# Chapter 4

Entropy and the second law of thermodynamics

4.1 Heat engines

In a cyclic transformation the final state of a system is by definition identical to the initial state. The overall change of the internal energy U hence vanishes,

$$\Delta U \; = \; 0, \qquad \Delta W = -\Delta Q \; .$$

A cycle transformation is by definition reversible and the *work done* by the system during a cycle is equal to the *heat absorbed.*
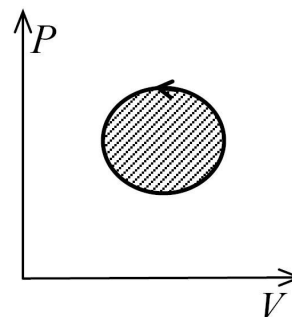
Work. The (negative) of the work

$$-\Delta W \; = \; \oint P dV \; = \; \text{area enclosed.}$$

corresponds for a reversible cyclic process to the area enclosed by the loop in the $V - P$ state diagram.

Heat engine. Work is converted by a cyclic process into heat, and vice versa. A cyclic process can hence be regarded as an *heat engine.*

Consider a heat engine operating between $T_1 > T_2$. Part of the heat that is transferred to the system from a heat bath with temperature T_1, Q_1, is converted into work, W, and the rest, Q_2, is delivered to a second bath with $T_2 < T_1$ (condenser). Following the first law of thermodynamics,

$$|Q_1| - |Q_2| \; = \; |W| \; .$$
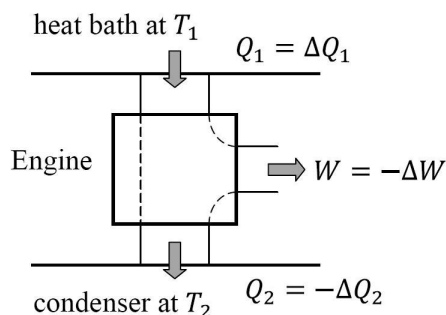
4.1.1   Carnot cycle

The *Carnot process* is a reversible cycle process bounded by two *isotherms* and two *adiabatic* lines.
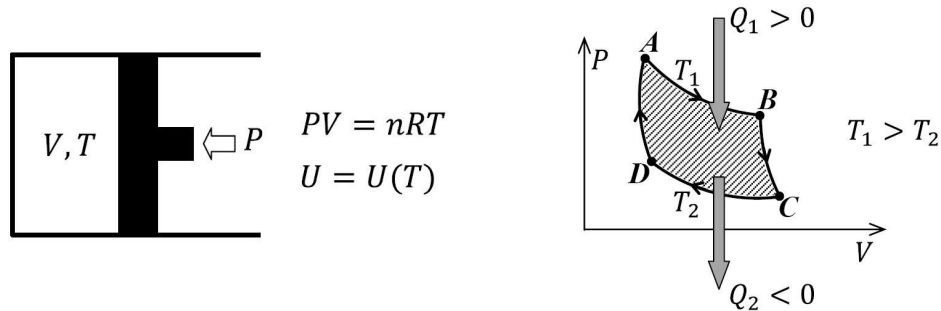
One Carnot cycle consists of four consecutive thermodynamic processes, which can be realized with an arbitrary working substance. We shall consider here however the case of an ideal gas.

(1)	$A \to B$	isothermal expansion	$T = T_1$	$V_A \to V_B$	Q_1 absorbed
(2)	$B \to C$	adiabatic expansion	$T_1 \to T_2$	$V_B \to V_C$	$\Delta Q = 0$
(3)	$C \to D$	isothermal compression	$T = T_2$	$V_C \to V_d$	Q_2 released
(4)	$D \to A$	adiabatic compression	$T_2 \to T_1$	$V_C \to V_a$	$\Delta Q = 0$

Work. We note that $Q_1 > 0$ (absorbed from hot bath) and $Q_2 < 0$ (released to cold bath). Total energy conservation, viz the first law of thermodynamics, dictates that

$$0 = \oint dU = \oint (\delta Q + \delta W) = Q + W = Q_1 + Q_2 + W \ ,$$

where $-W$ is the work performed by the system, equal to the area enclosed in the loop.

