

ENTROPIA E A SEGUNDA LEI DA TERMODINÂMICA

Paulo Seleglim Jr.
Universidade de São Paulo



Parte 1: Enunciados da 2ª lei, quantificando o nível de desordem de um sistema (ordem → desordem)

Parte 2: abordagens mecanicista e estatística (e também informacional)

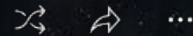
Parte 3: eficiência isentrópica e escoamentos compressíveis (aplicações de engenharia)



Curso de Termodinâmica e Aplicações de Engenharia

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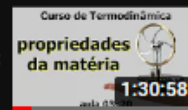
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No description

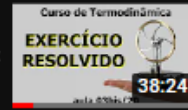


Prof. P. Seleglim



Aula 3 Propriedades Termodinâmicas e Diagramas de Equilíbrio

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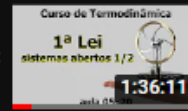
Aula 3bis Exercício Resolvido: TUTORIAL REFPROP

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Aula 4 Balanço de Energia em Sistemas Fechados

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Aula 5 Balanço de Energia em Sistemas Abertos - Regime Permanente

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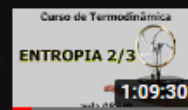
Aula 6 Balanço de Energia em Sistemas Abertos - Regime Transiente

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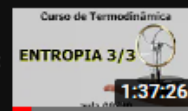
Aula 7 Entropia e a Segunda Lei da Termodinâmica

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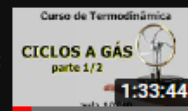
Aula 8 Entropia - Visões Mecanicista, Estatística e Informacional

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Aula 9 Entropia - Escoamentos Compressíveis e Eficiência Isentrópica

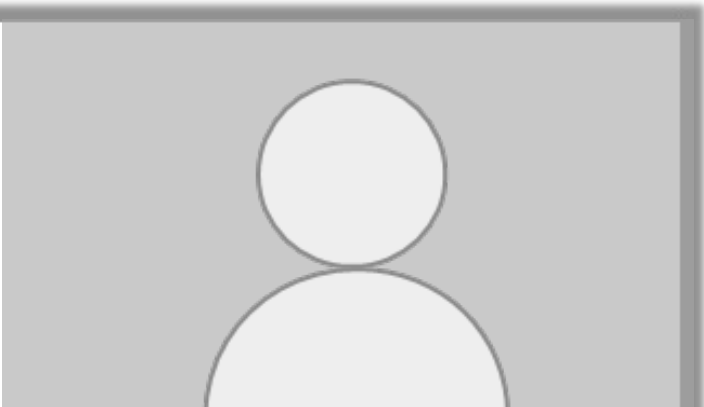
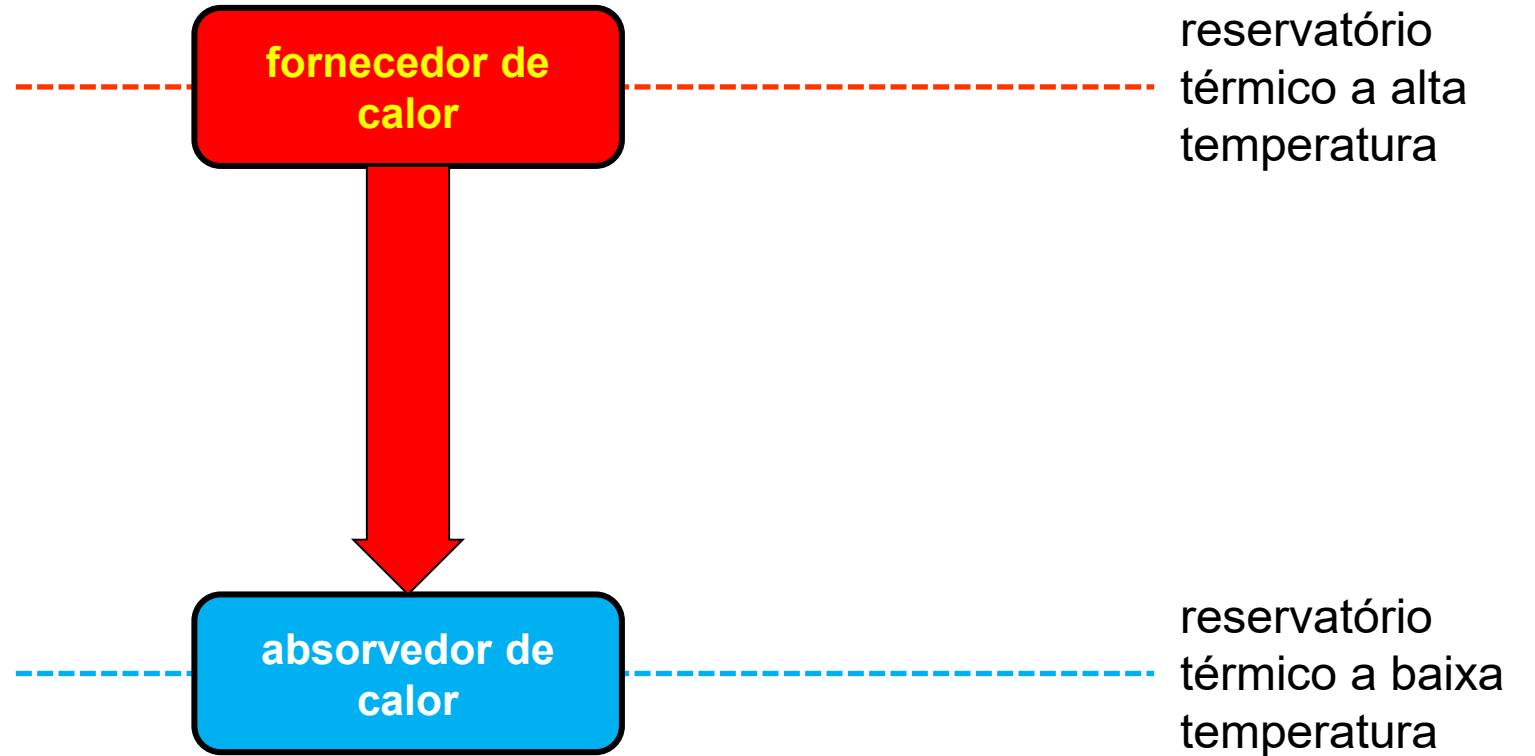
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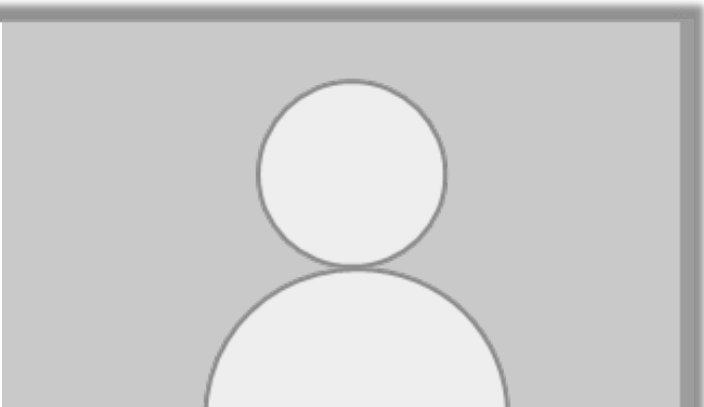
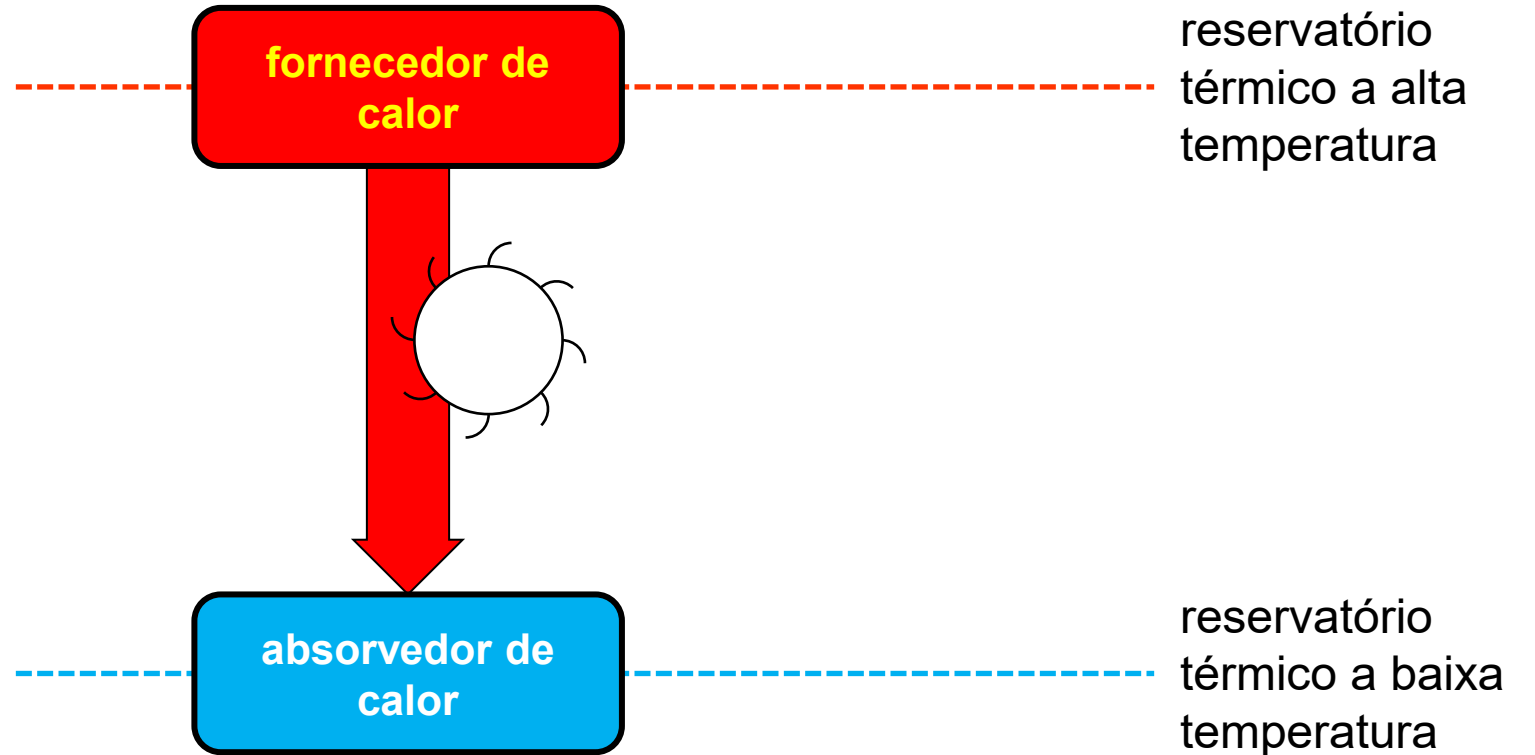
Aula 10 Ciclos de Potência a Gás - Parte 1 / Stirling, Otto, Diesel e Brayton

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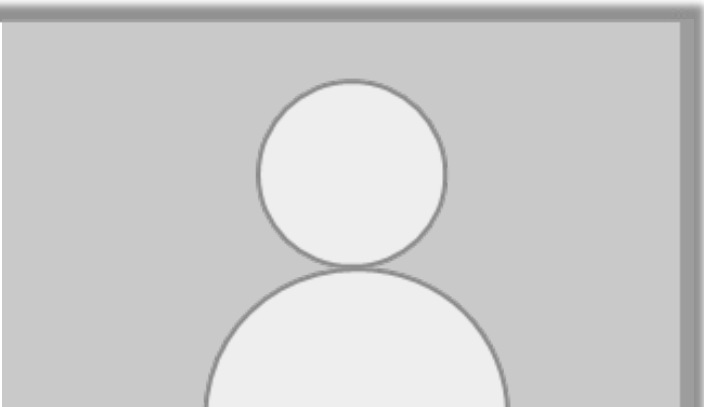
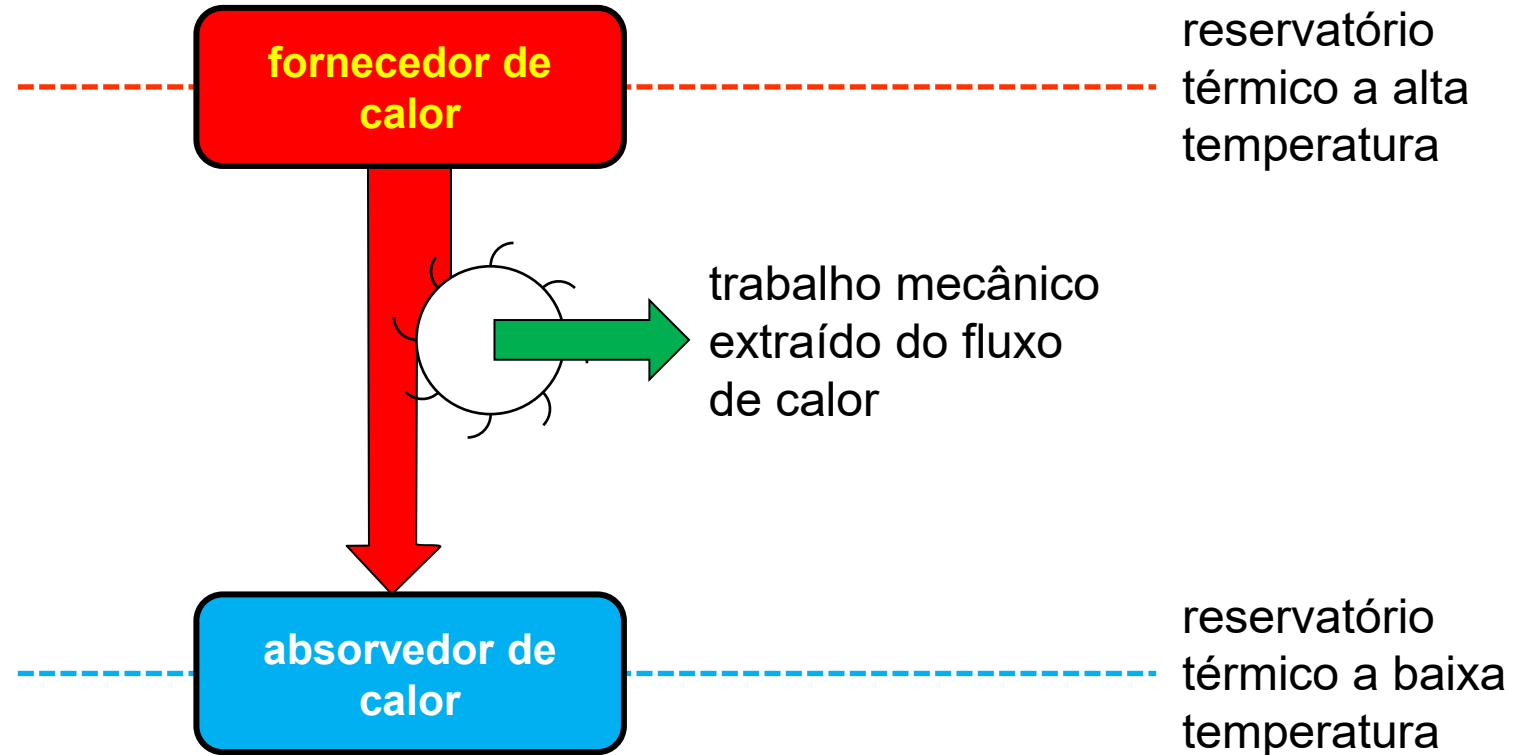
Sentido espontâneo do fluxo de energia



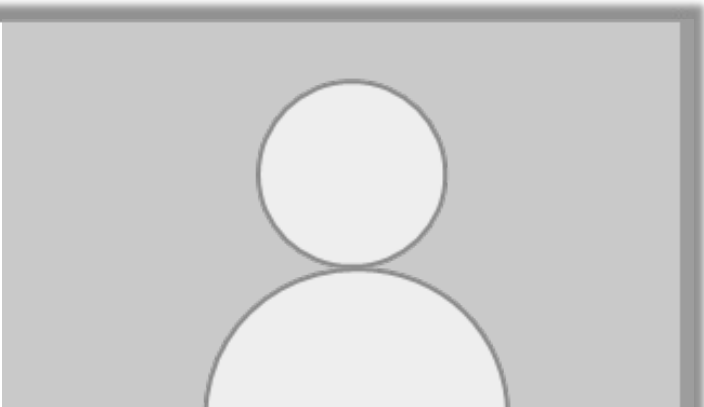
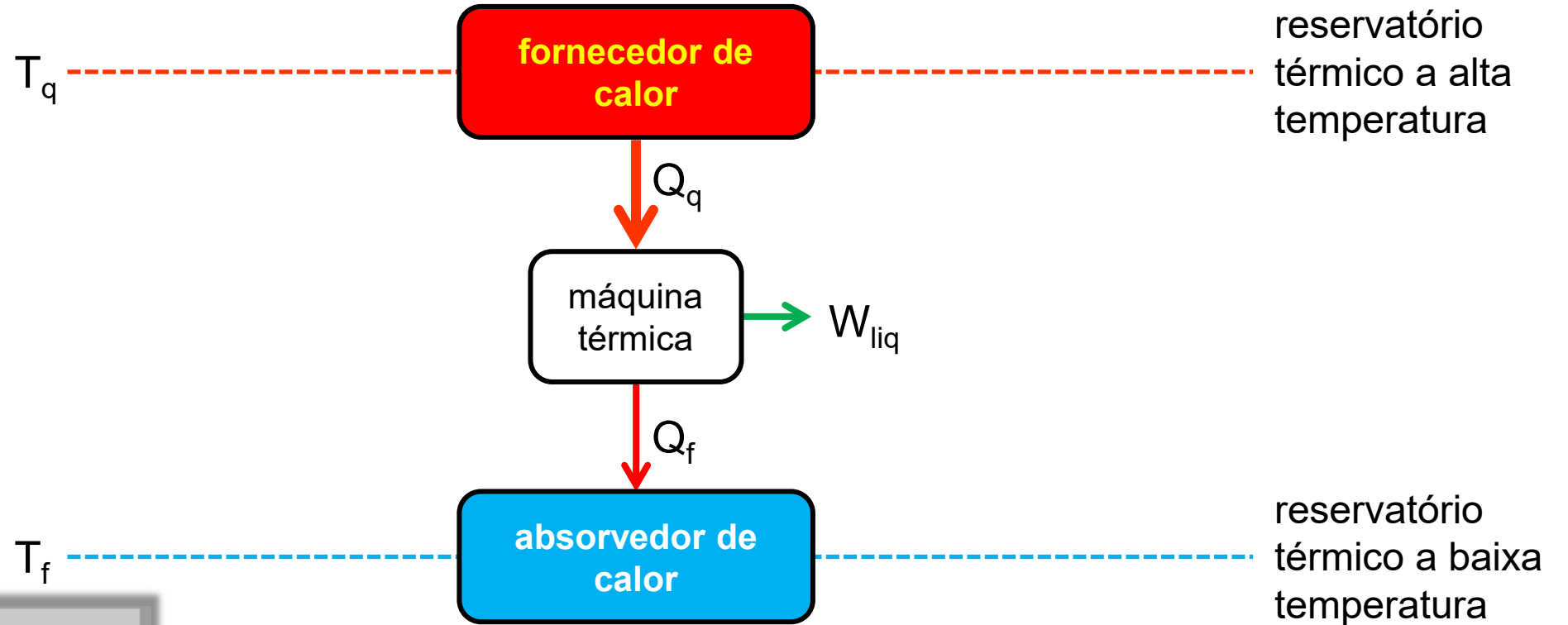
Sentido espontâneo do fluxo de energia



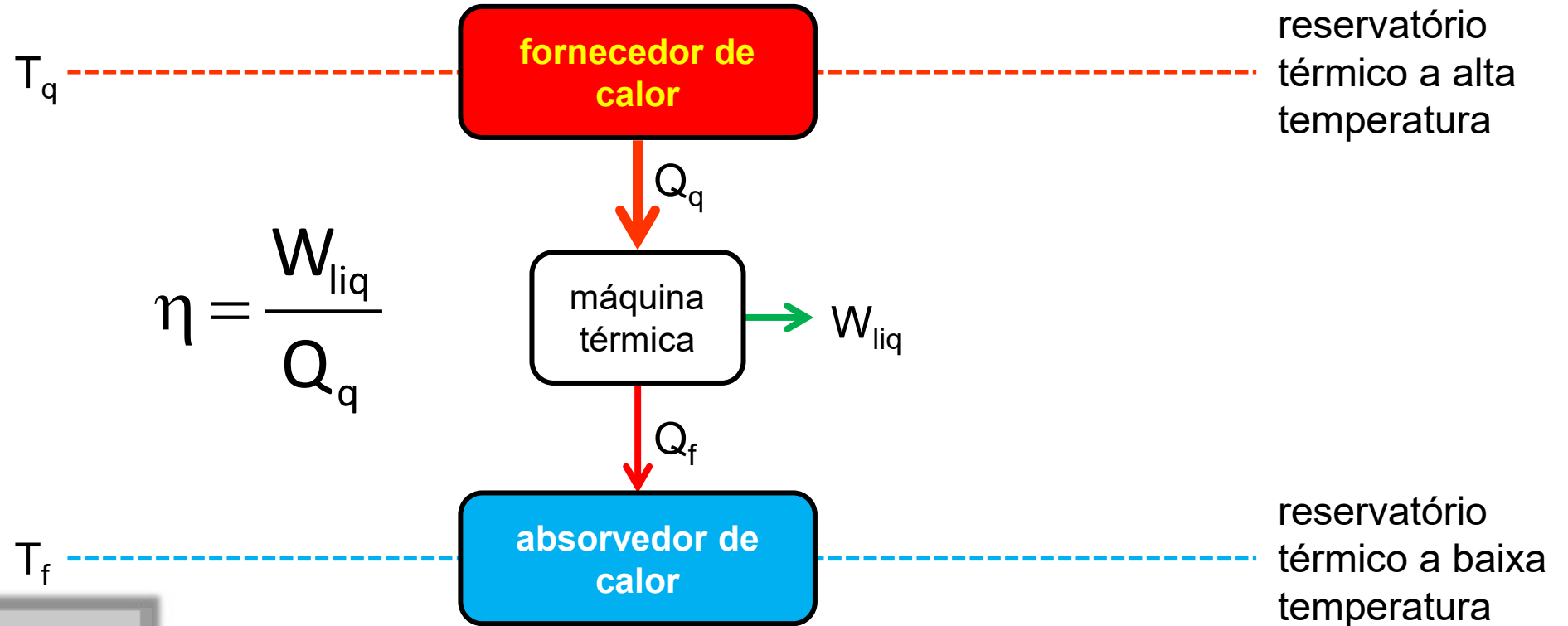
Sentido espontâneo do fluxo de energia



Sentido espontâneo do fluxo de energia

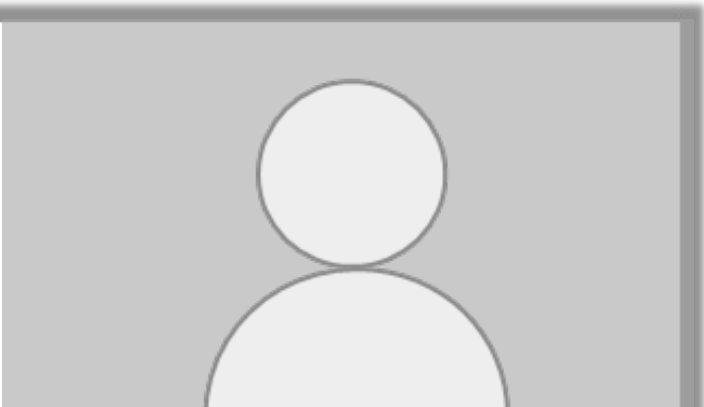


Sentido espontâneo do fluxo de energia



$$\eta = \frac{W_{liq}}{Q_q}$$

eficiência do ciclo de conversão



Sentido espontâneo do fluxo de energia

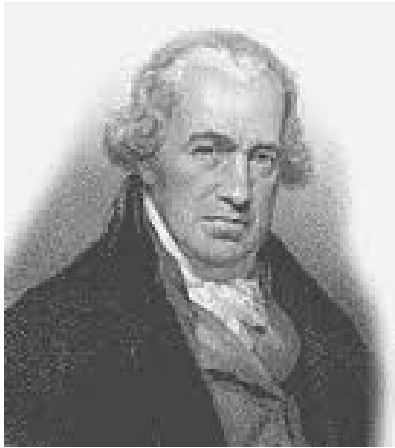
$$\eta = \frac{W_{\text{liq}}}{Q_{\text{q}}}$$

equivalente ao trabalho executado por xxx cavalos
unidade de potência → HP

custo proporcional a uma determinada quantidade de carvão (fonte de calor)



Sentido espontâneo do fluxo de energia

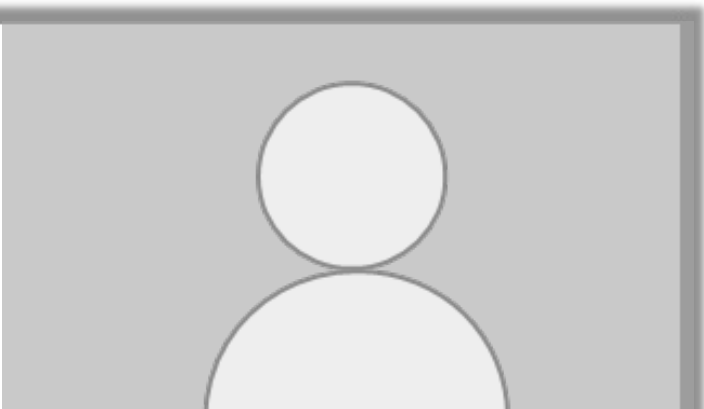
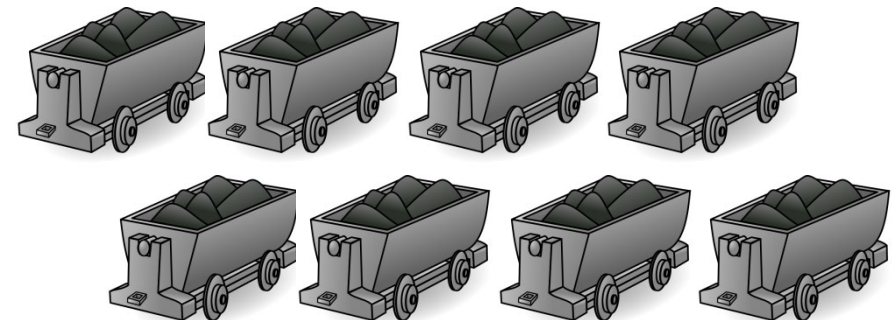
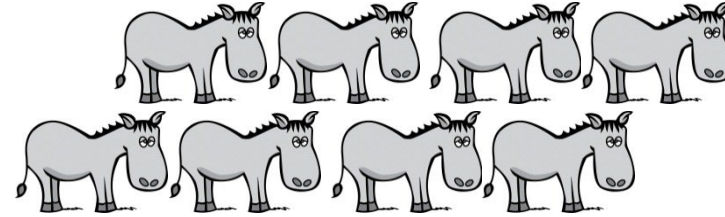


