Basic 12
Micro-nano Thermodynamics

Prof. I. Naruse
Dept. of Mechanical Science & Engineering
Nagoya University

Thermodynamics
・・・Progress limitation of phenomenon (Process)

||

Equilibrium

↓

Evaluation standard of system design

1) Thermodynamics for material
2) Thermodynamics for process
3) Thermodynamics for system

1) Thermodynamics for material

Energy of material: *E*
Entropy of material: *S*

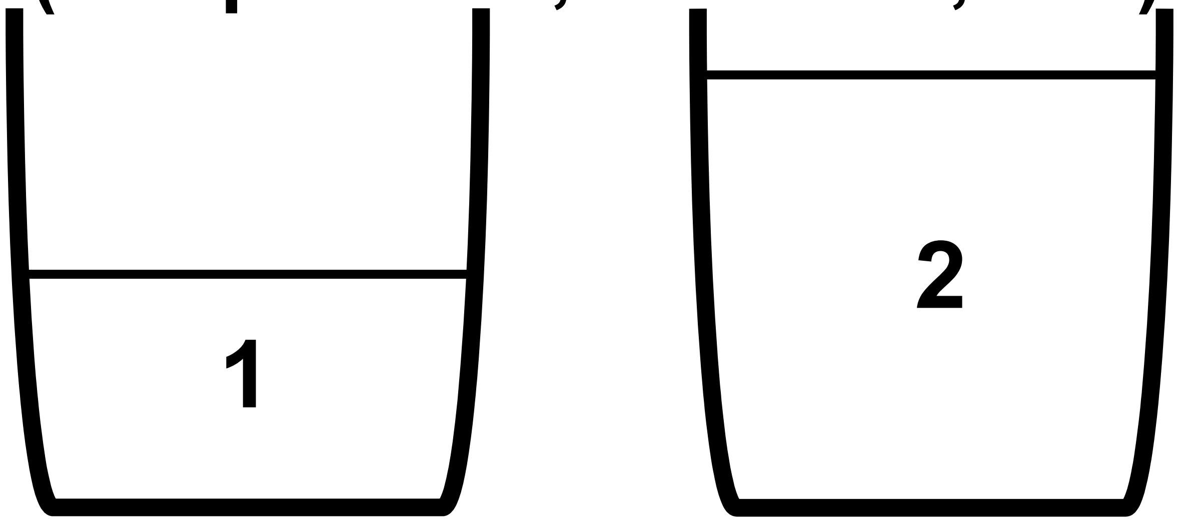
The number of material phases
Concentrations of material in each phase
Temperature
Pressure

Unit of energy: [J], [J/s]
Unit of entropy: [J/K], [J/(K·s)]

Explanation by Water model

Ex. 1 Water in a flask (Batch)

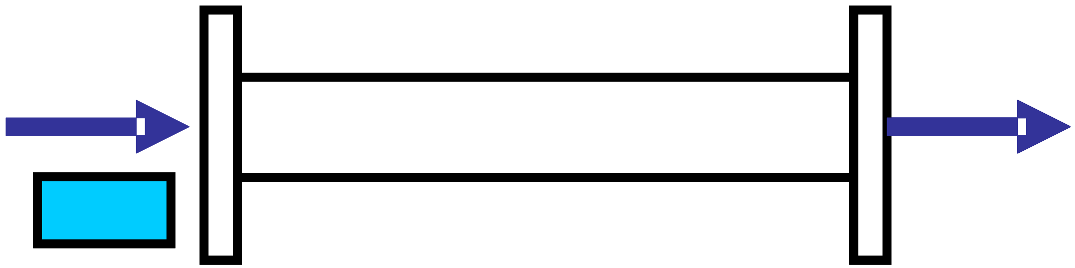
Same conditions
(Temperature, Pressure, etc.)



Energy	E [J]	$2E$ [J]
Entropy	S [J/K]	$2S$ [J/K]

Ex. 2 Water flow into a tube (Continuous)

1

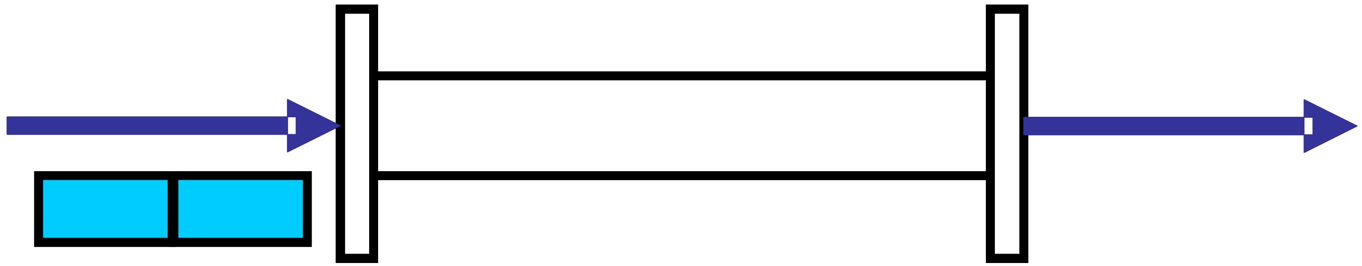


Energy *E* [J/s]

Entropy *S* [J/(K･s)]

Same conditions (Temperature, Pressure, etc.)

2



Energy 2*E* [J/s]

Entropy 2*S* [J/(K･s)]

Energy: E

- Volume changeable vessel：

  Enthalpy *H*

- Constant volume vessel：

  Internal energy *U*

What are energy and entropy?

Quantity of energy:

Enthalpy (Internal energy)

Quality of energy:

Expression by both enthalpy (Internal energy) and entropy

1) Calculation of enthalpy

Standard generation heat of material:

ΔH^0_{298} [J/mol]

Ex. CH_4 -74.5 kJ/mol

C and N_2 0 kJ/mol

(Pure material consisting of same element)

Enthalpy of material at temperature of *T* and the at atmospheric pressure : H^0_T

$$H_T^0 = n\Delta H_{298}^0 + n\int_{298}^{T} C_{p,m}\,\mathrm{d}T$$

n **: mol number of material [mol]**

$C_{p,m}$: Heat capacity of material [J/(K . mol)]

$$C_{p,m} = a + bT + cT^2$$

2) Calculation of entropy

Absolute entropy of material : S^0_{298} [J/(K·mol)]

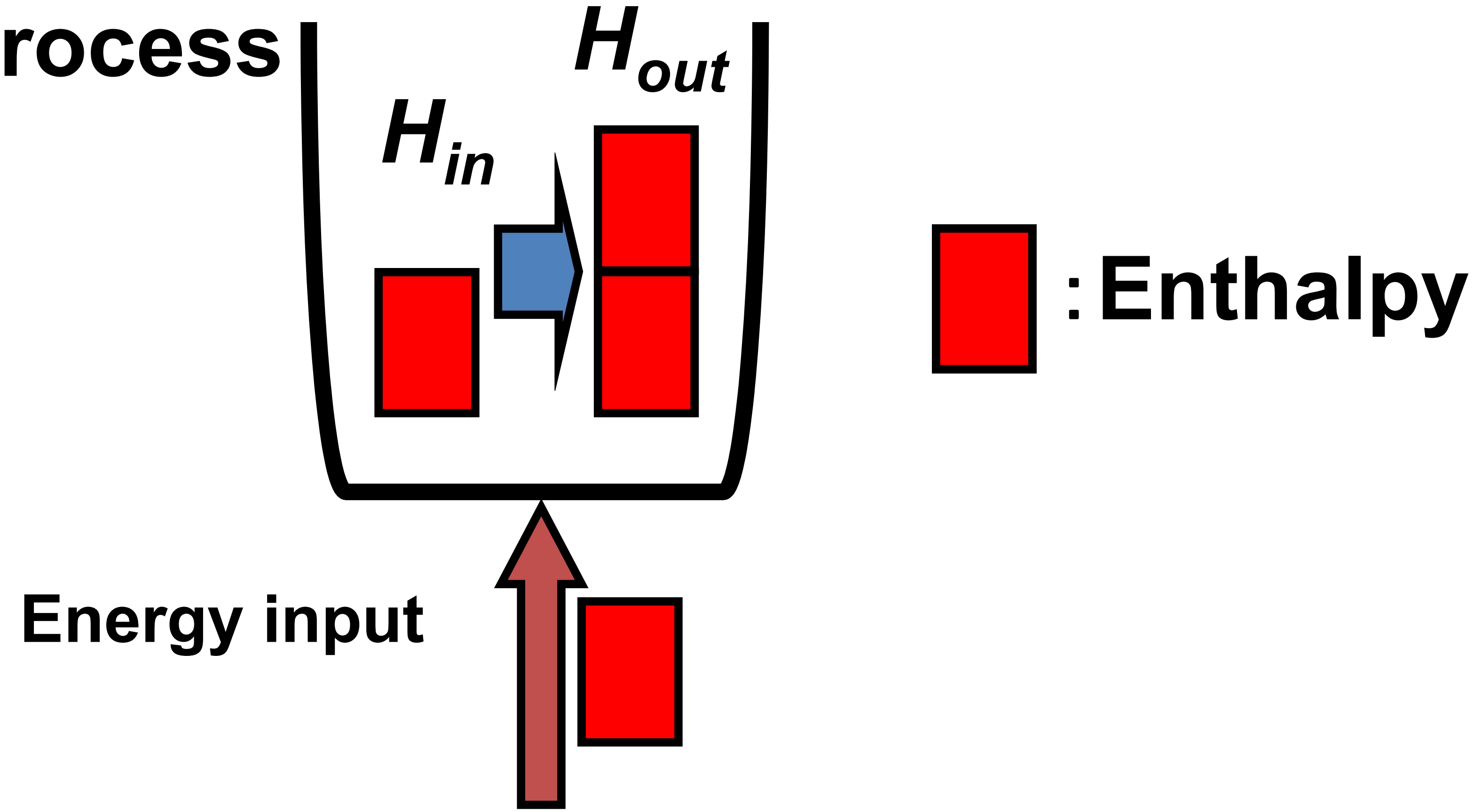
Ex. CH_4 186 [J/(K·mol)]

Absolute entropy of material at temperature of T and at the atmospheric pressure : S^0_T

