INSTITUTO SUPERIOR TÉCNICO

# 2019/2020

## Thermodynamics

**Prof. Tânia Sousa**
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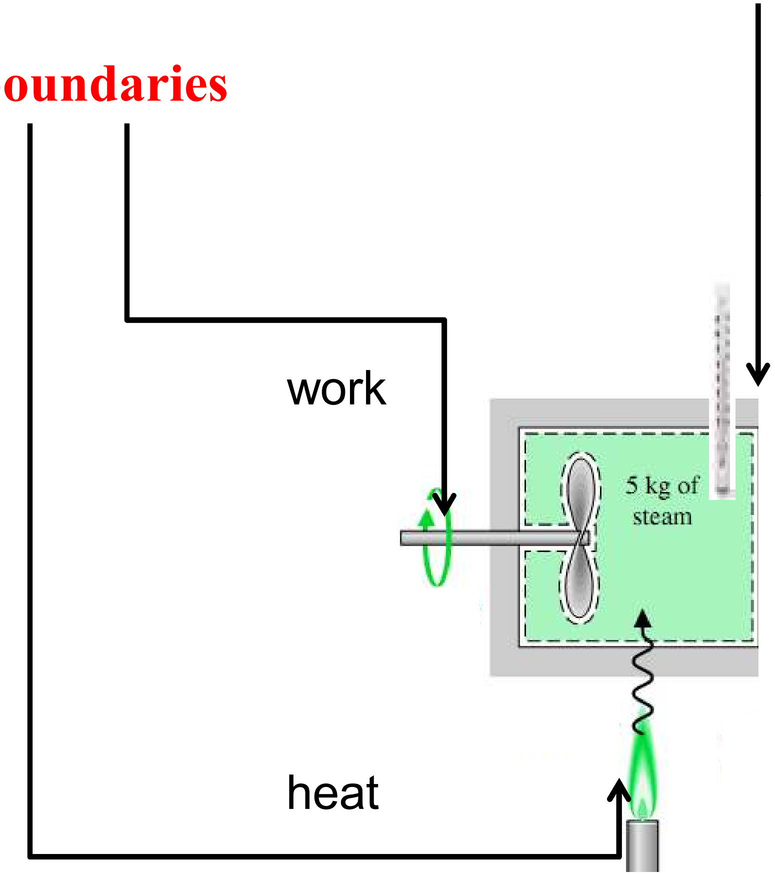
# Energy Balance in Closed Systems

**Energy change in the system**

**Flows at the boundaries**




*Moran et al., 2014*

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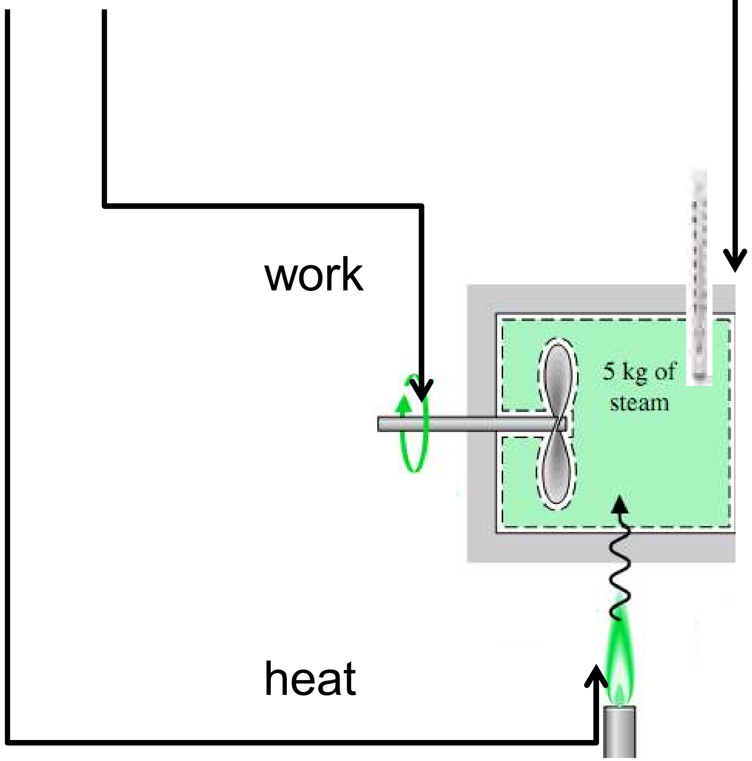
# Energy Balance in Closed Systems

## Energy Change = Heat + Work

**Energy change in the system**

**Flows at the boundaries**

$$\Delta E = \Delta\left(U + E_p + E_c\right) = Q + W$$



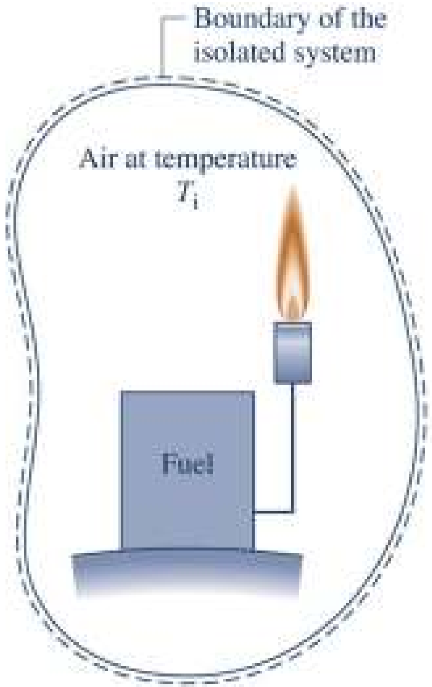

- $1^{st}$ Law: Energy Conservation
- Forms of E: U, $E_c$ and $E_p$
- Energy transfer by Q and W
- Sign of heat and work fluxes

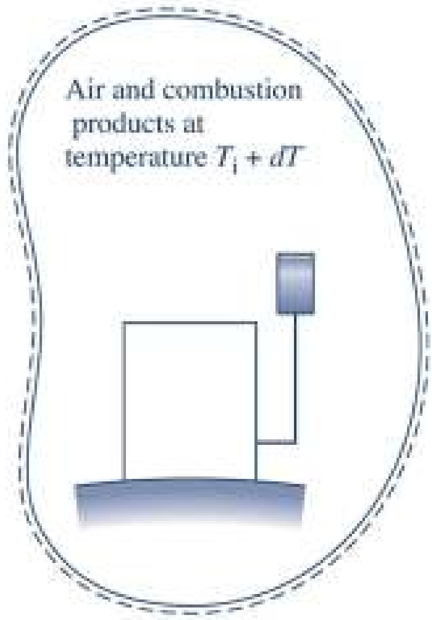
*Moran et al., 2014*

# Energy Balance in Closed Systems

# Energy Balance in isolated systems

- What happens to the total energy of the system?

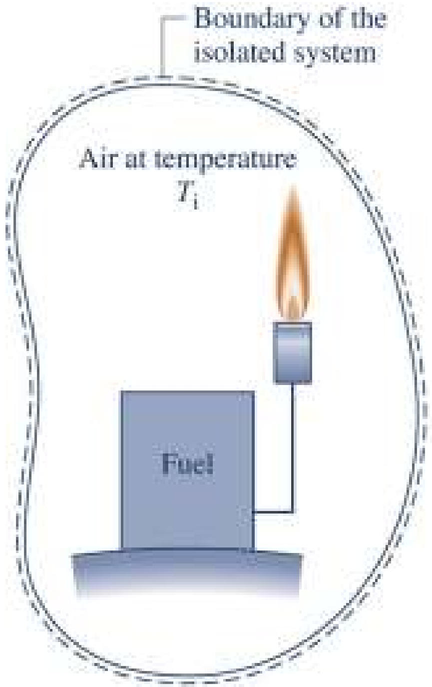


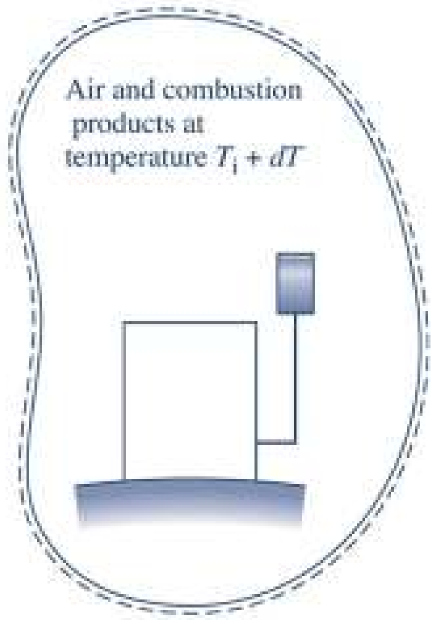




*Moran et al., 2014*

# Energy vs. Exergy

- What happens to the total energy of the system?

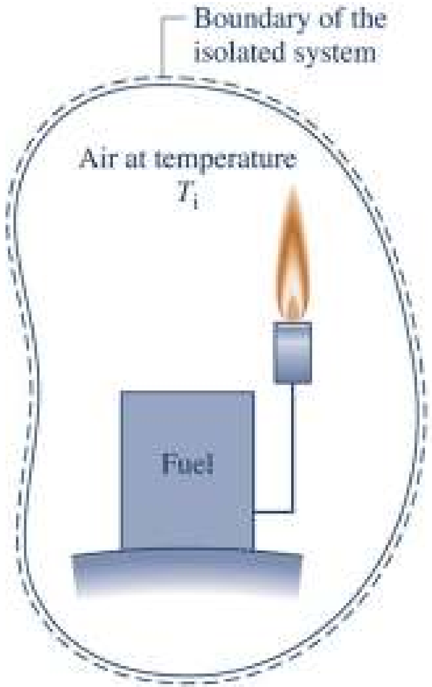


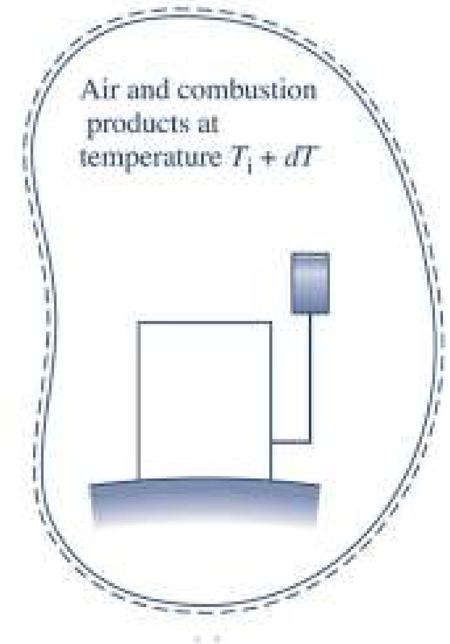




- It remains constant (system is isolated)

# Energy vs. Exergy

- Can the process occur from the right to the left?



# Is the first law enough?

- What happens if you put a dish with ice over a pan with boiling water?

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# Entropy Balance in Adiabatic Systems & Isolated Systems

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Entropy change = Entropy production

$$\Delta S = \sigma$$

- $2^{nd}$ Law: ?

