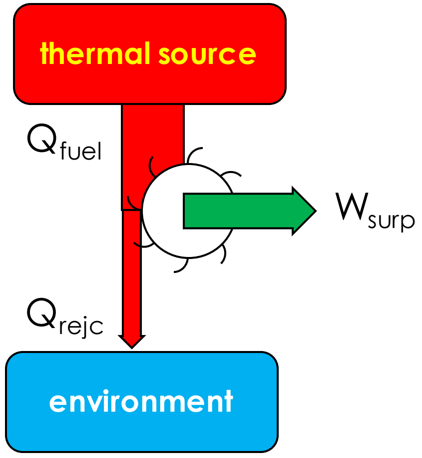
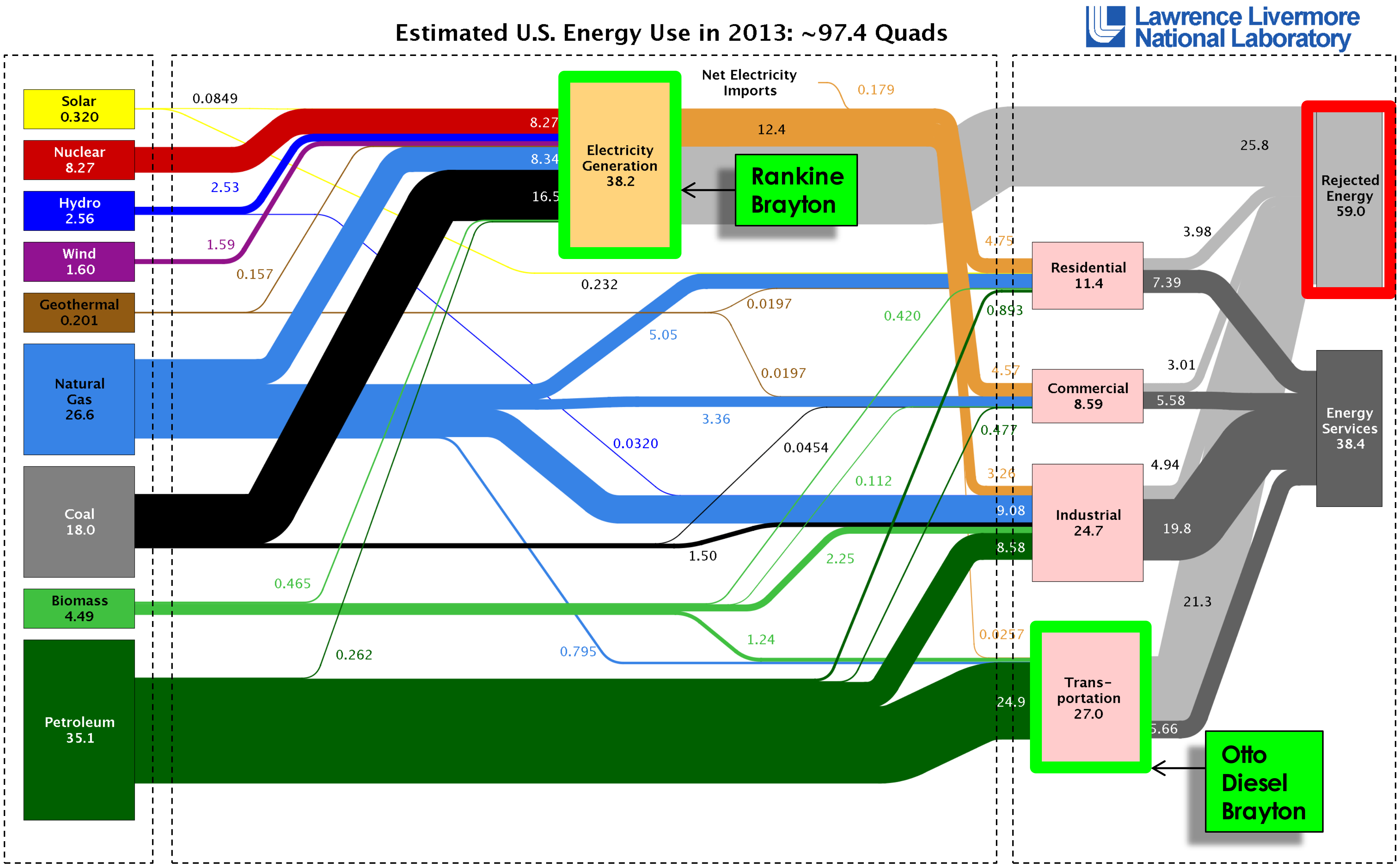
EXERGY ANALYSIS: integrating the 1st and 2nd laws of thermodynamics

Prof. Paulo Seleghim Jr.
Universidade de São Paulo



$$\eta = \frac{W_{surp}}{Q_{fuel}} \overset{2^{nd}}{<} 1$$



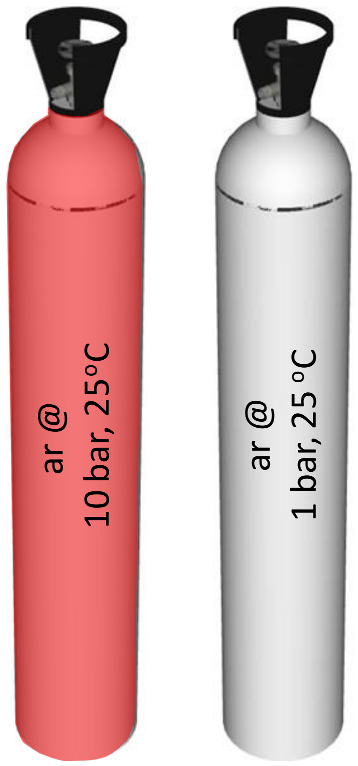
primary sources

energy vectors

application sectors

Sankey Diagram

How to maximize the conversion efficiency of an energy vector to useful energy ? (electricity, kinetic energy, etc.)



From which of these two systems is it possible to "generate" the greatest amount of mechanical work ?


P
∀
ar @
10 bar, 25°C
torque × rotação

ar @
10bar, 25^{O}c

10bar, 25^{O}c

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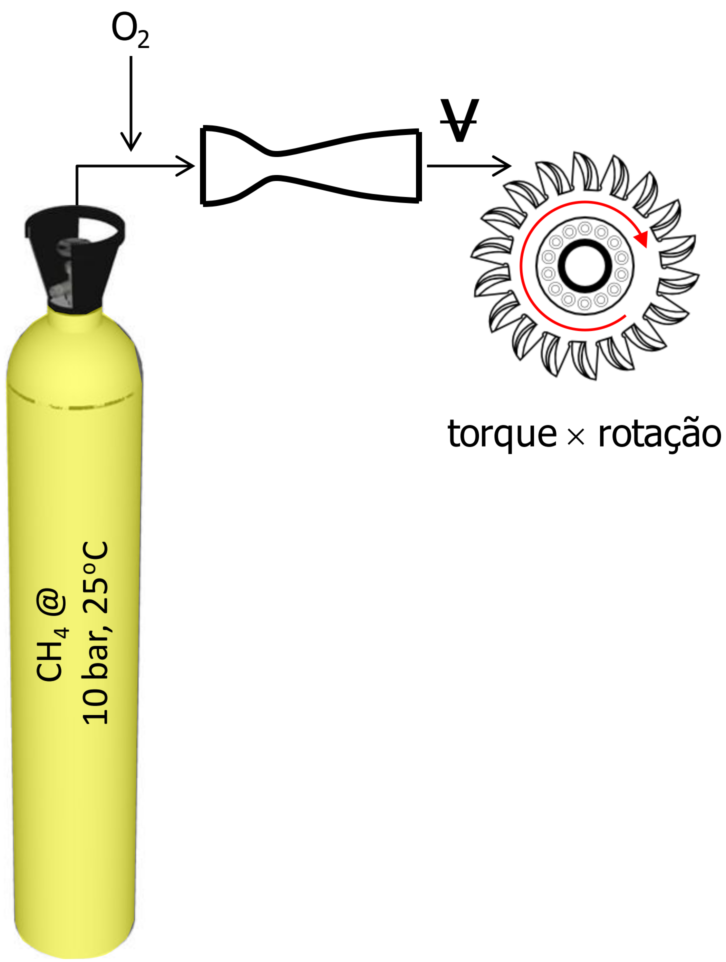
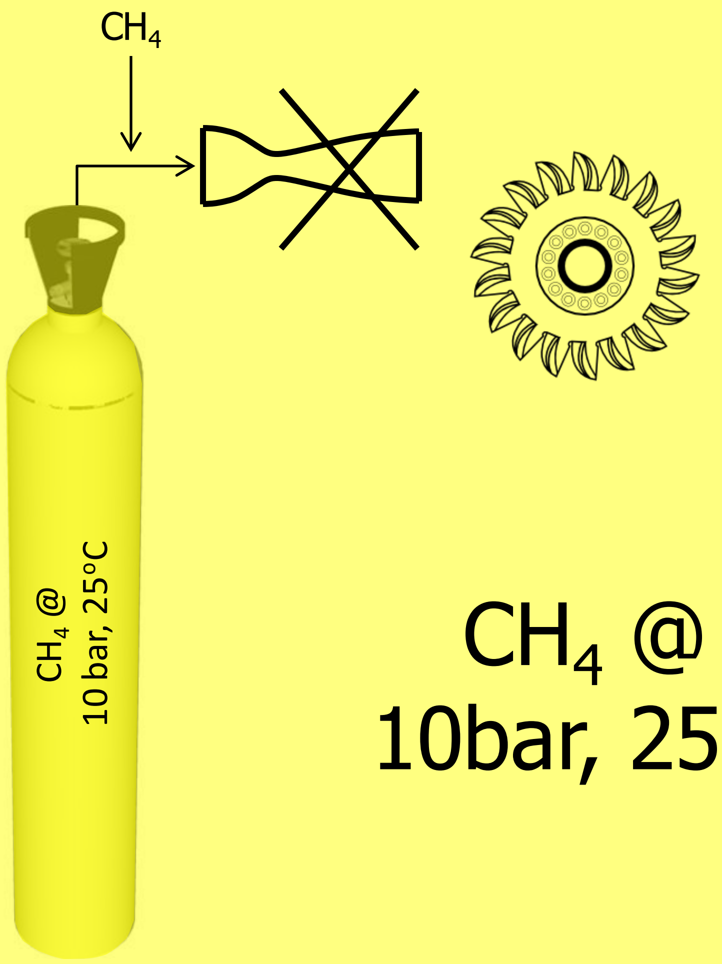


10bar, 25ºc



CH_4 @
10bar, 25^{O}c

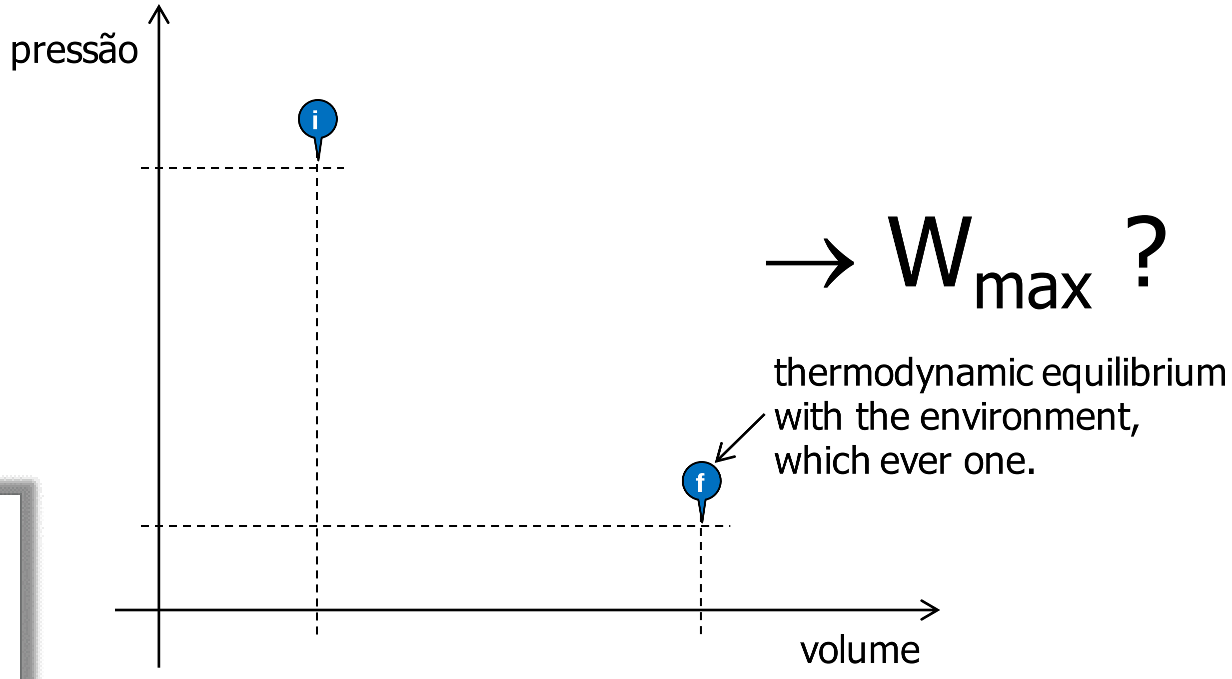
10bar, 25^{O}c

CONCLUSION:

the capacity to generate work is a **COMBINED** property of the thermodynamic state of the system (P and T) and the environment !

The maximum amount of work (mechanical energy) that one can obtain from a system is obtained by bringing it to equilibrium with the environment through a reversible transformation…

Nicolas Léonard Sadi Carnot
em 1824, aos vinte anos de idade



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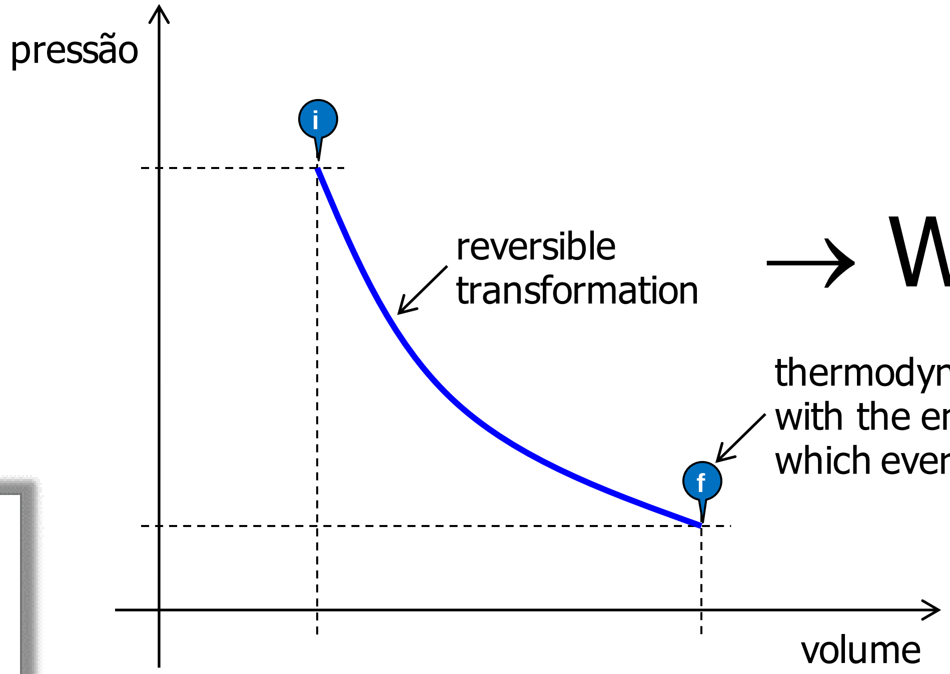

$\rightarrow W_{max}$?

thermodynamic equilibrium
with the environment,
which ever one.

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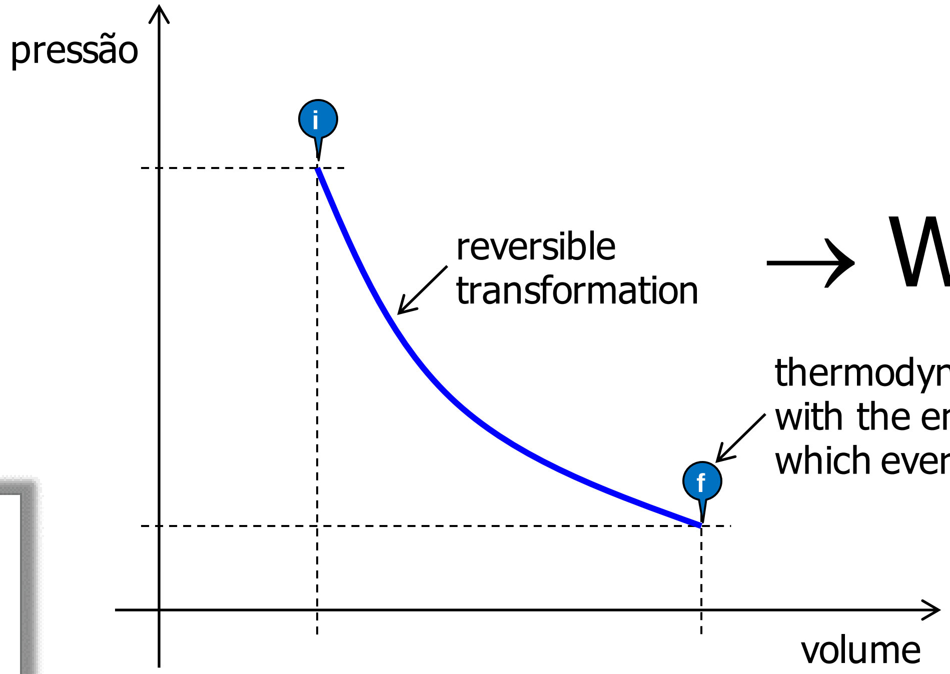
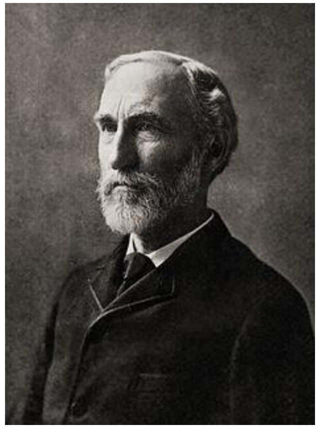


$\rightarrow W_{max}$?

thermodynamic equilibrium with the environment, which ever one.

- Air @ 1bar, 25^{O}c
- Ar @ 10bar, 25^{O}c
- CH_4 @ 10bar, 25^{O}c
- Vacuum...

DEFINITIONS

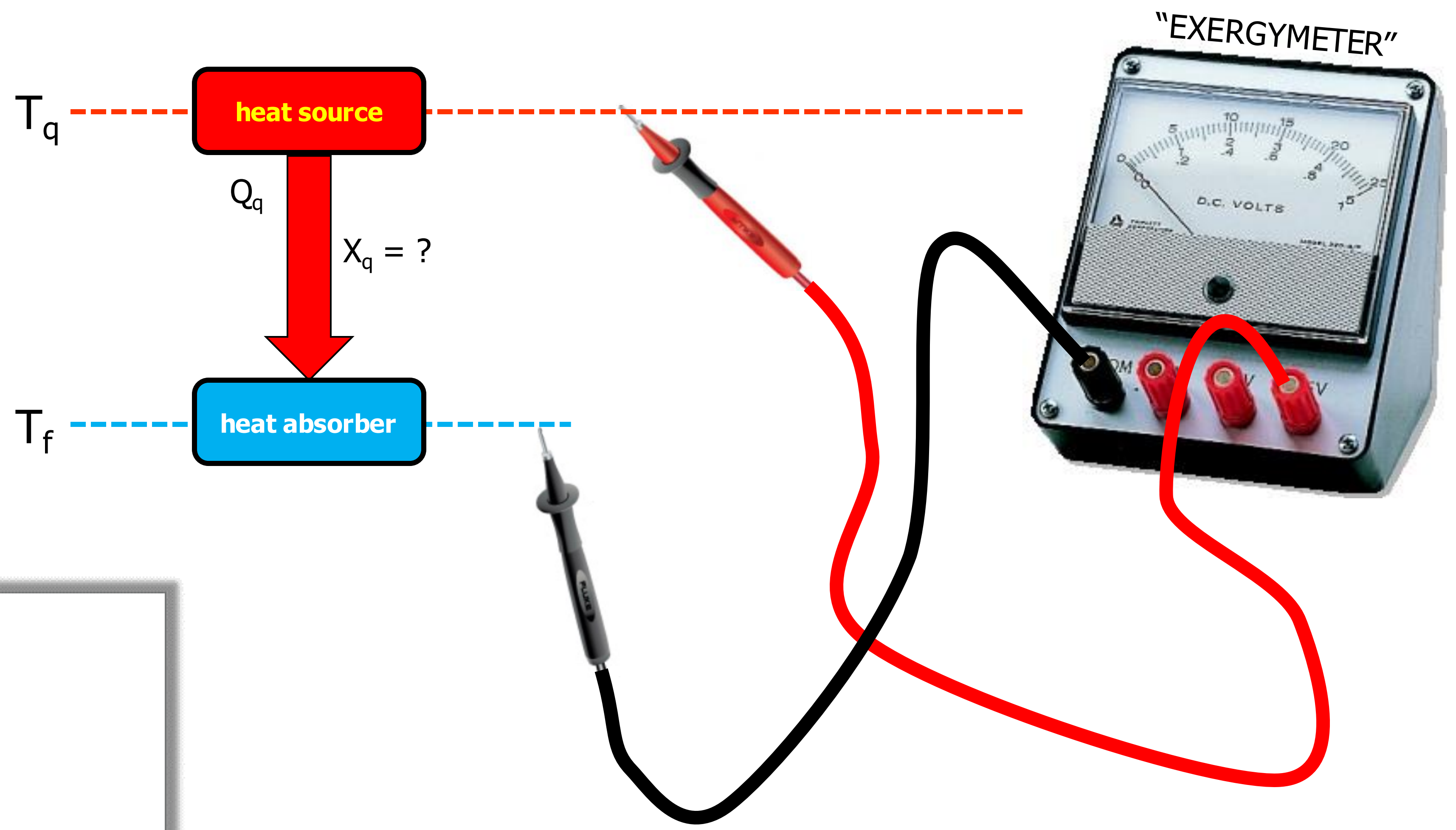

J. Willard Gibbs

"Useful work potential": is the maximum amount of mechanical energy that one can obtain from a system, the difference being inevitably lost to the environment due to the implications of the 2nd law.