$$S_T^0 = S_{298}^0 + \int_{298}^{T} \frac{C_{p,m}}{T} \mathrm{d}T$$

Ex. Heating process

- Batch process

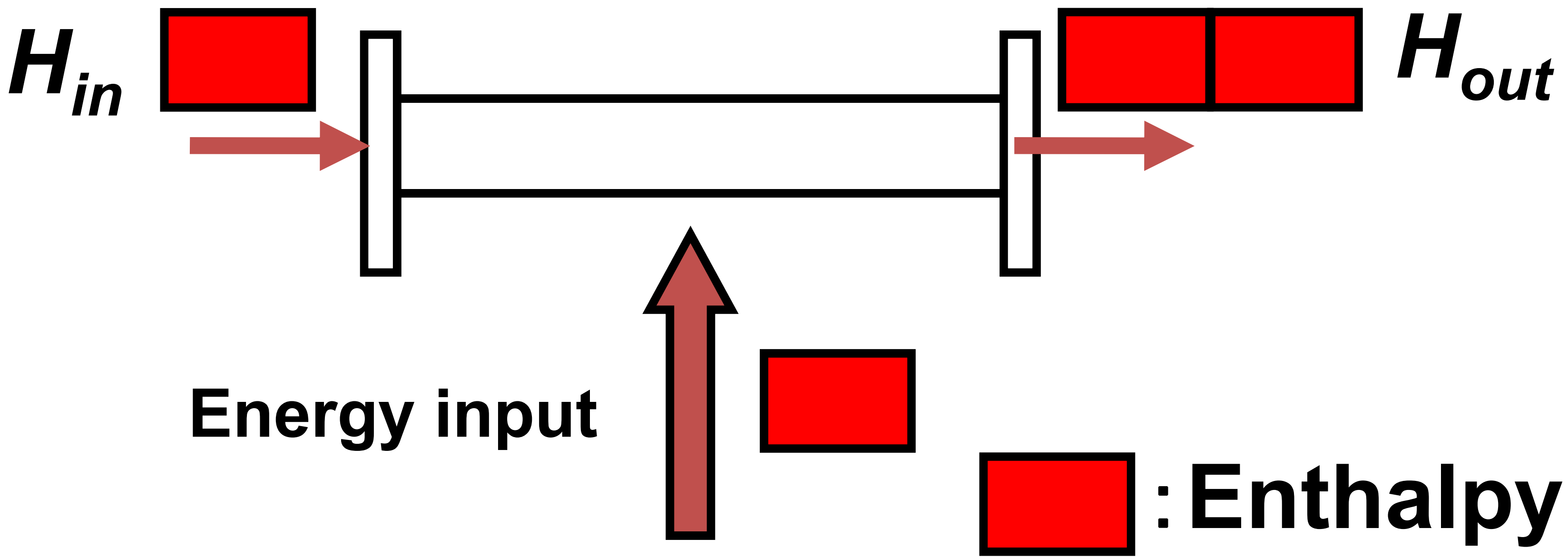


Enthalpy change before and after : ΔH

$$\Delta H = H_{out} - H_{in}$$

Ex. Heating process

・Continuous process

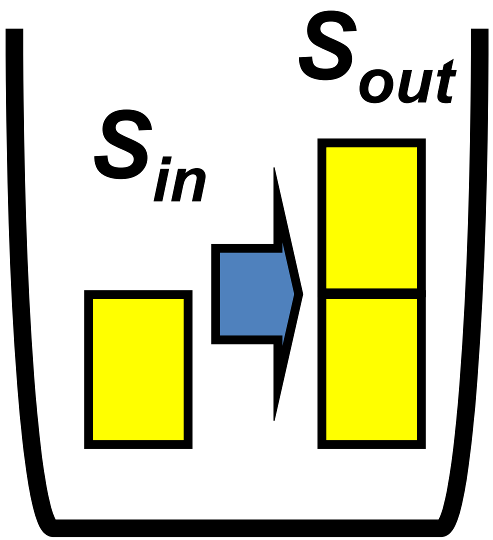


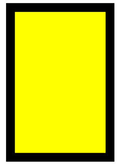
Enthalpy change before and after : ΔH

$$\Delta H = H_{out} - H_{in}$$

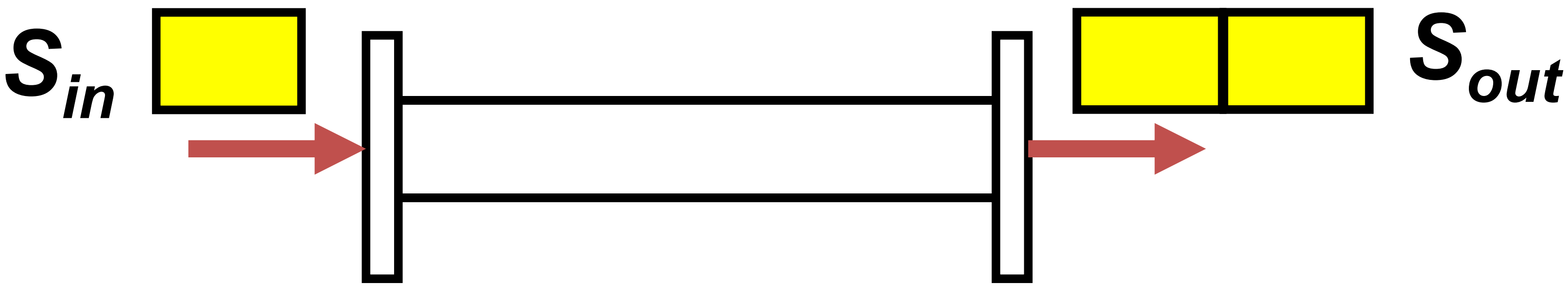
Ex. Heating process

- Batch process



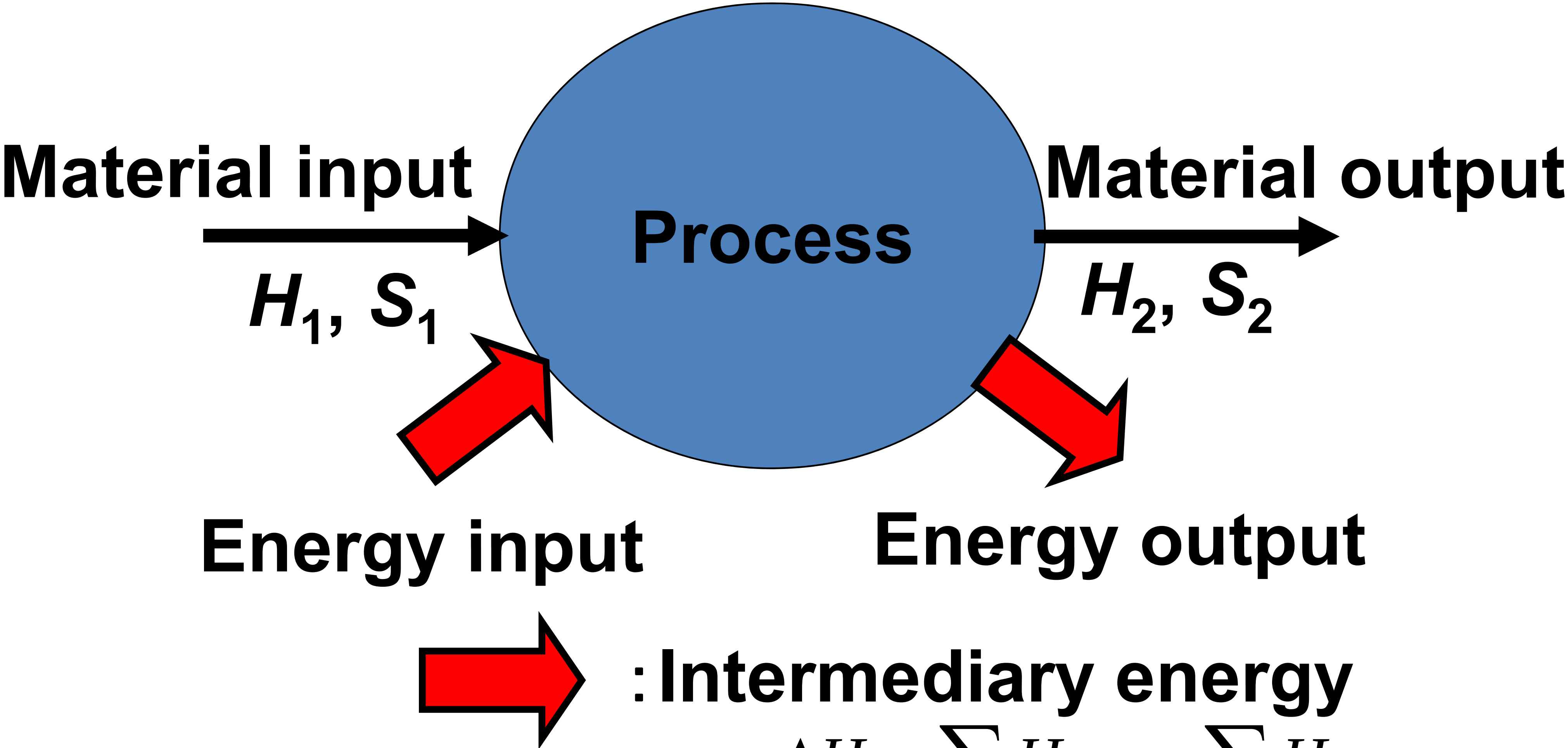


- Continuous process



Entropy change before and after : ΔS

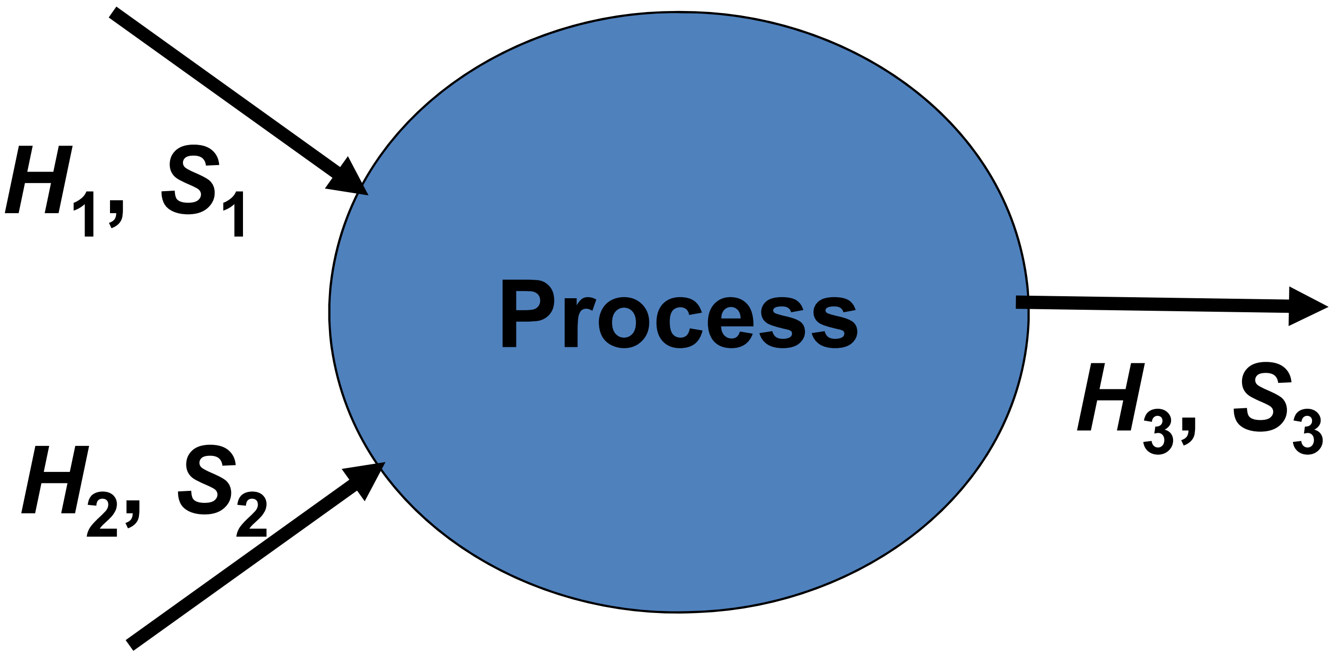
$$\Delta S = S_{out} - S_{in}$$



Enthalpy change $$\Delta H = \sum_j H_{out,j} - \sum_j H_{in,j}$$

Entropy change $$\Delta S = \sum_j S_{out,j} - \sum_j S_{in,j}$$

E.g.



Enthalpy change $$\Delta H = H_3 - (H_1 + H_2)$$

Entropy change $$\Delta S = S_3 - (S_1 + S_2)$$

ΔH: Intermediary energy

ΔH: Intermediary energy

Direction: **Positive or Negative of** ΔH

(Positive: Energy input, Negative Energy output)

Quantity: **Absolute value of** ΔH

Quality: **Degree of low level** d

$$d = \frac{\Delta S}{\Delta H} \qquad [1/K]$$

Degree of low level:

Larger d **indicates lower intermediary energy.**

What is the "Degree of low level"?

Assumption:

Evolution of 1 J intermediary energy

Temperature of heat source

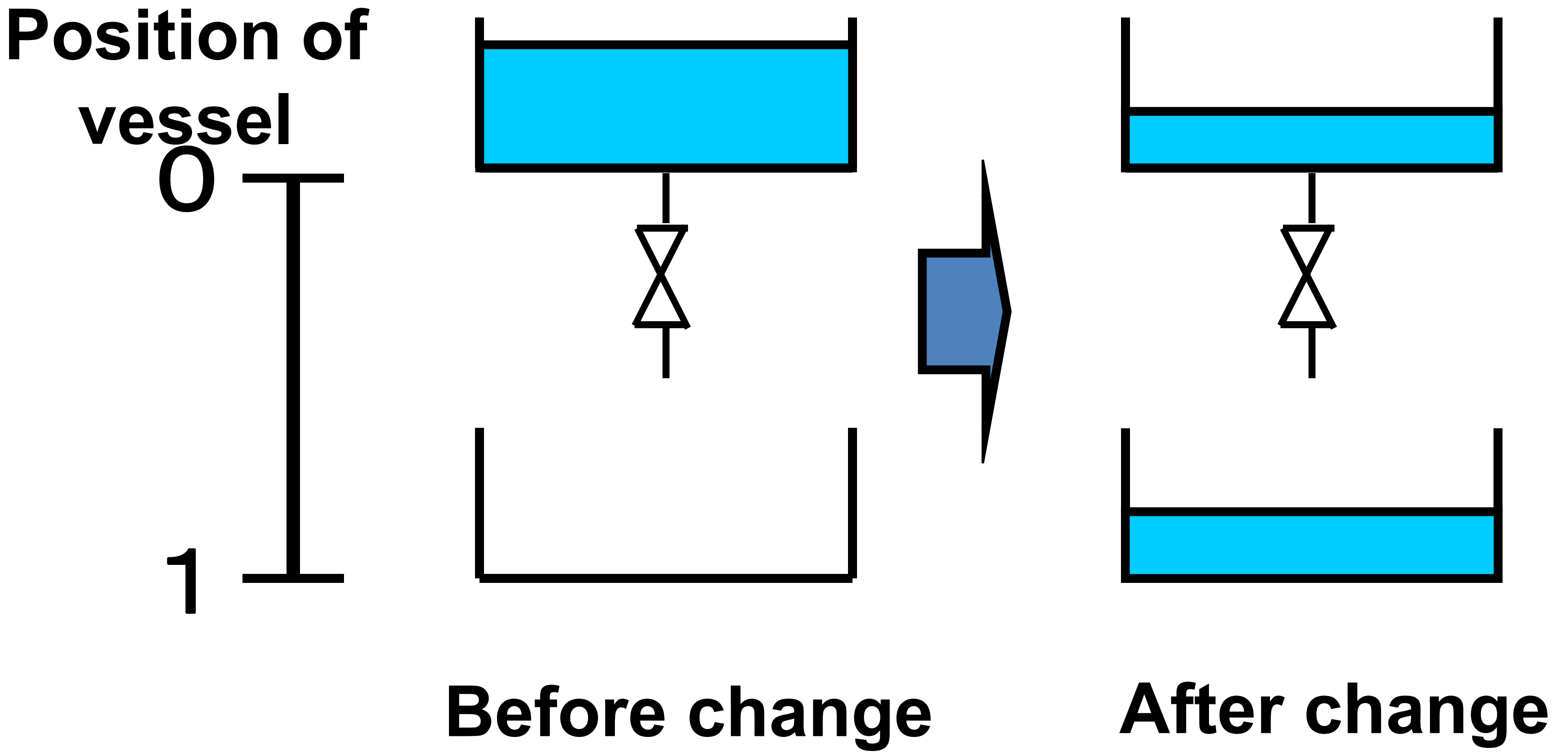
	1000K		300K
d	1/1000	$<$	1/300

Higher level of intermediary energy

Explanation of "Degree of low level" by Water model

Quantity of water = Mass of water

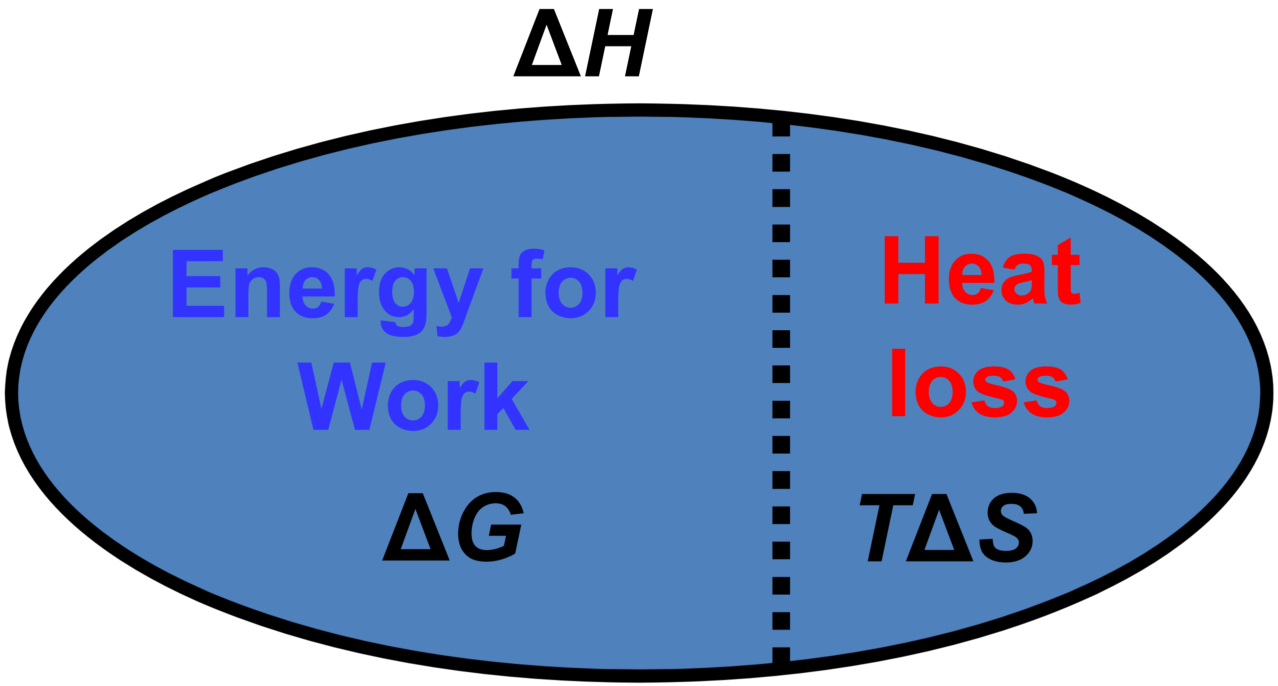
Degree of low level ⟹ **Position of vessel**



Content of enthalpy change: ΔH

ΔH = (Energy for Work)
+ (Energy for thermodynamic heat loss)

Thermal energy which is Impossible to use



Change of Gibbs' free energy $\Delta G = \Delta H - T\Delta S$

Process	Quantity of energy	Tempera-ture	ΔH	ΔS	Degree of low level d
Heat source	Output Q	T	$-Q$	$-Q/T$	$1/T$
Heat sink	Input Q	T	Q	Q/T	$1/T$
Work source	Output W	—	$-W$	0	0
Work sink	Input W	—	W	0	0

- **Heat source and sink・・・No work function**

$$\Delta G = 0$$

$$d = \frac{\Delta S}{\Delta H}$$

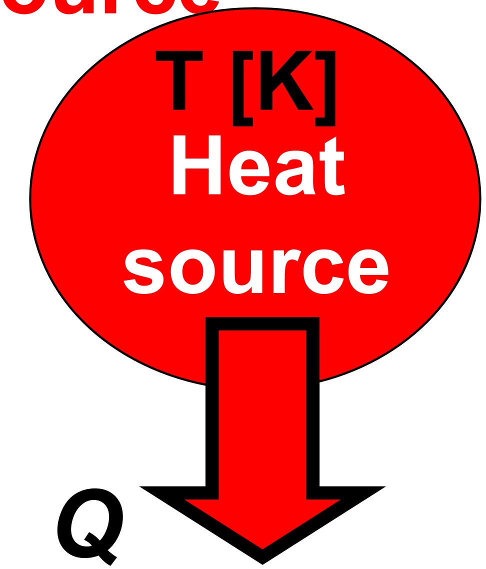
$$\Delta G = \Delta H - T\Delta S \longrightarrow \Delta S = \Delta H / T$$

- **Work source and sink・・・No thermal function**

$$\Delta S = 0$$

Even if the Work source or sink evolves or takes energy, Respectively, the quality of them dose not change.

