Preliminary version!

EXERGETICS

by

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EXERGY
ECOLOGY
DEMOCRACY

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Foreword

This is a first attempt to a guide book into the concept of exergy and its applications. The book is direct towards people with a basic skill in science and engineering. And I expect the reader to have strong patience with all mistakes and other imperfections.

The purpose is to give an understanding of the concept of exergy and its availability, enough for you to carry out exergy analysis within your work.

The size of the material is equivalent to about 200 hours study at graduate level. Since a lot need to be improved regarding the quality of the material I ask for your comments and suggestions. All proposals to improve the readers ability to understand the concept of exergy are highly appreciated.

For those who wants to put exergy into a social context I recommend the book *Time to turn* by Bo Lundberg, 1996, ISBN 91-26-94842-7. (A good book also for those who are not trained in science.) From my homepage: http://exergy.se/, you can also find more about exergy.

The present situation for mankind is very serious because of increasing lack of natural resources and increasing destruction of our living nature. Thus I recommend a better understanding of our situation and possibilities, and thus I regard an understanding of the concept of exergy as a nessessary part.

Finally, I am deeply grateful for the kind support of Dr. Darwish M. K. Al Gobaisi at the International Centre for Water and Energy Systems in Abu Dhabi, who have made this work possible. I also want to thank Mei Gong for preparing the manuscript.

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CONTENT

NOMENCLATURE

Symbol	Quantity [Unit according to the SI-systemet]
A	Area [m^2]
a, A	Specific free energy (= Helmholtz' function) [J/kg, Wh/kg] and free energy [J, Wh], $A = U - TS$. Sometimes the symbol F is also used.
COP	Coefficient of Peformance, for heat pumps: produced heat (energy) divided by used work (usually electricity) and for refrigerators: removed heat (energy) divided by used work (usually electricity) [no unit]
c	Velocity of light in vacuum ≈ 2.997925×10^8 m/s
c, C	Specific heat capacity [J/kg K] or heat capacity [J/K], gives the amount of heat (internal energy) which per unit mass is captured in a body as the temperature increases by one degree Celsius, i. e. one Kelvin
e, E	Specific exergy [J/kg, Wh/kg] or exergy, availability or available work [J, Wh]
E/Q	Exergy factor [no unit, %]
F	Power [N]
g	Constant of gravity ≈ 9.81 [m/s^2]
g, G	Specific free enthalpy (= Gibbs' function) [J/kg, Wh/kg] and free enthalpy [J, Wh], $G = H - TS$.
h	Hight [m]
h, H	Specific enthalpy [J/kg, Wh/kg] or enthalpy, $H = U + pV$ [J, Wh]. In German literature often signed by i and I.
H_0	Enthalpy for systems at environmental state, i.e. in equlibrium with the environment
I	Electric current [A]
m	Mass [kg]
n_i	Number of mole of substance i [mol]
n_{i0}	Number of mole of substance i for a systemet at equilibrium state [mol]
P	Pressure [Pa]
P_0	Environment pressure [Pa, bar] here 101.3 kPa = 1.013 bar
q, Q	Specific heat [J/kg, Wh/kg] och heat [J, Wh]
R	Molar gas constant ≈ 8.314 [J/mol K], state equation for ideal gases: $pV = nRT$
S	Entropy, gives degree of disorder, the following relation holds (2nd Law): $dS \geq \delta Q/T$ [J/K]
S	Distance [m]
S_0	Entropy of a system at environmental state [J/K]
s_i	Specific entropy, entropy per unit mass, of substance i, [J/kg K]
t	Time [s, h], 1yr = 8760 h = 31,536,000 s
T	Temperature [K] (0 K = –273.15˚C)
T_0	Environment temperature [K] usually 20˚C = 293.15 K
U	Electric potential [V]
u, U	Specific internal energy [J/kg, Wh/kg] or internal energy [J, Wh]
U	Overall heat transfer coefficient, gives the heat transfer rate per unit area of a substance, when the temperature difference is 1˚C, i.e. 1 K [W/m^2 K].
v	Velocity [m/s]
v, V	Specific volume [m^3/kg] and volume [m^3]
W	Work [J, Wh], by definition equal to exergy

x_i	Molar fraction of substance *i* [no unit]
Z	Hight [m]
μ_i	Chemical potential of substance *i* [J/mol], often equal to Gibbs function per mole
μ_{i0}	Chemial potential of substance *i* in environmetal state [J/mol]
η_{en}	Energy efficiency = Q_{out}/Q_{in} where Q states used energy [no unit or %]
η_{ex}	Exergy efficiency = E_{out}/E_{in} where E states used exergy [no unit or %]
ρ	Density [kg/m^3]
θ	Temperature in degrees Celsius, see T above [˚C]

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i	Indicates a substance, i.e. element or summation index
0	Indicates environmental state

INTRODUCTION

This guide-book will introduce the exergy concept into engineering work. Especially fundamental concepts of thermodynamics are treated to understand and be able to apply the exergy concept. It is offered to engineers of different background and experience. Thus, some parts might be well-known for some readers, but new for others. If you find yourself well aware with what is treated — go ahead but make sure you understand the content being treated.

In the text I use the following hints:

R: Read carefully through the indicated text and solve treated examples or problems.
L: Look breifly through the text indicated to be aware of what is treated.
S: Solve indicated problems.
Q: Question to answer, maybe a problem to calculate.

Indicated literature are written in short accordingly:

Exergy: *Exergy – a Useful Concept*, Wall, G., Ph.D. Thesis (1986).

The following complementary paper is also recommended:

> "Exergy, Ecology and Democracy — Concepts of a Vital Society", Wall, G., *Energy Systems and Ecology*, Int. Conf. Cracow, Poland, July 5-9, 1993, pp. 111-121.

These documents are found on the Internet: http://exergy.se/.

There are also a number of excellent textbooks available, however none of them includes the statistical treatment of entropy and the link to information theory, being carried out in this material. This is a selection of most of them:

Ahern, J. E., *The Exergy Method of Energy Systems Analysis*, Wiley (1980)
Barclay, F. J., *Combined Power and Process – an Exergy Approach*, MEP (1995)
Bejan, A., Tsatsaronis, G., Moran, M., *Thermal Design and Optimization*, Wiley (1996)
Bejan, A. *Advanced Engineering Thermodynamics* (1988)
Brodyansky, V. M., Sorin, M. V., Le Goff, P., *The Efficiency of Industrial Processes: Exergy Analysis and Optimization*, Elsevier (1994)
Edgerton, R. H., *Available Energy and Environmental Economics*, Lexington (1982)
Fratzscher, W., Brodjanskij, V. M., Michalek, K., *Exergie – Theorie und Anwendung*, VEB, Springer (1986)
Kotas, T. J., *The exergy Method of Thermal Plant Analysis*, Butterwoods (1985)
Moran, M. J., *Availability Analysis – A Guide to Efficient Energy Use*, ASME (1989)
Szargut, J., Morris, D. R., and Steward, F. R., *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Springer (1988)
Yantovskii, E. I., *Energy and Exergy Currents*, Nova (1994)

Moderna textbooks in thermodynamics also more often treats the exergy concept. Below are some examples:

Van Wylen, G. J. and Sonntag, R. E., *Fundamentals of Classical Thermodynamics*, Wiley (1985)
Moran, M. J., Shapiro, H. N., Fundamentals of Engineering Thermodynamics, Wiley (1995)

Hints: Usually the theory becomes clearer after you have worked through some exercises. Do not become frustrated if you do not understand everything immediately. Also Be prepared to repeat some sections more than one time. If you get stuck, sometimes it might be better to read another section to come back later with a new approach. If nothing else helps you should of course ask for help. You are always welcome to ask me through my email address: gw@exergy.se.

But: this self-instruction guide needs to be improved in many regards, e.g. poor language, misspelling and misprinting. Please, let me know your corrections or comments to improve the material!

When: you have worked yourself through this guide, then you are prepared to study done exergy analysis of real processes to later be able to carry out your own exergy analysis.

Good Luck!

FUNDAMENTAL CONCEPTS

Energy vs. Exergy
Energy vs. Exergy Power
Energy vs. Exergy Efficiency

Energy: The word energy is derived from the Greek: *en* (in or internal) and *ergon* (force or work). The concept was first formulated in the middle of the 19th century by lord Kelvin and Joule, after many scientists (Benjamin, Thomson, Carnot, Mayer and others) for decades had tried to find relations between mechanical work, power (horse power) and heat.

Energy can be defined as follows:

$$\boxed{\text{Energy = motion}^1\text{ or ability of motion}}$$

Motion might be a train running through the landscape or heat, i.e. moving molecules in a body of temperature above 0 K. At 0 K or -273.15˚C all motion is assumed to stop.

We differ between different kind of energy, such as:

Potential energy: A body of mass m [kg] at the height h [m] in a gravitational field with gravitational constant g [m/s^2], i.e. weight mg [N] has the potential energy

$$W_{\text{potential}} = mgh.$$

Kinetic energy: A body of mass m and velocity v [m/s] has the kinetic energy

$$W_{\text{kinetic}} = \frac{1}{2}mv^2 .$$

Pressure energy or external energy is energy stored as high pressure. A body with pressure P and volume V represents the pressure energy (cf. work below)

$$W_{\text{pressure}} = PV.$$

Internal energy U (molecular kinetic energy) is energy stored in a body usually as increased temperature. A body of mass m, specific heat c [J/K kg] and increased temperature T is storing the internal energy

$$U = mcT.$$

Electrical energy: just as a weight has potential energy in a gravitational field a charged partical has potential energy in a electrical field. An electric current of intensity I [A] and electric potential U [V] during time t [s] is equivalent to the electric energy

$$W_{\text{electric}} = UIt.$$

Chemical energy is energy stored in substances as binding energy between its components (atoms) and may be released as kinetic energy of the products at a chemical reaction. Values of some substances are listed below

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[1] Motion in a very general meaning, e.g. the molecular motion in a warm body.

Substance	g_{chemical} [MJ/kg]	g_{hemical} [kWh/kg]
Coal	32	9
Oil	42	12
Natural gas	50	14
Petrol	44	12
Dynamite	4	1
Firewood	14	4
Hydrogen	124	34

Nuclear energy is in the same way stored energy as binding energy between its internal components (nuclear particles) and may also be released as kinetic energy of the final products at a nuclear reaction (fission or fusion). This energy is actually stored as mass, i.e. we have the famous expression $E = mc^2$ which will be discussed later. Values of some substances are listed below

Substance	u_{nuclear} [MJ/kg]	u_{nuclear} [kWh/kg]
Uranium ore	30	8
Uranium (Light Water Reactor)	1.9×10^5	5.3×10^4
Uran (Breeder Reactor)	1.3×10^7	3.6×10^6
Deuterium (Fusion)	3.5×10^8	9.7×10^7
Mass ($E = mc^2$)	9×10^{10}	2.5×10^{10}

The following forms of energy are more than the other related to a process, that something happens, i.e. an energy conversion.

Work – if a force F [N] acts over the distance S [m] this is equal to the work:

$$W = FS.$$

Electromagnetic radiation as *light* and *heat radiation* emitted from a body of area A [m^2] and temperature T [K] during time t [s] gives the energy (“Black body radiation”)

$$Q_{\text{electromagnetic}} = \sigma T^4 At$$

where $\sigma \approx 5.67\times10^{-8}$ [W/m^{2}K^4] is usually refered to as the Stefan-Boltzmann’s constant.

Heat – can be transfered to or from a body by changing the temperature, i.e. the internal energy

$$Q_{\text{heat}} = \Delta U = U_2 - U_1 = mc(T_2 - T_1) = mc\Delta T.$$

Energy and mass

From the theory of relativity we know that energy and mass are equal (cf. nuclear energy above)

$$E = mc^2.$$

Einstein showed that the mass of a body depends on its speed according to

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$$

where c is the speed of light in vacuum about 3×10^8 m/s. Thus, a body has a larger mass when it is in motion than at rest. (We also note that the speed can never exceed the speed of light.) The kinetic energy of a body with rest mass m_0 and speed v becomes

$$E_{kin} = mc^2 m_0 c^2 = mc^2\left(1-\sqrt{1-\frac{v^2}{c^2}}\right) \approx m_0 c^2\left(1-\left(1-\frac{v^2}{2c^2}\right)\right) = \frac{m_0 v^2}{2}$$

The energy forms we will mainly use are *heat*, *light* and *mechanical work*. Most of the others may be regarded as subsidiary forms. The transformation between different forms of energy are called *conversion*.

Everything that happens involves conversion of energy

Whenever something happens energy is converted from one form to an other, i.e. an energy conversion. Everything that can be described as a change in time involves an energy conversion, from a supernova explosion to a thought of mind. The amount of energy being converted may be large or small, but without exception energy is converted in everything that happens.

Condensing power plants are main energy converters in the society of fossile or fissile fules, i.e. chemical or nuclear fuels into heat and electricity. The common principal in both cases is to boil water to get steam, which through pipes is forced to move in one direction, that can turn a turbine connected to an electric generator in order to produce electricity.

The SI unit of energy is J (Joule), Wh, kcal, eV. (1 eV = 0.16×10^{-18} J)

Some SI energy units:

2500 kcal = $2500\times1.16\times10^{-3}$ kWh = 2.9 kWh = 10.4 MJ;

1 kWh = 3.6×10^3 kJ = 3.6×10^6J; 1 TWh = 3.6 PJ

1 J = 1 Nm = 1 Ws

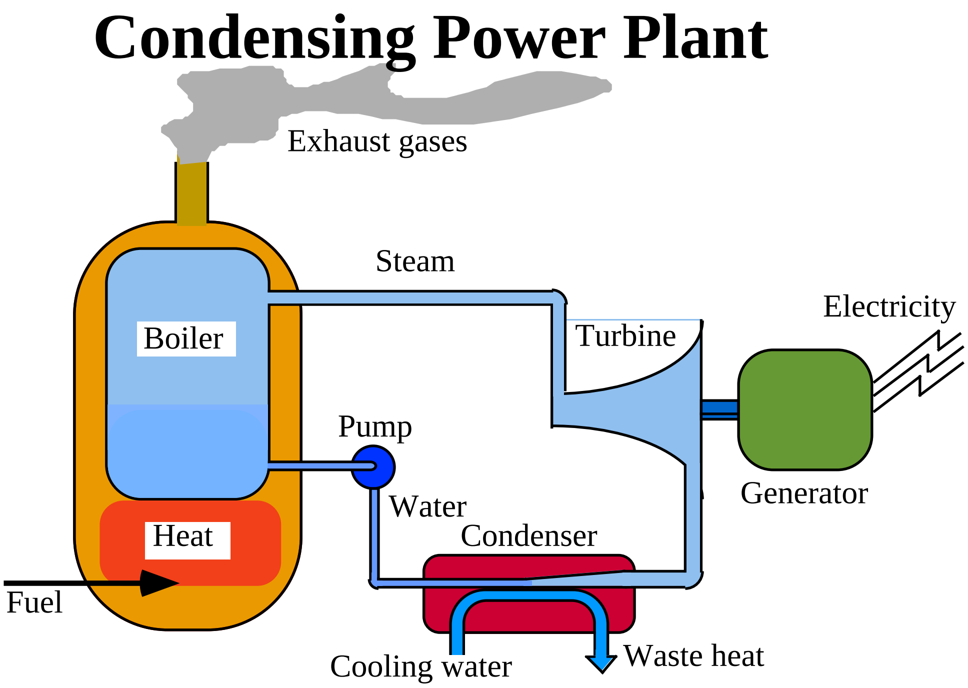

Fig. 1 The principle of condensing power plants is to boil water.

Prefix of multiple units

Factor	Prefix	Notation
10^{24}	yotta	Y
10^{21}	zetta	Z
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deca	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	µ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

Definition of 1 cal (between 1 – 100˚C approximately)

$$\boxed{\begin{array}{c}\text{1 cal heats 1 g water 1K}\\ \text{1 kcal heats 1 kg water 1K}\\ \text{1.16 Wh heats 1 kg water 1K}\\ \text{4.2 kJ heats 1 kg water 1K}\end{array}}$$

Exercise: How much energy is needed to make 1 kg of water at 5˚C to reach boiling temperature? Answer in kWh.

Solution:

$$\boxed{Q = \Delta U(5^\circ\text{C} \rightarrow 100^\circ\text{C}) = mc\Delta T}$$[2]

where

Q = heat added
U = internal energy
m = mass
c = specific heat [J/kg K]

$\theta^\circ\text{C} \Leftrightarrow T + 273.15\ \text{K}$
$\Delta\theta^\circ\text{C} \Leftrightarrow \Delta T\ \text{K}$

here: m = 1 kg
c = 4.2 kJ/kg K
$\Delta T = \Delta\theta = 100^\circ\text{C} - 5^\circ\text{C} = 95^\circ\text{C} \mathrel{\hat{=}} 95\ \text{K}$

$$Q = \Delta U = 1\times 4.2\times 95\left[\frac{\text{kg}\times\text{kJ}\times\text{K}}{\text{kg}\times\text{K}} = \text{kJ}\right] =$$

$$= 400\ \text{kJ} = 400\times 10^{3}\ \text{J} = 400\times 10^{3}\times 0.28\times 10^{-6}\ \text{kWh} = 0.11\ \text{kWh}$$

Answer: 0.11 kWh (1 J = $0.2777\ldots\times 10^{-3}$ Wh = $0.2777\ldots\times 10^{-3}\times 3600$ Ws = 1 Ws)

Energy power[3]**:**

$$\boxed{\text{Energy power} = \frac{\text{Energy}}{\text{Time}}}$$

Units for power are hp, W, J/s

1 hp = 735.5 W
1 W = 1 J/s

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[2] This will be treated further in the Chapter on thermodynamics below.

[3] As we soon will see it is important to distinguish between energy and exergy, which then is valid also for energy and exergy power.

Definition of 1 hp: lifts 75 kg 1 m in 1 second, i.e. 75×9.80665×1/1≈735.5 W [kg×m/s^2×m/s = Nm/s = J/s = W]

Exercise: What energy power is at least needed on a hot plate if 1 kg of water will start to boil in 5 minutes?

Solution: Energy power = $\dfrac{0.11}{\frac{5}{60}} = \dfrac{0.11\times 60}{5}$ = 1.32 [kWh/h = kW]

Q: How long time would it at least take with a 500 Watt plate?

Energy efficiency[4]

$$\boxed{\text{Energy efficiency} = \frac{\text{Utilized energy}}{\text{Used energy}}}$$

N.B.: Efficiency must always refer to a **system** or a **process**!

Exercise: What is the energy efficiency if we must use 1.5 kW for 7 minutes in the previous exercise?

Solution: The energy efficiency becomes $= \dfrac{0.11[\text{kWh}]}{1.5\times\frac{7}{60}[\text{kWh}]} = \dfrac{0.11\times 60}{1.5\times 7} \approx 0.63 = 63\%$.

Q: Try your own stove and pot. What energy efficiency do you get?

Units

Used units refer to the metric system. Please, get used to them!

Exercise: A. What is the energy power of a hot water-tap if the water is heated from 5˚C to 70˚C? The flow rate is 0.2 kg/s.
B. What current does this corresponds to at a voltage of 220 V?

Solution: A.

$$\begin{aligned} Q &= \Delta U = mc\Delta T \qquad m = 1 \text{ kg takes the time } 1/0.2 \text{ s} = 5 \text{ s} \\ \Delta T &= T_1 - T_2 = (70-5)^\circ\text{C} \\ c_{\text{Water}} &= 1 \text{ kcal/kg}^\circ\text{C} \approx 1.16 \text{ Wh/kg}^\circ\text{C} \approx 4.19 \text{ kJ/kg}^\circ\text{C} \end{aligned}$$

$$P = \frac{Q}{t} = \frac{mc\Delta T}{t}$$

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[4] Analogously, as for power we also distinguish between energy and exergy efficiency.

$$P = \frac{1 \times 1.16 \times (70 - 5)}{\frac{5}{3600}} = 54288 \approx 54 \times 10^{3} \left[\frac{\text{kg} \times \text{Wh} / (\text{kg}^\circ\text{C}) \times {}^\circ\text{C}}{\text{hr}} = \text{W} \right]$$

or if you count in SI units *mc* in J/˚C

$$P = \frac{1 \times 4.19 \times (70 - 5)}{5} \approx 54 \left[\frac{\text{kg} \times \text{kJ} \times {}^\circ\text{C}}{\text{kg} \times {}^\circ\text{C} \times \text{s}} = \text{kJ/ s} = \text{kW} \right]$$

Q: B. Try yourself by using the relation $P = UI$ (electric power=voltage×current).

Q: What is your conclusion from this?

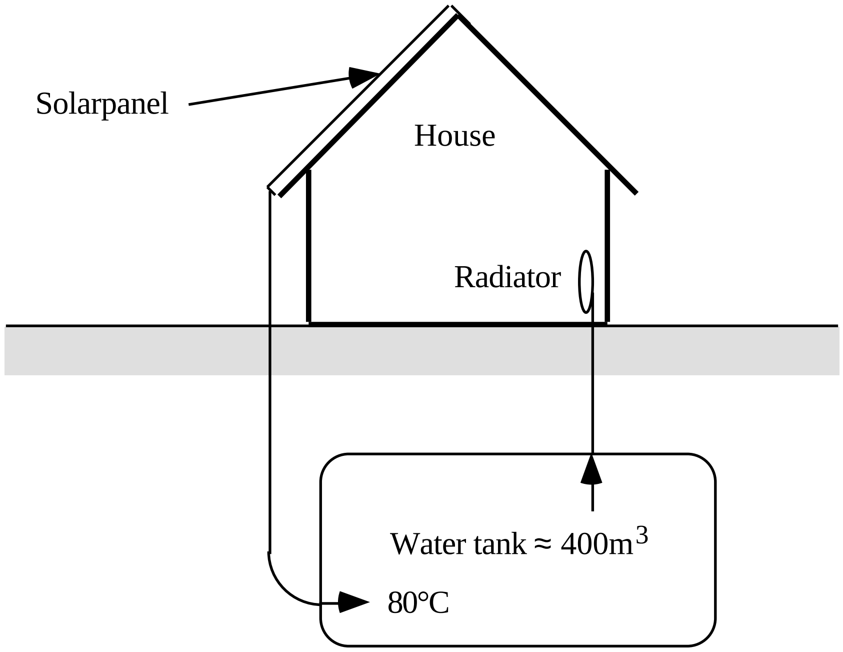
Exercise: Estimate the size of a water tank to support the heating needs of a single family dwelling, about 20,000 kWh/yr? The water temperature is 80˚C?
Assume the temperture is changed from 80 to 40˚C?

Solution: $Q = \Delta U = mc\Delta T = 20000 \times 10^{3}$ Wh

$$\text{Thus: } m = \frac{Q}{c\Delta T} \approx \frac{20000 \times 10^{3}}{1.16 \times (80 - 40)} = 431034\text{kg} \approx 431\text{ton} \approx 431\text{m}^{3}$$

Proposal of practical arrangement

Energy storage in a water tank



The tank is charged during the summer with 20 000 kWh solar energy and reach the temperature 80˚C by the winter season.

During the winter the tank is discharged 20 000 kWh and the temperature decrease to 40˚C by the summer. However, this proposal is far to simple to be economical. Better options are to store the heat directly in the ground (clay or rock).

Q: Consider the relation between heat contant and heat losses. What does this imply?

Additional illustrations of energy conversions

Thus, different forms of energy are convertible into each other. When you lift a stone you perform mechanical work, converting into increased potential energy of the stone. If the stone is dropped this converts to kinetic energy in the motion, which later converts to heat as it reaches the ground.

The combustion engine is an engineering application of energy conversions. The stored chemical energy in the fuel is released through combustion and it is converted to heat. The heat implies an increased pressure of the enclosed gas in the cylinder which forces the piston to move, i.e. the volume expands. Through the connecting rod and the crankshaft the linear motion is converted to a circular motion, i.e. rotation of the shaft. We have a torque, that may turns the wheels of a car, thus generating kinetic energy again. If the engine instead operates a pump the mechanical work may be converted to pressure energy by decreasing the volume of an enclosed gas, to potential energy by lifting a liquid to a higher level or to kinetic energy by increasing the flow rate.

In a hydro power plant the potential energy of water is converted to a torque of the turbine shaft, that is connected to an electric generator, where mechanical energy is converted to electrical energy. In an electric motor the electrical energy is converted back to a torque, that might operate a fan which may generate potential, kinetic and pressure energy in a gas.

As we see a certain form of energy may appear in many different parts of a process. Potential energy is for instance the input in a hydro power plant but might be the output in a pumping process. Electrical energy has the opposite position in these two cases.

But different forms of energy has different ability to convert into each other. Heat and electricity are the most familiar forms of energy used in daily life. Of these electrical energy may almost without exceptions be converted to any other form of energy without reducing the amount of energy. This makes electricity a high ranked form of energy, with high availability. Heat or rather internal energy at high temperature can only partly be converted to other forms of energy, e.g. mechanical energy. The rest of the energy is converted to heat at lower temperature. If this lower temperature is close to ambient, e.g. 30-40˚C it is hardly usable at all and must be low ranked. However, this low ranked heat might be useful for space heating, but when the temperature reaches ambient it is useless. The usefulness or availability of heat or internal energy is strongly depending on the temperature of the heat and the environment.

In a furnace we convert the highly ranked chemical energy in the fuel into relatively high ranked internal energy in the flame (high temperature), which is then converted into low ranked internal energy in the radiators (30-50˚C). To understand these kind of processes exergy is a very useful concept.

Exergy (*ex* = outer, *ergos* = work, cf. **energy**: *en* = internal)

The word exergy is derived from the Greek *ex* (out or outer) and *ergon* (force or work). The concept was first noticed in 1824 by Carnot in the relation of heat and work.

Exergy can be defined as:

Exergy = work (ordered motion) or
ability to do work (ordered motion)

Exercise: Compare the following two energy conversions. 1 kJ converted to 1 kg of water as:
(1) Internal energy, i.e. disordered motion of the water molecules.
(2) Kinetic energy, i.e. ordered motion of the water molecules.

Solution: 1. $\Delta U = mc\Delta T \quad \Delta T = \frac{\Delta U}{mc} = \frac{1}{1\times 4.2} \approx 0.24^\circ\mathrm{C} \left[\frac{\mathrm{kJ}}{\mathrm{kg}\times \mathrm{kJ}/(\mathrm{kg}^\circ\mathrm{C})} = {}^\circ\mathrm{C}\right]$, i.e. a hardly measurable change of the temperature.

2. $E_{kin} = \frac{mv^2}{2} \quad v = \sqrt{\frac{2E_{kin}}{m}} = \sqrt{\frac{2\times 1\times 10^3}{1}} \approx 44.7\,\mathrm{m/s} \approx 161\,\mathrm{km/h}$, i.e. a very extensive change of the speed.

What about units?: $\left[\sqrt{\frac{\mathrm{J}}{\mathrm{kg}}} = \sqrt{\frac{\mathrm{Nm}}{\mathrm{kg}}} = \sqrt{\frac{(\mathrm{kg}\times\mathrm{m/s^2})\mathrm{m}}{\mathrm{kg}}} = \mathrm{m/s}\right]$

Q: What happens if we try to make the processes above in the oppsite directions?

It is also important to distinguish between energy or exergy power and energy or exergy efficiency.

Exergy power:

$$\text{Exergy power} = \frac{\text{Exergy}}{\text{Time}}$$

Exergy efficiency

$$\text{Exergy efficiency} = \frac{\text{Utilized exergy}}{\text{Used exergy}}$$

Later we will see that everything that happens implies exergy consumption – the consumption of exergy is actually the driving force of everything that happens.

Everything that happens involves consumption of exergy

To remember

Energy = motion or ability of motion.

Everything that happens involves conversion of energy.

$$\text{Energy power} = \frac{\text{Energy}}{\text{Time}}$$

$$\text{Energy efficiency} = \frac{\text{Utilized energy}}{\text{Used energy}}$$

Exergy = work (ordered motion) or ability to do work (ordered motion)

$$\text{Exergy power} = \frac{\text{Exergy}}{\text{Time}}$$

$$\text{Exergy efficiency} = \frac{\text{Utilized exergy}}{\text{Used exergy}}$$

Everything that happens involves consumption of exergy

We will now introduce some thermodynamics and later come back to exergy.

THERMODYNAMICS (THERMOSTATICS)

The history of thermodynamics might be summerized accordingly:

1769, James Watt built the first steam engine, thus starting the development for heat engines. A theory of heat was needed to improve their performance.

1824, Sadi Carnot claimed that the efficiency of a heat engine relates to temperature, the so called Carnot factor.

1834, Clapeyron introduced the pressure-volume diagram to calculate work.

1842, Robert Meyer concluded the mechanical heat equivalence, which led to the definition of the 1st law of thermodynamics.

1845, Joule developed the kinetic theroy of gas, which explained heat as the result of molecular motions.

1850 and -51, lord Kelvin and Clausius formulated the 2nd law of thermodynamics, Kelvin also intorduced the scale of temperature.

1865, Clausius introduced the concept of entropy, which was an important aid to the theory of thermodynamics.

1872, Belpaire introduced the temperature-entropy diagram.

1873-78, Gibbs presented his phase rule, which increased the usability of thermodynamics into new areas. Gibbs also established a bas for the exergy concept.

1877, Boltzmann suggested that probabilty or order is linked to entropy.

1904, Mollier introduced the enthalpy-entropy diagram.

1906, Nernst formulats the 3rd law of thermodynamics.

1911, Planck generelised the 3rd law such that entropy and specific heat are zero at absolute zero temperature for a chemically homogenous body of limit density.

1905 and -15, Einstein published his works on the relation between energy and mass and the how the mass was related to its speed. Thus, thermodynamics was linked to the moderna physics, theory of athoms and quantum mechanics.

1948, Shannon verified the relation between entropy and probability, which linked thermodynamics to information theory through the statistical mechanics.

1953, Rant proposed the word exergy.

Thermodynamics may be regarded as the theory of energy and its behavior.

A system in thermodynamic equilibrium may be described by state variables. In thermodynamics the three state variables usually are pressure P, volume V and temperature T.

Temperature, heat and internal energy

Temperature may be described as disordered motion of the substances smallest parts – higher temperature implies faster motions. We distinguish between objects which we call hot or cold. A hot object we say has a high temperature and a cold object has a low temperature, but what we identify is based on that we touch the object, establish a contact. Steel we experience as colder than tree even though they have the same temperature. The reason is the difference in heat conductivity. Steel transfer heat more efficient than tree. The temperature should be regarded as a quality of heat, the intensity of the molecular motions, to be distinguished from the quantity of heat. This sometimes makes it difficult in practice to differentiate between temperature and heat content, which also historically was a problem.

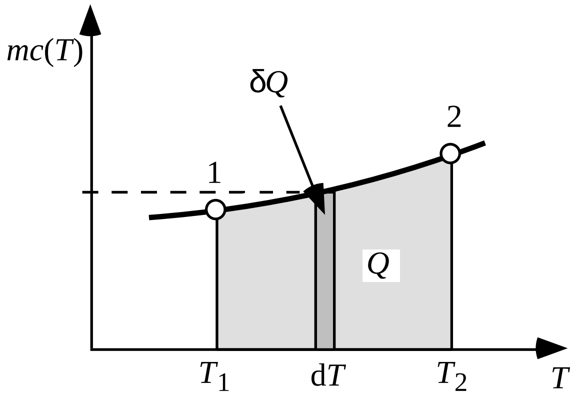
Q: Why can you walk barefooted on live coal without burning?

Thermodynamics is built up of a number of laws, which also defines a number of concepts. The zeroth law, which was defined after the first law, concerns the concept of temperature:

> Two systems in equilibrium with each other have the same temperature

Thus temperature of a system has meaning only if the system is in equilibrium. Temperature is a concept for the whole system. Thus, it is meaningless to talk about the temperature of a glass of lukewarm water where you just put a piece of ice.

The concepts of heat and heat content *Q* states the energy being transported between systems. Thus, it is principally wrong to say that a system contains heat, instead it contains energy. This energy, which is the sum of the containing particals’ kinetic and potential energies, we call internal energy *U*, or sometimes it is called thermal energy. One problem of understandng the concept of heat is that we can not experiance heat, instead what we experience when we feel “heat” is heat transfer.



Assume we add the heat *Q*, to increase the temperture from θ_1 (T_1) to θ_2 (T_2) of a substance of mass *m*, and specific heat *c*, i.e. we change the internal energy from U_1 till U_2. We have:

$$Q = \int_{U_1}^{U_2} dU = m\int_{T_1}^{T_2} c\,dT \approx m\hat{c}(T_2 - T_1) = m\hat{c}\Delta T$$

Q = heat [J]

U = internal energy [J]

m = mass [kg]

c = specific heat capacity [J/kg K], the heat needed to raise the temperature 1 K of 1 kg of the substance. *c* often increases with temperature (but not for water between 0 and 33.5˚C where it decreases!?). $\hat{c}$ is the average value of *c* in the temperature interval (T_1, T_2). *c* is also depending on how the state changes occurs when the temperature raises (see below for c_p och c_v).

C = mc = heat capacity [J/K]

T = temperature [K]

c_p = specific heat capacity when the state change occurs during constant pressure (*P* = constant), i.e. $c_P = \left(\frac{\partial q}{\partial T}\right)_{P=\text{constant}} = \frac{dh}{dT}$. The concept entalpy, *H* or specific enthalpy, *h* we will define and examine below.

c_v = specific heat capacity when the state change occurs during constant volume (*V* = constant), i.e. $c_V = \left(\frac{\partial q}{\partial T}\right)_{V=\text{constant}} = \frac{du}{dT}$.

Thus, the following holds: (1) supplied heat at constant pressure is equal to the increase in enthalpy and (2) supplied heat at constant volume is equal to the increase in internal energy.

For liquids or solids $c_p \approx c_V$ since these usually can be regarded as incompresible.

Gases needs more heat to raise the temperature at constant pressure than at constant volume, i.e. $c_p > c_V$. (The gas increases the volume to maintain constant pressure, i.e. perfomes work by expansion on the environment in addition to the change of internal energy given by the temperature change).

For gases the relation:

$$\frac{c_P}{c_V} = \kappa$$

has a typical value for specific gases. At low pressures, i.e. more ideal gases, κ becomes almost constant accordingly.[5]

One atomic gases as inert gases:	$\kappa \approx 1.66$
Two atomic gases as N_2, O_2, H_2 and air:	$\kappa \approx 1.40$
Three atomic gases as CO_2 and steam H_2O:	$\kappa \approx 1.30$

Before we look closer at the ideal gas model we need to define som further concepts:

ρ = dencity [kg/m^3]

v = specific volume [m^3/kg], $v = \frac{V}{m} = \frac{1}{\rho}$

M = molar weight of gas [kg/kmol], e.g. $M_{H_2} \approx 2$, $M_{\mathrm{Air}} \approx 29$ och $M_{O_2} \approx 32$

S: Calculate the molar weight of Carbon Dioxide and steam.

The ideal gas model

According to above the equilibrium state of a system is described by the state variables P, V and T. These are not independent of each other – for all substances there are state equations $f(P,V,T) = 0$. If the state equation is known all state variables may be calculated if we know two of them.

I reality the state equation of a substance is often too complicated to derive analytically, but from experiments we may get empirical relations. With modern computers, we may even describe liquids with fairly good correspondence between theory and practice.

An ideal gas is a gas were the molecules only interact by collisions, and they do not occupy any space, i.e. they are infinitely small.

For ideal gases there are three important experimental results:

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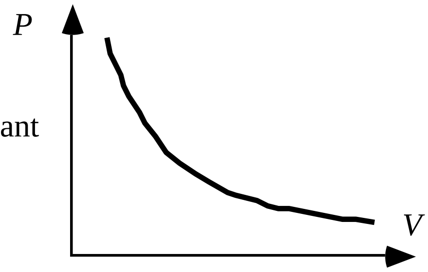
[5] The heat capacity may be regarded as the capacity of a substance to store energy by the embodied molecules. This can be done as kinetic energy from three dimensional motion and rotation. This energy depends linearly with temperature, thus not adding any temperature dependens from the heat capacity. This is valid for single atom gases as Ar, Ne and He. Contribution from vibrations and from electrons implies that the heat capacity becomes temperature dependent, especially for two atoms gases as H_2, O_2 and air. For many atoms gases as CO_2 and H_2O we have additional contributions from more possible states of vibrations, which make an even stronger temperature dependance in the heat capacity.

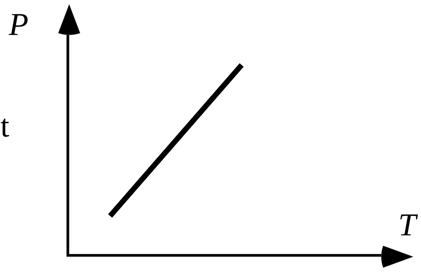
Boyles-Mariotte's law from 1660:

PV = constant, when T = constant



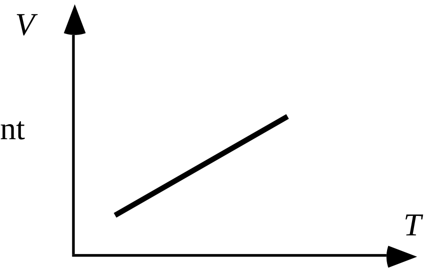
Charles' law stated 1787:

P/T = constant, when V = constant



Gay-Lussac's law from 1802:

V/T= constant, when P = constant



All these empirical realtions can be summerized in a state equation:

$$\boxed{PV = mRT}$$

called the ideal gas equation, where:

P = pressure [N/m^2 = Pa (Pascal)]
V = total volume [m^3]
m = mass [kg]
R = specific gas constant, $R = \frac{8314.3}{M}$) [J/kg K] were M is the molar mass of the substance, sometimes this symbol is also used for the universal gas constant, i.e. R = 8314.3 [J/kmol K], which is experimentally measured.
T = temperature [K]

If we insert the specific volume $v = \frac{V}{m}$

in the ideal gas equation we get:

$$\boxed{Pv = RT}$$

For the ideal gas we also have:

$$\boxed{c_P - c_V = R}$$

Q: Derive this relation from the definitions of c_P, c_V, the enthalpy ($h = u + Pv$) and the ideal gas equation.

Ex: A specific amount of air has the temperature 290 K and pressure 0.2 MPa. What is the pressure if the temperature increases to 310 K at constant volume? (For instance a car tyre subject to heat by friction.)

S: Assume ideal gas!

before: $P_1 V = mRT_1$

after: $P_2 V = mRT_2$

V = constant m = constant

$\frac{P_1}{P_2} = \frac{T_1}{T_2}$ $P_2 = \frac{P_1 T_2}{T_1} \approx \frac{2 \times 10^5 \times 310}{290} \approx 2.14 \times 10^5$ Pa = 0.214 MPa, i.e. 7% pressure increase. (We can also use Charles' law.)

Ex: If the volume in the previous example is 10 m^3 how much heat is needed?

S: Added heat becomes $Q = U_2 - U_1 \approx m\hat{c}_V (T_2 - T_1)$

From the ideal gas relation we get the mass of the air: $m = \frac{P_1 V}{RT_1}$

The state change appears during constant volume, but we only have data for c_P.

$\frac{c_P}{c_V} = \kappa \approx 1.4$ $c_V \approx \frac{c_P}{1.4}$

$\hat{c}_P \approx 1005$ [J/kg K] (Average value between 290 and 310 K, however $\hat{c}_P \approx 1.00$ [kJ/kg K] is also of course acceptable).

$$Q = \frac{P_1 V}{RT_1} \times \frac{c_P}{1.4} \times (T_1 - T_2) \approx \frac{2 \times 10^5 \times 10 \times 10^3}{\frac{8314.3}{29} \times 290} \times \frac{1005}{1.4} (310 - 290) \approx 341.84 \approx 342 [\mathrm{J}]$$

$$\left[\frac{\mathrm{Nm^3 \, kgK \, JK}}{\mathrm{m^2 \, JK \, kgK}} = \mathrm{Nm} = \mathrm{J} \right]$$

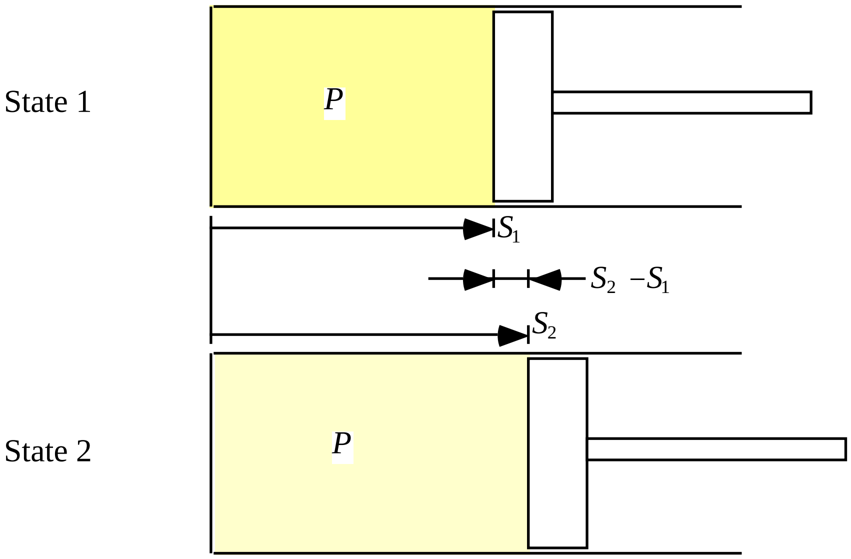
Work, Mechanical Work and Pressure-Volume Work

From Mechanics we have the following wellknown relation: *Work is equal the Force times the Distance,*

$$W = FS$$

where: W = work [Nm = J]
F = force [N]
S = distance [m]

Assume a cylinder with a mobile piston (no friction) with the cross section area A. in the cylinder we have a gas with pressure P.



What work is done by the gas if the piston is allowed to move a short distance, so that it does not influnce the pressure?

If A is the area which is subject to the pressure P, the force becomes $F = PA$

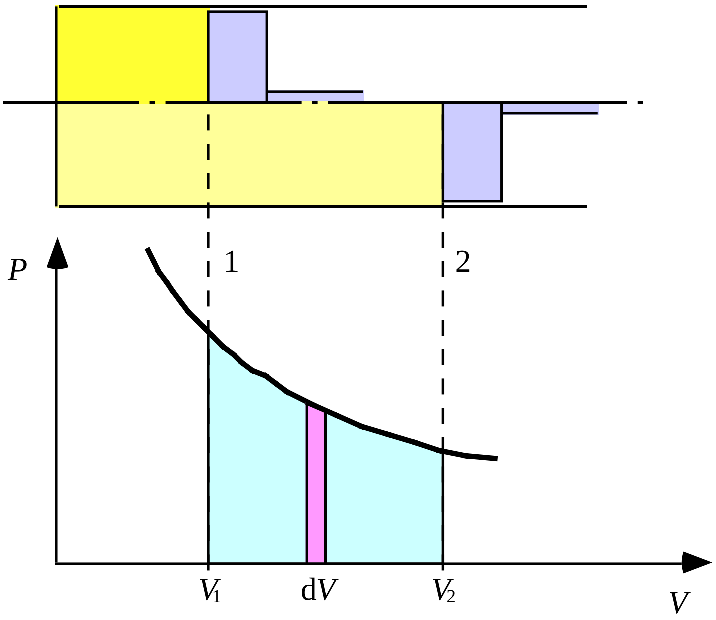
The piston moves the distance $S_2 - S_1$

The work done by the piston, assuming constant pressure becomes:

$$W = F(S_2 - S_1) = PA(S_2 - S_1) = P(V_2 - V_1)$$

Since the volume in state 1 is $V_1 = AS_1$ and in state 2 is $V_2 = AS_2$.

If we allow the piston to move out a longer distance the pressure will drop acording to the ideal gas equation $PV = mRT$.



The work one by the volume change dV is:

$$\delta W = P(V)\mathrm{d}V$$

The total work when the volume changes from V_1 to V_2 becomes:

$$W = \int_{V_1}^{V_2} P(V)\mathrm{d}V$$

W is sometimes called pressure-volume work.

If we draw P as a function of V, i.e. $P(V)$ in a PV-diagram, then W becomes the area under the curve $P(V)$ and between V_1 and V_2, i.e. the indicated area in the figure above.

Thus, the work performed by the gas depends on the shape of $P(V)$, i.e. how the state change occurs between 1 and 2.

The 1st Law of Thermodynamics — Nothing disappears

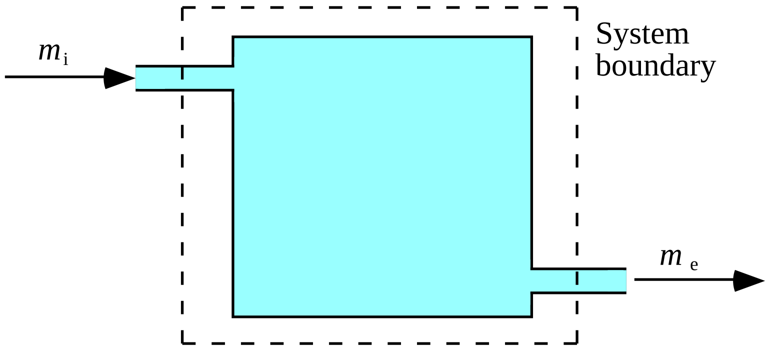
Energy can not be created or destroid.

A closed system is a system where nothing is allowed to cross the system boundary. The cylinder above is a partially closed system. The piston represents a moving boundary allowing work to be extracted, i.e. energy to cross.

The total energy of a closed system is constant. The energy before and after a change of state is the same, i.e. we have an energy balance. Energy is defined as that which is always conserved in every process.

Consequently, it is wrong to say energy production, instead use energy supply. By the same reason energy consumption is impossible, what we actually mean is that an energy form is consumed or that the energy is converted or maybe used but not consumed.

An open system is a system where mass may cross the system boundary. The mass of the system is determined from in and out flows, m_i and m_e (exit), see the figure below.



Ex: Water is falling 55 m at the rate of 500 m^3/s. Estimate the temperature rise, if we assume that all potential energy heats the water.

S: From energy conservation the potential energy, $E_{pot} = mgh$ [J], completely converts to increased internal energy, $\Delta U = mc\Delta T$, i.e. the temperature increases.

$$E_{pot} = \Delta U \qquad mgh = mc\Delta T \qquad gh = c\Delta T \qquad \Delta T = \frac{gh}{c} \approx \frac{9.81\times 55}{4.2\times 10^3} \approx 0.13[\mathrm{K}]$$

Units? $\left[\frac{\mathrm{Nm}}{\mathrm{kg}\frac{\mathrm{J}}{\mathrm{kgK}}} = \frac{\mathrm{NmkgK}}{\mathrm{kgJ}} = \frac{\mathrm{NmK}}{\mathrm{J}} = \mathrm{K}\right]$

Note that the flow rate is not needed.

Q: If you try to verify this by experiment, you might find that the temperature drops. Why, do you think?