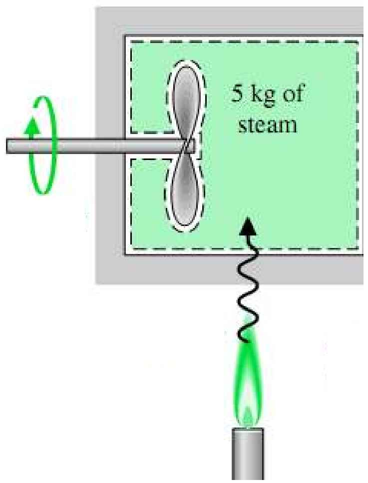
# Entropy Balance in Adiabatic Systems & Isolated Systems

Entropy change = Entropy production

$$\Delta S = \sigma$$

- $2^{nd}$ Law: In an adiabatic system the entropy must not decrease

# Entropy Balance in Closed Systems

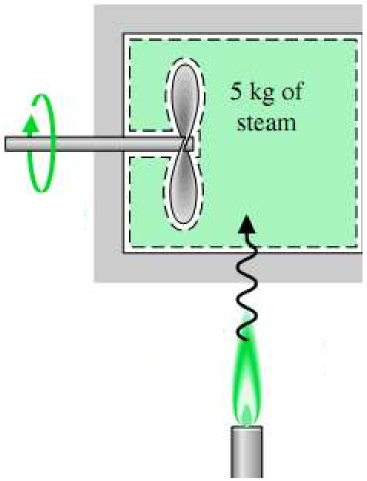


# Entropy Balance in Closed Systems

Entropy change = Entropy transfer in the form of heat + entropy production

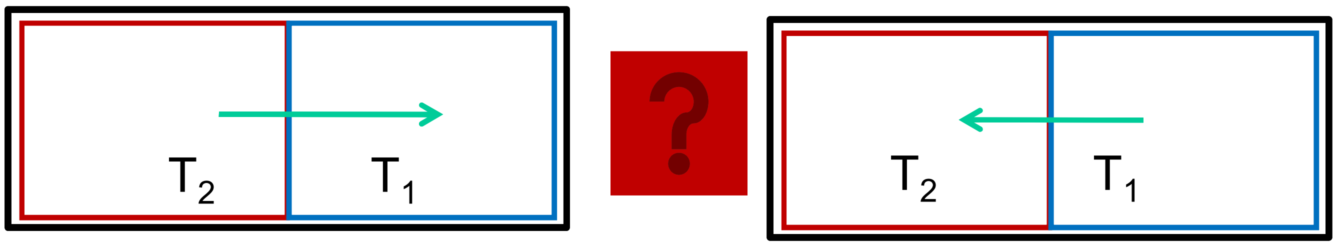
$$\Delta S = \frac{Q}{T} + \sigma$$

Entropy flows with heat but not with work



# Entropy Balance in Adiabatic Systems

- Suppose the combined system (contained in the black boundary) is adiabatic and that $T_2 > T_1$
- What happens to the entropy of the combined system in each case?

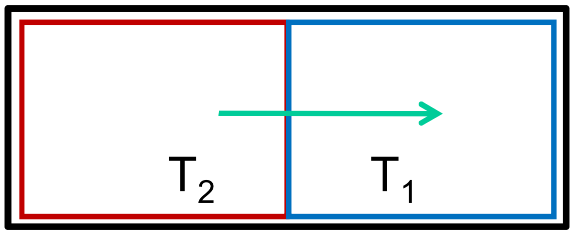


# Entropy Balance in Adiabatic Systems

$$\Delta S = \sigma > 0$$

$$\sigma > \sigma_1 + \sigma_2$$

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{Q}{T_1} - \frac{Q}{T_2} + \sigma_1 + \sigma_2$$

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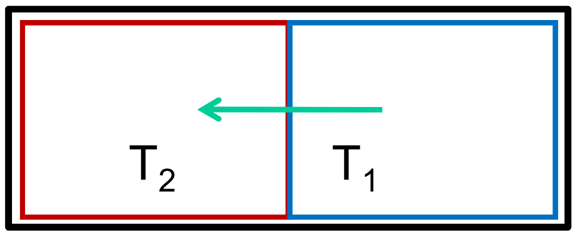
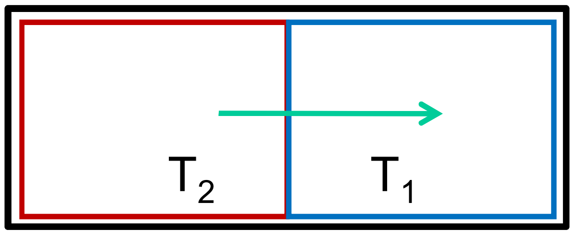
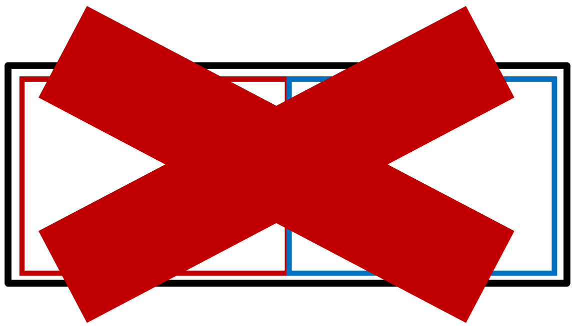


# Entropy Balance in Adiabatic Systems

- <u>2nd Law: In an adiabatic system the entropy must not decrease</u>

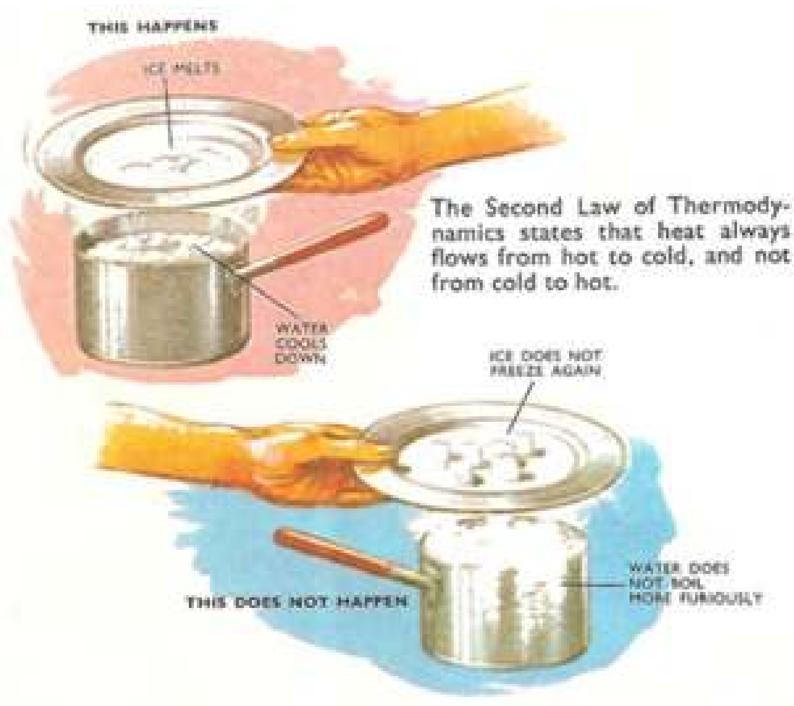


- 2nd Law: the arrow of time
- Entropy production in spontaneous processes

# Is the first law enough?

- What happens if you put a dish with ice over a pan with boiling water?



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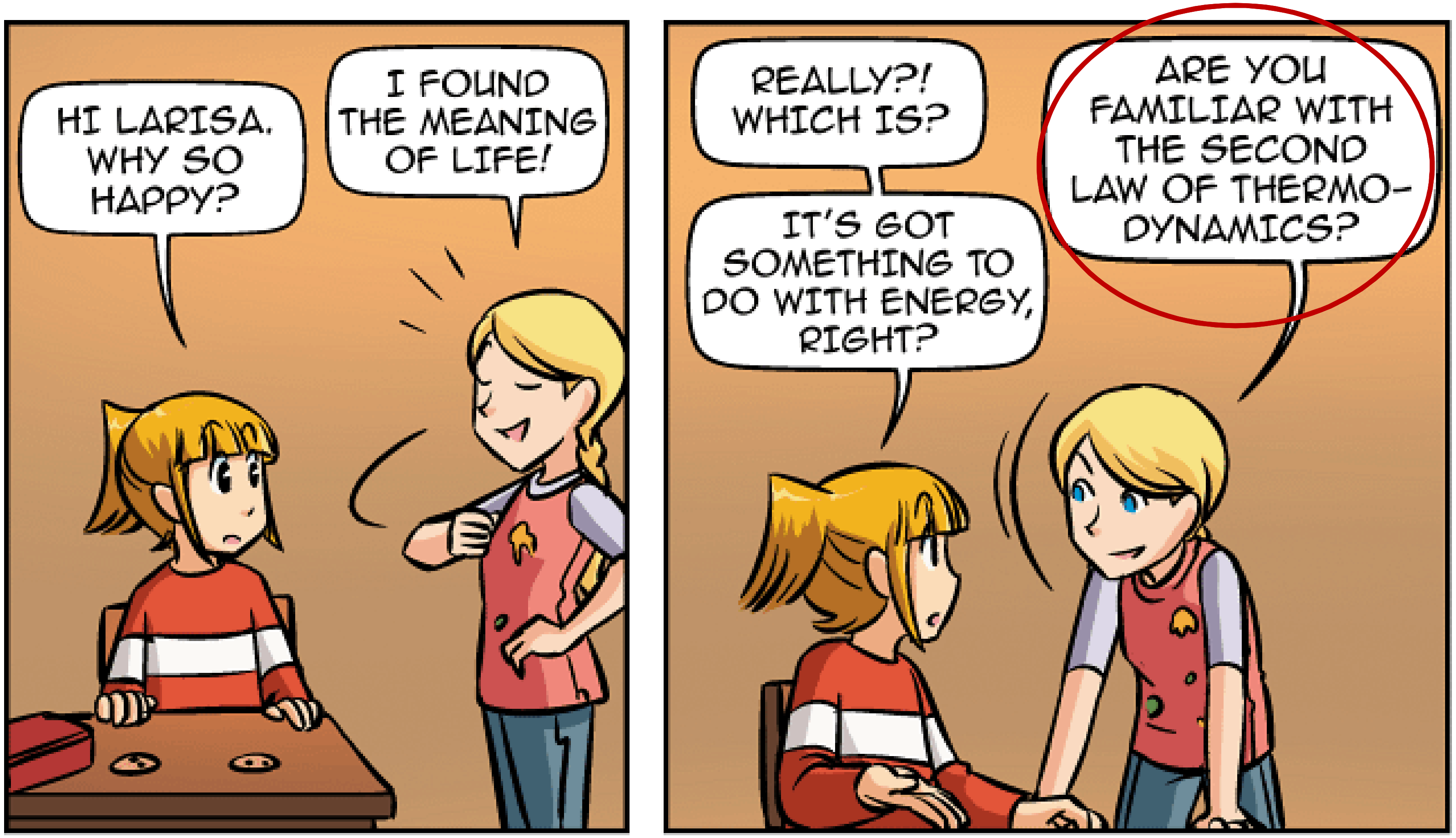
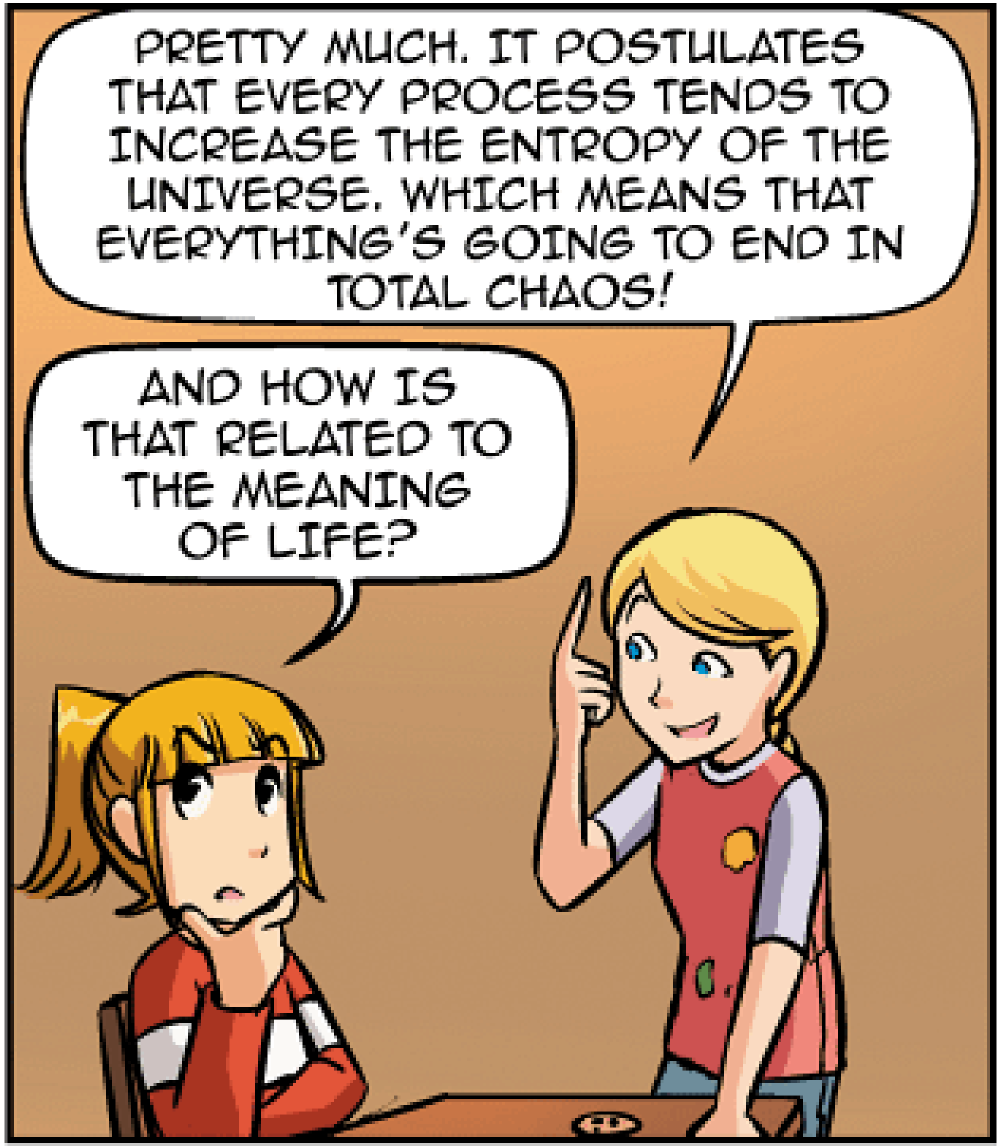
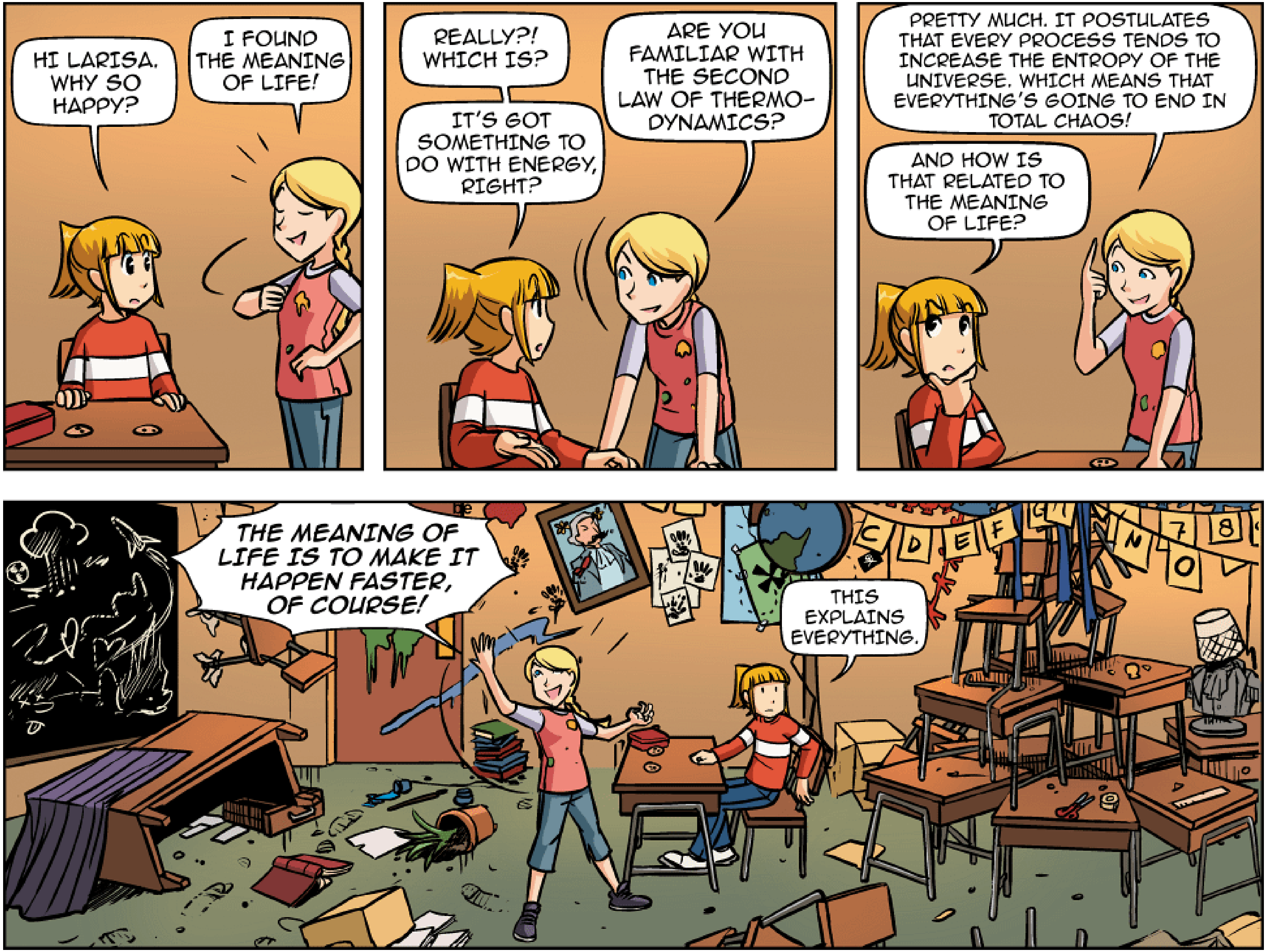