Heat source



$\Delta H = -Q$

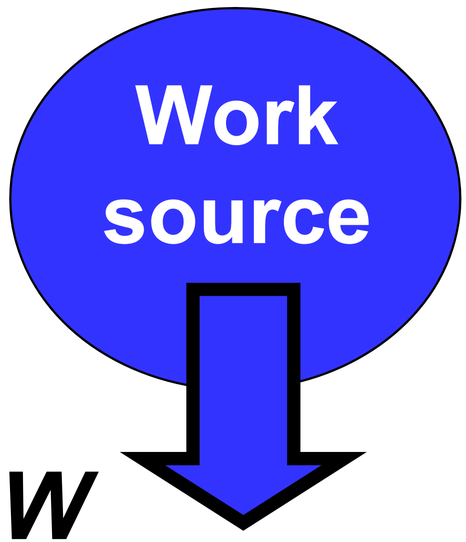
$\Delta S = -Q/T$

$d = 1/T$

$\Delta S = \Delta H / T$

$$d = \frac{\Delta S}{\Delta H}$$

Work source



$\Delta H = -W$

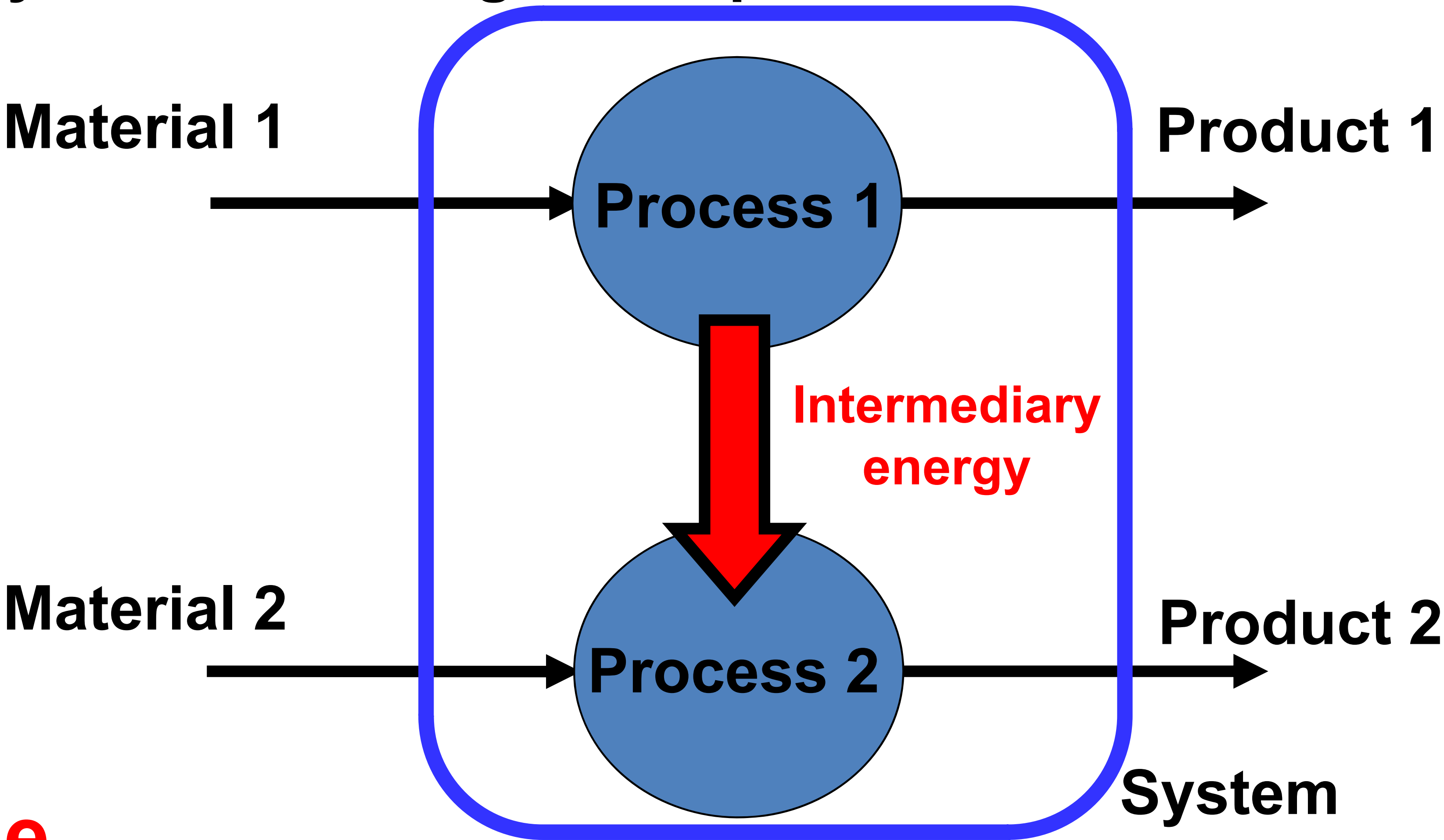
$\Delta S = 0$

$d = 0$

3) Thermodynamics for system

System: Assembly of processes

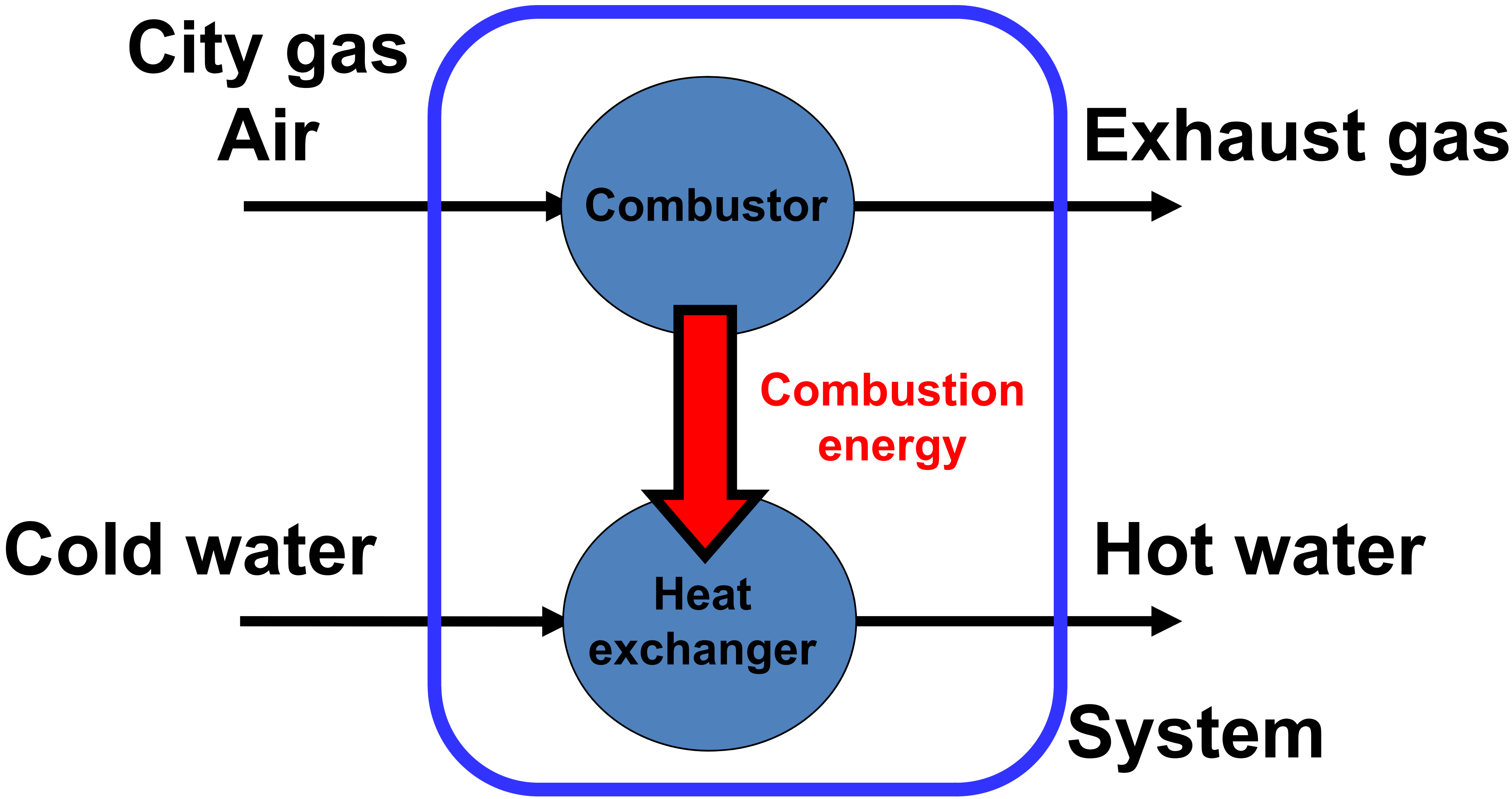
Ex. System consisting of two processes



Rule

The intermediary energy must not cross the system boundary.

Ex. Gas heating system for hot water



Thermodynamics for system

Rules

Only the materials can cross the system boundary.

The intermediary energy (Heat and Work) must not cross the system boundary.

The 1st law of thermodynamics

(Conservation low of energy)

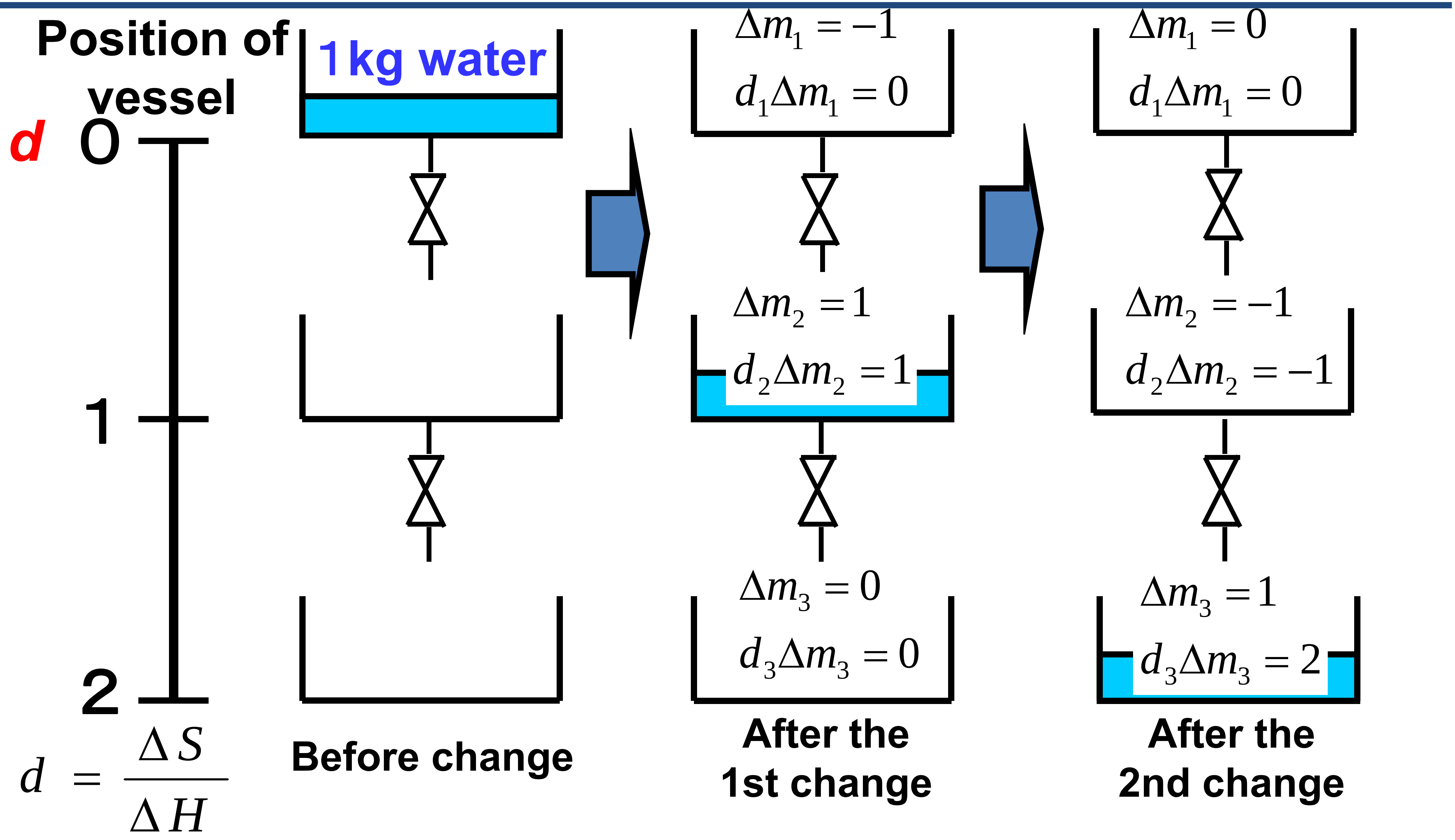
$$\sum_j \Delta H_j = 0$$

The 2nd law of thermodynamics

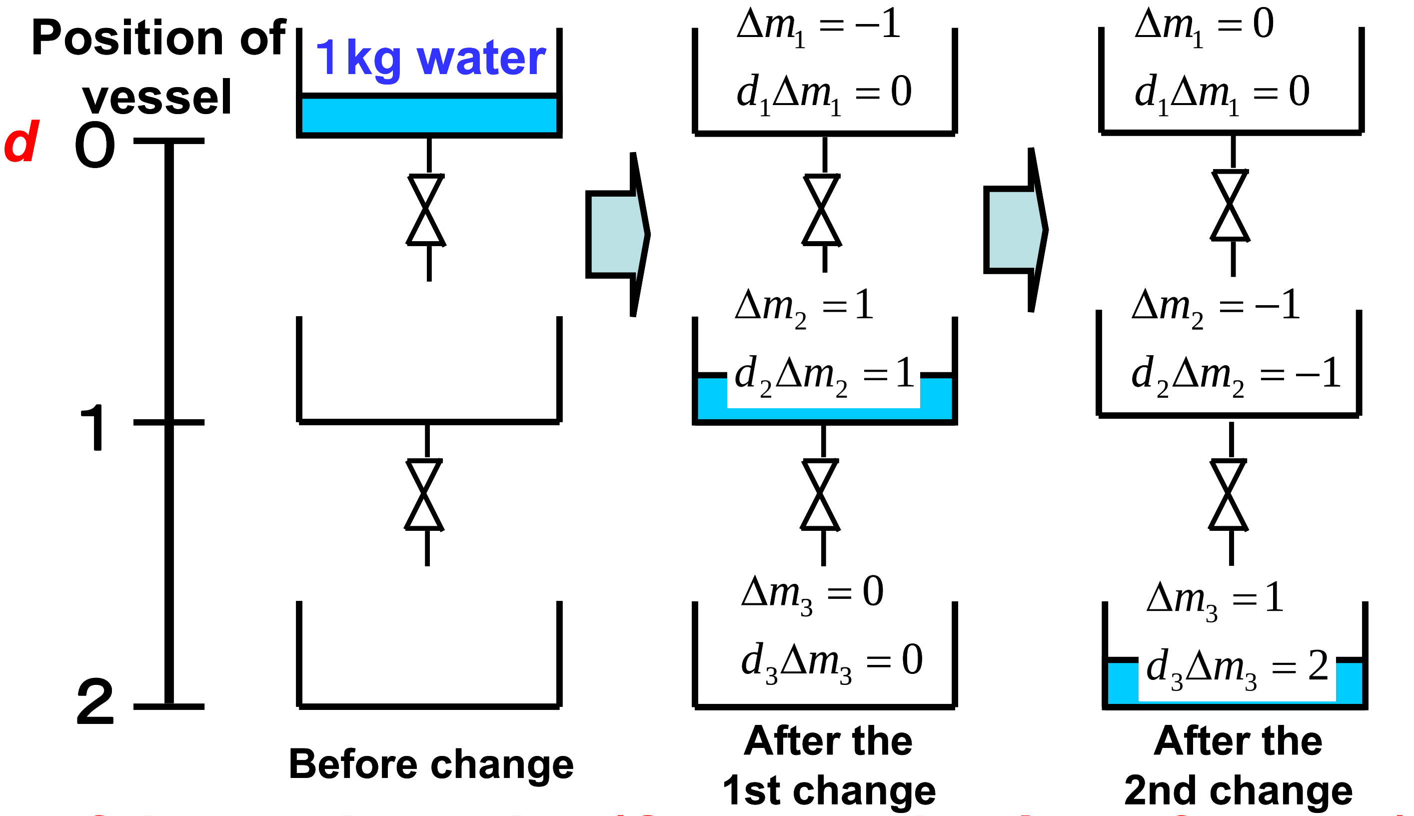
(Increase law of entropy)