Ex: Estimate the energy power from the water fall above?

S: Mass flow: $\dot{m}$ = 500 ton/s = 5×10^5 kg/s, i.e. in 1 second the energy $E_{pot} = mgh$ is converted. The energy power P, which is energy per unit time then becomes:

$$P = \frac{E_{pot}}{t} = \frac{mgh}{t} \approx \frac{5\times 10^5 \times 9.81\times 55}{1} = 269{,}775{,}000\mathrm{J/s} \approx 270\mathrm{MW}$$

Units? $\left[\frac{\mathrm{kgNm}}{\mathrm{skg}} = \frac{\mathrm{Nm}}{\mathrm{s}} = \frac{\mathrm{J}}{\mathrm{s}} = \mathrm{W}\right]$

We will now introduce *enthalpy*, H, which asigns the total energy of a system, i.e. the sum of the internal and external energies.

If the external energy is PV [J], where P = pressure [Pa = N/m^2] and V = volume [m^3] and the internal energy is, U [J], then the enthalpy is

$$H = U + PV$$

Work and Technical Work

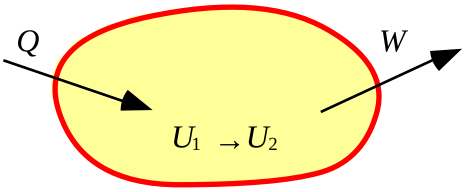
Closed system

Assume a system where no matter can cross the system boundary. We add heat, Q and extract work, W and the internal energy changes from U_1 to U_2, but nothing else happends. The 1st Law then becomes

$$Q = U_2 - U_1 + W = \Delta U + W$$

where Q = heat added [J]
U_1 = internal energy [J] before heat is added
U_2 = internal energy [J] after heat is added
W = extracted work [J].

Not that we regard input heat and output work as positive.

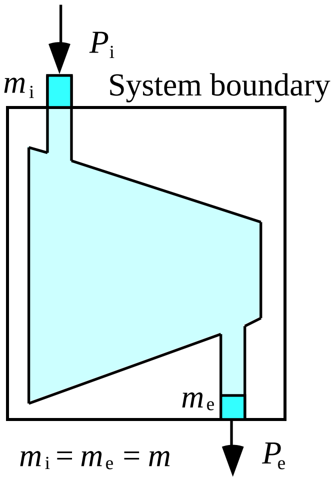


(Warning! By some authers input work is positive!)

Steady-State processes

In a steady state process the total mass and the total energy enclosed by the system boundary is always conserved. Such systems are pumps, compressors, fans, turbines, etc.

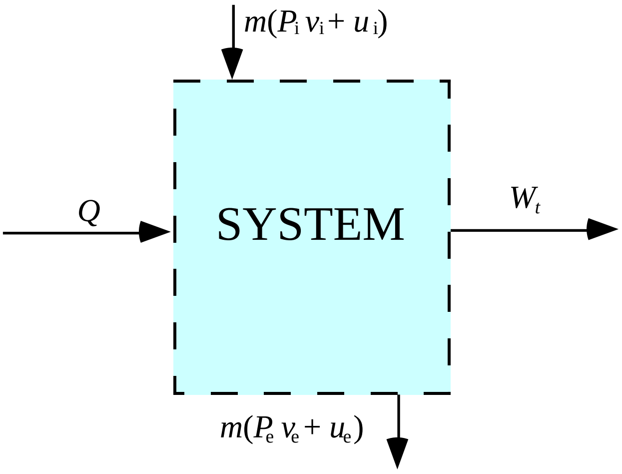
Assume a process with different inlet and outlet pressures.



The mass input is m_i, and from conservation the mass output m_e is the same as the input, i.e. $m_i = m_e = m$. Assume that the input specific internal energy is u_i [J/kg]. The surrounding air performs a specific external work $P_i v_i$ [J/kg] on the input mass.

Analogously for the output specific internal energy u_e and the mass performs an external work $P_e v_e$ on the surrounding air.

We also add heat Q [J] to the system, which also performes work W_t [J], we call this work technical work.



The total energy of the system is constant according to the 1st Law, i.e. energy input is equal to energy output.

$$Q + m(P_i v_i + u_i) = m(P_e v_e + u_e) + W_t$$

By introducing the enthalpy concept $h = Pv + u$ we get.

$$Q + mh_i = mh_e + W_t \qquad Q + H_i = H_e + W_t \qquad Q = H_e - H_i + W_t = \Delta H + W_t$$

An important case is when no heat is added, $Q = 0$, i.e. an adiabatic process.

$$W_t = H_i - H_e = \Delta H$$

Thus, the technical work is equal to the enthalpy change in an adiabatic process.

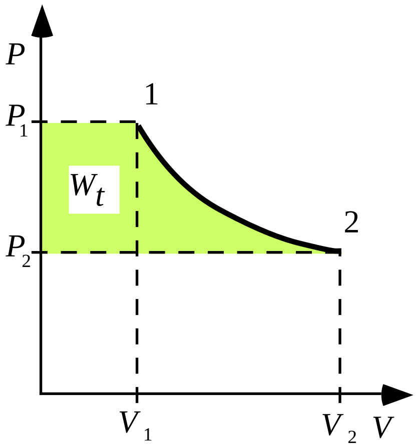
But, for a Steady-State process we also have that $Q = \Delta U + W = U_2 - U_1 + W$, where i=1 and e=2. U and W refers to the mass element m going through our system. We have

$$Q = \Delta U + W = \Delta H + W_t$$

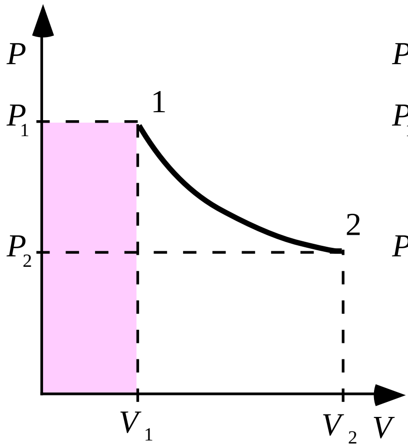
$$U_2 - U_1 + W = U_2 + P_2V_2 - U_1 - P_1V_1 + W_t$$

$$W_t = P_1V_1 - P_2V_2 + \int_{V_1}^{V_2} PdV$$

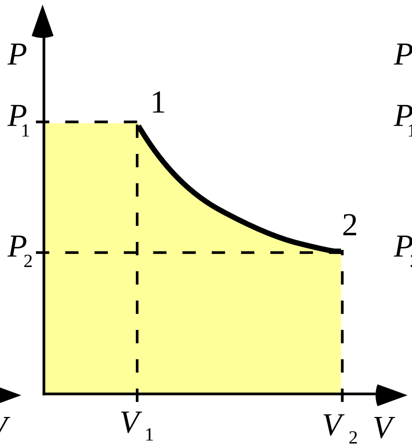
$$\text{since } W = \int_{V_1}^{V_2} PdV$$



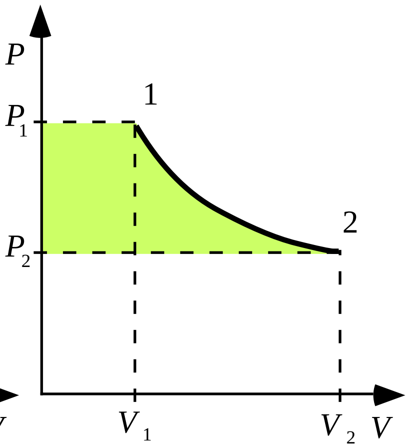
If we indicate the pressure as a function of the volume, $P(V)$, in a PV-diagram we see that W_t is the indicated area in the diagrams above and below.



P_1V_1



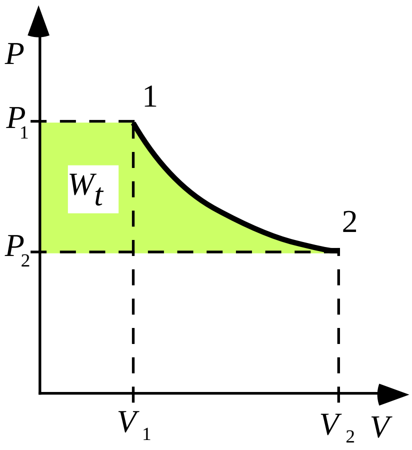
$P_1V_1 + \int_{V_1}^{V_2} PdV$

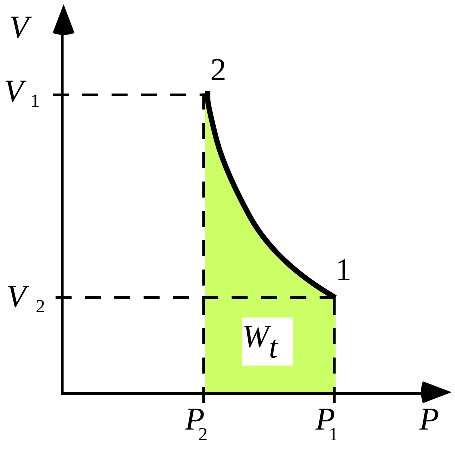


$P_1V_1 + \int_{V_1}^{V_2} PdV - P_2V_2$

The area can also be defined by the integral

$$W_t = \int_{P_2}^{P_1} VdP = \int_{P_1}^{P_2} VdP$$





Thus, we may write the energy balance for a closed system

$$Q = U_2 - U_1 + \int_{V_1}^{V_2} PdV$$

and for an open system

$$Q = H_2 - H_1 - \int_{p_1}^{p_2} VdP$$

Assume the heat is added during constant volume, dV = 0, then we have

$$Q_v = m\int_{T_1}^{T_2} c_v(T)dT \approx mc_v(T_2 - T_1)$$

which in combination with the energy balance of a closed system gives

$$Q_v \approx mc_v(T_2 - T_1) = U_2 - U_1 = \Delta U$$

Thus, for a closed system we have that the heat transfered at constant volume is equal to the change of the internal energy.

Instead, assume the heat is added during constant pressure, dP = 0, then we have

$$Q_P = m\int_{T_1}^{T_2} c_P(T)dT \approx mc_P(T_2 - T_1)$$

which in combination with the energy balance of an open system gives

$$Q_P \approx mc_P(T_2 - T_1) = H_2 - H_1 = \Delta H$$

Thus, for an open system we have that the heat transfered at constant pressure is equal to the change of the enthalpy.

This is valid for ΔU and ΔH at all change of state.

Ex/S: A closed isolated volume of 2 m^3 with air of pressure 0.5 MPa and temperature 293 K, receives 2500 kJ of heat.

The internal energy?

We have a closed system, thus

$Q = \Delta U + W$

No work is done $\Delta U = Q = 2500$ kJ

Final temperature of the gas?

$$V = \text{const.} \qquad Q \approx mc_v \Delta T \qquad \Delta T \approx \frac{Q}{mc_v}$$

The mass we can get from the ideal gas relation.
Air is approximatly an ideal gas with $\kappa \approx 1.40$, and for an ideal gas we have

$$\begin{cases} c_P - c_v = R \\ \dfrac{c_P}{c_v} = \kappa \end{cases} \qquad c_v(\kappa - 1) = R \qquad c_v = \frac{R}{\kappa - 1}$$

The temperature change:

$$\Delta T = \frac{Q}{mc_v} = \frac{Q}{\dfrac{P_1V_1}{RT_1} \times \dfrac{R}{\kappa - 1}} = \frac{QT_1(\kappa - 1)}{P_1V_1} \approx$$

$$\approx \frac{2500 \times 10^3 \times 293(1.4 - 1)}{5 \times 10^5 \times 2} \approx 293K$$

The final temperature $T_2 = T_1 + \Delta T \approx 586$ K

The final pressure?

From the ideal gas relation we get

State 1: $P_1V_1 = mRT_1$

State 2: $P_2V_2 = mRT_2$

By dividing these relations we get

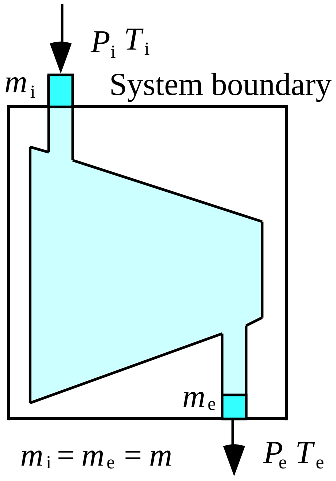
$$\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2} \text{ but since } V_1 = V_2$$

we get the final pressure

$$P_2 = \frac{P_1T_2}{T_1} \approx \frac{5 \times 10^5 \times 586}{293} \approx 10 \times 10^5 \,\text{Pa} = 1\text{MPa}$$

Ex: Air is compressed from 10 to 60 MPa, the temperature increases from 293 to 373 K and the flow rate is 3 kg/s. What is the work needed?

S: Assume we can neglect the heat leakage from the compressor, i.e. an adiabatic process.



The process is a adiabatic steady state process, i.e. $Q = 0$. The work output per second then becomes

$$W_t = H_i - H_e = m(h_i - h_e) \approx m\hat{c}_P\Delta T \approx 3 \times 1009 \times (293 - 373) \approx -242[\mathrm{kJ}]$$

The minus sign indicates that work is needed, 242 kJ per second, i.e. the needed exergy power is 242 kW.

State variables and State changes

Volume V, temperature T, enthalpy H and pressure P are called state variables. A state variable has a specific value for a certain state independent from how the state was attained. Thus, a state variable does not contain the history of the state. Work W, technical work W_t and heat Q are depending on how the state of the substance changes, i.e. they are "process related."

Variables may also be extensive, i.e. they are depending on the size of the system, as volume V and enthalpy H, or intensive, i.e. they are not depending of the size, as pressure P and temperature T.

The four most common state changes or processes are defined

Isochoric process V = constant, i.e. $dV = 0$

Isobaric process P = constant, i.e. $dP = 0$

Isothermal process T = constant, i.e. $dT = 0$

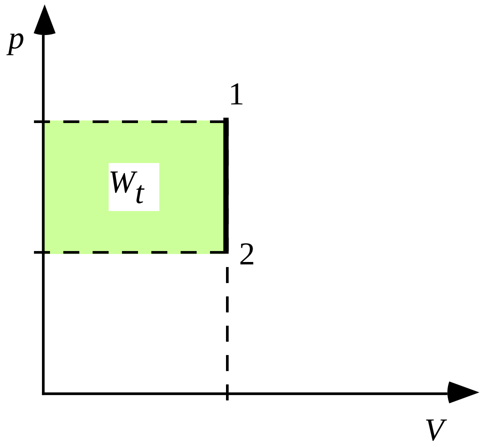
Adiabatic process $\delta Q = 0$, no heat lost or added to the system. (This is also called isentropic. Note the "curly" differential sign since the change is not unambiguous because it depends on the state change, as we just meantioned above.)

In all four cases we assume that the state changes are reversible. This means that the process is ideal, i.e. no losses occur when the system changes from 1 → 2 and back again

2 → 1. In reality there are no reversible processes. In real processes we have always losses – more or less. A real process must be irreversible, i.e. not reversibel, to have a direction.

Let us now see what this means for the work W, technical work W_t and heat Q for an ideal gas, i.e. $pV = mRT$.

<u>Isochoric process</u> $\dfrac{P}{T}$ = constant



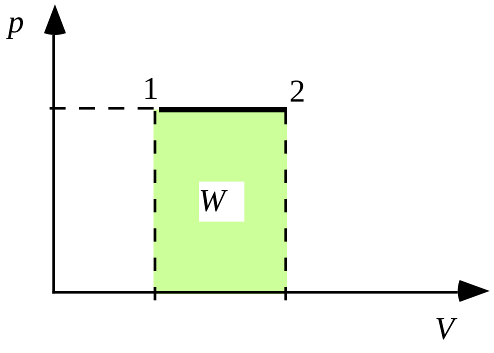
$$W = \int_{V_1}^{V_2} PdV = 0$$

$$W_t = \int_{P_1}^{P_2} Vdp = V(P_1 - P_2)$$

$$Q = m\int_{T_1}^{T_2} c_V(T)dT \approx m\hat{c}_V(T_2 - T_1)$$

where $\hat{c}_V$ is the average value in the temperature region $[T_1,T_2]$.

<u>Isobaric process</u> $\dfrac{V}{T}$ = constant



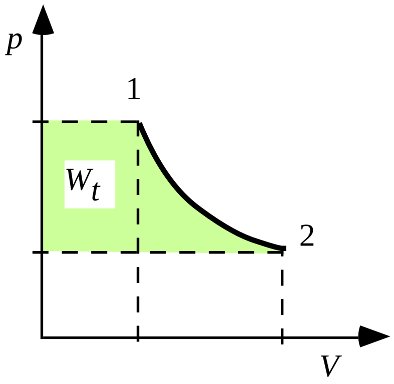
$$W = \int_{V_1}^{V_2} PdV = P(V_2 - V_1)$$

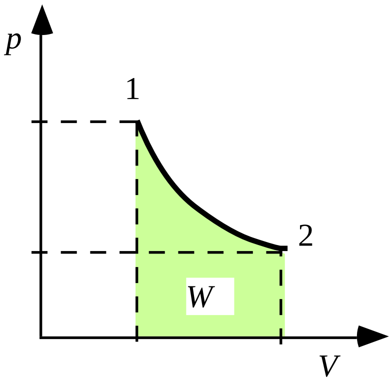
$$W_t = \int_{P_1}^{P_2} V dP = 0$$

$$Q = m\int_{T_1}^{T_2} c_P(T)dT \approx m\hat{c}_P(T_2 - T_1)$$

where $\hat{c}_P$ is the average value in the temperature region $[T_1, T_2]$.

Isothermal process PV = konstant





$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{mRT}{V} dV = mRT \ln\left(\frac{V_2}{V_1}\right) = mRT \ln\left(\frac{P_1}{P_2}\right)$$

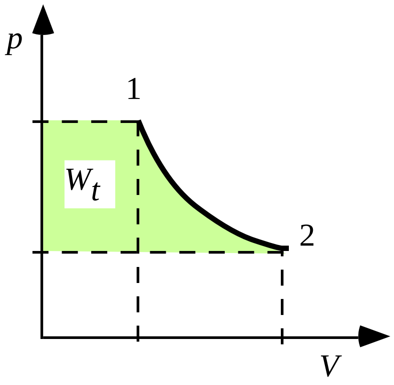
$$W_t = \int_{P_1}^{P_2} Vdp = \int_{P_1}^{P_2} \frac{mRT}{P} dP = mRT \ln\left(\frac{P_2}{P_1}\right) = mRT \ln\left(\frac{P_1}{P_2}\right)$$

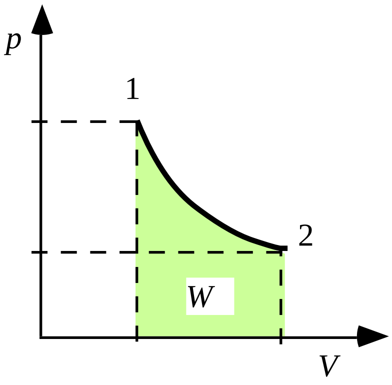
Thus we have $W = W_t$.

$$Q = U_2 - U_1 + \int_{V_1}^{V_2} PdV = W = W_t.$$

since $U_2 - U_1 = m\int_{T_1}^{T_2} c(T)dT = 0$.

Adiabatic process $\delta Q = 0$. For a reversible adiabatic process we have Poisson's relation PV^{κ} = constant, which also can be written $TV^{\kappa-1}$ = constant or $TP^{-(\kappa-1)/\kappa}$ = constant from the ideal gas model.





Q: Derive Poisson's relation, i.e. show that PV^{κ} = constant.

Hint: 1st Law and adiabatic process ($\delta Q = 0$) $PdV + dU = 0$, with $dU = mc_V dT$ we get $PdV + mc_V dT = 0$. By differentiating the ideal gas model we get: $PdV + VdP = mRdT$. Eliminate dT and we have: $PdV + VdP = \frac{R}{c_V} PdV$ or $(1 + \frac{R}{c_V})PdV + VdP = 0$. By using that $c_P = c_V + R$ and $\gamma = \frac{c_P}{c_V}$ we have: $\gamma \frac{dV}{V} = \frac{dP}{P}$ which after integration becomes $-\gamma \ln V = \ln P + \text{constant}$ or $PV^\gamma = \text{constant}$. From the ideal gas model $PV = mRT$ we also get the relations for T and P and for T and V as above.

Work is

$$W = \int_{V_1}^{V_2} PdV$$

but from the 1st law we have

$$Q = U_2 - U_1 + \int_{V_1}^{V_2} PdV = 0,$$

which gives

$$W = \int_{V_1}^{V_2} PdV = U_1 - U_2 = \Delta U.$$

but

$$\Delta U = m \int_{T_1}^{T_2} c_V(T) dT$$

which gives

$$\Delta U = m \int_{T_1}^{T_2} c_V(T) dT.$$

The technical work is

$$W_t = \int_{P_1}^{P_2} VdP$$

but

$$Q = H_2 - H_1 - \int_{P_1}^{P_2} VdP = 0,$$

and

$$\Delta H = m \int_{T_1}^{T_2} c_P(T) dT$$

which gives

$$W_t = m \int_{T_1}^{T_2} c_P(T) dT = m\kappa \int_{T_1}^{T_2} c_V(T) dT.$$

thus, we have $W_t = \kappa W$.

We will now study the polytropic process, which occurs during heat exchange with the environment.

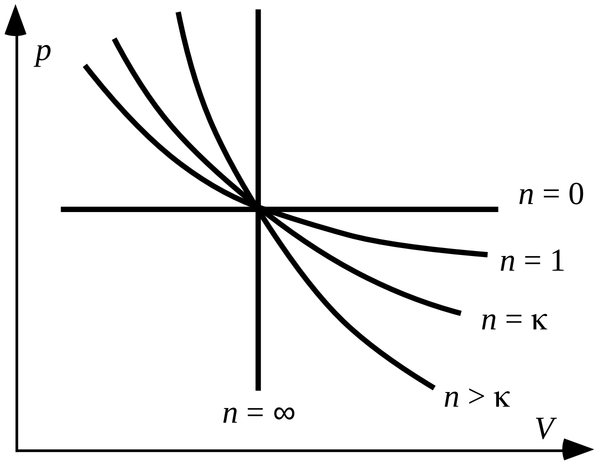
The process is characterized by

$$PV^n = \text{constant}$$

n is the polytropic coefficient and can have any value.

A polytropic process summerize all the processes above, where the value of *n* indicate the kind of process we have

Isochoric process	$n = \infty$
Isobaric process	$n = 0$
Isothermal process	$n = 1$
Isentropic process *(or adiabatic process)*	$n = \kappa$



Q: Show that when $n \to \infty$ a polytropic process becomes an isochoric process.
Hint: PV^n = constant we can write as $V^n = \frac{1}{P} \times \text{constant}$ or

$$V = \left(\frac{1}{P}\right)^{\frac{1}{n}} \times \text{constant} \to \left(\frac{1}{P}\right)^{0} \times \text{constant} = \text{constant} \text{ when } n \to \infty$$

Ex: A gas with c_P = 1.0 kJ/kg K and κ = 1.4 recieves the heat 100 kJ/kg. How much will the temperature rise if the heat is added at 1) constant pressure 2) constant volume?

S: 1) $\Delta Q = mc_P(T_2 - T_1) = mc_P \Delta T \qquad \Delta T = \frac{\Delta Q}{mc_P} = \frac{100 \times 10^3}{1 \times 1.0 \times 10^3} \approx 100\text{K}$.

$$2) \left.\begin{matrix} \Delta Q = mc_v(T_2 - T_1) = \Delta T \\ \kappa = \frac{c_P}{c_V} \end{matrix}\right\} \quad \Delta T = \frac{\Delta Q \kappa}{mc_P} \approx \frac{100 \times 10^3 \times 1.4}{1 \times 1.0 \times 10^3} = 140\text{K}$$

Ex: A gas with κ = 1.4 and the initial values P_1 = 0.4 MPa, V_1 = 3 m³ and T_1 = 473 K is adiabatically expanding to V_2 = 9 m³. Estimate final pressure, temperature and the works W and W_t.

S: For an adiabatic process we have PV^κ = constant, where $\kappa = \frac{c_P}{c_V}$, i.e.

$$P_1 V_1^\kappa = P_2 V_2^\kappa \qquad P_2 = P_1 \left(\frac{V_1}{V_2}\right)^\kappa = 4 \times 10^5 \left(\frac{3}{9}\right)^{1.4} \approx 0.86 \times 10^5 \text{Pa}.$$

$$TV^{\kappa-1} = \text{constant} \qquad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\kappa-1} \approx 473 \times \left(\frac{3}{9}\right)^{1.4-1} \approx 305\text{K}$$

$$W = \int_{V_1}^{V_2} PdV = \text{constant} \times \int_{V_1}^{V_2} \frac{1}{V^{\kappa}}dV = \frac{1}{\kappa - 1}(P_1V_1 - P_2V_2) \approx$$

$$\approx \frac{1}{1.41}(4 \times 10^5 \times 30.86 \times 10^5 \times 9) \approx 1.06 \times 10^6\text{J} \approx 1.06\text{MJ}$$

$$W_t = \kappa W \approx 1.4 \times 1.06 \approx 1.48 \text{ MJ}$$

The 2nd Law of Thermodynamics — Everything disperse

By experience we know that heat spontaneous goes from a warm body to a cold body, but never the opposite. We also know that the energy of heat can not completelly be transformed to work, even if we disregard losses as friction and heat losses. This implies the second law, which has been formulated in many ways:

Clausius:

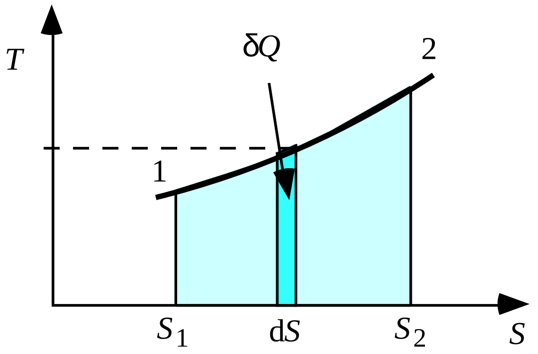
> Heat can not “by itself” go from a low to a higher temperature.

Lord Kelvin:

> Heat can not completely transfer to work.

From the concept entropy S, which was introduced by Clausius the year 1865, we may also make a formulation of the second law.

As we saw above work W and technical work W_t can be illustrated as areas in a pressure/volume diagram PV-diagram. Similarly heat Q can be illustrated as an area in a temperature/entropy diagram TS-diagram, see below.



If the area below the graph $T(S)$ and between S_1 and S_2 is the heat content Q, then we have

$$\delta Q = TdS$$

or

$$dS = \frac{\delta Q}{T},$$

with the unit J/K. When heat δQ is transferred to a system it is the temperature T of the heat that predicts the entropy dS that simultaneously is being transferred. By integration we get

$$\Delta S = \int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

The value of the integral is independent of the integration path, i.e. it is only depending on the values of S_1 and S_2. Thus, the entropy is a state variable, i.e. a function only depending on the state of the system. Therefore we may express the entropy as a function of the state variables pressure, volume, and temperature, $S(P,V,T)$. We will also notice that the entropy is an extensive variable, i.e. depends on the size of the system as mass, volume, and internal energy.

The 1st law says that energy is always conserved in any process. The 2nd law states that every process mostly take place in such a way that the entropy is constant for a reversible process or increases for an irreversible process, i.e.

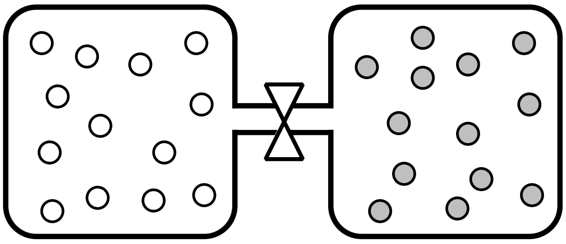
$$\boxed{\Delta S \geq 0}$$

Everything that happends implies an increase of the total entropy. Locally the entropy may decrease but only if the entropy increses even more somewhere else so that the total entropy increses.

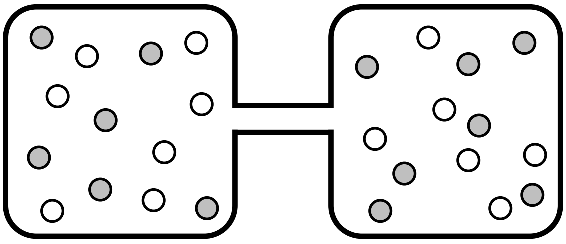
Entropy may also be regarded as a value of order. (This we will treat in the section on exergy of information.) Thus the 2nd law states that everything moves towards increased dissorder – increased disintegration. Locally we may still create increased order. In the case of creating order on the earth, as in the living nature, this is established by the order offered by the sun and the dissorder offered by the space.

So far all the state changes we have studied has been reversible. A reversible process is a process where you can always return to the initial state by running the process backwards. Such a process has no losses and assumes all processes to take place during thermodynamic equilibrium, i.e. no differences in temperature and pressure. This makes such processes infinite in time and unrealistic. By the second law we may say that we consider the irreversible processes which we have in reality.

Assume we have two containers with different gases, ○ and ●. We know which gas we have in each container, i.e. our system is ordered. If we open the valve connecting the container's gases will spontaneously diffuse into each other and we have lost some order since we do not know where the ○-gas or ●-gas is, S increases. We may not predict the exact distribution of ○ and ● in the two containers.



Case 1: Order ⇔ S_1 is small.



Case 2: Disorder ⇔ $S_2 > S_1$.

Also, we do not expect that the gases will spontaneously return to the initial state.

Let us see what this implies for different substances.

For a solid or liquid substance, i.e. an incompressible substance we have $\delta Q \approx \mathrm{d}U \approx mc\mathrm{d}T$, which gives

$$\Delta S = \int_1^2 dS \approx \int_{T_1}^{T_2} \frac{mcdT}{T} \approx mc\ln\left(\frac{T_2}{T_1}\right),$$

where we have assumed the specific heat capacity to be constant.

Ex: 1 kg water is heated from 20 to 90˚C. Estimate the entropy change when the specific heat is constant and compare with steam tables.

S: $\Delta S = mc\ln\left(\frac{T_2}{T_1}\right) \approx 1 \times 4.184\ln\left(\frac{273.15+90}{273.15+20}\right) \approx 0.8959$ kJ/K.
The steam tables gives $\Delta s \approx 1.1925 - 0.2966 = 0.8959$ kJ/kg K.
Thus, a very good resemblance.

For an ideal gas the relation becomes more complicated. From 1st law we have:

$$\delta Q = \mathrm{d}U + P\mathrm{d}V$$

and for an ideal gas we have:

$$\begin{cases} dU = mc_V dT \\ \dfrac{P}{T} = \dfrac{mR}{V} \end{cases}$$

Thus, the entropy change becomes

$$\Delta S = \int_1^2 \frac{\delta Q}{T} = \int_1^2 \frac{mc_V}{T}dT + \int_1^2 \frac{mR}{V}dV = m\int_1^2 \frac{c_V}{T}dT + mR\ln\left(\frac{V_2}{V_1}\right)$$

If the specific heat is constant, i.e. independent of the temperature we get

$$\Delta S = mc_V\ln\left(\frac{T_2}{T_1}\right) + mR\ln\left(\frac{V_2}{V_1}\right)$$

Analagously we have

$$\delta Q = \mathrm{d}H - V\mathrm{d}P$$

and for an ideal gas we have

$$\begin{cases} dH = mc_P dT \\ \dfrac{V}{T} = \dfrac{mR}{P} \end{cases}$$

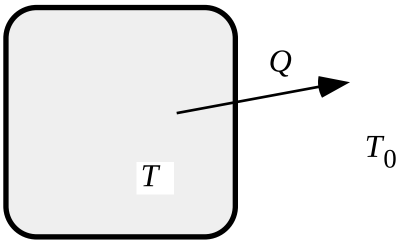
Thus the entropy change becomes

$$\Delta S = \int_1^2 \frac{\delta Q}{T} = \int_1^2 \frac{mc_P}{T}dT - \int_1^2 \frac{mR}{P}dP = m\int_1^2 \frac{c_P}{T}dT - mR\ln\left(\frac{P_2}{P_1}\right)$$

If the specific heat is constant we get

$$\Delta S = mc_P \ln\left(\frac{T_2}{T_1}\right) - mR \ln\left(\frac{P_2}{P_1}\right)$$

Ex: In a container 2 kg of steam is condensed at temperature T = 100˚C, and a heat Q = 4514 kJ is transferred to the surrounding air at temperature T_0 = 20˚C. Calculate the change in entropy in the container S, and the environment S_0. Also calculate the total entropy change S_{tot}. The temperature of the environment is constant.



S: If we assume that the heat is transfered at constant temperature we have for the entropy

$$S \geq \frac{Q}{T}$$

Container: $S \geq \frac{Q}{T} \approx \frac{-4514}{273+100} \approx -12.10$ kJ/K, the minus sign indicates that entropy and heat is transported out of the system.

Environment: $S_0 \geq \frac{Q}{T_0} \approx \frac{4514}{273+20} \approx 15.41$ kJ/K.

The total entropy change becomes:

$S_{\text{tot}} = S + S_0 \geq -12.10+15.41 = 3.31$ kJ/K ≥ 0, i.e. in accordance with the 2nd law.

We can summarize the following:

Laws

0th law defines the concept of temperature
1st law: $\delta Q = \mathrm{d}U + \delta W$, defines energy as a conserved quantity and work: $\delta W = P\mathrm{d}V$
2nd law: $\mathrm{d}S \geq 0$, $\mathrm{d}S_{\text{reversible}} = 0$, defines the concept of entropy throught heat: $\delta Q = T\mathrm{d}S$
3rd law defines the zero level for entropy

Concepts

Enthalpy: $H = U + PV$
Heat capacity: $\delta Q = C\mathrm{d}T$, C_v and C_P

Model

Ideal gas: $PV = n\overline{R}\,T = mRT$

Processes

Ideal gas: PV^n = constant $\begin{cases} n = 0 & \text{isobaric} \\ n = 1 & \text{isothermal} \\ n = \dfrac{C_P}{C_v} & \text{adiabatic} \\ n = \infty & \text{isochoric} \end{cases}$

Pricipally this is all you need to understand of classical thermodynamics to be able to manage this part of science. All other relations can be derived from these relations.

Remember!

The energy of a closed system is constant (1st law).

Energy forms may be destroyed and created, consumed and produced.

Energy production should be called energy supply

Energy consumption should be called energy use

Additional examples and solutions:

We are now ready to study additional examples to repeat thermodynamics.

Try to solve the problem before looking at the solution. If you do not succed, look at the solution part by part and try to solve as much as possible yourself. Simultaneously, repeat appropriate parts of the theory.

Ex: A bottle of the volume 0.02 m^3 containes hydrogen at 120 bar, 10˚C. What is the weight of the gas?

S: $V = 0.02\ m^3$

$P = 120\times10^5\ N/m^2$

$R = \dfrac{8314}{M_{H2}} \approx \dfrac{8314}{2} = 4157$ J/kg K

$T = 273.15+10 \approx 273+10 = 283$ K

$m = \dfrac{PV}{RT} \approx \dfrac{120\times10^5\times0.02}{4157\times283} \approx 0.204 \approx 0.20$ kg

Ex: 3 kg air of temperature 100˚C expandes isothermally in a closed volume from 0.1 m^3 to 0.3 m^3. How much heat must be added?

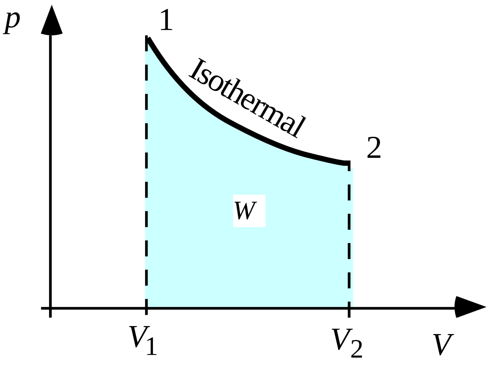
S: $m = 3$ kg, $T \approx (273+100)$ K = 373 K, $V_1 = 0.1$ m^3 and $V_2 = 0.3$ m^3.

For a isothermal process we have: $Q = mRT_1 \ln\left(\frac{V_2}{V_1}\right)$

The specific gas constant becomes $R_{\text{air}} \approx \frac{8314}{M_{\text{air}}} \approx \frac{8314}{29} \approx 287$ J/kg K.

Thus $Q \approx 287 \times 3 \times 373 \times \ln\left(\frac{0.3}{0.1}\right) \approx 352$ kJ ≈ 98 Wh.

In PV-diagram:



$W = Q$ since $Q = (U_2 - U_1) + W$ where

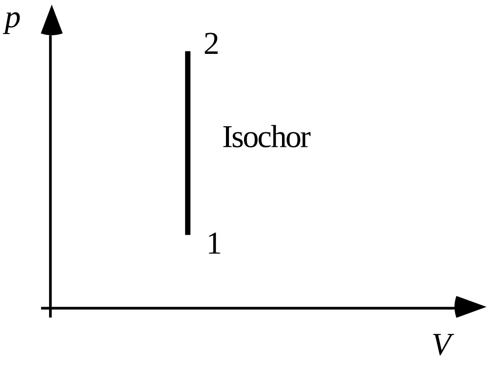
$U_2 - U_1 = mc_V(T_2 - T_1) = 0$.

Ex: A closed container of 20 liter with air at 20˚C, 1 bar receives heat until the pressure reaches 3 bar. How much heat is received?

S: Heat is being transfered at constant volume, thus the process is an isochor.

Transfered heat is, $Q = U_2 - U_1 = mc_V(T_2 - T_1)$, $c_v = \frac{R}{\kappa - 1}$, $\kappa_{\text{air}} = 1.4$,

$R_{air} = \frac{8314}{29}$ $c_v \approx \frac{8314}{29 \times 0.4} \approx 716.7$ J/kg K



The ideal gas model gives:

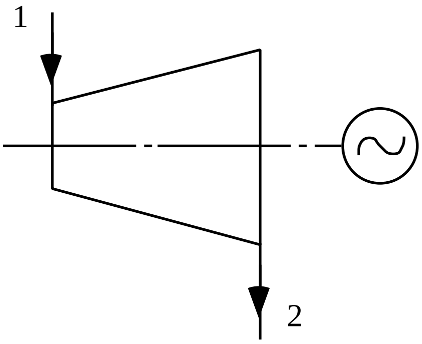
$$m = \frac{P_1 V_1}{RT_1} \approx \frac{1 \times 10^5 \times 0.02}{\frac{8314}{29} \times (273 + 20)} \approx$$

≈ 0.0238 [kg]

We get: $T_2 = \frac{P_2}{P_1} T_1 \approx \frac{3}{1} \times 293 = 879$ K

And the added heat becomes: $Q \approx 0.0238 \times 716.6 \times (879 - 293) \approx 10$ kJ

Ex: Air (2 kg/s) at 6 bar, 400˚C expandes in a turbine to the ambient pressure 1 bar. What is the maximal electric power to be utilized?



$P_1 = 6$ bar
$T_1 \approx (273+400) = 873$ K
$P_2 = 1$ bar
$\dot{m} = \frac{dm}{dt} = 2$ kg/s

S: The process is a steady state adiabatical process
Thus: $W_t = \kappa W = H_1 - H_2 = mc_P(T_1 - T_2)$

The power $\dot{W}_t$ is work W_t per time $\dot{W}_t = W_t$ per second $= \dot{m}\, c_P(T_1 - T_2)$

We have: $\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\kappa-1}{\kappa}} \approx \left(\frac{6}{1}\right)^{\frac{1.4-1}{1.4}} \approx 6^{0.286} \approx 1.67$, i.e. $T_2 \approx \frac{673}{1.67} \approx 403$ K.

The average value of $\hat{c}_P$ becomes: $\hat{c}_P = \frac{c_P(T_1) + c_P(T_2)}{2} \approx 1039$ J/kg K

(The specific heat is only depending on the temperature, since we assume an ideal gas, thus independent of the pressure difference $P_1 - P_2$)

We get $\dot{W}_t \approx 2 \times 1039 \times (673 - 403)\left[\frac{\text{kg} \times \text{J} \times \text{K}}{\text{s} \times \text{kg} \times \text{K}} = \text{J/s} = \text{W}\right] \approx 561.1 \approx 560$ kW

Problems

Try to solve these problems by yourself, without checking the solutions.

1. Which alternative use most energy? a) To remove the snow by truck that uses 5 liter diesel to remove 5 tonnes of snow. b) To melt the snow by a diesel burner with 80% efficiency. The enthalpy of melting is 334 kJ/kg.How much diesel will be used for 5 tonnes of snow?

2. Snow equivalent to 20 mm water falls over a city. What is the energy difference per m^2 if this instead was as rain? The difference causes an extra cooling effect, but also other effects. What other effects?

3. How much fuel oil is needed to raise the temperature of the indoor air from 0˚C to 20˚C in a house of 125 m^2 and hight 2.4 m? The efficiency of the heater is 65%. How is this effected if the volume is fixed or if the volume expands?

4. 10 kg hydrogen gas is heated 100K at constant volume. What is W and W_t? (*Hint:* use the definition of technical work and the ideal gas model!)

5. What is the volume of the gas in the previous problem if the initial state was +27˚C and 1 bar? (*Hint:* use the ideal gas model.)

6. 148 kJ of heat is isothermally added to 1 kg air of volume 0.5 m^3, so the final volume becomes 2 m^3. What was the initial temperature if R_{air} = 287 J/kg K? (*Hint:* use 1st law and the ideal gas model for an isothermal process!)

7. What was the initial pressure in the previous problem? (*Hint:* use the ideal gas model.)

8. A gas with $\kappa = 1.30$ expands adiabatic from P_1 = 6 bar to P_2 = 2 bar. How many percent does the volume increase? (*Hint:* adiabatic process.)

9. The air of a combustion engine is compressed polytropically from P_1 = 0.9 bar and T_1 = 40˚C. Determine the final pressure and temperature if the initial volume is 9 times the final volume and the polytropical coefficient is n = 1.35. (*Hint:* polytropical process.)

10. A closed container of 5 liter contains air at 1 bar, 20˚C. The air is heated to 50˚C. Calculate a) heat added b) final pressure (*Hint:* R = 285 J/kg K and the ideal gas model. Calculate the average value of c_P between 20-50˚C, and use the realtion for c_P and c_v.)

11. Air is adiabatically compressed from 1 bar, 20˚C to 6 bar. Calculate a) work needed b) temperature after compression c) change of internal energy of the air. (*Hint:* adiabatic process.)

12. Concider 0.6 m^3 of air at 2 bar, 20˚C. Calculate a) internal energy, U b) enthalpy, H if both of them are 0 at 1 bar, 0˚C. (*Hint:* isothermal and isobaric process.)

Answers

1. To melt the snow “costs” about 60 liter diesel.
2. 6.7 MJ/m^3 or 2 kWh/m^3
3. 12 MJ or 3.3 kWh
4. $W = 0$, W_t = – 4200 (4157) kJ, i.e. we must add the technical work 4.2 MJ
5. The volume of the gas is 125 m^3
6. The temperature of the air was 373 K ≈ 100˚C
7. The initial pressure was 2.1×10^5 Pa
8. The volume increase 130%
9. The final pressure is 17.5×10^5 Pa. The final temperature is 676 K ≈ 403˚C ≈ 400˚C
10. a) Added heat 130 (128) J, b) Final pressure 110 kPa
11. a) We add the work 200 (199) kJ/kg, b) Final temperature becomes 220 (216)˚C, c) $\Delta U \approx 140$ kJ/kg
12. a) Internal energy at 20˚C is 20 kJ b) Enthalpy at 20˚C is 28 kJ.

Solutions

1. To melt 1 kg snow you need 334 kJ 5 tonnes snow need $5000\times334\times10^3 \approx 1.7\times10^9 \approx 1.7$ GJ.

   Efficiency is 80%, i.e. $\frac{\text{Heat of melting}}{\text{Heat input}} = \frac{H_{\text{melt}}}{Q_{\text{input}}} = 0.8$

   $$Q_{\text{input}} = \frac{H_{\text{melt}}}{0.8} \approx \frac{1.7\times10^9}{0.8} \approx 2.1\times10^9 .$$

   1 liter diesel contains about 10kWh or 36 MJ.

   Needed amount becomes: $\frac{2.1\times10^9}{3.6\times10^7} \approx 58 \approx 60$ liter, which is more then 10 times what is needed for truck removal.

2. Per square meter we get 20×10^{-3} m^3 or 20 liter ice as snow, i.e. about 20 kg snow. To melt 1 kg snow we need 334 kJ 20 kg snow need $20\times334\times10^3 \approx 6.7\times10^6 \approx 6.7$ MJ ≈ 2 kWh, i.e. the energy difference between snow and rain is about 6.7 MJ/m^2 or 2 kWh/m^2.

3. Amount of air becomes 125×2.4 [m^3] $\times1.3$ [kg/m^3] ≈ 390 kg.

   Added heat is $Q = cm\Delta T \approx 1.0$ [kJ/kg K] $\times390$ [kg] $\times20$ [K] $= 7.8\times10^6$ J.

   The need of fuel oil is $Q_{\text{fuel}} = \frac{Q}{\eta} \approx \frac{7.8\times10^6}{0.65} = 12\times10^6\,\text{J} \approx 3.3$ kWh or about 1/3 liter.

4. Work $W = \int PdV = 0$, because an isochor process, i.e. dV = 0.

   Technical work $W_t = \int VdP$ (ideal gas model gives) $= mR\int dT = mR\Delta T \approx$

   $\approx 10[\text{kg}]\times\frac{8314.3[\text{J / kmolK}]}{2[\text{kg / kmol}]}\times100[\text{K}] \approx 4.157\times10^6\,\text{J} \approx 4.2$ MJ, i.e. we must add the technical work 4.2 MJ.

5. The ideal gas model gives:

   $$V = \frac{mRT}{P} \approx \frac{10[\text{kg}]\times\frac{8314.3[\text{J / kmol K}]}{2[\text{kg / kmol}]}(273.15+27)[\text{K}]}{1\times10^5[\text{Pa}]} \approx 125\ \text{m}^3.$$

6. 1st law gives: $Q = \Delta U + W = \int mc_v dT + W = 0 + W$, i.e. $Q = W$ of an isothermal process.

   Work $W = \int_1^2 PdV = \int_1^2 \frac{mRT}{V}dV = mRT\int_1^2\frac{dV}{V} = mRT\ln\frac{V_2}{V_1}$ of an ideal gas and isothermal process.

   We get: $T = \frac{Q}{mR\ln\frac{V_2}{V_1}} = \frac{148\times10^3[\text{J}]}{1[\text{kg}]\times287[\text{J/ kgK}]\ln\frac{2}{0.5}} \approx 373$ K or about 100°C.

