

# **Lecture 2.6**

## **The Second Law ...contd**

# .....understanding entropy

**Entropy is a thermodynamic property which decides adiabatic accessibility of states**

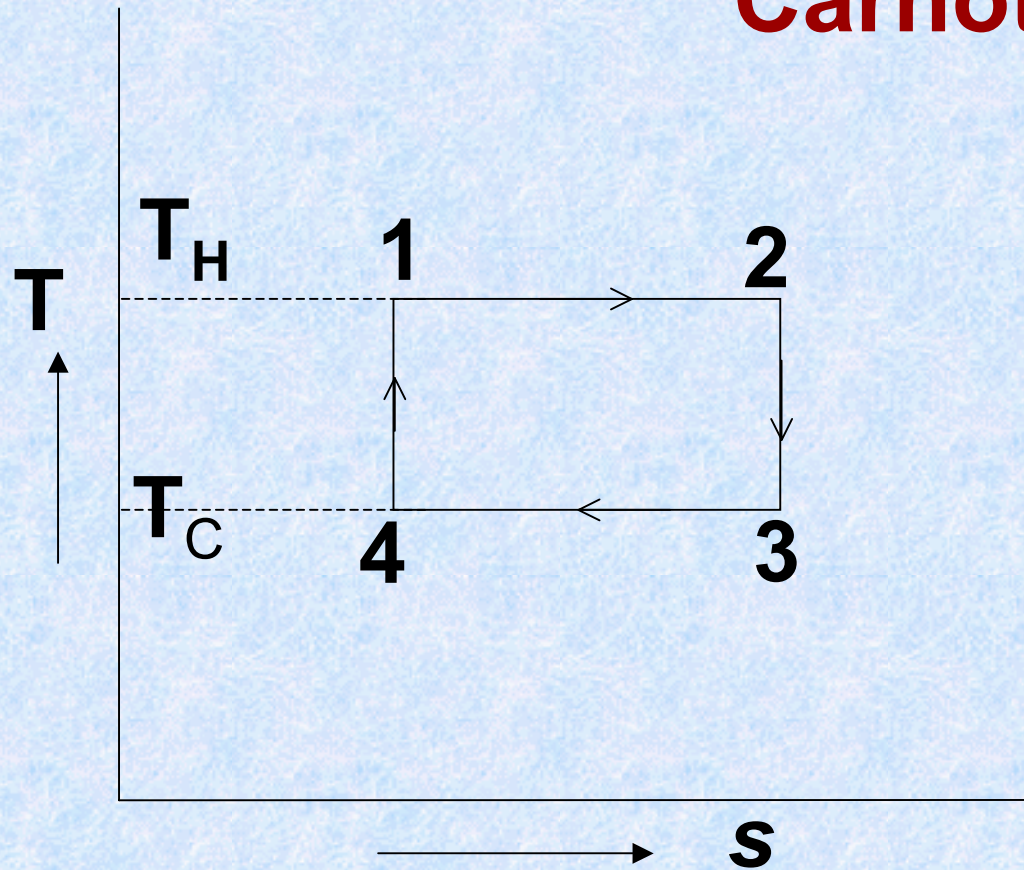
**In a reversible process**

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

**T should be absolute temperature !**

# The Concept of Absolute Temperature

## Carnot Cycle

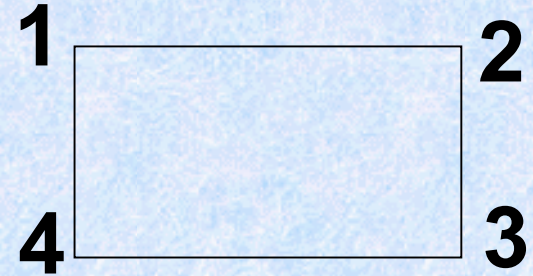


# Carnot Cycle.....

<u>Process</u>	<u>Nature</u>	<u>H.T.</u>
1-2	Isoth	$Q_H$
2-3	Adia	0
3-4	Isoth	$-Q_C$
4-1	Adia	0

# Carnot Cycle.....

For 1-2-3-4 to be a cycle



$$s_2 - s_1 = s_3 - s_4$$

or  $(s_2 - s_1) + (s_4 - s_3) = 0$

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

# Carnot Cycle.....

$$\begin{aligned} \therefore \eta_{carnot} &= \frac{\text{work done}}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \\ &= 1 - \frac{T_C}{T_H} \end{aligned}$$

**Since  $\eta_{carnot}$  depends only on the value of the two temperatures, above equation enables us to define an absolute temperature scale**

# Carnot Cycle.....

$$\therefore T_H = T_C / (1 - \eta_{carnot}) = T_C \left( \frac{Q_H}{Q_C} \right)$$

**Present Convention :choose  $T_C = 273.16$  K for Triple-point of water & determine the 'value' of any temperature from above equation using  $\eta_{carnot}$  as determined experimentally**

# MEASUREMENT OF ABSOLUTE TEMPERATURE

- ◆ **Difficulty of building heat engine operating on Carnot cycle**
- ◆ **Need for practically usable methods**
- ◆ **Constant volume gas thermometer**
- ◆ **Platinum resistance thermometers calibrated against easily reproducible states : triple points of O<sub>2</sub>, Hg ; M.P. of Ga, Zn etc.**

# The Concept of Absolute Temperature

- **Achieving Absolute Zero temperature**
- **It can be shown that the definition of absolute temperature (also called Thermodynamic temperature) implies that it is impossible to achieve temperatures below absolute zero.**

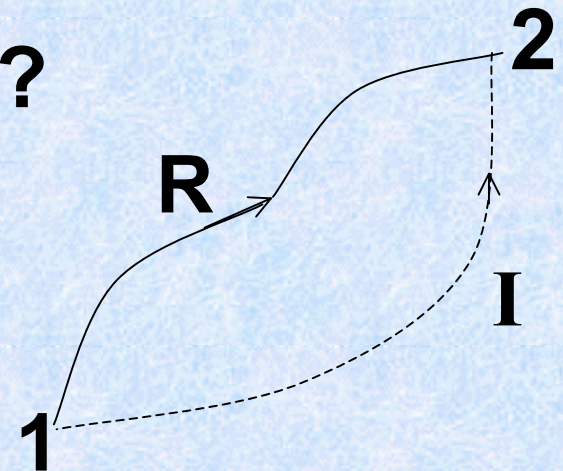
# DEFINING ABSOLUTE ZERO TEMPERATURE

**If a system undergoes a reversible isothermal process between two reversible adiabatics, without heat transfer, the temperature at which this process takes place is called absolute zero.**

# ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

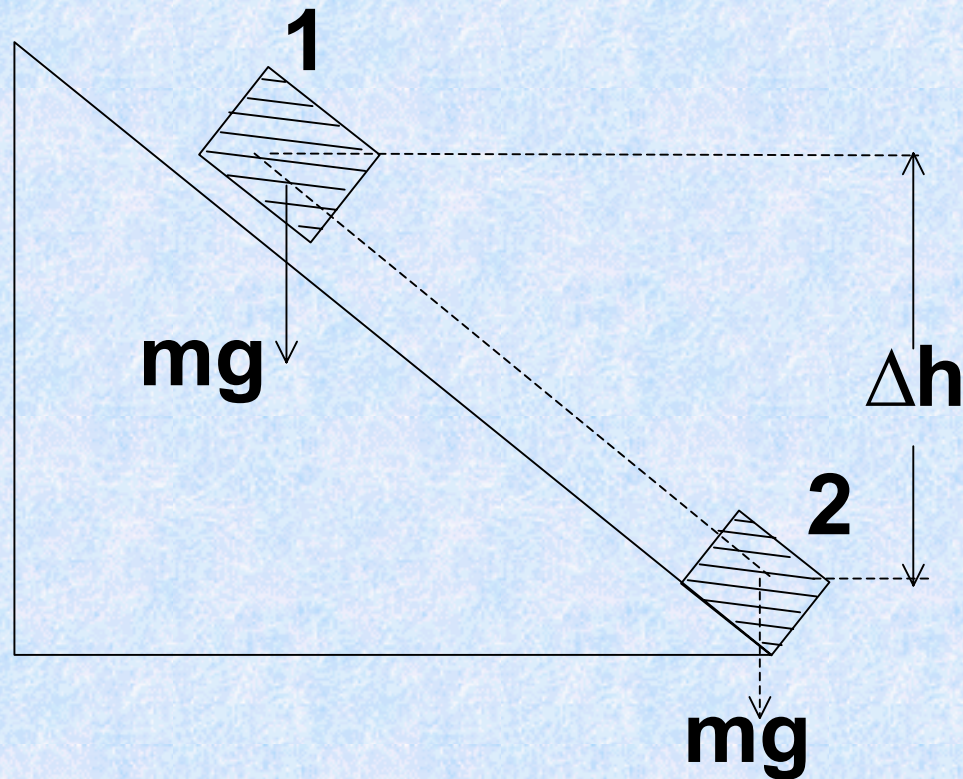
Entropy is a Property .....

$$(s_2 - s_1)_I = (s_2 - s_1)_R$$



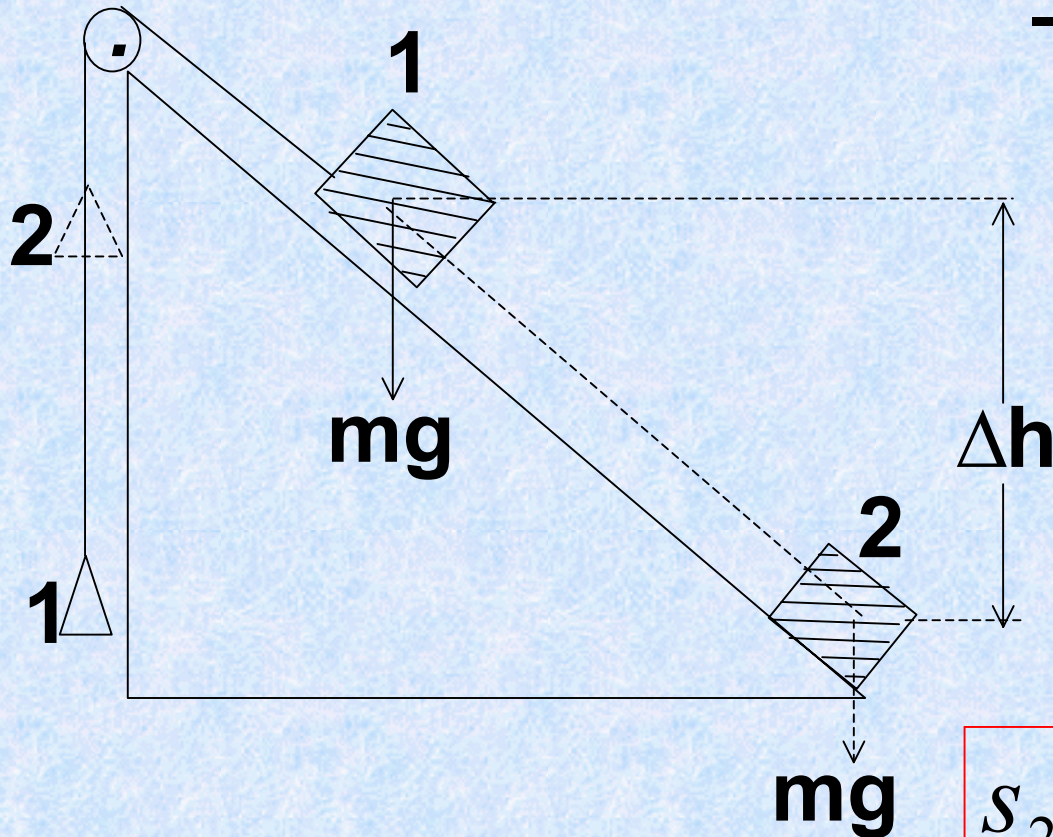
# ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

