

# **The Second Law of Thermodynamics**

**(Lecture 6)**

**1<sup>st</sup> semester, 2021**

**Advanced Thermodynamics (M2794.007900)**

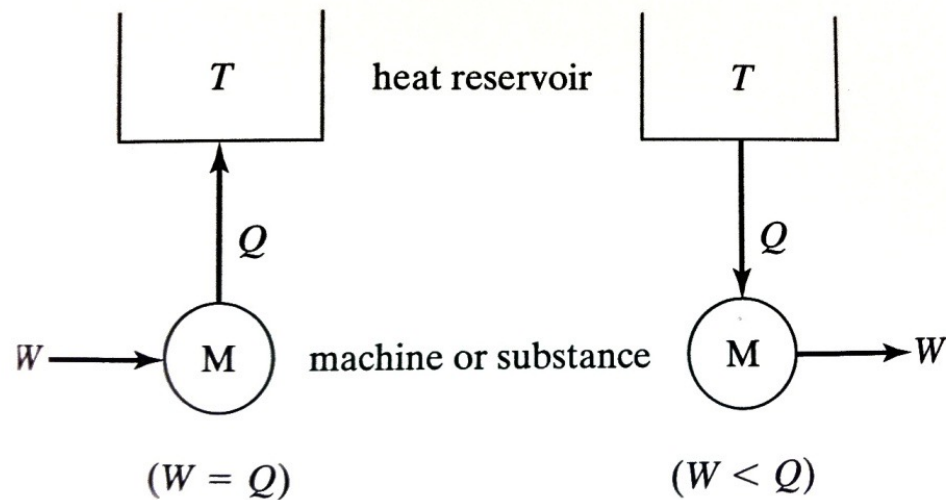
**Song, Han Ho**

(\* Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

# The Second Law of Thermodynamics

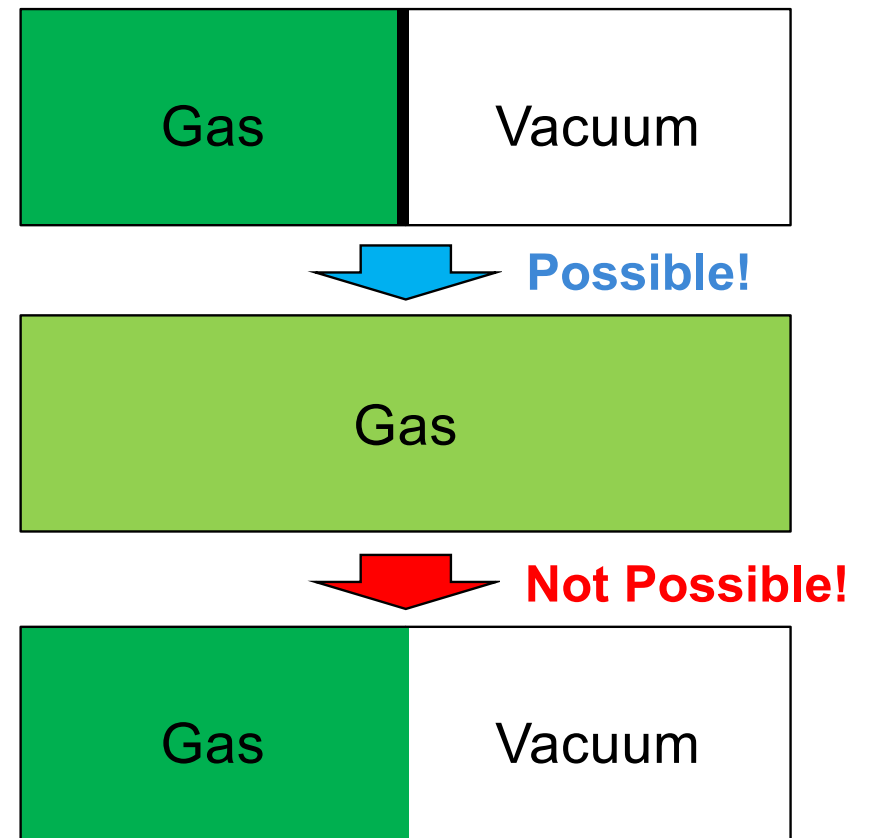
## Introduction

→ The first law of thermodynamics can't explain the followings.



