

The Second Law of Thermodynamics & The Entropy S

Meeting 8 *Section 4-2*

Related Links:

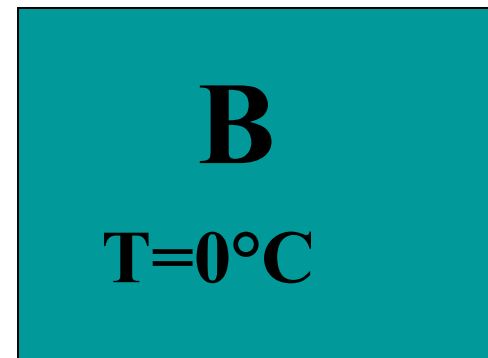
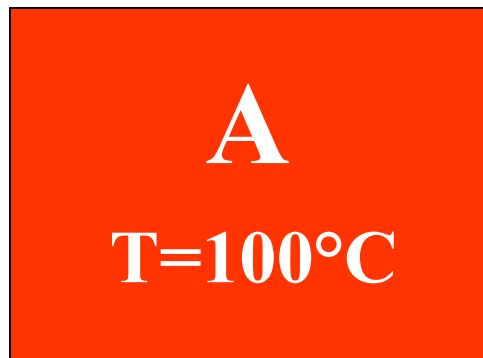
- 1) [Entropy Definitions](#) at Wikipedia
- 2) [Information Entropy](#) at Wikipedia
- 3) [Entropy](#) from MathWorld
- 4) [Entropy](#) from Georgia State Un. Phys Dept

Remember the First Law of Thermodynamics?

- **$Q - W = \Delta E$ (closed system)**
- **The equals sign is important- we can convert one form of energy to another.**
- **This law places no restriction on an energy conversion other than equality.**

TEAMPLAY

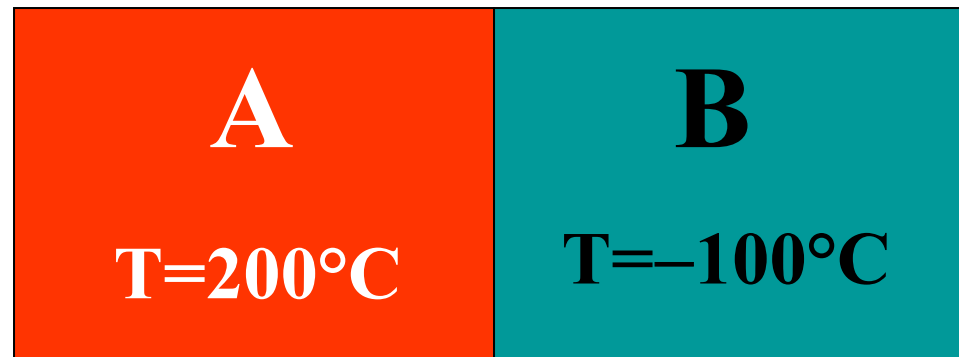
Consider the system below. We have substances A and B which are initially at 100°C and 0°C , respectively. Both have the same mass and specific heat.



STATE 1

TEAMPLAY

- **A&B are brought into contact and allowed to exchange energy with each other, but not to the surroundings.**
- **You come back in several days and find that the final temperature of B is $-100\text{ }^{\circ}\text{C}$. What is the final temperature of A?**
- **Is this what you would expect?**



STATE 2

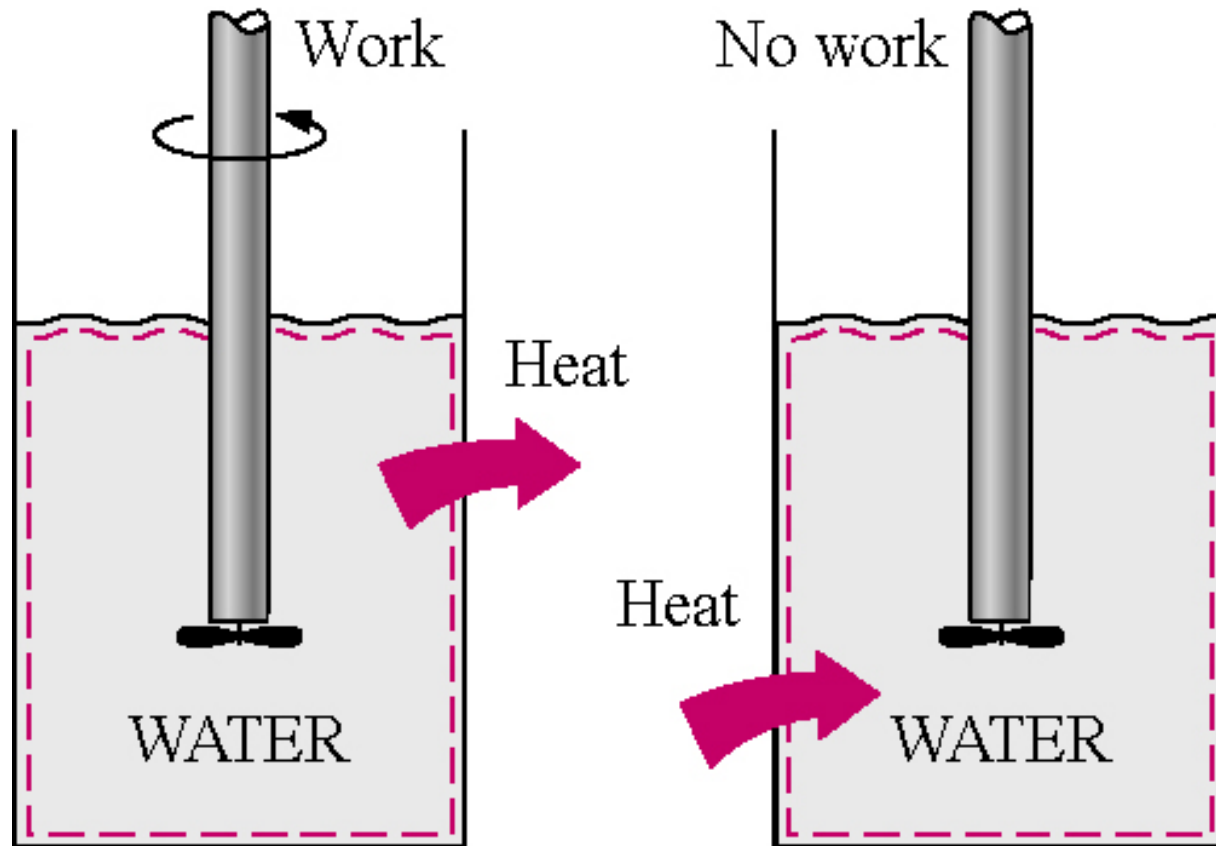
Second Law of Thermodynamics

- **The second law of thermodynamics states that processes occur in a certain direction, not in any direction. A process will not occur unless it satisfies both the first and the second laws of thermodynamics.**

2nd Law of Thermodynamics will help us:

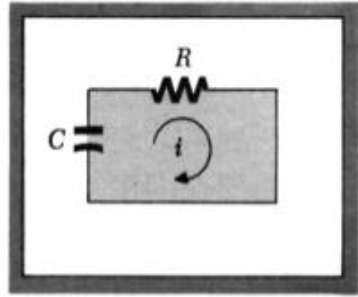
- determine the **direction of change (time arrow)** for a **spontaneous** process,
- establish the final equilibrium state,
- define **ideal performance** for energy conversion devices,
- determine the **quality** of energy,
- determine if a process is **irreversible**, and
- define an absolute temperature scale.

Work Always Converts Directly and Completely to Heat, But not the Reverse

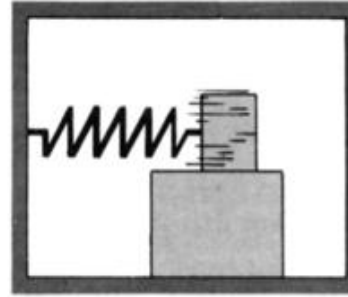


Reversible Process

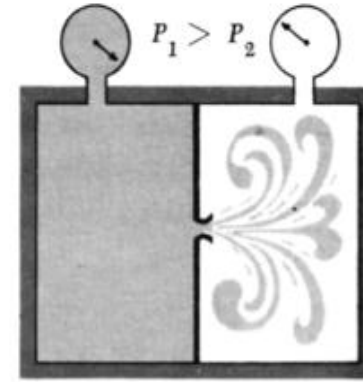
- **Reversible Process** - the system and the surroundings can be exactly restored to their initial states after the end of the process.



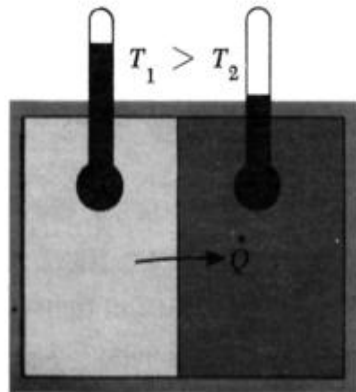
(a) Current flow through a resistance



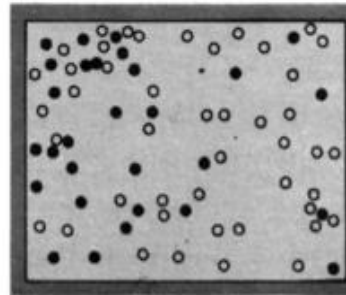
(b) Motion with friction



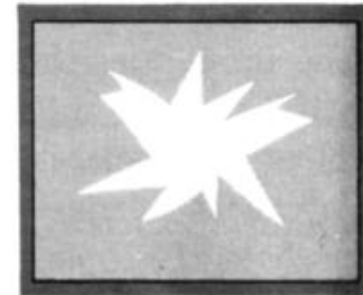
(c) Unrestrained expansion



(d) Energy transfer as heat



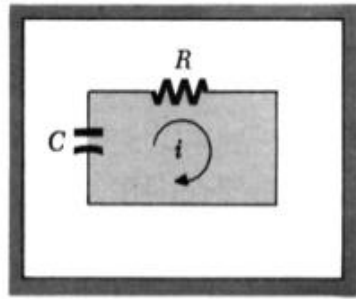
(e) Diffusion



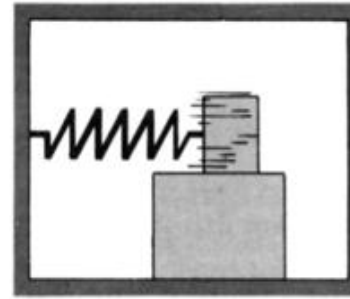
(f) Spontaneous chemical reaction

Irreversible Process: One Way Process

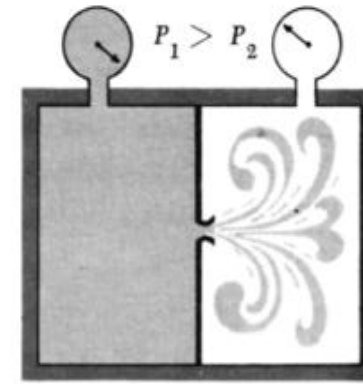
- the system and the surroundings cannot be exactly restored to the initial states after the end of the process.



