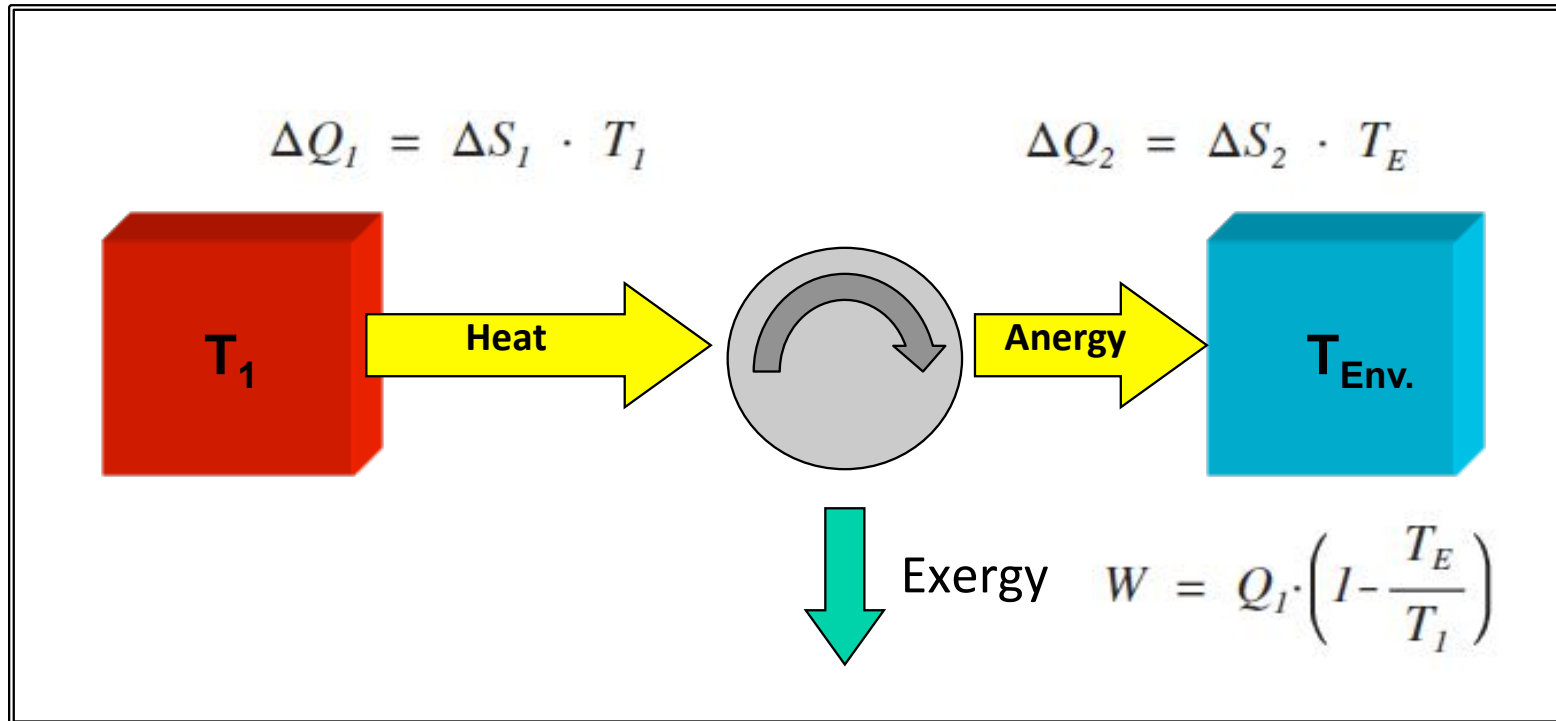


Thermodynamics of Energy Conversion & Storage

1. BASICS



1. BASICS

1.1. ENERGY: HEAT and WORK

1.1.1. History of Energy

1.1.2. Two forms of energy: heat and work

1.2. ENERGY STATISTICS

1.3. ENERGY UNITS

1.4. 1st and 2nd LAW OF THERMODYNAMICS

1.5. ENTROPY (S)

1.5.1. ENTROPY FROM HEAT

1.5.2. ENTROPY FROM PROBABILITY

1.6. ENERGY CONVERSION

1.6.1. ENERGY CONVERSION

1.6.2. GIBBS FREE ENERGY ΔG

1.6.3. SPONTANEOUS PROCESS

1.7. HEAT CONVERSION INTO WORK

1.7.1. EFFICIENCY (Conversion of Heat to Work)

1.8. EFFICIENCY (Conversion of Heat to Work)

1.8.1. EXERGIE & ANERGIE OF HEAT

1.8. EXERGY AND ANERGY

1.9. DEVELOPMENT OF THE EFFICIENCY

1.10. ENERGY CONVERSION PROCESS

1.10.1. Example Energy Conversion Process

1.11. USAGE versus COVERAGE

1.11.1. EXAMPLE PV USAGE versus COVERAGE (PRODUCTION)

1.11.2. EXAMPLE PV USAGE versus COVERAGE (STORAGE)

1.12. ENERGY and POWER

1.13. ENERGY CARRIER and ENERGY FLUX

1.13.1. Example space shuttle

1.14. RENEWABLE ENERGY CONVERSION AND STORAGE

1.1. ENERGY: Heat and Work

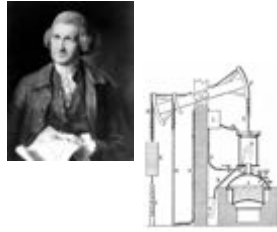
1.1.1. History of Energy

Steam turbine



Hero of ALEXANDRIA
10 - 70

1st Steam engine



Thomas NEWCOMEN
1712

Steam engine opt.