Efficiency. The *efficiency* of the Carnot engine is defined as

$$\boxed{\eta \equiv \frac{\text{performed work}}{\text{absorbed heat}} = \frac{-W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1}} \ .$$

η is 100% if there is no waste heat ($Q_2 = 0$). However, we will see that this is *impossible* due to the second law of thermodynamics.

4.2   Second law of thermodynamics

Definition by *Clausius*:

> *"There is no thermodynamic transformation whose* sole *effect is to deliver heat from a reservoir of lower temperature to a reservoir of higher temperature."*
>
> *Summary*: heat does not flow upwards.

Definition by *Kelvin*:

> *"There is no thermodynamic transformation whose* sole *effect is to extract heat from a reservoir and convert it entirely to work."*
>
> *Summary*: a perpetuum mobile of second type does not exist.

Equivalence. In order to prove that both definition are equivalent, we will show that the falsehood of one implies the falsehood of the other. For that purpose, we consider two heat reservoirs with temperatures T_1 and T_2 with $T_1 > T_2$.

If Kelvin's statement were false, we could extract heat from T_2 and convert it entirely to work. We could then convert the work back to heat entirely and deliver it to T_1 (there is no law against this). Thus, Clausius' statement would be negated.

If Clausius' statement were false, we could let an amount of heat Q_1 flow from T_2 to T_1 ($T_2 < T_1$). Then, we could connect a Carnot engine between T_1 and T_2 such as to extract Q_1 from T_1 and return an amount $|Q_2| < Q_1$ back to T_2. The net work output of such an engine would be $|Q_1| - |Q_2| > 0$, which would mean that an amount of heat $|Q_1| - |Q_2|$ is converted into work, without any other effect. This would contradict Kelvin's statement.

**Order vs. chaos.** From the microscopic point of view

- *heat transfer* is an exchange of energy due to the random motion of atoms;

- *work*'s performance requires an organized action of atoms.

In these terms, heat being converted entirely into work means chaos changing spontaneously to order, which is a very improbable process.

## 4.2.1 Universality of the Carnot cycle

The second law of thermodynamics has several consequences regarding the Carnot cycle.

– A 100% efficient Carnot engine would convert all heat absorbed from a warm reservoir into work, in direct contraction to the second law. We hence conclude that $\eta < 1$.

– All reversible heat engines operating between heat bath with temperatures T_1 and T_2 have the same efficiency.
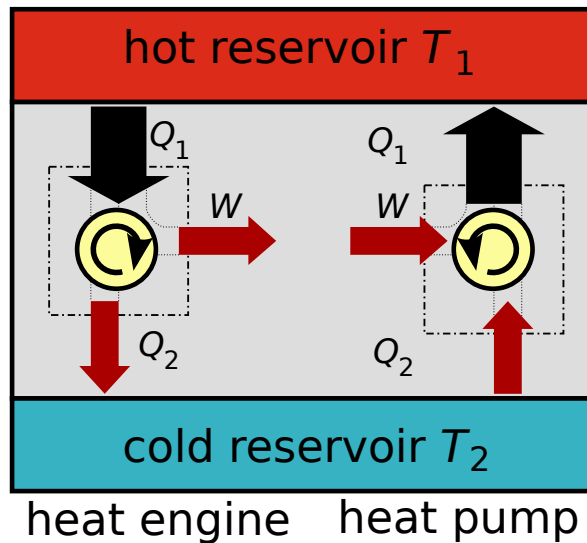
– No *irreversible* engine working between two given temperatures can be more efficient than a reversible thermodynamic process.