**Work → Heat**  
**100% conversion**  
**Possible!**

**Heat → Work**  
**100% conversion**  
**Not Possible!**



**Something is missing! We need a second fundamental law for a complete description of our world!**

# The Second Law of Thermodynamics

## The Mathematical Concept of Entropy

→ Let's define a new state variable, **entropy(S)**.

The first law of thermodynamics for a **reversible** process (subscript 'r' represents 'reversible'),

$$dU = \delta Q_r - \delta W_r$$

where  $\delta Q_r$  and  $\delta W_r$  are inexact differential.

Here,

$$\delta W_r = PdV \quad \text{or} \quad \frac{\delta W_r}{P} = dV$$

Here,  $dV$  is exact differential, and  $1/P$  is called **an integrating factor** for  $\delta W_r$ , an inexact differential. Then, how about  $\delta Q_r$ ?

$$\frac{\delta Q_r}{T} = dS$$

**Clausius's definition  
of the entropy S**

# The Second Law of Thermodynamics

## The Mathematical Concept of Entropy

→ Continue on.

$$dU = \delta Q_r - \delta W_r = TdS - PdV$$

**Gibbs Equation!**

→ Gibbs equation is one of the most important equations in thermodynamics.

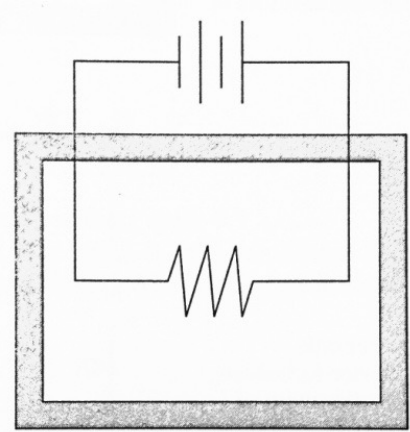
→ Here are two questions regarding the Gibbs equation:

1. Is  $dS$  an exact differential or is  $S$  (entropy) a **state variable**?
2. Does Gibbs equation apply for **irreversible** process, as well as for reversible process?

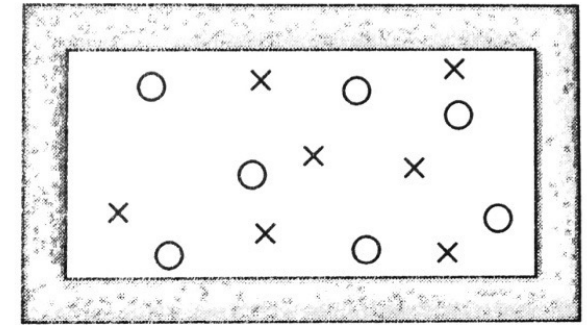
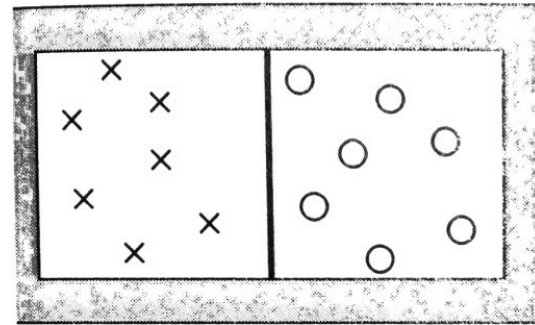
→ We will learn the answers throughout this lecture!

# The Second Law of Thermodynamics

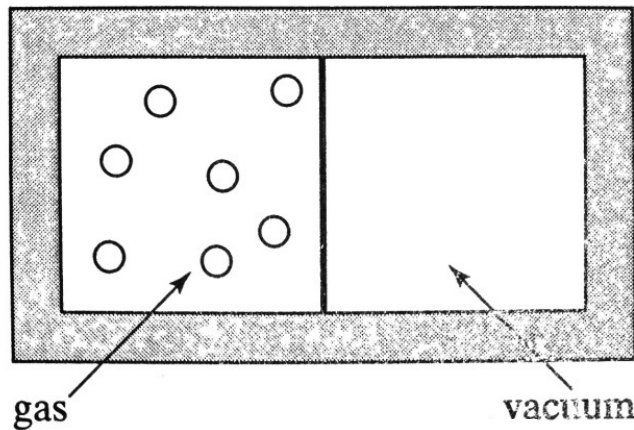
## Irreversible Processes (Examples)



