

The thermodynamic work function

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(Dated: May 19, 2026)

The thermodynamic work function is introduced as a fundamental physical principle. It symbolizes a positive vector of energy transformation in non-reactive systems, derived from the first and second laws. While the first law applies to any system and the second law applies to energy transformation among macroscopic systems, chemical reactions denote microscopic energy transformation inside a macroscopic system. This implies a different statistical mechanism and a change in paradigm between thermal physics and thermochemistry. The chemical work function thus supplants the classical Gibbs free energy concept. The dimensionless form is introduced as the fourth law of thermodynamics, showing that spontaneity and chemical equilibrium are related to Shannon entropy. The assumption that the second law applies to any process is proven false. Instead, spontaneous decreases in entropy are shown to exist when several small objects merge to form larger structures. This leads to a unified scientific understanding of inanimate matter and living nature across physics, chemistry, and biology, reaching out to even the social sciences.

I. INTRODUCTION

Energy is the most fundamental dynamic concept in all of physics. The attribute *dynamic* implies an inherent relation to time as a measure of energy transformation¹. Thermodynamics is the branch of physics that studies energy transformations and the relationships between different forms of energy, providing fundamental laws to understand and predict the behavior of classical² macroscopic³ systems. While state properties characterize a system in equilibrium at a particular moment in time, process properties describe the changes from one state to another. Associated forms of energy transformation include

- material flow,
- heat flow, defined as the spontaneous flow of energy from a warm to a cold object, and
- work, defined as any other form of energy transfer.

The investigation of process properties yields the *thermodynamic work function* introduced in this paper as a fundamental physical principle, the comprehension of which is relevant to all fields of science and human life.

Given the publication by Max Planck in 1913 [1, 2] that related Ludwig Boltzmann's multiplicity concept [3] to Rudolf Clausius' original formulation of entropy [4], the concept of a *work function* could have been introduced more than 100 years ago. Because it has not happened, the concept and its implications are thoroughly explained. The derivation starts from the Carnot cycle with an ideal gas as the working fluid. Section II thus provides a condensed introduction to basic concepts, including the differences between various forms of energy⁴, the ideal gas model, and the physical definition of entropy. Extensive state properties are normalized before introducing sign definitions and thermodynamic reference processes. The latter are combined in Section III to form a Carnot cooling cycle, investigating whether all the energy can be recovered. The result reveals the origin of technical work used to derive the work function of thermodynamic cycles. Its application is demonstrated in a process analysis that illustrates why thermal cycles cannot achieve efficiencies close to unity.

Section IV investigates reactive systems, highlighting a general change in paradigm between thermal physics and thermochemistry. The chemical work function is defined, supplanting the classical Gibbs free energy concept. The

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¹ The SI base unit of time is defined by the transition between two hyperfine ground states of cesium-133, an exemplary microscopic energy transformation process.

² Properties of quantum systems are not addressed.

³ Macroscopic relates to classical systems with particle numbers on the order of Avogadro's number, plus or minus a few orders of magnitude.

⁴ The physical meaning of energy forms often cannot be deduced from their historical names.

dimensionless form discloses the statistical mechanism towards chemical equilibrium, introduced as the *fourth law of thermodynamics*. It is independent of the second law, which holds only for energy transformation among non-reactive systems. Spontaneous decreases in entropy are generally possible as proven by an isolated ammonia reaction. This unites the thermodynamic understanding of inanimate matter and living nature.

The influence of force fields on the entropy of real systems is discussed in [Section V](#), showing that the Helmholtz free energy concept is a model rather than a true form of energy. This completes the physical understanding of classical concepts in the Guggenheim scheme. The impact of gravity is discussed in the context of black hole formation, calling for the reassessment of some astrophysical theories. Conclusively, the relevance of thermodynamic principles to human society is outlined.

[Section VI](#) summarizes major results and draws general conclusions.

II. BASIC THERMODYNAMIC CONCEPTS

A. Properties of the ideal gas

The ideal gas in this document is a monatomic ideal gas with $f = 3$ degrees of freedom. Its internal energy U is modeled by kinetic gas theory, yielding the equipartition theorem

$$U = \frac{1}{2} f N k_B T = \frac{3}{2} N k_B T \quad (1)$$

where N is the number of atoms, k_B is the Boltzmann constant, and T is the absolute temperature. Thus, $U = f(T)$ represents the thermal energy E_T of the gas. The total energy called enthalpy⁵ H is defined as

$$H = U + pV \quad (2)$$

where p is the pressure and V is the volume. While the classical definition of pressure is force F per unit area A , pressure is clearly a bulk rather than a surface property. Dimensional analysis suggests expansion by a spatial coordinate z , signifying molecular potential energy E_p per unit volume⁶

$$p = \frac{F \cdot z}{A \cdot z} = \frac{E_p}{V} \quad (3)$$

Other forms of energy may also be related to the unit volume, yielding, for example, the Bernoulli equation, which signifies volumetric energy conservation in steady-state, incompressible, frictionless, and adiabatic fluid flow

$$\frac{E_p}{V} + \frac{E_{\text{kin}}}{V} + \frac{E_{\text{grav}}}{V} = p + \frac{\rho}{2} w^2 + \rho g h = \text{const.} \quad (4)$$

where ρ is the density, w is the bulk velocity, g is the gravitational acceleration, and h is the hydrostatic height. The enthalpy

$$H = E_T + E_p \quad (5)$$

thus represents the total energy of a static fluid at a reference altitude, excluding macroscopic forms of energy such as kinetic bulk motion E_{kin} and gravitational potential energy E_{grav} . Substituting U in [Eq. \(2\)](#) by [Eq. \(1\)](#) and (pV) by the ideal gas model⁷

$$pV = N k_B T \quad (6)$$

yields

$$H = \frac{5}{2} N k_B T \quad (7)$$

i.e., contributions by E_T and E_p are fixed to $3/2$ vs. $2/2$ in the monatomic ideal gas. All components of H relate to energy that is *freely* redistributed among interacting atoms/molecules on microscopic⁸ scale, as explained by the second law of thermodynamics⁹.

⁵ The word ‘enthalpy’ was created by Heike Kamerlingh Onnes from ancient Greek, combining ($\acute{\epsilon}\nu$, en, ‘in’) with ($\theta\acute{\alpha}\lambda\pi\omega$, thálpō, ‘to warm’). This naming confuses the physical meaning with respect to U (which is the thermal component), while H is the total energy $H = E_T + E_p$.

⁶ In textbooks such as [\[5\]](#), the term pV is related to volumetric work. This is inconsistent because enthalpy is a state property, while work is a process property. State properties are independent of any process to reach the state.

⁷ Though the ideal gas model is sometimes called ‘ideal gas law’, it is an empirical model introduced by Émile Clapeyron in 1835 [\[6\]](#).

⁸ Microscopic relates to the atomic scale of matter with classical interactions.

⁹ If this was not the case, the temperature would not change together with the pressure during compression/expansion processes, cf. [Sections II E](#).

B. Properties of entropy

In contrast to classical kinetic gas theory, microscopic states must be described by *particle-wave functions*. The quantization of energy, the Heisenberg uncertainty principle, and the de Broglie wavelength constitute the basic prerequisites for defining entropy as a physical quantity. The theory is built on the following postulates:

- (i) Over sufficiently long timescales, energy moves around randomly in quantized amounts among the particles in a system.
- (ii) In an isolated system in equilibrium, all accessible microstates are equally probable, without preferring one over the other.
- (iii) On microscopic scale, any process that takes a system from state ($x \rightarrow y$) is reversible, so that the system can go back from ($y \rightarrow x$) without dissipation¹⁰.

Since atomic timescales are on the order of 10^{-10} s for gasses at ambient pressure and 10^{-15} s for solids, respectively, postulate (iii) is a prerequisite for the stability of matter. The atomic timescales and the size of macroscopic objects with particle numbers (and quantized amounts of energy) on orders around Avogadro's number $N_A \approx 10^{23}$ imply that microscopic energy transformation is driven by very large statistics. Because some macroscopic states comprise many (orders of magnitude) more microstates than others, the random energy redistribution drives interacting objects towards equilibrium, characterized by the state with the largest number of microstates. The size of macroscopic systems produces overwhelming probabilities, which makes energy transformation among macroscopic systems inherently irreversible.

The physical quantity that comprises these principles is the entropy S . Its definition, published by Max Planck in 1913 [1, 2], is

$$S = k_B \ln \Omega \quad (8)$$

where Ω is the multiplicity introduced by Ludwig Boltzmann in 1896 [3], also called the phase space. It is constructed of a spatial space component $\Omega_{\vec{r}}$ and a momentum space component $\Omega_{\vec{p}}$ with

$$\Omega = \Omega_{\vec{r}} \cdot \Omega_{\vec{p}} \quad (9)$$

signifying the number of ways (microstates) in which a number of atoms N with energy U can be arranged in a volume V , cf. Fig. 1 for a single particle. Entropy is thus a function of extensive state properties

$$S = S(U, V, N) \quad (10)$$

representing itself as an extensive state property. The essence of entropy and the second law is contained in the *dimensionless mechanism* of $(\ln \Omega)$ as outlined above and explained by statistical mechanics [5]. Only for historical reasons, entropy has units of (JK^{-1}) gained from the Boltzmann constant k_B . The original formulation of entropy¹¹ by Rudolf Clausius dating from 1864 [4], which is used until today as a 'definition' in classical thermodynamics (see e.g. [7–10]), signifies the **special case** of

$$S = S(U)_{V,N} \quad (11)$$

This 'definition' is problematic because $V = \text{const.}$ cannot be presumed in the majority of processes, while $N = \text{const.}$ cannot be presumed in reactive systems.

The entropy of the monatomic ideal gas is given by the Sackur-Tetrode equation

$$S(U, V, N) = k_B N \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right\} \quad (12)$$

published independently by Hugo Martin Tetrode and Otto Sackur in 1912 [11], where m is the mass of an atom and h is the Planck constant.

¹⁰ Dissipation describes the release of bound forms of energy to freely distributable forms, e.g. the conversion of kinetic energy of a macroscopic object into heat by friction. Because the energy in (iii) is freely distributable already, there can be no further dissipation.

¹¹ Clausius renamed his original 'equivalence value' to 'entropy', combining the word 'energy' with the Greek word ($\tau\rho\omicron\pi\eta$, trope), signifying 'transformation'.

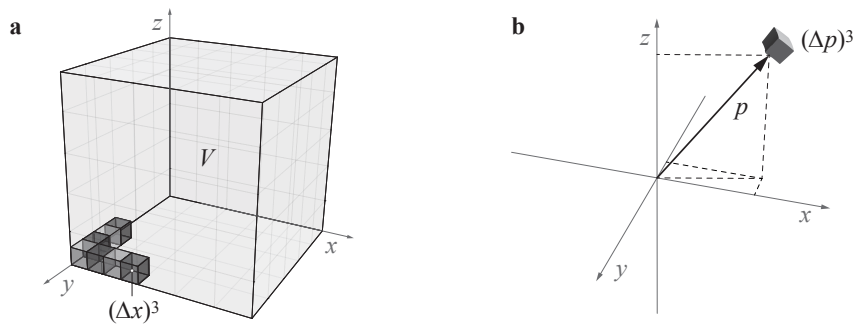


Figure 1. Illustration of a single particle with energy U in a volume V . The particle's position and momentum resolution is limited by the Heisenberg uncertainty theorem $\Delta x \cdot \Delta p \approx h$, enabling the distinction of discrete microstates, i.e., the particle's phase space. a) The particle can be found in any of the cubes Δx^3 , the number of cubes in V yields the spatial space multiplicity $\Omega_{\vec{r}}$; b) In each of the cubes Δx^3 , the momentum vector $\vec{p} = \sqrt{2mU}$ can point in a discrete number of directions $\Omega_{\vec{p}}$, obtained from the shell-like momentum space constructed by $(\vec{p} + \Delta p)$ and subdivided by Δp^3 .

C. Normalization of extensive state properties

To enable a universal description of states, extensive state properties are normalized either in units of mass or in molar units, retaining their extensive nature. While the former is applied to non-reactive systems in [Section III](#), the latter is needed to model reactive systems in [Section IV](#). Capital letters are used for absolute quantities, while lowercase letters are used for normalized quantities. The mass-specific entropy s , for example, is

$$\frac{S}{M} \left(\frac{U}{M}, \frac{V}{M}, \frac{N}{M} \right) = s(u, v, n) \quad (13)$$

where M is the unit mass, $n = N_A/\bar{M}$ is the particle number per unit mass, and \bar{M} is the molar mass. Rates of energy transformation in technical processes are obtained by scaling with the fluid's mass flow rate¹²

$$\dot{M} = M/\tau \quad (14)$$

where M is the fluid mass flowing through the system per unit time τ . In this context, $h = H/M$ signifies the mass-specific enthalpy in units of (J kg^{-1}). Because n is a fluid-specific constant, $\{u, h\}$ derived from [Eqs. \(1, 7\)](#) are only functions of temperature in the monatomic ideal gas.

D. Sign definitions

Classical thermodynamics is strongly related to the industrial revolution and the development of the steam engine. Its mechanical interpretation by Gustav Zeuner [12] and others is illustrated for a closed system in [Fig. 2a](#), where the heat $Q > 0$ yields technical work $L_t > 0$ (labor) of a power engine. This application-oriented sign declaration is still applied in parts of thermodynamic literature, cf. [9, 10]. Due to the sign inversion of energy vectors, with the heat-related unit vector on the inner surface and the work-related vector on the outer surface, thermodynamic changes in the system relate to thermodynamic changes in the surroundings.

Instead of a mechanical perspective, thermodynamic systems primarily deal with material and/or energy transformation. A system-oriented sign declaration is depicted in [Fig. 2b](#), where the unit vector of energy flow \vec{e} points into the system, irrespective the form of energy. Hence, the expansion work of a power engine has a negative sign, extracting energy from the system. This sign declaration is adopted in the other part of thermodynamic literature, cf. [7, 8], enabling an independent system description. Only the ambient temperature T_{amb} is needed as a boundary condition, which is considered constant due to the large size of the reservoir.

Following the first law of thermodynamics, energy is conserved. Energy can neither be created nor destroyed; it can only be transformed from one form to another. The first law is the basis of energy balances used to model arbitrary

¹² Mass flow rates can be measured more easily than molar flow rates, e.g. by the Coriolis force.

