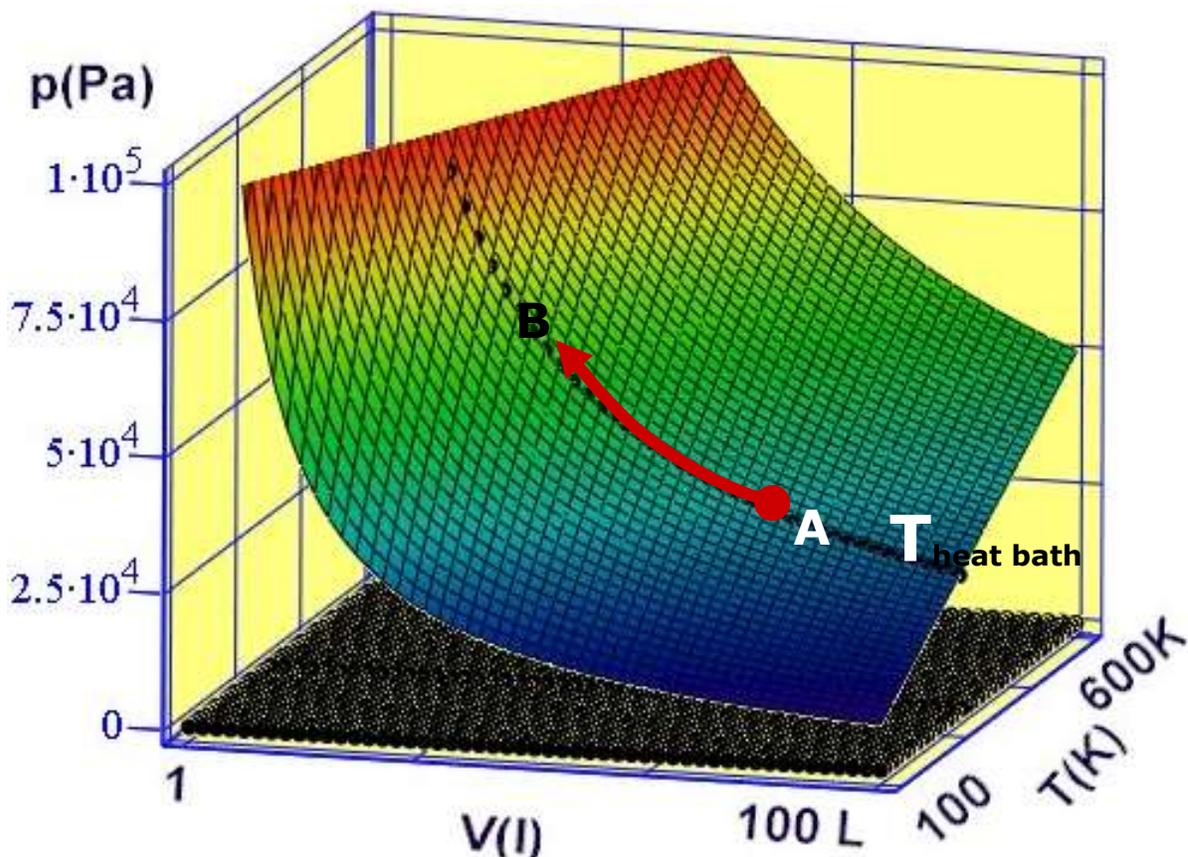
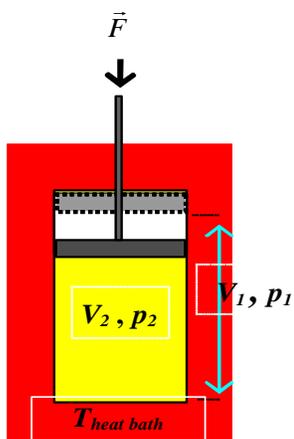


Reversible and irreversible processes

If the **energetics of a physical process**, such as emphasized in the First Law of Thermodynamics, is an important factor, experience tells that **other concepts** must play a role in its time evolution. For example, some processes are easily **reversible**, others cannot be inverted, they are **irreversible**. An example of the latter class of processes is the escape of the gas in a balloon, when a hole is pierced into its shell. The escaped gas will never return into the balloon. Another example is a frictional process, in which the dissipated energy is irreversibly lost into other degrees of freedom. Such processes seem to demonstrate inherently the progress of time, the direction of the "Arrow of Time". It will turn out later that this arrow points into the direction of increasing complexity.

Even though thermodynamic systems usually contain an enormous number of particles and are very complex, there are processes which transform state **A** to state **B** but are completely reversible. The figure illustrates the hyperplane of equilibrium states



Isothermal Compression

of an ideal gas containing these states. The arrow shows an isothermal path $\mathbf{A} \tau \mathbf{B}$. This path can be enforced by placing a cylinder containing an ideal gas in a heat bath, which is kept at fixed temperature $T = T_{\text{heat bath}}$, and by compressing the gas slowly. The downward motion of the piston (figure) transfers energy to the gas. This motion would heat the gas to a higher temperature, if no precaution were taken to cool the gas simultaneously. The compression has to be slow enough to allow the gas to equilibrate continuously by adapting to the new volume and the fixed temperature of the surrounding

heat bath. This is achieved by the gas generating the associated pressure required by the equation of state,

$$p_2 = Nk_B \frac{T_{\text{heat bath}}}{V_2} \quad (1)$$

The gas emits any excess internal energy continuously as heat, in order to remain at temperature $T = T_{\text{heat bath}}$. In each point along this trajectory, the system is in **local equilibrium with its surroundings**.