For the last two statements we consider two engines C and X (with X not necessarily reverisble) working between the baths at T_1 (warm) and T_2 (cold). We run the Carnot engine C in reverse, as a *refrigerator* $\bar{C}$, and feed the work output of X to $\bar{C}$.
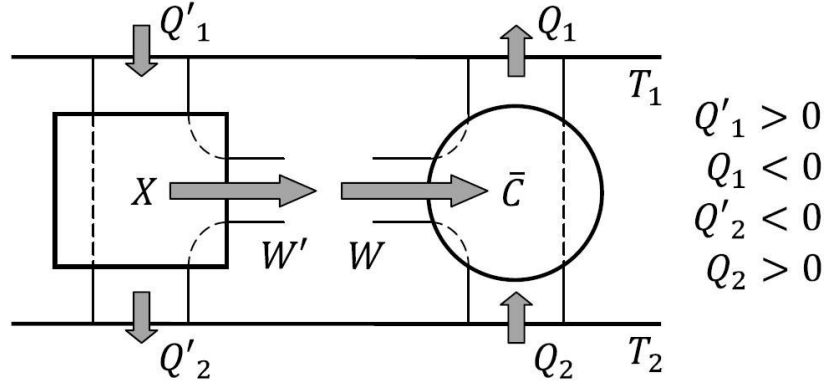
Work. The *total* work output of such a system is

$$W_{tot} \;=\; \left(|Q_1'| - |Q_2'|\right) - \left(|Q_1| - |Q_2|\right)\;.$$

– If we adjust the two engines such that $|Q_1'| = |Q_1|$, no *net* heat is extracted from the heat bath at T_1.

– In this case, an amount of heat $|Q_2| - |Q_2'|$ is extracted from the heat bath at T_2 and converted *entirely* to work, with no other effect.

This would violate the second law of thermodynamics, unless

$$|Q_2| \leq |Q_2'|.$$

Efficiencies. We divide this inequality by $|Q_1|$ and, using the fact that $|Q_1| = |Q_1'|$, get

$$\frac{|Q_2|}{|Q_1|} \leq \frac{|Q_2'|}{|Q_1'|}, \qquad \boxed{\frac{|Q_1| - |Q_2|}{|Q_1|} \geq \frac{|Q_1'| - |Q_2'|}{|Q_1'|}}, \qquad \boxed{\eta_C \geq \eta_X}\;.$$

The opposite inequality $\eta_C \leq \eta_X$ is also true if both X and C are reversible. In that case X could be run as a heat pump and C as a heat engine.

Universality. We made here use only of the fact that the Carnot machine is reversible. All reversible engines working between two heat baths have hence the same efficiency, since X could be, as a special case, a Carnot engine.

$$\boxed{\begin{array}{l} \Rightarrow \quad \text{The Carnot engine is } \textit{universal.} \\ \qquad \text{It depends } \textit{only} \text{ on the temperatures involved} \\ \qquad \text{and not on the working substance.} \end{array}}$$

Efficiency of irreversible heat engines. All reversible heat engines have the same efficiency η_C. Is it then possible that a heat engine X exist such that $\eta_X > \eta_C$? In this case we would have for $Q_1' = Q_1$ that $W' > W$, as shown above, and hence a violation of the second law.

> The efficiency of *irreversible* heat engines is lower that that of any reversible engine.

Irreversible heat pumps Exchanging X and C we may consider the case of *irreversible heat pumps*. One is then interested in the *figure of merit*

$$\frac{Q_2}{W} = \frac{\text{heat absorbed at low temperature}}{\text{work required}} \ .$$

Repeating the arguments for $Q_2' = Q_2$ we find that the second law requires $W' \leq W$ and hence $Q_2'/W' \geq Q_2/W$. The figure of merit of reversible heat pumps is consequently larger than the figure of merit of a irreversible heat pump.

4.3 Absolute temperature

The Carnot cycle is universal and may hence be used to define the temperature θ in an absolute way, i.e. independent of working substances.

$$\boxed{\frac{\theta_2}{\theta_1} \equiv \frac{|Q_2|}{|Q_1|}} \ , \qquad 1 - \eta = \frac{|Q_2|}{|Q_1|} = \frac{-Q_2}{Q_1} \ , \tag{4.1}$$

where η is the efficiency of a Carnot engine operating between the two reservoirs.

– The second law of thermodynamics implies that $|Q_2|$ is *strictly greater* than zero, $|Q_2| > 0$. The same holds for $|Q_1|$, which is anyhow larger (or equal) than $|Q_2|$.

Using (4.1) for defining the temperature via

$$\boxed{\theta_i \propto |Q_i|} \ , \qquad \boxed{\theta_i > 0} \ , \qquad i = 1, 2 \ ,$$

leads hence to strictly positive temperature θ.