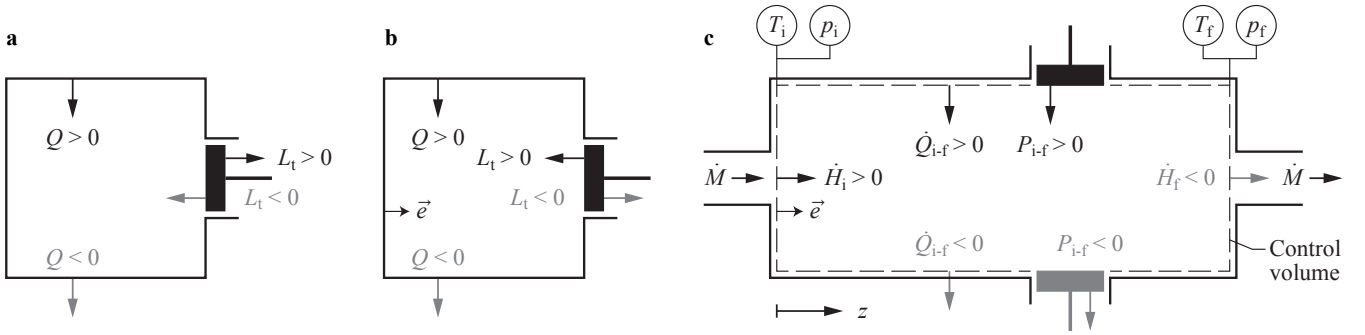


Figure 2. a) Sign declaration following a mechanical interpretation of technical work, cf. [9, 10, 12]. b) Sign declaration with a unit vector of energy flux \vec{e} pointing into the system for all forms of energy, cf. [7, 8]. c) Sign declaration based on \vec{e} in an open thermodynamic process, following the process coordinate z . Initial states ‘i’ have a positive sign and final states ‘f’ have a negative sign. Process properties ‘i-f’ can have positive and negative signs, respectively, depending on whether they increase or decrease the control volume’s energy.

control volumes¹³. Because individual energy conversions are not tracked *within* a control volume, all forms of energy flow must have the same unit vector \vec{e} in compliance with Figs. 2b and 2c.

The convertible energy flow rate associated with inlet and outlet mass flow rates \dot{M} is the enthalpy flow rate \dot{H} . Following the process coordinate z in Fig. 2c, inlet states into a control volume are referred to as *initial states* (index ‘i’), and outlet states are referred to as *final states* (index ‘f’). Process properties of heat flow rates \dot{Q} and power $P = \dot{L}_t$ are indicated by the index ‘i-f’. Following the unit vector \vec{e} , a heat flow rate $\dot{Q}_{i-f} > 0$ corresponds to heat input to the control volume, while $\dot{Q}_{i-f} < 0$ corresponds to heat rejection. Equivalently, power $P_{i-f} > 0$ signifies energy increase in the control volume by compression power, while $P_{i-f} < 0$ indicates energy decrease by expansion power. Processes may be formulated sequentially along the process coordinate z , a concept applied to reactive systems in Section IV.

E. Thermodynamic reference processes

In addition to normalized state properties and the sign declaration, the following two reference processes are needed to deduce the technical work function. The first process is the *isothermal* compression ($T = \text{const.}$) illustrated in Fig. 3, where L_t indicates the technical work exerted on a piston, and Q is the heat flowing through a cylinder surface A . In order to retain $\{T, U, H\} = \text{const.}$, any added work $+dL_t$ is released simultaneously in the form of heat $-dQ$. Following Fig. 3a, the transfer of heat is sometimes regarded ‘reversible’ in the idealized case, where the cylinder surface A is infinitely large. As a consequence, the temperature difference ΔT would approach zero. However, if $A \rightarrow \infty$, it follows that $\{V, L_t, Q\} \rightarrow \infty$ for any third dimension in space. With a finite heat transfer coefficient k , the heat transport equation resolved for ΔT is

$$\dot{Q} = \frac{Q}{\tau} = k A \Delta T \quad \rightarrow \quad \Delta T = \frac{1}{\tau k} \frac{Q}{A} \quad (15)$$

yielding ∞/∞ , which is mathematically undefined. It is therefore imperative to consider systems of finite size. If $A = \text{finite}$, it follows that $\{V, L_t, Q\} = \text{finite}$ as depicted in Fig. 3b. The only option for $\Delta T \rightarrow 0$ is $\tau \rightarrow \infty$ following Eq. (15). Consequently, the isothermal compression is an idealization known as *quasi-static*. Expansion is equivalent to compression, running in the opposite process direction.

The second *isentropic* reference process is an equivalent idealization with an adiabatic boundary condition, i.e., $Q = 0$. Given $s = \text{const.}$, the spatial space multiplicity $\Omega_{\vec{r}}$ is converted by compression work to momentum space multiplicity $\Omega_{\vec{p}}$, and vice versa during expansion, involving only energy transformations in the bulk fluid on microscopic scale.

In either reference process, $\tau \rightarrow \infty$ removes gradients for energy transfer over macroscopic system boundaries, yielding zero power density (i.e., zero energy fluxes¹⁴ \dot{Q}/A and P/A) regarding the heat flow rate \dot{Q} in the isothermal

¹³ Control volumes are not limited to physical volumes V . Investigations range from individual items to large and complex systems that comprise a multitude of energy transformation processes.

¹⁴ While a flow rate, sometimes called ‘total flux’, indicates the total amount of mass, particles, and energy entering or leaving the control volume per unit time, a flux or ‘flux density’ is a flow rate normalized per unit area.

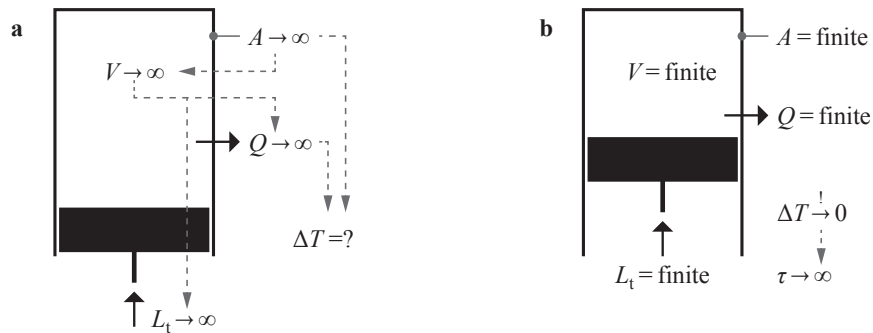


Figure 3. Illustrations of the isothermal piston compression process. a) Consideration of infinite size; b) Consideration of finite size

case

$$\dot{Q} = \frac{Q}{\tau} \rightarrow 0 \quad (16)$$

and regarding the mechanical compression/expansion power P in either case

$$P = \dot{L}_t = \frac{L_t}{\tau} \rightarrow 0 \quad (17)$$

which transforms these processes into states of equilibrium. It may be disputed whether an infinite series of equilibrium states constitutes a process, i.e., a change of states, and whether such a process is reversible. The answer is indeed irrelevant, as illustrated in Section III A by combining an *isentropic* compression with an *isothermal* compression, followed by an *isentropic* expansion and an *isothermal* expansion to create a Carnot cooling cycle.

III. THERMAL PHYSICS AND THE SECOND LAW

A. Ideal gas Carnot cooling cycle

An exemplary ideal gas Carnot cooling cycle is shown in Fig. 4, which is commonly called ‘left-handed’ due to the orientation in the T, s -diagram. Because Carnot cycles are considered reversible in classical thermodynamics, the aim is to recover all the technical work in continuous steady-state operation.

First, the isentropic compression ($1 \rightarrow 2$) and the isentropic expansion ($3 \rightarrow 4$) are examined. By the adiabatic boundary condition, all the compression work $l_{t,1-2} > 0$ added to the process increases the enthalpy $h_2 = h_1 + l_{t,1-2}$. Equivalently, the expansion work $l_{t,3-4} < 0$ reduces the enthalpy $h_4 = h_3 + l_{t,3-4}$. Because h is a function of temperature only

$$h = \frac{5}{2} n k_B T = f(T) \quad \rightarrow \quad \begin{pmatrix} h_3 = h_2 \\ h_4 = h_1 \end{pmatrix} \quad \rightarrow \quad l_{t,3-4} + l_{t,1-2} = 0 \quad (18)$$

i.e., the isentropic expansion work $l_{t,3-4} = l_{R,s}^-$ is fully recovered, index ‘R’, and used for the complete isentropic compression $l_{R,s}^+ = l_{t,1-2}$.

Next, the isothermal expansion ($4 \rightarrow 1$) is considered, where the mass-specific heat q_R^+ is absorbed at the constant cooling temperature T_c . At $\{u, h\} = \text{const.}$, all the energy added by q_R^+ is released in form of expansion work

$$l_{R,T}^- = l_{t,4-1} = -n k_B \ln \left(\frac{v_1}{v_4} \right) T_c < 0 \quad (19)$$

Because of $u = \text{const.}$, the multiplicity $\Omega_{\vec{p}}$ in momentum space is constant as well. The increase in entropy $(s_1 - s_4) > 0$ is caused by the increasing spatial space multiplicity $\Omega_{\vec{r}}$, i.e., by expansion¹⁵.

¹⁵ Eq. 11 cannot explain $s_1 > s_4$ given $u_1 = u_4$. The classical argument, whereby entropy would ‘flow’ with heat over the system boundary, is unphysical because entropy is a state property of the fluid and can only flow *with* the fluid. The argument is also inconsistent with adiabatic expansion (throttling), which implies entropy increase without heat flow. The classical argument in this case, stating that entropy would increase by ‘internal friction’, is in conflict with postulate (iii), cf. also the example of ‘free expansion’ in [5].

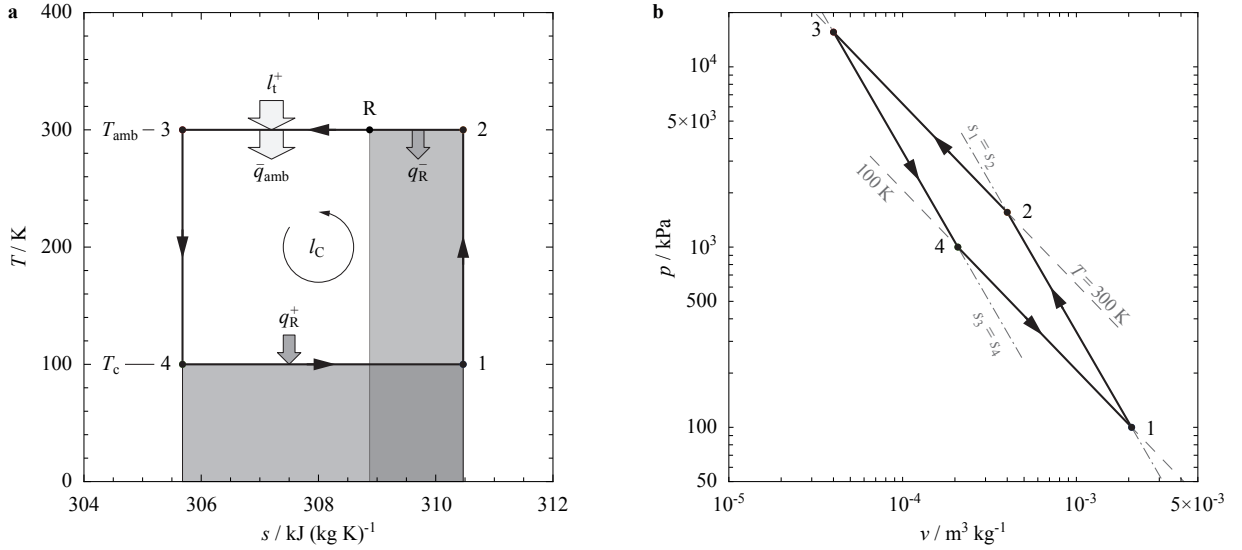


Figure 4. Exemplary Carnot cooling cycle in the T, s - and the p, v -diagram. State properties are calculated for the ideal gas, using the mass m of helium atoms in Eq. (12). Ambient and cooling temperatures are $T_{\text{amb}} = 300 \text{ K}$ and $T_c = 100 \text{ K}$, respectively, the minimum pressure is $p_1 = 100 \text{ kPa}$ and the isothermal pressure ratio is $p_3/p_2 = 10$. While the heat transformation is depicted in the T, s -diagram by the gray areas, the compression/expansion work could be shown in the p, v -diagram. For clarity, however, the four technical work areas $l_{t,i-f} = \int_i^f v dp$ are not indicated.

Finally, the isothermal compression ($2 \rightarrow 3$) is discussed. All the expansion work $l_{R,T}^-$ is first recovered to start the compression ($2 \rightarrow R$) with $l_{R,T}^+ = l_{t,2-R}$. To retain the isothermal condition $T_{2-R} = \text{const.}$, the heat q_R^- is released at the ambient temperature T_{amb} . Reaching thus the recovery point (R), all forms of expansion work l_R and heat q_R have been fully recovered, fulfilling the first law. Since these processes may be converted back and forth without loss in each loop of the continuous cycle, the remaining discussion reduces to the isothermal compression ($R \rightarrow 3$).

Due to the second law, the isothermal compression ($2 \rightarrow R$) decreases the entropy only by

$$s_R - s_2 = -\frac{T_c}{T_{\text{amb}}}(s_1 - s_4) \quad (20)$$

The sum of entropy changes up to the recovery point (R) therefore yields

$$\Delta s_{\text{irr}} = (s_1 - s_4) + (s_R - s_2) > 0 \quad (21)$$

To complete the cycle, further isothermal compression work $l_{t,R-3} > 0$ is needed to reduce the spatial space multiplicity from $\Omega_{\bar{r},R}$ to $\Omega_{\bar{r},3}$, and hence the entropy from s_R to s_3 . The additional energy input $l_t^+ = l_{t,R-3}$ is accompanied with simultaneous heat release q_{amb}^- to the surroundings, both to retain $\{T, u, h\} = \text{const.}$, and to fulfill the first law once again. As a consequence, the need for energy conservation (first law) and the energy transformation from T_c to T_{amb} (second law) cause the need for isothermal compression work in the Carnot cooling cycle

$$l_C = l_{t,R-3} = T_{\text{amb}} \Delta s_{\text{irr}} \quad (22)$$

In classical thermodynamics, the Carnot cycle is considered reversible, assuming that the work l_C^+ can be fully recovered when operating a ‘right-handed’ power cycle between the surroundings at T_{amb} and the cold object at T_c , which was previously created by the cooling cycle, to generate the work l_C^- . To understand the contradiction, a closer look on absolute energy scales is necessary. The quasi-static nature of the sub-processes in the cycle imply a mass flow rate of

$$\dot{M}_C = \lim_{\tau \rightarrow \infty} \frac{M \in \mathbb{R}^+}{\tau} = 0 \text{ kg s}^{-1} \quad (23)$$

All energy flow rates are therefore zero

$$P_C = \dot{M}_C l_C = 0 \text{ W} \quad ; \quad \dot{Q}_c = \dot{M}_C q_c = 0 \text{ W} \quad ; \quad \dot{Q}_{a,\text{tot}} = \dot{M}_C q_{a,\text{tot}} = 0 \text{ W} \quad (24)$$

i.e., the question of reversibility becomes obsolete. It also follows that $T_c < T_{\text{amb}}$ of any finite-sized object cannot be achieved. The normalized Carnot cycle is therefore commonly considered at *finite* power densities, i.e., at mass flow rates $\dot{M}_{\text{finite}} > 0$. This has the following consequences:

1. The creation of $T_c < T_{\text{amb}}$ is enabled, acting against the second law.
2. While *global* macroscopic gradients $T_c < T_{\text{amb}}$ are considered with respect to the application, consequential *local* macroscopic gradients for energy transformation in the individual compression and expansion processes are disregarded.
3. Hence, the Carnot cycle is an ambivalent model, to be interpreted at \dot{M}_{finite} as a tool for describing the minimum work l_{min} , or more precisely the minimum power $P_{\text{min}} = \dot{M}_{\text{finite}} l_C$, required to establish the global macroscopic gradients.