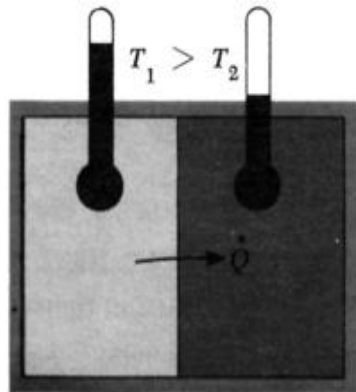
(a) *Current flow through a resistance*



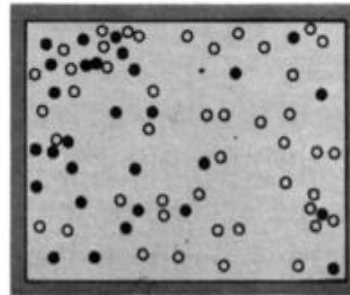
(b) *Motion with friction*



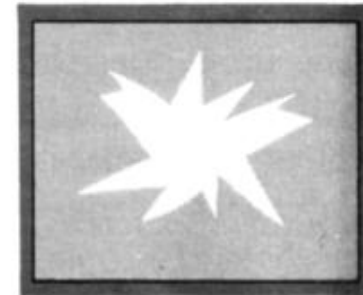
(c) *Unrestrained expansion*



(d) *Energy transfer as heat*



(e) *Diffusion*



(f) *Spontaneous chemical reaction*

Simple Statements Regarding irreversibility

- At the end of a real process, it is impossible to return both the system and surroundings to their original conditions (states).
- The system and the surroundings cannot be exactly restored to the initial states after the process. Many times the system can be restored to its initial state, but the environment cannot.
- In an irreversible process some sign, some signature, will be left in to the system or the surroundings that something has occurred.

Definitions

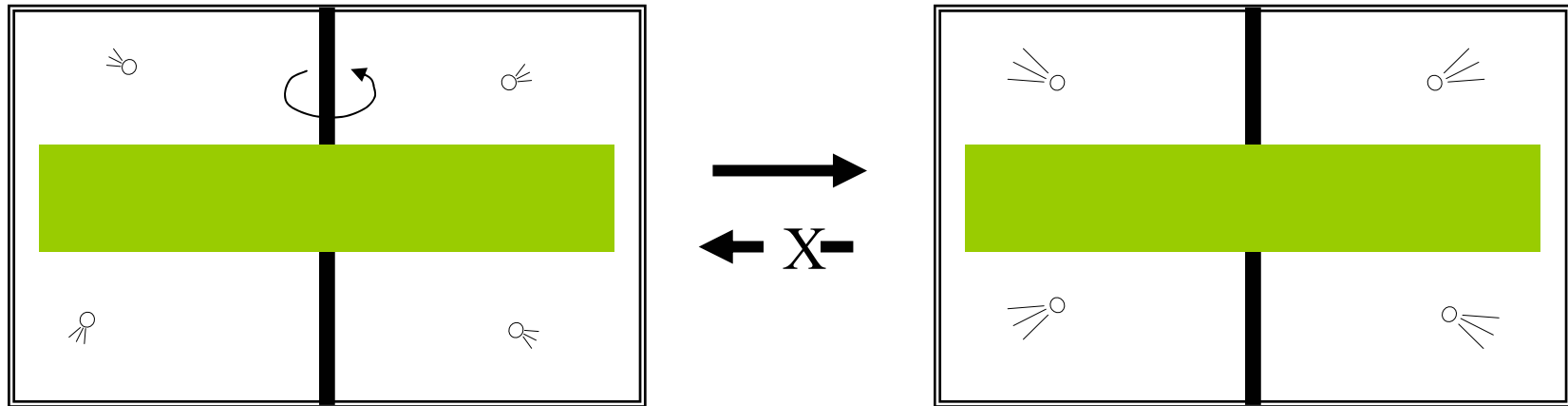
- **Internal irreversibilities**--
exist within the system only,
and are not in the
environment.
- **External irreversibilities**--
exist in the environment and
are not within the system.

The Second Law:

A View From the Microscopic

State of the Matter

Calor e Energia Mecânica (Análise Macroscópica e Microscópica)



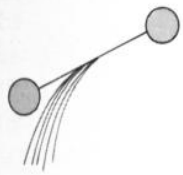
Estado inicial = volante com rotação, gás com rotação e a temperatura ambiente

Estado final = volante e gás estacionários a uma temperatura maior. Toda energia cinética do volante foi transformada em energia interna do gás.

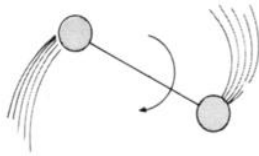
Diferenças entre Calor e Energia Mecânica

1. A primeira lei não impõe restrições ao sentido inverso do processo.
2. No estado inicial a maioria da energia é organizada: todas as moléculas do volante giram conjuntamente ao redor do eixo e transferem movimento ao gás. É muito 'fácil' extrair trabalho neste estado de 'organização' da energia.
3. No estado final a energia está 'desorganizada' microscopicamente pq. U aumentou. A capacidade de realizar trabalho diminui e o caos a nível molecular aumentou.

Modos de Energia a nível microscópico



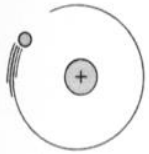
Molecular translation



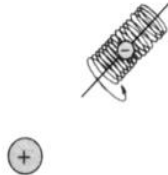
Molecular rotation



Molecular vibration



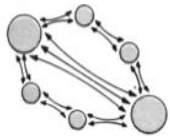
Electron translation



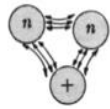
Electron spin



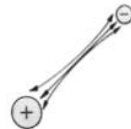
Nuclear spin



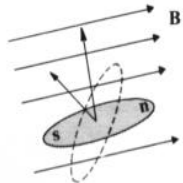
Molecular binding



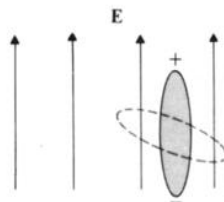
Nuclear binding



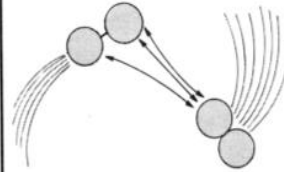
Coulomb binding



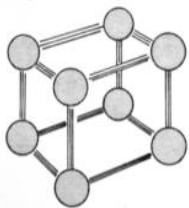
Magnetic-dipole moment



Electric-dipole moment



Intermolecular (weak)



Intermolecular (strong)

$$E = m_0 c^2$$



Mass equivalent



External field

Os átomos e moléculas possuem energia em virtude de sua: **translação da molécula e dos átomos**; **rotação da molécula e elétrons**; **vibração molecular**; e outras formas de interações

O conjunto de moléculas apresenta uma energia média devido a contribuição de cada parcela de energia de cada átomo e elétron. Em termos médios ela é representada pela energia interna da matéria:

$$du = CvdT \text{ (gás perfeito)}$$

Calor, Temperatura e o Nível de Organização

1. **Calor** é um modo de transferência de energia que ocorre quando há diferença de temperatura.
2. A transferência de calor vêm acompanhada com uma **mudança no nível de organização** das moléculas.
3. Quando se aumenta o nível de desorganização microscópica do sistema (molecular) diminui-se a disponibilidade de realizar trabalho.
4. **Entropia** é a variável termodinâmica (macroscópica) que mede o grau de desorganização do sistema a nível microscópico.
5. **Entropia** é uma propriedade de estado da matéria. Diferente de calor e trabalho ela não depende do caminho.
6. **Entropia** é uma propriedade extensiva: a entropia de um sistema complexo é a soma das entropias de suas partes.

Como se Mede o Grau de Desordem Microscópica de um Sistema?

Considere um sistema isolado formado por seis partículas, A, B, C, D, E e F cuja energia total é 4 e definida por quatro níveis quânticos: 0, 1, 2 e 4. Determine os possíveis estados deste sistema:

	(I)	(II)	(III)	(IV)
4	A			
2			AB	A
1		ABCD		BC
0	BCDEF	EF	CDEF	DEF
N. Estados:	(6)	(15)	(15)	(60)
Probabilidade:	0.06	0.15	0.15	0.64

O estado mais provável de ser encontrado é o estado (IV), porém como associar um parâmetro global (entropia) que avalie os graus de incerteza ou desorganização de um sistema?

Como se Mede o Grau de Desordem Microscópia de um Sistema?

- Todo o conjunto de probabilidade (p_i) reflete o grau de incerteza (aleatoriedade) do sistema.
- A entropia é uma função de (p_i) que serve para estimar o grau de incerteza.
- A entropia é extensiva, $S_C = S_A + S_B$

$$S_A = k \sum_{i=1}^N p_i \ln(p_i) \quad S_B = k \sum_{j=1}^M p_j \ln(p_j) \quad k \text{ const. Boltzmann}$$

- A probabilidade de cada estado C é determinada a partir das prob. Individuais de A e B: $p_{ij} = p_i \cdot p_j$

$$S_C = \sum_{j=1}^M \sum_{i=1}^N p_i p_j \ln(p_i p_j) \equiv \sum_{j=1}^M \sum_{i=1}^N p_i p_j \ln(p_i) + \sum_{j=1}^M \sum_{i=1}^N p_i p_j \ln(p_j)$$

$$\sum_{i=1}^N p_i \ln(p_i) \underbrace{\sum_{j=1}^M p_j}_{=1} + \sum_{j=1}^M p_j \ln(p_j) \underbrace{\sum_{i=1}^N p_i}_{=1}$$

$$S_A + S_B$$

2nd Law is not always easy to grasp:

- It's a **non-conservation law**
- It will be given as a **non-equality**
- It will typically be negatively stated
- tell us what we **can't do**
- No one statement covers all facets of the second law

2nd Law of Thermodynamics

- **It has implications for economics, theology and philosophy, and other fields. These make fun and interesting discussions...however, we'll focus on engineering applications of 2nd law.**
- **It is a matter of experience, of observations of what happens in nature....**experimental evidence.****

A sample of statements regarding direction of processes

- **All spontaneous processes result in a **more probable state.****
- **Heat energy cannot of itself pass from a colder to hotter body.**
- **Once you open a can of worms, the only way to recan them is with a larger can.**

Definições para Entropia

1. Todo sistema possui entropia. Ela mede o grau (a nível microscópico) da desorganização do sistema, nossa incerteza sobre o estado microscópico.
2. Uma transformação **espontânea** leva a um aumento de entropia, **S**, pois do ponto de vista microscópico o sistema procura o estado mais provável.
3. A entropia de um sistema que sempre apresenta um único estado microscópico é zero ($T = 0 \text{ K} \rightarrow S = 0$)

Definições para Entropia

1. Entropia é extensiva; entropia do sistema é a soma das entropias das partes
2. A entropia de um sistema isolado ($Q = W = 0$) nunca diminui, $dS \geq 0$.
3. Processo Cíclico Reversível não gera entropia $P_s = 0$. Processo Irreversível, $P_s \geq 0$

Definição Termodinâmica Entropia

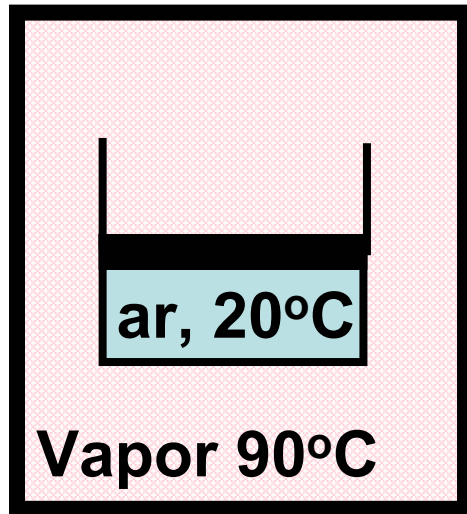
- A partir de grandezas macroscópicas a entropia é definida por:

$$dS = \frac{\delta Q_{\text{REV}}}{T} \rightarrow \delta Q_{\text{REV}} = TdS$$

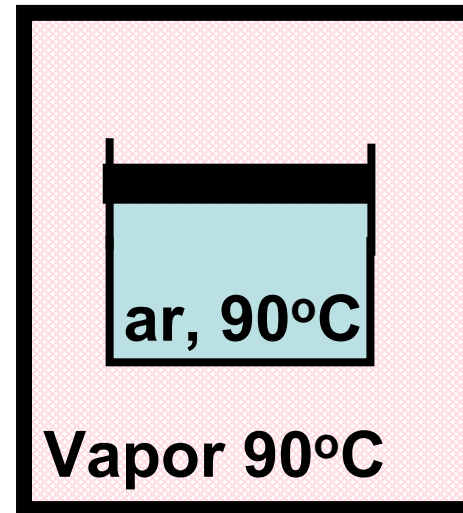
- A temperatura passa a ser um fator integrante para o calor.
- A razão $\delta Q/T$ define a propriedade entropia que não depende do caminho!