James WATT
1783

1st Steam locomotive



George STEPHENSON
1828

Standard Oil Company



John D. ROCKEFELLER
1865

Patent Motorwagen



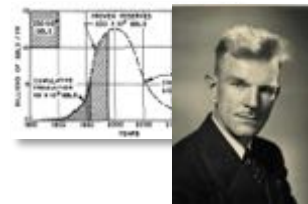
Carl BENZ
1886

1st motorized flight



Wilbur & Orville WRIGHT
1903

Model for oil mining



M. King HUBBERT
1957

Club of Rome



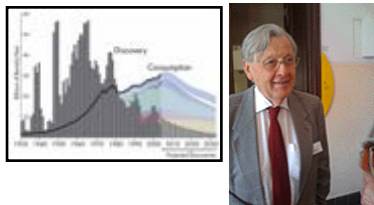
Jimmy" CARTER
1978

Solar energy & H₂



Carl-J. WINTER
1989

Fossil resource model



Colin J. CAMPBELL
1998

REWTHA



Sir David J. C. MACKAY
2008

CO₂ Air Capture



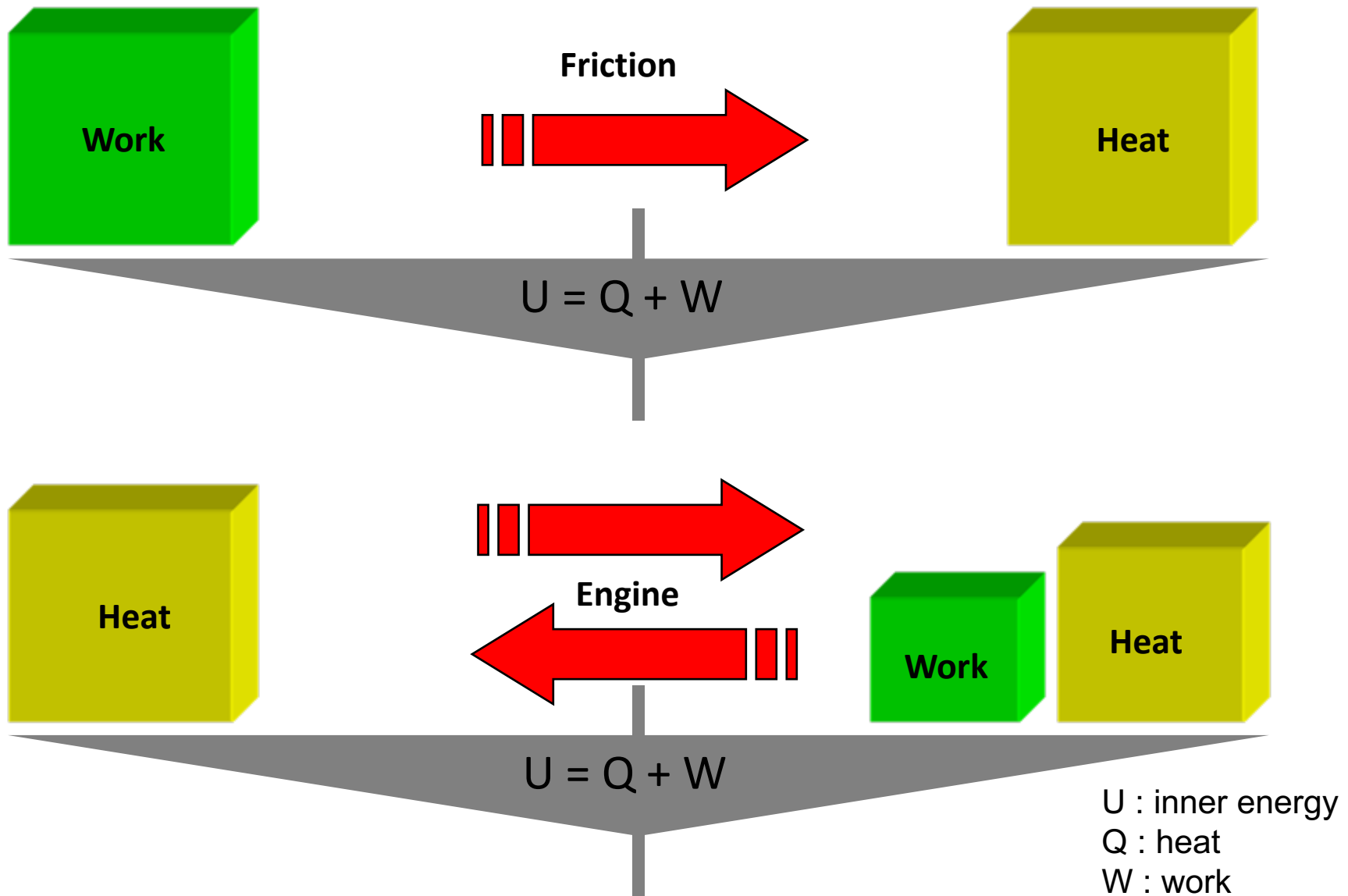
Klaus S. LACKNER
2009

Gapminder



Hans ROSLING
2009

1.1.2. Two forms of ENERGY: HEAT and WORK



QUESTIONS

Q 1.1.: How does nature convert work into heat?

Q 1.2.: What technology converts work into heat?

Q 1.3.: How does nature convert heat into work?

Q 1.4.: What technology converts heat into work?

SOLUTIONS

Q1.1.: How does nature convert work into heat?

Friction in fluids, gases, between solids, impact, deformation

Q1.2.: What technology converts work into heat?

Breaks, electric heater, Heat pump

Q1.3.: How does nature convert heat into work?

evaporation of water and condensation, wind, streams

Q1.4.: What technology converts heat into work?

piston engines, turbines

1.2. ENERGY STATISTICS

1.2.1. IEA World Energy Outlook

<https://www.iea.org/newsroom/news/2016/november/world-energy-outlook-2016.html>

1.2.2. Our World in Data



Our World in Data:

<https://ourworldindata.org>



QUESTIONS

Q1.5. How much energy (and power) does a human being consume?

Q1.6. How much can a human body work? How do we measure the work?

SOLUTION

Q1.5. How much energy (and power) does a human being consume?

$$\text{Food } 2060 \text{ kcal/day} = 8640 \text{ kJ/day} = 8640 \text{ kJ}/(24\text{h} \cdot 3600 \text{ sec}) \\ = 100 \text{ W}$$

Q1.6. How much can a human body work? How do we measure the work?

Clime a mountain 400m/hour, walk horizontal 4 km/h

$$P = m \cdot g \cdot h/t = 70 \text{ kg} \cdot 9.81 \text{ m/s}^2 \cdot 400 \text{ m/h} = 76 \text{ J} \cdot \text{s}^{-1} = 76 \text{ W}$$

$$W = m \cdot g \cdot h = 70 \text{ kg} \cdot 9.81 \text{ m/s}^2 \cdot 400 \text{ m/h} \cdot 4\text{h} = 1000 \text{ kJ}$$

1.3. ENERGY UNITS

Name	Symb.	J	kWh	TWa	kg SKE
Joule	J	1.000	$2.778 \cdot 10^{-7}$	$3.171 \cdot 10^{-20}$	$3.41 \cdot 10^{-8}$
Erg	erg	$1.000 \cdot 10^{-7}$	$2.778 \cdot 10^{-14}$	$3.171 \cdot 10^{-27}$	$3.41 \cdot 10^{-15}$
Calorie	cal	4.1855	$1.160 \cdot 10^{-6}$	$1.327 \cdot 10^{-19}$	$1.427 \cdot 10^{-7}$
Electronvolt	eV	$1.600 \cdot 10^{-19}$	$4.500 \cdot 10^{-26}$	$5.073 \cdot 10^{-39}$	$5.456 \cdot 10^{-27}$
Kilowatthour	kWh	$3.600 \cdot 10^6$	1.000	$1.141 \cdot 10^{-13}$	$1.228 \cdot 10^{-1}$
Megatonns Oil Eq.	Mtoe	$4.186 \cdot 10^{16}$	$1.163 \cdot 10^{10}$	$1.02 \cdot 10^{-1}$	$1.427 \cdot 10^9$
Mega British thermal unit	MBtu	$1.055 \cdot 10^9$	293.1	$3.345 \cdot 10^{-11}$	$3.598 \cdot 10^1$
Terajoule	TJ	$1.000 \cdot 10^{12}$	$2.778 \cdot 10^5$	$3.171 \cdot 10^{-8}$	$3.410 \cdot 10^4$
Terawattyear	TWa	$3.160 \cdot 10^{19}$	$8.778 \cdot 10^{12}$	1.000	$1.078 \cdot 10^{12}$
kg SKE	kg SKE	$2.930 \cdot 10^7$	8.139	$9.291 \cdot 10^{-13}$	1.000

QUESTIONS

Q1.7. Convert 1 kWh in kJ

Q1.8. Convert 1 kJ in Wh

Q1.9. Convert 1 eV in J·mol⁻¹

Q 1.10. Convert 1 kcal in kJ

SOLUTION

Q1.7. Convert 1 kWh in kJ

$$1 \text{ kWh} = 1 \text{ kJ} \cdot \text{s}^{-1} \cdot \text{h} = 1 \text{ kJ} \cdot \text{s}^{-1} \cdot 3600 \text{ s} \cdot \text{h}^{-1} \cdot \text{h} = 3600 \text{ kJ}$$

Q1.8. Convert 1 kJ in Wh

$$1 \text{ kJ} = 1 \text{ kW} \cdot \text{s} = 1000 \text{ W} \cdot \text{s} \cdot \text{h} \cdot (3600 \text{ s})^{-1} = 0.278 \text{ Wh}$$

Q1.9. Convert 1 eV in J·mol⁻¹

$$1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ As} \cdot \text{V} = 96.4 \text{ kJ} \cdot \text{mol}^{-1}$$

Q 1.10. Convert 1 cal in J

$$1 \text{ kcal} = 4.187 \text{ kJ} \text{ (heat 1 kg H}_2\text{O by 1}^\circ\text{C or lift 4.2 kg by 1 m up)}$$

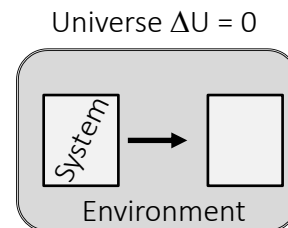
1.4. 1st and 2nd LAW OF THERMODYNAMICS

1st law:

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

Energy conservation

System, Environment, Universe



Ludwig Eduard Boltzmann

(* 20. 2 1844 in Wien;
† 5. 9. 1906 in Duino,
Österreich-Ungarn)

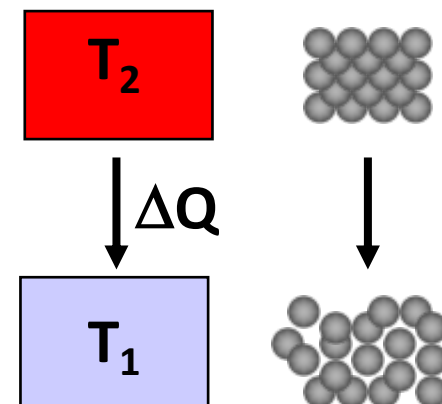
2nd law:

$$\Delta S \geq 0$$

$$\Delta S = \frac{\Delta Q}{T} \quad \text{and} \quad \Delta S = k \cdot \ln(P_{n,m})$$

Heat spontaneously moves from hot to cold

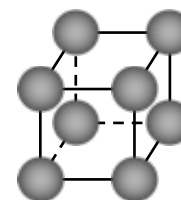
Disorder spontaneously increases



3rd law:

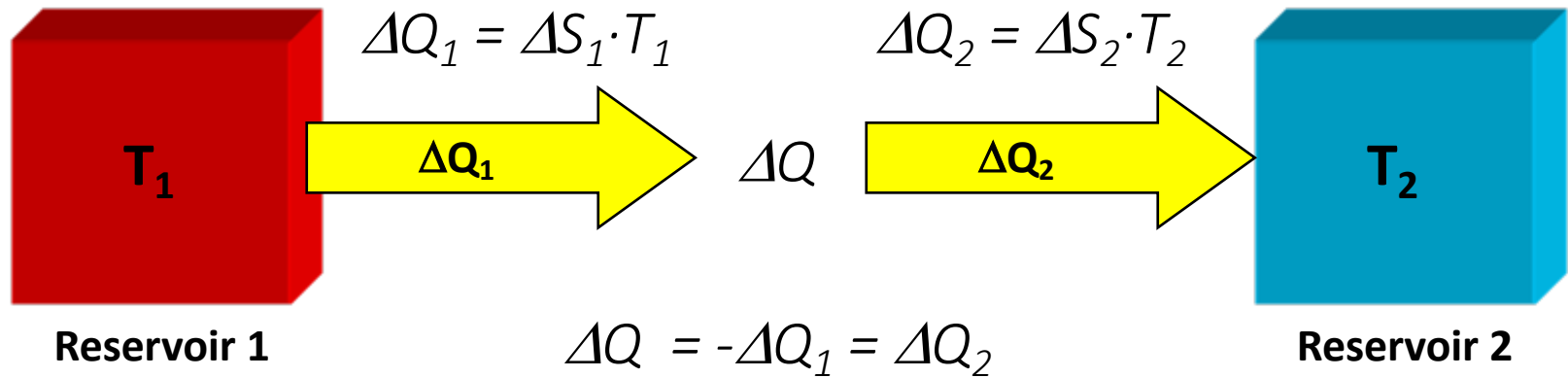
$$\Delta S_{\text{minimal}} \text{ at } T = 0 \text{ K}$$

At 0K the entropy in an ideal crystal is minimal.



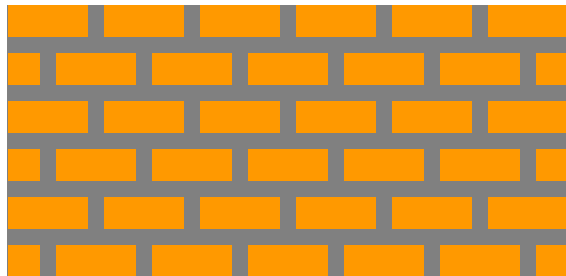
1.5. ENTROPY (S)

ENTROPY = HEAT/TEMPERATURE



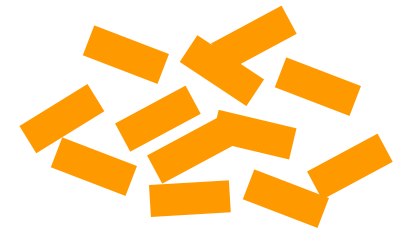
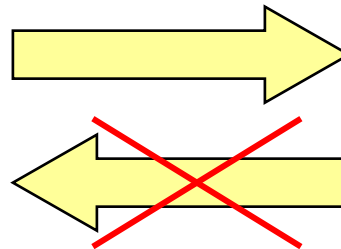
$$\Delta S = -\Delta Q_1 / T_1 + \Delta Q_2 / T_2$$

ENTROPY = DISORDER (Probability)



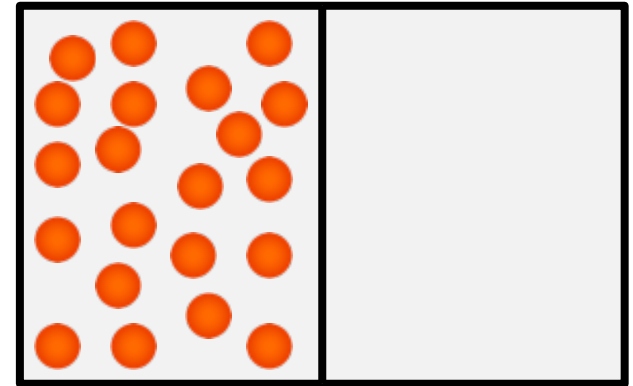
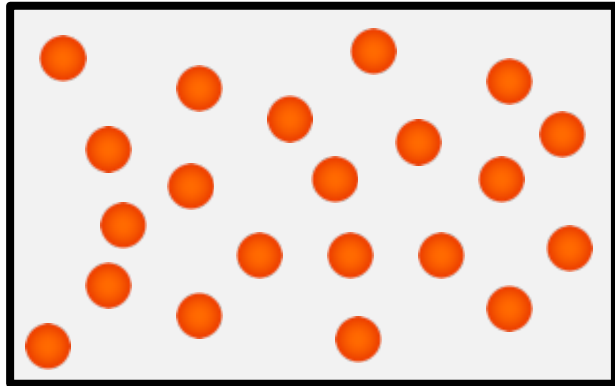
$$S = k \cdot \ln(P)$$

Boltzmann constant $k = R/N_A$
 $k = 1.38064852 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$



1.5.1. ENTROPY FROM HEAT

$$\Delta S = \frac{\delta Q}{T}$$



isothermal compression $T = \text{const.}$ $\Delta U = \Delta Q + \Delta W = 0$

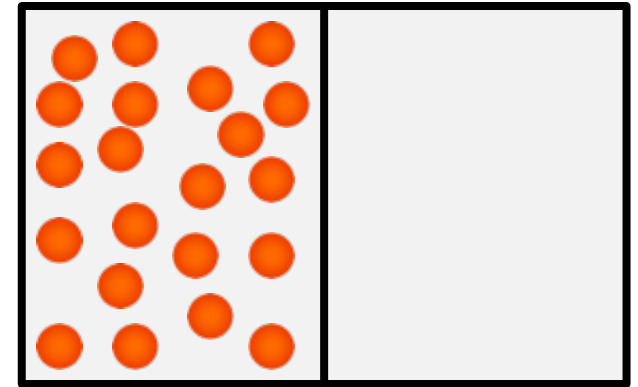
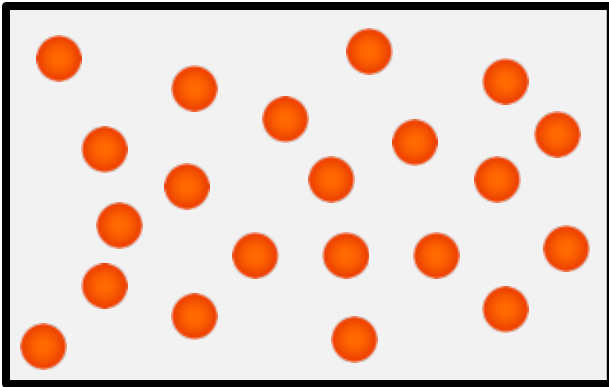
$$\begin{aligned}\Delta W &= -\int_V^{V/2} p \cdot dV = -n \cdot R \cdot T \int_V^{V/2} \frac{dV}{V} = -n \cdot R \cdot T \cdot \ln\left(\frac{V/2}{V}\right) \\ &= n \cdot R \cdot T \cdot \ln(2)\end{aligned}$$

$$\Delta Q = -\Delta W$$

$$\Delta S = \frac{\delta Q}{T} = -n \cdot R \cdot \ln(2)$$

1.5.2. ENTROPY FROM PROBABILITY

$$\Delta S = k \cdot \ln(P)$$



the probability to find all the molecules in half of the volume is

$$\begin{aligned}\Delta S &= k_B \cdot \ln \left(\frac{1}{2} \right)^N \\ &= - N \cdot k_B \cdot \ln(2) \\ &= - n \cdot R \cdot \ln(2)\end{aligned}$$