The inconsistency in the classical understanding is, that reversibility of the Carnot cycle is assumed with a list of conditions, which is then generalized *beyond* these conditions, where the system *is* irreversible. From a statistical mechanics' point of view, all macroscopic systems are irreversible due to macroscopic gradients, which cause the spontaneous and irreversible flow of energy against the gradient. Microscopic systems, on the other hand, are reversible in the absence of macroscopic gradients, following postulate (iii).

Looking at a real-world application in air-conditioning, for example, the temperature of a confined volume is temporarily reduced by a cooling system or increased by a heat pump, respectively, both adopting the same left-handed cycle¹⁶. The work of the Carnot cycle is a fraction of the total technical work, i.e., the minimum work. Once the cycles are switched off, the volume approaches T_{amb} spontaneously, i.e., all the work used to create and maintain $T \neq T_{\text{amb}}$ is lost in form of ambient heat. None of this work can ever be recovered once T_{amb} is reached.

B. Physical expression of the work function

For a cooling temperature $T_c = \text{const.}$, the Carnot cooling cycle yields the minimum work

$$l_C = l_{\text{min}} \quad (25)$$

since local macroscopic gradients $\{\Delta T, \Delta p\}$ for energy transport over macroscopic system boundaries (heat, work) and local macroscopic gradients Δp for convective mass transport (fluid flow) inside the system are not included. By the second law, these gradients create additional entropy $\Delta s_{\text{irr},i-f} > 0$ in all sections of a system. The entropy increase caused by these gradients is related to $s = s(u, v, n)$ in the following ways:

- Regarding $ds_{\text{irr}}(du)_{v,n}$, the irreversibility of heat transfer from T_h (hot) to T_c (cold) is given by

$$ds_{\text{irr},u} = \frac{T_h - T_c}{T_h T_c} dq = \frac{\Delta T}{\bar{T}^2} dq > 0 \quad (26)$$

scaling with $\Delta T = T_h - T_c$ and the inverse square of the absolute geometric mean temperature $\bar{T} = \sqrt{T_h T_c}$ ¹⁷.

- Regarding $ds_{\text{irr}}(dv)_{u,n}$ representing adiabatic expansion (fluid flow, throttling), the fundamental equation and the definition of enthalpy yield

$$ds_{\text{irr},v} = -\frac{v(T,p)}{T} dp > 0 \quad (27)$$

scaling with the specific volume and the inverse absolute temperature.

- Regarding $ds_{\text{irr}}(dn)_{u,v}$, the entropy of mixing

$$ds_{\text{irr},n} = -n k_B \sum x_j \ln x_j > 0 \quad (28)$$

applies to fluid mixtures, where x_j is the concentration of species j .

¹⁶ While the warm heat exchanger rejects heat $q_{\text{amb}} < 0$ in a cooling system, the cold heat exchanger absorbs ambient heat $q_{\text{amb}} > 0$ in a heat pump.

¹⁷ In fact, the 'thermal dimension' of the Carnot cycle in Fig. 4a up to point 'R' can be abstracted as a counter-flow heat exchanger, where q_R is released at T_h and absorbed at T_c . With these temperatures and the specific heat q_R , Eq. (26) yields the same result as Eq. (21), underlining the irreversibility of the cycle.

Because entropy cannot decrease spontaneously in non-reactive systems, the sum of $\Delta s_{\text{irr},i-f}$ from all sections must be depleted by heat rejection at T_{amb} and compensated by work

$$\sum l_{i-f} = T_{\text{amb}} \sum \Delta s_{\text{irr},i-f} \quad (29)$$

showing that l_{min} and $\sum l_{i-f}$ are equivalent following Eqs. (22, 25, 29). The total technical work of real left-handed cycles is thus caused by the same physical mechanism

$$l_t = T_{\text{amb}} \sum \Delta s_{\text{irr}} \quad (30)$$

Equation (30) discloses that the need of work is created in all sections of a left-handed cycle, independently of where the technical work is provided. Therefore, an expression for $\Delta s_{\text{irr},i-f}$ is sought to formulate work functions l_{i-f} , which uncover this need to enable continuous steady-state operation. The derivation of l_{i-f} implies the application of the first law and the second law, considering the unit vector \vec{e} in all forms of energy flow as defined in Section IID and depicted in Fig. 5. The derivation starts from the adiabatic flow process shown in Fig. 5a. By the second law, the entropy balance with $\Delta s_{\text{irr},i-f} > 0$ is

$$s_i + \Delta s_{\text{irr},i-f} - s_f = 0 \quad (31)$$

yielding with Eq. (29) while preserving the sign convention for s_i and s_f

$$l_{i-f,\text{ad}} = -T_{\text{amb}} (s_i - s_f) \quad (32)$$

The next step is the diabatic flow process depicted in Fig. 5b. The mass-specific heat flow q_{i-f} can be positive or negative, changing the entropy balance due to $s(u)$ by $\Delta s_{u,i-f}$ to

$$\Delta s_{\text{irr},i-f} = -(s_i - s_f) - \Delta s_{u,i-f} \quad (33)$$

Because $\Delta s_{u,i-f} = f(T_{i-f})$, Eq. (33) must not be multiplied by T_{amb} to obtain the work function. Rather, q_{i-f} is subtracted directly from Eq. (32)

$$l_{i-f,q} = -T_{\text{amb}} (s_i - s_f) - q_{i-f} \quad (34)$$

and substituted by the energy balance (first law)

$$h_i + q_{i-f} - h_f = 0 \quad (35)$$

yielding

$$l_{i-f,q} = (h_i - h_f) - T_{\text{amb}} (s_i - s_f) \quad (36)$$

Apart from the opposite sign, Eq. (36) is known from different concepts in classical thermodynamics, such as ‘minimum liquefaction work’ and ‘exergy’ [7–10]

$$\Delta e = \Delta h - T_{\text{amb}} \Delta s = (h_f - h_i) - T_{\text{amb}} (s_f - s_i) \quad (37)$$

the latter being meaningful only in power cycles¹⁸. Because a flux or a flow rate is proportional to the negative gradient of a property in accordance with Fourier’s and Fick’s laws, corresponding to $-\Delta$, the work function of Eq. (36) signifies an *energy vector* pointing in the process direction

$$\vec{l}_{i-f,q} = \vec{h}_{i-f} - T_{\text{amb}} \vec{s}_{i-f} \quad (38)$$

Whichever classical concept signifies a **special case**, Eq. (36) is incomplete because technical work $l_{t,i-f}$ can be exerted on the control volume beside q_{i-f} as illustrated in Fig. 5c. This case is presented in the isothermal compression/expansion processes in Section III A, for instance. Considering first $l_{t,i-f}$ separately from q_{i-f} , quasi-static adiabatic compression/expansion $l_{\text{is},i-f}$ is isentropic. Finite power densities generally imply $l_{t,i-f} - l_{\text{is},i-f} > 0$ to overcome quasi-static equilibria. The energy difference contributes either to $\Delta s_{\text{irr},i-f}$, or to q_{i-f} in the diabatic case. Substituting finally q_{i-f} in Eq. (34) with the energy balance of Fig. 5c

$$h_i + q_{i-f} + l_{t,i-f} - h_f = 0 \quad (39)$$

yields the **work function**

$$\boxed{\vec{l}_{i-f} = \vec{h}_{i-f} + \vec{l}_{t,i-f} - T_{\text{amb}} \vec{s}_{i-f}} \quad (40)$$

The sum of work functions, i.e., the closed integral of work energy vectors, equals the total technical work of thermodynamic cycles as explained in Sections III C and III D.

¹⁸ The concept originates from Josiah Willard Gibbs [13], who introduced the notation of ‘available energy of the body’ in 1873. It was later renamed ‘exergy’ following a proposal by Zoran Rant [14].

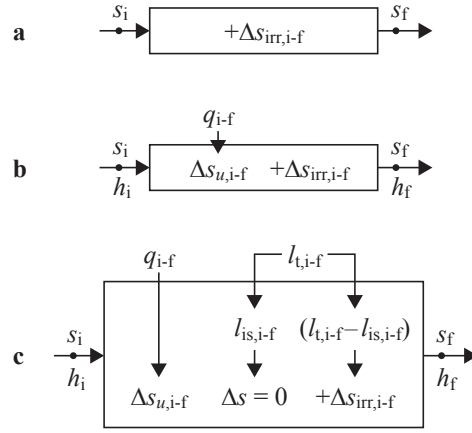


Figure 5. Derivation of the work function l_{i-f} of a process section with initial states (i) and final states (f) as defined in Section II D. a) Adiabatic flow process; b) Diabatic flow process; c) Diabatic flow process with technical work.

C. Validation of the work function

The derivation of Eq. (40) is straightforward because the entropy changes Δs_{irr} in the Carnot cooling cycle and $\Delta s_{\text{irr},i-f}$ in real processes with finite power density have the same positive signs. This is not the case in right-handed power cycles due to the opposite orientation in the T, s -diagram. Though Eq. (30) is not evident in this case, the first law and the second law must apply equivalently. The work function defined by Eq. (40) is therefore validated for the Carnot power cycle shown in Fig. 6a.

As already explained by Eq. (18), the isentropic compression/expansion processes cancel each other out

$$\vec{l}_{t,\text{II-III}} + \vec{l}_{t,\text{IV-I}} = 0 \quad (41)$$

Adding the two remaining isothermal processes and considering

$$(h_{\text{I}} - h_{\text{II}}) = 0 \quad ; \quad (h_{\text{III}} - h_{\text{IV}}) = 0 \quad (42)$$

$$(s_{\text{I}} - s_{\text{II}}) + (s_{\text{III}} - s_{\text{IV}}) = 0 \quad (43)$$

the sum of the isothermal work functions is reduced from

$$\vec{l}_{\text{C}} = \vec{l}_{\text{I-II}} + \vec{l}_{\text{III-IV}} \quad (44)$$

following Eq. (40) to their technical work contributions $\vec{l}_{t,i-f}$

$$\vec{l}_{\text{C}} = \vec{l}_{t,\text{I-II}} + \vec{l}_{t,\text{III-IV}} \quad (45)$$

Then, the expression for isothermal compression/expansion work

$$\vec{l}_{t,i-f}(T) = -n k_{\text{B}} \underbrace{\ln \frac{v_{\text{f}}}{v_{\text{i}}}}_{(s_{\text{f}} - s_{\text{i}})} T \quad (46)$$

together with Eq. (43) leads to

$$\vec{l}_{\text{C}} = -n k_{\text{B}} \left(T_{\text{amb}} \ln \frac{v_{\text{II}}}{v_{\text{I}}} + T_{\text{h}} \ln \frac{v_{\text{IV}}}{v_{\text{III}}} \right) \quad (47)$$

$$= \underline{(s_{\text{II}} - s_{\text{I}})(T_{\text{h}} - T_{\text{amb}})} < 0 \quad (48)$$

i.e., the enclosed surface in the T, s -diagram in Fig. 6a with a negative sign, as expected. The result proves two important points:

- (i) the generality of the work function, holding also for systems with mixed-sign entropy changes, and

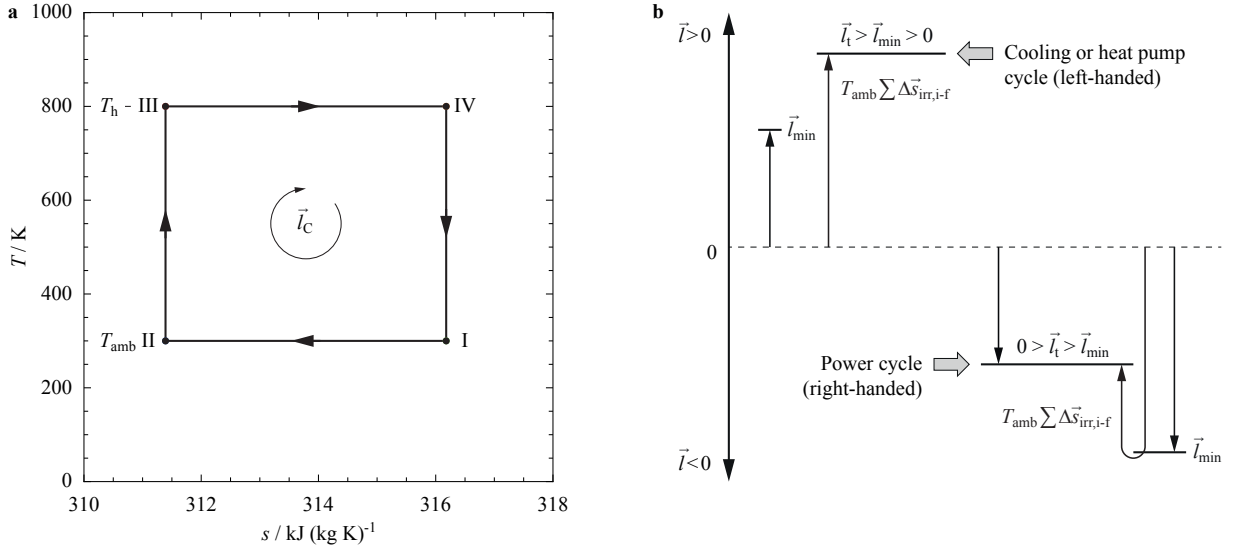


Figure 6. a) Carnot power cycle equivalent to Fig. 4, operating between $T_{\text{amb}} = 300$ K and the heating temperature $T_h = 800$ K with a minimum pressure $p_I = 100$ kPa and an isothermal pressure ratio $p_{II}/p_I = 10$. b) Minimum work \vec{l}_{min} and technical work \vec{l}_t of left-handed cooling and heat pump cycles vs. right-handed power cycles following the sign definitions of Section IID.

(ii) the necessity of the parameter $\vec{l}_{t,i-f}$ introduced in Eq. (40) in processes with technical work.