$$\sum_j \Delta S_j \geq 0$$

Explanation of the 1st and 2nd law of thermodynamics by Water model



Δ*H*→ Change of water mass : Δ*m* **_d_→ Position of water**



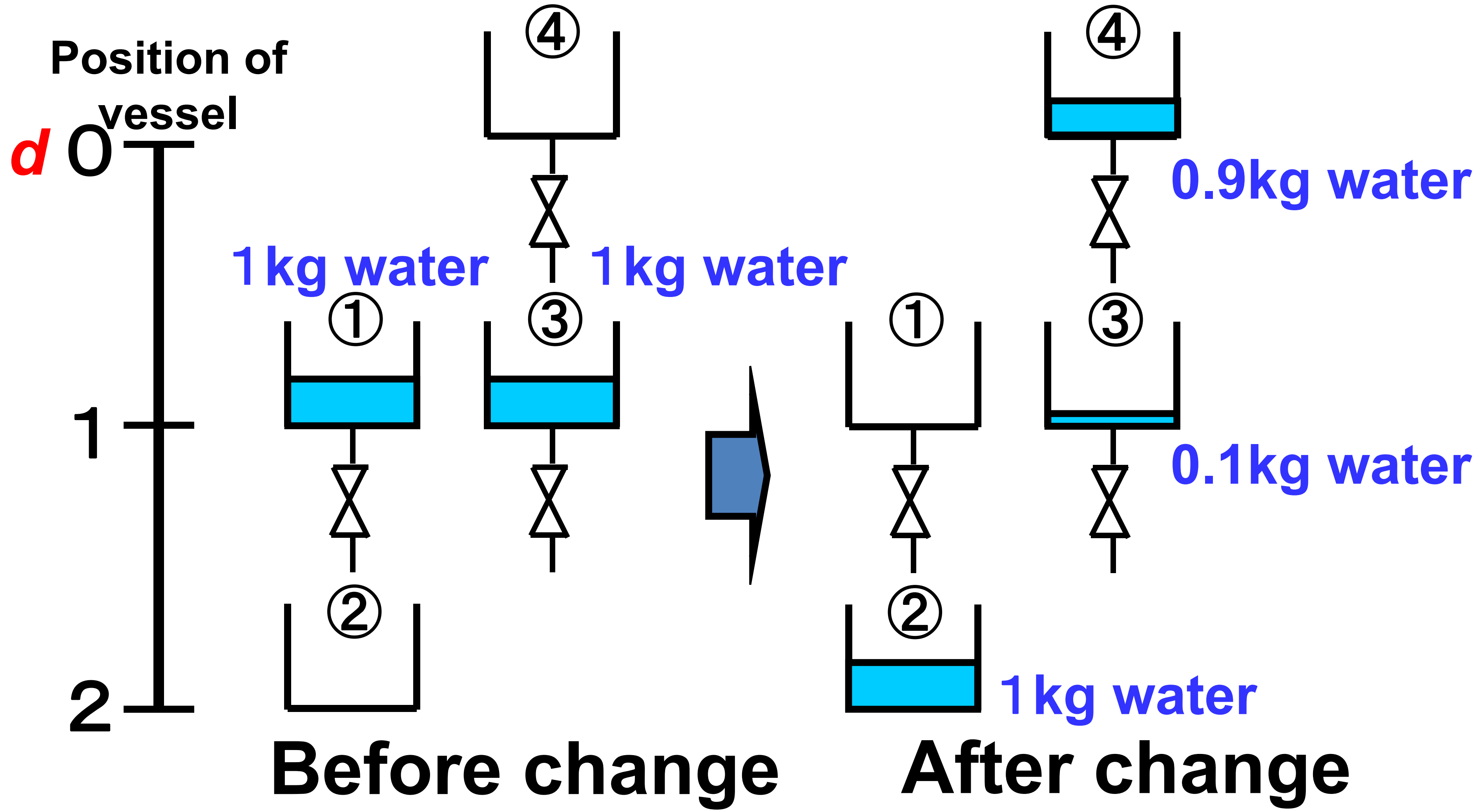
The 1st law of thermodynamics (Conservation low of energy)

$$\sum_j \Delta H_j = \sum_j \Delta m_j = \Delta m_1 + \Delta m_2 + \Delta m_3 = 0$$

The 2nd law of thermodynamics (Increase law of entropy)

$$\sum_j \Delta S_j = \sum_j d_j \Delta m_j = d_1 \Delta m_1 + d_2 \Delta m_2 + d_3 \Delta m_3 = 1 \geq 0$$

Ex.

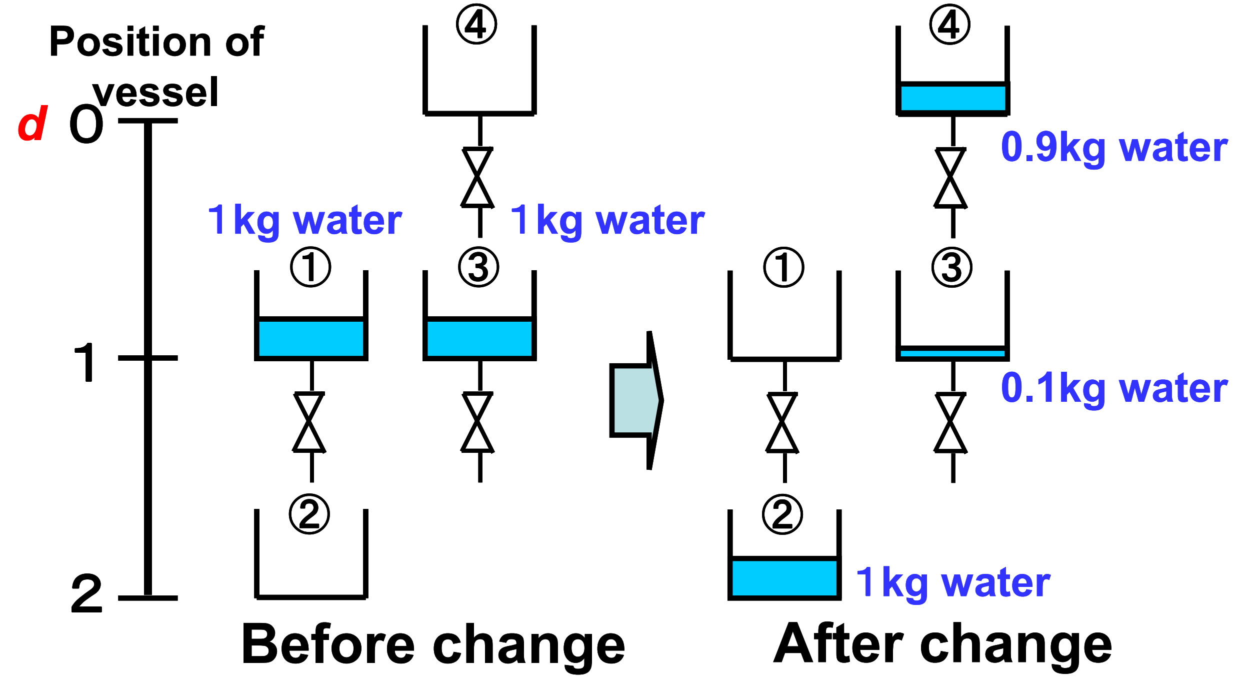


① $\Delta m_1 = -1,\ d_1 \Delta m_1 = -1$

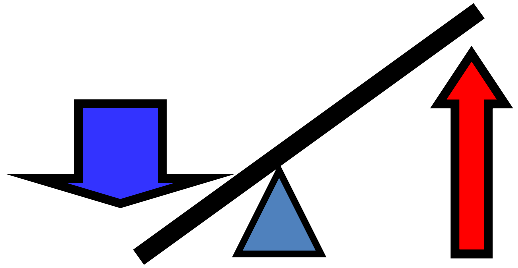
② $\Delta m_2 = 1,\ d_2 \Delta m_2 = 2$

③ $\Delta m_3 = -0.9,\ d_3 \Delta m_3 = -0.9$

④ $\Delta m_4 = 0.9,\ d_4 \Delta m_4 = 0$



Energy leverage



① $\Delta m_1 = -1,\ d_1 \Delta m_1 = -1$ ② $\Delta m_2 = 1,\ d_2 \Delta m_2 = 2$

③ $\Delta m_3 = -0.9,\ d_3 \Delta m_3 = -0.9$ ④ $\Delta m_4 = 0.9,\ d_4 \Delta m_4 = 0$

The 1st law of thermodynamics (Conservation low of energy)

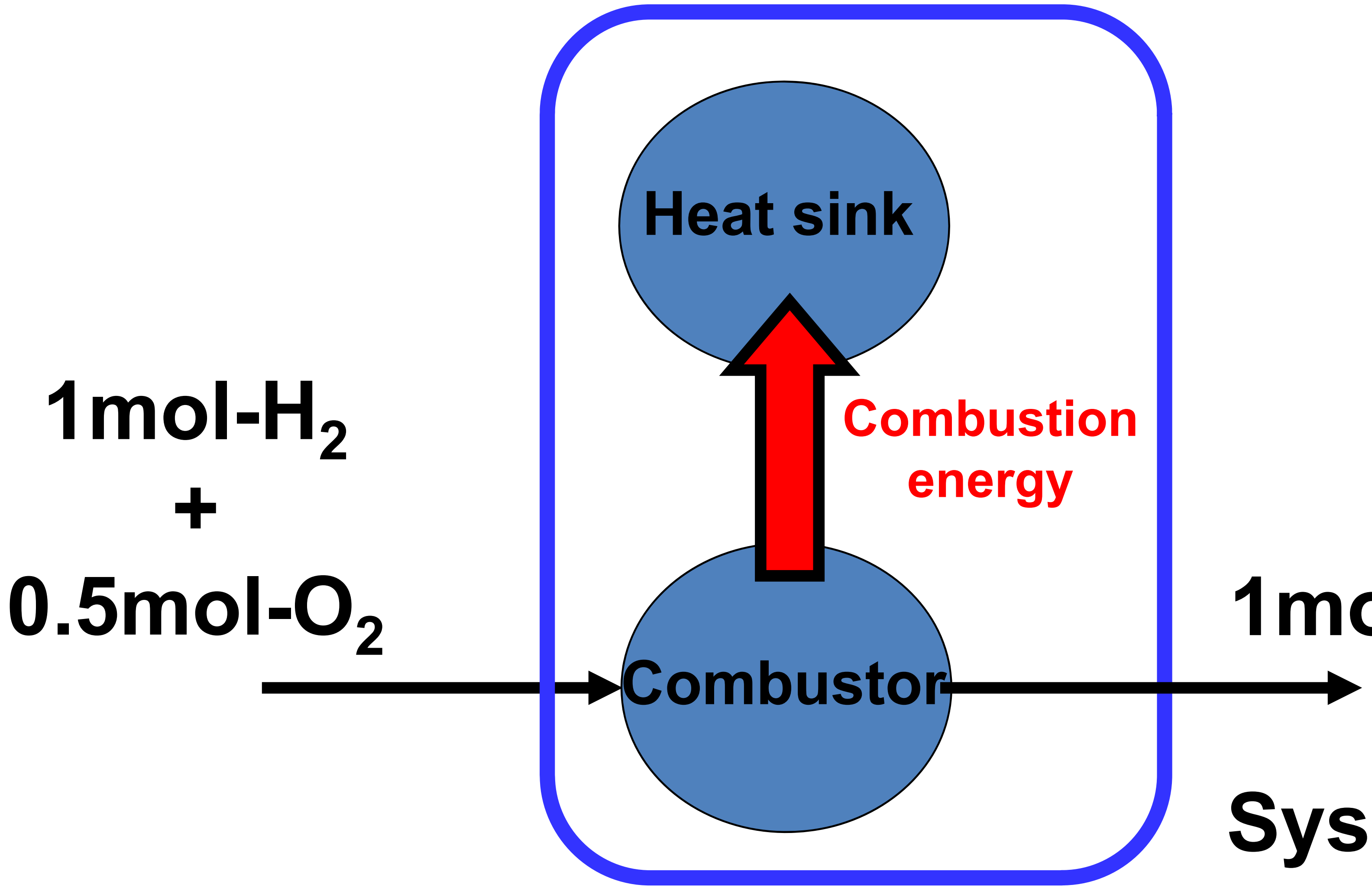
$$\sum_j \Delta H_j = \sum_j \Delta m_j = \Delta m_1 + \Delta m_2 + \Delta m_3 + \Delta m_4 = 0$$

The 2nd law of thermodynamics (Increase law of entropy)

