# D Thermodynamics and entropy



## 23 Thermodynamic averages

### 23.a Generalized grandcanonical ensembles

Until now we have worked with the canonical ensemble, but also allowed that the particle number is not fixed, but is allowed to fluctuate. By adding a term $-\mu\hat{N}$ to the Hamiltonian we obtained the grandcanonical ensemble described by $\rho = \mathrm{e}^{-\beta(H-\mu\hat{N})}/Y$. Similarly one may add other quantities to $H$ as we already did by introducing a canonical ensemble with given pressure instead of volume. One obtains generally

$$\rho = \mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)}/Y \tag{23.1}$$

or if we introduce the generalized potential $K$ by

$$\mathrm{e}^{-\beta K} = Y = \mathrm{tr}\,\mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)} \tag{23.2}$$

then we may write

$$\rho = \mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i-K)} \tag{23.3}$$

Note, that $K$ is a function of $T$ or $\beta$ and of the $f_i$s. Examples of such external forces $f_i$ and their corresponding conjugate operators $\hat{Q}_i$ are

| $f_i$ | $\hat{Q}_i$ |
|---|---|
| External forces | operators (conjugate quantities) |
| chem. potential | particle number |
| − pressure | volume |
| stress tensor | $V\cdot$ strain tensor |
| velocity | momentum |
| frequency | anguar momentum |
| magnetic field | magnet. moment |
| electric field | electr. moment |

Taking the derivative with respect to $f_i$ we obtain $Q_i = \langle\hat{Q}_i\rangle$ from $K$,

$$\frac{\partial K}{\partial f_i} = -k_{\mathrm{B}}T\frac{\partial \ln Y}{\partial f_i} = -k_{\mathrm{B}}T\frac{1}{Y}\beta\mathrm{tr}(\hat{Q}_i\mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)}) = -\mathrm{tr}(\hat{Q}_i\rho) = -\langle\hat{Q}_i\rangle = -Q_i. \tag{23.4}$$

One can show by means of the cyclic invariance of the trace, that this does not only hold for oerators $\hat{Q}_i$ which commute with $H-\sum_i f_i\hat{Q}_i$. Thus one obtains generally the expectation values of the operators $\hat{Q}_i$ from the derivatives of $K$. Finally we consider what we obtain from the derivative of $K$ with respect to $\beta$,

$$\begin{aligned}\frac{\partial K}{\partial\beta} &= -\frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\ln Y\right) = \frac{1}{\beta^2}\ln Y - \frac{1}{\beta Y}\frac{\partial Y}{\partial\beta}\\ &= \frac{1}{\beta^2}\mathrm{tr}((\beta(H-\sum_i f_i\hat{Q}_i)+\ln Y)\rho)\end{aligned} \tag{23.5}$$

This expression may be written

$$\frac{\partial K}{\partial\beta} = \frac{1}{\beta}(E-\sum_i f_iQ_i - K) \tag{23.6}$$

as well as

$$\frac{\partial K}{\partial \beta} = -\frac{1}{\beta^2}\langle \ln \rho \rangle \tag{23.7}$$

since $\ln \rho = -\beta(H - \sum_i f_i \hat{Q}_i - K)$. Thus we obtain

$$\mathrm{d}K = -\sum_i Q_i \mathrm{d}f_i + k_\mathrm{B}\langle \ln \rho \rangle \mathrm{d}T. \tag{23.8}$$

## 23.b Entropy

We have found for the canonical and the generalized canonical ensembles

$$\begin{array}{llllll} \text{Ensemble} & Y & K & f & Q & \mathrm{d}K \\ \text{canonical} & Z & F & - & - & \mathrm{d}F = -S\mathrm{d}T \\ \text{canonical} & \tilde{Z} & G & -P & V & \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \\ \text{grandcanonical} & Y & J & \mu & N & \mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu. \end{array} \tag{23.9}$$

From (23.8) it follows that the entropy for these ensembles should be defined as

$$S = -k_\mathrm{B}\langle \ln \rho \rangle. \tag{23.10}$$

For the microcanonical ensemble we had

$$\rho_i = \begin{cases} 1/W & E_i \le E, \\ 0 & E_i > E. \end{cases} \tag{23.11}$$

This yields with the definition (23.10)

$$S = -k_\mathrm{B}\sum_i \rho_i \ln \rho_i = k_\mathrm{B} \ln W \tag{23.12}$$

in accordance with the original definition. Note, that

$$\lim_{\rho \to 0} \rho \ln \rho = 0. \tag{23.13}$$

Then we may define the entropy operator

$$\hat{S} = -k_\mathrm{B} \ln \rho \tag{23.14}$$

which reads for our generalized canonical ensembles

$$\hat{S} = \frac{1}{T}(H - \sum_i f_i \hat{Q}_i - K) \tag{23.15}$$

Then we obtain

$$\mathrm{d}K = -S\mathrm{d}T - \sum_i Q_i \mathrm{d}f_i \tag{23.16}$$

and

$$E = K + TS + \sum_i f_i Q_i. \tag{23.17}$$

For classical systems $\rho$ under the logarithm has to be multiplied by $N!h^{3N}$,

$$S = -k_\mathrm{B}\int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \rho \ln(N!h^{3N}\rho). \tag{23.18}$$

First we know, that only one quantum state fits into $\Delta p \Delta x = h$. The probability that it is occupied is obtained by multiplying $\rho$ by the corresponding phase space, that is by the appropriate power of $h$.

Since equal particles are indistinguishable all $N!$ permutations of the coordinates $(p_i, x_i)$ contribute to the state. Therefore the phase-space for an $N$-particle state (of equal particles) has to be multiplied by $N!$. One may object, that for bosons one and the same state can be occupied multiply, and that then the factor $N!$ is an overestimate. This is correct. If however, the occupation probability is that large, that this plays a role, then the classical calculation is no longer valid. Similar is the argument, that those regions of the phase-space, in which two fermions have practically the same coordinates should not be taken into account. Here, too, the following applies: If the occupation is so large that this plays a role for the final result, then one has to perform a quantum mechanical calculation. The first quantum correction had been calculated in section 17.