– This means that the *absolute zero* $\theta = 0$ is a limiting value that can *never* be reached since this would violate the second law of thermodynamics.

Ideal gas. The proportionality $\theta \sim |Q|$ is defined such that

$$T = \frac{PV}{Nk_B} \equiv \theta.$$

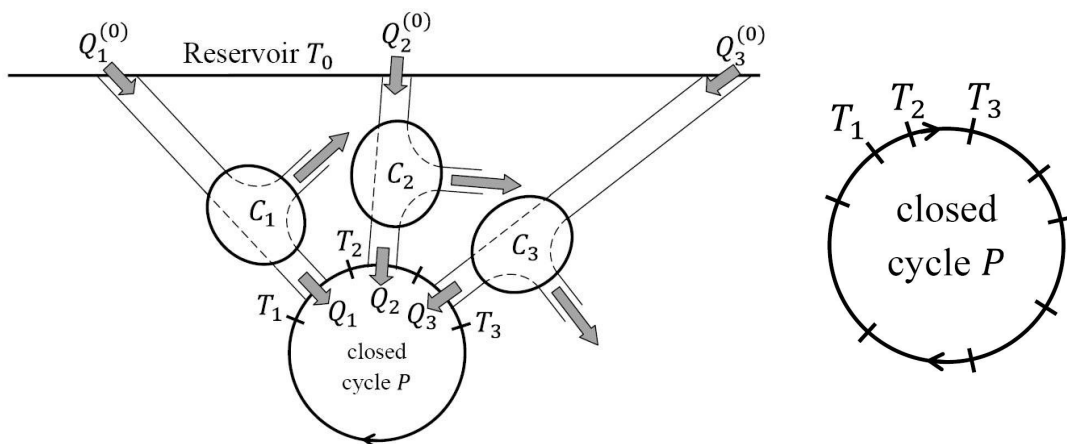when the an ideal gas is used as the working substance in a Carnot engine.

4.3.1   Clausius's inequality

The temperature defined by (4.1) allows to transform the differential of the heat, δQ, which is not reversible into a reversible expression.

The inequality

$$\oint_{P_c} \frac{\delta Q}{T} \leq 0$$

holds for arbitrary cyclic processes P. The equality holds when P_c is *reversible*.

Proof of Clausius's 's inequality. For a derivation we divide the cycle P_c into n segments so that on each segment its temperature T_i $(i = 1, \ldots, n)$ is constant.

Reference reservoir. We consider now a reservoir at reference temperature $T_0 > T_i(\forall i)$ and introduce Carnot engines between the reservoir at T_0 and T_i. Energy is conserved both by the Carnot engine and by the cycle P_c,

$$W_i = Q_i - Q_i^{(0)}, \qquad W = -\sum_{i=1}^{n} Q_i \, ,$$

where $(-W)$ is the work performed by P. Note that W is negative/positive for a heat engine/pump and that Q_i is the heat flowing into P_c at T_i, viz out of C_i.

Temperature. The definition

$$\frac{Q_i^{(0)}}{T_0} = \frac{Q_i}{T_i}$$

of absolute temperature allows us then to rewrite the total heat $Q_T^{(0)}$ absorbed from the reservoir at T_0 as

$$Q_T^{(0)} = \sum_{i=1}^{n} Q_i^{(0)}, \qquad \boxed{Q_T^{(0)} = T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i}} \, . \tag{4.2}$$

Global balance. The work W_T performed by the overall system composed of cycle P_c and of the n Carnot engines is given by the overall energy balance

$$W_T = W + \sum_{i=1}^{n} W_i = -\sum_{i=1}^{n} Q_i - \sum_{i=1}^{n} \left(Q_i^{(0)} - Q_i \right) = -\sum_{i=1}^{n} Q_i^{(0)} = -Q_T^{(0)} .$$

If $Q_T^{(0)} > 0$, the combined machine would convert heat from the reservoir at T_0 completely into mechanical work.

- Kelvin's principle state, that no reversible or irreversible process can convert heat fully into mechanical work.