1.6. ENERGY CONVERSION

Universe

U : inner energy

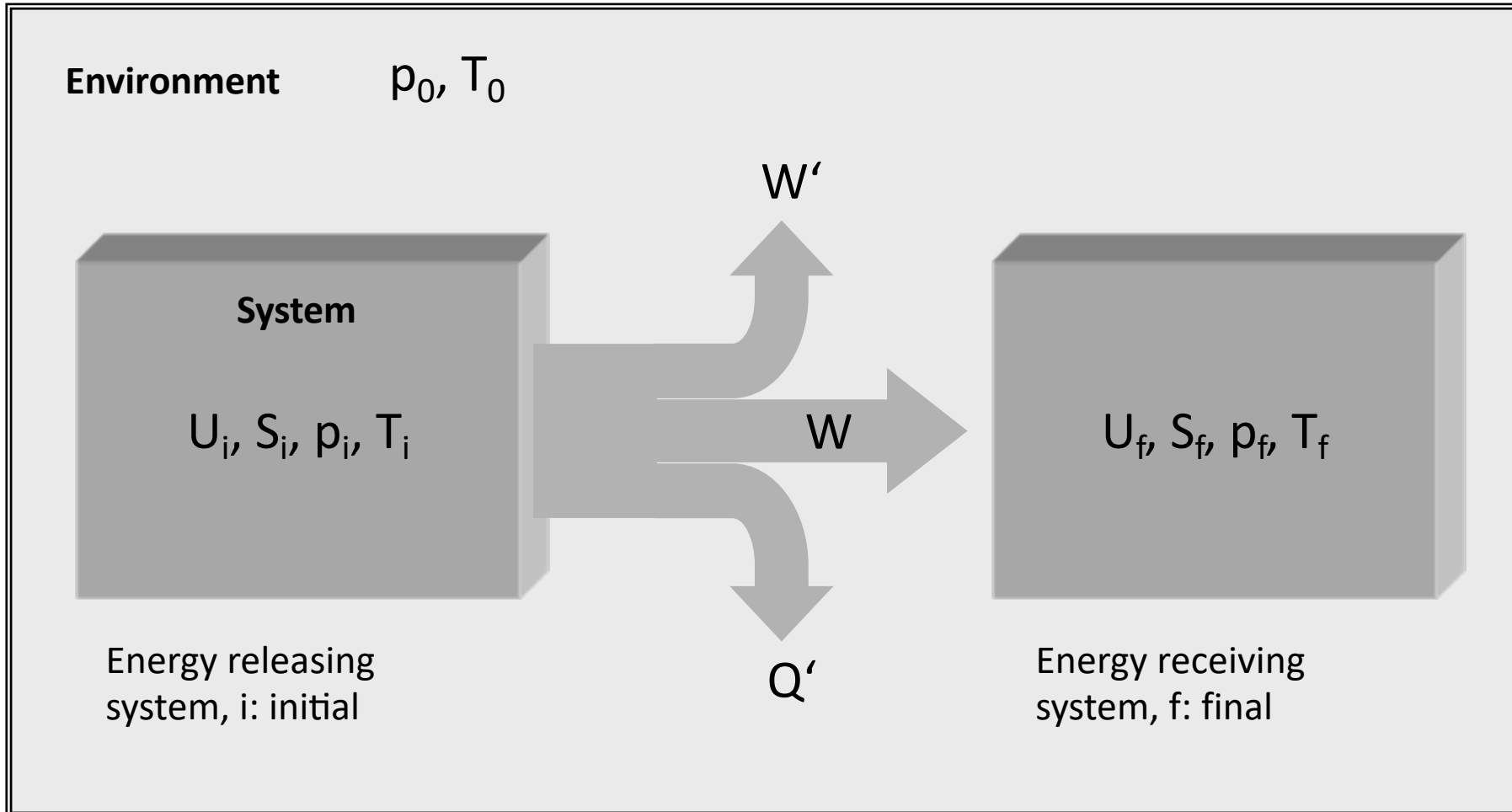
S : entropy

Q : heat

W : work

p : pressure

T : temperature



1.6.1. ENERGY CONVERSION ΔS_{tot}

$$-\Delta U = W + W' + Q' \quad \text{with} \quad \Delta U = U_0 - U$$

$$\Delta S = S_0 - S \quad \text{with} \quad \Delta S' = \frac{Q'}{T_0}$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S' = S_0 - S + \frac{Q'}{T_0}$$

$$Q' = T_0 \cdot (\Delta S_{\text{tot}} - \Delta S)$$

for the work $W = -\Delta U' - W' - Q'$

$$\begin{aligned} W + T_0 \cdot \Delta S_{\text{tot}} &= -\Delta U - W' + T_0 \cdot \Delta S \\ &= (U - U_0) + p_0 \cdot (V - V_0) - T_0 \cdot (S - S_0) \end{aligned}$$

for $\Delta S_{\text{tot}} = 0$: $W = (U - U_0) + p_0 \cdot (V - V_0) - T_0 \cdot (S - S_0)$ *Exergy*
and $T_0 \cdot \Delta S_{\text{tot}} = \text{Anergy}$

1.6.2. GIBBS FREE ENERGY ΔG

$$\Delta S_{\text{Universe}} = \Delta S_{\text{tot}} = \Delta S + \Delta S' = S_0 - S + \frac{Q'}{T_0}$$

$$\Delta S' = -\frac{\Delta H}{T} = -\frac{Q'_{\text{rev}}}{T_0} \quad \Delta p = 0$$

$$-T \cdot \Delta S_{\text{tot}} = \Delta H - T \cdot \Delta S$$

$$\Delta G = -T \cdot \Delta S_{\text{tot}}$$

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$G = H - T \cdot S \quad \text{or} \quad \Delta G = \Delta H - \Delta(T \cdot S)$$

ΔG is a state function (independent of the path)

1.6.3. SPONTANEOUS PROCESS

$\Delta S_{\text{Universe}} > 0$ *spontaneous process*

$\Delta S_{\text{Universe}} < 0$ *spontaneous process in opposite direction*

$\Delta S_{\text{Universe}} = 0$ *process in equilibrium*

$$\Delta G = -T \cdot \Delta S_{\text{Universe}} = \Delta H - T \cdot \Delta S$$

$\Delta G < 0$ *spontaneous process* ($\Delta H < 0, \Delta S > 0$)

($\Delta H < 0, \Delta S < 0$ at low T)

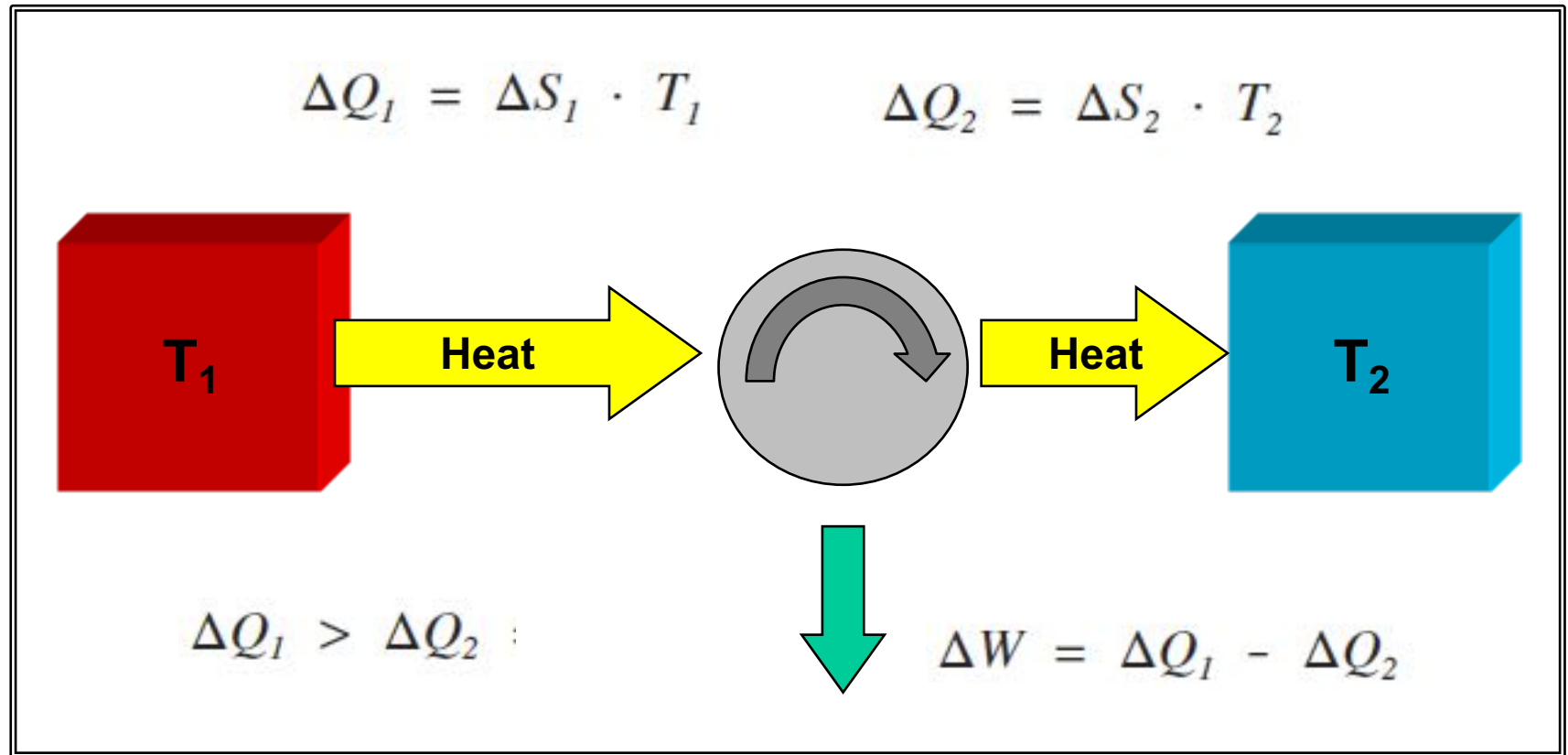
($\Delta H > 0, \Delta S > 0$ at high T)

$\Delta G > 0$ *spontaneous process in opposite direction* ($\Delta H > 0, \Delta S < 0$)

$\Delta G = 0$ *process in equilibrium* ($\Delta H = -T \cdot \Delta S$)

1.7. HEAT CONVERSION INTO WORK

Nicolas Léonard Sadi Carnot
(* 1. Juni 1796 in Paris;
† 24. August 1832 Paris)



1.7.1. EFFICIENCY (Conversion of Heat to Work)

Energy conservation: $Q_1 = W + Q_2$

Entropy change: $\Delta S = -S_1 + S_2 = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2}$