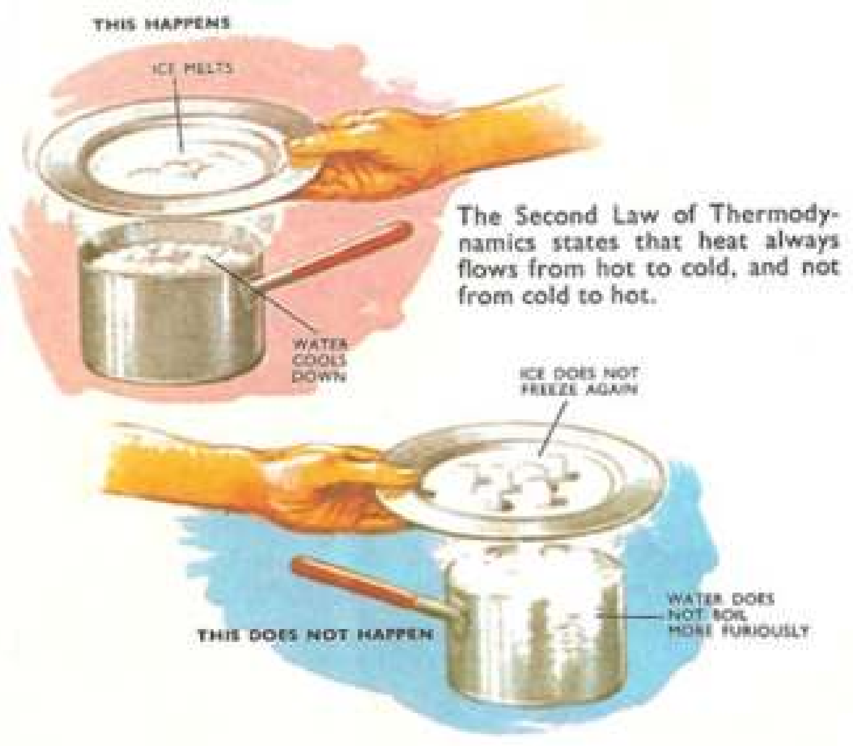

PRETTY MUCH. IT POSTULATES THAT EVERY PROCESS TENDS TO INCREASE THE ENTROPY OF THE UNIVERSE. WHICH MEANS THAT EVERYTHING'S GOING TO END IN TOTAL CHAOS!
AND HOW IS THAT RELATED TO THE MEANING OF LIFE?




*Sandra and Woo* by Oliver Knörzer (writer), Powree (artist) and Lisa Moore (colorist) - www.sandraandwoo.com

# The state variable: Entropy

- Entropy is the state variable that gives unidirectionality to time in physical processes ocurring in isolated & adiabatic systems.




I have a bottle of beer next to a mug of coffee.

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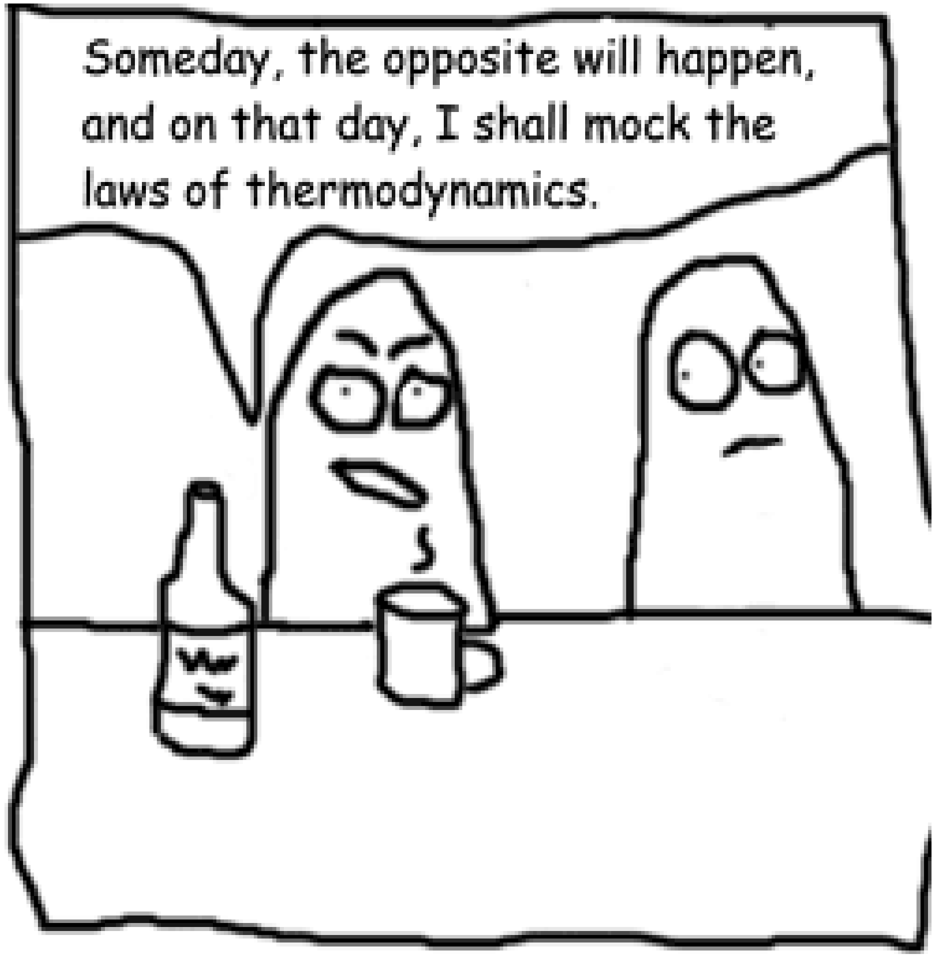
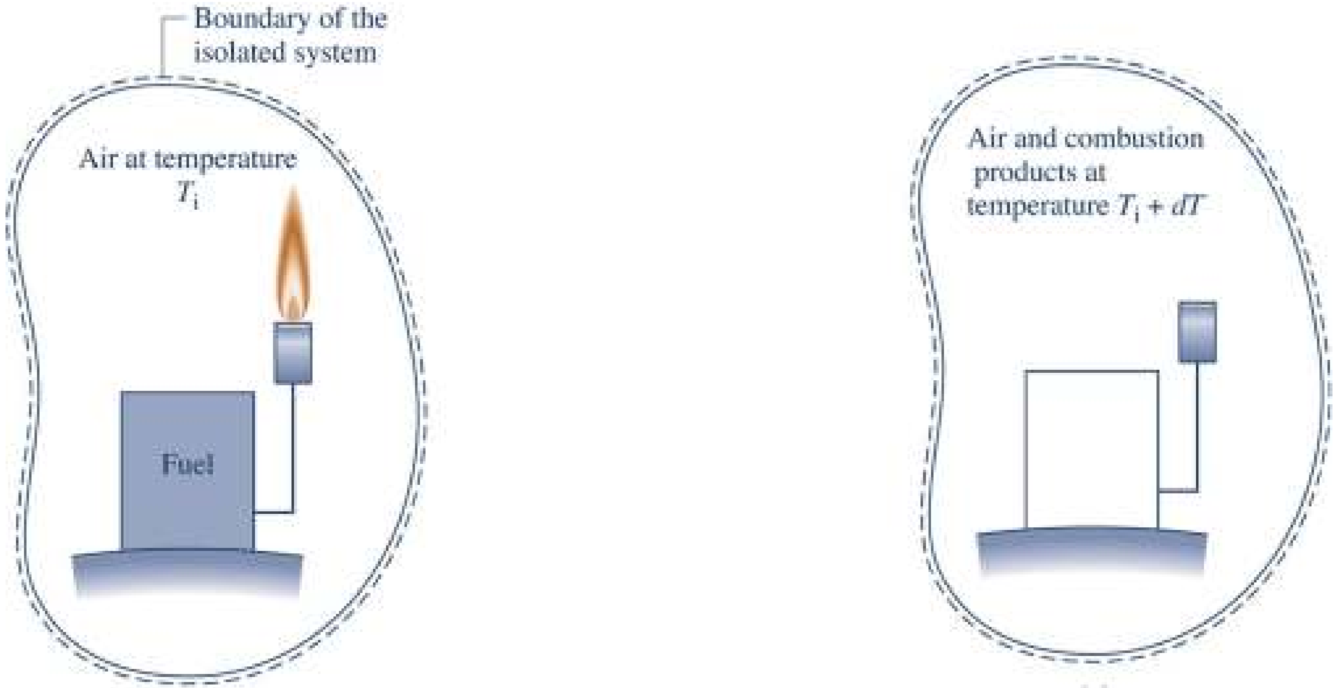

Someday, the opposite will happen, and on that day, I shall mock the laws of thermodynamics.