Differences between the minimum work \vec{l}_{min} and the technical work \vec{l}_t in real cycles are illustrated in Fig. 6b, showing that finite power densities increase the work ($\vec{l}_t > \vec{l}_{\text{min}}$) of *any* macroscopic cycle. Left-handed cooling and heat pump cycles need technical work ($\vec{l}_t > 0$) to create and maintain non-equilibrium conditions with regard to the surroundings, while right-handed power cycles exploit non-equilibria to extract technical work ($\vec{l}_t < 0$) from the thermodynamic system to use this energy elsewhere.

D. Application to non-reactive cycles

Example 1. The application of the work function to non-reactive systems is demonstrated for the air liquefaction cycle shown in Fig. 7a. The following key application rules apply:

- i) The work function Eq. (40) can be applied to individual flow sections or to grouped process areas with several inlet and outlet streams¹⁹.
- ii) In cases of dissimilar mass flow rates, the work functions are scaled with either the relative mass flow rates²⁰

$$m_{i-f} = \dot{M}_{i-f} / \dot{M}_{\text{ref}} \quad (49)$$

regarding a chosen reference to obtain the mass-specific work in (J kg^{-1}), or with the absolute mass flow rates \dot{M}_{i-f} to obtain the power in (W).

- iii) To ensure a closed energy balance, i.e., a closed integral over all work energy vectors, open process streams are notionally closed, as indicated by the dotted lines in Fig. 7a for both the liquid air stream²¹ and the exhaust stream.
- iv) All process sections with sources of entropy change must be included²².

¹⁹ Grouping is useful to analyze the influence of process components, such as the counter-flow heat exchangers (CFHX) indicated in Fig. 7a.

²⁰ In the example of Fig. 7a, 80% of the total flow rate is used for pre-cooling the 20% cold stream m_{cold} , which is partially liquefied by throttling into the phase separator. Vapor fractions are indicated by x_9 with regard to m_{cold} , and by x with regard to the total mass flow rate, respectively.

²¹ The work $(1-x)\vec{l}_{11-1}$ in Fig. 7a represents the minimum liquefaction work $\vec{l}_{\text{min,liq}}$, i.e., the minimum work of an idealized cycle to liquefy ambient air from $\{T_{\text{amb}}, p_{\text{amb}}\}$ to state {11} when all local macroscopic gradients are neglected.

²² While the flow separation {6-7-13} has no influence, the mixing point {12-14-15} in Fig. 7a must be included. In the case of air, the entropy of mixing is nonzero because of the concentration change caused by the phase separation. An additional effect is associated with $T_{12} \neq T_{14} \neq T_{15}$, signifying a direct-contact heat exchanger, which is also relevant in pure fluids.

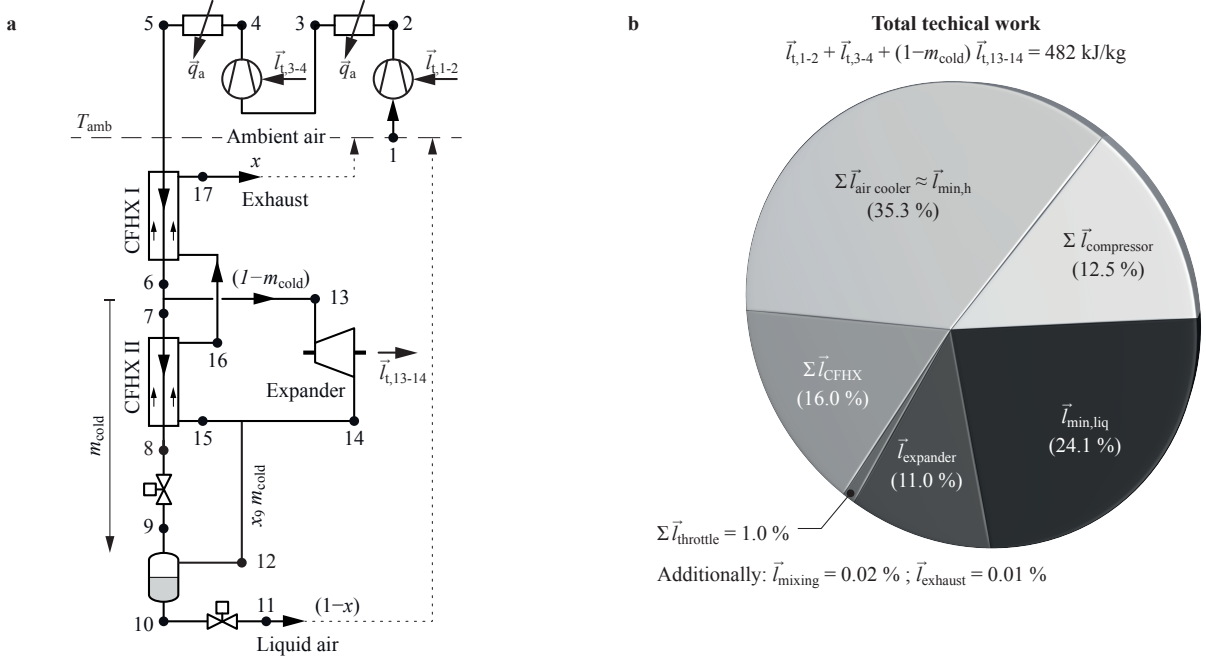


Figure 7. a) Open Claude air liquefaction cycle, using the fluid properties of pseudo-pure air from CoolProp [15]. Ambient conditions are $T_{\text{amb}} = 300 \text{ K}$ and $p_{\text{amb}} = p_1 = 100 \text{ kPa}$, compressed to $p_2 = 700 \text{ kPa}$ and $p_4 = 4000 \text{ kPa}$, given $\Delta p_{i-f} = -50 \text{ kPa}$ pressure drop in each flow section, $\eta_{\text{is}} = 0.8$ of both compressors and expander, $\Delta T_{\text{min,ac}} = 10 \text{ K}$ in the air coolers and $\Delta T_{\text{min,CFHX}} = 3 \text{ K}$ in the counter-flow heat exchangers, and a cold stream fraction $m_{\text{cold}} = 0.2$. b) Work functions grouped by components yielding the total technical work represented by the surface of the pie chart (0.1 % rest due to rounding).

The correct implementation of these rules yields *exact* agreement between the total technical work applied in the two compressors and gained in the expander

$$\vec{l}_{t,\text{tot}} = \vec{l}_{t,1-2} + \vec{l}_{t,3-4} + (1 - m_{\text{cold}}) \vec{l}_{t,13-14} \quad (50)$$

and the sum of the work functions

$$\vec{l}_{t,\text{tot}} \stackrel{!}{=} \sum m_{i-f} \vec{l}_{i-f} \quad (51)$$

providing a coherent tool to validate the process analysis. Because work functions signify an energy vector pointing in the process direction, the following sign rules apply:

- a positive vector $\vec{l}_{i-f} > 0$ indicates a spontaneous process;
- a negative vector $\vec{l}_{i-f} < 0$ indicates a non-spontaneous process;
- $\vec{l}_{i-f} = 0$ corresponds to equilibrium.

For example, the work function of the second air cooler is $\vec{l}_{4-5} > 0$, i.e., the specific heat $\vec{q}_{4-5} < 0$ can be rejected to the surroundings spontaneously, irrespective of other processes in the cycle. The same applies to the evaporation of liquid air $\vec{l}_{11-1} > 0$, which can spontaneously absorb heat $\vec{q}_{11-1} > 0$ from the surroundings. On the other hand, the cool-down of the high-pressure stream in the first counter-flow heat exchanger cannot happen independently due to $\vec{l}_{5-6} < 0$. The process of heat transfer is facilitated only in combination with the low-pressure stream yielding $\vec{l}_{5-6} + x \vec{l}_{16-17} > 0$. Further, ambient air cannot compress itself spontaneously because $(\vec{h}_{1-2} - T_{\text{amb}} \vec{s}_{1-2}) < 0$. Only the inclusion of the technical work $\vec{l}_{t,1-2}$ facilitates the process yielding $\vec{l}_{1-2} > 0$ following Eq. (40).

The results of the exemplary process analysis are depicted in Fig. 7b, where the surface of the pie chart represents the total technical work $\vec{l}_{t,\text{tot}}$ following Eq. (50). Although the compressors provide all the work (or rather the power $P = \dot{M} l_t$), they are only ‘responsible’ for 12.5% caused by their isentropic efficiency $\eta_{\text{is}} = 0.8$. Apart from the effect of expansion due to pressure losses, the air cooler contribution represents mainly the minimum work $l_{\text{min,h}}$ for heat

rejection at $T_h > T_{\text{amb}}$, since the air-side flow is not considered. It is the largest fraction due to significant temperature differences with the surroundings. Equivalently, the counter-flow heat exchangers (CFHX) have a perceptible impact due to the temperature differences required for heat transfer and operation at low temperatures, cf. Eq. (26). The impact of throttling follows Eq. (27) and is small, partly because of the small flow rate compared to the expander, which causes 11 % of the total technical work owing to $\eta_{\text{is}} = 0.8$. The minimum liquefaction work is 24.1 %, i.e., the thermodynamic process efficiency is

$$\eta_{\text{th}} = \frac{\vec{l}_{\text{min,liq}}}{\vec{l}_t} = 24.1 \% \quad (52)$$

Equation (52) is the general form of the so-called Carnot efficiency

$$\frac{\eta}{\eta_{\text{C}}} = \frac{\frac{\vec{q}_c}{\vec{l}_t}}{\frac{\vec{q}_c}{\vec{l}_c}} = \frac{\vec{l}_{\text{min}}}{\vec{l}_t} = \left(\frac{T_{\text{amb}} - T_c}{T_c} \right) \frac{\vec{q}_c}{\vec{l}_t} \quad (53)$$

that signifies a **special case** for providing a cooling capacity \vec{q}_c at a constant cooling temperature T_c ²³. In general, the efficiency of any technical system may be improved by a larger technical effort that reduces local macroscopic gradients. To fulfill any purpose, however, reasonable power densities are needed, which implies that thermodynamic cycles cannot reach efficiencies η_{th} close to unity. Considering time as the base unit of energy transformation, energy flow rates and power densities are usually more important than the absolute values of energy.

Before concluding the introduction of the work function, its sign rule **b)** requires a discussion in the context of right-handed power cycles, where the sum of work functions is negative (cf. Sections III C). This result indicates that the power cycle cannot occur *without* an energy source, i.e., a process that creates and maintains $T_h > T_{\text{amb}}$. Typically, the energy may be provided by the combustion of a fuel. In combination with the corresponding *chemical work function*, the integral of work energy vectors (or better power vectors) will be positive for the energy conversion to take place.

IV. THERMOCHEMISTRY AND THE FOURTH LAW

A. Change in paradigm

The transition from thermal physics to thermochemistry implies a crucial change in paradigm:

- I) In non-reactive classical systems, the energy locked in chemical bonds is not part of the distributable energy H . The second law describes the redistribution of thermal energy dU , molecular potential energy $p dV$ and particles dN among *weakly coupled macroscopic systems*, yielding equilibria at $\max(S_{\text{total}})$ with tremendous probabilities, cf. [5] for the derivation.
- II) In reactive systems, the energy of chemical bonds is modeled as part of H because it is redistributed among the particles during the chemical conversion. The system is characterized by a *strong coupling of microscopic energy transformation inside a macroscopic system*. The mechanism of chemical conversions differs from the second law. It is introduced as the **fourth law of thermodynamics**.

B. Classical equilibrium concept

The classical concept to model thermodynamic equilibria is the ‘Gibbs free energy’

$$G = H - T S \quad (54)$$

(also called ‘free enthalpy’) introduced by Josiah Willard Gibbs in 1875 [16] as a mathematical concept. Because all the energy in H is already *freely* redistributed, as explained by statistical mechanics [5] and Footnote 9, the question remains what kind of energy G may be related to.

²³ The example process operates at $T_c \neq \text{const.}$, with 43 % of q_c relating to sensible cooling between T_{amb} and the dew point, followed by -2.8 K temperature glide during liquefaction at $p_{\text{amb}} = \text{const.}$ due to air being a zeotropic mixture.

From first principles, absolute values of H and S can only be determined for idealized systems, for instance, the ideal gas and the Einstein solid²⁴. This applies also to the third law of thermodynamics, attributed to Walther Nernst [17], which requires $\{S, C_v\} \rightarrow 0$ at $T \rightarrow 0$, where C_v is the heat capacity at constant volume²⁵. Therefore, only *changes* are modeled by equations of state of real substances with respect to arbitrary reference states. Common fluid libraries [15, 18] provide the following options:

- NBP: $h = 0 \text{ kJ kg}^{-1}$, $s = 0 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for saturated liquid at the normal boiling point,
- ASHRAE: $h = 0 \text{ kJ kg}^{-1}$, $s = 0 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for saturated liquid at -40°C ,
- IIR: $h = 200 \text{ kJ kg}^{-1}$, $s = 1 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for saturated liquid at 0°C .

The definition of individual user values is also possible.

Because the references of H and S are both arbitrary and independent, the combination of H and S cannot constitute a coherent form of energy with respect to H ! The problem only disappears when applying Eq. (54) to changes of states, i.e., a *process*

$$\Delta G = \Delta H - T \Delta S \quad (55)$$

which eliminates the arbitrary references. G must hence be understood as a *model* that combines physical quantities, i.e., the distributable energy H and the phase space S , in which H is being redistributed. For the same reason, *any* concept that includes the absolute values of U or H in combination with S must be considered a model, which also applies to the ‘Helmholtz free energy’

$$F = U - T S \quad (56)$$

introduced by Gibbs together with H and G in [16], cf. Section (V A).