J. Watt desenvolveu o conceito de "cavalo-vapor" para facilitar a venda de sua máquina térmica (ele ficou muito rico...)

$$\eta = \frac{W_{\text{liq}}}{Q_{\text{q}}}$$

equivalente ao trabalho executado por xxx cavalos
unidade de potência → HP

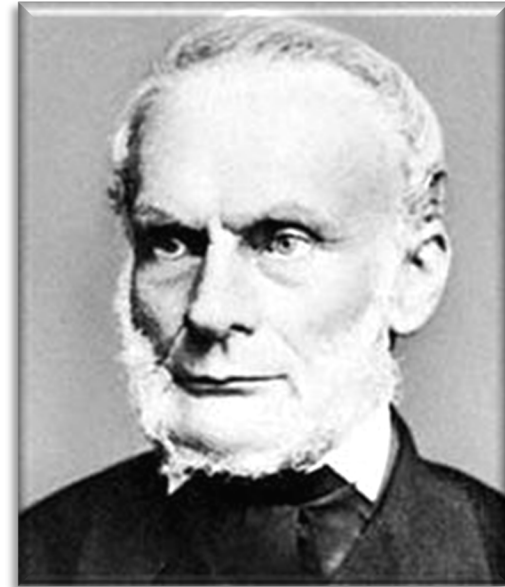
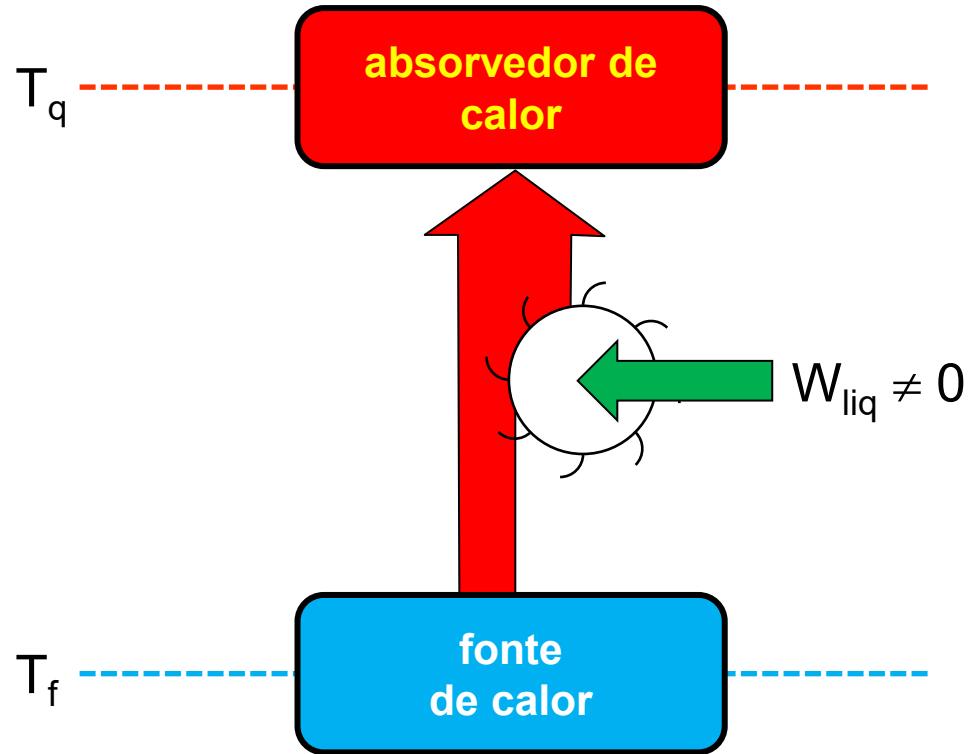
custo proporcional a uma determinada quantidade de carvão (fonte de calor)



A SEGUNDA LEI DA TERMODINÂMICA...



Segunda lei da termodinâmica: enunciado de Clausius

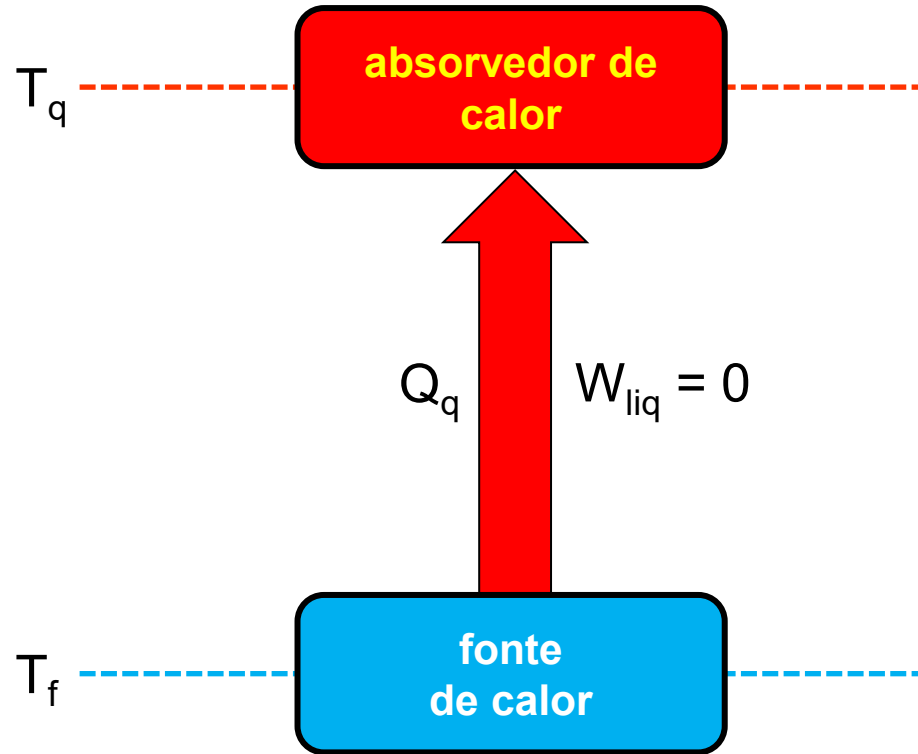


Rudolf Julius Emanuel Clausius
(1822 –1888)

R. Clausius.

POSSÍVEL

Segunda lei da termodinâmica: enunciado de Clausius

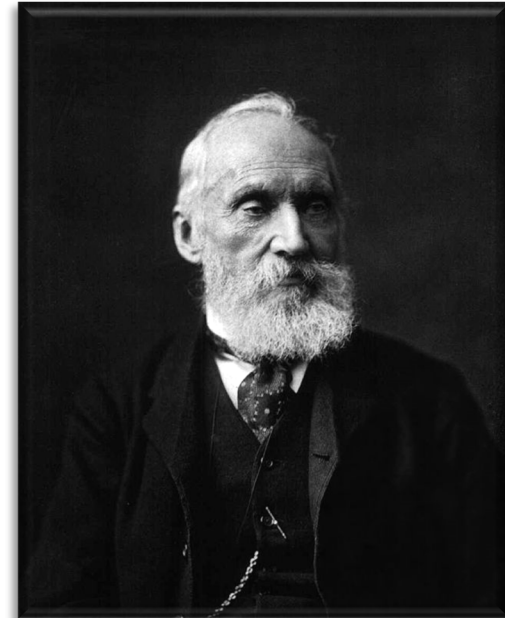
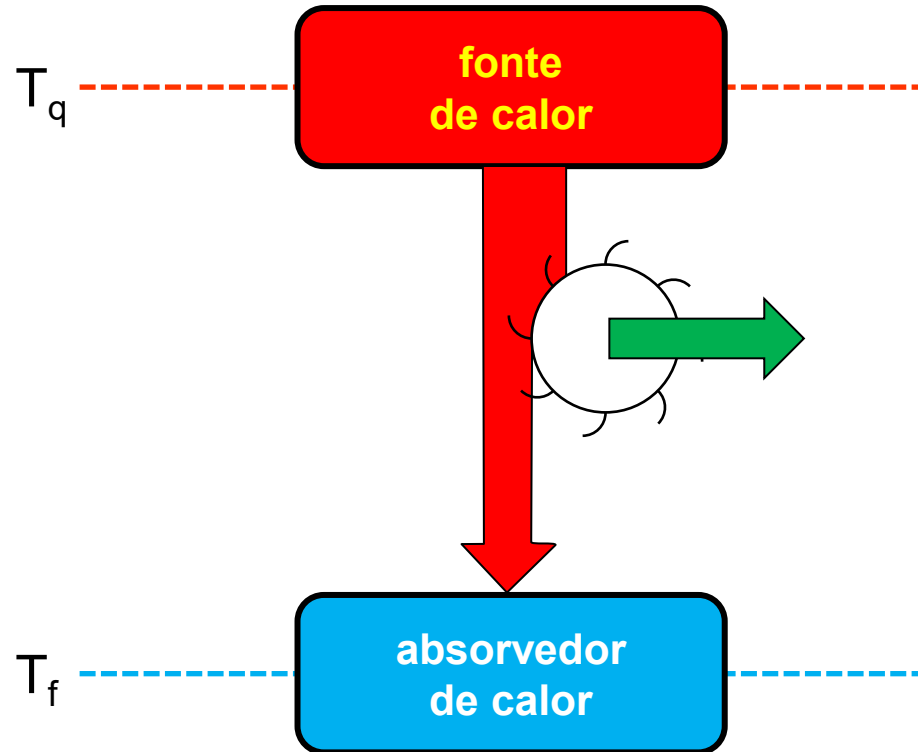


Rudolf Julius Emanuel Clausius
(1822 –1888)

R. Clausius.

IMPOSSÍVEL

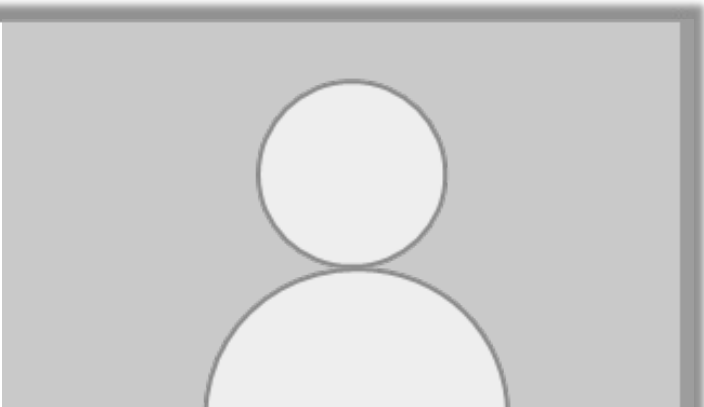
Segunda lei da termodinâmica: Kelvin-Planck



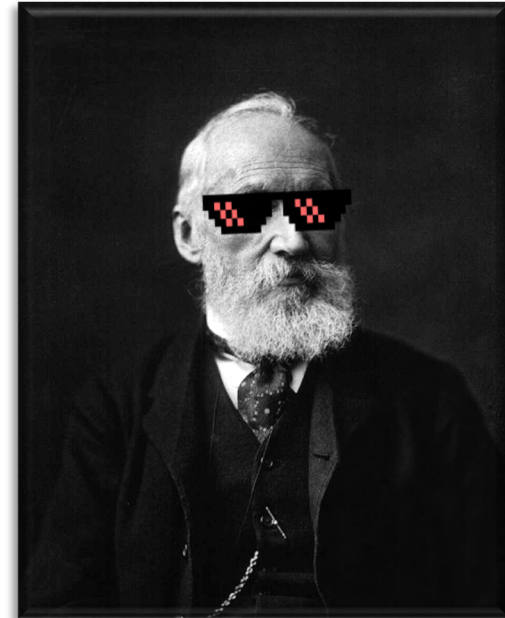
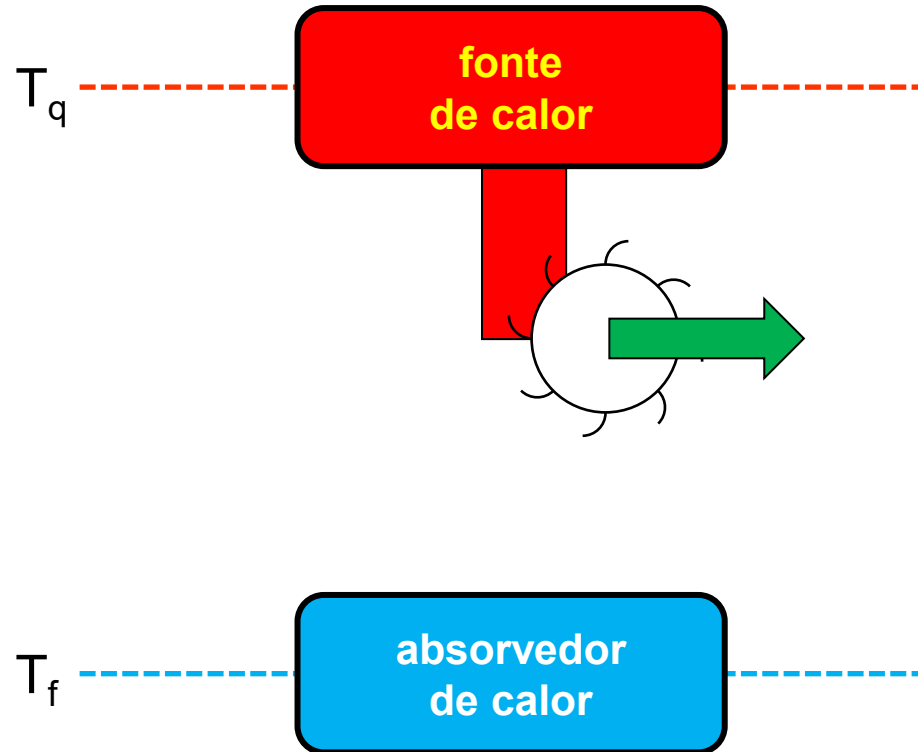
William Thomson, 1st Baron Kelvin
(1824 – 1907)

Kelvin PNP

POSSÍVEL



Segunda lei da termodinâmica: Kelvin-Planck



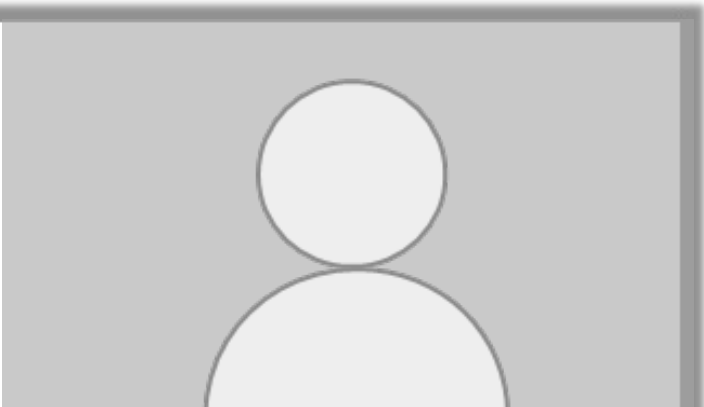
William Thomson, 1st Baron Kelvin
(1824 – 1907)

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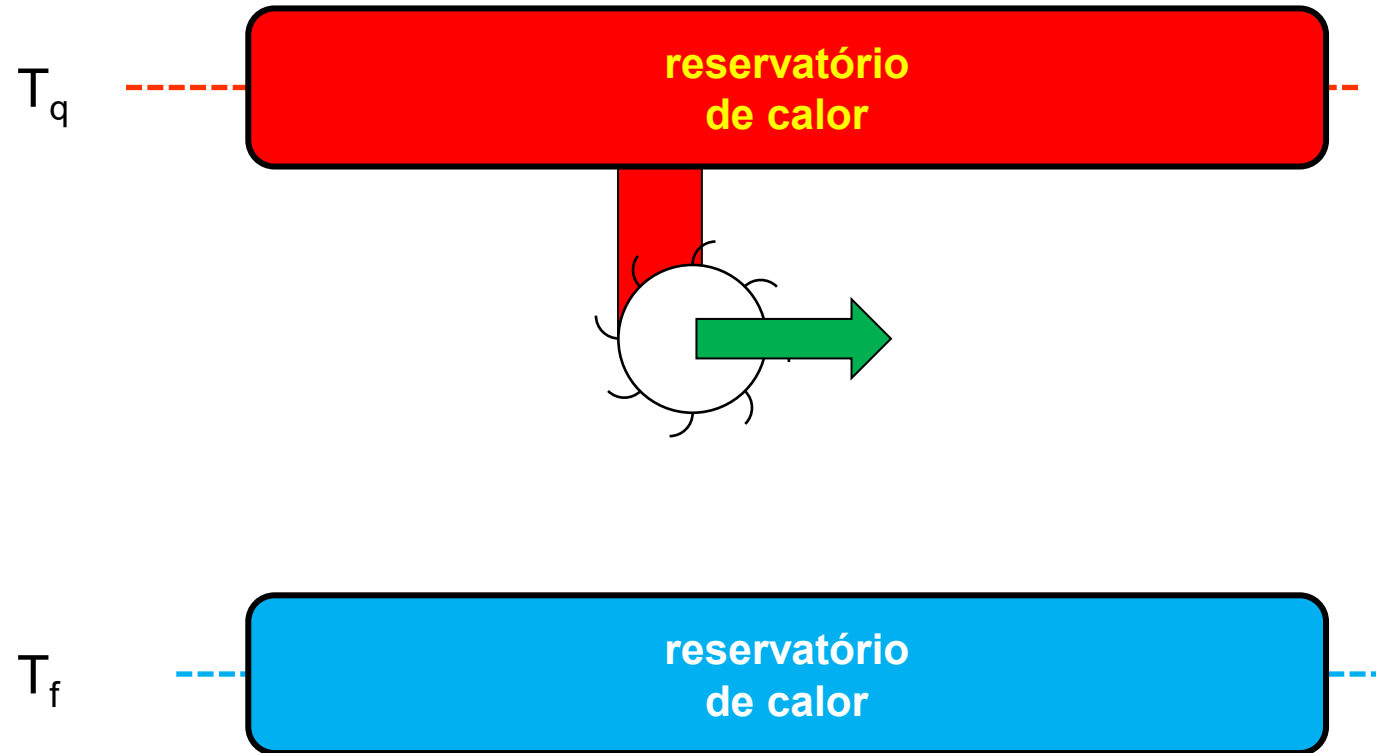
IMPOSSÍVEL



Equivalência dos dois enunciados da segunda lei



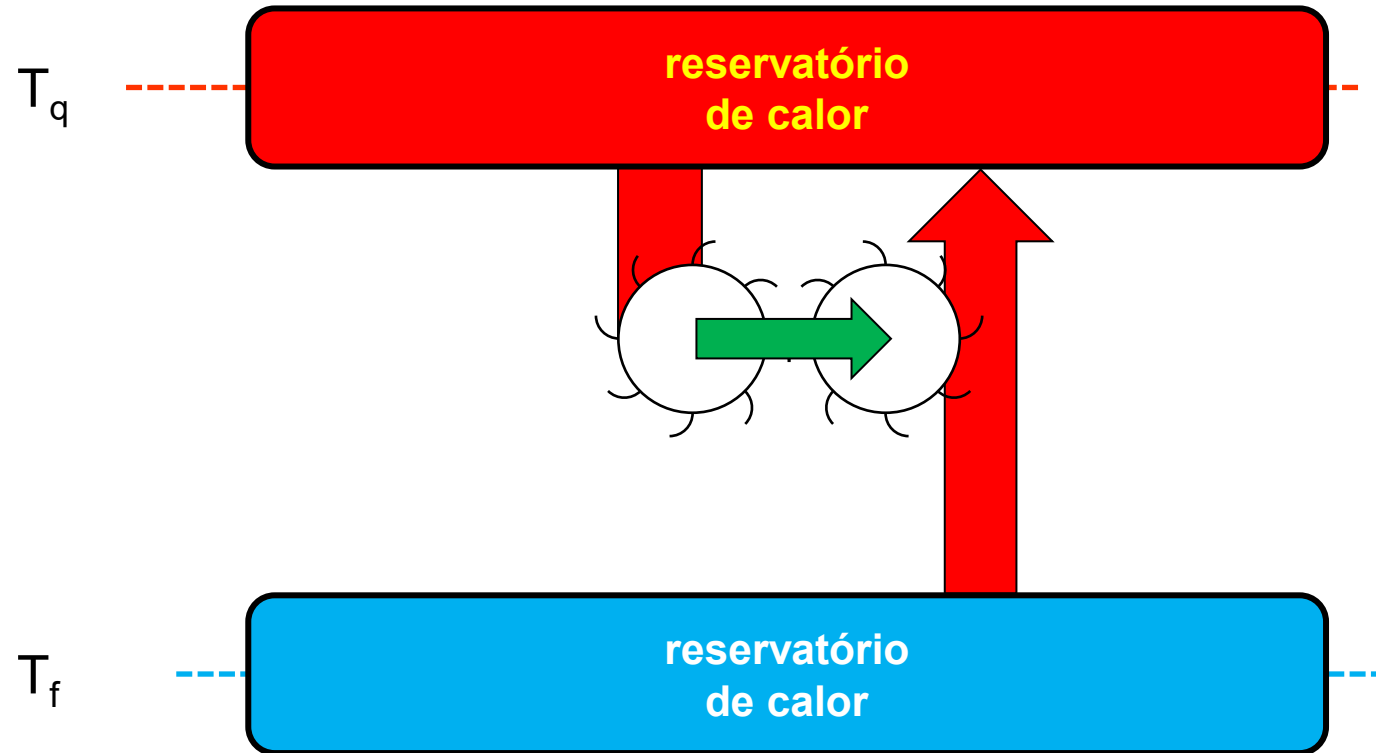
Equivalência dos dois enunciados da segunda lei



POSSÍVEL
por hipótese



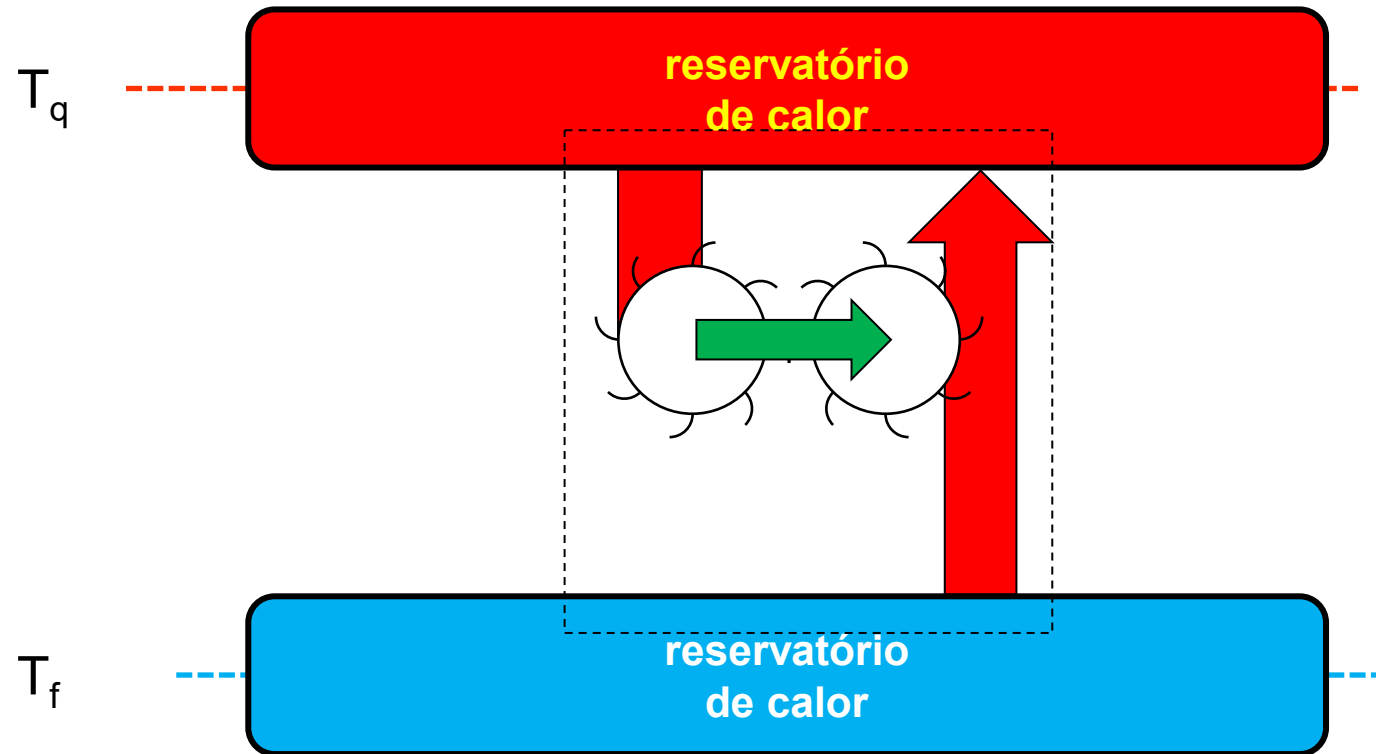
Equivalência dos dois enunciados da segunda lei



