Fisica do Calor
(4300159)

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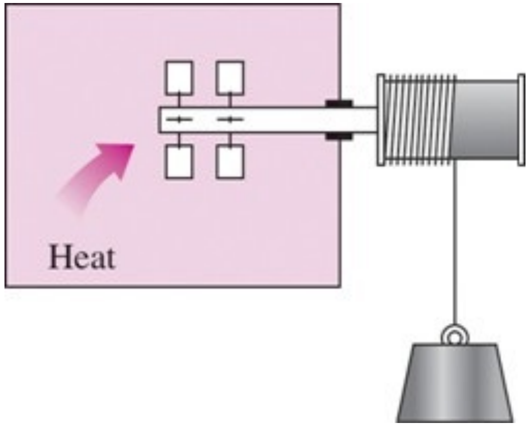
C01

Segunda Lei

Data	Programa do curso
August 9	Temperatura e escalas
August 12	Expansão Térmica
August 16	Calorimetria
August 19	Condução, convenção Radiação (Corpo Humano)
August 23	Equação de Estado
August 26	Propriedades moleculares da Matéria
August 30	**(Aula de Exercícios e Revisão)**
September 2	**Aula Modelo do Gas Ideal**
September 6	Feriado
September 9	Feriado
September 13	**Prova 3 1/4 - Temperatura e Calor** - Capacidade Têrmica
September 16	Velocidade molecular (Corpo Humano)
September 20	**(Aula de Exercícios e Revisão)**
September 23	**Prova 3 2/4 - Propriedades da Matéria - Aula Fases da matéria**
September 27	Prova 1: Temperatura, Calor e Propriedades da Matéria
September 30	Calor e trabalho
October 4	A primeira lei da Termodinâmica
October 7	Processos termodinâmicos
October 11	Semana de Ensino (IFUSP)
October 14	Semana de Ensino (IFUSP)
October 18	Termodinâmica do Gas Ideal
October 21	**(Aula de Exercícios e Revisão)**
October 25	**Prova 3 3/4 - Primeira Lei da Termodinâmica - Aula Processos adiabaticos**
October 28	Processos reversíveis e irreversíveis (Corpo Humano)
November 1	Maquinas térmicas, Ciclo de Otto e Refrigerador (Corpo Humano)
November 4	Segunda Lei da Termodinâmica
November 8	Ciclo de Carnot
November 11	**(Aula de Exercícios e Revisão)**
November 15	Feriado
November 18	Entropia Micro estados
November 22	**Prova 3 4/4 - Segunda Lei da Termodinâmica - Aula Micro estados**
November 25	Prova 2: Primeira e Segunda Lei da Termodinâmica
November 29	Prova Sub

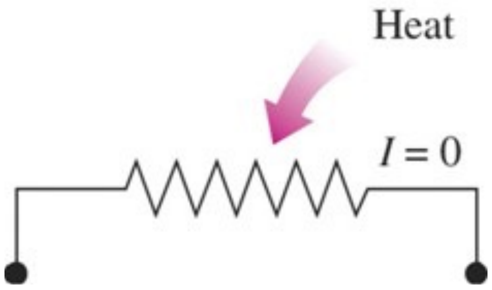
Segunda Lei da Termodinâmica

Um copo de café
nunca esquenta em
um ambiente frio



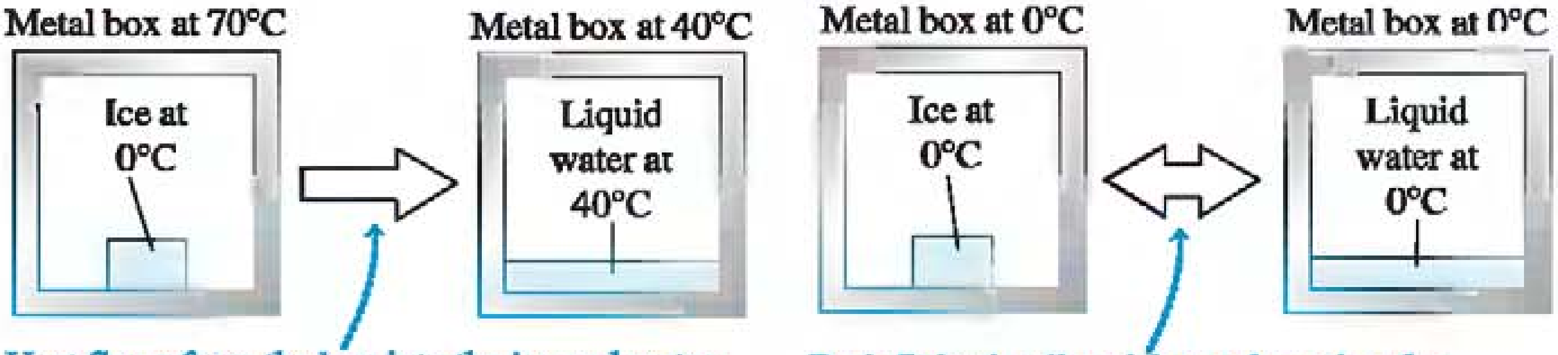
Transferir calor para uma
roda com remos não vai
fazer ela rodar

Transferir calor para uma
resistência não vai gerar
eletricidade



Esses processos não podem ocorrer, mesmo que eles não violem a primeira lei da termodinâmica

Irreversibilidade!!!



(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.

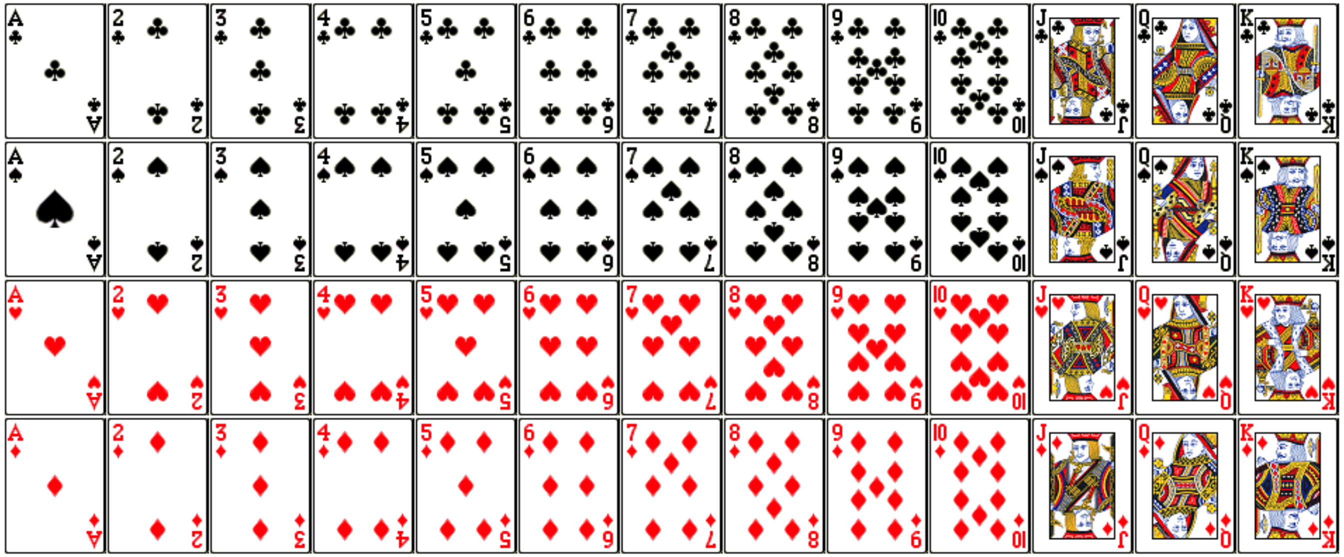
Heat flows from the box into the ice and water, never the reverse.

(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.

By infinitesimally raising or lowering the temperature of the box, we can make heat flow into the ice to melt it or make heat flow out of the water to refreeze it.

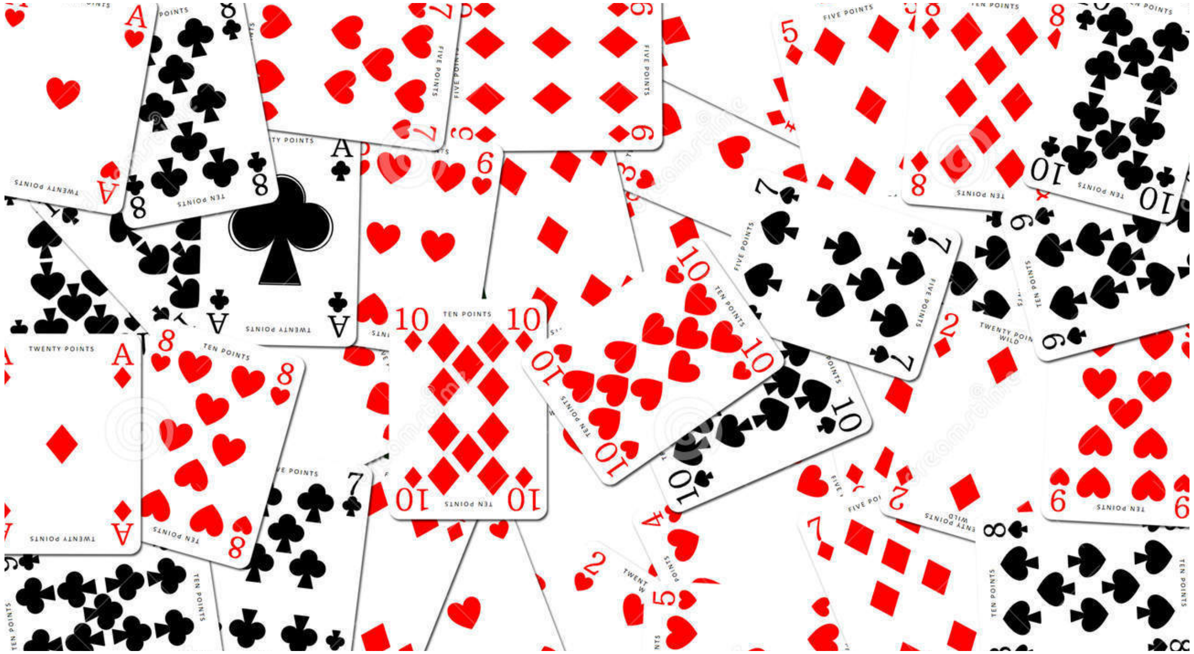
Idealizado reversível, muito
proximo ao equilíbrio
termodinâmico

Qual a probabilidade de voce colocar as cartas na mesa, aleatoriamente, e obter essa sequencia?

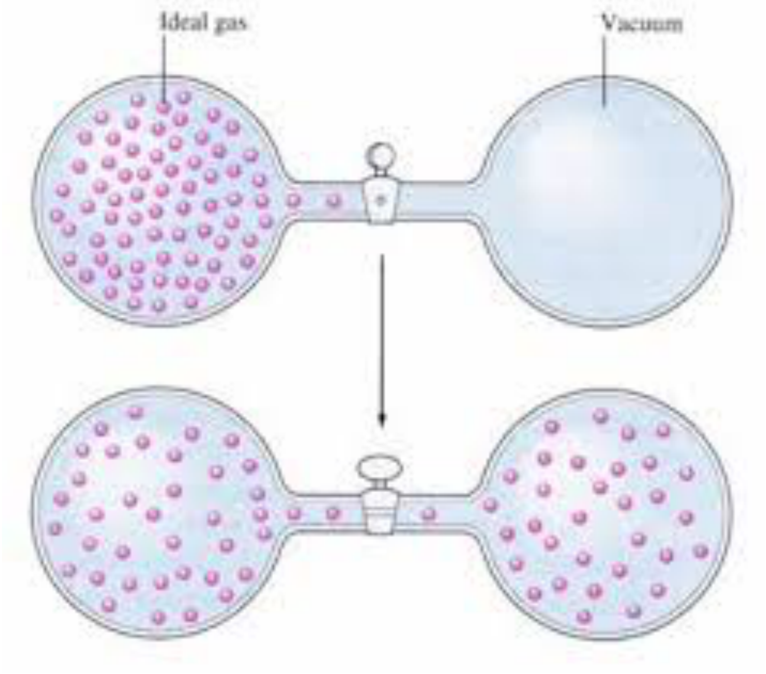


E algo assim ?

Porque ?