No, not today.
Not Today?

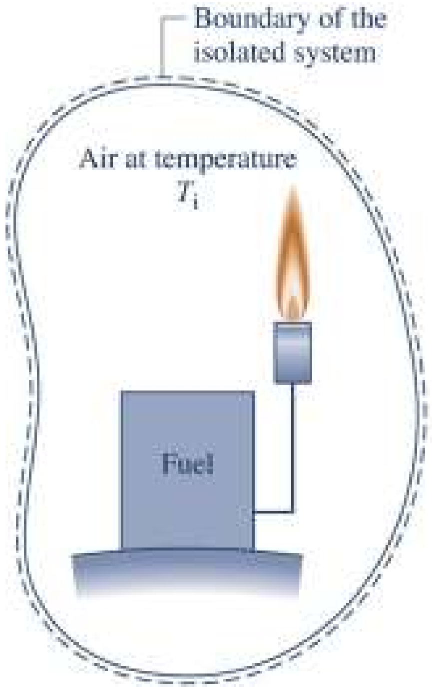
# Entropy

- What happens to the total entropy of the system?

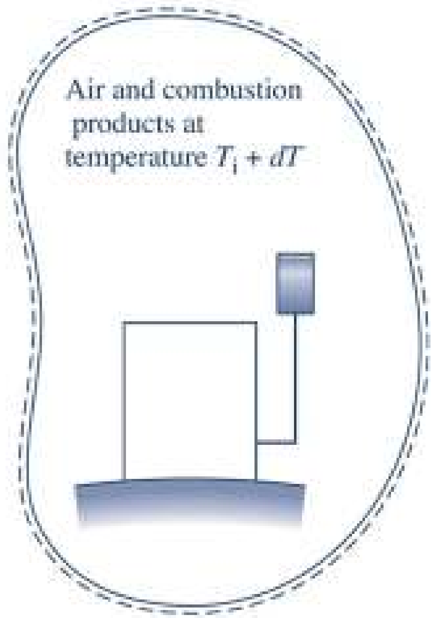


# Energy vs. Exergy

- Which system has a greater potential for use?




Fuel-air combination




Warm air mixture

# Energy vs. Exergy

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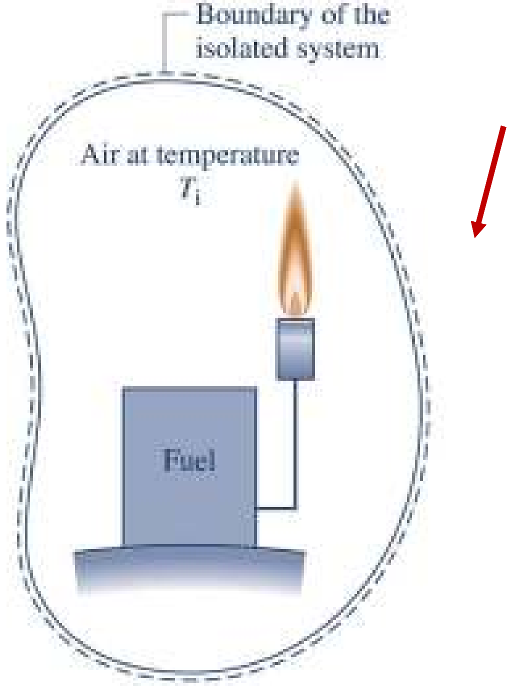
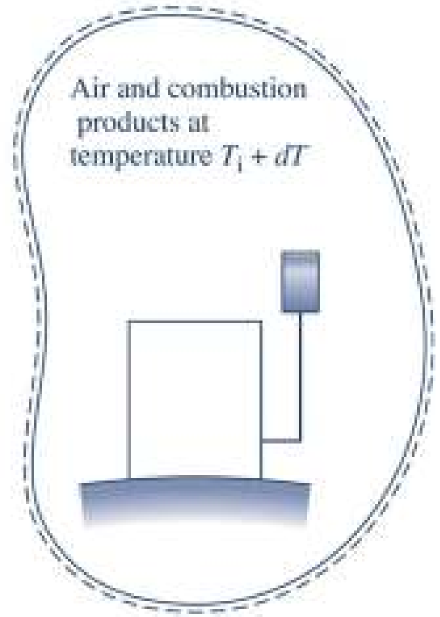



Fuel-air combination

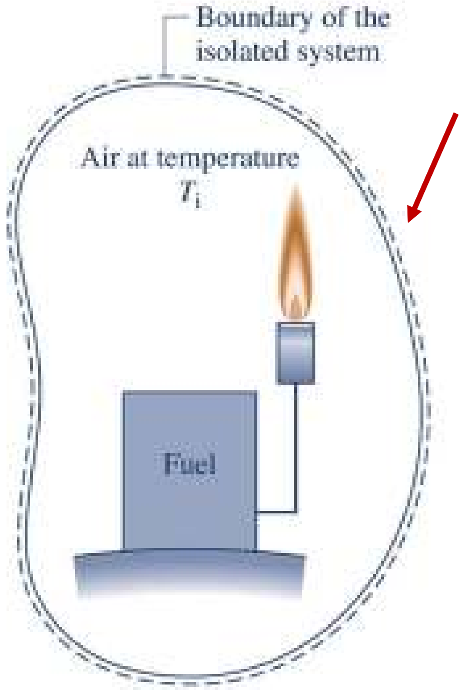



Warm air mixture

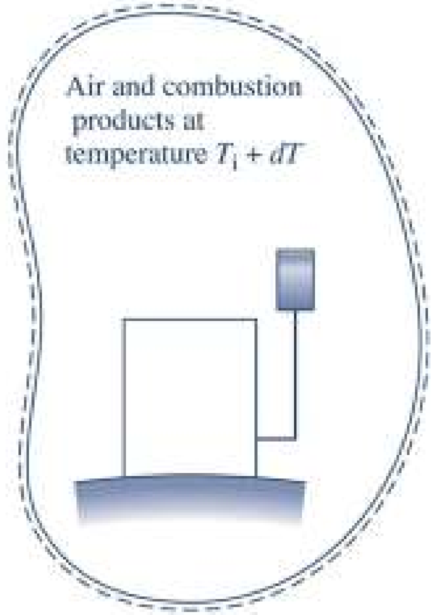
- “The fuel might be used to generate electricity, produce steam, or power a car whereas the final warm mixture is clearly unsuited for such applications.”

# Energy vs. Exergy

- Which system has a greater potential for use?




Fuel-air combination

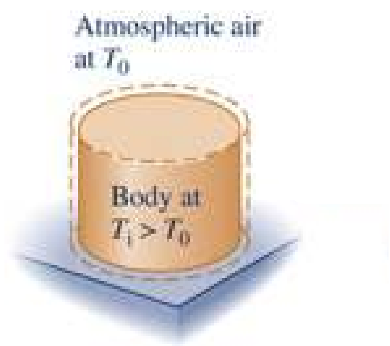



Warm air mixture

- "During the process the initial potential for use (and economic value) is predominately ***destroyed*** owing to the irreversible nature of that process. "

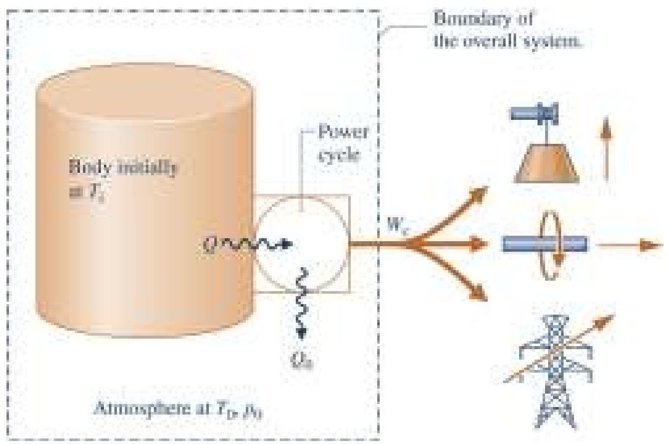
# Energy vs. Exergy

- Exergy is the property that quantifies the potential for use and it is exergy that has economic value.
- Exergy is a property that takes into account the second law of thermodynamics
- How can we make use of a body at $T_i > T_0$?



# Energy vs. Exergy

- Controlled cooling to produce work




*Moran et al., 2014*

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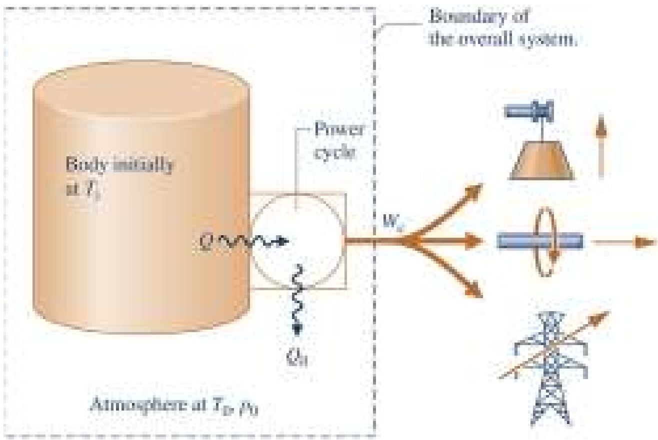
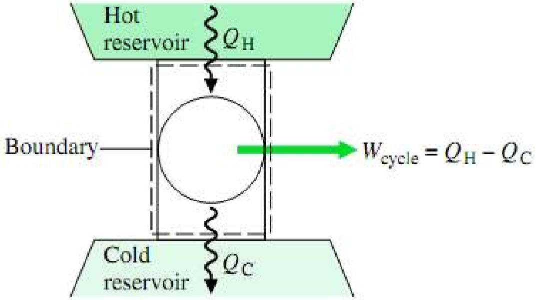


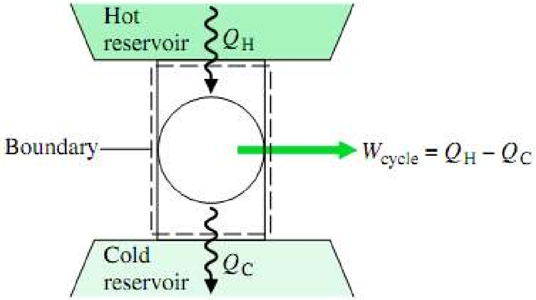

*Moran et al., 2014*

- The amount of maximum work depends on what?