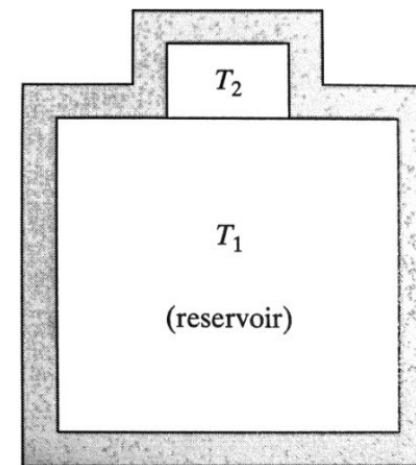
**Dissipative work**



**Mixing of two gases**



**Free expansion**



**Thermal equilibrium process ( $T_2 > T_1$ )**

# The Second Law of Thermodynamics

## Classical Statements of Second Law

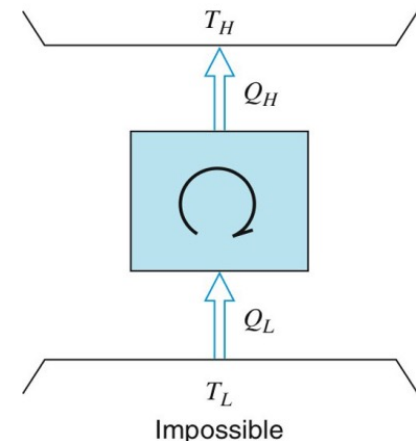
→ Historically, the impossibility of certain process was first introduced in the following two famous statements of **the second law**:

- **Clausius** statement

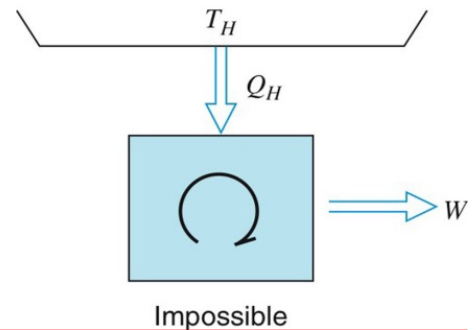
“It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to hotter body.”

- **Kelvin-Planck** statement

“It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and the exchange of heat with a single reservoir.”



**Clausius statement**



**Kelvin-Planck statement**

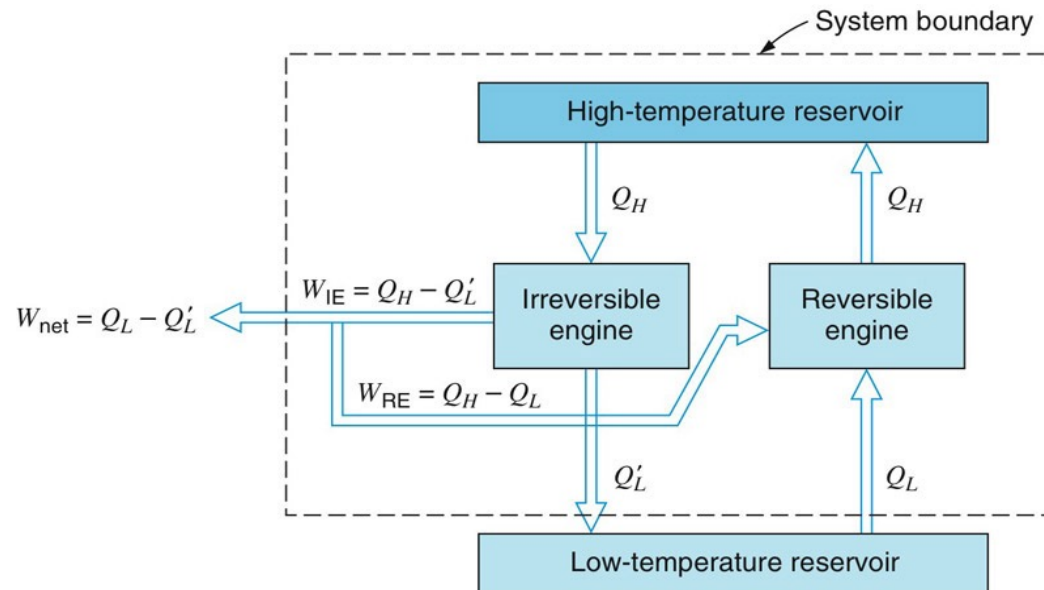
# The Second Law of Thermodynamics

## Carnot's Theorem

### → First Proposition

“It is impossible to construct an engine that operates between two given reservoirs and is more efficient than a reversible engine (or Carnot engine) operating between the same two reservoirs.”