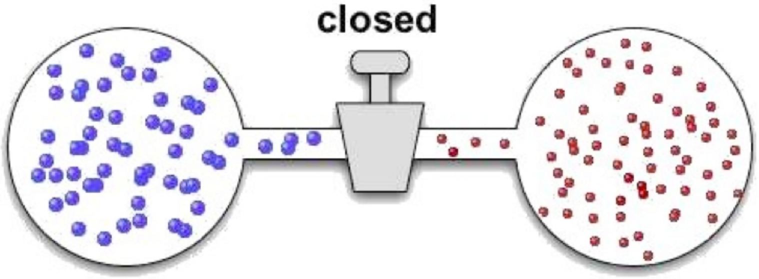
Expansão livre



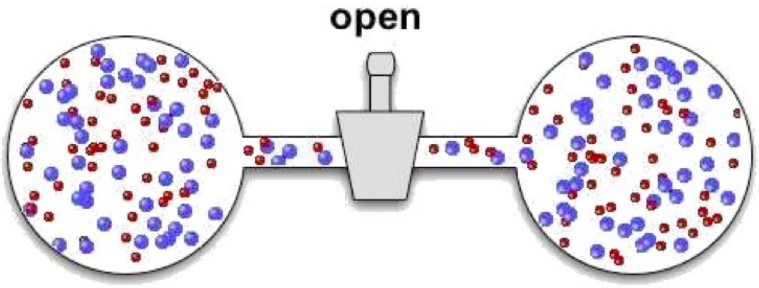
Mais ordenado

Menos ordenado

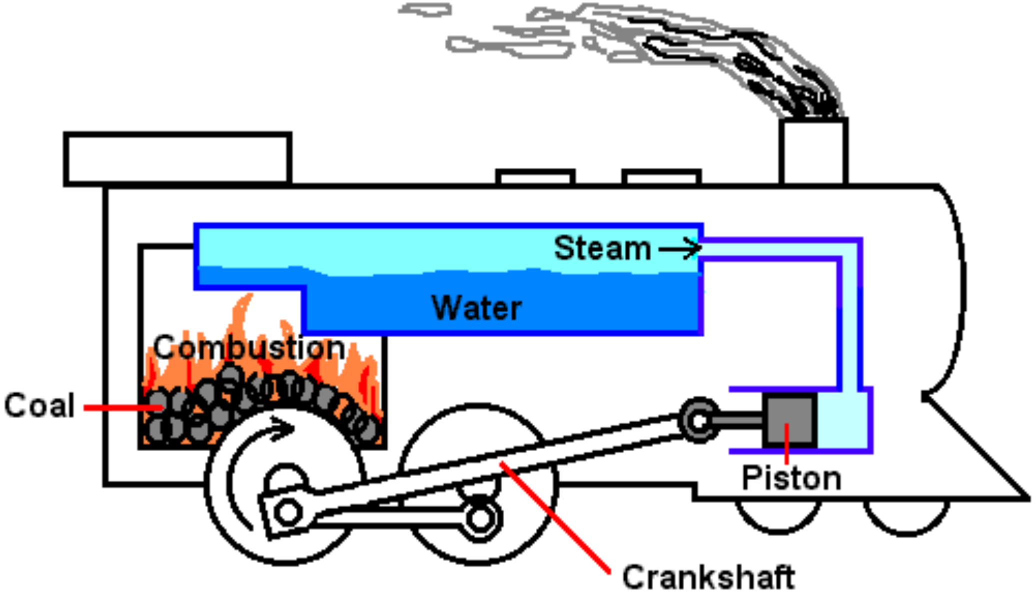
Mais ordenado



Menos ordenado



Maquinas Térmicas



Outras maquinas térmicas?

Stirling Engine

Reservatórios de calor e de frio

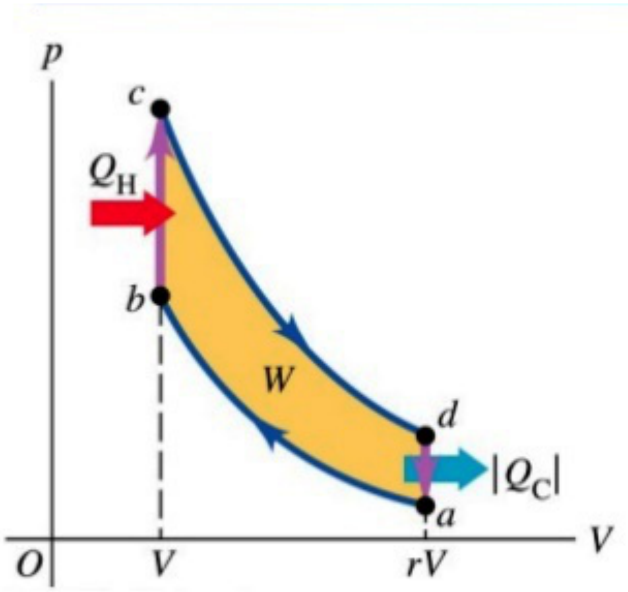
Todas as maquinas térmicas trabalham com dois reservatórios, o quente e o frio.
A maquina absorve calor, executa um trabalho mecânico, e descarta parte do calor em um reservatório frio.

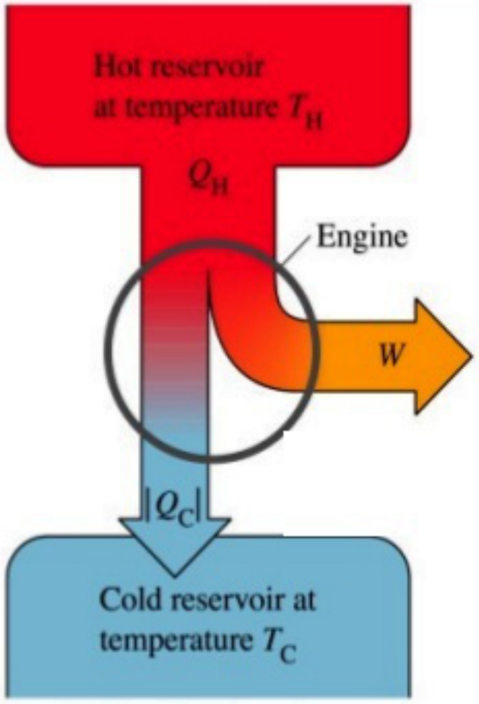
Em um sistema cíclico, Energia final e inicial são o mesmo:

$$\Delta U = 0 = Q - W$$

$$Q = W$$

Diagrama de Fluxo de Energia e Eficiencia





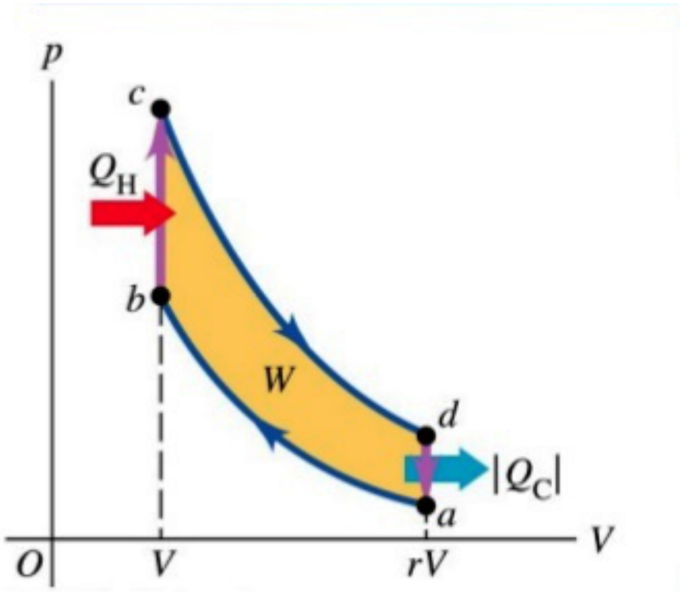
$$\begin{aligned} W &= Q_H + Q_C \\ &= |Q_H| - |Q_C| \end{aligned}$$

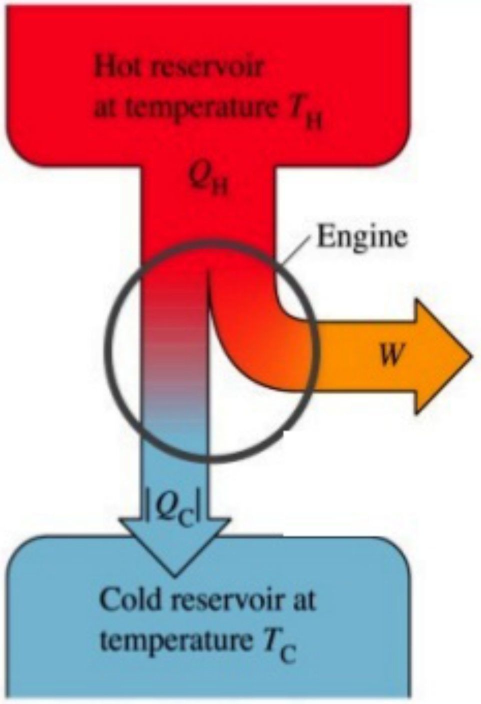
Idealmente, gostaríamos que todo o calor fosse convertido em trabalho, nesse caso: $W = Q_H$

$$Q_C = 0$$

ISSO NUNCA OCORRE

Diagrama de Fluxo de Energia e Eficiencia

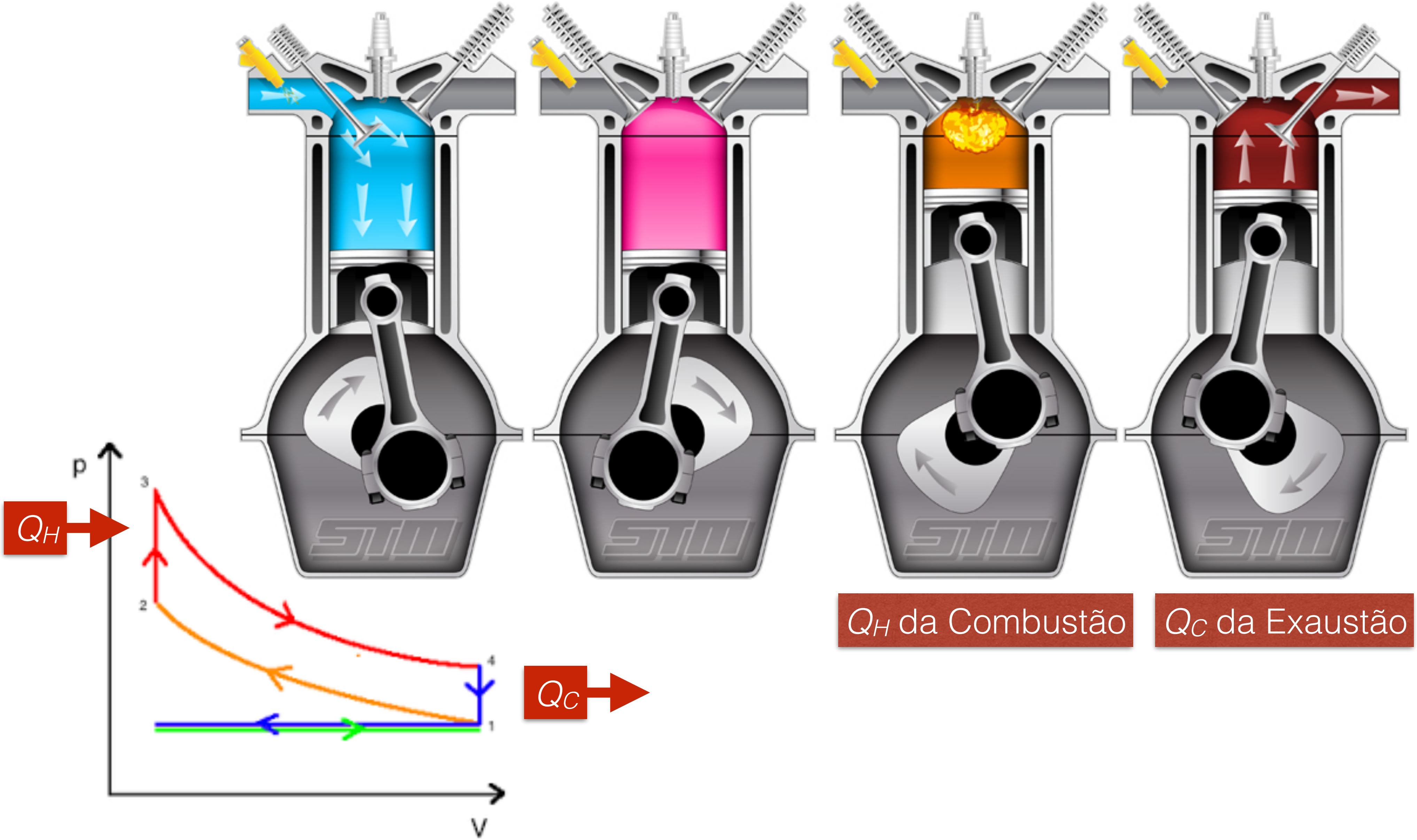




$$\begin{aligned} W &= Q_H + Q_C \\ &= |Q_H| - |Q_C| \end{aligned}$$

Eficiencia: $$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left|\frac{Q_C}{Q_H}\right|$$