- There is no law forbidding to convert work into heat, that is $Q_T^{(0)} \leq 0$ is allowed.

Clausius's inequality Using (4.2) we obtain finally with

$$T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i} = Q_T^{(0)} \leq 0, \qquad \boxed{\oint_P \frac{\delta Q}{T} \leq 0}$$

Clausius's inequality.

Reversible processes. We may reverse a process, if it is *reversible*. This implies that both $\oint_{P_c} \delta Q/T \leq 0$ and $\oint_{P_c} \delta Q/T \geq 0$ are valid. This implies that

$$\boxed{\oint_{P_c} \frac{\delta Q}{T} = 0}_{P_c \text{ reversible}} \tag{4.3}$$

Both the total work W_T and the total heat $Q_T^{(0)}$ extracted from the reference reservoir T_0 then vanish.

4.3.2 Entropy

The equality (4.3) implies that

$$\boxed{\int_A^B \frac{\delta Q}{T} \equiv S(B) - S(A)} \tag{4.4}$$

depends only on the end points A and B and not on the particular path, as long as it reversible, and that

$$\boxed{dS = \frac{\delta Q}{T}} \tag{4.5}$$

is an *exact* differential.

Entropy. Eq. (4.4) states that there exists a state function S, defined up to an additive constant, whose differential is $dS = \delta Q/T$. It is denoted *entropy*,

Irreversible processes. We consider that the states A and B occurring in (4.4) are connected both by a reversible path P_R and by an irreversible path P_I?

Clausius' inequality for the combined cycle yields

$$\int_A^B \left(\frac{\delta Q}{T}\right)_R + \int_B^A \left(\frac{\delta Q}{T}\right)_I \leq 0$$

and hence

$$\boxed{\int_B^A \left(\frac{\delta Q}{T}\right)_I \leq -\int_A^B \left(\frac{\delta Q}{T}\right)_R = S(A) - S(B)}.$$

Therefore, in general

$$\boxed{\int_B^A \frac{\delta Q}{T} \leq S(A) - S(B)}, \tag{4.6}$$

where the equality holds for a reversible process.

Thermally isolated systems. From (4.6) it follows with

$$\boxed{\Delta S \geq 0}_{\delta Q = 0}$$

that the entropy can only increase for *thermally isolated* systems which does not exchange heat with a reservoir.

$$\boxed{\text{``The entropy of an isolated system can only increase.''}}$$

Notes.

– The joint system of a *system* and its *environment* is called "universe". Defined in this way, the "universe" is an *isolated* system and, therefore, its entropy never decreases. However, the entropy of a non-isolated system may decrease at the expense of the system's environment.

– Since the entropy is a state function, $S(B) - S(A)$ is *independent* of the path, regardless whether it is reversible or irreversible. For an irreversible path, the entropy of the environment changes, whereas for a reversible one it does not.

– Remember that the entropy difference is

$$S(B) - S(A) = \int_A^B \frac{\delta Q}{T}$$

only when the path is *reversible*; otherwise the difference is larger that the integral.
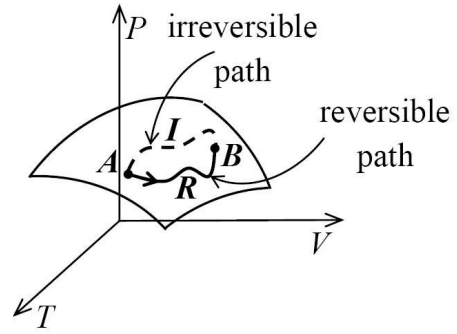
4.4   Entropy as a thermodynamic variable

For a reversible process in a closed system the first law of thermodynamics can be written as

$$\delta U \; = \; \delta Q + \delta W, \qquad \boxed{dU \; = \; TdS - PdV} \;, \qquad \delta Q \; = \; TdS \; . \qquad (4.7)$$

This representation implies that the entropy S and the volume V are the two state variables for which the differential of the internal energy $U = U(S,T)$ becomes exact. In this section we transform one basic pair of state variables to another, namely from (S,V) to (T,V), when one of the variables, here the entropy S, takes also the role of a thermodynamic potential.