A chemical reaction is a process of energy transformation. Normalization of extensive state properties is needed in terms of molar rather than mass units, indicated by lowercase symbols with an overbar

$$\Delta \bar{g} = \Delta \bar{h} - T \Delta \bar{s} \quad (57)$$

Eq. (57) is used to calculate the molar chemical conversion energy $\Delta_f \bar{g}_j^\ominus$ of reacting species j , called the ‘free enthalpy of formation’

$$\Delta_f \bar{g}_j^\ominus = \Delta_f \bar{h}_j^\ominus - T \Delta_f \bar{s}_j^\ominus \quad (58)$$

using chemical reference data of $\{\Delta_f \bar{h}_j^\ominus, \Delta_f \bar{s}_j^\ominus\}$ tabulated for IUPAC²⁶ standard states $\{T^\ominus = 25^\circ \text{C}; p^\ominus = 0.1 \text{ MPa}\}$ and referring to 1 mol of each species²⁷. Because the mole numbers \bar{N}_j of reactants and products may differ and change during chemical reactions, the molar quantities are scaled with the stoichiometric coefficients ν_j provided by the reaction equation as a result of the conservation of the chemical elements

$$\frac{\Delta_f \bar{g}_j^\ominus}{1} = \frac{\Delta_r \bar{G}_j^\ominus}{\nu_j} \quad (59)$$

The capital symbol and the index ‘r’ identify $\Delta_r \bar{G}_j^\ominus$ as an absolute quantity scaled to the dimensions of a chemical reaction. Using molar heat capacities $\bar{c}_{p,j}(T, p^\ominus)$ to convert $\{\Delta_f \bar{h}_j^\ominus, \Delta_f \bar{s}_j^\ominus\}$ to reaction temperatures T leads to the so-called ‘standard Gibbs reaction enthalpy’ at standard pressure p^\ominus

$$\Delta_r \bar{G}^\ominus(T) = \sum_j \Delta_r \bar{G}_j^\ominus(T) = \sum_j \nu_j (\Delta_f \bar{h}_j^\ominus(T) - T \Delta_f \bar{s}_j^\ominus(T)) \quad (60)$$

The (partial) pressure dependence is finally obtained by

$$\Delta_r \bar{G}(T, p, \xi) = \Delta_r \bar{G}^\ominus(T) + \bar{R} T \ln Q(T, p, \xi) \quad (61)$$

$$= \Delta_r \bar{H}(T, p, \xi) - T \Delta_r \bar{S}(T, p, \xi) \quad (62)$$

²⁴ In solids, $H = U$ due to $p \rightarrow 0$.

²⁵ Real solids have frozen-in residual entropy for several reasons, including random orientations of molecules, the mixing of nuclear isotopes or different elements, and the multiplicity of nuclear spins, cf. [5].

²⁶ IUPAC: International Union of Pure and Applied Chemistry.

²⁷ Instead of the common nomenclature $\Delta_f \bar{G}_j^\ominus$, the lowercase symbol $\Delta_f \bar{g}_j^\ominus$ indicates the normalized molar character.

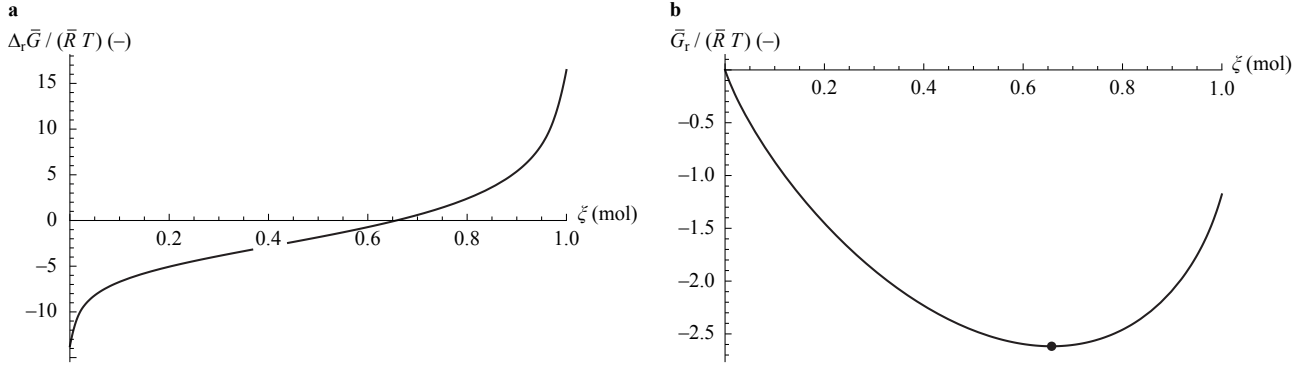


Figure 8. **Example 2** showing the classical illustration of chemical equilibrium, using the ammonia reaction Eq. (65) in terms of the extent of reaction ξ for initial amounts $\bar{N}_i(\text{N}_2, \text{H}_2, \text{NH}_3) = (1 \text{ mol}, 3 \text{ mol}, 0 \text{ mol})$ at constant temperature $T = 400^\circ\text{C}$ and constant pressure $p = 30 \text{ MPa}$. a) The chemical equilibrium is found at $\xi_{\text{eq}} = 0.66$ for $\Delta_r \bar{G} = 0$ following Eq. (61). b) The integration of Eq. (61) from 0 mol to ξ mol yields the common representation, whereby systems minimize their reaction Gibbs free energy \bar{G}_r .

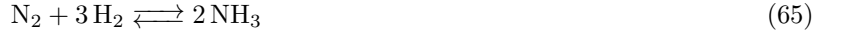
where \bar{R} is the universal gas constant and Q is the reaction quotient

$$Q = \prod a_j^{\nu_j} \quad (63)$$

with activities $a_j = f_j/p^\ominus$ calculated, in the case of gas reactions, from fugacities $f_j(T, p, x_j)$ with molar concentrations x_j . $Q = Q(T, p, \xi)$ depends on the progress of a chemical reaction, quantified by the extent of reaction ξ defined as the normalized change in mole numbers of the limiting species j

$$\xi = \frac{\Delta \bar{N}_j}{\nu_j} = \frac{\bar{N}_j(\xi) - \bar{N}_{j,i}}{\nu_j} \quad (64)$$

Example 2. Before advancing the classical concept, its application is briefly demonstrated for the ammonia reaction



where 4 mol of reactants form 2 mol of products. Fugacities f_j are obtained from the REFPROP fluid library [18]. Exemplary results in terms of ξ for initial amounts $\bar{N}_i(\text{N}_2, \text{H}_2, \text{NH}_3) = (1 \text{ mol}, 3 \text{ mol}, 0 \text{ mol})$ at constant temperature $T = 400^\circ\text{C}$ and constant pressure $p = 30 \text{ MPa}$ are shown in Fig. 8. The curve in Fig. 8a corresponds to Eq. (61) in units of $(\bar{R}T)$, illustrating the equilibrium condition $\Delta_r \bar{G} = 0$ at $\xi_{\text{eq}} = 0.66$, which corresponds to a product concentration of $x_{\text{NH}_3}(\xi_{\text{eq}}) = 0.49$. The reaction is spontaneous at $\Delta_r \bar{G} < 0$ and non-spontaneous at $\Delta_r \bar{G} > 0$, respectively. The integration of Eq. (61) from 0 mol to ξ mol is depicted in Fig. 8b. The arbitrary integration constant set to $\bar{G}_r(0) = 0$ confirms that absolute values of \bar{G}_r are physically meaningless. The common representation in Fig. 8b causes the misconception that chemical systems ‘minimize their free energy’, which is physically untenable.

C. Chemical work function

Eq. (61) shows similarity to the work function Eq. (40). Because chemical reactions signify a linear sequential process without cyclic dependence on the ambient temperature, T_{amb} in Eq. (40) is replaced by the reaction temperature T . And since molecular energy transformation is *reversible* in accordance with postulate (iii), equilibria between forward and reverse reactions can be shifted by varying process parameters.

To obtain a chemical work function \vec{L}_r that is compatible both with Eq. (40) and the sign convention in Section IID, the signs of the changes Δ in Eqs. (61,62) must be inverted

$$\vec{L}_r(T, p, \xi) \equiv -\Delta_r \bar{G}(T, p, \xi) = -[\Delta_r \bar{G}^\ominus(T) + \bar{R}T \ln Q(T, p, \xi)] \quad (66)$$

$$= -[\Delta_r \bar{H}(T, p, \xi) - T \Delta_r \bar{S}(T, p, \xi)] \quad (67)$$

The necessity of the sign inversion is explained in Section IV F. A formally correct modeling implies a sign change of the stoichiometric coefficients in process direction, i.e., $\vec{\nu}_j$ of reactants entering the reactor are positive, while those

of products leaving the reactor are negative²⁸. Consequently, the extent of reaction ξ is redefined along the process coordinate to form a balance of normalized mole numbers of the limiting species j

$$\xi = \frac{\vec{N}_j}{\vec{\nu}_j} = \frac{\bar{N}_{j,i} - \bar{N}_j(\xi)}{\bar{\nu}_j} = \bar{n}_{j,i} - \bar{n}_j(\xi) \quad (68)$$

transforming Eq. (67) to the equivalent expression

$$\vec{L}_r(T, p, \xi) = \vec{H}_r(T, p, \xi) - T \vec{S}_r(T, p, \xi) \quad (69)$$

Tentatively, \vec{L}_r is interpreted as a positive energy vector pointing in the process direction of the chemical formula. As in Section III D, the following sign rules apply:

- a) a positive vector $\vec{L}_r > 0$ indicates a spontaneous chemical conversion;
- b) a negative vector $\vec{L}_r < 0$ indicates a non-spontaneous condition; and
- c) $\vec{L}_r = 0$ corresponds to chemical equilibrium.

It follows that \vec{L}_r corresponds to the concept of chemical affinity A introduced by Théophile De Donder in 1922 [19] together with the extent of reaction ξ

$$\vec{L}_r \hat{=} A = - \sum \nu_j \mu_j = \sum \bar{\nu}_j \mu_j \quad (70)$$

where μ_j is the chemical potential of species j . The chemical work function \vec{L}_r thus symbolizes the positive driving force that determines the reaction kinetics, as recently discussed in [20], in analogy with the temperature difference ΔT (or better the temperature vector \vec{T}) in heat transfer and the pressure vector \vec{p} in volume and potential energy transformation, respectively.

D. Spontaneity criterion

With regard to Eqs. (67,69), possible sign combinations of \vec{H}_r , \vec{S}_r and \vec{L}_r are summarized in Tab. I. This table is common knowledge in chemistry, however, it deserves a discussion in a larger thermodynamic context. The following mechanisms apply:

- [i] $\vec{H}_r = f(\vec{U}_r, \vec{V}_r)$ is the distributable reaction energy vector, i.e., energy can be released from (source term) or stored in (sink term) chemical bonds. Without violating the first law, this mechanism also applies to weaker molecular interactions modeled by the excess enthalpy concept, which describes the enthalpy deviation of a real non-reactive mixture from that of an ideal mixture.
- [ii] $\vec{H}_r < 0$ yields an endothermic reaction that absorbs heat from the system, while $\vec{H}_r > 0$ yields an exothermic reaction associated with the release of heat to the system. The sign of \vec{H}_r contains no information on whether a reaction takes place; i.e., both endothermic and exothermic reactions exist.
- [iii] Vectors of \vec{U}_r , \vec{V}_r , and \vec{N}_r can generally occur, all affecting the reaction entropy vector $\vec{S}_r(\vec{U}_r, \vec{V}_r, \vec{N}_r)$.
- [iv] While the second law commonly associates spontaneity with entropy increase, Class (4) in Tab. I indicates spontaneity despite entropy decrease!
- [v] $\vec{S}_r > 0$ is possible in chemical reactions due to $\vec{H}_r > 0$ (see item [i]) and $\vec{N}_r > 0$. This means that larger numbers of smaller reactant particles can form fewer and larger (heavier) product particles.
- [vi] Equivalent to \vec{H}_r , the sign of \vec{S}_r contains no information on whether a reaction takes place.

²⁸ For the example reaction Eq. (65), the classical product-oriented perspective defines $\nu_{N_2} = -1$, $\nu_{H_2} = -3$ and $\nu_{NH_3} = 2$, while the sign convention of Section II D implies $\bar{\nu}_{N_2} = 1$, $\bar{\nu}_{H_2} = 3$ and $\bar{\nu}_{NH_3} = -2$.

Table I. Possible sign combinations of \vec{H}_r , \vec{S}_r and \vec{L}_r in chemical reactions

Class	$\vec{H}_r = -\Delta_r \bar{H}$	$\vec{S}_r = -\Delta_r \bar{S}$	$\vec{L}_r = -\Delta_r G$	Reaction
(1)	\ominus	\ominus	\ominus at low T ; \oplus at high T	Spontaneous at high T
(2)	\ominus	\oplus	\ominus at all T	Non-spontaneous
(3)	\oplus	\oplus	\oplus at all T	Spontaneous
(4)	\oplus	\oplus	\oplus at low T ; \ominus at high T	Spontaneous at low T
	Any	Any	Zero	Chemical equilibrium

[vii] Irrespective of the sign of \vec{S}_r , chemical reactions are *reversible* because they occur on a molecular level, cf. postulate (iii).

[viii] The process variable that comprises all possible sign combinations of \vec{H}_r and \vec{S}_r is the chemical work function \vec{L}_r . The spontaneity of chemical reactions is determined by the sign of \vec{L}_r as explained above.

It is a core belief in science that entropy always increases. The ammonia reaction of [Example 2](#) falls into Class (4) of [Tab. I](#), though the temperature is not really ‘low’ due to kinetic limitation. Executing the exothermic reaction at $T = \text{const.}$ implies heat rejection from the system to the surroundings. Classical theory assumes that both the reaction entropy $\vec{S}_r > 0$ and the system entropy $\vec{S}_{\text{sys}} > 0$ decrease *only* because the global entropy of the system and the Universe

$$\max(S_{\text{global}}) = \max(S_{\text{sys}} + S_{\text{Univ}}) \quad (71)$$

reaches a maximum in equilibrium, following the second law. This mistaken assumption is corrected in the following.

E. Analytic modeling of an isolated Class (4) reaction

A chemical reaction involves two integrated processes, where molecular chemical conversions take place in the bulk of a macroscopic system. The system’s temperature $T(\xi)$ and the pressure $p(\xi)$ are influenced by the reaction enthalpy $\vec{H}_r(T, p)$, the system’s heat capacitance $C_{\text{sys}}(T, p, \xi)$, and the system’s boundary conditions, e.g. isothermal, adiabatic, diabatic, $p = \text{const.}$, $V = \text{const.}$, etc. $\vec{H}_r(T, p)$, $C_{\text{sys}}(T, p, \xi)$, $T(\xi)$ and $p(\xi)$ are therefore fully coupled, yielding an implicit expression that can be solved numerically.

Once $T(\xi)$ and $p(\xi)$ are known, the reaction entropy $\vec{S}_r(T, p, \xi)$ is calculated, showing, besides $T(\xi)$, a strong dependence on concentrations $x_j(\xi)$ and partial pressures $p_j(\xi)$, respectively. The chemical conversion is then determined *exclusively* by the chemical work function $\vec{L}_r(T, p, \xi)$ following [Eq. \(69\)](#).