Maquinas de combustão interna
Ciclo de Otto



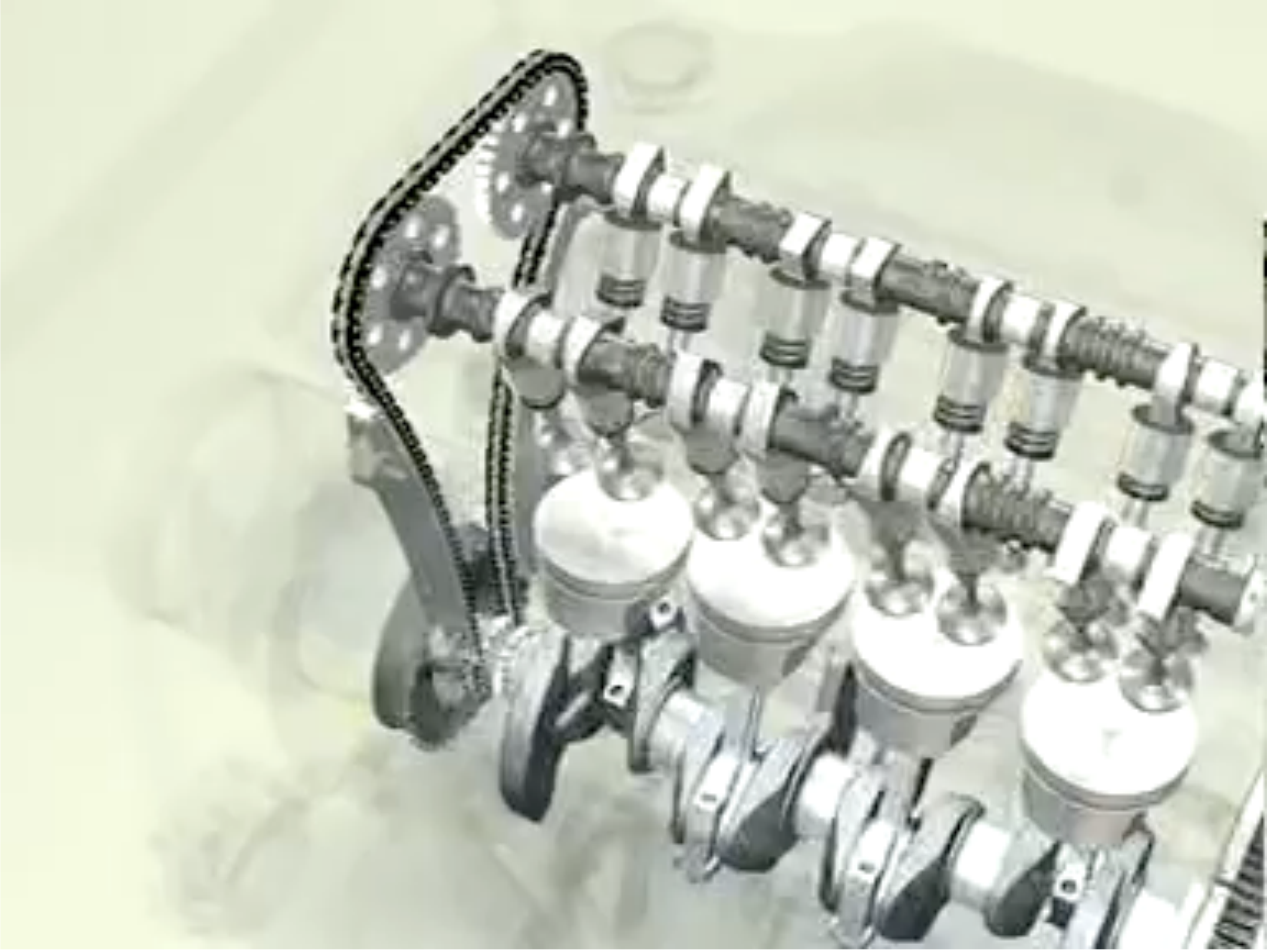
Q_H

Q_C

Q_H da Combustão

Q_C da Exaustão

Maquinas de combustão interna
Ciclo de Otto



Maquinas de combustão interna
Ciclo de Otto

Eficiência:

$$Q_H = nC_V(T_c - T_b) > 0$$
$$Q_C = nC_V(T_a - T_d) < 0$$

$$e = \frac{Q_H + Q_C}{Q_H} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b}$$

Para os processos adiabaticos:

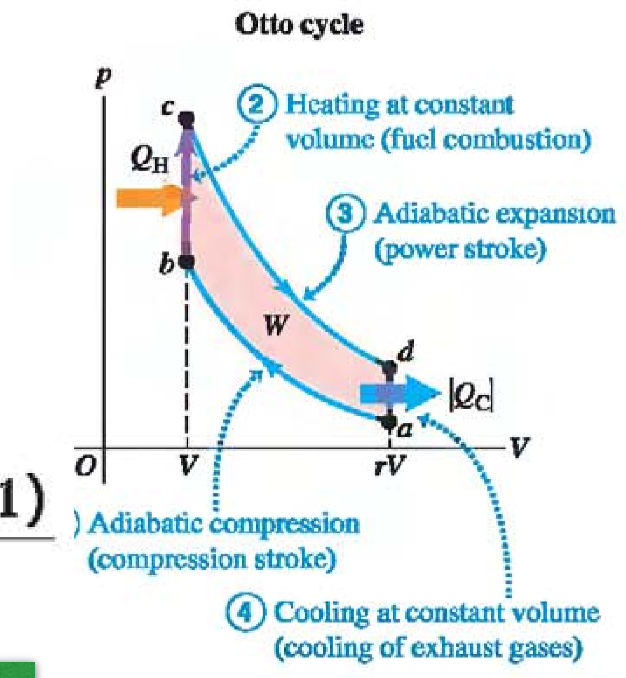
$$T_a(rV)^{\gamma-1} = T_b V^{\gamma-1}$$

$$e = \frac{T_d r^{\gamma-1} - T_a r^{\gamma-1} + T_a - T_d}{T_d r^{\gamma-1} - T_a r^{\gamma-1}} = \frac{(T_d - T_a)(r^{\gamma-1} - 1)}{(T_d - T_a) r^{\gamma-1}}$$

$$e = 1 - \frac{1}{r^{\gamma-1}}$$

Para $r = 8$, $e = 0.56$
$r_{\max}$ = 10~13 (gasolina Premium)

20.6 The *pV*-diagram for the Otto cycle, an idealized model of the thermodynamic processes in a gasoline engine.

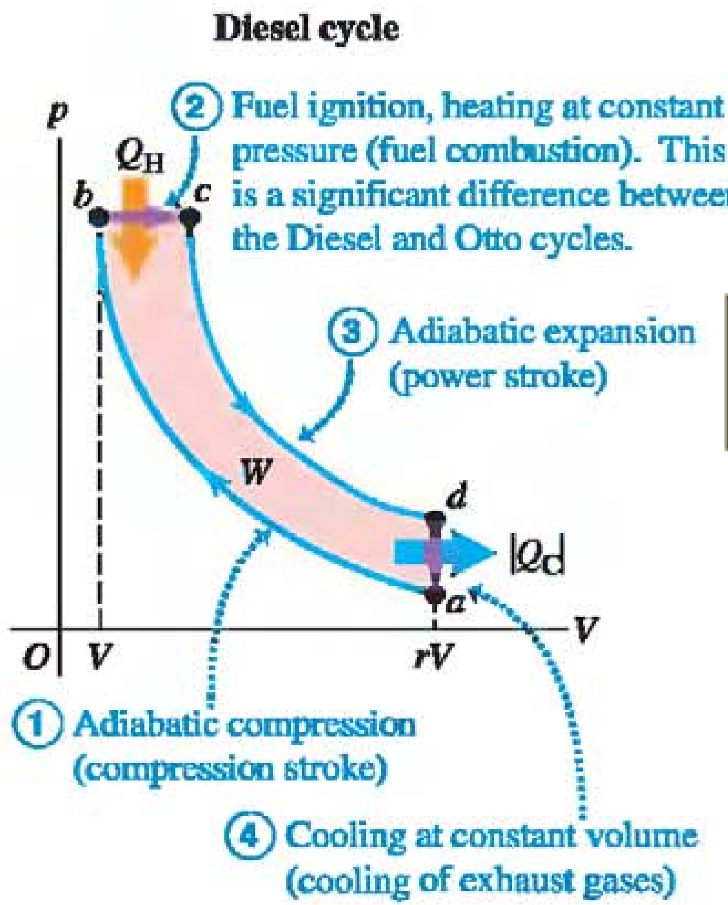


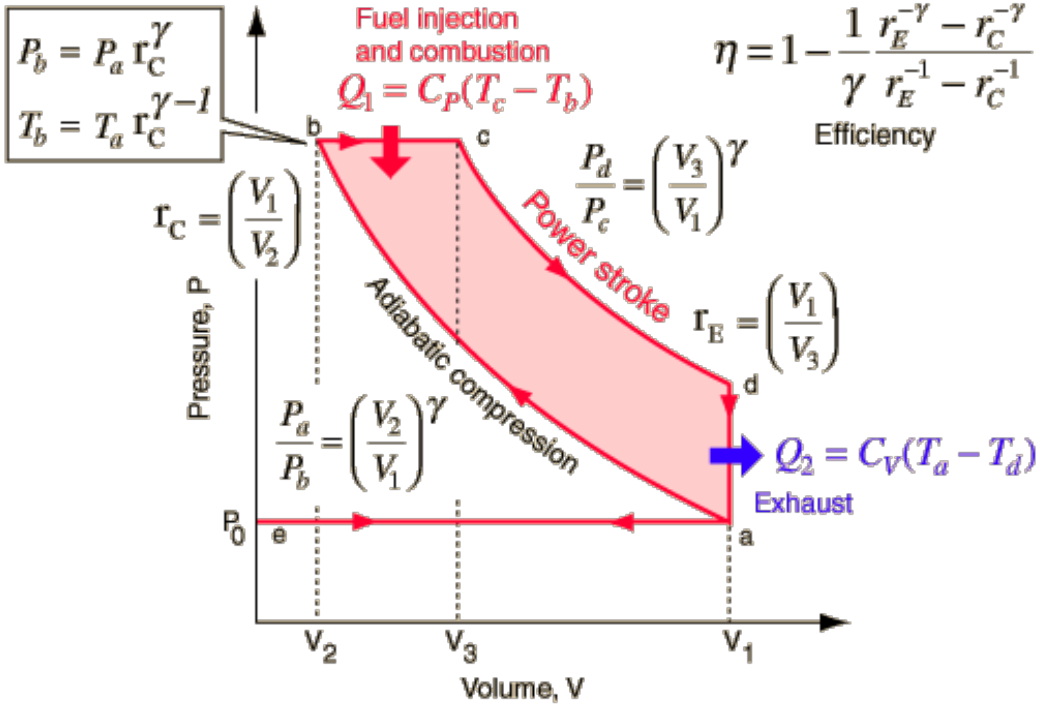
Quais as idealizações aqui? Quais as outras fontes de perdas?

Ciclo do Diesel

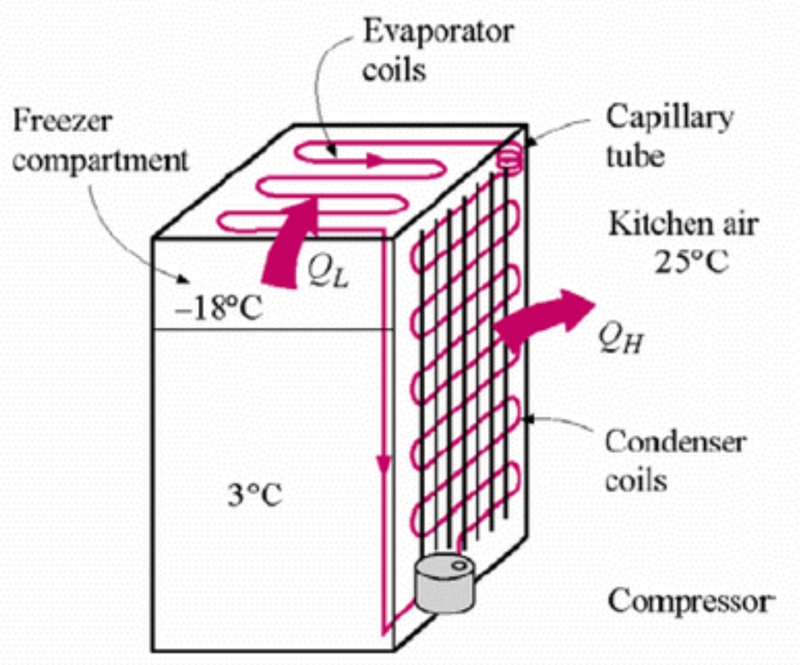
20.7 The pV-diagram for the idealized Diesel cycle.