# 24 Second derivatives of thermodynamic potentials and fluctuations

## 24.a The Derivatives

We now consider the second derivatives of the thermodynamic potentials with respect to their natural variables. The first derivative was

$$-\frac{\partial K}{\partial f_i} = Q_i = \mathrm{tr}(\hat{Q}_i \underbrace{\mathrm{e}^{-\beta(H-\sum_j f_j \hat{Q}_j - K)}}_{\rho}). \tag{24.1}$$

The second turns out to be

$$\begin{aligned} \frac{\partial Q_i}{\partial f_j} &= \beta \mathrm{tr}(\hat{Q}_i \hat{Q}_j \rho) + \beta \underbrace{\frac{\partial K}{\partial f_j}}_{-Q_j} \mathrm{tr}(\hat{Q}_i \rho) \\ &= \frac{1}{k_\mathrm{B}T}\left(\langle \hat{Q}_i \hat{Q}_j\rangle - Q_i Q_j\right) = \frac{1}{k_\mathrm{B}T}\langle \Delta\hat{Q}_i \Delta\hat{Q}_j\rangle \end{aligned} \tag{24.2}$$

with $\Delta\hat{Q}_i = \hat{Q}_i - Q_i$ (section 3). Here we assume that $\hat{Q}_i$ or $\hat{Q}_j$ commutes with $H - \sum_i f_i \hat{Q}_i$. Then we obtain for the grand-canonical ensemble

$$\frac{\partial N}{\partial \mu} = \frac{1}{k_\mathrm{B}T}\langle(\Delta\hat{N})^2\rangle = \frac{1}{k_\mathrm{B}T}(\Delta N)^2 = O(N^1). \tag{24.3}$$

The estimate $O(N^1)$ is obtained since we take the derivative of an extensive quantity ($N$) with respect to an intensive one ($\mu = O(N^0)$). Therefore normally the fluctuation of the particle number is of order $O(N^{1/2})$, thus small against the particle number in macroscopic systems. (Normally means: If $\frac{\partial N}{\partial \mu}$ remains finite.)
Further we consider

$$\frac{\partial Q_i}{\partial \beta} = -T\langle \hat{Q}_i \hat{S}\rangle + \beta \frac{\partial K}{\partial \beta} Q_i \tag{24.4}$$

and therefore

$$\frac{\partial Q_i}{\partial T} = -\frac{1}{k_\mathrm{B}T^2}\frac{\partial Q_i}{\partial \beta} = \frac{1}{k_\mathrm{B}T}\langle \hat{Q}_i \hat{S}\rangle + \frac{1}{k_\mathrm{B}T}\underbrace{\frac{\partial K}{\partial T}}_{-S} Q_i = \frac{1}{k_\mathrm{B}T}\langle \Delta\hat{Q}_i \Delta\hat{S}\rangle \tag{24.5}$$

with

$$\hat{S} = \frac{1}{T}\left(H - \sum_i f_i \hat{Q}_i - K\right), \quad \Delta\hat{S} = \frac{1}{T}\left(\Delta H - \sum_i f_i \Delta\hat{Q}_i\right). \tag{24.6}$$

We observe

$$\frac{\partial S}{\partial T} = \frac{1}{k_\mathrm{B}T}\langle(\Delta\hat{S})^2\rangle. \tag{24.7}$$

For the canonical ensemble one obtains

$$\frac{\partial S}{\partial T} = \frac{1}{k_\mathrm{B}T^3}\langle(\Delta H)^2\rangle = O(N^1). \tag{24.8}$$

Thus also the energy fluctuations are normally of order $O(N^{1/2})$ and thus negligible against the average energy for macroscopic systems.

## 24.b Special second derivatives

We consider now the specific heat. It is the amount of heat which has to be fed into the system divided by the change of temperature. Thus we have

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T}. \tag{24.9}$$

What is obtained in detail depends on the way the process is performed. If volume and particle number are kept fixed then one obtains

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_{V,N}. \tag{24.10}$$

The formulation $\left.\frac{\partial S}{\partial T}\right|_{V,N}$ means that we differentiate $S$ with respect to $T$ at fixed $V$ and $N$. This is equivalent to the partial derivative of the function $S(T,V,N)$ with respect to $T$. Since, however, one often changes the variables in thermodynamics, it would be necessary to distinguish different functions for different variables. Instead one prefers to indicate which quantities are kept fixed. If, however, pressure and particle number are fixed, then one obtains

$$C_P = T\left.\frac{\partial S}{\partial T}\right|_{P,N}. \tag{24.11}$$

For an ideal classical monatomic gas one obtains

$$S = k_{\mathrm{B}}N\ln\left(\frac{V}{N}(k_{\mathrm{B}}T)^{3/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\mathrm{e}^{5/2}\right), \qquad C_V = \frac{3}{2}k_{\mathrm{B}}N, \tag{24.12}$$

$$S = k_{\mathrm{B}}N\ln\left(\frac{1}{P}(k_{\mathrm{B}}T)^{5/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\mathrm{e}^{5/2}\right), \qquad C_P = \frac{5}{2}k_{\mathrm{B}}N. \tag{24.13}$$

Similarly one distinguishes between adiabatic and isothermal compressibility,

$$\kappa = -\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P} \tag{24.14}$$

Similarly the magnetic susceptibility $\chi = \frac{\mathrm{d}M}{\mathrm{d}H}$ and the volume expansion coefficient depend on the way the change of the system is performed

$$\alpha = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T}. \tag{24.15}$$

# 25 Thermodynamic Relations

## 25.a from the potentials

A number of thermodynamic relations can be obtained by differentiating the potentials. For example one obtains from

$$\begin{aligned} \mathrm{d}E &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N, && (25.1) \\ \mathrm{d}I &= T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N && (25.2) \end{aligned}$$

relations between the specific heats

$$\begin{aligned} \left.\frac{\partial E}{\partial T}\right|_{V,N} &= T\left.\frac{\partial S}{\partial T}\right|_{V,N} = C_V, && (25.3) \\ \left.\frac{\partial I}{\partial T}\right|_{P,N} &= T\left.\frac{\partial S}{\partial T}\right|_{P,N} = C_P, && (25.4) \\ \left.\frac{\partial E}{\partial T}\right|_{P,N} &= T\left.\frac{\partial S}{\partial T}\right|_{P,N} - P\left.\frac{\partial V}{\partial T}\right|_{P,N} = C_P - PV\alpha_P. && (25.5) \end{aligned}$$

