increases with the strength of the external field and decreases for rising temperatures.

TEOS (*Curie's law*):

$$M = \frac{C}{T}H \quad (C.. \,\mathrm{const.})$$

$(\frac{\partial U}{\partial M})_T = H - T(\underbrace{\frac{\partial H}{\partial T}}_{\frac{M}{C}})_M = 0$ **(*)**

The internal energy does thus not depend on the magnetic moment.

$\mathrm{dS} = \frac{\mathrm{dU} - H\,\mathrm{dM}}{T} = \frac{C_M}{T}\,\mathrm{dT} - \frac{M}{C}\,\mathrm{dM}$

reversible adiabatic processes: dS=0
$\Rightarrow \frac{C_M}{T}\,\mathrm{dT} = \frac{M}{C}\,\mathrm{dM}$

⇒ cooling by adiabatic demagnetization, socalled *magnetic refrigeration*

Thermodynamic cycle The cycle is performed as a refrigeration cycle, analogous to the Carnot cycle, and can be described at a starting point whereby the chosen working substance is introduced into a magnetic field (i.e. the magnetic flux density is increased). The working material is the refrigerant, and starts in thermal equilibrium with the refrigerated environment.

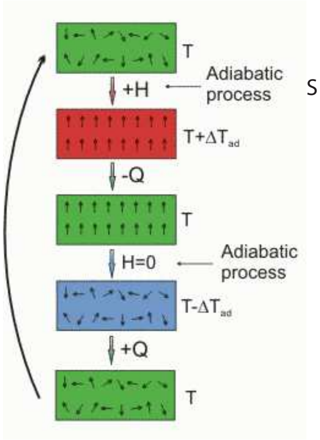
1. *Adiabatic magnetization:* The substance is placed in an insulated environment. The increasing external magnetic field (+H) causes the magnetic dipoles of the atoms to align, thereby decreasing the material's magnetic entropy and heat capacity. Since overall energy is not lost (yet) and therefore total entropy is not reduced (according to thermodynamic laws), the net result is that the item heats up (T + $\Delta \mathrm{T}_{ad}$).

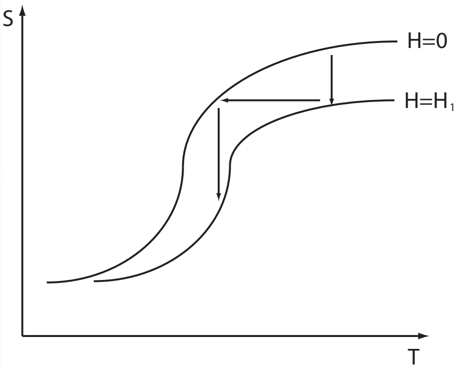
2. *Isomagnetic enthalpic transfer:* This added heat can then be removed by a fluid or gas - gaseous or liquid helium for example (-Q). The magnetic field is held constant to prevent the dipoles from reabsorbing the heat. Once sufficiently cooled, the magnetocaloric material and the coolant are separated (H=0).

3. *Adiabatic demagnetization:* The substance is returned to another adiabatic (insulated) condition so the total entropy remains constant. However, this time the magnetic field is decreased, the thermal energy causes the magnetic moments to overcome the field, and thus the sample cools (i.e. an adiabatic temperature change). Energy (and entropy) transfers from thermal entropy to magnetic entropy (disorder of the magnetic dipoles).

4. *Isomagnetic entropic transfer:* The magnetic field is held constant to prevent the material from heating back up. The material is placed in thermal contact with the environment being refrigerated. Because the working material is cooler than the refrigerated environment (by design), heat energy migrates into the working material (+Q).

Once the refrigerant and refrigerated environment are in thermal equilibrium, the cycle begins anew.





10.3 Ferromagnetism

Ferromagnetic materials contain many atoms with unpaired spins. When these tiny magnetic dipoles are aligned in the same direction, they create a measurable macroscopic field. These permanent dipoles (often called simply "spins" even though they also generally include orbital angular momentum) tend to align in parallel to an external magnetic field, an effect called *paramagnetism.* Ferromagnetism involves an additional phenomenon, however: the dipoles tend to align spontaneously, without any applied field. This is a purely quantum-mechanical effect. According to classical electromagnetism, two nearby magnetic dipoles will tend to align in opposite directions (which would create an antiferromagnetic material). In a ferromagnet, however, they tend to align in the same direction because of the Pauli principle: two electrons with the same spin cannot also have the same "position", which effectively reduces the energy of their electrostatic interaction compared to electrons with opposite spin. At long distances (after many thousands of ions), the exchange energy advantage is overtaken by the classical tendency of dipoles to anti-align. This is why, in an equilibriated (non-magnetized) ferromagnetic material, the dipoles in the whole material are not aligned. Rather, they organize into magnetic domains (also known as Weiss domains) that are aligned (magnetized) at short range, but at long range adjacent domains are anti-aligned. The transition between two domains, where the magnetization flips, is called a domain wall (i.e., a Bloch/Nel wall, depending upon whether the magnetization rotates parallel/perpendicular to the domain interface) and is a gradual transition on the atomic scale (covering a distance of about 300 ions for iron). Thus, an ordinary piece of iron generally has little or no net magnetic moment. However, if it is placed in a strong enough external magnetic field, the domains will re-orient in parallel with that field, and will remain re-oriented when the field is turned off, thus creating a "permanent" magnet. This magnetization as a function of the external field is described by a hysteresis curve. Although this state of aligned

domains is not a minimal-energy configuration, it is extremely stable and has been observed to persist for millions of years in seafloor magnetite aligned by the Earth's magnetic field (whose poles can thereby be seen to flip at long intervals). The net magnetization can be destroyed by heating and then cooling (annealing) the material without an external field, however. As the temperature increases, thermal motion, or entropy, competes with the ferromagnetic tendency for dipoles to align. When the temperature rises beyond a certain point, called the Curie temperature, there is a second-order phase transition and the system can no longer maintain a spontaneous magnetization, although it still responds paramagnetically to an external field. Below that temperature, there is a spontaneous symmetry breaking and random domains form (in the absence of an external field).
For $T > \Theta$, with Θ = Curie temperature

TEOS (Curie-Weiss law)

$$M = \frac{C}{T - \Theta} H$$

$(\frac{\partial U}{\partial M})_T =$(*)$= H - T(\underbrace{\frac{\partial H}{\partial T}}_{\frac{M}{C}})_M = -\frac{\Theta}{C} M$

Internal energy thus depends on the magnetization(cf. real vs ideal gas)!

For $T < \Theta \Rightarrow$ hysteresis $\Rightarrow$ complicated...