Caso Estudo

- Sistema isolado ($Q = W = 0$) contém um cilindro/pistão com ar a 20°C e vapor saturado H_2O a 90°C no estado inicial. No estado final o pistão se expande, o vapor encontra-se a 90°C e $x = 0.5$ enquanto que o ar está a 90°C



INICIAL



FINAL

- Considere o sistema ar mais vapor e avalie a variação da entropia do sistema.

Caso Estudo – página 2

- Para um sistema isolado, ($Q = W = 0$) a entropia nunca diminui, $dS \geq 0$
- A variação de entropia é igual a variação de S do vapor e do ar

$$\int_1^2 dS = \int_1^2 dS_{\text{VAPOR}} + dS_{\text{AR}} \geq 0$$
$$\int_1^2 dS_{\text{AR}} - \int_1^2 \frac{\delta Q}{T_{\text{VAPOR}}} \geq 0 \quad \text{ou} \quad dS \geq \frac{\delta Q}{T}$$

- A entropia nunca diminui num processo adiabático ($Q = 0$).

Caso Estudo – página 3

- A variação de entropia em um processo é sempre maior ou igual (processo reversível) a razão calor/temperatura.

$$\int_1^2 dS \geq \int_1^2 \frac{\delta Q}{T} \quad \rightarrow \quad \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + P_S$$

- A desigualdade é transformada inserindo-se um termo de Produção de Entropia, P_S .
- P_S é sempre uma grandeza positiva, $P_S \geq 0$

Caso Estudo – página 4

$$\int_1^2 dS \geq \int_1^2 \frac{\delta Q}{T} \quad \rightarrow \quad \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + P_S$$

- As conseqüências da desigualdade são:
 1. A entropia de um sistema pode diminuir somente por remoção de calor;
 2. A entropia de um sistema pode crescer por adição de calor ou pela presença de uma irreversibilidade;
 3. A entropia de um sistema não pode diminuir num processo adiabático;

Processos Cíclicos

$$\oint dS = \oint \frac{\delta Q}{T} + P_S$$

1. Num ciclo, a variação de S é nula!

$$\oint dS = 0$$

2. A produção de S é sempre positiva,

$$P_S \geq 0$$

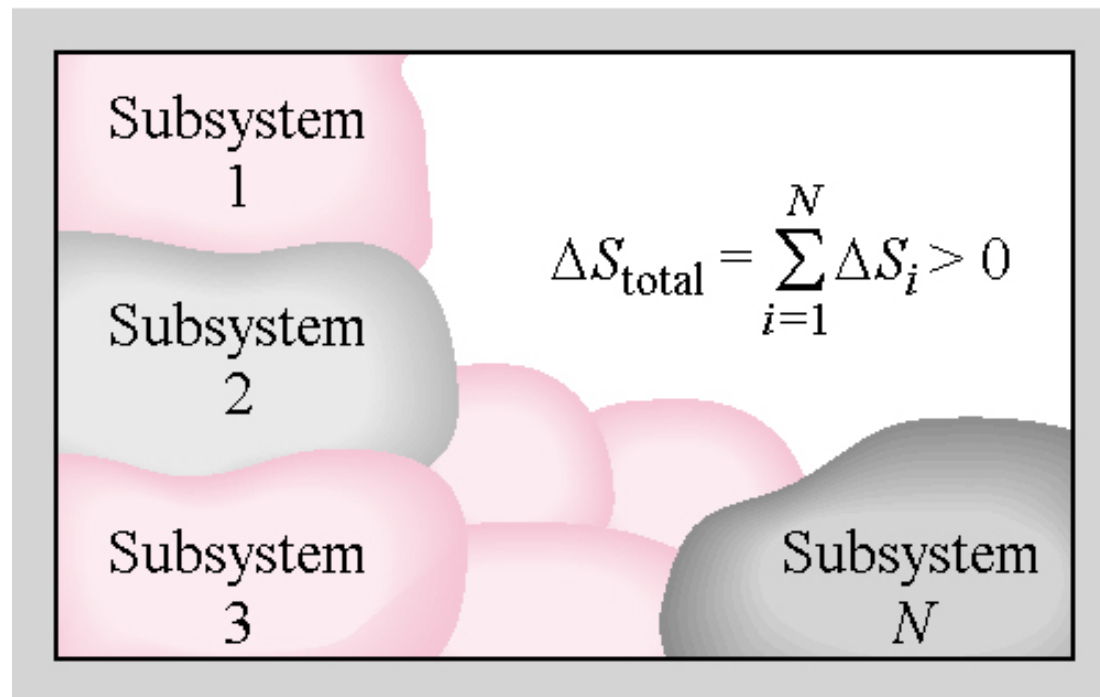
3. Logo se segue a desigualdade de Clausius:

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

The Entropy Change of an Isolated System

The entropy change of an isolated system is the sum of the entropy changes of its components, and is never less than zero

(Isolated)



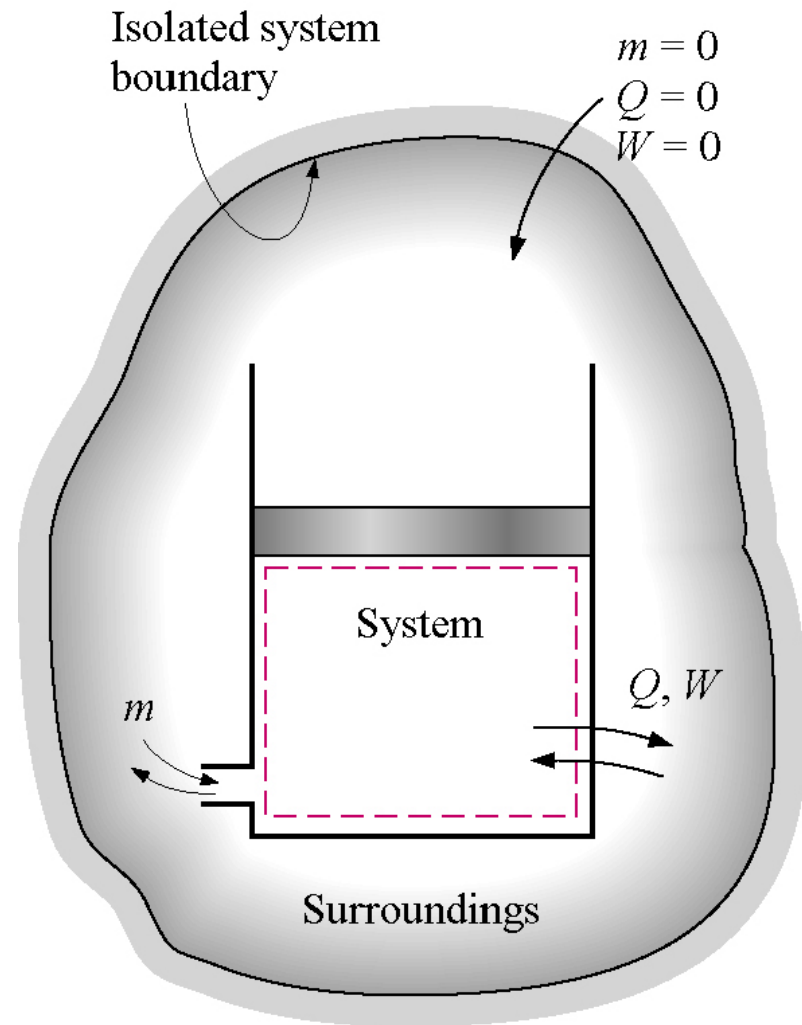
Principle of increase of entropy (second law)

- **Isolated system:**
- For an isolated system composed of several subsystems exchanging energy among themselves

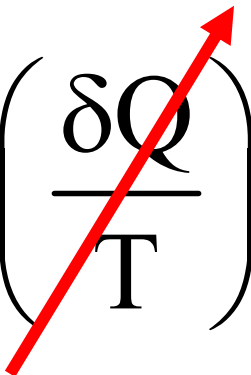
$$\Delta S_{\text{isolated}} \geq \int_1^2 \frac{\delta Q}{T} = 0$$

($\because Q = 0$)

- The total entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.



For An Isolated System

$$\Delta S_{\text{isolated}} = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{isolated}} + P S_{\text{gen}}$$


- Isolated system: $\dot{m} = Q = W = 0$
- If we include the surroundings as part of the system, it is the universe and is adiabatic (isolated)
- Irreversibilities will always increase the entropy of the universe

Heat or Thermal Energy Reservoir

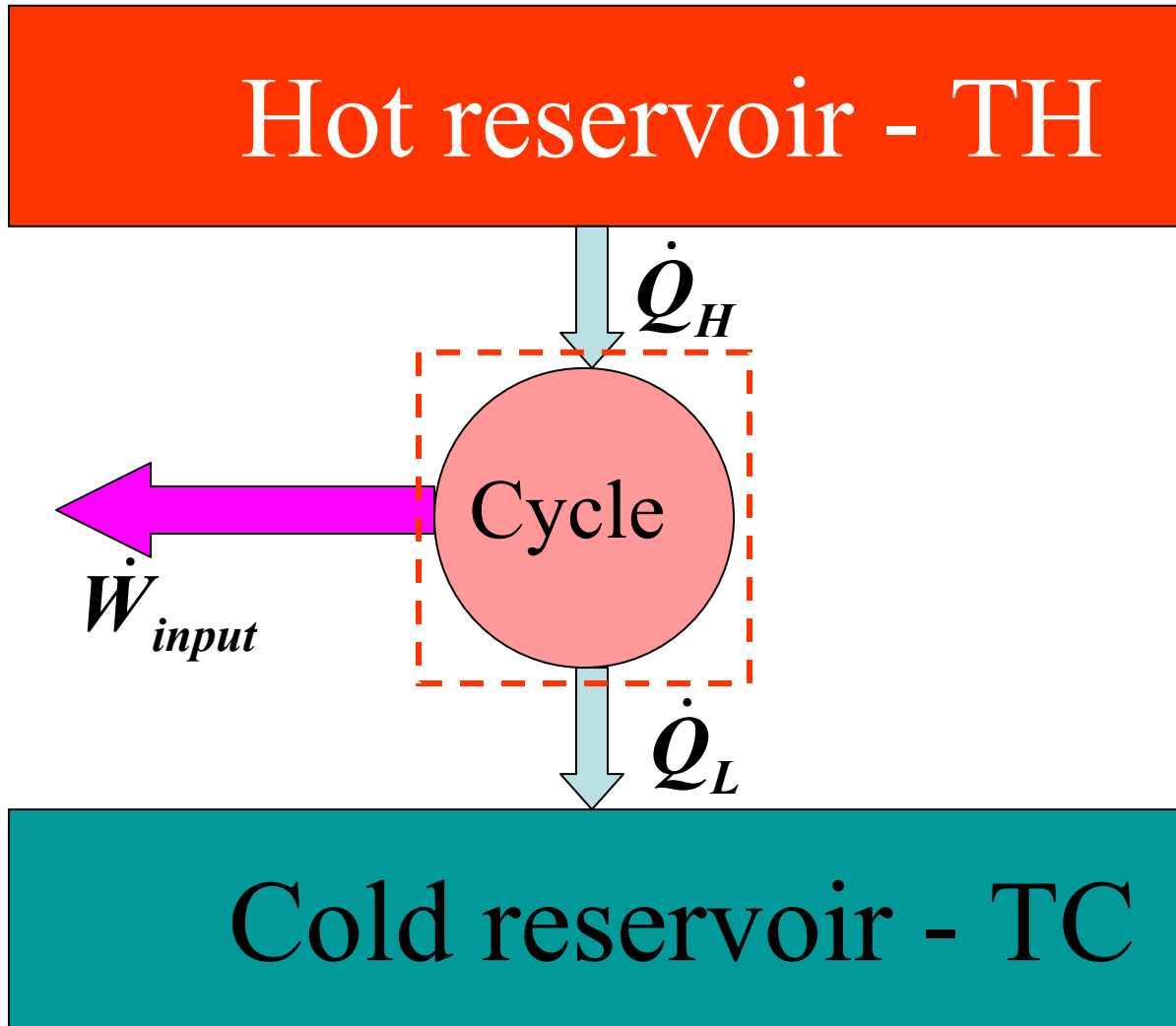
A heat or thermal energy reservoir is a closed system (with large thermal energy capacity mC_v) from which heat is removed or heat is added without a temperature change. Its sole distinguishing property is its temperature T .