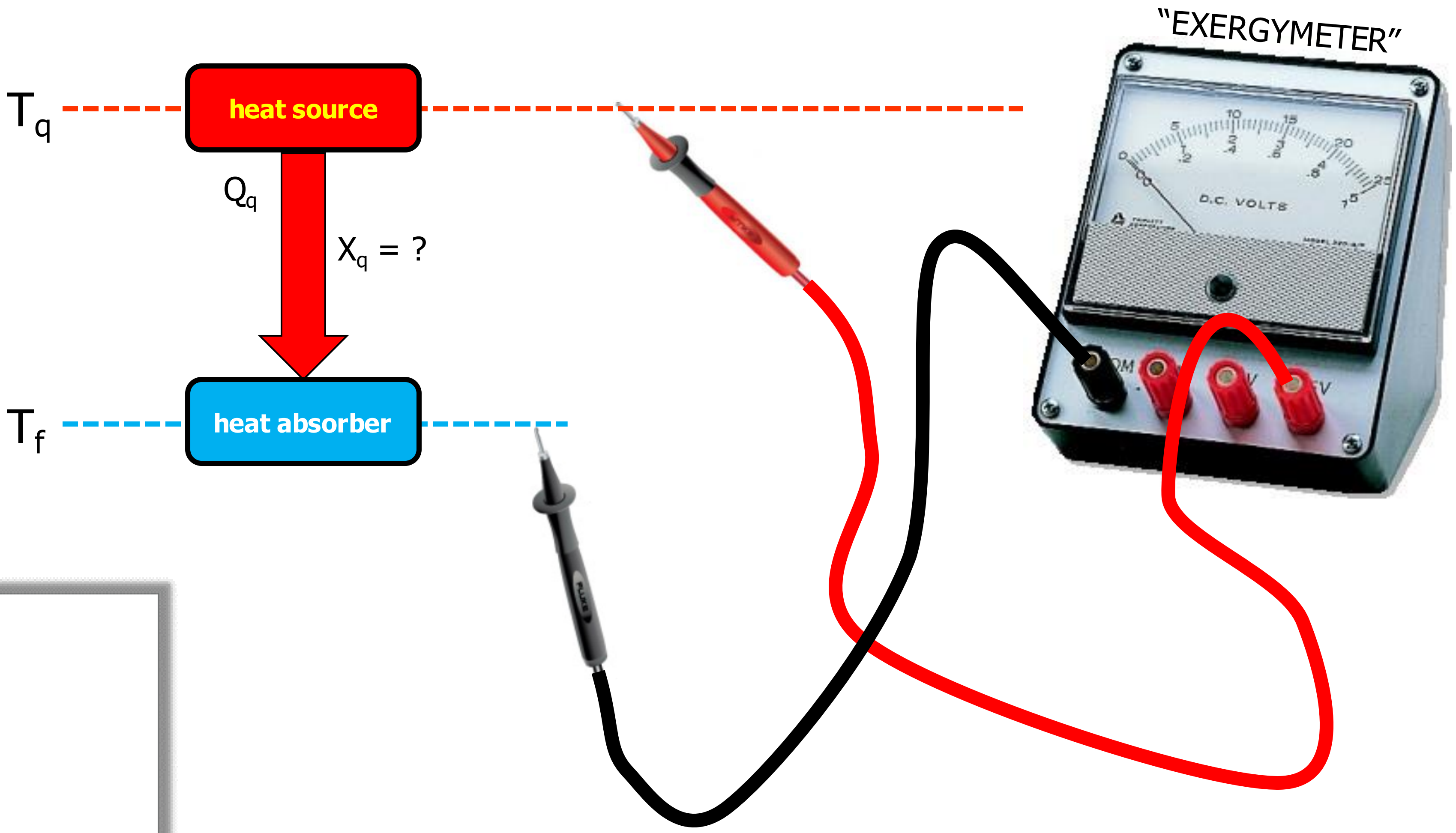
EXERGY ⇨

Available energy
Exergetic energy
Availability
Reversible work
Etc.

Exergy associated with the heat supplied by a thermal source…



Exergy associated with the heat supplied by a thermal source... is equal to the work produced by a reversible cycle operating between the thermal reservoirs and the environment



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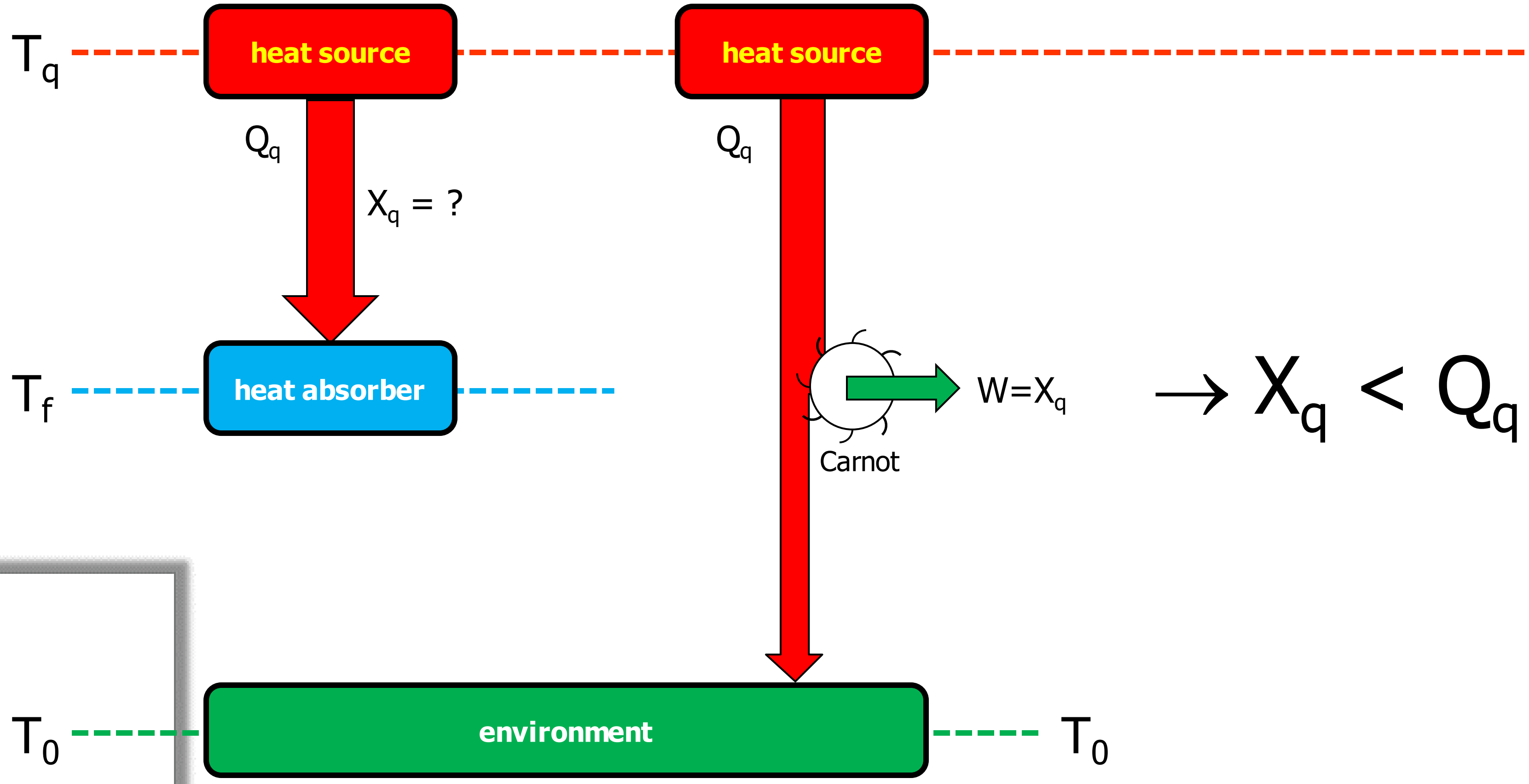

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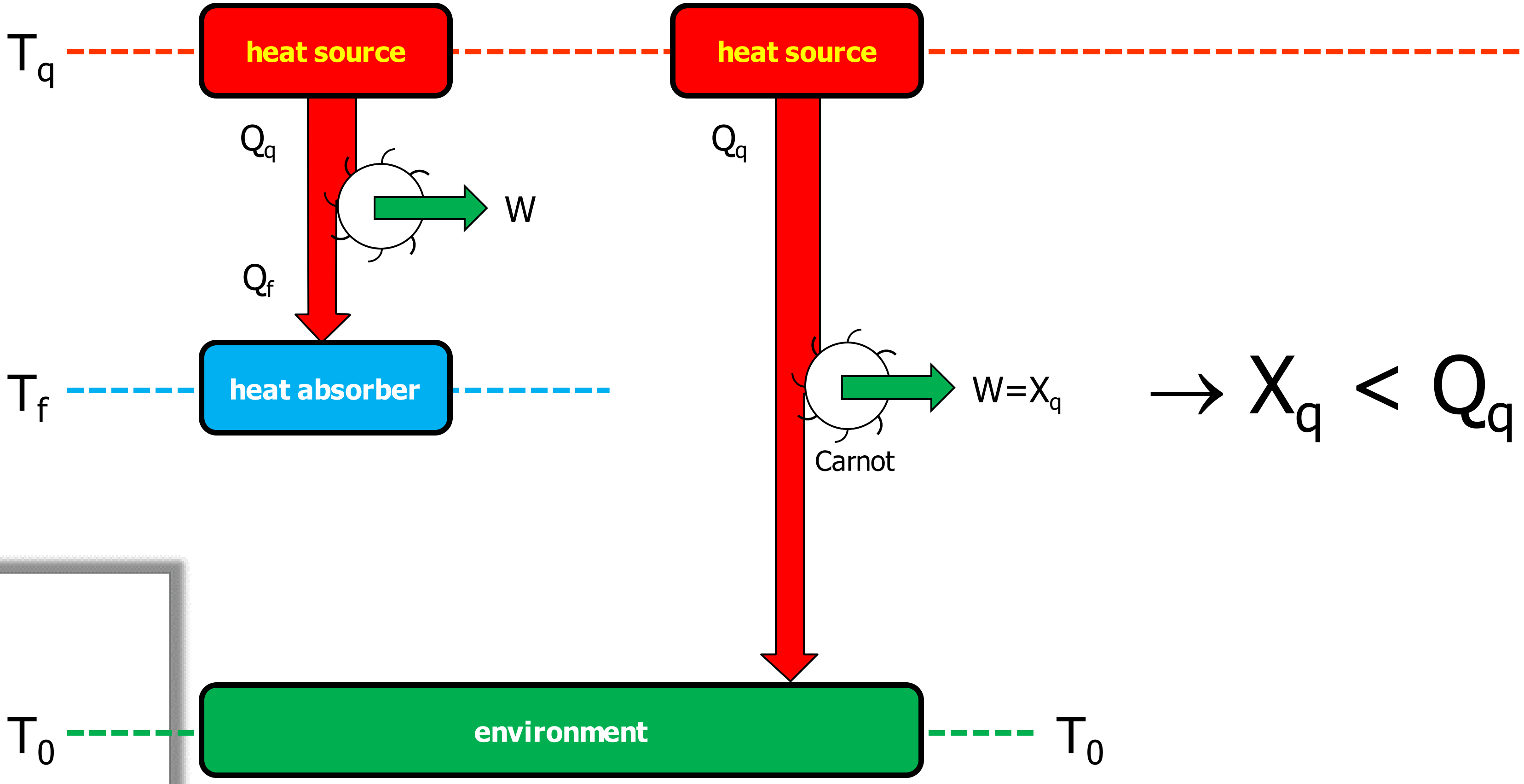

$\rightarrow X_q < Q_q$

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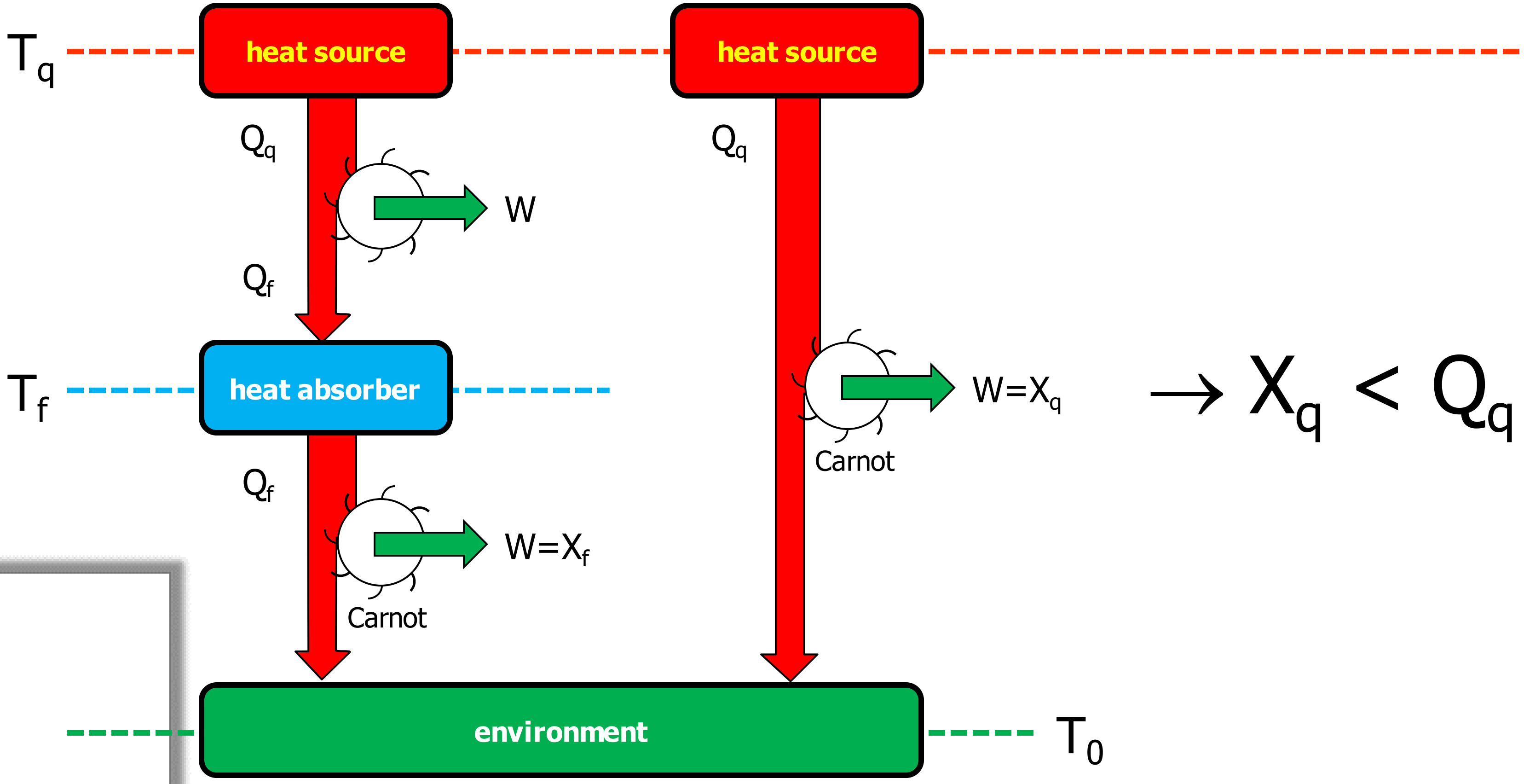

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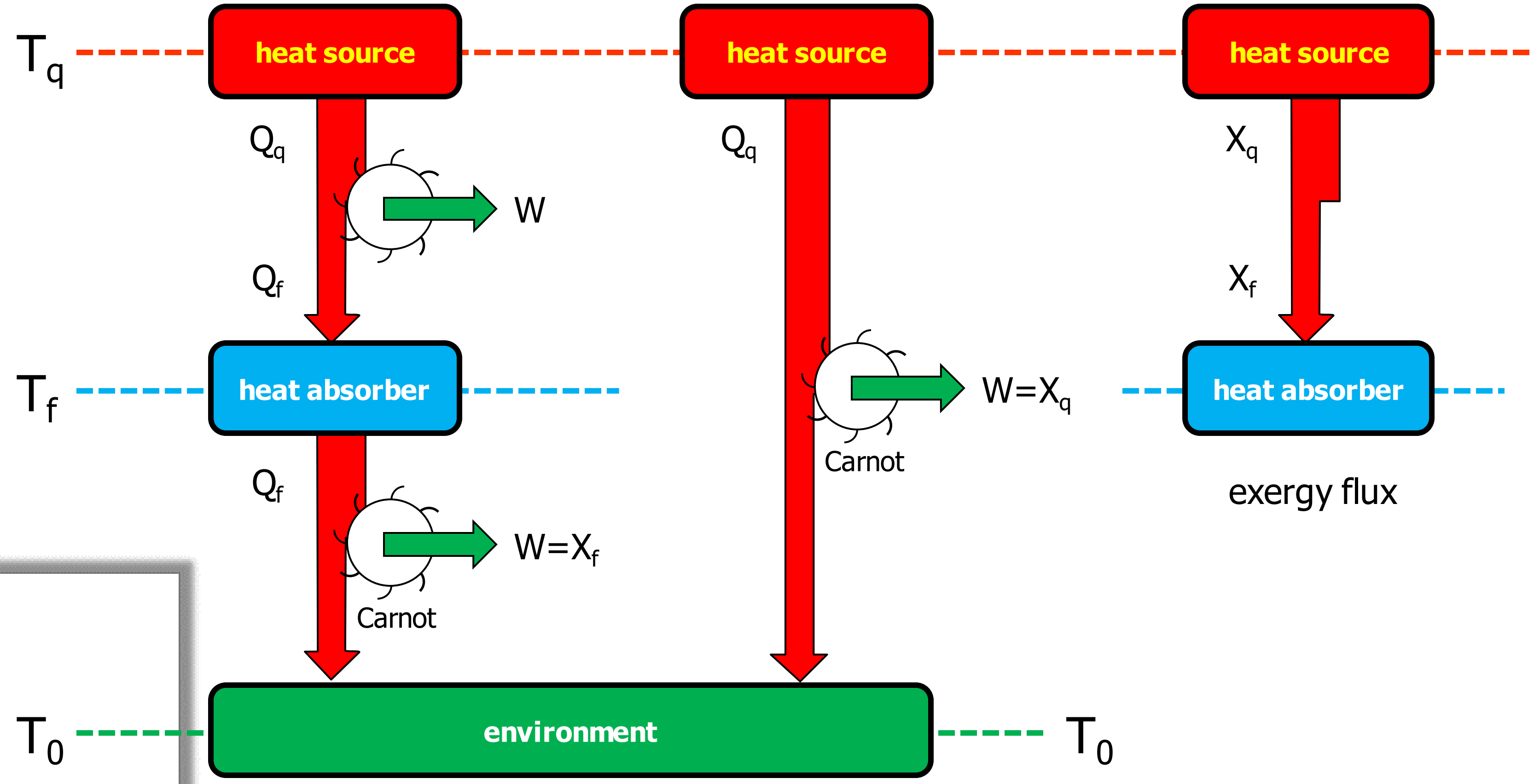

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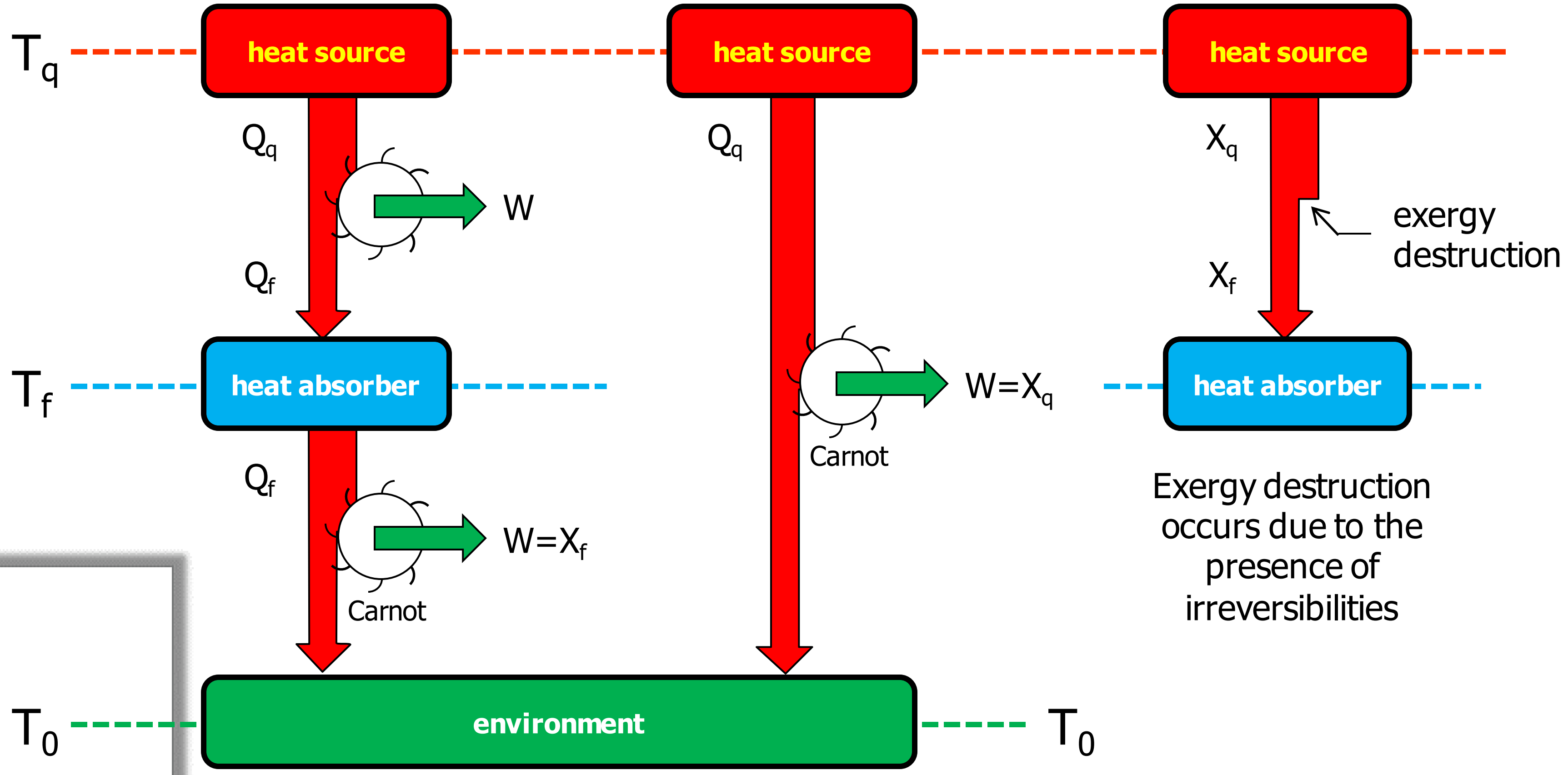