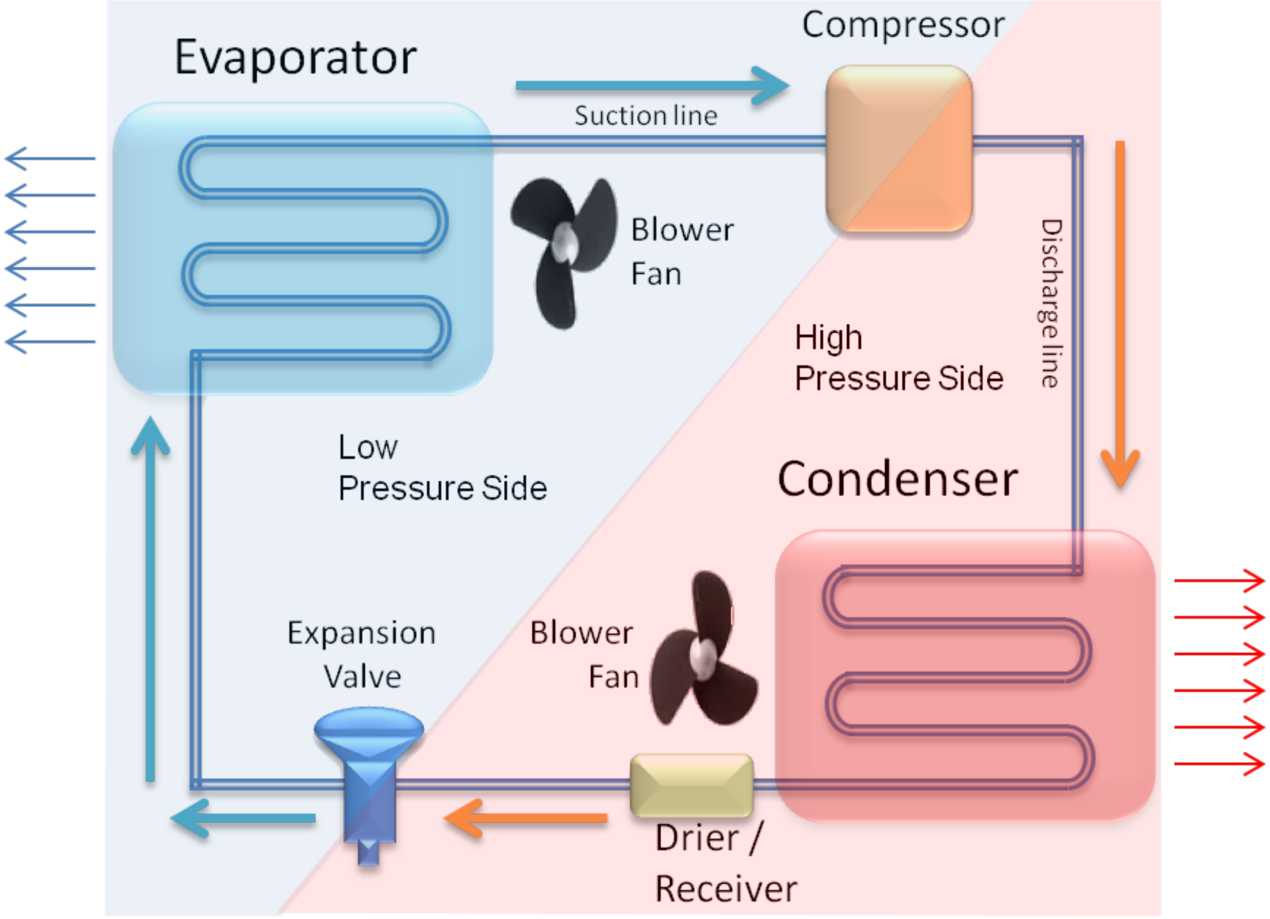
$$r = 15 \sim 20$$
$$e = 0.65 \sim 0.7$$



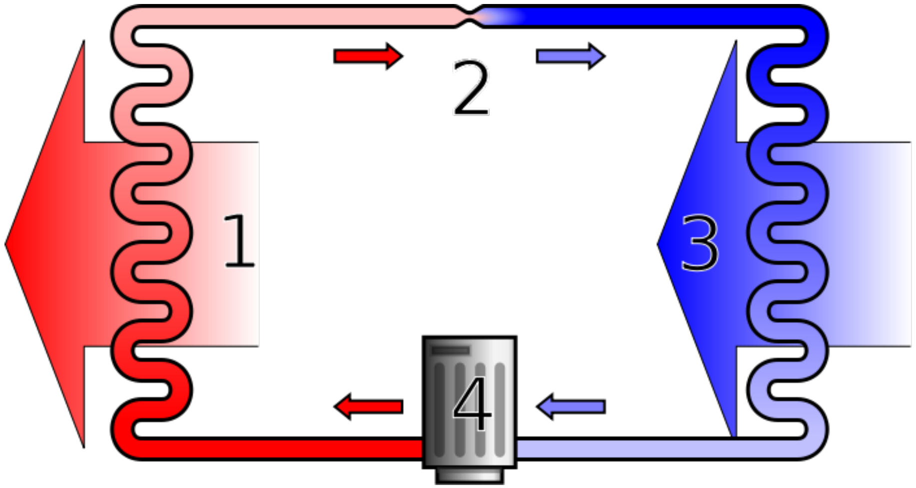


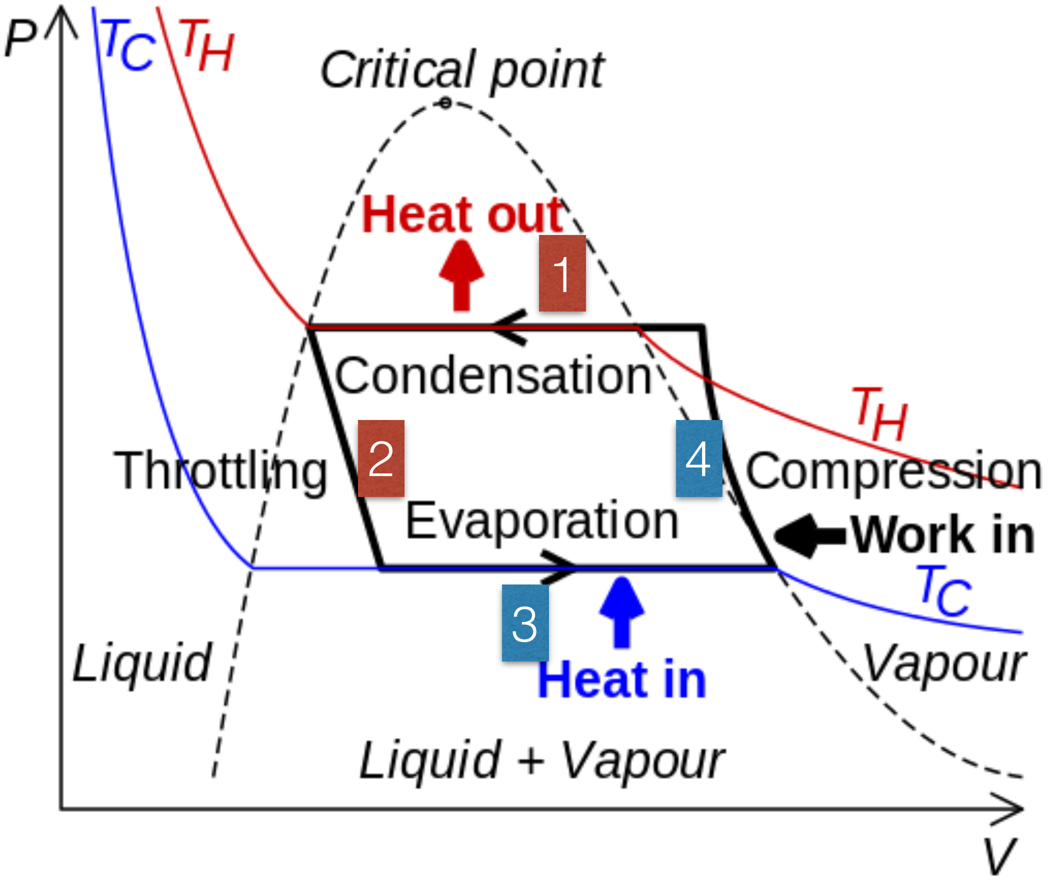
Refrigerador





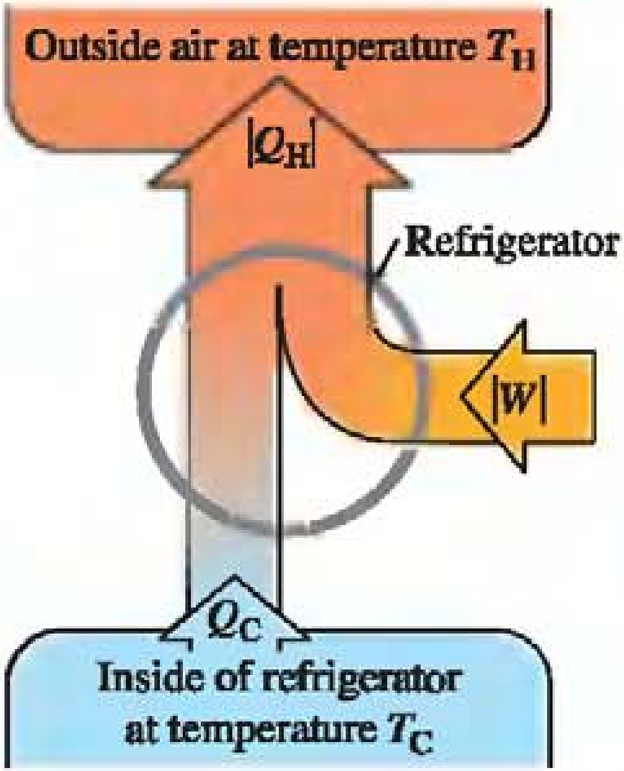
Refrigerador





Refrigerador

20.8 Schematic energy-flow diagram of a refrigerator.



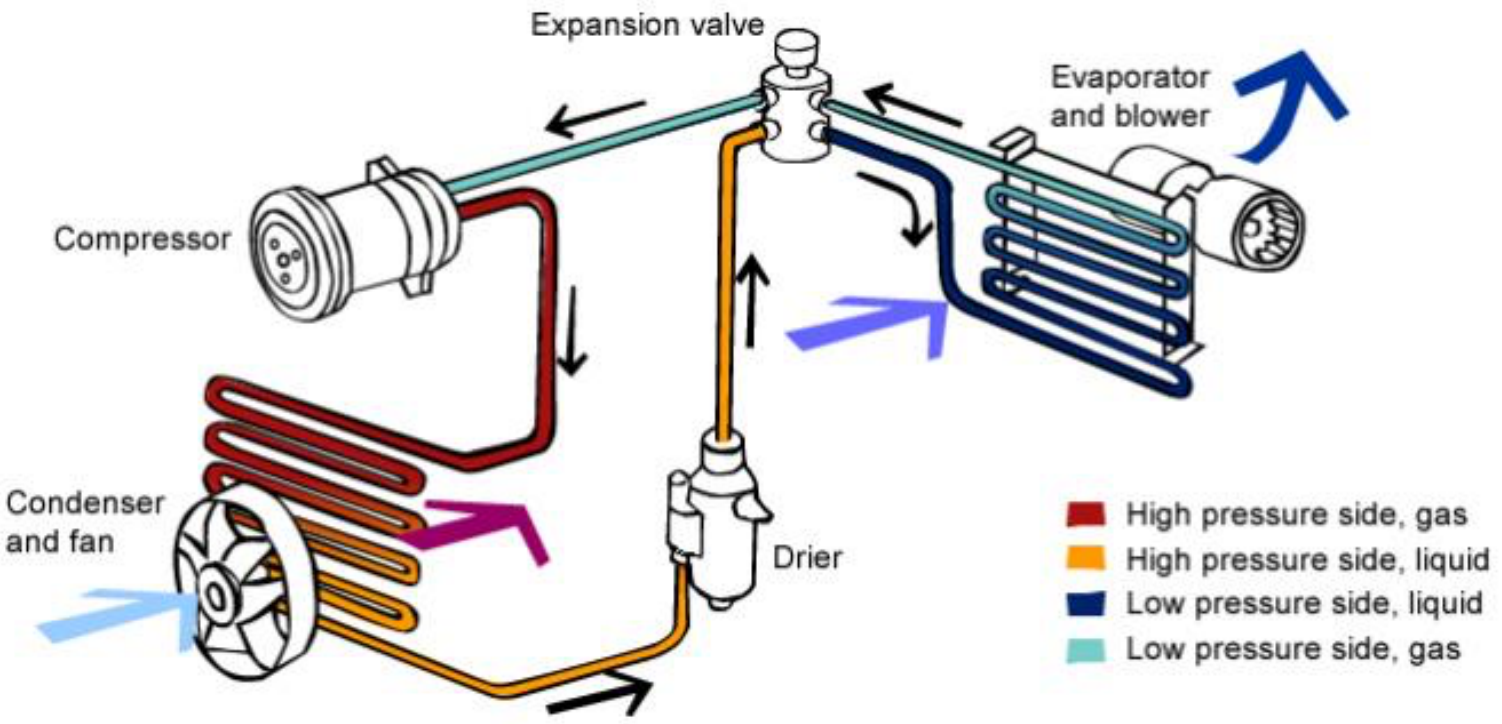
$$Q_H + Q_C - W = 0$$

$$|Q_H| = |Q_C| + |W|$$

Coeficiente de performance:

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

Ar-condicionado



Valores típicos:

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|/\Delta T}{|W|/\Delta T} \begin{array}{l} \rightarrow 10\ \text{kBtu/h ou 3 kW} \\ \rightarrow 1200\ \text{W} \end{array}$$

Sempre é necessário trabalho? calor pode ser transferido de um ambiente frio para um quente sem trabalho?