7. The ideal gas model gives:

   $$P = \frac{mRT}{V} = \frac{1[\text{kg}]\times287[\text{J/ kgK}]\times373[K]}{0.5[\text{m}^3]} \approx 2.14\times10^5\ \text{Pa}.$$

8. For an adiabatic process we have PV^κ = constant, where $\kappa = \frac{c_P}{c_v}$, i.e.

$$P_1V_1^\kappa = P_2V_2^\kappa \Leftrightarrow \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^\kappa \Leftrightarrow \frac{V_2}{V_1} = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\kappa}} \approx \left(\frac{6\times10^5}{2\times10^5}\right)^{\frac{1}{1.3}} \approx 3^{0.77} \approx 2.33,\ \text{i.e.}$$

the volume increases 133%.

9. For a polytropical process we have PV^n = constant, where n is the polytropic coefficient, i.e. the final pressure becomes P_2:

$$P_1V_1^n = P_2V_2^n \Leftrightarrow P_2 = P_1\left(\frac{V_1}{V_2}\right)^n \approx 0.9\times10^5\left(\frac{9V_2}{V_2}\right)^{1.35} \approx 0.9\times10^5\times9^{1.35} \approx$$

$$\approx 17.5\times10^5\,\text{Pa}$$

From the ideal gas model ($PV = mRT$) we can rewrite this as:

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{n-1} \approx (40+273.15)\left(\frac{9V_2}{V_2}\right)^{(1.35-1)} \approx 313\times9^{0.35} \approx 676\ \text{K} \approx 403^\circ\text{C}.$$

10. a) To determine Q we must know c_v in the temperature interval $[T_1,T_2]$ and the mass m. The mass we get from the ideal gas model ($PV = mRT$, where R is the special gas constant, i.e. "per kg" according to $R = \frac{\overline{R}}{M}$, where $\overline{R}$ is the general gas constant and M is mol):

$$m = \frac{P_1V_1}{RT_1} \approx \frac{1\times10^5\times5\times10^3}{\frac{8314}{29}\times293.15} \approx 5.95\times10^{-3}\ \text{kg.}$$

$$P_1V_{1^n} = P_2V_{2^n} \Leftrightarrow P_2 = P_1\left(\frac{V_1}{V_2}\right)^n \approx 0.9\times10^5\left(\frac{9V_2}{V_2}\right)^{1.35} \approx 0.9\times10^5\times9^{1.35} \approx$$

$$\approx 17.5\times10^5\ \text{Pa.}$$

From the ideal gas model ($PV = mRT$) the relation above can be written as

We have for c_P and c_v: $\kappa = \frac{c_P}{c_v}$ and for air we have $\kappa \approx 1.4$. From tables we get the average value for c_P in temperature range 20-50˚C to:

$$\hat{c}_P = c_P(20^\circ\text{C},50^\circ\text{C}) \approx \frac{c_P(20^\circ\text{C})+c_P(50^\circ\text{C})}{2} \approx \frac{c_P(20^\circ\text{C})+\frac{c_P(40^\circ\text{C})+c_P(60^\circ\text{C})}{2}}{2}$$

$$\approx \frac{1005+\frac{1005+1009}{2}}{2} \approx 1006\ \text{J/kg}^\circ\text{C. Which gives } \hat{c}_v = \frac{\hat{c}_P}{\kappa} \approx 719\ \text{J/kg}^\circ\text{C.}$$

We can now determine the added heat from the definition of the heat capacity:

$$Q = m\hat{c}_v(T_2-T_1) = m\hat{c}_v\Delta\theta_{21} \approx 5.95\times10^3\times719\times30 \approx 128[\text{kg}\frac{\text{J}}{\text{kgK}}K = \text{J}]$$

(Always check the dimentions!)

b) To determine the final pressure we must know how the pressure changes during the process, since it is an isochoric process we have (according to the ideal gas model): $P\times\text{constant} = T$ or

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \Leftrightarrow P_2 = P_1\frac{T_2}{T_1} \approx 1\times10^5\,\frac{323.15}{293.15} \approx 1.10\times10^5 \text{ Pa} = 110 \text{ kPa.}$$

11. a & b) The process is adiabatic, i.e.:

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} \approx 293.15\left(\frac{6\times10^5}{1\times10^5}\right)^{\frac{1.4-1}{1.4}} \approx 489 \text{ K, i.e. } \theta_2 \approx 489–273 \approx 216^\circ\text{C.}$$

We may now calculate the average value of the specific heat at constant pressure accordingly:

$$\hat{c}_P = c_P(20^\circ\text{C},216^\circ\text{C}) \approx \frac{c_P(20^\circ\text{C}) + c_P(216^\circ\text{C})}{2} \approx \frac{1005+1027}{2} \approx 1016 \text{ J/kg K.}$$

Added work, i.e. technical work, when we have an open process, can be calculated: $w_t = h_1 - h_2 = \int_2^1 c_P dT \approx \hat{c}_P(T_1 - T_2) \approx 1016\times(293.15–489.15) \approx –199$ kJ/kg. (The minus sign indicate that work is beeing added to the process!)

c) The change of the internal energy can be calculated:

$$u_2 - u_1 = \int_1^2 c_V dT = \int_1^2 \frac{c_P}{\kappa}\,dT = \frac{\int_1^2 c_P dT}{\kappa} = \frac{-w_t}{\kappa}$$

, i.e. the internal energy increases by, $\Delta u_{21} \approx -\frac{(-199)}{1.4} \approx 140$ kJ/kg.

12. The mass m we get from the ideal gas model ($PV = mRT$) accordingly:

$$m = \frac{P_2V_2}{RT_2} \approx \frac{2\times10^5\times0.6}{287\times293.15} \approx 1.4 \text{ kg.}$$

a) For the internal energy: $U_2 - U_1 = m\int_1^2 c_V dT = \int_1^2 \frac{c_P}{\kappa}\,dT \approx m\frac{\hat{c}_P}{\kappa}(T_2 - T_1) \approx$

$$\approx m\frac{c_P(0^\circ\text{C},20^\circ\text{C})}{\kappa}(T_2 - T_1) \approx m\,\frac{\frac{c_P(0^\circ\text{C}) + c_P(20^\circ\text{C})}{2}}{\kappa}(T_2 - T_1) \approx$$

$$\approx 1.4\frac{\frac{1005+1005}{2}}{1.4}(293.15 - 273.15) \approx 20 \text{ kJ} \qquad U_2 \approx 20 + U_1 \approx 20 + 0 \approx 20 \text{ kJ.}$$

a) Analagously for the enthalpyt: $H_2 = H_1 + m\int_1^2 c_P dT \approx H_1 + m\hat{c}_p(T_2 - T_1) \approx 0 + 1.4\times1005\times(293.15–273.15) \approx 28$ kJ.

EXERGY

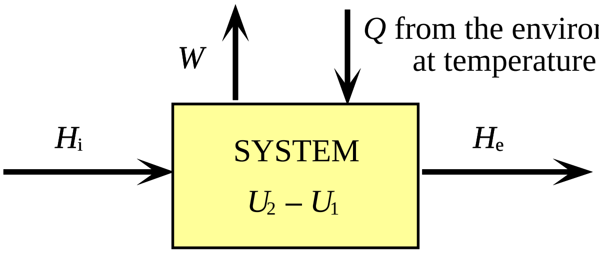
We have now concluded that it is a fundamental law of nature that energy neither can be created nor distryed (the First Law of Thermodynamics). Energy is available in many different forms and may be converted between these forms. However, a strict limitation is always active. Different energies has different qualities, indicating to what extent they are theoretically convertible to mechanical work. This limitation, a Law of Nature, implies that the total energy quality always decreases in each conversion (the Second Law of Thermodynamics).

The quality of energy is described by the concept of entropy. High entropy is equal to low quality of energy. The Second Law states that conversions are possible only if the total entropy increases. By introducing exergy, we may treat energy and entropy simultaneously, i.e. “kill two birds with one stone”.

At this stage, introducing exergy is mere a matter of putting a name to something we already know. By reading the more verbal treatment of the exergy concept you are well prepared for the more analytic treatment.

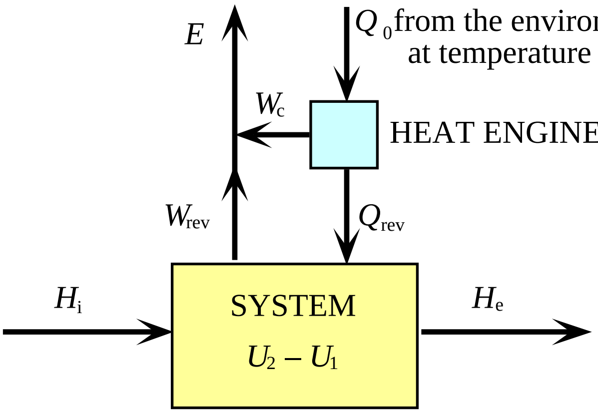
Exergy of a general process

Assume a general (irreversible) process:



The processen involves a change of the internal energy of the system, $U_2 - U_1$, and a change of the enthalpy of the flow through the system, H_e and H_i. Thus, the process is a combination of a closed and open system.

Let us make the process reversible by adding a reversibel heat engine as below.



We can now describe the process in detail.

The work from the heat engine is W_c, and the total maximal work we may extract from the system at a reversible process E (= exergy) is

$$E = W_{\text{rev}} + W_{\text{c}}$$

If we apply the first law on the modified system with a reversible process, we get

$$Q_{\text{rev}} + H_{\text{i}} = U_2 - U_1 + W_{\text{rev}} + H_{\text{e}}$$

i.e.,

$$W_{\text{rev}} = Q_{\text{rev}} + H_{\text{i}} - H_{\text{e}} - (U_2 - U_1)$$

Since, all processes are reversible the heat exchange with the environment must go through the heat engine, as is shown in the Fig above. The first law applied to the heat engine gives

$$W_{\text{c}} = Q_0 - Q_{\text{rev}}$$

and the second law gives

$$\frac{Q_0}{T_0} = S_{\text{rev}}$$

were S_{rev} is the entropy related to the heat Q_{rev}. The work from the heat engine becomes:

$$W_{\text{c}} = T_0 S_{\text{rev}} - Q_{\text{rev}}$$

the second law for the system gives:

$$S_{\text{rev}} = S_2 - S_1 + S_{\text{e}} - S_{\text{i}}$$

Thus the work from the heat engine becomes

$$W_{\text{c}} = T_0(S_2 - S_1 + S_{\text{e}} - S_{\text{i}}) - Q_{\text{rev}}$$

By replacing W_{rev} and W_{c} in the Eq. for E, we get

$$E = Q_{\text{rev}} + H_{\text{i}} - H_{\text{e}} - (U_2 - U_1) + T_0(S_2 - S_1 + S_{\text{e}} - S_{\text{i}}) - Q_{\text{rev}}$$

Which may be rewritten as

$$E = H_{\text{i}} - T_0 S_{\text{i}} - (H_{\text{e}} - T_0 S_{\text{e}}) + (U_1 - T_0 S_1) - (U_2 - T_0 S_2) = E_{\text{i}} - E_{\text{e}} + E_1 - E_2$$

As we see Q_{rev} disappears in the expression for the reversible work that can be extracted from a general process, which involves heat at ambient temperature T_0. This reversible work, which is the maximum work that can be extracted, we call the exergy. This is the part of the energy, which is completely convertible into any other forms of energy, i.e. especially work. Other forms of energy, e.g. kinetic and potential mechanical energies and electrical energy may just be directly added. Let us now look closer to special cases of this general exergy expression.

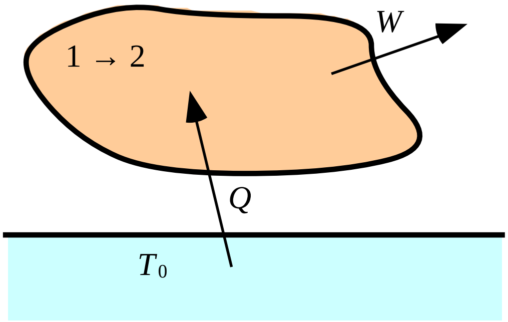
R: Appendix B in this material or Appendix A in G. Wall, “Exergy — A Useful Concept within Resource Accounting”, 1977, pp. 40-43, that you find on the Internet: http://exergy.se/. (This is an alternative derivation of the exergy concept based on a closed system in an infinite environment. Thus the environmental relations are stressed, but as we will see the environment only plays the role of referens state. And, the exergy can be related to any referens state.)

Exergy, work and entropy production

We will now derive an expression for the total entropy production and the relation to exergy.

Consider a defined thermodynamic system going through a process from state 1 to 2, where work W is extracted. Futher more heat Q is added from a reservoir, e.g. the environment at temperature T_0, see Fig. below.

The situation is completely general the only restriction is that the system is defined.



The first law gives:

$$Q = U_2 - U_1 + W \tag{1}$$

The entropy change of the system is $S_{sys} = S_2 - S_1$. Futher has the entropy of the reservoir also changed. The reservoir has delivered the heat Q. The entropy change change of the reservoir then becomes

$$S_{res} = \frac{Q}{T_0} \tag{2}$$

We use S^{tot} to indicate the total entropy change of the system and the environment, which becomes

$$S^{tot} = S_{sys} + S_{res} = S_2 - S_1 - \frac{Q}{T_0} \tag{3}$$

By eliminating Q from Eqs. 3 and 1 we get

$$W = U_1 - U_2 - T_0(S_1 - S_2) - T_0 S^{tot} \tag{4}$$

The total entropy change S^{tot} is always positive (second law)

$$S^{tot} > 0 \tag{5}$$

so we will from now on call S^{tot} the total entropy production.

Equations 4 and 5 gives an upper limit of the work W which may be extracted from the process. This upper limit is given from a reversible process, since the total entropy production S^{tot} of such a process is zero.

We now assume a reversible process, which utilizes the given heat reservoir and converts the system from state 1 to 2. Any kind of extra apparatus is alloved. However, these should be in the same state efter the reversible process as they were before. The maximal extractible work, i.e. the exergy then becomes according to Eq. 4:

$$E = U_1 - U_2 - T_0(S_1 - S_2) \tag{6}$$

If we combine Eqs. 4 and 6 we have an important relation

$$W = E - T_0 S^{\text{tot}} \tag{7}$$

The exergy obiously gives an upper limit to the work which is extracable from the process, since the entropy production S^{tot} is always positive. Thus the available work W is limited by the exergy E.

At an irreversible process as above with the entropy production S^{tot}, this corresponds to a loss of available work or exergy. Thus, for an irreversible process we have:

$$\begin{cases} W_{\text{loss}} = E_{\text{loss}} = T_0 S^{\text{tot}} \\ S^{\text{tot}} \geq 0 \end{cases} \tag{8}$$

Thus, the relation between exergy and entropy is very fundamental. We may say that exergy is the concept which linkes the universial concept of entropy with the the conditions on the Earth through the temperature. In the section on exergy and information we will develop this fundamental relation further.

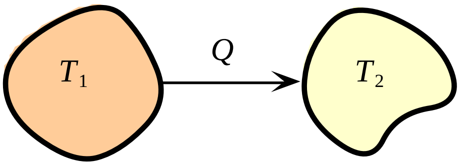
Exergy loss = Ambient temperature × Entropy production

This relation may also be expressed as the following: the maximal available exergy is equal to the ambient temperature times the maximal entropy production.

The result of this section may be expressed in many ways as we will see in the comming sections. This simple conclusion is still a very fundamental realtion. We will now calculate the entropy production of some simple cases.

Heat transfer

Assume a certain amount of heat Q is transfered from a body with the temperature T_1 to a body with the temperature T_2. The entropy change for the bodies are $-Q/T_1$ and Q/T_2. We may regard this as if the heat flow is removing the entropy Q/T_1 from "T_1" and adding the entropy Q/T_2 to "T_2", and that the difference gives the entropy production. The heat exchange has occurred through some intermediate medium. This medium is in the same state after the process as before. The intermediate medium does not change its entropy.



The total entropy change then becomes

$$S^{tot} = \frac{Q}{T_2} - \frac{Q}{T_1} \tag{9}$$

If a heat Q is transfered from T_1 to T_2 and further to T_3 then we get for each transfer

$$S_{12}^{\text{tot}} = \frac{Q}{T_2} - \frac{Q}{T_1} \quad \text{and} \quad S_{23}^{\text{tot}} = \frac{Q}{T_3} - \frac{Q}{T_2} \tag{10}$$

and for the total transfer we get

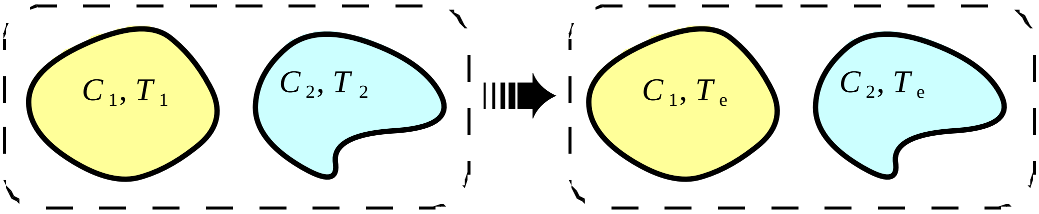
$$S_{13}^{\text{tot}} = \frac{Q}{T_3} - \frac{Q}{T_1} \tag{11}$$

We could have stated Eq. 11 directly from Eq. 9.

It is important to note that the entropy production becomes less if the heat transfer occurs at higher temperature. The entropy production at heat tranfer from 610 K to 600 K is only one forth as big as if the same energy of heat is transfered from 310 K to 300 K.

Temperature exchange between two bodies

We have two bodies with the heat capacities C_1, C_2 and the temperatures T_1 and T_2. The volumes are constant, e.g. two buckets of water with different temperatures.



Heat is exchanged to reach equilibrium at temperature T_e. First law, i.e. energy conservation gives:

$$T_e = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2} \tag{12}$$

The total entropy production becomes:

$$S^{\text{tot}} = \int_{T_1}^{T_e} \frac{C_1 dT}{T} + \int_{T_2}^{T_e} \frac{C_2 dT}{T} = C_1 \ln\frac{T_e}{T_1} + C_2 \ln\frac{T_e}{T_2} \tag{13}$$

if we assume that the heat capacities are constant, i.e. do not depend on temperature.

Ex: Convince yourself that the total entropy production always is positive.

S: To check this we set $x = T_2/T_1$, which gives:

$$S^{\mathrm{tot}} = C_1 \ln \frac{C_1 + xC_2}{C_1 + C_2} + C_2 \ln \frac{\frac{C_1}{x} + C_2}{C_1 + C_2} \tag{14}$$

The entropy production is of course zero if $x = 1$. The derivative with respect to x becomes:

$$\frac{dS^{\mathrm{tot}}}{dx} = \frac{C_1 C_2}{C_1 + C_2 x}\left(1 - \frac{1}{x}\right) \tag{15}$$

The derivative is positive for $x>1$ and negative for $0<x<1$. Thus, the entropy production is positive for $0<x<\infty$.

Friction

Assume w_{f} to be the frictional work of a process, and assume this becomes heat, i.e. no other effects. If the temperature of the frictional heat is T, the entropy production becomes, according to Eq. 2 ($Q = -w_{\mathrm{f}}$):

$$s = \frac{w_{\mathrm{f}}}{T} \tag{16}$$

As we see the entropy production becomes less with increasing temperature, i.e. the friction work is transfered to frictional heat of higher quality.

Q: Have you any ideas how this could be used? Do you know where?

If the frictional work W_{f} generates heat at temperature T_1 and if the temperature then decreases to T_2 we get the entropy production from Eq. 9 and 16:

$$S^{\mathrm{tot}} = \frac{W_{\mathrm{f}}}{T_1} + W_{\mathrm{f}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{W_{\mathrm{f}}}{T_2} \tag{17}$$

Thus, we get the same entropy production as if the temperature of the frictional heat originally was T_2.

The total entropy production from friction is given by contributions defined by Eq. 16. The produced frictional heat also creates additional contributions to the total entropy production according to Eq. 9, and finally the total entropy production becomes according Eq. 17.

Thus, if the total frictional work is W_{f}, and if all frictional heat is lost to the environment at temperature T_0, then the total entropy production from frictional work and heat transfer to the environment becomes:

$$S^{\mathrm{tot}} = \frac{W_{\mathrm{f}}}{T_0} \tag{18}$$

All frictional heat finally reaches the environment, however the entropy production will appear at many sub processes.

System in contact with a heat reservoir

Our system is now in contact with a heat reservoir of temperature T_0 during the process 1 to 2. The initial and final emperatures must then be equal to T_0:

$$T_1 = T_2 = T_0 \tag{19}$$

We also assume that the volume is constant:

$$V1 = V2 \tag{20}$$

The process will then not generate any work on the environment.

This kind of process usually occur for liquids and solids. The temperature might of course change during the process.

The exergy, i.e. the available reversible work then becomes according to Eqs. 6, 19 and the definition of Helmholtz' function or free energy, $A = U - TS$:

$$E = A_1 - A_2 \tag{21}$$

From Eq. 7 we get:

$$W \leq A_1 - A_2 \tag{22}$$

Thus, the decrease of Helmholz free energy of the system gives the upper limit of the available work of the process.

System in contact with a heat and pressure reservoir

In many processes the inital and final pressure is the same, i.e.:

$$P_1 = P_2 = P_0 \tag{23}$$

And often P_0 is the ambient pressure, towards which the system performes a work $P_0(V_2 - V_1)$ during the process. The available work then becomes:

$$W' = W - P_0(V_2 - V_1) \tag{24}$$

The exergin then becomes according to Eq. 21, the definition of enthalpy $H = U + PV$ and Gibbs' function or free enthalpy $G = H - TS$:

$$E = G_1 - G_2 \tag{25}$$

For the available work we get:

$$W' \leq G_1 - G_2 \tag{26}$$

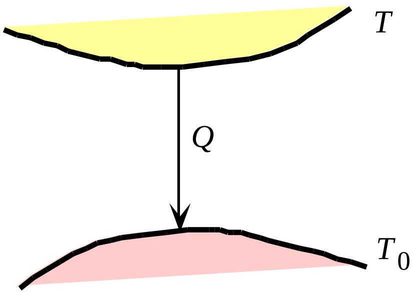
Thus, the decrease of free enthalpy *G* for the system gives the upper limit of the available work of the process, i.e. similarly as above for Helmholz' function.

The Eqs. 22 and 26 explains why we use free energy for *A* and free enthalpy for *G*. It is important to notice the conditions of these relations. As we have seen Helmholtz' och Gibbs' functions are special cases of the exergy for special processes. In Appendix 2, you will find a more detailed analysis between exergy and these and other concepts.

Exergy of heat and cold

We will now derive expressions for available work in some basic cases where heat transfer is involved. The ambient temperature is T_0.

Let us first assume that heat *Q* is transfered between two reservoirs at temperatures *T* and T_0, and $T > T_0$ and find the exergy involved. A reversible heat engine working between the temperatures *T* and T_0 gives the maximal available work. By assuming that the heat is completely lost we may calculate the maximal entropy production and the exergy beeing lost, i.e. the available exergy which is able to utilize.



From above we have:

$$E = T_0 S^{\text{tot}} = T_0\left(\frac{Q}{T_0} - \frac{Q}{T}\right) = Q\left(1 - \frac{T_0}{T}\right) \qquad (T>T_0) \qquad (1)$$

If the temperature $T < T_0$, this only change the direction of the heat flow *Q*, which then will go from T_0 to *T*, the exergy now becomes:

$$E = T_0\left(\frac{Q}{T} - \frac{Q}{T_0}\right) = Q\left(\frac{T_0}{T} - 1\right) \qquad (T<T_0) \qquad (2)$$

The ratio between the exergy *E* and the energy of the transfered heat *Q* we call the **exergy factor** *E*/*Q*. Thus, by multiplying the energy by the exergy factor we get the exergy. The exergy factor of heat from a heat reservoir, i.e. at constant temperature *T*, that differ from the ambient temperature T_0 is

$$\frac{E}{Q} = \left|\frac{T - T_0}{T}\right| \qquad (3)$$

This is a generalisation of the Carnot relation, since it also covers temperature below ambient. Let us exemplify this.

Ex: What is the exergy factor of heat at 20˚C (≈ 293 K) in an environment at 5˚C (≈ 278 K)? One example of this is exergy needed to maintain the inside temperature at +20˚C when the outside temperature is 5˚C.

S: From Eq.3 we have:

$$\frac{E}{Q} = \left| \frac{293-278}{293} \right| = \frac{15}{293} \approx \frac{15}{3}\% \approx 5\%$$

So, the exergy factor of heat at 20˚C in an environment at 5˚C is approximatly 5 %. Thus, the exergy efficiency of an electric heat radiator (electric short circuit), which maintain the indoor temperature at +20˚C when the outdoor temperature is +5˚C is about 5 %. However, the energy efficiency is 100%.

Let us look closer to the relation between energy and exergy efficiencies and exergy factor.

Ex: Estimate the energy efficiency of an oil furnace when the exergy efficiency is 3%, the exergy factors for in and out flows are 0.9 and 0.04 respectively?

S: We have the following relations:

$$\text{Exergy factor} = \frac{\text{Exergy}}{\text{Energy}}\ \text{, i.e.,}\ \frac{E}{Q}$$

$$\text{Energy efficiency} = \frac{\text{Energy output}}{\text{Energy input}}\ \text{, i.e.,}\ \eta_{\text{en}} = \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

$$\text{Exergy efficiency} = \frac{\text{Exergy output}}{\text{Exergy input}}\ \text{, i.e.,}\ \eta_{\text{ex}} = \frac{E_{\text{out}}}{E_{\text{in}}}$$

From these relations we may derive the following relation:

$$\eta_{\text{en}} = \frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{Q_{\text{out}}\dfrac{E_{\text{out}}}{E_{\text{out}}}}{Q_{\text{in}}\dfrac{E_{\text{in}}}{E_{\text{in}}}} = \frac{E_{\text{out}}\dfrac{Q_{\text{out}}}{E_{\text{out}}}}{E_{\text{in}}\dfrac{Q_{\text{in}}}{E_{\text{in}}}} = \eta_{\text{ex}}\frac{\dfrac{Q_{\text{out}}}{E_{\text{out}}}}{\dfrac{Q_{\text{in}}}{E_{\text{in}}}} = \eta_{\text{ex}}\frac{\dfrac{E_{\text{in}}}{Q_{\text{in}}}}{\dfrac{E_{\text{out}}}{Q_{\text{out}}}}$$

Numerical values gives:

$$\eta_{\text{en}} = 0.03\frac{0.9}{0.04} = 0.675 \approx 70\%$$

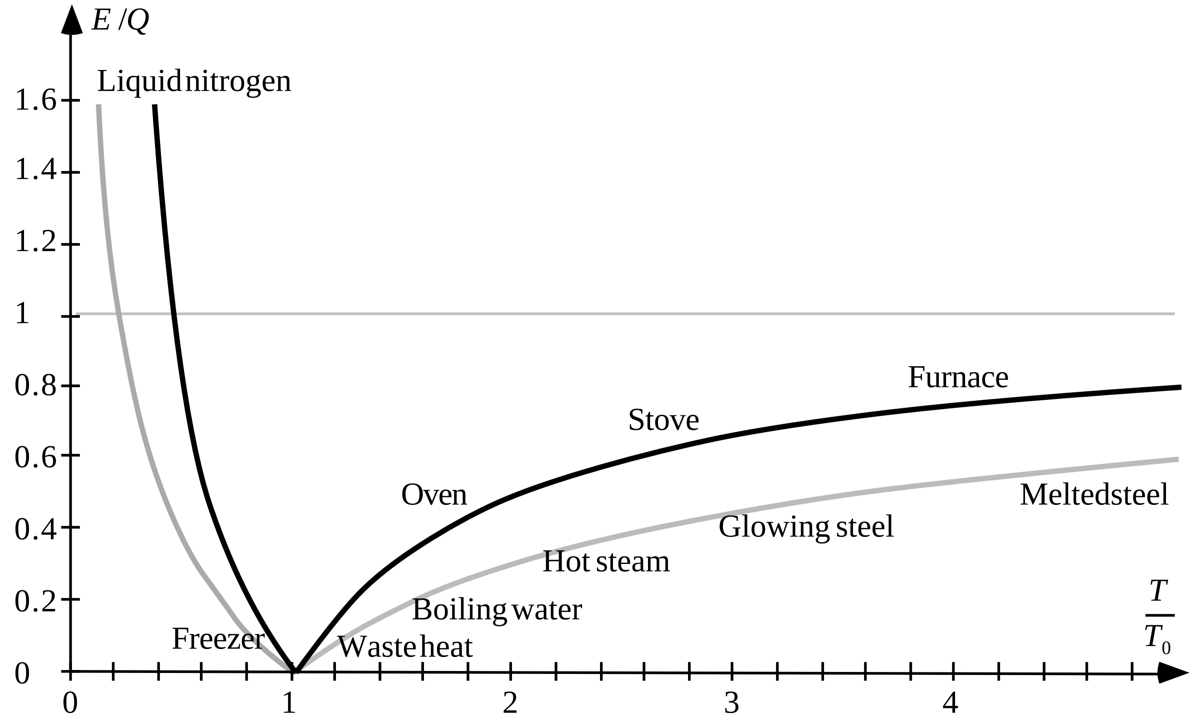
The energy efficiency becomes about 70 %.

S: Calculate the exergy factor for heat transfered between the following temperatures in degrees Celsius and 0˚C:

	–270	–200	–100	–20	0	20	100	200	500	1000	5000
$\frac{E}{Q}$	…	…	…	…	…	…	…	…	…	…	…

Check your values with the black line in the Fig. below.

The upper black curve, in Fig. below illustrates Eq. 3. (Den skuggade kurvan kommer vi att beskriva nedan.) As we see cold has exergy, when energy is regarded as negative. We also see that the exergy factor strongly increase for low temperatures, which explains the difficulty to reach absolute zero temperature, i.e. 0K or −273.15˚C. At high temperatures the exergy factor comes closer to 1 (the dotted line), i.e. exergy E and energy Q of the heat becomes almost the same. As we know, high temperatures generate more work in a heat engine.



Equation 3 is useful to describe the exergy need to maintain the temperature in hot spaces, e.g. furnaces, stoves, ovens, or houses, as well as in cold spaces, e.g. refrigerators and freezers, or to keep a pleasant indoor climate by air-conditioning a hot summer day.

Exergy reflects better than energy that heat or cold is more ”expensive” when we need it the most. Thus, it is easier to generate cold in winter and heat in summer. By using the energy concept it seems equal, since energy is not affected by the ambient conditions. So, from an energy point of view it seems independent of whether it is summer or winter. Thus, district heat should be more expensive in the winter than in the summer. This is an example of something obvious which is not explained by the energy concept, but is imideately explained by the exergy concept.

The exergy of a body with temperature T is slightly more complicated to calculate since the temperature of the body as well as the delivered heat decreases when heat is removed. Assume that the heat capacity of the body is $C(T)$. Let us calculate the exergy when the temperature decrease from T to T_0. The heat content of a temperature change dT' is $C(T')\mathrm{d}T'$, then the exergy becomes an integral from T_0 to T:

$$E=\int_{T_0}^{T} C(T')\left(1-\frac{T_0}{T'}\right)dT' \qquad (4)$$

It is not hard to see that this relation holds at both $T>T_0$ and $T<T_0$.

If the heat capacity is not depending on temperature, the exergy becomes

$$E=C\left(T-T_0-T_0\ln\frac{T}{T_0}\right)=C(T-T_0)\left(1-\frac{T_0}{T-T_0}\ln\frac{T}{T_0}\right) \qquad (5)$$

Since

$$Q=C(T-T_0) \qquad (7)$$

the exergy factor E/Q becomes:

$$\frac{E}{Q}=\left|1-\frac{T_0}{T-T_0}\ln\frac{T}{T_0}\right| \qquad (8)$$

Where the absolut signs make sure that the relation also holds for $T<T_0$. This relation is indicated by the gray line in the Fig. above.

In the derivation of exergy for a body we have neglected change in volume, which is usually acceptable for solids and for liquids.

S: Calculate the exergy factor for heat transfered between a body at the following temperatures in degrees Celsius and 0˚C:

θ˚C	–270	–200	–100	–20	0	20	100	200	500	1000	5000
$\frac{E}{Q}$	…	…	…	…	…	…	…	…	…	…	…

Check your values with the gray line in the Fig. above.

(Please observe that at low temperatures the heat capacity C can not be regarded as constant.)

In the Fig. above the exergies of some bodies at different temperatures are indicated, e.g. liquid nitrogen, waste heat, boiling water, hot steam, glowing steel, and melted steel.

Let us compare the exergy factors between the two cases, reservoir and body, at temperature T, see the exercises above. If T=100˚C then the exergy factor of the reservoir is 0.27 and for the body 0.15, i.e. almost half.

As we would expect the exergy factor E/Q is lower for a body since the temperature decreases with the heat released. At low temperatures, $T<T_0$, and for temperatures close to ambient, T_0, the exergy factor E/Q of a body is about half that of a reservoir. For high temperatures the exergy factors for a reservoir and a body become closer. Thus, it is important to make sure what kind of heat source is available, reservoir or body, for the system to be studied.

We will now examine district heat more in detail. District heat is regarded as a body, thus, the exergy factor becomes from Eq. 8:

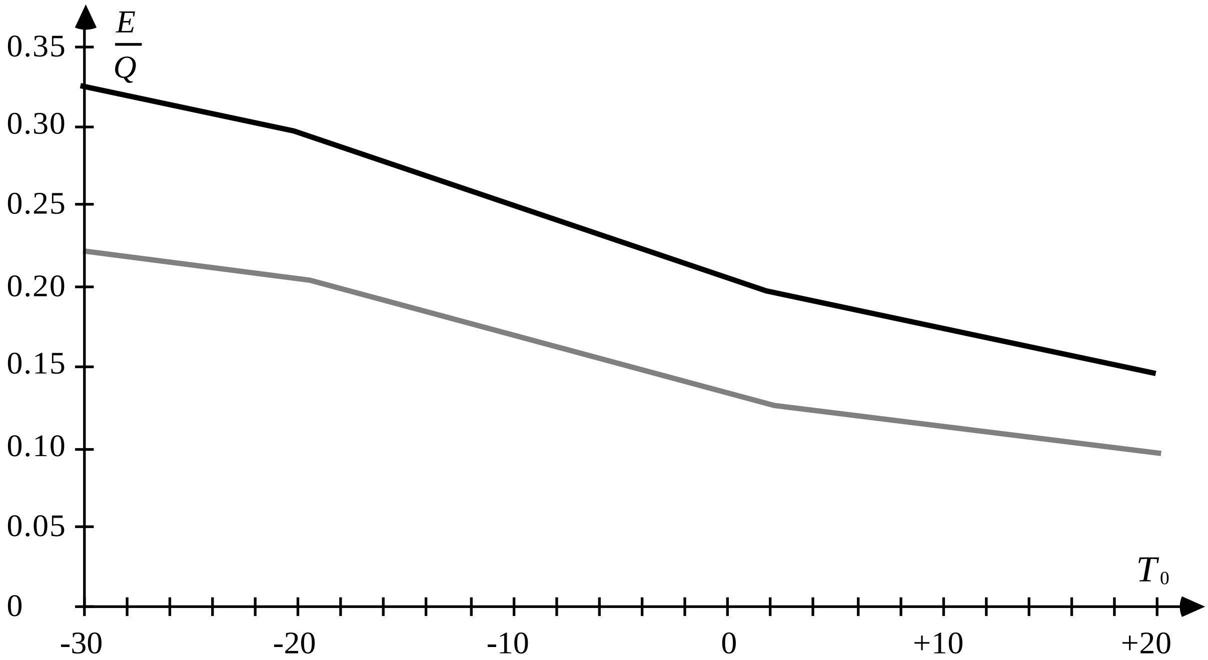
$$\frac{E}{Q} = 1 - \frac{T_0}{T_{\text{supply}} - T_0} \ln \frac{T_{\text{supply}}}{T_0} \tag{9}$$

where T_{supply} is the temperature of the supplied heat($T_{\text{supply}} > T_0$). Assume this to be 85˚C when $T_0 > +2$˚C and that it increses linearly with decreasing outdoor temperature to 120˚C when $T_0 < -20$˚C. Then, we get the lower gray curve in Fig. below. We see that the exergy factor is vaying stepwise between about 0.10 and 0.22 when the temperature decreases from +20 to –30˚C.

However, since a part of the supplied exergy is returned, we may calculate the utilized exergy to:

$$\frac{E}{Q} = 1 - \frac{T_0}{T_{\text{supply}} - T_{\text{return}}} \ln \frac{T_{\text{supply}}}{T_{\text{return}}} \tag{10}$$

where T_{return} is the temperature of the returned exergy, which we assume to 55˚C. Then, we get the upper black curve in the Fig. below. As we expected the exergy factor becomes higher, since the heat now is taken out at a higher average temperature. It now varies stepwise between about 0.15 and 0.32.



Ex: Calculate the exergy factor of district heat when the outdoor temperature is 0˚C? Also calculate the exergy factor of the utilized heat, see Eq. 10 above?

S: First we must find the temperature on the supplied district heatT_{supply} at the prevailing outdoor temperature T_0. When –20˚C $< T_0 <$+2˚C we have:

$$T_{\text{supply}} = 85 + (120 - 85) \times \frac{2 - T_0}{2 - (-20)}$$

which gives $T_{\text{supply}} \approx 88.2^\circ\text{C} \approx 361\text{K}$. Numbers in Eq. 9 give:

$$\frac{E}{Q} = 1 - \frac{273}{361-273}\ln\frac{361}{273} \approx 1 - \frac{273}{88}\ln(1.3223) \approx 0.13$$

Thus, the exergy factor of the supplied heat is 0.13.
If we assume the return temperature to be 55°C, i.e. 328K, then we get for the utilized heat:

$$\frac{E}{Q} = 1 - \frac{273}{361-328}\ln\frac{361}{328} \approx 1 - \frac{273}{33}\ln(1.1006) \approx 0.21$$

Thus, the exergy factor of the utilized heat is 0.21.

S: Verify the expression for the utilized district heat in Eq. 10 above.

We will return to exergy of heat and cold when we analyze the exergy conversions in industrial processes.

Add something about district cold also, this is interesting from the point of putting a price on the energy. How do you price cold delivered to the consumer, when the consumer is delivering the heat?

Exergy of black body radiation

For black body radiation[6] we have the following relations for energy and entropy emission rates per unit area:

$$\dot{u} = \sigma T^4 \tag{1}$$

$$\dot{s} = \frac{4}{3}\sigma T^3 \tag{2}$$

(Please, note that $d\dot{u} = Td\dot{s}$.)

where $\sigma = \dfrac{2\pi^5 k^4}{15h^3c^2} \approx 5.67 \times 10^8 \left[\text{W/ K}^4\text{m}^2\right]$ is called the Stefan-Boltzmanns constant.

Consider the reversible process, radiation from a black body at temperature T is transmitted to another black body at temperature, T_0:

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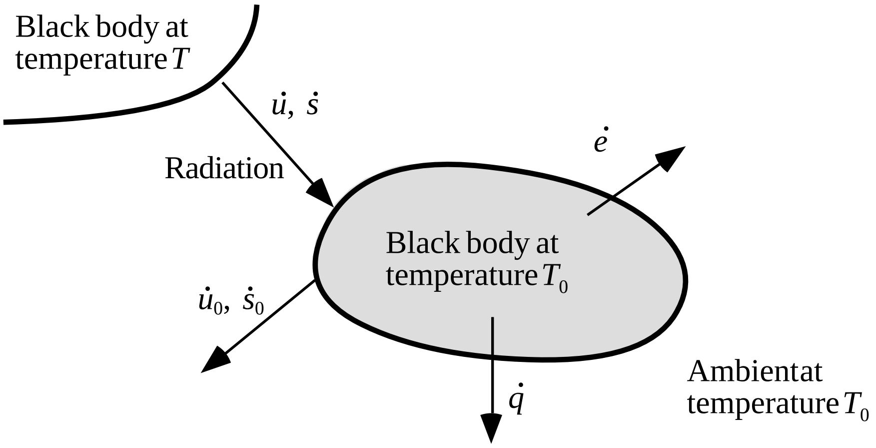
[6] A black body by definition absorbs all incoming radiation.



The exergy flow $\dot{e}$, which is associated with the heat radiation is derived by applying the first and second law to an ideal reversible process. This process converts the radiation to exergy and heat at ambient temperature. Assume that the converter can not receive radiation without emit radiation, the principal of detailed balance.

The converter receives energy and entropy according to Eqs. 1 and 2. Simultaneously, it emits energy, $\dot{u}_0$ and entropy, $\dot{s}_0$ according to Eqs. 1 and 2.

$$\dot{u}_0 = \sigma T_0^4$$

$$\dot{s}_0 = \frac{4}{3}\sigma T_0^3$$

The first law gives:

$$\dot{u} = \dot{u}_0 + \dot{e} + \dot{q} \tag{3}$$

Since the the process is reversibel, there is no entropy production, and the second law gives.

$$\dot{s} = \dot{s}_0 + \frac{\dot{q}}{T_0} \tag{4}$$

The work or exergy that can be extracted from the radiation becomes

$$\begin{aligned}\dot{e} &= \dot{u} - \dot{u}_0 - \dot{q} = \dot{u} - \dot{u}_0 - T_0(\dot{s} - \dot{s}_0) = \\ &= \sigma\left[T^4 - T_0^4 - \frac{4}{3}T_0(T^3 - T_0^3)\right] = \sigma T^4\left[1 + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 - \frac{4}{3}\frac{T_0}{T}\right]\end{aligned} \tag{5}$$

Thus, the exergy factor of black body radiation is

$$\frac{\dot{e}}{\dot{u}} = 1 + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 - \frac{4}{3}\frac{T_0}{T} \tag{6}$$

Let us apply this result to sunlight[7], where T_{sun} = 6000 K and $T_{\text{earth}} = T_0$ = 300 K, the exergy factor becomes from Eq. 6

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[7] The sun and the earth can be regarded as almost black bodies.

$$\left(\frac{\dot{e}}{\dot{u}}\right)_{\text{sunlight}} = 1 + \frac{1}{3}\left(\frac{300}{6000}\right)^4 - \frac{4}{3}\times\frac{300}{6000} \approx 0.933$$

Q: What is the exergy factor for heat at heat transfer? What does the differens indicate?

Ex: Compare the energy and Exergy efficiencies of the following solar collectors, all working in full sunlight, i.e. 1000 W/m^2 and the ambient temperature is 15˚C:

1. A flat solar panel for heat generation of 1m^2 which heats 3 dl of water from 10 to 40˚C per minut.
2. A concetration solar collector of 1 m^2 which gives 1 g steam at ambient pressure per minut from water at 10˚C.
3. Solar cell 95×65 mm which gives 0.45 V and 400 mA.

S: 1. Energy power in $P_{\text{en, in}} \approx 1000\times1 = 1000$ W

Exergy power in $P_{\text{ex, in}} \approx 1000\times0.933\times1 = 933$ W

Energy power out $P_{\text{en,out}} = \dot{C}\Delta T \approx \frac{0.3}{60}\times 4200(40-10) = 630\text{W}$

Exergy power out $P_{\text{ex,out}} = \dot{C}\left(\Delta T - T_0 \ln\frac{T_{\text{out}}}{T_{\text{in}}}\right) \approx$

$\approx \frac{0.3}{60}\times 4200\left(40-10-288.15\times\ln\frac{313.15}{283.15}\right) \approx 20.6\text{W}$

Energy efficiency $\eta_{\text{en}} \approx \frac{630}{1000} = 63\%$

Exergy efficiency $\eta_{\text{ex}} \approx \frac{20.6}{933} \approx 2.2\%$

2. Energy power in $P_{\text{en, in}} \approx 1000\times1 = 1000$ W

Exergy power in $P_{\text{ex, in}} \approx 1000\times0.933\times1 = 933$ W

Energy power out $P_{en,ut} = \dot{C}\Delta T + \dot{H}_{\text{phase}} \approx$

$$\approx \frac{0.001}{60}\left[4200(100-10) + 2.3\times10^6\right] = 44.6\text{W}$$

Exergy power out $P_{\text{ex,out}} = \dot{C}\left(\Delta T - T_0 \ln\frac{T_{ut}}{T_{in}}\right) + \dot{H}_{\text{phase}}\times\frac{T_{\text{out}} - T_0}{T_{\text{out}}} \approx$

$\approx \frac{0.001}{60}\left[4200\left(100-10-288.15\times\ln\frac{373.15}{283.15}\right) + 2.3\times10^6\times\frac{100-15}{373.15}\right] \approx$

$\approx 0.7 + 8.7 = 9.4$ W

Energy efficiency $\eta_{\text{en}} \approx \frac{44.6}{1000} \approx 4\%$

Exergy efficiency $\eta_{\text{ex}} \approx \frac{9.4}{933} \approx 1\%$

3. Energy power in $P_{\text{en, in}} \approx 1000\times95\times65\times10^{-6} \approx 6.2$ W

Exergy power in $P_{\text{ex, in}} \approx 0.933\times6.175 \approx 5.8$ W

Energy power in $P_{\text{en, out}} = UI \approx 0.45\times0.4 = 0.18$ W

Exergy power in $P_{\text{ex, out}} = UI \approx 0.18$ W

$$\text{Energy efficiency } \eta_{\text{en}} \approx \frac{0.18}{6.2} \approx 2.9\%$$

$$\text{Exergy efficiency } \eta_{\text{ex}} \approx \frac{0.18}{5.8} \approx 3.1\%$$

Q: What are suitable applications of these different collectors?

Exergy of materials

A simplified introduction to the exergy of substances and materials is given below.

Assume the pressure P and the temperature T to be constant, i.e. $P = P_0$ and $T = T_0$, then we have from the general expression of exergy, see App. 2:

$$E = \sum_i n_i(\tilde{\mu}_i - \tilde{\mu}_{i0}) \tag{1}$$

where $\tilde{\mu}_i$ is the generalized chemical potential of substance i in its present state and
$\tilde{\mu}_{i0}$ is the generalized chemical potential of substance i in its environmental state.

Further, assume that that the substance only depart from the environment in chemical potential μ and concentration c. Also, assume that the general chemical potential may be written

$$\tilde{\mu}_i = \mu_i^0 + RT_0 \ln c_i \tag{2}$$

where μ_i^0 is the chemical potential for the material (substance) i in relation to its standard state, given from chemical tables, usually the pure element. Then the exergy becomes

$$E = \sum n_i(\mu_i^0 - \mu_{i0}^0) + RT_0 \sum n_i \ln \frac{c_i}{c_{i0}} \tag{3}$$

where μ_{i0}^0 is the chemical potential for the material in the environment in relation to its standard state.

For only one material we have

$$E = n\left[\mu^0 - \mu_0^0 + RT_0 \ln \frac{c}{c_0}\right] \tag{4}$$

Ex./S: Let us calculate the exergy of the Swedish iron ore production.