$$\Delta T = \frac{Q}{mC_v} \cong 0$$

Thermal Energy Reservoir

- **Bodies that can absorb or reject finite amounts of heat isothermally are called thermal energy reservoirs or heat reservoirs.**
- **Oceans, lakes, rivers, etc.**
- **Atmospheric air**
- **Two-phase systems (constant T)**
- **Heat sources (Furnaces) -- supply heat**
- **Heat sinks (Condensers) -- absorb heat**

Carnot Efficiency



Consider a Carnot Cycle operating between a Hot and Cold temperature reservoirs

Carnot Efficiency

The cycle efficiency is expressed as the ratio of heats:

$$\eta_{\text{Carnot}} = 1 - \frac{Q_L}{Q_H}$$

Considering a **REVERSIBLE CYCLE**, the Clausius inequality becomes an equality

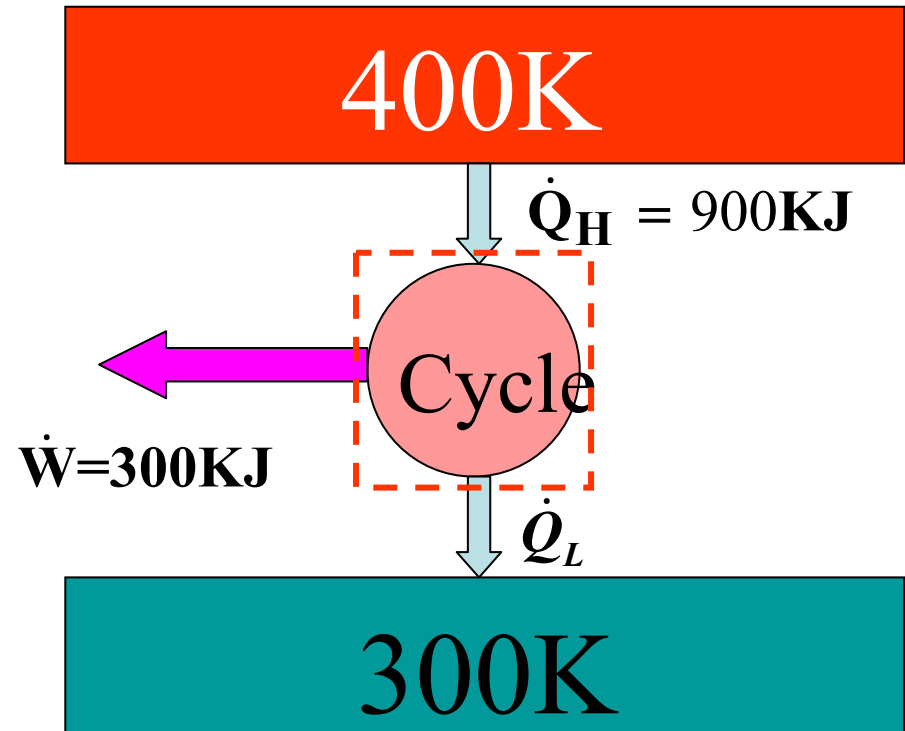
$$\oint \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

and the heat ratio is the same as the thermal reservoirs temperature:

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \rightarrow \frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

TEAMPLAY

Um inventor diz que ele desenvolveu uma máquina que recebe 900 kJ de calor de uma fonte a 400 K e produz 300 kJ de trabalho, enquanto rejeita calor a uma fonte a 300 K. É razoável o que afirma o inventor? Porque?



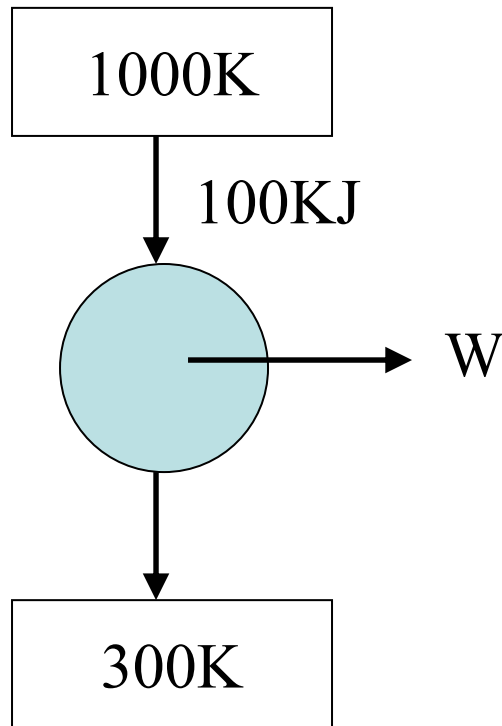
Carnot Efficiency

- The Carnot efficiency depends on the thermal reservoirs temperature

$$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{L}}}{T_{\text{H}}}$$

- This expression sets an **upper-bound** for thermal engines efficiency, otherwise the 2nd law is violated!
- It does not depend on the material, neither on the details of the engine but only on the thermal reservoirs temperature!

Ex4.13) 100 KJ de calor é adicionada a um ciclo de Carnot a 1000K. O ciclo rejeita calor a 300K. Quanto trabalho o ciclo produz e quanto calor ele rejeita?



Ciclo de Carnot

$$W=?$$

$$Q_c=?$$

$$\eta_c = \frac{W}{Q_h} = 1 - \frac{T_c}{T_h} = 1 - \frac{3}{10}$$

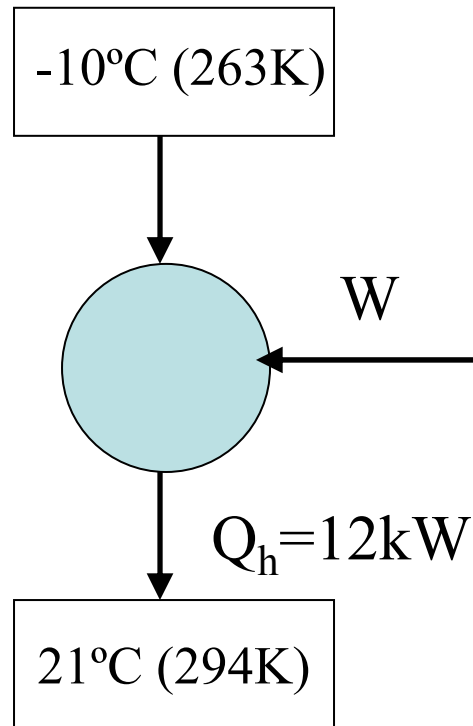
$$\eta_c = 0,7 \rightarrow W = 0,7 \times 100$$

$$W = 70\text{KJ}$$

$$\oint Q = \oint W \rightarrow (100 - Q_c) = 70$$

$$Q_c = 30\text{KJ}$$

- Ex4.18)** Uma casa precisa de 12KW de aquecimento quando o ar externo está a -10C e a temp interna está a +21C. (a) qual é a potência mínima requerida por uma bomba de calor aquecer a casa nestas condições;
 (b) Liste os fatores que exigiriam uma maior potência que o mínimo.



$$\eta_{bc} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

$$\eta_{bc} = \frac{1}{1 - \frac{T_L}{T_H}} = 9,484$$

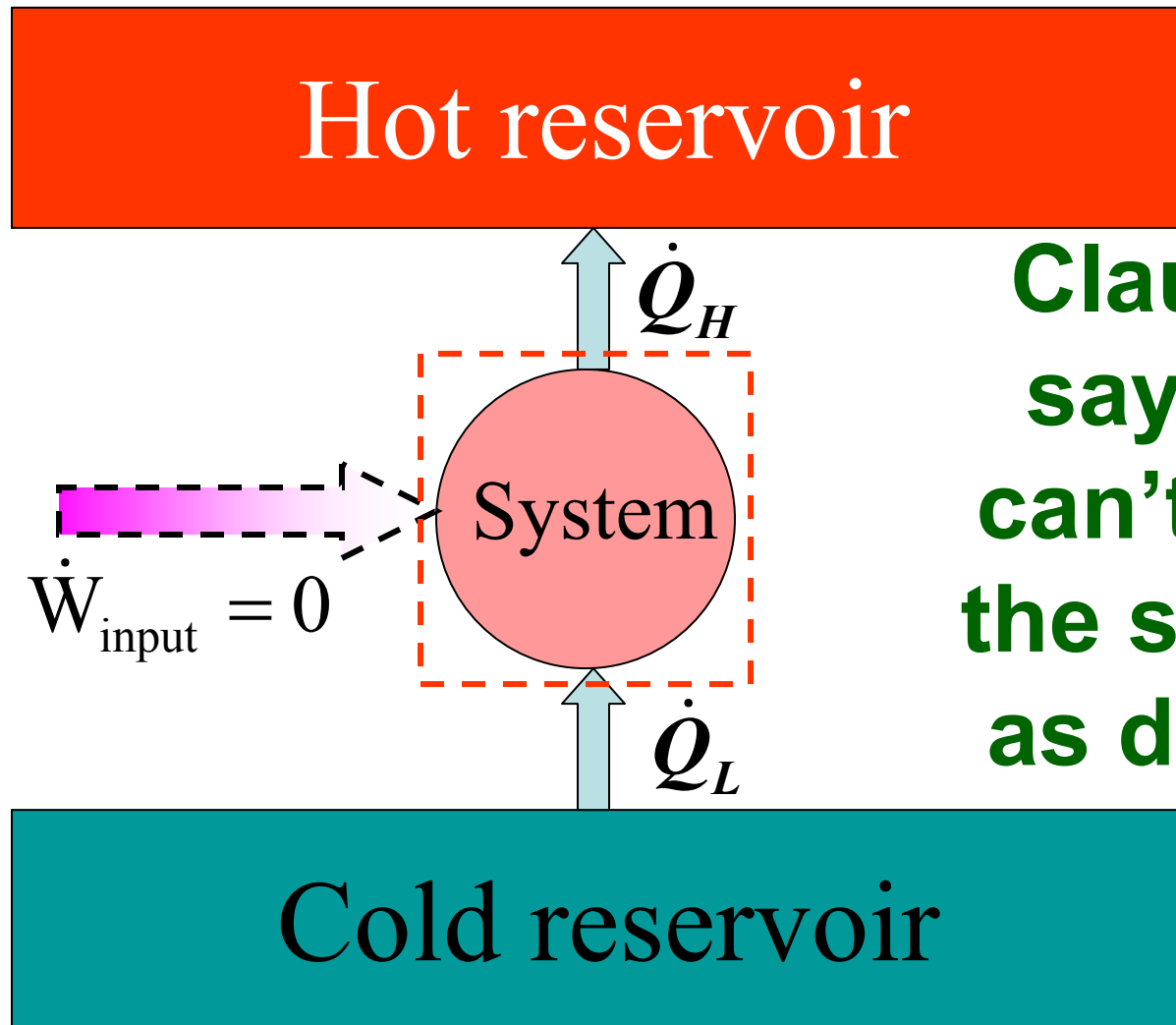
$$W = \frac{Q_H}{\eta_{bc}} = 1,265kW$$

O trabalho mínimo necessário é aquele do ciclo operando reversivelmente.
 Causas irreversibilidades: atrito mecânico do fluido, expansões no ciclo, diferenças de temperaturas, ...