Differential of the entropy. Inserting dS and dU/T,

$$dS \; = \; \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV, \qquad dU \; = \; \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \;,$$

into (4.7) leads to

$$\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \; = \; \frac{1}{T} \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{\equiv\, c_V} dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial V}\right)_T dV + P \right) dV \;,$$

where we have used (3.7), namely that $(\delta Q/\delta T)_V = (\partial U/\partial T)_V = C_V$. Comparing coefficients we then find with

$$\boxed{\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T} \\[2mm] \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \end{aligned}} \qquad\qquad (4.8)$$

the partial derivatives of the entropy, as a state function, with respect, with respect to T and V.

4.4.1   Entropy of the ideal gas

We recall (3.9) and (3.6), namely that the specific heat C_V and the free energy U of the ideal gas are

$$C_V \; = \; \frac{3}{2}nR \qquad U \; = \; \frac{3}{2}nRT \qquad \left(\frac{\partial U}{\partial V}\right)_T = 0 \; .$$

Using the partial derivatives (4.8) and the equation of state $PV = nRT$ of the ideal gas then leads with

$$dS \; = \; \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V}$$

to the entropy difference

$$S(T,V) - S(T_0,V_0) \; = \; \frac{3nR}{2}\log\left(\frac{T}{T_0}\right) + nR\log\left(\frac{V}{V_0}\right) \; . \qquad (4.9)$$

Note that the number of moles n is here constant.

4.4.2   Maxwell equations

The commutativity of differentiation operations, *Schwarz's theorem*, can be used to derive relations between thermodynamic quantities. For the case of the differential (4.7) this implies that $\partial^2 U/(\partial S \partial V) = \partial^2 U/(\partial V \partial S)$ and hence

$$dU = TdS - PdV, \qquad \frac{\partial T}{\partial V} = -\frac{\partial P}{\partial S}, \qquad \boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}, \qquad (4.10)$$

where we used an inversion for the last step. The relation $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$ is denoted a *Maxwell equation*.

4.4.3   Energy equation

The entropy is not an experimentally controllable variable, in contrast to T, V and P, which allow to measure the *thermal equation of state*

$$P = P(T, V) . \qquad (4.11)$$

We however use (4.7) to deduce an relation, *the energy equation*, which allows to determine the *caloric equation of state* $U = U(T, V)$.

Energy equation. We use the commutativity of differentiation operations, as in Sect. 4.4.2, but this time for the derivatives of the entropy:

$$\begin{aligned}
\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right) &= \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right) \\
&= \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right) = \frac{\partial}{\partial T}\left(\frac{1}{T}\left[\frac{\partial U}{\partial V} + P\right]\right) \\
&= -\frac{1}{T^2}\left[\frac{\partial U}{\partial V} + P\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial V} + \frac{\partial P}{\partial T}\right] .
\end{aligned}$$

Canceling identical terms we get

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \qquad \Rightarrow \qquad \text{ENERGY EQUATION.} \qquad (4.12)$$

The derivative of the internal energy is written with (4.12) in terms of *measurable* quantities. It is fulfilled for an ideal gas, for which $PV = nRT$ and $(\partial U/\partial V)_T = 0$.

4.5   Eulers's cyclic chain rule

The partial derivative $(\partial P/\partial T)_V$ entering the energy equation (4.12) may be related to thermodynamic coefficients as well. The involved type of variable transformation is can be applied to a large set of thermodynamic quantities.

Implicit variable dependencies. We are dealing in general with a set of variables, e.g. P, V and T, which are related we a equation of state

$$f(P,V,T) = 0, \qquad \frac{\partial f}{\partial P}dP + \frac{\partial f}{\partial T}dT + \frac{\partial f}{\partial V}dV = df(P,V,T) = 0 \ .$$

From the relative partial derivatives of the state variables

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial f/\partial T}{\partial f/\partial P}, \qquad \left(\frac{\partial T}{\partial V}\right)_P = -\frac{\partial f/\partial V}{\partial f/\partial T}, \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{\partial f/\partial P}{\partial f/\partial V}$$

it follows that

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1} \tag{4.13}$$

The importance of (4.13), *Euler's chain rule*, lies in the fact that one does not know the equation-of-state function $f(P,V,T)$ explicitly, only that it exists.