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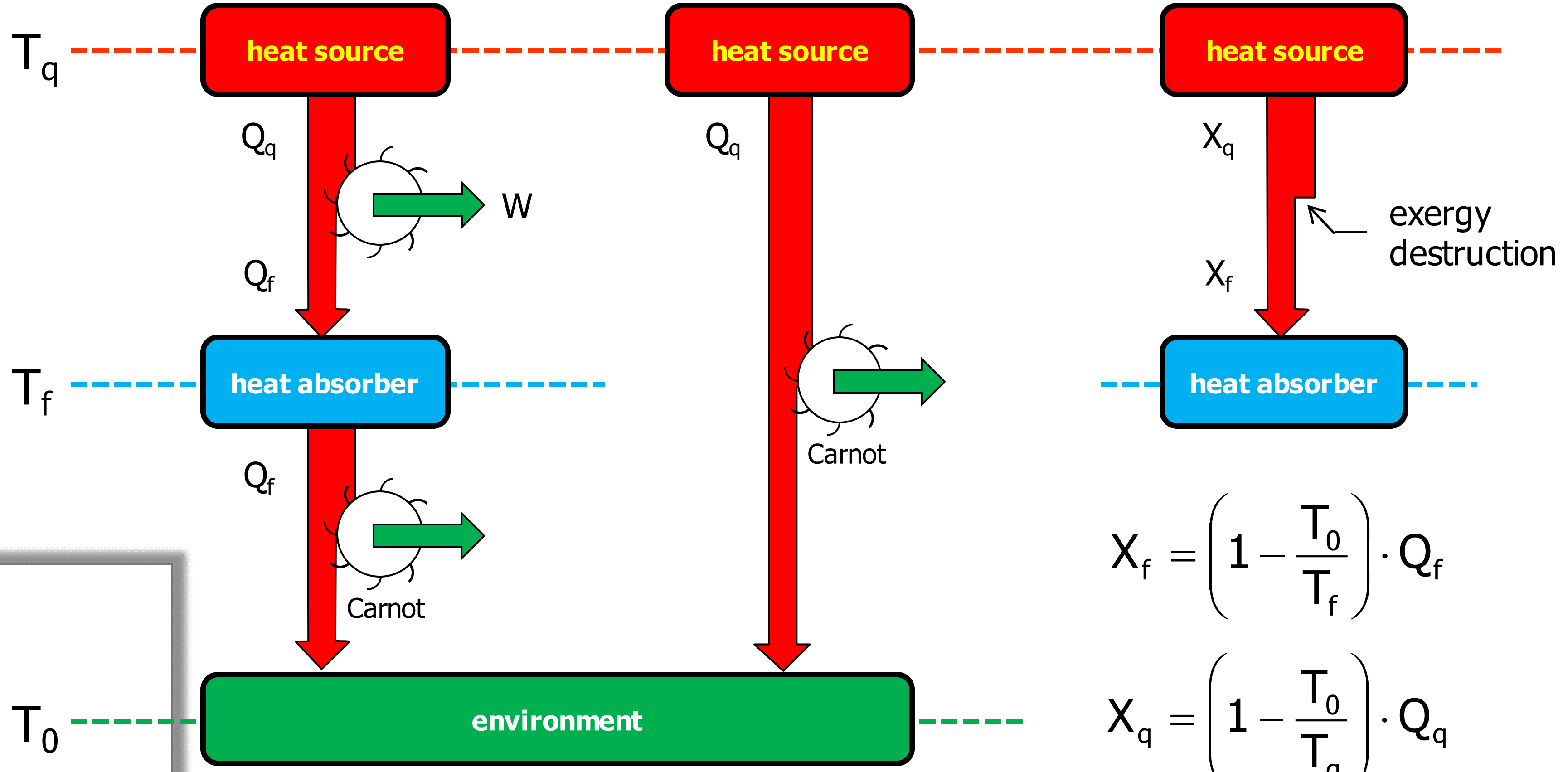
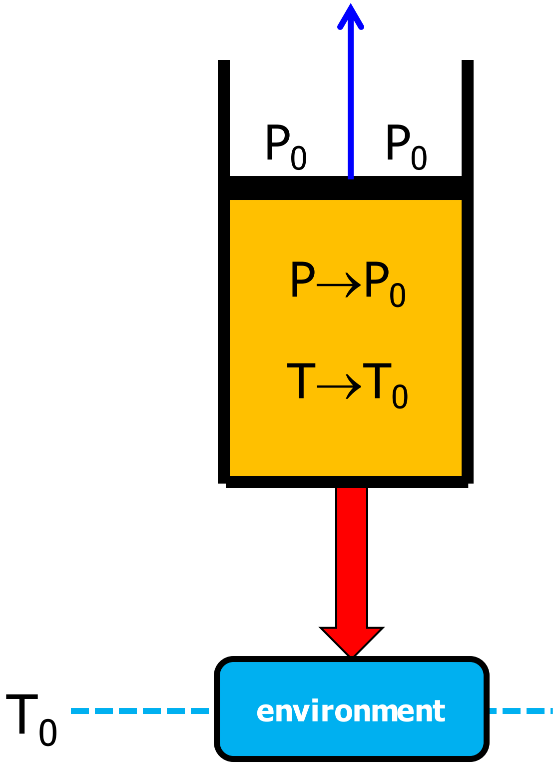


$$X_f = \left(1 - \frac{T_0}{T_f}\right) \cdot Q_f$$

$$X_q = \left(1 - \frac{T_0}{T_q}\right) \cdot Q_q$$

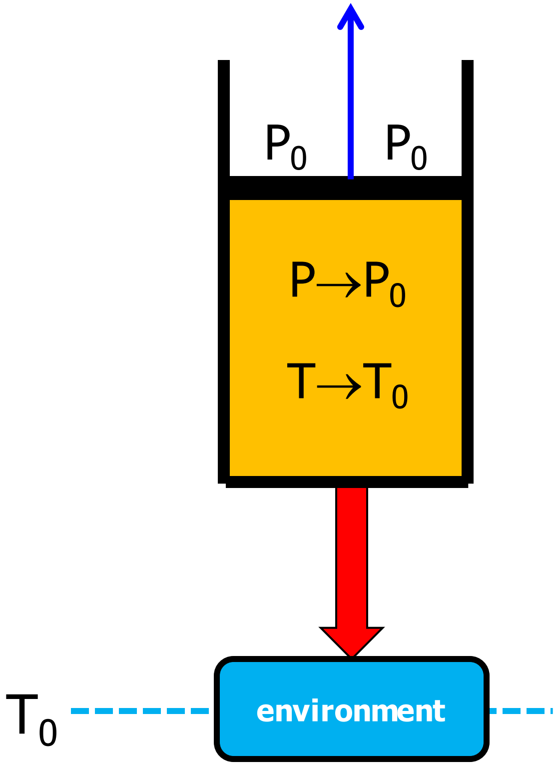
Closed system analysis

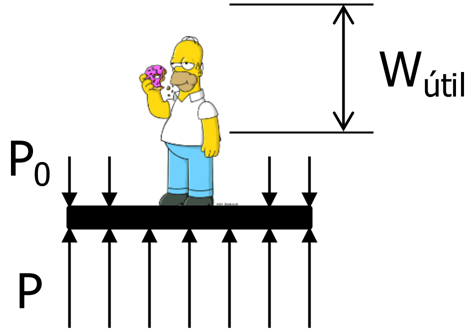
Variation of the amount of exergy in a closed system



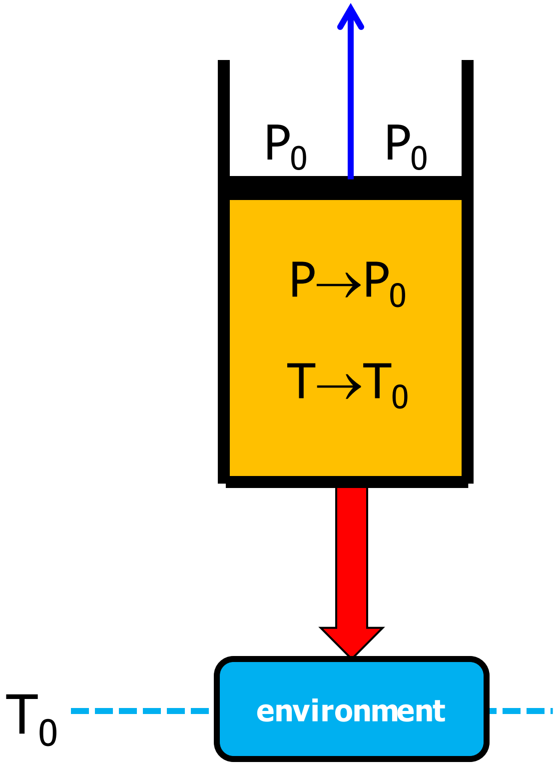
Expansion of the system with exportation of mechanical work until it reaches the equilibrium with the environment…

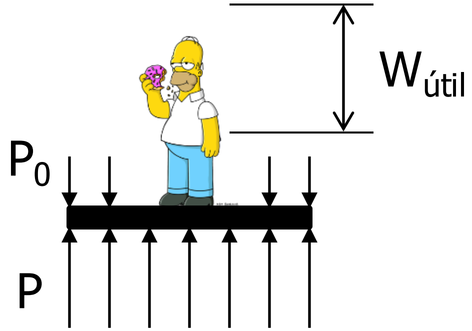
Variation of the amount of exergy in a closed system





Variation of the amount of exergy in a closed system

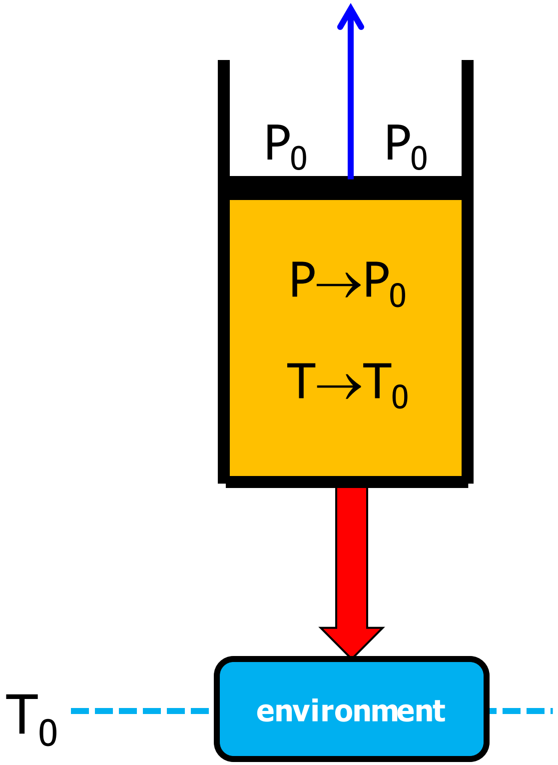


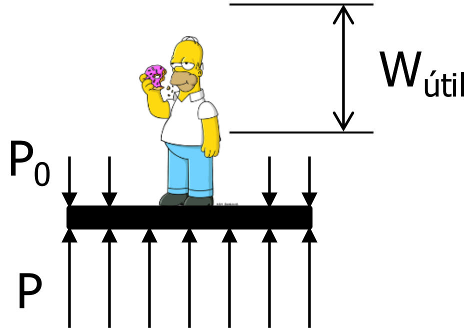


$$\delta W = P \cdot dV$$

work going out of the system

Variation of the amount of exergy in a closed system

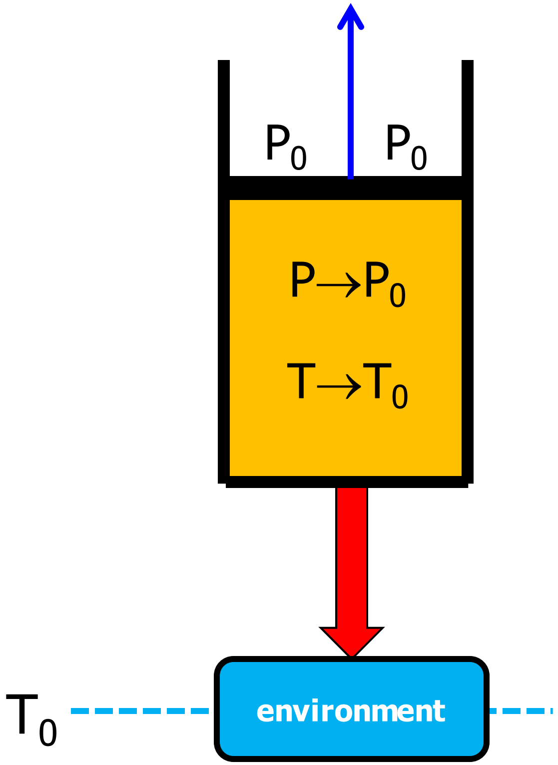


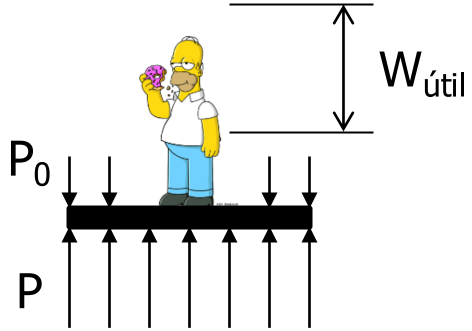


$$\delta W = P \cdot dV$$

$$\delta W = (P - P_0) \cdot dV + P_0 \cdot dV$$

Variation of the amount of exergy in a closed system





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$$\delta W = \delta W_{útil} + P_0 \cdot dV$$

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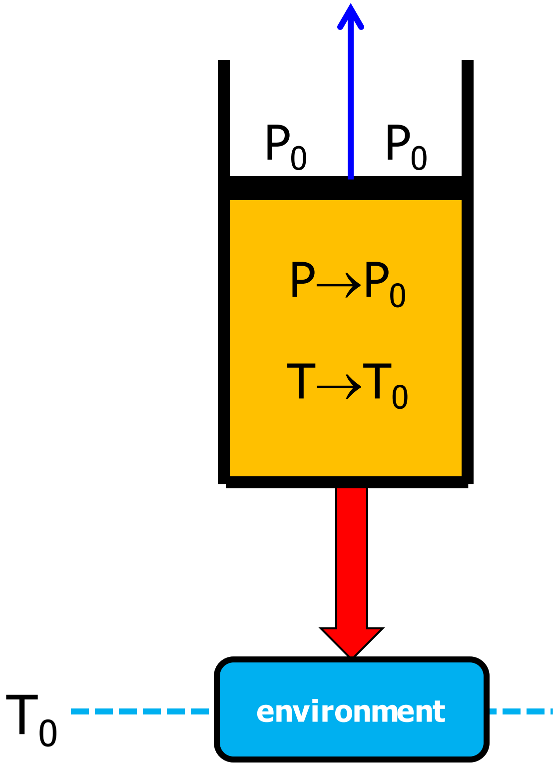

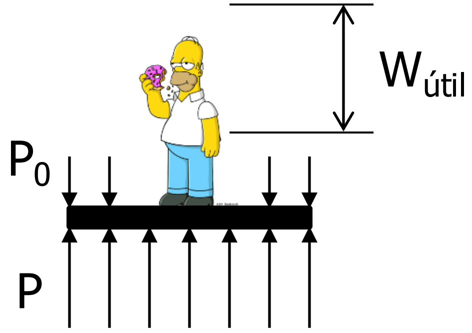

$$\delta W = P \cdot dV$$

$$\delta W = (P - P_0) \cdot dV + P_0 \cdot dV$$

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$$W = W_{útil} + \int P_0 \cdot dV$$

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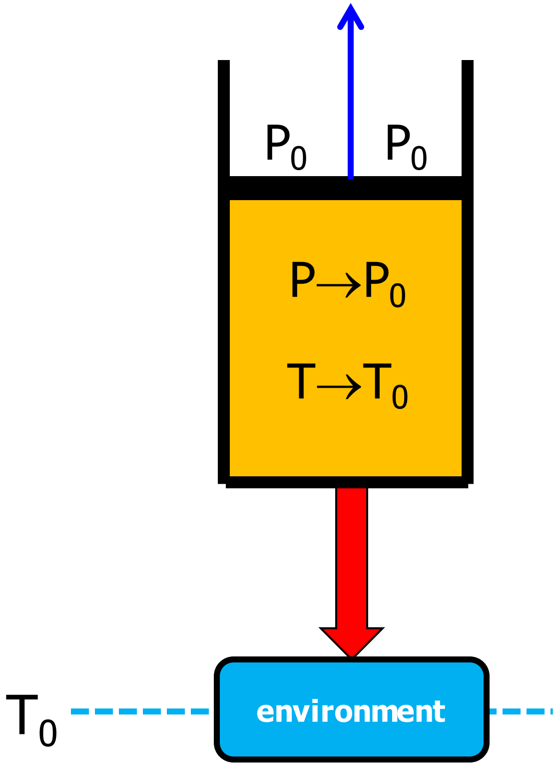

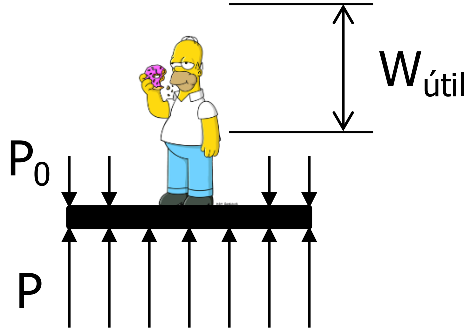

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$$W = W_{útil} + P_0 \cdot (V_2 - V_1)$$

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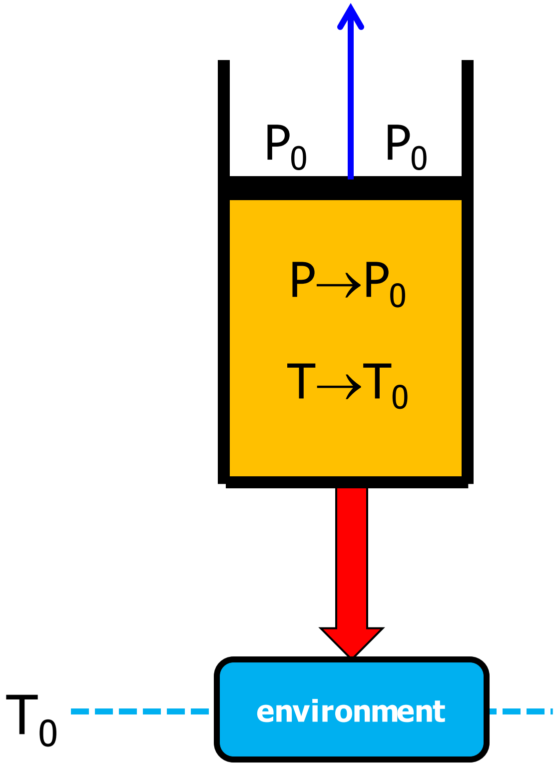

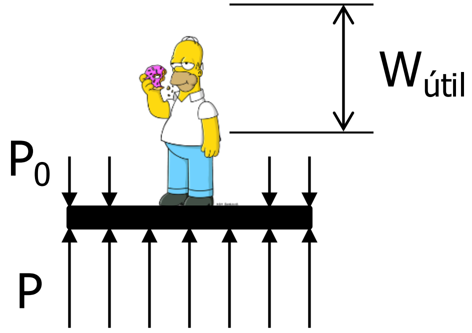

$$\boxed{W = W_{útil} + W_{env}}$$

$$\delta W = P \cdot dV$$

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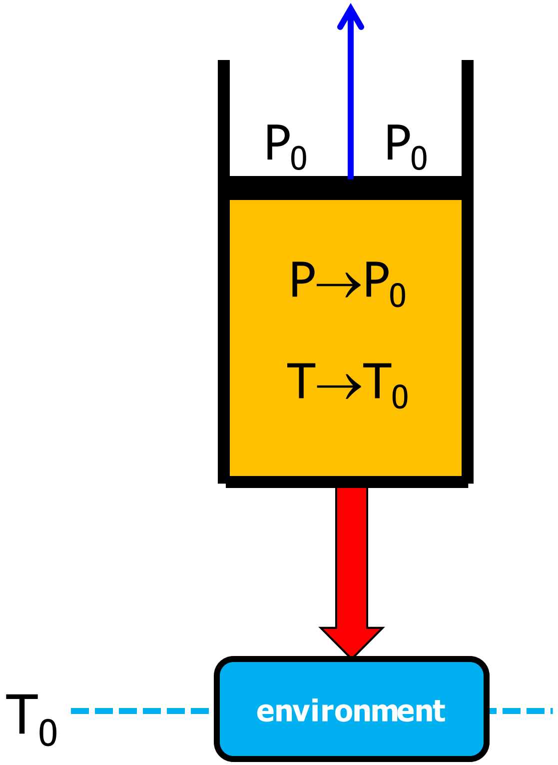
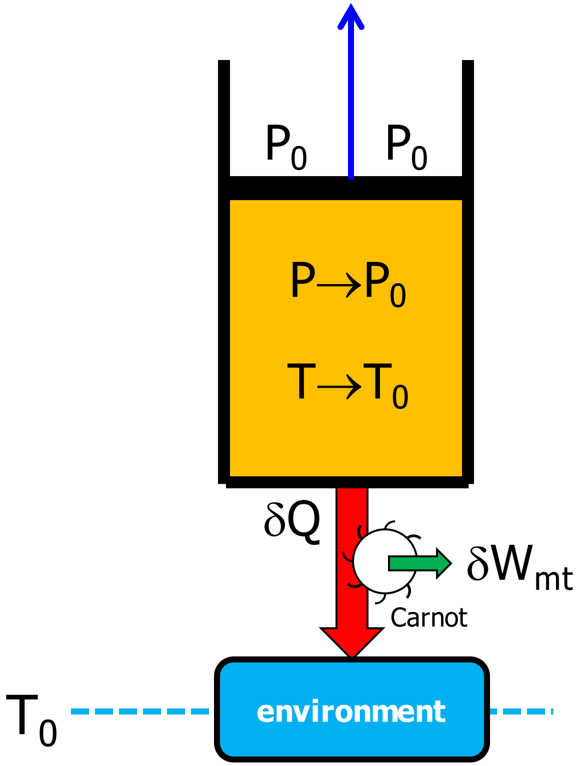


$$\delta W = \delta W_{útil} + P_0 \cdot dV$$

$$\delta Q\big|_{rev} \overset{def}{=} T \cdot dS$$

Variation of the amount of exergy in a closed system



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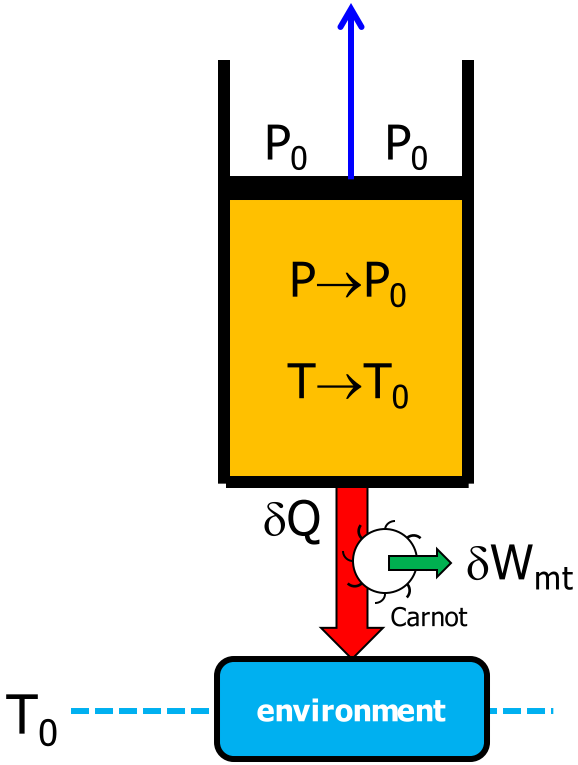

$$\Rightarrow \quad \delta W = \delta W_{útil} + P_0 \cdot dV$$

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$$\delta W_{mt} = \left(1 - \frac{T_0}{T}\right) \cdot \delta Q$$