POSSÍVEL
por hipótese



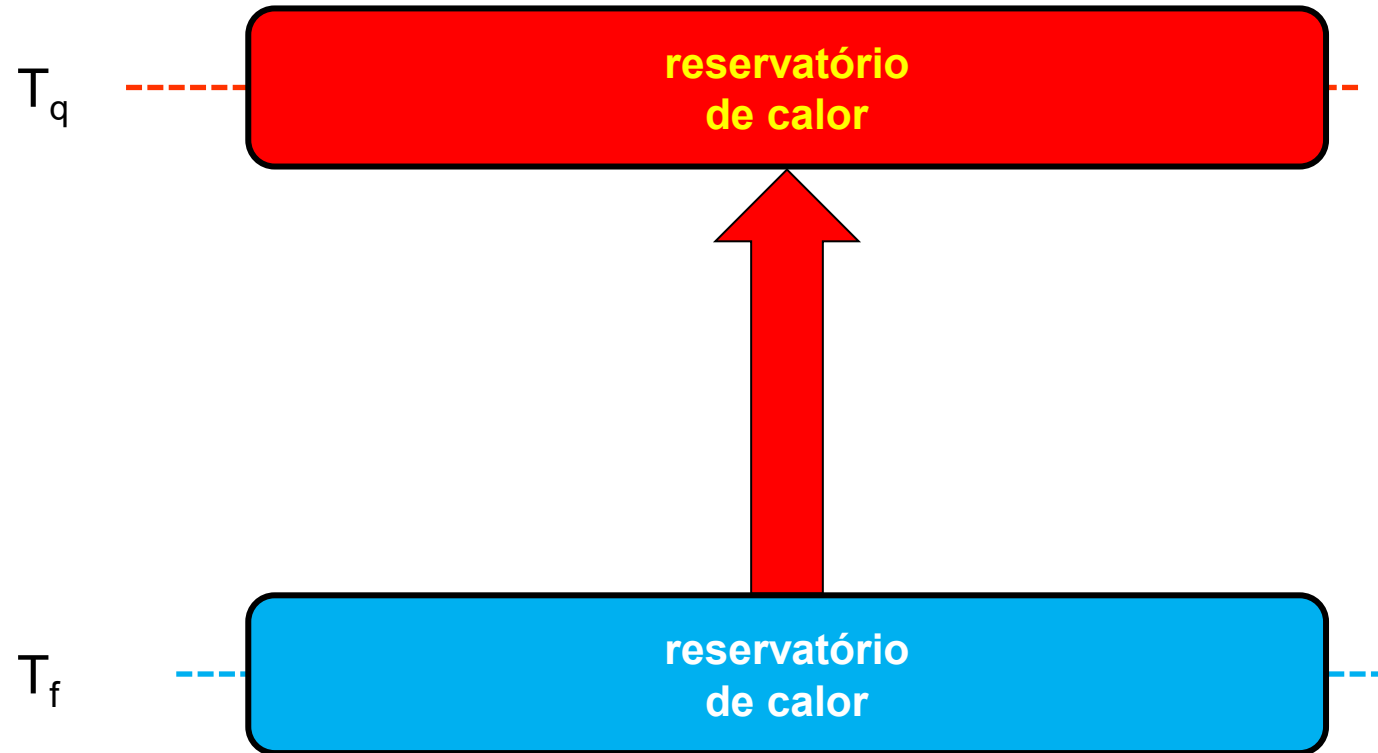
Equivalência dos dois enunciados da segunda lei



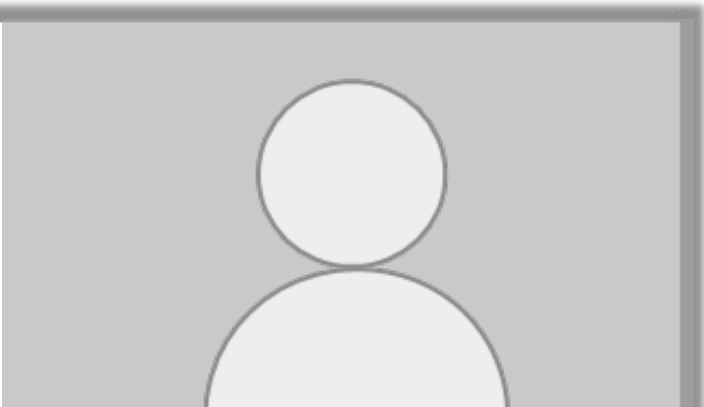
POSSÍVEL
por hipótese



Equivalência dos dois enunciados da segunda lei



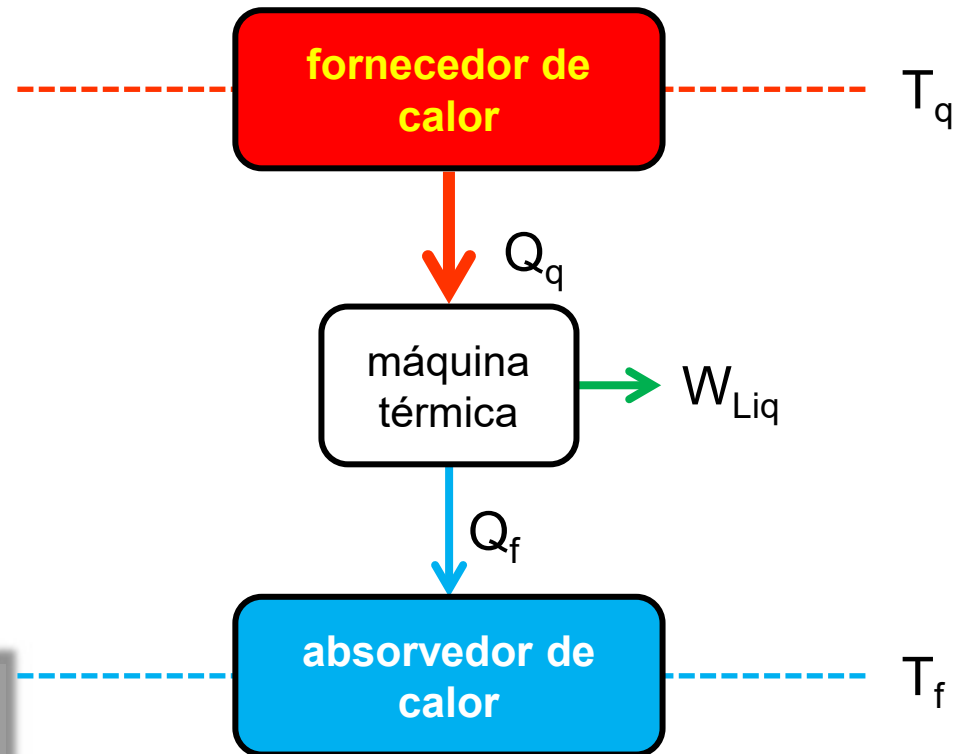
→ POSSÍVEL



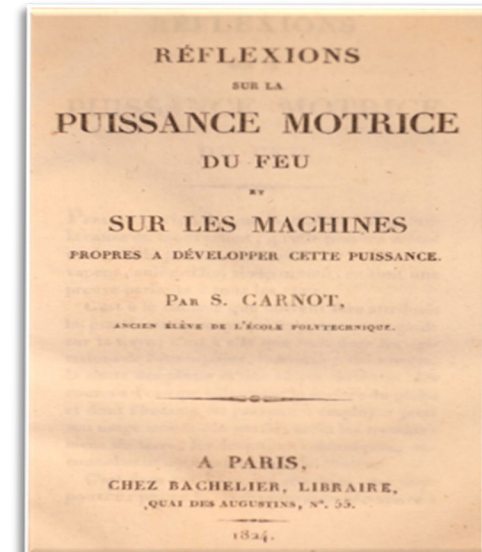
A MÁXIMA EFICIÊNCIA DE CONVERSÃO $Q \rightarrow W...$



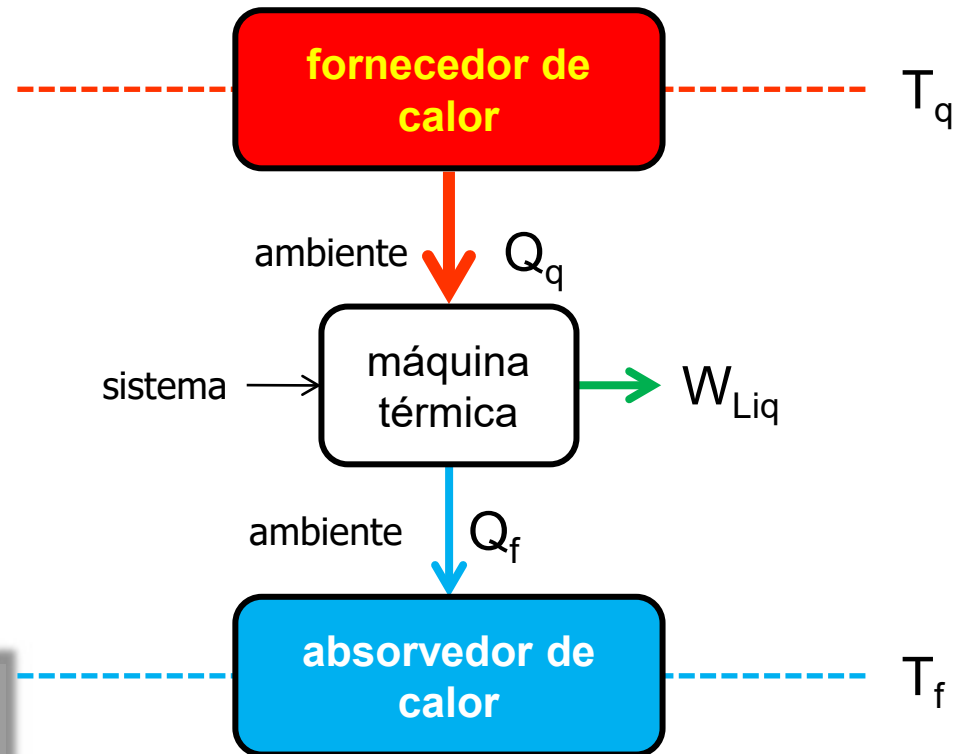
Máxima eficiência de conversão



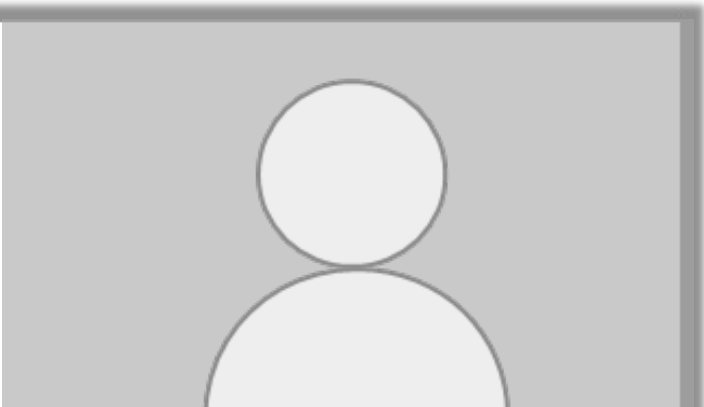
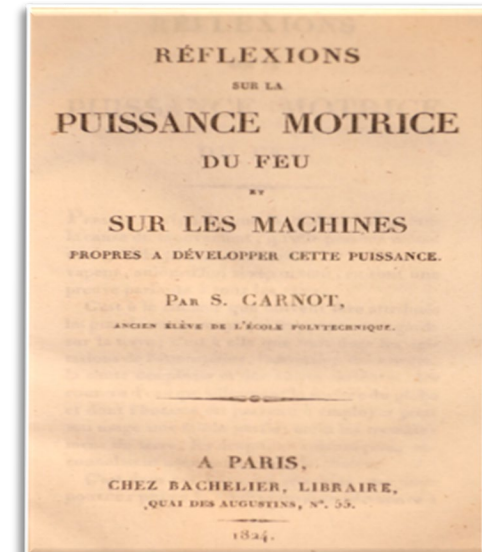
Nicolas Léonard Sadi Carnot em 1824, aos vinte anos de idade



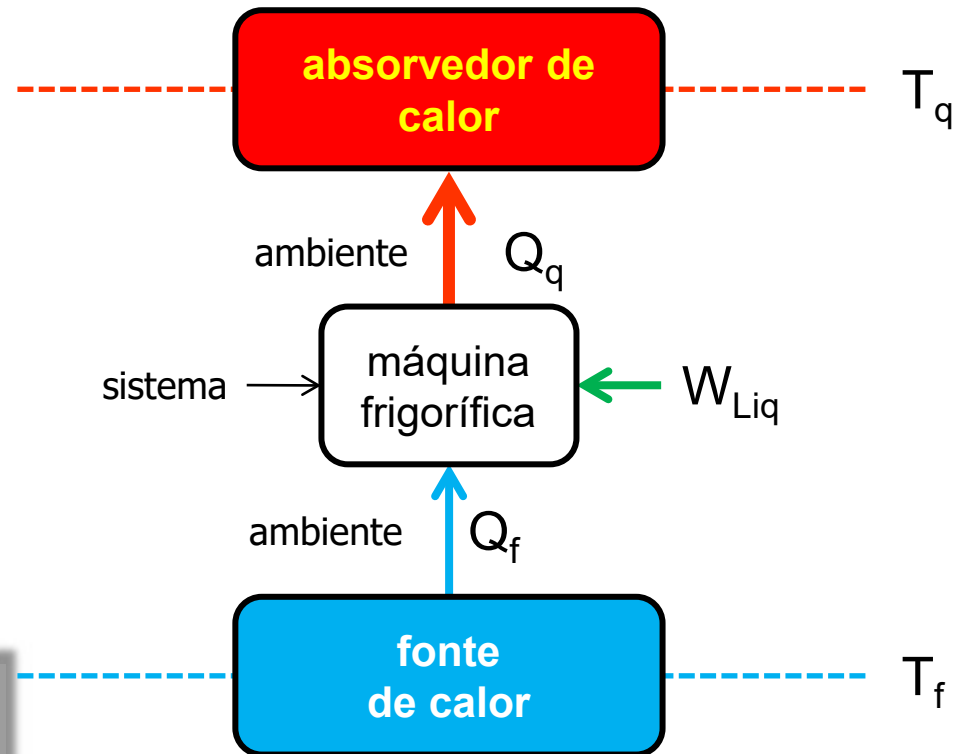
Máxima eficiência de conversão



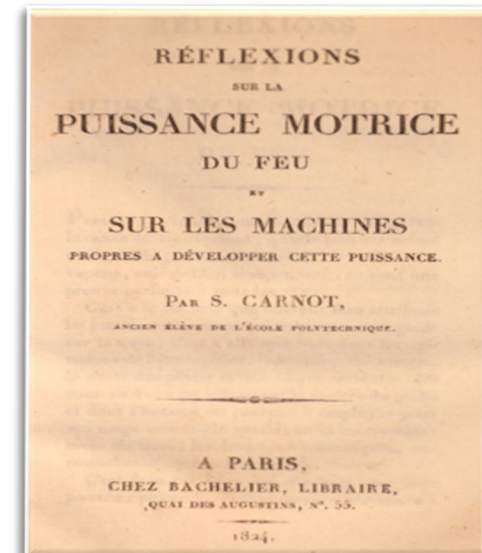
Nicolas Léonard Sadi Carnot em 1824, aos vinte anos de idade



Máxima eficiência de conversão

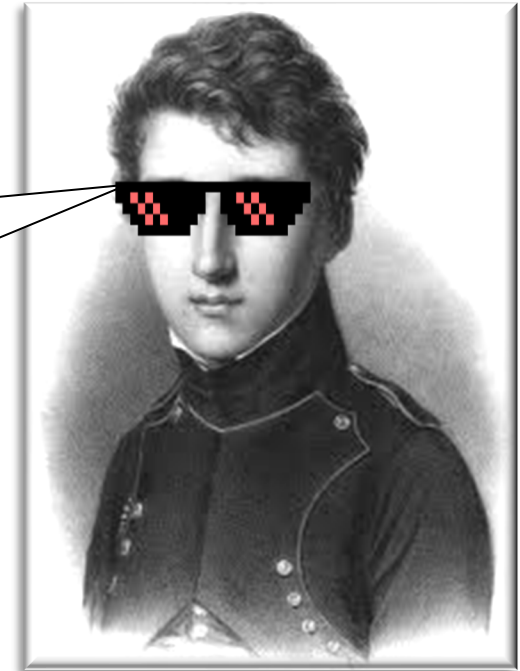


Nicolas Léonard Sadi Carnot em 1824, aos vinte anos de idade



Máxima eficiência de conversão

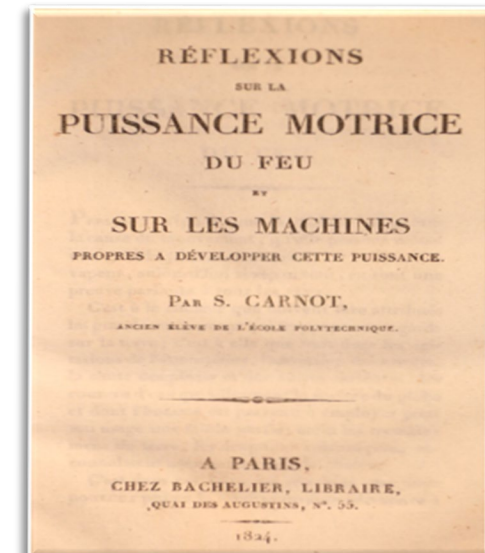
*"Le moteur peut être **actionné en sens inverse** et le résultat net serait alors la consommation d'un **travail égal** à celui produit par le fonctionnement en **sens direct** et le transfert de la **même quantité de chaleur**, mais dans ce cas du corps froid au corps chaud..*



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

**Máxima Eficiência:
ocorre quando a máquina
térmica é reversível !!!**

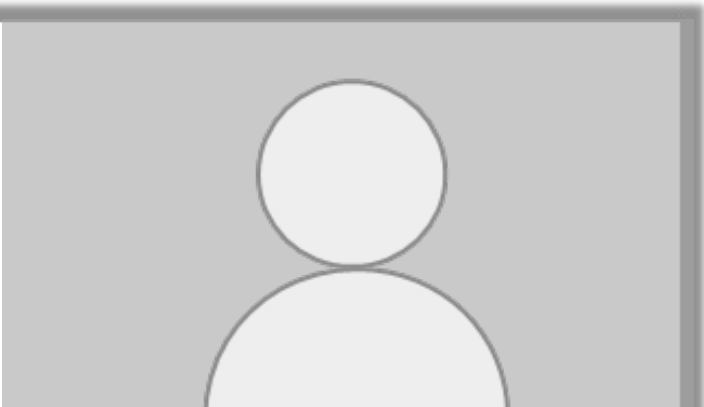
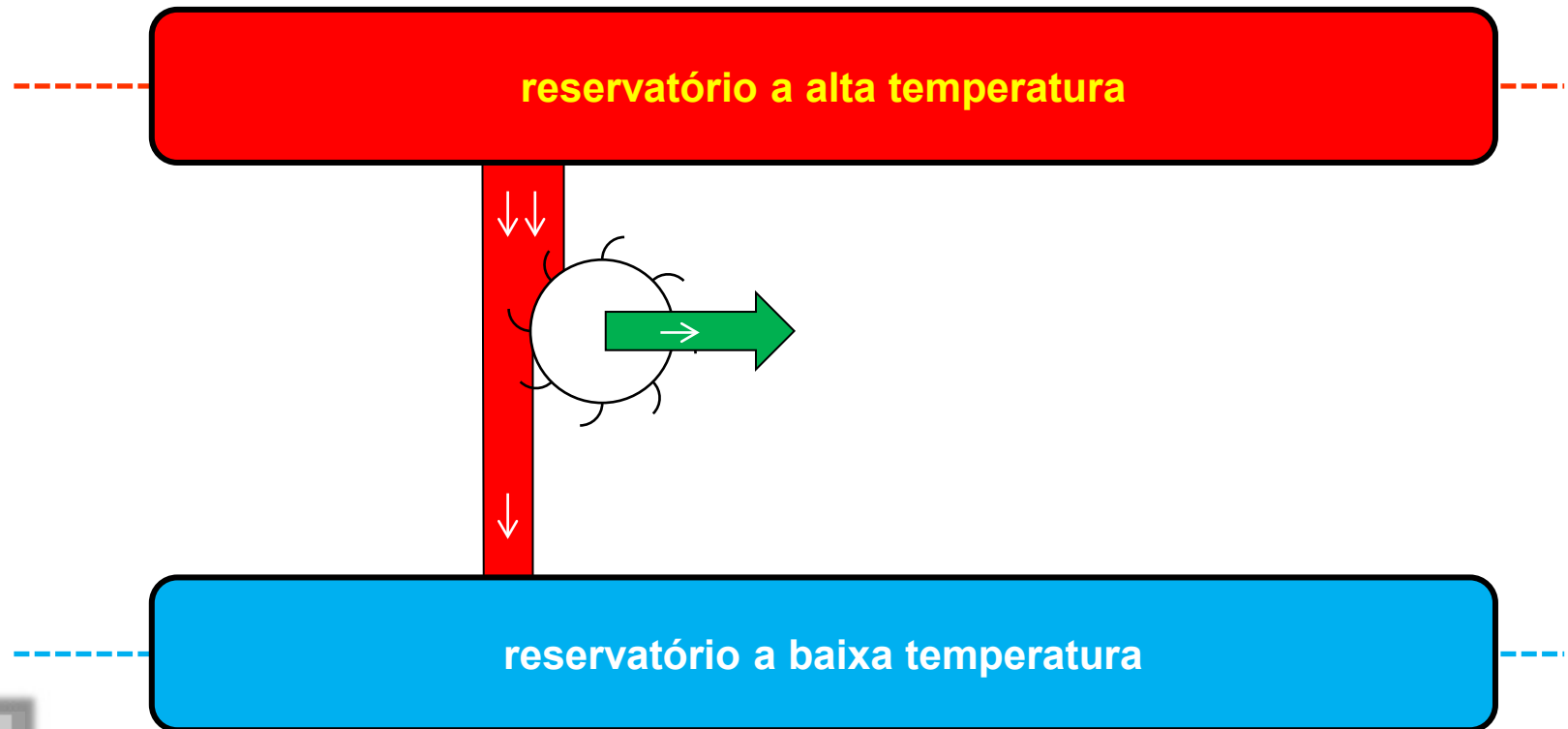
Reversibilidade estrita: ocorre quando a troca de calor e a realização de trabalho entre o **sistema e o ambiente** for nulo para o processo combinado (original e inverso), o que sabemos ser IMPOSSÍVEL !



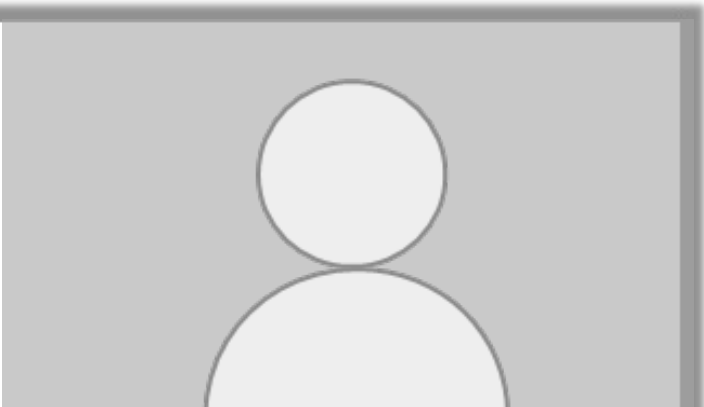
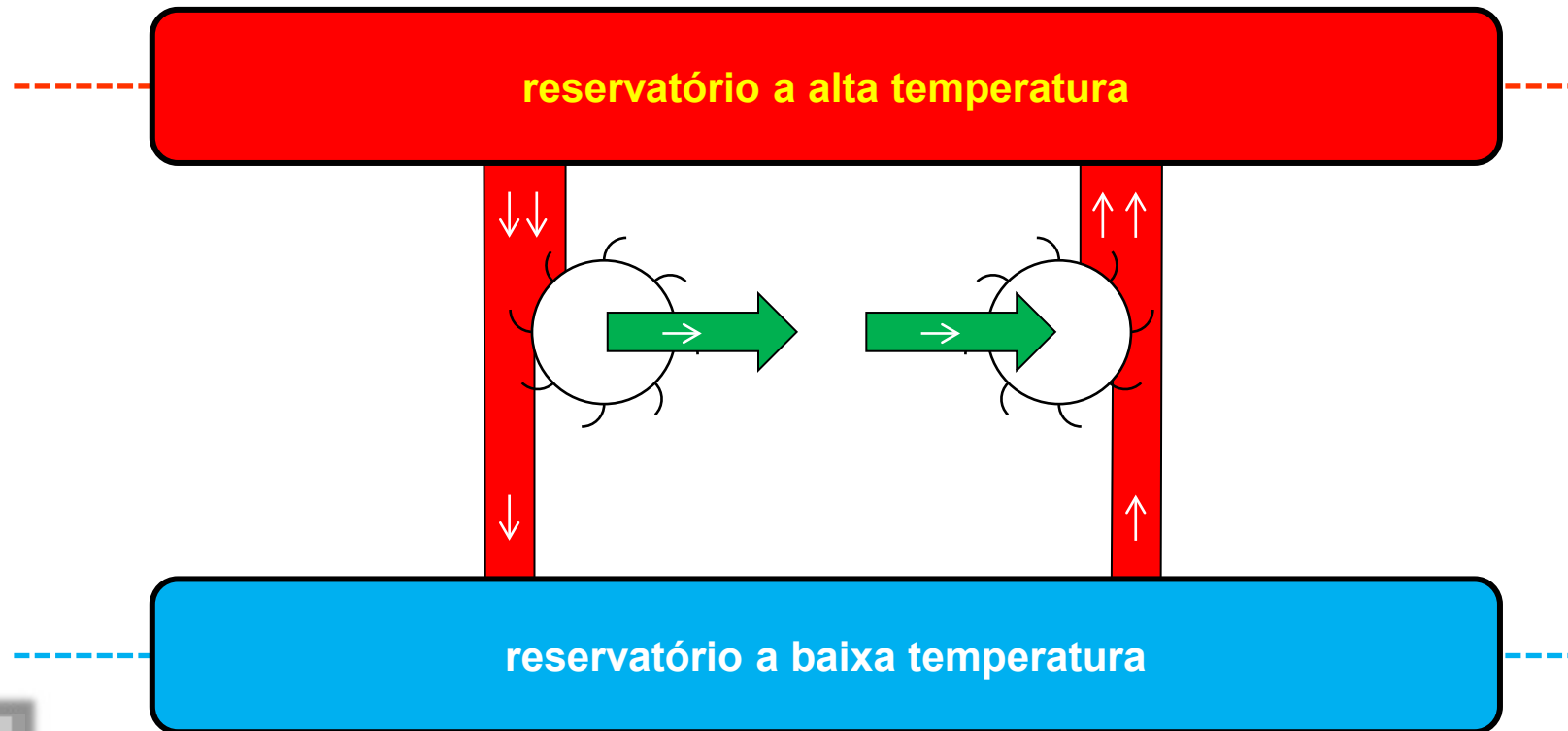
O QUE SIGNIFICA REVERSIBILIDADE ESTRITA ?