## 25.b from the conditions of integrability

The mixed second derivatives of the potentials have to agree (condition of integrability). Then one obtains from

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \qquad (25.6)$$

the condition

$$-\frac{\partial^2 F}{\partial V \partial T} = \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}. \qquad (25.7)$$

Similarly

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N \qquad (25.8)$$

yields

$$-\frac{\partial^2 G}{\partial P \partial T} = \left.\frac{\partial S}{\partial P}\right|_{T,N} = -\left.\frac{\partial V}{\partial T}\right|_{P,N}. \qquad (25.9)$$

These relations are called Maxwell-relations.

## 25.c Functional (Jacobi-) determinant

The Jacobian

$$\frac{\partial(f,g)}{\partial(x,y)} := \frac{\partial f}{\partial x}\frac{\partial g}{\partial y} - \frac{\partial f}{\partial y}\frac{\partial g}{\partial x} \qquad (25.10)$$

obeys the chain-rule

$$\frac{\partial(f,g)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(u,v)}\frac{\partial(u,v)}{\partial(x,y)}. \qquad (25.11)$$

Note that

$$\frac{\partial(f,y)}{\partial(x,y)} = \left.\frac{\partial f}{\partial x}\right|_y \qquad (25.12)$$

and

$$\partial(f,g) = -\partial(g,f) \qquad (25.13)$$

holds.

Now we derive a relation between the specific heats and the compressibilities. We transform

$$\begin{aligned}\frac{\partial(P,S,N)}{\partial(V,T,N)} = \frac{\partial(P,S,N)}{\partial(V,S,N)}\frac{\partial(V,S,N)}{\partial(V,T,N)} &= \frac{\partial(P,S,N)}{\partial(P,T,N)}\frac{\partial(P,T,N)}{\partial(V,T,N)} \\ = \left.\frac{\partial P}{\partial V}\right|_{S,N}\left.\frac{\partial S}{\partial T}\right|_{V,N} &= \left.\frac{\partial S}{\partial T}\right|_{P,N}\left.\frac{\partial P}{\partial V}\right|_{T,N} \\ = -\frac{1}{V\kappa_S}\frac{C_V}{T} &= \frac{C_P}{T}\left(-\frac{1}{V\kappa_T}\right), \end{aligned} \tag{25.14}$$

from which we obtain

$$\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V} \tag{25.15}$$

We derive another connection between the specific heats

$$C_P = T\left.\frac{\partial S}{\partial T}\right|_{P,N} = T\left.\frac{\partial S}{\partial T}\right|_{V,N} + T\left.\frac{\partial S}{\partial V}\right|_{T,N}\left.\frac{\partial V}{\partial T}\right|_{P,N}. \tag{25.16}$$

We convert further

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N} = \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)}\frac{\partial(P,T,N)}{\partial(T,V,N)} = \left.\frac{\partial V}{\partial T}\right|_{P,N}\cdot(-\left.\frac{\partial P}{\partial V}\right|_{T,N}) \tag{25.17}$$

and therefore

$$C_P = C_V + T(V\alpha_P)^2\frac{1}{V\kappa_T} = C_V + TV\frac{\alpha_P^2}{\kappa_T}. \tag{25.18}$$

The integrability condition (25.7)

$$\left.\frac{\partial P}{\partial T}\right|_{V,N} = \left.\frac{\partial S}{\partial V}\right|_{T,N} \tag{25.19}$$

yields

$$\frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(T,S,N)}{\partial(T,V,N)} \tag{25.20}$$

and thus

$$\partial(P,V,N) = \partial(T,S,N) \tag{25.21}$$

and similarly

$$\partial(P,V,\mu) = \partial(T,S,\mu), \quad \partial(P,V,T) = \partial(\mu,N,T). \tag{25.22}$$

## 25.d Homogeneity

If numerator and denominator of a Jacobian contain the same two intensive variables ($T$, $P$, $\mu$) and one extensive variable, then from homogeneity it follows, that the Jacobian determinant is the ratio of the two extensive variables,

$$\frac{\partial(V,P,T)}{\partial(N,P,T)} = \left.\frac{\partial V}{\partial N}\right|_{P,T} = \frac{V}{N}. \tag{25.23}$$

This relation can be used to determine the isothermal compressibility from the grand canonical potential,

$$\begin{aligned}\kappa_T &= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{T,N} = -\frac{1}{V}\frac{\partial(V,N,T)}{\partial(P,N,T)} = -\frac{1}{N}\frac{\partial(V,N,T)}{\partial(P,V,T)} = \left(\frac{1}{N}\left.\frac{\partial N}{\partial P}\right|_{T,V}\right) \\ &= -\frac{1}{N}\frac{\partial(V,N,T)}{\partial(\mu,N,T)} = -\frac{V}{N^2}\frac{\partial(V,N,T)}{\partial(\mu,V,T)} = \frac{V}{N^2}\left.\frac{\partial N}{\partial\mu}\right|_{T,V}\end{aligned} \tag{25.24}$$

Considering that $N = -\frac{\partial J}{\partial\mu}$ the compressibility is obtained from the second derivative of the grand canonical potential with respect to $\mu$.

# 26 Positivity of Entropy: Third Law of Thermodynamics

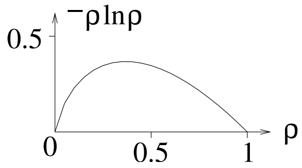
## 26.a Positivity

For all eigenvalues of the density matrix one has $0 \leq \rho_n \leq 1$ and thus $-\rho_n \ln \rho_n \geq 0$ and therefore

$$S = -k_{\mathrm{B}} \sum_n \rho_n \ln \rho_n \geq 0. \tag{26.1}$$

The entropy is never negative. It can only vanish, if each eigenvalue $\rho_n$ equals either 0 or 1. Since $\sum_n \rho_n = 1$, then one of the eigenvalues equals one and the other ones vanish. Thus the entropy vanishes only for a pure state.