$$\eta_{irr} < \eta_{rev}$$



$$\text{if } \eta_{irr} > \eta_{rev}, \\ Q'_L < Q_L$$

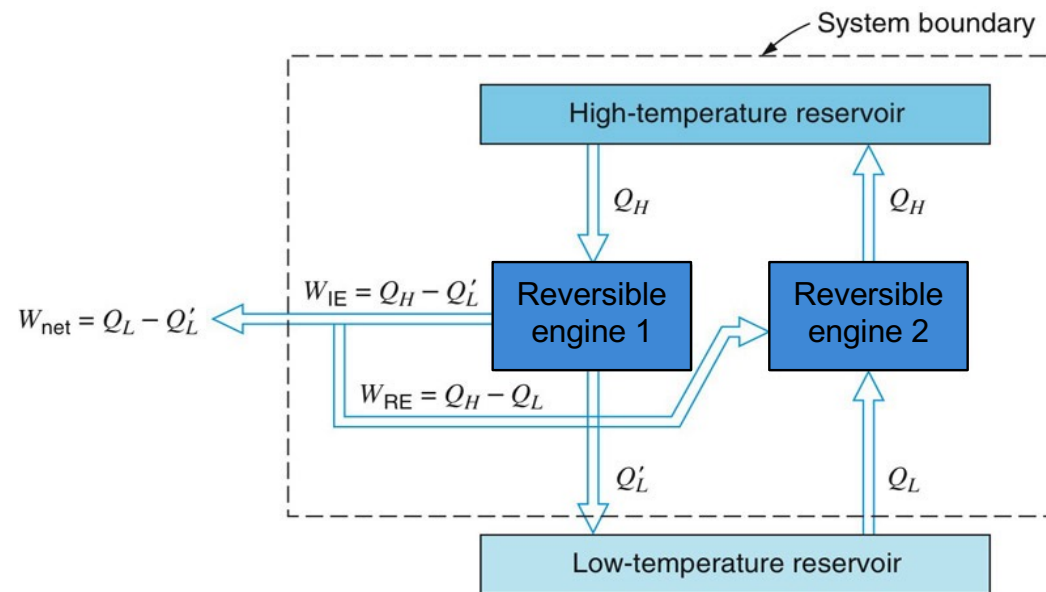
# The Second Law of Thermodynamics

## Carnot's Theorem

### → Second Proposition

“All engines that operate on the Carnot cycle between two given reservoirs have the same efficiency, independent of working substance.”

$$\eta_{rev} = f(T_H, T_L) \quad \text{or} \quad \eta = \frac{w}{q_H} = \frac{q_H - q_L}{q_H} = 1 - \frac{q_L}{q_H} = 1 - \frac{T_L}{T_H}$$





# The Second Law of Thermodynamics

## The Clausius Inequality and the Second Law

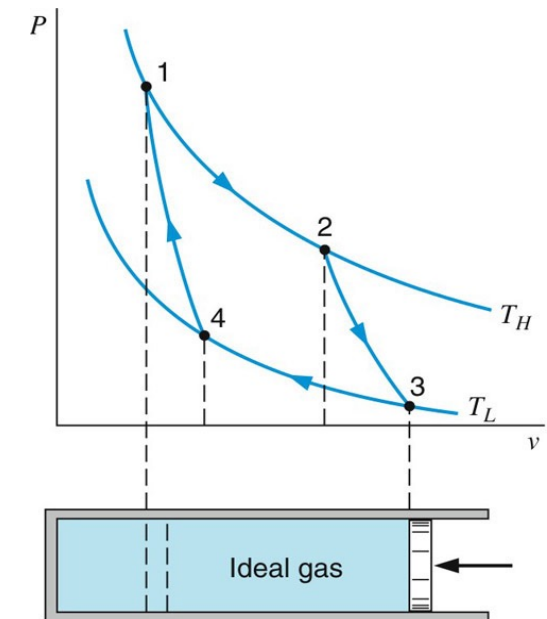
- The second law of thermodynamics leads to the **inequality of Clausius** for both reversible and irreversible heat engines (or refrigerators).