## Entropy Increase due to Friction



# ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

.....due to Friction



$$\Delta W_{in} = -mg \Delta h$$

$$\Delta Q_{in} = mg \Delta h$$

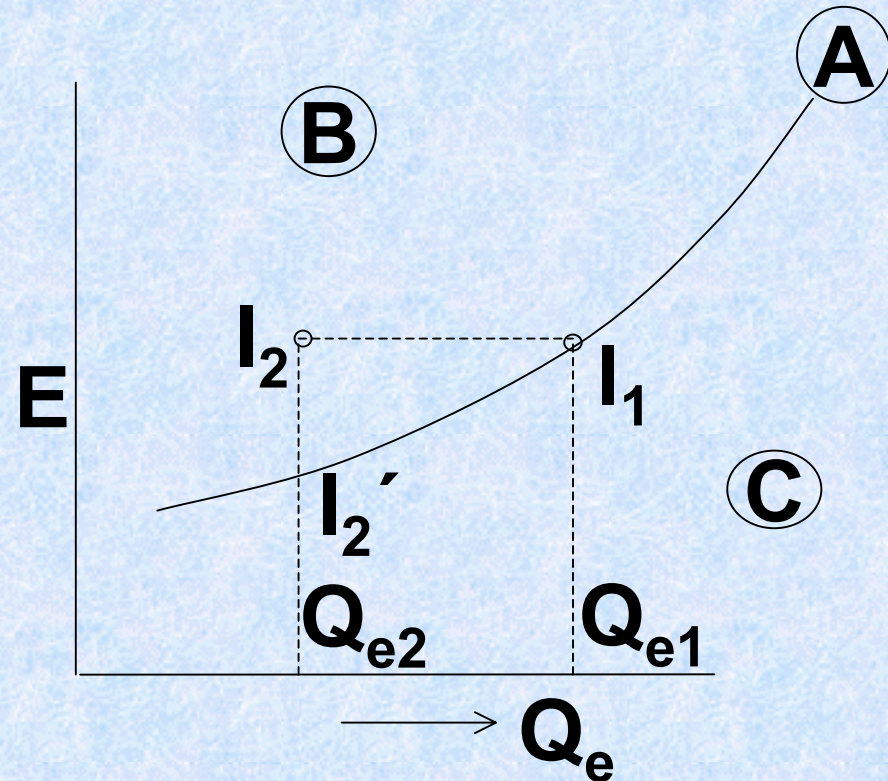
$$s_2 - s_1 = mg \Delta h / T$$

# ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

.....due to short-circuiting of a battery

$$W_{on} = \int V dQ_e = V_{avg} (Q_{e2} - Q_{e1})$$

$$S_2 - S_1 = \frac{Q_{avg}}{T_{avg}} = \frac{V_{avg} (Q_{e1} - Q_{e2})}{T_{avg}}$$



# ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

## Other examples

- **Free expansion of a compressible fluid**
- **Heat transfer between two reservoirs having finite temperature difference**

**End of Lecture**

# **Lecture 2.7**

## **The Second Law .....Corollaries**

# .....Recap

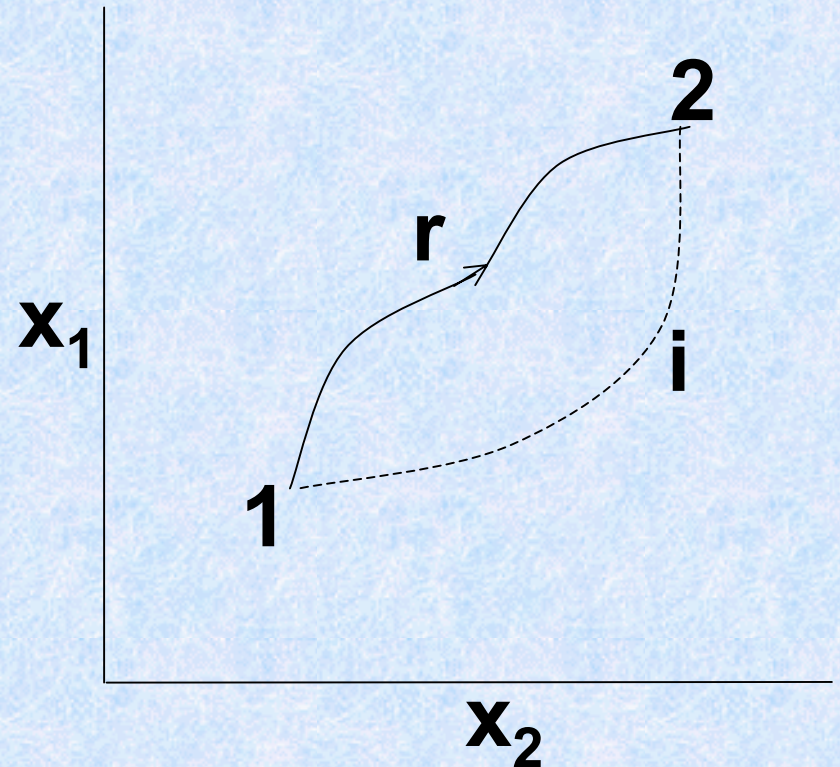
- **Caratheodory's formulation of 2nd Law**
- **Reversible & Irreversible processes**
- **Concept of Entropy**
- **Concept of Absolute Temperature**
- **Entropy change in an irreversible process**

# Work done in an Irreversible Process

$$r : \Delta E = \Delta Q_r + \Delta W_r$$

$$i : \Delta E = \Delta Q_i + \Delta W_i$$

$$\Delta W_i = \Delta W_r + \Delta Q_r - \Delta Q_i$$



Is  $\Delta Q_r - \Delta Q_i > < = 0$ ?

# Work done in an Irreversible Process

- \* Assume 1 - 2 in close proximity so that the temp  $T$  doesn't change much during the process
- $\Delta S$  is same in both the processes
- $\Delta Q_r = T \Delta S$   
 $\therefore \Delta Q_r - \Delta Q_i = T \Delta S - \Delta Q_i$

# Work done in an Irreversible Process

Consider the 3 possibilities

$$T \Delta S - \Delta Q_i > 0$$

$$T \Delta S - \Delta Q_i < 0$$



Which of these two is correct ?

or

$$T \Delta S - \Delta Q_i = 0$$

**X**



Process 1 is irreversible & this eq. is valid only for reversible process.

# Work done in an Irreversible Process

Since above discussion is general, it should also apply to the special case of an adiabatic process, i.e.  $\Delta Q_i = 0$

For this special case, these inequalities give

$$T \Delta S > 0 \text{ or } T \Delta S < 0$$

Which is correct ?

# Work done in an Irreversible Process

Since in an irreversible adiabatic process the entropy can only increase

$$\therefore T \Delta S > 0$$

Therefore for any irreversible process

$$T \Delta S - \Delta Q_i > 0$$

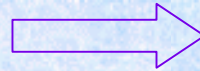
$$\Delta S > \Delta Q_i/T$$

Recall, for a reversible process

$$\Delta S = \Delta Q_r/T$$

# Work done in an Irreversible Process

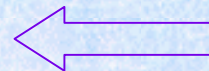
$$T\Delta S - \Delta Q_i > 0$$



$$\Delta Q_r - \Delta Q_i > 0$$



$$(-\Delta W_i) < (-\Delta W_r)$$



$$\Delta W_i > \Delta W_r$$



**Work output in an irreversible process is smaller**



**Work input in irreversible process is greater**

# Work done in an Irreversible Process

**Conclusion** : Starting from a given initial state, to reach the same final state work input required is larger in an irreversible process.

In a work producing cycle  $W_{\text{irr}} < W_{\text{rev}}$

# Work done in an Irreversible Process

Condition under which this result is derived?

Pts 1-2 close to each other,  $T \approx T_1 \approx T_2$   
= temp of thermal reservoir

It is possible to have work output in an irreversible process  $>$  that in a reversible process between the same end states

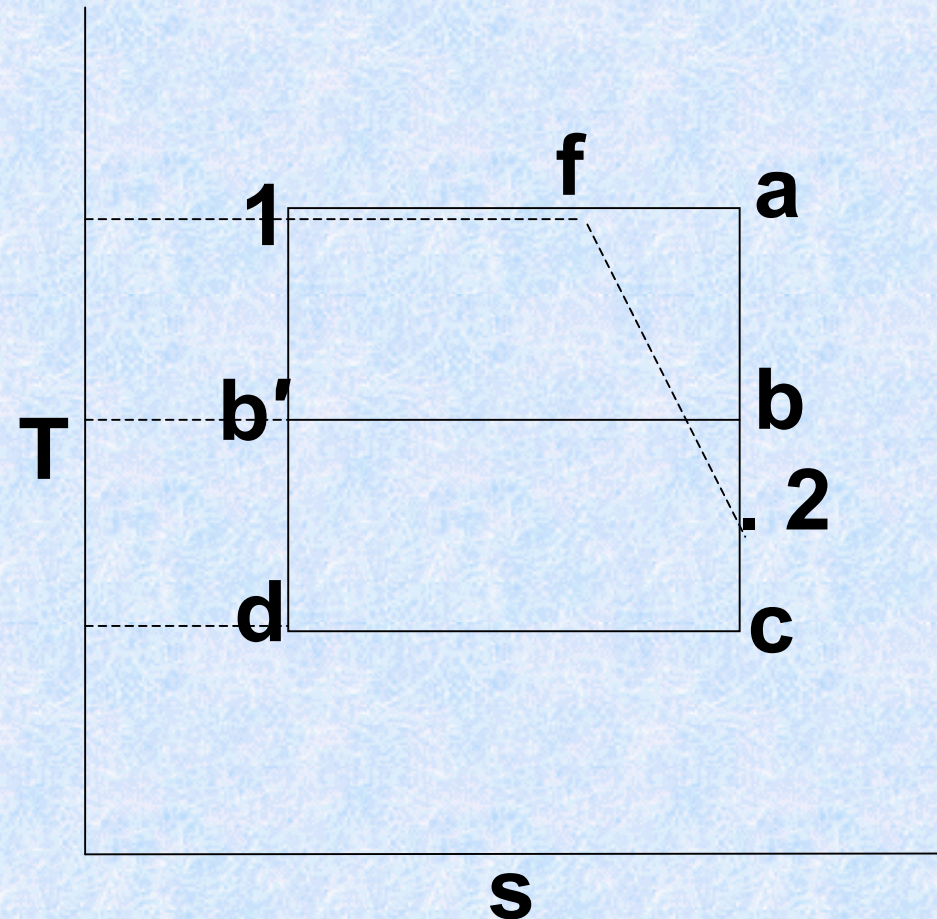
# Work done in an Irreversible Process

## Reversible paths

1 - a - 2

1 - b' - b - 2

1 - c' - c - 2



# Work done in an Irreversible Process

$$T_a > T_b > T_c \quad Q_a > Q_b > Q_c$$

$$\bullet E_2 - E_1 = Q_a + W_{\text{on},a} = Q_b + W_{\text{on},b} = Q_c + W_{\text{on},c}$$

$$\therefore W_{\text{on},a} < W_{\text{on},b} < W_{\text{on},c}$$



$$W_{\text{by},a} > W_{\text{by},b} > W_{\text{by},c}$$

since  $E_2 < E_1$

$W_{\text{on}}$  is -ve

1-f-2 irreversible  $W_{\text{by},f} < W_{\text{by},a}$

But  $W_{\text{by},f}$  can be  $> W_{\text{by},c}$  !