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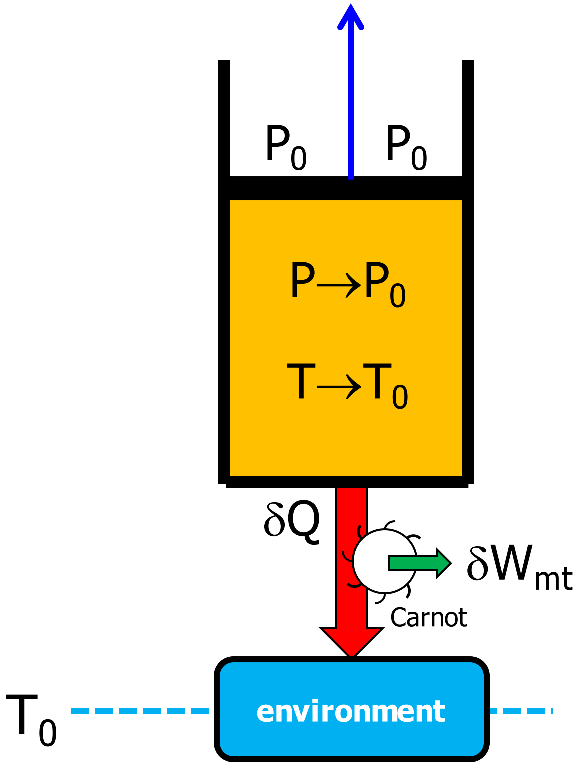

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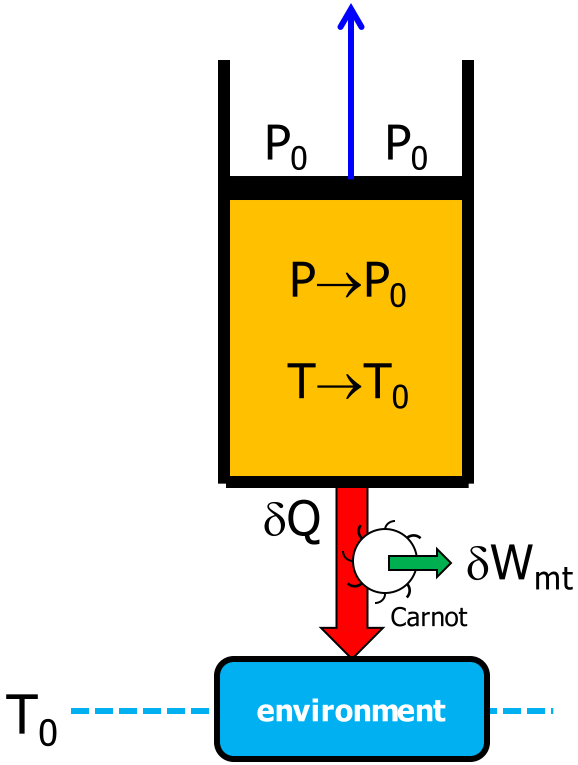

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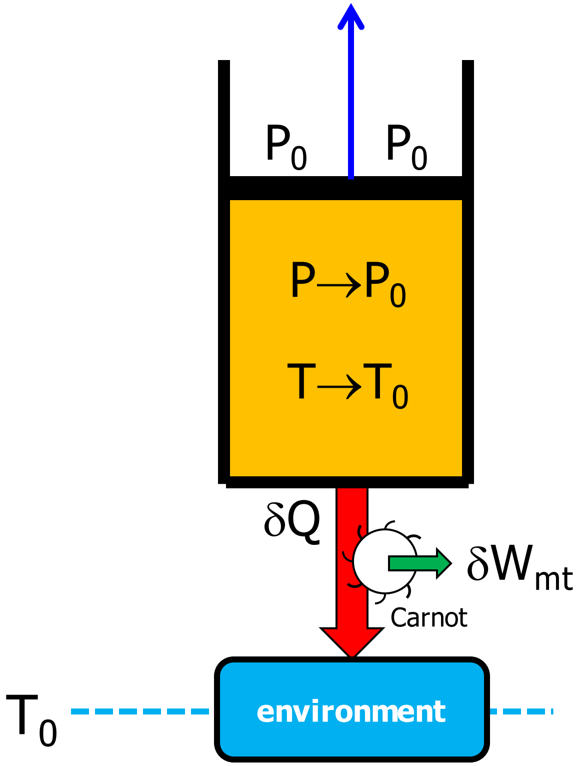
$$dU = \underset{\substack{\downarrow \\ \text{heat going out} \\ \text{of the system}}}{-\delta Q} - \delta W$$

Variation of the amount of exergy in a closed system



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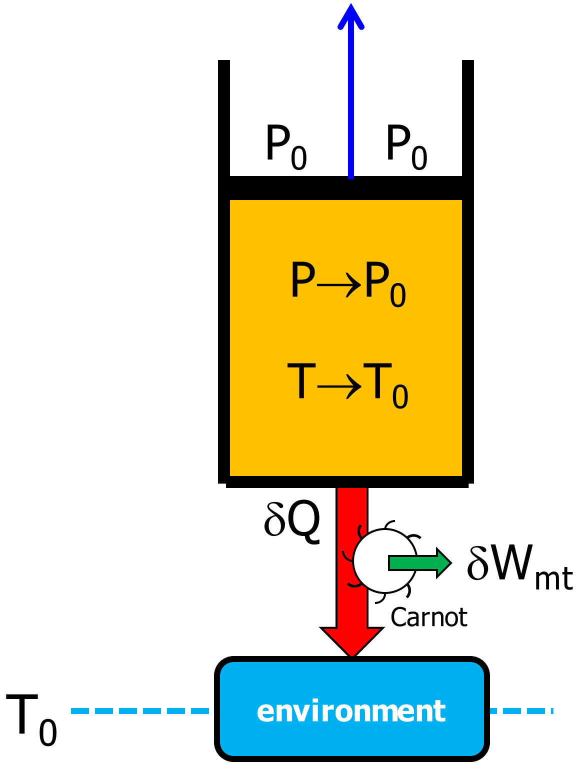
$$dU = -\delta Q - \delta W$$

$$dU = -(\delta W_{mt} + T_0 dS) - (\delta W_{útil} + P_0 dV)$$

Variation of the amount of exergy in a closed system



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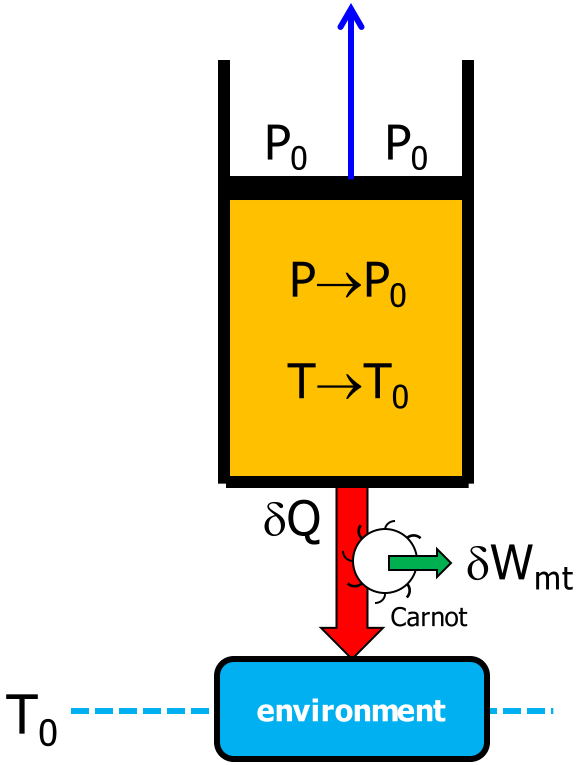
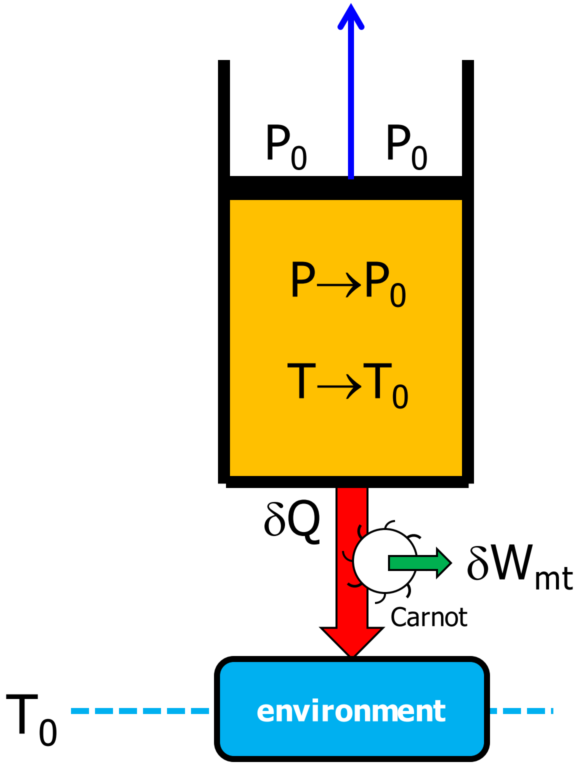


$$\Rightarrow dU = -(\delta W_{mt} + T_0 dS) - (\delta W_{útil} + P_0 dV)$$

$$\delta W_{útil\ total} = \delta W_{mt} + \delta W_{útil}$$

Variation of the amount of exergy in a closed system



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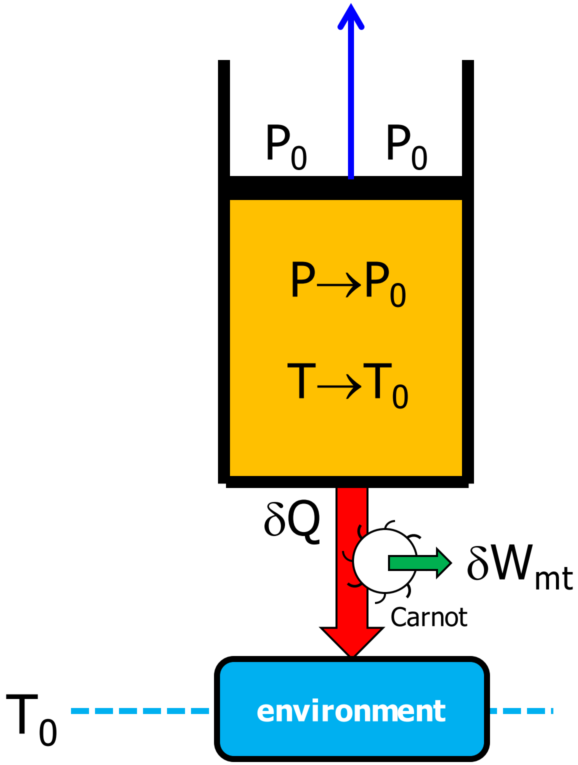

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$$\int_{inicial}^{0} \delta W_{útil\ total} = \ldots$$

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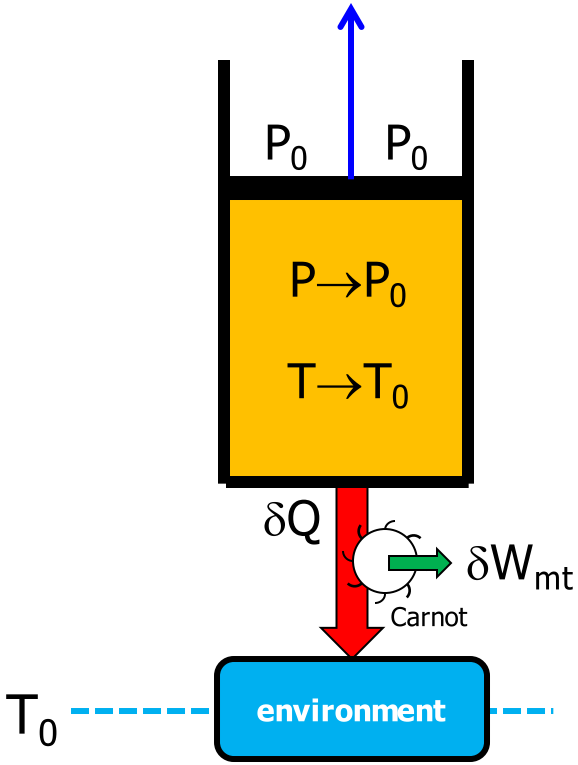

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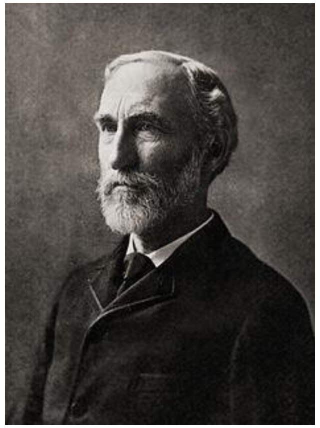
$$\delta W_{útil\ total} = -dU - P_0 dV - T_0 dS$$

$$\int_{inicial}^{0} \delta W_{útil\ total} = \ldots$$

$$W_{útil\ total} = (U - U_0) + P_0 (V - V_0) - T_0 (S - S_0)$$

DEFINITIONS

Available energy
Exergetic energy
Availability
Reversible work
Etc.



J. Willard Gibbs

Exergy...

$$X \stackrel{\text{def}}{=} (U - U_0) + P_0(V - V_0) - T_0(S - S_0)$$

Available energy
Exergetic energy
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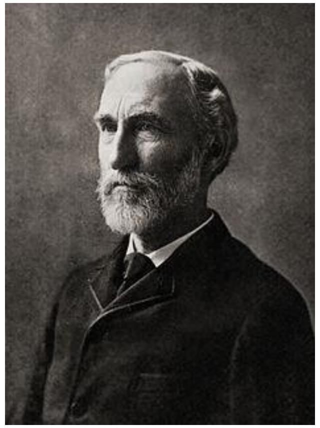

J. Willard Gibbs

DEFINITIONS

Exergy...

$$X \overset{\text{def}}{=} (U - \boxed{U_0}) + \boxed{P_0}(V - \boxed{V_0}) - T_0(S - \boxed{S_0})$$

accounts the influence of the environment

properties of the system when in equilibrium with the envirnoment

DEFINITIONS

Exergy...

Available energy
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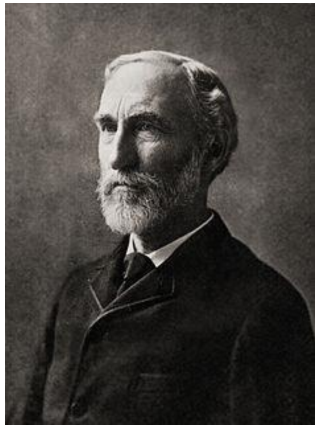

J. Willard Gibbs

$$X \overset{\text{def}}{=} \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}}$$

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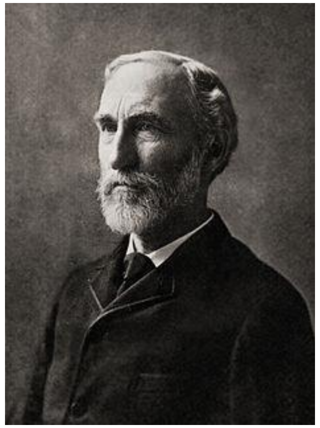

J. Willard Gibbs

Exergy...

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$$X \overset{\text{def}}{=} \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}} + \underbrace{EP + EC}_{\text{mechanical exergy}}$$

DEFINITIONS

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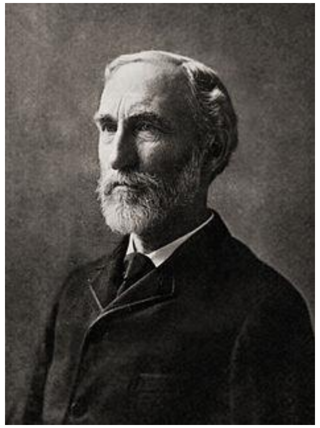
Etc.



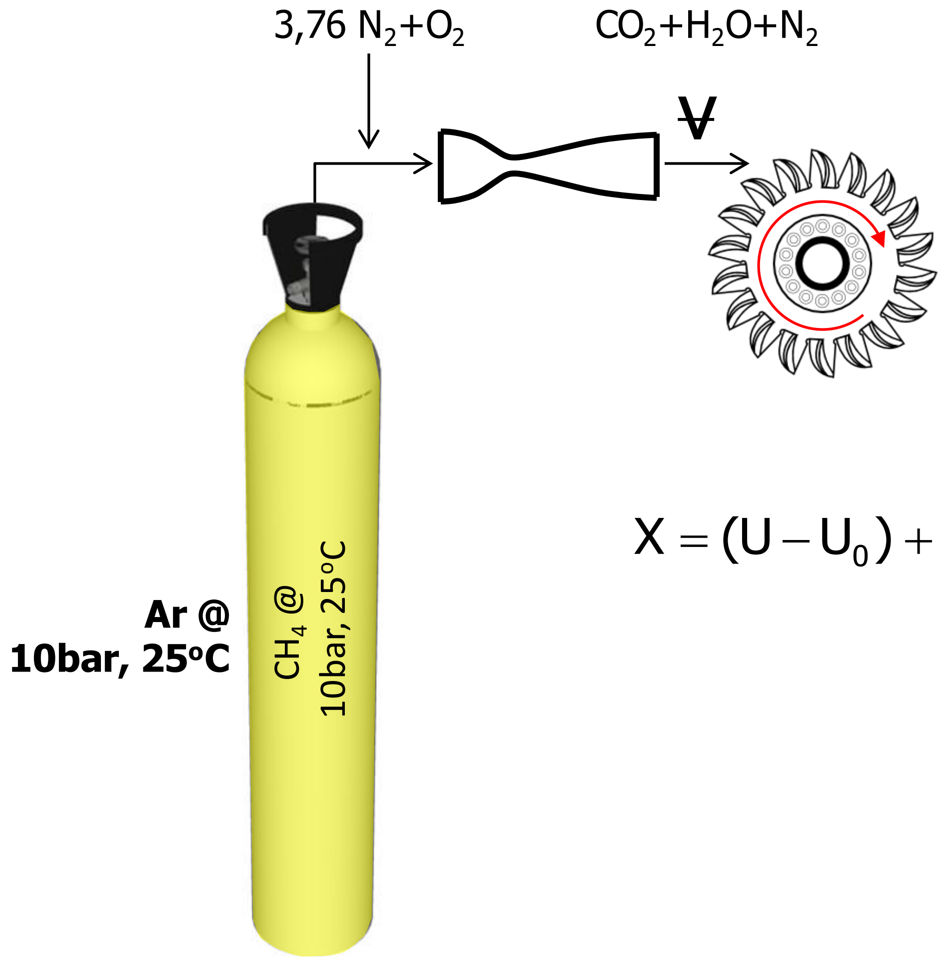
J. Willard Gibbs

Exergy...

$$X \stackrel{\text{def}}{=} \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}}$$

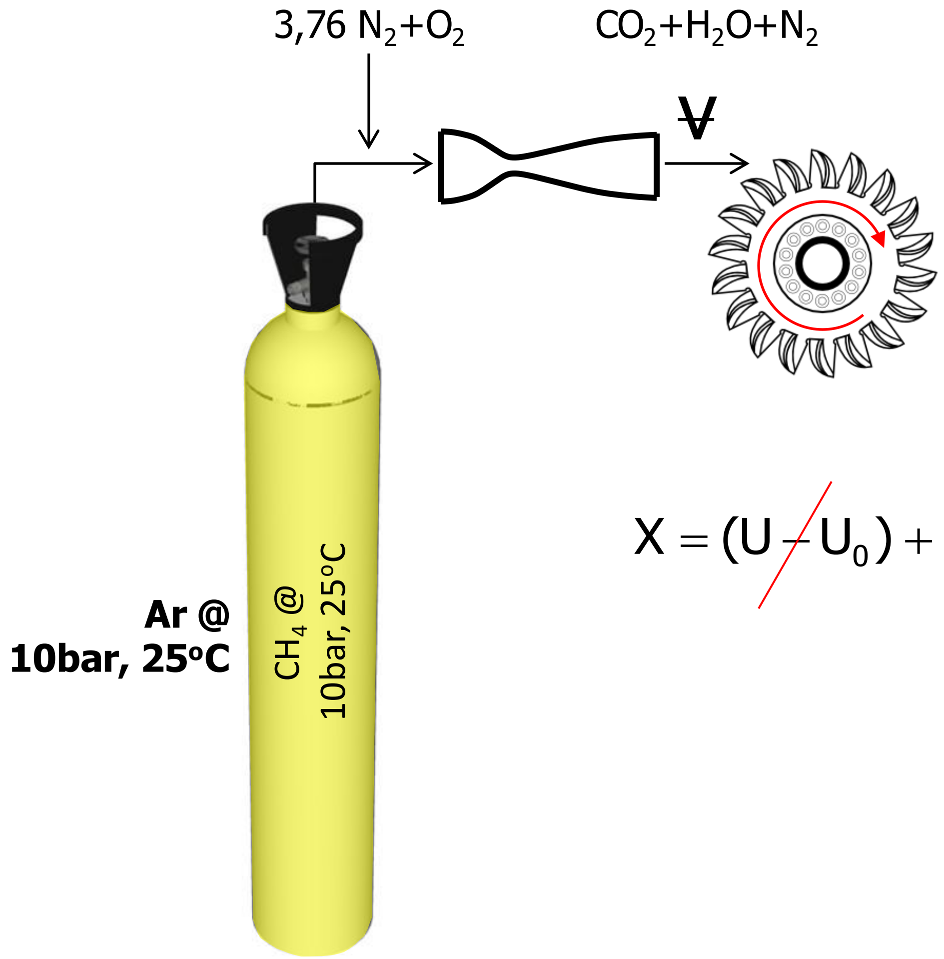
$$X \stackrel{\text{def}}{=} \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}} + \underbrace{EP + EC}_{\text{mechanical exergy}}$$

$$X \stackrel{\text{def}}{=} \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{thermodynamic exergy}} + \underbrace{EP + EC}_{\text{mechanical exergy}} + \underbrace{EQ}_{\text{chemical exergy}}$$



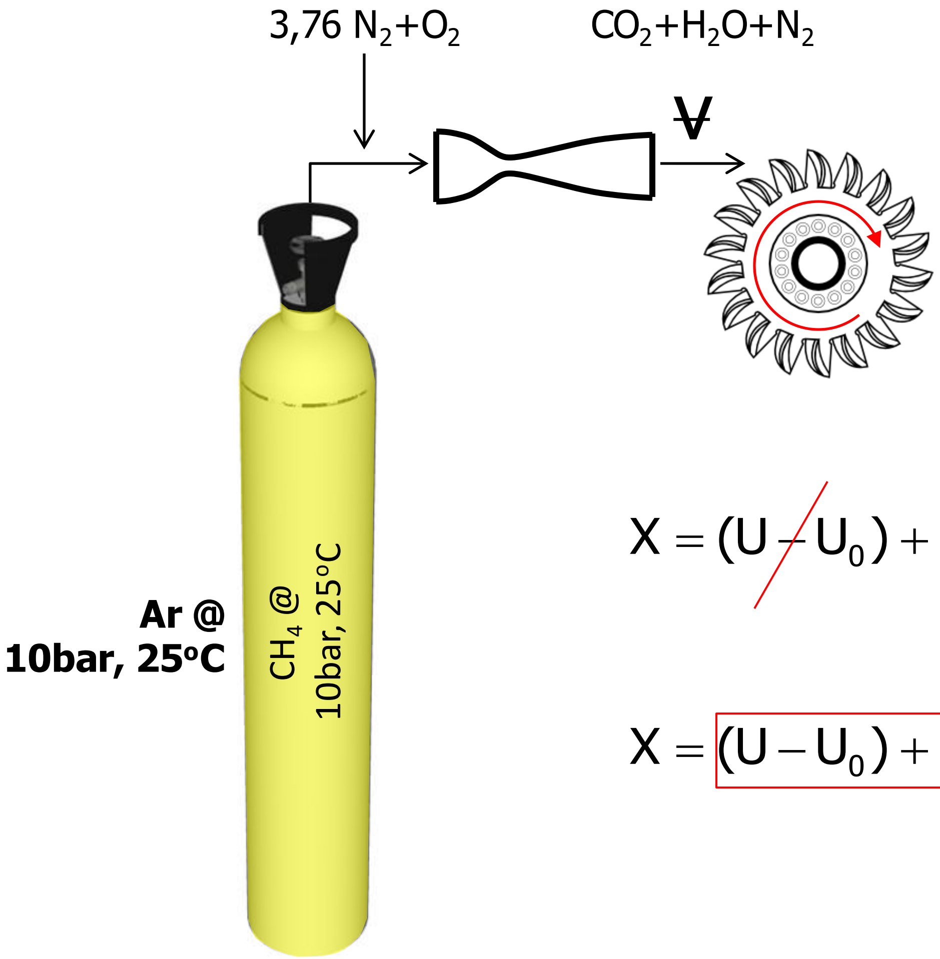
Chemical exergy is the maximum amount of work when its constituents are chemically transformed to those of the environment

$$X = (U - U_0) + P_0(V - V_0) - T_0(S - S_0) + EP + EC + EQ$$



Chemical exergy is the maximum amount of work when its constituents are chemically transformed to those of the environment