The Swedish iron ore has an average content of iron of about 60% (weight) and usually consists of magnetite (Fe_3O_4). The molar weight of iron is 55.8 g, which implies that 1 kg of iron ore contains 600/55.8 = 10.7 mol of iron = 3.58 mol magnetite = 0.83 kg magnetite.[8]

Assume that the reference (environmental) state of iron is hematite (Fe_2O_3) in solid form and with molar concentration 2.7×10^{-4} and that oxygen O_2 is in gaseous form at partial pressure 20.40 kPa in the environment [Szargut (1980)].

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[8] Since we lack data on molar fraction of iron in iron ore, we use instead kg iron per kg iron ore.

The chemical potentials of iron in magnetite and hematite then becomes [kJ/mol]:[9]

$$\mu^0(\mathrm{Fe}_{\text{magnetite}}) \approx \frac{1}{3}(-1015.5 + 2 \times 3.84) \approx -335.9$$
$$\mu^0(\mathrm{Fe}_{\text{hematite}}) \approx \frac{1}{2}(-742.2 + 1.5 \times 3.84) \approx -368.2$$

Where 3.84 kJ is the amount of exergy relised when the partial pressure of 1 mol of oxygen gas (O_2) decreases from 101.325 kPa to 20.40 kPa at 15˚C.

$$RT_0 \ln\left(\frac{c}{c_0}\right) \approx 8.314 \times (273.15 + 15) \times \ln\left(\frac{101.325}{20.40}\right) \approx 3840\,\mathrm{J}$$

Thus, the specific exergy of iron ore and iron then becomes, [MJ/kg]:[10]

$$e_{\text{ironore}} \approx 10.7\left\{[-335.9 - (-368.2)] \times 10^3 + 8.31 \times 288 \times \ln\left(\frac{0.83 \times 0.43}{2 \times 2.7 \times 10^4}\right)\right\} \approx$$
$$\approx 0.51$$
$$e_{\text{iron}} \approx 17.9\left\{[0 - (-368.2)] \times 10^3 + 8.31 \times 288 \times \ln\left(\frac{1}{2 \times 2.7 \times 10^4}\right)\right\} = 6.91$$

where 1 kg iron corresponds to 17.9 mol.

These values are in correspondance with those of others (McGannon, 1971, Gyftopoulos et al., 1974).

The Swedish mining of iron ore amounted to 26.9 Mton in 1980, by assuming this to be magnetite it corresponds to 14 PJ. The Swedish steel production was 3.5 Mton, i.e. about 24 PJ of exergy. To produce this 5.7 Mton of ore, i.e. about 3 PJ, about 34 PJ of electricity and about 77 PJ of coal and other fuels where needed. The exergy efficiency then becomes 21%.

Ex./S: Let us also apply this to desalination and calculate the exergy of fresh water. Assume that the reference (environmental) state of water is sea water. Sea water has an average content of water, H_2O of about 96.5% (weight) and the molar weight is 18 g, which implies that 1 kg of sea water contains 965/18 ≈ 53.6 mol of water. The rest is mainly sodium clorid (NaCl) with a molar weight of 58.5 g, i.e. 1 kg of water contains 35/58.5 ≈ 0.598 mol of NaCl. However, when NaCl is disolved in water it becomes Na+ and Cl- ions, i.e. separate molecules. Thus 1 kg of water contains 53.6 mol of H_2O, 0.598 mol of Na+ and 0.598 mol of Cl-, i.e. together about 54.8 mol. The mol concentration of water in sea water then becomes about 97.8%. The exergy of pure water at ambient temperature 15˚C then becomes

$$E = RT_0 \ln\left(\frac{c}{c_0}\right) \approx 8.314 \times (273.15 + 15) \times \ln\left(\frac{1}{0.978}\right) \approx 54.9\,\mathrm{J/mol}$$

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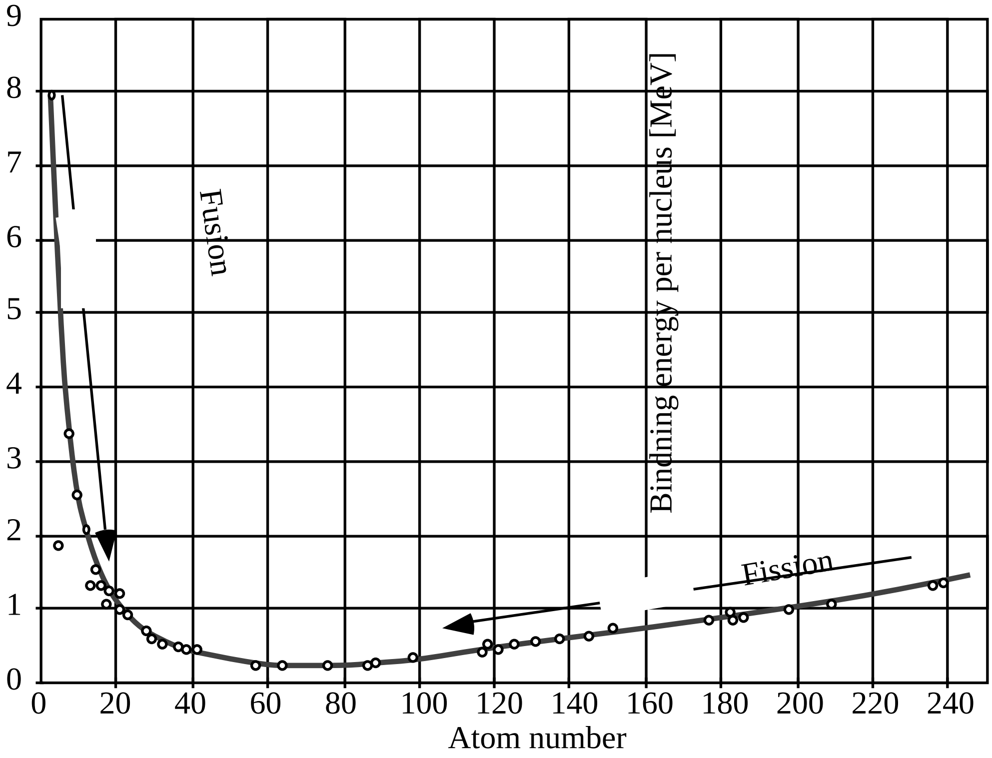
[9] *Handbook of Chemistry and Physics,* CRC, vol. 63, sida D-72: $\Delta G_f°(Fe_2O_3)$ = –177.4 kcal/mol = –742.2 kJ/mol, $\Delta G_f°(Fe_3O_4)$ = –242.7 kcal/mol = –1015.5 kJ/mol.

[10] 3 of 7 atoms in the magnetite molecule is iron atoms, i.e. the iron concentration in magnetite is 3/7≈0.43.

where the chemical potentials vanishes since we assume no chemical effects. The exergy of of pure water then becomes about 3.05 kJ/kg or about 0.847 kWh/m^3. If we instead assume 4.5% of salt and the ambient temperature of 30˚C, then we get 72.0 J/mol, 4.0 kJ/kg or 1.1 kWh/m^3. These exergies of fresh water corresponds to the minimum amount of exergy needed to produce it from the assumed sea water, respectively. The exergy of sodium cloride, on the other hand, becomes 184 kJ/kg and 182 kJ/kg respectively, i.e. less when the salt content in sea water increases.

Exergy of nuclear fuel

When the nuclear particles regroup into more probable states, exergy is released. In fission this occurs by splitting heavy atoms and in fusion by putting together light atoms into heavy atoms.



The exergy per nucleus in an atom as function of atom numbers.

The differens in binding energies between the initial and the final state is released as scattered motion in the produced particles, like neutrons and new elements. The energy can be expressed as a change of mass, a mass shift, through the well known relation

$$E=mc^2$$

where c is the speed of light in vacuum. However, the lost mass is very small compared to the rest initial mass, e.g. in fission uranium-235 losses about 1‰ of its mass and in fusion to helium deuterium (^{2}H) losses about 64‰ of its mass. Thus, we write instead

$$U = \Delta mc^2 \tag{1}$$

where we also use U for internal energy, in this case nuclear.

Since, a part of the released energy in most cases appear as neutrinos, which can be regarded as invisable and non interactive, i.e. useless, we may write nuclear exergy as

$$E = \Delta mc^2 - E_{\text{neutrino}} \tag{2}$$

The energy of the neutrios may sometime exceeds to 5% of the totally released energy.

Q: Estimate from the Fig. above the available exergy of 1 kg uranium? Compare this with the extracted exergy (electricity), which in todays Light Water Reactors is about 1 TJ/kg uranium. What is this difference due to and what consequences does it bring to the waste?

Exergy and information

Even though, thermodynamics treats the physics of systems which from a macroscopic point of view may be very small (about 10^{-15} cm^3) are they still from microscopic point of view very big, therefor containing a large amount of particles (10^{-15} cm^3 contains about 10^9 atoms). Thus, a detailed knowledge of the motion of every particle is impossible. In statistical mechanics we consider the large amout of particles and use statistical methods do explain the macroscopic phenomena as the result of microscopic rules. Statistical mechanics, by this means the theoretical basis of understanding thermodynamics.

Statistical mechanics is also strongly linked to information theory, where we study uncomplete knowledge. Thus, many concepts and relations are valid in all these fields, thermodynamics, statistical mechanics and information theory. Let us therefor look closer into information theory.

Assume a system of N unique particles. The number of allowed states Ω of the system is exponentially depending on N. Let the probability of the j:th state be P_j and the sum of the probabilities of all states to be 1, i.e. the system is in at least one state

$$\sum_{j=1}^{\Omega} P_j = 1$$

The entropy of the system is then defined from statistical mechanics as

$$S = -k \sum_{j=1}^{\Omega} P_j \ln P_j$$

where k is the Boltzmann's constant, 1.38054×10^{-23} J/K.

The probabilities at equilibrium P_j^0 are such that they maximize the entropy S independent of other restrictions on the system.

$$S_{\text{eq}} = S_{\text{max}} = -k \sum_{j=1}^{\Omega} P_j^0 \ln P_j^0$$

The available negentropy, negative entropy, of the system then becomes

$$-\left(S-S_{eq}\right)=S_{eq}-S=k\left(\sum_{j=1}^{\Omega}P_j\ln P_j-\sum_{j=1}^{\Omega}P_j^0\ln P_j^0\right)$$

From information theory we have the information or the information capacity I in binary units (bits)

$$I=\frac{1}{\ln 2}\left(\sum_{j=1}^{\Omega}P_j\ln P_j-\sum_{j=1}^{\Omega}P_j^0\ln P_j^0\right)$$

Let us exemplify by a system of N different particles with 2 possible states each, e.g. 0 or 1. The we have $\Omega = 2^N$. If there are no other restictions then all P_j^0 must be 2^{-N}, see the Table below.

N			$\Omega = 2^N$	P_j^0
1	□	0,1	$2^1=2$	$\frac{1}{2}$
2	□□	00,01,10,11	$2^2=4$	$\frac{1}{4}$
3	□□□	000,001,010,100,011,101,110,111	$2^3=8$	$\frac{1}{8}$
etc.				

Total information about the system (one of P_j equals 1 and all the others equal 0) gives $I = N$,

$$I=\frac{1}{\ln 2}\left[0-\sum_{j=1}^{2^N}2^{-N}\ln\left(2^{-N}\right)\right]=\frac{1}{\ln 2}\left[-2^N\frac{1}{2^N}(-N)\ln 2\right]=N$$

For every particle there is information corresponding to a “yes” or “no” to a specific question. Every such answer corresponds to one binary unit (bit) of information.

Thus, negentropy and information are very closelly linked

$$S_{\mathrm{eq}}-S=k'I$$

where $k' = k\ln 2 \approx 1.0\times10^{-23}$ [J/K].

One bit of information, thus, is equvalent to 1.0×10^{-23} J/K of negentropy.

Exergy and negentropy is also related from a relation we already know:

$$E=T_0(S_{\mathrm{eq}}^{\mathrm{tot}}-S^{\mathrm{tot}})$$

tot means the total system, here we only use system. From these relations we now get the following relation between exergy and information

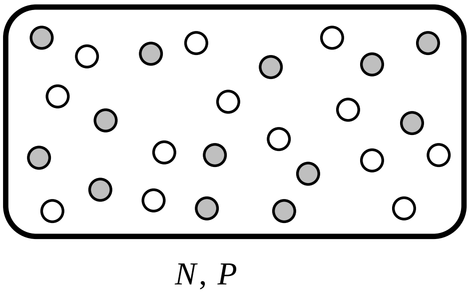
$$E=k'T_0I$$

where $k'T_0 \approx 2.9\times10^{-21}$ [J] is the amount of exergy related to 1 bit of information at room temperature.

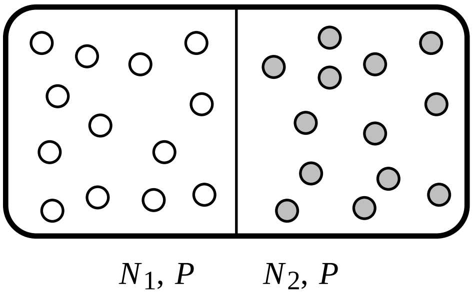
It is important to observe that information or information capacity, not necessary need to be meaningful from a human point of view. Information is here used as a measure of order or structure.

Whithin science information is just as fundamental as energy and matter. By small amount of information, processes converting huge amount of energy and matter can be controlled. As we have seen there is a fundamental relation between exergy and information, defined from information theory. However, as we will see information usually has a very small exergy value. Thus, it should be treated as a resource of one’s own.

Let us apply the concepts above on a physical system. Consider a container of volume$V$, with an ideal mixture of two different ideal gases 1 and 2, see the Fig. below. The total number of molecules is N, divided into N_1 and N_2 respectivelly. The molar concentration then becomes $x_1 = N_1/N$ and $x_2 = N_2/N = 1 - x_1$.



The gases are mixed in the container
with pressure P.



The gases are separated with the
same pressure P.

If we randomly pick one molecule from a specific place in the left container in the Fig. we face a probability $P = (x_1,\ x_2)$[11] to get a specific molecule. The information we gain when we discover which molecule it is, becomes according to above

$$I = \frac{1}{\ln 2}\left[x_1 \ln\left(\frac{1}{x_1}\right) + x_2 \ln\left(\frac{1}{x_2}\right)\right]$$

Let us now split the container in two parts with the volumes $V_1 = x_1 V$ and $V_2 = x_2 V$ respectively, and arrange the molecules so that V_1 only contains molecules 1 and V_2 only contains molecules 2, see the right part of the Fig. above. If we now randomly pick one molecule from a specified part of the container, then we know which molecule we get, and our knowledge and information increase by 0. By mixing the molecules information is lost, i.e. I per molecule, which can be related to a loss of exergy as above. Let us look closer to this.

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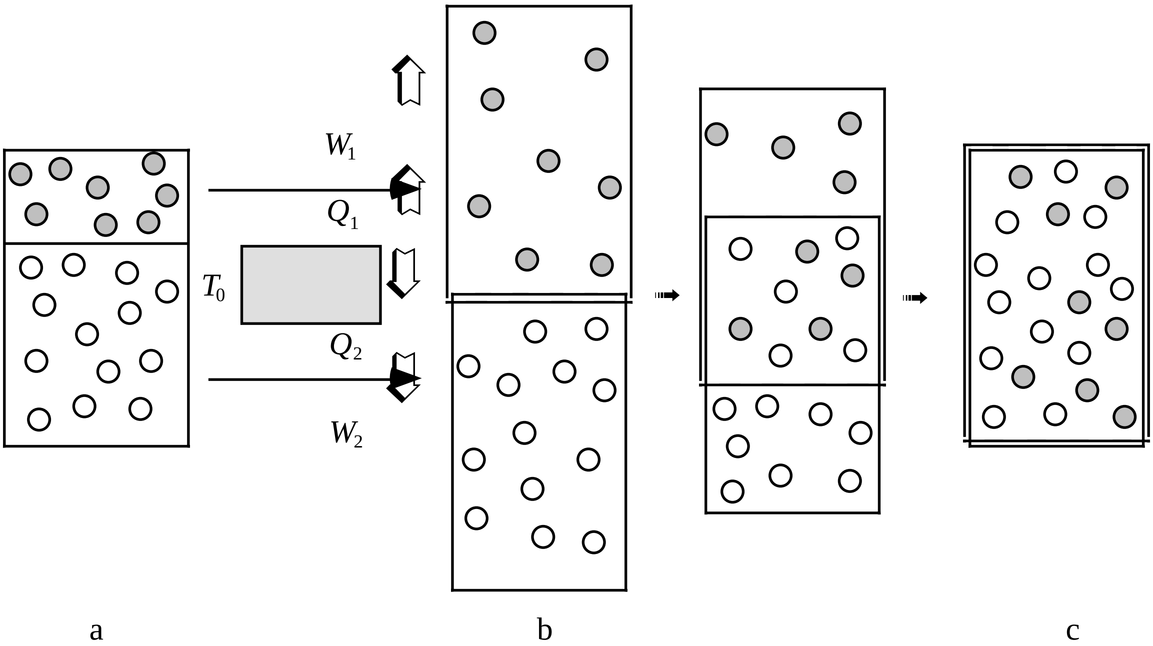
[11] Please note that we here are forced to use the same symbol for pressure and probability. This problem usually occurs when you simultaneously treat different fields of science.

Mixing entropy

Let us now calculate the maximal available work when we mix the two gases 1 and 2 as above. We may than get an expression of the amount of exergy, which should be related to the information *I*, i.e. we will check the relation above.

Assume the container is in thermal equilibrium with the ambient at temperature T_0. Since the initial and final volumes are the same we may set the ambient pressure to 0. First allow gas 1 and 2 independently expand isothermaly, see the processen a to b in the Fig. below. The gases are then mixed reversible by ideal semi permeable walls, see process b to c. Please note there is no net force on the containers during the mixing process b to c, and also there is not heat flow. So, the mixing is completely reversible, i.e. the entropy is constant.



A reversible mixing of the gases through an isothermal expansion (a to b), followed by an iso-exergetic mixing (b to c).

When the gases are regarded as ideal the ideal gas model is valid, i.e. $PV = nRT = NkT$ and the work is obtainable as

$$W_i = \int_{V_i}^{V} P_i dV' = \int_{V_i}^{V} \frac{N_i kT_0}{V'} dV' = N_i kT_0 \ln\left(\frac{V}{V_i}\right) = NkT_0 x_i \ln\left(\frac{1}{x_i}\right)$$

which gives

$$W = W_1 + W_2 = NkT_0 \left[x_1 \ln\left(\frac{1}{x_1}\right) + x_2 \ln\left(\frac{1}{x_2}\right) \right] = NkT_0 \ln 2 I$$

Thus, we have the following relation between the exergy per molecule *E* and information per molecule *I* in the ordered system

$$E = kT0 \ln 2I \qquad (2)$$

which is analougus to what we had above.

Since the internal energy U for an ideal gas only is a function of the temperature, we have for the isothermal process (a to b) that

$$Q_1 + Q_2 = W_1 + W_2$$

according to the first law. Thus, the entropy production S for the expansion (a to b) becomes

$$S = \frac{Q}{T_0} = Nk \ln 2I$$

If we assume the molecules to be identical, 1 or 2, then $I = 1$, i.e. each molecule in the ordered system is carrying 1 bit of information. The container may then be regarded as a binary memory, and in principle one molecule is enough to store 1 bit of information. In practice you need to make the reading easy and storing safe, and therfore repeat the information by using several molecules, i.e. so-called redundancy. Therefore, it is unadvisable to say that the ordered system contains N bits of information.

By information capacity we define the amount of information that a system kan store or transfer. This amount of information is limited by the available exergy, as above.

Since information needs so small amount of exergy the demand of high efficiency[12] has been weak. However, one area where increasing efficiency is an absolute necessity is in highly packed integrated circuits, where the exergy losses are converted into heat which may otherwise overheat the circuit. Increased efficiency also makes the circuits faster and more powerful.

A limited efficiency is usually needed since it imply that the storage and transfer of information becomes less sensitive for noise and other disturbances. Signals in electronic systems are always subjet to thermal noise, and the amount of exergy per bit must be several magnitudes above the noise level kT. However, the information transfer in biological systems when reproducing information and syntezising proteins is far more efficient, and the exergy use is sometimes only 10-100 kT/bit. Even though, the probability of errors, or mutations, is very low.[13] This is possible because of the specific environment in which the information is transferred. Thus, the transfer of genetic information occurs in a “shielded” environment. This is similar to integrated circuits operating at super conductivity conditions.

Q: Give examples of phenomena which seriously may damage the transfer of genetic information.

Exergy is a measure of how much a system differ from equilibrium with the environment. The more a system differs from the environment the more information is needed to describe the system and the more information capacity can be carried by the system. The relation between exergy and information (or information capacity) is therefor as we have seen of fundamental significance.

Ex: The net flow rate of information to the earth from the sun is about:

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[12] The relation between transferred or treated information and the used information capacity, both measurable in exergy.

[13] It should also be noticed that errors in the information transfer of biological systems is a necessity. The evolution is completely depending on mutations, i.e. errors in the reproduction of DNA.

$$\frac{P_{\mathrm{ex}}}{kT_0 \ln 2} \approx \frac{P_{\mathrm{en}} \times 0.933}{kT_0 \ln 2} \approx \frac{1.2 \times 10^{17} \times 0.933}{1.38 \times 10^{23} \times 300 \times 0.693} \approx 4 \times 10^{37} \left[\mathrm{bits} / \mathrm{s}\right]$$

> Of this mankind make use of only a tiny fraction or about 5×10^{13} bits. The relation between used and available information capacity becomes about 10^{-24}. The same relation for energy is about 3×10^{-5}. Thus, mankind is a poor user of available information or exergy. One reason to this will be mentioned below.

Information must be stored and transported safely. To reach this we must use redandancy (over-explicitness) in codes and in copying, which implies access dissipation of energy to make the process irreversible (safe) enough. The explicitness in the process increases on behalf of the information capacity. In biological systems there is a continuous debugging or control of the transferred information. (As you might know this becomes even more necessary in our increasingly computerized society, with the belonging flourish computer viruses.)

In daily communication of information the exergy use is often far to high. Thus the exergy per bit value becomes high, which implies that only a fraction of the available information capacity is utilized, as mentioned before. In the living nature the solar exergy is converted inte highly ordered structures in the green plants. From an energy point of view this is a small amount, but from an exergy or an information point of view huge amount is beeing utilized.

Let us compare the efficiency of information transfer, exergy per bit, for different systems, see Table below. This has the dimension temperature, T_{transfer}. The lower temperature the more efficient is the information transfer, but if this temeprature becomes to low the thermal noise in the environment may ruin the information.

	Exergy per bit [J/bit]	T_{transfer} [K]
Electrisk typewriter	1	10^{23}
Radio receiver	5×10^{-4}	5×10^{19}
Television	2×10^{-5}	2×10^{18}
Computer memory	10^{-12}	10^{11}
Human speech	10^{-16}	10^{7}
Human ear	10^{-17}	10^{6}
Human eye	5×10^{-18}	5×10^{5}
Protein biosynthesis in a cell	4.6×10^{-21}	460

The sensitivity of the retina is such that the human eye functions near the quantum mechanical limit. It is in fact enough with only a few quanta to cause a reaction in the eye. Storage of information in a computer memory has a characteristic temperature of about 10^5 times the temperature for sight. But on the other hand the time resolution, and thus the rate, is about 10^5 times higher than for the eye. The conclusion is that living creatures and computers are each efficient in their use of exergy to receive and transfer information. The biosynthesis in a cell is after all many times more efficient.

Electronic circuits, man’s ear and eye, and protein biosynthesis are drawn in a logarithmic information rate (frequency) - power diagram in the Fig. below. The minimum power requirements of integrated circuits has been calculated by Landauer (1961) and

Bennet (1973). Brillouin (1956) has shown that an elementary process in a circuit, such as a measurement, a storage or a logic operation, requires an energy conversion which is large in relation to $kT \approx 4\times10^{-21}$ J (at room temperature). This is necessary to avoid thermal fluctuations which are the cause of noise in electronic circuits, Brownian movement, etc. The room temperature is marked with a straight line. A process must ordinarily be far above this line to avoid serious disruption from thermal fluctuations. The protein biosynthesis {54} is surprisingly close to this critical line. The transfer from messenger RNA to proteins, which uses half of the power requirements, is actually below this line. This is possible because all of 4.3 bits of information are transferred at each transformation. The ear and the eye occupy strikingly large areas in the diagram, covering many orders of magnitude. Electronics is probably the best technology we know today, from an exergy efficient viewpoint. But, as Fig. 4.1 shows, life itself is far more efficient in its use of exergy to construct biological matter.

Biological structures live by transforming energy from one form to another. The solar exergy is used to build up complicated organic matter. This information is transferred from generation to generation. The information which is stored in the genetic matter (DNA molecule) directs the construction of matter. When biological material, e.g. wood or cellulose, is used as construction material, it is these structures and this information that we benefit from.

Both exergy and information are measures of the deviation from a reference environment. The exergy is the maximal amount of work that can be derived from such a deviation, but the work is also needed to maintain and transfer information. Thus, the relationship between exergy and information is very close.

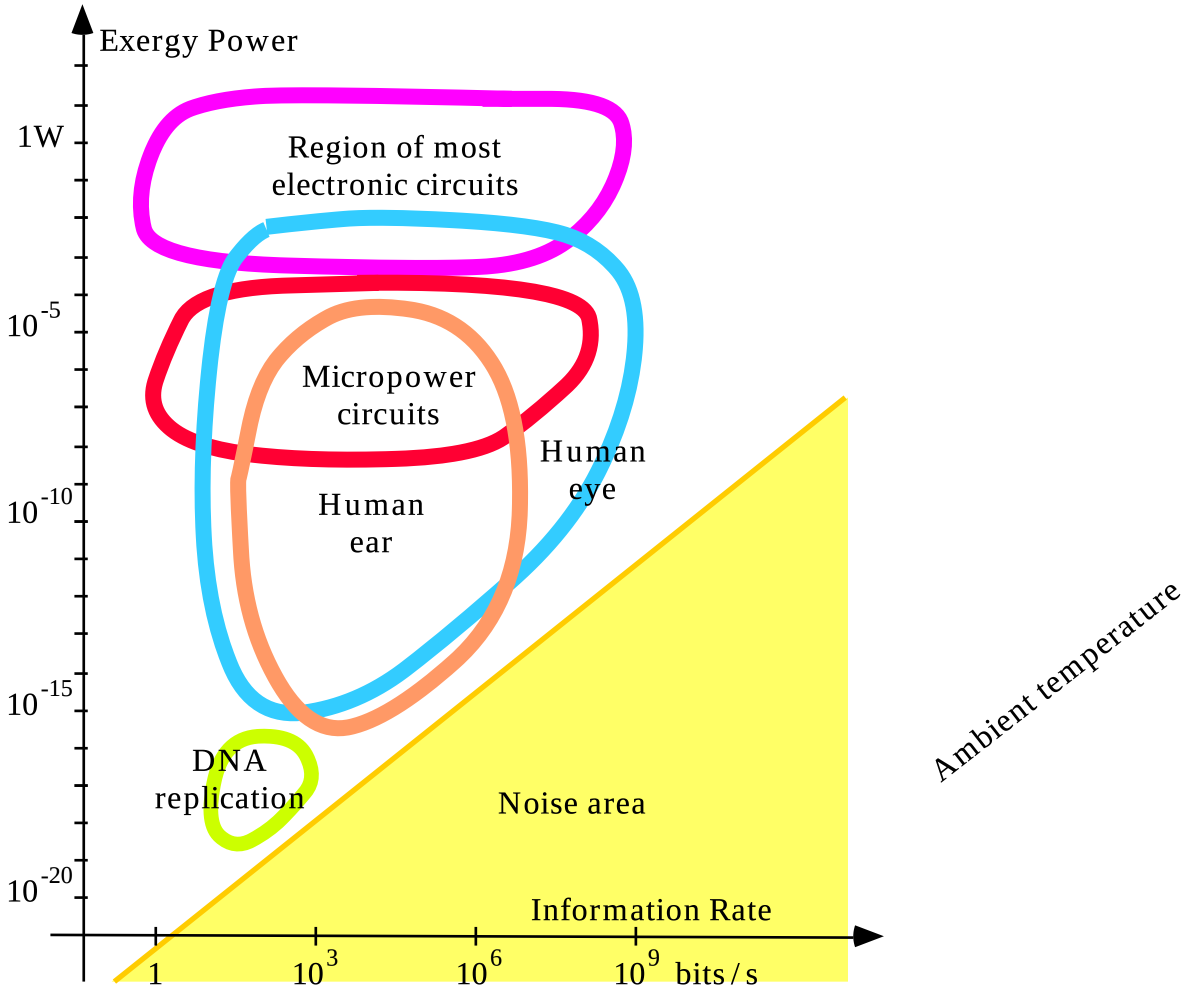

Fig. Information rate - power diagram of information transfer

Q: Consider the total information flow towards the earth during its lifetime. What “happened”, from a information perspective after about 2-3 billion years, and what was then the total amount of information that had reached the earth? What “happened”, after another 2-3 billion years? The sun is now about middle age, so if the evolution continues, what do you think will “happen” in the future, after another 2-3 billion years and another 2-3 billion years? Why is this so hard to understand?

This is my personal ideas about this. Let us consider the total information flow towards the earth during its lifetime, i.e. about 10 billion years, see Figure below. Matter and the laws of nature was there from the start. After about 2-3 billion years, when the earth had received about 10^{54} bits of information life was a fact on the earth. Then after another 2-3 billion years the ability to be aware of one self appeared, i.e. to be conscious, the mind or the soul. The sun, which is “father”[14] of our solar system is now about middle age, so if the evolution continues, what will appear in the future, after another 2-3 billion years and another 2-3 billion years? To answer this question is as difficult for us as it would have been for the living organisms some billions of years ago, or a bacteria of today to realize Homo Sapiens. Matter has organized itself into things as life, from attractive forces acting

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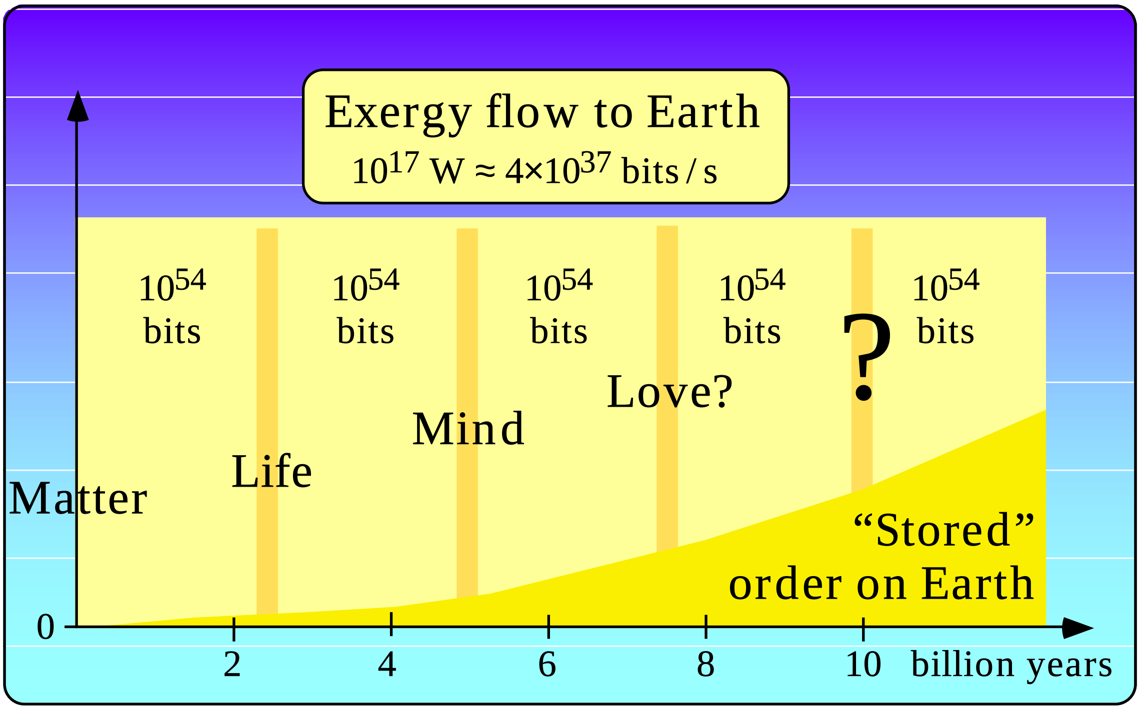
[14] The original inhabitants of America, i.e. the American Indians use to say father sun and mother earth to describe the forces that creates our world.

on a microscopic level. In the same way minds might organize itself into some form of immaterial structure, where love might be one attractive force of importance. In this immaterial universe, which is far beyond the so called Cyberspace, each mind would be just as simple or stupid as molecules in the material world. However, this is just speculations that is up to every one to fantasize about. The main reason for bringing up this subject is to give a perspective of the human culture, its believes, myths and opinion about the importance of itself, especially the European culture, i.e. the white man.



Finally let us compare the efficiency of a modern personal computer with other means of information transfer, see the Table below and excersice 16 and 17.

Information system	Efficiency
Reading text by lamplight	10^{-20} - 10^{-21}
Motorola Power PC or Intel Pentium processor	10^{-13}
DNA-replication, protein synthesis	10^{-1} - 10^{-2}

As we see a personal computer is far mor efficient than reading by lamplight, but compared with living nature a computer is still very poor. Todays most sofisticated computers are nothing but steam engines compared to future computers — please, remember this!

Summary

Let us close this Chapter with a schematic table of some forms of energy listed by decreasing quality, from "extra superior" to "valueless". The quality of the energy is indicated by the exergy factor. The quality index ranges from 1 for potential energy, kinetic energy and electricity (which are pure exergy and thus can be totally transformed into all other forms of energy) to 0 for the exergy-lacking heat radiation from the earth. The quality index of heat energy varies considerably from 0.6 for hot steam to zero for heat radiation from the earth.

The quality of different forms of energy.

	Form of energy	Quality index (Exergy factor)
Extra superior	Potential energy[1]	1
	Kinetic energy[2]	1
	Electrical energy	1
Superior	Nuclear energy[3]	almost 1
	Sunlight	0.93
	Chemical energy[4]	0.95
	Hot steam	0.6
	District heating	0.3
Inferior	Waste heat	0.05
Valueless	Heat radiation from the earth	0

[1] e.g. highly situated water resources
[2] e.g. waterfalls
[3] e.g. the energy in nuclear fuel
[4] e.g. oil, coal, gas or peat

CYCLIC PROCESSES

Cyclic processes in general

First we will consider cyclic processes in general.

A cyclic process is a process where the working medium, e.g. a gas goes through a number of states in a cyclic pattern, i.e. each state is repeted in every cycle. We also assume the process to be reversible.

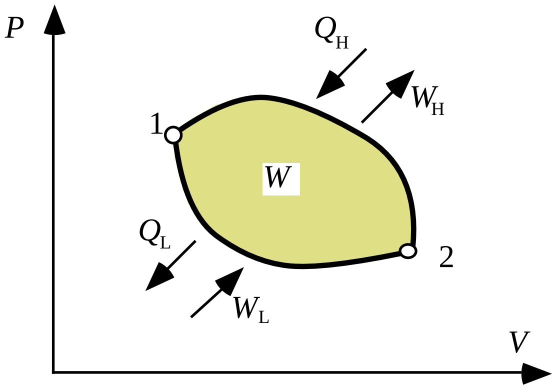
The first law applied to the state change 1 to 2 along the upper curve in th e Fig. below gives:

$$Q_H = U_2 – U_1 + W_H$$

where Q_H is added heat and W_H is the performed work, represented by the area between the higher curve 1 to 2 and the V-axis, i.e. $\int PdV$. When the medium is returned to the initial state along the lower curve 2 to 1, we get as above:

$$–Q_L = U_1 – U_2 + (–W_L)$$

where the heat $–Q_L$ is added and the work $–W_L$ is extracted, now represented by the area between the lower curve 2 to 1 and the V-axis.



For the complete cycle we have:

$$Q_H – Q_L = U_2 – U_1 + W_H + U_1 – U_2 – W_L$$

$$Q_H – Q_L = W_H – W_L = W$$

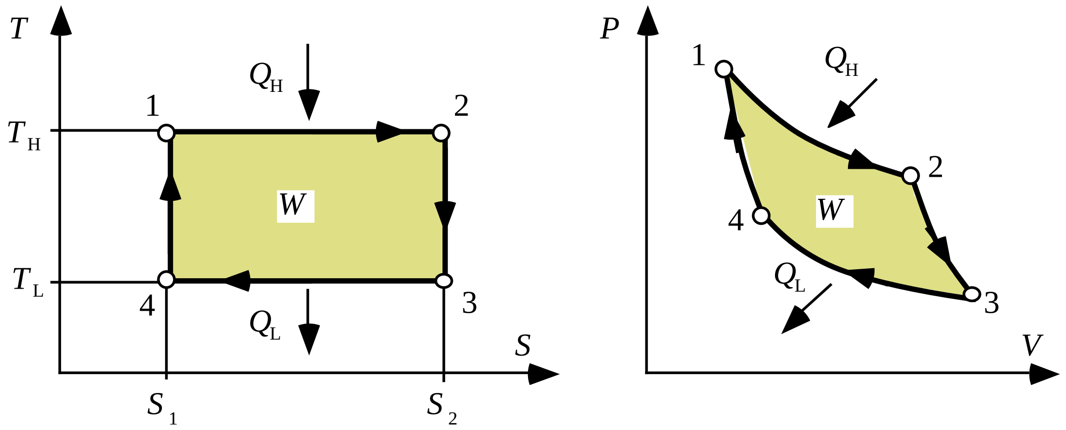
Thus, the net supply of heat $Q_H – Q_L$ is equvalent to the net amount of performed work W, which is indicated by the liny area in the Fig.

We can now define a thermal efficiency, η_t, of the cycle as the relation between the work output and supplied heat.

$$\eta_t = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

The Carnot cycle

We will now study the Carnot cycle, the cycle which has the highest theoretical efficiency for thermal engines (Sadi Carnot showed this 1824). Acording to the second law heat must go from high to low temperature inorder to produce work. The maximal work, to be extracted for two heat reservoirs at temperatures T_H and T_L, is the rectangular area in a TS-diagram. This cycle consists of two isothermal (T = constant) and two adiabatic or isentropic (S = constant) processes, see Fig. below.



A Carnot process consists of two reversible adiabatic and two reversible isothermal processes.

1-2: isothermal “expansion”
2-3: adiabatic expansion
3-4: isothermal “compression”
4-1: adiabatic compression

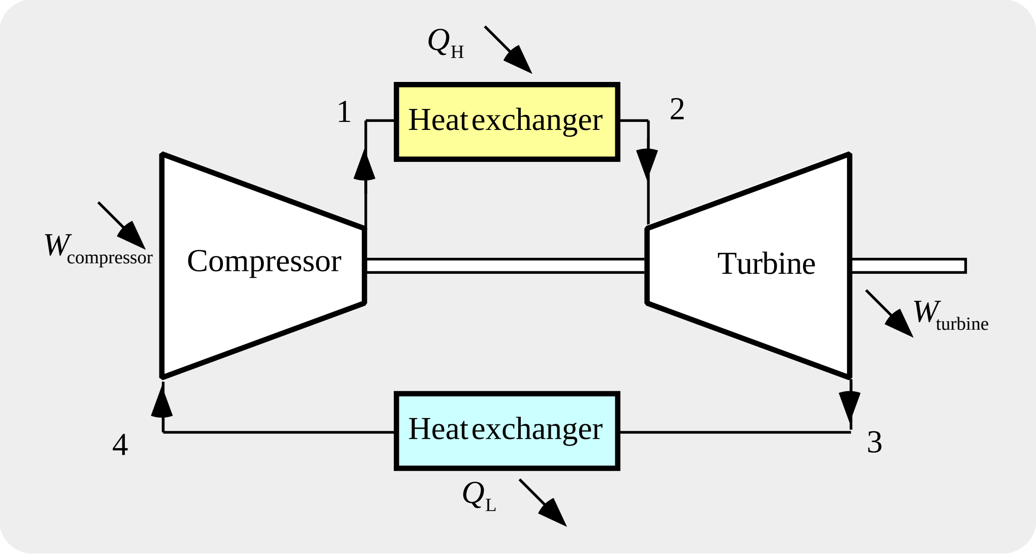
From the Fig. we see: $Q_H = T_H(S_2 - S_1)$ and $Q_L = T_L(S_2 - S_1)$, which gives the work W and the efficiency η_{Carnot}:

$$W = Q_H - Q_L = (T_H - T_L)(S_2 - S_1)$$

$$\eta_{Carnot} = \frac{W}{Q_H} = \frac{(T_H - T_L)(S_2 - S_1)}{T_H\left(S_2 - S_1\right)} = 1 - \frac{T_L}{T_H}$$

Assume the following heat engine to realize the Carnot cycle. An ideal gas is contained in a system of two heat exchangers, a turbine and a compressor, see Fig. below. The turbine and the compressor are on the same axis, and the compressor is powered by the turbine so the output work is

$$W = W_{turbine} - W_{compressor}$$



We must assume that process is ideal to be able to describe it, which means no heat leakages or friction, i.e. completely reversibel conditions. The high temperature in the upper heat exchanger is T_H and in the lower T_L and $T_H > T_L$.

Let us follow one unit mass through the cycle.

1-2: isotherm, the heat Q_H at temperature T_H is received in the upper heat exchanger.

2-3: reversible adiabatic, $Q = 0$, the gas is expanded in the turbine and work $W_{turbine}$ is extracted, the temperature decrease to T_L.

3-4: isotherm, the heat Q_L at temperature T_L is emitted in the lower heat exchanger.

4-1: reversible adiabatic, $Q = 0$, the gas is compressed, which uses work $W_{compressor}$, and the temperature increase to T_H.

Let us now analyze the process step by step.

Isotherms: 1-2: $Q_H = RT_H \ln\frac{V_2}{V_1}$

3-4: $Q_L = -RT_L \ln\frac{V_4}{V_3} = RT_L \ln\frac{V_3}{V_4}$

Adiabatics: 2-3: $T_H V_2^{\kappa-1} = T_L V_3^{\kappa-1}$

4-1: $T_L V_4^{\kappa-1} = T_H V_1^{\kappa-1}$

which gives

$$\frac{T_H}{T_L} = \left(\frac{V_3}{V_2}\right)^{\kappa-1} = \left(\frac{V_4}{V_1}\right)^{\kappa-1} \qquad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

The thermal efficiency of the Carnot cycle becomes:

$$\eta_t = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{RT_L \ln \frac{V_3}{V_4}}{RT_H \ln \frac{V_2}{V_1}} = 1 - \frac{T_L}{T_H} = \frac{\Delta T}{T_H} = \eta_{\text{Carnot}}\,.$$

Which is what we should expect.

—Why is this efficiency not reachable in practice? At first, we have a temperature difference in the heat exchangers and all mechanical parts suffer from friction.

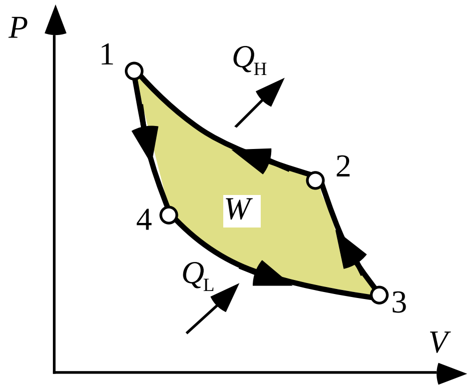
Ex: The surface water in a lake becomes warm in the summer about 20˚C, whereas the bottom water is only 4˚C. What is the highest thermal efficiency we can achieve with this temperature difference?

S: The highest efficiency is the Carnot efficency, thus:

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \approx 1 - \frac{273+4}{273+20} \approx 0.0546 = 5.5\%$$

Inverse Carnot cycle

Above we used the Carnot cycle as a heat engine to extract work from two heat reservoirs. We will now reverse the cycle, which is possible because it is reversible. Then instead work will be used to produced heat, Q_H according to the relation$W = Q_H - Q_L$.



One example of this is a heat pump or a refrigerator, which is actually the same thing. In the heat pump we use the produced heat and in the refrigerator we use the simultaneously produced cold, i.e. the removal of heat.

For the refrigerator we have a coefficient of performance (COP) for the produced cold,

$$\text{COP}_{\text{cold}} = \frac{\text{Removed heat}}{\text{Used work}}$$

For a Carnot process we have:

$$\text{COP}_{\text{cold, Carnot}} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} = \frac{1}{\frac{T_H}{T_L} - 1}$$

since $\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$ for a Carnot cycle.

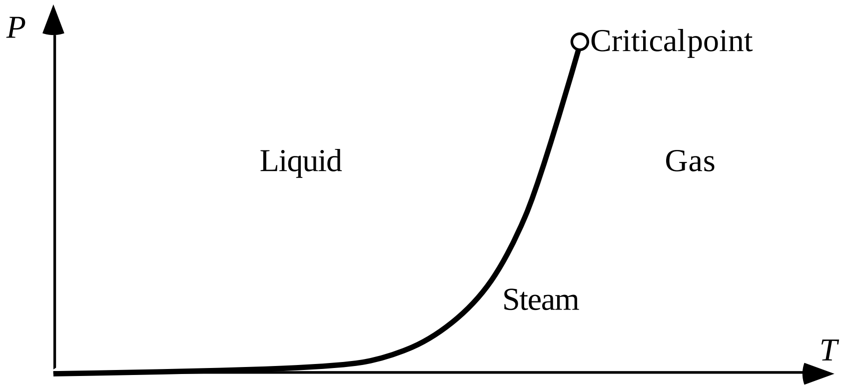
For a heat pump we get analogously,

$$\mathrm{COP_{heat}} = \frac{\text{Delivered heat}}{\text{Used work}}$$

$$\mathrm{COP_{heat,\ Carnot}} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} = \frac{1}{1 - \frac{T_L}{T_H}} = \frac{1}{\eta_{\text{Carnot}}}$$

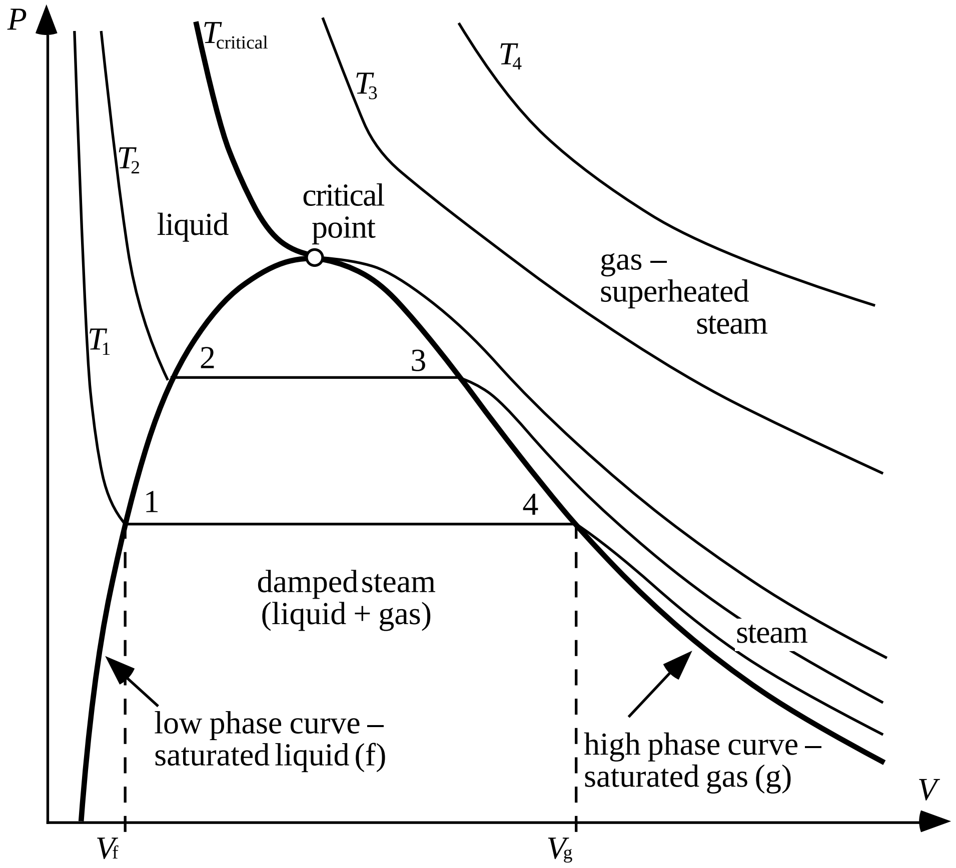
Thermodynamics of steam

Before we study steam cycles we will treat the thermodynamics of steam. Since, steam is a gas close to condensation, it can not be treated as an ideal gas. Steam cycles are the most common cycles in power industry, e.g. fossile and nuclear fueled power plants. Let us first look at the steam pressure curve, which shows the different phases of water in a *PV*-diagram, se the Fig. below.