Clausius Statement of 2nd Law of Thermodynamics:

It is impossible to operate a cyclic device in such a manner that the sole effect external to the device is the transfer of heat from one heat reservoir to another at a higher temperature.

We need to have some work input to make it happen.



**Clausius
says we
can't have
the system
as drawn:**

Clausius Proof

The path integral of the heat flux and temperature is:

$$\oint \frac{dQ}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L}$$

Since there is no work, then $Q_H = Q_L$ (1st Law), therefore the path integral becomes:

$$\oint \frac{dQ}{T} = Q \left(\frac{1}{T_L} - \frac{1}{T_H} \right) > 0$$

This clearly does not comply with the Clausius inequality:

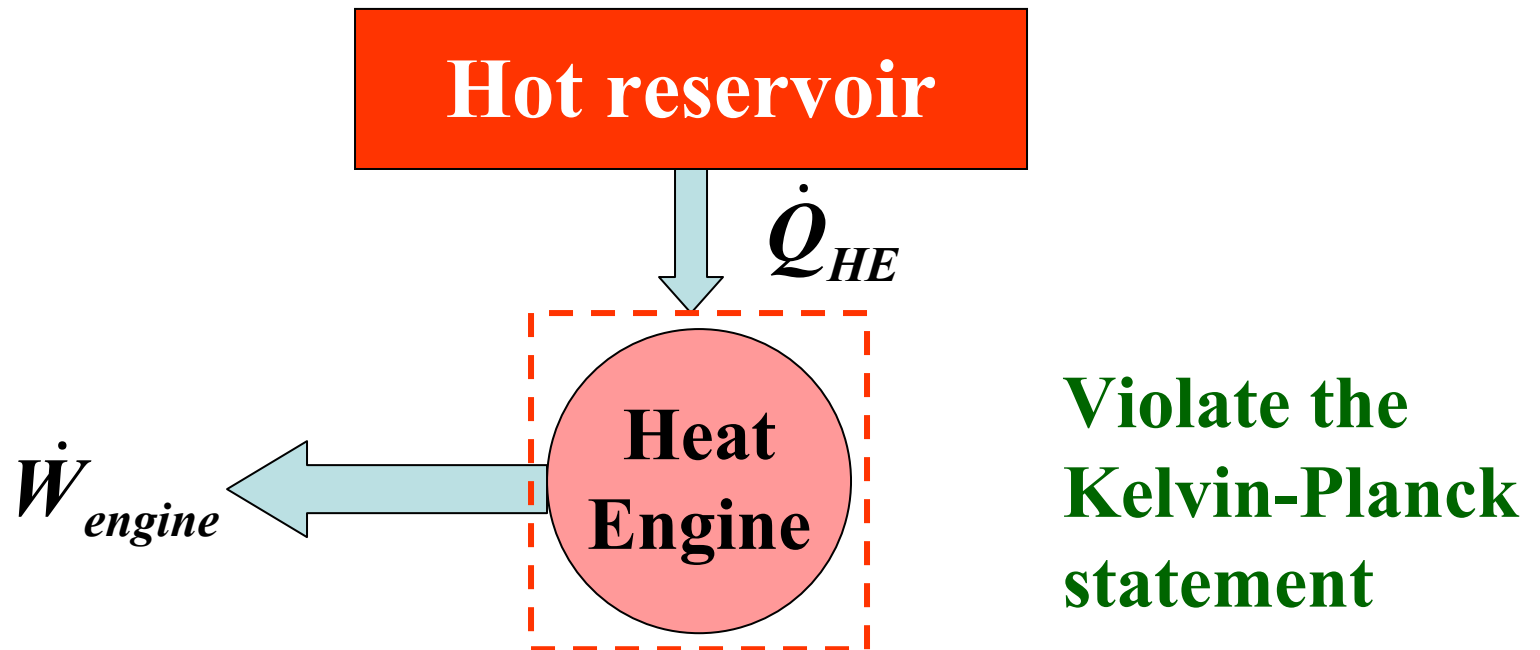
$$\oint \frac{\delta Q}{T} \leq 0$$

Kelvin-Planck Statement of 2nd Law of Thermodynamics:

*If we can't transfer heat from a cold thermal energy reservoir to a hot thermal energy reservoir in the absence of a work interaction, **let's try something else.***

Let's assume we have a heat engine that absorbs heat and converts it all to work energy

The system below operates in a cycle..Will it work?



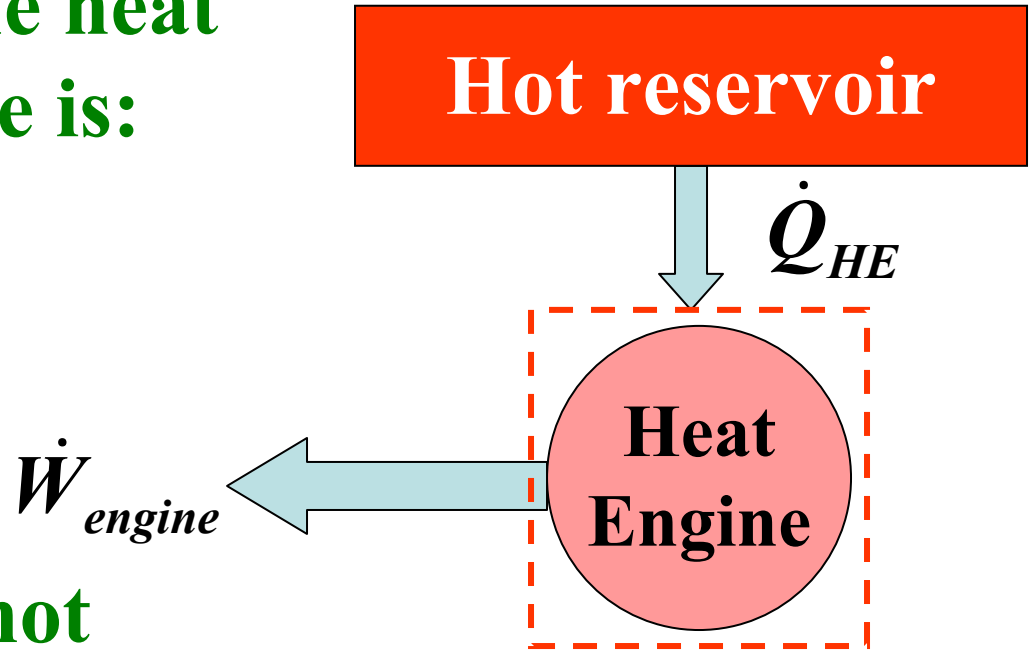
Kelvin Planck Proof

The path integral of the heat flux and temperature is:

$$\oint \frac{dQ}{T} = \frac{Q_H}{T_H} > 0$$

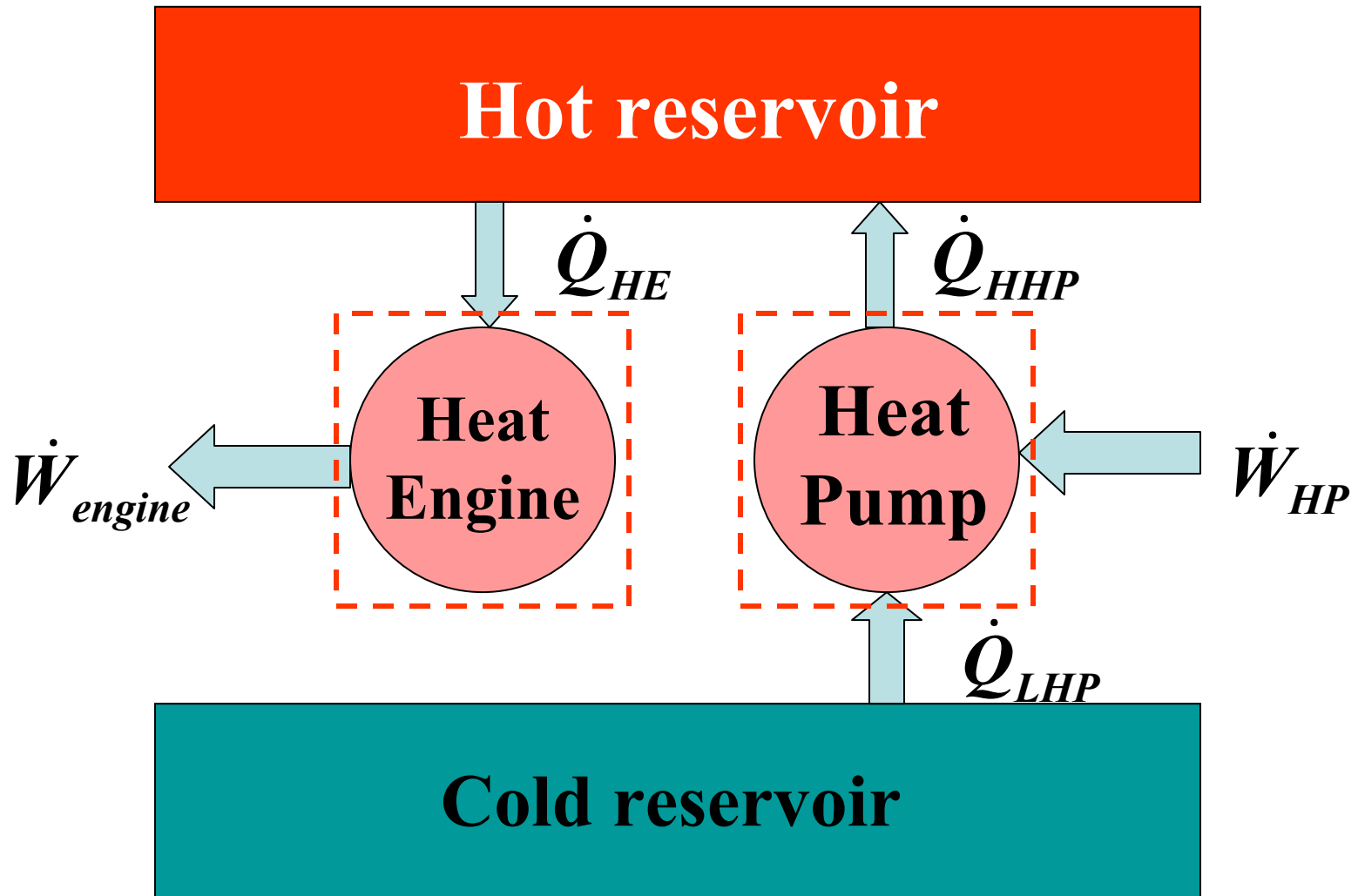
This clearly does not comply with the Clausius inequality:

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

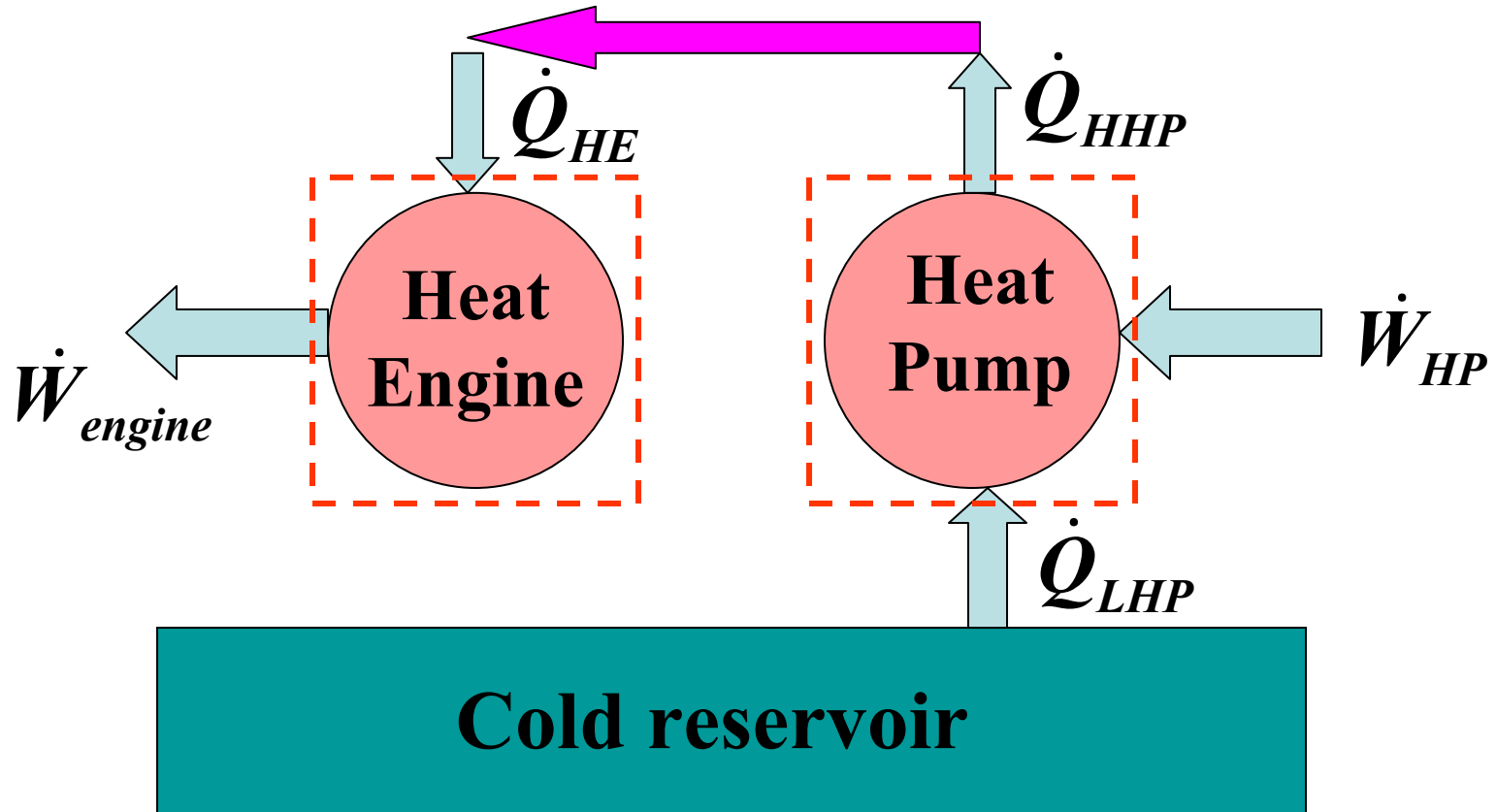


**Perpetual Mode 2nd Kind. Check it out!
Let's add a heat pump.**

$$\dot{Q}_{HHP} = \dot{Q}_{HE}$$



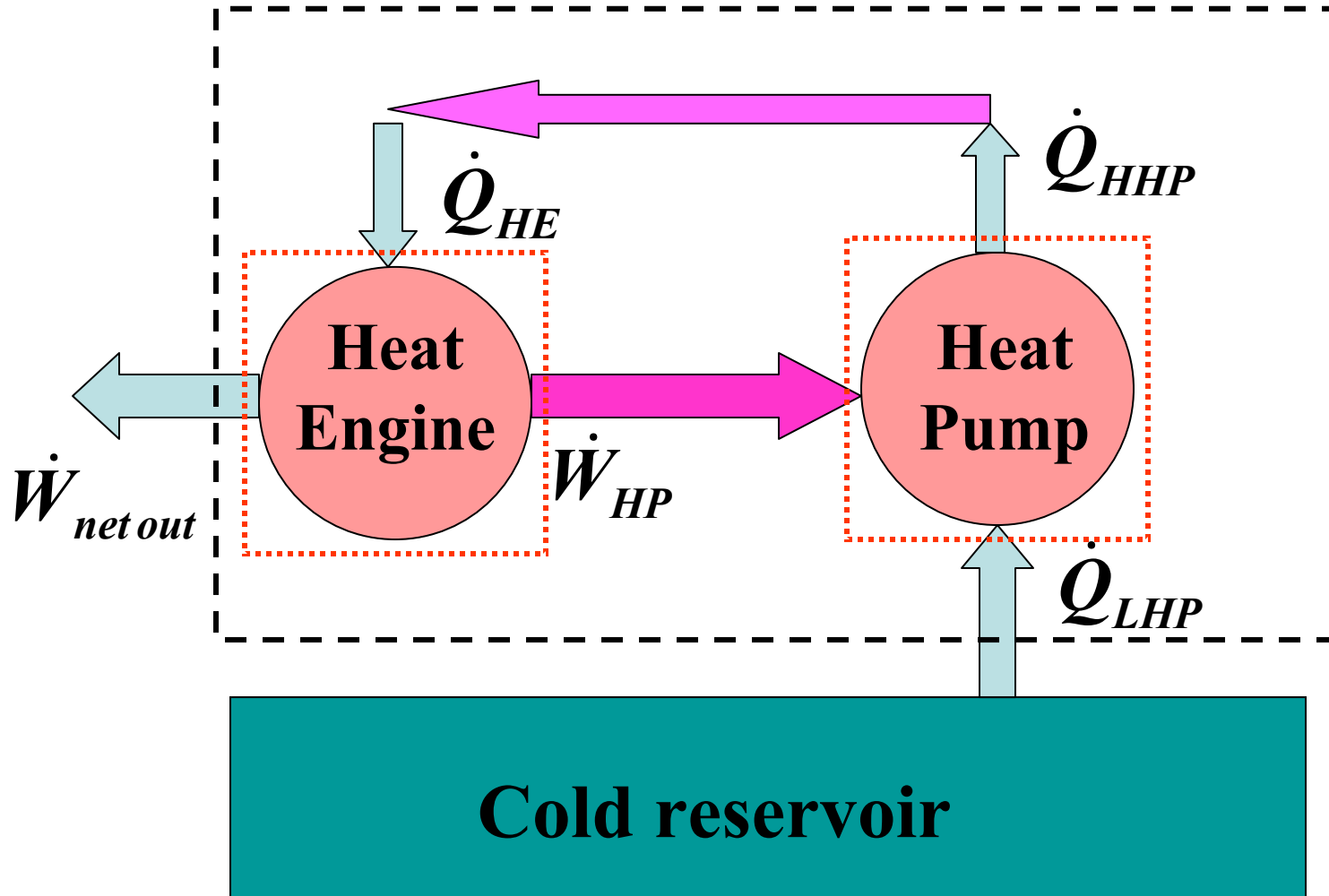
Since $\dot{Q}_{HHP} = \dot{Q}_{HE}$, we can eliminate heat source



We know $\dot{W}_{engine} = \dot{W}_{HP} + \dot{Q}_{LHP}$,

so we can use engine to drive heat pump

Final System



Main characteristics of the combined system

- Net work output
- Extract energy from a low temperature source (cold reservoir)
- Does not require any external work (electrical or otherwise)
- Can **perpetually extract energy** from ground, water, air or any low temperature source
- **You can run the Titanic (the ship) with energy from water!**

TEAMPLAY

O projeto da termoelétrica de Carioba II (Americana-SP 2000) prevê uma geração de 950 MW queimando gás natural e operando num ciclo Rankine (vapor) a uma pressão máxima de 6 MPa.

Determine a mínima quantidade de calor que ela rejeitará ao rio Piracicaba. Se ela tomar do rio 4 m³/s de água para fins de resfriamento calcule qual o aumento na temperatura desta água ao retornar ao rio.

TEAMPLAY page 1

O menor calor rejeitado ocorre se ela operar reversivelmente num ciclo de Carnot.

- Eficiência de Carnot:

$$\eta_C = 1 - 298/549 = \underline{0.46}$$

- Eficiência Térmica:

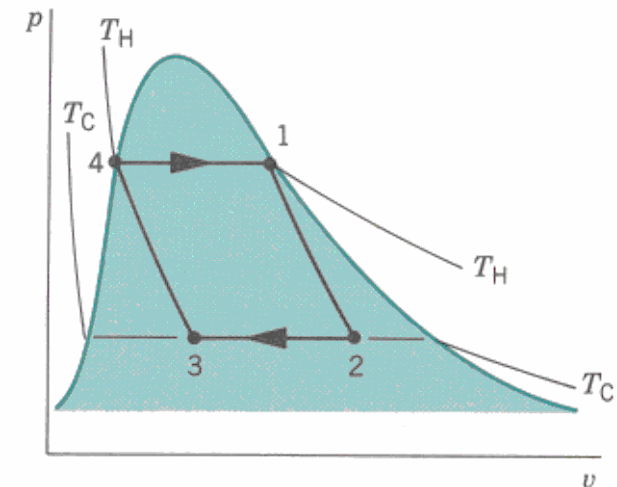
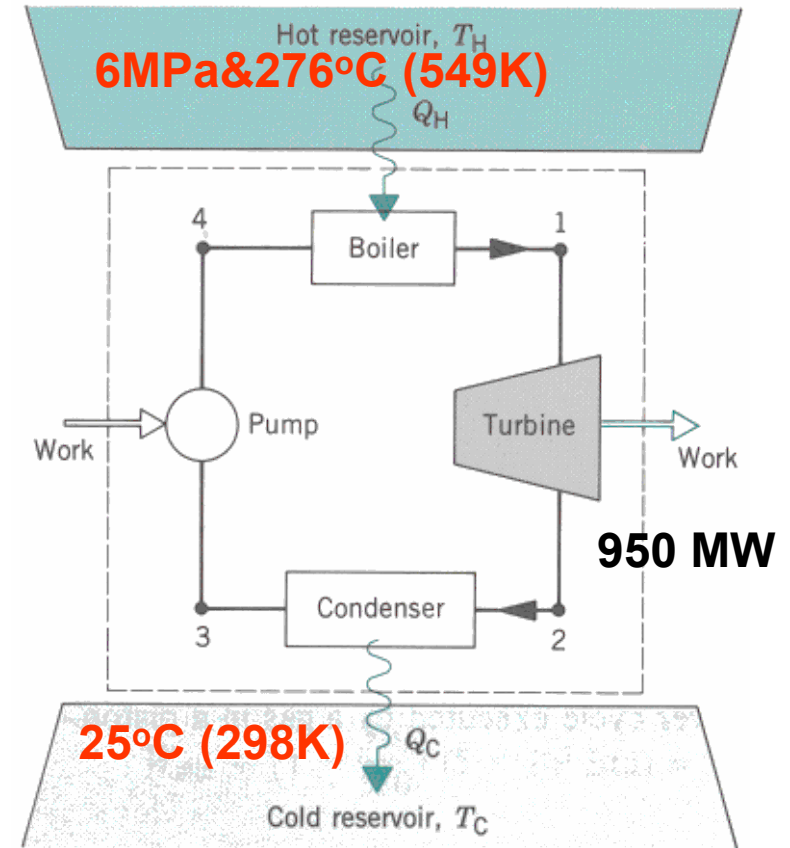
$$\eta_T = W/Q_H = \underline{0.46}$$