# BASIC EQ. OF THERMODYNAMICS

**Combining the expressions for entropy change in reversible and irreversible processes**

$$dS \geq \frac{dQ}{T} \geq \frac{dE - dW}{T} \\ \geq \frac{\left( dE + \sum f_i'' dx_i'' \right)}{T}$$

# BASIC EQ. OF THERMODYNAMICS

$$TdS \geq dE + \sum f_i'' dx_i''$$

$$TdS \geq dE - \sum f_i'' dx_i'$$

$$\left\{ \text{If } dx_i' = - dx_i'' \right.$$

**For a reversible process**  $f_i'' = f_i'$

# BASIC EQ. OF THERMODYNAMICS

For a reversible process

$$Tds = dE - \sum f_i' dx_i'$$

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**Basic equation of thermodynamics  
applicable to all processes !!**

**End of Lecture**

# **Lecture 2.8**

## **The Second Law .....Corollaries**

# SECOND LAW FOR CYCLIC PROCESSES

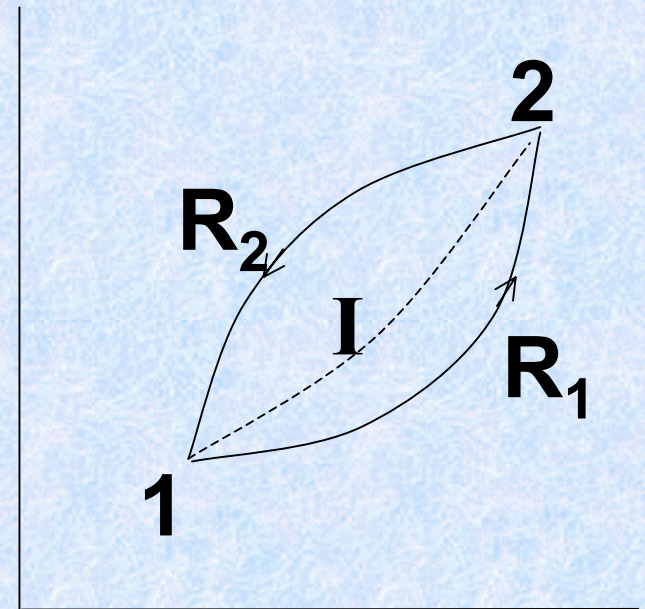
For all cycles

$$\oint dS = 0$$

for reversible cycle  $R_1 - R_2$

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

$$\therefore \oint dS = 0 \Rightarrow \oint \frac{dQ}{T} = 0 \text{ ----- } I$$



# SECOND LAW FOR CYCLIC PROCESSES

For irreversible cycle I – R<sub>2</sub>

Process I

$$dS > \frac{dQ}{T} \Rightarrow \int_I dS > \int_I \frac{dQ}{T}$$

Process R<sub>2</sub>

$$dS = \frac{dq}{T} \Rightarrow \int_{R_2} dS = \int_{R_2} \frac{dq}{T}$$

# SECOND LAW FOR CYCLIC PROCESSES

For irreversible cycle I – R<sub>2</sub>

$$\therefore \oint dS = \int_I dS + \int_{R_2} dS > \oint \frac{dQ}{T}$$

$$\int \frac{dQ}{T} < 0 \text{ ----- II}$$

# SECOND LAW FOR CYCLIC PROCESSES

Combine I & II to get  
Clausius Inequality

$$\oint \frac{dQ}{T} \leq 0$$

Applying to power cycles

$$\frac{Q_h}{T_h} - \frac{Q_c}{T_c} \leq 0$$

or

$$\frac{Q_h}{Q_c} \leq \frac{T_h}{T_c} \quad ; \quad \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$$

# SECOND LAW FOR CYCLIC PROCESSES

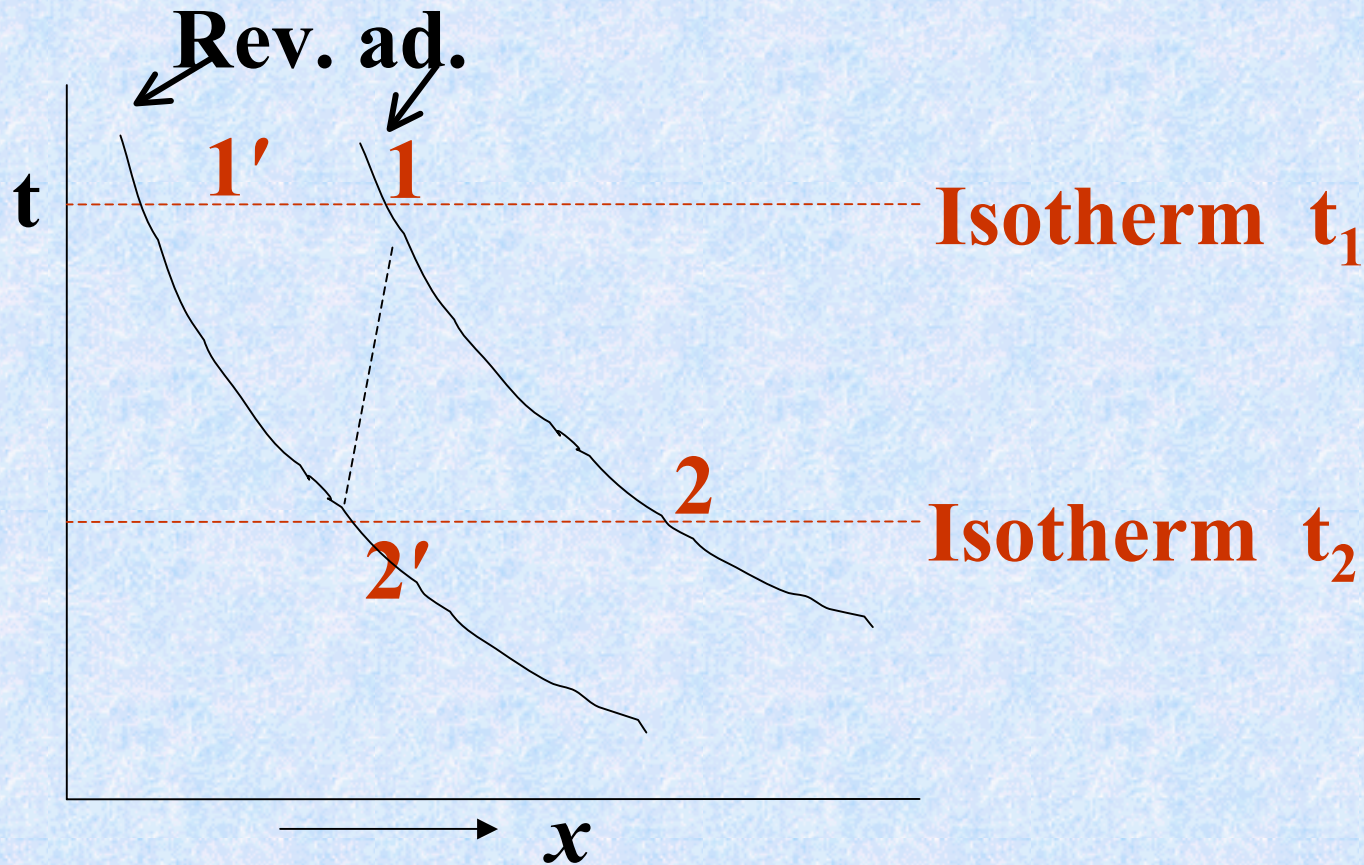
$$\therefore \eta = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h}$$

⇒ ( $\eta < 1$ ) : Kelvin Planck Statement of 2<sup>nd</sup> Law

**Carnot Cycle (Reversible Engine)**  
is the most efficient in  
conversion of heat to Work.

Similarly derive Clausius Statement of  
2<sup>nd</sup> Law by considering a Reversed CC.

# EQUIVALENCE OF CARATHEDORY'S FORMULATION with Kelvin-Planck Statement

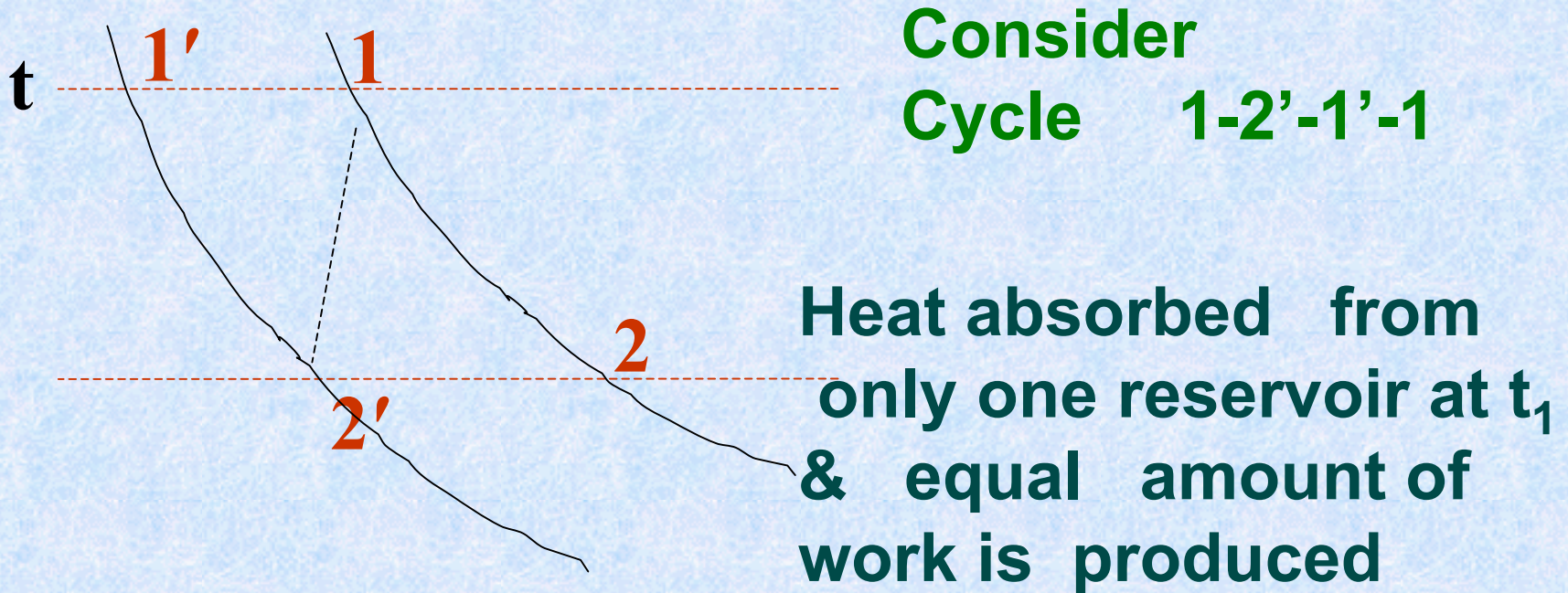


# EQUIVALENCE OF CARATHEDORY'S FORMULATION with Kelvin-Planck Statement

Caratheodory: 2'  
inaccessible  
adiabatically from 1

Suppose this is not true i.e. 2' is  
then adiabatically accessible from 1  
(say process 1-2')