To the left of the curve we have only water as liquid, to the right only steam and gas. On the curve we have liquid and steam simultaneously, and at the critical point the difference between liquid and gas vanishes, i.e. a liquid is a compressed gas.

We will also study the transition between gas and liquid in a *PV*-diagram, see Fig. below.



Let us "walk" along an isotherm, $T = T_1$, and start at the left end in the *PV*-diagram. Here we are in the liquid region, and if the pressure drops the volume increases only slitly, the liquid is almost incompressible. At 1 we have saturated liquid that starts to boil, and along 1 to 4 the liquid gradually boils to gas, the volume increases but the pressure is constant, and at 4 all liquid has turned to saturated gas. if we continue to right the pressure will decrease and the volume increase, as for an ideal gas.

By doing the same procedure for different temperatures we get a lot of data, for saturated liquid and saturated gas. By connecting these we get the phase curves for saturated liquid and saturated gas, and between them we have the damped steam. Where liquid and gas appear simultaneously.

The critical piont we find at the top, where saturated liquid becomes saturated gas without increasing volume. The critical point for water is:

$$P_{critical} = 221.29\times10^5\text{Pa}$$
$$T_{critical} = 647.3\text{ K} \rightarrow \theta_{critical} = 374.15^\circ\text{C}$$
$$v_{critical} = 3.1\times10^{-3}\text{ m}^3/\text{kg}$$

At temperatures higher than $T_{critical}$=374.15˚C water can only appear as gas. Along the isotherm $T = T_{critical}$ to the critical point the liquid turns to gas with no change of volume.

From now we asign saturated gas by g and saturated liquid by f (fluid).

The specific gas content or quality of the steam, *x*, is the relative amount of gas in the damped steam, i.e.

$$x = \frac{\text{kg gas}}{\text{kg damped steam}}$$

The specific liquid content then becomes 1–x, i.e.

$$1 - x = \frac{\text{kg liquid}}{\text{kg damped steam}}$$

Thespecific volume$v$ [m^3/kg] of the damped steam (liquid + gas) at a specific temperature can be calculated from:

$$v = xv_g + (1–x)v_f$$

Ex: A container contains a damped steam at 3 bar. The volume is 20 liter and the mass of the mixture is 0.04 kg. What is the gas content?

S: First calculate the specific volume of the damped steam!

$$v = \frac{20 \times 10^{-3}}{0.04} = 0.5 \left[\text{m}^3 / \text{kg}\right]$$

From steam tables we find for P= 3 bar:

v_f = 0.00107 m^3/kg
v_g = 0.60567 m^3/kg

By rewriting the relation between x, v, v_f and v_g we get:

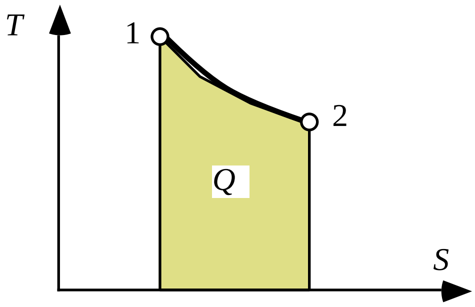
$$v = v_f(1 - x) + v_g x \qquad x = \frac{v - v_f}{v_g - v_f} = \frac{0.5 - 0.00107}{0.60567 - 0.00107} \approx 0.8.$$

TS-diagram

Since $dS = \frac{\delta Q}{T}$, where S is entropy and δQ is heat added of temperature T, then we can calculate the added heat, Q, of a process 1 to 2, as:

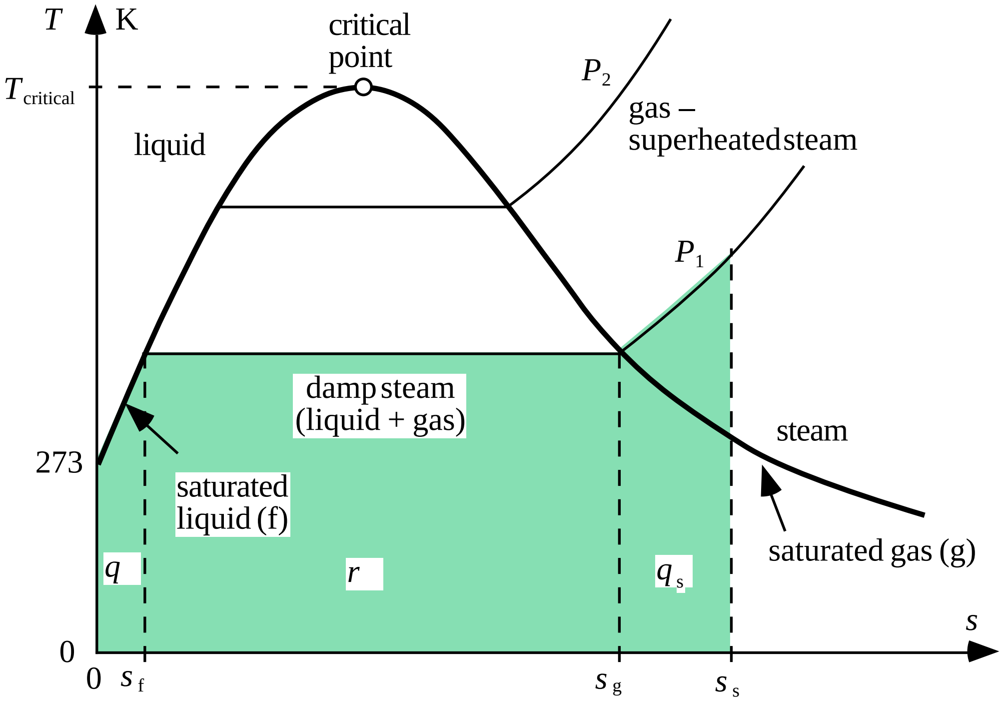
$$Q_{1-2} = \int_1^2 TdS$$

In a TS-diagram the added heat is the area below the curve T(S) and between state 1 and 2, as shown in the Fig. below.



In technical applications one usually set$h$ ≡ 0 and s ≡ 0 for water as liquid at 0˚C and the corresponding saturation pressure.

Let us make a *Ts*-diagram for steam, see Fig. below.



The isobars almost follow the curve of saturated liquid up to the boiling point.

When we add heat to the water at konstant pressure we have $q = h_2 - h_1$ [J/kg], i.e. the added heat is equal to the change of enthalpy.

Assume we have 1 kg 0 degreee (273 K) water at p_1 to be heated to boiling point. The added heat q then becomes

$$q = h_f - 0 = h_f$$

where h_f is the enthalpy at the boiling point and pressure P_1, i.e. at the saturation curve. Thus, q becomes the area in the *Ts*-diagram below the isobar $P = P_1$.

The heat of evaporation, r, we get in the same way if we add heat during constant pressure P_1, i.e.

$$r = h_g - h_f$$

where h_g is the enthalpy of the saturated gas and h_f is the enthalpy of the saturated liquid. r is also the surface in the *Ts*-diagram below the isobar $P = P_1$, in the damped zone.

To determine the enthalpy of damped steam we use the specific gas content, x. In the same way as we got the specific volume of the damped steam we can now determine the specific enthalpy h [J/kg] of the damped steam

$$h = xh_g + (1–x)h_f$$

if we use that $r = h_g - h_f$ we get

$$h = h_f + xr.$$

Similarly, we also get the specific entropy s [J/kg K] of the damped steam

$$s = xs_g + (1–x)s_f$$

The heat content of the superheated steam then becomes

$$h_s = q + r + q_s = h_f + r + q_s = h_g + q_s$$

R: Become acquainted with steam tables!

Ex: Liquid water at $P = 10$ bar and $\theta = 120$˚C is heated to steam with $x = 0.90$ at constant pressure. What is the specifik heating need?

S: From steam tables we get at $P = 10$ bar saturation state 179.88 ≈ 180˚C and $h_f = 762.63$ kJ/kg.
If we assume thatc_P is constant in the interval 120-180˚C then the enthalpy of water at 120˚C becomes

$h_{180} = c_P(180 - 0)$
$h_{120} = c_P(120 - 0)$

Which gives $h_{120} = \dfrac{h_{180}}{180} \times 120 \approx \dfrac{762.6}{180} \times 120 \approx 509\,[\text{kJ/ kg}]$

For the damped steam we get

$$h = xh_g + (1-x)h_f \approx 0.90 \times 2778 + (1-0.9) \times 762.6 \approx 2576 \text{ [kJ/kg]}$$

The added heat then becomes

$$q = h - h_{120} \approx 2576 - 509 = 2067 \text{ kJ/kg}$$

Ex: We have a closed 4 m^3 container with 800 kg of water at pressure 0.1 bar. How much heat is required to increase the pressure to 20 bar?

S: The volume is constant, so we have

$$q = c_V \Delta T = u_2 - u_1 = h_2 - h_1 - v(P_2 - P_1)$$

the specific volume is $v = \dfrac{4}{800} = 0.005 \text{ m}^3/\text{kg}$

We assume only water in the container, which will be damped steam. From steam tables we get:

State 1: $P = 0.1$ bar
$v_f = 1.01 \times 10^{-3}$ m^3/kg
$v_g = 14.67$ m^3/kg
$v = 0.005$ m^3/kg

From$v = v_g x_1 + (1-x_1)v_f$, we get $x_1 = 0.00027$

When we know x_1 we can calculate the enthalpy, i.e. the heat content of the damped steam at $P = 0.1$ bar.

$h_1 = h_g x_1 + (1-x_1)h_f \approx 192.5$ kJ/kg

State 2: $P = 20$ bar

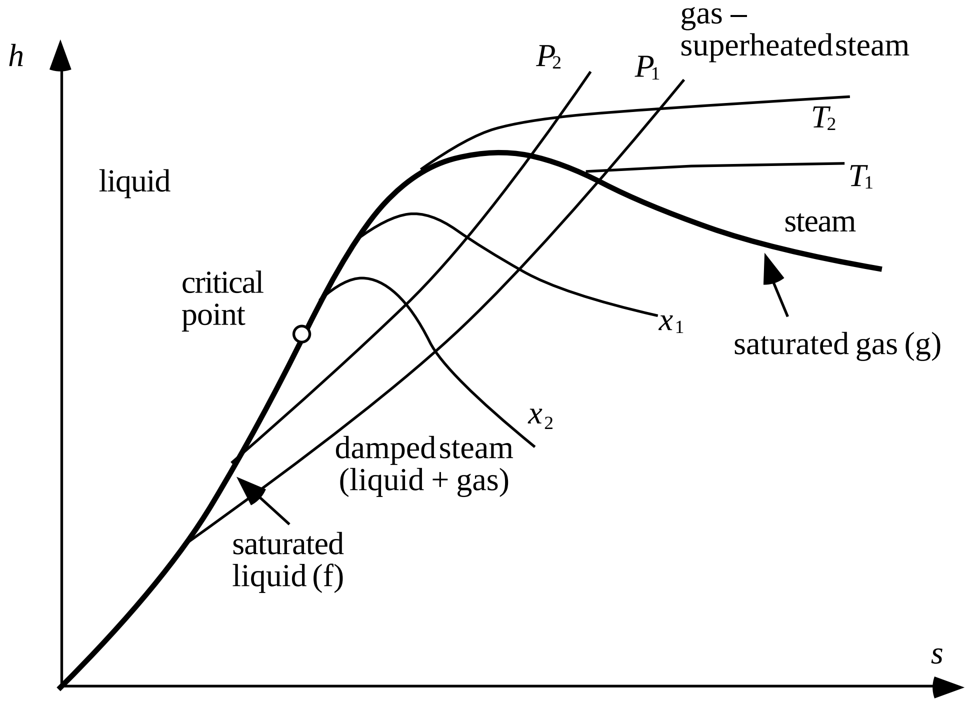
In the same way we get $x_2 = 0.0388$ and $h_2 = 981.9$ kJ/kg.

The added heat then becomes

$Q = m[h_2 - h_1 - v(P_2 - P_1)] \approx 800[981.9\times10^3 - 192.5\times10^3 - 0.005(20\times10^5 - 0.1\times10^5)] \approx 623$ MJ

Mollier or hs-diagram

In the same way we have drawn *PV*-diagrams and *Ts*-diagrams for steam we can also make *hs*-diagrams or Mollier-diagrams. In the Mollier-diagram we also have curves for isobars and isotherms. See Fig. below or a steam table.



Ex: 10 kg steam per second at $P = 20$ bar, $\theta = 400^\circ$C expands adiabaticaly (isentropicaly) to $P = 2$ bar. Determine the available power.

S: The available power is work per unit time, and from the first law for an adiabatic process, i.e. $Q = 0$, we have

$W_t = H_1 - H_2 = m(h_1 - h_2)$

The steam expands adiabatically, i.e. the entropy s is constant.

State 1: $P_1 = 20$ bar, $\theta_1 = 400^\circ$C, gives $h_1 \approx 3.25$ MJ/kg

State 2: $P_2 = 2$ bar, s = constant. Find the point P_1, θ_1, then find $P_2 = 2$ bar along the line s = constant and get $h_2 = 2.70$ MJ/kg.

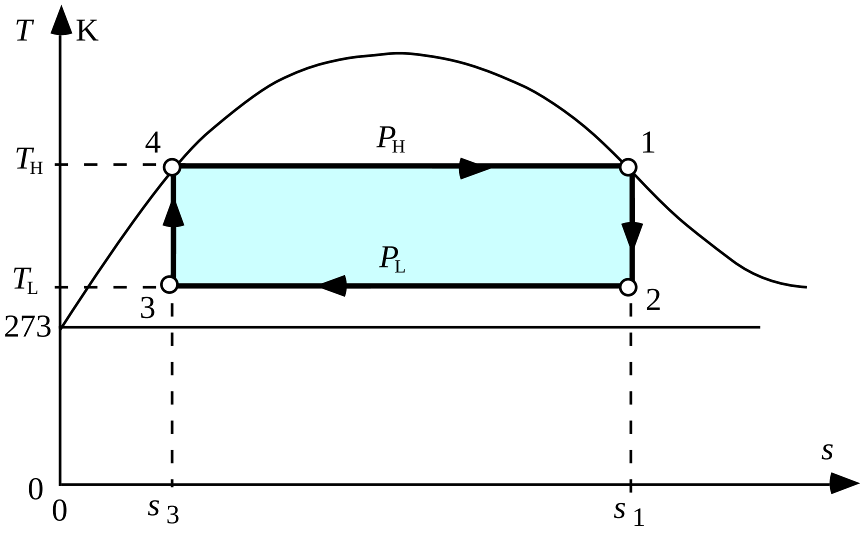
$$w_t = h_1 - h_2 \approx 3.25\text{-}2.70 = 0.55 \text{ MJ/kg} = 550 \text{ kJ/kg}$$

So, when 10 kg steam per second expands the available power is $\dot{W}_t$ = 5500 kW.

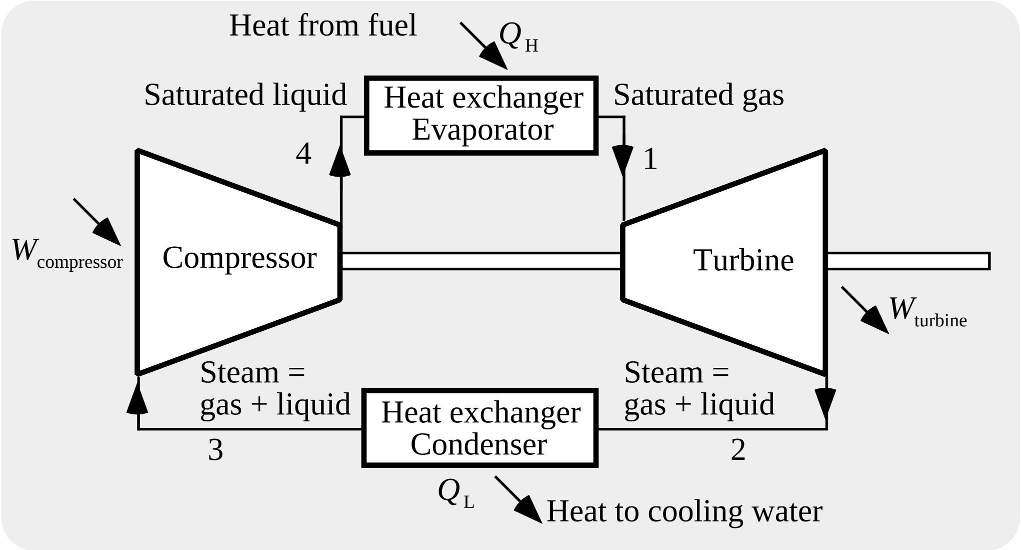
Steam power processes

Steam is often used in industry for heating, drying and cleaning. The power industry uses steam to transfer the power or exergy in a fuel (combustion or fission) trough a steam generator in a furnace to motion in a turbine connected to a electric generator.

As we have seen the Carnot process is the most efficient process to transfer exergy of heat to mechanical exergy (work). In the *TS*-diagram below the Carnot cycle is shown for a steam process.



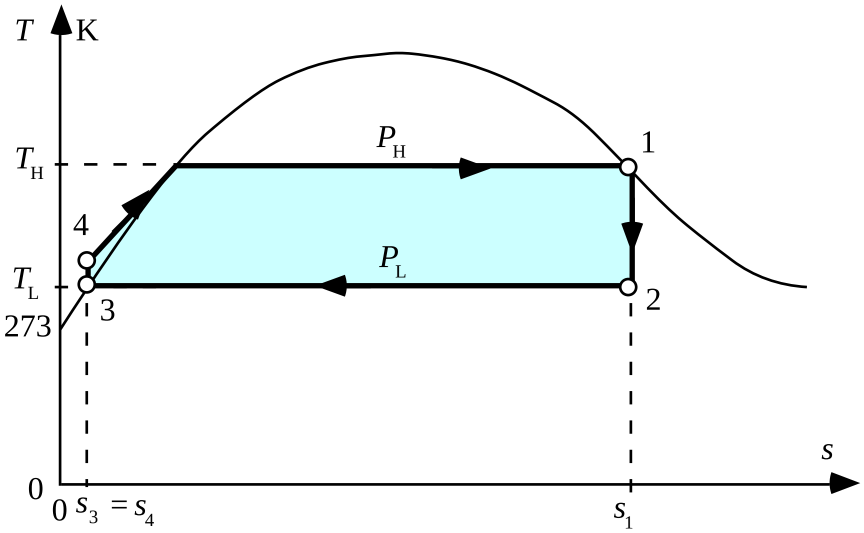
An example of such a heat power plant is shown below.



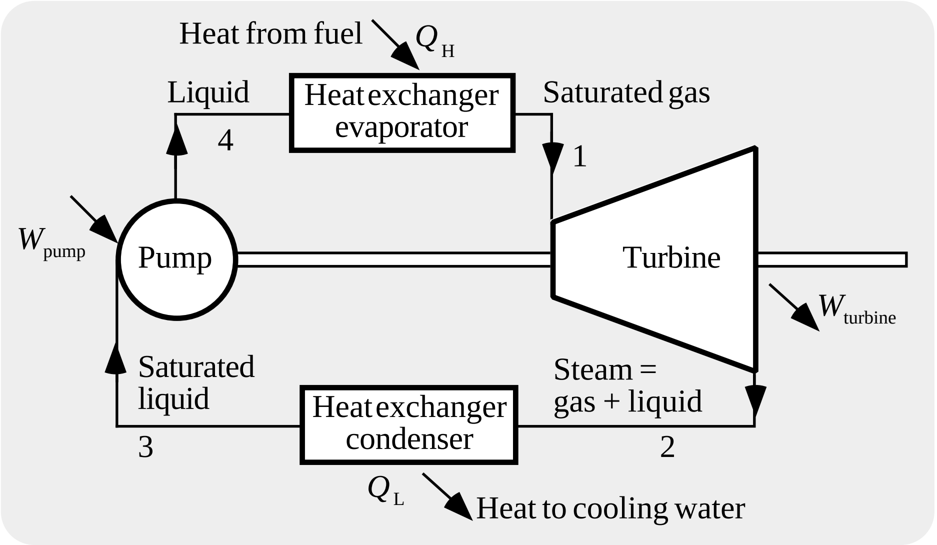
In the evaporator (steam generator) water is converted from saturated liquid, 4 to saturated gas, 1. The heat is usually extracted from the exhaust gases by heat exchangers, and the evaporation occurs at constant pressure P_H and constant temperatureT_H. In the turbine the saturated gas expands adiabatically to 2 with a lower pressure P_L. The steam is this state of high quality, i.e. tha gas content is high. According to the first law of a steady state reversible adiabatic process, we have:

$$W_{\text{turbine}} = H_1 - H_2$$

The steam is condensed at constant pressure P_L and constant temperature T_L, to state 3. The steam in this state is of low quality, i.e. the gas content is low and the liquid content is high. By a heat exchanger the heat is delivered to cooling water. After that the steam is compressed adiabatically to its initial state 4. In this compression the remaining gas will turn to liquid, i.e. the compressor faces a very big change in volume implying an big and expensive compressor. Thus, it is more economical to cool the steam to saturated liquid at pressure P_L and temperature T_L, see Fig. below.



This process is called Clausius- Rankine process or just Rankine process. The pressure increase from state 3 to 4 can now instead be obtained with a pump, se Fig. below. State 4 will now be in the liquid region since the pressure increase is reversible, $s_3 = s_4$. The heating of the liquid to saturated liquid will now occur in the evaporator instead.



Ex: Determine how the energy and exergy conversions change when we choose a Rankine process instead of a Carnot process in the case $P_H = 5$ bar and $P_L = 1$ bar. Also estimate the thermal energy and exergy efficiencies ($T_0 = 293.15$ K).

S: The processes are identical beside states 3 and 4.
In state 1 we have saturated gas at $P_H = 5$ bar, i.e. from steam tables we get

$h_1 \approx 2748.79$ kJ/kg
$s_1 \approx 6.8219$ kJ/kg K
$e_1 = h_1 - T_0 s_1 \approx 2748.79 - 293.15 \times 6.8219 \approx 748.95$ kJ/kg

We now must detrmine the quality of steam in state 2, x_2. The entropy in states 2 and 1 are the same, i.e.

$s_1 = s_2 \approx x_2 7.3590 + (1 - x_2)1.3028 \approx 6.8219 \qquad x_2 \approx 0.91131.$

From steam tables, we can now calculate the enthalpy and exergy in state 2:

$h_2 \approx 417.550 + 0.91131 \times 2257.71 \approx 2475.03$ kJ/kg
$s_2 \approx 0.08869 \times 1.3028 + 0.91131 \times 7.3590 \approx 6.8219$ kJ/kg K
$e_2 = h_2 - T_0 s_2 \approx 2475.03 - 293.15 \times 6.8219 \approx 475.19$ kJ/kg

In state 4 we have for the Carnot process saturated liquid at $P_H = 5$ bar, i.e. from steam tables we get:

$h_4 \approx 640.16$ kJ/kg
$s_4 \approx 1.8604$ kJ/kg K
$e_4 \approx 640.16 - 293.15 \times 1.8604 \approx 94.78$ kJ/kg

For the Rankine process we have liquid at $P_H = 5$ bar and $s_4 = s_3$. Let us therefor wait to calculate this state. First we determine the exergy in state 3 for the Carnot process. Then we need to know the quality of the steam, x_3. The entropy in states 3 and 4 are the same, i.e. from steam tables we get

$s_4 = s_3 \approx x_3 7.3590 + (1 - x_3)1.3028 \approx 1.8604 \qquad x_3 \approx 0.09207.$
$h_3 \approx 417.550 + 0.09207 \times 2257.71 \approx 625.42$ kJ/kg
$s_3 \approx 0.90793 \times 1.3028 + 0.09207 \times 7.3590 \approx 1.86039$ kJ/kg K
$e_3 \approx 625.42 - 293.15 \times 1.86039 \approx 80.05$ kJ/kg

For the Rankine process it is easier since we have saturated liquid

$h_3 \approx 417.550$ kJ/kg
$s_3 \approx 1.3028$ kJ/kg K
$e_3 \approx 417.550 - 293.15 \times 1.3028 \approx 35.63$ kJ/kg

Thus we know, for state 4 that $P_H = 5$ bar and $s_4 = s_3 \approx 1.3028$ kJ/kg K, which principally is enough to determine the state in detail, but it is better to first calculate the pumping work. We know the specific volume of the liquid to be pumped and the pressure levels. If we assume the liquid to be incompressible we get:

$w_{\text{pump}} = v(P_H - P_L) \approx 0.00107(5 - 1)10^5/1000 \approx 0.43$ kJ/kg

Where we used the average value of the specific volume in the two states. As we see the pump work is almost negligible. Thus, the stae becomes

$h_4 = h_3 + w_{\text{pump}} \approx 417.55 + 0.43 \approx 417.98$ kJ/kg
$s_4 = s_3 \approx 1.3028$ kJ/kg K
$e_4 \approx 417.98 - 293.15 \times 1.3028 \approx 36.06$ kJ/kg, but also as above, i.e.:
$e_4 = e_3 + w_{\text{pump}} \approx 35.63 + 0.43 \approx 36.06$ kJ/kg.

Thus, for the enthalpy we have:
$h_1 \approx 2748.79$, $h_2 \approx 2475.03$, $h_3 \approx 625.42$ (Carnot), $h_3 \approx 417.55$ (Rankine), $h_4 \approx 640.16$ kJ/kg (Carnot), and $h_4 \approx 417.98$ (Rankine) and we get the following values for the energy conversion:
For the Carnot process the compressor work becomes:
$w_{\text{compressor}} = h_4 - h_3 \approx 640.16 - 625.42 \approx 15$ kJ/kg.
For the Rankine process the pump work becomes:
$w_{\text{pump}} = h_4 - h_3 \approx 417.98 - 417.55 \approx 0.43$ kJ/kg, as we already know.
For the Carnot process the heat to cooling water becomes:
$q_L = h_2 - h_3 \approx 2475.03 - 625.42 \approx 1850$ kJ/kg.
For the Rankine process the heat to cooling water becomes:
$q_L = h_2 - h_3 \approx 2475.03 - 417.55 \approx 2057$ kJ/kg.
For the Carnot process the added heat becomes:
$q_H = h_1 - h_4 \approx 2748.79 - 640.16 \approx 2109$ kJ/kg.
For Rankine process the added heat becomes:
$q_H = h_1 - h_4 \approx 2748.79 - 417.98 \approx 2331$ kJ/kg.
The utilized energy in the turbine, which is the same in both cases becomes:
$w_{\text{turbine}} = h_1 - h_2 \approx 2748.79 - 2475.03 \approx 274$ kJ/kg.

For the exergy we have: $e_1 \approx 748.95$, $e_2 \approx 475.19$, $e_3 \approx 80.05$ (Carnot), $e_3 \approx 35.63$ (Rankine), $e_4 \approx 94.78$ kJ/kg (Carnot), and $e_4 \approx 36.06$ (Rankine), which implies:
Carnot: $w_{\text{compressor}} = e_4 - e_3 \approx 94.78 - 80.05 \approx 15$ kJ/kg, as above.
Rankine: $w_{\text{pump}} = e_4 - e_3 \approx 36.06 - 35.63 \approx 0.43$ kJ/kg, as above.
Carnot: $q_L = e_2 - e_3 \approx 475.19 - 80.05 \approx 395$ kJ/kg.
Rankine: $q_L = e_2 - e_3 \approx 475.19 - 35.63 \approx 440$ kJ/kg.
Carnot: $q_H = e_1 - e_4 \approx 748.95 - 94.78 \approx 654$ kJ/kg.
Rankine: $q_H = e_1 - e_4 \approx 748.95 - 36.06 \approx 713$ kJ/kg.
Carnot and Rankine: $w_{\text{turbine}} = e_1 - e_2 \approx 748.95 - 475.19 \approx 274$ kJ/kg, as above.

The thermal energy efficiency, i.e. $\dfrac{\text{Net work output}}{\text{Added energy as heat}}$ becomes in the two cases:

$$\eta_{\text{en,Carnot}} = \frac{w_{\text{turbine}} - w_{\text{compressor}}}{q_H} \approx \frac{274 - 15}{2109} \approx 12.3\%$$

$$\eta_{\text{en,Clausius-Rankine}} = \frac{w_{\text{turbine}} - w_{\text{pump}}}{q_H} \approx \frac{w_{\text{turbine}}}{q_H} \approx \frac{274}{2331} \approx 11.8\%$$

The thermal exergy efficiency, i.e. $\frac{\text{Net work output}}{\text{Added exergy as heat}}$ becomes in the two cases:

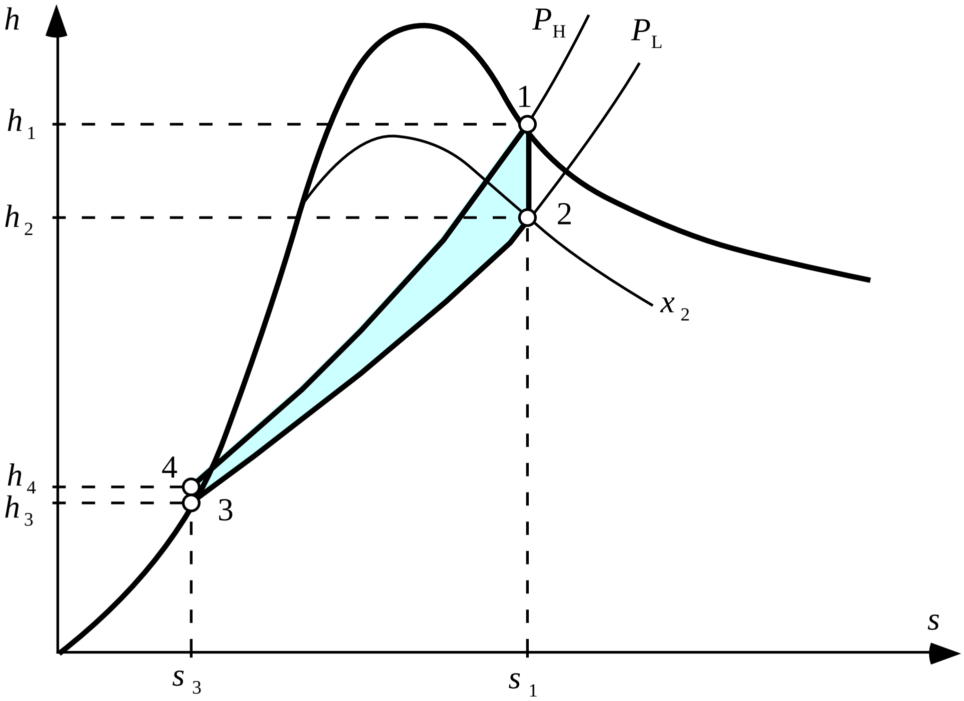
$$\eta_{\text{ex,Carnot}} = \frac{w_{\text{turbine}} - w_{\text{compressor}}}{q_{\text{H}}} \approx \frac{274 - 15}{654} \approx 39.6\%$$

$$\eta_{\text{ex,Clausius-Rankine}} = \frac{w_{\text{turbine}} - w_{\text{pump}}}{q_{\text{H}}} \approx \frac{w_{\text{turbine}}}{q_H} \approx \frac{274}{713} \approx 38.4\%$$

As we expect the Rankine process has a lower efficiency than the Carnot process, which is the most efficient process.

Q: Check that we have both energy and exergy balances for the processes, i.e. that both the first and second law is valid. What is the reason for the big difference between the thermal energy and exergy efficiencies and why are they so poor?

Let us now also put the Rankine process in a Mollier diagram, i.e. a *hs*-diagram, see the Fig. below.



Let us see how to improve the efficiency of the Rankine process:

1. Increase the pressure before the turbine, which means that the conversion 1-2 is moved to left in the *hs*-diagram above. The difference $h_1 - h_2 = e_1 - e_2 = w_{\text{turbine}}$ then increases, i.e. more work out.
2. Lowering the pressure after the turbine implies that the cooling loss $q_L = e_2 - e_3$ reduces and we utilize exergy which otherwise would be lost with the cooling water.
3. Superheating; in a real turbine we can not allow the quality of the steam to become less than about 0.90, i.e. in state 2. The liquid will otherwise ruin the turbine blades. Therefor the gas in state 1 must be superheated, which principally also increases the efficiency – according to Carnot. However, material restrictions in the turbine, put an upper limit of about 600˚C in today's conventional constructions.

4. Feed water heating; an important reason of the poor efficiency is that a large amount of the heating content of the steam is due to evaporation. By pre heating of the water to the evaporator the efficiency could be improved. This is usually done by draining the turbine of steam, which is mixed with the feed water to increase its temperature.

In the treatment above we have assumed no losses in the components. In reality we have a lot of losses, but with adequate combination of high pressures and superheating before the turbine, low pressures after the turbine, and feed water heating we can still reach efficiencies of about 40%.

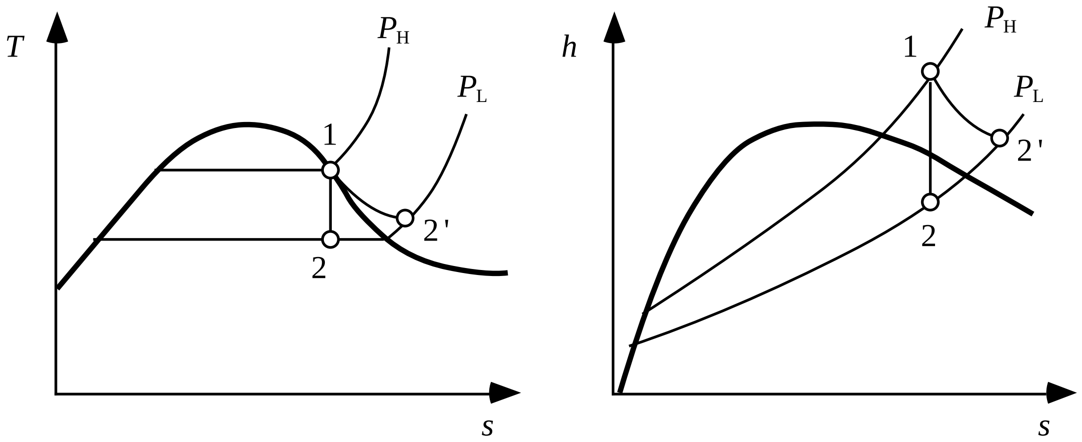
We will now look closer at the losses. Before, we concluded that the available work from a reversible adiabatic steady state process, i.e. $Q = 0$ and S = constant, is $W_t = W_s = H_1 - H_2 = E_1 - E_2$.

In reality we have losses, i.e. $Q \neq 0$ and $S \neq$ constant, so the output work is less and we must add more work to the kompressor or the pump. We can represent the internal losses by the energy and exergy efficiency of the turbine, $\eta_{t,en}$ och $\eta_{t,en}$, which are defined:

$$\eta_{t,en} = \frac{\text{Actual work}}{\text{Reversible work}} = \frac{w_a}{w_s} = \eta_{t,ex} = \eta_t$$

Let us see what this implies for the turbine and the compressor in the Carnot process.

Turbine



The maxumum work appear when ΔS = 0, but as we said before ΔS>0 fo all real processes. 1-2 gives maximum work, $h_1 - h_2$ and 1-2' gives the real work, $h_1 - h_{2'}$, see Fig. above. As we see $h_1 - h_2 > h_1 - h_{2'}$. The above is valid if no heat losss occur. The efficiency of the turbine becomes:

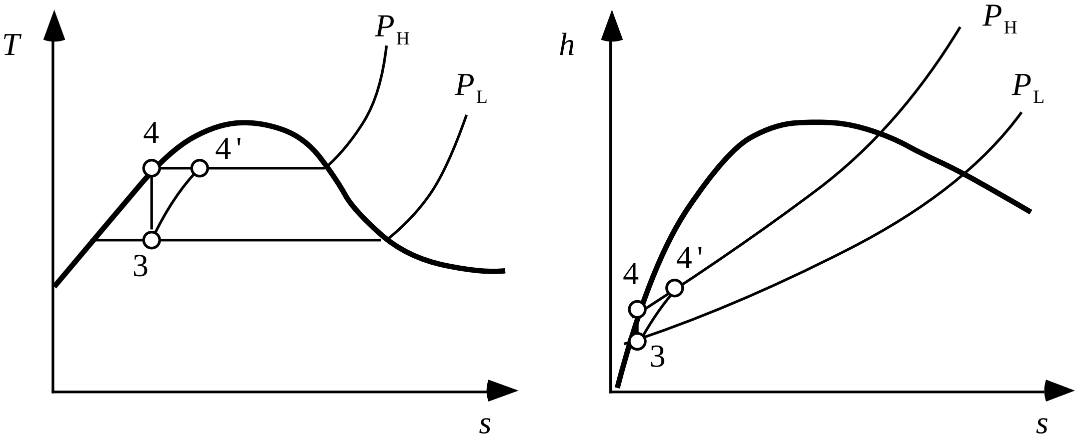
$$\eta_t = \frac{h_1 - h_{2'}}{h_1 - h_2}$$

which usually is about 0.80-0.85.

Compressor

The energy and exergy efficiencies of the compressor becomes accordingly:

$$\eta_{c,en} = \frac{\text{Reversible work}}{\text{Actual work}} = \frac{w_s}{w_a} = \eta_{c,ex} = \eta_c$$

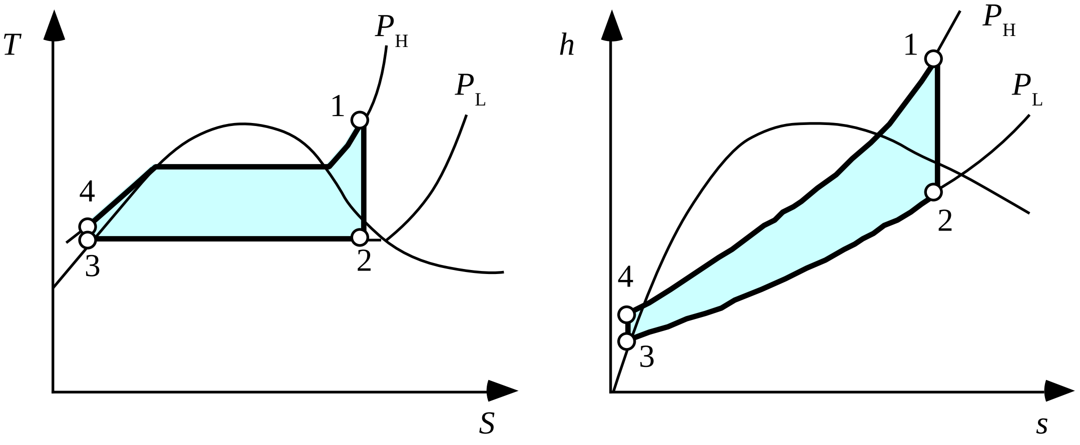


$\Delta S>0$ for the compressor since the process is irreversible, thus, we have

$$\eta_k = \frac{h_3 - h_4}{h_3 - h_{4'}}$$

which is usually about 0.80-0.85.

Let us now return to the Rankine cycle and see how it ususally looks, see Fig. below.



For a reversible Rankine cycle we have:

4-1 Liquid water converts to steam at pressure P_H, we add heat Q_H.
1-2 The steam expands adiabatically, i.e. $\Delta S = 0$, to pressure P_L, just below saturation. Work is transfered through the turbine to an electric generator in a power plant.
2-3 The steam is condensed at pressure P_L, we remove heat Q_L.
3-4 Liquid water is pumped isentropically, i.e. $\Delta S = 0$, to the boiler and the pressure increases to P_H. We feed the pump work W_p.

Net produced work becomes from first law:

$$W_{net} = Q_H - Q_L - W_p$$

The pump work becomes, if we assume the liquid water to be incompressible and the specific volume $v = 0.001$ m^3/kg.

$$W_p \approx 0.001\Delta P = 0.001(P_H - P_L) \text{ [J/kg]}$$

The theoretical thermal energy efficiency of the Rankine cycle then becomes:

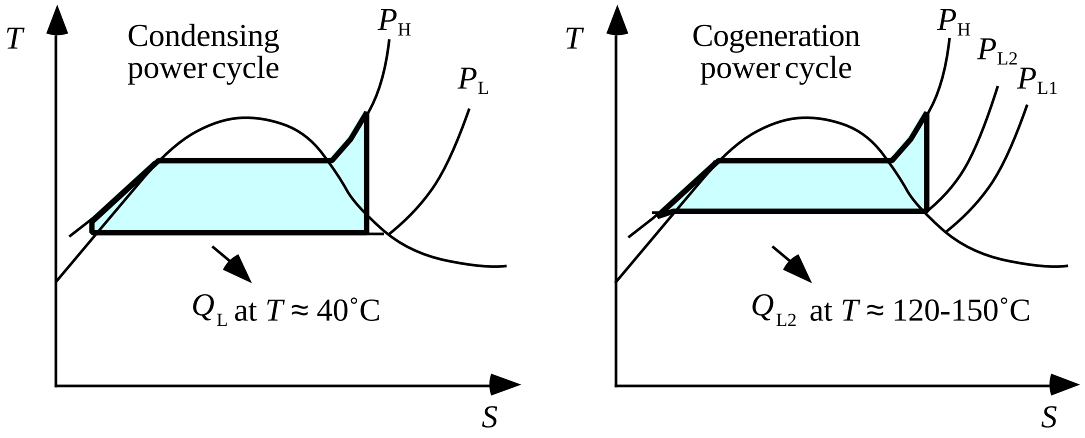
$$\eta_{tt,en} = \frac{\text{Output work}}{\text{Input enthalpy}} = \frac{h_1 - h_2}{h_1 - h_4}$$

And analogusly for the theoretical thermal exergy efficiency:

$$\eta_{tt,ex} = \frac{\text{Output work}}{\text{Input exergy}} = \frac{e_1 - e_2}{e_1 - e_4}$$

As we already have concluded it is advantageously to superheat the steam to extract more work from the turbine. In practice the pressure is below 200 bar and the temperature below 550-600˚C at the admission state 1. As we see from the Fig. of the Rankine cycle above, the actual work is depending of the pressure dropp between the admission state 1 and the final state 2. The lower pressure (back pressure) the more work we get, however, the content of liquid water in the steam must not exceed 10-12 weight-%, which gives the lower limit of the pressure.

An other way to improve the steam power cycle is back pressure och cogeneration. If we have a simultaneous need of power and heat this may be a good solution.



In the condensing power cycle we extract more power, but the low condensing temperature makes the heat useless. In the cogeneration power cycle we extract less power, but the condensing temperature is now high enough to make the heat useful. The heat can be used for process heat or space heating. In this way the energy efficiency increases, but the exergy efficiency is more or less the same.

There are a number of efficiencies to describe the different losses in a steam power plant. Let us just mention some of them in energy units.

- Combustion losses in the boiler, the boiler energy efficiency:

$$\eta_b = \frac{\text{Energy in steam}}{\text{Energy in fuel}} \approx 0.9 \text{ for big plants.}$$

- The theoretical thermal energy efficiency depends on the design of the steam power cycle:

$\eta_{tt} \approx 0.5$ for a good design.

- The efficiency of the turbine (energy and exergy):

$\eta_t \approx 0.8\text{-}0.9$

- Mechanical (friction) and electrical losses in the turbine and generator. The energy and exergy efficiencies are usually:

$\eta_{m+el} \approx 0.9\text{-}0.95$ for big plants.

The total energy efficiency from fuel to electricity then becomes about

$\eta_{tot} = \eta_b\eta_{tt}\eta_t\eta_{m+el} \approx 0.35\text{-}0.4$ (NB, the pump is not included!)

Losses are also due to the use of power at the power plant, e.g. for pumps, fans and internal transportations. These losses often adds to between 2 and 5% of produced electricity.

Ex: A steam turbine has the admission state 60 bar, 500˚C, and the steam flow 10 ton/h. What is the power output if the back-pressure is 6 bar? ($\eta_t = 0.80$)

S: From above we have:

$$\eta_t = \frac{\text{Acual work}}{\text{Reversible work}} = \frac{h_1 - h_{2'}}{h_1 - h_2}$$

Reversible work: $w_s = h_1 - h_2$

Actual work: $w_a = h_1 - h_{2'} = \eta_t(h_1 - h_2)$

From steam tables we get: $h_1 = 3425$ kJ/kg and $h_2 = 2810$ kJ/kg

(We find h_2 by first finding state 1 in the Mollier chart and then follow an isentropic line until it cross the pressure $P_L = 6$ bar then we have state 2.

$$P_{\text{turbine}} = \dot{m}\eta_t(h_1 - h_2) \approx \frac{10 \times 10^3}{3600} \times 0.8 \times (3425 - 2810) \approx 1370\text{kW}$$

In addition to this we also have mechanical and electrical losses, i.e. $\eta_{m+el} \approx 0.9\text{-}0.95$, so P_{el} in reality becomes even less.