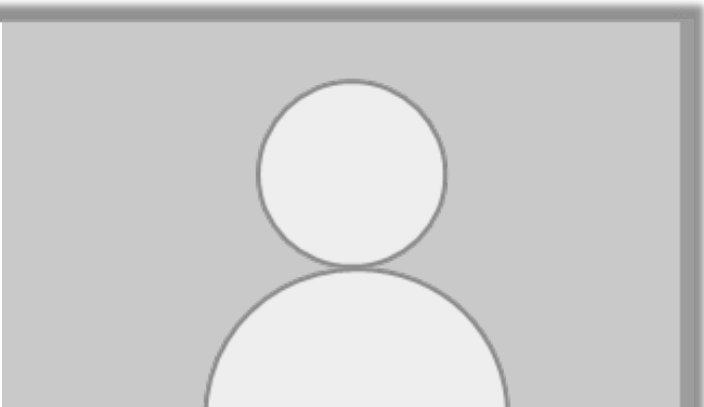
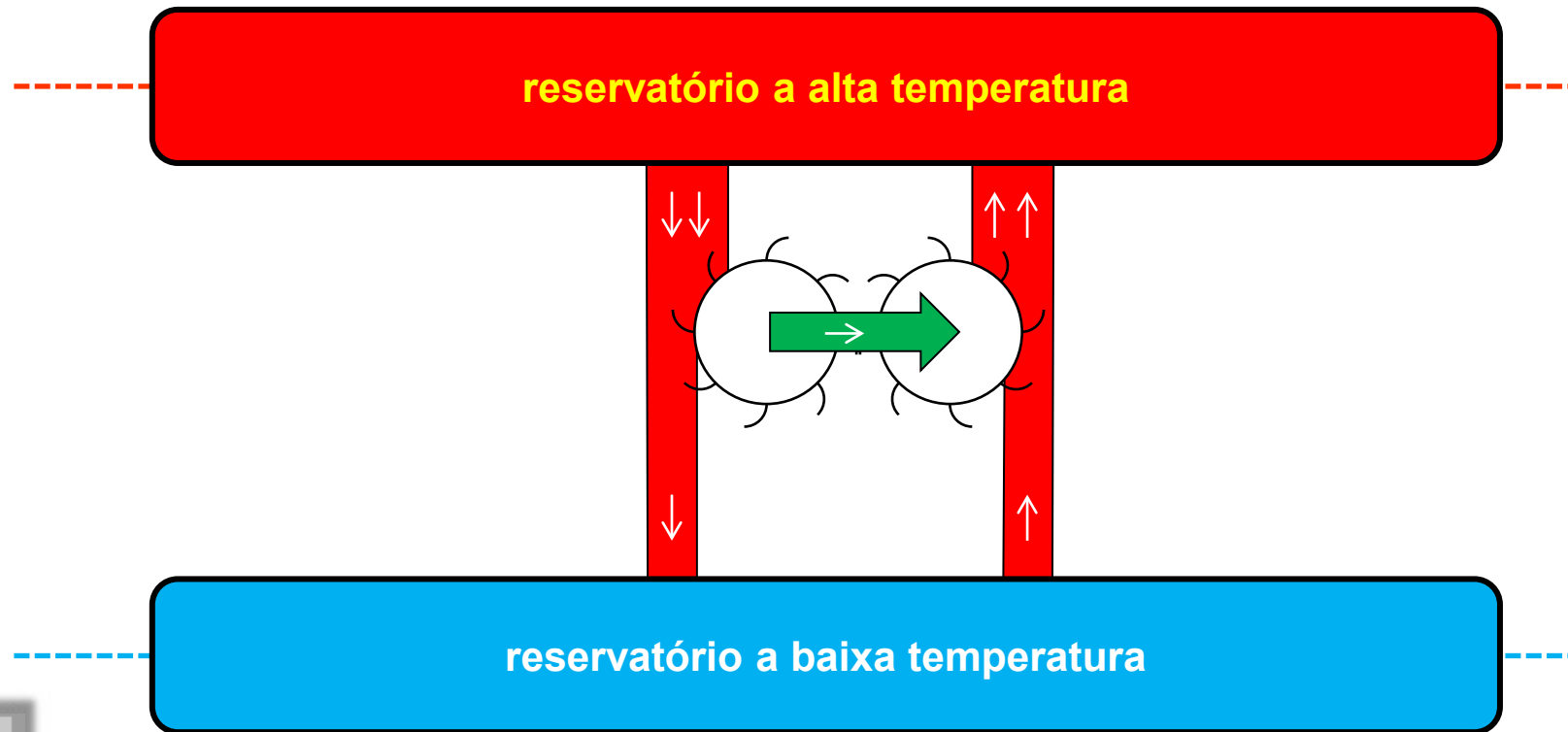
O conceito de reversibilidade estrita...



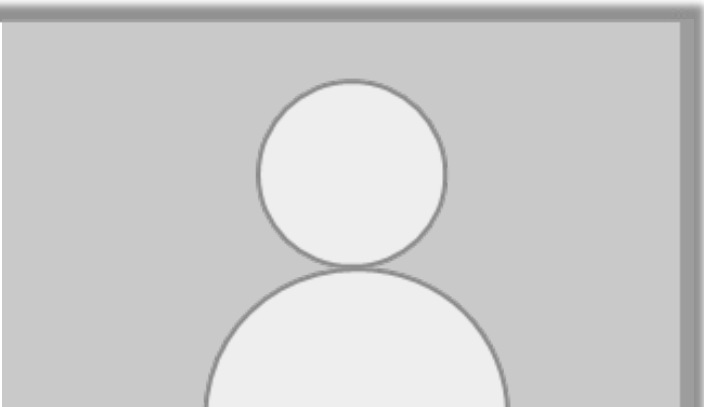
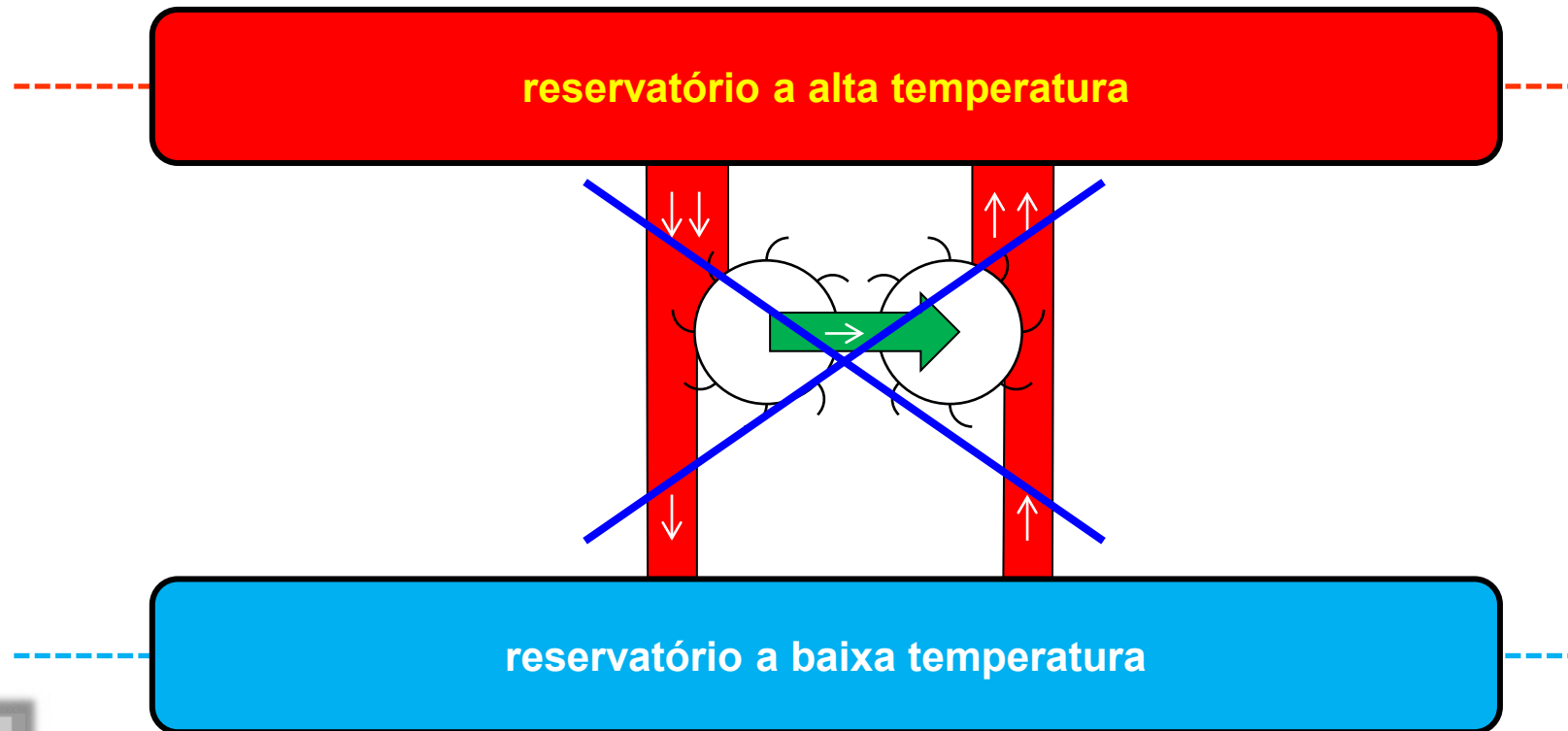
O conceito de reversibilidade estrita...



O conceito de reversibilidade estrita...



O conceito de reversibilidade estrita...



O conceito de reversibilidade estrita...



reservatório a alta temperatura

reservatório a baixa temperatura



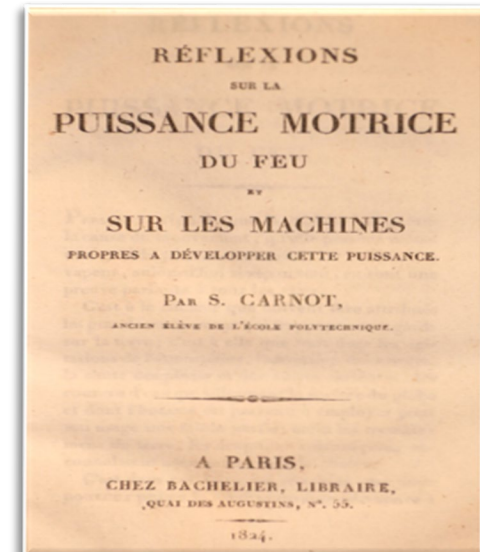
Máxima eficiência de conversão

- $\eta < 1$ para $\Delta T < \infty$
- $\eta_{\text{rev}} > \eta_{\text{irrev}}$
- $\eta_{\text{rev},m} = \eta_{\text{rev},n} \quad \forall m,n$
- $\eta_{\text{rev}} = f(T_f, T_q)$

↑
É a diferença de temperaturas entre os reservatórios quente e frio influi na eficiência, e não a diferença de pressão como se pensava...



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



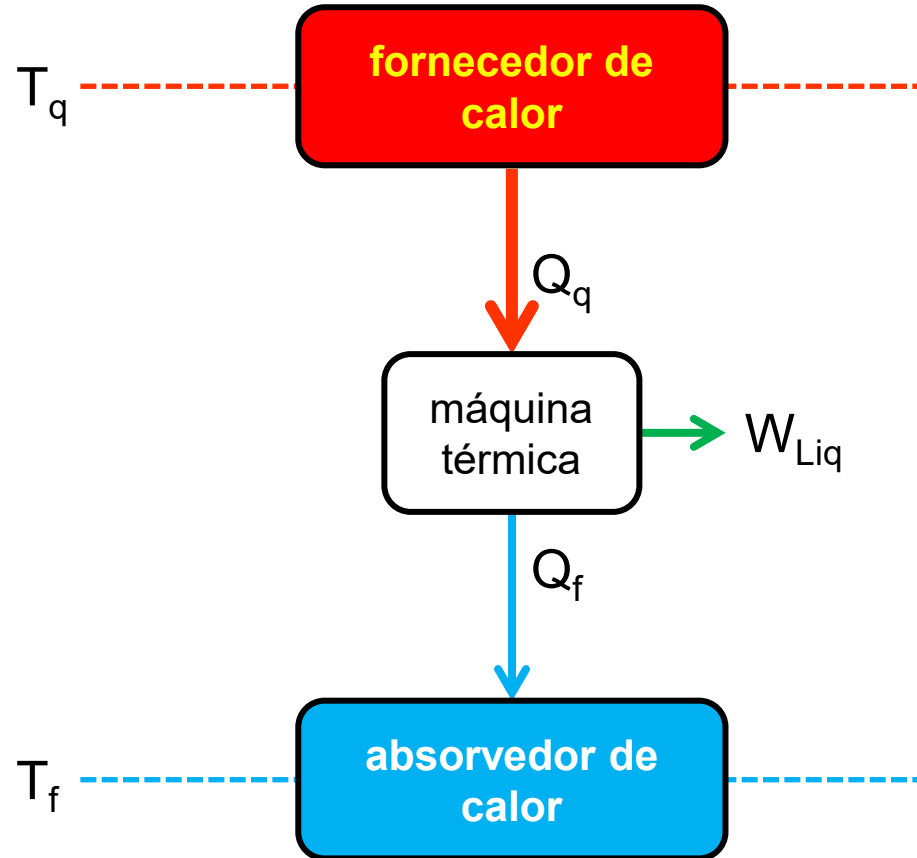
A ESCALA TERMODINÂMICA DE TEMPERATURA



A escala termodinâmica de temperatura



$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$

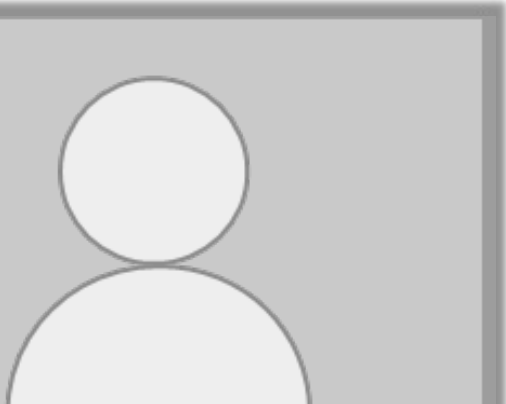


primeira lei

$$\eta = \frac{W_{\text{liq}}}{Q_q} = \frac{Q_q - Q_f}{Q_q}$$
$$\eta = 1 - \frac{Q_f}{Q_q}$$

postulado de Carnot

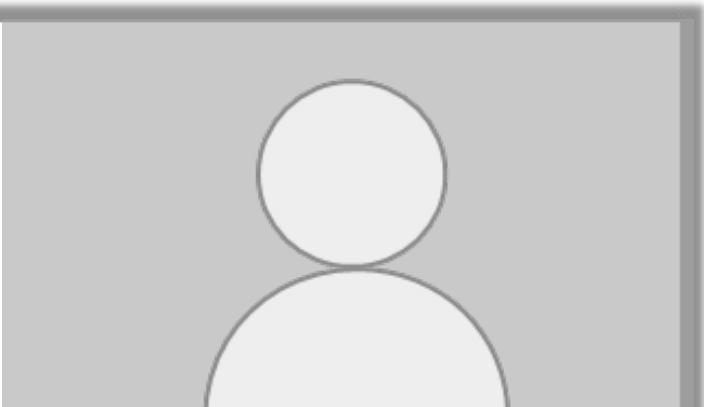
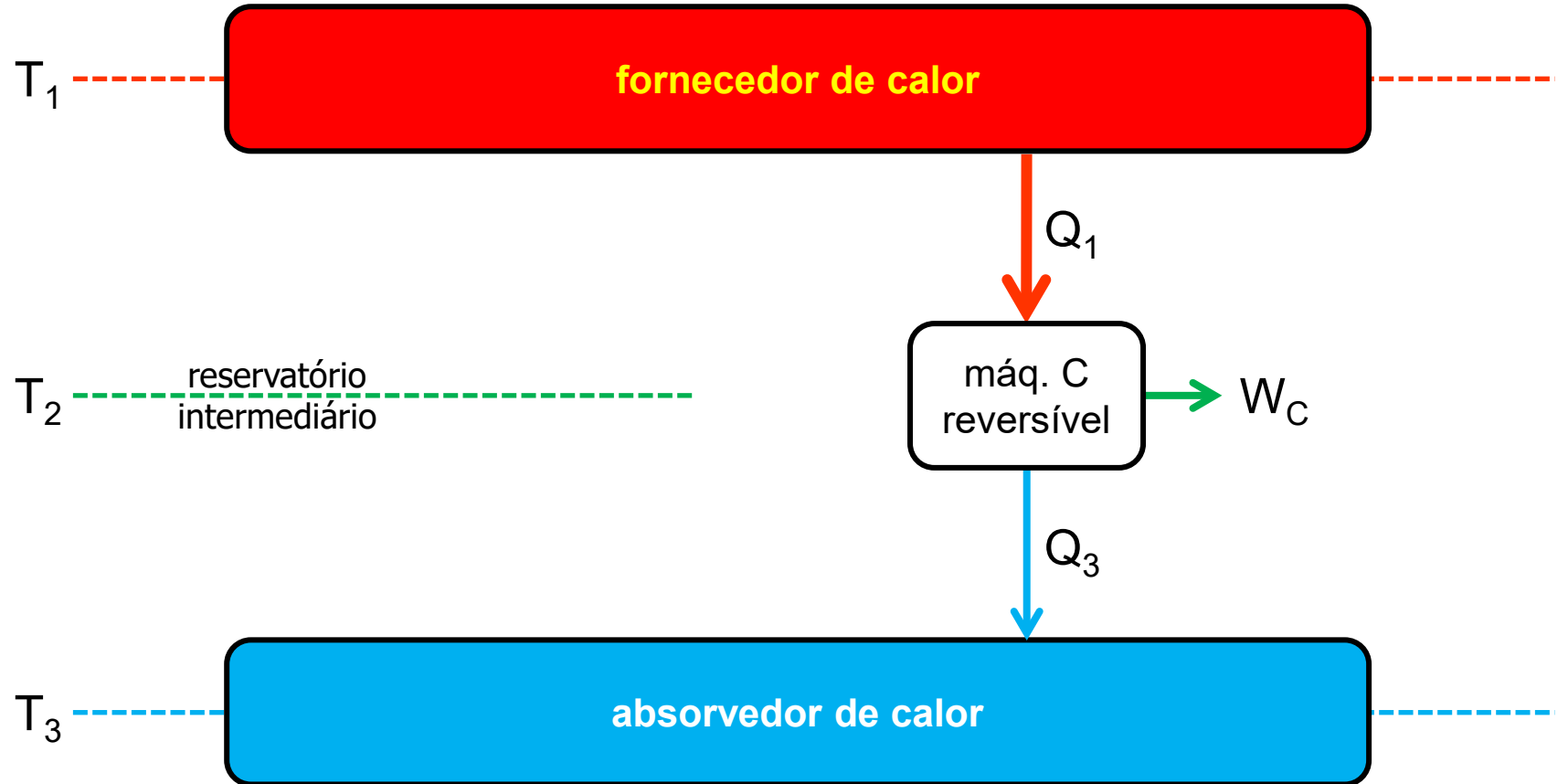
$$\eta = 1 - \frac{Q_f}{Q_q} \stackrel{c}{=} f(T_f, T_q)$$



A escala termodinâmica de temperatura



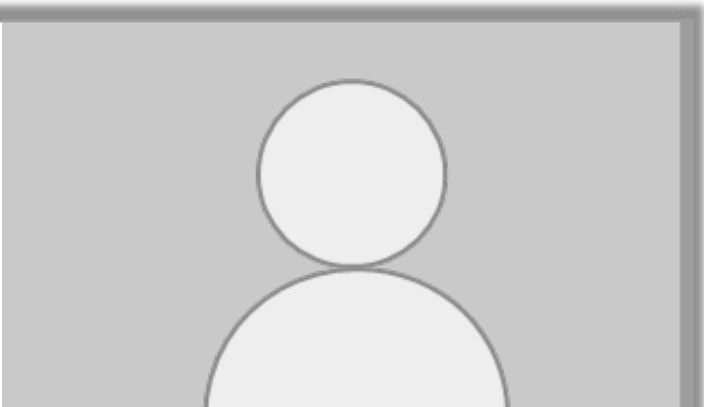
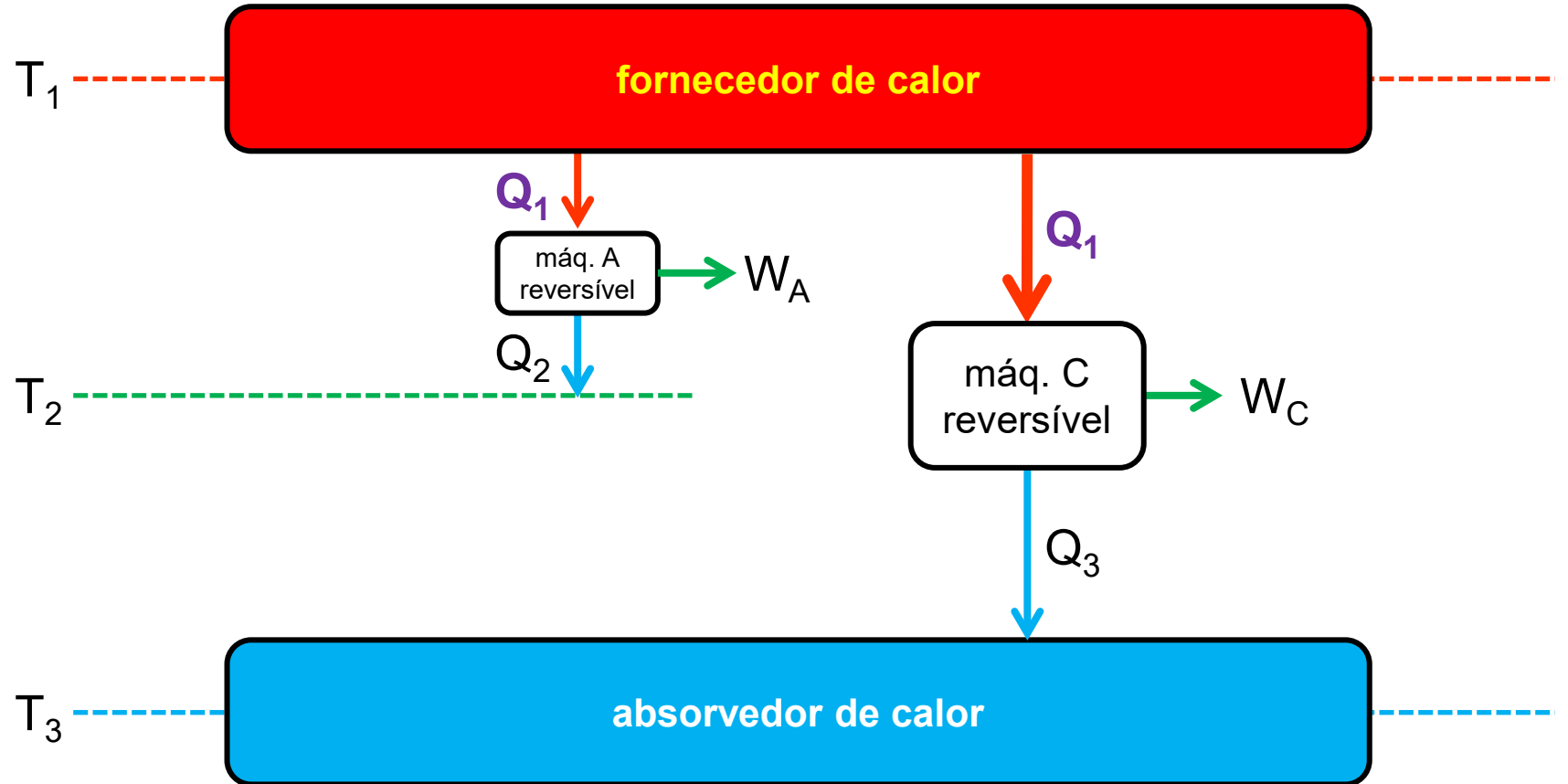
$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$