Example 3. To demonstrate the physical mechanism of chemical energy conversion, a *hypothetical* reaction



is used, where all reactants and the product have monatomic ideal gas properties. This allows analytic modeling at a manageable level of complexity, using the state properties described in [Section II](#). With respect to [Example 2](#), the stoichiometric coefficients are $\vec{\nu}_X = 1$, $\vec{\nu}_Y = 3$, $\vec{\nu}_Z = -2$, the molar masses are $\bar{M}_X = 28 \text{ g mol}^{-1}$, $\bar{M}_Y = 2 \text{ g mol}^{-1}$, and $\bar{M}_Z = 17 \text{ g mol}^{-1}$, and the initial amounts are $\bar{N}_{i,X} = 1 \text{ mol}$, $\bar{N}_{i,Y} = 3 \text{ mol}$, and $\bar{N}_{i,Z} = 0 \text{ mol}$. The reaction takes place in an adiabatic vessel at $V = \text{const.}$, which excludes any thermodynamic changes in the ambient surroundings

$$\Delta S_{\text{amb}} \stackrel{!}{=} 0 \quad (73)$$

This enables a complete and independent system description based on the sign convention in [Section II D](#).

At a given initial temperature T_i , initial pressure p_i , and initial mole number $\bar{N}_{i,\text{sys}} = \sum_j \bar{N}_{i,j}$, the system volume is

$$V_{\text{sys}} = \bar{N}_{i,\text{sys}} \frac{\bar{R} T_i}{p_i} = \text{const.} \quad (74)$$

Because all the species j have monatomic ideal gas properties, the reaction enthalpy is

$$\vec{H}_r(T) = \bar{H}(T) \sum_j \vec{\nu}_j \quad (75)$$

with $\bar{H}(T)$ from Eq. (7) in molar units. The temperature of the coupled system is determined numerically from

$$T(\xi) = \xi \cdot \vec{H}_r(T_i) + C_{p,\text{sys}}(\xi) \cdot (T(\xi) - T_i) \quad (76)$$

with the temperature-independent system heat capacitance

$$C_{p,\text{sys}}(\xi) = \frac{5}{2} \bar{R} \bar{N}_{\text{sys}}(\xi) \quad (77)$$

The system's boundary conditions affect the system pressure $p(\xi)$, yielding

$$p(\xi) = \bar{N}_{\text{sys}}(\xi) \frac{\bar{R} T(\xi)}{V_{\text{sys}}} \quad (78)$$

from the ideal gas model. The reaction entropy $\vec{S}_r(T, p, \xi)$ is then obtained from

$$\vec{S}_r(T, p, \xi) = \sum_j \bar{\nu}_j \bar{s}_j(T, p_j, m_j) \quad (79)$$

where the molar entropies \bar{s}_j of species j are calculated from the Sackur-Tetrode equation with partial pressures p_j and the particle masses $m_j = \bar{M}_j / \bar{N}_A$

$$\bar{s}_j(T, p_j, m_j) = \bar{R} \left(\ln \left[\left(\frac{2\pi m_j}{h^2} \right)^{\frac{3}{2}} \frac{(k_B T)^{\frac{5}{2}}}{p_j} \right] + \frac{5}{2} \right) \quad (80)$$

The system entropy \bar{S}_{sys} is finally given by²⁹

$$\bar{S}_{\text{sys}}(T, p, \xi) = \sum_j \bar{N}_j(\xi) \bar{s}_j(T, p_j, m_j) \quad (81)$$

and the change in the system's entropy

$$\Delta \bar{S}_{\text{sys}}(\xi) = \bar{S}_{\text{sys}}(T(\xi), p(\xi), \xi) - \bar{S}_{\text{sys}}(T_i, p_i, \xi_i) \quad (82)$$

To apply this model in the classical regime where the Sackur-Tetrode equation is valid, the thermal de Broglie wavelengths Λ_j of all the species j must be well below the length scale of the available particle volume

$$\Lambda_j = \frac{h}{\sqrt{2\pi m_j k_B T}} \ll \left(\frac{V}{N} \right)^{\frac{1}{3}} \quad (83)$$

Using the ideal gas model for a given initial pressure p_i , the initial temperature T_i must be well above the maximum of the species' critical temperatures $T_{\text{crit},j}$

$$T_i \gg \max \left[T_{\text{crit},j}(\xi) = \left\{ \left(\frac{h^2}{2\pi m_j k_B} \right)^{\frac{3}{2}} \frac{p_j(\xi)}{k_B} \right\}^{\frac{2}{5}} \right] \quad (84)$$

The results for $p_i = 30$ MPa and $T_i = 100$ K are plotted in Fig. 9, showing that the chemical equilibrium coincides with the maximum of the system entropy. This **special case** is misconceived in classical theory, assuming that the chemical equilibrium is *caused* by the second law, which would hold for *any* kind of process. This interpretation entails the following fundamental problems:

- I) The isolated macroscopic system does not interact with any other macroscopic system; i.e., the mechanism of the second law does not apply.
- II) In the case of interaction by heat transfer across the system boundary, the assumption of Eq. (71) infers equilibrium between the system and the Universe, including *thermal* equilibrium! The Universe would hence 'draw' all the thermal energy from exothermic reactions due to

$$\left| \Delta S_{\text{sys}}(U_{\text{sys}} - dU, V_{\text{sys}}, N_{\text{sys}}) \right| \ll \Delta S_{\text{Univ}}(U_{\text{Univ}} + dU, V_{\text{Univ}}, N_{\text{Univ}}) \quad (85)$$

yielding complete conversions.

As a consequence, the chemical equilibrium must be understood as an independent physical mechanism!

²⁹ Because the partial pressures p_j are used in Eq. (80), the mixing and pressure correction terms are already included.

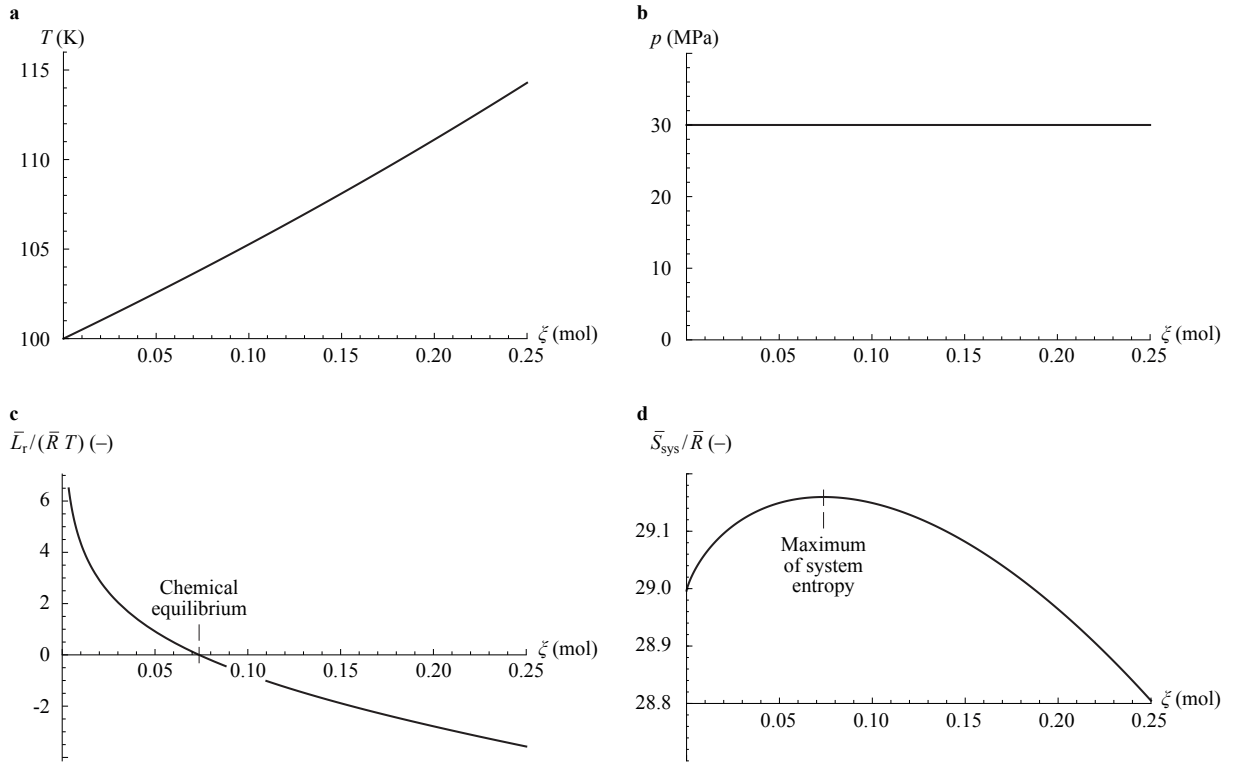


Figure 9. **Example 3** of the hypothetical reaction Eq. (72) in an adiabatic vessel of constant volume, considering all species j with monatomic ideal gas properties, using stoichiometric coefficients $\bar{\nu}_X = 1$, $\bar{\nu}_Y = 3$, $\bar{\nu}_Z = -2$, molar masses $\bar{M}_X = 28 \text{ g mol}^{-1}$, $\bar{M}_Y = 2 \text{ g mol}^{-1}$, and $\bar{M}_Z = 17 \text{ g mol}^{-1}$, and initial amounts $\bar{N}_{i,X} = 1 \text{ mol}$, $\bar{N}_{i,Y} = 3 \text{ mol}$, and $\bar{N}_{i,Z} = 0 \text{ mol}$. a) Temperature $T(\xi)$ with $T_i = 100 \text{ K}$. b) Pressure $p(\xi)$ with $p_i = 30 \text{ MPa}$. c) Chemical work functions following Eq. (69), yielding a chemical equilibrium at $\xi_{\text{eq}} = 0.0737$. d) Total system entropy, where $\max(\bar{S}_{\text{sys}})$ coincides with the chemical equilibrium.

F. The fourth law of thermodynamics

To understand the mechanism of chemical conversions, the chemical work function Eq. (69) must be written in dimensionless form

$$\frac{\vec{L}_r}{\bar{R}T} = \frac{\vec{H}_r}{\bar{R}T} - \frac{T}{\bar{R}} \frac{\vec{S}_r}{\bar{R}} \quad (86)$$

The second term on the right has dimensions of

$$\frac{\vec{S}_r}{\bar{R}} = \frac{k_B \ln \Omega}{\text{mol}} \frac{1}{k_B \bar{N}_A} = \ln \Omega \quad (87)$$

The symbol Ω in Eq. (87) is replaced by $\delta\Gamma_r$, signifying the phase space volume required for the conversion of a single formula unit. In the case of **Example 3**, 1 X particle and 3 Y particles must be close enough to enable the formation of 2 Z particles³⁰.

In relation to the second term, the first term in Eq. (86) can be interpreted as the total reaction phase space volume Γ_r

$$\frac{\vec{H}_r}{\bar{R}T} = \ln \Gamma_r \quad (88)$$

³⁰ The hypothetical example is equivalent to the ammonia reaction, where 1 N_2 molecule and 3 H_2 molecules are required to form 2 NH_3 molecules. The thermal prerequisites to enable the chemical conversion are provided by the system temperature.

Substituting Eqs. (87,88) in Eq. (86) yields the basic form of Fisher information [21] and Shannon entropy [22], respectively

$$\frac{\vec{L}_r}{\bar{R}T} = \ln \Gamma_r - \ln \delta\Gamma_r = \ln \left(\frac{\Gamma_r}{\delta\Gamma_r} \right) = \ln \Omega_r \quad (89)$$

where Ω_r signifies the **multiplicity** in the reaction phase space Γ_r . Starting at $\xi = 0$, $\delta\Gamma_r$ is small because only/mainly reactants are present. Example 3 yields $\Omega_r(\xi = 0) \approx 10^{16}$, signifying the number of possible unit conversions among the $\bar{N}_{i,X} = 1$ mol and $\bar{N}_{i,Y} = 3$ mol reactant particles. As the reaction proceeds along ξ , $\delta\Gamma_r$ increases strongly due to the presence of product particles and the influence of mixing. When the equilibrium is reached at $\vec{L}_r/(\bar{R}T) = 0$, the size of $\delta\Gamma_r$ required for a single unit conversion reaches the size of Γ_r ; i.e., $\Omega_r = 1$ and $\ln \Omega_r = 0$. Because fractional conversions of a formula unit are not possible when $\delta\Gamma_r > \Gamma_r$, the lower limit of the chemical work function is zero, equivalent to the physics of thermal entropy. This mechanism explains why the experimental establishment of chemical equilibria is extremely slow; it takes ‘ages’ until the reactants find each other in the entire Γ_r at $\xi \rightarrow \xi_{\text{eq}}$.

The derivation demonstrates that the process towards chemical equilibrium is a dimensionless mechanism, which becomes an energy vector only by multiplication with $\bar{R}T$. The multiplication, however, enables modeling based on macroscopic state properties. While the statistical mechanics of weakly coupled macroscopic and non-reactive systems drives thermodynamic equilibria towards $\Omega \rightarrow \text{max}$, the statistical mechanism of chemical energy conversion drives chemical equilibria towards $\Omega_r \rightarrow 1$. This mechanism constitutes the **fourth law of thermodynamics**, whereby the *configurational* entropy S_r of chemical reactions is zero in equilibrium

$$\boxed{\frac{\vec{L}_r}{\bar{R}T} = S_r = \ln \Omega_r} \quad (90)$$

Eq. (90) is being validated against the Classes in Tab. I. The reaction phase space is constructed of quantum-mechanical wave functions, where the logarithm of negative numbers yields complex numbers

$$\ln(-x) = \ln x + i\pi \quad (91)$$

The application to Class (1) leads to

$$\ln(-\Gamma_r) - \ln(-\delta\Gamma_r) = (\ln \Gamma_r + i\pi) - (\ln \delta\Gamma_r + i\pi) = \ln \Gamma_r - \ln \delta\Gamma_r = \ln \left(\frac{\Gamma_r}{\delta\Gamma_r} \right) \quad (92)$$

i.e., the result is physically possible and equivalent to Class (4). In the case of Classes (2) and (3), negative signs in either the first or the second term yield negative multiplicity values $\Omega_r < 1$, which are impossible in classical systems. This confirms the Class (2) behavior. Because Class (3) comprises exothermic ($\vec{H} > 0$) and entropic ($\vec{S} < 0$) reactions, the chemical work function \vec{L} is large and positive at any temperature, causing complete conversions³¹ with a reaction entropy $S_r(\xi = 1.0) > 0$. Eqs. (90,91) suggest that chemical equilibria between forward and reverse reactions are quantum-mechanically excluded in Class (3).

Eventually, the derivation of Eq. (90) leads to the following conclusions:

- i) Entropy is a dimensionless mechanism of energy transformation in nature. The units in Eq. (8) are only contributed by the Boltzmann constant k_B for historical compatibility, cf. [5].
- ii) Because entropy cannot be negative, the sign inversion implemented in Eq. (69) is *imperative* for physical understanding. Energy transformation processes must be modeled in the process direction.
- iii) The work function Eq. (40) in Section III has the equivalent structure of Eq. (89) when expressed in dimensionless form. Therefore, dimensionless work functions constitute the basic driving forces of energy transformation to be applied in kinetic modeling.