$-\rho \ln \rho$ *versus* $\rho$




The statement of the positivity requests the quantum nature of the system.
Formally in a part of the phase-space of a classical system $\rho$ can be larger then $1/(N!h^{3N})$, which yields a negative contribution to the entropy. This, however, would violate fundamental principles of quantum mechanics and such a phase-space density cannot be a good description of a physical system.

## 26.b Third Law of Thermodynamics

We consider a large but finite system with discrete energy levels. The ground-state be $g$-fold degenerate. At absolute zero only the ground-states are occupied,

$$S(T = 0) = k_{\mathrm{B}} \ln g. \tag{26.2}$$

$g$ may even be macroscopically. An isotropic ferromagnet with total spin $\tilde{S} = O(N)$ has the degeneracy $g = 2\tilde{S} + 1$, that is $S(T = 0) = k_{\mathrm{B}} \ln(2\tilde{S} + 1) = O(\ln N)$. We see, however, that

$$\lim_{N\to\infty} \lim_{T\to 0} \frac{S}{N} = 0. \tag{26.3}$$

This is the statement of the third law of thermodynamics. It is possible to construct theoretical models with $S(T = 0) \propto N$. (This can be done e.g. for ice-models. In these models the oxygen atoms are connected by hydrogen bridges, where the hydrogen is closer or remoter to one or the other oxygen. All states in which two hydrogen atoms are close to each oxygen are considered energetically degenerate.) It seems that in reality such high degeneracies are lifted.

# 27 Extremal Properties of the Entropy

## 27.a An Inequality

$\rho$ and $\rho'$ be two statistical operators with eigenstates

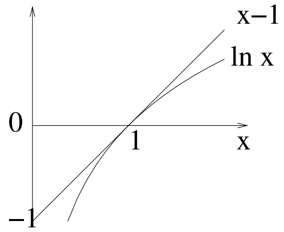
$$\rho|n\rangle = \rho_n|n\rangle, \quad \rho'|\nu\rangle = \rho'_\nu|\nu\rangle. \tag{27.1}$$

Then one has

$$\begin{aligned} \mathrm{tr}(\rho'(\ln\rho - \ln\rho')) &= \sum_{n,\nu}\langle\nu|\rho'|n\rangle\langle n|\ln\rho - \ln\rho'|\nu\rangle \\ &= \sum_{n,\nu}\rho'_\nu\langle\nu|n\rangle\langle n|\nu\rangle(\ln\rho_n - \ln\rho'_\nu). \end{aligned} \tag{27.2}$$

Now one has $\ln x \le x - 1$, which follows from $\ln x = \int_1^x \frac{\mathrm{d}x'}{x'}$ and $\frac{1}{x'} < 1$ for $x' > 1$ and $\frac{1}{x'} > 1$ for $x' < 1$

*Graphical representation of the inequality* $\ln x \le x - 1$




$$\ln\rho_n - \ln\rho'_\nu = \ln\frac{\rho_n}{\rho'_\nu} \le \frac{\rho_n}{\rho'_\nu} - 1 \tag{27.3}$$

and

$$\mathrm{tr}(\rho'(\ln\rho - \ln\rho')) \le \sum_{n,\nu}|\langle\nu|n\rangle|^2(\rho_n - \rho'_\nu) = \sum_n \rho_n - \sum_\nu \rho'_\nu = 1 - 1 = 0, \tag{27.4}$$

that is

$$S' = -k_\mathrm{B}\sum_\nu \rho'_\nu \ln\rho'_\nu \le -k_\mathrm{B}\mathrm{tr}(\rho'\ln\rho). \tag{27.5}$$

The equal-sign holds only, if for each term in (27.4) either $\langle\nu|n\rangle = 0$ or $\rho_n = \rho'_\nu$, from which $\rho = \rho'$ follows.

## 27.b Microcanonical Ensemble

The statistical operator $\rho'$ be composed from the states $|\nu\rangle$ of the Hilbert-space spanned by the eigenstates $|n\rangle$ of the Hamiltonian in the energy-interval $E - \Delta < E_n \le E$. $\rho$ describes the microcanonical ensemble

$$\rho = \frac{1}{W(E) - W(E-\Delta)}\sum_{n,E-\Delta<E_n\le E}|n\rangle\langle n|. \tag{27.6}$$

Then one obtains

$$S' \le -k_\mathrm{B}\mathrm{tr}(\rho'\ln\rho) = k_\mathrm{B}\mathrm{tr}(\rho'\ln(W(E) - W(E-\Delta)) = S. \tag{27.7}$$

The microcanonical ensemble has the largest entropy of all ensembles which are composed from states in the energy-interval $E - \Delta ... E$. A similar statement holds, if energy is replaced by enthalphy.

## 27.c Generalized (grand)canonical Ensemble

$\rho$ be the statistical operator of the generalized canonical ensemble

$$\rho = \mathrm{e}^{-\beta(H-\sum_i f_i \hat{Q}_i - K)} \tag{27.8}$$

and $\rho'$ be an arbitrary statistical operator. Then one obtains

$$S' \le k_\mathrm{B}\beta \mathrm{tr}(\rho'(H - \sum_i f_i \hat{Q}_i - K)) = \frac{1}{T}(E' - \sum_i f_i Q'_i - K). \tag{27.9}$$

With $K = E - \sum_i f_i Q_i - TS$ one obtains

$$S' \le S + \frac{1}{T}(E' - E + \sum_i f_i(Q_i - Q'_i)). \tag{27.10}$$

$\alpha$) Be $\rho'$ an ensemble with given expectation values $E' = E$, $Q'_i = Q_i$. Then one finds: The generalized canonical ensemble has the largest entropy of all ensembles with given expectation value of the energy and of the operators $\hat{Q}_i$. $\beta$) From the inequality (27.10) one obtains

$$K \le E' - TS' - \sum f_i Q'_i. \tag{27.11}$$

This allows for a variational principle in order to determine an upper bound for $K$ for given $T$ and $f_i$s: One varies $\rho'$ and looks for that with the lowest $E' - TS' - \sum f_i Q'_i$ as an approximation. This is a generalization of the variational principle to determine the groundstate ($T = 0$), $E \le E'$.