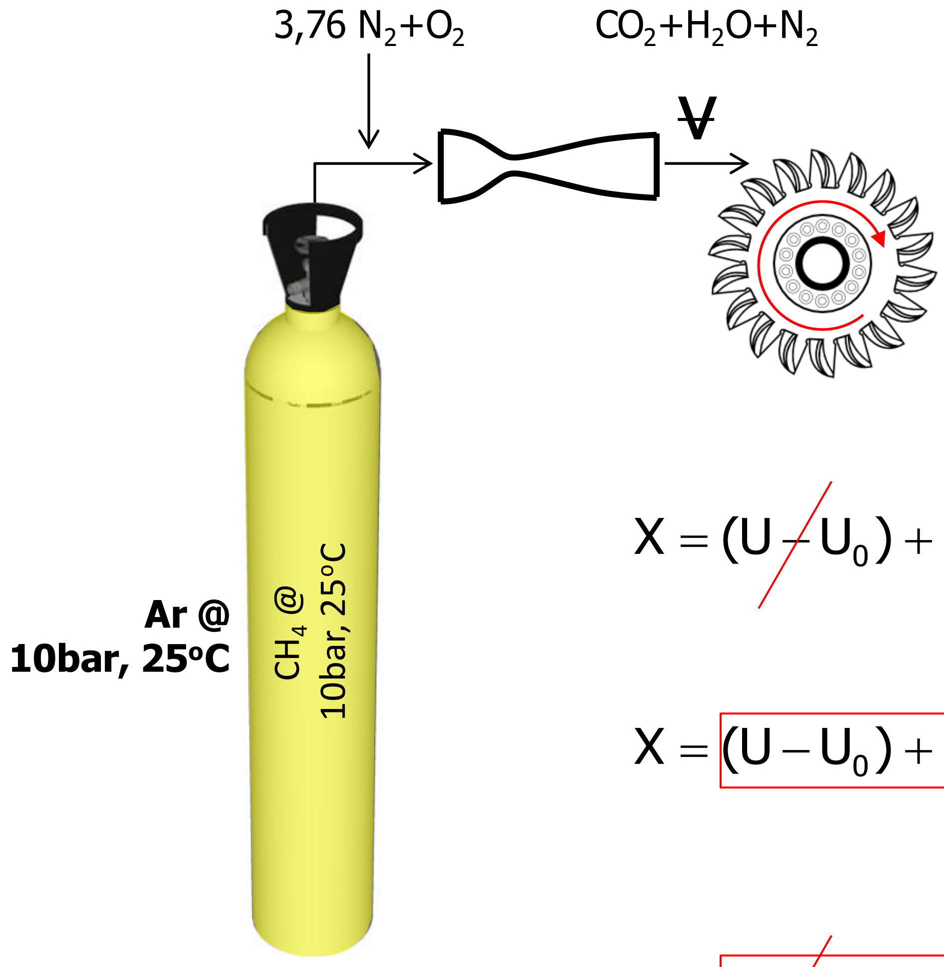
$$X=(U\cancel{-}U_0)+P_0(V\cancel{-}V_0)-T_0(S\cancel{-}S_0)+\cancel{EP}+\cancel{EC}+EQ$$



Chemical exergy is the maximum amount of work when its constituents are chemically transformed to those of the environment

$$X = (U \cancel{-} U_0) + P_0(V \cancel{-} V_0) - T_0(S \cancel{-} S_0) + \cancel{EP} + \cancel{EC} + EQ$$

$$X = \boxed{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)} + \cancel{EP} + \cancel{EC} + \cancel{\boxed{EQ}}$$



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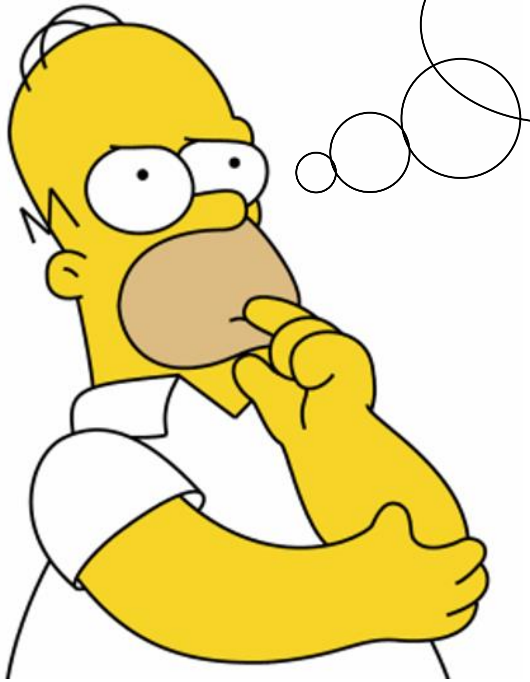
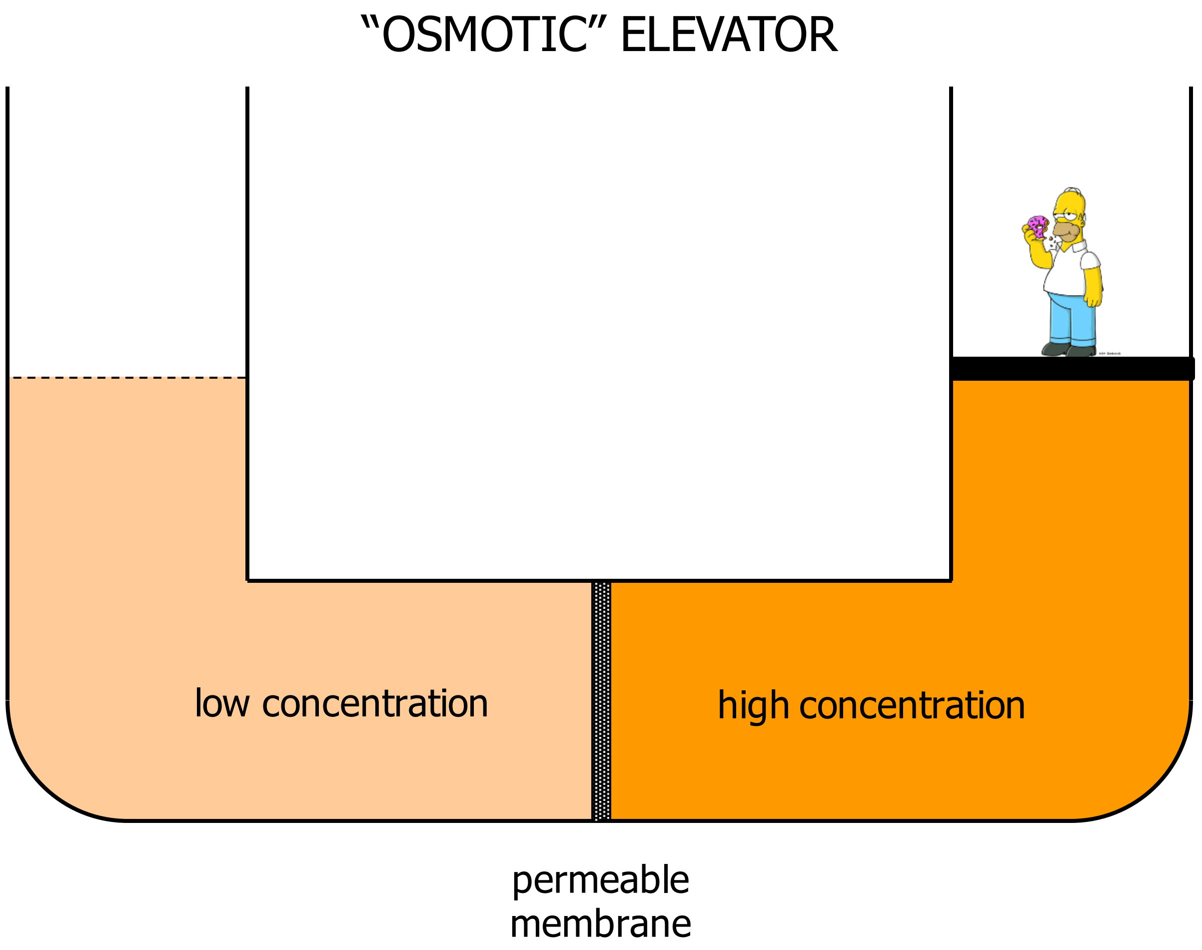
$$X = \boxed{(U \cancel{-} U_0) + P_0(V \cancel{-} V_0) - T_0(S \cancel{-} S_0)} + \cancel{EP} + \boxed{EC} + \cancel{EQ}$$

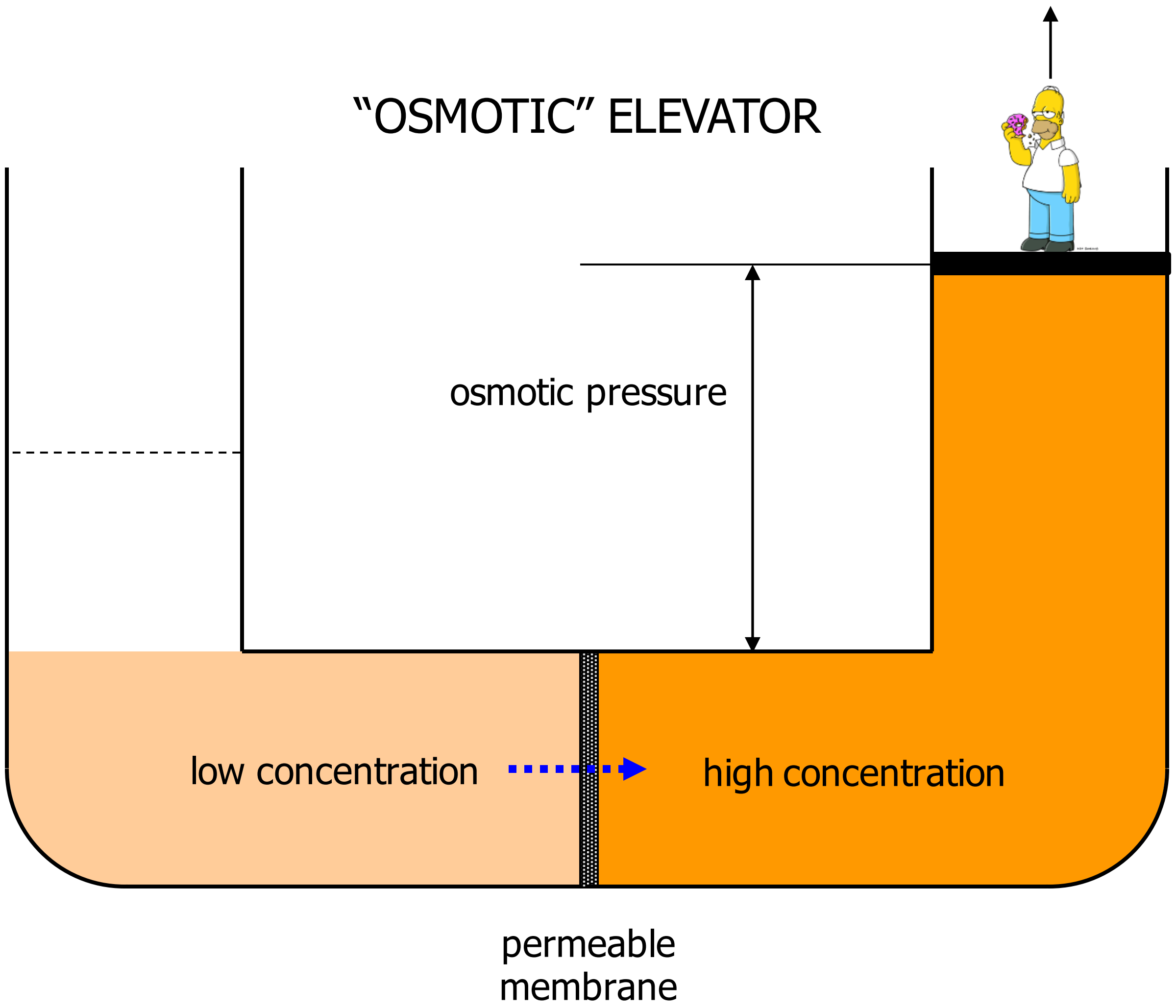


The potential to generate work (organized energy) exists when there are differences between the system and the environment. Those differences may be in terms of thermodynamic properties, chemical composition…

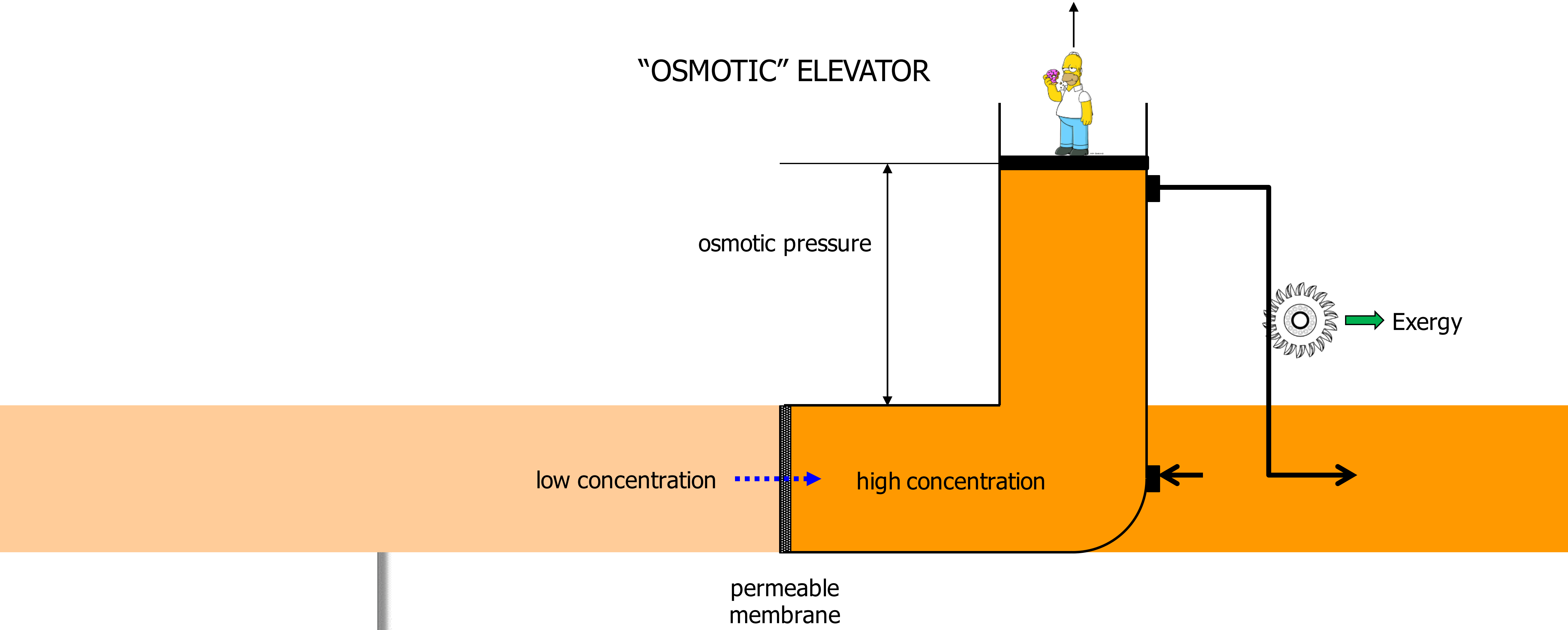
Potential to generate work from differences in chemical composition



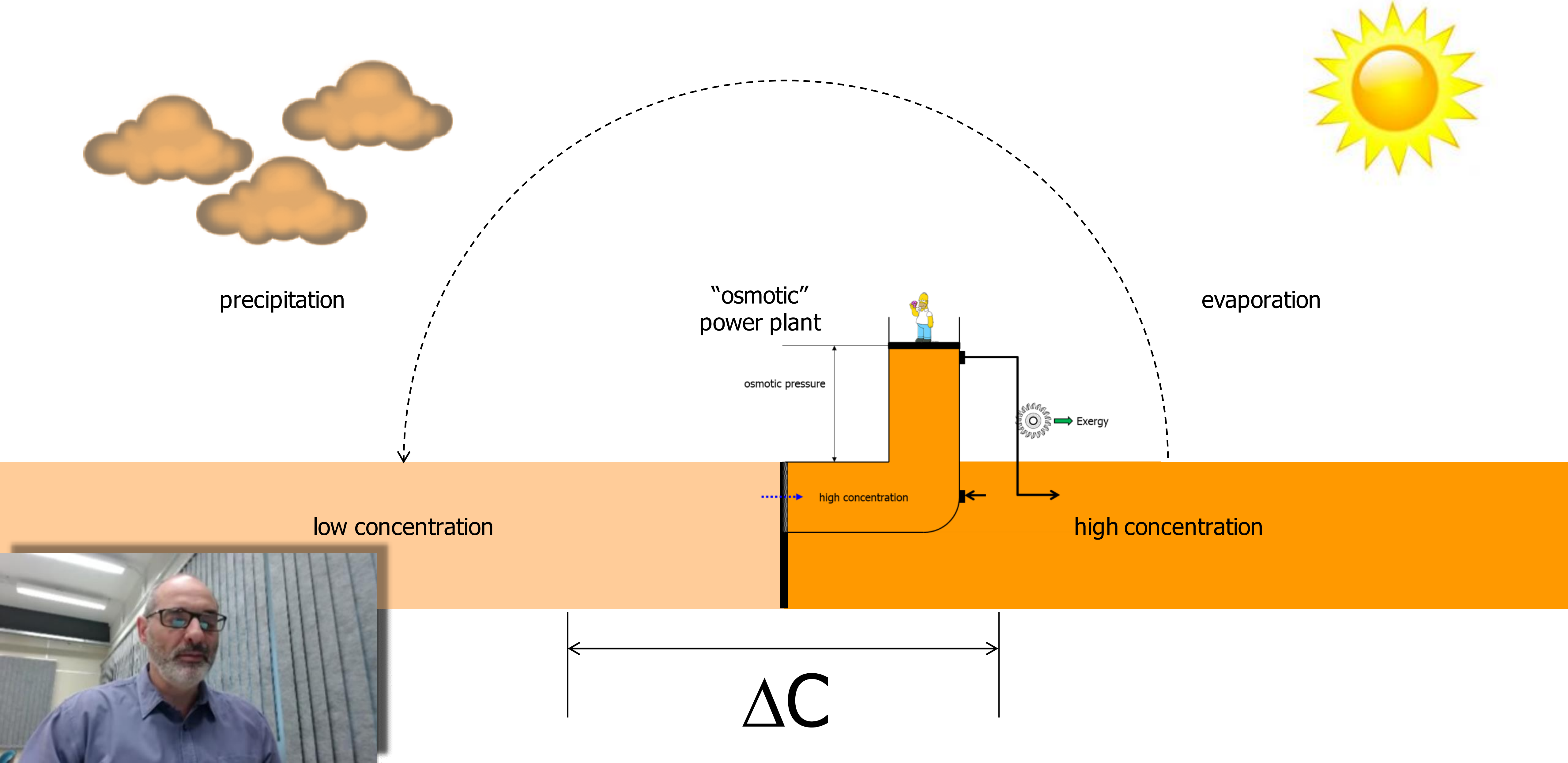
Potential to generate work from differences in chemical composition