- Calor Absorvido, Q_H :

$$Q_H = 950/0.46 = 2065 \text{ MW}$$

- Calor Rejeitado, 1ª Lei:

$$Q_H - Q_L = W_{liq} \rightarrow Q_L = 1115 \text{ MW}$$



TEAMPLAY page 2

- Aquecimento da água:

$$Q_L = MC(T_f - T_i)$$

$$\Delta T = 1115 \cdot 10^6 / 4000 \cdot 4180 = 66.7^\circ\text{C}$$

- Se considerarmos as irreversibilidades, a eficiência do ciclo passa a ser 80% da de Carnot:

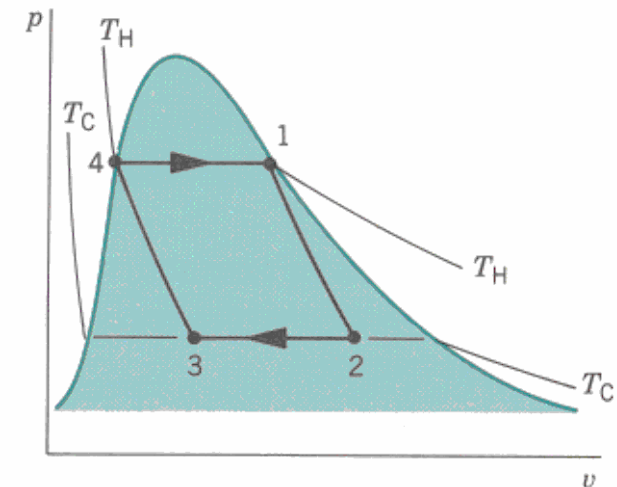
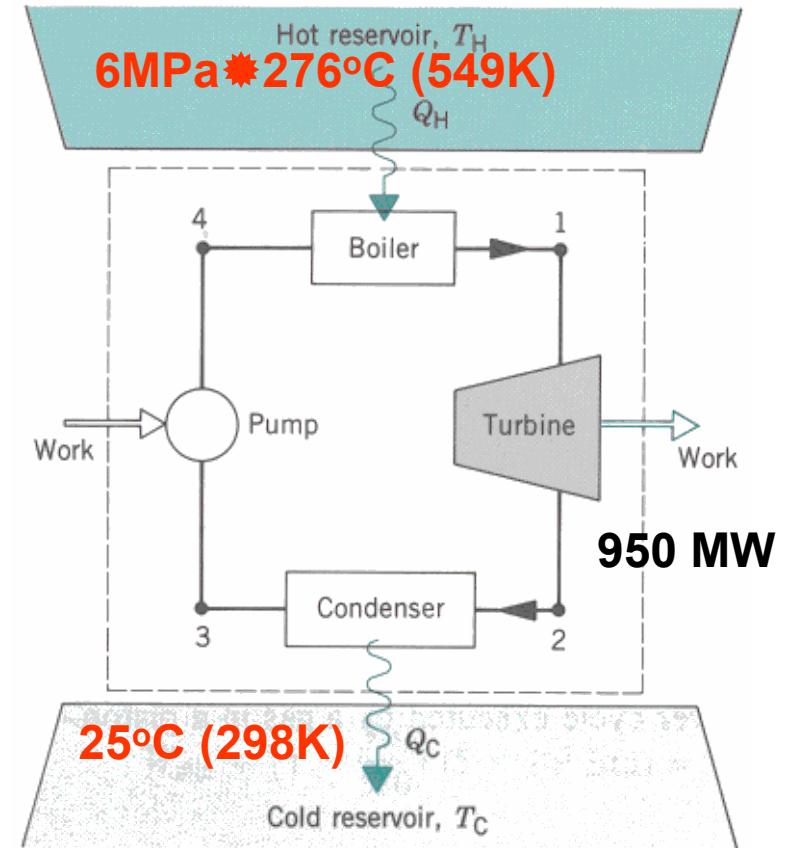
$$\eta_T = 0.8 \eta_C = \underline{0.37}$$

- Calor Absorvido, Q_H :

$$Q_H = 950 / 0.37 = 2567 \text{ MW}$$

- Calor Rejeitado, 1a Lei:

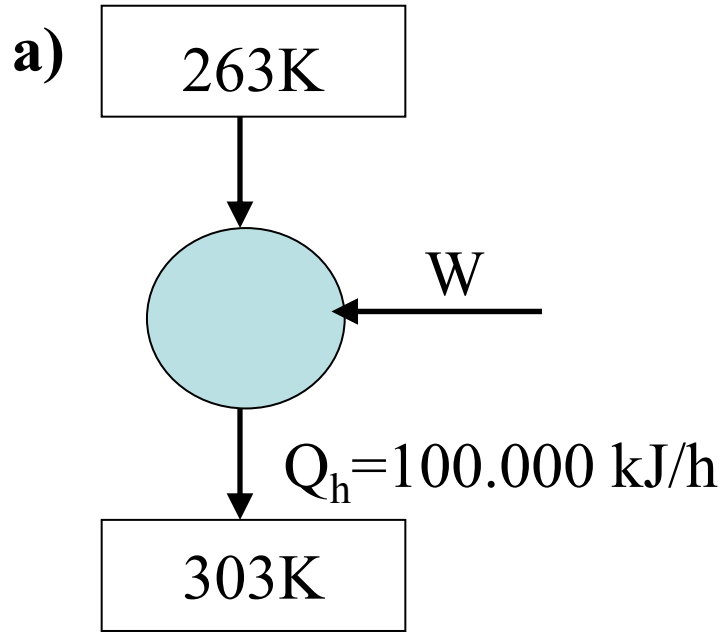
$$Q_H - Q_L = W_{liq} \rightarrow Q_L = 1617 \text{ MW}$$



Ex4.22) Aquecer uma casa com bomba de calor. Necessita-se de 100000 KJ/h para manter o interior da casa a +30C quando fora o ar está a -10C.

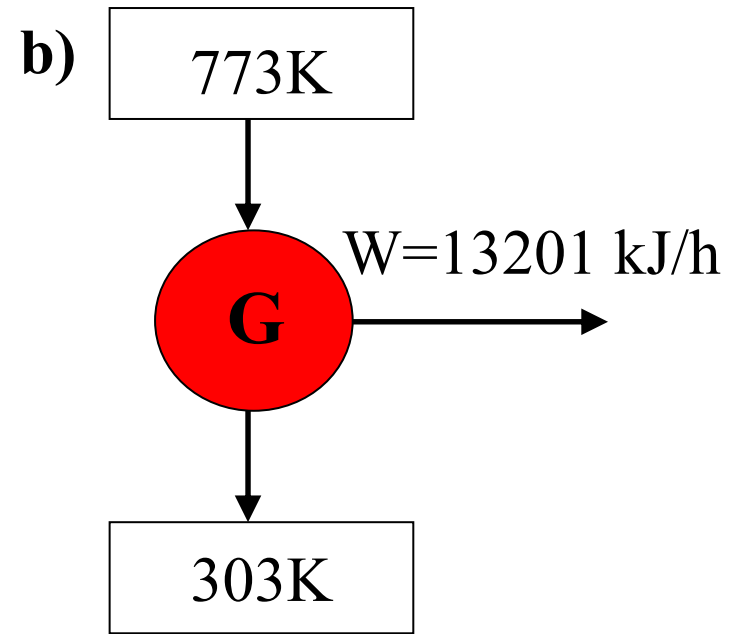
- (a)** Qual é a potência mínima para acionar a bomba de calor?
- (b)** Compare esta potência com a potência elétrica se o aquecimento fosse com resistências elétrica
- (c)** Se a bomba de calor fosse acionada por uma máquina térmica operando entre 500C e 30C, qual é o mínimo calor requerido pela caldeira? Compare esta potência térmica com a potência necessária se a casa utilizasse aquecimento a gás.

Ex4.22)



$$\eta_{bc} = 7,575 \rightarrow W \geq 13201 \frac{\text{kJ}}{\text{h}}$$

Potência necessária para aquecimento elétrico:
100.000kJ/h



$$\eta_T = 1 - \frac{T_L}{T_H} = 0,608$$

$$\eta_T = \frac{W}{Q_H} \rightarrow Q_H = \frac{13201}{0,608}$$

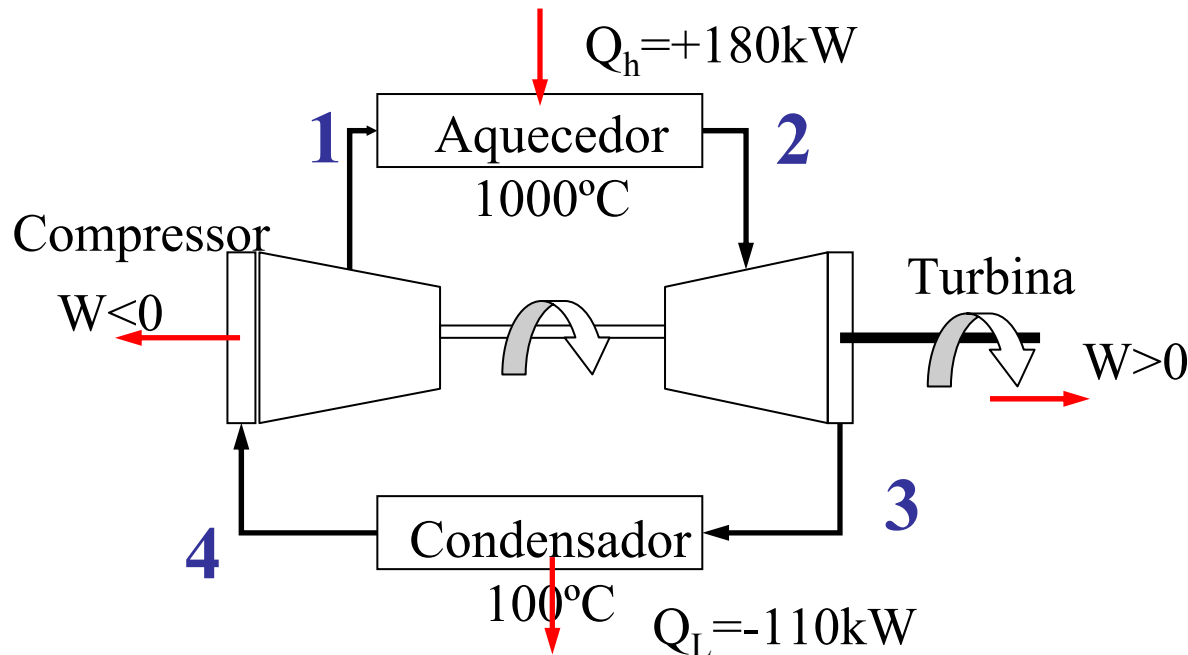
$$\eta_T = 21711 \frac{\text{kJ}}{\text{h}}$$

Razão Consumo Gás:
21711/100.000 \approx 1:5

Ex4.17) Uma central de potência com turbina a gás operando num ciclo fechado usa ar como fluido de trabalho, veja esquema da figura.