# The Carnot Efficiency – Power Cycle




# The Carnot Efficiency – Power Cycle




- First law: $\Delta E = Q_H - Q_C - W_{cycle} = 0 \Rightarrow W_{cycle} = Q_H - Q_C$
- Second law: $\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} + \sigma = 0 \Rightarrow Q_C \neq 0$

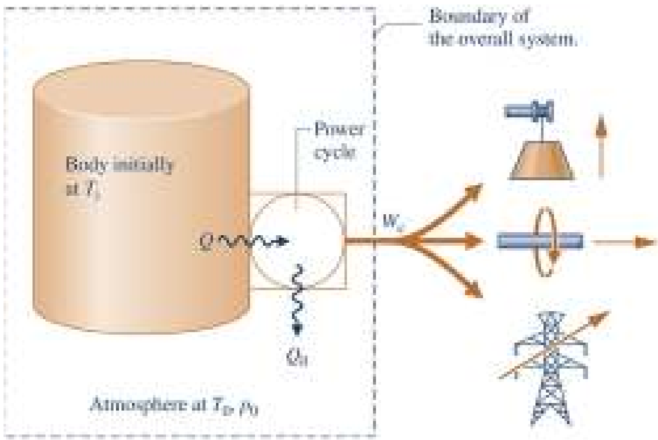
- Ideal (Reversible) Cycle:

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

$$\eta_{ideal} = \frac{W_{cycle}}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

# Energy vs. Exergy

- Controlled cooling to produce work

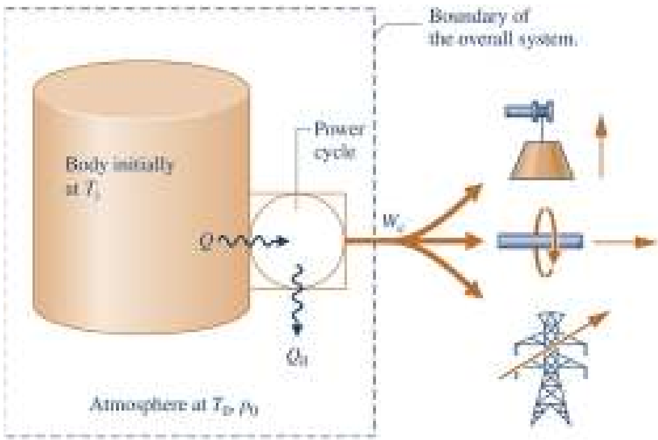



*Moran et al., 2014*

- Exergy is the maximum theoretical value for the work $W_c$.
- What happens to the exergy of the body with time?

# Energy vs. Exergy

- Controlled cooling to produce work




*Moran et al., 2014*

- Exergy is the maximum theoretical value for the work $W_c$.
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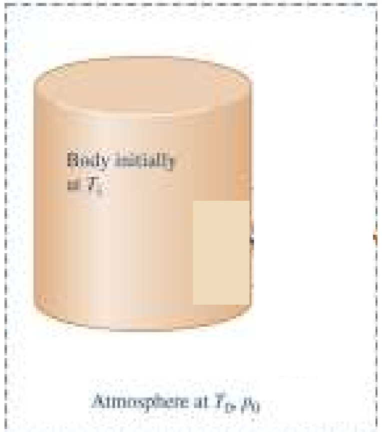
# Energy vs. Exergy

- Could we produce work if $T_i < T_0$?



# Energy vs. Exergy

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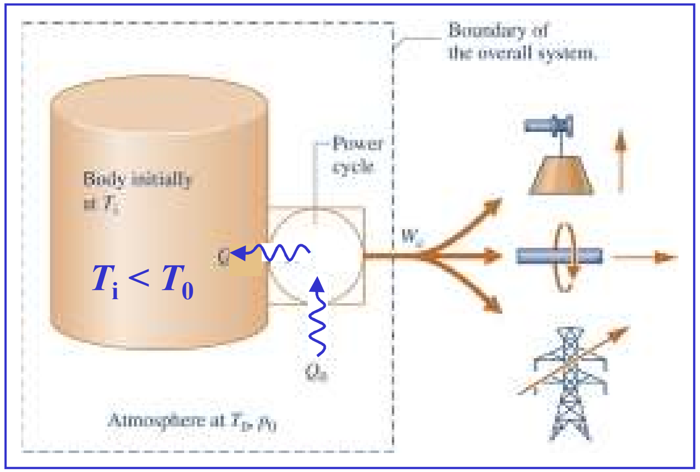
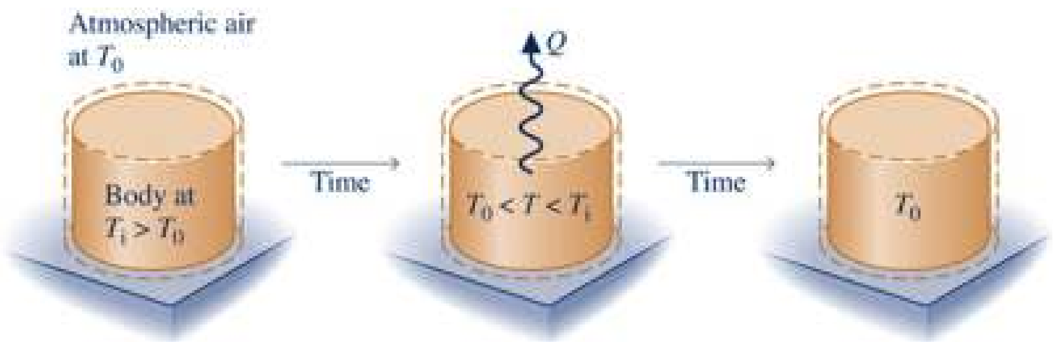



*Moran et al., 2014*

- The potential for developing work $W_c$ exists because the initial state of the body differs from that of the environment, i.e., $T_i < T_0$.

# Defining Exergy

- Reference environment: $T_0$ and $P_0$
- Exergy is the maximum $W_{\mathbf{c}}$ obtainable from the system plus the environment as the system comes into equilibrium with the environment (goes to the dead state $T_0$ & $P_0$).
- What happened in the case of spontaneous cooling?

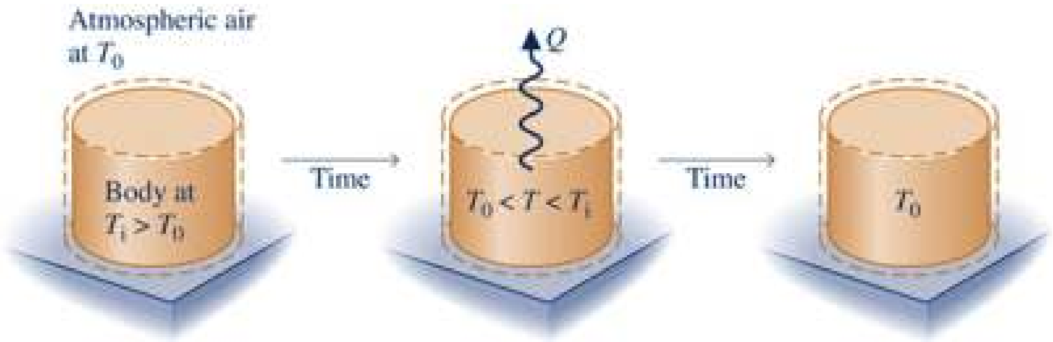


# Defining Exergy

- Reference environment: $T_0$ and $P_0$

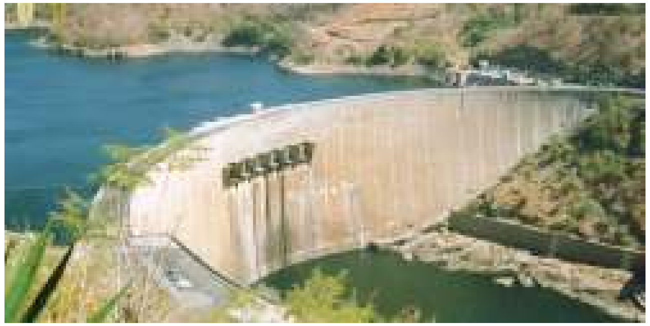
- Exergy is the maximum $W_c$ obtainable from the system plus the environment as the system comes into equilibrium with the environment (goes to the dead state $T_0$ & $P_0$).

- $W_c$ is null because exergy is destroyed by irreversibilities (spontaneous processes)



# Defining Exergy

- If temperature and/or pressure of a system differ from that of the environment, the system has **thermomechanical** exergy. Another contribution, called **chemical exergy**, arises when there is a chemical composition difference between the system and environment.

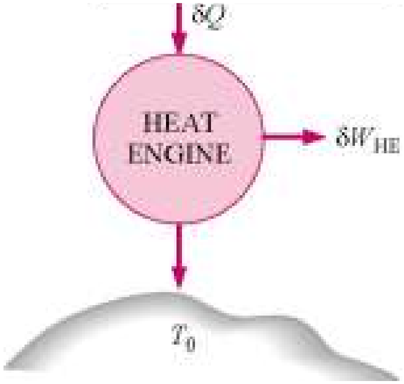


# Exergy Balance in Closed Systems

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \underline{\int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q + \left[W + p_0(V_2 - V_1)\right]} - \underline{T_0\sigma}$$

# Exergy Balance in Closed Systems

- Exergy transfer by heat
  - What is the maximum amount of work that can be produced with Q?



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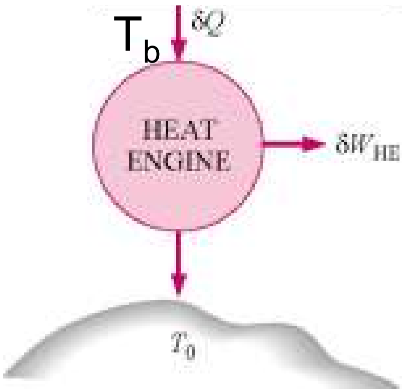



$$W_{max} = \int \left(1 - \frac{T_0}{T_b}\right) \delta Q$$

Cengel & Boles

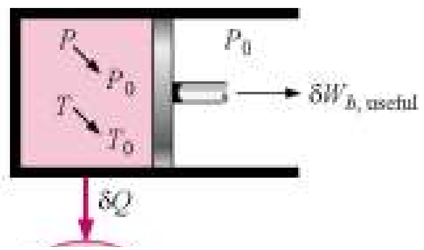
$$E_q = \left[\begin{array}{c} \textit{exergy} \text{ transfer} \\ \text{accompanying heat} \\ \text{transfer} \end{array}\right] = \int_1^2 \left(1 - \frac{T_0}{T_b}\right) \delta Q$$

# Exergy Balance in Closed Systems

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \underline{\int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q + \left[W + p_0(V_2 - V_1)\right]} - \underline{\quad T_0\sigma \quad}$$

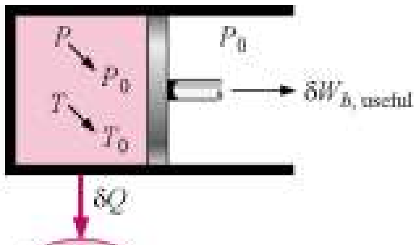
# Exergy Balance in Closed Systems

- Exergy transfer by work
  - What is the maximum amount of useful work that can be used from W?



# Exergy Balance in Closed Systems

- Exergy transfer by work




$$W = W_{b,useful} - \int P_0\, dV$$

$$W_{b,useful} = W + P_0(V_2 - V_1)$$

Work associated with expansion

Cengel & Boles

Total work that exits the system

$$E_w = \begin{bmatrix} exergy \text{ transfer} \\ \text{accompanying work} \end{bmatrix} = [W + p_0(V_2 - V_1)]$$

# Exergy Balance in Closed Systems

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q + \left[W + p_0(V_2 - V_1)\right] - T_0\sigma$$

# Exergy Balance in Closed Systems

- Exergy destruction: irreversibilities destroy exergy

$$E_d = T_0 \sigma$$

- $2^{nd}$ Law?

# Exergy Balance in Closed Systems

- Exergy destruction: irreversibilities destroy exergy

$$E_d = T_0\sigma$$

- 2nd Law?

$$E_d: \begin{cases} = 0 & \text{(no irreversibilities present within the system)} \\ > 0 & \text{(irreversibilities present within the system)} \\ < 0 & \text{(impossible)} \end{cases}$$

# Exergy Balance in Closed Systems

Exergy Change = exergy transfer by heat - exergy transfer by work - exergy dissipation

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \underbrace{\int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q - \left[W + p_0(V_2 - V_1)\right]}_{\text{exergy transfers}} - \underbrace{T_0\sigma}_{\text{exergy destruction}}$$

- What happens to the exergy of an isolated system?

# Exergy Rate Balance for Closed Systems

- The exergy rate balance?

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \underbrace{\int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q + [W + p_0(V_2 - V_1)]}_{\text{exergy transfers}} - \underbrace{T_0\sigma}_{\text{exergy destruction}}$$

# Exergy Rate Balance for Closed Systems

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$$\frac{dE}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W} + p_0\frac{dV}{dt}\right) - \dot{E}_d$$

- Steady-state?