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

- For Carnot (reversible) engines,

$$\frac{q_H}{q_L} \left( \text{or } \frac{Q_H}{Q_L} \right) = \frac{T_H}{T_L}$$

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



Carnot cycle in P-v diagram

## The Second Law of Thermodynamics

### The Clausius Inequality and the Second Law

- For irreversible heat engines operating between the same T reservoirs as for the Carnot (reversible) engine,

$$W_{\text{irr}} < W_{\text{rev}} \longrightarrow Q_H - Q_{L \text{ irr}} < Q_H - Q_{L \text{ rev}}$$

Then,

$$Q_{L \text{ irr}} > Q_{L \text{ rev}}$$

Finally,

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L \text{ irr}}}{T_L} < 0$$

- For both reversible and irreversible heat engines,

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

where equality is for reversible engines. Similarly, the inequality of Clausius can be demonstrated for both rev. and irrev. refrigerators.

# The Second Law of Thermodynamics

## The Clausius Inequality and the Second Law

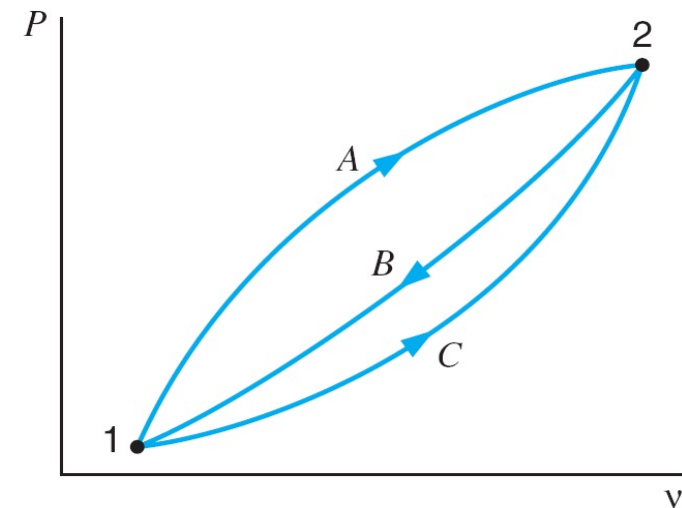
- Consider the reversible processes A, B, and C.
- Applying the inequality of Clausius,

$$1 \xrightarrow{A} 2 \xrightarrow{B} 1$$
$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B$$

$$1 \xrightarrow{C} 2 \xrightarrow{B} 1$$
$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_C + \int_2^1 \left( \frac{\delta Q}{T} \right)_B$$

- Then,

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

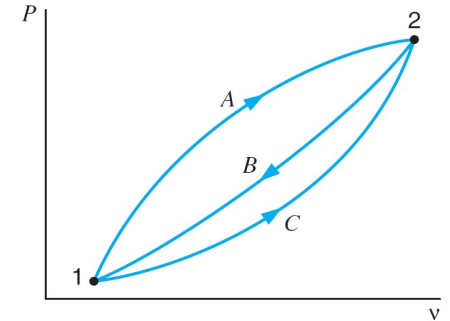


# The Second Law of Thermodynamics

## The Clausius Inequality and the Second Law

→ Continue on.

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$



→ So,  $\left( \frac{\delta Q}{T} \right)_{rev}$  is independent of the path, or **a point function**.

→ Define this point function as **entropy**, or **S**.

$$dS \equiv \left( \frac{\delta Q}{T} \right)_{rev}$$

→ Then, the change in entropy can be evaluated as,

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_{rev}$$

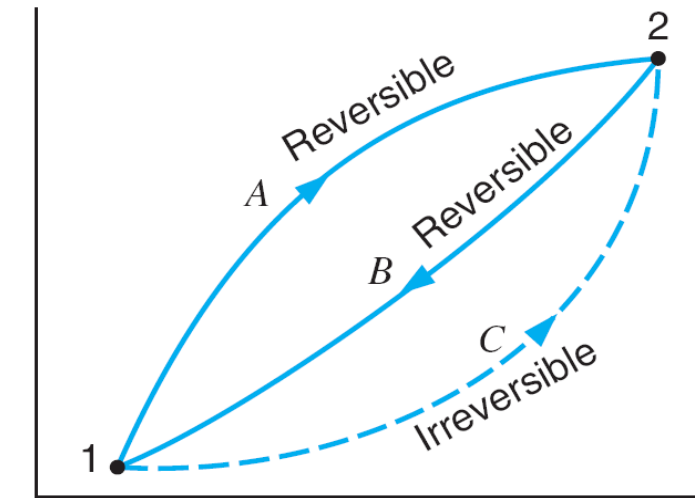
# The Second Law of Thermodynamics

## The Clausius Inequality and the Second Law

→ Consider **reversible** processes **A & B** and **irreversible** process **C**. From the inequality of Clausius,