# EQUIVALENCE OF CARATHEDORY'S FORMULATION WITH Kelvin-Planck Statement



**THIS VIOLATES K-P STATEMENT**

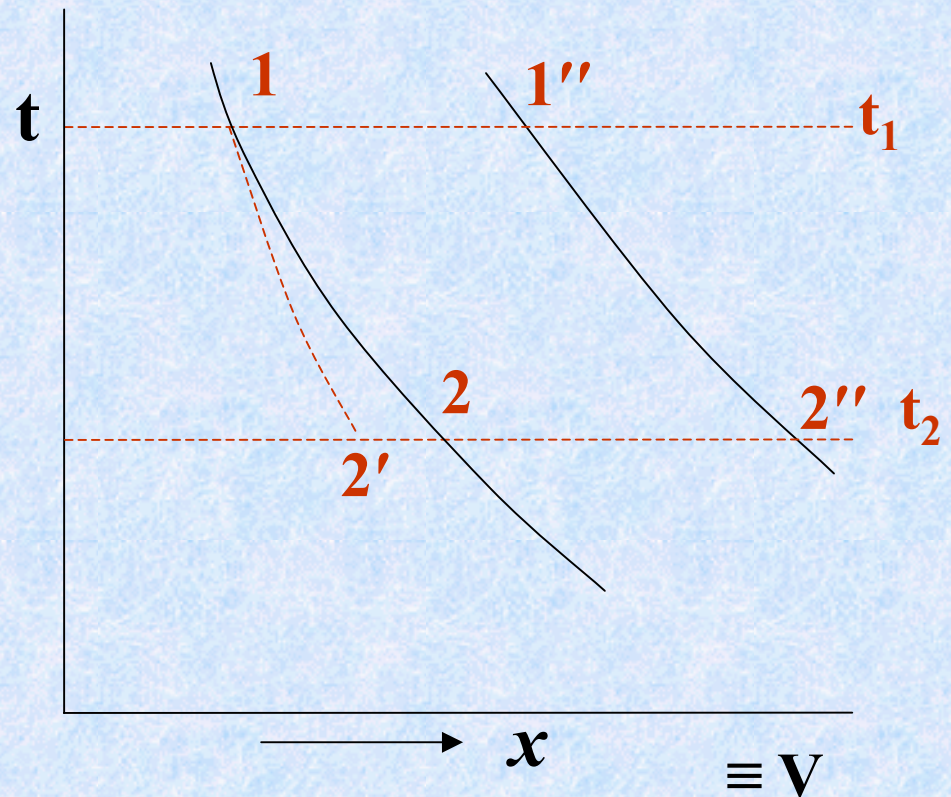
# Equivalence of Caratheodory's formulation with Clausius Statement

Caratheodory : 1-2' can't be an adiabatic process

NB 2' has been so located that

$$Q_{1-1''} = Q_{2'-2''}$$

{both +ve}



# Equivalence of Caratheodory's formulation with Clausius Statement

Assuming Caratheodory's axiom is incorrect  
1-2' could be an adiabatic process.

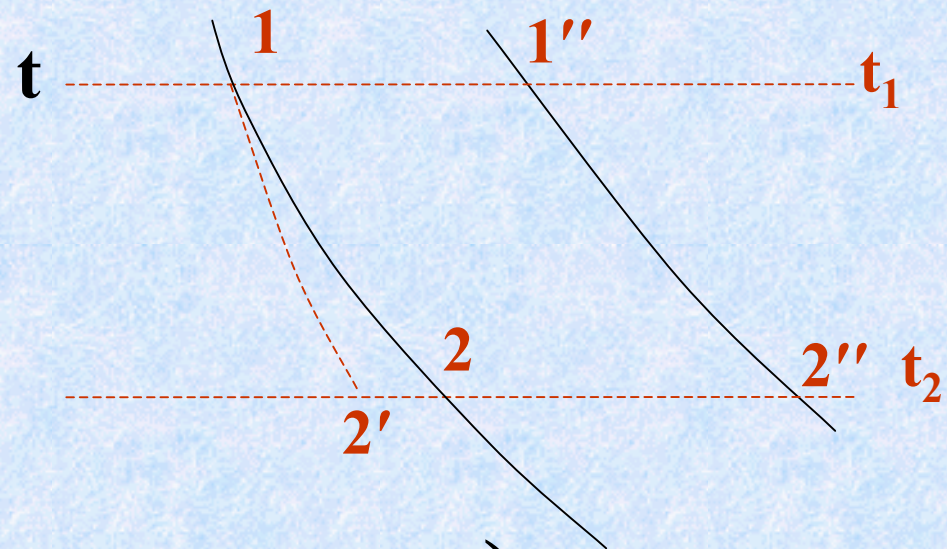
Then consider cycle 1- 2'- 2'' -1''- 1

It has two heat transfers, viz

$$Q_{2'2''} \rightarrow +ve$$

$$Q_{1''-1} \rightarrow -ve$$

$$\Sigma (Q_{1''-1} + Q_{2'2''}) = 0$$



# Equivalence of Caratheodory's formulation with Clausius Statement

$Q_{\text{net}} = 0 = W_{\text{net}} \Rightarrow$  Heat  $|Q_{2'2''}|$  has been absorbed at low temp.  $t_2$  & delivered to high temp.  $t_1$ , without any work input



**VIOLATION OF CLAUSIUS STATEMENT**

**End of Lecture**

# **Lecture 2.9**

## **The Second Law .....Corollaries & Applications**

# ENTROPY MAX PRINCIPLE

for any process

$$dS \geq \frac{dQ}{T} \Rightarrow dS = \frac{dQ}{T} + d\sigma$$

where  $d\sigma \geq 0 \equiv$  **entropy gen.**

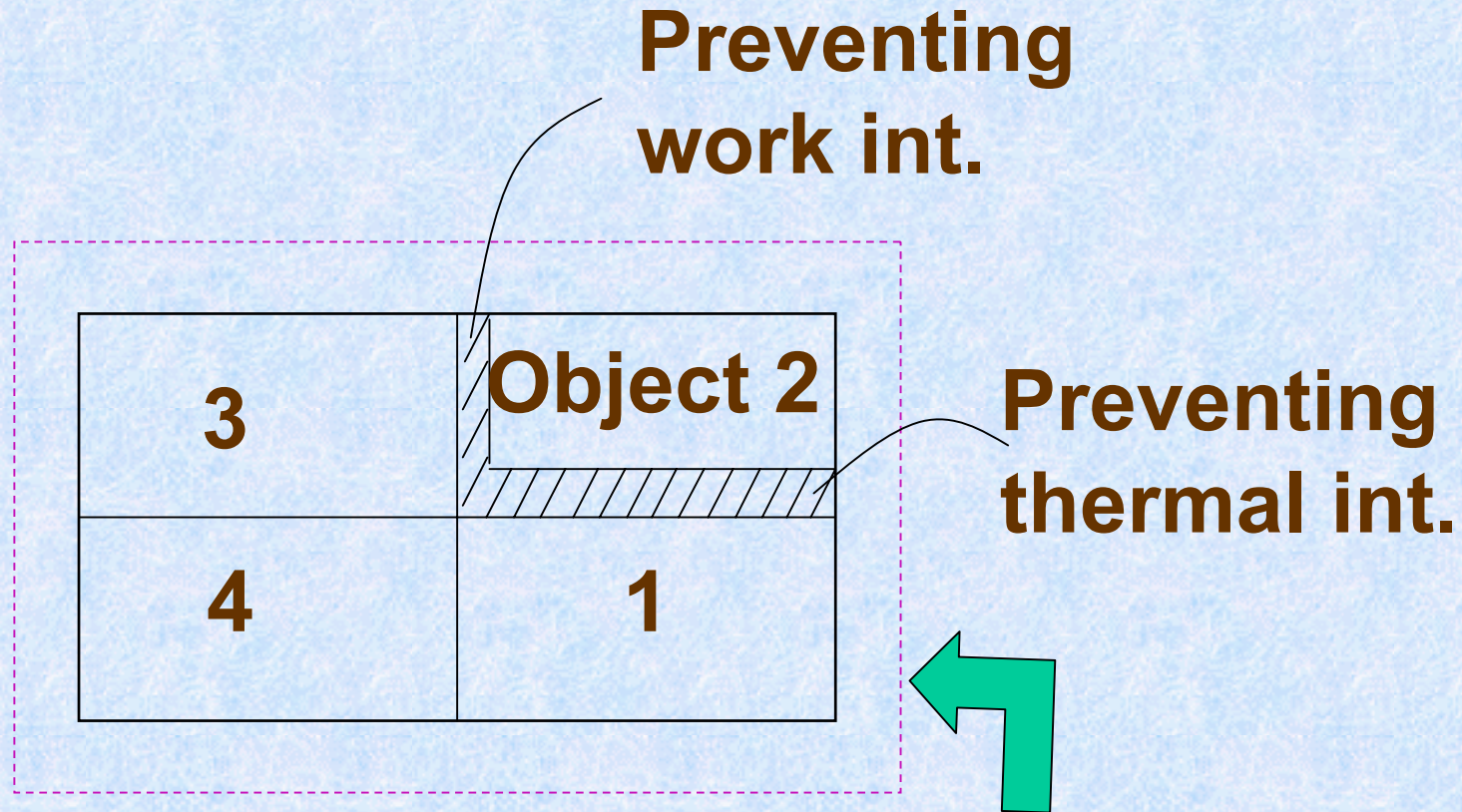
In rate terms:  $\frac{dS}{dt} = \frac{\dot{Q}}{T} + \frac{d\sigma}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma}$

**In the absence of thermal interaction**

$$ds = d\sigma \geq 0$$

**Principle of Increase of entropy**

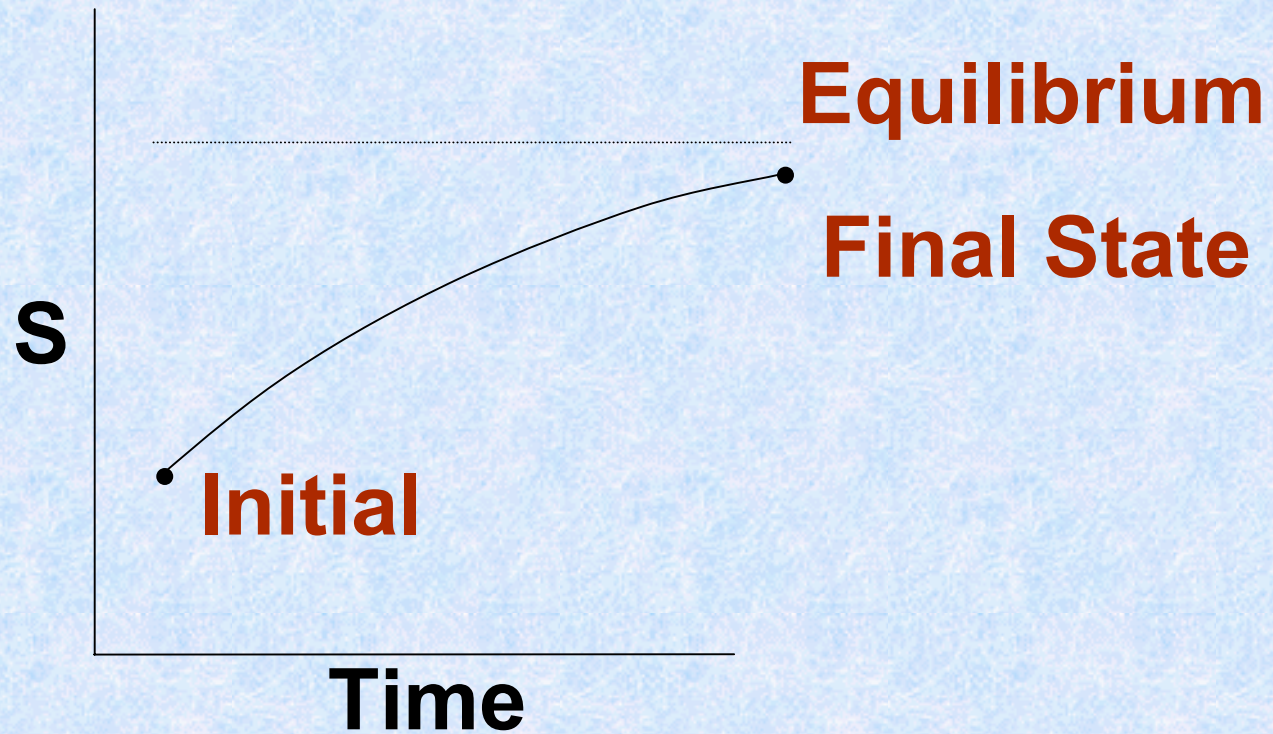
# ENTROPY MAX PRINCIPLE



Composite system is isolated

**The entropy reaches maximum possible value at the equilibrium**

# ENTROPY MAX PRINCIPLE



Trend to Equilibrium

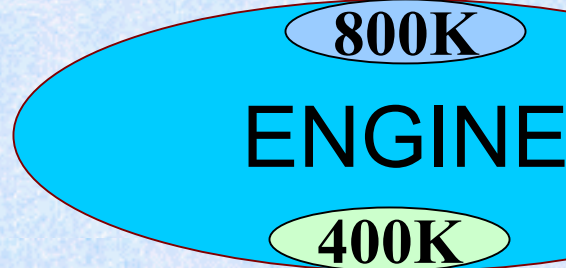
# Examples of Second Law Analysis

A heat engine operates in a cycle between two thermal reservoirs at 300K and 900K and produces 100kW power. Find the heat rejection and entropy generation when the engine is internally reversible but receives heat and rejects heat at 800K and 400k respectively

$$T_h = 900 \text{ K}$$

 $Q_h$ 

First Law in  
rate terms:

 $100 \text{ kW}$  $Q_c$ 

$$T_c = 300 \text{ K}$$

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} = \dot{Q} + \dot{W}$$

For this cycle:

$$0 = \Sigma Q - 100$$

$$Q_h - Q_c = 100$$

Since the engine is internally  
reversible :  $Q_h/800 - Q_c/400 = 0$

$$Q_h = 200 \text{ kW}$$

$$Q_c = 100 \text{ kW}$$

# Example 1....

Second Law in rate terms:

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T} + \frac{d\sigma}{dt}$$

For this cycle :

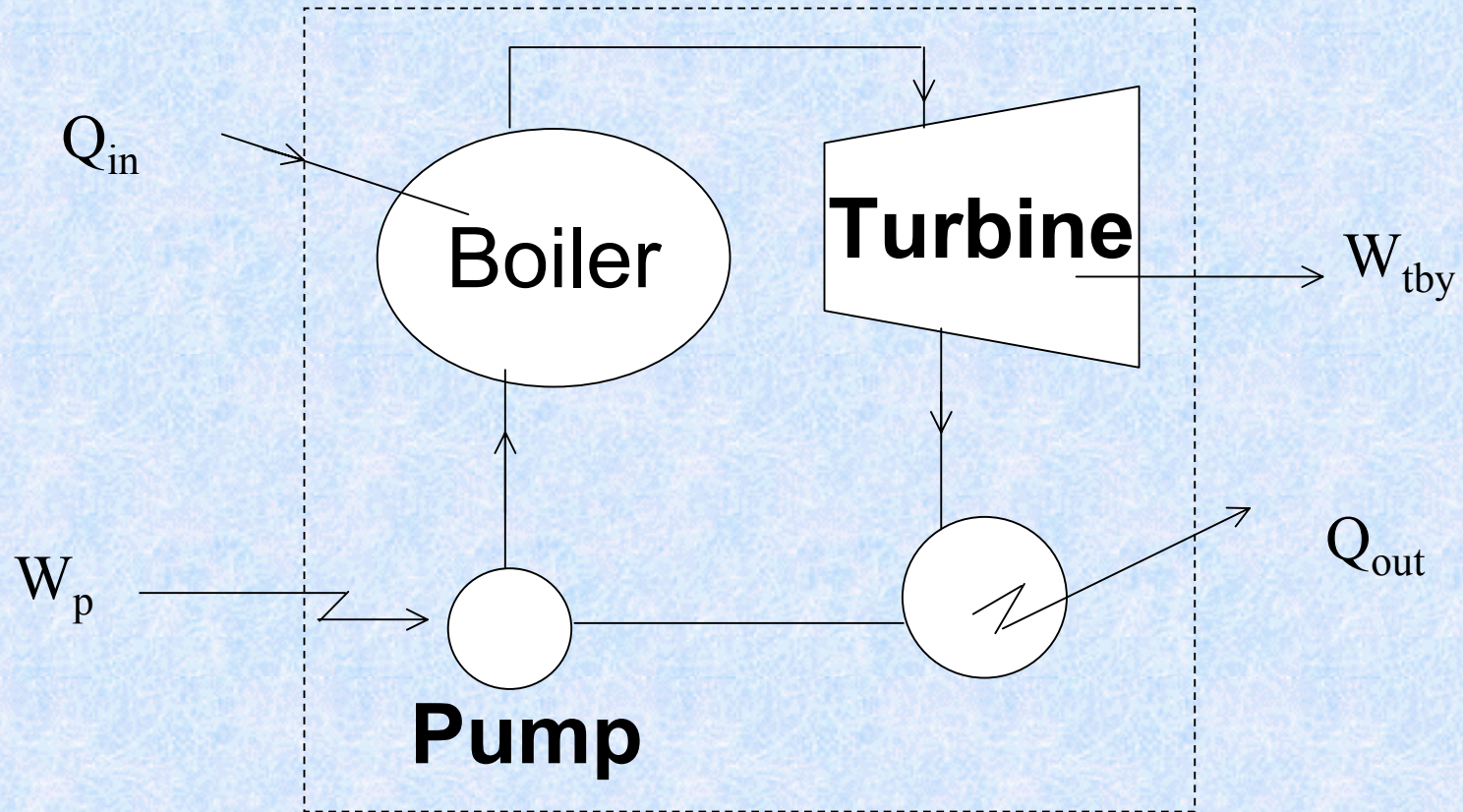
$$\frac{d\sigma}{dt} = - \left\langle \frac{Q_h}{900} - \frac{Q_c}{300} \right\rangle$$

This gives entropy generation rate as:  
- [ 200/900 - 100/300 ] = 0.111 kW / K

## EXAMPLE 2

A simple steam power cycle producing **100 MW** of power receives heat at **900K** in the boiler and rejects heat at **320K**. The condensate pump consumes **50kW** of power, and the boiler consumes **54 tonnes/hour** of coal. Assuming that the combustion of **1Kg** of coal releases **20MJ** of heat determine the thermal efficiency and entropy generation in the cycle.

# EXAMPLE 2.....



## EXAMPLE 2 .....

**First Law (for System within dashed line boundaries)**

$$\frac{dE}{dt} = \dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{P,in} - \dot{W}_{T,by}$$

**Under steady state conditions,  $\frac{dE}{dt} = 0$**

$$\Rightarrow \dot{Q}_{in} - \dot{Q}_{out} = \dot{W}_{T,by} - \dot{W}_{P,in}$$

**Here**

$$\begin{aligned}\dot{Q}_{in} &= \frac{54 \times 1000}{3600} \times 20 \text{ MJ/S} \\ &= 300 \text{ MW}\end{aligned}$$

$$\begin{aligned}\dot{Q}_{out} &= 300 - 100 \\ &= 200 \text{ MW}\end{aligned}$$

$$\eta = \frac{100}{300} = 33.3\%$$

## EXAMPLE 2 .....

**Second Law ( for system within dashed line boundaries)**

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T} + \dot{\sigma}$$

**Under steady state conditions,**  $\frac{dS}{dt} = 0$

$$\Rightarrow \dot{\sigma} = -\sum \left( \frac{\dot{Q}}{T} \right)$$

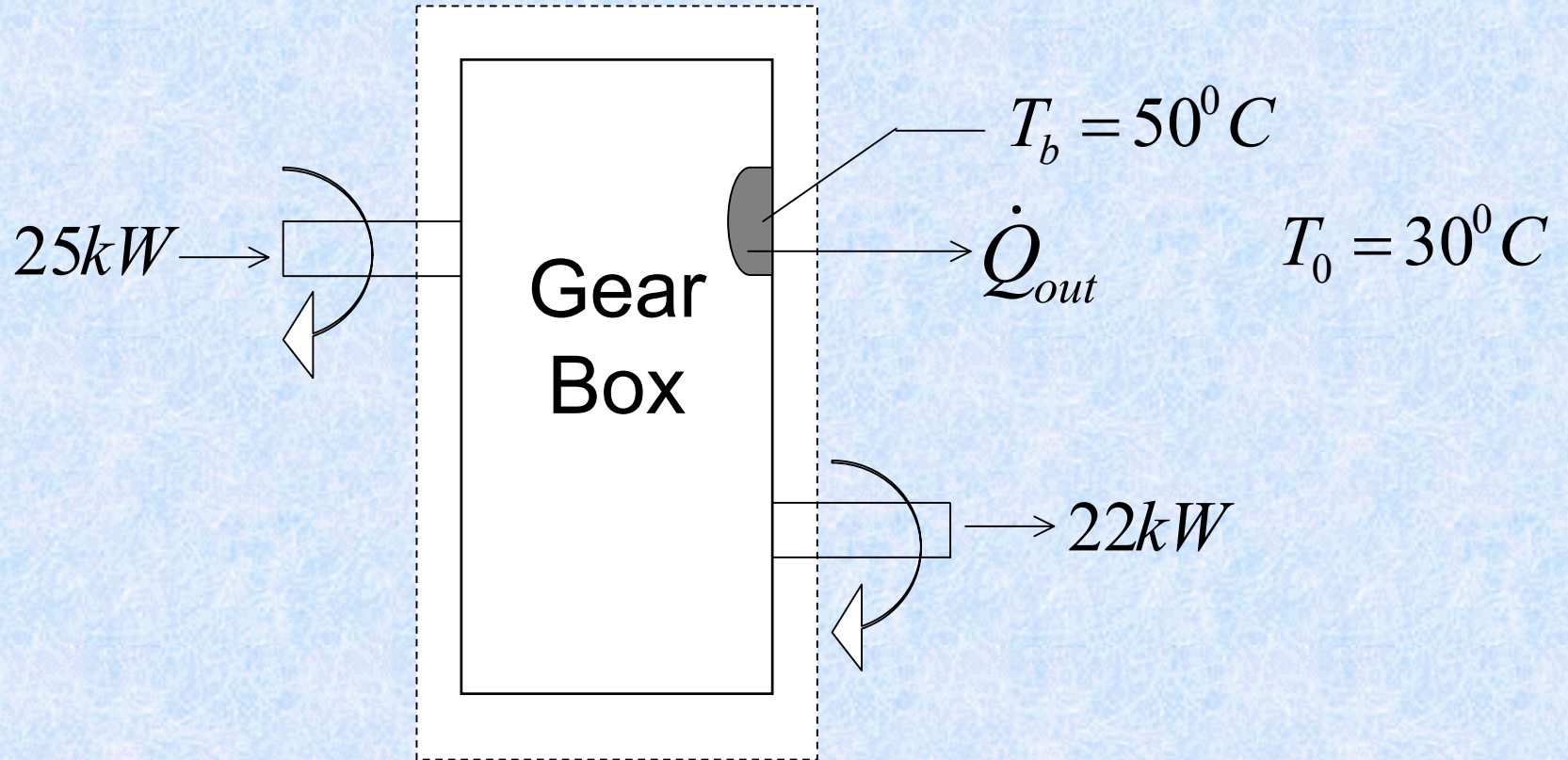
**Here**

$$\begin{aligned} \dot{\sigma} &= -\left( \frac{300}{900} - \frac{200}{320} \right) \frac{MW}{K} \\ &= .2917 MW/K \end{aligned}$$

## EXAMPLE 3

The gear box of a machine is operating under steady-state conditions. The input shaft receives **25 kW** from a prime mover and transmits **22kW** to the output shaft, the rest being lost due to friction etc. The gear box surface is at an average temperature of **50°C** and loses heat to the surroundings at **30°C**. Estimate the rate of entropy production inside the gear box.