Reversible: $\Delta S = 0$

$$\underline{\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = S}$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{S \cdot T_1 - S \cdot T_2}{S \cdot T_1} = \frac{T_1 - T_2}{T_1} = \frac{\Delta T}{T_1} = 1 - \frac{T_2}{T_1}$$

η : Efficiency

Irreversible: $\Delta S > 0$

$$\left| \frac{Q_1}{T_1} \right| < \left| \frac{Q_2}{T_2} \right| \xrightarrow{Q_1 < 0} \frac{T_2}{T_1} > \frac{Q_2}{Q_1}$$

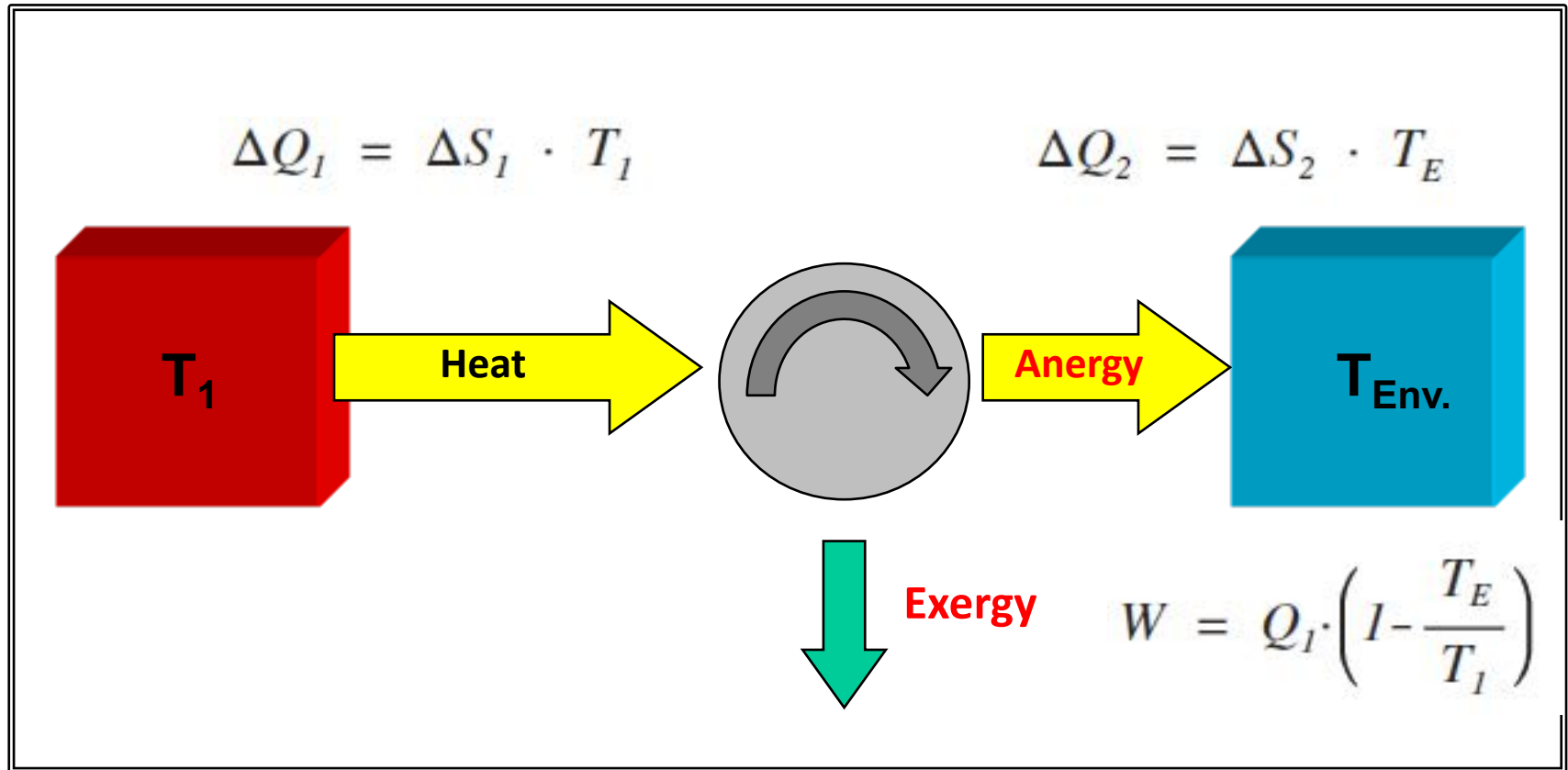
$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

Impossible: $\Delta S < 0$

$$\left| \frac{Q_1}{T_1} \right| > \left| \frac{Q_2}{T_2} \right| \rightarrow \frac{T_2}{T_1} < \frac{Q_2}{Q_1}$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} > 1 - \frac{T_2}{T_1}$$