$$1 \xrightarrow{A} 2 \xrightarrow{B} 1$$
$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B = 0$$

$$1 \xrightarrow{C} 2 \xrightarrow{B} 1$$
$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_C + \int_2^1 \left( \frac{\delta Q}{T} \right)_B < 0$$



$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A > \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

→ Because entropy is a point function,

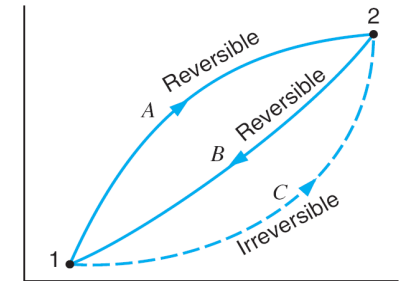
$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 dS_A = \int_1^2 dS_C \longrightarrow \int_1^2 dS_C > \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

# The Second Law of Thermodynamics

## The Clausius Inequality and the Second Law

→ As path C was an arbitrary irreversible process, in general,

$$dS \geq \frac{\delta Q}{T}$$
$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$



$$\int_1^2 dS_C > \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

→ For a reversible process, the second law is

$$dS = \left( \frac{\delta Q}{T} \right)_{\text{rev}}$$

→ For an irreversible process, the second law is

$$dS > \left( \frac{\delta Q}{T} \right)_{\text{irr}}$$

If any irreversible effects occur while the amount of heat ( $\delta Q$ ) is transferred, the change of entropy will be greater than for the reversible process.

## The Second Law of Thermodynamics

### The Clausius Inequality and the Second Law

- Interesting fact around the second law for our universe:

$$dS \geq \frac{\delta Q}{T} = 0 \text{ (for isolated system)}$$

“The entropy of an isolated system increases in any irreversible process and is unaltered in any reversible process. This is the principle of increasing entropy.”

- This indicates that there is a direction for the sequence of natural events.

**The law of increasing entropy = The arrow of time**

# The Second Law of Thermodynamics

## Combined First and Second Laws

→ Here are two questions regarding the Gibbs equation again:

$$dU = \delta Q_r - \delta W_r = TdS - PdV$$

1. Is  $dS$  an exact differential or is  $S$  (entropy) a state variable?
2. Gibbs equation applies for **irreversible** process, as well as for reversible process?

→ Let's consider the second question.

The first law in most general form,

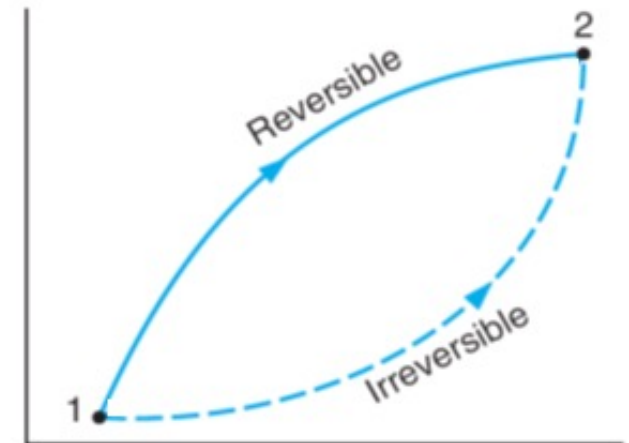
$$dU = \delta Q - \delta W$$

From the second law for an irreversible process,

$$TdS = \delta Q_r > \delta Q \text{ or } \delta Q_r = \delta Q + \varepsilon \ (\varepsilon > 0)$$

Then, substitute this into the first law for reversible process,

$$dU = \delta Q_r - \delta W_r = \delta Q + \varepsilon - \delta W_r$$





# The Second Law of Thermodynamics

## Combined First and Second Laws

→ Continue on.