- (a) Identifique as interações das transf. de calor e trabalho considerando o ar como sistema.
- (b) se 180KW são fornecidos ao aquecedor e 110KW são rejeitados no condensador, determine a potência líquida e a eficiência da central.
- (c) *Determine a máxima eficiência possível operando a T_h e T_c de 1000C e 100C*

parte (a)



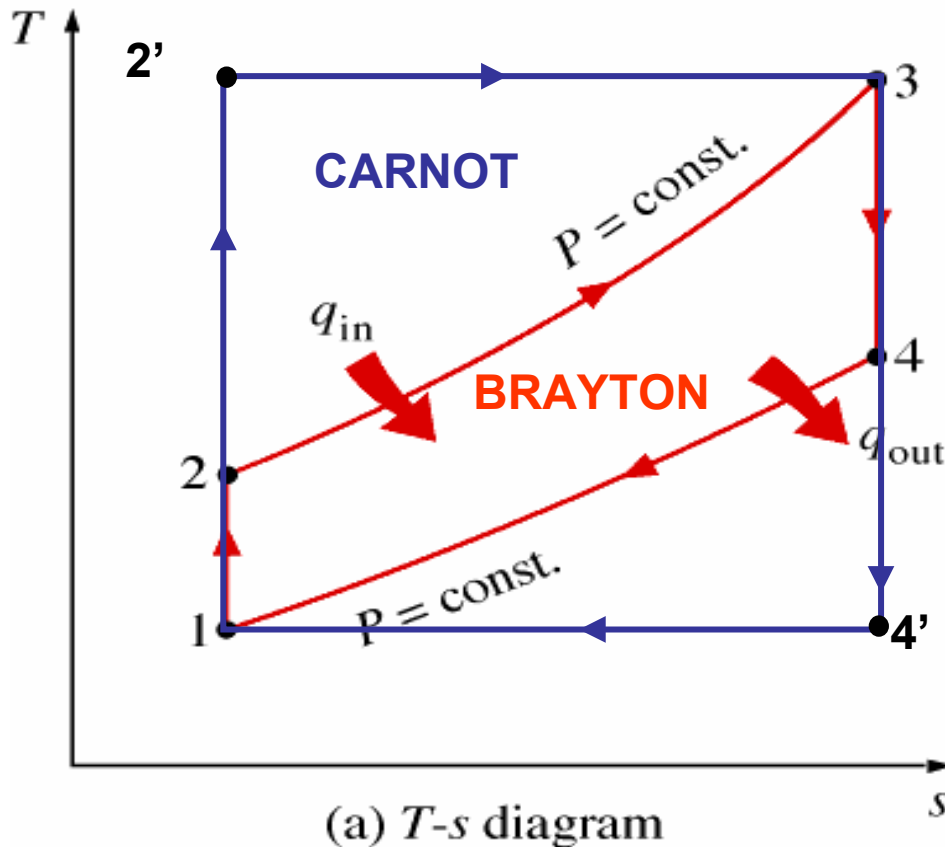
parte (b)

$$1^\circ \text{ Lei: } \oint Q = \oint W$$

$$W_{\text{liq}} = 180 - 110 = 70 \text{ kW}$$

$$\eta_T = \frac{W_{\text{liq}}}{Q_h} = \frac{70}{180} = 0,39\%$$

The highest efficient cycle operating between two temperatures is the Carnot Cycle

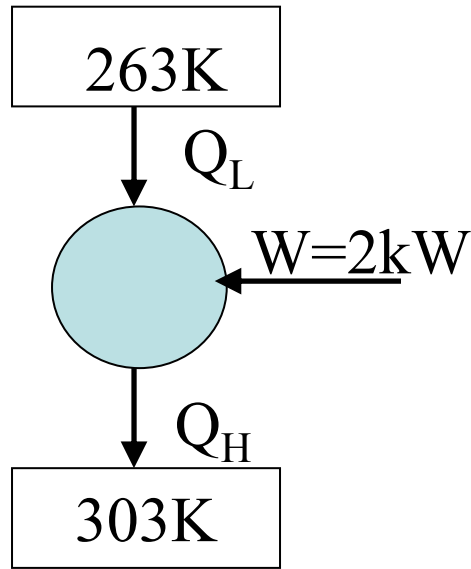


$$\eta = 1 - \frac{Q_L}{Q_H}$$

Compare the areas in the Ts diagram, they represent the heat

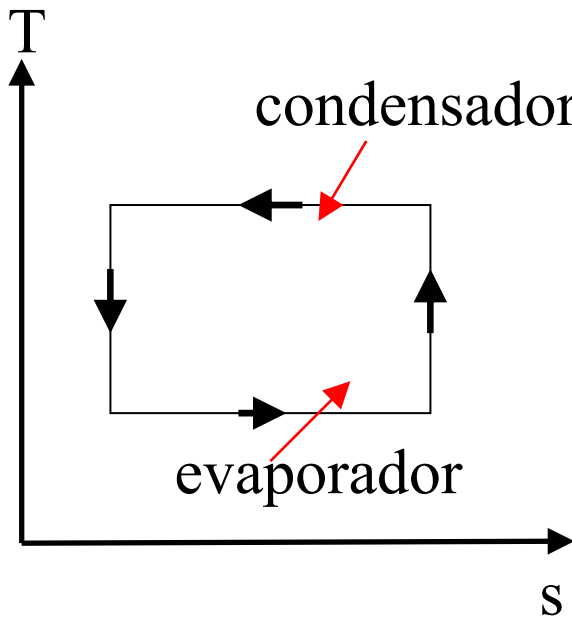
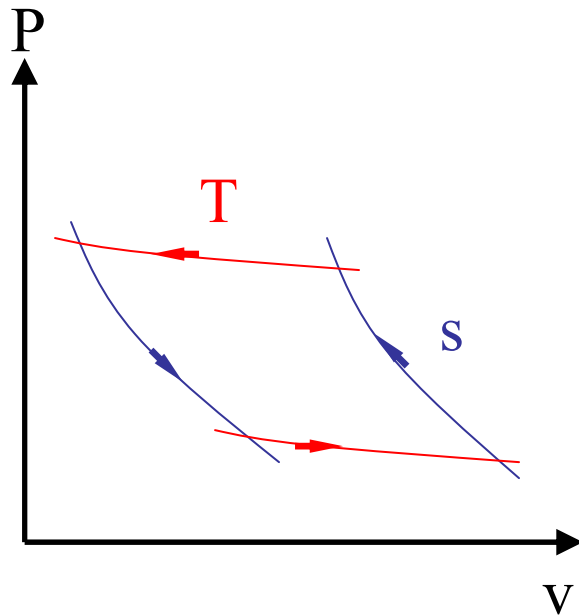
$$\eta = 1 - \frac{373}{1273} \cong 0,70$$

Ex4.23)



$$\eta_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$\eta_R = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{1}{\frac{303}{263} - 1} = 6,57$$



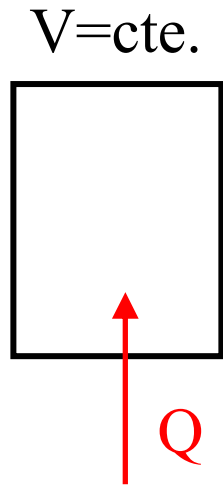
$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

$$Q_H = \frac{T_L}{T_H} Q_L$$

$$Q_H = \frac{303}{263} 6,57 \times 2$$

$$Q_H = 15,14 \text{ kW}$$

Ex4.24)



Adição de calor a volume constante

1º Lei: $Q - W = \Delta U$ onde: $[W = 0]$

$$\Delta U = C_v \Delta T = Q$$

Energia Interna aumenta ($Q > 0$)

Temperatura aumenta ($\Delta U > 0$)

Pressão aumenta ($PV = MRT$) [$T \uparrow$]

Entalpia aumenta ($H = U + PV$)

Entropia:

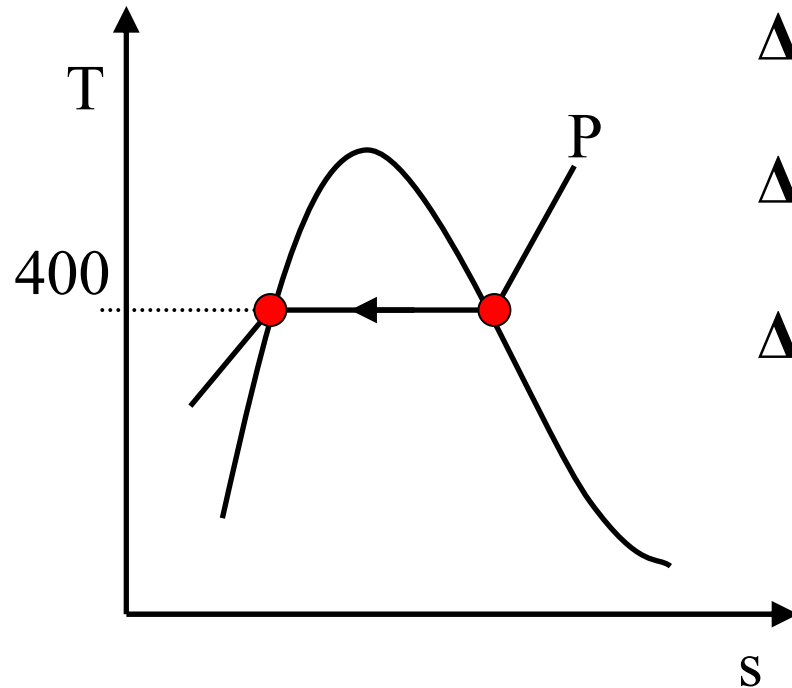
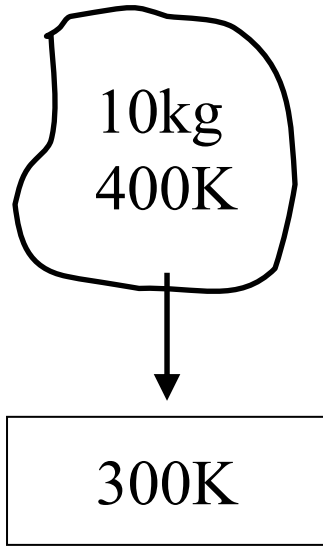
$$\Delta S = c_v \ln\left(\frac{T_2}{T_1}\right) + k \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S > 0 \rightarrow T_2 > T_1$$

**Troca de calor com
diferença de temperatura
→ Processo Irreversível**

$$\Delta S_{\text{sist+viz}} > 0$$

Ex4.27)



$$\int dS = \oint \frac{\partial Q}{T} + \int dI$$

$$\Delta S_{\text{sist}} = \frac{-100}{400} = -0,25 \frac{\text{kJ}}{\text{°K}}$$

$$\Delta S_{\text{viz}} = \frac{+100}{300} = +0,33 \frac{\text{kJ}}{\text{°K}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sist}} + \Delta S_{\text{viz}}$$

$$\Delta S_{\text{univ}} = \left(\frac{1}{3} - \frac{1}{4} \right) = \frac{1}{12} = 83,33 \frac{\text{J}}{\text{°K}}$$