³¹ A typical example is the decay of hydrogen peroxide $2 \text{H}_2\text{O}_2 \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2$. Though Class (3) reactions are considered complete and irreversible in practice, the reaction quotient Q in Eq. (66) causes $\vec{L} \rightarrow 0$ at $\xi \rightarrow 0.9999\dots$. This is an artefact of the classical model.

G. Isolated ammonia reaction

Example 4. To further illustrate the problem of the classical theory, the ammonia reaction Eq. (65) is modeled with real fluid properties from REFPROP [18] in an isolated reactor (adiabatic, $V_{\text{sys}} = \text{const.}$). The following methodology is applied to determine the states in the control volume:

- 1) Equivalent to Eq. (73), the boundary conditions exclude thermodynamic changes in the surroundings.
- 2) The constant volume V_{sys} is calculated from the initial molar density $\bar{\rho}_i(T_i, p_i, \xi_i)$ of the initial mixture $\sum_j x_j(\xi_i)$ using REFPROP [18] and the initial total mole numbers $\bar{N}_{i,\text{tot}}$

$$V_{\text{sys}} = \frac{\bar{N}_{i,\text{tot}}}{\bar{\rho}_i} \quad (93)$$

- 3) The temperature of the adiabatic system $T(\xi)$ is determined numerically from the energy balance between the reaction enthalpy vector $\vec{H}_r(T)$ and the system's heat capacitance $\bar{C}_{p,\text{sys}}(T, \xi)$ ³²

$$\int_0^\xi \int_{T_i}^T \frac{1}{T - T_i} \vec{H}_r(T') d\xi' dT' + \int_0^\xi \int_{T_i}^T \frac{1}{\xi} C_{p,\text{sys}}(T', \xi') d\xi' dT' = 0 \quad (94)$$

where

$$C_{p,\text{sys}}(T, \xi) = \sum_j \bar{N}_j(\xi) c_{p,j}(T) \quad (95)$$

- 4) The system pressure $p(\xi)$ is calculated with REFPROP [18] based on $T(\xi)$, the molar densities $\bar{\rho}_{\text{sys}}(\xi)$, and the mixture compositions $\sum_j x_j(\xi)$

$$p(\xi) = f(T(\xi), \bar{\rho}_{\text{sys}}(\xi), \xi) = f\left(T(\xi), \frac{\bar{N}_{\text{tot}}(\xi)}{V_{\text{sys}}}, \xi\right) \quad (96)$$

- 5) The chemical work function \vec{L}_r is calculated following Eq. (66) using $T(\xi)$ and $p(\xi)$.
- 6) The system entropy change is finally obtained from molar entropies of the mixtures $\bar{s}_{\text{sys}}(T, p, \xi)$ using REFPROP [18], scaled with the system's total mole numbers $\bar{N}_{\text{tot}}(\xi)$

$$\Delta S_{\text{sys}}(\xi) = \bar{N}_{\text{tot}}(\xi) \cdot \bar{s}_{\text{sys}}(T(\xi), p(\xi), \xi) - \bar{N}_{i,\text{tot}} \cdot \bar{s}_{\text{sys}}(T_i, p_i, \xi_i) \quad (97)$$

The results of the isolated reaction are depicted in Fig. 10, using the initial conditions of Example 2. Fig. 10a shows the system temperature $T(\xi)$ resulting from Eq. (94) with $T_i = 400^\circ\text{C}$. Ammonia properties are available in REFPROP [18] for $T \leq 1000\text{ K}$, limiting the modeling to $\xi_{\text{max}} \approx 0.4\text{ mol}$. With $p_i = 30\text{ MPa}$, Eq. (96) yields the pressure $p(\xi)$ depicted in Fig. 10b. The chemical work function \vec{L}_r is plotted in Fig. 10c (full line) in comparison to Example 2 (dashed line). The reaction is spontaneous due to $\vec{L}_r > 0$ until equilibrium is reached at $\xi_{\text{eq}} = 0.23$. The system entropy change $\Delta \bar{S}_{\text{sys}}$ is shown in Fig. 10d. Because the mixing term has an infinite positive gradient at $(\xi \rightarrow 0)$, $\Delta \bar{S}_{\text{sys}}$ rises initially but quickly decreases due to the strongly negative standard term, resulting from $\Delta \bar{S}_{\text{sys}} = f(\Delta \bar{U}, \Delta \bar{N}_{\text{tot}})_V$ when 4 mol of reactants form 2 mol of products. The sign change and the predominantly negative value of $\Delta \bar{S}_{\text{sys}}$ do not influence the reaction's spontaneity, determined exclusively by $\vec{L}_r > 0$.

Example 4 provides **conclusive evidence of spontaneous entropy decrease** on macroscopic scales. On a fundamental philosophical level, Class (4) in Tab. I defines the thermodynamic conditions for the spontaneous creation of larger objects from smaller ones, thus signifying the spontaneous creation of *structures* as a synonym for entropy decrease. This **special case** may be interpreted as the **thermodynamic prerequisite for life**, distinguishing biology from general chemistry.

³² The pressure dependence of both $\vec{H}_r(T, p)$ and $\bar{C}_{p,\text{sys}}(T, p, \xi)$ has a negligible influence on $T(\xi)$.

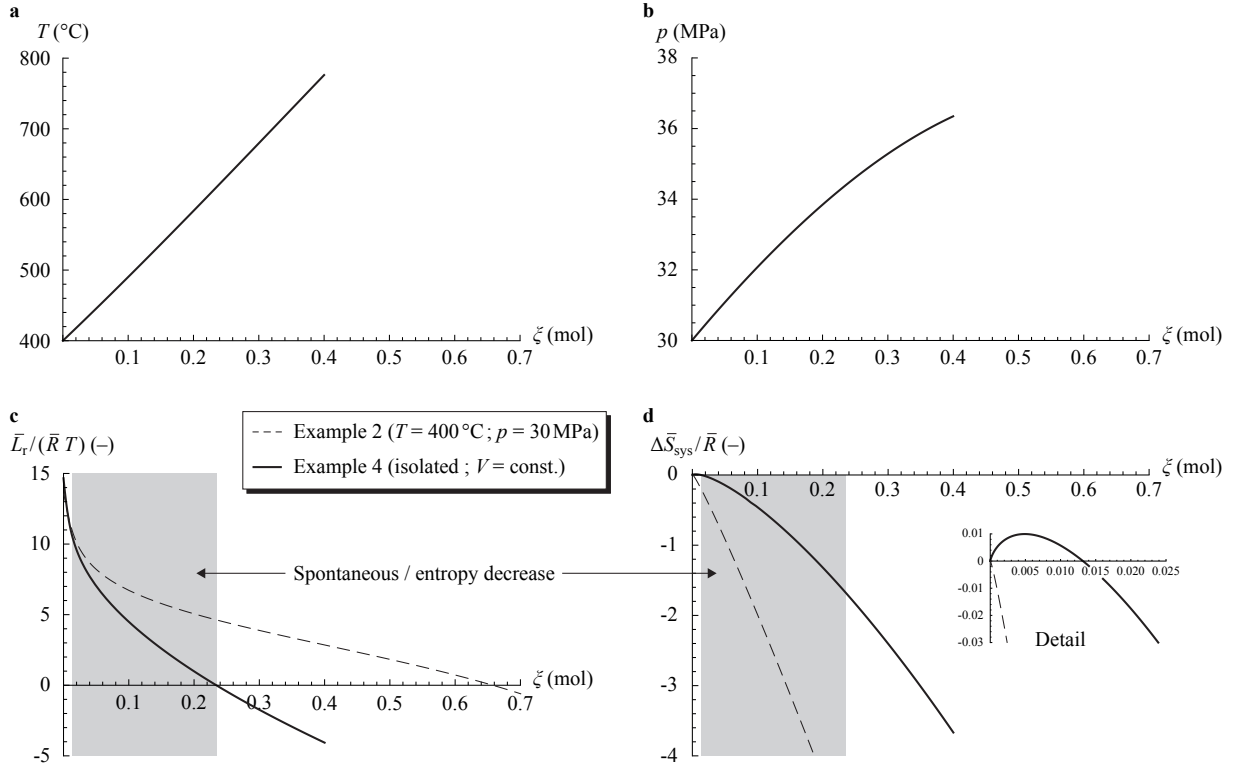


Figure 10. **Example 4** of an isolated ammonia reaction (adiabatic, $V_{\text{sys}} = \text{const.}$), using the initial conditions of **Example 2**. a) System temperature $T(\xi)$ resulting from Eq. (94). b) System pressure $p(\xi)$ due to $T(\xi)$, $\bar{p}_{\text{sys}}(\xi)$, and the mixture composition $\sum_j x_j(\xi)$. c) Chemical work function Eq. (66) with $T(\xi)$ and $p(\xi)$ (full line) in comparison to **Example 2** (dashed line). d) System entropy change Eq. (97) with $T(\xi)$ and $p(\xi)$ (full line) in comparison to **Example 2** (dashed line). The detail shows initial entropy increase due to the infinite positive gradient of the mixing term at $(\xi \rightarrow 0)$. $\Delta \bar{S}_{\text{sys}}$ becomes negative at $\xi > 0.013$ mol (full line) and $\xi > 3 \times 10^{-6}$ mol (dashed line). In view of $\Delta S_{\text{amb}} = 0$, the gray areas indicate the range of spontaneous entropy decrease in the macroscopic system of **Example 4**.

In the thermodynamic sense, life can be seen as a sequence of multiscale chemical reactions with a positive chemical work function and system entropy decrease, encoded in the DNA.

These *biochemical reactions* fulfill the basic prerequisites for spontaneous structural growth in nature, such as the growth of a tree. With regard to the famous Rede Lecture by C.P. Snow on “*The Two Cultures and the Scientific Revolution*” [23], the fourth law introduced by Eq. (90) provides the missing conceptual link between inanimate matter and living nature.

The thermodynamic work function is further applied to human society in Section V C in an attempt to build a bridge from the natural sciences to the social sciences.

H. Independence of chemical and diffusive equilibria

The *cardinal error* of physical chemistry is the generalization of the *ideal gas* model illustrated by **Example 3**, from which the coupled equilibrium condition

$$\Delta_r \bar{G} = \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_j \nu_j \mu_j = 0 \quad (\text{invalided}) \quad (98)$$

is deduced. The right part is known as the *Gibbs-Duhem equation* introduced also by Josiah Willard Gibbs in 1875 [16]. Substituting $\Delta_r \bar{G}$ with $-\bar{L}_r$, ν_j with $-\bar{\nu}_j = \partial n_j / \partial \xi$, and μ_j with

$$\mu_j = -T \left(\frac{\partial \bar{S}_j}{\partial n_j} \right)_{T,p} \quad (99)$$

signifying the diffusive component in statistical mechanics (cf. [5]) yields, in dimensionless form

$$\frac{\vec{L}_r}{\bar{R}T} = \frac{1}{\bar{R}} \sum_j \frac{\partial n_j}{\partial \xi} \left(\frac{\partial \bar{S}_j(\xi)}{\partial n_j} \right)_{T,p} = \frac{1}{\bar{R}} \sum_j \left(\frac{\partial \bar{S}_j(\xi)}{\partial \xi} \right)_{T,p} = 0 \quad (100)$$

$$\downarrow$$

$$S_r = \frac{\max(S_{\text{sys}})}{\bar{R}} \quad (\text{invalided}) \quad (101)$$

In addition to the theoretical derivation of Eq. (90) that clearly shows the independence of the fourth law, the isolated ammonia reaction modeled with *real* fluid properties in Example 4 proves that Eq. (98) does not hold in reality! There is absolutely no physical relationship between the chemical equilibrium in a reactive system (left side) of Eq. (98) and the diffusive equilibrium among non-reactive systems (right side)³³. Consequently, the relationship between the chemical work function and the affinity concept in Eq. (70) must be considered with caution as well.

Ultimately, it is important to note that there is no universality claim on the fourth law. It is valid in situations where the chemical elements are conserved. This does not apply to nuclear reactions, which require a relativistic model in terms of energy and mass conservation.

I. Scales and terminology

An obstacle to overall understanding is the use of terminology in scientific disciplines, where either same things have different names, or different things have the same name. The latter is a potential issue in Eq. (90), where the configurational entropy S_r is not to be mistaken for the reaction entropy \vec{S}_r in Eq. (69), which is an intrinsic part of Eq. (90)!

It is central to note that chemical reactions happen on a microscopic (molecular) scale inside a macroscopic (molar) system. The stoichiometric coefficients $\vec{\nu}_j$ relate to the molecular scale to conserve the chemical elements, while the reaction enthalpy \vec{H}_r and the reaction entropy \vec{S}_r are scaled to the reaction's molar dimension to consider \vec{H}_r in the thermal system behavior. Inherently, though, chemical conversions are *microscopic*, requiring the following changes in terminology and nomenclature, both to establish a clear interface with molecular dynamics (MD), and to overcome the change in paradigm in Sections IV A:

- a) The enthalpy of formation $\Delta_f \bar{h}_j^\ominus$ of species j becomes the standard molar binding energy $\Delta \bar{e}_{b,j}^\ominus$, where the Δ indicates the reference with respect to pure species, the overbar the molar unit, and the superscript \ominus the relation to IUPAC standard states.
- b) The entropy of formation $\Delta_f \bar{s}_j^\ominus$ becomes the standard molar μ -space $\Delta \bar{\mu}_j^\ominus$, following the μ -space³⁴ concept introduced by Gibbs in 1902 [24] and the established terminology in MD.
- c) The reaction enthalpy \vec{H}_r^\ominus becomes the reaction energy $\vec{E}_r^\ominus = \sum_j \vec{\nu}_j \Delta \bar{e}_{b,j}^\ominus$.
- d) The reaction entropy \vec{S}_r becomes $\bar{R} \ln[\delta \Gamma_r] = \sum_j \vec{\nu}_j \Delta \bar{\mu}_j^\ominus$, following Eqs. (87) to (89) that adopt the established nomenclature of Γ -space in MD.
- e) The chemical work function Eq. (69) finally becomes

$$\boxed{\vec{L}_r = \vec{E}_r - \bar{R} T \ln[\delta \Gamma_r]} \quad (102)$$

In dimensionless form, Eq. (102) is equivalent to Eq. (89), underlining that the fourth law is a truly *universal* dimensionless mechanism applicable to any scale. The Universe itself is a reactive system that follows the fourth law and not the second law; i.e., it does not interact with another macroscopic system. The improved terminology concludes a coherent theory of thermodynamic work functions, being compatible with the relevant disciplines in modern physics. It may provide a stepping stone towards a *Grand Unified Theory* (GUT) [25].

³³ A macroscopic diffusive process is non-existent in Example 4.