1.8. EXERGY AND ANERGY



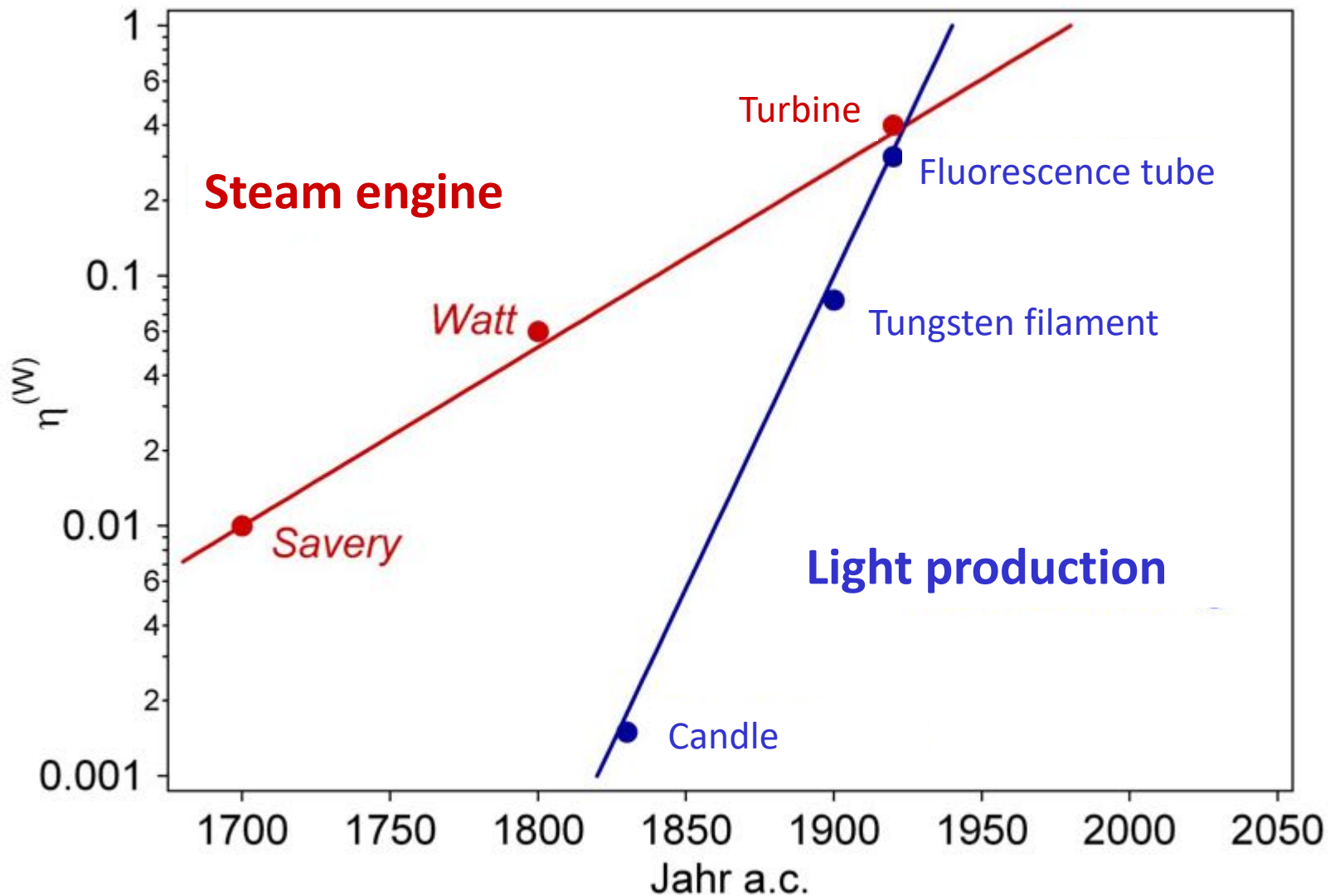
Special case: $T_2 = T_E$

$$W = Q_1 \cdot \left(1 - \frac{T_E}{T_1} \right) \quad \text{Exergy}$$

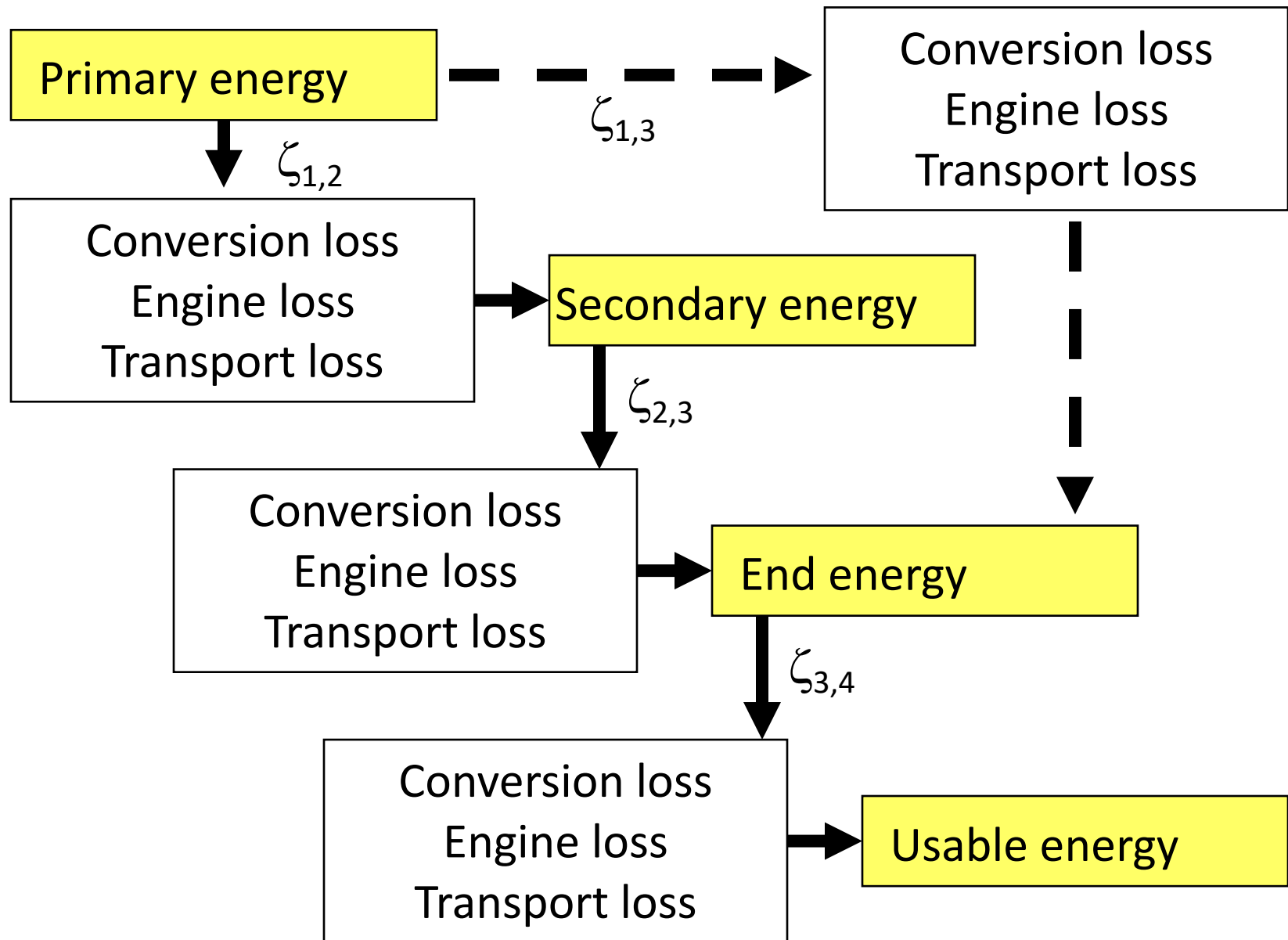
$$Q_2 = Q_1 - W = Q_1 \cdot \left(\frac{T_E}{T_1} \right) \quad \text{Anergy}$$

The heat $Q_1 = \text{Exergy} + \text{Anergy}$ is the sum of Exergy and Anergy.