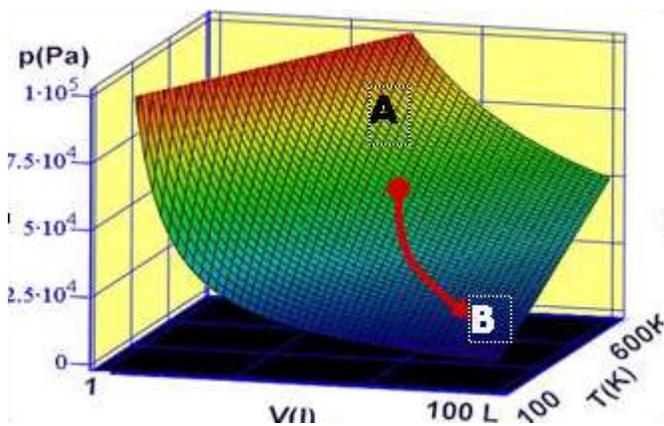
As has been shown before, it is straightforward to calculate the work ΔW_{mech} done by the ideal gas in an *isothermal* ($T = T_{\text{heat bath}}$) *expansion/compression* $\mathbf{V}_1 \tau \mathbf{V}_2$:

$$\Delta W_{\text{mech}} = -\int_{V_1}^{V_2} p(V) dV = -\int_{V_1}^{V_2} \frac{Nk_B T}{V} dV = Nk_B T \ln\left(\frac{V_1}{V_2}\right) \quad (2)$$

using $pV = Nk_B T$. The relative sizes of \mathbf{V}_1 and \mathbf{V}_2 determine the sign of ΔW_{mech} , e.g., $\Delta W_{\text{mech}} < 0$ for $\mathbf{V}_1 < \mathbf{V}_2$ (expansion). In either case, the temperature T is held constant, and therefore the internal energy remains constant. The **loss ΔU** in internal energy associated with the expansion **is compensated exactly, and continuously, during a reversibly expansion/compression** by an inflow of heat energy into the gas from the surroundings:

$$\underline{\underline{\Delta W_{mech}}}\Big|_{T=const} = -\int_{V_1}^{V_2} p(V)dV = \underline{\underline{-\Delta q}}\Big|_{T=const} \quad (3)$$

It is obvious that such a procedure can be made in a reversible fashion. One only has to ascertain that on the return path, the gas assumes the equilibrium pressure compatible with the isothermal equation of state, for the present volume V (piston position) and the external temperature $T = T_{heat\ bath}$. Upon slow retraction of the piston, allowing the system to continuously equilibrate, eventually the gas will return to its initial state **A**. The heat bath '**guides**' the system tracing its way back exactly along the path it went from **A** to **B**.



Adiabatic expansion or compression processes for isolated ideal-gas systems also belong to the class of reversible processes of interest to thermodynamics. The figure illustrates such a trajectory **A** \rightarrow **B**. The only energy transfer between an isolated system and its surroundings is accomplished by work done by or on the system, in the present example, just pV work. Along the path on the state surface indicated in the figure, the gas performs a certain amount of work,

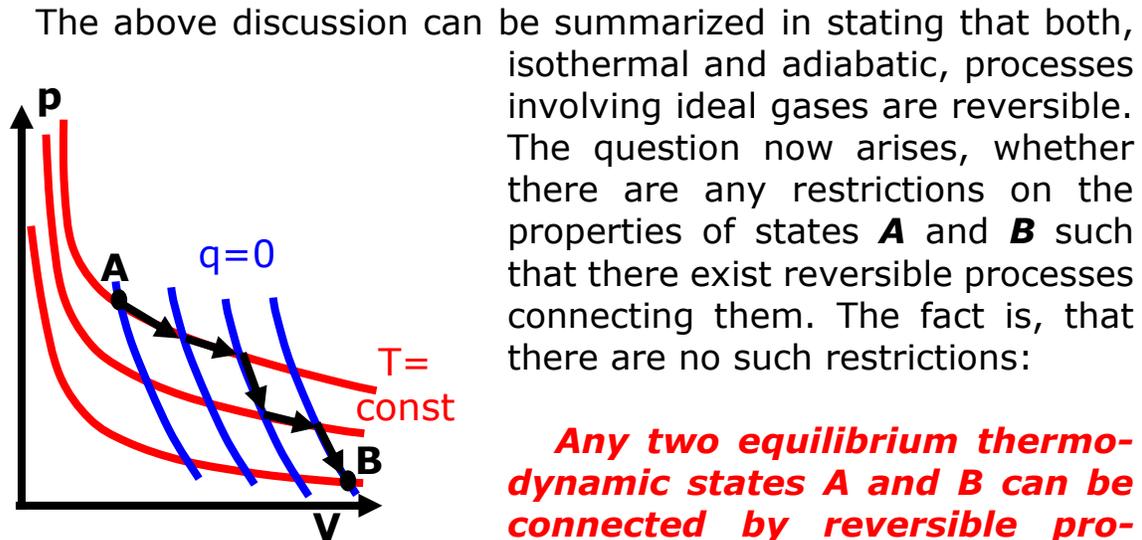
$$\Delta W = -\int_{V_A}^{V_B} p(V)dV = -p_A V_A^\gamma \int_{V_A}^{V_B} \frac{dV}{V^\gamma} = \frac{p_A V_A^\gamma}{\gamma - 1} (V_A^{1-\gamma} - V_B^{1-\gamma}) < 0 \quad (4)$$