# Exergy Rate Balance for Closed Systems

- The exergy rate balance

$$\underbrace{E_2 - E_1}_{\text{exergy change}} = \underbrace{\int_1^2 \left(1 - \frac{T_0}{T_b}\right)\delta Q + [W + p_0(V_2 - V_1)]}_{\text{exergy transfers}} - \underbrace{T_0\sigma}_{\text{exergy destruction}}$$

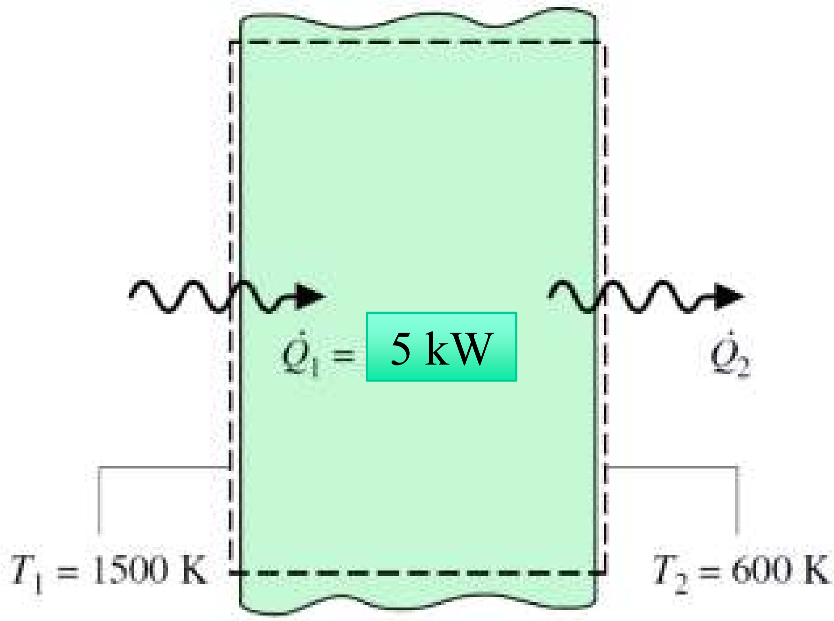
$$\frac{dE}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W} + p_0\frac{dV}{dt}\right) - \dot{E}_d$$

- Steady-state

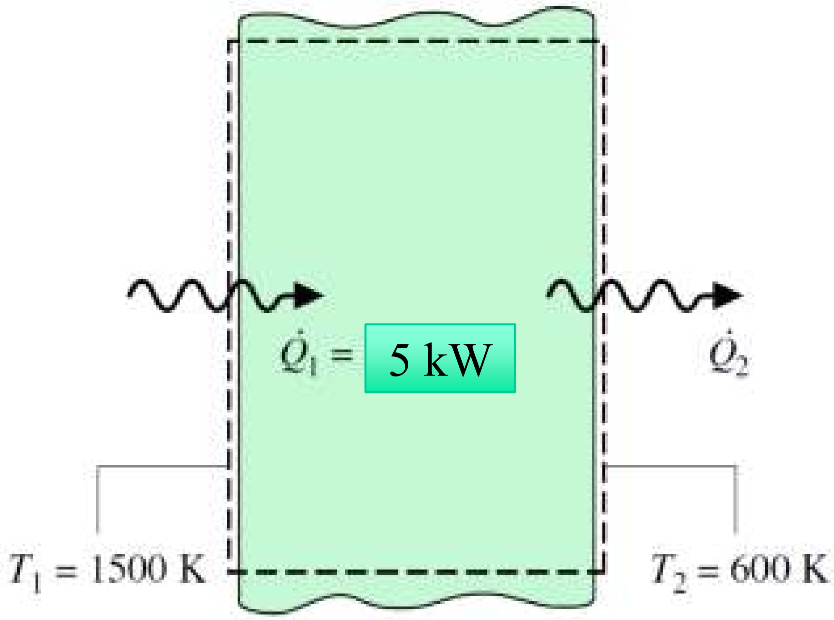
$$0 = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \dot{W} - \dot{E}_d$$

$$0 = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \dot{W} - \dot{E}_d$$

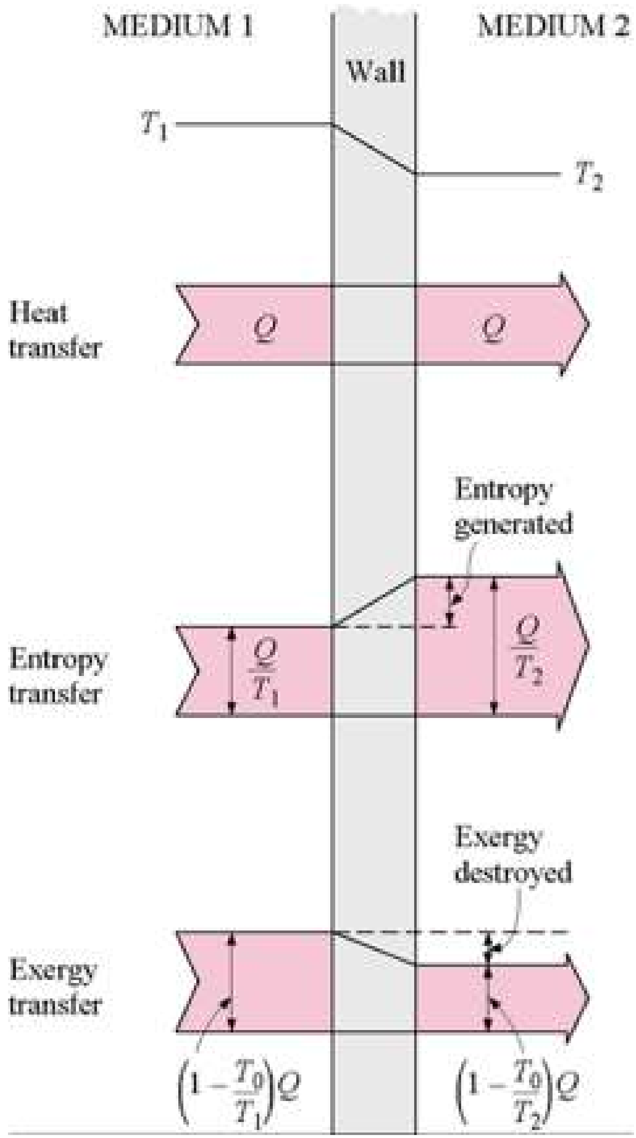
Let $T_0 = 300$ K.



Let $T_0 = 300$ K.

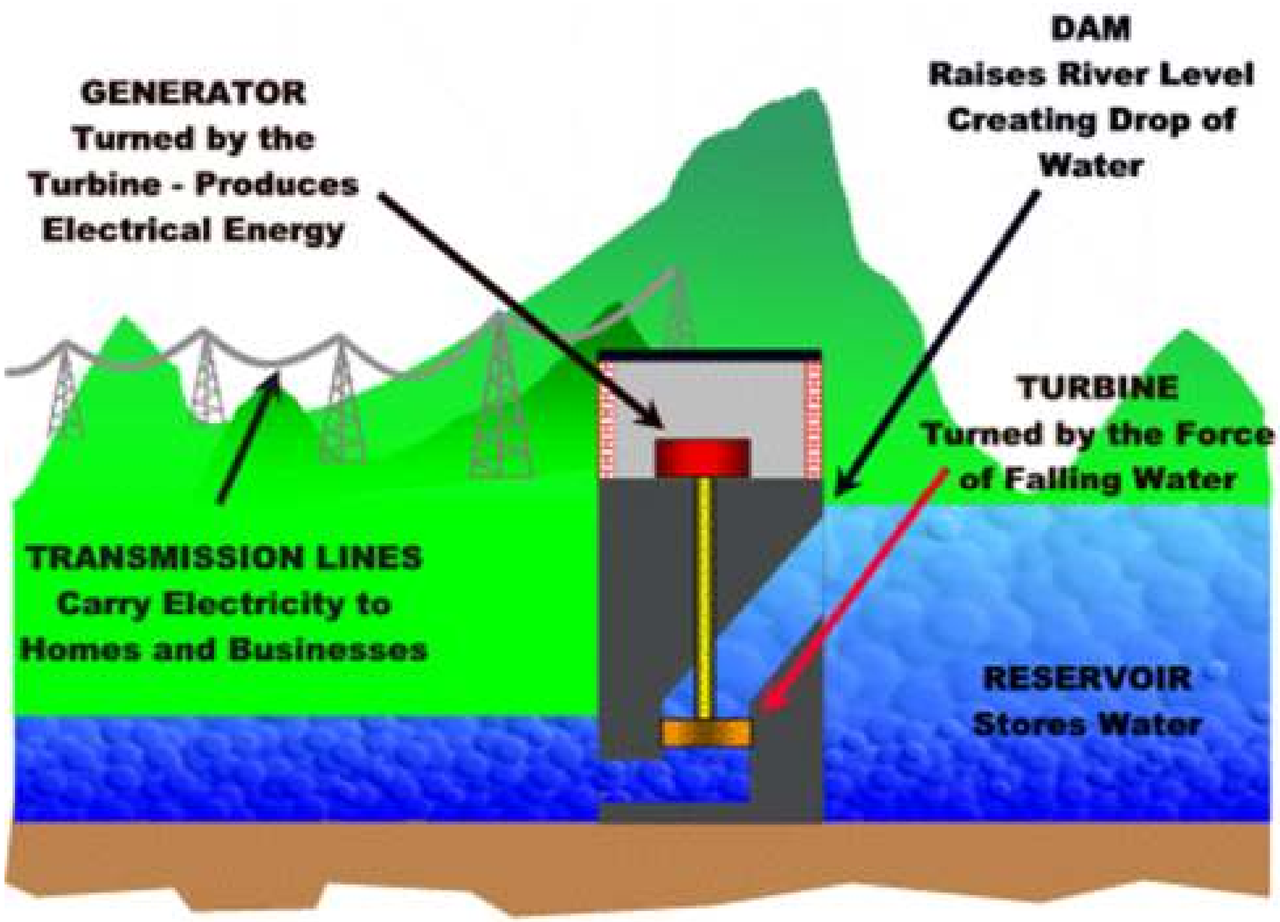


$\dot{Q}_1$ = 5 kW
$\dot{Q}_2$
$T_1$ = 1500 K
$T_2$ = 600 K

MEDIUM 1
MEDIUM 2
Wall
$T_1$
$T_2$
Heat transfer
$Q$
$Q$
Entropy generated
Entropy transfer
$\frac{Q}{T_1}$
$\frac{Q}{T_2}$
Exergy destroyed
Exergy transfer
$\left(1 - \frac{T_0}{T_1}\right)Q$
$\left(1 - \frac{T_0}{T_2}\right)Q$

# Energy Balance in Open Systems



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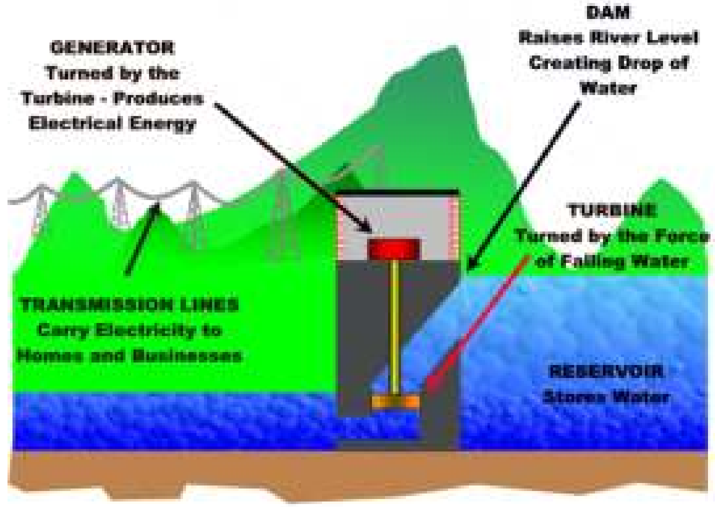
# Energy Balance in Open Systems

## Mass Change = Σ Mass Flows

$$\frac{dm}{dt} = \sum_i \dot{m}_{in,i} - \sum_j \dot{m}_{out,j}$$




## Energy Change = Heat + Work + Energy in Mass Flow

$$\frac{dE}{dt} = \underbrace{\dot{Q} + \dot{W} + \sum_i \dot{m}_{in,i}\left(h_i + \frac{v_i^2}{2} + gz_i\right) - \sum_j \dot{m}_{out,j}\left(h_j + \frac{v_j^2}{2} + gz_j\right)}$$