³⁴ The symbol μ is not related to the chemical potential.

V. THE INFLUENCE OF FORCE FIELDS

A. Real fluid properties

In all systems, particles exert forces on each other. The binding forces that hold atoms and molecules together are the same as those acting during chemical reactions, yielding the formation or breaking of ionic, covalent, or metallic bonds. Weaker interactions between molecules include dipole-dipole interactions and hydrogen bonds. The sum of all forces yields complex intra- and intermolecular force fields that constitute the potential energy

$$E_p = \int_{\text{all } j} F_j(r) dr \quad (103)$$

where r is the distance between the centers of moving particles.

The enthalpy of the ideal gas contains potential energy $E_p = pV = Nk_B T$ according to Eqs. (3) to (7), though it is not considered in statistical mechanics, which assumes a randomized (stochastic) redistribution of (U, V, N) . Force fields limit this random motion, yielding a deviation from postulate (ii) that presumes *equal* probability of microstates. This is illustrated by a simple example: While a neutral particle may occupy the whole spatial space $\Omega_{\bar{r}}$ confined by two electrodes, an electron is driven by an electric field from the negative anode to the positive cathode; i.e., microstates towards the cathode are *more* probable.

Compared to the stochastic ideal gas model, force fields thus reduce the entropy in its spatial space component $\Omega_{\bar{r}}$. Accordingly, equations of state (EOS) describe real fluid properties in terms of corrections to the ideal gas model, Eq. (6). For instance, the virial EOS corrects the potential energy E_p in dimensionless form by

$$\frac{p\bar{V}}{RT} = 1 + \frac{B_2(T)}{\bar{V}} + \frac{B_3(T)}{\bar{V}^2} + \dots \quad (104)$$

whereby the virial coefficient $B_2(T)$ represents two-body interactions, $B_3(T)$ three-body interactions, etc. In the case of simple atoms, such as noble gasses, Eq. (104) can be truncated after the second term, and quantum mechanics provides the analytic expression

$$B_2(T) = -2\pi \int_0^\infty r^2 \left(e^{-\frac{U(r)}{k_B T}} - 1 \right) dr \quad (105)$$

where $U(r)$ is the potential energy between two atoms.

Modern EOS are based on the ‘Helmholtz free energy’ F cited already in Eq. (56). Using the molar density $\bar{\rho}$ as a parameter in

$$\bar{F} = \bar{F}(T, \bar{\rho}) = \bar{F}\left(T, \frac{1}{\bar{V}}\right) = \bar{F}_{\text{ideal}} + \bar{F}_{\text{res}} \quad (106)$$

enables the description of real fluid properties depending on both thermal energy E_T via T and potential energy E_p via \bar{V} , respectively. All other fluid properties are derived consistently from Eq. (106). \bar{F}_{ideal} corresponds to Eq. (56), in molar units, and the residual part \bar{F}_{res} is adapted to experimental data using fit functions.

Comparing Eqs. (106) and (104) reveals a direct relation between \bar{F}_{res} and $B_2(T)$, truncating Eq. (104) after the second term for a low-pressure fluid. Considering the analytic relation

$$0 = \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T_1} \quad (107)$$

between $B_2(T)$ and the inversion temperature T_1 defined by a Joule-Thomson coefficient of $\mu_{JT} = 0$, it can be shown that³⁵

$$0 = \frac{d\bar{F}_{\text{res}}(T, p)}{dT} - \frac{\bar{F}_{\text{res}}(T, p)}{T_1} \quad (108)$$

\bar{F} must therefore be understood as a *model* similar to the virial EOS, rather than a physical form of energy. This renders the reference problem discussed in Section IV irrelevant.

³⁵ Using, for example, the current EOS of ⁴He from REFPROP [18] with $p = 1$ kPa yields $T_1(\mu_{JT}(p)) = 45.645$ K. The calculation based on Eq. (108) leads to $T_1(\bar{F}_{\text{res}}(T, p)) = 45.647$ K.

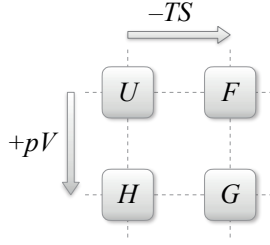


Figure 11. Guggenheim scheme of classical thermodynamics, representing the relationship between ‘thermodynamic potentials’. U is the thermal energy E_T , pV the molecular potential energy E_p , and $H = E_T + E_p$ the total energy of a static fluid, all representing state properties in contrast to G and F . $\bar{L} = -\Delta\bar{G}$ signifies the work function of both reactive and non-reactive energy transformations. \bar{F} is a model to describe real fluid properties, i.e., a type of an equation of state.

The classical ‘thermodynamic potentials’ U , H , G , and F assembled in the Guggenheim scheme of Fig. 11 are ‘quantities with units of energy’ rather than physical potentials³⁶. When Josiah Willard Gibbs introduced these concepts in 1875 [16], the microscopic picture of entropy was not yet available. Following the discussions above, the physical meaning of these quantities can now be summarized as follows:

- (a) The internal energy U is the thermal energy E_T .
- (b) The product pV is the molecular potential energy E_p , i.e., the physical definition of pressure is potential energy per unit volume (rather than force per unit area).
- (c) The enthalpy $H = E_T + E_p$ is the total energy of a static fluid, being freely redistributed inside the fluid following statistical mechanics. The energy of chemical bonds is not included in case of non-reactive systems, and considered in case of reactive systems.
- (d) While U , pV and H are state properties, G and F do not correspond to physical forms of energy.
- (e) $\bar{L}/\bar{R}T = -\Delta\bar{G}/\bar{R}T$ signifies configurational entropy as the basic dimensionless driving force of energy transformation. The multiplication with $\bar{R}T$ yields thermodynamic work functions in both non-reactive and reactive systems, which enable the calculation of energy transformations based on macroscopic state properties.
- (f) The Helmholtz energy \bar{F} is a model used to describe the potential energy of real fluids, resulting from complex intra- and intermolecular force fields. These alter the random motion of atoms and molecules, and hence the phase space volume compared to the ideal gas model, which serves as a reference. \bar{F} is a type of an equation of state, not a physical form of energy.

B. The impact of gravity

Entropy is a dimensionless mechanism that regulates the redistribution of energy and particles in the phase space volume. In many instances, the effect of force fields is not a ‘small’ correction to ideal gas behavior. Gravitation particularly restricts the phase space of objects in the spatial space component Ω_r . For instance, the spatial space of planets is restricted to their orbits around stars, instead of a random occupation in the Universe. Gravity also restricts the spatial space of people essentially to the ground.

The historical ‘heat death paradox’ of the Universe by William Thomson [26, 27] relies on Clausius’ classical entropy expression and the paradigm that entropy could never decrease. The universal validity of the second law, however, is shown to be false in Section IV. It applies only to energy transformations among weakly coupled non-reactive macroscopic systems.

In general, nature is composed of reactive systems, where energy transformations follow the fourth law introduced by Eq. (90), and where macroscopic entropy decrease is possible when several smaller objects merge to act as one. Because black hole formations are reactive processes with $\Delta S = f(\Delta U, \Delta V, \Delta N)$, the Bekenstein-Hawking model on black hole thermodynamics [28, 29] needs to be reassessed, potentially solving the conflict with the soft-hair and quantum hair theories [30, 31]. Stephen Hawking’s area law of colliding black holes [32] is independent of the second law. It states that the surface area of the final black hole is larger than the sum of the initial black hole areas, which is confirmed by recent results from LIGO and Virgo [33].

³⁶ Physical potentials are positive and facilitate energy transformation; they are not the energy being transformed.

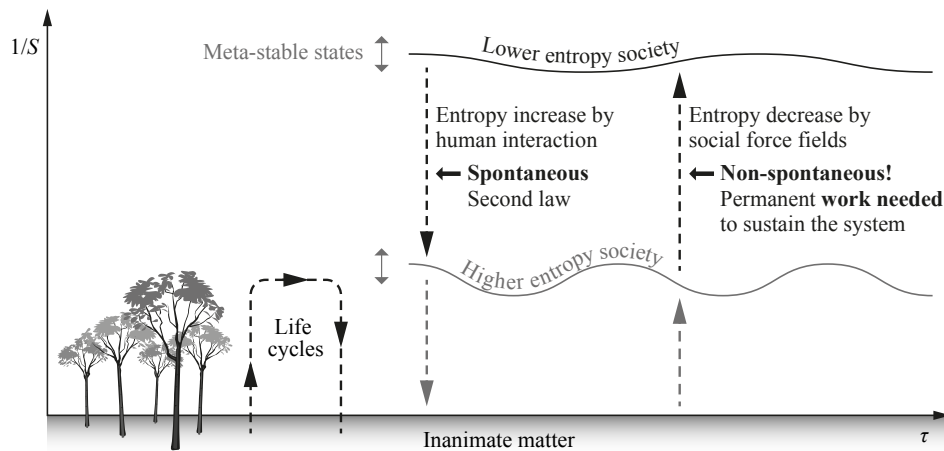


Figure 12. Illustration of living systems in terms of entropy changes. Just like anything else in nature, human societies are subject to thermodynamic energy transformations. The permanent entropy increase due to macroscopic interactions (second law) must be compensated by a societal work function. Different timescales of changing boundary conditions and societal countermeasures yield metastable states. Higher organizational levels correspond to lower entropy and higher effort.

C. Thermodynamics of living systems

The thermodynamic interpretation of life in Section IV G symbolizes the growth of living entities through the creation of multiscale structures from dispersed materials, corresponding to the spontaneous decrease in entropy. Once the structures have matured, life is preserved by continuous energy transformations until the end of the life cycle, characterized by decomposition with entropy increase.

Just like anything else in nature, human societies are subject to the laws of thermodynamics. Societies are ‘living’ (dynamic) systems characterized by a statistically sufficient size³⁷, inferring the applicability of thermodynamic work functions. While the exchange of energy U , space V , and objects N among individuals yields a permanent increase in entropy, societal work functions stabilize systems on certain levels, as illustrated in Fig. 12.

From a thermodynamic point of view, the worst situation in human societies corresponds to ‘ideal gas behavior’, i.e., erratic and unpredictable human interaction. To limit the randomness of ideas and conduct, human societies have developed *social* force fields beyond the physical ones, such as culture, religion, and constitutional order with human laws and legislation. To compensate for the second law, i.e., the mechanism of decomposition, the societal work function requires *permanent contributions* by the members of society to sustain the system. Because, on average, all members must work *more*³⁸ than they receive, appropriate participation from all groups must be ensured. Yet, the permanently changing external and internal conditions, along with differing timescales, cause the metastability of states in which perfection and equilibrium are unattainable. Politics must hence be understood as ‘change management’ rather than ‘administration’, aiming to rebalance the multitude of interests in a vast societal parameter space. Its failure may lead to destruction and a fallback to physical force fields.

The thermodynamic system response of societies is comparable to left-handed cycles explained in Section III, both creating and sustaining higher ordered states compared to the surroundings. When the ‘ambient temperature’ increases, a society needs to adjust its societal work function to stabilize the state. This can be achieved either by working more, or alternatively, the internal *systemic* entropy increase must be limited. In the former case, the twentieth-century model of economic growth and wealth distribution increasingly conflicts with biophysical planetary boundaries and absolute resource scarcity [35]. To achieve the latter option, civic education and the evolution of cultural norms are essential prerequisites. Constructive contributions from information technology are inevitable to restrain information entropy, i.e., Shannon entropy [22], which is defined as the measure of uncertainty or randomness in a data source. Collectively, these interventions enhance public comprehension, synchronize collective behavior, and minimize systemic friction within and between societies, thereby mitigating the risk of structural conflict. With the same work, societies can achieve more; conversely, less energy and fewer resources are needed to sustain the status quo.

³⁷ Because the mechanism of entropy becomes overwhelming already at about $N \geq 10^5$, entropy and the work functions are meaningful concepts in a societal context. In contrast to quantum mechanics, which can only deal with much smaller systems, thermodynamics neither enables nor aims to predict individual ‘personal’ states; only statistical conclusions can be drawn regarding the entire system behavior. These, however, are extremely reliable.

³⁸ John F. Kennedy, inaugural address 1961: “And so, my fellow Americans: ask not what your country can do for you – ask what you can do for your country.” [34].

Thermodynamic work functions describe the basic principles of energy transformation in nature, confirming that “*Thermodynamics has something to say about everything, but does not tell us everything about anything*” [36]. At least, it answers the question about the meaning of human life: Simply to be a constructive member of society!

VI. SUMMARY AND CONCLUSIONS

This paper introduces the thermodynamic work function as a fundamental physical principle. It is inferred from the first law of energy conservation and the second law of energy transformation among non-reactive macroscopic systems, considering the physical definition of entropy from statistical mechanics.

The transition from thermal physics to thermochemistry implies a crucial change in paradigm, whereby the energy of chemical bonds becomes part of the distributable energy. In contrast to the second law, chemical conversions are characterized by microscopic energy transformation inside a macroscopic system, yielding a different statistical mechanism of energy transformation. The chemical work function thus supplants the classical Gibbs free energy concept. Its dimensionless form reveals the mechanism of spontaneity and chemical equilibrium based on configurational Shannon entropy, introduced as the fourth law of thermodynamics. Scaling with $\bar{R}T$ enables the calculation based on macroscopic state properties. Work functions, in general, should hence be considered the physical basis of kinetic modeling.

The assumption that the second law applies to any process is proven false. Instead, spontaneous decreases in entropy are shown to exist when several small objects merge to form larger structures. The isolated ammonia reaction with real fluid properties provides conclusive evidence. The corresponding class of multiscale bio-chemical reactions can be seen as the basic thermodynamic prerequisite for the growth of living entities in nature, thus yielding a unified scientific understanding across physics, chemistry, and biology.

Furthermore, the influence of force fields on real system behavior is discussed, showing that the classical Helmholtz free energy concept is a model rather than a true form of energy. This enhances the physical understanding of classical concepts in the Guggenheim scheme. The impact of gravity on real system behavior is discussed in the context of black hole formation, calling for the reassessment of some astrophysical theories.

Last but not least, the relevance of thermodynamic principles to living systems is briefly outlined in an attempt to build a bridge from the natural sciences to the social sciences and the humanities. On macroscopic scales, energy transformations take place in a 6N-dimensional phase space Ω , constructed of particle-wave functions, with real and imaginary dimensions. While the real dimension is relatively well-explored in physics, the imaginary dimension is the realm that hosts imagination, thought, theory, language, culture, dreams, emotion, love, and religion. There is no doubt that imagination affects reality, and the discussion of chemical reaction classes may be an example. This is the place to find new physics, I believe.

ACKNOWLEDGMENTS

The author would like to thank the reviewers and the members of his team for their constructive criticism, which helped to sharpen the argumentation.

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