Expansion and compression coefficients. Using (4.13), we get

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_P \, (\partial V/\partial P)_T} = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}, \qquad \boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}}, \tag{4.14}$$

where have made use of the thermodynamic coefficients
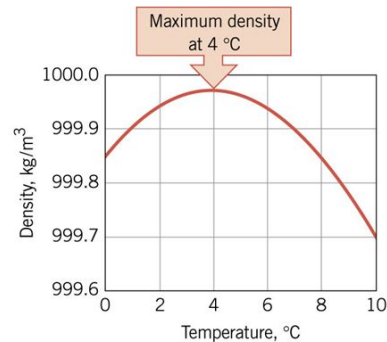
$$\boxed{\begin{aligned} \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P & \text{(coefficient of thermal expansion)} \\[2mm] \kappa_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T & \text{(isothermal compressibility)} \\[2mm] \kappa_S &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S & \text{(adiabatic compressibility)} \end{aligned}}$$

Using (4.14) the energy equation (4.12) reads

$$\left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V = T\frac{\alpha}{\kappa_T} \ . \tag{4.15}$$

Mayer's relation between C_P and C_V. The energy equation (4.15) can be used to rewrite Mayer's relation (3.12), which we derived considering the chain rule for $(\partial U/\partial T)_P$, as

$$C_P = C_V + \underbrace{\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]}_{T\alpha/\kappa_T}\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha},$$

which leads then to

$$\boxed{C_P - C_V = \frac{\alpha^2}{\kappa_T} TV > 0} \,. \qquad (4.16)$$

Note that the thermal expansion κ_T is normally positive. Water close to the freezing point has however an anomalous $\kappa_T < 0$.

4.5.1 Entropy differentials

The rewritten energy equation (4.15) can be used to rewrite also the the differential (4.8) of the entropy as

$$TdS = C_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV = C_V dT + T\frac{\alpha}{\kappa_T} dV \,. \qquad (4.17)$$

T **and** V **as independent variables.** Expression (4.17) for the differential of the entropy implies that the absorbed heat δQ can be expressed likewise in terms of directly measurable coefficients,

$$\boxed{\delta Q = TdS = C_V dT + \frac{\alpha}{\kappa_T} TdV} \,, \qquad (4.18)$$

where T and V are here the independent variables.

T **and** P **as independent variables.** We use the Maxwell equation (4.10), $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$,

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP \,,$$

and obtain

$$\boxed{TdS = C_P dT - \alpha TV dP} \,, \qquad (4.19)$$

where the independent variables are now T and P.

V **and** P **as independent variables.** We note that dT can be rewritten in terms of dV and dP as

$$dT = \left(\frac{\partial T}{\partial V} \right)_P dV + \left(\frac{\partial T}{\partial P} \right)_V dP = \frac{1}{\alpha V} dV + \frac{\kappa_T}{\alpha} dP \,,$$

where we have used (4.14), viz $(\partial P/\partial T)_V = \alpha/\kappa_T$, in the last step. Inserting dT into (4.19) we obtain

$$\boxed{TdS = \frac{C_P}{\alpha V} dV + \left(\frac{C_P \kappa_T}{\alpha} - \alpha TV \right) dP} \qquad (4.20)$$

for TdS, where the independent pair of state variables is now V and P.

4.6   Third law of thermodynamics (Nernst law)

Analyzing experimental data, Nernst has concluded that in the limit $T \to 0$ the entropy becomes a constant independent of other thermodynamic parameters such as volume and pressure,

$$\left(\frac{\partial S}{\partial V}\right)_{T \to 0} = \left(\frac{\partial S}{\partial P}\right)_{T \to 0} = 0 \ . \tag{4.21}$$

The entropy is defined via (4.4) only up to constant, which can be selected hence such that

$$\boxed{\lim_{T \to 0} S(T) = 0} \ . \tag{4.22}$$

This equation is equivalent in statistical mechanics, as we will discus in Sect. 8.2, that nearly all states of matter are characterized by a unique ground state. Macroscopically degenerate ground state leading to finite $T = 0$ entropies are observed only for exotic phases of matter.