calculated from the adiabatic equation of state of an ideal gas,

$$pV^\gamma = const = p_A V_A^\gamma \quad (5)$$

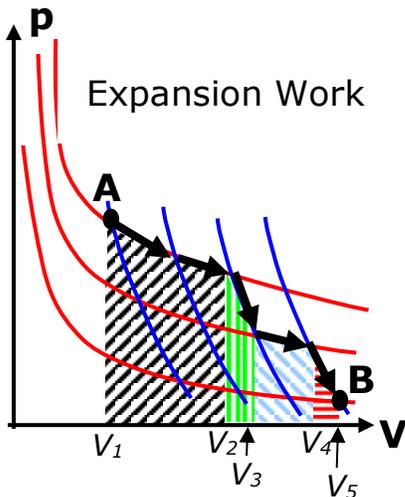
Since the expansion work is negative, the internal energy U of the ideal gas, i.e., its temperature, decreases. To make an adiabatic expansion reversible, again the process (piston movement) has to be slow enough such that the gas temperature drops uniformly over the entire volume, and the system remains at

equilibrium at all times. The same procedure reversed will then return the system along the same path, back to its starting point **A**.



Any two equilibrium thermodynamic states *A* and *B* can be connected by reversible processes *A* τ *B*.

This can be seen easily, because isotherms and adiabats represent a curvilinear coordinate system (grid) on the hyper-plane of all equilibrium states. Any state on this plane, i.e., any equilibrium state of an ideal gas, is situated at an intersection of an isotherm with an adiabat. Therefore, as illustrated in the figure, any two states on the state hyper-plane can be connected by a series of isotherms and adiabats. Each segment of such a composite path is reversible, and so is the sum, the entire path. The total work done along such a path is the sum of all amounts of work done along each of the individual segments.



For the example illustrated in the figure,

$$\Delta w_{\text{mech}} = -\int_{V_A}^{V_B} p(V) dV = -\sum_{i=1}^4 \int_{V_i}^{V_{i+1}} p(V) dV \quad (6)$$

Similarly, the total heat absorbed along such a path is the sum of all amounts of heat energy absorbed along each of the individual segments. For the example illustrated in the figure,

$$q = \sum_{i=1}^4 \Delta q_{i \rightarrow i+1} = \Delta q_{1 \rightarrow 2} + \Delta q_{3 \rightarrow 4} = + \int_{V_1}^{V_2} p(V) dV + \int_{V_3}^{V_4} p(V) dV \quad (7)$$

The system absorbs heat only on the isothermal legs 1 τ 2 and 3 τ 4 of the process and in amounts equal in magnitude, but opposite in sign, to the work done on these parts. On the adiabatic legs 2 τ 3 and 4 τ 5, no heat is exchanged with the surroundings.

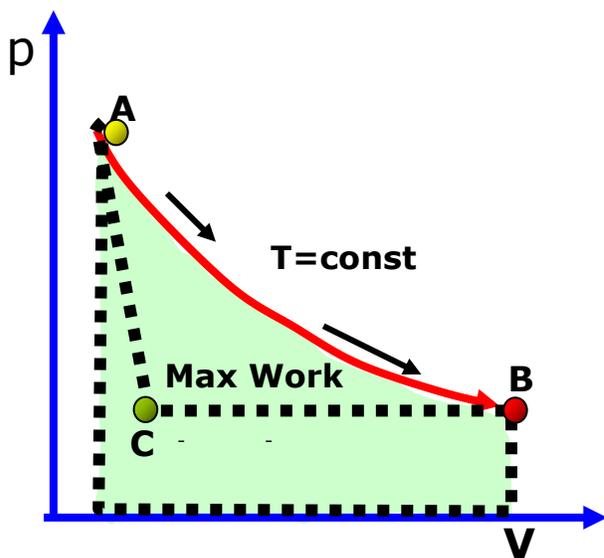
The particular values of work and heat exchange represented in Eqs. (6) and (7) pertain only to the exact pathway chosen for the process $A \xrightarrow{\text{process 1}} B$. For another process, $A \xrightarrow{\text{process 2}} B$, connecting the same two states, the relations between work and heat exchange are obviously different. The sums and integrals over work and heat differentials in Eqs. (6) and (7), respectively, depend clearly on the particular path chosen for each leg of the transition, for example, whether it is isothermal or adiabatic. Because of this path dependence of the respective integrals, the differentials of work and heat are sometimes termed "inexact differentials" denoted by dw and dq , respectively. Such notation has been chosen in the literature to alert the reader and remind him of the path dependence of the corresponding integral.

Regardless of the path dependence of the sums and integrals over work and heat, the sum of all work done and all heat absorbed equals the change ΔU in internal energy, going from state **A** to state B. More generally, **the change in any state variable remains the same on all possible pathways** $A \xrightarrow{\text{process X}} B$.