Comparing these two equations,

$$dU = \delta Q - \delta W \quad \text{and} \quad dU = \delta Q + \varepsilon - \delta W_r$$
$$\rightarrow \delta W = \delta W_r - \varepsilon$$

Here,  $\varepsilon$  is called **lost work**, associated with irreversibility.

Finally,

$$dU = \delta Q - \delta W = (\delta Q_r - \varepsilon) - (\delta W_r - \varepsilon) = \delta Q_r - \delta W_r = TdS - PdV$$

This indicates that the Gibbs equation is applied to **ANY** process.

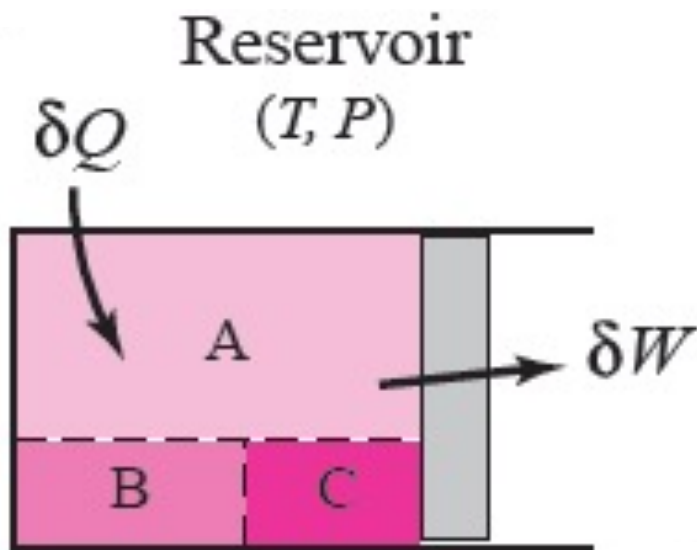
→ Two interesting examples:

- Free expansion:  $\delta Q, \delta W = 0$  but  $PdV, TdS = \text{finite}$
- Adiabatic stirring:  $\delta Q = 0$  but  $TdS = \text{finite}$ ,  $PdV = 0$  but  $\delta W \neq 0$

# The Second Law of Thermodynamics

## Determining Entropy in Real System (extra topic)

- For simple substances, Q.M. & S.M. can be used to directly enumerate microstates (statistical thermodynamics).  $\rightarrow S = k \ln \Omega$
- For complex substances, the Gibbs equation is used.



## Gibbs Equation (EOS for Entropy)

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

# The Second Law of Thermodynamics

## 2<sup>nd</sup> Law of Thermodynamics (extra topic)

$$[S]: \underbrace{dS_{system}}_{\text{accumulation}} = \underbrace{\delta S_{in} - \delta S_{out}}_{\text{transfers}} + \underbrace{\delta S_{produced}}_{\geq 0 \text{ (2<sup>nd</sup> Law)}} - \underbrace{\delta S_{destroyed}}_{= 0 \text{ (2<sup>nd</sup> Law)}}$$

Transfers of Entropy:

*Work*  $\rightarrow 0$  (reversible work modes only)

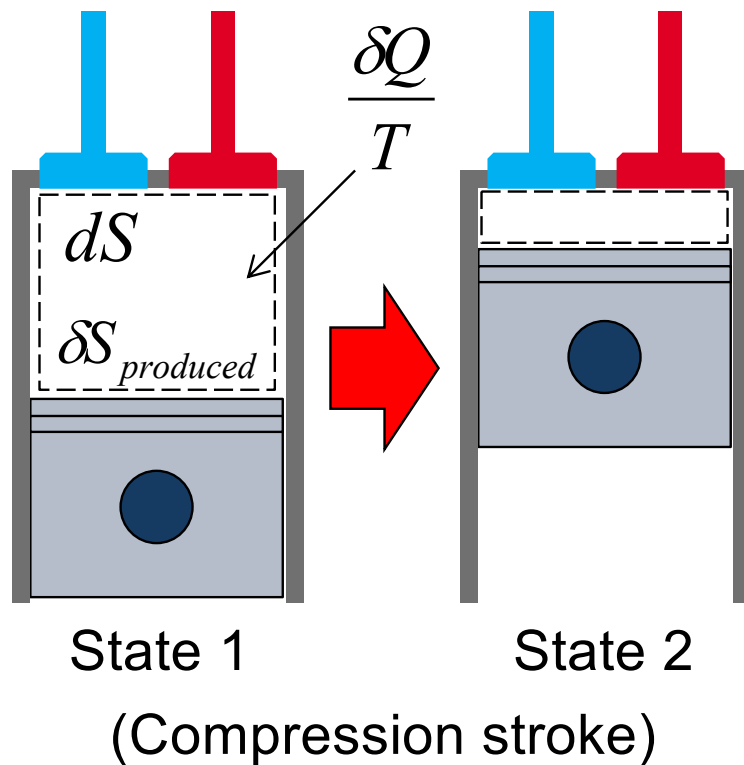
*Heat*  $\rightarrow \frac{\delta Q}{T}$  (Irreversible work modes as heat)