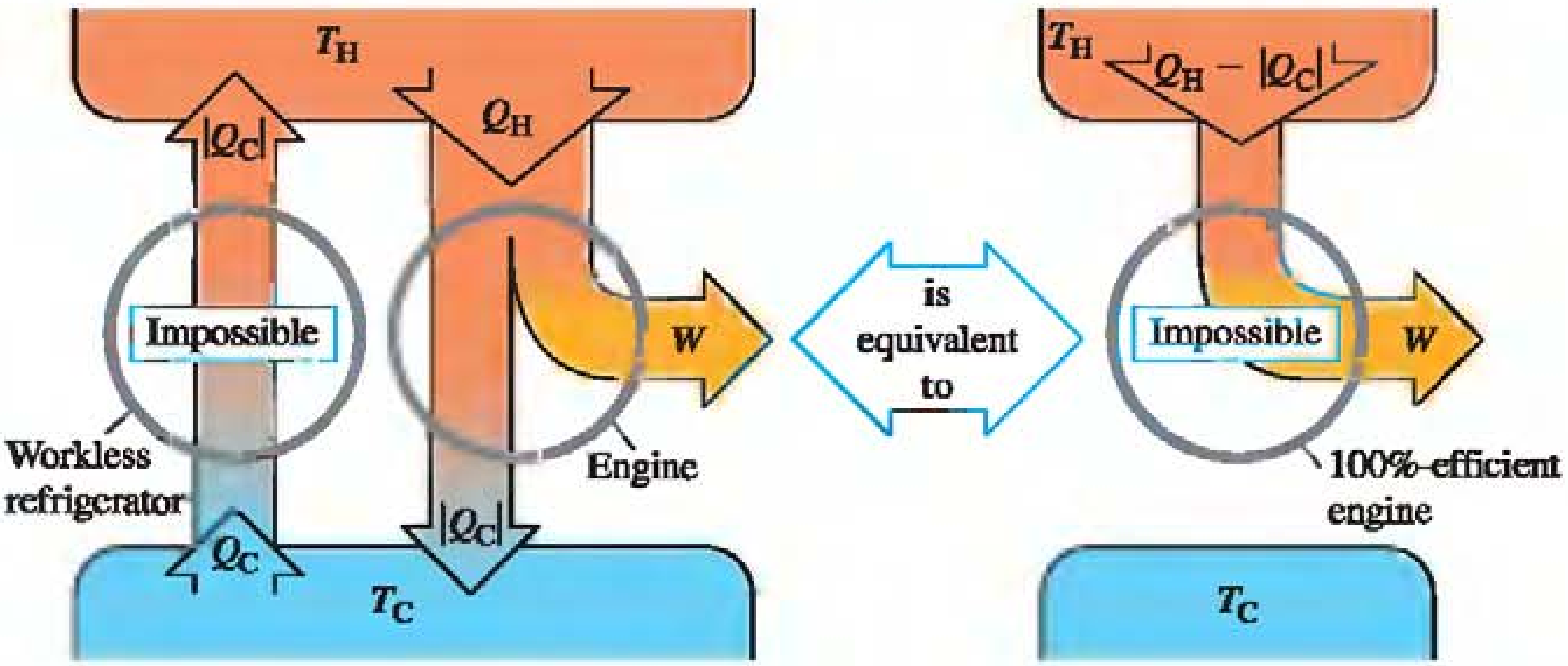
Segunda Lei

> É impossível para qualquer sistema passar por um processo em que absorve calor de um reservatório em uma única temperatura e converta todo o calor em trabalho mecânico, com o sistema terminando no mesmo estado em que começou.
>
> — *Kelvin-Planck*

> É impossível qualquer processo transferir, como único resultado, calor de um reservatório frio para um quente.
>
> — *Clausius*

Segunda Lei

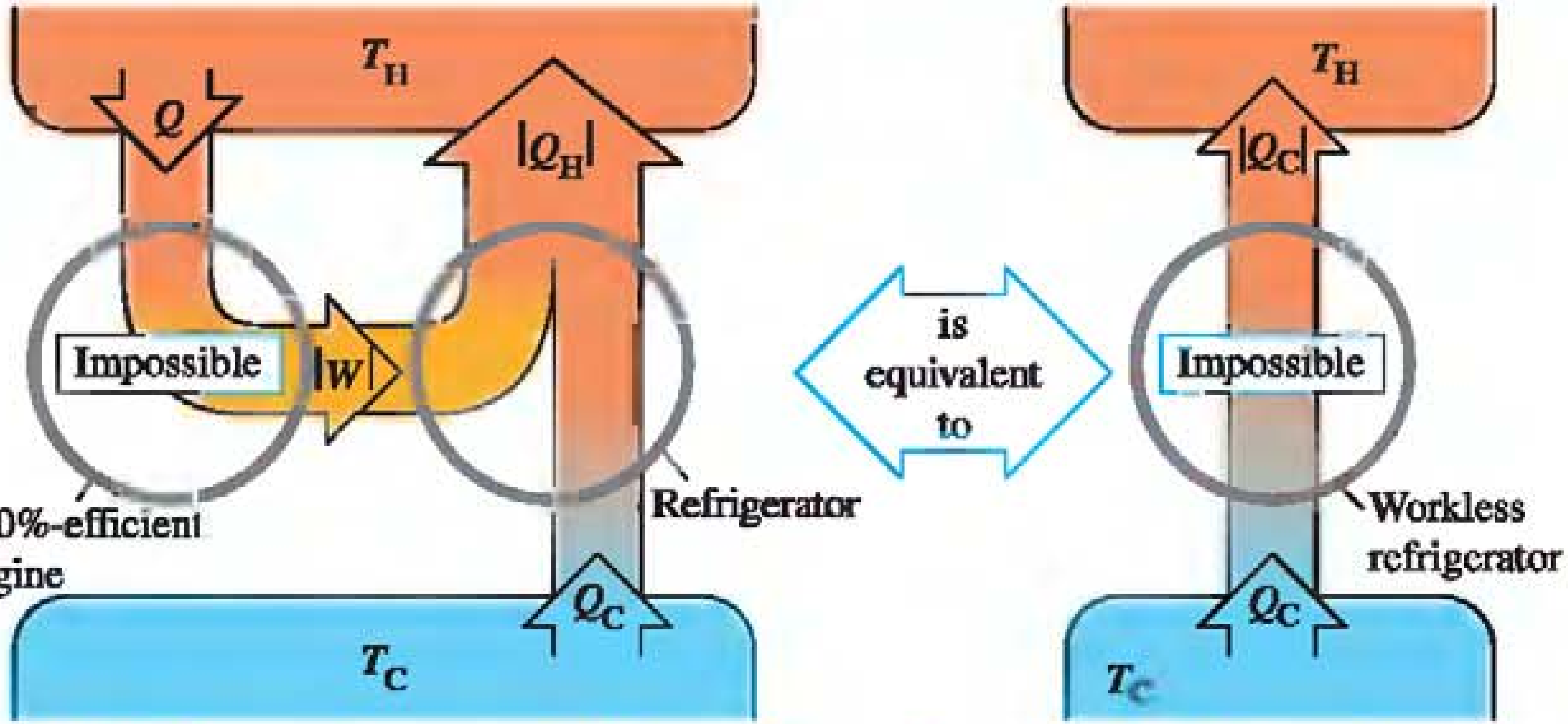
(a) The "engine" statement of the second law of thermodynamics



If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

Segunda Lei

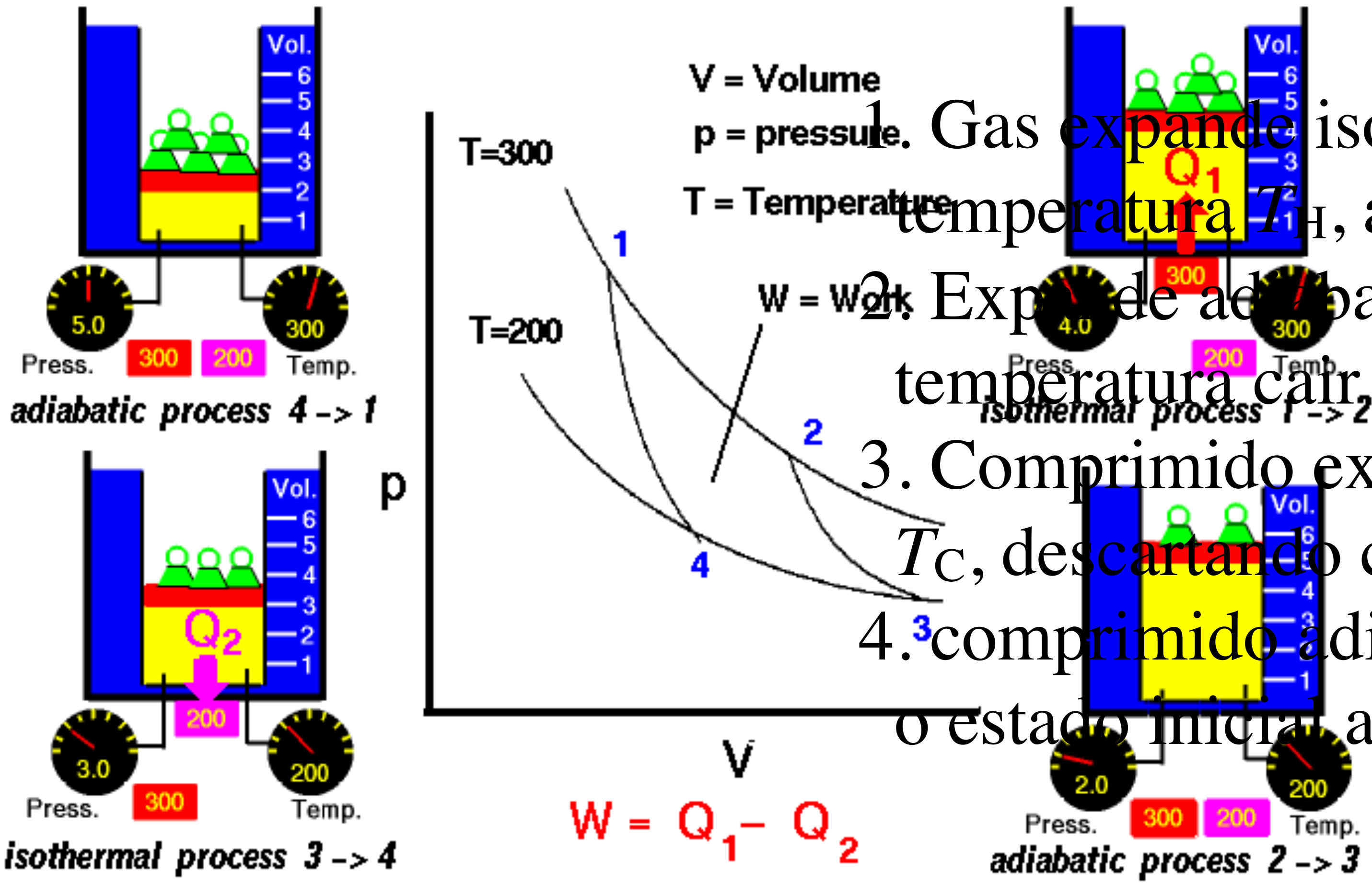
(b) The "refrigerator" statement of the second law of thermodynamics



If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

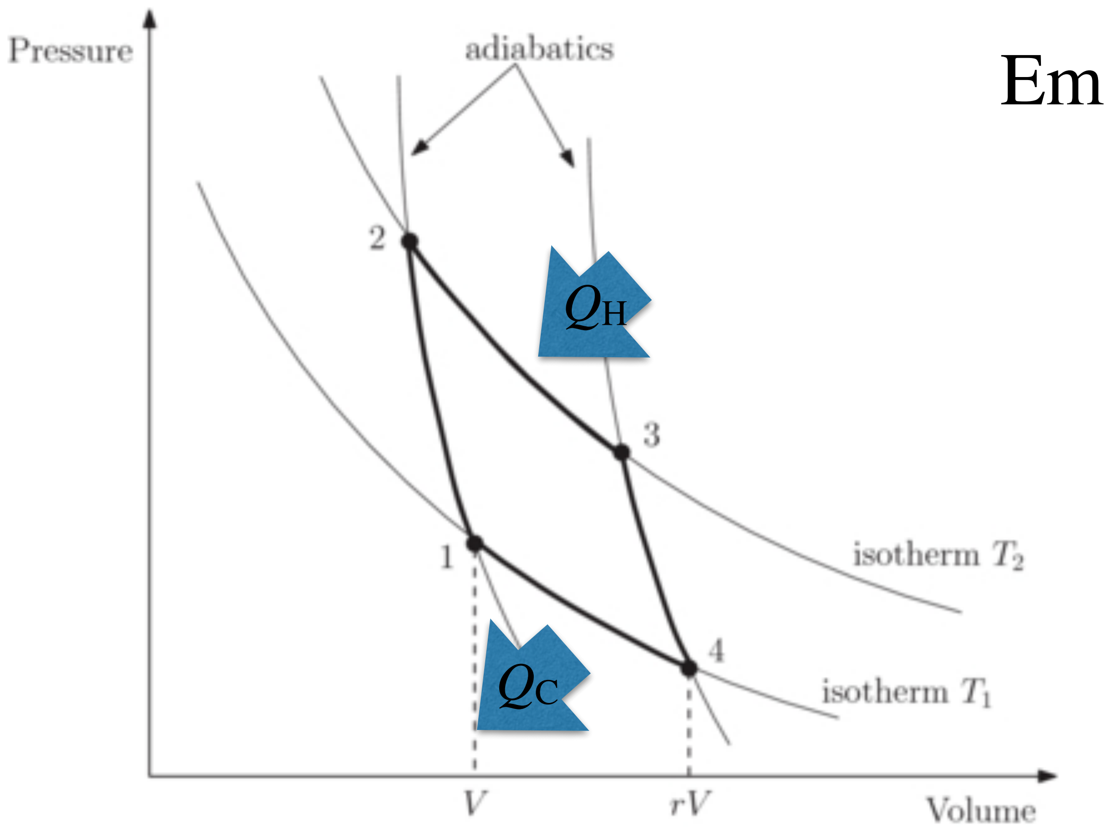
Ciclo de Carnot

Ciclo hipotético, idealização de uma máquina termina que maximiza a eficiência mantendo a consistência com a segunda lei.