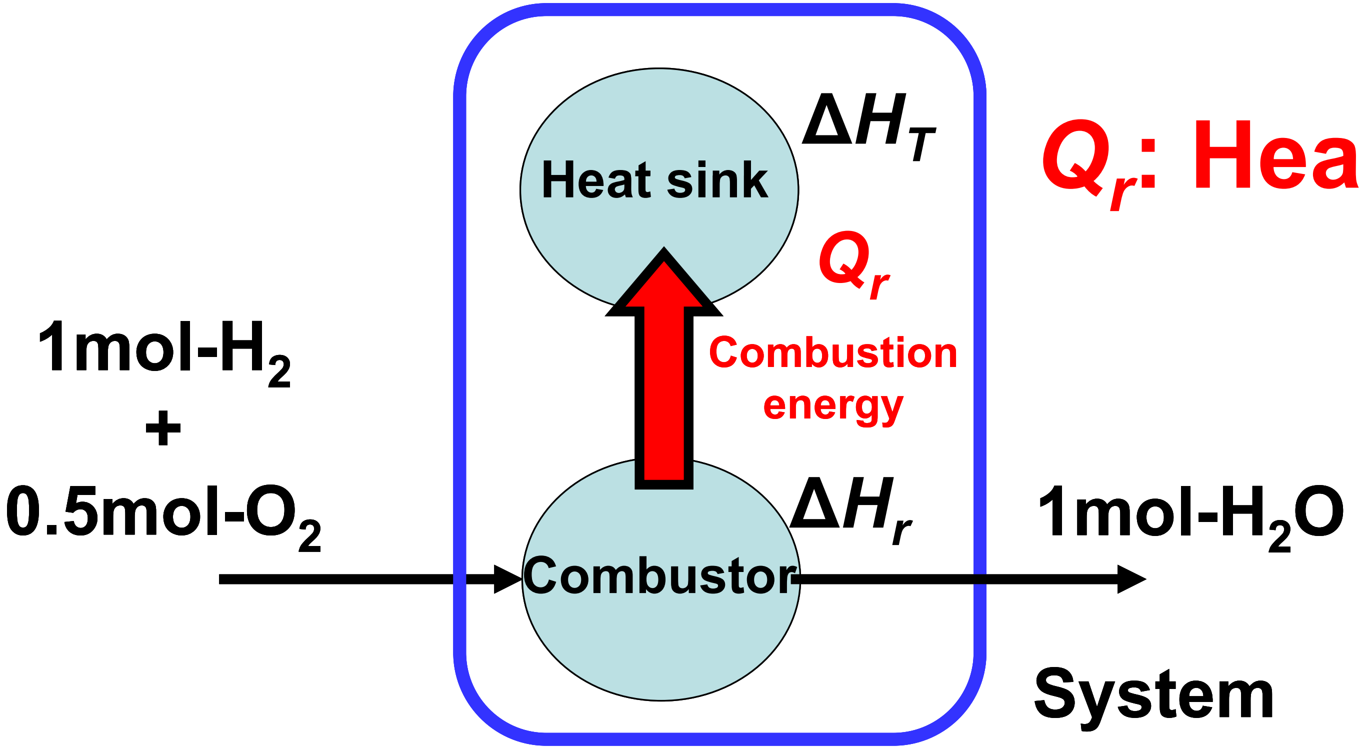
$$\sum_j \Delta S_j = \sum_j d_j \Delta m_j = d_1 \Delta m_1 + d_2 \Delta m_2 + d_3 \Delta m_3 + d_4 \Delta m_4 = 0.1 \geq 0$$

Applications of thermodynamics

Ex. Combustion of H_2 with O_2 $H_2 + 1/2O_2 \rightarrow H_2O$



Relationship between enthalpy change (ΔHr) and reaction heat (Qr)



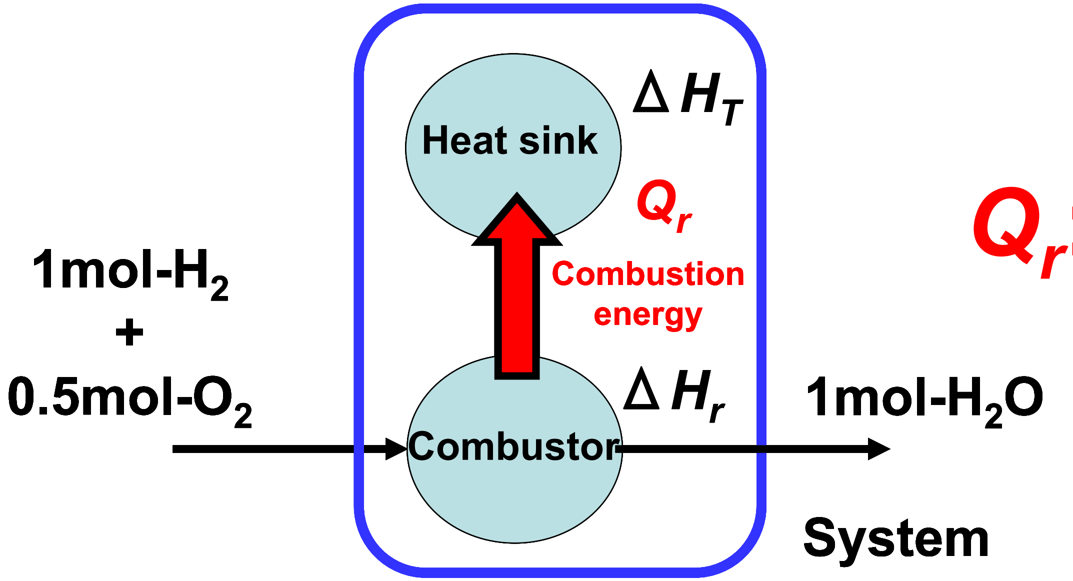
Q_r: Heat of reaction

Energy change by reaction: ΔH_r

Energy change in heat sink: ΔH_T

From the 1st law $\Delta H_r + \Delta H_T = 0$

$$\Delta H_T = Q_r \longrightarrow \Delta H_r = -Q_r$$



Q_r: Heat of reaction

$$\Delta H_r = -Q_r$$

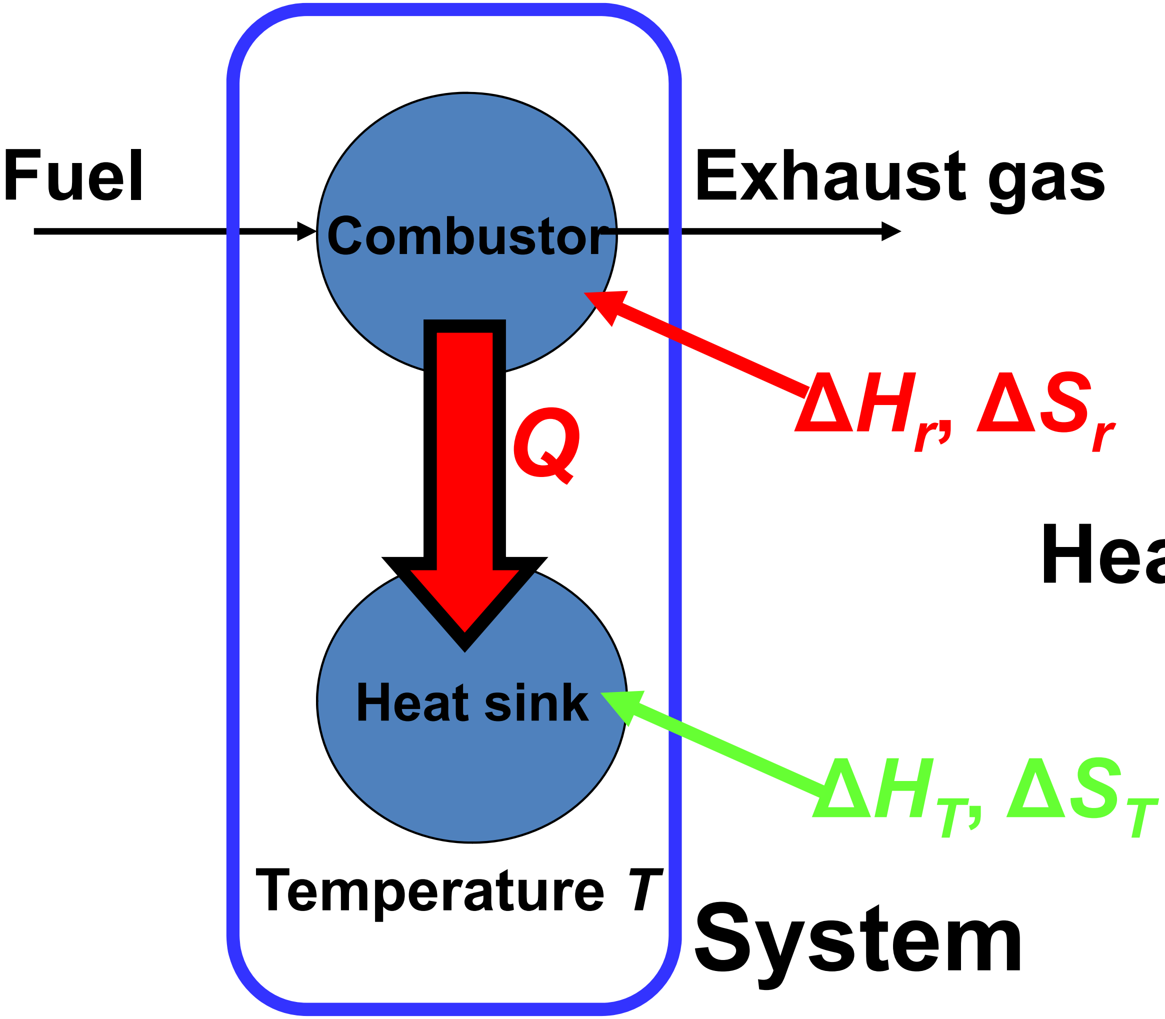
Exothermic reaction

$$Q_r > 0 \longrightarrow \Delta H_r : \text{Negative}$$

Endothermic reaction

$$Q_r < 0 \longrightarrow \Delta H_r : \text{Positive}$$

Exothermic reaction system



The 1st law

$$\Delta H_r + \Delta H_T = 0$$

The 2nd law

$$\Delta S_r + \Delta S_T \geqq 0$$

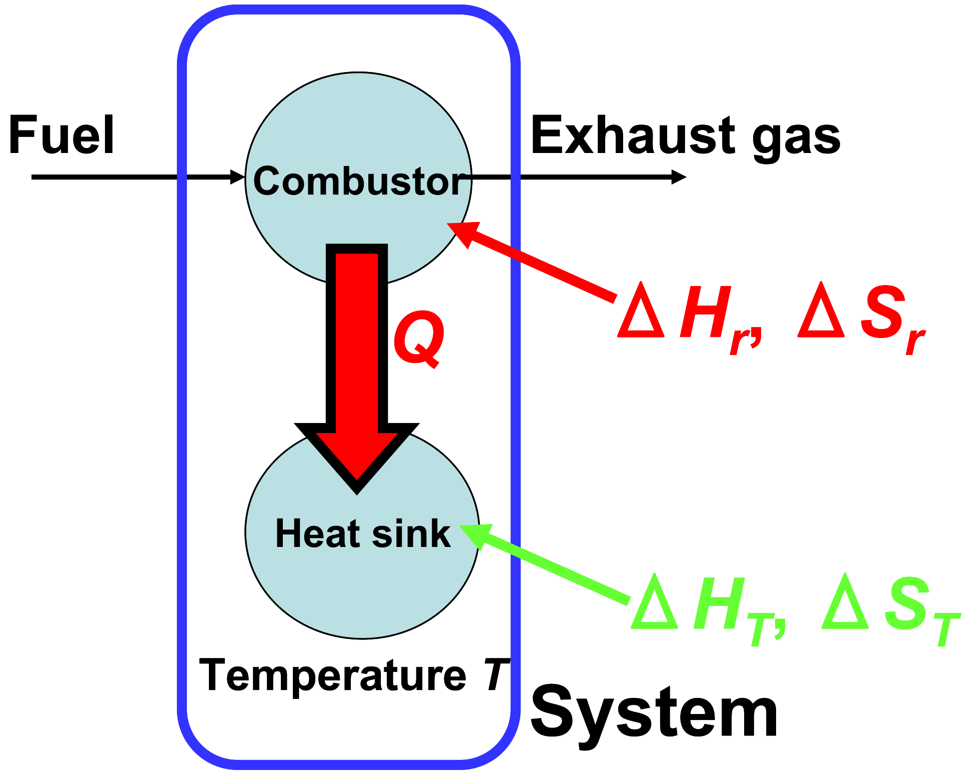
Heat sink

$$\Delta H_T = Q$$

$$\Delta S_T = Q/T$$ より

$$\Delta H_r + Q = 0$$

$$\Delta S_r + (Q/T) \geqq 0$$



$$\Delta H_r + Q = 0$$
$$\Delta S_r + (Q/T) \geqq 0$$
↓
$$\Delta S_r - (\Delta H_r/T) \geqq 0$$

Multiply (-T) by both sides

$$\Delta H_r - T\Delta S_r \leqq 0$$

Condition to occur exothermic reaction

$$\Delta H_r \leqq T\Delta S_r$$

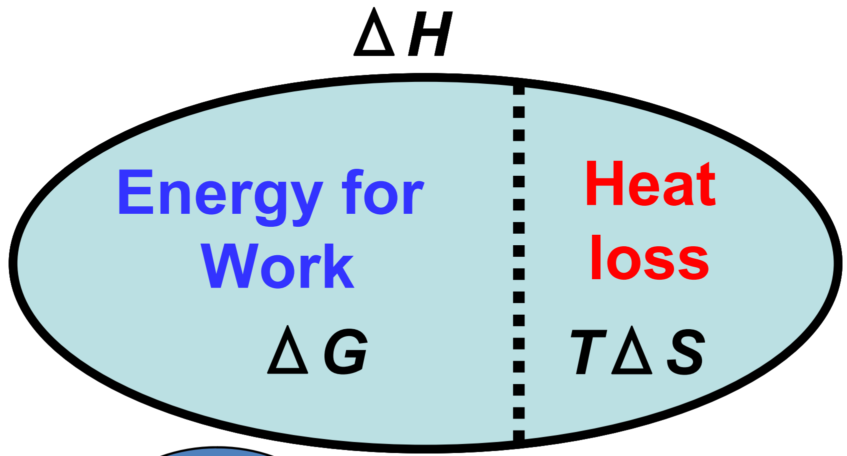
$\Delta H - T\Delta S \equiv \Delta G$: Change of Gibbs' free energy