Ex: a) An industrial cogeneration plant is working with the admission state 100 bar, 500˚C and back-pressure 5 bar. What is the maximum electricity production if the heating need is 15 MW, $\eta_t = 0.82$ and $\eta_{el+m} = 0.94$.
b) The plant is used only for production of electricity, and the pressure after the turbine is 0.08 bar. Determine the electric power and the specific amount of steam at

the real state after the turbine. c) Calculate the exergy output in the two cases. (T_0 = 20˚C)

S: a) P_H = 100 bar & θ = 500˚C h_1 = 3.37 MJ/kg

P_{L2} = 5 bar & s = constant h_2 = 2.65 MJ/kg

$$\eta_t = \frac{h_1 - h_{2'}}{h_1 - h_2} \qquad h_{2'} = h_1 - \eta_t(h_1 - h_2) \approx 3.37 - 0.82 \times (3.37 - 2.65) \approx 2.78$$

The condensing heat is used when the steam is condensed. The actual enthalpy after the turbine is $h_{2'}$. If h_3 is the state when all the steam is condensed, i.e. saturated liquid, then we get from steam tables:

P_{L2} = 5 bar and saturated liquid h_3 = 0.64 MJ/kg

The condensing heat is $q_L = h_{2'} - h_3$ = 2.78 – 0.64 = 2.14 MJ/kg

We know that the heating need is 15 MW (15 MJ/s). From this we can determine how much steam that must be condensed per second.

$$\frac{15 \times 10^6}{2.14 \times 10^6} \approx 7\,[\text{kg / s}]$$

Thus, 7 kg steam is expanded in the turbine per second, which gives:

$$P_{el} = \dot{W}_{el} = \dot{m}(h_1 - h_2)\eta_t\eta_{m+el} \approx 7 \times (3.37 - 2.65) \times 0.82 \times 0.94 \approx 3.9\,[\text{MW}].$$

b) The theoretical state after the turbine now instead becomes, from steam tables:

P_{L1} = 0.08 bar & s = constant h_2 = 2.06 MJ/kg

The real state is 2': $h_{2'} = h_1 - \eta_t(h_1 - h_2)$ = 2.30 MJ/kg

Thus, we have at this state: $h_{2'}$ = 2.30 MJ/kg and P_2 = 0.08 bar, and from the hs-diagram we get the gas content of the steam to: $x \approx 0.88$

The electric output becomes:

$$P_{el} = \dot{W}_{el} = \dot{m}(h_1 - h_2)\eta_t\eta_{m+el} \approx 7 \times (3.37 - 2.06) \times 0.82 \times 0.94 \approx 7.1\,[\text{MW}]$$

c) The exergy in the produced heat in the cogeneration case becomes:

$$P_{L,ex} = \dot{W}_{L,ex} = \dot{m}\left[(h_3 - h_0) - T_0(s_3 - s_0)\right] \approx$$
$$\approx 7 \times [(640.16 - 83.90) - (273.15 + 20)(1.8604 - 0.296)] \approx 684\,[\text{kW}] \approx 0.7\,[\text{MW}]$$

The total exergy power then becomes: $P_{ex} = P_{L,ex} + P_{el} \approx 0.7 + 3.9 \approx 4.6$ [MW]

And in the case of pure condensation: $P_{ex} = P_{el} \approx 7.1$ [MW]

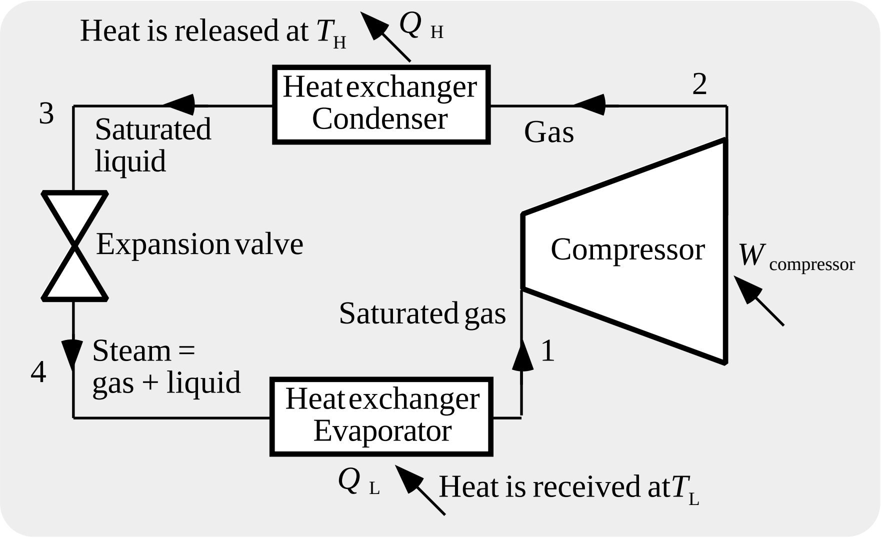
Let us summerize:
a) Cogeneration gives the energy power: 3.9 MW electricity and 15 MW heat.
b) The plant gives 7.1 MW electricity and the steam quality is 0.88.
c) $P_{ex,a} \approx 4.6$ MW ($P_{en,a} \approx 18.9$ MW) and $P_{ex,b} \approx 7.1$ MW ($\approx P_{en,b}$)

Refrigerators and heat pumps

We have seen that heat can move from lower to higher temperature by adding work to a Carnot cycles going backwards. This is what happens in refrigerators and heat pumps.

The most common systems are based on expansion, compression and absorption. We will treat the compression process, since it is the most common.

The compression process is similar to a steam power cycle running backwards, see the Fig. below. In short the boiling temperature of the refrigerant, i.e. the working fluid, is moved by changing the pressure. A liquid boils (evaporates) at a low pressure, i.e. takes up heat at low temperature, and then it condenses at high pressure, i.e. gives away heat at high temperature.



For an ideal process we have:

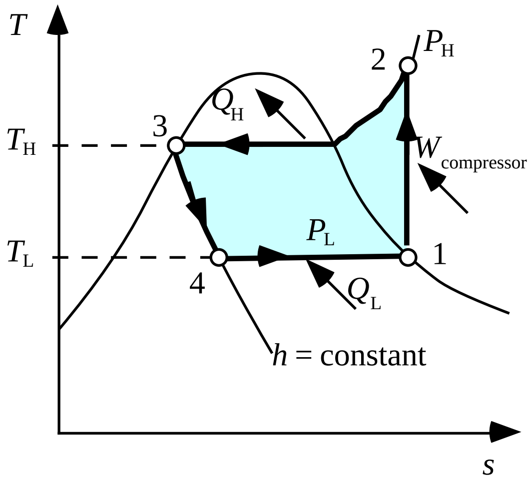
1-2 The refrigerant is adibatically, i.e. $\Delta s = 0$, compressed to pressure P_H.

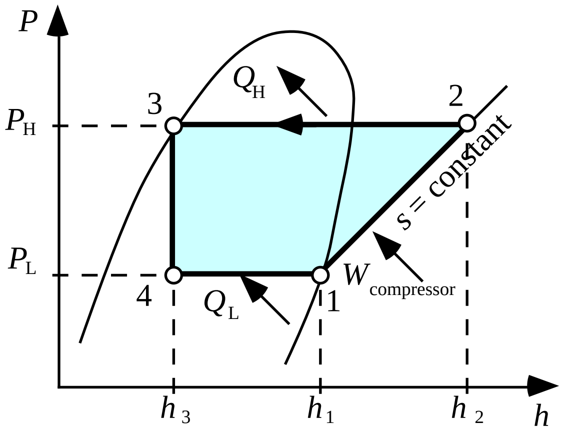
2-3 The superheated refrigerant (gas) condenses at pressure P_H and then releases heat Q_H at temperature T_H.

3-4 The refrigerant expands by an expansion valve to pressure P_L. The expansion occurs at constant enthalpy (H = constant) since neither heat or work is involved (first law).

4-1 The refrigerant is in the damp region (gas+liquid). The liquid part evaporates and takes up the heat Q_L at temperature T_L.

In the Figs. below we see the process in a *Ts* and *Ph*-diagram.





In the ideal process the expansion occurs at constant enthalpy, which implies that energy is neither added nor removed. However, a lot of exergy is lost in the expansion.

Let us apply the first law:

$$W_{\text{compressor}} = Q_H - Q_L$$

$$Q_L = H_1 - H_4 = H_1 - H_3, \text{ since } H_3 = H_4$$

$$W_{\text{compressor}} = H_2 - H_1$$

$$Q_H = H_2 - H_3$$

The efficiency as a refrigerator is defined by the Coefficient of Performance, $\text{COP}_{\text{cooling}}$:

$$\text{COP}_{\text{cooling}} = \frac{\text{Received heat}}{\text{Added work}} = \frac{Q_L}{W_{\text{compressor}}} = \frac{H_1 - H_3}{H_2 - H_1}$$

The efficiency as a heat pump is similarly defined by $\text{COP}_{\text{heating}}$:

$$\text{COP}_{\text{heating}} = \frac{\text{Released heat}}{\text{Added work}} = \frac{Q_H}{W_{\text{compressor}}} = \frac{H_2 - H_3}{H_2 - H_1}$$

The highest COP we get for a Carnot process.

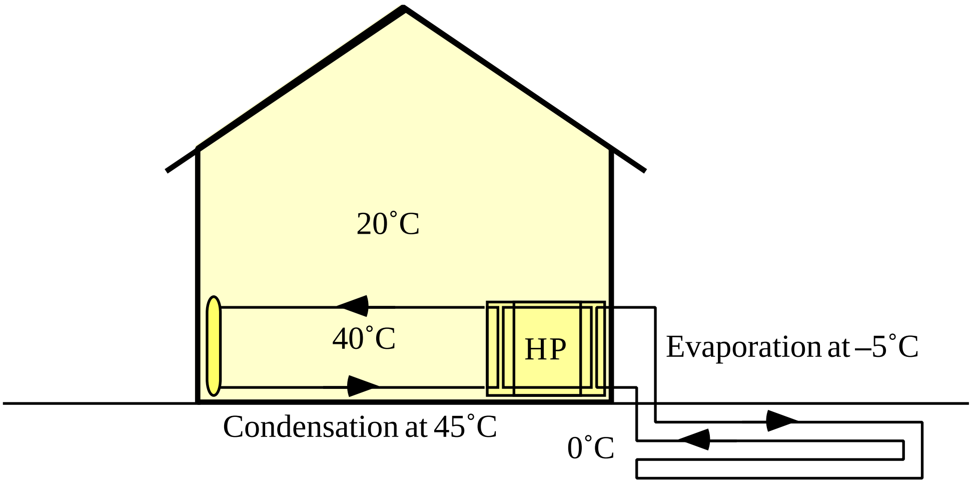
$$\text{COP}_{\text{coolingCarnot}} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}$$

$$\text{COP}_{\text{heatingCarnot}} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L} = 1 + \text{COP}_{\text{cooling}}$$

N.B.! T is the absolute temperature, i.e. in Kelvin.

In practice $\text{COP}_{\text{cooling}} = 0.4 \text{ to } 0.6 \times \text{COP}_{\text{cooling, Carnot}}$ and if all heat from the heat pump is beeing used then $\text{COP}_{\text{heating}} = 1 + 0.4 \text{ to } 0.6 \times \text{COP}_{\text{cooling, Carnot}}$.

Ex: A house is keept at 20˚C by a compressor heat pump acold winter day (–20˚C). The heat source is the gound at 0˚C. The refrigerant is R-12, working between –5˚C and 45˚C, which gives 40˚C in the radiatorers. a) Calculatethe $\text{COP}_{\text{heating}}$ if the system works idealy between –5˚C and 45˚C. b) What is then the $\text{COP}_{\text{heating,Carnot}}$? c) Estimate the COP in practice.



S: a) From steam tables for R-12, we find:

State 1, θ_L = –5˚C, saturated gas $P_L \approx 2.61$ bar & $h_1 \approx 349$ kJ/kg.

State 3, θ_H = 45˚C, saturated liquid $P_H \approx 10.84$ bar & $h_3 \approx 244$ kJ/kg.

We now have to determine the enthalpy at state 2. Look for state 1 in the a *Ph*-diagram. Assume reversible process, i.e. *s* is constant. Follow the isentropic curve to P_H = 10.8 bar, and find $h \approx 376$ kJ/ kg.

$$\text{COP}_{\text{heating}} = \frac{h_2 - h_3}{h_2 - h_1} \approx \frac{376 - 244}{376 - 349} \approx 4.9$$

b) $$\text{COP}_{\text{heating,Carnot}} = \frac{T_H}{T_H - T_L} \approx \frac{45 + 273}{(45 + 273) - (-5 + 273)} \approx 6.4$$

c) In practice we have $\text{COP}_{\text{heating}} \approx 1 + 0.4$ to $0.6\times\text{COP}_{\text{cooling, Carnot}} \approx 1 + 0.4$ to $0.6\times \dfrac{-5+273}{(45+273)-(-5+273)} \approx$ 3.1-4.2. Thus the result above seem to optimistic, after all we did assume no losses.

Ex: A one stage refrigerator should have the cooling power 58 kW. The refrigerant is ammonia, evapoating at –10˚C and condensating at 25˚C. Determine: a) ammonium flow, b) COP, c) ammonium flow and COP when super cooling occure at 15˚C in the condenser and d) the theoretically highest COP in b) and c).

S: From the *Ph*-diagram for ammonia, we have:

At evaporation: θ_L = –10˚C, P_L= 2.9 bar and h_1 = 1452 kJ/kg

At condensation: θ_H = 25˚C, P_H = 10.0 bar and h_3 = 318 kJ/kg

At condensation and super cooling: $\theta_{H'}$ = 15˚C, $P_{H'}$ = 10.0 bar and $h_{3'}$ = 270 kJ/kg
From the *Ph*-diagram we have $h_2 \approx 1620$ kJ/kg
Cooling power: $P_{\text{cooling}} = \dot{m}\,(h_1 - h_3)$ where $\dot{m}$ is the refrigerant flow

Coefficient of Performance: $\text{COP}_{\text{cooling}} = \dfrac{h_1 - h_3}{h_2 - h_1}$

The theoretically highest COP: $\mathrm{COP}_{\mathrm{Carnot}} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}}$

a) $\dot{m} = \dfrac{P_{\mathrm{cooling}}}{h_1 - h_3} \approx \dfrac{58}{1452 - 318} \approx 0.051\ [\mathrm{kg/s}]$

b) $\mathrm{COP}_{\mathrm{cooling}} = \dfrac{h_1 - h_3}{h_2 - h_1} \approx \dfrac{1452 - 318}{1620 - 1452} \approx 6.6$

c) $\dot{m} = \dfrac{P_{\mathrm{cooling}}}{h_1 - h_{3'}} \approx \dfrac{58}{1452 - 270} \approx 0.049\ [\mathrm{kg/s}]$ and

$\mathrm{COP}_{\mathrm{cooling}} = \dfrac{h_1 - h_{3'}}{h_2 - h_1} \approx \dfrac{1452 - 270}{1620 - 1452} \approx 6.8$

d) Case b: $\mathrm{COP}_{\mathrm{Carnot}} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} \approx \dfrac{273 - 10}{273 + 15 - (273 - 10)} \approx 7.5$

Case c: $\mathrm{COP}_{\mathrm{Carnot}} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} \approx \dfrac{273 - 10}{273 + 25 - (273 - 10)} \approx 10.5$

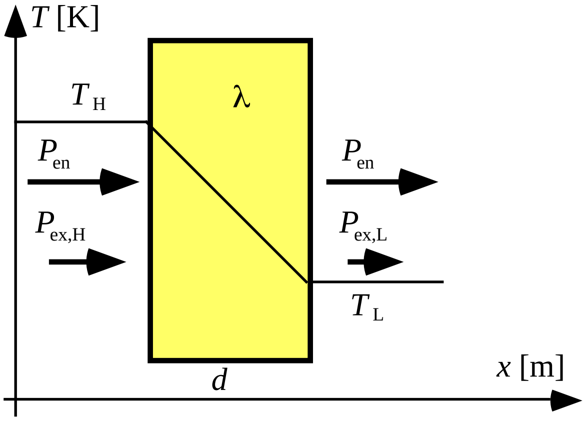
HEAT TRANSFER

Heat[15] is as we have mentioned before a consequence of that two bodies with different temperature exchange internal energy. From the second law of thermodynamics heat (internal energy) will spontaneously go from the warmer to the colder body. Heat should therefor rather be regarded as a process like work, they are not true forms of energy like mechanical and electrical energies. How heat is being transfered is a very complicated science, i.e. involving material properties. This makes this area to a scientific field beside thermodynamics. Heat can principally be transfered in three different ways:

1. Heat conduction
2. Heat convection, by self-convection or by external force
3. Heat radiation

Heat conduction

In a solid body heat is transferred from the warmer to the colder part by direct contact between the micro particles in the body. The temperature drops linearly through a homogenous body of rectangular shape.



The energy power P_{en} that is transferred through conduction is:

$$P_{en,l} = \frac{\lambda}{d} A (T_H - T_L) \ \text{[W = J/s]}$$

where T_H and T_L are the different temperatures [K], since it is a difference it is also valid for ˚C,
A is the area which the heat flow is facing [m^2],
d is the distance the heat flow has to transfer [m] och
λ is the heat conduction [W/m˚C or W/mK] for the body.

The exergy power P_{ex} that is transferred through the body consists of firstly the exergy flow in to the body at the temperature T_H:

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[15] Heat is here reagarded both as energy and exergy.

$$P_{\mathrm{ex,l,H}} = \left(\frac{E}{Q}\right)_{\mathrm{H}} P_{\mathrm{en,l}} = \frac{T_{\mathrm{H}} - T_0}{T_{\mathrm{H}}} P_{\mathrm{en,l}}$$

where T_0 is the environmental temperature, and secondly of the exergy flow that leaves the body at the temperature T_{L}:

$$P_{\mathrm{ex,l,L}} = \left(\frac{E}{Q}\right)_{\mathrm{L}} P_{\mathrm{en,l}} = \frac{T_{\mathrm{L}} - T_0}{T_{\mathrm{L}}} P_{\mathrm{en,l}}$$

The difference between these flows becomes:

$$\Delta P_{\mathrm{ex,l}} = P_{\mathrm{ex,l,H}} - P_{\mathrm{ex,l,L}} = \frac{T_{\mathrm{H}} - T_0}{T_{\mathrm{H}}} P_{\mathrm{en,l}} - \frac{T_{\mathrm{L}} - T_0}{T_{\mathrm{L}}} P_{\mathrm{en,l}} =$$

$$= \frac{(T_{\mathrm{H}} - T_0)T_{\mathrm{L}} - (T_{\mathrm{L}} - T_0)T_{\mathrm{H}}}{T_{\mathrm{H}}T_{\mathrm{L}}} P_{\mathrm{en,l}} = \frac{T_0(T_{\mathrm{H}} - T_{\mathrm{L}})}{T_{\mathrm{H}}T_{\mathrm{L}}} P_{\mathrm{en,l}} =$$

$$= \frac{\lambda}{d} A \frac{T_0}{T_{\mathrm{H}}T_{\mathrm{L}}} (T_{\mathrm{H}} - T_{\mathrm{L}})^2$$

This is the exergy needed to “fuel” the process, i.e. to maintain the temperature difference.

The heat conductivity, λ, denotes how much heat passes per unit time through 1 m^2 of the body when this is 1 m thick and the temperature difference is 1 K (here equals 1˚C). λ is a material constant. The higher the λ the more heat is conducted through the material. If we want a good heat insultator, then we should look for a small λ. Metals are good heat conductors ($\lambda \approx 45$ for steel), which is an advantage in e.g. heat radiators, whereas mineral wool ($\lambda \approx 0.036$) and other porous materials are poor heat conductors, because of enclosed stationary air. In liquids and gases we also have to consider convections, i.e. mass flows, because of the temperature dependence of the density. This we will study below, but first some numerical examples.

Ex: A glass window has an area of 1m^2, outside temperature is –5˚C and inside is +17˚C. The thichness of the glass is 5 mm. What is the heat rate (energy power) through the window, if we only consider heat conduction?

S: A = 1 m^2, θ_{H} = 17˚C, θ_{L} = –5˚C, d = 5 mm = 5×10^{-3} m, λ = 0.9 W/m˚C at 20˚C, from tables. The λ value is depending on the temperature, however in most cases we can neglect this dependence. From the equations above we get the energy power:

$$P_{\mathrm{en,l}} = \frac{\lambda}{d} A(T_{\mathrm{H}} - T_{\mathrm{L}}) = \frac{\lambda}{d} A(\theta_{\mathrm{H}} - \theta_{\mathrm{L}}) = \frac{0.9}{5\times10^3} \times 1 \times [17 - (-5)] = 3960 \approx 4\ [\mathrm{kW}]$$

Thus, a conciderable amount of energy and energy loss.

Ex: What is the exergy loss in the example above?

S: The energy power leaking trough the window is $P_{\mathrm{en,l}}$ as above. Assume the environmental temperature is equal to the outdoor temperature, i.e. $T_0 = T_{\mathrm{L}}$ then the exergy will be zer for the heat when it reaches the outside temperature. The exergy factor at the temperature T_{H} becomes:

$$\left(\frac{E}{Q}\right)_{\mathrm{H}} = \frac{T_{\mathrm{H}} - T_0}{T_{\mathrm{H}}} = \frac{T_{\mathrm{H}} - T_{\mathrm{L}}}{T_{\mathrm{H}}} = \frac{\theta_{\mathrm{H}} - \theta_{\mathrm{L}}}{T_{\mathrm{H}}} \approx \frac{17-(-5)}{273.15+17} \approx 0.075 = 7.5\%.$$

The exergy loss then becomes:

$$\Delta P_{\mathrm{ex}} = P_{\mathrm{ex,l}} = \frac{E}{Q} P_{\mathrm{en,l}} \approx 0.075 \times 3960 \approx 300 \; [W]$$

The needed exergy power to maintain the temperature difference, thus, is far less than the energy power. Let us compare this with a situation when we try to keep a leaking bucket, which leaks 300 liter per hour full of water. Then adding more than 300 liters per hour will only flow away, and to pour on more 4000 liter per hour is ridiculous!

Since, the heat transfer is towards the environment the exergy flow only becomes a loss, i.e. no exergy is being transfered.

Ex: Let us compare dry and wet mineral wool. The area is 2 m^2 and the temperatures are 0˚C on outside and +20˚C on inside, the thickness is 10 cm. What are the energy flows and the exergy losses in the two cases?

S: We have: A = 2 m^2, θ_{H} = 20˚C, θ_{L} = 0˚C, d = 10 cm = 0.1 m, λ = 0.04 for dry wool and for water we have λ = 0.60 from tables. The energy flows in the two cases become, if we neglect the wool in the wet case:

$$P_{\mathrm{en,l,dry}} = \frac{\lambda}{d} A (T_{\mathrm{H}} - T_{\mathrm{L}}) = \frac{\lambda}{d} A (\theta_{\mathrm{H}} - \theta_{\mathrm{L}}) = \frac{0.036}{0.1} \times 2 \times (20-0) = 14.4 \; [\mathrm{W}]$$

$$P_{\mathrm{en,l,wet}} = \frac{0.60}{0.1} \times 2 \times (20-0) = 240 \; [\mathrm{W}]$$

Thus, insulation is very sensitive for water or moist. (Moist is also good if you want to grow mold and fungi.)

The exergy factor becomes, in both cases, since $T_0 = T_{\mathrm{L}}$:

$$\frac{E}{Q} = \frac{\theta_{\mathrm{H}} - \theta_{\mathrm{L}}}{T_{\mathrm{H}}} \approx \frac{200}{273.15+20} \approx 0.068$$

Thus, the exergy losses becomes:

$$\Delta P_{\mathrm{ex,dry}} = P_{\mathrm{ex,l,dry}} = \frac{E}{Q} P_{\mathrm{en,l,dry}} \approx 0.068 \times 14.4 \approx 1 \; [W]$$

$$\Delta P_{\mathrm{ex,wet}} = P_{\mathrm{ex,l,wet}} = \frac{E}{Q} P_{\mathrm{en,l,wet}} \approx 0.068 \times 240 \approx 16 \; [W]$$

The energy or exergy need to maintain the the temperature difference increase by 16 times if the insulation is wet.

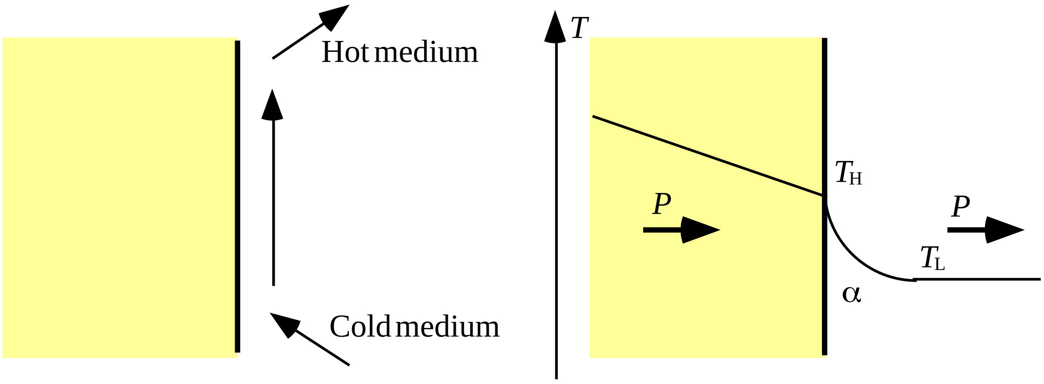
Heat conduction is of course also acting in gases and liquids, but heat transfer in these phases mainly instead relates to mass transfer or convection, see below. This implies that heat conduction is only of interest in gases and liquids if mass transfer is not aloud.

Heat convection

Convection is heat transfer by transfer of mass. The heat you can feel over a hot radiator is due to that hot air rises when its density decreases, i.e. the air becomes lighter. In the same way water on the stove is heated when the bottom becomes warm, the water rises and replaces by colder heavier water, i.e. natural stirring. This does not occur in a microwave oven, where the heat is beeing generated inside the substance, so we need to manually “convect” the water, stir it. Thus, we differ between free and forced convection.

Free convection – free current

A wall of temperature T_H is in contact with a gas (or liquid) of temperature T_L, $T_H > T_L$. From heat conduction, i.e. direct contact heat is being transferred to the medium in contact with the wall. This medium the gets a higher temperature and lower density and rises. Then the left space is being replaced by colder media, and so on. A free current of the media has evolved.



Transfered energy power by convection then becomes:

$$P_{\mathrm{en,c}} = \alpha A (T_H - T_L)$$

where α = heat transfer coefficient [W/m²K]

A is the area exposed to convection [m²]

The heat transfer coefficient α, denotes how much heat [W] is transferred per unit time and unit area at a temperature difference of 1 K [˚C] when we have convection.

As for heat conduction the exergy power becomes:

$$P_{\mathrm{ex,c,H}} = \frac{T_H - T_0}{T_H} P_{\mathrm{en,c}} = \alpha A \frac{T_H - T_0}{T_H} (T_H - T_L)$$

$$P_{\mathrm{ex,c,L}} = \frac{T_{\mathrm{L}} - T_0}{T_{\mathrm{L}}} P_{\mathrm{en,c}} = \alpha A \frac{T_{\mathrm{L}} - T_0}{T_{\mathrm{L}}} (T_{\mathrm{H}} - T_{\mathrm{L}})$$

$$\Delta P_{\mathrm{ex,c}} = \frac{T_0 (T_{\mathrm{H}} - T_{\mathrm{L}})}{T_{\mathrm{H}} T_{\mathrm{L}}} P_{\mathrm{en,c}} = \alpha A \frac{T_0}{T_{\mathrm{H}} T_{\mathrm{L}}} (T_{\mathrm{H}} - T_{\mathrm{L}})^2$$

Ex: Assume hot water surrounding a pipe with the diameter 55 mm and length 4 m. How much heat (energy and exergy) per unit time is transferred from the water to the pipe if the water temperature is 50˚C and the pipe is 20˚C ans if the heat transfer coefficient is 5000 W/m²K? (θ_0 = 0˚C)

S: The area A is the area of the pipe, i.e. $A = \pi dL \approx 3.14\times55\times10^{-3}\times4 \approx 1$ m², θ_{H} = 50˚C, θ_{L} = 20˚C, d = 5 mm = 5×10^{-3} m. From the relations above we have:

$$P_{\mathrm{en,c}} = \alpha A(T_{\mathrm{H}}–T_{\mathrm{L}}) = \alpha \pi dL(\theta_{\mathrm{H}}–\theta_{\mathrm{L}}) \approx 5000\times3.14\times55\times10^{-3}\times4(50–20) \approx 104 \text{ [kW]}$$

The exergy power becomes:

$$P_{\mathrm{ex,c,H}} = \frac{T_{\mathrm{H}} - T_0}{T_{\mathrm{H}}} P_{\mathrm{en,c}} = \frac{\theta_{\mathrm{H}} - \theta_0}{T_{\mathrm{H}}} P_{\mathrm{en,c}} \approx \frac{500}{273 + 50} \times 104 \approx 16 \text{ [kW]}$$

$$P_{\mathrm{ex,c,L}} = \frac{T_{\mathrm{L}} - T_0}{T_{\mathrm{L}}} P_{\mathrm{en,c}} = \frac{\theta_{\mathrm{L}} - \theta_0}{T_{\mathrm{L}}} P_{\mathrm{en,c}} \approx \frac{20 - 0}{273 + 20} \times 104 \approx 7 \text{ [kW]}$$

$$\Delta P_{\mathrm{ex,c}} = \frac{T_0 (T_{\mathrm{H}} - T_{\mathrm{L}})}{T_{\mathrm{H}} T_{\mathrm{L}}} P_{\mathrm{en,c}} \approx \frac{273 \times (50 - 20)}{(273 + 50) \times (273 + 20)} \times 104 \approx 9 \text{ [kW]}$$

Thus more than half of the exergy being transferred is lost in the process.

Forced convection

Force convection appear when we increase the convection by external forces, e.g. by a pump or a fan. As we are familiar with the heat transfer increases with the speed of the fluid, e.g. we experince more heat losses when it is windy.

We have the following relationas for the heat transfer coefficient at forced convection:

Air and steam

In pipes between +20˚C and +100˚C

$$\alpha = c_1(v\rho)^{0.79} \text{ [W/m}^2\text{K]}$$

where c_1 is a constant depending on the shape of the pipe and the flowing medium, the following approximate values are usually used:

Pipe diameter [mm]	10	20	50
c_1 for air	8.1	7.2	6.4
c_1 for steam	13.5	12.0	10.7

v is the speed of the flowing medium [m/s]
ρ is the density of the flowing medium [kg/m^3]

For flat areas

$\alpha = 5.8+3.95v \qquad v<5$ m/s

$\alpha = 7.15v^{0.78} \qquad v>5$ m/s

Water in pipes

$\alpha = c_2 v^{0.87} \qquad$ [W/m^2]

At pipe diameters between 10 and 30 mm and temperatures between 10 to 50˚C c_2 is evaluated from:

$c_2 = 3370 + 55\theta$ (θ is the temperature in ˚C)

For condensing water we have $\alpha \approx 10000$ W/m^{2}K.

Ex: A hot pipe, length 10 m and diameter 10 cm, with water at the temperature 60˚C passes a cold area at environmental temperature 0˚C. How much energy and exergy is lost in this area? Assume that the area of the pipe can be regarded as a flat surface, and assume that the surface of the pipe has the same temperature as the flowing water.

S: The area A becomes: $A = \pi dL \approx 3.14\times10\times10^{-2}\times10 = 3.14$ m^2.

The heat transfer coefficient becomes from above (air surrounding a flat area): $\alpha = 5.8 + 3.95v = 5.8$ W/m^{2}K, since $v = 0$ m/s.

The energy power becomes: $P_{\text{en,c}} = \alpha A(\theta_{\text{H}}-\theta_{\text{L}}) = 5.8\times3.14\times(60-0) \approx 1.1$ [kW]

The exergy power, being lost, becomes: $\Delta P_{\text{ex,c}} = \dfrac{T_0(T_{\text{H}}-T_{\text{L}})}{T_{\text{H}}T_{\text{L}}}P_{\text{en,c}} =$

$$= \frac{T_{\text{H}}-T_{\text{L}}}{T_{\text{H}}}P_{\text{en,c}} = \frac{\theta_{\text{H}}-\theta_{\text{L}}}{T_{\text{H}}}P_{\text{en,c}} \approx \frac{60-0}{273+60}\times1100 \approx 200 \text{ [W]}$$

A very efficient heat transfer occures if the convection appears simultaneaously as a phase change, e.g. if a liquid is evaporation from a surface. This we experience when we are wet or when we are sweating. At the evaporation heat is taken from the skin, which then becomes extra cold.

Heat radiation

A body of temperature above the absolute zero (0K or –273.15˚C) emits electromagnetic radiation, as light and heat radiation. High frequency radiation (blue light, ultra violet, or x-ray) has more energy than low frequency radiation (red, infra-red or heat radiation). The radiation is a way of transporting energy or exergy between body which are not in physical contact. Thus, energy and exergy can be transported in vacuum and long distances. The energy and exergy flow from the sun to the earth is one example of this.

As we know the color has an important effect on the radiation. Dark clothes absorbs more heat than light clothes. Á *black* body, by definition absorbs all incoming radiation and it is at all temperatures the most emitting and absorbing body. A *white* body, by definition reflects all incoming radiation. A *gray* body absorbs an equal amount of the incoming radiation at all frequencies. A *colored* body radiates at certain frequencies defined by the color.

A *reflecting surface* reflects the radiation at the same angle as the incoming radiation and a matt surface reflects the incoming radiation in all directions, as scattered light.

The so called *emission coefficient* ε denotes the amont of the radiation which is emitted, i.e. leaves the surface. A surface with a low emission coefficient emitts less of the radiation to the environment and more of the radiation is reflected back into the body. A mirror reflects most of the incoming radiation and only a small part is absorbed. A shiny and white surface has a low emission coefficient, wheras a matt and black surface has a highr emission coefficient and high absorbtion. A surface that absorbes all incoming radiation or emitts all outgoing radiation, has the emission coefficient $\varepsilon = 1$, i.e. a black body.

Q: Perhaps you have seen a little wheel with wings on a vertical axis in a small glass bulb. Usually four wings, like a water-wheel, one side black the other side white. If you put it in the sunlight it starts to move, in which direction and why?

The emitted radiation per unit area and time from a black body is determined by Stefan-Boltzmanns law:

$$P_{\mathrm{en,r}} = \sigma A T^4 \approx 5.67 \times 10^{-8} A T^4 \left[= 5.67 A \left(\frac{T}{100} \right)^4 \right]$$

The energy power from a gray body instead becomes:

$$P_{\mathrm{en,r}} = \varepsilon \sigma A T^4 \approx \varepsilon\, 5.67 \times 10^{-8} A T^4 \left[= \varepsilon 5.67 A \left(\frac{T}{100} \right)^4 \right]$$

where A is the emitting surface [m^2]

ε is the emission coefficient or absorbtion coefficient, which is found in tables.

T is the temperature in Kelvin.

As we see the radiation depends on the temperature raised to the 4th power, which implies that when the temperature doubles the radiation increase by a factor of 16!

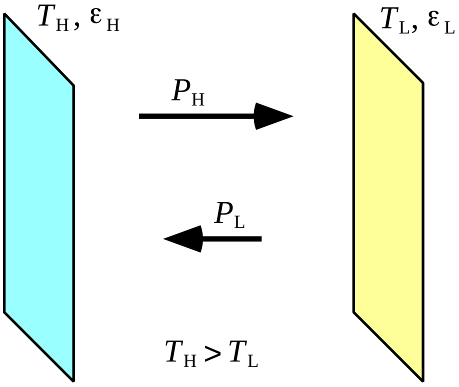
Q: Assume that we concentrate sunlight by a big concave mirror. What is the maximal temperature we could get in the focus and why? There are two different explanations!

From above we have that the exergy of radiation is:

$$P_{\mathrm{ex,r}} = \left[1 + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 - \frac{4}{3}\frac{T_0}{T}\right] P_{\mathrm{en,r}}$$

Radiation between different bodies

Since every body (over 0K) emitts radiation we must consider the exchange of radiation between different bodies to be able to calculate the net radiation from the warmer to the colder body. Let us first concider two paralell surfaces of equal size, but with different temperaturesT_{H}, T_{L} and emission coefficients ε_{H}, ε_{L}, see below.



We have the following radiation situation between the surfaces

$$\begin{cases} P_{\mathrm{en,r,H}} = \varepsilon_{\mathrm{H}}\sigma A T_{\mathrm{H}}^4 \approx \varepsilon_{\mathrm{H}}\, 5.67\times 10^{-8} A T_{\mathrm{H}}^4 \\ P_{\mathrm{en,r,L}} = \varepsilon_{\mathrm{L}}\sigma A T_{\mathrm{L}}^4 \approx \varepsilon_{\mathrm{L}}\, 5.67\times 10^{-8} A T_{\mathrm{L}}^4 \end{cases}$$

The hot surface the receives the energy power $P_{\mathrm{en,r,L}}$ and the surface will absorb the energy power $\varepsilon_{\mathrm{H}}P_{\mathrm{en,r,L}}$, while the rest $(1\text{-}\varepsilon_{\mathrm{H}})P_{\mathrm{en,r,L}}$ is reflected back to the surface of lower temperature, where the energy power $\varepsilon_{\mathrm{L}}(1\text{-}\varepsilon_{\mathrm{H}})P_{\mathrm{en,r,L}}$ is absorbed, while the rest $(1\text{-}\varepsilon_{\mathrm{L}})(1\text{-}\varepsilon_{\mathrm{H}})P_{\mathrm{en,r,L}}$ is reflected back, etcetera. The net energy flow, which of course always is directed towards the surface of lower temperature, T_{L} becomes:

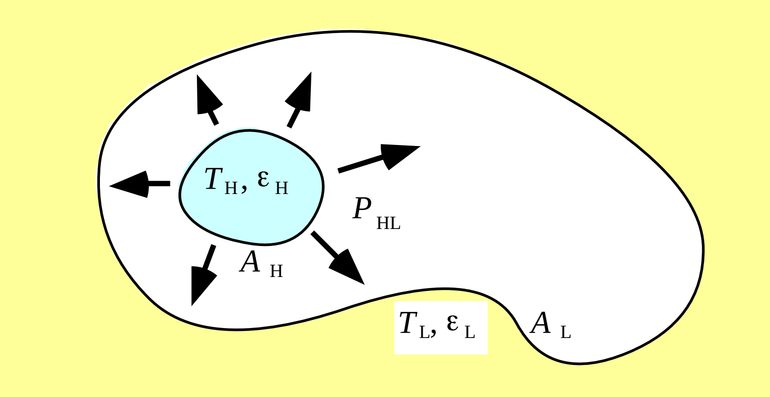
$$P_{\mathrm{en,r,HL}} = \frac{1}{\dfrac{1}{\varepsilon_H} + \dfrac{1}{\varepsilon_L} - 1}\sigma A\left(T_{\mathrm{H}}^4 - T_{\mathrm{L}}^4\right)$$

which is valid for all colored surfaces (black or white) ans liquid surfaces.

The net exergy flow becomes from above:

$$P_{\mathrm{ex,r,HL}} = \frac{1}{\frac{1}{\varepsilon_{\mathrm{H}}}+\frac{1}{\varepsilon_{\mathrm{L}}}-1}\,\sigma A\left\{T_{\mathrm{H}}^4\left[1+\frac{1}{3}\left(\frac{T_0}{T_{\mathrm{H}}}\right)^4-\frac{4}{3}\frac{T_0}{T_{\mathrm{H}}}\right]-T_{\mathrm{L}}^4\left[1+\frac{1}{3}\left(\frac{T_0}{T_{\mathrm{L}}}\right)^4-\frac{4}{3}\frac{T_0}{T_{\mathrm{L}}}\right]\right\}$$

For a hot surface completely covered by an other surface at lower temperature, see Fig below, we get the net energy flow:



$$P_{\mathrm{en,r,HL}} = \frac{1}{\frac{1}{\varepsilon_{\mathrm{H}}A_{\mathrm{H}}}+\frac{1}{A_{\mathrm{L}}}\left(\frac{1}{\varepsilon_{\mathrm{L}}}-1\right)}\,\sigma\left(T_{\mathrm{H}}^4-T_{\mathrm{L}}^4\right)$$

which is valid for all kinds of rooms where the hot body can be randomly placed. If the net power P is negativ then $T_{\mathrm{H}}<T_{\mathrm{L}}$. The exergy net power becomes as above:

$$P_{\mathrm{ex,r,HL}} = \frac{1}{\frac{1}{\varepsilon_{\mathrm{H}}A_{\mathrm{H}}}+\frac{1}{A_{\mathrm{L}}}\left(\frac{1}{\varepsilon_{\mathrm{L}}}-1\right)}\,\sigma\left\{T_{\mathrm{H}}^4\left[1+\frac{1}{3}\left(\frac{T_0}{T_{\mathrm{H}}}\right)^4-\frac{4}{3}\frac{T_0}{T_{\mathrm{H}}}\right]-T_{\mathrm{L}}^4\left[1+\frac{1}{3}\left(\frac{T_0}{T_{\mathrm{L}}}\right)^4-\frac{4}{3}\frac{T_0}{T_{\mathrm{L}}}\right]\right\}$$

Often the radiation conditions are more complicated and thus difficult to calculate, but from handbooks and tables you usually find enough instructions. Other wise, you have to simplify the problem to be able to solve it.

Ex: How much heat (energy and exergy) does a naked person loose (surface temperature 35˚C, $\varepsilon_{\mathrm{H}} = 0.7$ and area 1.5 m^2) from radiation in a room with black walls, $\varepsilon_{\mathrm{L}} = 1$, $\theta_{\mathrm{L}} = 20$˚C and area 20 m^2? ($T_0 = T_{\mathrm{L}}$)

S: We have a body contained in an other body, thus we have for the energy power, see relation above, where $T_{\mathrm{H}} \approx 35+273 = 308$ [K] and $T_{\mathrm{L}} \approx 20+273 = 293$ [K]:

$$P_{\mathrm{en,r,HL}} \approx \frac{1}{\frac{1}{0.7\times1.5}+\frac{1}{20}\left(\frac{1}{1}-1\right)}\,5.67\times10^{-8}\times1.5\times\left(308^4-293^4\right)\approx 145\ [\mathrm{W}]$$

The person will probably freeze, which we also might guess.
For the exergy we have:

$$P_{\text{ex,r,HL}} \approx \frac{1}{\dfrac{1}{0.7 \times 1.5} + \dfrac{1}{20}\left(\dfrac{1}{1} - 1\right)} 5.67 \times 10^{-8} \times$$

$$\times 1.5 \times 308^4 \left[1 + \frac{1}{3} \times \left(\frac{293}{308}\right)^4 - \frac{4}{3} \times \frac{293}{308}\right] \approx 3.7 \text{ [W]}$$

Thus, there are three ways for energy and exergy to be transfered as heat between bodies: conduction, which was simple to describe, convection and radiation, which were more complicated to describe. At temperatures close to ambient, i.e. ±20-30°C we can assume the following reletaion:

$$P_{\text{en,total}} = P_{\text{en,conduction}} + P_{\text{en,convection}} + P_{\text{en,radiation}} \approx UA\,(T_{\text{H}} - T_{\text{L}})$$

Hereby, all phenomena are summarized in one expression and concept, the over all heat coefficient *U*. Analogously, we have for the exergy flows:

$$P_{\text{ex,total,H}} = P_{\text{ex,conduction,H}} + P_{\text{ex,convection,H}} + P_{\text{ex,radiation,H}} \approx \frac{T_{\text{H}} - T_0}{T_{\text{H}}} P_{\text{en,total}}$$

$$P_{\text{ex,total,L}} = P_{\text{ex,conduction,L}} + P_{\text{ex,convection,L}} + P_{\text{ex,radiation,L}} \approx \frac{T_{\text{L}} - T_0}{T_{\text{L}}} P_{\text{en,total}}$$

The exergy loss then becomes:

$$\Delta P_{\text{ex,total}} = P_{\text{ex,total,H}} - P_{\text{ex,total,L}} \approx \frac{T_0 \left(T_{\text{H}} - T_{\text{L}}\right)}{T_{\text{H}} T_{\text{L}}} P_{\text{en,total}} \approx UA \frac{T_0}{T_{\text{H}} T_{\text{L}}} \left(T_{\text{H}} - T_{\text{L}}\right)^2$$

As we see, the energy is always conserved, the first law, whereas exergy is always lost, the second law. We also see that the exergy loss increases by the square of the temperature difference T_{H}–T_{L}, which is an important conclusion.

Q: Which form of heat has the highest exergy factor:

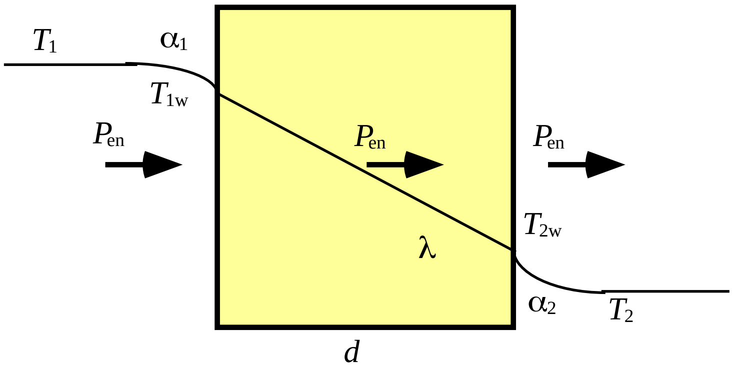
conduction: $\left(\dfrac{P_{\text{ex}}}{P_{\text{en}}}\right)_{\text{conduction}} = \dfrac{T - T_0}{T}$

or radiation: $\left(\dfrac{P_{\text{ex}}}{P_{\text{en}}}\right)_{\text{radiation}} = \left[1 + \dfrac{1}{3}\left(\dfrac{T_0}{T}\right)^4 - \dfrac{4}{3}\dfrac{T_0}{T}\right]$

Thus, which form of heat is most ordered?

Over all heat coefficient, *U*

Regard the heat transport through a homogenous wall



Since the same energy flow passes all layers we can put up the following equations, we neglect the radiation since the temperature differences $(T_1 - T_{1w})$ and $(T_{2w} - T_2)$ are assumed to be small:

$$\begin{cases} P_{en} = \alpha_1 A (T_1 - T_{1w}) \\ P_{en} = \dfrac{\lambda}{d} A (T_{1w} - T_{2w}) \\ P_{en} = \alpha_2 A (T_{2w} - T_2) \end{cases}$$

By writing the expressions for the temperature differences we get:

$$\begin{cases} \dfrac{P_{en}}{\alpha_1 A} = T_1 - T_{1w} \\ \dfrac{P_{en} d}{\lambda A} = T_{1w} - T_{2w} \\ \dfrac{P_{en}}{\alpha_2 A} = T_{2w} - T_2 \end{cases}$$

By adding all these expressions we get:

$$\frac{P_{en}}{\alpha_1 A} + \frac{P_{en} d}{\lambda A} + \frac{P_{en}}{\alpha_2 A} = T_1 - T_{1w} + T_{1w} - T_{2w} + T_{2w} - T_2$$

or:

$$\frac{P_{en}}{A}\left(\frac{1}{\alpha_1} + \frac{d}{\lambda} + \frac{1}{\alpha_2}\right) = T_1 - T_2$$

which can be written:

$$P_{en} = UA(T_1 - T_2)$$

where the overall heat coefficient is defined as $U = \dfrac{1}{\dfrac{1}{\alpha_1} + \dfrac{d}{\lambda} + \dfrac{1}{\alpha_2}}$ or $\dfrac{1}{U} = \dfrac{1}{\alpha_1} + \dfrac{d}{\lambda} + \dfrac{1}{\alpha_2}$.