A escala termodinâmica de temperatura



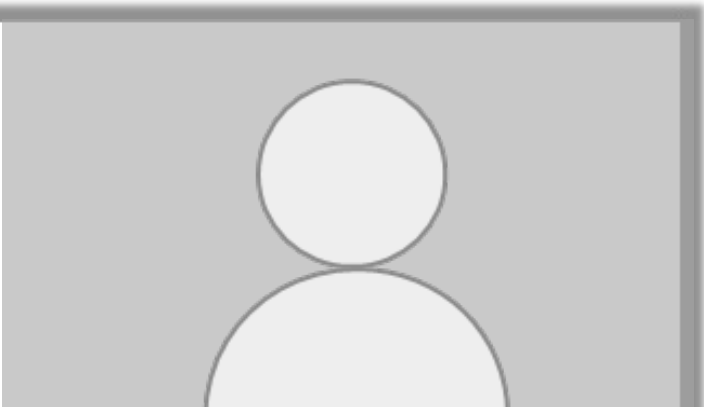
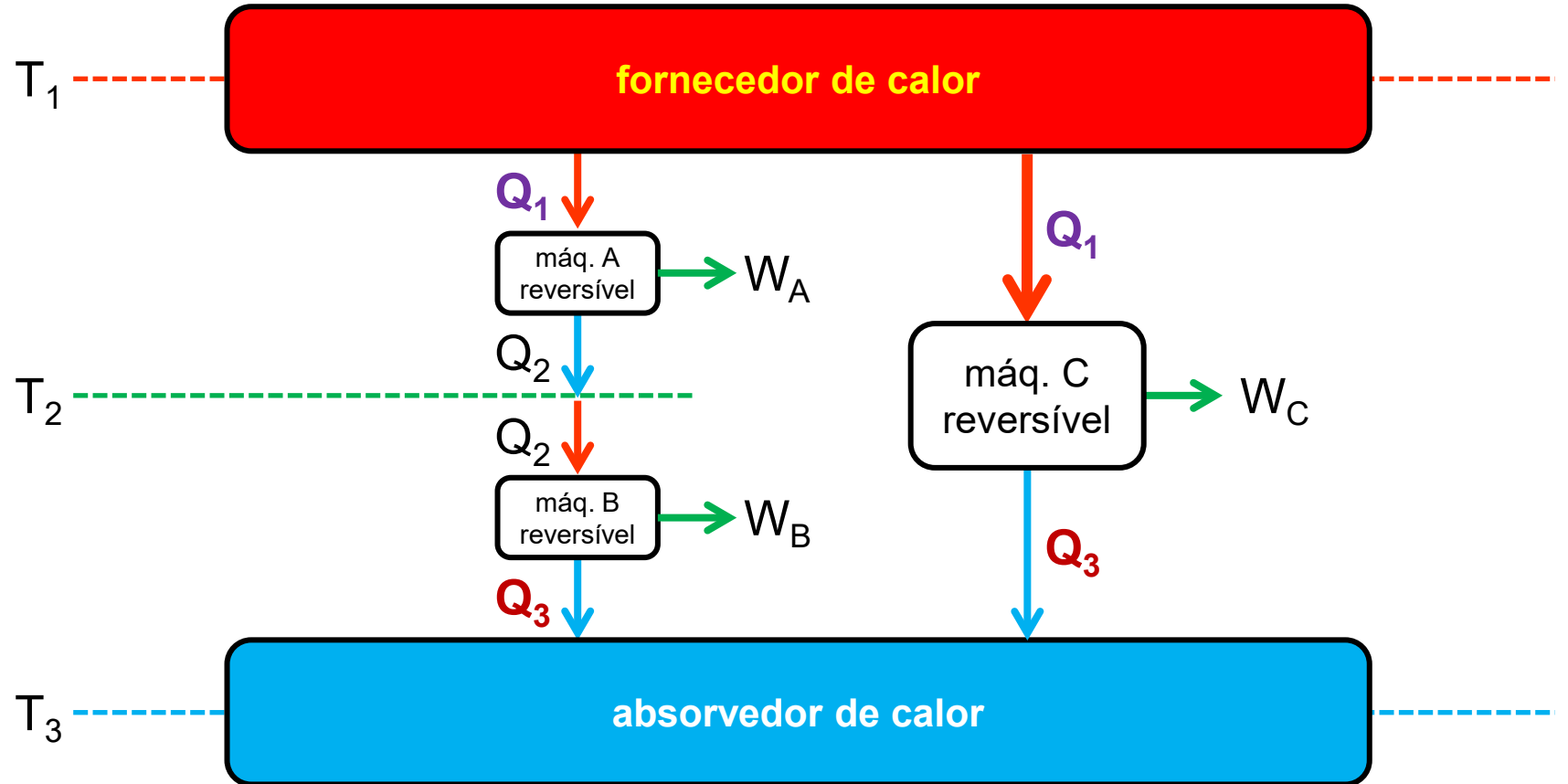
$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$



A escala termodinâmica de temperatura



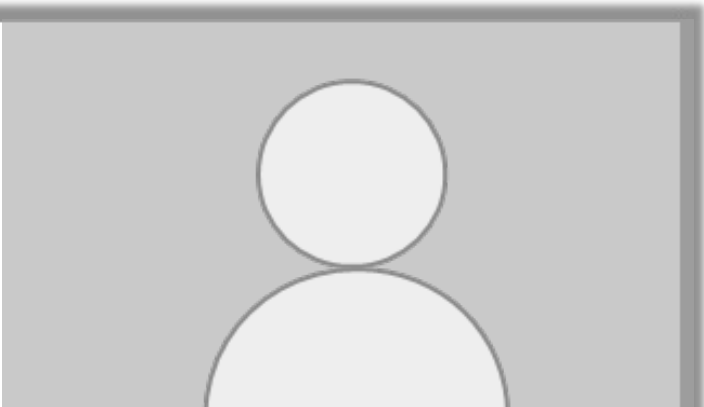
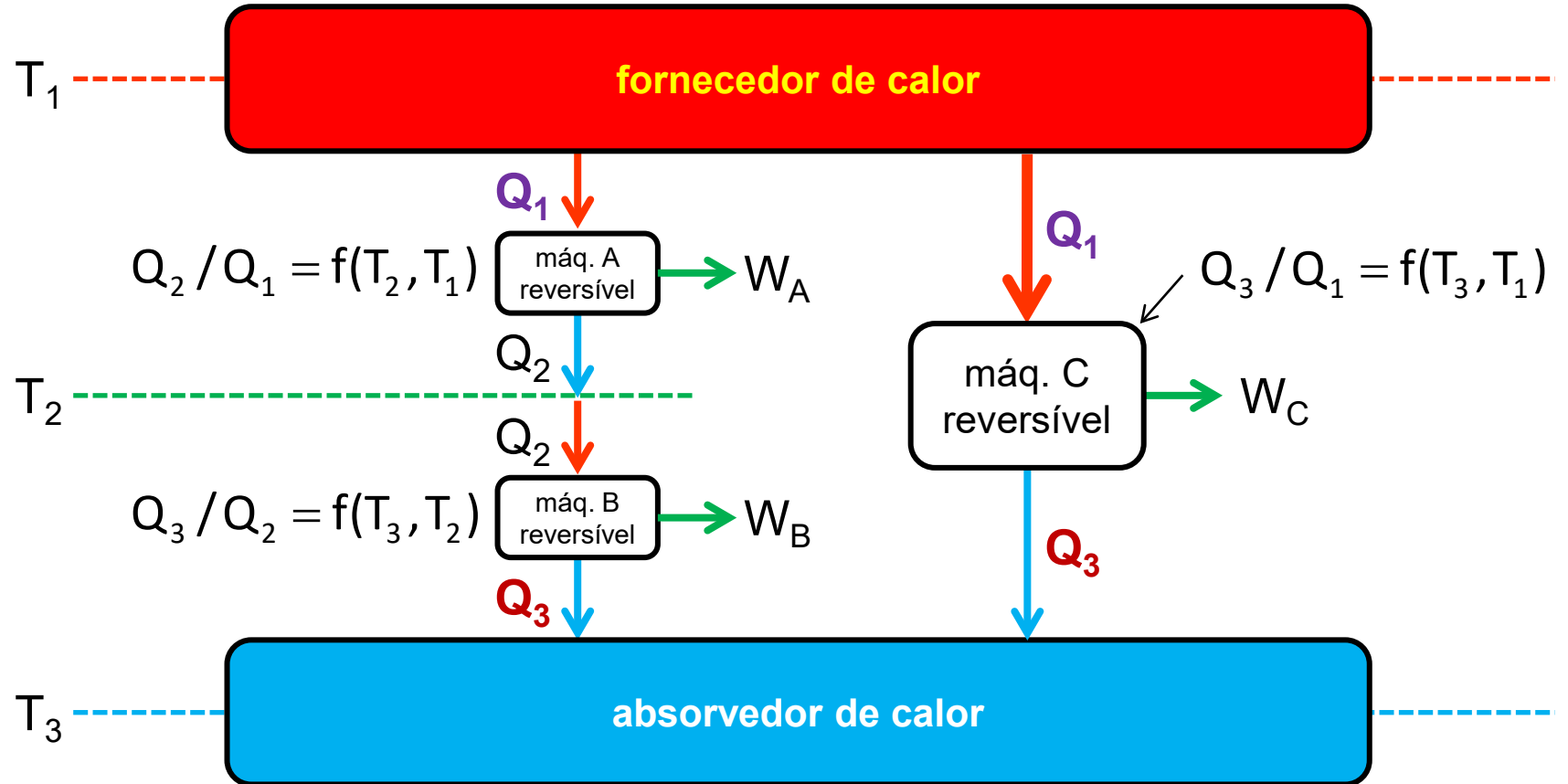
$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$



A escala termodinâmica de temperatura



$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$



A escala termodinâmica de temperatura



$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$

$$\frac{Q_3}{Q_1} = \frac{Q_3}{Q_2} \cdot \frac{Q_2}{Q_1}$$

$$Q_3 / Q_1 = f(T_3, T_1)$$

$$Q_2 / Q_1 = f(T_2, T_1)$$

$$Q_3 / Q_2 = f(T_3, T_2)$$



$$f(T_3, T_1) = f(T_3, T_2) \cdot f(T_2, T_1)$$

não pode depender de T_2 pq arbitrária



A escala termodinâmica de temperatura



$$f(T_3, T_1) = f(T_3, T_2) \cdot f(T_2, T_1)$$

independe de T_2

só pode ser satisfeito se \Rightarrow

$$f(T_x, T_y) = \frac{\phi(T_x)}{\phi(T_y)}$$

$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$

$$f(T_3, T_1) = \frac{\phi(T_3)}{\phi(T_1)} \quad f(T_3, T_2) = \frac{\phi(T_3)}{\phi(T_2)} \quad f(T_2, T_1) = \frac{\phi(T_2)}{\phi(T_1)}$$

$$\frac{Q_3}{Q_1} = \frac{\phi(T_3)}{\phi(T_1)} \quad \frac{Q_3}{Q_2} = \frac{\phi(T_3)}{\phi(T_2)} \quad \frac{Q_2}{Q_1} = \frac{\phi(T_2)}{\phi(T_1)}$$



A escala termodinâmica de temperatura



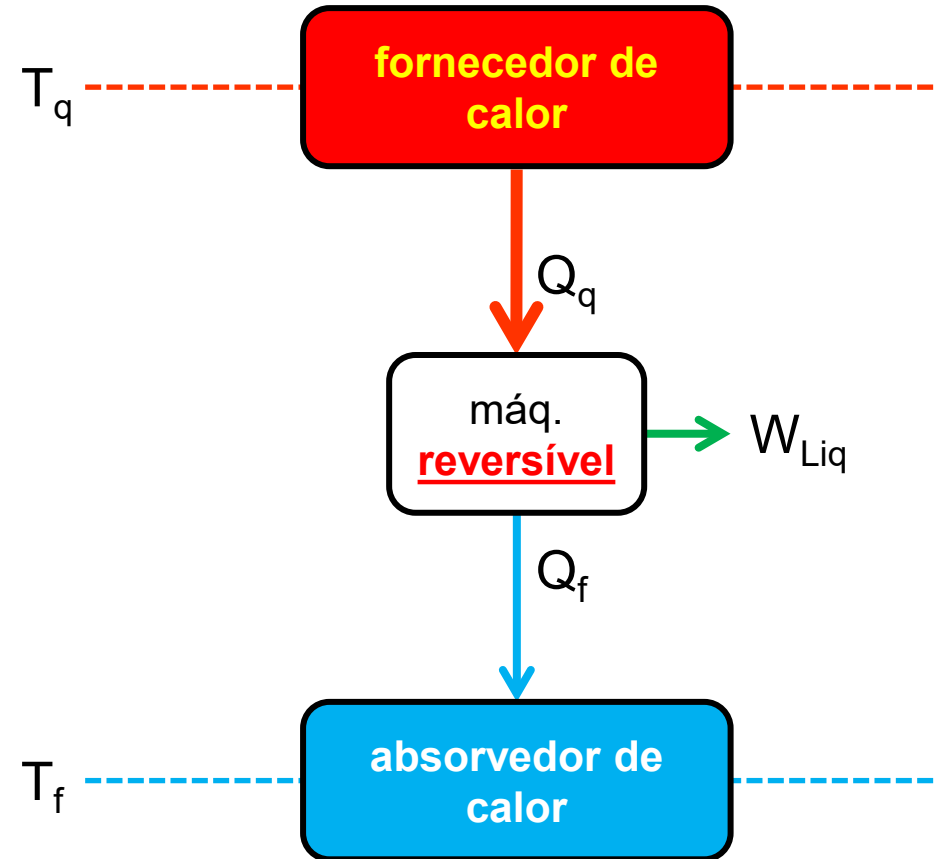
$$\eta = 1 - \frac{Q_f}{Q_q} = f(T_f, T_q)$$

$$\left. \frac{Q_f}{Q_q} \right|_{\text{rev}} = \frac{\phi(T_f)}{\phi(T_q)}$$

$$\phi(T) \stackrel{\text{def}}{=} T$$

$$\eta = 1 - \frac{Q_f}{Q_q} = 1 - \frac{T_f}{T_q}$$

escala absoluta
de temperatura

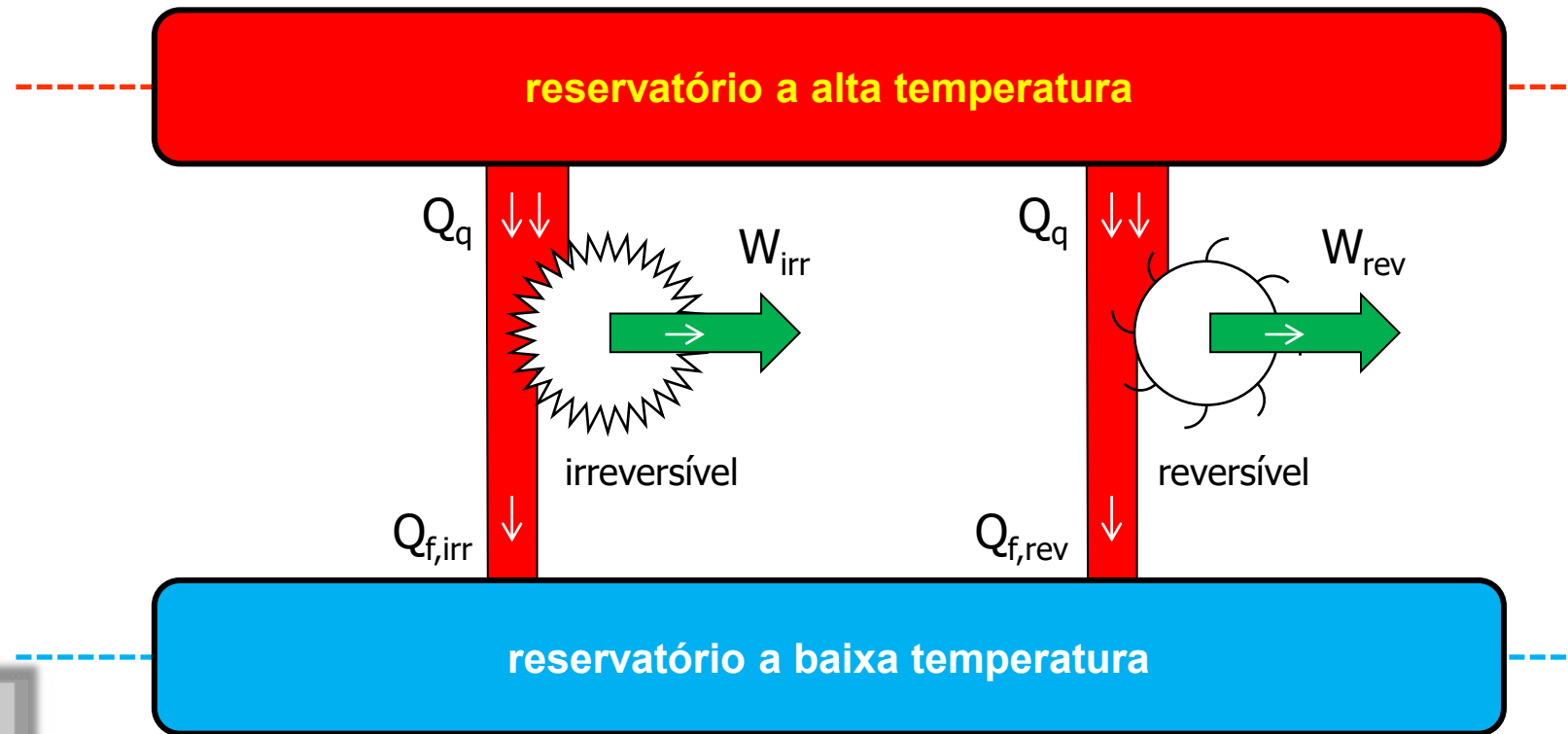


Lord Kelvin →

A desigualdade de Clausius: uma outra manifestação da 2ª lei da termodinâmica



Máxima eficiência de conversão: $\eta_{\text{rev}} > \eta_{\text{irrev}}$



$$\eta_{\text{irr}} = \frac{W_{\text{irr}}}{Q_q} = 1 - \frac{Q_{f,\text{irr}}}{Q_q}$$

$$\eta_{\text{rev}} = \frac{W_{\text{rev}}}{Q_q} = 1 - \frac{Q_{f,\text{rev}}}{Q_q}$$

$$\overset{\text{hip.}}{\eta_{\text{irr}}} > \eta_{\text{rev}}$$

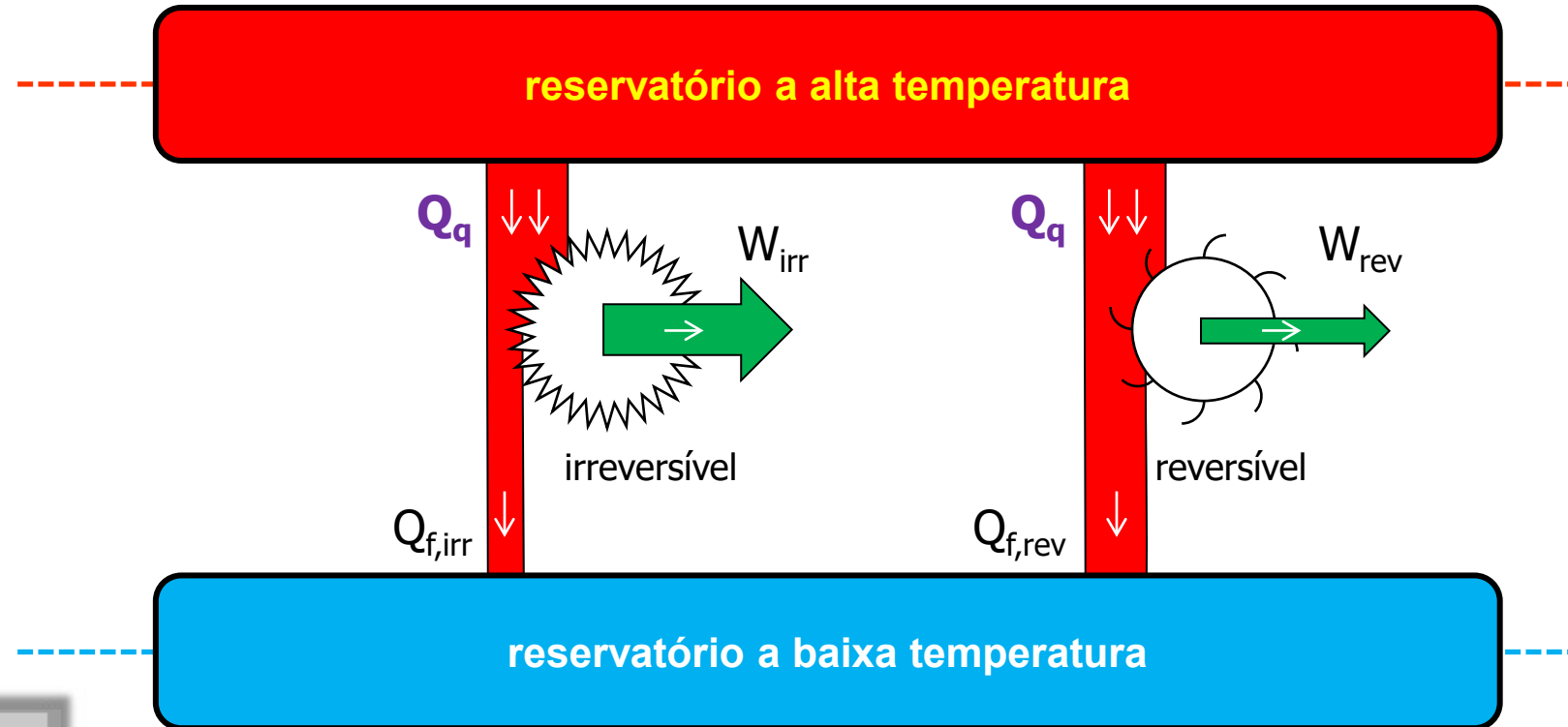
$$\eta_{\text{irr}} = \frac{W_{\text{irr}}}{Q_{\text{q}}} = 1 - \frac{Q_{\text{f,irr}}}{Q_{\text{q}}} > \eta_{\text{rev}} = \frac{W_{\text{rev}}}{Q_{\text{q}}} = 1 - \frac{Q_{\text{f,rev}}}{Q_{\text{q}}}$$

$$W_{\text{irr}} > W_{\text{rev}}$$

$$Q_{\text{f,irr}} < Q_{\text{f,rev}}$$



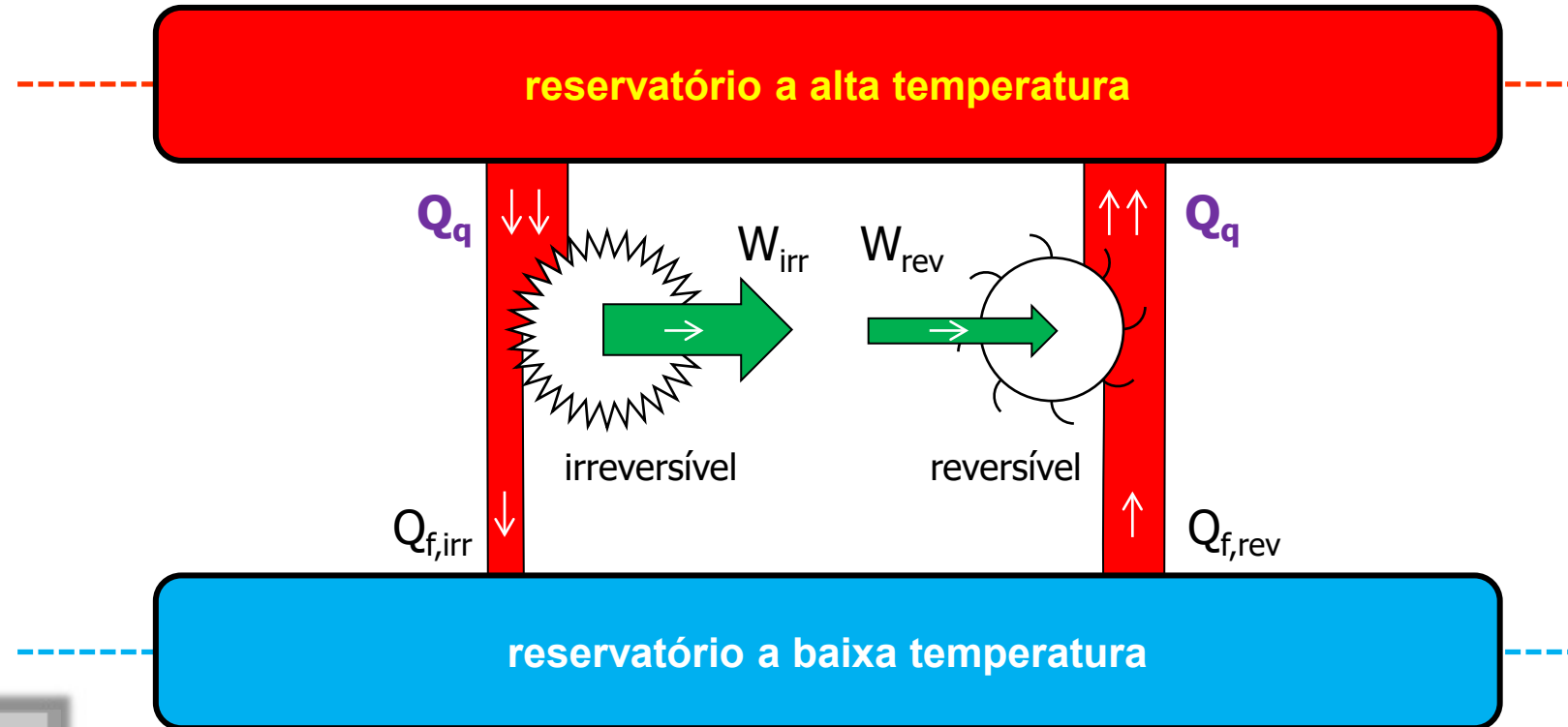
$$\eta_{\text{irr}}^{\text{hip.}} > \eta_{\text{rev}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