## 27.d Information entropy

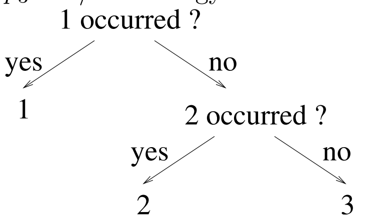
The expression

$$S = -k_\mathrm{B} \sum_n \rho_n \ln \rho_n \tag{27.12}$$

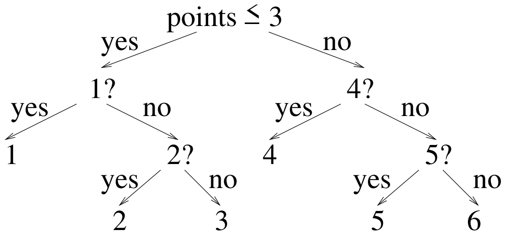
is closely related with the measure for information. For events $n$ with a-priori probabilities $\rho_n$, $\sum_n \rho_n = 1$ one defines the information, that the event $n$ occurs as $-\mathrm{ld}\rho_n$. Here ld is the logarithm to basis 2, $\mathrm{ld}\rho = {}^2\log \rho = \ln\rho/\ln 2$. A rare event carries a larger amount of information, a frequent one only a small amount. Compare the amount of information of the two statements: "I hit the jackpot" and "I have drawn a blank". The averaged information is

$$I = -\sum_n \rho_n \mathrm{ld}\rho_n. \tag{27.13}$$

Obviously the relation is $S = k_\mathrm{B} I/\ln 2$. The meaning of $I$ is the following:
$\alpha$) If one follows an optimal strategy of questions, then one needs *in the average* at least $I$ questions with answers yes or no (bits), in order to find out which event did occur.
$\beta$) There is always a strategy, so that *in the average* less than $I+1$ such questions are necessary to find out which event occurred. Example 1: Three events happen with probabilities $p_1 = 1/2$, $p_2 = 1/4$, $p_3 = 1/4$. Strategy:




One obtains $I = 3/2$, the average number of questions is $3/2$.
Example 2: One throws dices. Six possible events with probability $p_i = 1/6$. Strategy:




One finds $I = \mathrm{ld}6 = 2.584$. The average number of questions is $8/3 = 2.667$.
Apart from the factor in front the entropy $S$ is an information entropy. It is characteristic for the microcanonical and the canonical ensembles that the missing information (on the state of the system) is maximal under the conditions given (energy boundaries or energy-expectation value). That is besides these conditions *nothing* is known on the state of the system.

Literatur/literature: Ash, Information Theory (Bibl. Ang. Math.), L. Brillouin, Science and Information Theory.

# 28 Second Law of Thermodynamics

The second law of thermodynamics says: The thermodynamic entropy of a closed system obeys $\mathrm{d}S/\mathrm{d}t \geq 0$. Thus the thermodynamic entropy of a closed system can only increase or stay constant as a function of time.

## 28.a Constance of information entropy

First we consider the development of the information entropy of a closed system. We represent $\rho(t)$ by its eigenstates at a certain time

$$\rho(t) = \sum_n |n(t)\rangle \rho_n \langle n(t)|. \tag{28.1}$$

The states $|n(t)\rangle$ need not be eigenstates of the hamiltonian. They develop according to

$$|m(t')\rangle = \mathrm{e}^{-\mathrm{i}H(t'-t)/\hbar}|m(t)\rangle, \quad \langle n(t')| = \langle n(t)|\mathrm{e}^{\mathrm{i}H(t'-t)/\hbar}. \tag{28.2}$$

Thus one obtains, that the states at time $t'$ are also orthonormal

$$\langle n(t')|m(t')\rangle = \langle n(t)|m(t)\rangle = \delta_{n,m}. \tag{28.3}$$

Therefore one has

$$\rho(t') = \sum_n |n(t')\rangle \rho_n \langle n(t')|, \tag{28.4}$$

where $\rho(t')$ is expanded in its eigenstates, too. The eigenvalues $\rho_n$ are unchanged. Then one obtains for the information entropy

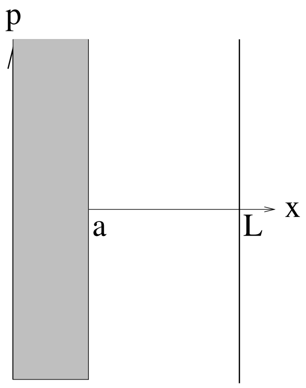
$$S(t') = -k_\mathrm{B} \sum_n \rho_n \ln \rho_n = S(t). \tag{28.5}$$

Thus the information entropy of a closed system is constant. This holds for classical systems, too.

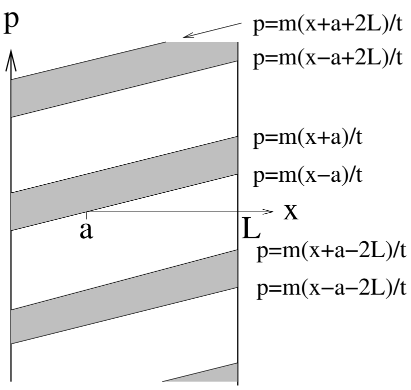
## 28.b Reversible and irreversible expansion of an ideal classical gas

Let us now consider an ideal classical gas which is heat insulated.
First we consider what happens, if the system undergoes a **slow expansion**. Then the system delivers the energy $P\mathrm{d}V$. Thus one has $\mathrm{d}E = -P\mathrm{d}V$ und thus $T\mathrm{d}S = 0$, that is $S =$const. This is an adiabatic process. The process is reversible, both $\mathrm{d}V/\mathrm{d}t > 0$ and $\mathrm{d}V/\mathrm{d}t < 0$ are possible without change of entropy.
Next we consider a **fast expansion**: The wall should move faster then the average thermal velocity, or we remove suddenly a wall of the vessel. Then the system does (nearly) not deliver energy. The pressure exerted on the wall is much less then the internal pressure, $\mathrm{d}E \approx 0$. Since for fixed energy the entropy increases (in equilibrium) with the volume, we have $\dot{S} > 0$, $\dot{V} > 0$. The process is irreversible, since it is not possible to capture the particles in the original volume without doing work.
Now there is the question: Does the entropy increase? Does the system approach equilibrium?
For this purpose we consider what happens to an ideal gas, if we remove the wall at time $t = 0$. Up to this time all atoms be in the box $0 \leq x \leq a$. For $t > 0$ the atoms can move freely in the larger box $0 \leq x \leq L > a$.