# EXAMPLE 3



## EXAMPLE 3

Since the gear box is operating in steady state,

First Law  $0 = 25 - 22 - \dot{Q}_{out} \Rightarrow \dot{Q}_{out} = 3 \text{KW}$

Second Law  $\dot{\sigma} = -\sum \left( \frac{\dot{Q}}{T} \right) = \frac{\dot{Q}_{out}}{T} = \frac{3 \times 1000}{323} = 9.289 \text{ W/K}$

**Entropy production outside the box?**

**End of Lecture**

# **Lecture 2.9**

## **The Second Law .....Corollaries & Applications**

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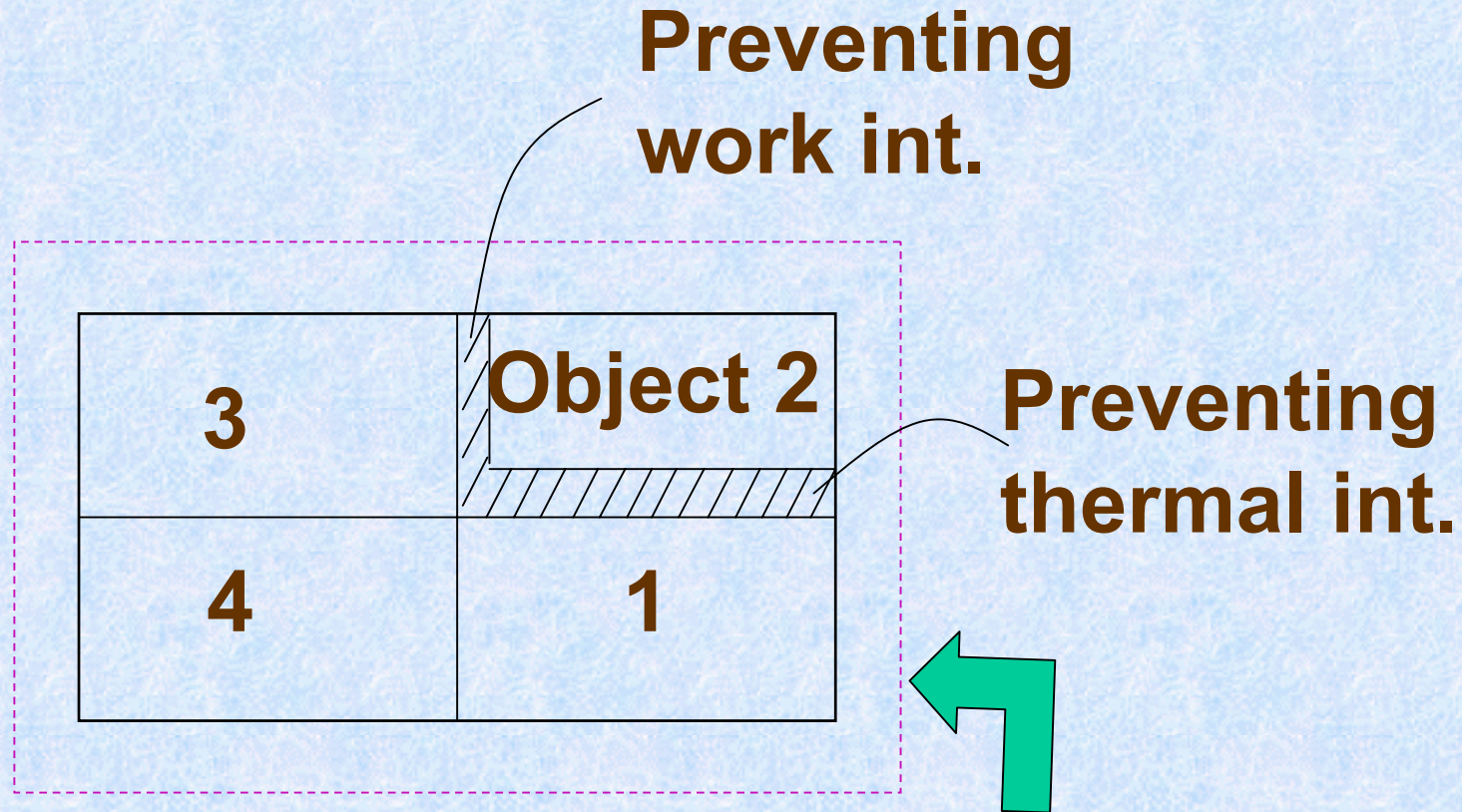
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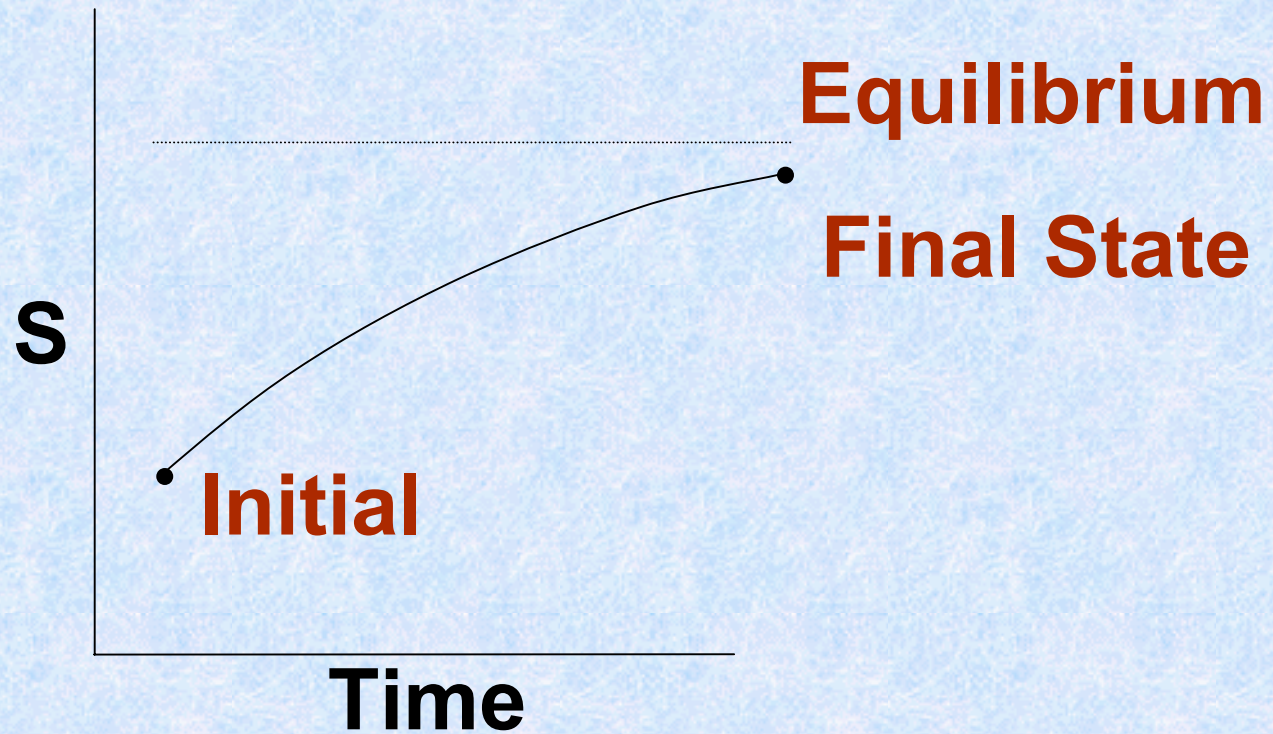
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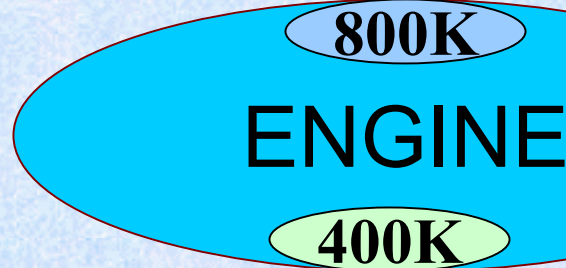
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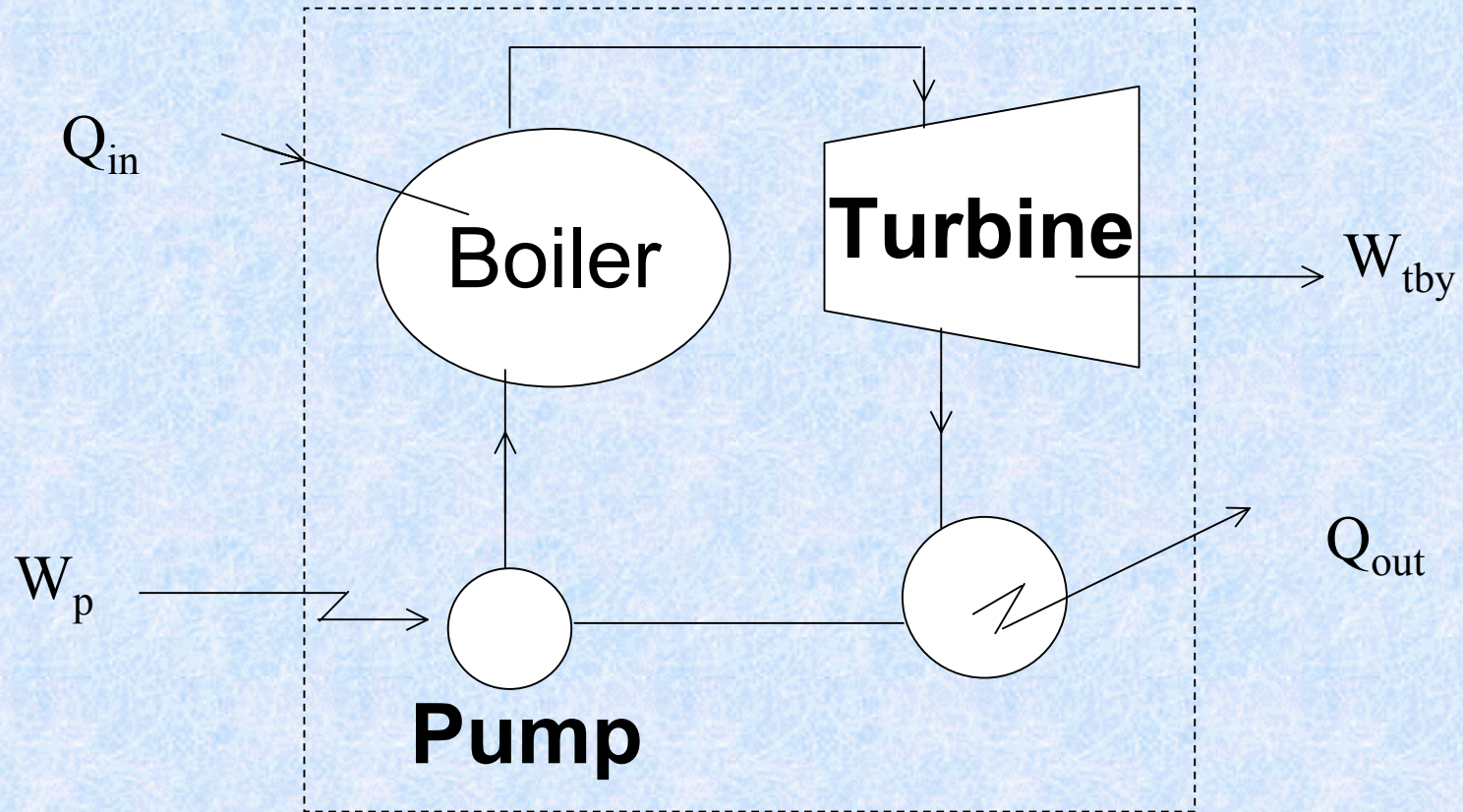
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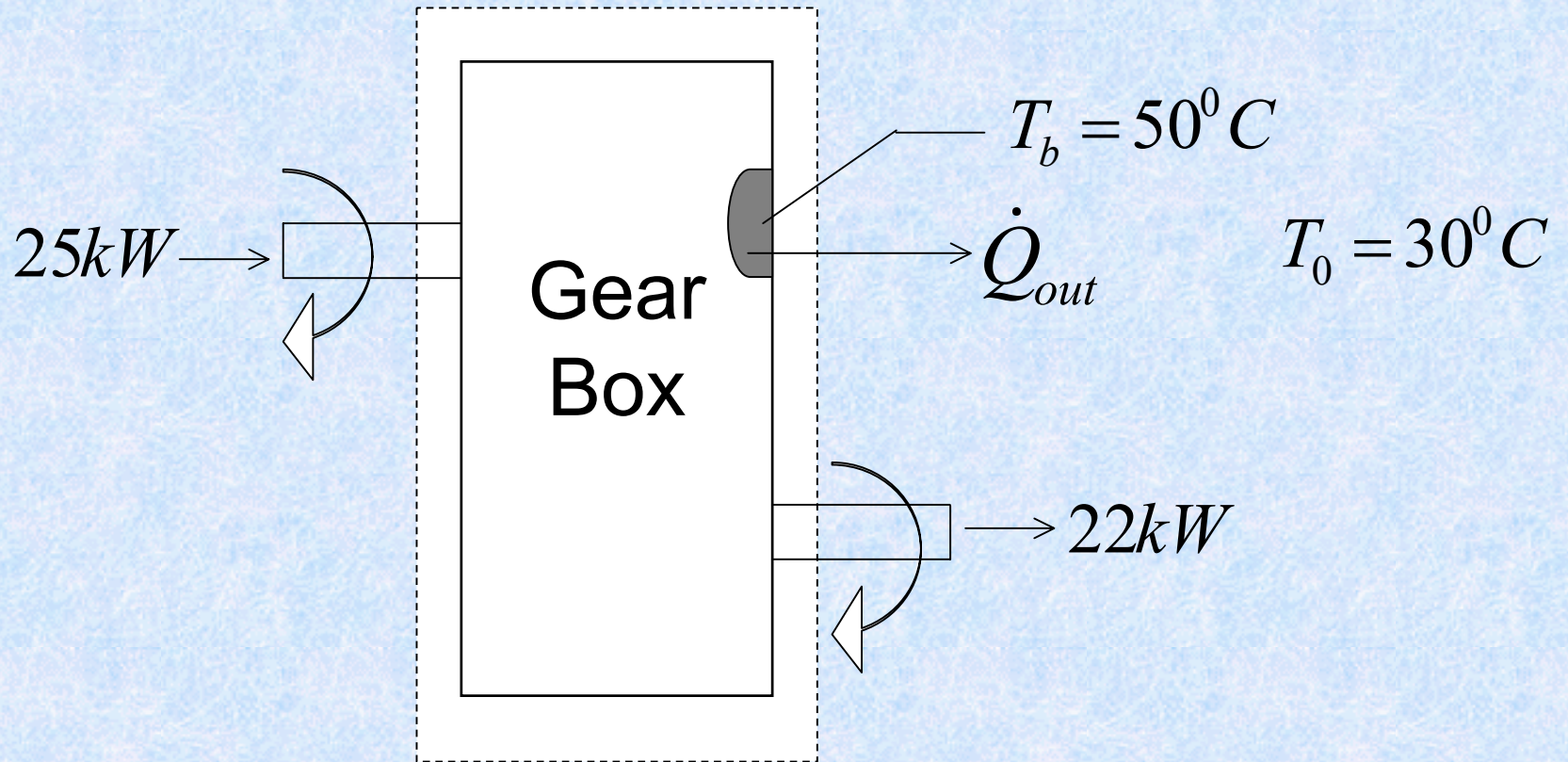
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**End of Lecture**