1.9. DEVELOPMENT OF THE EFFICIENCY

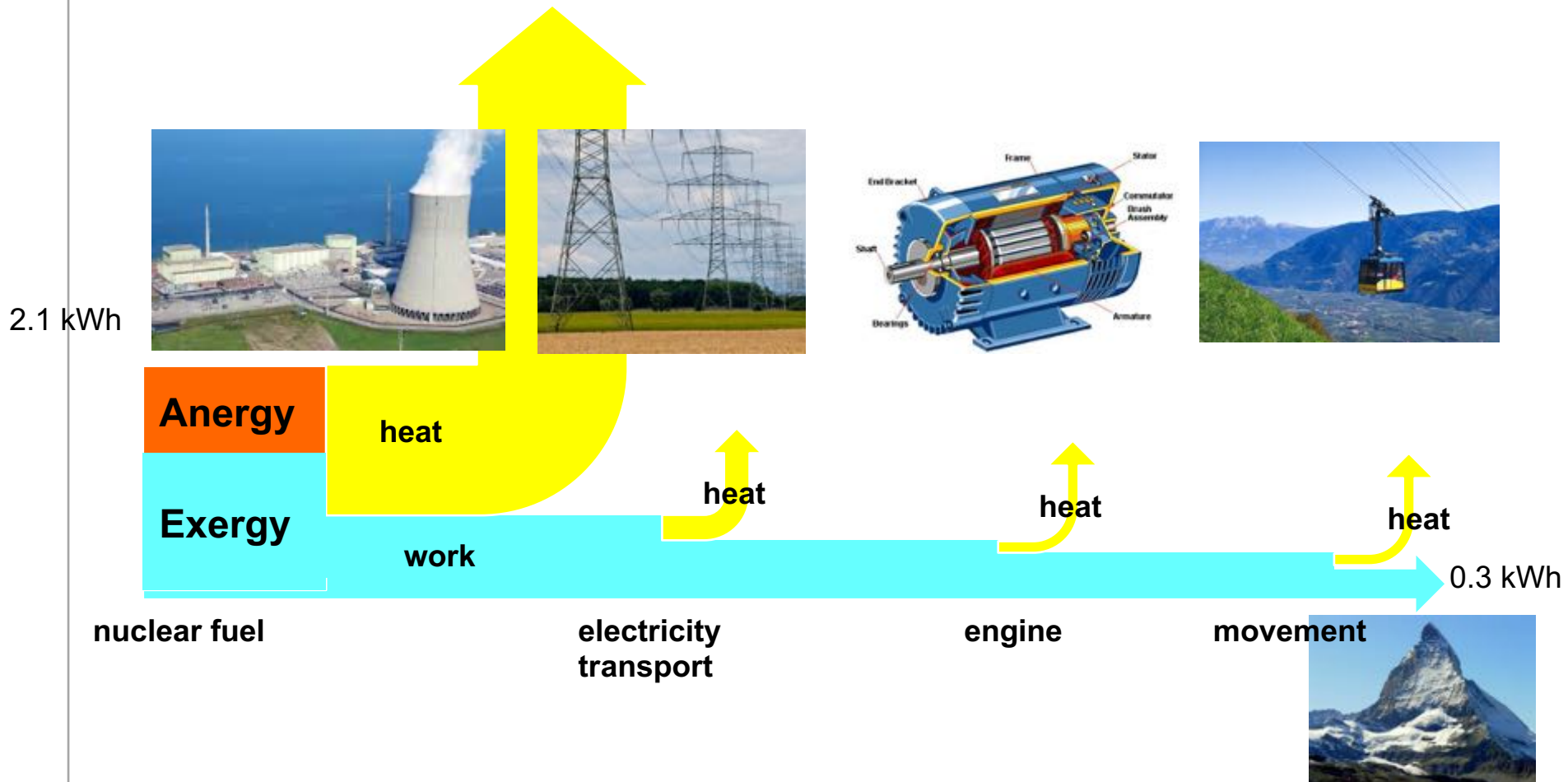


1.10. ENERGY CONVERSION PROCESS

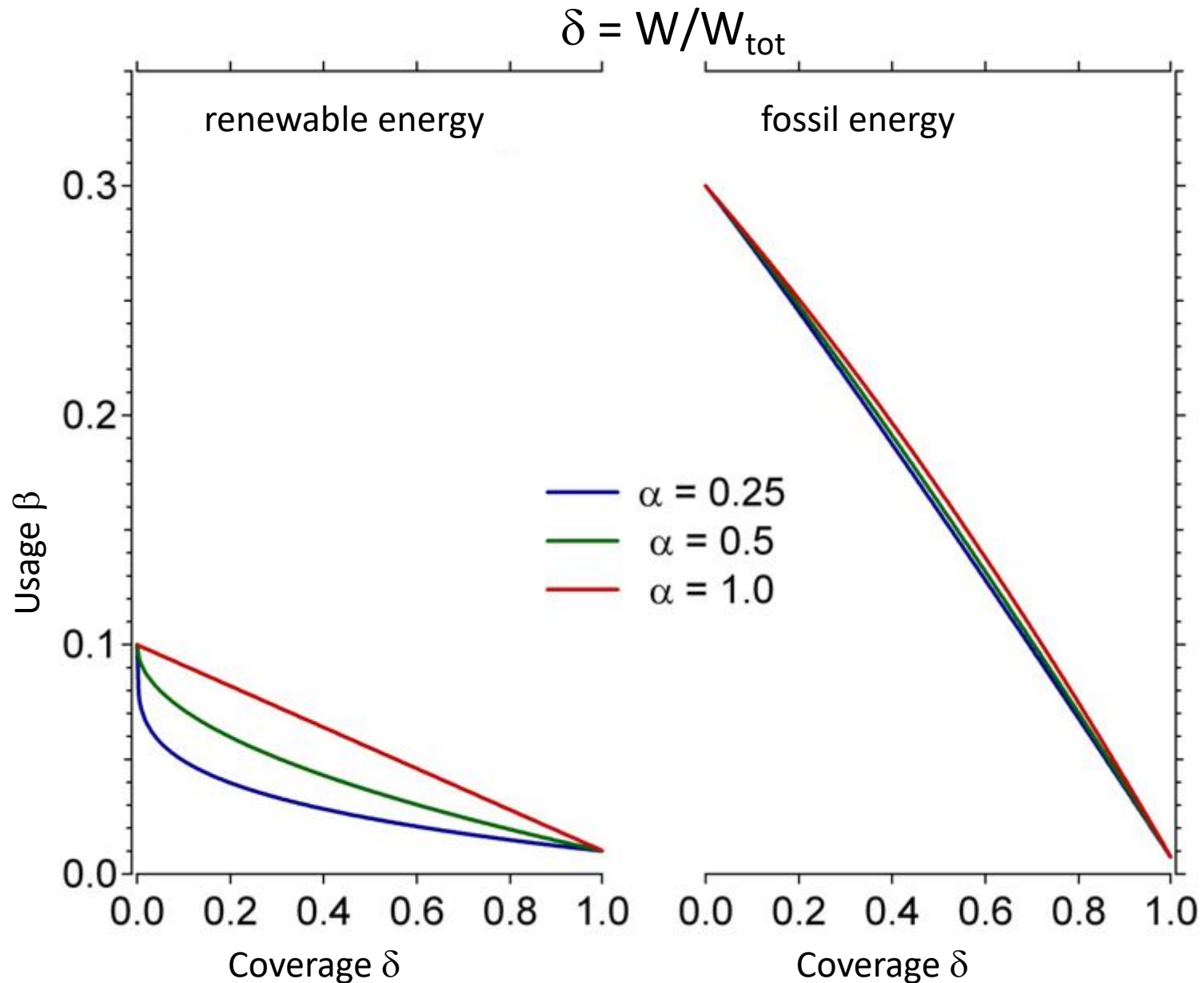


1.10.1. ENERGY CONVERSION PROCESS

Example: Move from the valley to the mountain,
potential energy = $100 \text{ kg} \cdot 9.81 \text{ m/s}^2 \cdot 1000 \text{ m} = 1 \text{ MJ} = 0.3 \text{ kWh}$

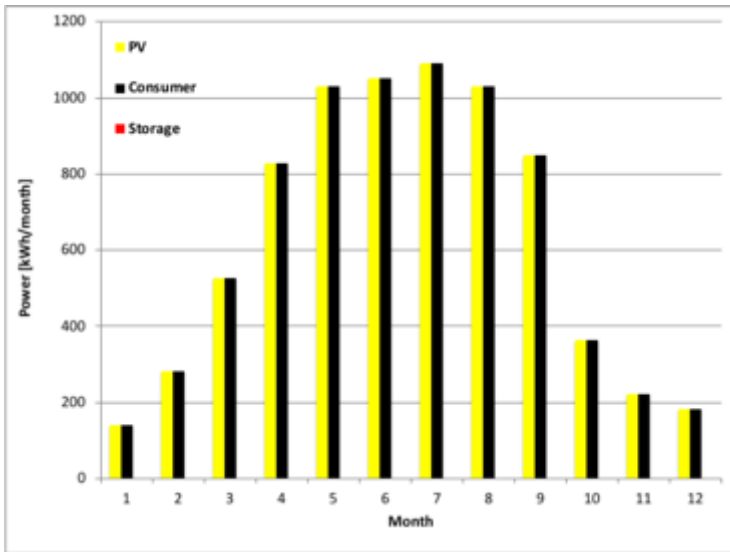


1.11. USAGE versus COVERAGE



1.11.1. EXAMPLE: PHOTOVOLTAICS

Photovoltaics $\eta = 25\%$



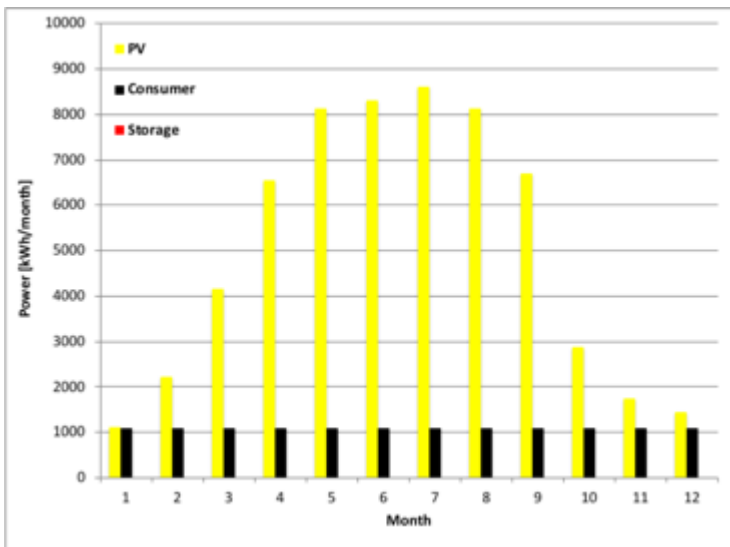
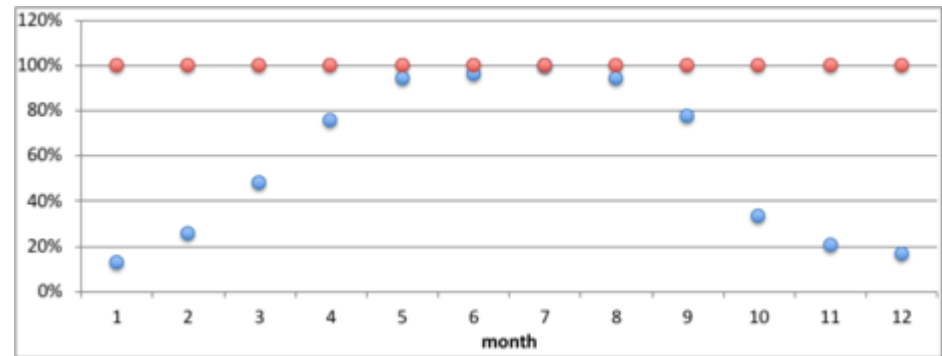
Min. production