*All atoms in the box $0 \leq x \leq a$ at time $t = 0$.*



*At times $t > 0$ free motion in the box $0 \leq x \leq L$.*




Now a streak structure develops: In the (x,p) space occupied and unoccupied regions change frequently. The information entropy (microscopic entropy) is conserved. For $t \to \infty$ the stripes become smaller and smaller. Then one replaces $\rho$ by an $\rho$ averaged in some region of the $\Gamma$-space: coarse graining. The assumption is, that one cannot draw any use out of the streak structure. The situation becomes more apparent, if one takes the interaction into account. Then the averaged one-particle density $\rho_1(p,x)$ does no longer show a streak structure, but the $N$-particle density $\rho$.

We have assumed that the particles are reflected ideally at the walls. If this is not the case, then the system is coupled to its surroundings. This induces a fading of the streak structure and consequently an increase of the entropy of the gas in the box. A pure state coupled to another system will not remain in generally a pure state, but develop into a mixture with increasing entropy.

## 28.c Thermodynamical entropy

The thermodynamical entropy is the maximal information entropy for a system with given expectation values (e.g. for energy, volume, etc.) One replace the actual $\rho$ by an averaged one. This averaging (coarse graining) yields practically no difference for expectation values like $\langle H \rangle$, $\langle \hat{Q}_i \rangle$, but an essential difference for the entropy. Generally one has

information entropy $\leq$ thermodynamical entropy

In considering expectation values one need not confine oneself to quantities of the whole system. One may for example introduce space-dependent densities, or as we will show in the following, averaged occupation numbers for particles of different momenta.

## 28.d Boltzmann-equation

If we now assume, that we can describe the system by the average occupation $\bar{n}$. Then the following picture emerges: The entropy can be expressed in terms of the occupation numbers. It turns out, that again eqs. (16.20, 16.21) hold (for simplicities' sake we leave aside the other quantum numbers)

$$S = k_{\mathrm{B}} \sum_{\mathbf{k}} ((\pm(1 \pm \bar{n}_{\mathbf{k}}) \ln(1 \pm \bar{n}_{\mathbf{k}}) - \bar{n}_{\mathbf{k}} \ln \bar{n}_{\mathbf{k}})) \tag{28.6}$$

This is immediately clear for fermions (lower sign), since there the $n_{\mathbf{k}}$ assume only the values 0 and 1. Thus the probabilities $w_n$ for $n$-fold occupation are given by $w_0 = 1 - \bar{n}$, $w_1 = \bar{n}$ with the contribution

$$-k_{\mathrm{B}}(w_0 \ln w_0 + w_1 \ln w_1) = -k_{\mathrm{B}}(1 - \bar{n}) \ln(1 - \bar{n}) - k_{\mathrm{B}} \bar{n} \ln \bar{n} \tag{28.7}$$

to the entropy. For bosons we have the contribution to the entropy $-k_{\mathrm{B}} \sum_n w_n \ln w_n$. One adds by means of Lagrange parameters $\kappa$ and $\lambda$ the conditions for total probability 1 and average occupation $\bar{n}$, so that

$$-k_{\mathrm{B}} \sum_n w_n \ln w_n + \kappa(\sum_n w_n - 1) + \lambda(\sum_n n w_n - \bar{n}) \tag{28.8}$$

has to be varied. The variation of $w_n$ yields

$$-k_{\mathrm{B}}(1 + \ln w_n) + \kappa + \lambda n = 0. \tag{28.9}$$

If one solves the equation with respect to $w_n$ and determines $\kappa$ and $\lambda$ from the auxiliary conditions, then one obtains the distribution (16.11) and evaluates the entropy (16.20).
The change of entropy in the course of time is then given by

$$\dot{S} = k_\mathrm{B} \sum_{\mathbf{k}} \dot{\bar{n}}_{\mathbf{k}} \left(\ln(1 \pm \bar{n}_{\mathbf{k}}) - \ln \bar{n}_{\mathbf{k}}\right) \tag{28.10}$$

From Fermi's golden rule we now that the transition probability from a many-particle state $n$ to $m$ is given by

$$\Gamma_{m,n} = \frac{2\pi}{\hbar}\delta(E_n - E_m)|\langle n|V|m\rangle|^2 \tag{28.11}$$

We apply this to a system interacting via two-particle interaction and consider the scattering of two atoms with momenta $\hbar\mathbf{k}_3$ and $\hbar\mathbf{k}_4$ into atoms with momenta $\hbar\mathbf{k}$ und $\hbar\mathbf{k}_2$.
Then we obtain for the average occupation of the one-particle state with momentum $\hbar\mathbf{k}$ die Boltzmann-equation (integrated over local space)

$$\dot{\bar{n}}_{\mathbf{k}} = \frac{1}{2} \sum_{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \left(\langle \hat{n}_{\mathbf{k}_3}\hat{n}_{\mathbf{k}_4}(1 \pm \hat{n}_{\mathbf{k}})(1 \pm \hat{n}_{\mathbf{k}_2})\rangle - \langle \hat{n}_{\mathbf{k}}\hat{n}_{\mathbf{k}_2}(1 \pm \hat{n}_{\mathbf{k}_3})(1 \pm \hat{n}_{\mathbf{k}_4})\rangle\right) \tag{28.12}$$

The factor $\frac{1}{2}$ has been introduced, since otherwise the scattering from $\mathbf{k}_3$, $\mathbf{k}_4$ and from $\mathbf{k}_4$, $\mathbf{k}_3$ would be counted twice. We note, that $\Gamma$ contains two $\delta$-factors because of energy conservation and momentum conservation,

$$\Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \propto \delta(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} - \epsilon_{\mathbf{k}_4})\delta(\mathbf{k} + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \tag{28.13}$$