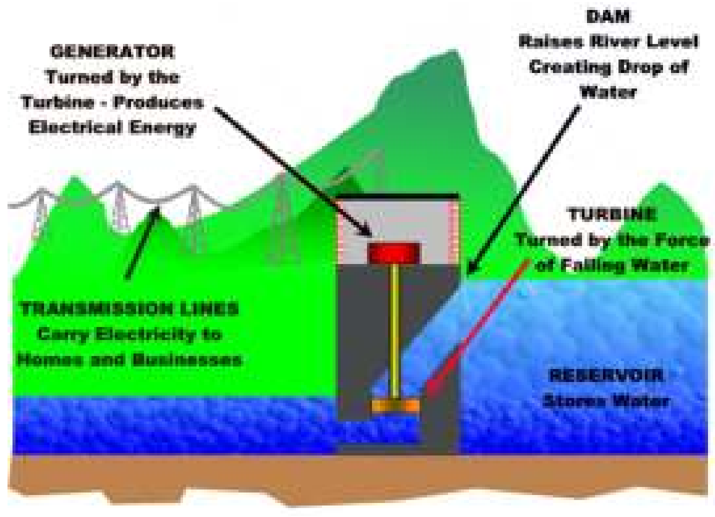
**Enthalpy of component j**

$$h_i = u_i + p_i v_i$$

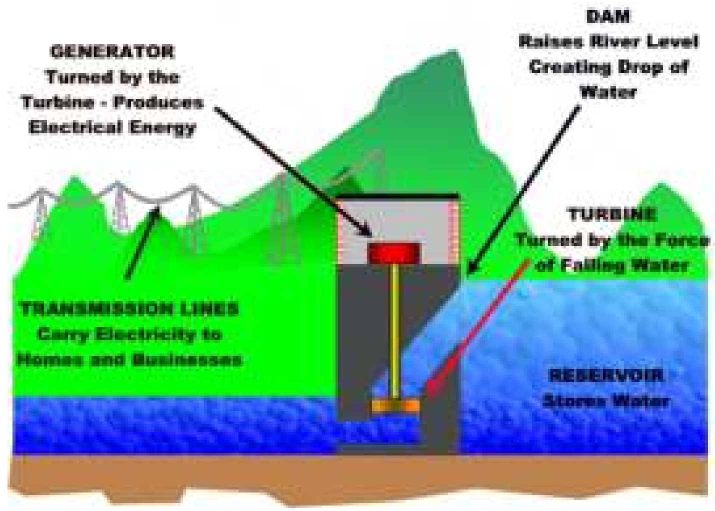
**Flows at the boundaries**

# Energy Balance in Open Systems

# Entropy Balance in Open Systems



# Entropy Balance in Open Systems




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

# Exergy Rate Balance for Control Volume Systems

- The exergy rate balance for closed systems

$$\frac{dE}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W} + p_0\frac{dV}{dt}\right) - \dot{E}_d$$

- The exergy rate balance for open systems

# Exergy Rate Balance for Control Volume Systems

- The exergy rate balance for closed systems

$$\frac{d\mathsf{E}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W} + p_0\frac{dV}{dt}\right) - \dot{\mathsf{E}}_d$$

- The exergy rate balance for open systems

$$\frac{d\mathsf{E}_{cv}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W}_{cv} + p_0\frac{dV_{cv}}{dt}\right) + \sum_i \dot{m}_i \mathsf{e}_{fi} - \sum_e \dot{m}_e \mathsf{e}_{fe} - \dot{\mathsf{E}}_d$$

- Steady-state?

# Exergy Rate Balance for Control Volume Systems

- The exergy rate balance for closed systems

$$\frac{d\mathsf{E}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W} + p_0\frac{dV}{dt}\right) - \dot{\mathsf{E}}_d$$

- The exergy rate balance for open systems

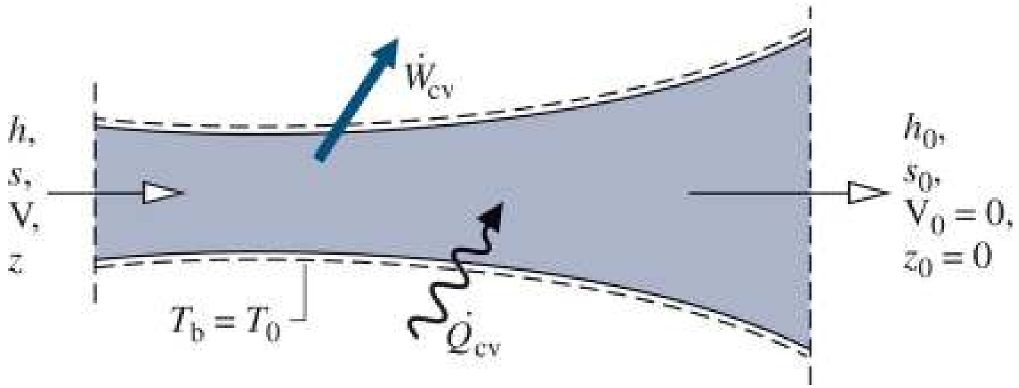
$$\frac{d\mathsf{E}_{cv}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \left(\dot{W}_{cv} + p_0\frac{dV_{cv}}{dt}\right) + \sum_i \dot{m}_i \mathsf{e}_{fi} - \sum_e \dot{m}_e \mathsf{e}_{fe} - \dot{\mathsf{E}}_d$$

- Steady-state?

$$0 = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j + \dot{W}_{cv} + \dot{m}(\mathsf{e}_{f1} - \mathsf{e}_{f2}) - \dot{\mathsf{E}}_d$$

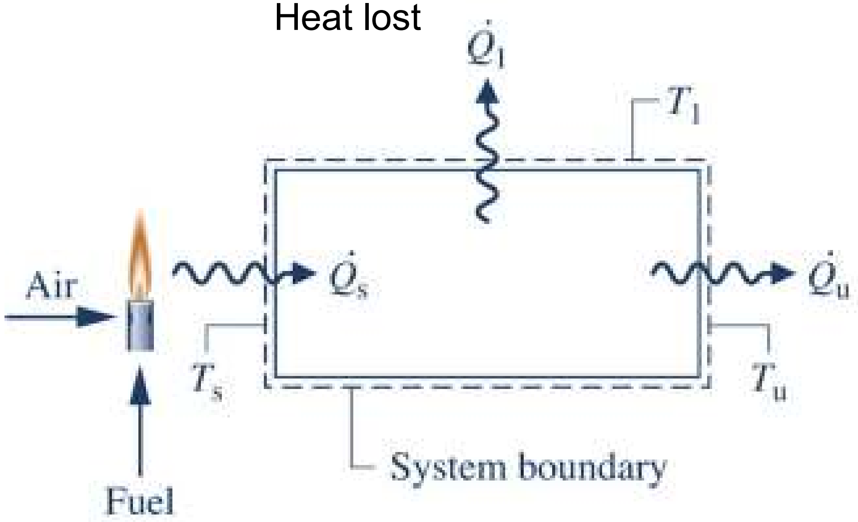
# The specific flow exergy

- What is the specific flow exergy?



# Energy & Exergy Efficiencies

- Energy and exergy balances at steady-state?

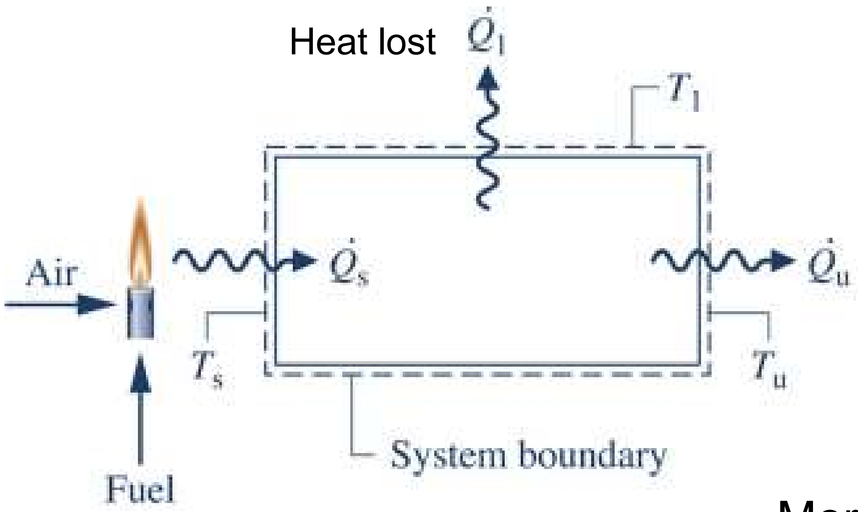



$T_0$

Moran et al., 2014

# Exergetic Efficiency

- Energy and exergy balances at steady-state




$T_0$

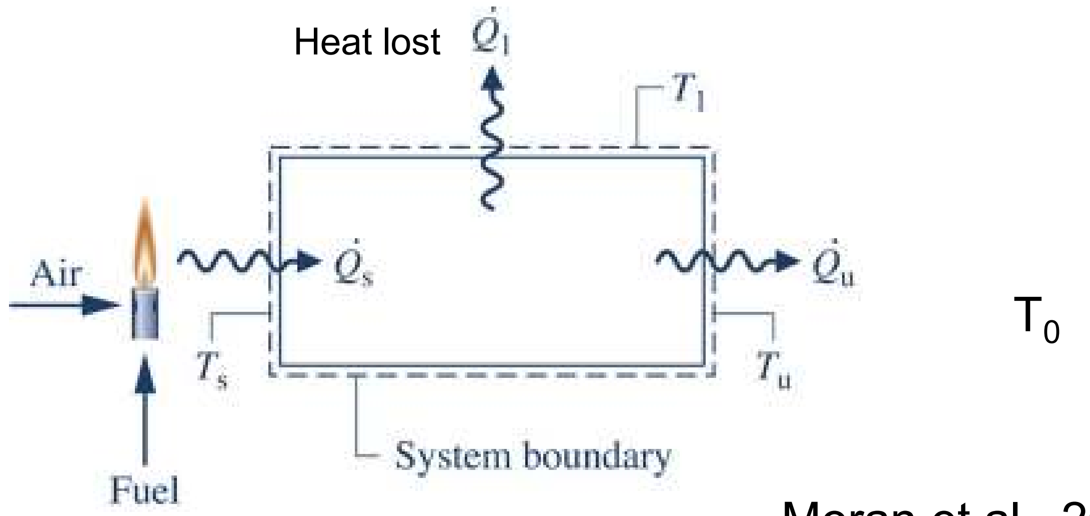
Moran et al., 2014

$$\frac{dE^{0}}{dt} = (\dot{Q}_s - \dot{Q}_u - \dot{Q}_l) - \dot{W}^{0}$$

$$\frac{d\mathsf{E}^{0}}{dt} = \left[\left(1 - \frac{T_0}{T_s}\right)\dot{Q}_s - \left(1 - \frac{T_0}{T_u}\right)\dot{Q}_u - \left(1 - \frac{T_0}{T_l}\right)\dot{Q}_l\right] - \left[\dot{W}^{0} - p_0\frac{dV^{0}}{dt}\right] - \dot{\mathsf{E}}_d$$

# Exergetic Efficiency

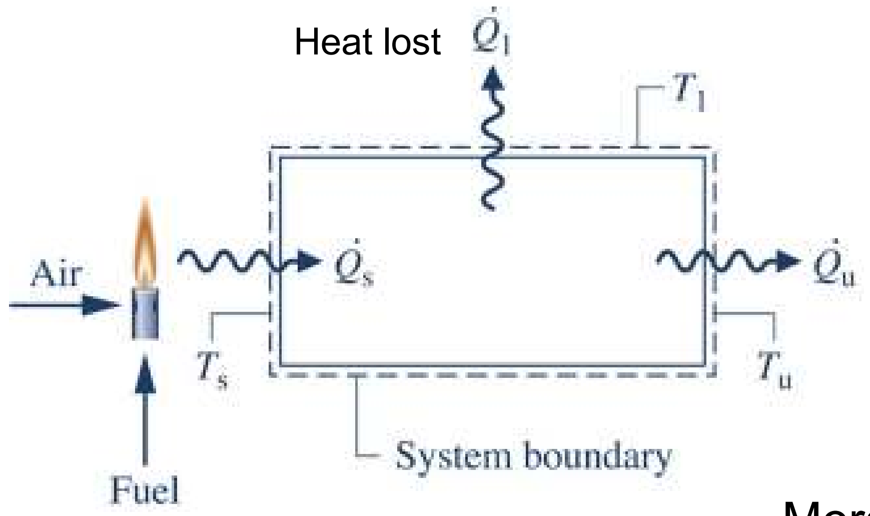
- Energy efficiency?