This realization has important practical consequences for the evaluation of state quantities. State variables are characteristics of a given state and independent on the sequence or history of processes through which the system has evolved to that state. Therefore, one can deduce the properties of the final state **B** in a process 1, $A \xrightarrow{1} B$, from the properties of state **A** and the changes produced in a, conveniently chosen, hypothetical reversible process 2: $A \xrightarrow{2} B$. Convenient choices are always

isothermal and adiabatic processes, or combinations thereof, since one can easily calculate the changes in all state variables along such pathways. The above example illustrates this point. A well-known application of this principle for the determination of energy changes in chemical reactions is Hess' Law.

Consider as another illustrative example the two processes of **a)** an isothermal reversible and **b)** and an irreversible expansion of an ideal gas. During the reversible expansion, the pressure decreases steadily, although the temperature is held constant. The work done by the gas in the isothermal expansion is given by the negative integral of the isotherm between V_A and V_B , i.e., the area under the curve within the two limits. It has not decreased the internal energy of the gas, which is equal to $(3/2)k_B T$ per particle before, during, and after the expansion. It is evident that the work done by the system in an isothermal expansion is the maximum that it can do, $|w_{rev}| = w_{max}$. Here, the condition is that $U_A = U_B$. It is fulfilled by replenishing continuously the energy content of the gas with heat from the surroundings, as this energy is expended in pV work done by the gas. Without contact with a heat bath, the work done by the system would lead to its cooling, a decrease in temperature, internal energy and a diminished capability of the system to do further work on the surroundings (e.g. on a piston).



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Keeping the sign convention in mind, according to which work done by the system is counted as negative, because it decreases the internal energy, this statement is equivalent to saying that

$$w_{rev} = w_{min} < 0 \quad (8)$$

Now consider the **irreversible expansion** of the same gas in a process $A \rightarrow C \rightarrow B$, with $U_A > U_C (> U_B) > U_B = U_A$, indicated by

the dashed lines in the pV diagram shown in the figure. Removing the external force retaining the gas at the initial volume V_A suddenly will let the gas expand spontaneously and rapidly to an intermediate volume $V_C < V_B$.

This expansion **process** $V_A \rightarrow V_C$ **is spontaneous and irreversible**. It is irreversible because the system has cooled, lost internal energy and gained entropy. Under no conceivable circumstances will the gas compress spontaneously back to the initial volume V_A and initial pressure p_A . Since this leg of the process $V_A \rightarrow V_B$ is irreversible, the entire process is irreversible. Reestablishing the initial state A requires more heat energy than the work done by the system in an irreversible process.

In the initially rapid expansion, $V_A \rightarrow V_C$, the gas pressure will drop precipitously from p_A to $p_C = p_B$. Relatively little, if any, work will be done on the surroundings in this stage of the irreversible expansion. There can be turbulence, pressure, and temperature differentials across the volume in a rapid, non-equilibrium (dissipative) expansion process. At $\{p_C, V_C, T\}$, the **gas is not necessarily in an equilibrium state** with pressure, volume, and temperature described by the equation of state. This decompression, which is associated with little change in volume, requires that internal energy of the gas has been lost by irradiating heat to the outside, thus cooling the gas. After having settled down to p_B , the gas may expand and eventually do some work against an external force, until the final volume V_B is reached. Along this segment, if in contact with a heat bath, some heat can flow back into the gas countering further cooling. In detail, the process may not be known precisely and may be very different from the dashed line in the figure. In any case, the work corresponding to the entire irreversible path is represented by the negative area under the trajectory in $\{p, V\}$ space (dashed curve in the figure).

This work done in the irreversible process is clearly less in magnitude than the work done along the reversible, isothermal path, i.e., $|W_{irrev}| < |W_{max}| = |W_{rev}|$. This means that, accounting for the negative sign, that

$$W_{rev} = W_{max} < W_{irrev} \quad (9)$$

However, ***initial and final state of both, reversible and irreversible processes A τ B are the same.*** In the reversible case, the gas has performed maximum work against an external force. In the irreversible case, little work was done by the gas. Its initial energy was partially lost as waste heat to the surroundings. Therefore, one has the following relations between the various forms of energy for the two types of processes:

$$\Delta U = w_{rev} + q_{rev} = w_{irrev} + q_{irrev} \quad (10)$$

Since it was argued that $w_{irrev} > w_{rev}$, the opposite inequality must hold for the heat transfer in the two processes:

$$q_{irrev} < q_{rev} \quad (11)$$

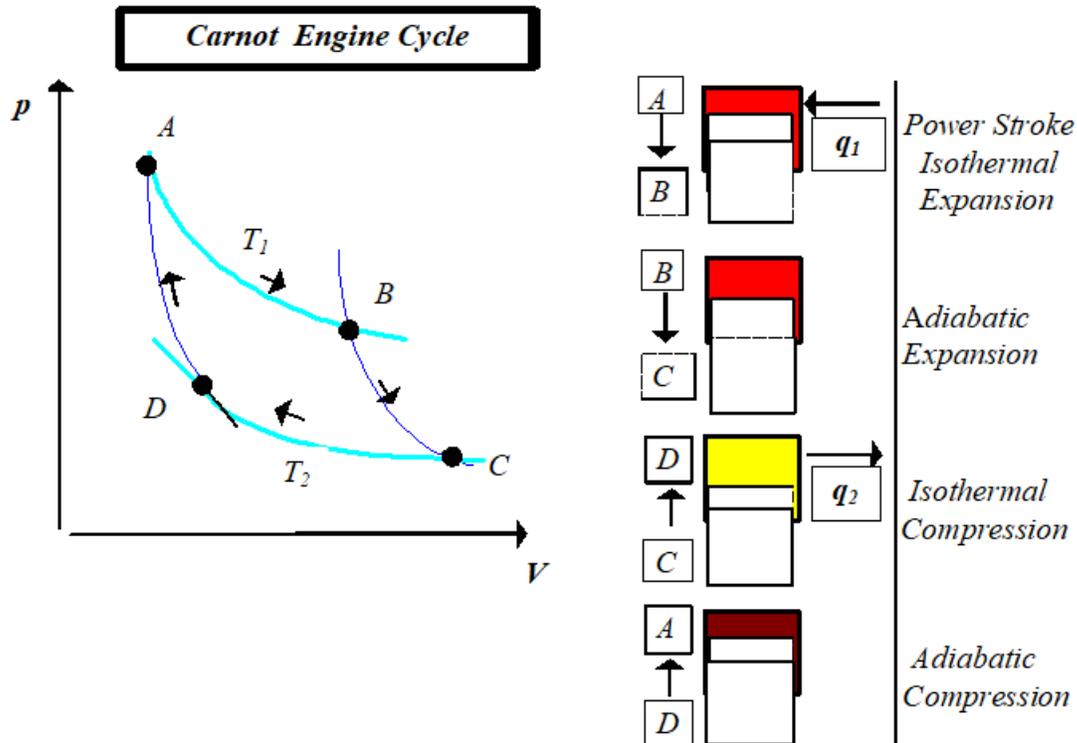
Consistent with these conclusions, the work required to compress a system is always larger, when it is irreversible than when it is reversible, since some of the irreversibly applied work is converted into heat, which is irradiated to the outside. In any reversible compression, the excess energy is also irradiated as heat. This can in principle never be prevented. However, in an irreversible process, even more energy is irradiated as heat, wasting some of the applied work.

Carnot Processes

Particularly instructive are cyclic, reversible Carnot processes, which form the basis of many modern 'high-tech' or 'low-tech' engines. Thermodynamic processes occurring in engines running with ***ideal gases*** have been considered by Carnot in 1824. Engines that run continuously in cycles can be graphically represented in pV or other diagrams. For ***ideal gases, cycles consisting of two isothermal and two adiabatic legs are termed Carnot cycles.*** It turns out that such Carnot engines are the most efficient ones that can be built. Practical engines have only a fraction of the theoretically possible Carnot efficiency.

The figure below attempts to illustrate the basic processes that drive a Carnot engine, e.g., an idealized internal-combustion motor with 4-stroke cylinders. It makes a connection between the

movement of a piston in an engine cylinder and the evolution of



the cylinder gas in a pV diagram. It pictures a pV diagram with two isotherms ($\Delta T = 0$) and two adiabats ($q = 0$).

For the isothermal expansion $A \rightarrow B$, the temperature remains constant ($T = T_1$) and, hence, the kinetic energy of the gas particles remains constant. Therefore, the loss of internal energy due to pressure-volume work done by the system during expansion has to be balanced by a **flow q of heat** energy from the surroundings into the system. In **adiabatic processes**, such as in the expansion $B \rightarrow C$ **no heat exchange** can take place. Here, the pV work done by the gas in the expansion decreases the internal energy of the gas and, hence, decreases the temperature ($T = T_2 < T_1$).

The right-hand column of the figure shows the sequence of "strokes" of a thermodynamic engine that is simulated by the pV diagram. A piston moves in a cylinder up and down, alternatingly expanding or compressing the gas in the volume in the cylinder head.

- At point A the power stroke begins. Here, the compressed gas expands and drives the piston down. The cylinder is in contact

with a "**heat source**" supplying heat $q_1 > 0$ to the gas keeping its temperature at $T = T_1$.

- At point B , the heat contact with the hot source is broken, while the gas is still expanding. Now, the expansion is adiabatic. No heat is supplied to the cylinder, and the gas cools off to $T_2 < T_1$. Expansion is continuing until point C is reached.

So far, the system has absorbed heat, but also performed work. This work is given by the area under the curve ABC ,

$$w_{mech} = -\int_A^C p(V)dV = -q_1 - \int_B^C p(V)dV \quad (12)$$

- From point C on, the piston moves upwards, compressing the gas again, at first isothermally. Since $T = T_2$, compressional heat $q_2 < 0$ has to be released by the system into the surroundings. It has to be in contact with a "**cold source (heat sink)**".
- This contact is broken at point D , from where on the compression is adiabatic, leading to an increase in temperature from T_2 back to T_1 . This completes the Carnot cycle, which can begin anew.

During the path from C to D , the system has produced heat, but consumed work, i.e., work had to be done on the system. This work is given by the area under the curve CDA ,

$$w_{mech} = -\int_C^A p(V)dV = -q_2 - \int_D^A p(V)dV \quad (13)$$

Generally, this compression work is smaller in magnitude than that performed by the system in expansion, because the **pressure is lower on the return path**. The difference in works done by and on the gas is the useful work that can be extracted from the engine.