1. Gas expande isotermicamente a temperatura T_{H}, absorvendo calor
2. Expande adiabaticamente ate a temperatura cair para T_{C}
3. Comprimido exotermicamente a T_{C}, descartando calor.
4. comprimido adiabaticamente até o estado inicial a T_{H}

Ciclo de Carnot



Em uma isotermica

$$\Delta U = 0$$

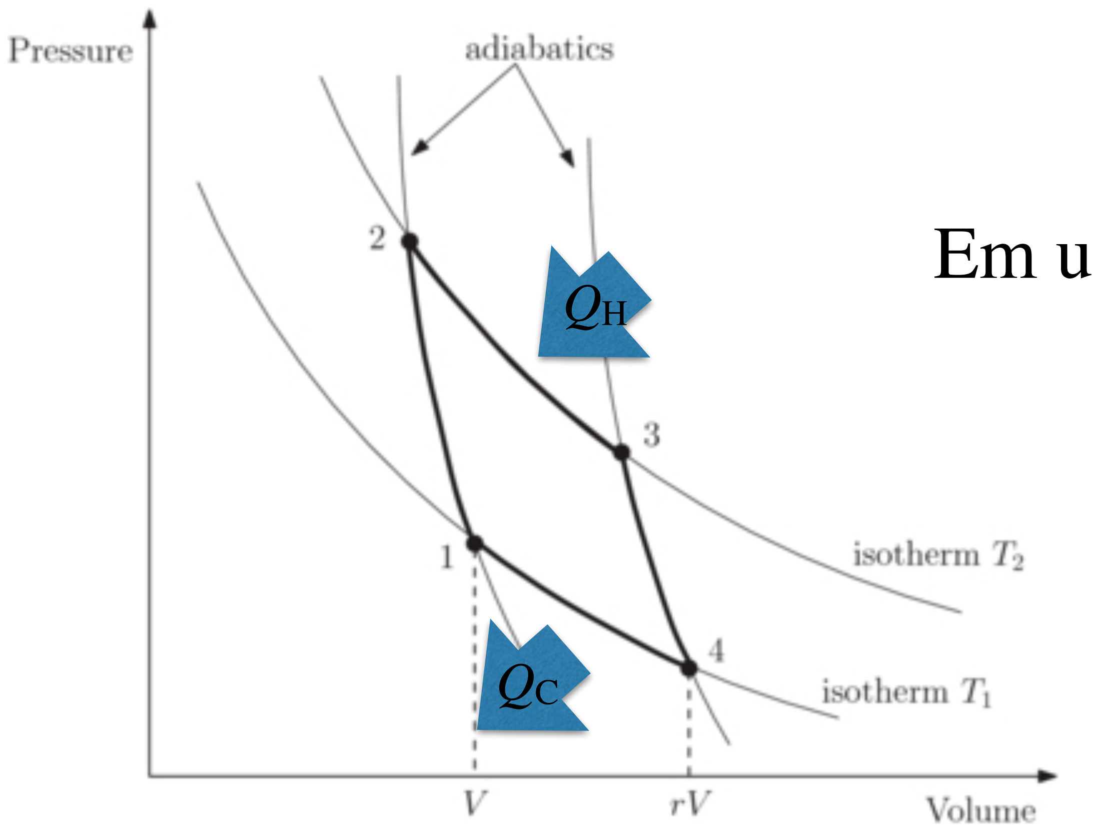
$$Q_H = W_{2-3}$$

$$Q_H = nRT_H \ln \frac{V_3}{V_2}$$

$$Q_C = -nRT_C \ln \frac{V_4}{V_1}$$

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \frac{\ln \frac{V_4}{V_1}}{\ln \frac{V_3}{V_2}}$$

Ciclo de Carnot



$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}\frac{\ln\frac{V_4}{V_1}}{\ln\frac{V_3}{V_2}}$$

Em uma curva adiabatica

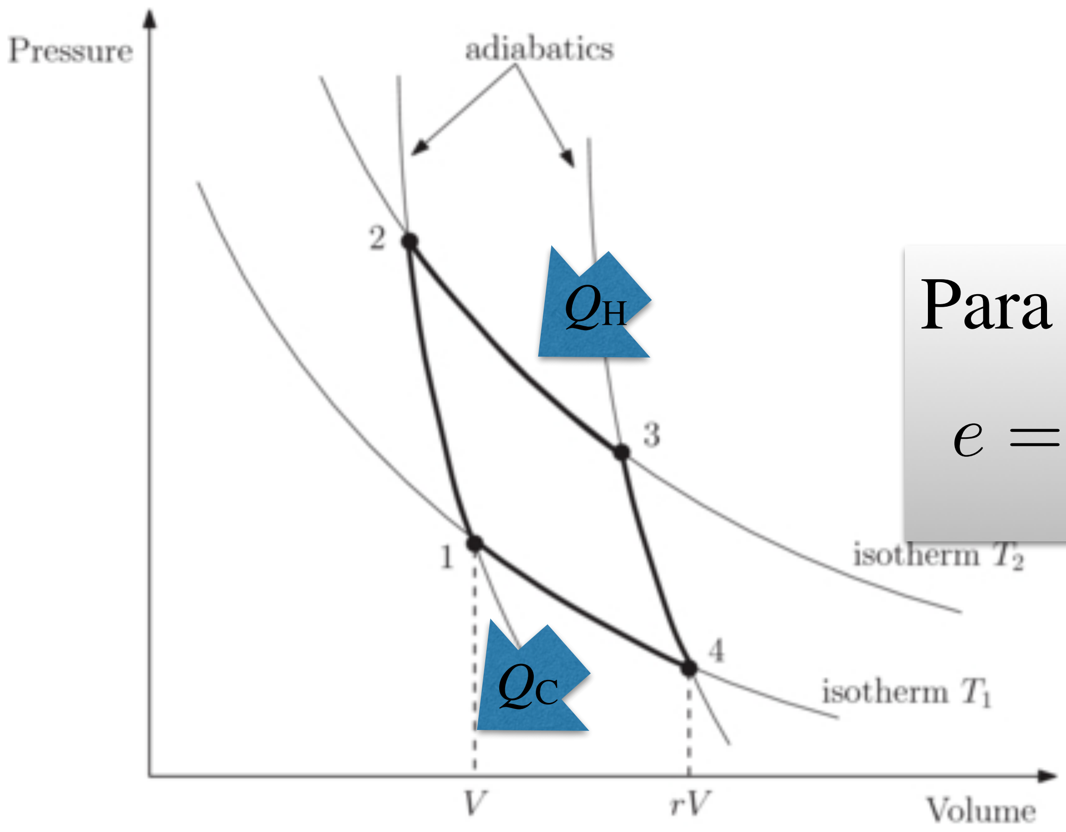
$$T_H V_3^{\gamma-1} = T_C V_4^{\gamma-1}$$

$$T_H V_2^{\gamma-1} = T_C V_1^{\gamma-1}$$

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \qquad \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H}$$

Ciclo de Carnot



$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H}$$

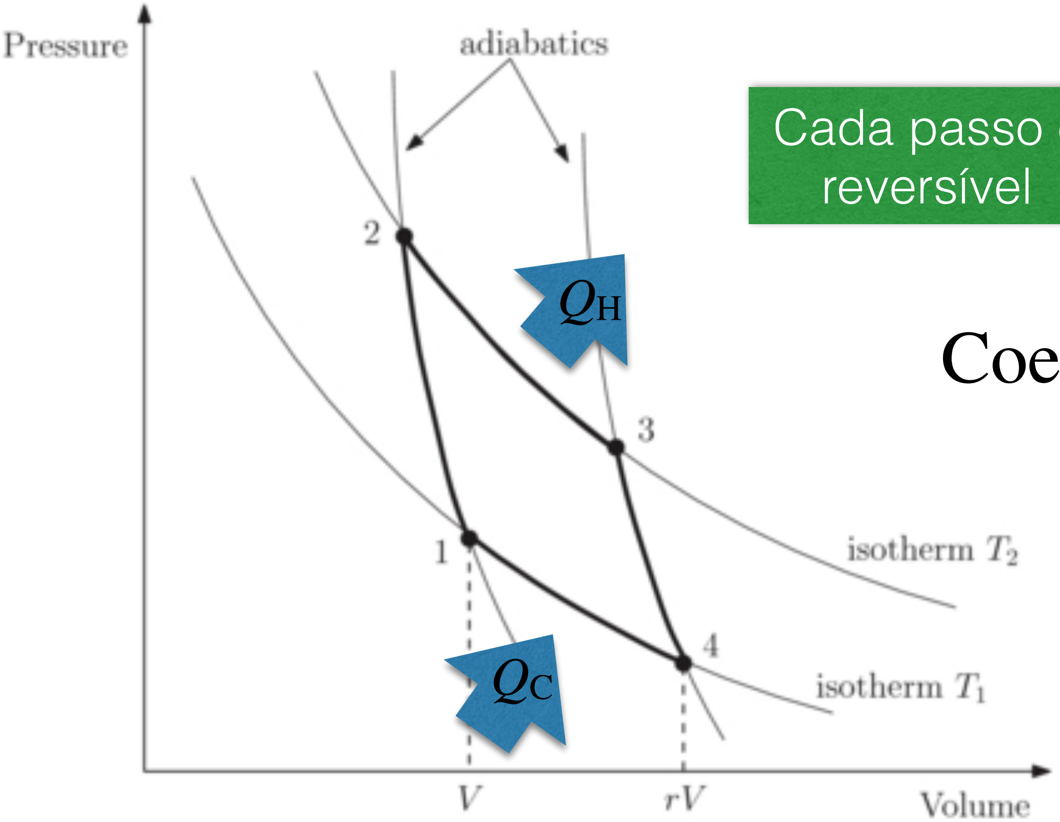
Para uma máquina termica:

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|}$$

Para uma máquina de Carnot:

$$e = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$

Ciclo de Carnot (refrigerador)



Cada passo é reversível

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H}$$

Coeficiente de performance (Geral):

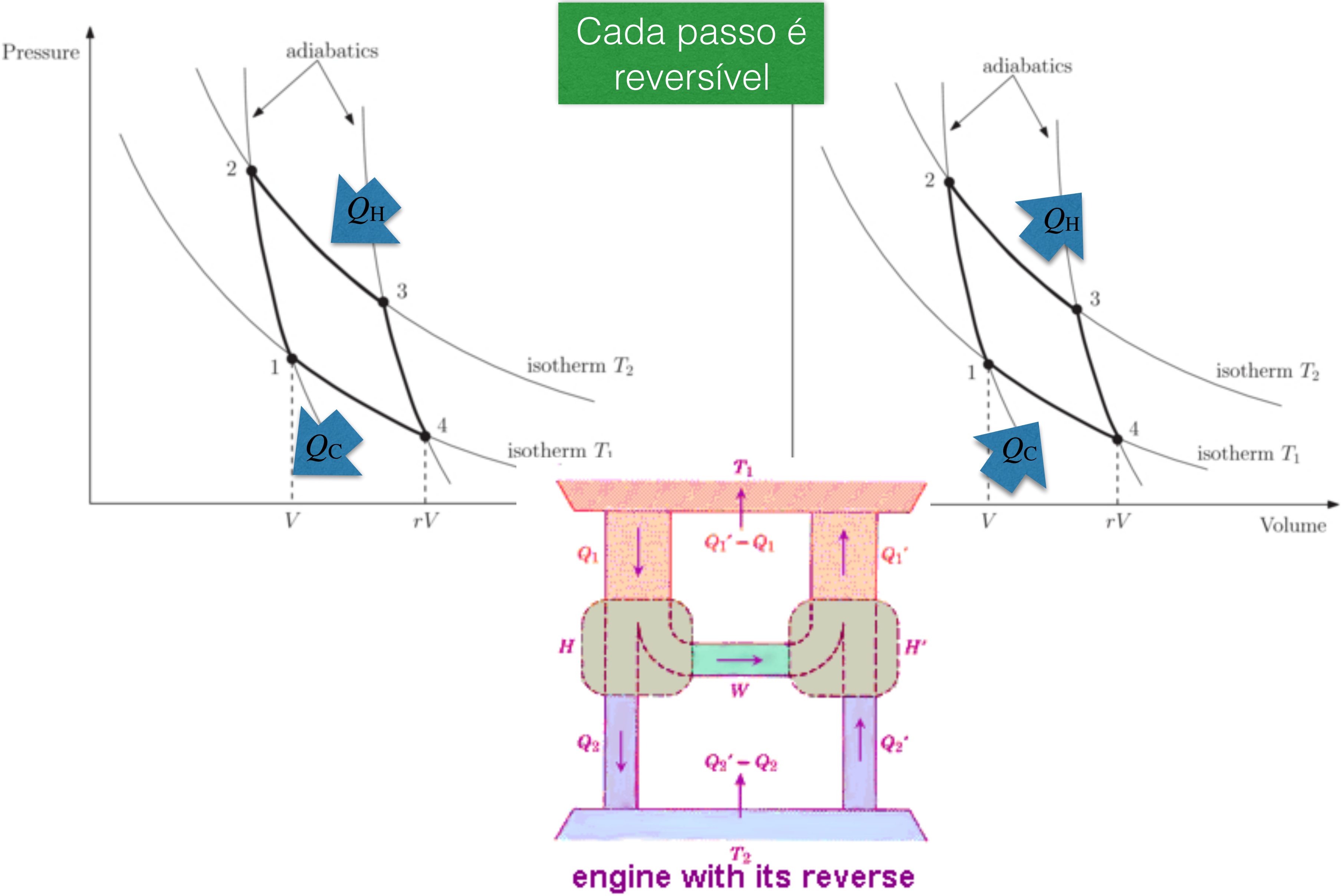
$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