Moran et al., 2014

# Exergetic Efficiency

- Energy efficiency



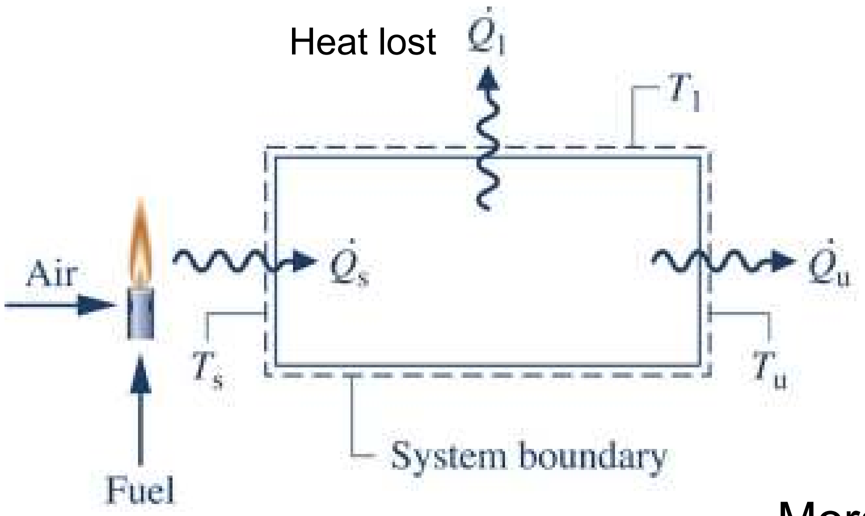

$T_0$

Moran et al., 2014

$$\eta = \frac{\dot{Q}_u}{\dot{Q}_s}$$

# Exergetic Efficiency

- Exergy efficiency?

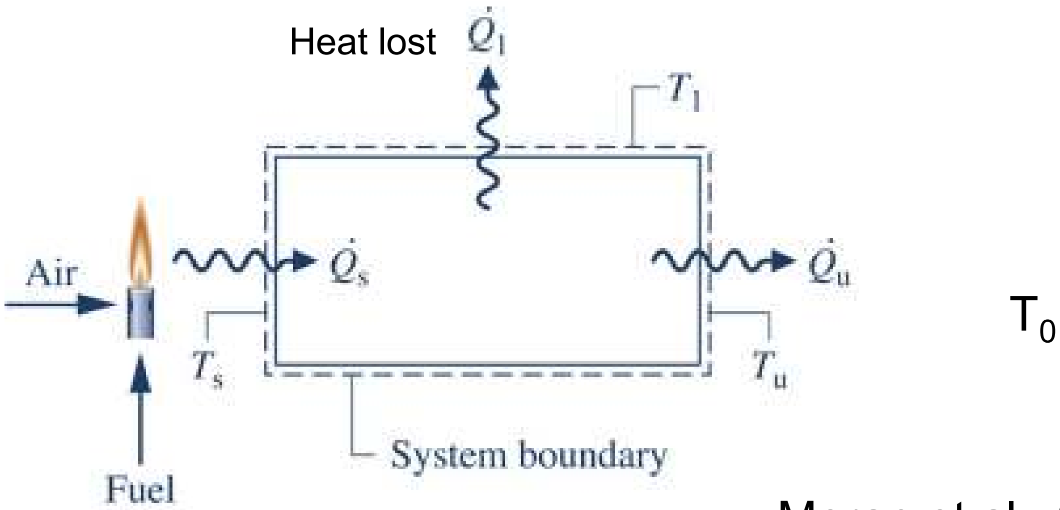



$T_0$

Moran et al., 2014

# Exergetic Efficiency

- Exergy efficiency




Moran et al., 2014

$$\varepsilon = \frac{(1 - T_0/T_u)\dot{Q}_u}{(1 - T_0/T_s)\dot{Q}_s}$$

$$\varepsilon = \eta\left(\frac{1 - T_0/T_u}{1 - T_0/T_s}\right)$$

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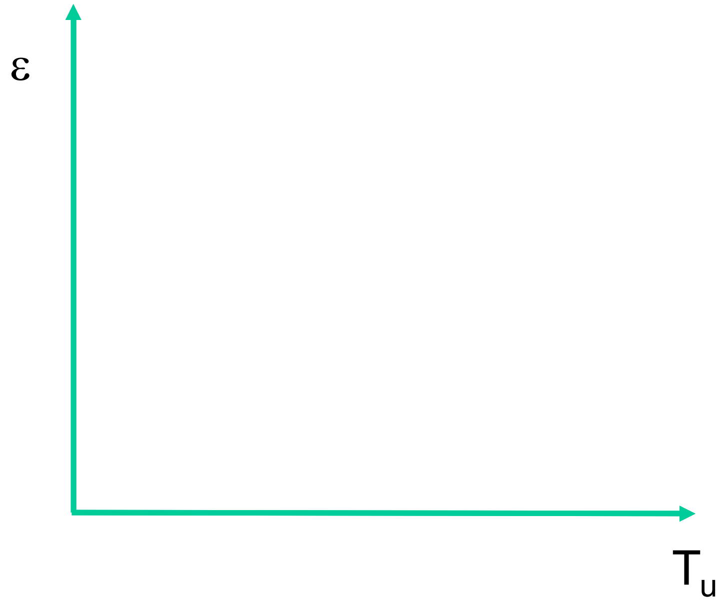
# Exergetic Efficiency

- How does exergy efficiency varies assuming $T_s$=2200K, $\eta$=100% ?

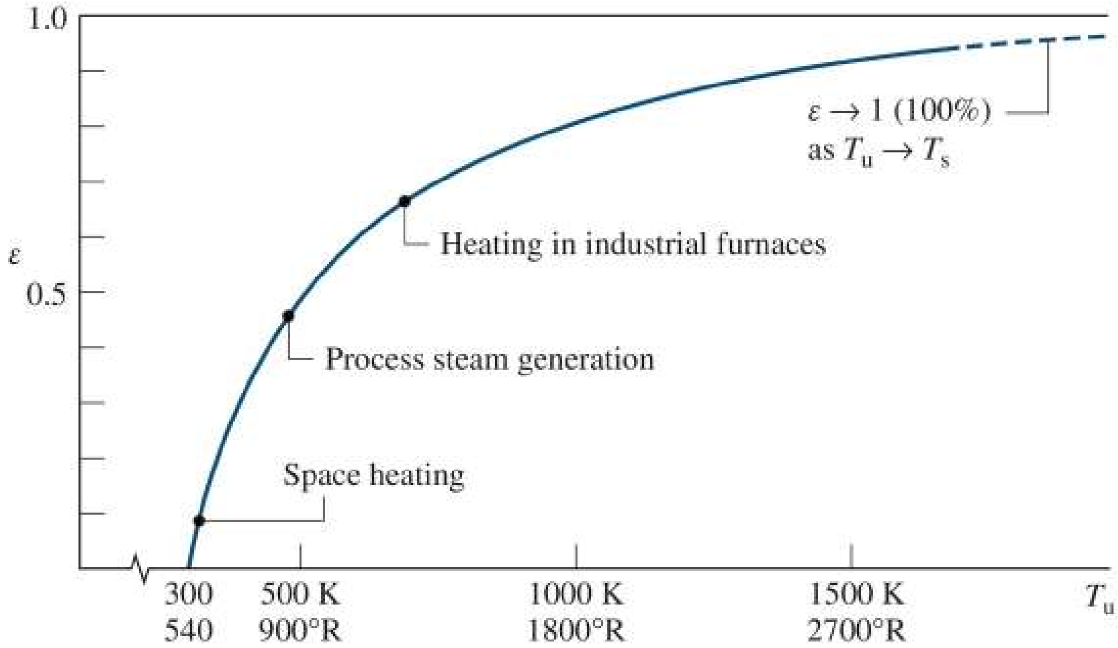



$$\varepsilon = \eta\left(\frac{1 - T_0/T_u}{1 - T_0/T_s}\right)$$

Moran et al., 2014

# Exergetic Efficiency

- Exergy efficiency




$T_s$=2200K
η=100%

Moran et al., 2014

- Exergy analysis: (mis)match between energy used and end-use

# Exergy efficiencies

- 2nd Law efficiency

$$\varepsilon = \frac{W_{max,output}}{W_{max,input}} \longleftarrow \eta = \frac{E_{output}}{E_{input}}$$

# Exergy efficiencies

- 2nd Law efficiency

$$\varepsilon = \frac{W_{max,output}}{W_{max,input}} \longleftarrow \eta = \frac{E_{output}}{E_{input}}$$

- For a device which converts one form of mechanical energy to another $\varepsilon = \frac{W_{output}}{W_{input}} = \eta$

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# Household appliances with electric motors

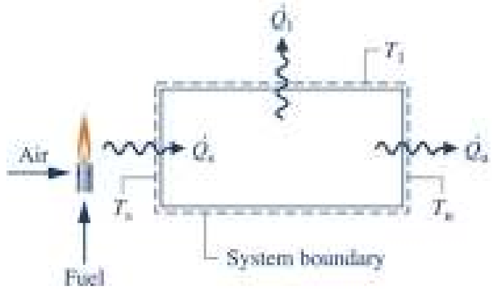
# Exergy efficiencies

- 2nd Law efficiency

$$\varepsilon = \frac{W_{max,output}}{W_{max,input}} \longleftarrow \eta = \frac{E_{output}}{E_{input}}$$

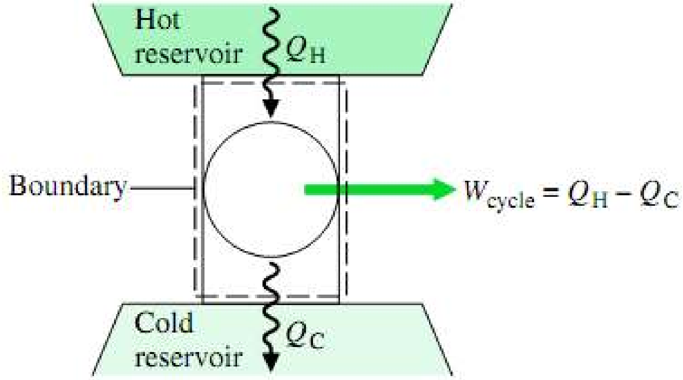
- When the input or output of a device is heat then heat must be downgraded into equivalent units of mechanical work (Cullen & Allwood, 2010)

$$\varepsilon = \frac{(1 - T_0/T_u)\dot{Q}_u}{(1 - T_0/T_s)\dot{Q}_s}$$

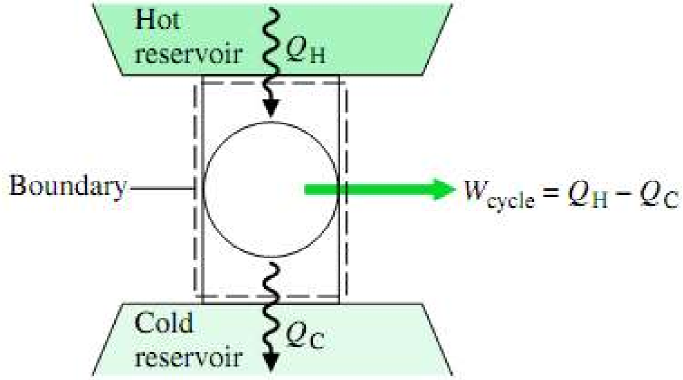



# Exergy Efficiency – Power Cycle

?



# Exergy Efficiency – Power Cycle




$$\varepsilon = \frac{\eta}{\eta_{ideal}}$$

# Exergy efficiencies

- Second law efficiencies are bounded (thay are less than or equal to 100%) - > they provide information on how much you can improve your efficiency.

# Exergy efficiencies

- Exergy losses vs. Exergy destruction

$$\frac{d\mathsf{E}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j - \left(\dot{W} - p_0\frac{dV}{dt}\right) - \dot{\mathsf{E}}_\mathrm{d}$$

$$\varepsilon = \frac{\eta}{\gamma_{ideal}}$$

# Exergy efficiencies

- 2nd Law efficiency

$$\varepsilon = \frac{W_{max,output}}{W_{max,input}} \longleftarrow \eta = \frac{E_{output}}{E_{input}}$$

- When the input is work (electricity) and the output is neither work nor heat (e.g. light or music then

$$\varepsilon = \frac{W_{output}}{W_{max,input}} = \qquad = \frac{\eta}{\eta_{ideal}} = \frac{\eta}{683\ lm/W}$$