Colocando o calor e o trabalho em escala

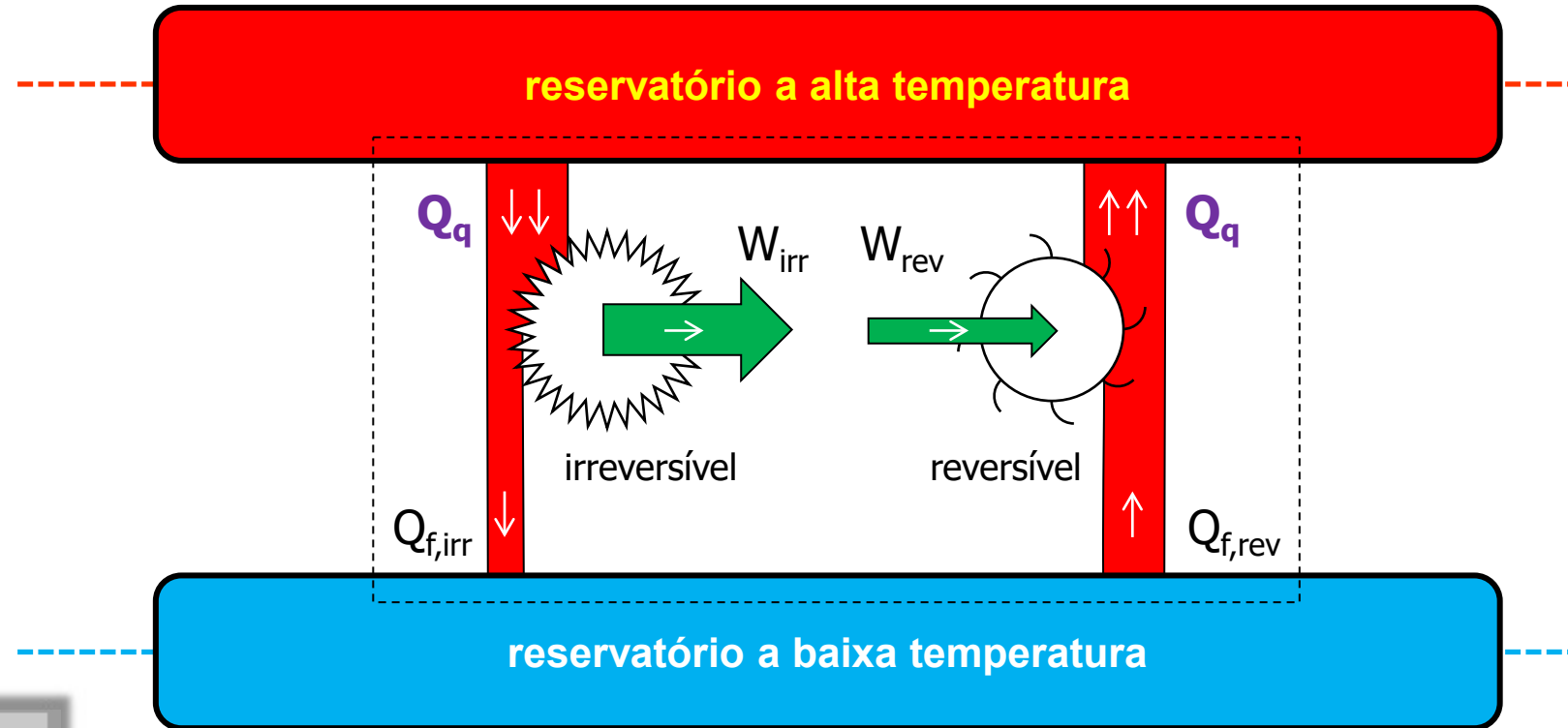


$$\eta_{\text{irr}}^{\text{hip.}} > \eta_{\text{rev}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



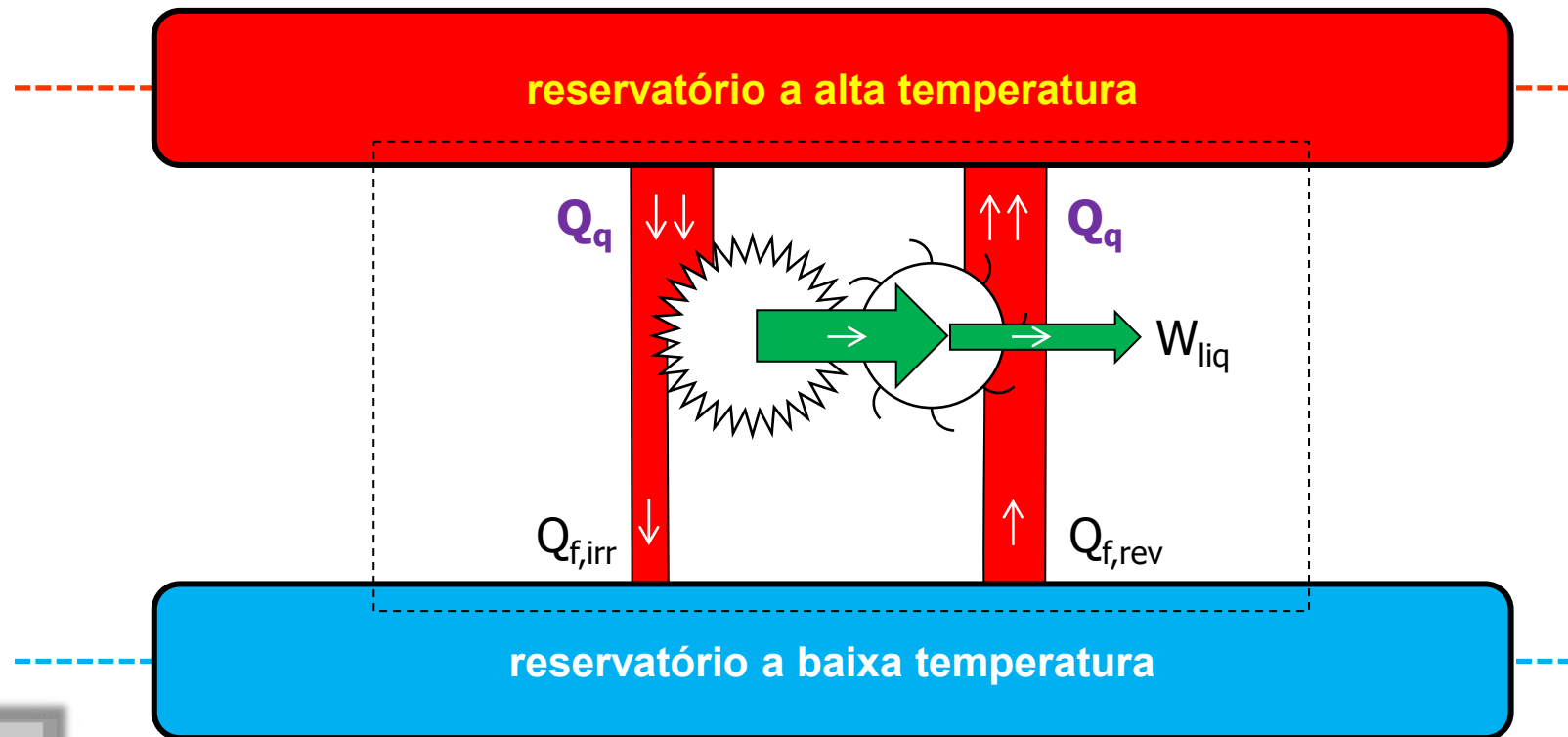
Invertendo o sentido do ciclo da máquina reversível

$$\overset{\text{hip.}}{\eta_{\text{irr}} > \eta_{\text{rev}}} \Rightarrow \begin{cases} Q_{\text{f,irr}} < Q_{\text{f,rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



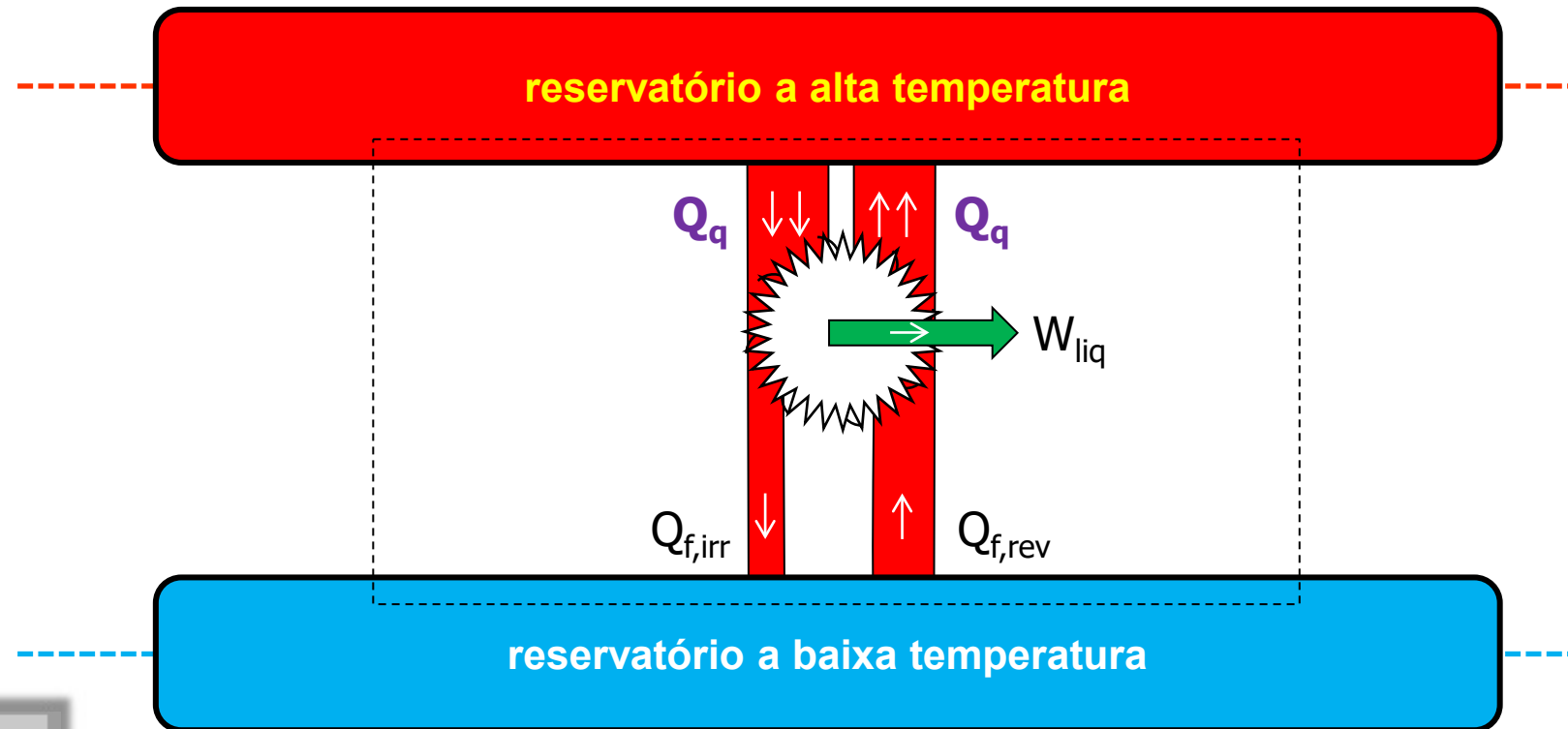
Analisando a máquina combinada

$$\eta_{\text{irr}}^{\text{hip.}} > \eta_{\text{rev}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



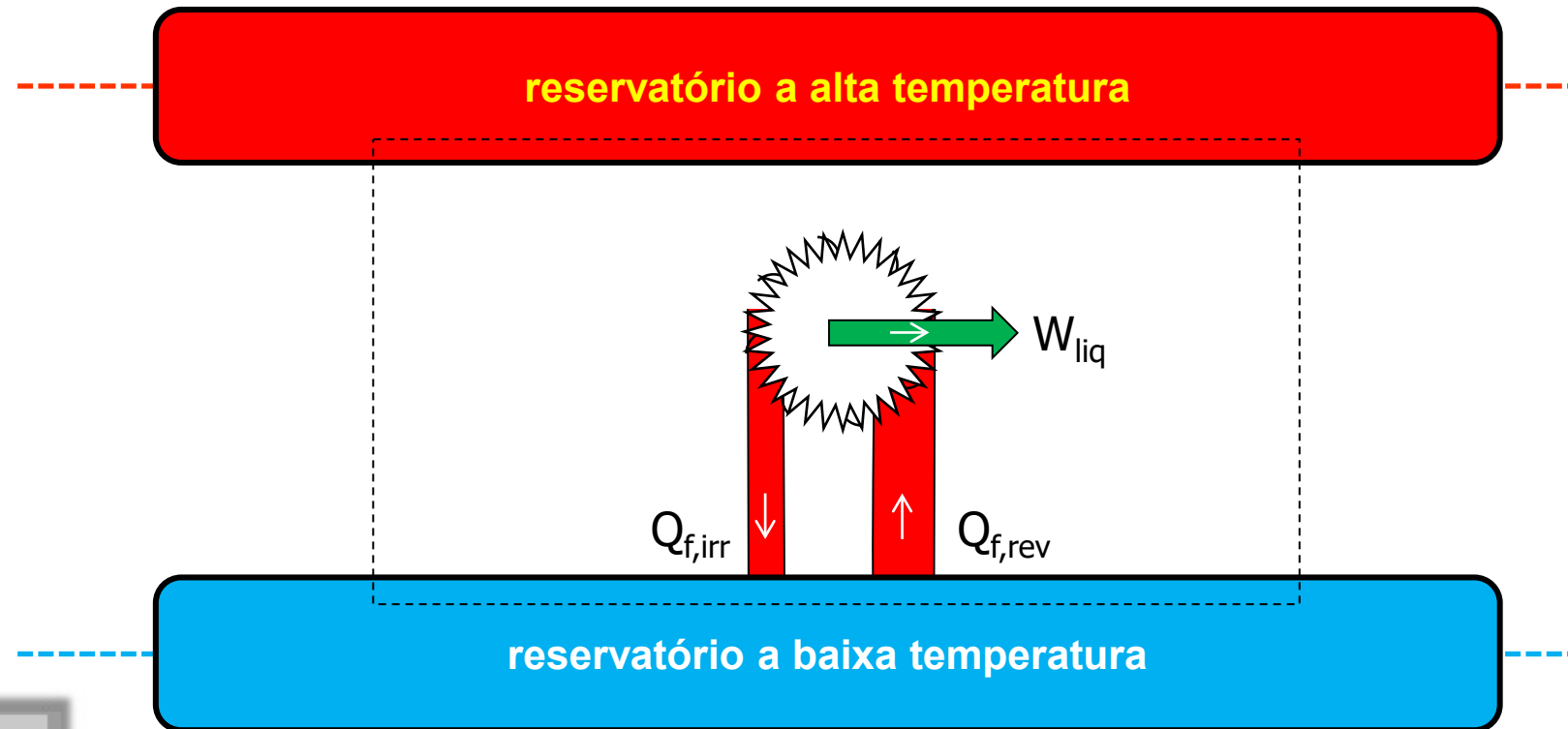
O trabalho total é positivo (exportado)

$$\eta_{\text{irr}}^{\text{hip.}} > \eta_{\text{rev}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



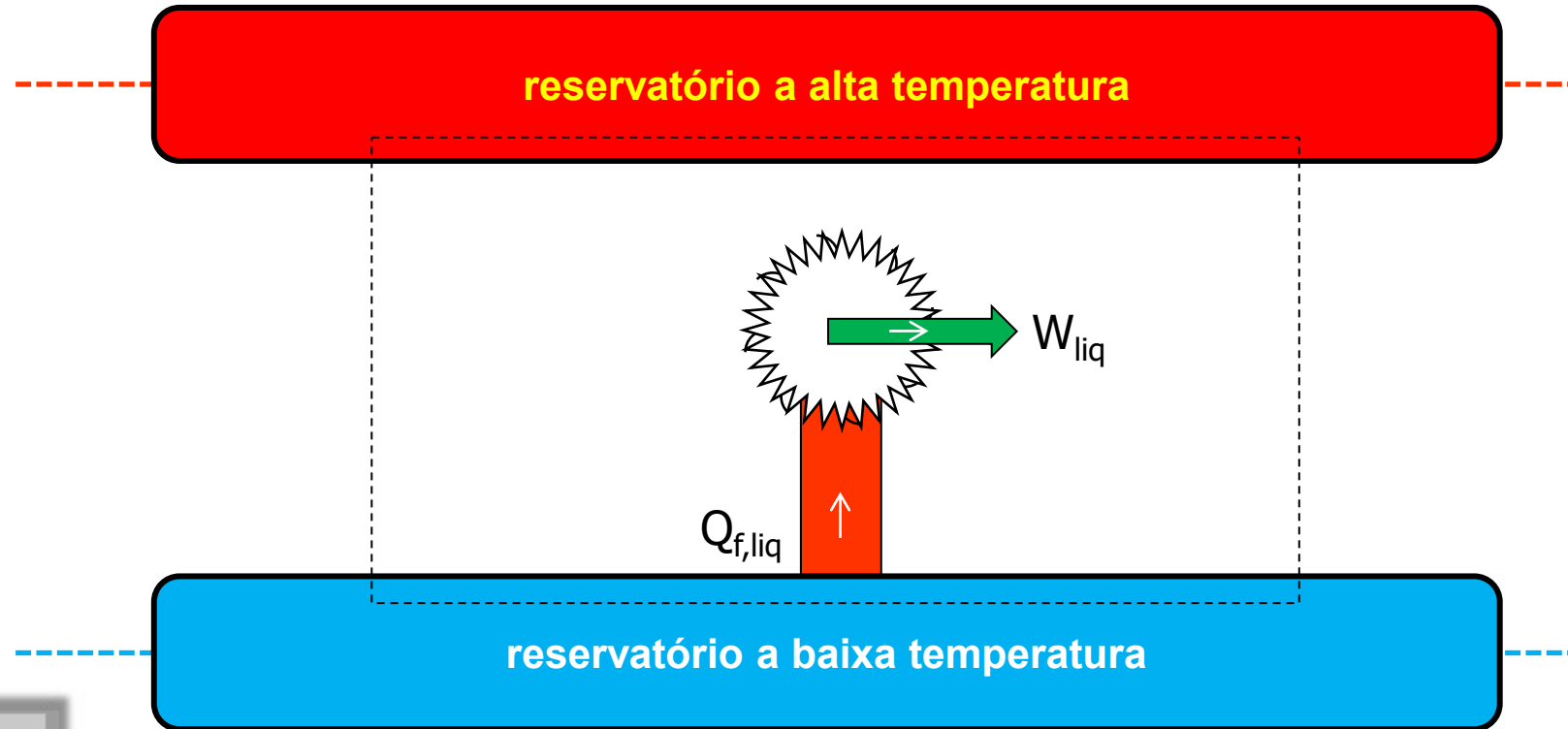
O calor trocado com a fonte quente é cancelado

$$\eta_{\text{irr}}^{\text{hip.}} > \eta_{\text{rev}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



O calor absorvido da fonte fria é positivo

$$\overset{\text{hip.}}{\eta_{\text{irr}} > \eta_{\text{rev}}} \Rightarrow \begin{cases} Q_{f,\text{irr}} < Q_{f,\text{rev}} \\ W_{\text{irr}} > W_{\text{rev}} \end{cases}$$



ABSURDO !

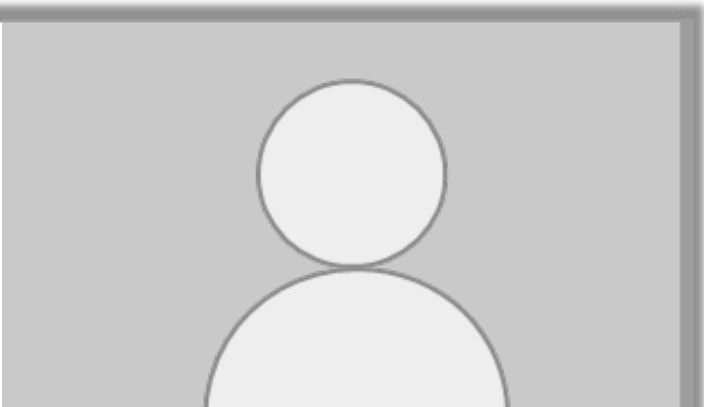
Portanto a hipótese não pode ser verdadeira.

A desigualdade de Clausius: uma outra manifestação da 2ª lei...

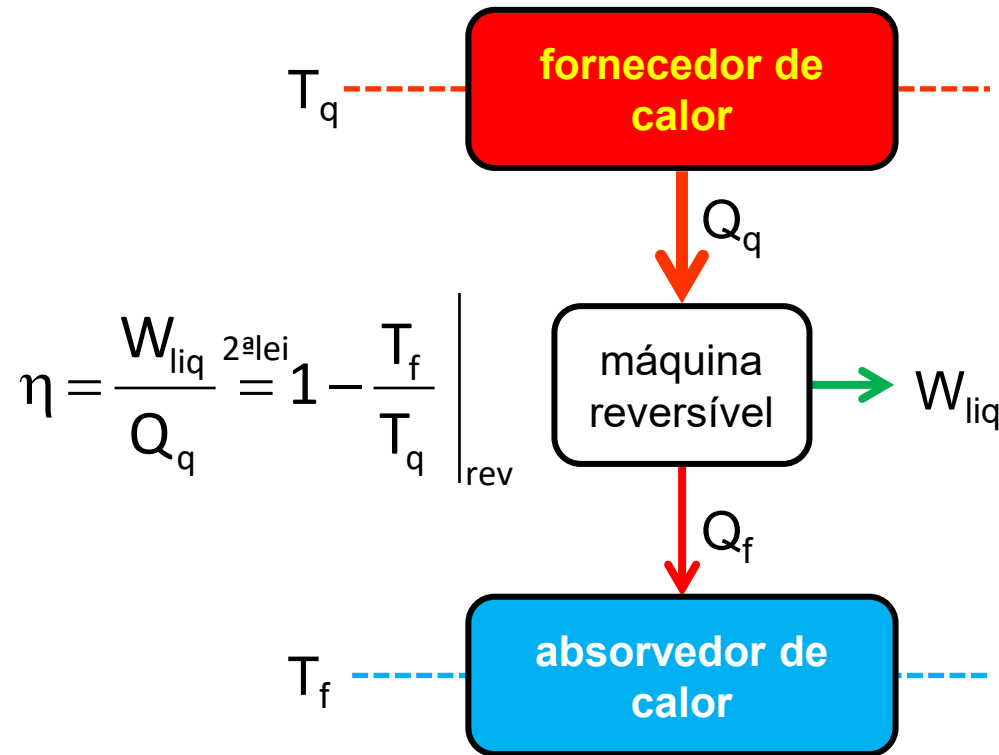
$$\int \frac{\delta Q}{T} \leq 0$$
$$\left\{ \begin{array}{l} \int_{\text{rev}} \frac{\delta Q}{T} = 0 \\ \int_{\text{irrev}} \frac{\delta Q}{T} < 0 \end{array} \right.$$



Rudolf Julius Emanuel Clausius
(1822 – 1888)



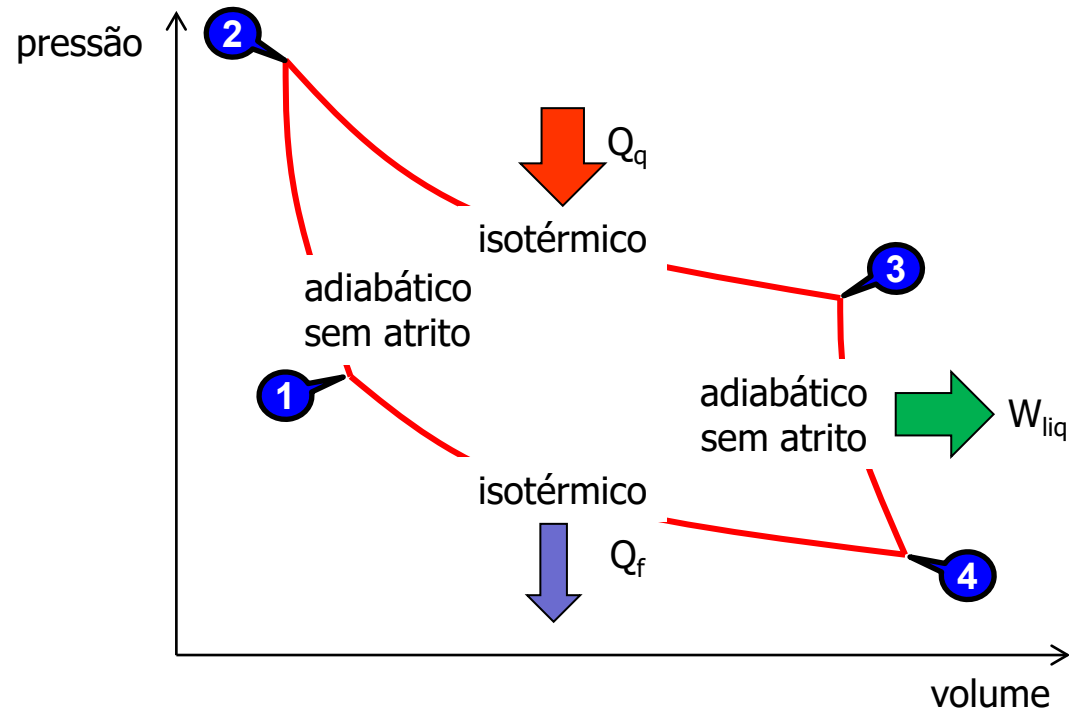
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



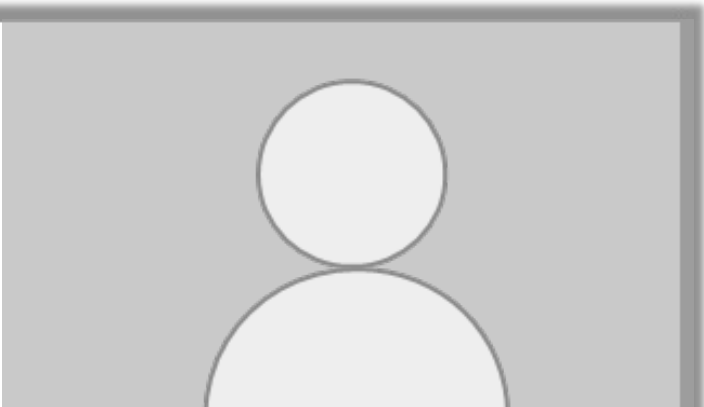
Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\eta = \frac{W_{liq}}{Q_q} \stackrel{1^{\text{a}} \text{ lei}}{=} 1 - \frac{Q_f}{Q_q} \stackrel{2^{\text{a}} \text{ lei}}{=} 1 - \frac{T_f}{T_q} \Rightarrow \frac{Q_f}{T_f} = \frac{Q_q}{T_q}$$