The amount of net work performed by the engine is given by the area enclosed by the cyclic path in the figure. It is positive only because of the temporal contact with the hot and cold sources. Otherwise, the system would move up and down an adiabat, and no net work would be done. The net work that a Carnot engine can

do comes from the difference in heat energies absorbed and emitted: **Heat is absorbed at a high temperature**, and a **smaller amount is transferred to the cold sink at a lower temperature**. Obviously, not all of the absorbed heat can be converted into useful work, some must be dumped to the heat sink. This is the content of the

Second Law of Thermodynamics

*No process is possible, in which the **only** result is the absorption of heat from a reservoir and its **complete** conversion into work. (Kelvin)* (14)

This law notes a **surprising dissymmetry of nature**: Heat cannot be converted completely into work, but work can be converted completely into heat, e.g., by friction, a dissipative process. Effects such as **friction** make processes irreversible. It is interesting to investigate, in what fundamental sense reversible and irreversible processes differ.

A partial answer to this question can be obtained from considering the, obviously reversible, Carnot process involving an ideal gas. Such a cycle is illustrated in the figure on p.9. In the isothermal parts of the cycle, **absorbed heat**, q_1 , and **work done**, w_1 , are equal in magnitude. Hence, one can calculate the heat energy

$$q_1 = -w_1 = Nk_B T_1 \cdot \ln\left(\frac{V_B}{V_A}\right) > 0 \quad (15)$$

Similarly, one calculates the outflow of heat on the path $C \rightarrow D$,

$$q_2 = -w_3 = Nk_B T_2 \cdot \ln\left(\frac{V_D}{V_C}\right) < 0 \quad (16)$$

Here, the sign of q_2 is negative to indicate the heat *loss* suffered by the system.

Along the adiabatic legs of the cycle, no heat is exchanged with the surroundings. Furthermore, the work done by the engine during expansion, $B \rightarrow C$, is equal in magnitude to that required to

compress the gas again during the adiabatic leg **D** → **A**. The amount is simply the difference in internal energies,

$$w_2 = C_V \cdot (T_2 - T_1) = -w_4 < 0 \quad (17)$$

Here, $C_V = N(3/2)k_B$ is the **heat capacity** of an ideal gas of N structureless particles. For the balance of energies, then only the isothermal legs of the Carnot cycle are essential.

The flow of energy in and out of the system is reflected entirely in the balance of heat energies transferred. The **difference between the heat absorbed (q_1) and the heat emitted (q_2) is available for conversion into useful work**. In the Carnot cycle, this conversion is complete. One can calculate this useful work easily, once the volumes entering Eqs. (15) and (16) are known. In fact, one only needs a relation between the ratios (V_B/V_A) and (V_D/V_C). Such a relation exists for the adiabats (isentropes) connecting the corresponding points in the Carnot cycle. Since for **adiabatic expansion** of an ideal gas, $TV^{\gamma-1} = \text{const.}$ (with $\gamma = C_P/C_V > 1$), one has

$$T_1 \cdot V_B^{\gamma-1} = T_2 \cdot V_C^{\gamma-1} \quad (18)$$

and

$$T_1 \cdot V_A^{\gamma-1} = T_2 \cdot V_D^{\gamma-1} \quad (19)$$

Taking the ratios of the *l.h.s.* and the *r.h.s.* of Eqs. (18) and (19), one finally gets the volumes connected through an isothermal expansion simply scale:

$$V_B/V_A = V_D/V_C \quad (20)$$

Hence, the logarithmic factors in Eqs. (15) and (16) are equal, leading to

$$\frac{q_1}{T_1} = nR \cdot \ln\left(\frac{V_B}{V_A}\right) = nR \cdot \ln\left(\frac{V_D}{V_C}\right) = -\frac{q_2}{T_2} \quad (21)$$

In other words, some kind of a “reduced” heat, the heat normalized to the temperature, i.e., the quantity (q/T), seems to be a more natural variable than the heat flow q itself:

- *Equal amounts of $S := q/T$ are absorbed at the high temperature level (T_1) and dumped again at the lower temperature (T_2).*

This **extensive observable $S = (q/T)$** has the name **entropy**.

This name has not been chosen arbitrarily. The variable has a deep connection to the microscopic entropy discussed in another section.

Equation (21) is equivalent to the conclusion that the entropy of a system undergoing **any reversible** (Carnot) process is conserved:

$$\Delta S = \oint_{\text{rev}} dS = \oint_{\text{rev}} \frac{dq}{T} = 0 \quad (22)$$

Whatever gains or losses in entropy the system incurs along a given path is made up by the corresponding entropy losses and gains experienced by the surroundings, with which the system is in equilibrium. However, it is important to note that both, system and surroundings, separately conserve their respective entropies.

The line integral in Equ. (22) is taken over a closed path on the state hyper-plane representing an arbitrary reversible process. The fact that ΔS for the system is equal to zero along a closed path implies that **S is a state function (dS is an exact differential)**. **Along a specified path**, e.g., one where conveniently $T = \text{const.}$, **dq can be treated as an ordinary differential**. This makes it possible to evaluate any integrals of the type $\int_A^B dq$. In contrast, in evaluating an integral of the type $\int_A^B dS = \int_A^B dq/T$, it is not necessary to specify the path. All such integrals have exactly the same numerical value depending only on initial and final states, **A** and **B**, respectively.