Heat capacities vanish for $T \to 0$**.** The heat capacities disappear at $T = 0$ as a consequence of (4.22):

$$\lim_{T \to 0} C_V = \lim_{T \to 0} T \left(\frac{\partial S}{\partial T}\right)_V = 0,$$

$$\lim_{T \to 0} C_P = \lim_{T \to 0} T \left(\frac{\partial S}{\partial T}\right)_P = 0 \ .$$

The ideal gas does not fulfill the third law. The heat capacities (3.9) and (3.11) of the ideal gas are constant,

$$C_V = \frac{3}{2}nR, \qquad C_P = \frac{5}{2}nR \ ,$$

in contradiction with the third law. This is because the idea gas corresponds the high-temperature limit of the state of matter, which undergoes further gas $\to$ liquid $\to$ solid transitions upon cooling.

No thermal expansion for $T \to 0$**.** The Maxwell equation (4.10), $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$, implies

$$\lim_{T \to 0} \alpha = \lim_{T \to 0} \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \lim_{T \to 0} \frac{-1}{V} \left(\frac{\partial S}{\partial P}\right)_T = 0 \ ,$$

where the last step follows from the fact that any derivative of a constant vanishes.

The absolute $T = 0$ **(zero point) is unattainable.** We analyze what happens when we are trying to reach low and lower temperatures by subsequently performing adiabatic and isothermal transformations.
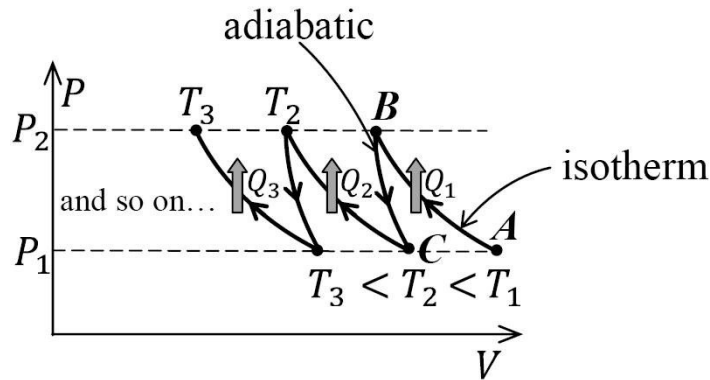
Using a gas as a working substance, cooling is achieved by the *Linde method* through a sequence isothermal and adiabatic transformations.

$A \to B$ isothermal compression

> Work is performed on the gas and an amount of heat $Q_1 < 0$ is transferred from the substance to be cooled (characterized by a low temperature T_1), to the reservoir (having a higher temperature) in a reversible process. The entropy of the substance being cooled diminishes consequently by

$$\Delta S_1 \;=\; \frac{Q_1}{T_1} \; .$$

$B \to C$ adiabatic expansion

> The gas cools by performing work. The entropy remains however with $\delta Q = 0$ constant.
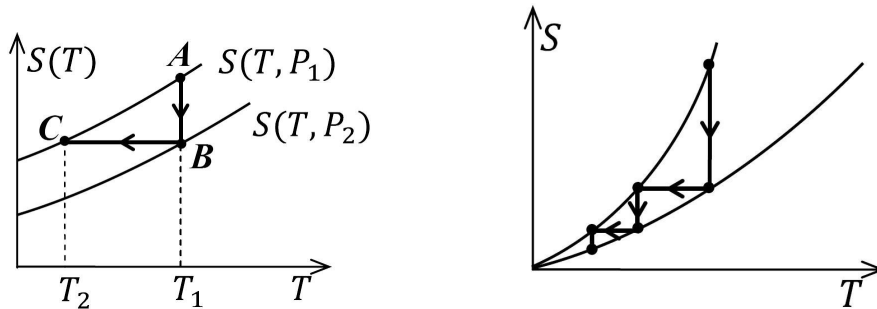
Note that all entropy curves converge to $S(T \to 0) \to 0$. The process becomes hence progressively ineffective and an infinite number of Linde iterations would be needed to reach the limit $T \to 0$.