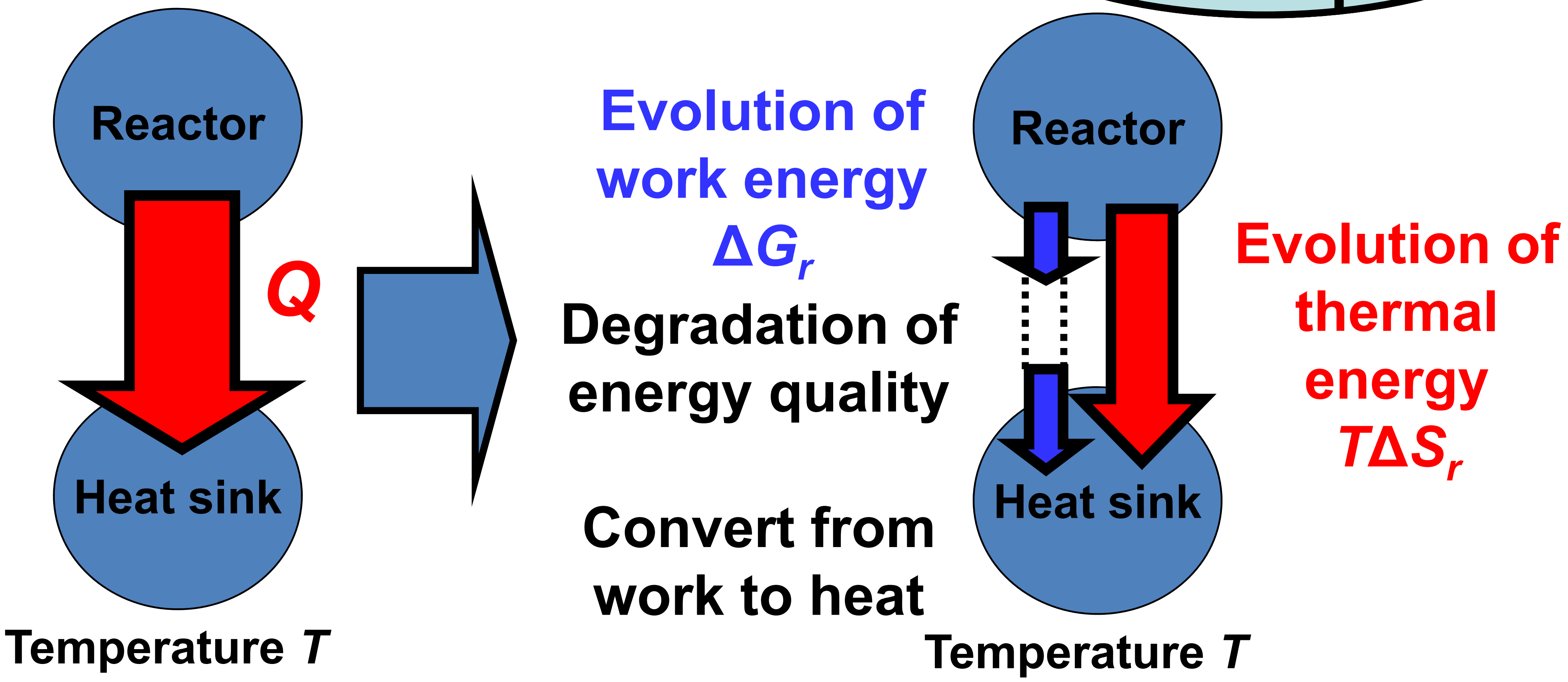
Condition to occur exothermic reaction

$$\Delta G_r \leqq 0$$

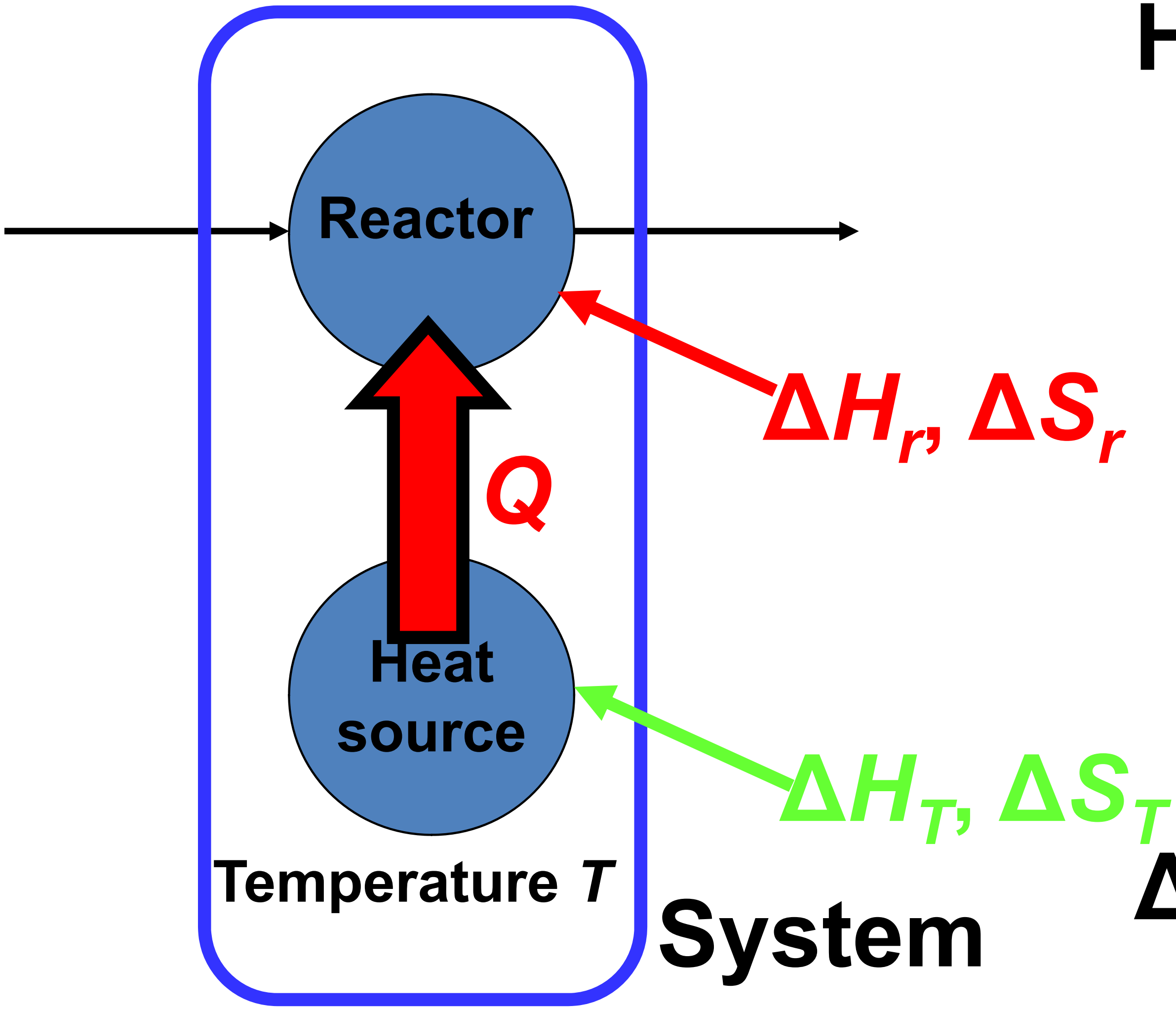
Content of enthalpy change: ΔH

$$\Delta H = \Delta G + T\Delta S$$





Endothermic reaction system



Heat source

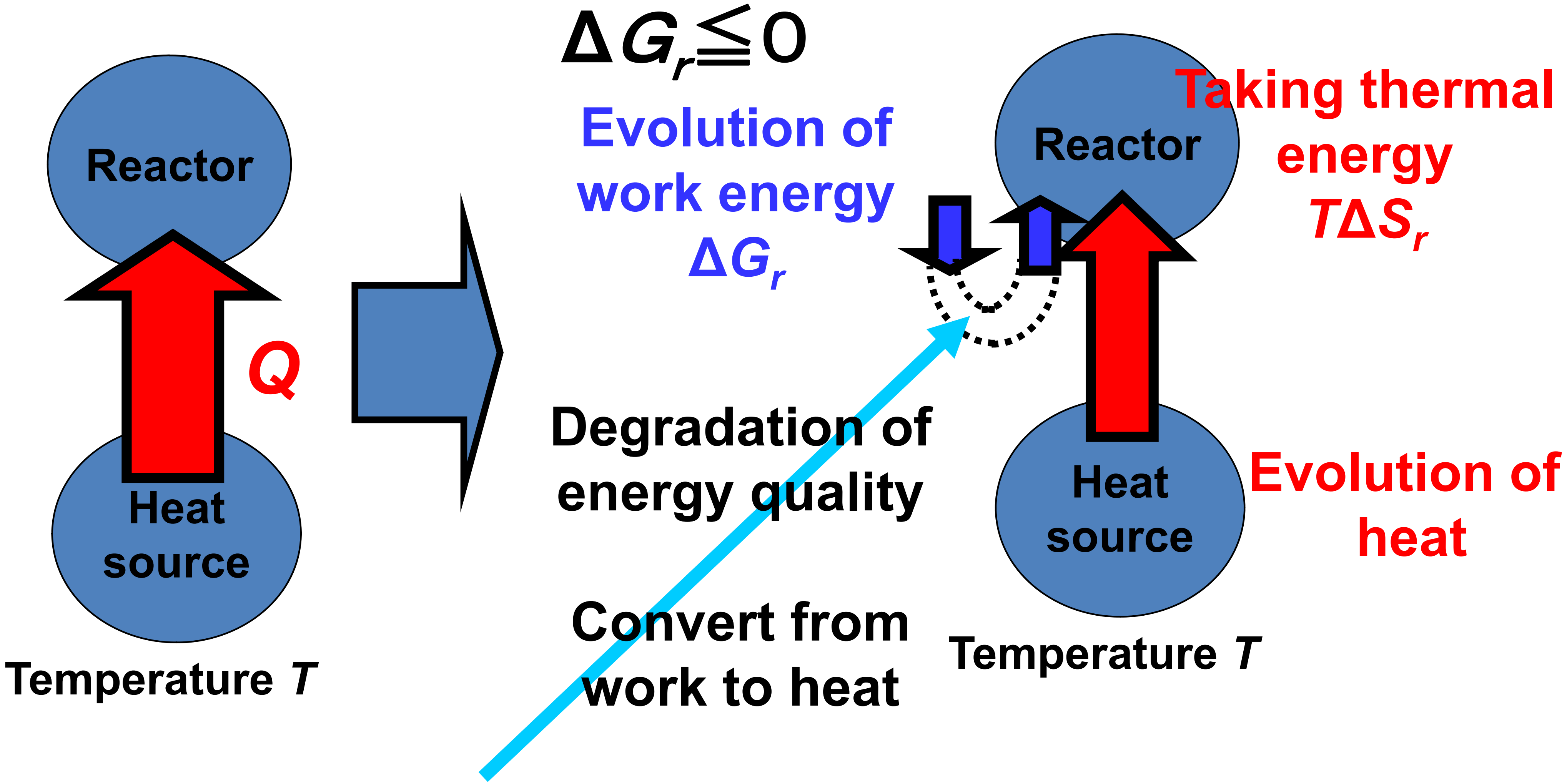
$$\Delta H_T = -Q$$
$$\Delta S_T = -Q/T$$

$$\Delta H_r - Q = 0$$
$$\Delta S_r - (Q/T) \geqq 0$$

$$\Delta S_r - (\Delta H_r/T) \geqq 0$$

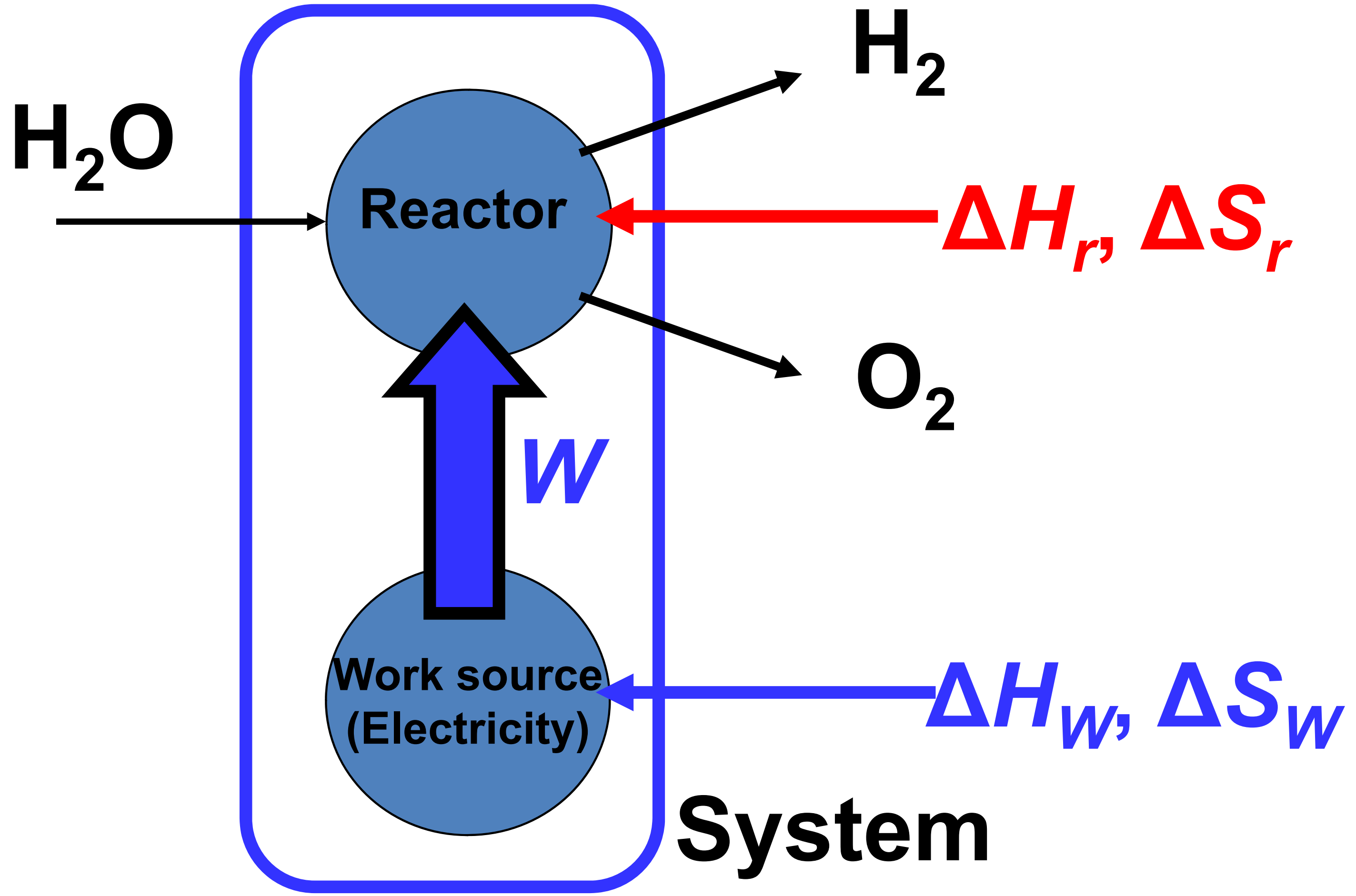
The condition for the endothermic reactions is the same as the for the exothermic reactions.