Para uma refrigerador de Carnot:

$$K = \frac{|Q_C|/|Q_H|}{|Q_H|/|Q_H| - |Q_C|/|Q_H|} = \frac{T_C}{T_H - T_C}$$

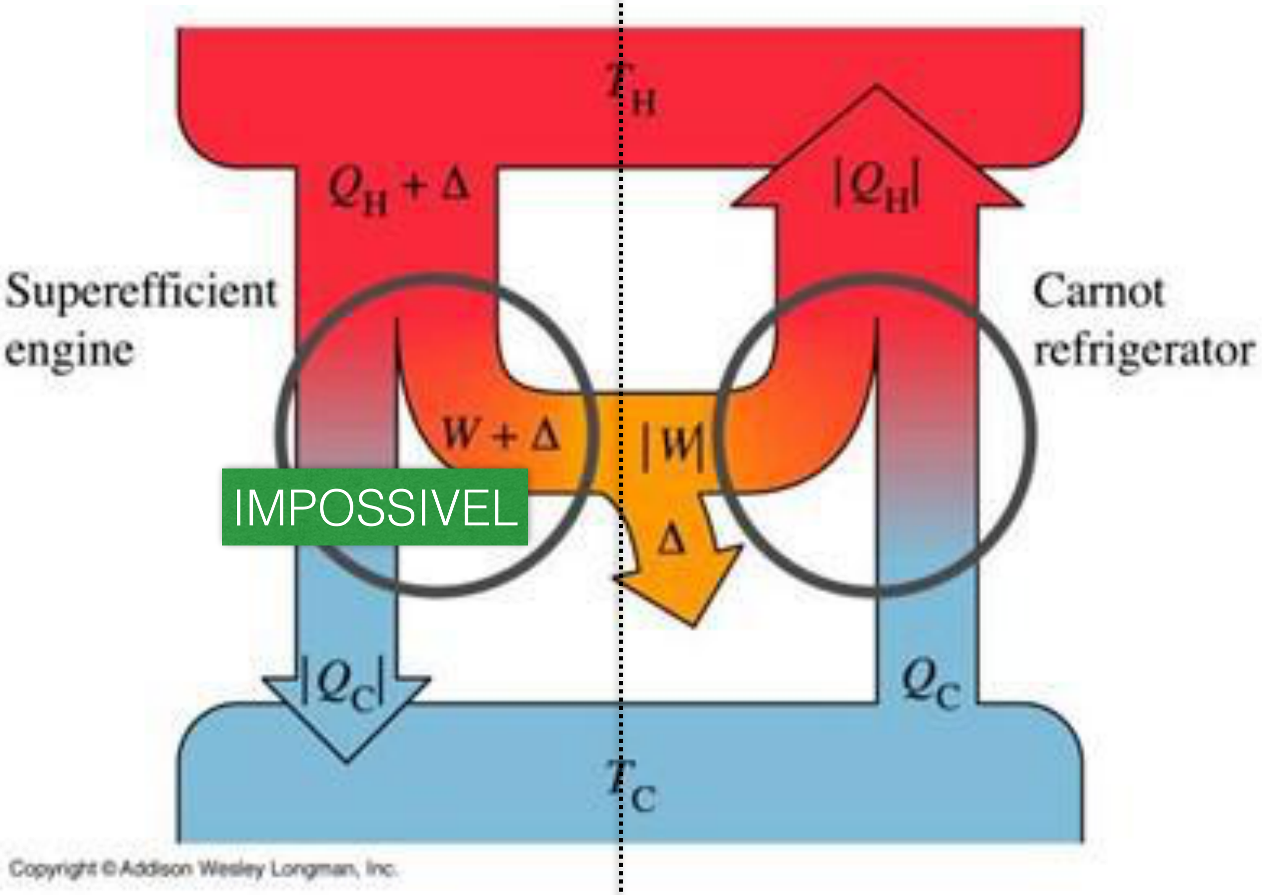
Ciclo de Carnot e a Segunda Lei

Cada passo é reversível



engine with its reverse

Maquina mais eficiente que ciclo de Carnot



IMPOSSIVEL

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Nenhuma maquina pode ser mais eficiente que uma maquina operando no ciclo de Carnot

— Outra forma de falar a Segunda lei

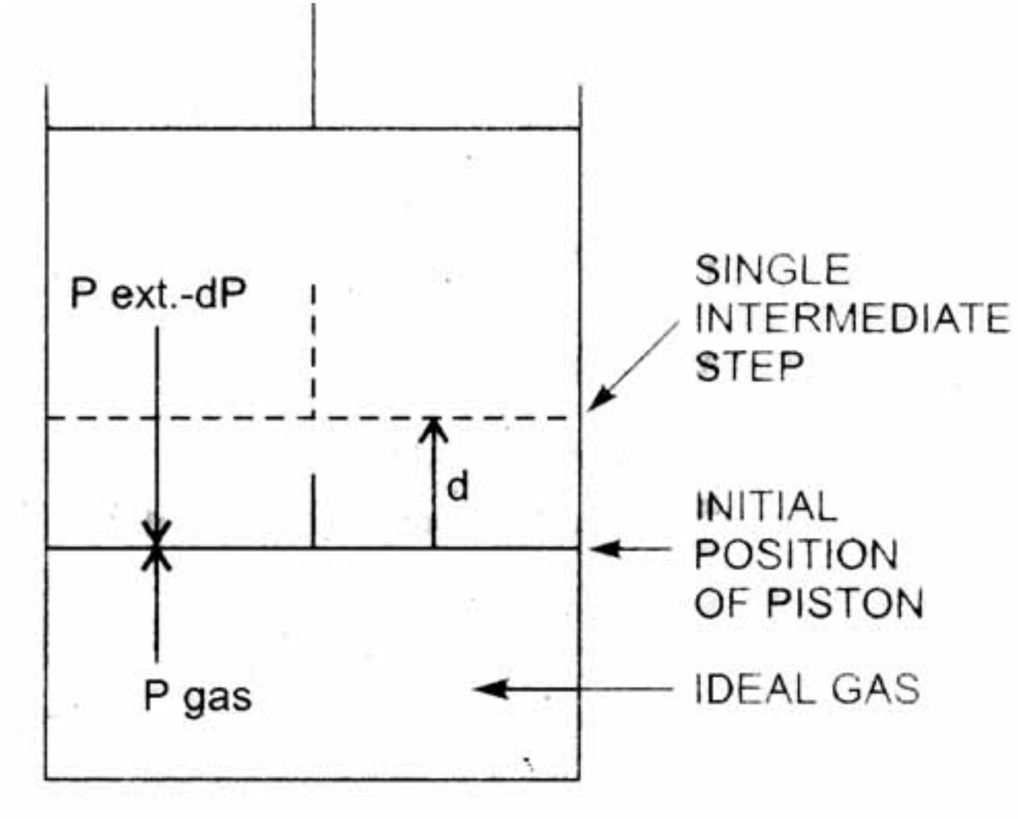
Entropia

Entropia nos da uma medida quantitativa da desordem

Expansão infinitesimal isotermica

Calor entra no sistema

Moléculas se movem em um volume maior, posições mais aleatórias (menos previsíveis)



Isothermal reversible expansion work

Entropia

$$dU = 0$$

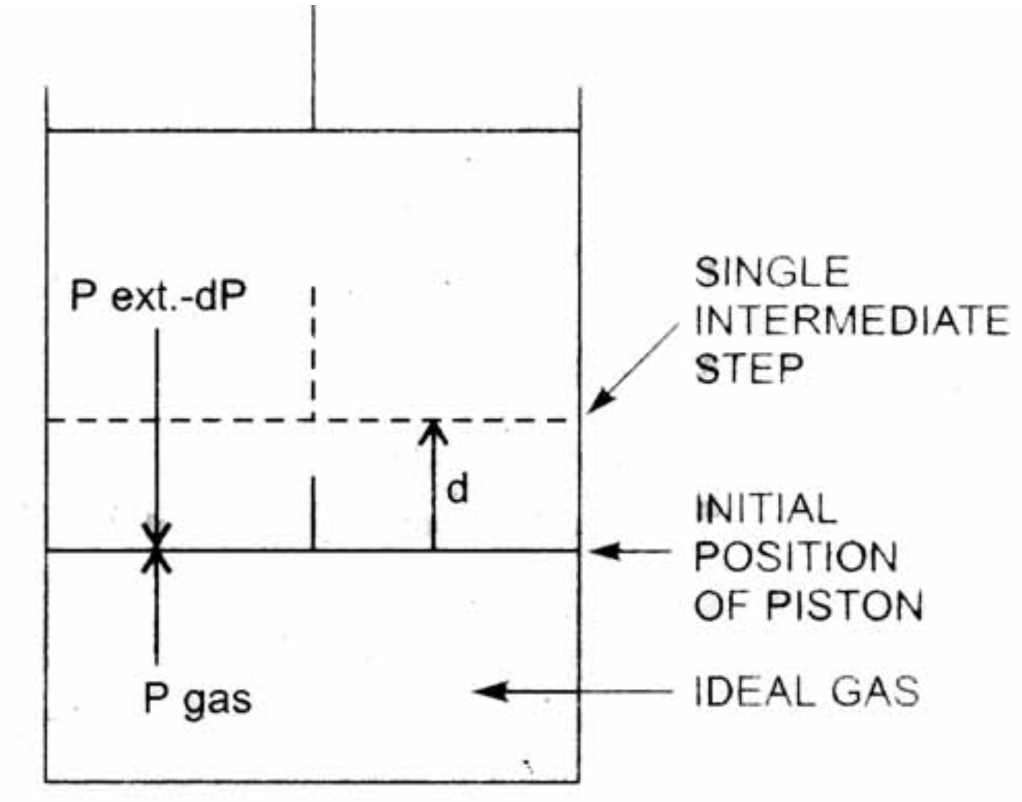
$$dQ = dW = pdV = \frac{nRT}{V}dV$$

$$\frac{dV}{V} = \frac{1}{nR}\frac{dQ}{T}$$

↓

Fração da
variação
volumétrica → Quantificação
do aumento
da desordem

$$\frac{dQ}{T}$$



Isothermal reversible expansion work

Entropia

Definimos mudanças infinitesimais de entropia durante um processo infinitesimal reversível na temperatura absoluta T