One can now compare transitions **A** \rightarrow **B** associated with reversible or irreversible processes. As discussed in the context of Equ.

(11), the amount of heat exchanged is larger in a reversible than in an irreversible process. Therefore,

$$q_{irr} < q_{rev} = dS \cdot T \quad (23)$$

and one concludes that for any process involving such thermodynamic systems and states,

$$dS \geq dq/T \quad (24)$$

where dq is the **heat absorbed** ($dq > 0$) or **emitted** ($dq < 0$) **by the system in a process $A \rightarrow B$** , as measured in an experiment. T is the temperature of the surroundings. Equation (24) is valid including the signs of dS and dq .

The equal sign applies to reversible processes, as proven previously (cf. Equ. (23)). **This is another form of the Second Law.** In integral form, this **Second Law of Thermodynamics** reads

$$\Delta S_{A \rightarrow B} \geq \int_A^B \frac{dq}{T} \quad (25)$$

As discussed in the context of the Carnot cycle, entropy can be gained or lost by the system, if it can interact with its surroundings.

For **adiabatic** ($q = 0$) **changes $A \rightarrow B$, of an isolated system in its own intrinsic thermal equilibrium and $\Delta S_{A \rightarrow B} = 0$.**

The system plus its surroundings may be thought of forming a larger, isolated system that is only able to undergo adiabatic transitions. If this "Universe" is of the type of homogeneous systems considered here and if it is in thermal equilibrium, $\Delta S_{A \rightarrow B} = 0$ should be valid for any of its transitions. If on the other hand, this "Universe" is not in its intrinsic equilibrium, it can be partitioned into one or more smaller subsystems. In the simplest case, it could be divided into one subsystem (the entity previously called "system") and a larger remainder (previously called "surroundings"),

which are not (yet!) in thermal equilibrium. Any process involving this subsystem and its surroundings should then lead to an increase $\Delta S_{A \rightarrow B} > 0$ in entropy of the universe. In other words, (another way of stating the Second Law of Thermodynamics):

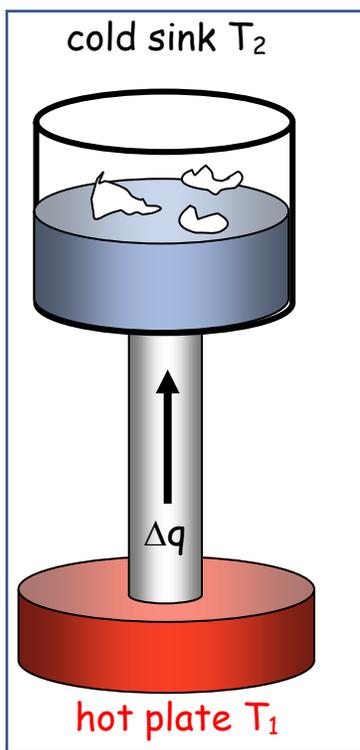
The combined entropy of a system and its surroundings never decreases!

For the Carnot process considered above, contributions to the integral in Equ. (25) only come from a path along an isotherm ($T = \text{const.}$). the differential **dq can be treated like an exact differential**. Adiabatic expansion and compression take place with $dq = 0$, hence the term **isentropes** for such processes.

The equal sign in Equ. (25), for which $\Delta S_{A \rightarrow B} = 0$, is valid only for a non-spontaneous, reversible process. Since for a reversible process involving an **isolated system at equilibrium**, $dS = 0$, the entropy **S must have an extremum**. Whether this extremum is a maximum or a minimum depends on higher-order variations of entropy with process variables. Maximum entropies are achieved when $d^2S = 0$ but $d^2S < 0$. To calculate these higher-order variations, the functional dependence of S on all process variables needs to be established. That is one of the tasks of the microscopic theory of statistical thermodynamics which makes a **connection between entropy, density of accessible system states, and probability**.

It turns out that **S is at a maximum** in the above reversible processes. Irreversible processes (transitions), the only ones that occur spontaneously, are driven into the direction of increasing entropy, **$dS > 0$** , with thermal equilibrium being the final stage of a sequence of such processes. In the following, the entropy changes are calculated for a few examples.

As stated above, irreversible processes encounter or, rather, are driven by entropy gains. For example, **frictional work** ΔW_{fr} on



a system at temperature T is irreversibly dissipated, with $\Delta S_{A \rightarrow B} = \Delta W_{fr}/T > 0$.