The unit of U is W/m^{2}K, i.e. it gives the energy that per unit time and unit area passes through the construction when the temperature difference is 1 K [˚C]. The U-coefficient depends on the construction, d and λ and the heat transfer coefficients, α_1 and α_2. We also see that at heat insulation, e.g. in houses the *U*-coefficient should be small, but at heat conduction, e.g. in heat exchangers the *U*-coefficient should be large.

For a construction with several layers of materials, i and air, i.e. a sandwich construction we write the *U*-coefficient accordingly:

$$\frac{1}{U}=\frac{1}{\alpha_1}+\frac{1}{\alpha_2}+\sum_i\frac{d_i}{\lambda_i}+\sum\frac{1}{U_{\text{air}}}$$

where U_{air} combine conduction, convection and radiation for each air layer.

Ex: A wall with the area 20 m^2 has a mineral wool insulation with thickness 170 mm. The indoor temperature is +20˚C and outdoor is –5˚C. How much heat (energy and exergy) per unit time leaks trough the wall if the wind velocity is 1m/s? ($\theta_0 = -5$˚C)

S: We have the following data: d = 170 mm = 0.17 m, A = 20 m^2, θ_1= +20˚C, θ_2= –5˚C and λ = 0.04 W/m˚C.

$P_{\text{en}} = UA(\theta_1-\theta_2)$ where $\frac{1}{U}=\frac{1}{\alpha_1}+\frac{d}{\lambda}+\frac{1}{\alpha_2}$, since we only have one layer.

For flat surfaces we have from tables $\alpha = 5.8+3.95v$ if $v<5$ m/s

α_1 is the inside heat transfer coefficient

inside is $v = 0 \Rightarrow \alpha_1 = 5.8$ W/m^2˚C

α_2 is the outside heat transfer coefficient

outside is $v = 1$ m/s $\Rightarrow \alpha_2 = 5.8+3.95 = 9.75$ W/m^2˚C

$$\frac{1}{U}=\frac{1}{5.8}+\frac{0.17}{0.04}+\frac{1}{9.75}\approx 5$$

$$U=\frac{1}{5}=0.2\ \text{[W/m}^2\text{K]}$$

$$P_{\text{en}} = UA(\theta_1-\theta_2) = 0.2\times20(20-(-5)) = 0.2\times20\times25 = 100\text{ W}$$

$$T_{\text{L}}=T_0 \qquad P_{\text{ex,L}}=0 \qquad \Delta P_{\text{ex}}=P_{\text{ex,H}}\approx\frac{T_0(T_{\text{H}}-T_{\text{L}})}{T_{\text{H}}T_{\text{L}}}P_{\text{en,total}}=$$

$$=\frac{T_0(T_{\text{H}}-T_0)}{T_{\text{H}}T_0}P_{\text{en,total}}=\frac{T_{\text{H}}-T_0}{T_{\text{H}}}P_{\text{en,total}}=\frac{\theta_{\text{H}}-\theta_0}{T_{\text{H}}}P_{\text{en,total}}\approx\frac{20-(-5)}{273+20}\times100\approx8.5\ \text{[W]}$$

Thus, 100 W energy is leaking out and 8.5 W exergy is lost.

There are two ways of determine the over all heat coefficient *U*: the λ-method and *U*-method.

λ-method

In this method we consider each layer of the construction. The λ-value for a layer is the average value of the λ-values of the different areas in proportion to its area perpendicular to the direction of the heat flow, i.e. λ_a, for a mixed layer is

$$\lambda_a = \frac{\sum_i \lambda_i A_i}{\sum_i A_i} = \frac{\lambda_1 A_1 + \lambda_2 A_2 + \lambda_3 A_3 + \ldots}{A_1 + A_2 + A_3 + \ldots}$$

where λ_i is the λ-value of layer i [W/mK]
A_i is the layer i's area perpenduicular to the heat flow [m^2].

The overall heat coefficient U [W/m^{2}K] then becomes:

$$U_\lambda = \frac{\lambda_a}{d}$$

where d is the thickness [m].
λ-method gives a slightly to high U-value compared to experiments.

Q: Why?

U-method

We now consider each cross-section of the construction along the direction of the heat flow. The U-value for each section is calculated separately, and the total U-value is given by the sum of the the U-values for each cross-section in proportion to its area, i.e.

$$U = \frac{\sum_i U_i A_i}{\sum_i A_i} = \frac{U_1 A_1 + U_2 A_2 + U_3 A_3 + \ldots}{A_1 + A_2 + A_3 + \ldots}$$

where U_i is the U-value of section i [W/m^{2}K]
A_i is the area of section i perpendicular to the direction of the heat flow [m^2]
The U-method give a slightly lower U-value compared to experiments.

Q: Why?

Ex: Assume a wall, 20 m^2, that from outside consists of 100 mm wood ($\lambda = 0.14$ W/mK), 100 mm mineral wool ($\lambda = 0.036$ W/mK) between wood bars (10% of the area) and towards the inside a board, 40 mm ($\lambda = 0.05$ W/mK). How much heat leaks trough the construction per unit time if the outdoor temperature is –5˚C and the indoor temperature is +20˚C? a) According the λ-method b) According the *U*-method.

S: a) λ-method: We calculate λ_a for the mineral woll and the wood bars:

$$\lambda_a = \frac{\lambda_1 A_1 + \lambda_2 A_2}{A_1 + A_2} = \frac{0.036 \times 0.9 + 0.14 \times 0.1}{0.9 + 0.1} \approx 0.046 \ \ [\mathrm{W/m^2K}]$$

The *U*-value for the construction becomes

$$\frac{1}{U} = \sum_i \frac{d_i}{\lambda_i} \approx \frac{0.1}{0.14} + \frac{0.1}{0.046} + \frac{0.04}{0.05} \approx 3.69 \qquad U_{\mathrm{wall}} \approx 0.27 \ \ [\mathrm{W/m^2K}]$$

The energy power becomes $P_{\mathrm{en}} = UA(\theta_1 - \theta_2) \approx 0.27 \times 20 \times 25 = 135$ [W]

The exergy power becomes $P_{\mathrm{ex}} = \frac{\theta_1 - \theta_2}{T_1} P_{\mathrm{en}} \approx \frac{20 - (-5)}{273 + 20} \times 135 \approx 11.5$ [W]

b) *U*-method: the *U*-value where we have the wood bars becomes

$$\frac{1}{U_{\mathrm{wood}}} = \sum_i \frac{d_i}{\lambda_i} \approx \frac{0.1}{0.14} + \frac{0.1}{0.14} + \frac{0.04}{0.05} \approx 2.23 \qquad U_{\mathrm{wood}} = 0.45 \ \ [\mathrm{W/m^2K}]$$

The *U*-value where we have the mineral wool becomes

$$\frac{1}{U_{\mathrm{mineral\ wool}}} = \sum_i \frac{d_i}{\lambda_i} \approx \frac{0.1}{0.14} + \frac{0.1}{0.036} + \frac{0.04}{0.05} \approx 4.29 \qquad U_{\mathrm{mineral\ wool}} = 0.23 \ \ [\mathrm{W/m^2K}]$$

The *U*-value for the construction becomes

$$U = \frac{U_1 A_1 + U_2 A_2}{A_1 + A_2} \approx \frac{0.45 \times 0.1 + 0.23 \times 0.9}{0.1 + 0.9} \approx 0.25 \ \ [\mathrm{W/m^2K}]$$

The energy power becomes $P_{\mathrm{en}} = UA(\theta_1 - \theta_2) \approx 0.25 \times 20 \times 25 = 125$ [W]

The exergy power becomes $P_{\mathrm{ex}} = \frac{\theta_1 - \theta_2}{T_1} P_{\mathrm{en}} \approx \frac{20 - (-5)}{273 + 20} \times 125 \approx 10.7$ [W]

Thus, the λ-method gives that 135 W energy is leaking out and that 11.5 W exergy is lost, but the *U*-method gives 125 W energy and 10.7 W exergy respectively.

Ex: Determine the *U*-value, the positionläget where the temperature is 0˚C and where condensation may occure in the following wall, from outside to inside: 100 mm wood, 100 mm mineral wool and 40 mm board.

	Inside	Outside
Air speed [m/s]	0	4
Temperature [˚C]	20	–10
Relative humidity [%]	80	50

A: From tables we get

The U-value ≈ 0.23 W/m²K, the relative humidity excides 100% between the wood and the mineral wool, where condensation may occure.

The temperature 0˚C passes in the mineral wool. The temperature increases linearly in the wool. If we assume that 0˚C is x mm in the mineral wool from the outside, then we have:

$\frac{x}{100} = \frac{0 - (-4.6)}{12.9 - (-4.6)}$ $x \approx 26$ mm. (The problem can also be solved graphically.)

Heat exchangers

We will now look closer into heat exchangers, which are used to transfer heat between two different media by heat transfer. We find heat exchangers as heat radiators, hot water tanks, solar panels and car engine cooler. There are two main kinds of heat exchangers, parallel and counter flow. Let us assume a simple model one tube in an other, see Fig. below.

In a parallel heat exchanger the final temperature of the colder flow never can exceed the final temperature of the hot flow, i.e. $T_{H2} > T_{C2}$. However, in a counter flow heat exchanger we may have that $T_{H2} < T_{C2}$.

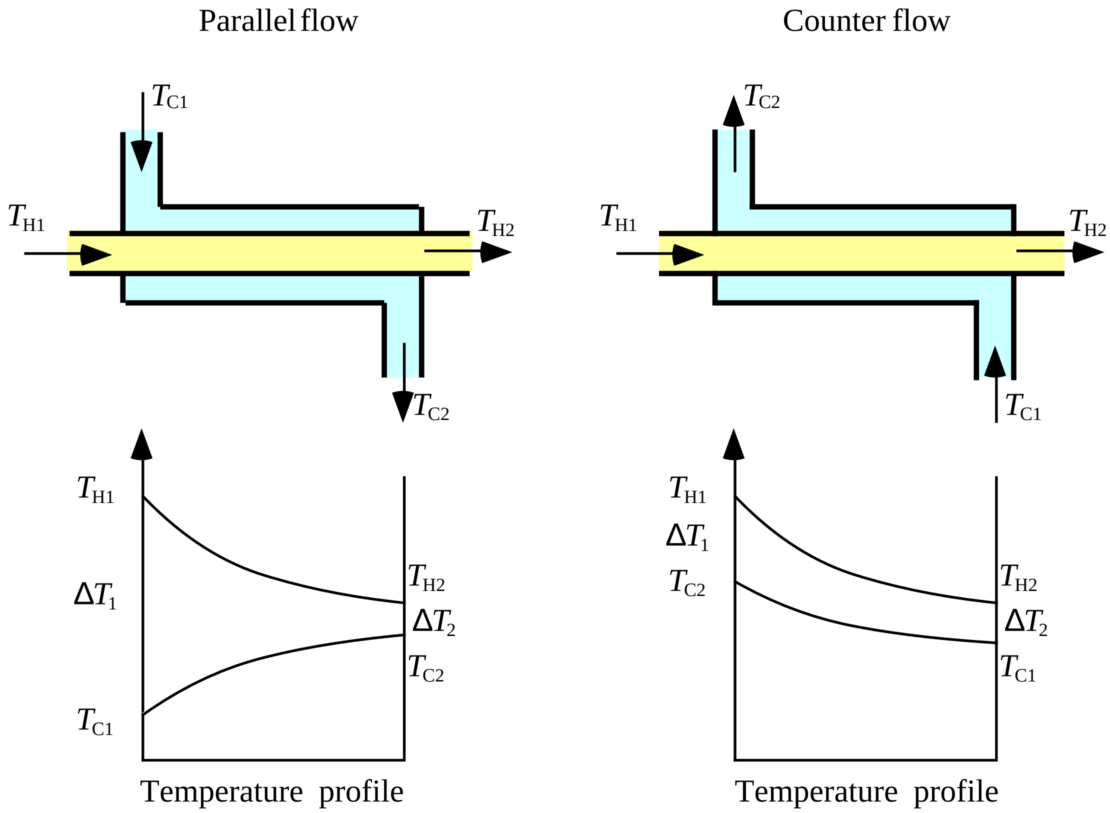
The energy power being transfered in a heat exchanger can be determined from

$$P_{en} = UA\Delta T_m \text{ [W]}$$

where U is the overall heat coefficient [W/m²K]
A is the area of heat transfer [m²]
ΔT_m is the average temperature differens, i.e.

$$\Delta T_m = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

where ΔT_1 and ΔT_2 is defined according to the Fig. below. (To use temperatures in degres Celsius is also allowed because the realion only contains temperature differences.)



Ex: In a counter flow heat exchanger 2 kg per second of lubrucation oil for a ship engine is cooled from 70˚C to 40˚C by water. The water is then heated from 20˚C to 40˚C. The transfer surface is 6 m². What is the *U*-value if the heat capacity of the oil *c* is 1.9 kJ/kgK? What are the exergy losses if the ambient temperature is θ_0 = 20˚C? *Use*: $P_{en} = \dot{m}c(\theta_1 - \theta_2)$

S: $\Delta\theta_1$ = 70–40 = 30˚C and $\Delta\theta_2$ = 40–20 = 20˚C

The average temperature difference is: $\Delta\theta_m = \dfrac{\Delta\theta_1 - \Delta\theta_2}{\ln\left(\dfrac{\Delta\theta_1}{\Delta\theta_2}\right)} = \dfrac{30-20}{\ln\left(\dfrac{30}{20}\right)} \approx 24.7\text{˚C}$

The transfered energy power becomes: $P_{en} = UA\Delta\theta_m$

For the oil we have: $P_{en} = \dot{m}c(\theta_{H1} - \theta_{H2})$, where $\dot{m}$ is the massflow [kg/s], i.e.

$P_{en,oil}$ = 2×1.9(70–40) = 114 [kW]

For the water we have: $P_{en,oil} = P_{en,water} = UA\Delta\theta_m$, i.e.

$114\times10^3 = U\times6\times24.7 \qquad U \approx 770$ [W/m²K]

For water we further hav: $P_{en} = \dot{m}_{water}c_{water}(\theta_{H1} - \theta_{H2})$, i.e.

$$\dot{m}_{water} = \frac{P_{en}}{c_{water}(\theta_{H1} - \theta_{H2})} \approx \frac{114}{4.18\times(40-20)} \approx 1.4 \ \ [\text{kg/s}]$$

For a heat content, which decreases its temperature with the heat revealed, we have, acourding to the section above on exergy of heat and cold, if the heat capacity is constant.

$$\frac{E}{Q} = 1 - \frac{T_0}{T - T_0}\ln\frac{T}{T_0}$$

which gives the following exergy flows for the hot oil:

$$P_{\mathrm{ex,H1}} = \dot{m}_{\mathrm{oil}} c_{\mathrm{oil}} \left(T_{\mathrm{H1}} - T_0 - T_0 \ln\frac{T_{\mathrm{H1}}}{T_0} \right)$$

$$P_{\mathrm{ex,H2}} = \dot{m}_{\mathrm{oil}} c_{\mathrm{oil}} \left(T_{\mathrm{H2}} - T_0 - T_0 \ln\frac{T_{\mathrm{H2}}}{T_0} \right)$$

The exergy power that the oil looses in the heat exchanger then becomes:

$$\Delta P_{\mathrm{ex,H}} = P_{\mathrm{ex,H1}} - P_{\mathrm{ex,H2}} = \dot{m}_{\mathrm{oil}} c_{\mathrm{oil}} \left(T_{H1} - T_{H2} - T_0 \ln\frac{T_{H1}}{T_{H2}} \right) =$$

$$= \dot{m}_{\mathrm{oil}} c_{\mathrm{oil}} \left(\theta_{\mathrm{H1}} - \theta_{\mathrm{H2}} - T_0 \ln\frac{T_{\mathrm{H1}}}{T_{\mathrm{H2}}} \right) \approx$$

$$\approx 2 \times 1.9 \times \left(70 - 40 - (273 + 20)\ln\frac{273 + 70}{273 + 40} \right) \approx 12.1 \ \ [\mathrm{kW}]$$

Similarly we have for the water on the cold side. The exergy power being received by the water in the heat exchanger becomes:

$$\Delta P_{\mathrm{ex,C}} = P_{\mathrm{ex,C2}} - P_{\mathrm{ex,C1}} = \dot{m}_{\mathrm{water}} c_{\mathrm{water}} \left(\theta_{C2} - \theta_{C1} - T_0 \ln\frac{T_{C2}}{T_{C1}} \right) \approx$$

$$\approx 1.4 \times 4.18 \times \left(40 - 20 - (273 + 20)\ln\frac{273 + 40}{273 + 20} \right) \approx 3.7 \ \ [\mathrm{kW}]$$

Thus, the exergy loss in the heat exchanger becomes:

$$\Delta P_{\mathrm{ex}} = \Delta P_{\mathrm{ex,H}} - \Delta P_{\mathrm{ex,C}} \approx 8.4 \ [\mathrm{kW}]$$

The exergy efficiency of the heat exchanger becomes:

$$\eta_{\mathrm{ex}} = \frac{\Delta P_{\mathrm{ex,C}}}{\Delta P_{\mathrm{ex,H}}} \approx \frac{3.7}{12.1} \approx 31\%$$

The energy efficiency is of course as we assumed 100%.

Ex: A condensor heats water by steam at temperature 100˚C. The water temperture increases from 30˚C to 75˚C and the condensor has a surface of 200 m^2 and the *U*-value is 3000 W/m^{2}K. How much hot water is produced per hour? What are the exergy losses and the exergy efficiency when θ_0 = 20˚C?

S: When steam is condensed the heat of evaporation is delivered to the colder flow. The temperature differences at the in and out let becomes: $\Delta\theta_1 = 100–30 = 70$˚C and $\Delta\theta_2 = 100–75 = 25$˚C. The average temperature then becomes:

$$\Delta\theta_\mathrm{m} = \frac{\Delta\theta_1 - \Delta\theta_2}{\ln\left(\frac{\Delta\theta_1}{\Delta\theta_2}\right)} = \frac{70-25}{\ln\left(\frac{70}{25}\right)} \approx 44˚\mathrm{C}$$

The energy power which is being transfered to the water becomes: $P_\mathrm{en} = UA\Delta\theta_\mathrm{m} \approx 3000\times200\times44 = 26.4$ [MW].

The water is being heated from 30 to 75˚C. Added energy power to the water is $P_\mathrm{en,w} = \dot{m}c(\theta_1 - \theta_2)$ where $c \approx 4.18$ [kJ/kgK], i.e. the specific heat capacity of water from table. Thus we have

$$P_\mathrm{en,w} = \dot{m}c(\theta_1 - \theta_2)$$

which gives

$$\dot{m} = \frac{P_\mathrm{en}}{c(\theta_1 - \theta_2)} \approx \frac{26.4\times10^6}{4.18\times10^3\times(75-30)} \approx 140 \ \ [\mathrm{kg/s}]$$

From above we get the following exergy power being releaved from the steam

$$\Delta P_\mathrm{ex,H} = \frac{T_\mathrm{H} - T_0}{T_\mathrm{H}} P_\mathrm{en} = \frac{\theta_\mathrm{H} - \theta_0}{T_\mathrm{H}} P_{en} \approx \frac{100-20}{273+100}\times 26.4 \approx 5.7 \ \ [\mathrm{MW}]$$

since the temperature is constant at the heat transfer.

In the same way as in the previous example we have for the water, which receives heat, that the exergy power received becomes:

$$\Delta P_\mathrm{ex,C} = P_\mathrm{ex,C2} - P_\mathrm{ex,C1} = \dot{m}_\mathrm{water} c_\mathrm{water} \left(\theta_\mathrm{C2} - \theta_\mathrm{C1} - T_0 \ln\frac{T_\mathrm{C2}}{T_\mathrm{C1}}\right) \approx$$

$$\approx 140\times 4.18 \times \left(75 - 30 - (273+20)\ln\frac{273+75}{273+30}\right) \approx 2.6 \ \ [\mathrm{MW}]$$

The exergy loss at the heat exchange then becomes:

$$\Delta P_\mathrm{ex} = \Delta P_\mathrm{ex,H} - \Delta P_\mathrm{ex,C} \approx 3.1 \ [\mathrm{MW}]$$

The exergy efficiency becomes:

$$\eta_\mathrm{ex} = \frac{\Delta P_\mathrm{ex,C}}{\Delta P_\mathrm{ex,H}} \approx \frac{2.6}{5.7} \approx 46\%$$

Please, remember that the energy efficiency usually is assumed to 100%!

COMBUSTION

First some common concepts:

nm^3 – *normal cubic meter*. The gas volume is usually measured in nm^3, which is the amount of gas at the temperature 0˚C, i.e. 273.15 K and the pressure 1 bar, i.e. 0.1 MPa. Normal cubic meter, nm^3.

mol – one *mol* is the number of molecules or atoms that are in 0.012 kg of the element carbon, C 12. Thus, one mol is a *number,* actually 6.023×10^{27} pieces. This means that 1 mol of a substance has the same weight in gram as is given by its atom weight, and 1 kmol corresponds to kg.

H_s – *Calorimetricheatvalue* or *high heat value* – is measured by the amount of enthalpy beeing released when a certain mass is combusted in a bomb calorimeter, principally a completely isolated container. The combustion products are cooled so that the moist in the fuel and the produced steam is condensated. This means that the the enthalpy of the generated steam is included in H_S.

H_i – *Effective heat value* or *low heat value* – is the enthalpy released at normal combustion, i.e. the generated steam is excluded. Thus $H_i \le H_s$.

The combustion reaction $2H_2 + O_2 \rightarrow 2H_2O$ means that if 1 kmol H_2, i.e. 2 kg, burns you get 1 kmol H_2O, i.e. 18 kg. In weight, you get 9 times as much water as hydrogen. Thus, if we know the amount of hydrogen and moist in the fuel we may approximatelly calculate H_i from H_s. The enthalpy of steam is about 2.5 MJ/kg at 293 K (≈20˚C).

For solid and liquid fules we have accordingly:

$$H_i = H_s - 2.5(9H + F) \text{ [MJ/kg]}$$

where H is the weight percentage of hydrogen
F is the weight percentage of moist (water)

For dry fire wood, independent of kind we have $H_i \approx 19.2$ MJ/kg and for damped:

$$H_i = 19.2 - 21.7F \text{ [MJ/kg]}$$

Ex: At fuel oil combustion, $H_i = 42$ MJ/kg the air surplus is 40%. Calculate the amount of exhaust gas and the combustion temperature?

S: $H_i = 42$ MJ/kg → theoretical amount of exhaust gas $g_o = 11.8$ nm^3/kg, from tables and theoretical amount of air (dry air) $l_o = 11.1$ nm^3/kg

The air surplus is 40%, i.e. $\frac{l - l_o}{l_o} = 0.4$ a*irfactor*: $m = \frac{l}{l_o} = 1.4$

Real amount of exhaust gas $g = g_o + l_o(m - l) = 11.8+11.1(1.4-1) = 16.24$ nm^3/kg

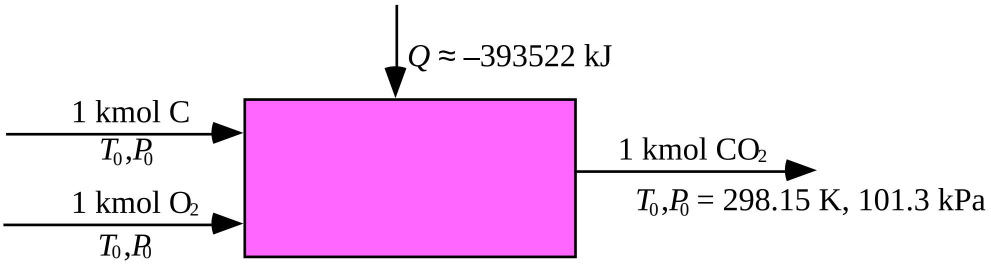
The heat content of the exhaust gas $h_{\max} = \frac{H_i}{g} = \frac{42}{16.24} \approx 2600 \text{kJ / nm}^3$

and from tables we get ≈1920 K.

Ex: A boiler combusts 2 kg oil/hr, H_i = 42 MJ/kg, with an air surplus of 20%. The temperature of the exhaust gases are 620 K. Estimate the heat power, losses and efficiency of the boiler.

Enthalpy, Gibbs' function and exergy of fuels

When we have chemical reactions it is necessary to define a common reference state. This is usually defined at 25˚C (298.15 K) and 101.3 kPa (T_0,P_0) and that gases are treated as ideal gases. Regard the following stationary combustion process, solid carbon is combusted with oxygen (ideal gas), where both are supplied at the reference state, T_0,P_0. The produced carbon dioxide (ideal gas) is leaving the combustion chamber at the reference state, T_0,P_0. If we could measure the heat transfer to the process (the reaction chamber) it would be –393,522 kJ/kmol CO_2 (the minus sign because heat is released, an exothermic reaction).



The chemical reaction is:

$$C + O_2 \rightarrow CO_2$$

The first law gives:

$$Q + H_R = H_P$$

where the indices *R* and *P* refer to reactants and products. First law is usually written

$$Q + \sum_R n_i \bar{h}_i = \sum_P n_e \bar{h}_e$$

where the sum involves all reactants and products respectively, *n* the number of mol and $\bar{h}$ indicates the enthalpy per mol of the substance. The enthalpy of formation is tabulated for most substances in standard states at T_0,P_0. Usually this is put to zero for the substance in its standard state, pure and normal form. For carbon, C this is pure carbon in solid state and for oxygen as O_2 in gas state, i.e. $(\bar{h}_f^0)_{C,s,graphite} = 0$ and $(\bar{h}_f^0)_{O_2,g} = 0$. Thus the enthalpy of formation for carbon dioxide becomes, $(\bar{h}_f^0)_{CO_2,g}$ = –393522 kJ/kmol. If we instead assume the enthalpy of formation of O_2 and of CO_2 as gases to zero, i.e. $(\bar{h}_f^0)_{O_2,g} = 0$ and $(\bar{h}_f^0)_{CO_2,g} = 0$, then we get the enthalpy of formation of C as solid $(\bar{h}_f^0)_{C,s,graphite}$, or shorter $\bar{h}_C$= 393522 kJ/kmol. This is usually called the heat content of the fuel at constant pressure (and temperature), in the same way the internal energy of formation U_C the heat content at constant volume (and temperature). Sometimes you also say the "high" and "low" heat content as above. The high value refers to the case when water in the exhaust gases is as liquid, and the low value when it is as gas. Note, that this sometimes gives confusing values of the energy efficiency.

The enthalpy at an arbitrary temperature is:

$$h_{T,P} = (h_f^0) + \Delta h_{T_0,P_0 \to T,P}$$

where $\Delta h_{T_0,P_0 \to T,P}$ represents the difference in enthalpy between a given state at T,P and at T_0,P_0.

If we apply the second law to this combustion process and change the heat extracted Q by the maximal extractable (reversible process) exergy E we get

$$E = E_R - E_P.$$

As above this can be written

$$E = \sum_R n_i \bar{e}_i - \sum_P n_e \bar{e}_e$$

where the sum includes all reactants and products respectively and $\bar{e}$ is the exergy per mol of the substance in relation to its environmental state, which is called exergy of formation and is tabulated for the most common substance, see App. 4.

When the reactants and the products are in pressure and temperature equilibrium with the environment we can write

$$E = \sum_R n_i \bar{g}_i - \sum_P n_e \bar{g}_e$$

where g is the Gibbs' function per mol.

Let us calculate the change in Gibbs' function when forming CO_2 from the reaction

$$C + O_2 \to CO_2$$

where C, O_2 and CO_2 are all separated and at T_0,P_0.

The change in Gibbs' function can be calculated accordingly

$$G_P - G_R = H_P - H_R - T_0(S_P - S_R)$$

i.e.

$$\sum_P n_e (\bar{g}_f^0)_e - \sum_R n_i (\bar{g}_f^0)_i = \sum_P n_e (\bar{h}_f^0)_e - \sum_R n_i (\bar{h}_f^0)_i - T_0 \left[\sum_P n_e (\bar{s}_{298}^0)_e - \sum_R n_i (\bar{s}_{298}^0)_i \right]$$

From tables, e.g. Table A.13, Van Wylen, G. J. and Sonntag, R. E., *Fundamentals of Classical Thermodynamics,* Wiley (1985) we get

$$(\bar{g}_f^0)_P - (\bar{g}_f^0)_R \approx (\bar{h}_f^0)_{CO_2} - 0 - 298.15[(\bar{s}_{298}^0)_{CO_2} - (\bar{s}_{298}^0)_C - (\bar{s}_{298}^0)_{O_2}]$$
$$\approx -393522 - 298.15(213.795 - 5.686 - 205.142) \approx -394407 \text{ kJ/kmol}.$$

If the Gibbs' function for the reactants are set to zero, i.e. $(\bar{g}_f^0)_R = 0$, the Gibbs' function for forming CO_2 becomes

$$(\bar{g}_f^0)_P = (\bar{g}_f^0)_{CO_2} \approx -394407 \text{ kJ/kmol}.$$

If we instead assume Gibbs' function of O_2 and CO_2 to zero, as we did above for the enthalpy, we have that $\bar{g}_{\mathrm{C}} = (\bar{g}_f^0)_{\mathrm{C}} \approx 394407$ kJ/kmol. Thus, we see that $h_{\mathrm{C}} < g_{\mathrm{C}}$, i.e. the enthalpy is less than the Gibbs' function for C, because the entropy S of the products are much larger than for the reactants – "heat" $Q = T_0 S$ is captured by the products.

Let us now calculate the exergy change for this reaction. The reactants and the products are now instead related to their individual environmental states. The difference between the enthalpy and Gibbs' function is that in Gibbs' function we also include the change of entropy of the reactants and the products in relation to their individual standard states. The difference between Gibbs' function and the exergy is that in exergy we also include the environment state, i.e. in what regard the reactants and products differ from environmental state, e.g. in concentration or chemically. From tables of exergy for different substances, App. 4 we have

$$(\bar{e}_f^0)_{\mathrm{C,s,graphite}} \approx 410260 \text{ kJ/kmol}$$
$$(\bar{e}_f^0)_{\mathrm{O_2,g}} \approx 3970 \text{ kJ/kmol}$$
$$(\bar{e}_f^0)_{\mathrm{CO_2,g}} \approx 19870 \text{ kJ/kmol,}$$

which gives the exergy change

$$\bar{e}_{\mathrm{C}} = \sum_R n_i \bar{e}_i - \sum_P n_e \bar{e}_e \approx 410260 + 3970 - 19870 = 394360.$$

Let us summarize, for C we have

Enthalpy	$\bar{h}_C \approx 393522$ kJ/kmol
Gibbs' function	$\bar{g}_C \approx 394407$ kJ/kmol
Exergy	$\bar{e}_C \approx 394360$ kJ/kmol

The relation between the exergy and enthalpy for C is

$$\frac{\bar{e}_{\mathrm{C}}}{\bar{h}_{\mathrm{C}}} \approx \frac{394360}{393522} \approx 1.002 \text{ or } 100.2\%$$

Q: Why is enthalpy less than exergy?

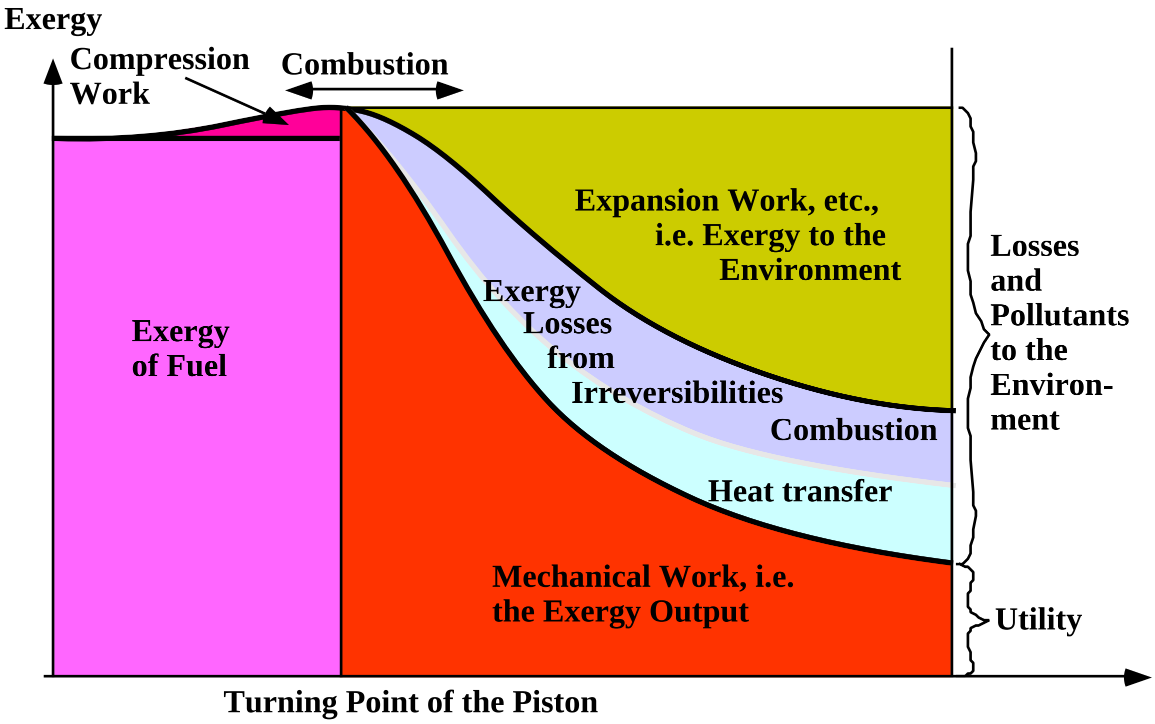
We have seen that from exergy tables of different substances we may calculate the exergy change of any chemical reaction.

In same way as for enthalpy we may also calculate exergy at any temperature

$$\bar{e}_{T,P} = (\bar{e}_f^0)_{T_0,P_0} + \Delta\bar{e}_{T_0,P_0 \to T,P}$$

the term $\Delta\bar{e}_{T_0,P_0 \to T,P}$ represents the difference in exergy between a given state at T,P and the exergy at T_0,P_0. This exergy sometimes is called the thermal exergy to differ from the chemical exergy.

Finally, we will just see what happens with the exergy in a real process, e.g. an combustion engine, se the figure below.



As we see most of the exergy is used to get the exhaust gases into the environment, i.e. a pressure-volume work, $P_0\Delta V$, performed on the surrounding air.

Q: Reflect on what this means for a car with a combustion engine.

Example: 1000 ton of CO_2 or 1000 ton of cooling water

Let us compare an emission of 1000 ton of CO_2 at ambient pressure and temperature with 1000 ton of cooling water. From exergy tables we have for the different chemical compounds of C and H:

Substance	State	Mol mass m [kg/kmol]	Enthalpy of formation $(\bar{h}_f^0)$ [kJ/mol]	Exergy $(\bar{e}_f^0)$ [kJ/mol]
C	s, graphite	12.01115	393.509	410.26
C	s, diamond	12.01115	395.406	413.16
CCl_4	l	153.823	578.95	473.1
CN	g, cyano	26.01785	858.00	845.0
C_2N_2	g, cyanogen	52.0357	1096.14	1118.9
CO	g	28.0105	282.984	275.10
CO_2	g	44.0095	0	19.87
…				
H_2O	g	18.01534	0	9.5
H_2O	l	18.01534	–44.012	0.9
H_3PO_4	s	98.0013	–76.26	104.0
H_2S	g	34.080	946.61	812.0
H_2SO_4	l	98.077	153.25	163.4
…				

Thus we have for 1000 ton of CO_2

$$E_{\mathrm{CO}_2} = \frac{19.87 \times 1000 \times 1000}{44.0095}\left[\frac{\mathrm{kJ} \times \mathrm{kg}}{\mathrm{mol} \times \dfrac{\mathrm{kg}}{\mathrm{kmol}}}\right] \approx 4.5 \times 10^5 [\mathrm{MJ}] = 0.45 [\mathrm{TJ}]$$

For water the chemical exergy becomes:

$$E_{\mathrm{H_2O},chemical} = \frac{0.9 \times 1000 \times 1000}{18.01534} \approx 5 \times 10^4 [\mathrm{MJ}] = 0.05 [\mathrm{TJ}]$$

The thermal exergy becomes:

$$E_{thermal} = \int_{T_0}^{T} C(T')\left(1 - \frac{T_0}{T'}\right) dT' \qquad (4)$$

If the heat capacity C is not depending on temperature, the exergy becomes

$$E_{thermal} = C\left(T - T_0 - T_0 \ln \frac{T}{T_0}\right) \qquad (5)$$

Assume $C = 4.2$ kJ/kg and T_o=298.15K, then $E_{thermal}$=0.4 TJ correspond to a temperature increase for 1000 ton of water of about 400K, i.e. some of the water will be steam. The exergy of the water at boiling temperature, i.e. at 373.15 K is

$$E_{thermal} = 4.2 \times 10^3 \times 1000 \times 10^3 \left(373.15 - 298.15 - 298.15 \ln \frac{373.15}{298.15}\right) \approx 3.4 \times 10^{10} [\mathrm{J}]$$

(5)

Thus 0.4–0.034=0.366 TJ = 366 GJ is left for steam production at ambient pressure. The enthalpy of steam is about 2300 kJ/kg so the exergy of steam becomes

$$e_{steam} = h_{steam}\left(1 - \frac{T_0}{T}\right) \approx 2300\left(1 - \frac{298.15}{373.15}\right) \approx 462 \left[\frac{\mathrm{kJ}}{\mathrm{kg}}\right]$$

The mass converted to steam them becomes

$$m_{steam} \approx \frac{E_{steam}}{462} \approx \frac{366}{462}\left[\frac{\mathrm{GJ}}{\mathrm{kJ/kg}}\right] \approx 0.792 \times 10^6 [\mathrm{kg}] = 792 [\mathrm{ton}]$$

Thus, from an exergy point of view, an emission of 1000 ton of CO_2 is equivalent to 792 ton of steam and 208 ton of water at 373.15 K, if the environment is at ambient pressure and temperature, i.e. 101.3 kPa and 298.15 K.

APPENDIX

Appendix 1 Internal energy and entropy

To be written.

Appendix 2 Exergy

A derivation of the exergy concept can be made from simple thermodynamic relations of state changes which are related to the concept of work.

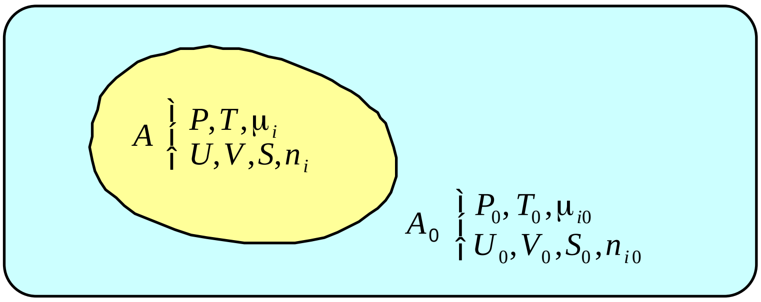


Fig. 1 The system A in an environment A_0

Assume we have a system A in a very large homogenous environment (reservoir) A_0 which is defined by the intensive parameters P_0, T_0 och $\tilde{\mu}_{i0}$ (pressure, temperature and generalized chemical potential[16]). The intensive parameters of A are P, T and $\tilde{\mu}_i$. The corresponding extensive parameters of A and A_0 are U, V, S and n_i (internal energy, volume, entropy and number of mol of different substances) respectively U_0, V_0, S_0 och n_{i0} för A_0, Fig. l. Also assume that A and A_0 each are in internal equilibrium.

Assume that all extensive parameters of A are much smaller than those of A_0 and futher that the total system $A \quad A_0$ is isolated from the surrounding except for the extraction of work W which is extracted from the total system, then we have the following relations

$$\begin{cases} U << U_0 \\ V << V_0 \\ n_i << n_{i0} \end{cases} \tag{1}$$

$$\begin{cases} U + U_0 + W = \text{constant} \\ V + V_0 = \text{constant} \\ n_i + n_{i0} = \text{constant} \end{cases} \tag{2}$$

$$\begin{cases} dU + dU_0 + dW = 0 \\ dV + dV_0 = 0 \\ dn_i + dn_{i0} = 0 \end{cases} \tag{3}$$

Interaction between A and A_0 can take place in a controlled way through the interface of A. Since A is small, Eq. 1, this does not change the intensive parameters of A_0,

$$\begin{cases} dT_0 = 0 \\ dP_0 = 0 \\ d\tilde{\mu}_{i0} = 0 \end{cases} \tag{4}$$

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[16] The generelized chemical potential includes all potentials realted to the substance, e.g. chemical, electrical, magnetical, mechanical, and gravitational potentials.

The entropy differential of the environment A_0 is

$$dS_0 = \frac{1}{T_0}(dU_0 + P_0 dV_0 - \sum_i \tilde{\mu}_{i0} dn_{i0}) \tag{5}$$

which can be written by using Eq. 3

$$dS_0 = -\frac{1}{T_0}\left(dU + P_0 dV - \sum_i \tilde{\mu}_{i0} dn_i\right) - \frac{dW}{T_0} \tag{6}$$

The total entropy differential of the system *and* the environment is

$$dS^{\text{tot}} = dS + dS_0 = -\frac{1}{T_0}\left(dU + P_0 dV - T_0 dS - \sum_i \tilde{\mu}_{i0} dn_i\right) - \frac{dW}{T_0} \tag{7}$$

This may be written as

$$dS^{\text{tot}} = -\frac{1}{T_0}(dE + dW) \tag{8}$$

where we have introduced **exergy** E,

$$E = U + P_0 V - T_0 S - \sum_i \tilde{\mu}_{i0} n_i \tag{9}$$

If we use the Gibbs relation

$$U = TS - PV + \sum_i \tilde{\mu}_i n_i \tag{10}$$

in (9) we get

$$E = S(T - T_0) - V(P - P_0) + \sum_i n_i(\tilde{\mu}_i - \tilde{\mu}_{i0}) \tag{11}$$

which shows that E vanishes at equilibrium, i.e.

$$\left.\begin{aligned} P &= P_0 \\ T &= T_0 \\ \tilde{\mu}_i &= \tilde{\mu}_{i0} \end{aligned}\right\} \Leftrightarrow E = 0 \tag{12}$$

Assume now that A evolves towards equilibrium with its environment A_0 and the work ΔW is performed during this process. The exergy is then changed by -E from E to 0 and the total entropy S^{tot} is changed by ΔS^{tot}. By integrating (8) we then get

$$\Delta S^{\text{tot}} = -\frac{1}{T_0}\left(-E + \Delta W\right) \tag{13}$$

and thus

$$\Delta W = E - T_0 \Delta S^{\text{tot}} \tag{14}$$

Since according to the second law

$$\Delta S^{\text{tot}} \geq 0 \tag{15}$$

we get

$$\Delta W \leq E \tag{16}$$

where equality only holds when $\Delta S^{\text{tot}} = 0$, i.e. reversible processes.

Thus, the exergy E is the maximum work that can be extracted from a system through interaction with its environment.

We may subtract from (A.7) the corresponding equation at equilibrium, i.e.

$$E_{\text{eq}} = U_{\text{eq}} + P_0 V_{\text{eq}} - T_0 S_{\text{eq}} - \sum_i \tilde{\mu}_{i0} n_{i,\text{eq}} \tag{17}$$

Since E vanishes at equilibrium, i.e. $E_{\text{eq}} = 0$ we then find

$$E = U - U_{\text{eq}} + P_0 \left(V - V_{\text{eq}} \right) - T_0 \left(S - S_{\text{eq}} \right) - \sum_i \tilde{\mu}_{i0} \left(n_i - n_{i,\text{eq}} \right) \tag{18}$$

which is a useful relation for practical determinations of exergy.

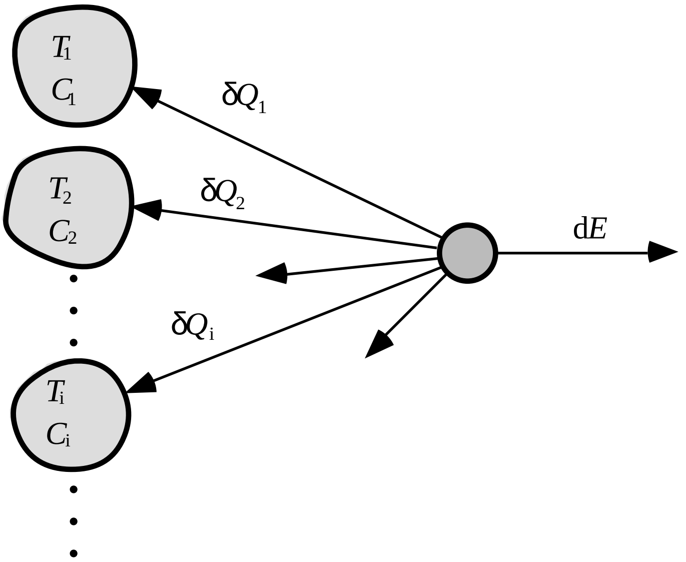
In special cases exergy differences are related to differences of other, better known, thermodynamic potentials, e.g. Gibbs' function, Helmholtz's function and enthalpy as described in the Table below. By differentiating the definition of exergy, Eq. 9, we can easily find the following realtions to these potentials

Table
Relations between differences in exergy and in other thermodynamic potentials.

Case	$\Delta E = \Delta X$	Definition of X	Usually named
$\Delta n_i = 0$	$\Delta E = \Delta G_0$	$G_0 = U + P_0 \text{V} - T_0 S$	
$\Delta n_i = 0$, $\Delta V = 0$	$\Delta E = \Delta F_0$	$F_0 = U - T_0 S$	
$\Delta n_i = 0$, $\Delta S = 0$	$\Delta E = \Delta H_0$	$H_0 = U + P_0 \text{V}$	
$\Delta n_i = 0$, $P = P_0$, $T = T_0$	$\Delta E = \Delta G$	$G = U + PV - TS$	Gibbs' function
$\Delta n_i = 0$, $\Delta V = 0$, $T = T_0$	$\Delta E = \Delta F$	$F = U - TS$	Helmholz's function
$\Delta n_i = 0$, $\Delta S = 0$, $P = P_0$	$\Delta E = \Delta H$	$H = U + PV$	Enthalpy

Appendix 3 Heat exchange between many systems

Let us derive an expression for the exergy when heat is exchanged between many systems.