Potential to generate work from differences in chemical composition

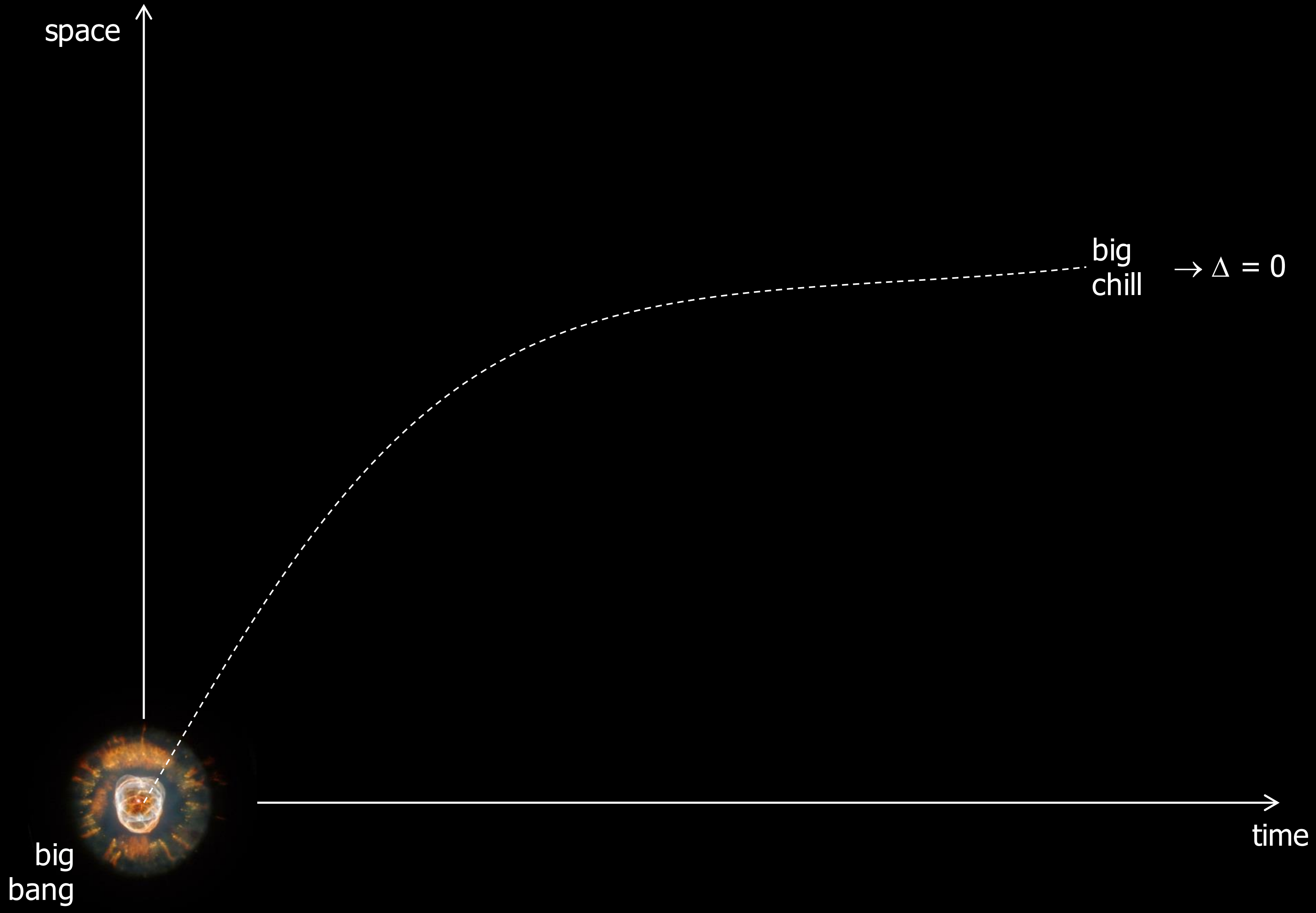


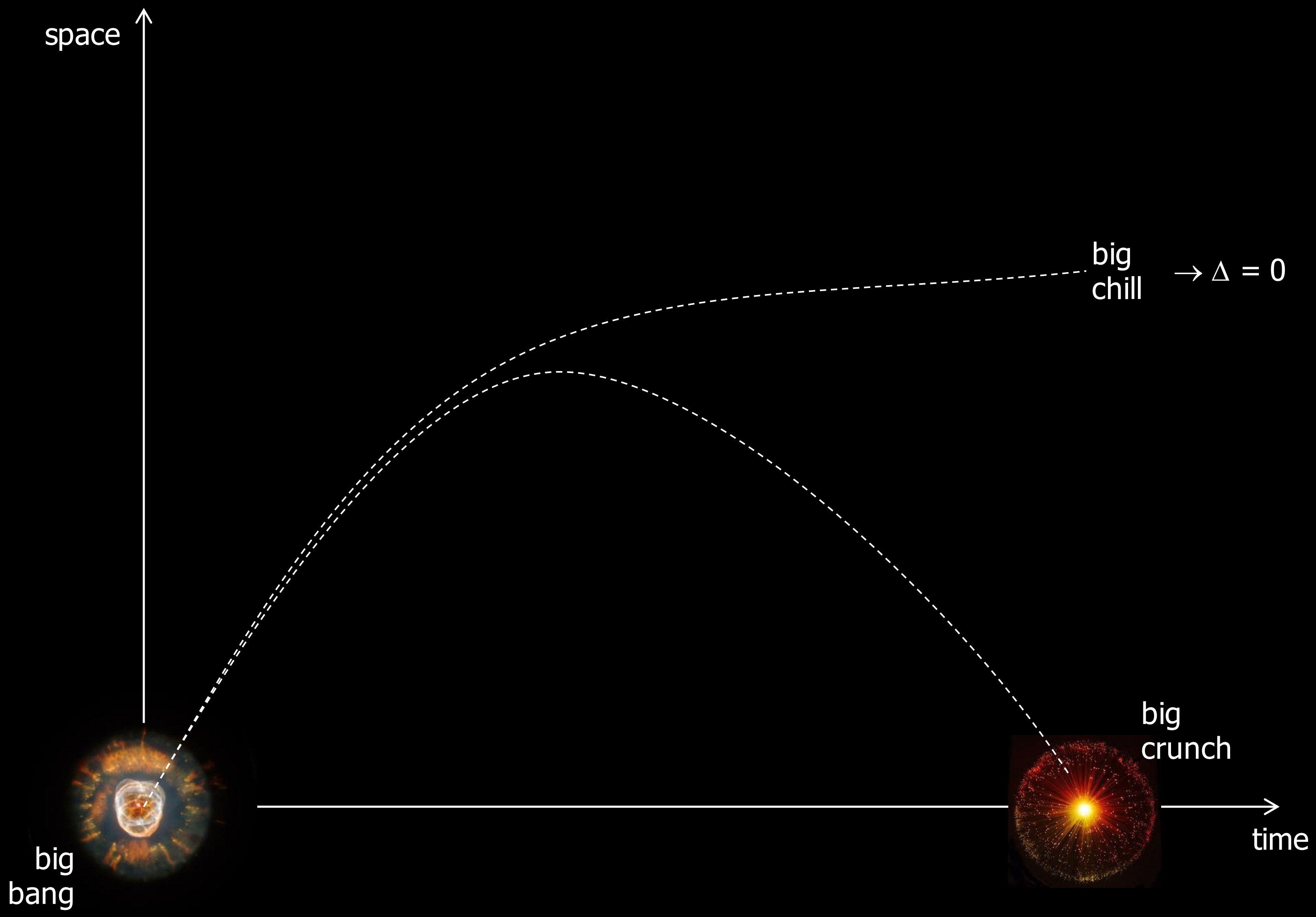
Potential to generate work from differences in chemical composition

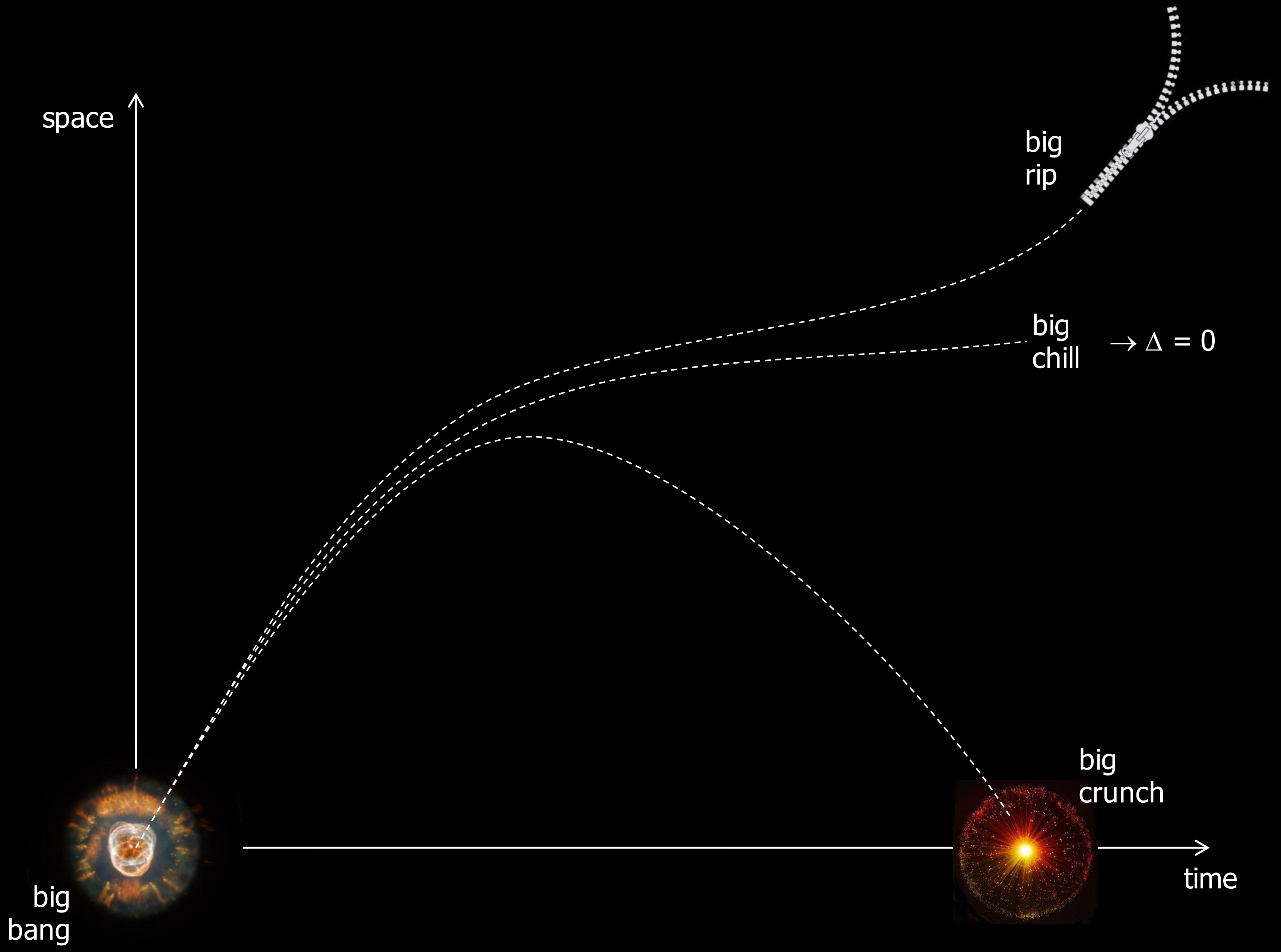


But if exergy can only be destroyed, this means the total exergy of the universe is decreasing and that all differences tend to equalize, pressures and temperatures become the same, differences in chemical composition disappear…


space
time
big
bang

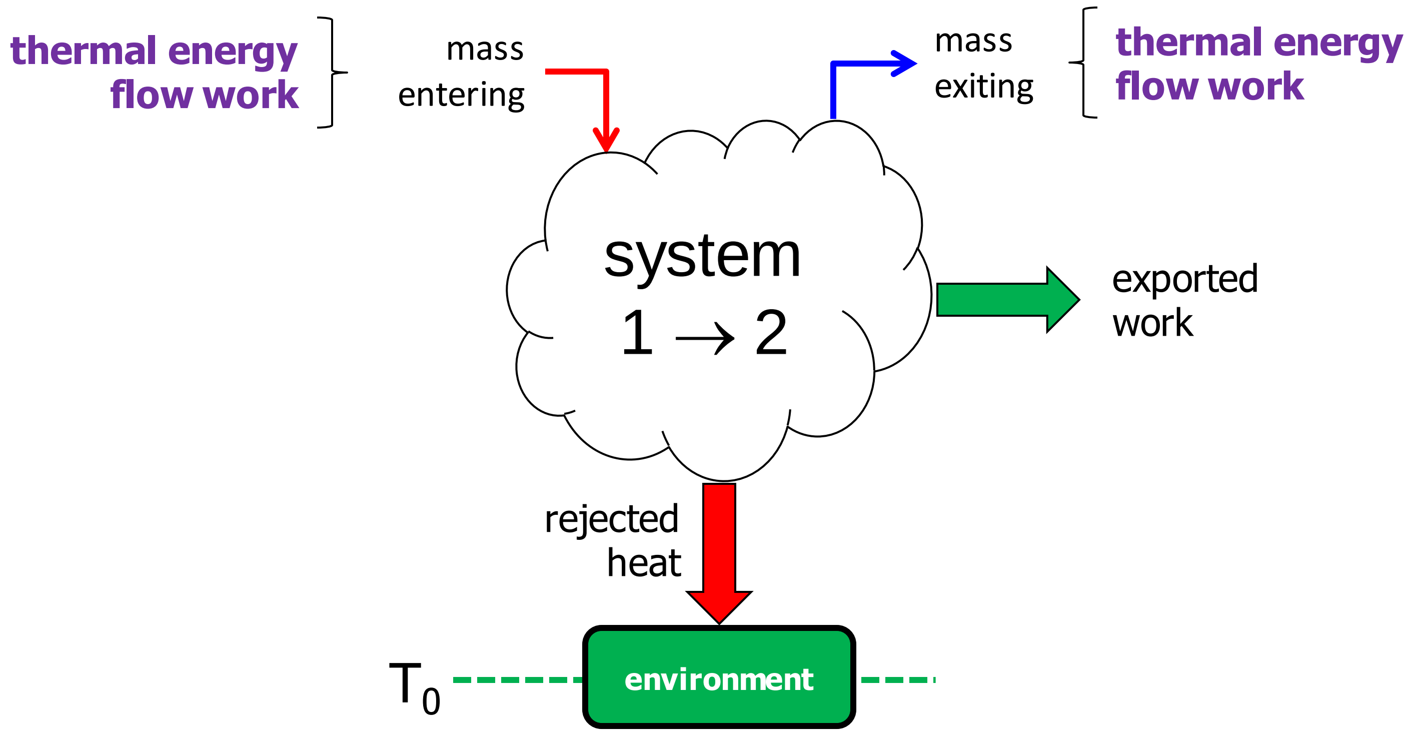

space
big
chill
$\rightarrow \Delta = 0$
big
bang
time


space
big
chill
$\rightarrow \Delta = 0$
big
crunch
time
big
bang

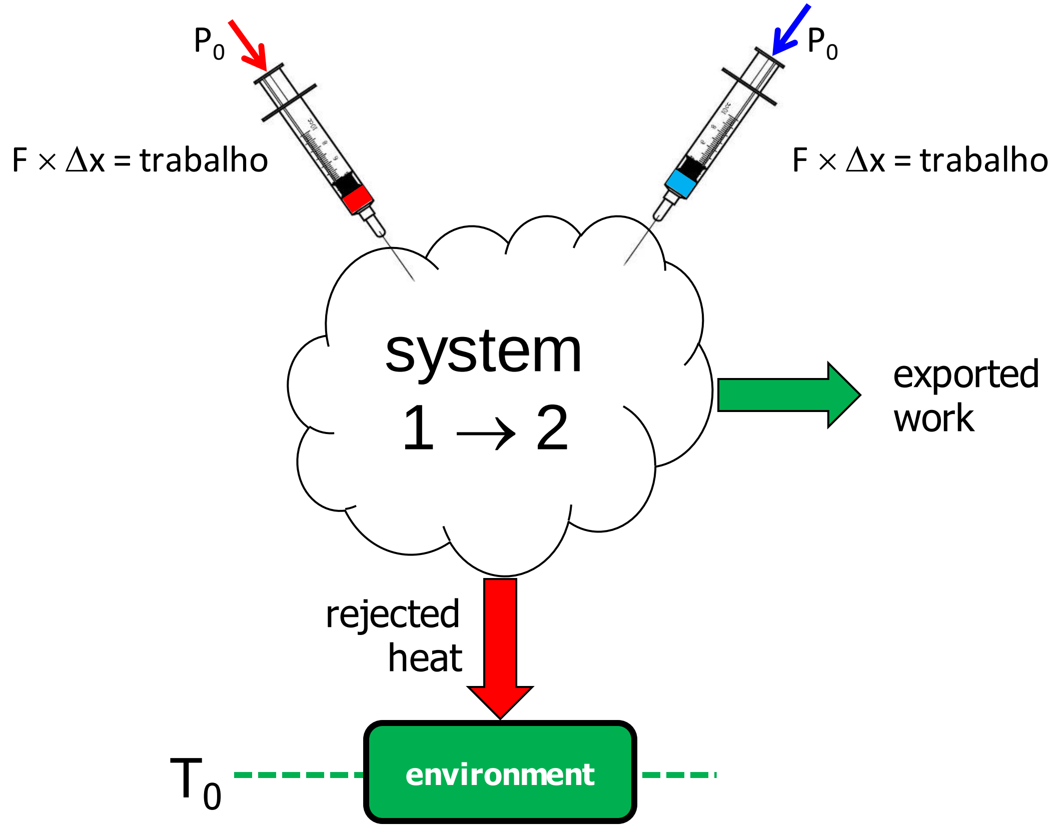

space
big
rip
big
chill
→ Δ = 0
big
crunch
time
big
bang

Open system analysis

Flow exergy and exergy flux of an open system



Flow exergy and exergy flux of an open system



$$W_{fluxo} = (P \cdot A) \cdot \Delta x = P \cdot V$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

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$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = X_{sist.\ fechado} + X_{fluxo}$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = \underbrace{(U - U_0) + P_0(V - V_0) - T_0(S - S_0)}_{\text{exergia termodinâmica}} + \underbrace{(P - P_0)V}_{\text{exergia de fluxo}}$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = \boxed{(U} - \boxed{U_0)} + \cancel{P_0(}V - \boxed{V_0)} - T_0(S - S_0) + \boxed{(P} - \cancel{P_0)}V$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = \boxed{(U} - \boxed{U_0)} + P_0 \cancel{(}V - \boxed{V_0)} - T_0(S - S_0) + \boxed{(P} - P_{\cancel{0}}\cancel{)}V$$

$$X = (H - H_0) - T_0(S - S_0)$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = \boxed{(U} - \boxed{U_0)} + P_{\cancel{0}}\cancel{(}V - \boxed{V_0)} - T_0(S - S_0) + \boxed{(P} - P_{\cancel{0}}\cancel{)}V$$

$$X = (H - H_0) - T_0(S - S_0)$$

$$X = (H - H_0) - T_0(S - S_0) + EP + EC + EQ$$

$$W_{fluxo} = P \cdot (A \cdot \Delta x) = P \cdot V$$

$$X_{fluxo} = P \cdot V - P_0 \cdot V = (P - P_0) \cdot V$$

$$X = (\boxed{U} - \boxed{U_0}) + \cancel{P_0}\cancel{(}V - \boxed{V_0}) - T_0(S - S_0) + \boxed{(P} - \cancel{P_0}\cancel{)}V$$

$$X = (H - H_0) - T_0(S - S_0)$$

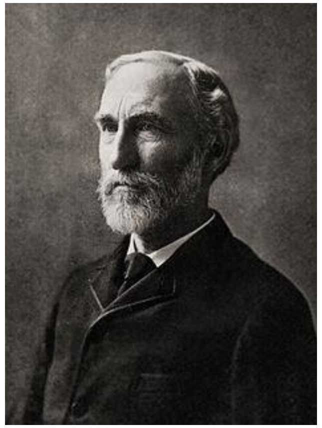
$$X = (H - H_0) - T_0(S - S_0) + EP + EC + EQ$$

$$x = (h - h_0) - T_0(s - s_0) + ep + ec + eq$$

second law efficiency
rational efficiency
etc.

DEFINITIONS

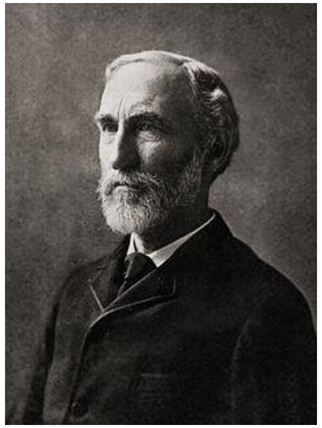
Exergetic efficiency is the ratio of the 1st law efficiency of a thermal cycle to the efficiency of a reversible cycle operating between the same temperatures



J. Willard Gibbs

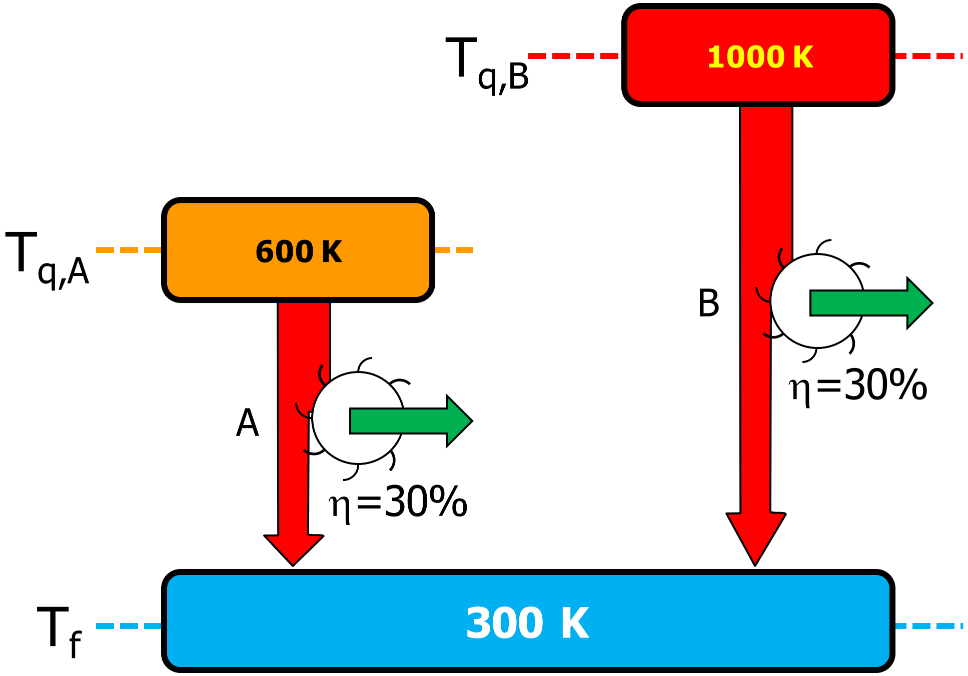
DEFINITIONS

second law efficiency
rational efficiency
etc.



J. Willard Gibbs

Exergetic efficiency is the ratio of the 1st law efficiency of a thermal cycle to the efficiency of a reversible cycle operating between the same temperatures



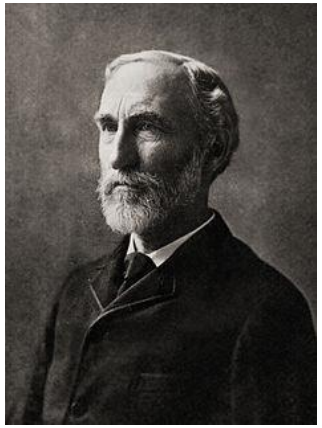
$$\eta_{2alei} \overset{def}{=} \eta_{term} / \eta_{rev}$$

$$\eta_{rev,A} = 1 - T_f / T_{q,A}$$

$$\eta_{2alei} = 0{,}3/(1 - 300/600)$$

$$\eta_{2alei} = 0{,}60$$

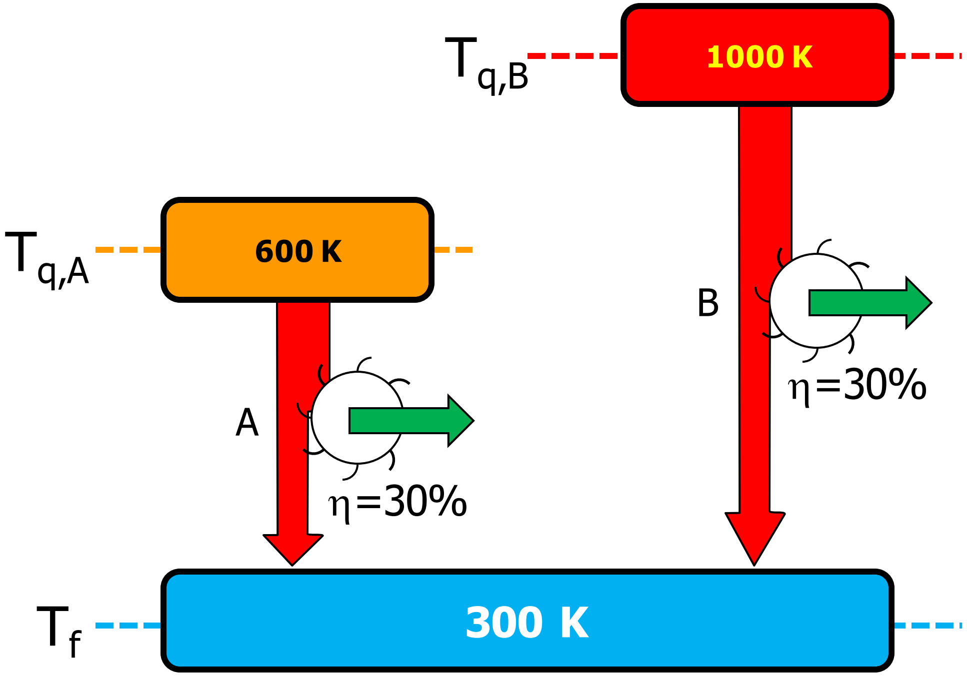
second law efficiency
rational efficiency
etc.