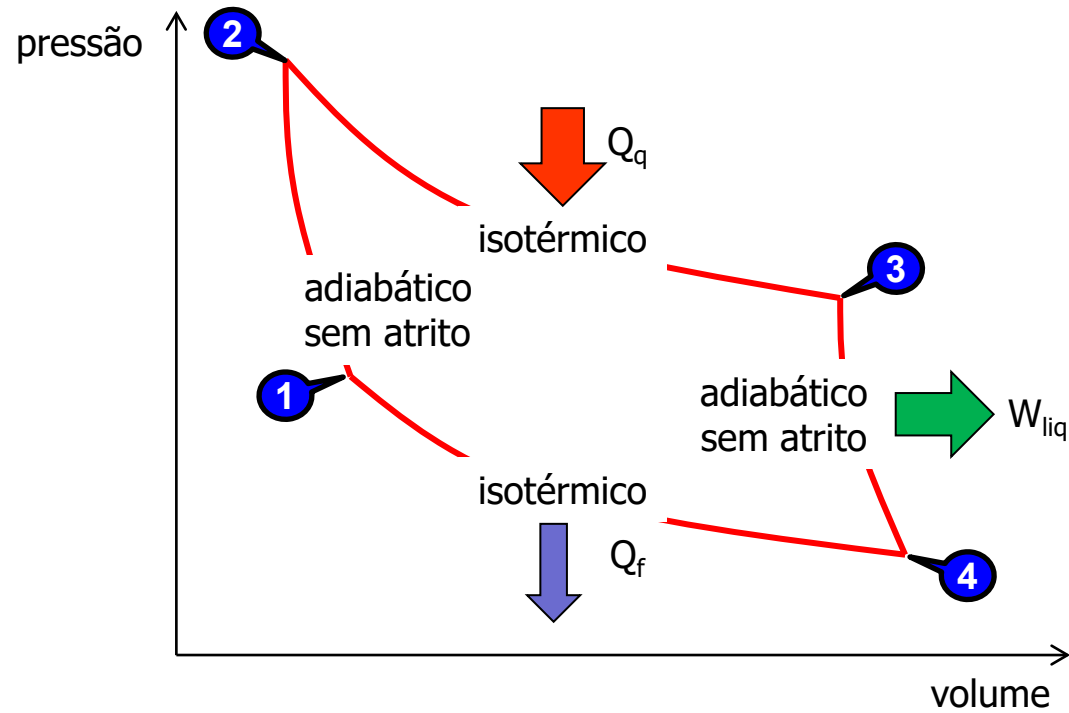
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



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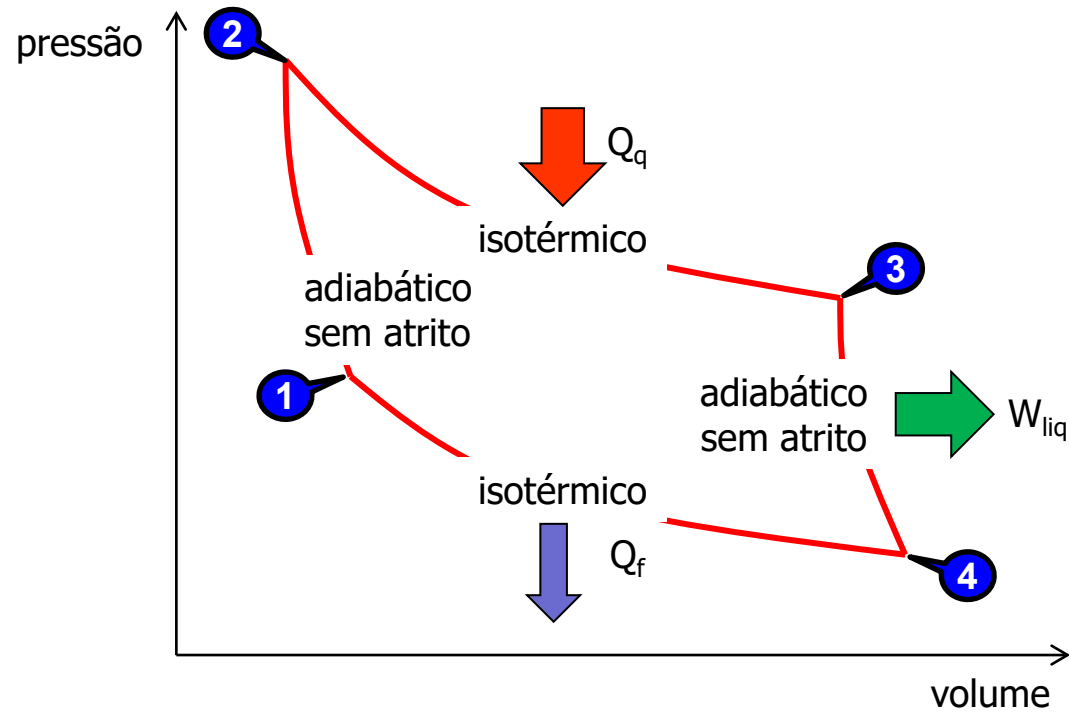
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\oint_{\text{rev}} \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

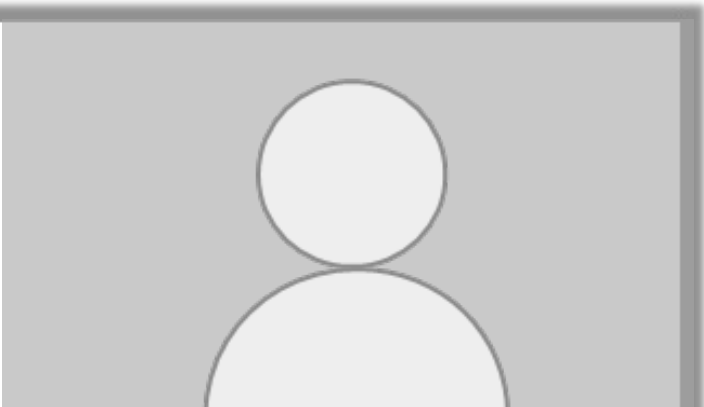
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



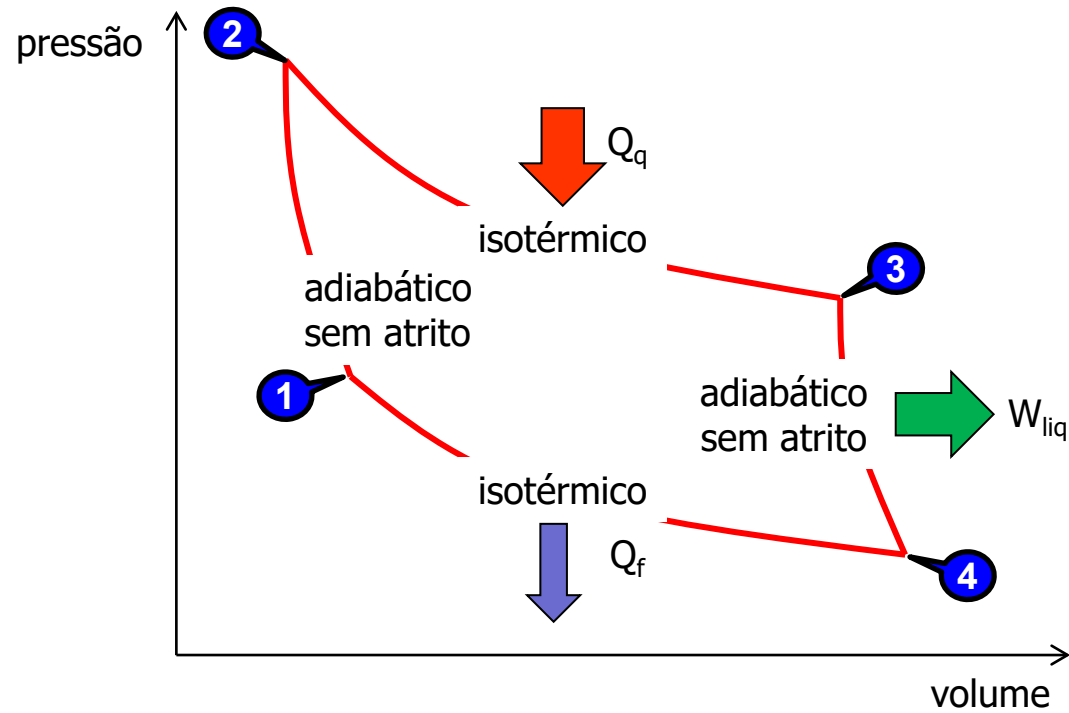
Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\oint_{\text{rev}} \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

(Note: The first and third terms in the original image are crossed out with red lines.)



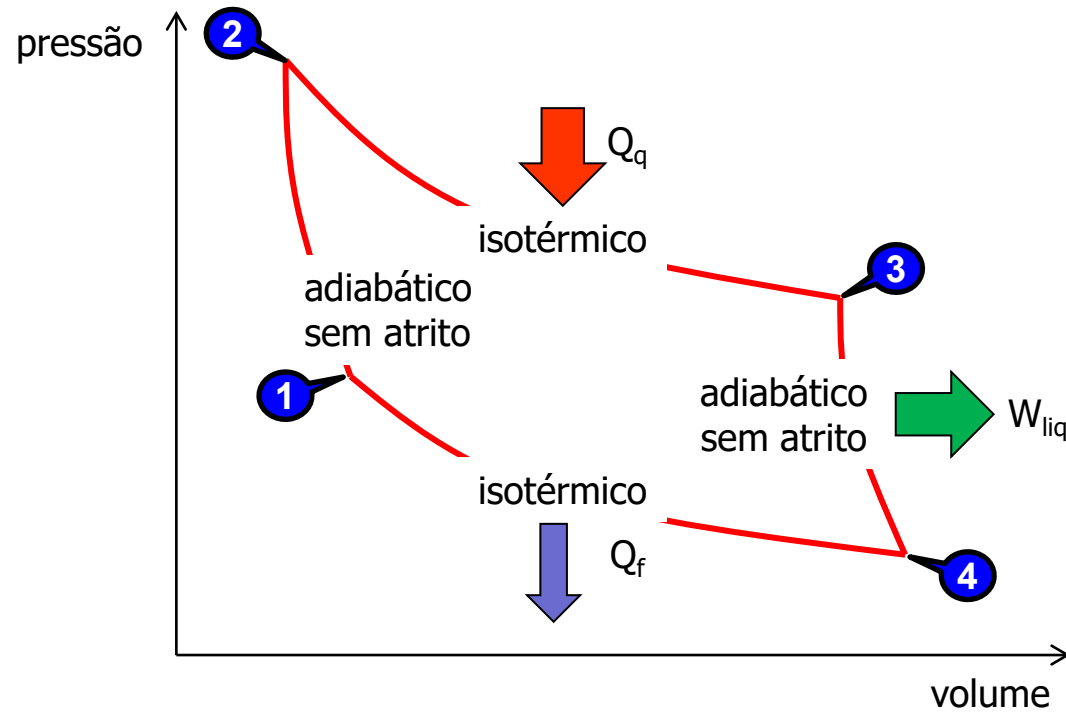
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



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(1822 – 1888)

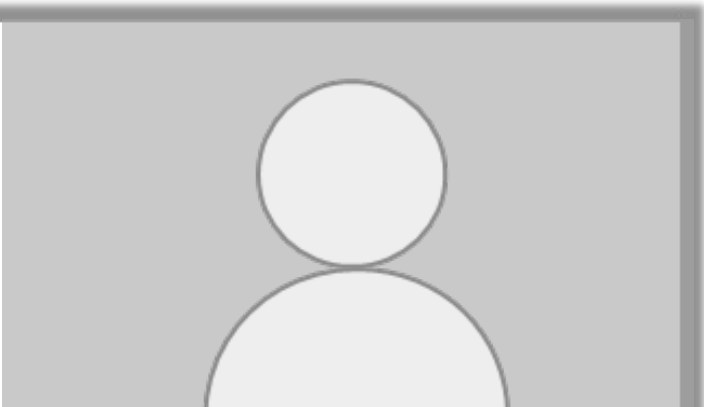
$$\oint_{\text{rev}} \frac{\delta Q}{T} = \int_2^3 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

A desigualdade de Clausius: uma outra manifestação da 2ª lei...

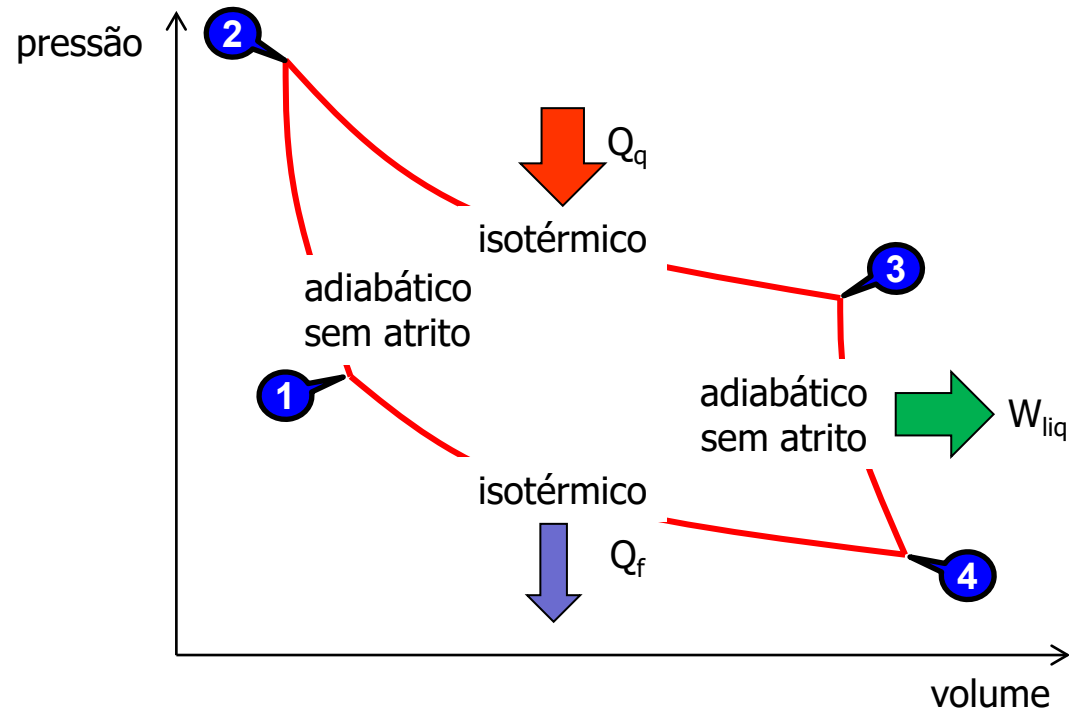


Rudolf Julius Emanuel Clausius
(1822 –1888)

$$\oint_{\text{rev}} \frac{\delta Q}{T} = \int_2^3 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T} = \frac{Q_q}{T_q} - \frac{Q_f}{T_f} \quad \frac{Q_f}{T_f}^{\text{rev}} = \frac{Q_q}{T_q}$$



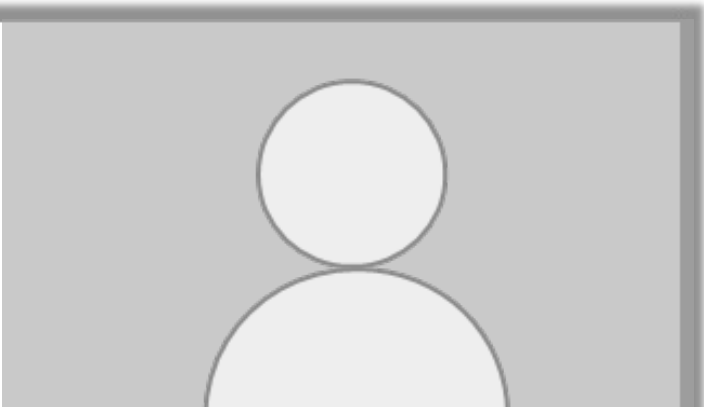
A desigualdade de Clausius: uma outra manifestação da 2ª lei...



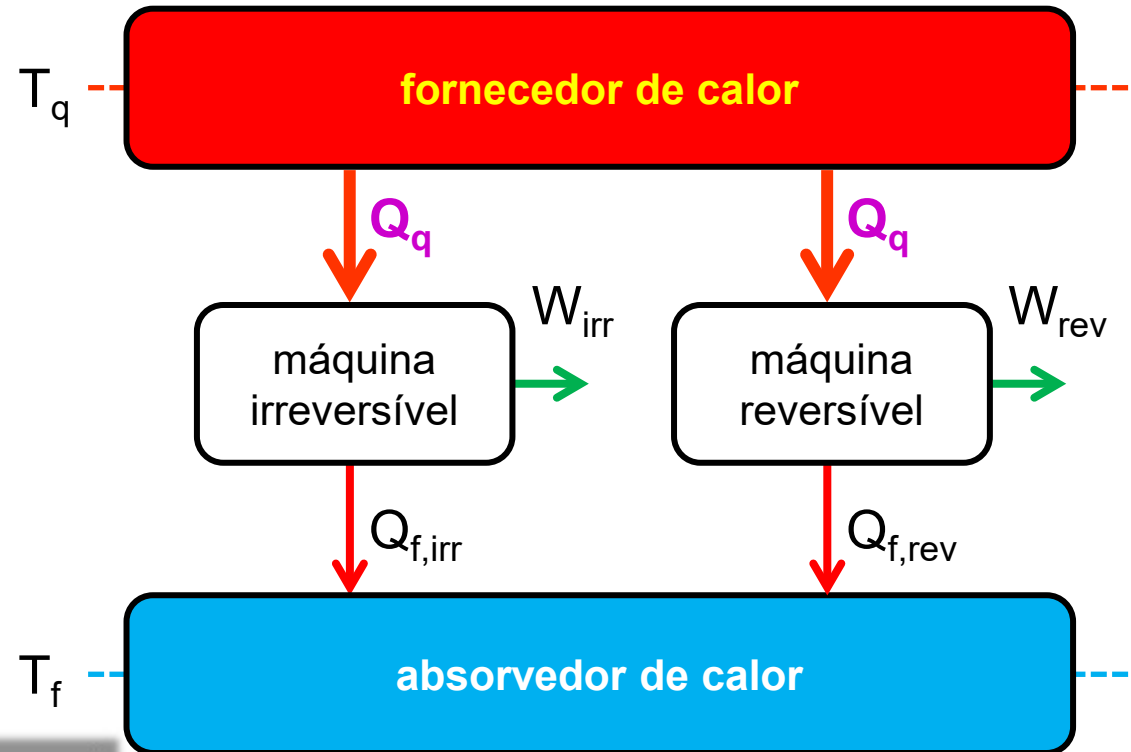
Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\Rightarrow \oint_{\text{rev}} \frac{\delta Q}{T} = 0$$

$$\frac{Q_f}{T_f} \stackrel{\text{rev}}{=} \frac{Q_q}{T_q}$$



A desigualdade de Clausius: uma outra manifestação da 2ª lei...

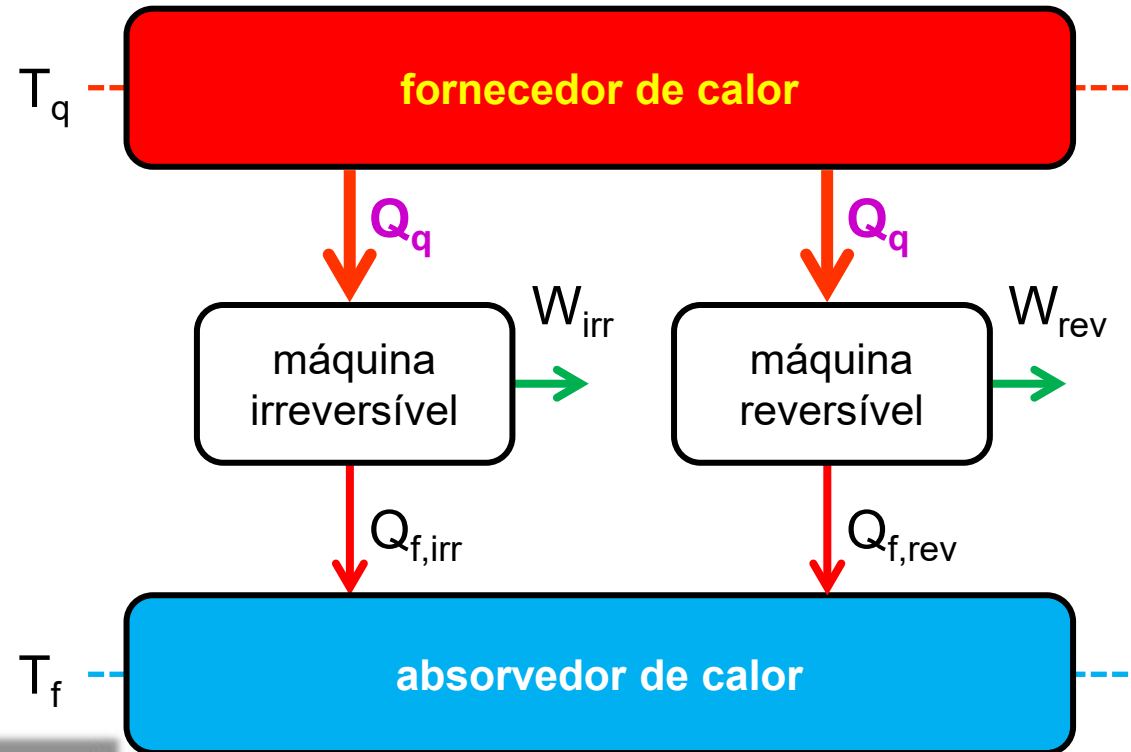


Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\eta_{rev} > \eta_{irr} \stackrel{2^a \text{ lei}}{\Rightarrow} \begin{cases} Q_{f,rev} < Q_{f,irr} \\ W_{rev} > W_{irr} \end{cases}$$

$$\frac{Q_f}{T_f} \stackrel{rev}{=} \frac{Q_q}{T_q}$$

A desigualdade de Clausius: uma outra manifestação da 2ª lei...

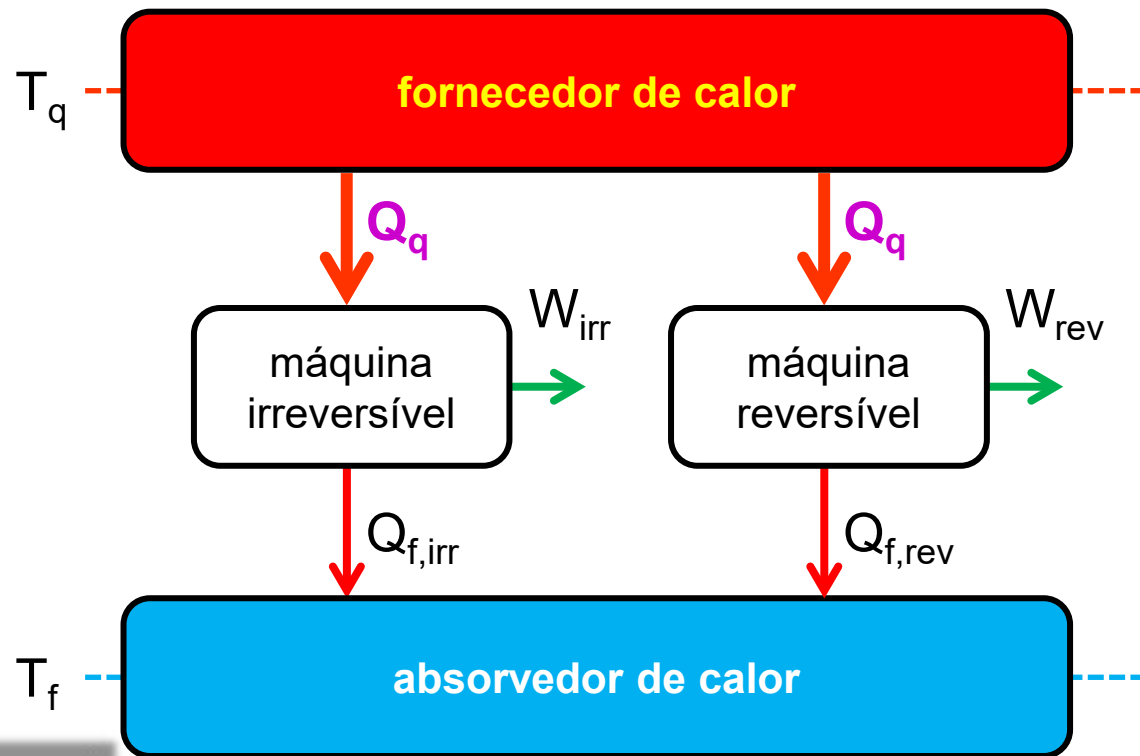


Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\oint_{\text{irrev}} \frac{\delta Q}{T} = \frac{Q_q}{T_q} - \frac{Q_{f,\text{irr}}}{T_f} < \frac{Q_q}{T_q} - \frac{Q_{f,\text{rev}}}{T_f} = 0$$

$$\eta_{\text{rev}} > \eta_{\text{irr}} \Rightarrow \begin{cases} Q_{f,\text{rev}} < Q_{f,\text{irr}} \\ W_{\text{rev}} > W_{\text{irr}} \end{cases}$$

A desigualdade de Clausius: uma outra manifestação da 2ª lei...