Endothermic reaction $\Delta Hr > 0$



Driving force for reaction

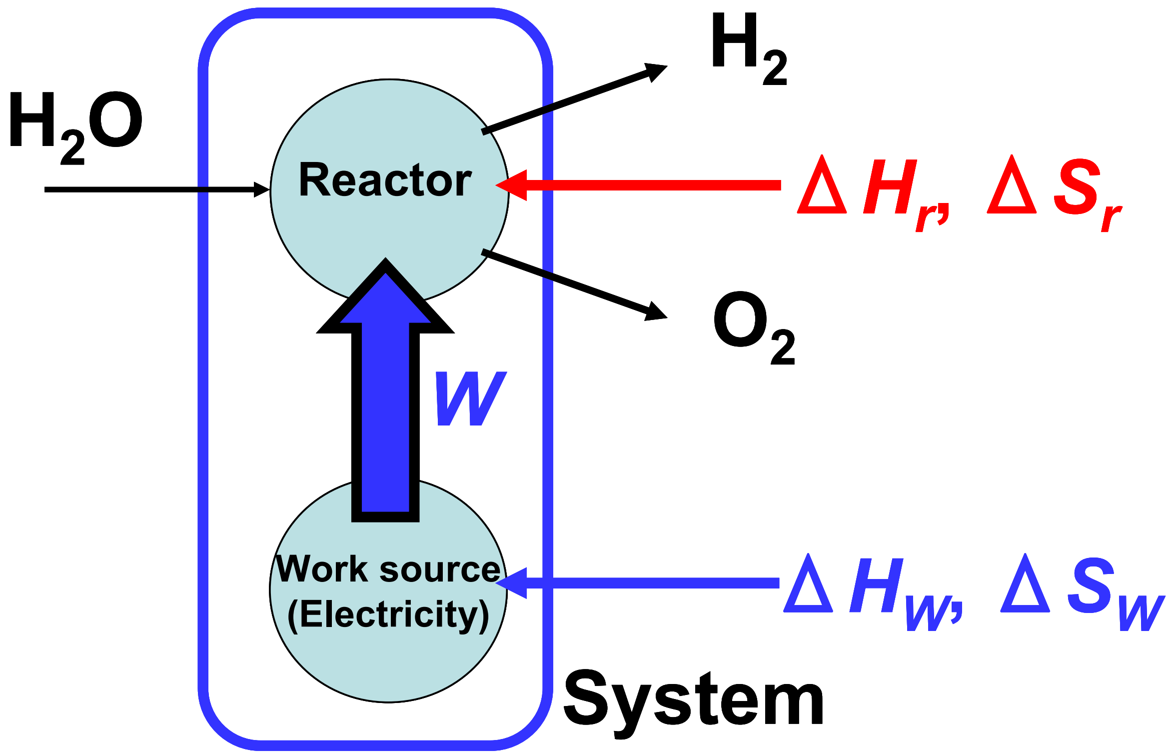
Ex. 1 Thermodynamic analysis of electric decomposition of water



$$\Delta H_W = -W$$
$$\Delta S_W = 0$$

The 1st law $\Delta H_r + \Delta H_W = 0$ $\qquad \Delta H_r - W = 0$

The 2nd law $\Delta S_r + \Delta S_W \geqq 0$ $\qquad \Delta S_r \geqq 0$



$$\Delta H_r - W = 0$$

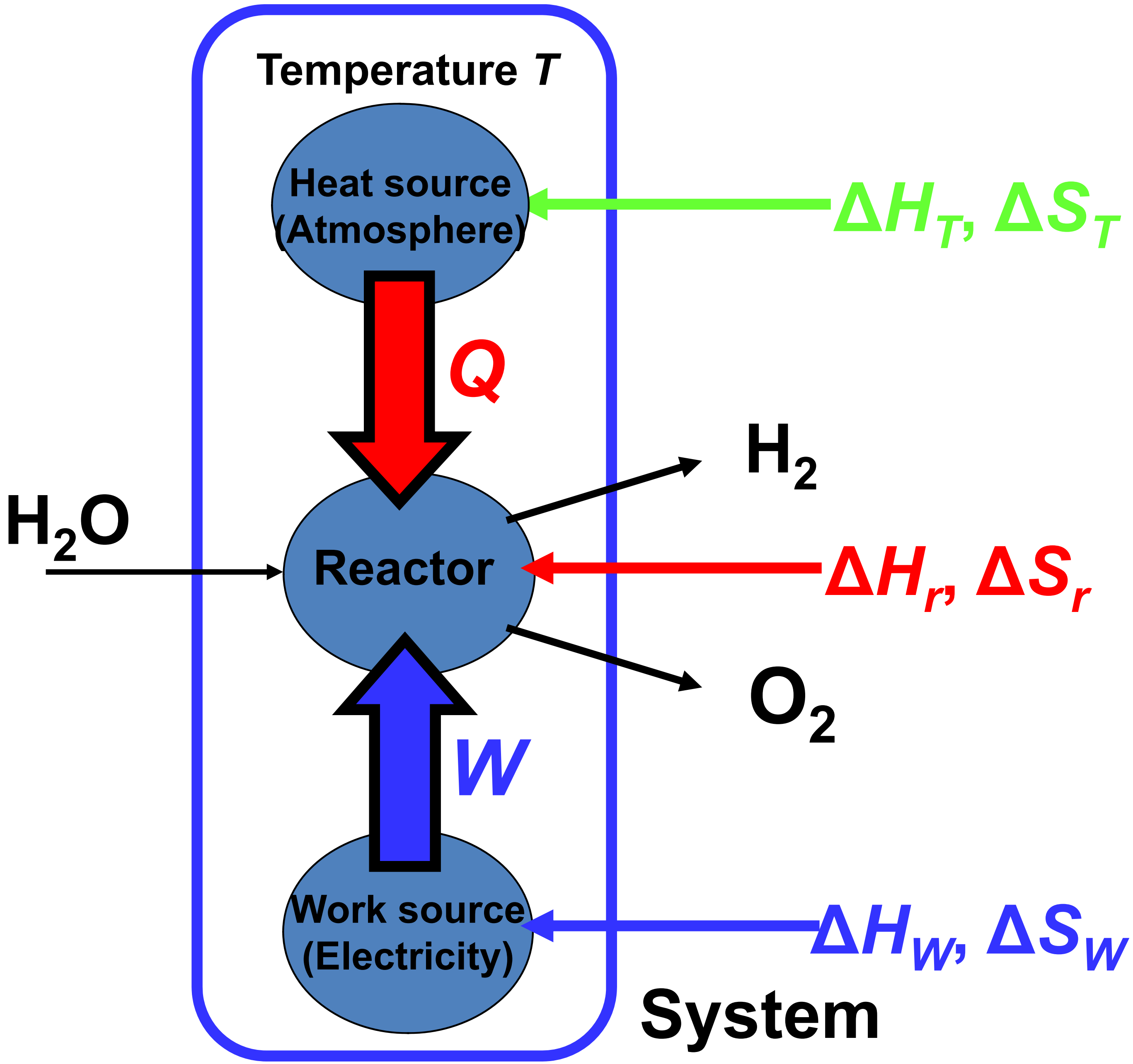
↓

$$\Delta H_r = W$$

Experimental result $W \leqq \Delta H_r$

Electric decomposition of water occurs by electric energy less than the theoretical heat of reaction.

Why?


Temperature T
Heat source (Atmosphere)
ΔH_T, ΔS_T
Q
H2
H2O
Reactor
ΔH_r, ΔS_r
O2
W
Work source (Electricity)
ΔH_W, ΔS_W
System

The 1st law $\Delta H_r + \Delta H_W + \Delta H_T = 0$

The 2nd law $\Delta S_r + \Delta S_W + \Delta S_T \geqq 0$

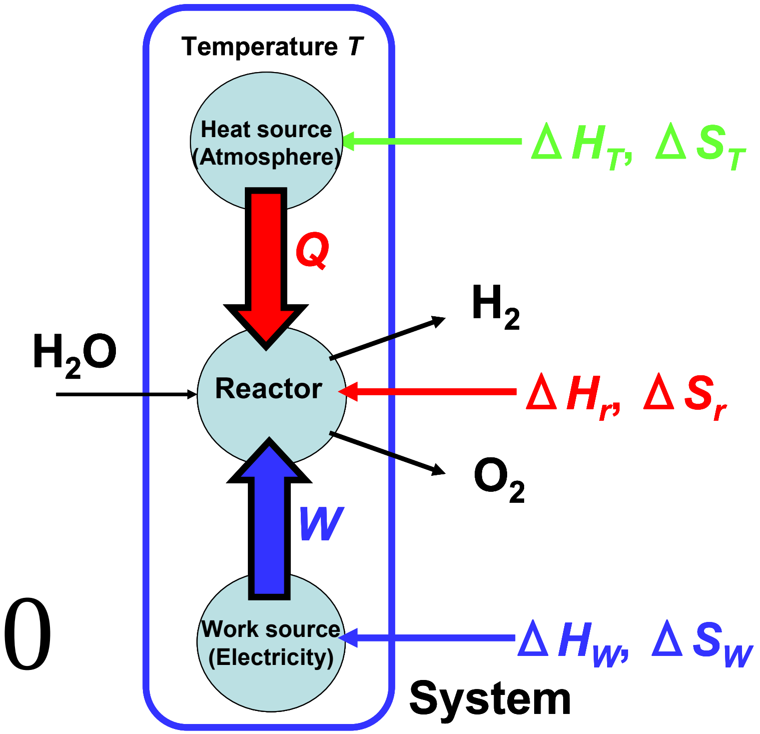
$\Delta H_r - W - Q = 0$

$\Delta S_r - Q/T \geqq 0$

$Q = \Delta H_r - W$

$$\Delta S_r - \frac{\Delta H_r - W}{T} \geq 0$$

$$W \geq \Delta H_r - T\Delta S_r = \Delta G_r$$

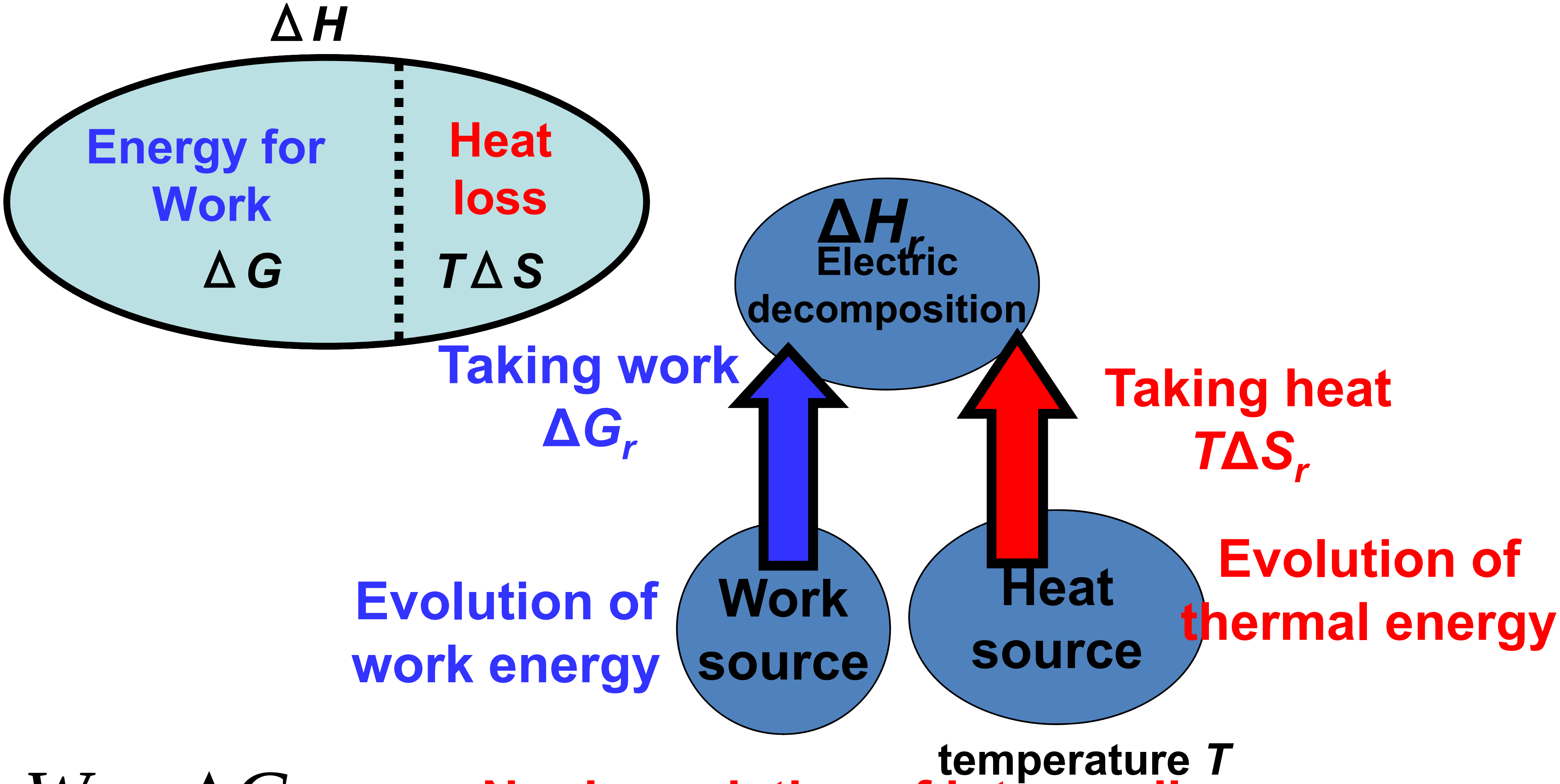


The reactor takes thermal energy of $T\Delta S_r$ from atmosphere.

Experimental results:

Consumed electricity ≒ Theoretical electricity

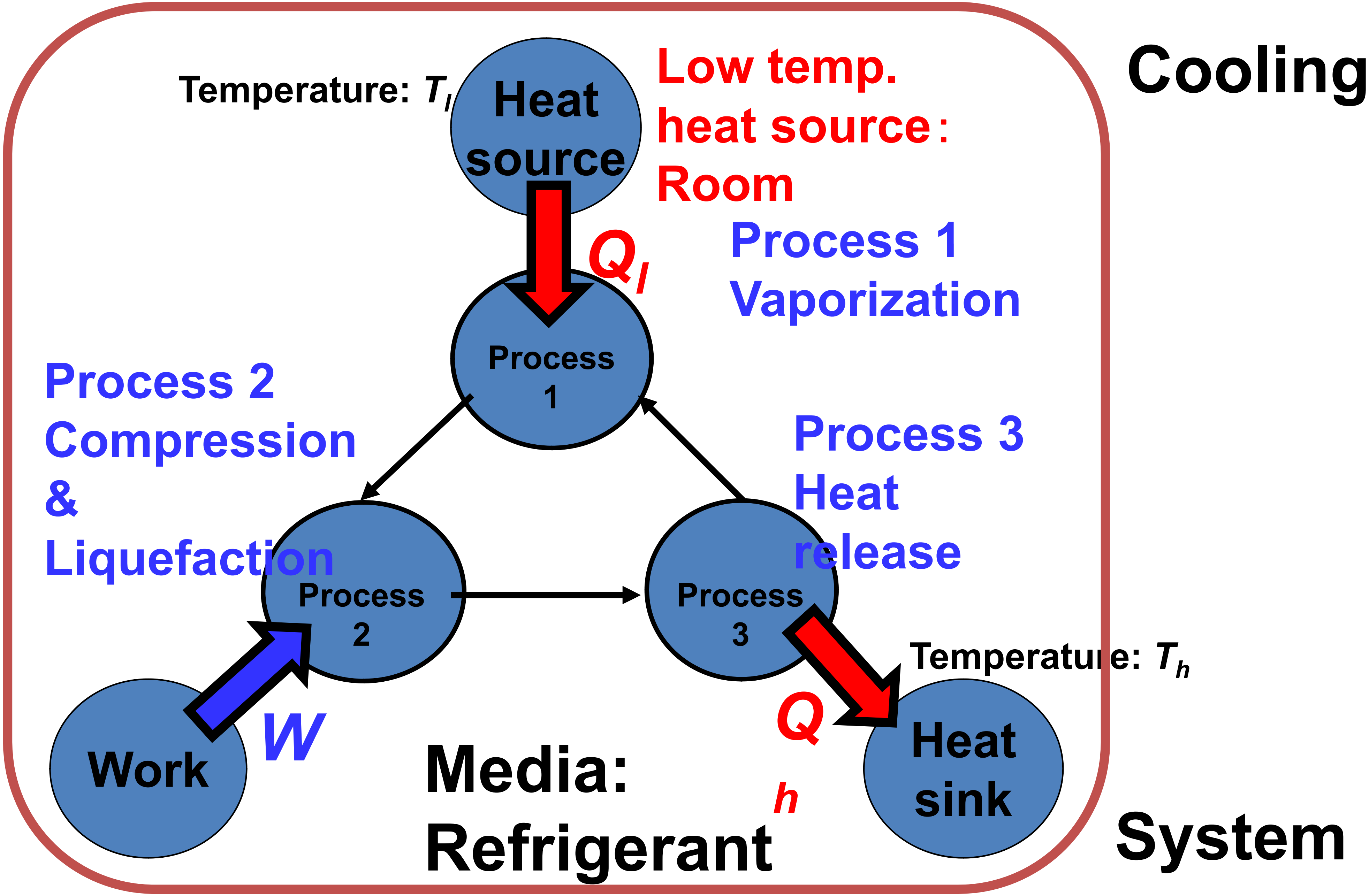
The electricity Is reduced at high atmospheric temperature.