J. Willard Gibbs

DEFINITIONS

Exergetic efficiency is the ratio of the 1st law efficiency of a thermal cycle to the efficiency of a reversible cycle operating between the same temperatures



$$\eta_{2^a lei} \stackrel{def}{=} \eta_{term} / \eta_{rev}$$

$$\eta_{rev,B} = 1 - T_f / T_{q,B}$$

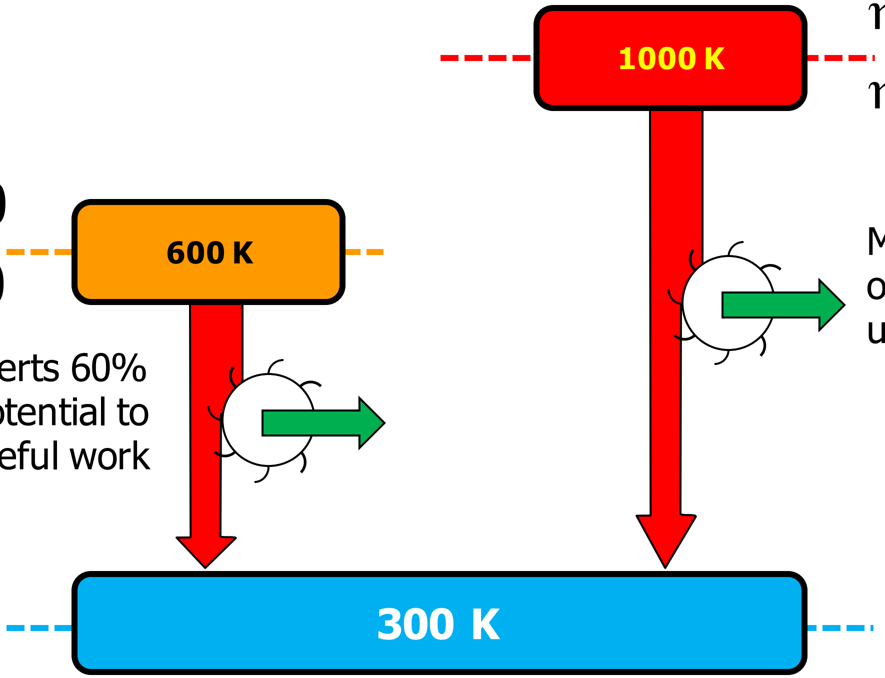
$$\eta_{2^a lei} = 0{,}3 / (1 - 300 / 1000)$$

$$\eta_{2^a lei} = 0{,}43$$

$\eta_{term} = 0{,}30$

$\eta_{2^a lei} = 0{,}43$

Machine B converts 43% of its work potential to useful work



$\eta_{term} = 0{,}30$

$\eta_{2^a lei} = 0{,}60$

Machine A converts 60% of its work potential to useful work

$$\eta_{2^a lei} = \frac{W_{útil}}{W_{rev}} \Rightarrow \eta_{2^a lei} = \frac{\text{recovered exergy}}{\text{supplied exergy}} = 1 - \frac{\text{destroyed exergy}}{\text{supplied exergy}}$$

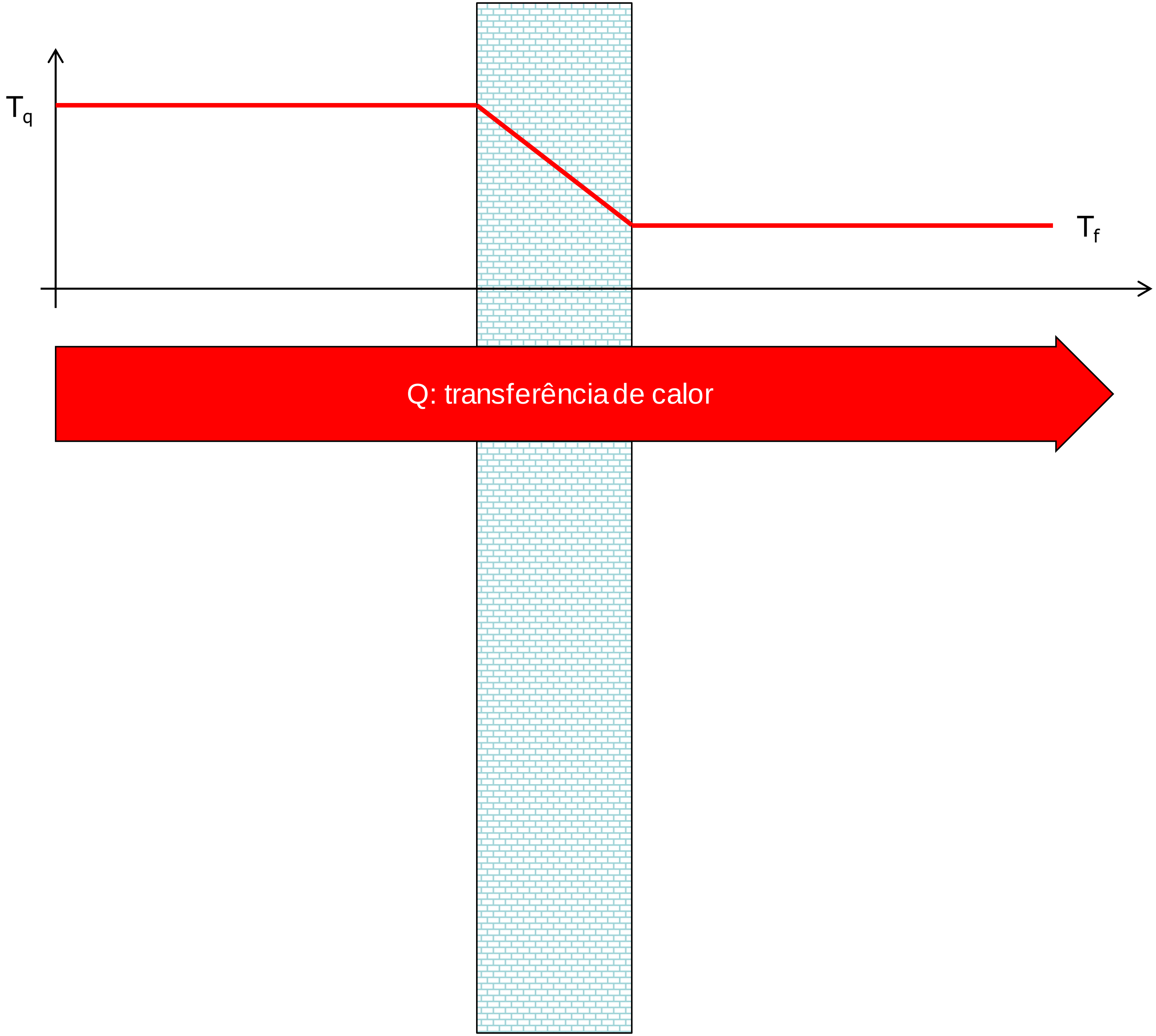
Exergy transfer mechanisms

- Heat, work and mass flow

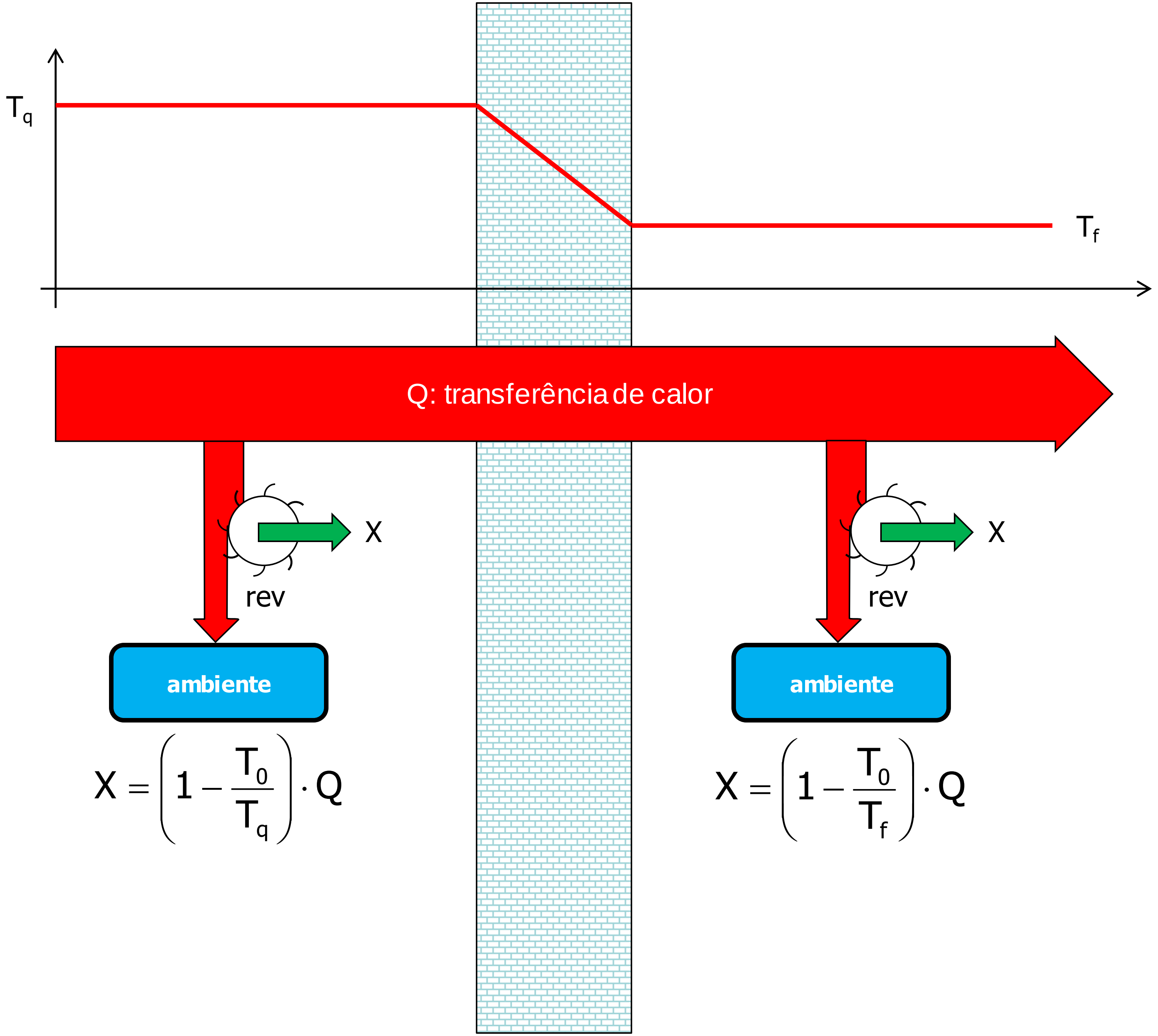
$$X \overset{\text{def}}{=} \underbrace{(U-U_0)+P_0(V-V_0)-T_0(S-S_0)}_{\text{thermodynamic exergy}} + \underbrace{EP+EC}_{\text{mechanical exergy}} + \underbrace{EQ}_{\text{chemical exergy}}$$

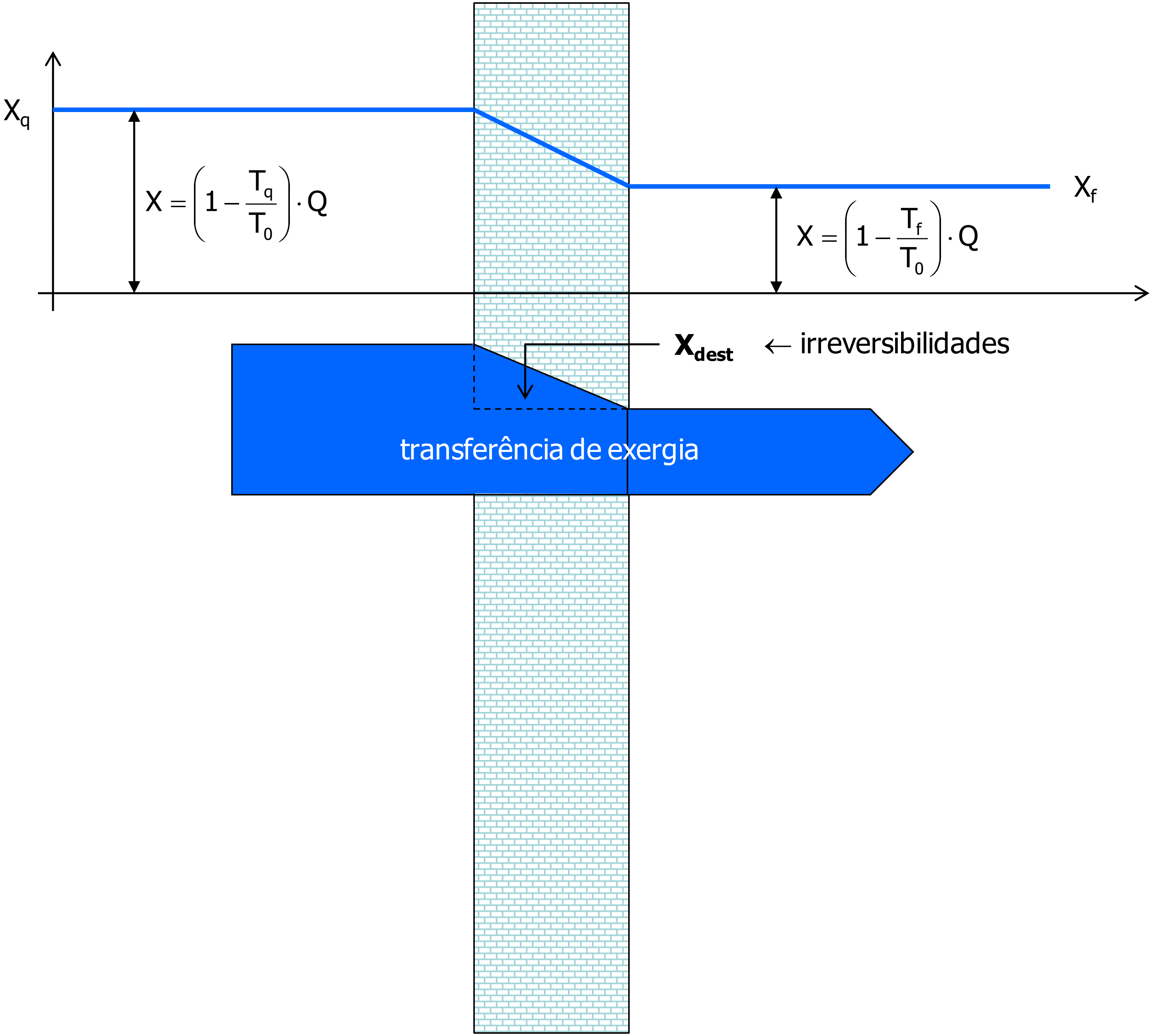
Exergy is a themodynamic property, i.e. a state property

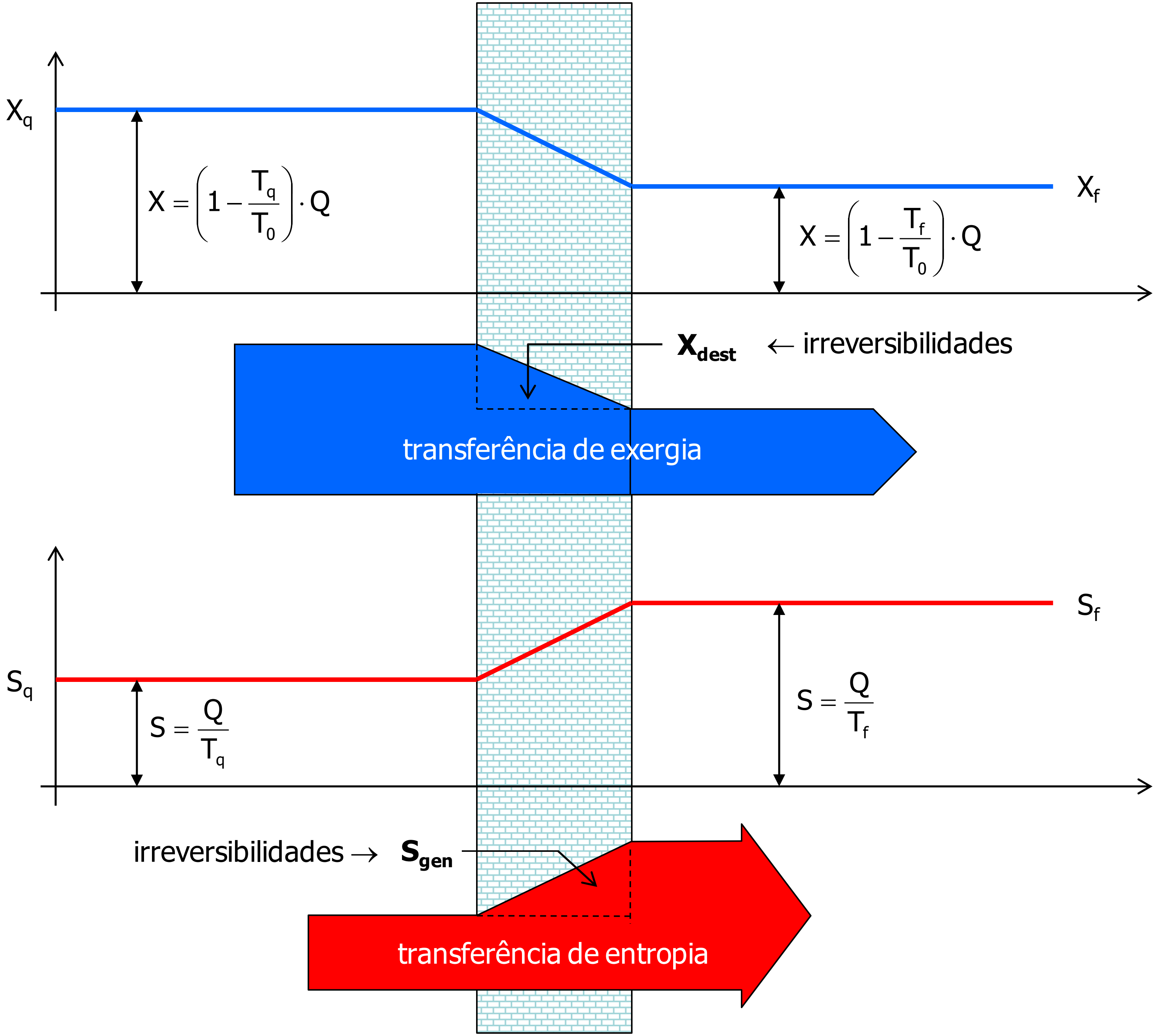
Exergy transfer through heat…



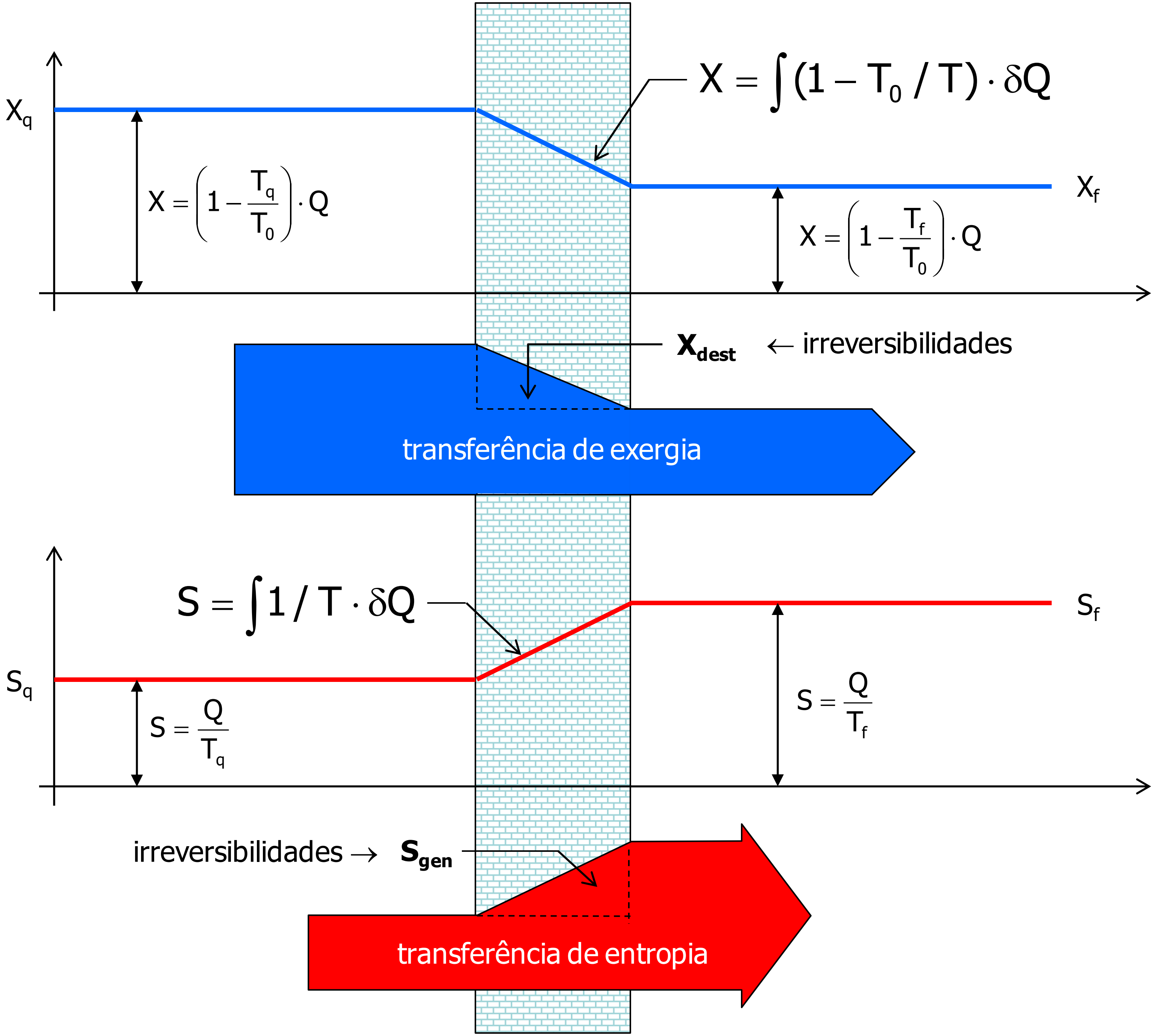
T_q
T_f
Q: transferência de calor


T_q
T_f
Q: transferência de calor
X
rev
X
rev
ambiente
ambiente
$X = \left(1 - \frac{T_0}{T_q}\right) \cdot Q$
$X = \left(1 - \frac{T_0}{T_f}\right) \cdot Q$


X_q
$X = \left(1 - \frac{T_q}{T_0}\right) \cdot Q$
X_f
$X = \left(1 - \frac{T_f}{T_0}\right) \cdot Q$
$\mathbf{X_{dest}}$ ← irreversibilidades
transferência de exergia