Consumption: 13320 kWh

Production: 7600 kWh

coverage = 58%

usage = 25% · 100%



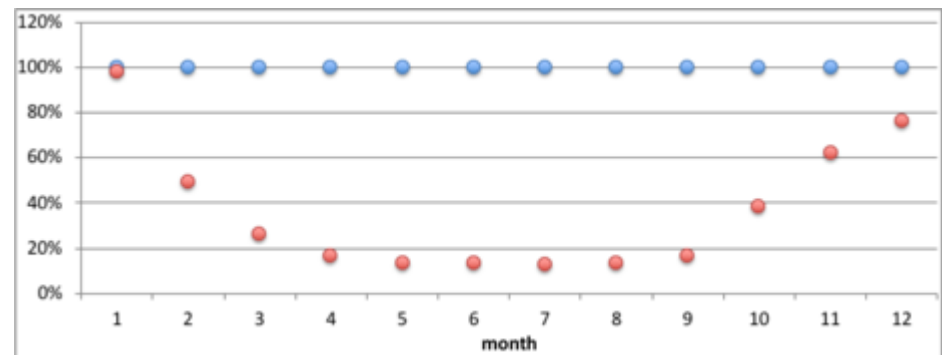
Max. production

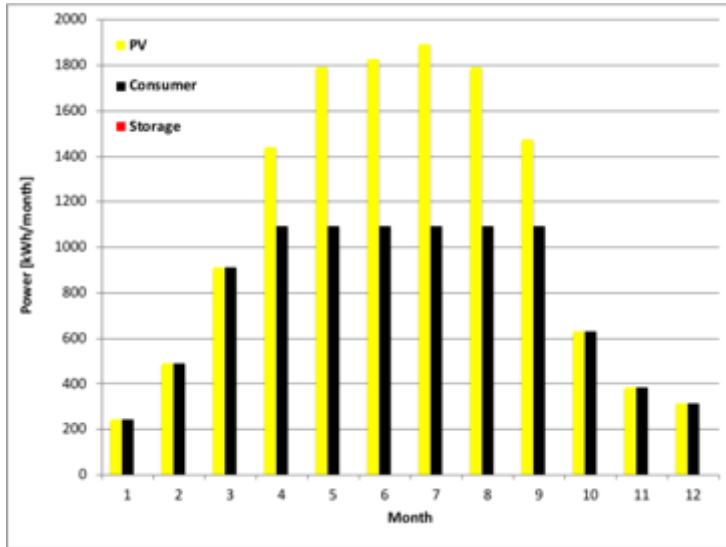
Consumption: 13320 kWh

Production: 64000 kWh

coverage = 100%

usage = 25% · 21%





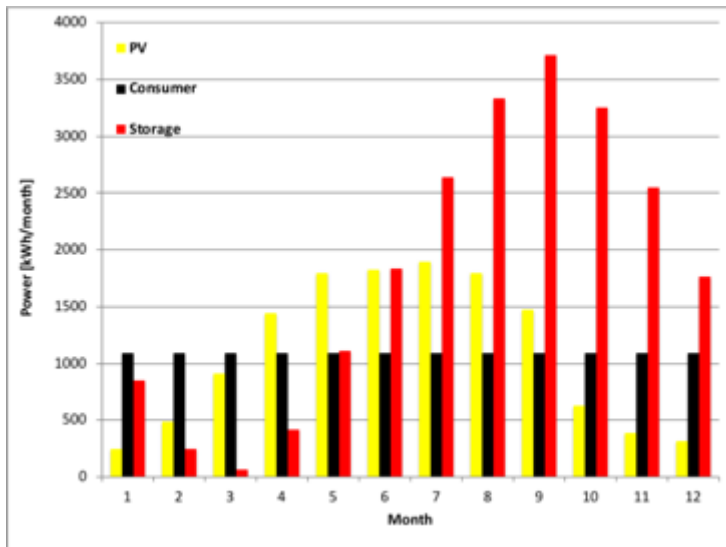
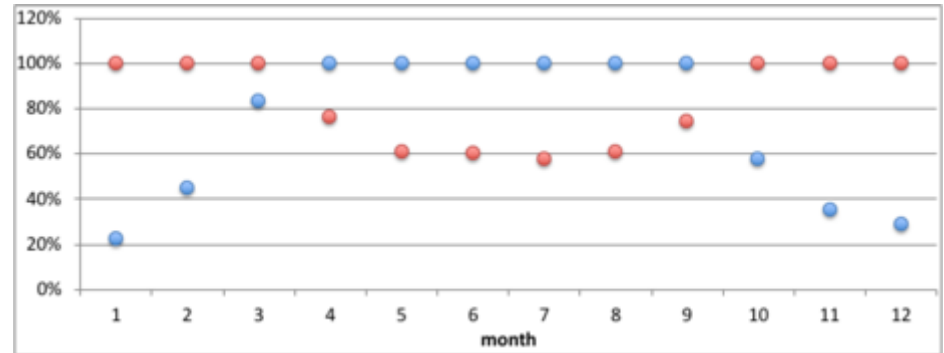
Equal production and consumption

Consumption: 13320 kWh

Production: 13200 kWh

coverage = 20 - 100%

usage = 25% · (60 - 100%)



Equal production and consumption and storage

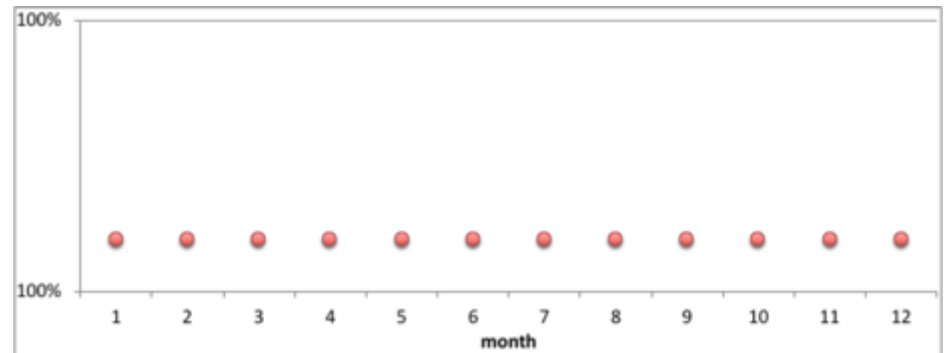
Consumption: 13320 kWh

Production: 13320 kWh

Storage: 5900 kWh

coverage = 100%

usage = 100%



1.12. ENERGY and POWER

Energy
(E or E/m or E/V)



8000 kJ = 2.4 kWh



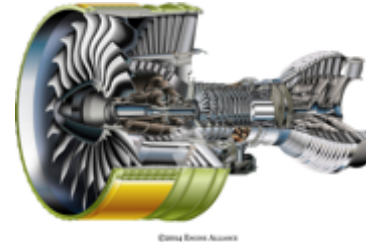
1300 MWh



Power
($P = dE/dt$)



8000 kJ/day = 100 W

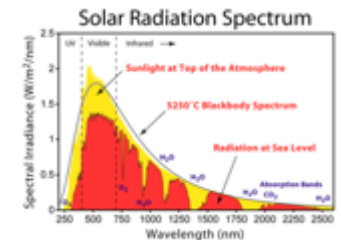


160 MW



33'000 TW

Intensity
($I = dP/dA$)



1.3 kW/m²

1.13. ENERGY CARRIER and ENERGY FLUX



$$\text{Energy: } W + Q$$

$$\text{Power: } P = \frac{d(W+Q)}{dt}$$



1.13.1. EXAMPLE Space Shuttle

1535 m³ liq. H₂, 120t

m = 2'000 t, 2 solid state rockets 590 t (500t fuel, energy density 2.78 kWh/kg) each

Reaction: $10\text{Al} + 6\text{NH}_4\text{ClO}_4 \rightarrow 4\text{Al}_2\text{O}_3 + 2\text{AlCl}_3 + 12\text{H}_2\text{O} + 3\text{N}_2$



1.13.1. EXAMPLE Space Shuttle

1535 m³ liq. H₂, 120t

m = 2'000 t, 2 solid state rockets 590 t (500t fuel, energy density 2.78 kWh/kg) each

Reaction: $10\text{Al} + 6\text{NH}_4\text{ClO}_4 \rightarrow 4\text{Al}_2\text{O}_3 + 2\text{AlCl}_3 + 12\text{H}_2\text{O} + 3\text{N}_2$



t = -60s



t = -10s



t = 0s ignition



t = 2s take off



t = 42s speed of sound



t = 120s release buster rockets

1.14. RENEWABLE ENERGY CONVERSION AND STORAGE

Energy carrier

Energy flux

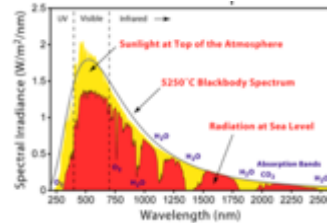
Conversion

Storage

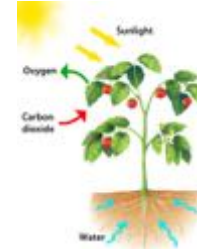
Sun (H)



Intensity



Photosynthesis



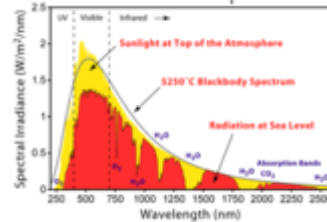
Biomass / Oil



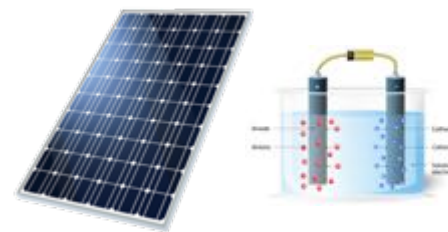
Sun (H)



Intensity



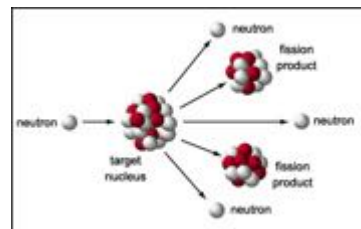
Photovoltaik/Electrolysis



Hydrogen


nuclear fuel (U²³⁵)


fission (n)



Turbine



Battery



EXERCISES 1

- 1) Describe the forms of work and heat you know, e.g. potential energy $W = m \cdot g \cdot h$ or heat capacity $Q = m \cdot c \cdot dT$. Make an example to each form with the corresponding quantity.
- 2) Calculate the energy consumed of an average human (J/day) and convert into power (Watts).
- 3) Compare in view of energy and entropy the heating of 1kg of water from 10°C to 100°C by using a coal fire (800°C).
- 4) Calculate the Exergy and Anergy of coal fire (800°C), in the steam entering the turbine (400°C), in boiling hot water (100°C) and in a heated room (22°C) when the temperature of the environment is at 15°C .
- 5) Calculate the primary energy necessary and the increase of entropy for drinking a cup of tea. Describe the energy chain from primary to usable energy and all the conversion steps.