*Matter*  $\rightarrow s \delta N$

# The Second Law of Thermodynamics

## 2<sup>nd</sup> Law of Thermodynamics (extra topic)

$$[S]: \underbrace{dS_{system}}_{\text{accumulation}} = \underbrace{\delta S_{in} - \delta S_{out}}_{\text{transfers}} + \underbrace{\delta S_{produced}}_{\geq 0 \text{ (2<sup>nd</sup> Law)}} - \underbrace{\delta S_{destroyed}}_{= 0 \text{ (2<sup>nd</sup> Law)}}$$



(Closed System)

Differential:

$$dS = \frac{\delta Q}{T} + \delta S_{produced}$$

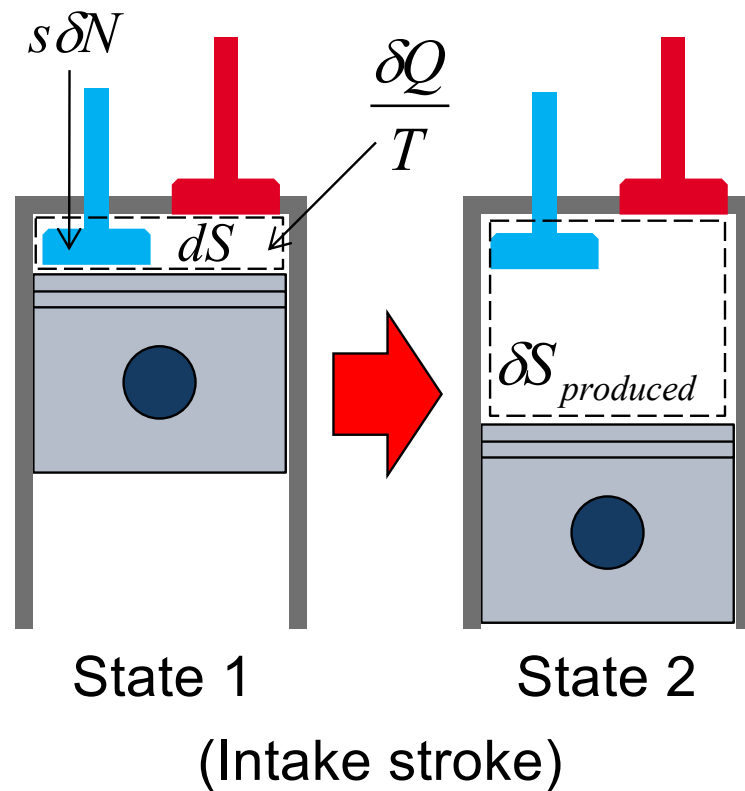
Whole process 1  $\rightarrow$  2:

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + \int_1^2 \delta S_{produced}$$

# The Second Law of Thermodynamics

## 2<sup>nd</sup> Law of Thermodynamics (extra topic)

$$[S]: \underbrace{dS_{system}}_{\text{accumulation}} = \underbrace{\delta S_{in} - \delta S_{out}}_{\text{transfers}} + \underbrace{\delta S_{produced}}_{\geq 0 \text{ (2<sup>nd</sup> Law)}} - \underbrace{\delta S_{destroyed}}_{= 0 \text{ (2<sup>nd</sup> Law)}}$$



(Open System)

Differential:

$$dS = \frac{\delta Q}{T} + s \delta N + \delta S_{produced}$$

Whole process 1 → 2:

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + \int_1^2 s \delta N + \int_1^2 \delta S_{produced}$$