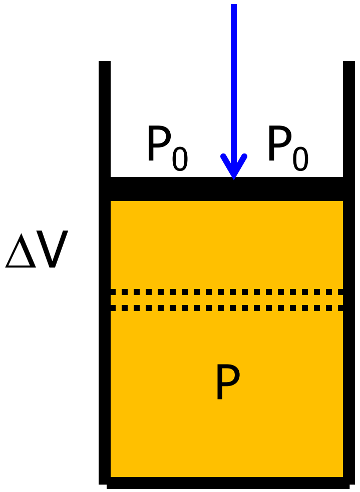
X_q
$X = \left(1 - \frac{T_q}{T_0}\right) \cdot Q$
X_f
$X = \left(1 - \frac{T_f}{T_0}\right) \cdot Q$
$\mathbf{X_{dest}}$ ← irreversibilidades
transferência de exergia
S_q
$S = \frac{Q}{T_q}$
S_f
$S = \frac{Q}{T_f}$
irreversibilidades → $\mathbf{S_{gen}}$
transferência de entropia



X_q
$X = \int (1 - T_0 / T) \cdot \delta Q$
$X = \left(1 - \frac{T_q}{T_0}\right) \cdot Q$
X_f
$X = \left(1 - \frac{T_f}{T_0}\right) \cdot Q$
X_{dest} ← irreversibilidades
transferência de exergia
$S = \int 1 / T \cdot \delta Q$
S_q
S_f
$S = \frac{Q}{T_q}$
$S = \frac{Q}{T_f}$
irreversibilidades → S_{gen}
transferência de entropia

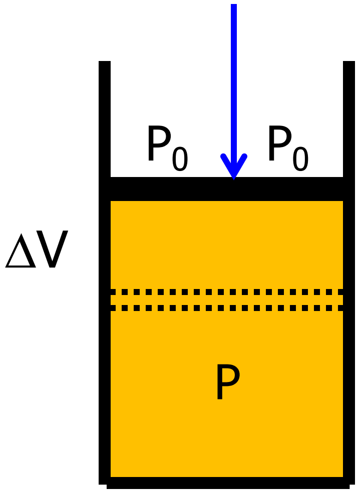
Exergy transfer through work…

potential to generate useful work= exergy



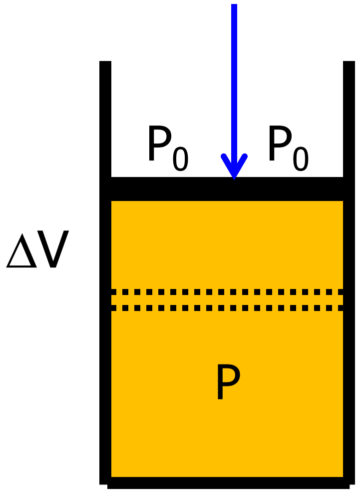
$$X_{work} = W_{boundary} - W_{neighborhood}$$

potential to generate useful work= exergy

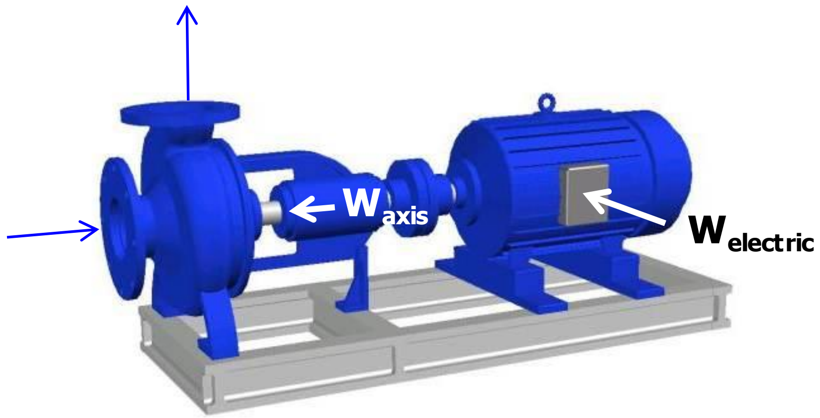


$$X_{work} = \underbrace{W_{boundary}}_{\int PdV} - \underbrace{W_{neighborhood}}_{P_0 \Delta V}$$

potential to generate useful work= exergy



$$X_{work} = \underbrace{W_{boundary}}_{\int PdV} - \underbrace{W_{neighborhood}}_{P_0 \Delta V}$$

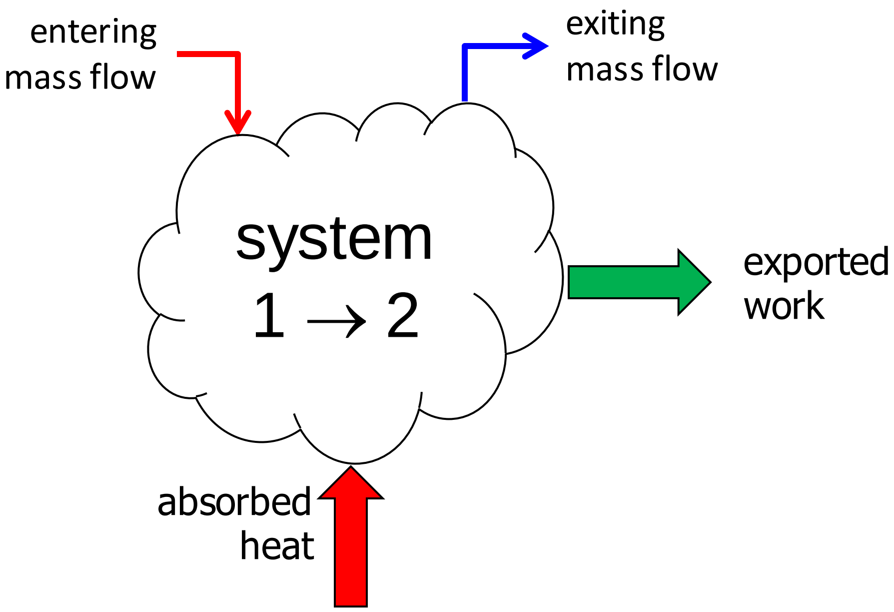


$$X_{work} = W_{axis}$$

$$X_{work} = W_{electric}$$

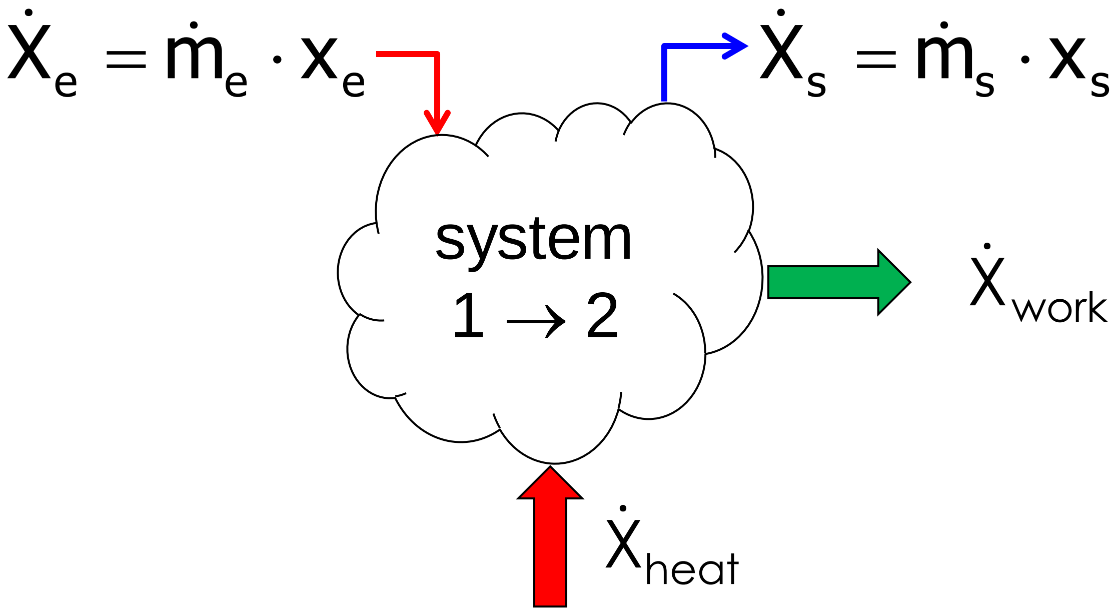
Exergy transfer through mass flow…

Mass contains exergy, energy, entropy, etc.



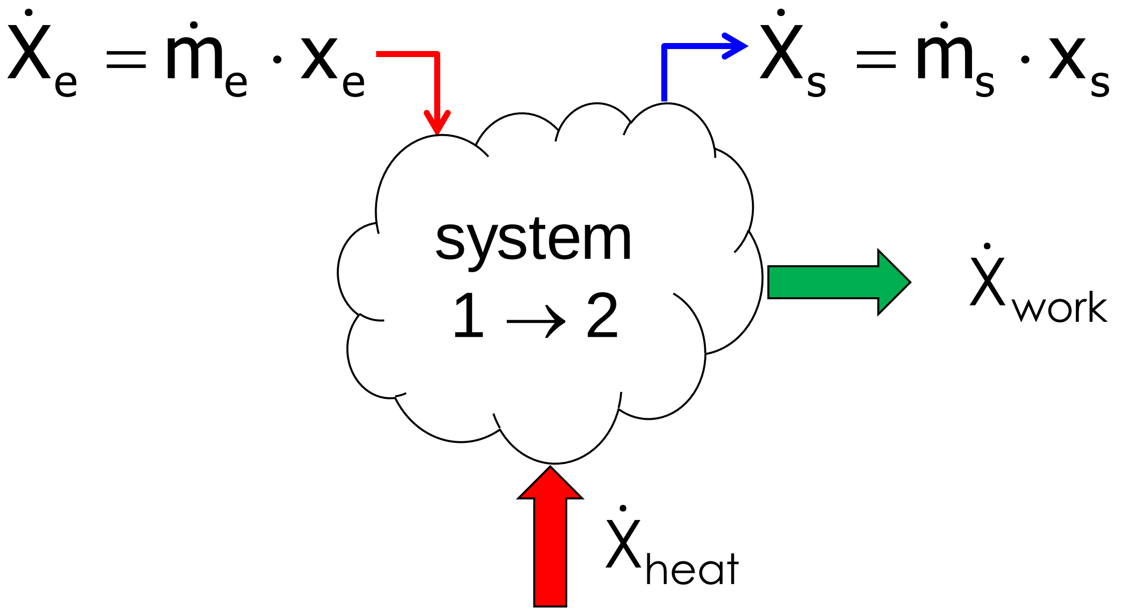
$$x = (h - h_0) - T_0(s - s_0) + ep + ec + eq$$

Mass contains exergy, energy, entropy, etc.



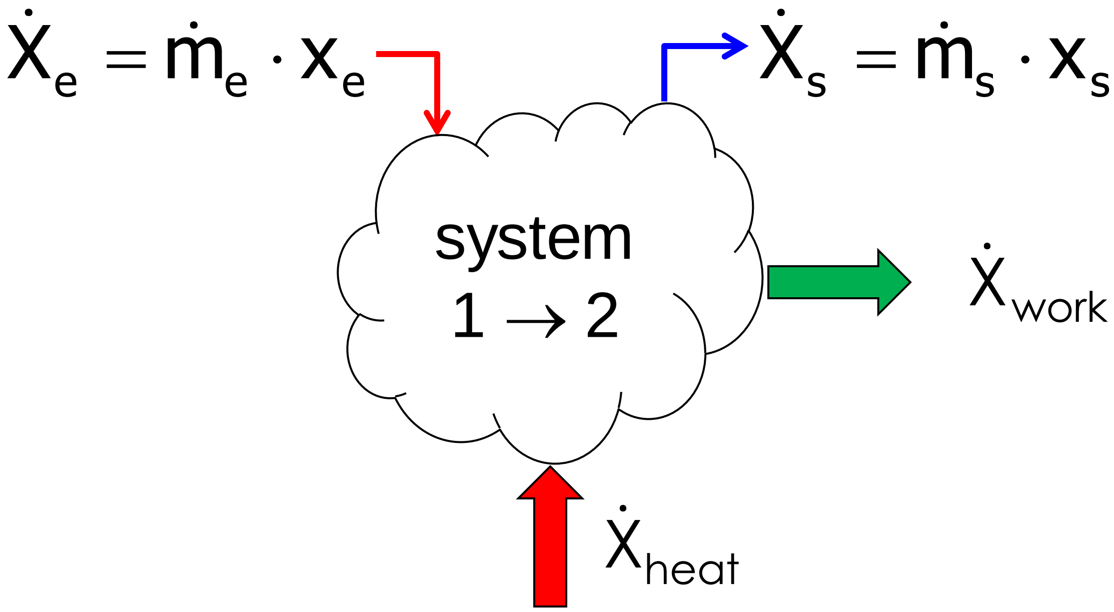
$$x = (h - h_0) - T_0 (s - s_0) + ep + ec + eq$$

Mass contains exergy, energy, entropy, etc.



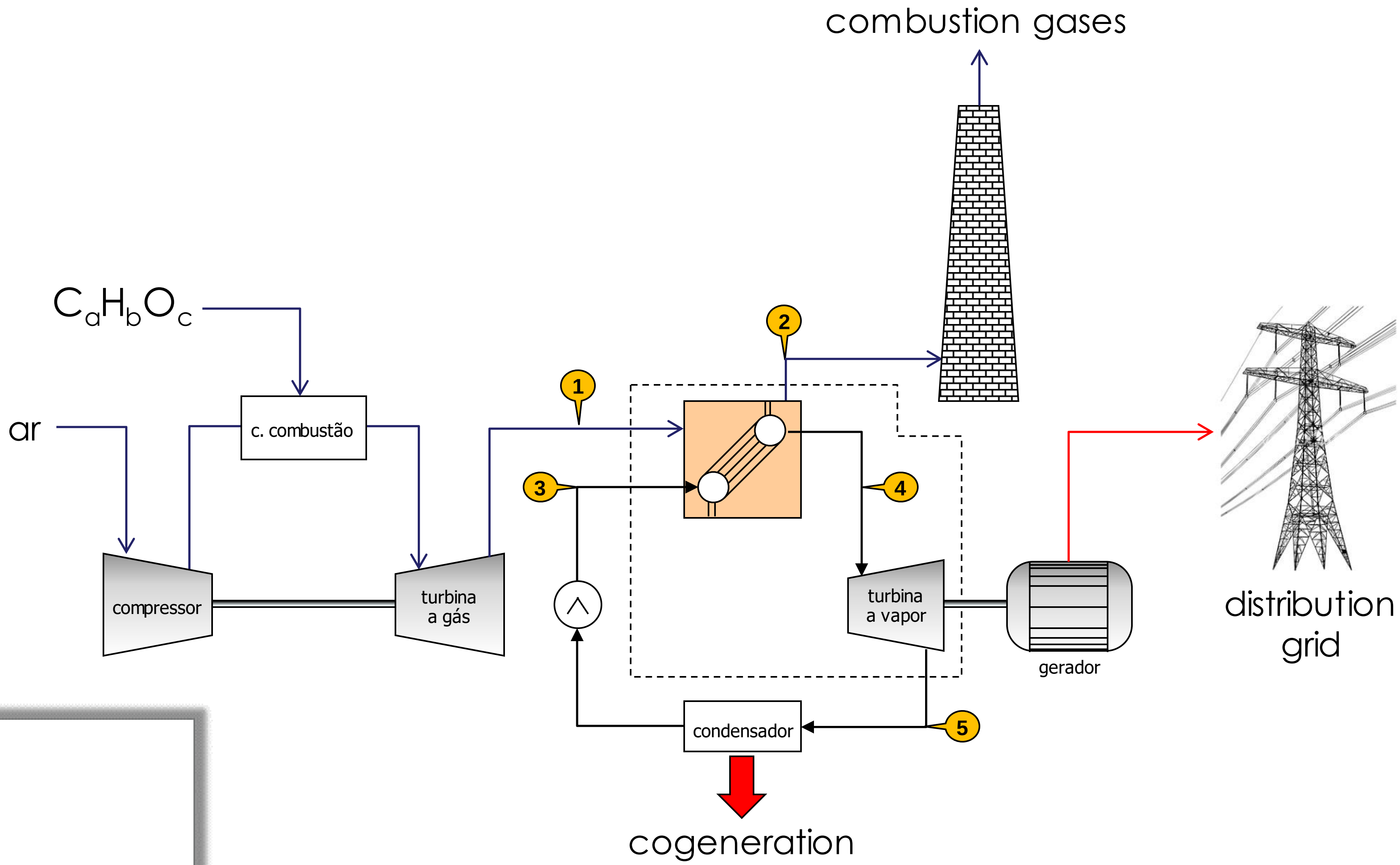
$$\dot{X}_{heat} - \dot{X}_{work} + \dot{X}_{e,mflow} - \dot{X}_{s,mflow} - \dot{X}_{destroyed} = dX_{vc} / dt$$

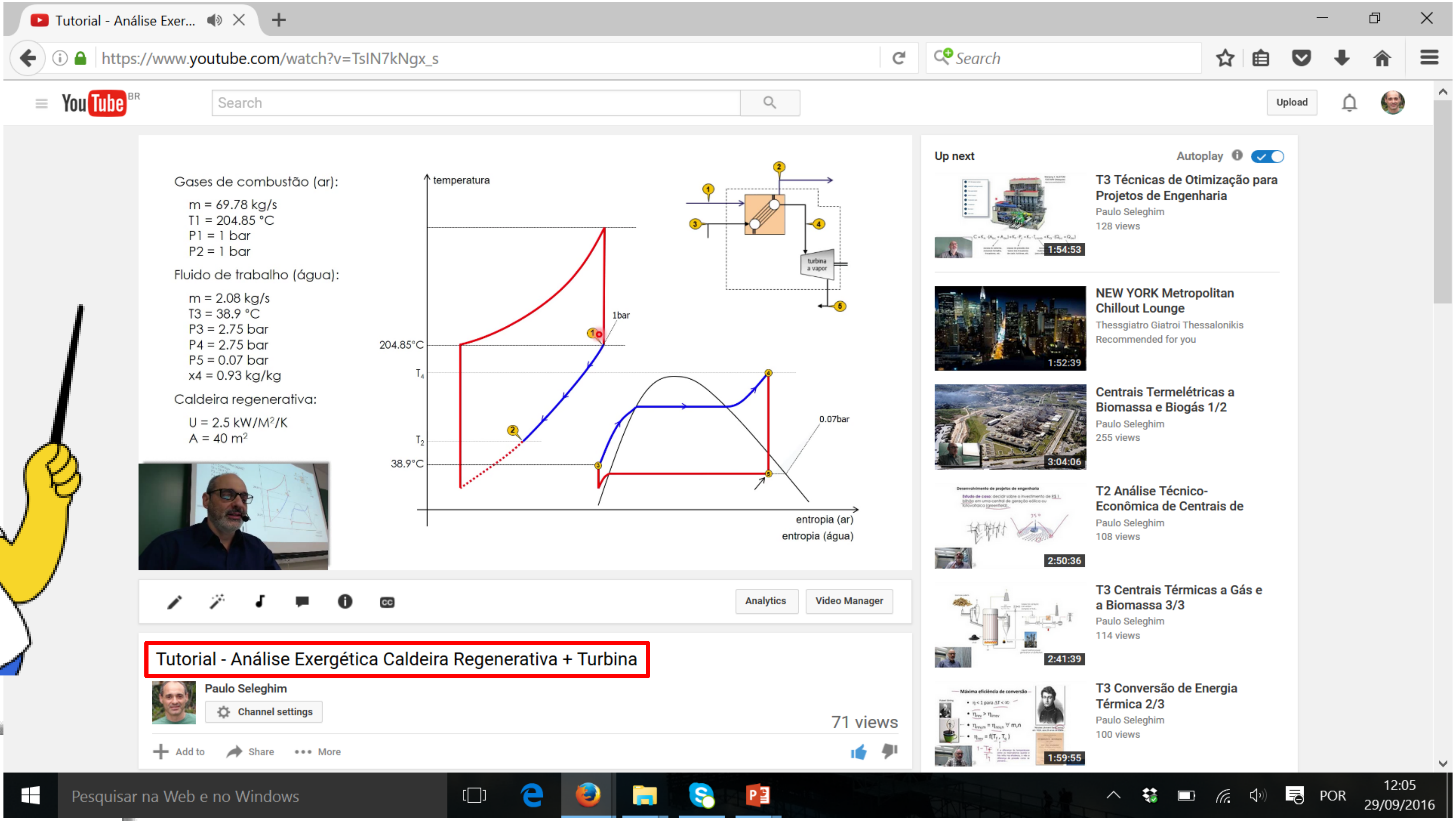
Mass contains exergy, energy, entropy, etc.



$$\sum\left(1-\frac{T_0}{T_k}\right)\dot{Q}_k-\left(\dot{W}-P_0\frac{dV_{vc}}{dt}\right)+\sum\dot{m}_e x_e-\sum\dot{m}_s x_s-\dot{X}_{dest}=\frac{dX_{vc}}{dt}$$

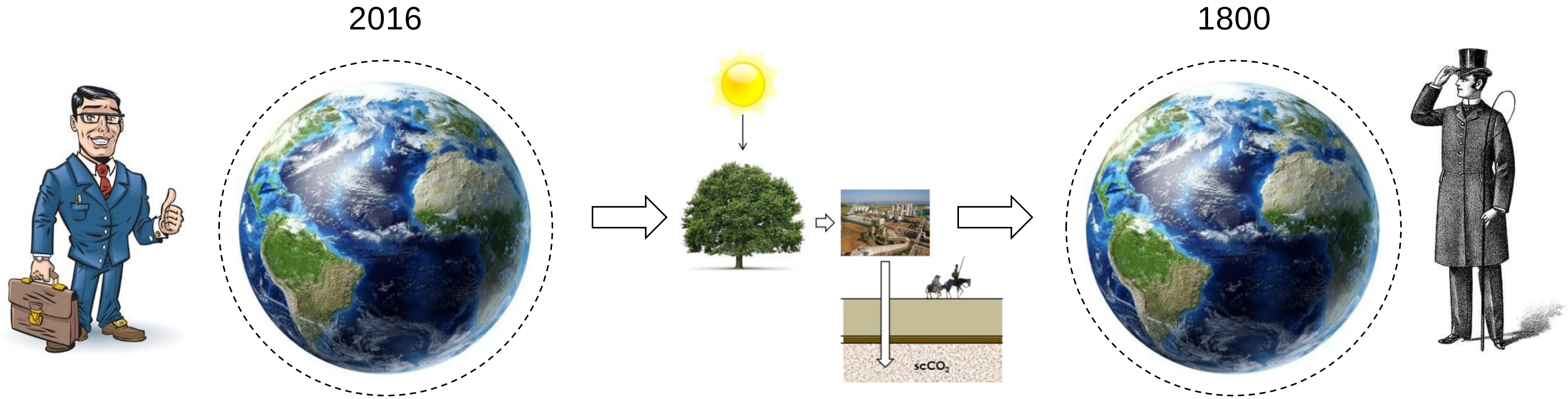
Exergetic analysis: combined cycle thermal power plant





https://youtu.be/TsIN7kNgx_s

Next classes: “Sun Powered CCS Industrial Plants”



How much exergy is necessary to reconstitute earth’s atmosphere to its original constitution...
Exergetic analysis of separation processes…