The factors $\hat{n}_{\mathbf{k}_3}\hat{n}_{\mathbf{k}_4}$ in the expectation value in (28.12) are immediately obvious. The rate of the transitions from $\mathbf{k}_3$ and $\mathbf{k}_4$ is of course proportional to the corresponding occupations. There is also a back-scattering from $\mathbf{k}$, $\mathbf{k}_2$. This is described by the second expectation value in (28.12). If the gas is dilute, then one may replace the factors $1 \pm \hat{n}$ in the expectation values by 1. For fermions the factor can easily be understood. If the state with momentum $\hbar\mathbf{k}$ is already occupied, then it is not possible to scatter anything into this state, thus the factor $1 - \hat{n}$. For bosons one obtains instead a factor $1 + \hat{n}$. The process is stimulated, if the state is already occupied.
One assumes, that there is no correlation between the occupations, thus one puts

$$A := \langle \hat{n}_{\mathbf{k}_3}\hat{n}_{\mathbf{k}_4}(1 \pm \hat{n}_{\mathbf{k}})(1 \pm \hat{n}_{\mathbf{k}_2})\rangle = \bar{n}_{\mathbf{k}_3}\bar{n}_{\mathbf{k}_4}(1 \pm \bar{n}_{\mathbf{k}})(1 \pm \bar{n}_{\mathbf{k}_2}). \tag{28.14}$$

and similarly for the other expectation value

$$B := \bar{n}_{\mathbf{k}}\bar{n}_{\mathbf{k}_2}(1 \pm \bar{n}_{\mathbf{k}_3})(1 \pm \bar{n}_{\mathbf{k}_4}) \tag{28.15}$$

This is an essential approximation. It is called molecular chaos. It assumes that correlations do not play an essential role. Then one obtains

$$\dot{S} = \frac{k_\mathrm{B}}{2} \sum_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}(\ln(1 \pm n_{\mathbf{k}}) - \ln n_{\mathbf{k}})(A - B). \tag{28.16}$$

If we take into account, that $\Gamma$ and $A - B$ are invariant against interchange of $\mathbf{k}$ and $\mathbf{k}_2$, and that by the exchange of the pair $\mathbf{k}, \mathbf{k}_2$ with the pair $\mathbf{k}_3, \mathbf{k}_4$ again $\Gamma$ is invariant and $A - B$ changes sign, then we may write

$$\dot{S} = \frac{k_\mathrm{B}}{8} \sum_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4}(\ln B - \ln A)(B - A) \tag{28.17}$$

Obviously the entropy $S$ increases until one has $A = B$ or equivalently $\ln B = \ln A$ for all terms with $\Gamma \neq 0$. If $\ln B = \ln A$, then one has

$$\nu_{\mathbf{k}} + \nu_{\mathbf{k}_2} = \nu_{\mathbf{k}_3} + \nu_{\mathbf{k}_4} \text{ with } \nu_{\mathbf{k}} = \ln \frac{\bar{n}_{\mathbf{k}}}{1 \pm \bar{n}_{\mathbf{k}}}. \tag{28.18}$$

Since $\Gamma \neq 0$ holds only for energy-conservation and momentum-conservation and in our case there is also particle-conservation one has $A = B$ for

$$\nu_{\mathbf{k}} = -\beta(\epsilon_{\mathbf{k}} - \mathbf{v}\hbar\mathbf{k} - \mu) \tag{28.19}$$

which yields

$$\bar{n}_{\mathbf{k}} = \frac{1}{\mathrm{e}^{\beta(\epsilon_{\mathbf{k}} - \mathbf{v}\hbar\mathbf{k} - \mu)} \mp 1} \tag{28.20}$$

As long as momentum-conservation is not perturbed (e. g. by the walls of a vessel) the particles can move with an averaged velocity $\mathbf{v}$. For $\mathbf{v} = \mathbf{0}$ this is the Bose- and Fermi-distribution, resp.

# 29 Carnot Cycle

A Carnot cycle is a process where some medium works reversible between two heat reservoirs and returns to its original state. If the machine works optimally then the total entropy is conserved. If the entropy increases, then one looses reversible (e.g. mechanical) energy to the second-rate heat energy. In reality each periodically working machine produces entropy, the more, the faster it runs. A reversible process is an idealization: It shows the limit of what can be reached.
Principle of the Carnot process: A cycle in four steps $\alpha$) isothermal change at $T = T_1$. The working medium takes an amount of heat $Q_1 = T_1 \Delta S$ out of the reservoir with temperature $T_1$. $\beta$) The system goes adiabatically ($S$ =const., heat insulated) to the temperature $T_2$. $\gamma$) a second isothermal change, $T = T_2$, the working medium gives to the second reservoir the amount $Q_2 = T_2 \Delta S$. $\delta$) the system goes adiabatically ($S$ =const.) back to temperature $T_1$.
We consider now the **heat balance** and observe

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{29.1}$$

This can be used to determine the temperature scale without ideal gas.
For the **energy balance** one finds: The working medium takes the amount $Q_1 = T_1 \Delta S$ of heat and delivers $Q_2 = T_2 \Delta S$ of heat. Energy conservation requires, that the work $A$ done by this medium is

$$A = Q_1 - Q_2 = (T_1 - T_2)\Delta S. \tag{29.2}$$

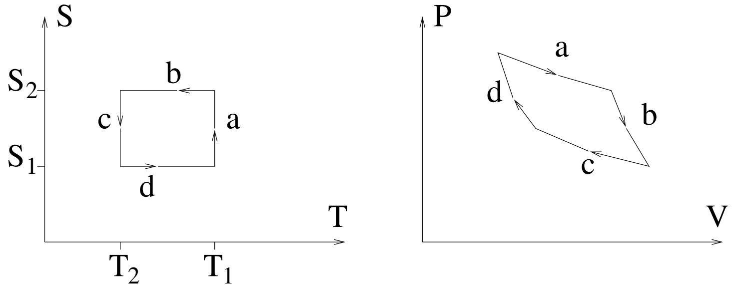
## 29.a Various Applications

The Carnot cycle can be used in various ways:

### 29.a.$\alpha$ Heat engines

In the $T, S$- and the $P, V$-diagram one obtains the following picture

*Carnot cycle of the heat engine in the $ST$ and the $PV$-diagram*




The work delivered is $A = \oint P \mathrm{d}V$. In (25.21) we have shown that $\partial(P, V, N) = \partial(T, S, N)$. Therefore the net heat

$$Q_1 - Q_2 = \oint T \mathrm{d}S = \oint P \mathrm{d}V = A \tag{29.3}$$

fed into the system equals the work $A$ done by the system. The enclosed areas in both figures are equal. The ideal efficiency is the ratio of the obtained work $A$ to the heat $Q_1$ fed into the machine,

$$\eta = \frac{A}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} < 1. \tag{29.4}$$

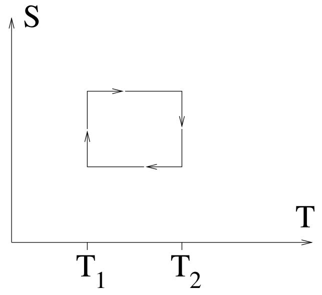
### 29.a.$\beta$ Heat Pump

The heat pump works the other way around. One feeds work $-A$ into these machines (mechanical or electrical) and extracts heat at the higher temperature $T_2$. The ideal efficiency is obtained from the ratio of the heat $Q_2$ to the work $-A$.

$$\eta = \frac{Q_2}{-A} = \frac{T_2}{T_2 - T_1} = \frac{1}{1 - T_1/T_2} > 1. \tag{29.5}$$

The heat pump does not only convert work into heat, but pumps moreover heat from the cold reservoir to the warm one.

*Carnot cycle of the heat pump*




### 29.a.$\gamma$ Refrigerator

The refrigerator works in the same direction as the heat pump. However, now one is interested in the heat which is extracted from the colder reservoir. Thus the efficiency is now given by the ratio of the heat $Q_1$ to the work $-A$, in the ideal case

$$\eta = \frac{Q_1}{-A} = \frac{T_1}{T_2 - T_1}. \tag{29.6}$$

For a conventional refrigerator, where $T_2 - T_1 \ll T_1$, one can have $\eta > 1$. For a real low-temperature machine where $T_1 \ll T_2 - T_1$ one has an efficiency $\eta \ll 1$.
Do not forget to insert the temperatures $T$ in kelvin for these calculations.

## 29.b Exergy

There is much talk about the energy crisis. In reality it is not an energy crisis. After all energy is conserved. However, we know meanwhile that heat is in a certain sense a second class energy. It can only be transformed in a limited amount into an energy of first class like mechanical or electrical energy. Therefore one asks the question: If one has a certain substance in a given environment, how much work can one extract from this substance by bringing it into equilibrium with the environment? This work is called exergy.
We assume, that we work with two species of particles and that the reservoir (environment) has temperature $T_0$, pressure $P_0$, and the chemical potentials $\mu_{a0}$ and $\mu_{b0}$.
Now we perform several steps, in which the system will deliver mechanical work against the external pressure

$$A = \int (P - P_0)\mathrm{d}V = \int P\mathrm{d}V - P_0(V_0 - V) \tag{29.7}$$

with

$$P\mathrm{d}V = -\mathrm{d}E + T\mathrm{d}S + \mu_a \mathrm{d}N_a + \mu_b \mathrm{d}N_b. \tag{29.8}$$

In a first step we keep $S$, $N_a$, and $N_b$ fixed and change $V$ until our substance has the temperature of the environment, $T = T_0$. Then we have

$$P\mathrm{d}V = -\mathrm{d}E, \quad \mathrm{d}S = 0, \quad \mathrm{d}N_a = 0, \quad \mathrm{d}N_b = 0. \tag{29.9}$$

In a second step we keep $T_0$, $N_a$, $N_b$ fixed and change the volume of our substance until $\mu_a = \mu_{a0}$. Then we have

$$P\mathrm{d}V = -\mathrm{d}E + T_0\mathrm{d}S, \quad \mathrm{d}N_a = 0, \quad \mathrm{d}N_b = 0. \tag{29.10}$$

In a third step we introduce a semipermeable membrane, which allows particles $a$ to pass but is impermeable to particles $b$. If we move this membrane, then we have

$$P\mathrm{d}V = -\mathrm{d}E + T_0\mathrm{d}S + \mu_{a0}\mathrm{d}N_a, \quad \mathrm{d}N_b = 0. \tag{29.11}$$

In total the system has done the work

$$\begin{aligned} A &= -\int \mathrm{d}E + T_0 \int \mathrm{d}S + \mu_{a0} \int \mathrm{d}N_a - P_0(V_0 - V) \\ &= E - E_0 + T_0(S_0 - S) + \mu_{a0}N_{a0} - \mu_{a0}N_a - P_0V_0 + P_0V. \end{aligned} \tag{29.12}$$

If we consider that the substance $b$ is in equilibrium with the reservoir after the third step, $N_b = N_{b0}$, and that

$$E_0 = T_0S_0 - P_0V_0 + \mu_{a0}N_{a0} + \mu_{b0}N_{b0}, \tag{29.13}$$

then we obtain for the work, which can maximally be extracted from the substance

$$A = E - T_0S + P_0V - \mu_{a0}N_a - \mu_{b0}N_b. \tag{29.14}$$

This is the exergy of the substance. It is simultaneously the minimum amount of work required to produce this substance in the given environment.
If we add an index $_0$ to the unprimed quantities in eq. (27.10) and remove the primes from the primed quantities, then we obtain for the potential $K_0 = E_0 - \mu_{a0}N_{a0} + P_0V_0 - T_0S_0 = \mu_{b0}N_{b0}$ the inequality

$$S \leq S_0 + \frac{1}{T}(E - E_0 + \mu_{a0}(N_{a0} - N_a) - P_0(V_0 - V)) \tag{29.15}$$

and thus $A \geq 0$. As expected this work can never be negative.