We have:

Energy conservation: $$\sum_i \delta Q_i + dE = 0 \tag{1}$$

Entropy conservation: $$\sum_i dS_i = 0 \qquad \text{(reversible process)} \tag{2}$$

We have for the entropy: $$dS_i = \frac{\delta Q_i}{T_i} \tag{3}$$

and for the heat: $$\delta Q_i = C_i(T_i)dT_i \tag{4}$$

Eqs. l and 4: $$dE = \sum_i C_i(T_i)dT_i \tag{5}$$

Eqs. 2, 3, and 4: $$\sum_i \frac{C_i(T_i)dT_i}{T_i} = 0 \tag{6}$$

Integration gives: $$E = -\sum_i \int_{T_i^0}^{T_i^{\mathrm{f}}} C_i(T_i)dT_i \tag{7}$$

$$\sum_i \int_{T_i^0}^{T_i^{\mathrm{f}}} \frac{C_i(T_i)dT_i}{T_i} = 0 \tag{8}$$

where T_i^0 is the initial temperatures and T_i^{f} is the final temperature.

Thus, we have two equations which completely describes the available exergy of the system. If $T_i^{\mathrm{f}} = T^f$ for all *i* then Eq. 8 gives T^f which in Eq. 7 gives the exergy.

Assume that the heat capacities are constants and that the final temperature is the same for all subsystems, i.e. $C_i(T_i) = C_i$ and $T_i^{\mathrm{f}} = T^f$:

$$E = \sum_i C_i T_i^0 - T^{\mathrm{f}} \sum_i C_i \tag{9}$$

$$T^{\mathrm{f}} = \left(\prod_i (T_i^0)^{C_i} \right)^{\frac{1}{\sum_i C_i}} \tag{10}$$

Equation 9 may be written:

$$E = \sum_i C_i (T^0 - T^{\mathrm{f}}) \tag{11}$$

where

$$T^0 = \frac{\sum_i C_i T_i^0}{\sum_i C_i} \tag{12}$$

T^0 is a weighted arithmetic average value and T^{f} is a weighted geometric average value.

We can also find that the work obtainable from the system becomes:

$$\Delta S^{\mathrm{tot}} = \sum_i C_i (\ln T^0 - \ln T^{\mathrm{f}}) \tag{13}$$

And the exergy becomes:

$$E = -T^* \Delta S^{\mathrm{tot}} \tag{14}$$

where

$$T^* = -\frac{T^0 - T^{\mathrm{f}}}{\ln T^0 - \ln T^{\mathrm{f}}} \tag{15}$$

Thus, we are able to calculate the exergy of a system of arbitrary numbers of bodies with arbitrary heat capacity and temperature and with a reference environment. Let us look at some simple special cases, which we already are familiar with.

Ex: Assume only two systems, one limited and the other unlimited (ambient). We get:

$$E = C T_0 \left(\frac{T}{T_0} - 1 - \ln \frac{T}{T_0} \right) = C \left(T - T_0 - T_0 \ln \frac{T}{T_0} \right)$$

where T and C are temperature and heat capacity of the limited system and T_0 is ambient temperature. This we recognize from before.

Ex: Assume all subsystems are identical, but with different temperatures, i.e.:

$C_{\mathrm{i}} = C$ for all i then we get:

$$E = nC\left\{ \sum_i \frac{T_i^0}{n} - \left(\prod_i T_i^0 \right)^{\frac{1}{n}} \right\}$$

where n is number of subsystems. For $n = 2$ we get:

$$E = C\left(\sqrt{T_1^0} - \sqrt{T_2^0} \right)^2$$

Appendix 4 Reference states[†]

Table A.4.1 Enthalpy and exergy of formation for unorganic substances at reference state (T_0 = 298.15 K, P_0 = 101.325 kPa)

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
Ag	s	107.870	47.48	70.2
Ag_2CO_3	s	275.749	–17.38	115.0
AgCl	s	143.323	0	22.2
AgF	s	126.868	47.60	118.5
$AgNO_3$	s	169.875	–76.91	43. I
Ag_2O	s	231.739	63.91	57.6
Ag_2O_2	s	247.739	70.69	172.1
Ag_2S	s, α	247.804	787.79	709.5
Ag_2SO_4	s	311.802	104.50	139.6
Al	s	26.9815	930.69	888.4
Al_4C_3	s	143.959	4694.51	4588.2
$AlCl_3$	s	133.3405	467.18	444.9
Al_2O_3	s, α, corundum	101.9612	185.69	200.4
$Al_2O_3\cdot H_2O$	s, boermite	119.9765	128.35	195.3
$Al_2O_3\cdot 3H_2O$	s, gibbsite	156.0072	24.13	209.5
Al_2S_3	s	150.155	3313.81	2890.7
$Al_2(SO_4)_3$	s	342.148	596.80	529.7
Al_2SiO_5	s, andalusite	162.046	28.03	43.9
Al_2SiO_5	s, kyanite	162.046	25.94	45.1
Al_2SiO_5	s, sillimanite	162.046	0	15.4
$Al_2Si_2O_5(OH)_4$	s, kaolinite	258.1615	68.25	197.8
$3AI_2O_3\cdot 2SiO_2$	s, mullite	426.0536	630.11	618.8
Ar	g	39.948	0	11.69
As	s	74.9216	462.44	494.6
As_2O_5	s	229.8402	0	216.9
Au	s	196.967	0	15.4
AuCl	s	232.42	45.49	62.2
$AuCl_3$	s	303.326	123.09	155.5
AuF_3	s	253.962	246.46	437.3
Au_2O_3	s	441.932	–80.81	114.7
B	s	10.811	636.39	628.5
B_2O_3	s	69.6202	0	69.4
Ba	s, II	137.34	747.77	747.7
$BaCO_3$	s, II	197.35	–75.18	26.3
$BaCl_2$	s	208.25	48.69	61.3
BaF_2	s	175.34	–53.24	57.2
BaO	s	153.34	194.15	224.6
BaO_2	s	169.34	113.38	169.3
$Ba(OH)_2$	s	171.36	45.93	132.9
BaS	s	169.40	1012.88	901.9

[†] Szargut, J., Morris, D. R., and Steward, F. R., *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Springer (1988)

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
$BaSO_4$	s, barite	233.40	0	3.4
Bi	s	208.980	286.94	274.5
Bi_2O_3	s	465.958	0	61.4
Bi_2S_3	s	514.152	2607.05	2237.3
Br_2	l	159.812	—	101.2
C	s, graphite	12.01115	393.509	410.26
C	s, diamond	12.01115	395.406	413.16
CCl_4	l	153.823	578.95	473.1
CN	g, cyano	26.01785	858.00	845.0
C_2N_2	g, cyanogen	52.0357	1096.14	1118.9
CO	g	28.0105	282.984	275.10
CO_2	g	44.0095	0	19.87
CS_2	l	76.139	1934.09	1694.7
Ca	s, II	40.08	813.57	712.4
CaC_2	s	64.10	1541.18	1468.3
$CaCO_3$	s, aragonite	100.09	0	1.0
$CaCO_3 \cdot MgCO_3$	s, dolomite	184.411	0	15.1
$CaCl_2$	s	110.99	178.21	87.9
CaF_2	s	78.077	0	11.4
$CaFe_2O_4$	s	215.77	161.07	104.0
$Ca_2Fe_2O_4$	s	271.85	321.00	194.7
$Ca_2Mg_5Si_8O_{22}(OH)_2$	s, tremolite	812.41	425.49	81.6
$Ca(NO_3)_2$	s	164.0898	–124.90	–18.1
CaO	s	56.08	178.44	110.2
$CaO \cdot Al_2O_3$	s	158.04	351.66	275.4
$CaO \cdot 2Al_2O_3$	s	260.00	541.71	460.4
$3CaO \cdot Al_2O_3$	s	270.20	716.72	500.6
$12CaO \cdot 7Al_2O_3$	s	1386.68	3415.71	2526.8
$CaO \cdot Al_2O_3 \cdot 2SiO_2$	s, anortite	222.038	273.92	218.3
$Ca(OH)_2$	s	74.09	69.04	53.7
$Ca_3(PO_4)_2$	s, α	310.18	0	19.4
CaS	s	72.14	1056.57	844.6
$CaSO_4$	s, anhydrite	136.14	104.88	8.2
$CaSO_4 \cdot 1/2H_2O$	s, α	145.15	83.16	12.1
$CaSO_4 \cdot 2H_2O$	s, gypsum	172.17	0	8.6
$CaSiO_3$	s, volastonite	116.16	90.24	23.6
Ca_2SiO_4	s, β	172.24	232.28	95.7
Ca_3SiO_5	s	282.32	424.94	219.8
Cd	s, ν	112.40	357.10	293.8
Cd	s, α	112.40	356.51	293.2
CdCO3	s	172.41	0	40.6
$CdCl_2$	s	183.31	126.04	73.4
CdO	s	128.40	98.95	67.3
$Cd(OH)_2$	s	146.41	38.26	59.5
CdS	s	144.46	920.60	746.9
$CdSO_4$	s	208.46	149.24	88.6
$CdSO_4 \cdot H_2O$	s	226.48	84.79	80.6
Cl_2	g	70.906	160.44	123.6

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
Cl	g	35.453	201.90	87.1
Co	s, α, hexagonal	58.9332	297.06	265.0
$CoCO_3$	s	118.9426	–22.38	45.8
$CoCl_2$	s	129.839	144.96	118.8
CoO	s	74.9326	59.12	52.8
Co_3O_4	s	240.7872	0	38.2
$Co(OH)_2$	s, pink	92.9479	–0.86	50.7
CoS	s	90.997	942.27	792.2
$CoSO_4$	s	154.995	134.22	99.8
Cr	s	51.996	569.86	544.3
Cr_3C_2	s	180.010	2415.85	2372.0
Cr_7Cl	s	400.005	5007.63	4874.2
$CrCl_2$	s	122.902	361.91	311.9
$CrCl_3$	s	158.355	281.05	261.6
Cr_2O_3	s	151.990	0	36.5
Cs	s	132.905	362.68	404.4
CsCl	s	168.358	0	51.5
$CsNO_3$	s	194.910	–80.22	18.2
Cs_2O	s	281.809	407.75	521.8
Cs_2SO_4	s	361.872	30.53	127.0
Cu	s	63.54	201.59	134.2
$CuC0_3$	s	123.55	0	31.5
CuCl	s	98.99	144.57	76.2
$CuCl_2$	s	134.45	141.95	82.1
$CuFe_2O_4$	s	239.23	60.62	36.1
CuO	s	79.54	44.27	6.5
Cu_2O	s	143.08	234.56	124.4
$Cu(OH)_2$	s	97.55	–6.37	15.3
CuS	s	95.60	873.87	690.3
Cu_2S	s	159.14	1049.10	791.8
$CuS0_4$	s	159.60	155.65	89.8
Cu_2SO_4	s	223.14	377.15	253.6
D_2	g	4.02946	249.199	263.8
D_2O	g	20.02886	0	31.2
D_2O	l	20.02886	–45.401	22.3
F_2	g	37.9968	406.07	466.3
Fe	s, α	55.847	412.12	376.4
Fe_3C	α, cementite	179.552	1654.97	1560.2
$FeCO_3$	s, siderite	115.856	65.06	125.9
$FeCl_2$	s	126.753	230.77	197.6
$FeCl_3$	s	162.206	253.29	230.2
$FeCr_2O_4$	s	223.837	107.10	129.1
$Fe_{0.947}O$	s, wustite	68.8865	124.01	113.3
FeO	s	71.846	140.16	127.0
Fe_2O_3	s, hematite	159.692	0	16.5
Fe_3O_4	s, magnetite	231.539	117.98	121.6
$Fe(OH)_3$	s	106.869	–48.14	39.6
FeS	s, α	87.911	1037.54	885.6

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
FeS_2	s, pyrite	119.975	1684.72	1428.7
$FeSO_4$	s	151.909	209.11	173.0
FeSi	s	83.933	1249.42	1157.3
$FeSiO_3$	s	131.931	118.07	161.7
Fe_2SiO_4	s, fayalite	203.778	255.30	236.2
$FeTiO_3$	s	151.75	118.90	131.4
H_2	g	2.01594	241.818	236.1
H	g	1.00797	338.874	331.3
HCl	g	36.461	108.82	84.5
HDO	g	19.0213	0.21	18.8
HDO	l	19.0213	–44.38	10.0
HF	g	20.0064	52.82	80.0
HNO_3	l	63.0129	–53.19	43.5
H_2O	g	18.01534	0	9.5
H_2O	l	18.01534	–44.012	0.9
H_3PO_4	s	98.0013	–76.26	104.0
H_2S	g	34.080	946.61	812.0
H_2SO_4	l	98.077	153.25	163.4
He	g	4.0026	0	30.37
Hg	l	200.59	63.82	115.9
Hg_2CO_3	s	461.189	–12.39	179.8
$HgCl_2$	s	271.50	0	60 8
Hg_2Cl_2	s	472.09	22.86	144.5
HgO	s, red, orthorhombic	216.59	–27.01	57.3
HgS	s, red	232.65	731.08	674.8
$HgSO_4$	s	296.65	81.73	146.0
Hg_2SO_4	s	497.24	110.36	223.4
I_2	s	253.8088	—	174.7
K	s	39.102	356.63	366.6
$KAlSi_3O_4$	s, adularia	278.337	66.26	99.9
K_2CO_3	s	138.213	–43.58	85.1
KCl	s	75.555	0	19.6
$KClO_4$	s	138.553	6.67	136.0
KF	s	58.100	–7.77	62.2
KNO_3	s	101.1069	–135.90	–19.4
K_2O	s	94.203	350.04	413.1
KOH	s	56.109	52.72	107.6
K_2S	s	110.268	1024.40	943.0
K_2SO_3	s	158.266	300.47	302.6
K_2SO_4	s	174.266	4.62	35.0
K_2SiO_3	s	154.288	75.9	137.9
Kr	g	83.80	0	34.36
Li	s	6.939	328.10	393.0
Li_2CO_3	s	73.887	–166.33	70.1
LiCl	s	42.392	0	70.7
Li_2O	s	29.877	57.38	225.7
LiOH	s	23.946	–35.73	74.1
Li_2SO_4	s	109.940	–52.86	204.3

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
Mg	s	24.312	725.71	633.8
$MgAl_2O_4$	s, spinel	142.273	274.17	230.3
$MgCO_3$	s	84.321	23.43	37.9
$MgCl_2$	s	95.218	244.65	165.9
$MgFe_2O_4$	s	200.004	121.53	77.9
MgO	s	40.311	124.38	66.8
$Mg(OH)_2$	s	58.327	42.73	40.9
$Mg(NO_3)_2$	s	148.3218	–64.34	57.4
$Mg_3(PO_4)_2$	s	262.879	76.59	130.0
MgS	s	56.376	1105.11	901.6
$MgSO_4$	s	120.374	166.22	80.7
$MgSiO_3$	s	100.396	87.73	22.0
Mg_2SiO_4	s	140.708	188.35	74.9
$Mg_3Si_2O_5(OH)_4$	s, chrysolite	277.134	117.06	61.3
$Mg_3Si_4O_{10}(OH)_2$	s, talc	379.289	140.26	36.5
Mg_2TiO_4	s	160.52	231.48	134.3
Mn	s, α	54.9381	520.03	482.3
Mn_3C	s	176.82545	1958.20	1862.3
$MnCO_3$	s	114.9475	19.42	81.8
$MnCl_2$	s	125.844	199.18	165.4
$MnFe_2O_4$	s	230.630	118.36	121.4
MnO	s	70.9375	134.81	119.4
MnO_2	s	86.9369	0	21.1
Mn_2O_3	s	157.8744	81.09	89.4
Mn_3O_4	s	228.8119	172.26	171.6
$Mn(OH)_2$	s, amorphous	88.9528	66.47	107.3
MnS	s, green	87.002	1031.23	873.5
$MnSO_4$	s	151.000	180.20	142.4
$MnSiO_3$	s	131.022	110.08	102.3
Mo		95.94	745.09	730.3
Mo_2C		203.89	1838.88	1824.6
MoO_2	s	127.94	156.15	201.2
MoO_3	s	143.94	0	68.2
Mo_2S_3	s	288.07	3302.43	2891.2
MoS_2	s	160.068	1960.78	1723.1
N_2	g	28.0134	0	0.72
N_2, atmospheric	g	28.1541	0	0.69
NH_3	g	17.0305	316.62	337.9
NH_4CL	s	53.491	249.43	331.3
NH_4NO_3	s	80.04348	118.08	294.8
$(NH_4)_2SO_4$	s	132.138	511.84	660.6
NO	g	30.0061	90.25	88.9
NO_2	g	46.0055	33.18	55.6
N_2O	g	44.0128	82.05	106.9
N_2O_4	g	92.0110	9.163	106.5
N_2O_5	g	108.0104	11.30	125.7
Na	s	22.9898	330.90	336.6
$NaAlO_2$	s	81.9701	128.40	151.7

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
$NaAlSi_2O_6 \cdot H_2O$	s, analcime	220.055	35.41	104.2
$NaAlSi_3O_8$	s, low albite	262.2245	72.75	105.5
Na_2CO_3	s	105.9891	75.62	41.5
NaCl	s	58.443	0	14.3
$NaHCO_3$	s	84.0071	–101.94	21.6
NaI	s	149.8942		136.1
$NaNO_3$	s	84.9947	–135.62	–22.7
Na_2O	s	61.9790	243.82	296.2
NaOH	s	39.9972	23.79	74.9
Na_2S	s	78.044	1014.84	921.4
Na_2SO_3	s	126.042	297.63	287.5
Na_2SO_4	s	142.041	0	21.4
Na_2SiO_3	s	122.064	11.31	66.1
$Na_2Si_2O_5$	s	182.149	13.28	67.6
Na_4SiO_4	s	184.043	151.45	256.6
Ne	g	20.183	0	27.19
Ni	s	58.71	239.74	232.7
Ni_3C	s	188.14	1180.09	1142.9
$NiCO_3$	s	11 8.72	–49.93	36.4
$NiCl_2$	s	129.62	94.85	97.2
NiO	s	74.71	0	23.0
$Ni(OH)_2$	s	92.72	–48.13	25.5
NiS	s	90.77	883.15	762.8
Ni_3S_2	s	240.26	1967.14	1720.2
$NiSO_4$	s	154.77	92.25	90.4
$NiSO_4 \cdot 6H_20$	s, α, tetragonal, green	262.86	–266.75	53.6
O_2	g	31.9988	0	3.97
O	g	15.9994	249.17	233.7
O_3	g	47.9982	142.67	169.1
P	s, α, white	30.9738	840.06	875.8
P	s, red, triclinic	30.9738	822.49	863.6
P_4O_{10}	s, hexagonal	283.8892	376.21	825.3
Pb	s	207.19	305.64	232.8
$PbCO_3$	s	267.20	0	23.5
$PbCl_2$	s	278.10	106.67	42.3
PbO	s, yellow	223.19	88.32	46.9
PbO	s, red	223.19	86.65	45.9
PbO_2	s	239.19	28.24	19.4
Pb_3O_4	s	685.57	198.53	105.2
$Pb(OH)_2$	s	241.20	32.48	20.6
PbS	s	239.25	930.64	743.7
$PbSO_4$	s	303.25	111.12	37.2
$PbSiO_3$	s	283.27	70.88	31.2
Pb_2SiO_4	s	506.46	159.07	75.5
Rb	s	85.47	350.38	388.6
Rb_2CO_3	s	230.95	–33.90	152.4
RbCl	s	120.92	0	48.6
Rb_2O	s	186.94	370.60	491.3

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
S	s, rhombic	32.064	725.42	609.6
SO_2	g	64.0628	428.59	313.4
SO_3	g	80.0622	329.70	249.1
Sb	s, III	121.75	485.97	435.8
Sb_2O_3	s	291.50	263.07	251.2
Sb_2O_4	s	307.50	62.63	83.7
Sb_2O_5	s	323.60	0	52.3
Se	s, black	78.96	–	346.5
Si	s	28.086	910.94	854.6
SiC	s, α, hexagonal	40.097	1241.69	1204.6
$SiCl_4$	l	169.898	544.81	481.9
SiO_2	s, α, quartz	60.085	0	1.9
SiO_2	s, α, cristobalite	60.085	1.46	2.8
SiO_2	s, amorphous	60.085	7.45	7.9
SiS_2	s	92.214	2149.23	1866.3
Sn	s, I, white	118.69	580.74	544.8
Sn	s, II, gray	118.69	578.65	544.9
$SnCl_2$	s	189.60	416.08	386.4
SnO	s	134.69	294.97	289.9
SnO_2	s	150.69	0	29.1
SnS	s	150.75	1205.74	1056.1
SnS_2	s	182.82	1863.8	1604.6
Sr	s	87.62	826.34	730.2
$SrCO_3$	s	143.63	0	6.2
$SrCl_2$	s	158.53	157.93	72.6
SrO	s	103.62	234.30	170.2
SrO_2	s	119.62	191.96	140.4
SrS	s	119.68	1098.99	891.8
$SrSO_4$	s	183.68	98.66	7.1
Ti	s	47.90	944.75	906.9
TiC	s	59.91	1154.16	1136.7
TiO	s	63.90	425.14	418.5
TiO_2	s, rutile	79.90	0	21.4
Ti_2O_3	s	143.80	368.66	385.5
Ti_3Os	s	223.70	375.10	413.2
TiS_2	s	112.03	2060.45	1875.9
U	s	238.03	1230.10	1190.7
UCl_3	s	344.39	577.35	550.1
UCl_4	s	379.84	499.39	475.2
UCl_5	s	415.30	536.93	513.6
UO_2	s	270.03	145.19	162.9
UO_3	s	286.03	0	43.9
U_3O_8	s	842.085	115.49	218.5
V	s	50.942	775.30	721.1
VC	s	62.953	1067.96	1032.6
VO	s	66.941	343.51	318.9
VO_2	s	82.940	57.74	61.9
V_2O_3	s	149.882	322.60	299.7

Substance	State	Molar mass [kg/kmol]	Enthalpy [kJ/mol]	Exergy [kJ/mol]
V_2O_5	s	181.881	0	32.5
W	s	183.85	842.87	827.5
WC	s	195.86	1195.84	1199.5
WO_2	s	215.85	253.18	297.5
WO_3	s	231.85	0	69.3
WS_2	s	249.98	2084.51	1796.6
Xe	g	131.30	0	40.33
Zn	s	65.37	419.27	339.2
$ZnCO_3$	s	125.38	0	23.9
$ZnCl_2$	s	136.28	583.93	93.4
$ZnFe_2O_4$	s	241.06	74.08	36.4
ZnO	s	81.37	70.99	22.9
$Zn(OH)_2$	s, β	99.38	19.18	25.7
ZnS	s, sphalerite	97.43	938.71	747.6
$ZnSO_4$	s	161.43	161.87	82.3
Zn_2SiO_4	s	222.82	112.74	17.8

Table A.4.2 Entalpy and exergy of formation for organic substances at reference state (T_0 = 298.15 K, P_0 = 101.325 kPa)

Chemical formula	Namne	State	Molar mass	Enthalpy	Exergy
				of formation	
			kg/kmol	[kJ/mol]	[kJ/mol]
CH_2	Methylene	g	14.02709	1032.9	1030.5
CH_3	Methyl	g	15.03506	889.9	900.5
	Aliphatic saturated hydrocarbons C_nH_{2n+2}				
CH_4	Methane	g	16.04303	802.33	831.65
C_2H_6	Ethane	g	30.07012	1427.79	1495.84
C_3H_8	Propane	g	44.09721	2045.4	2154.0
C_4H_{10}	*n*-Butane	g	58.1243	2658.4	2805.8
C_5H_{12}	*n*-Pentane	g	72.15139	3274.3	3463.3
		l		3247.2	3461.8
C_6H_{14}	*n*-Hexane	g	86.17848	3889.3	4118.5
		l		3857.6	4114.5
C_7H_{16}	*n*-Heptane	l	100.20557	4464.7	4761.7
C_8H_{18}	*n*-Octane	l	114.23266	5074.4	5413.1
C_9H_{20}	*n*-Nonane	l	128.25975	5684.2	6064.9
$C_{10}H_{22}$	*n*-Decane	l	142.28684	6294.0	6716.8
$C_{11}H_{24}$	*n*-Undecane	l	156.31393	6908.6	7376.9
$C_{12}H_{26}$	*n*-Dodecane	l	170.34102	7518.8	8029.4
$C_{13}H_{28}$	*n*-Tridecane	l	184.36811	8129.0	8682.0
$C_{14}H_{30}$	*n*-Tetradecane	l	198.3952	8739.2	9334.5
$C_{15}H_{32}$	*n*-Pentadecane	l	212.42229	9349.4	9984.8
$C_{16}H_{34}$	*n*-Hexadecane	l	226.44938	9959.6	10639.7
	Cycloparaffins C_nH_{2n}				
C_3H_6	Cyclopropane	g	42.08127	1959.2	2043.2
C_4H_8	Cyclobutane	g	56.10836	2388.7	2516.2
C_6H_{12}	Cyclohexane	g	84.16254	3691.4	3914.3
		l		3658.3	3909.2
C_6H_{12}	Methylcyclopentane	l	84.16254	3673.5	3910.8
C_7H_{14}	Methylcyclohexane	g	98.18963	4295.5	4556.9
C_8H_{16}	Ethylcyclohexane	g	112.21672	4914.3	5228.5
		l		4873.8	5205.9
C_9H_{18}	n-Propylcyclohexane	l	126.24381	5483.3	5857.7
$C_{10}H_{20}$	n-Butylcyclohexane	l	140.2709	6094.3	6511.5
	Olefins (ethylenic hydrocarbons) C_nH_{2n}				
C_2H_4	Ethylene	g	28.05418	1323.1	1361.1
C_3H_6	Propylene	g	42.08127	1927.7	2003.9
C_4H_8	1-Butylene	g	56.10836	2542.9	2659.7

Chemical formula	Namne	State	Molar mass	Enthalpy	Exergy
				of formation	
			kg/kmol	[kJ/mol]	[kJ/mol]
C_6H_{12}	1-Hexylene	g	84.16254	3772.9	3970.5
		l		3742.2	3967.9
C_7H_{14}	1-Heptylene	g	98.18963	4388.0	4625.5
		l		4338.5	4604.6
	Acetylene hydrocarbons C_nH_{2n-2}				
C_2H_2	Acetylene	g	26.03824	1255.6	1265.8
C_3H_4	Propyne	g	40.06533	1850.9	1899.5
C_4H_6	1-Butyne	g	54.09242	2465.6	2552.3
C_6H_{10}	1-Hexyne	g	82.1466	3696.3	3865.1
C_7H_{12}	1-Heptyne	g	96.17369	4311.4	4520.5
C_8H_{14}	1-Octyne	g	110.20078	4923.2	5170.3
C_9H_{16}	1-Nonyne	g	124.22787	5537.9	5825.1
	Diene hydrocarbons C_nH_{2n-2}				
C_3H_4	Propadiene	g	40.06533	1472.1	1523.8
C_5H_8	Pentadiene	g	68.11951	2789.2	2914.8
	Aromatic hydrocarbons (benzene derivatives)				
C_6H_6	Benzene	g	78.11472	3171.6	3303.6
		l		3137.7	3298.5
C_7H_8	Toluene	g	92.14181	3774.4	3943.4
		l		3736.4	3931.0
C_8H_{10}	Ethylbenzene	g	106.1689	4390.0	4598.8
		l		4347.7	4587.9
C_8H_{10}	*o*-Xylene	l	106.1689	4332.8	4573.1
C_9H_{12}	*n*-Propylbenzene	l	120.19599	4957.5	5249.1
$C_{10}H_{14}$	*n*-Butylbenzene	l	134.22308	5567.7	5892.0
$C_{16}H_{26}$	*n*-Decylbenzene	l	218.38562	9198.3	9700.8
	Solid hydrocarbons				
$C_{10}H_8$	Naphthalene	s	128.17526	4984.2	5255.0
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	s	134.22308	5533.0	5880.0
$C_{10}H_{10}$	2-Methylnaphthalene	s	142.20235	5574.9	5881.4
$C_{11}H_{16}$	Pentamethylbenzene	s	148.25017	6131.6	6516.0
$C_{12}H_{18}$	Hexamethylbenzene	s	162.27726	6739.1	7171.0
$C_{14}H_{10}$	Anthracene	s	178.2358	6850.9	7218.1
$C_{14}H_{10}$	Phenanthrene	s	178.2358	6835.9	7201.8
$C_{14}H_{14}$	1,1-Diphenylethan	s	182.26768	7250.9	7665.9
$C_{18}H_{38}$	*n*-Octadecane	s	254.50356	11116.7	11937.4
$C_{19}H_{16}$	Triphenylmethane	s	244.33937	9579.7	10109.2
$C_{24}H_{18}$	1,3,5-Triphenylbenzene	s	306.41106	11850.1	12490.3

Chemical formula	Namne	State	Molar mass kg/kmol	Enthalpy of formation [kJ/mol]	Exergy of formation [kJ/mol]
$C_{25}H_{20}$	Tetraphenylmethane	s	320.43815	12544.1	13231.6
	Organic compounds containing oxygen				
CH_2O	Formaldehyde	g	30.02649	519.4	538.4
CH_2O_3	Formic acid	g	46.02589	259.1	301.3
		l		213.0	291.7
CH_4O	Methanol	l	32.04243	638.4	718.0
C_2H_6O	Ethyl alcohol	g	46.06952	1278.2	1363.9
		l		1235.9	1357.7
C_2H_6O	Dimethyl ether	g	46.06952	1328.1	1419.5
C_2H_4O	Acetic aldehyde	g	44.05358	1105.5	1163.3
C_2H_4O	Ethyleneoxyde	g	44.05358	1220.5	1284.4
$C_2H_6O_2$	Ethylene glycol	l	62.06892	1058.6	1207.3
$C_2H_4O_2$	Acetic acid	g	60.05298	834.1	919.0
		l		786.6	908.0
C_3H_8O	Propylalcohol-2	l	60.09661	1830.6	1998.6
C_3H_6O	Acetone	g	58.08067	1690.9	1791.5
		l		1659.6	1788.5
C_4H_8O	Butylaldehyde-1	l	72.10776	2296.5	2463.3
C_4H_8O	Butylketone-2	l	72.10776	2264.1	2432.6
C_4H_40	Furane	g	68.07588	2024.4	2118.8
		l		1996.7	2118.2
$C_4H_8O_2$	Butyric acid	l	88.10716	2018.8	2215.8
$C_4H_8O_2$	Ethyl acetate	l	88.10716	2073.6	2269.6
$C_5H_{12}O$	Amyl alcohol	l	88.15079	3060.7	3311.7
$C_5H_{12}O$	2-Methylbutanol-2	l	88.15079	3017.2	3275.7
$C_5H_{10}O$	Cyclopentanol	l	86.13485	2878.7	3109.7
$C_5H_6O_2$	Furfuryl alcohol	l	98.10237	2418.6	2687.7
$C_6H_{14}O$	Hexyl alcohol-l	l	102.17788	3668.9	3961.1
$C_6H_{12}O$	Cyclohexanol	l	100.16194	3465.4	3750.8
$C_7H_{16}O$	Heptyl alcohol-l	l	116.20497	4285.6	4619.2
C_7H_8O	Benzyl alcohol	l	108.14121	3563.4	3795.8
$C_4H_{10}O_4$	Erythrite	s	122.1219	1874.7	2193.0
$C_4H_6O_4$	Succinic acid	s	118.09002	1356.9	1609.4
$C_4H_4O_4$	Malonic acid	s	116.07408	1271.3	1495.7
$C_4H_4O_4$	Fumaric acid	s	116.07408	1249.1	1471.5
C_6H_6O	Phenol	s	94.11412	2925.9	3128.5
$C_6H_{14}O_6$	Dulcite	s	182.17488	2729.6	3196.3
$C_6H_{14}O_6$	Mannit	s	182.17488	2739.6	3204.8
$C_6H_{12}O_6$	α-D-Galactose	s	180.15894	2529.6	2928.8
$C_6H_{12}O_6$	L-Sorbose	s	180.15894	2544.6	2939.0
$C_7H_6O_2$	Benzoic acid	s	122.12467	3097.2	3343.5
$C_7H_6O_3$	Hydroxybenzoic acid	s	138.12407	2888.1	3151.2
$C_8H_4O_3$	Phthalic acid anhydride	s	148.11928	3173.8	3434.8
$C_8H_6O_4$	Phthalic acid	s	166.13462	3094.3	3412.6

Chemical formula	Namne	State	Molar mass kg/kmol	Enthalpy of formation [kJ/mol]	Exergy [kJ/mol]
$C_{12}H_{10}O$	Diphenyl ether	s	170.2129	5903.1	6282.4
$C_{12}H_{22}O_{11}$	β-Lactose	s	342.30254	5154.2	5988.1
$C_{12}H_{22}O_{11}$	Saccharose	s	342.30254	5166.2	6007.8
$C_{12}H_{24}O_{12}$	α-Lactose monohydrate	s	360.31788	5152.2	6043.3
$C_{12}H_{24}O_{12}$	β-Maltose monohydrate	s	360.31788	5173.2	6063.4
$C_{16}H_{34}O$	Cetyl alcohol	s	242.44878	9731.3	10493.9
$C_{16}H_{32}O_2$	Palmitin acid	s	256.43224	9290.3	10052.3
$C_2H_2O_4$	Oxalic acid	s	90.03584	202.7	368.7
	Organic compounds containing nitrogen and oxygen				
$C_2H_4N_4$	Dicyanodiamide	s	84.08098	1296.5	1477.4
$C_3H_6N_6$	Melamine	s	126.12147	1835.6	2120.5
$C_5H_5N_5$	Adenine	s	135.1291	2664.9	2941.0
$C_6H_4N_2$	2-Cyanopyridine	s	104.11218	3106.1	3246.9
$C_{12}H_{11}N$	Diphenylamine	s	169.22817	6188.1	6540.7
CH_4ON_2	Urea	s	60.05583	544.7	689.0
$CH_6O_2N_2$	Ammonium urethane	s	78.06037	474.8	666.7
$C_2H_5O_2N$	Aminoacetic acid	s	75.06765	867.6	1049.5
$C_3H_7O_2N$	D,L-Alanine	s	89.09474	1462.4	1689.4
$C_4H_7O_4N$	L-Aspartic acid	s	133.10469	1445.2	1743.8
$C_4H_8O_3N_2$	L-Asparagine	s	132.11996	1749.9	2061.3
$C_4H_2O_4N_2$	Alloxan	s	142.07154	813.1	1053.8
$C_4H_7ON_3$	Creatinine	s	113.11989	2179.7	2440.6
$C_4H_9O_2N_3$	Creatine	s	131.13523	2123.1	2442.8
$C_4H_6O_3N_4$	Allantoin	s	158.11742	1580.0	1909.9
$C_5H_9O_4N$	D-Glutamic acid	s	147.13178	2047.9	2393.2
$C_5H_4ON_4$	Hypoxanthine	s	136.11383	2337.3	2602.4
$C_5H_4O_2N_4$	Xanthine	s	152.11323	2068.8	2361.7
$C_5H_5O_3N_4$	Uric acid	s	169.1206	1950.6	2289.1
$C_5H_5ON_5$	Guanine	s	151.1285	2385.2	2691.2
$C_9H_9O_3N$	Hypuric acid	s	179.17698	4014.3	4388.1
$C_{12}H_5O_{12}N_7$	1,3,5-Hexanitrodiphenylamine	s	439.21335	5397.2	6167.8
	Organic compounds containing sulfur				
C_2H_6S	Ethyl mercaptan	l	62.134	2164.9	2134.0
C_2H_6S	Dimethyl sulfide	l	62.134	2173.2	2145.4
C_3H_8S	Propyl mercaptan	l	76.161	2784.3	2794.7
C_3H_8S	Methylethyl sulfide	l	76.161	2783.6	2795.0
$C_4H_{10}S$	Butyl mercaptan	l	90.188	3386.2	3438.7
$C_4H_{10}S$	2-Methylpropyl mercaptan	l	90.188	3378.9	3434.3
$C_4H_{10}S$	Diethyl sulfide	l	90.188	3392.9	3446.3
$C_4H_{10}S$	Methylpropyl sulfide	l	90.188	3386.2	3442.6

Chemical formula	Namne	State	Molar mass kg/kmol	Enthalpy of formation [kJ/mol]	Exergy of formation [kJ/mol]
C_4H_4S	Thiophene	l	84.140	2865.9	2847.0
$C_4H_{10}S_2$	Ethylbutyl disulfide	l	122.252	4117.1	4055.4
$C_5H_{12}S$	Amyl mercaptan	l	104.215	3994.8	4091.3
C_5H_6S	2-Methylthiophene	l	98.168	3374.5	3396.5
C_5H_6S	3-Methylthiophene	l	98.168	3376.1	3398.2
C_6H_6S	Thiophenol	l	110.179	3876.6	3916.1
$C_6H_{14}S_2$	Dipropyl disulfide	l	150.306	5336.5	5358.4
$C_6H_{10}O_4S_2$	Milk acid β,β'-dithiane	s	210.272	4053.1	4168.6
C_3H_7OSN	1-Cysteine	s	105.159	2219.3	2285.8
$C_6H_{12}O_4S_2N_2$	1-Cystine	s	240.302	4212.8	4415.5

Table A.4.3 Enthalpy and exergy of formation for organic substances by groups

Group	Gases		Liquids	
	Enthalp of formation [kJ/mol]	Exergy of formation [kJ/mol]	Entalpy of formation [kJ/mol]	Exergy of formation [kJ/mol]
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$	398.57	462.77	403.54	462.64
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$	509.77	557.40	485.75	545.27
$-\overset{\vert}{\mathrm{C}}\mathrm{H}_2$	614.91	654.51	607.38	651.46
$-\mathrm{CH}_3$	713.47	747.97	715.35	752.03
$=\overset{\vert}{\mathrm{C}}-$	440.53	513.35	443.16	473.02
$=\overset{\vert}{\mathrm{C}}\mathrm{H}$	551.86	576.31	535.08	569.95
$=\mathrm{CH}_2$	660.26	678.74	680.26	675.68
$=\mathrm{C}=$	543.04	554.23	539.28	559.21
$\equiv\mathrm{C}-$	510.20	519.58	494.34	515.27
$\equiv\mathrm{CH}$	625.37	630.28	623.86	634.34
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$ (ring)	413.34	461.01	379.03	425.11
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$ (ring)	522.78	561.37	468.76	543.05
$-\overset{\vert}{\mathrm{C}}\mathrm{H}_2$ (ring)	629.05	662.29	614.16	653.63
$=\overset{\vert}{\mathrm{C}}-$ (ring)	442.71	466.41	—	—
$=\overset{\vert}{\mathrm{C}}\mathrm{H}$ (ring)	559.18	576.65	542.95	568.28
$\leftrightarrow \mathrm{C}^{\swarrow\!\!\nearrow}_{\nwarrow\!\!\searrow}$	414.22	436.03	416.14	435.03
$-\mathrm{C}^{\swarrow\!\!\nearrow}_{\nwarrow\!\!\searrow}$	415.47	440.00	426.22	436.45
$\mathrm{HC}^{\swarrow\!\!\nearrow}_{\nwarrow\!\!\searrow}$	528.26	549.91	519.93	547.15

Group	Gases		Liquids	
	Enthalp	Exergy	Entalpy	Exergy
	of formation		of formation	
	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
$-\mathrm{O}-$	–111.59	–89.11	–131.17	–86.52
$=\mathrm{O}$	–246.86	–245.09	–91.46	
$-\mathrm{O}-$ (ring)	–117.42	–97.12	–126.27	–106.64
$\mathrm{O}\genfrac{}{}{0pt}{}{\nearrow}{\searrow}$	–89.96	–83.59	–84.43	–73.13
$-\mathrm{OH}\left(\text{to } -\overset{\vert}{\underset{\vert}{\mathrm{C}}}-\right)$	–68.42	–165.48	–137.54	–80.08
$-\mathrm{OH}\left(\text{to } -\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}\right)$	63.90	–66.78	–85 11	–52
$-\mathrm{OH}\ (\text{to } -\overset{\vert}{\mathrm{C}}\mathrm{H}_2)$	–56.66	–42.89	–84.82	–51.34
$-\mathrm{OH}\ (\text{to } -\mathrm{CH}_3)$	–77.00	–25.52	–76.87	–33.97
$-\mathrm{OH}\ (\text{to } -\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}\ \text{ ring})$	-65.16	–46.78	–70.47	–58.16
$-$ OH (attached to aromatic)	–66.12	–52.01	81.64	–47.57
$-\overset{\vert}{\mathrm{C}}=\mathrm{O}$	262.38	293.87	231.58	281.36
$-\overset{\substack{\mathrm{H}\\ \vert}}{\mathrm{C}}=\mathrm{O}$	388.64	412.68	356.72	400.21
$-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{O}-$	65.69	108.30	35.90	101.15
$-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{O}-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-$	296.94	382.66	244.81	362.70
$-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{OH}$	—	168.04	—	155.11
$-\mathrm{O}-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-\mathrm{H}$	207.01	250.09	183.96	
$-\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{C}}-$ (ring)	—	305.66	—	277.76

Group	Gases		Liquids	
	Enthalp of formation [kJ/mol]	Exergy of formation [kJ/mol]	Entalpy of formation [kJ/mol]	Exergy of formation [kJ/mol]
$-\overset{\overset{H}{\vert}}{C}=O$ (attached to aromatic)	382.87	415.07	379.60	410.21
$-\overset{\vert}{N}-$	97.03	142.05	64.60	131.09
$-\overset{\vert}{N}H$	181.49	213.38	137.18	195.56
$-NH_2$	258.43	290.20	235.43	284.39
$=\overset{\vert}{N}$	56.82	72.98	–103.43	
$\equiv N$	24.18	23.06	0	29.97
$-\overset{\vert}{N}H$ (ring)	186.19	209.24	151.20	199.37
$-NH_2$ (attached to aromatic)	237.80	240.16	216.84	269.24
$-\overset{\vert}{N}H$ (attached to aromatic)	153.58	196.27		
$-\overset{\vert}{N}-$ (attached to aromatic)	77.07	134.06		
$N^{\swarrow\!\!\nearrow}_{\nwarrow\!\!\searrow}$	69.08	81.68	72.34	83.33
$-NO_2$	–42.30	1.45	–58.32	12.16
$-O-NO-$	19.66	18.89	—	—
$-O-O_2$	–89.91	–89.77	–121.71	–23.88
$-N=C-$	585.26	592.73	551.97	584.03
$N\equiv C-$	516.93	527.50	510.53	522.14
$-S-$	761.07	636.88	741.74	642.32
$-SH$	862.06	724.36	848.67	732.26
$=SO$	692.04	553.78	696.47	566.88
$-\overset{\vert}{\underset{\vert}{SO}}$	660.53	562.95	686.39	
$-\overset{\vert}{SO}_2$	439.87	373.78	414.68	

Group	Gases		Liquids	
	Enthalp of formation [kJ/mol]	Exergy of formation [kJ/mol]	Entalpy of formation [kJ/mol]	Exergy of formation [kJ/mol]
− S − (ring)	764.08	633.45	755.42	687.25
S ⤢ ⤡	781.15	653.56	762.45	654.41
− F	–15.00	16.25	–8.85	34.70
− Cl	46.08	26.24	42.89	32.01
− F (attached to aromatic)	15.08	45.16	–8.85	34.70
− Cl (attached to aromatic)	46.08	26.24	42.89	32.01
Ortho (1,2)	4.35	7.66	0.0	0.0
Meta (1,3)	1.76	3.47	0.0	0.0
Para (1,4)	1.26	4.60	0.0	0.0
1,2,3 Position	12.89	20.08	0.0	0.0
1,2,4 Position	9.05	13.60	0.0	0.0
1,3,5 Position	6.28	14.27	0.0	0.0
1,2,3,5 Position	14.06	26.94	0.0	0.0
1,2,3,5 Position	12.80	23.93	0.0	0.0
1,2,4,5 Position	12.38	24.27	0.0	0.0
1,2,3,4,5 Position	17.99	35.36	0.0	0.0
1,2,3,4,5,6 Position	19.66	62.34	0.0	0.0
3 Atom saturated ring	62.30	49.04	83.68	83.68
4 Atom saturated ring	50.84	43.76	87.82	82.30
5 Atom saturated ring	–50.38	–45.52	0.00	0.00
6 Atom saturated ring	–83.05	–61.25	–28.79	0.00
7 Atom saturated ring	–73.81	–46.32		
8 Atom saturated ring	–72.59	–33.47		
Pentene ring	–50.38	–45.52	0.00	0.00
Hexene ring	–83.05	–61.25	–28.79	0.00

Table A.4.4 Exergy of substances in ideal water solution (molarity 1 mol/kg H_2O), (T_0 = 298.15 K, P_0 = 101.325 kPa)

Chemical formula	Exergy		
	Unsolved [kJ/mol]	Solved	
		Form	[kJ/mol]
AgCl	59.4	Ag^{2+}, Cl^-	77.9
$CaCl_2$	—	Ca^{2+}, $2Cl^-$	19.7
CuCl	—	Cu^+, Cl	114.7
$CuCl_2$	—	Cu^{2+}, $2Cl^-$	61.2
$FeCl_2$	—	Fe^{2+}, $2Cl^-$	158.7
H_2CO_3	29.57	$2H^+$, CO_3^{2-}	124.6
		H^+, HCO_3^-	65.6
HCl	48.9	H^+, Cl^-	48.5
HF	56.6	H^+, F^-	74.6
HNO_3	20.9	H^+, NO_3	13.0
H_3PO_4	80.6	$3H^+$, PO_4^{3-}	204.4
		$2H^+$, HPO_4^{2-}	134.1
H_2S	817.9	—	—
H_2SO_4	—	$2H^+$, SO_4^{2-}	108.6
KCl	15.0	K^+, Cl^-	14.6
KNO_3	–19.8	K^+, NO_3^-	–20.7
KOH	46.9	K^+, OH	46.9
K_2SO_4	—	$2K^+$, SO_4^{2-}	41.3
LiCl	58.1	Li^+, Cl	29.7
$MgCl_2$	—	Mg^{2+}, 2Cl	40.4
NH_3	327.4	—	—
NH_4OH	328.8	NH4, OH	322.1
Na_2CO_3	—	$2Na^+$, CO_3^{2-}	37.7
NaCl	5.5	Na^+, Cl^-	5.1
$NaHCO_3$	21.4	Na^+, HCO_3^-	21.4
$NaNO_3$	–29.4	Na^+, NO_3^-	–30.2
NaOH	37.7	Na^+, OH^-	37.7
Na_2SO_4	—	$2Na^+$, SO_4^{2-}	22.2
O_2	20.3	—	—
$PbCl_2$	—	Pb^{2+}, $2Cl^-$	69.5
$ZnCl_2$	—	Zn^{2+}, $2Cl^-$	53.2
$ZnSO_4$	51.8	Zn^{2+}, SO_4^{2-}	80.2