Another, familiar example for a dissipative process is **heat conduction**, illustrated on the left for a system consisting of a hot-plate at T_1 , a cold sink at $T_2 < T_1$, filled with a water-ice mix, and a thermal conductor connecting separate parts of the system. In such a heat conduction process, an amount Δq of heat energy is transferred from a source at high temperature T_1 to a sink at a lower temperature T_2 . Define state **A** as the initial state with a significant internal temperature gradient and state **B** as another state, where a small amount Δq of heat has been transferred to the cold part of the system. If neither temperature T_1 or T_2 have yet changed much in the process, the entropy

change is calculated easily. It increases by

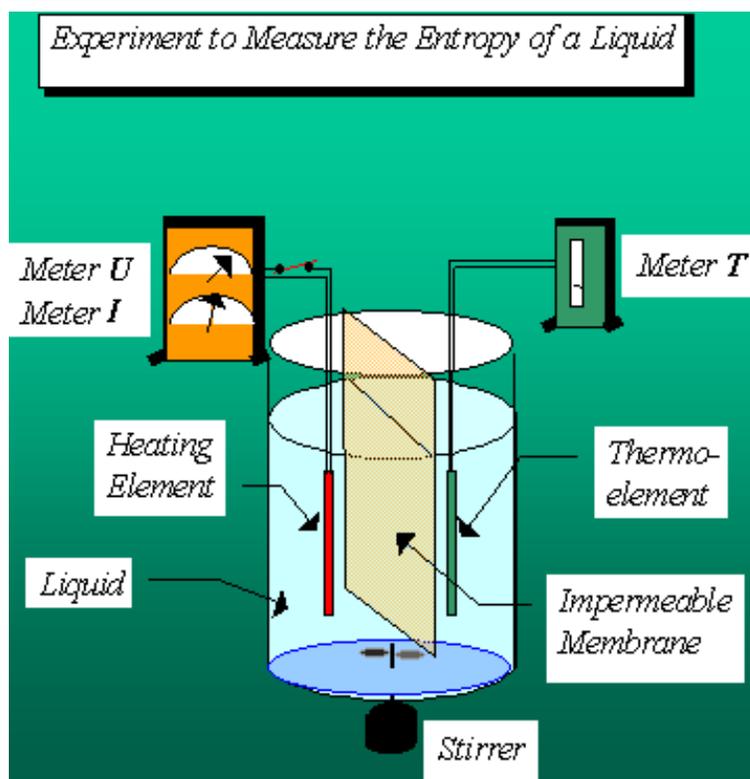
$$\Delta S_{A \rightarrow B} \geq (\Delta q/T_2) - (\Delta q/T_1) > 0 \quad (26)$$

It is straightforward to formulate the problem more rigorously in differential calculus. This familiar process has an obviously **irreversible character**.

In general, the entropy of a substance can be measured by transferring specified amounts Δq_i of heat energy to a sample and measuring the resulting temperature gains $\Delta T_i = (T_i - T_{i-1})$:

$$S(T = T_N) = S(T_0) + \sum_{i=1}^N \frac{\Delta q_i}{T_{i-1} + \Delta T_i / 2} \quad (27)$$

A setup such as shown in the figure on p. 17 is typically used to determine the entropy of liquids. Here, an electric heating element is used to introduce slowly well known amounts of heat into the liquid. The rise of the temperature is monitored and recorded using a modern thermo-element as thermometer.



The thermometer is shielded from the heating element, and the liquid is well stirred during the entire experiment. For gases, one can design a similar experimental setup.

Results of entropy measurements are collected in the table for different representative materials at room temperature. As seen from this table, materials in crystalline form have the

lowest entropy, just a few J/K per mole of substance. Water and other liquids have higher entropy values, and gases have the highest entropies. It is interesting that the highly structured Diamond phase of carbon has lower entropy than its less ordered graphite form.

Substance	Entropy (298 K, 1at)
Diamond	$2.4 \text{ J K}^{-1}\text{mol}^{-1}$
Carbon	$5.74 \text{ J K}^{-1}\text{mol}^{-1}$
Water	$69.9 \text{ J K}^{-1}\text{mol}^{-1}$
Alcohol	$160.7 \text{ J K}^{-1}\text{mol}^{-1}$
Oxygen (gas)	$205.0 \text{ J K}^{-1}\text{mol}^{-1}$
CO_2	$213.6 \text{ J K}^{-1}\text{mol}^{-1}$

One also observes higher entropies for gases with more complex structure than for simpler molecules that have fewer degrees of freedom. It is a general trend that the entropy increases with the number of degrees of freedom and with temperature.

Transitions in phase of a pure substance are very obvious situations in which the number of degrees of freedom of the substance changes. For example, it requires absorption of a certain amount of "latent" heat to convert a solid into a liquid and a liquid into a vapor (gas). As will be discussed in detail elsewhere, each phase change occurs in the vicinity of a characteristic temperature of the substance. Water vaporizes at the temperature of $T_{vap} = 373\text{ K}$ at normal pressure. It then requires heat transfer in the amount of $\Delta H_{vap} = 40.7\text{ kJ}$ per mole to actually turn into vapor. The associated entropy increase in this phase transition can be measured to,

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}} \quad (28)$$

In the case of water, this entropy gain amounts to $\Delta S_{vap} = 109.0\text{ J/K}$ per mole. Similar relations appear to be valid for solid-liquid phase transitions, suggesting that the concepts developed here in the context of gases have much more general relevance.

At low temperatures, all substances have very small entropies, consistent with the following formulation of the

3rd Law of Thermodynamics

$$S(T=0) = 0 \quad (29)$$

As will be seen in the discussion of the microscopic origin of this law, strictly Equ. (29) is only correct to a good approximation. In the following, the entropy is calculated for gases and processes connecting different thermodynamic states. One important task consists in deriving an expression for the entropy in terms of other state variables, variables that can perhaps be measured more easily than the entropy.