Rudolf Julius Emanuel Clausius
(1822 – 1888)

$$\Rightarrow \oint_{\text{irrev}} \frac{\delta Q}{T} < 0$$

$$\eta_{\text{rev}} > \eta_{\text{irr}} \Rightarrow \begin{cases} Q_{f,\text{rev}} < Q_{f,\text{irr}} \\ W_{\text{rev}} > W_{\text{irr}} \end{cases}$$

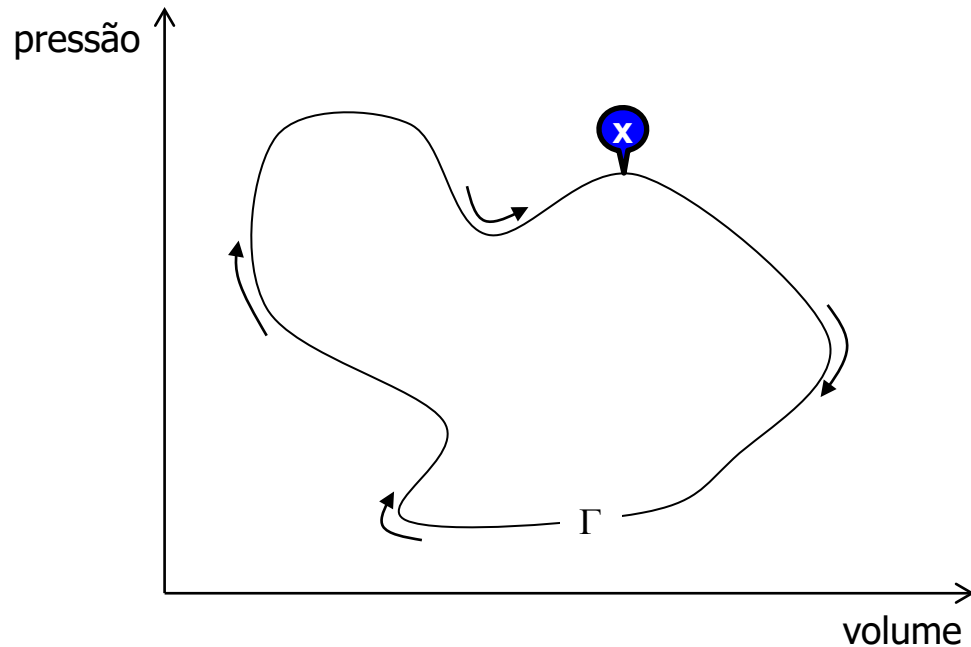


ENTROPIA:

uma propriedade de estado...



Definição termodinâmica clássica de entropia (estatística, informacional)



$x \Rightarrow$ propriedade termodinâmica

$$\oint_{\Gamma} dx = 0$$

qualquer que seja a trajetória Γ

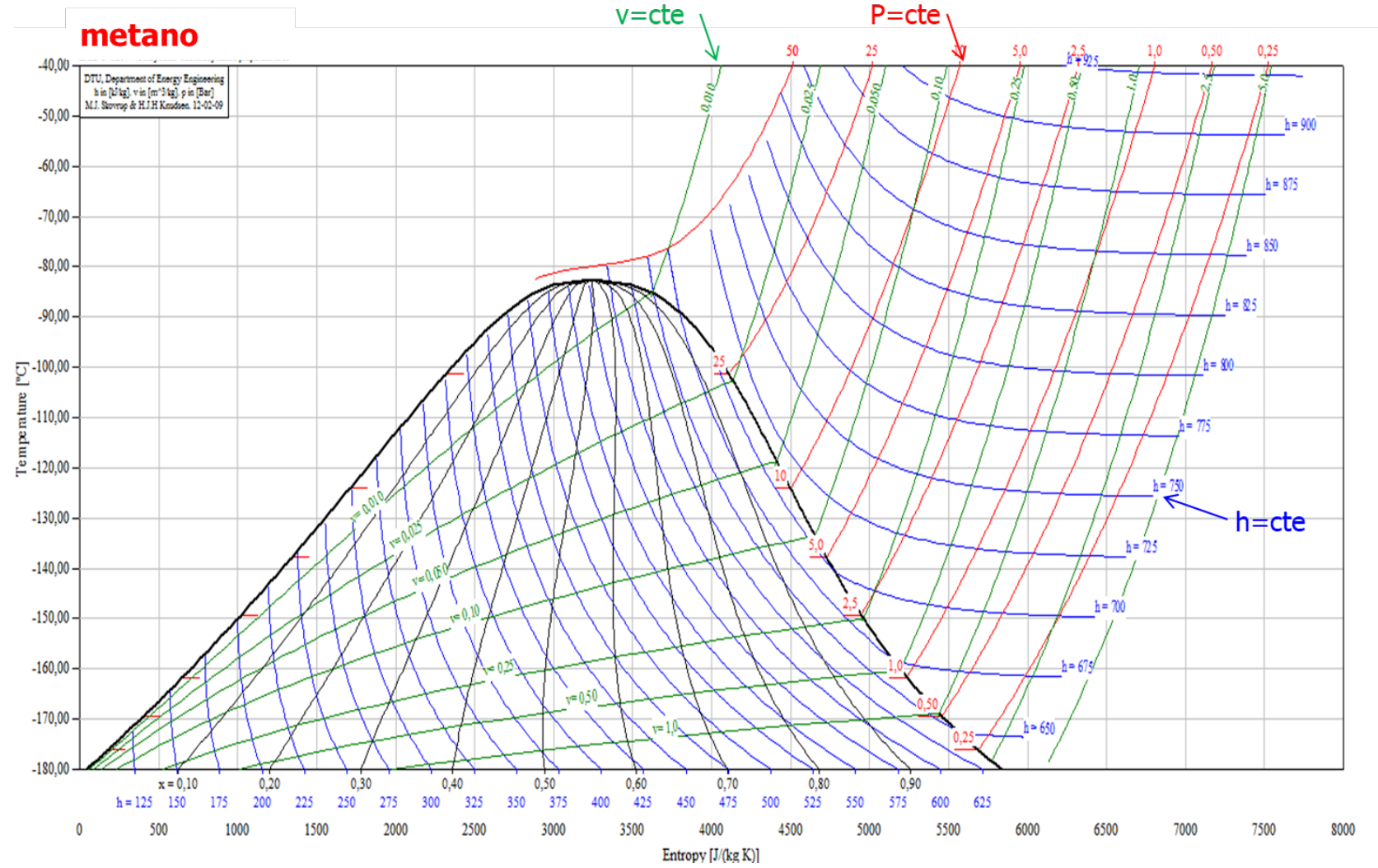
$$\oint \frac{\delta Q}{T} \Big|_{\text{rev}} = 0 \Rightarrow$$

$$dS \stackrel{\text{def}}{=} \frac{\delta Q}{T} \quad [S] = \frac{\text{kJ}}{\text{K}} \text{ ou } \frac{\text{kJ}}{\text{kgK}}$$

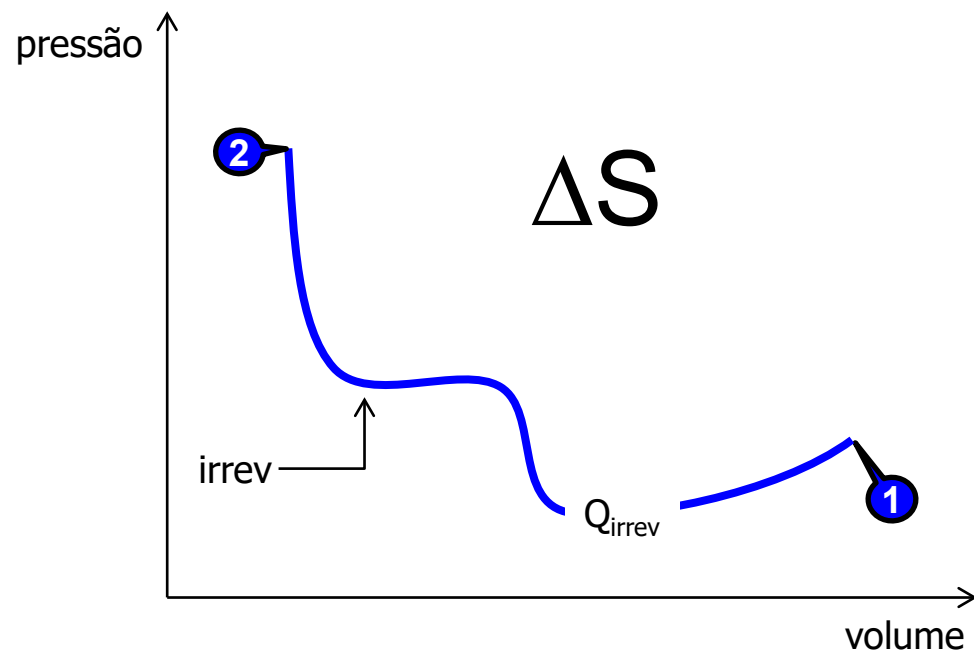
$$S_x - S_0 = \int_0^x \frac{\delta Q}{T} \Big|_{\text{rev}}$$

metano

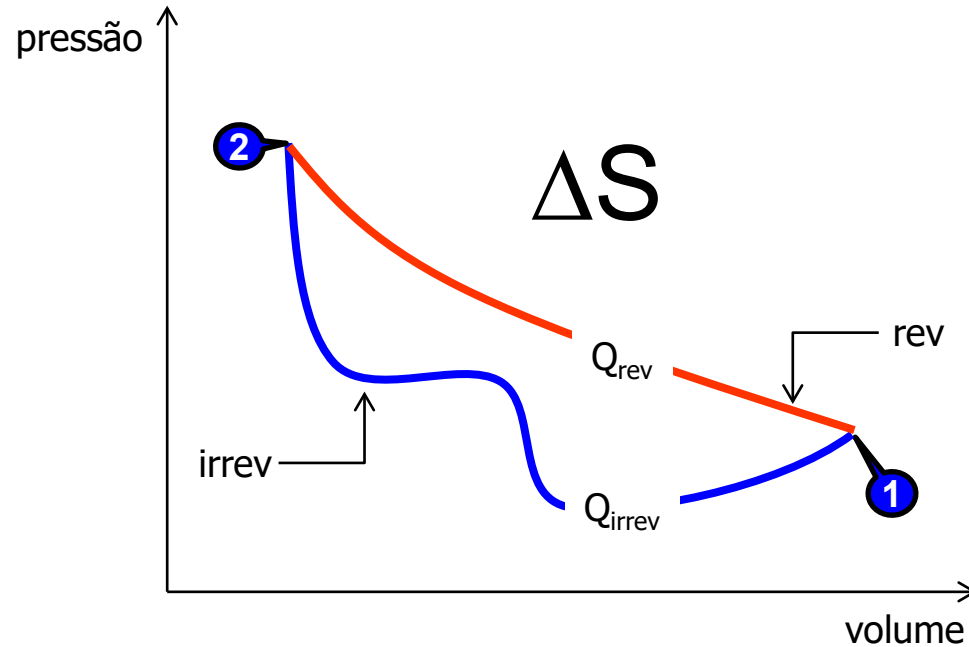
DTU, Department of Energy Engineering
h in [kJ/kg], v in [m³/kg], p in [Bar]
M.J. Sørvog & H.J.H. Kauden, 12-02-09



ΔS é sempre calculada por uma trajetória reversível



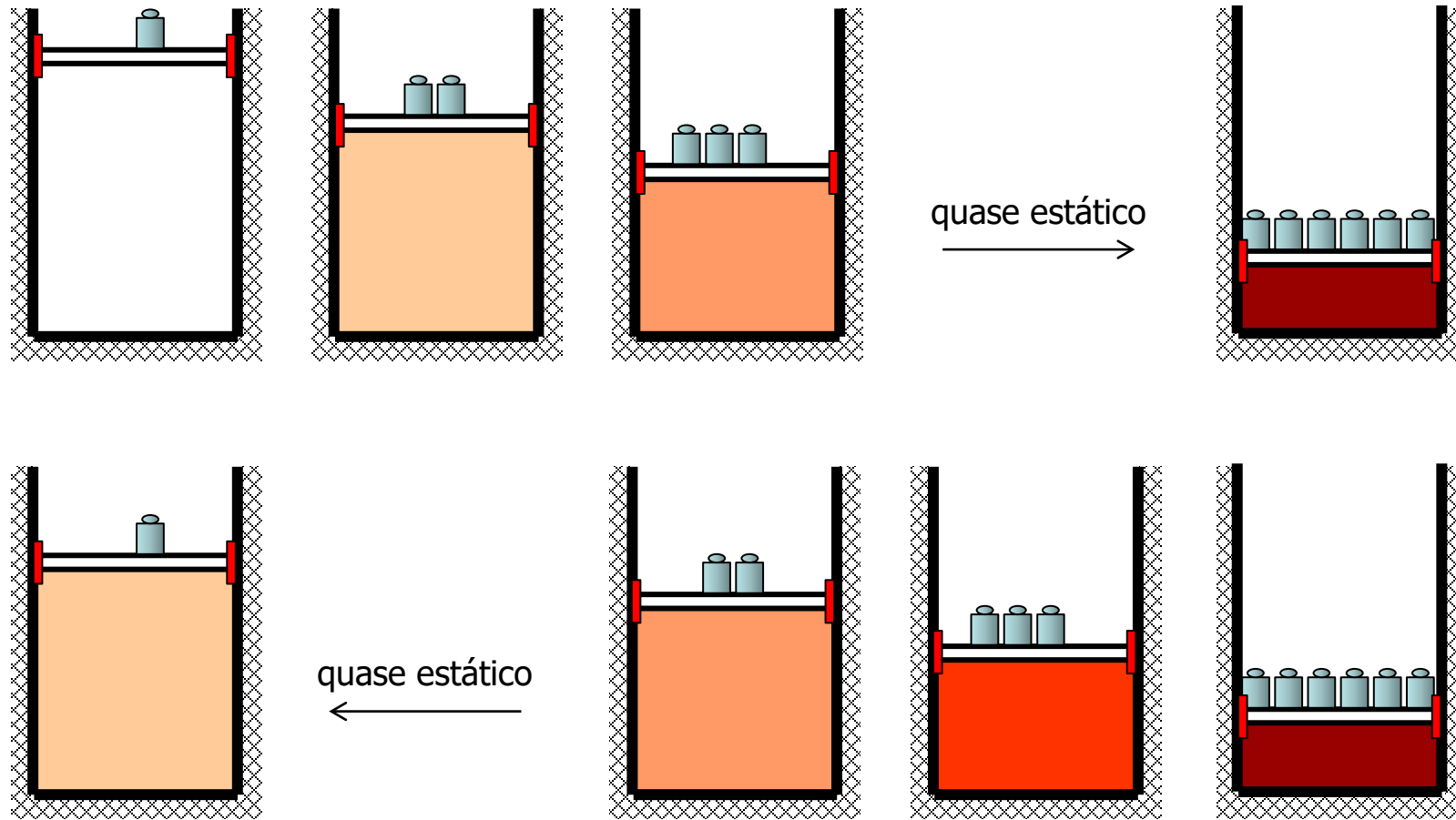
ΔS é sempre calculada por uma trajetória reversível



Fontes de irreversibilidades:

- Transferência de calor ΔT finito
- Atritos internos
- Compressão/expansão não resistida
- Mistura de substâncias diferentes
- Reações químicas espontâneas
- Passagem de corrente elétrica por uma resistência finita
- Deformação inelástica de sólidos

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \Big|_{\text{rev}} \neq \int_1^2 \frac{\delta Q}{T} \Big|_{\text{irrev}}$$



O calor gerado pela pelo fricção do êmbolo com a camisa é sempre aditivo, portanto não é possível inverter perfeitamente a transformação !

Processos de geração e de transferência de entropia

Clausius: $\oint \frac{\delta Q}{T} \leq 0$

$$\oint_{\Gamma} \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} \Big|_{\text{irrev}} + \int_2^1 \frac{\delta Q}{T} \Big|_{\text{rev}} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} \Big|_{\text{irrev}} + (S_1 - S_2) \leq 0$$

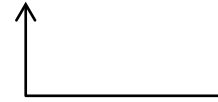
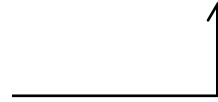
$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \Big|_{\text{irrev}} \quad \Rightarrow \quad dS \geq \frac{\delta Q}{T}$$



Processos de geração e de transferência de entropia

$$dS \geq \delta Q / T$$

Varição da entropia de um sistema fechado durante processo irreversível



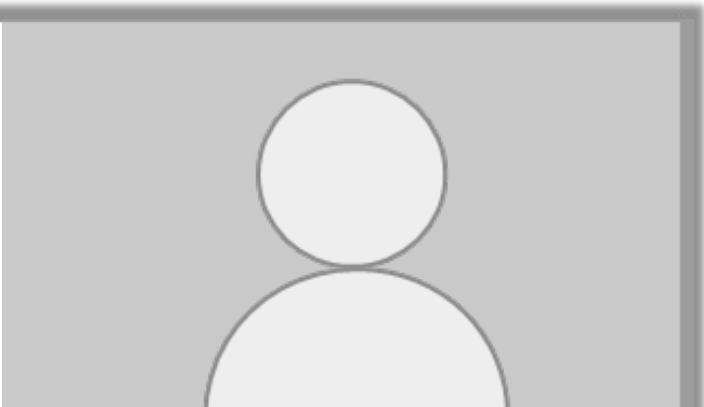
Transferência de entropia via transferência de calor

$$\Delta S_{\text{sistema}} = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$$

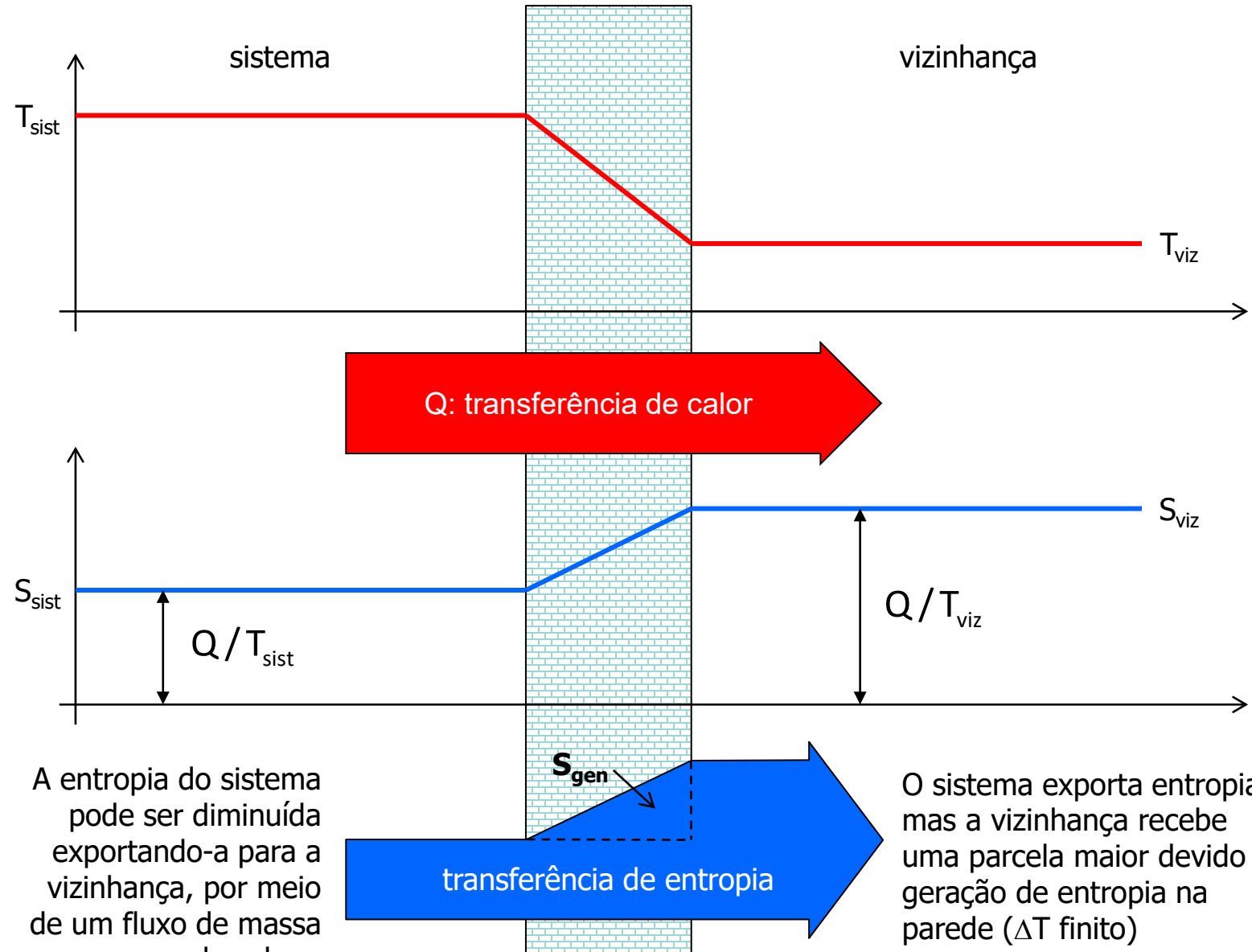


Entropia gerada durante o processo irreversível

$$S_{\text{gen}} \begin{cases} > 0 \text{ proc. irreversível} \\ = 0 \text{ proc. reversível} \\ < 0 \text{ proc. impossível} \end{cases}$$



Processos de geração e de transferência de entropia

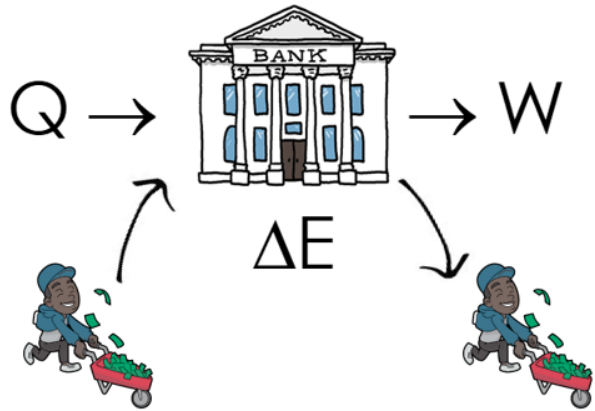


A entropia do sistema pode ser diminuída exportando-a para a vizinhança, por meio de um fluxo de massa ou de calor...

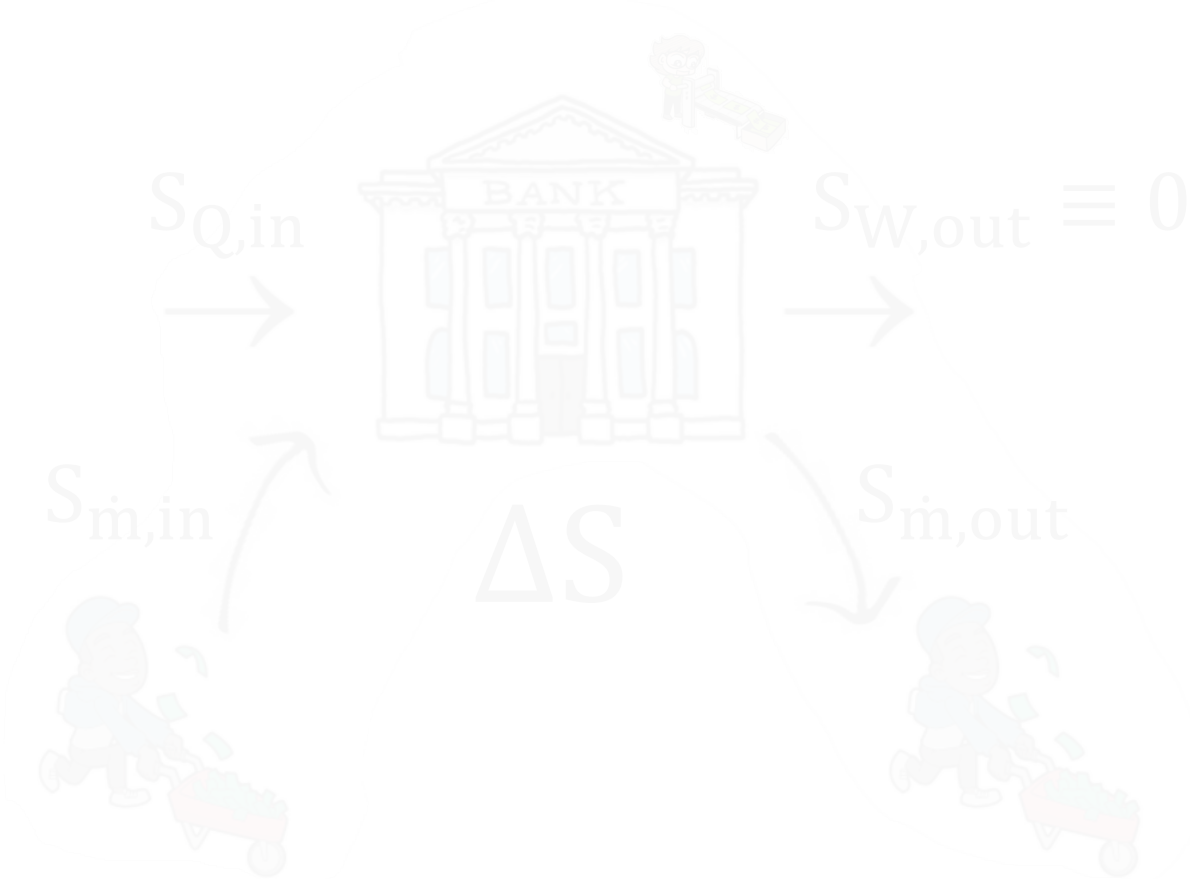
O sistema exporta entropia mas a vizinhança recebe uma parcela maior devido a geração de entropia na parede (ΔT finito)

INVENTÁRIO DE ENTROPIA...

1ra Lei TD: conservação da energia



$$\frac{dE_{VC}}{dt} = \dot{Q} - \dot{W} - \sum_{sai} \dot{m}_k \theta_k + \sum_{entra} \dot{m}_k \theta_k$$



$$\frac{dS_{CV}}{dt} = \sum_{i=0}^n \frac{Q_i}{T_i} + \sum_{i=0}^n \dot{m}_{i,in} s_{i,in} - \sum_{i=0}^n \dot{m}_{i,out} s_{i,out} + \dot{\sigma}_{CV}$$

$\frac{dS_{cv}}{dt}$ = rate of entropy change
 $\sum_j \frac{\dot{Q}_j}{T_j}$ = rates of entropy transfer
 $\sum_e \dot{m}_e s_e + \dot{\sigma}_{cv}$ = rate of entropy production





ENTROPIA