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# ENTROPY MAX PRINCIPLE

for any process

$$dS \geq \frac{dQ}{T} \Rightarrow dS = \frac{dQ}{T} + d\sigma$$

where  $d\sigma \geq 0 \equiv$  **entropy gen.**

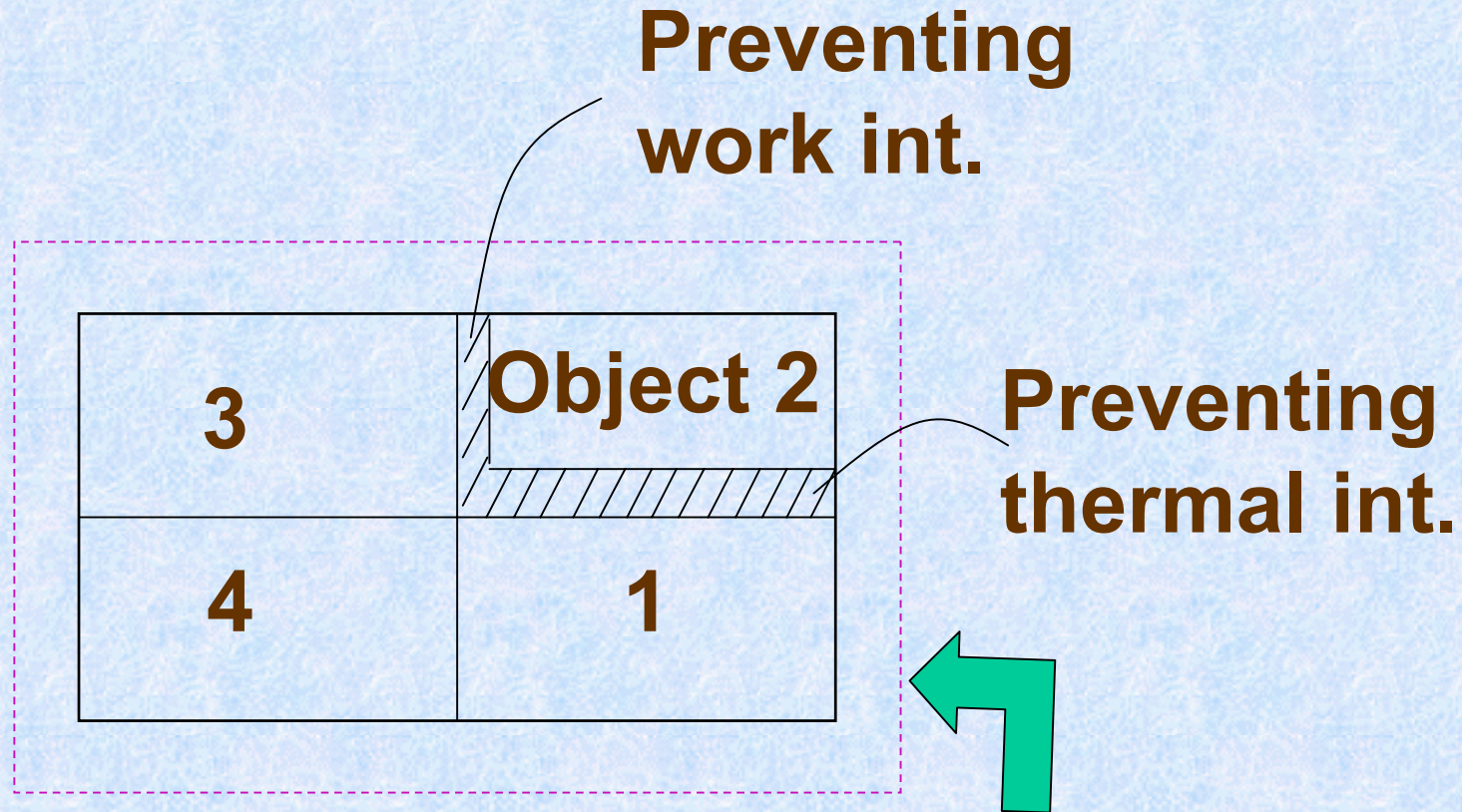
In rate terms:  $\frac{dS}{dt} = \frac{\dot{Q}}{T} + \frac{d\sigma}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma}$

**In the absence of thermal interaction**

$$ds = d\sigma \geq 0$$

**Principle of Increase of entropy**

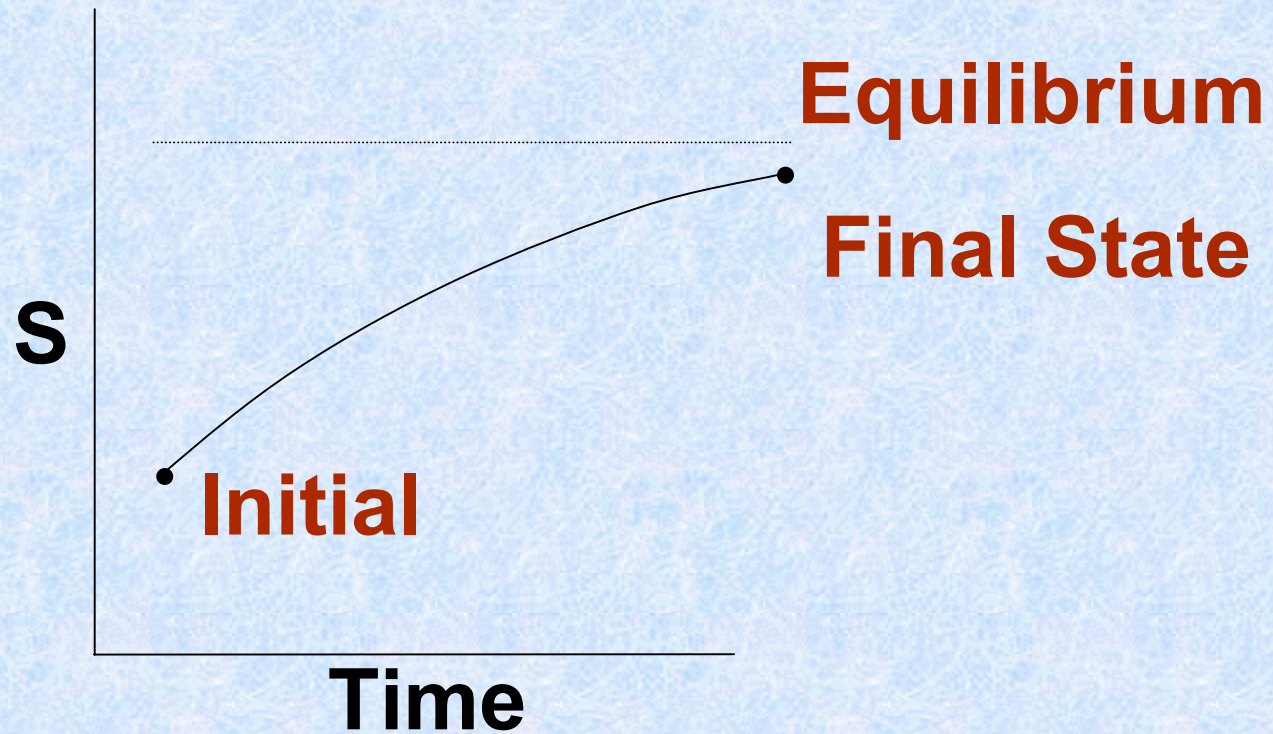
# ENTROPY MAX PRINCIPLE



Composite system is isolated

**The entropy reaches maximum possible value at the equilibrium**

# ENTROPY MAX PRINCIPLE



Trend to Equilibrium

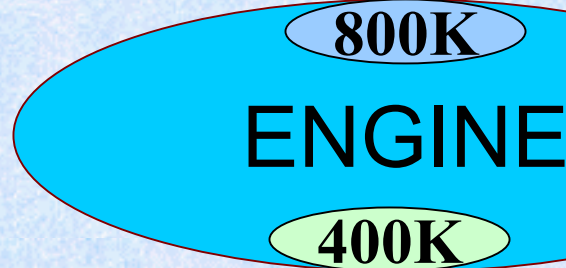
# Examples of Second Law Analysis

A heat engine operates in a cycle between two thermal reservoirs at 300K and 900K and produces 100kW power. Find the heat rejection and entropy generation when the engine is internally reversible but receives heat and rejects heat at 800K and 400k respectively

$$T_h = 900 \text{ K}$$

 $Q_h$ 

First Law in  
rate terms:

 $100 \text{ kW}$  $Q_c$ 

$$T_c = 300 \text{ K}$$

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} = \dot{Q} + \dot{W}$$

For this cycle:

$$0 = \Sigma Q - 100$$

$$Q_h - Q_c = 100$$

Since the engine is internally  
reversible :  $Q_h/800 - Q_c/400 = 0$

$$Q_h = 200 \text{ kW}$$

$$Q_c = 100 \text{ kW}$$

# Example 1....

Second Law in rate terms:

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T} + \frac{d\sigma}{dt}$$

For this cycle :

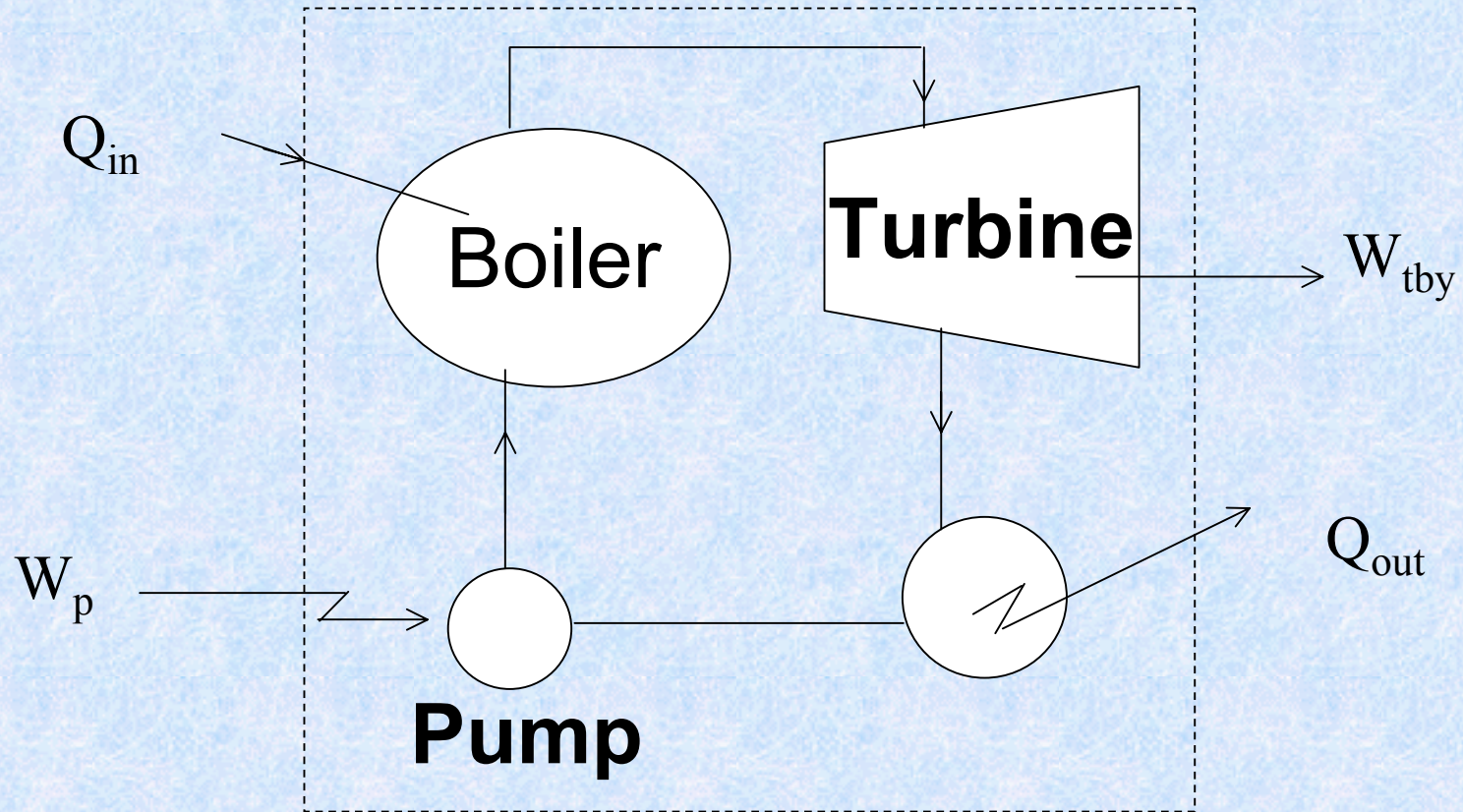
$$\frac{d\sigma}{dt} = - \left\langle \frac{Q_h}{900} - \frac{Q_c}{300} \right\rangle$$

This gives entropy generation rate as:  
- [ 200/900 - 100/300 ] = 0.111 kW / K

## EXAMPLE 2

A simple steam power cycle producing **100 MW** of power receives heat at **900K** in the boiler and rejects heat at **320K**. The condensate pump consumes **50kW** of power, and the boiler consumes **54 tonnes/hour** of coal. Assuming that the combustion of **1Kg** of coal releases **20MJ** of heat determine the thermal efficiency and entropy generation in the cycle.

# EXAMPLE 2.....



## EXAMPLE 2 .....

**First Law (for System within dashed line boundaries)**

$$\frac{dE}{dt} = \dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{P,in} - \dot{W}_{T,by}$$

**Under steady state conditions,  $\frac{dE}{dt} = 0$**

$$\Rightarrow \dot{Q}_{in} - \dot{Q}_{out} = \dot{W}_{T,by} - \dot{W}_{P,in}$$

**Here**

$$\begin{aligned}\dot{Q}_{in} &= \frac{54 \times 1000}{3600} \times 20 \text{ MJ/S} \\ &= 300 \text{ MW}\end{aligned}$$

$$\begin{aligned}\dot{Q}_{out} &= 300 - 100 \\ &= 200 \text{ MW}\end{aligned}$$

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## EXAMPLE 2 .....

**Second Law ( for system within dashed line boundaries)**

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T} + \dot{\sigma}$$

**Under steady state conditions,**  $\frac{dS}{dt} = 0$

$$\Rightarrow \dot{\sigma} = -\sum \left( \frac{\dot{Q}}{T} \right)$$

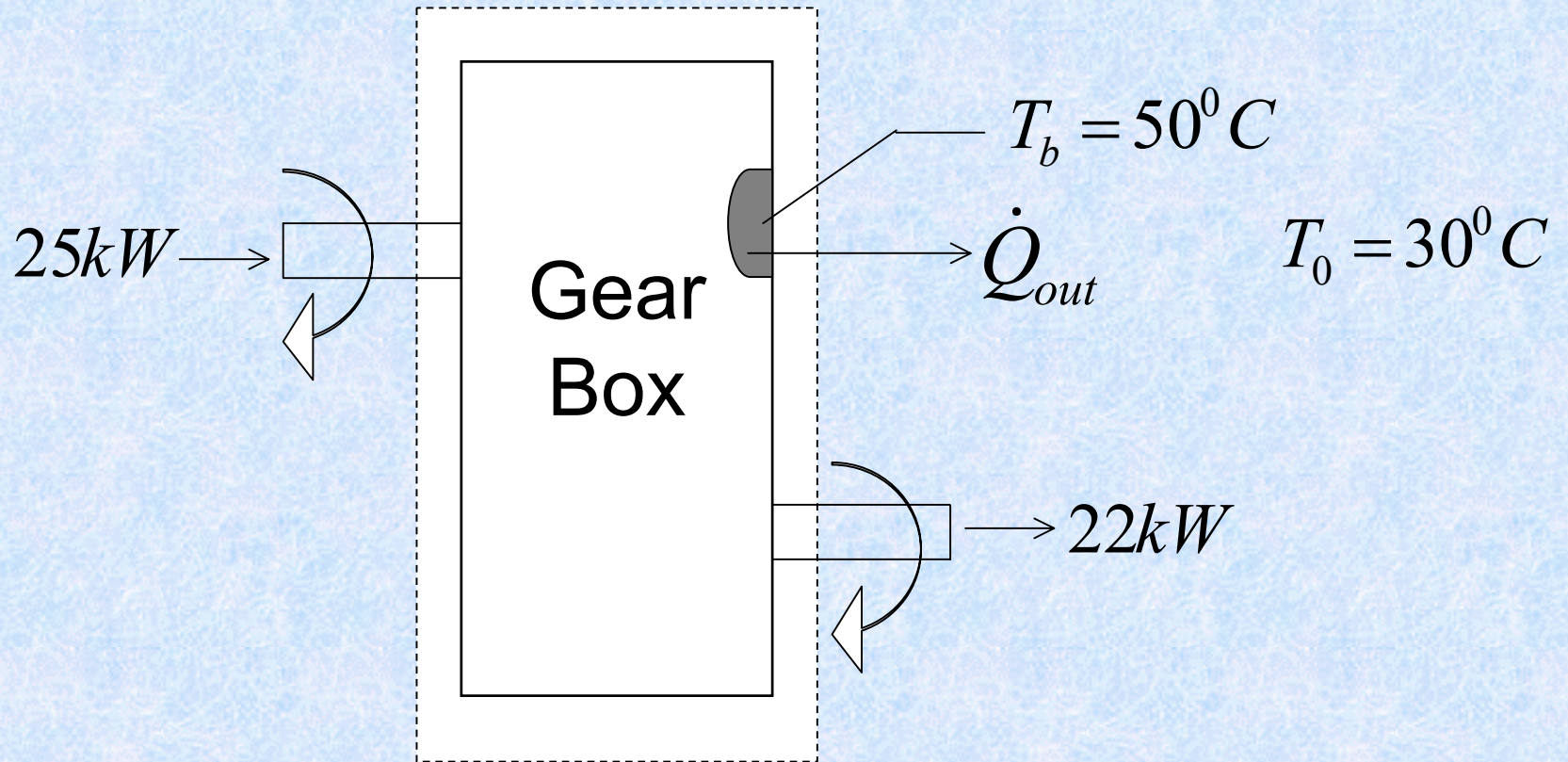
**Here**

$$\begin{aligned} \dot{\sigma} &= -\left( \frac{300}{900} - \frac{200}{320} \right) \frac{MW}{K} \\ &= .2917 MW/K \end{aligned}$$

## EXAMPLE 3

The gear box of a machine is operating under steady-state conditions. The input shaft receives **25 kW** from a prime mover and transmits **22kW** to the output shaft, the rest being lost due to friction etc. The gear box surface is at an average temperature of **50°C** and loses heat to the surroundings at **30°C**. Estimate the rate of entropy production inside the gear box.

# EXAMPLE 3



## EXAMPLE 3

Since the gear box is operating in steady state,

First Law  $0 = 25 - 22 - \dot{Q}_{out} \Rightarrow \dot{Q}_{out} = 3 \text{KW}$

Second Law  $\dot{\sigma} = -\sum \left( \frac{\dot{Q}}{T} \right) = \frac{\dot{Q}_{out}}{T} = \frac{3 \times 1000}{323} = 9.289 \text{ W/K}$

**Entropy production outside the box?**

**End of Lecture**