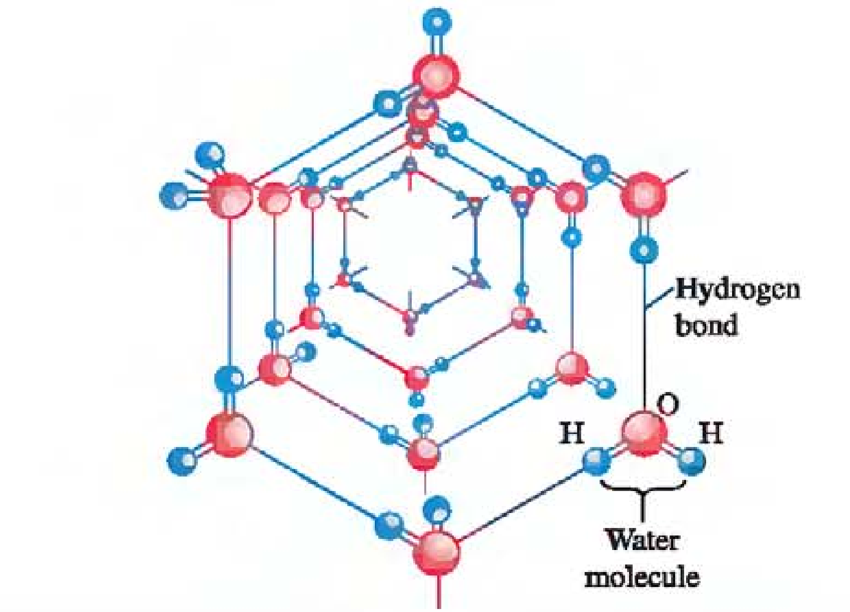
$$dS = \frac{dQ}{T}$$

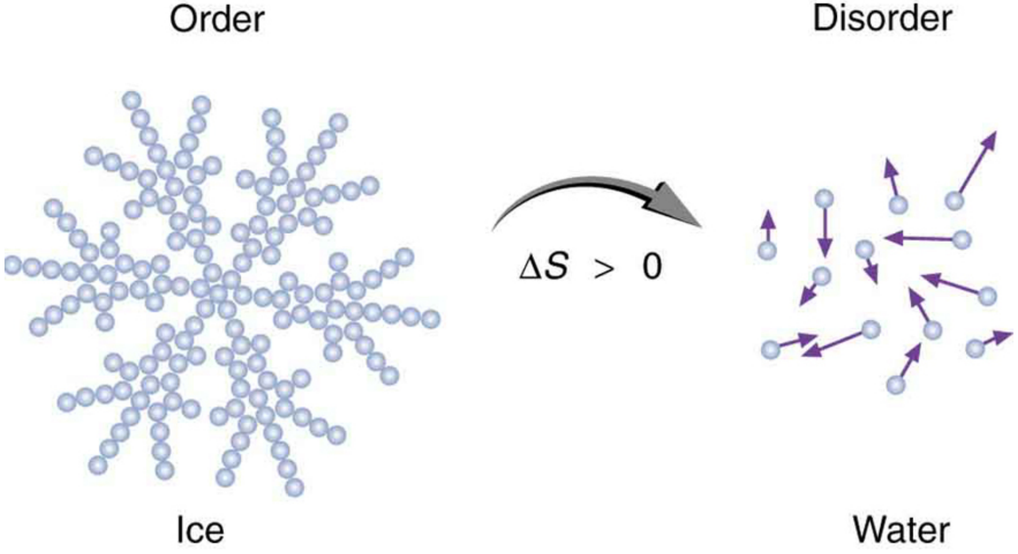
Para um processo reversível:

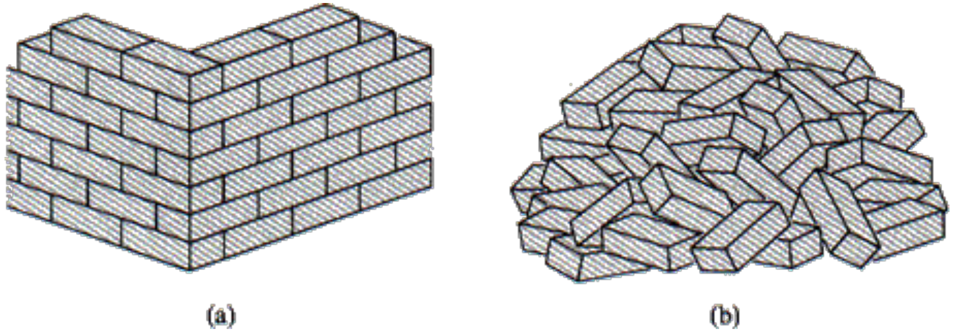
$$\Delta S = \frac{Q}{T} \qquad \text{J/K}$$

Alta temperatura -> Alta aleatoriedade das moléculas
Adicionar calor em uma substância que esta fria, adicionamos bastante aumento fracional… (pensar no oposto)

20.18 Water molecules are arranged in a regular, ordered way in an ice crystal. When the ice melts, the hydrogen bonds between molecules are broken, increasing the water's disorder and its entropy.







Entropia

Para um processo reversível qualquer, genérico:

$$\Delta S = \int_1^2 \frac{dQ}{T}$$

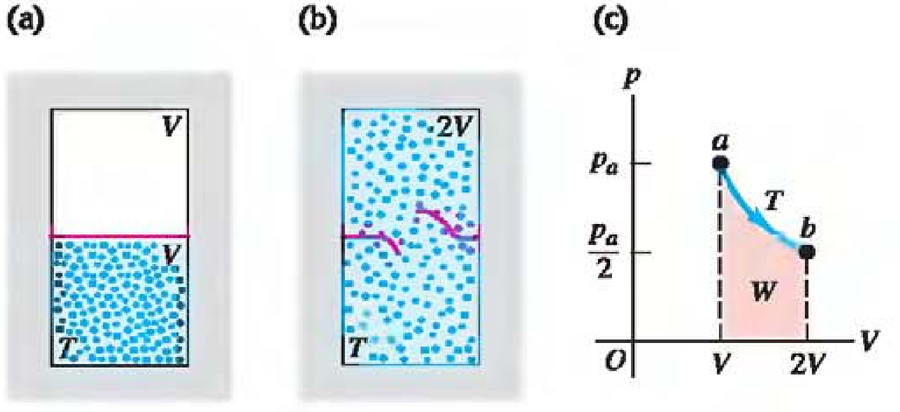
Entropia é uma medida do estado.
A Equação acima é valida apenas para processos reversíveis.
Como fazer para um processo irreversível?

Example 20.8 Entropy change in a free expansion

A thermally insulated box is divided by a partition into two compartments, each having volume V (Fig. 20.19). Initially, one compartment contains n moles of an ideal gas at temperature T, and the other compartment is evacuated. We then break the partition, and the gas expands to fill both compartments. What is the entropy change in this free-expansion process?

SOLUTION

IDENTIFY: For this process, $Q = 0$, $W = 0$, $\Delta U = 0$, and therefore (because the system is an ideal gas) $\Delta T = 0$. We might think that the entropy change is zero because there is no heat exchange. But Eq. (20.19) can be used to calculate entropy changes for *reversible* processes only; this free expansion is *not* reversible, and there *is* an entropy change. The process is adiabatic because $Q = 0$, but it is not isentropic because $\Delta S \neq 0$. As we mentioned at the beginning of this section, entropy increases in a free expansion because the positions of the molecules are more random than before the expansion.



20.19 (a,b) Free expansion of an insulated ideal gas. (c) The free-expansion process doesn't pass through equilibrium states from a to b. However, the entropy change $S_b - S_a$ can be calculated by using the isothermal path shown or *any* reversible path from a to b.

SET UP: To calculate ΔS, we recall that the entropy change depends only on the initial and final states. We can devise a *reversible* process having the same endpoints, use Eq. (20.19) to calculate its entropy change, and thus determine the entropy change in the original process. An appropriate reversible process in this case is an isothermal expansion from V to $2V$ at temperature T. The gas does work W during this substitute expansion, so an equal amount of heat Q must be supplied to keep the internal energy constant. We find the entropy change for this reversible isothermal process using Eq. (20.18); the entropy change for the free expansion will be the same.

EXECUTE: We found in Example 19.1 (Section 19.2) that the work done by n moles of ideal gas in an isothermal expansion from V_1 to V_2 is $W = nRT\ln(V_2/V_1)$. Using $V_1 = V$ and $V_2 = 2V$, we have

$$Q = W = nRT\ln\frac{2V}{V} = nRT\ln 2$$

Thus the entropy change is

$$\Delta S = \frac{Q}{T} = nR\ln 2$$

which is also the entropy change for the free expansion with the same initial and final states. For 1 mole,

$$\Delta S = (1\text{ mol})(8.314\text{ J/mol}\cdot\text{K})(\ln 2) = 5.76\text{ J/K}$$

EVALUATE: The entropy change is positive, as we predicted. The factor $(\ln 2)$ in our answer is a result of the volume having increased by a factor of 2. Can you show that if the volume had increased in the free expansion from V to xV, where x is an arbitrary number, the entropy change would have been $\Delta S = nR\ln x$?

Example 20.9 Entropy and the Carnot cycle

For the Carnot engine in Example 20.2 (Section 20.6), find the total entropy change in the engine during one cycle.

SOLUTION

IDENTIFY: All four steps in the Carnot cycle are reversible (see Fig. 20.13), so we can use the expression for the change in entropy in a reversible process.

SET UP: We find the entropy change ΔS for each step and then add the entropy changes to get the total ΔS for the cycle as a whole.

EXECUTE: There is no entropy change during the adiabatic expansion or adiabatic compression. During the isothermal expansion at $T_{\mathrm{H}} = 500\ \mathrm{K}$ the engine takes in 2000 J of heat, and its entropy change, from Eq. (20.18), is

$$\Delta S_{\mathrm{H}} = \frac{Q_{\mathrm{H}}}{T_{\mathrm{H}}} = \frac{2000\ \mathrm{J}}{500\ \mathrm{K}} = 4.0\ \mathrm{J/K}$$

During the isothermal compression at $T_{\mathrm{C}} = 350\ \mathrm{K}$ the engine gives off 1400 J of heat, and its entropy change is

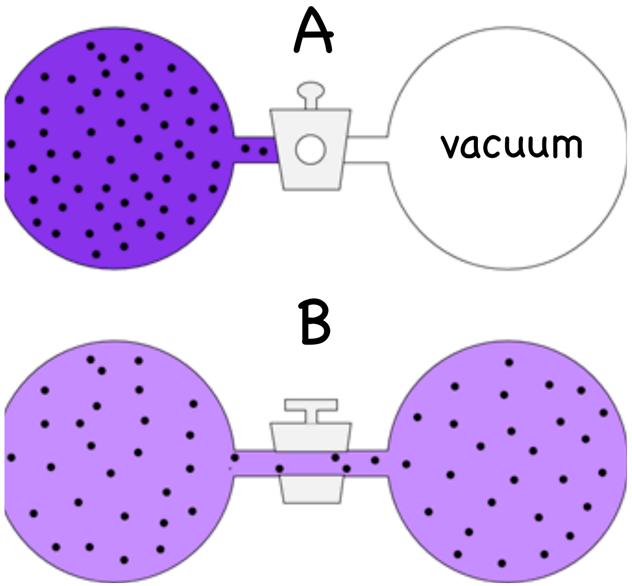
$$\Delta S_{\mathrm{C}} = \frac{Q_{\mathrm{C}}}{T_{\mathrm{C}}} = \frac{-1400\ \mathrm{J}}{350\ \mathrm{K}} = -4.0\ \mathrm{J/K}$$

The total entropy change in the engine during one cycle is $\Delta S_{\mathrm{total}} = \Delta S_{\mathrm{H}} + \Delta S_{\mathrm{C}} = 4.0\ \mathrm{J/K} + (-4.0\ \mathrm{J/K}) = 0$.

EVALUATE: The result $\Delta S_{\mathrm{total}} = 0$ tells us that when the Carnot engine completes a cycle, it has the same entropy as it did at the beginning of the cycle. We'll explore this result in the following subsection.

What is the total entropy change of the engine's *environment* during this cycle? The hot (500 K) reservoir gives off 2000 J of heat during the reversible isothermal expansion, so its entropy change is $(-2000\ \mathrm{J})/(500\ \mathrm{K}) = -4.0\ \mathrm{J/K}$; the cold (350 K) reservoir absorbs 1400 J of heat during the reversible isothermal compression, so its entropy change is $(+1400\ \mathrm{J})/(350\ \mathrm{K}) = +4.0\ \mathrm{J/K}$. Thus each individual reservoir has an entropy change; however, the sum of these changes—that is, the total entropy change of the system's environment—is zero.

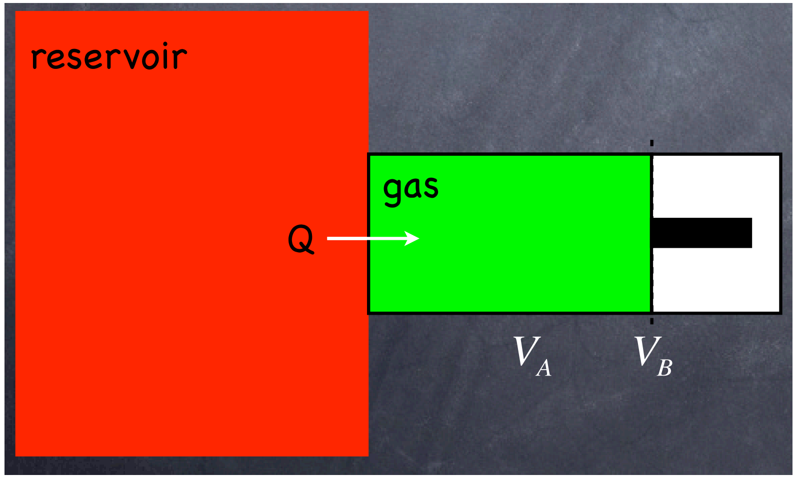
These results apply to the special case of the Carnot cycle, for which *all* of the processes are reversible. In this case we find that the total entropy change of the system and the environment together is zero. We will see that if the cycle includes irreversible processes (as is the case for the Otto cycle or Diesel cycle of Section 20.3), the total entropy change of the system and the environment *cannot* be zero, but rather must be positive.



Expansão livre

$$\Delta S_{\text{sistema}} = \Delta S_{\text{gas}} = nR\ln\frac{V_B}{V_A} > 0$$

“Trabalho perdido”



Expansão Isotermica quasi-estatica

$$\begin{aligned}\Delta S_{\text{sistema}} &= \Delta S_{\text{gas}} + \Delta S_{\text{reservatorio}}\\ &= \frac{+Q}{T} + \frac{-Q}{T} = 0\end{aligned}$$