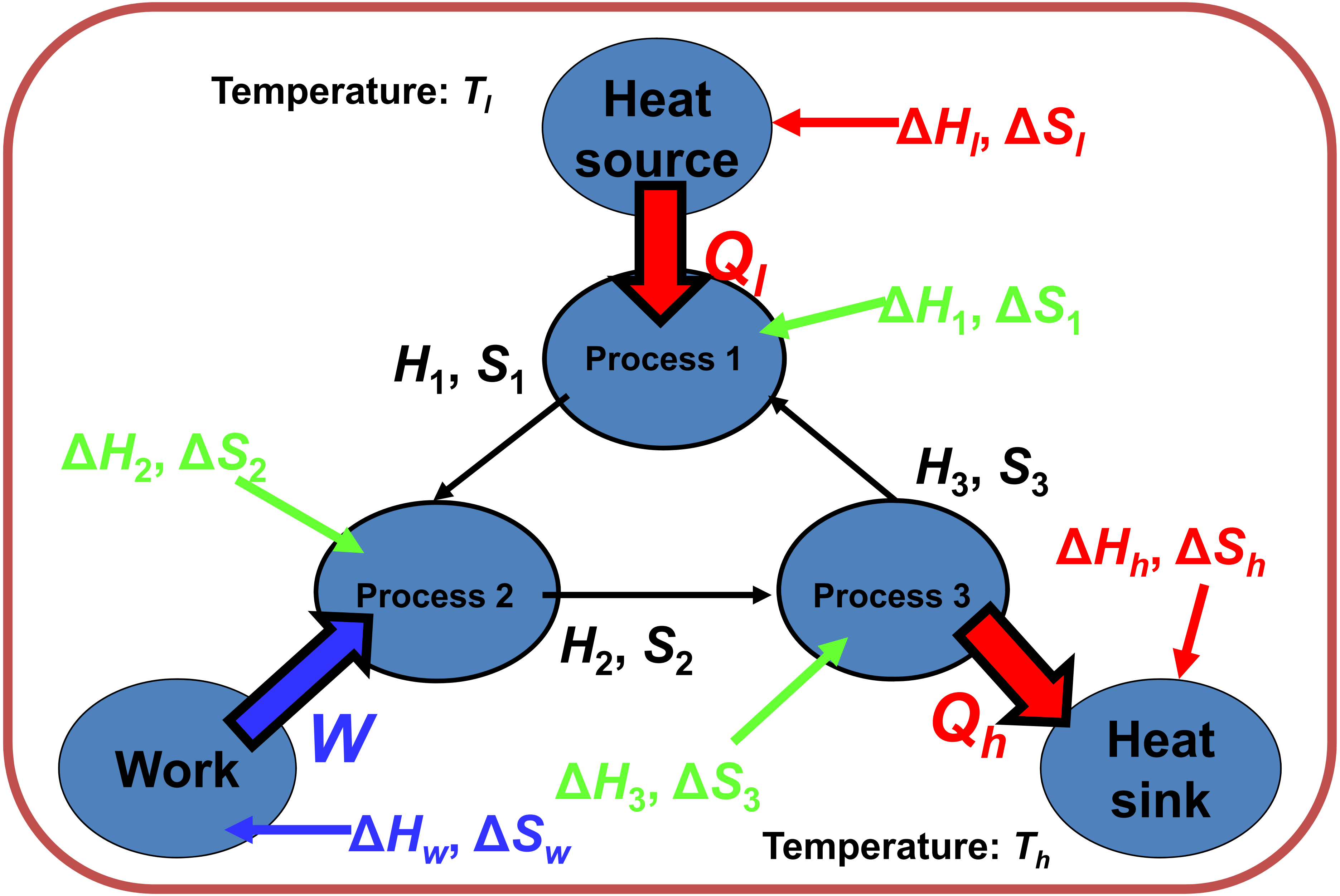


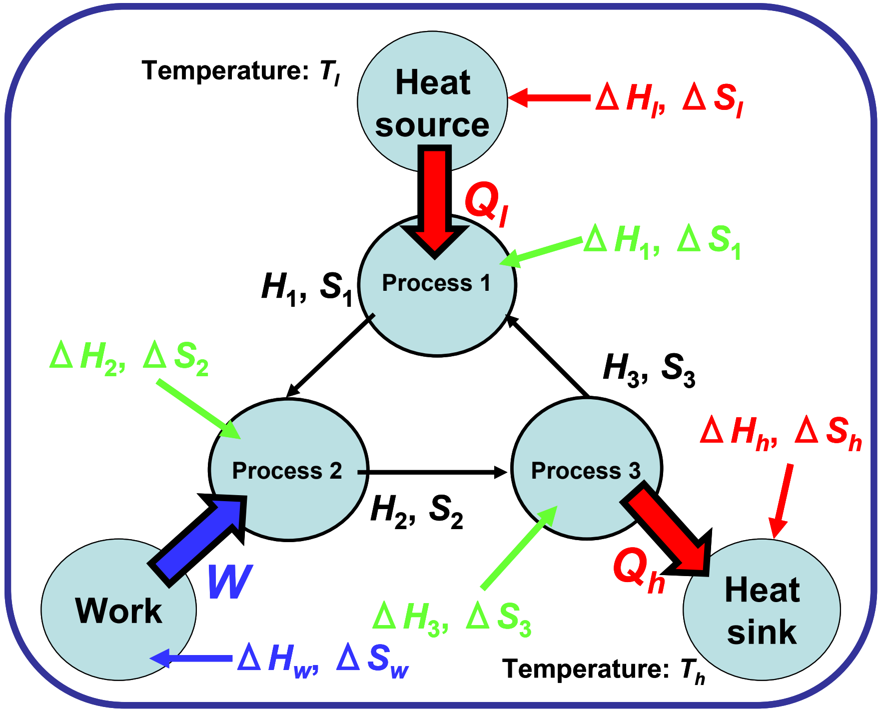
$W = \Delta G_r$ ··· **No degradation of intermediary energy**

$W > \Delta G_r$ ··· **Increase of electric energy and low thermal energy from heat sink**

Ex. 2 Thermodynamic analysis of heat pump



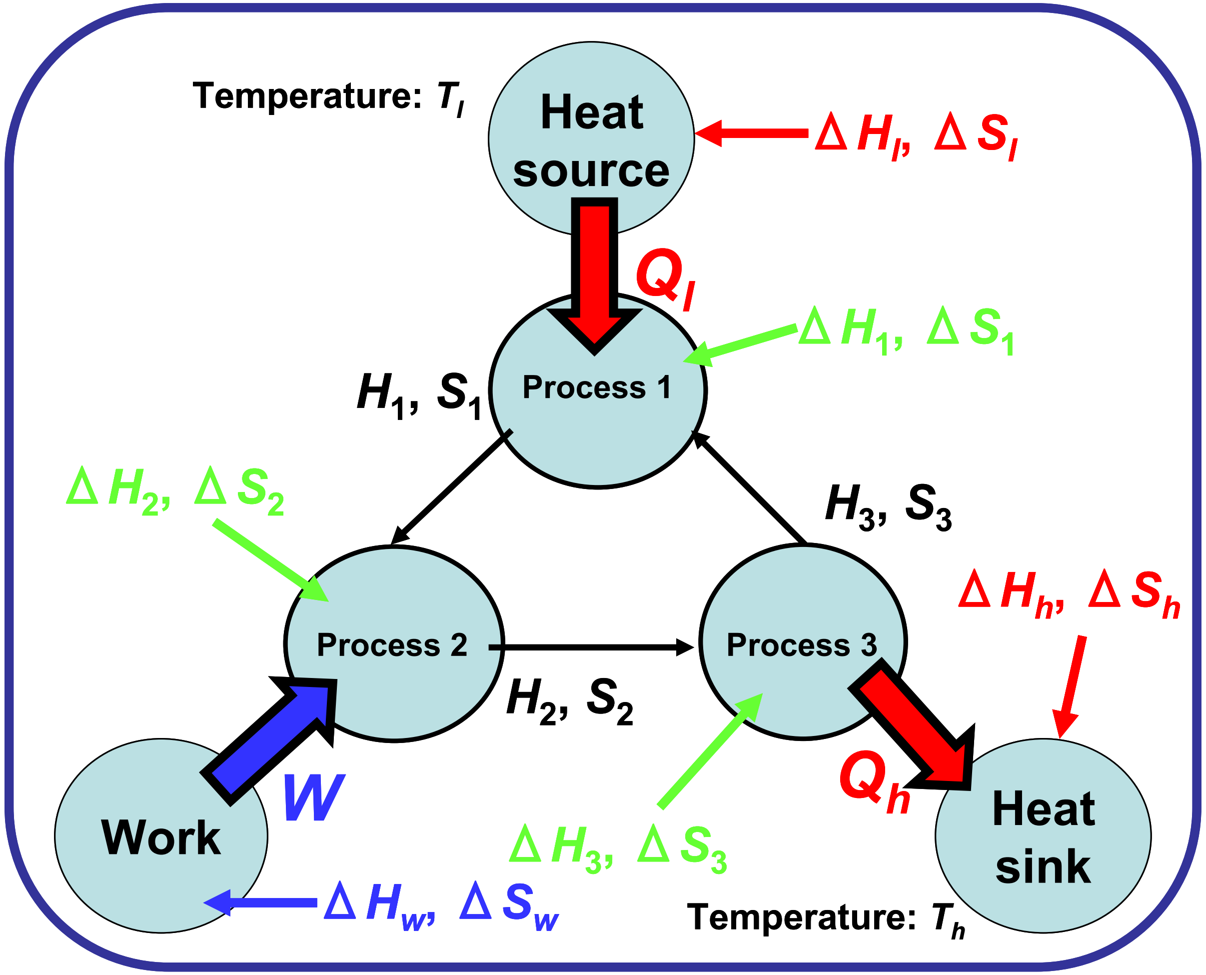

Temperature: T_l
Heat source
ΔH_l, ΔS_l
Q_l
ΔH_1, ΔS_1
Process 1
H_1, S_1
ΔH_2, ΔS_2
H_3, S_3
ΔH_h, ΔS_h
Process 2
Process 3
H_2, S_2
W
Work
Q_h
Heat sink
ΔH_3, ΔS_3
ΔH_w, ΔS_w
Temperature: T_h



The 1st law $$\underbrace{\Delta H_1 + \Delta H_2 + \Delta H_3}_{=\,0} + \Delta H_l + \Delta H_w + \Delta H_h = 0$$

The 2nd law $$\underbrace{\Delta S_1 + \Delta S_2 + \Delta S_3}_{=\,0} + \Delta S_l + \Delta S_w + \Delta S_h \geq 0$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = (H_1 - H_3) + (H_2 - H_1) + (H_3 - H_2) = 0$$
$$\Delta S_1 + \Delta S_2 + \Delta S_3 = (S_1 - S_3) + (S_2 - S_1) + (S_3 - S_2) = 0$$



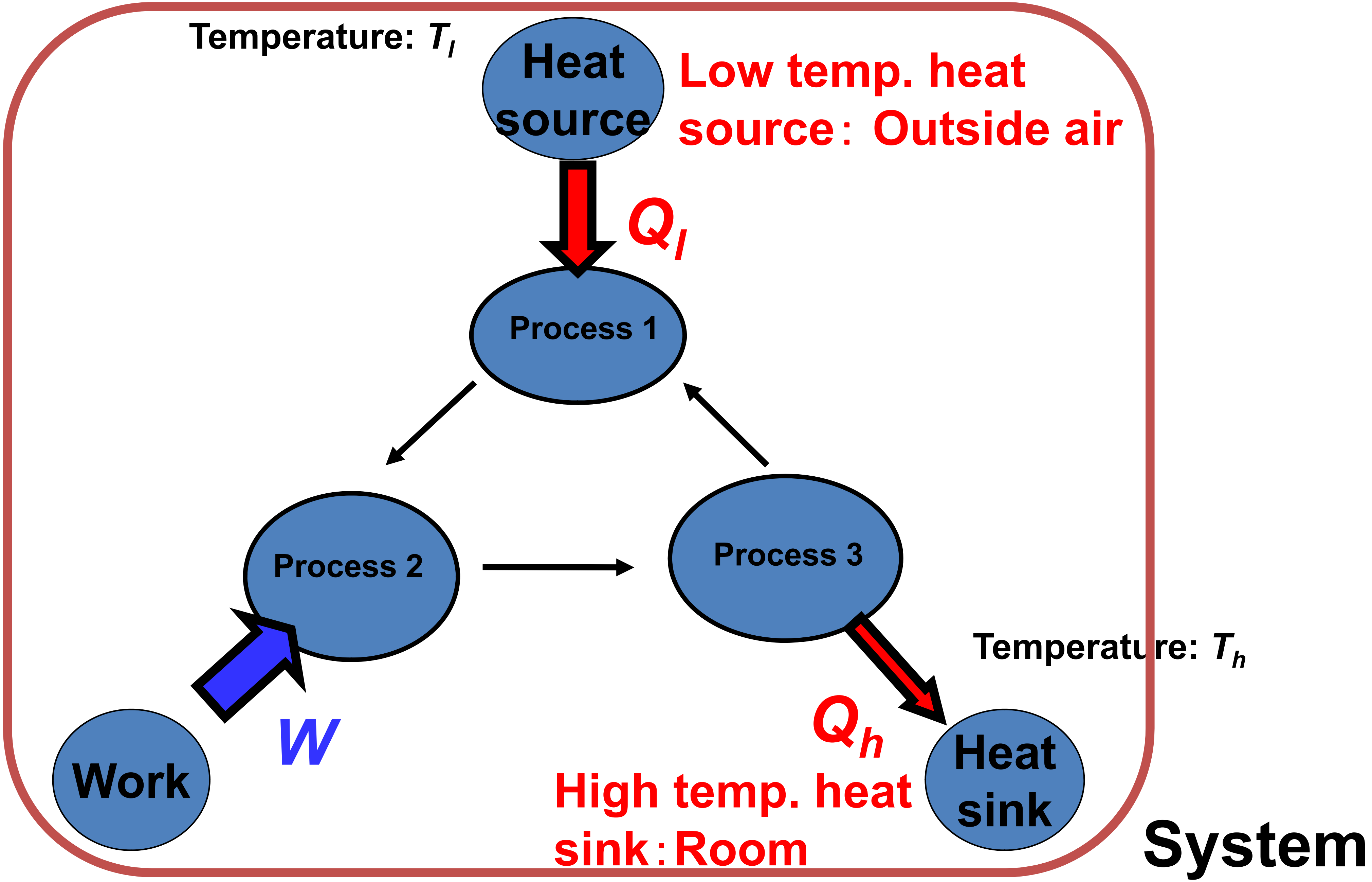
$$\Delta H_l + \Delta H_w + \Delta H_h = 0$$

$$-Q_l - W + Q_h = 0$$

$$\Delta S_l + \Delta S_w + \Delta S_h \geq 0$$

$$-\frac{Q_l}{T_l} + (0) + \frac{Q_h}{T_h} \geq 0$$

Room heating



Room heating

$$-Q_l - W + Q_h = 0$$

$$-\frac{Q_l}{T_l} + \frac{Q_h}{T_h} \geq 0$$

$$Q_l = -W + Q_h$$

$$\frac{W - Q_h}{T_l} + \frac{Q_h}{T_h} \geq 0$$

$$W - Q_h + \frac{T_l}{T_h} Q_h \geq 0$$

$$W \geq \frac{T_h - T_l}{T_h} Q_h$$

Cooling

$$W \geq \frac{T_h - T_l}{T_l} Q_l$$

Room heating

$$W \geq \frac{T_h - T_l}{T_h} Q_h$$

Heat at T_l in the air is taken. $T_h > T_l$

The room at T_h is heated at heating rate of Q_h.

Ex. Outside temp.: －3℃(=270K)

Room temp.: 27℃(=300K)

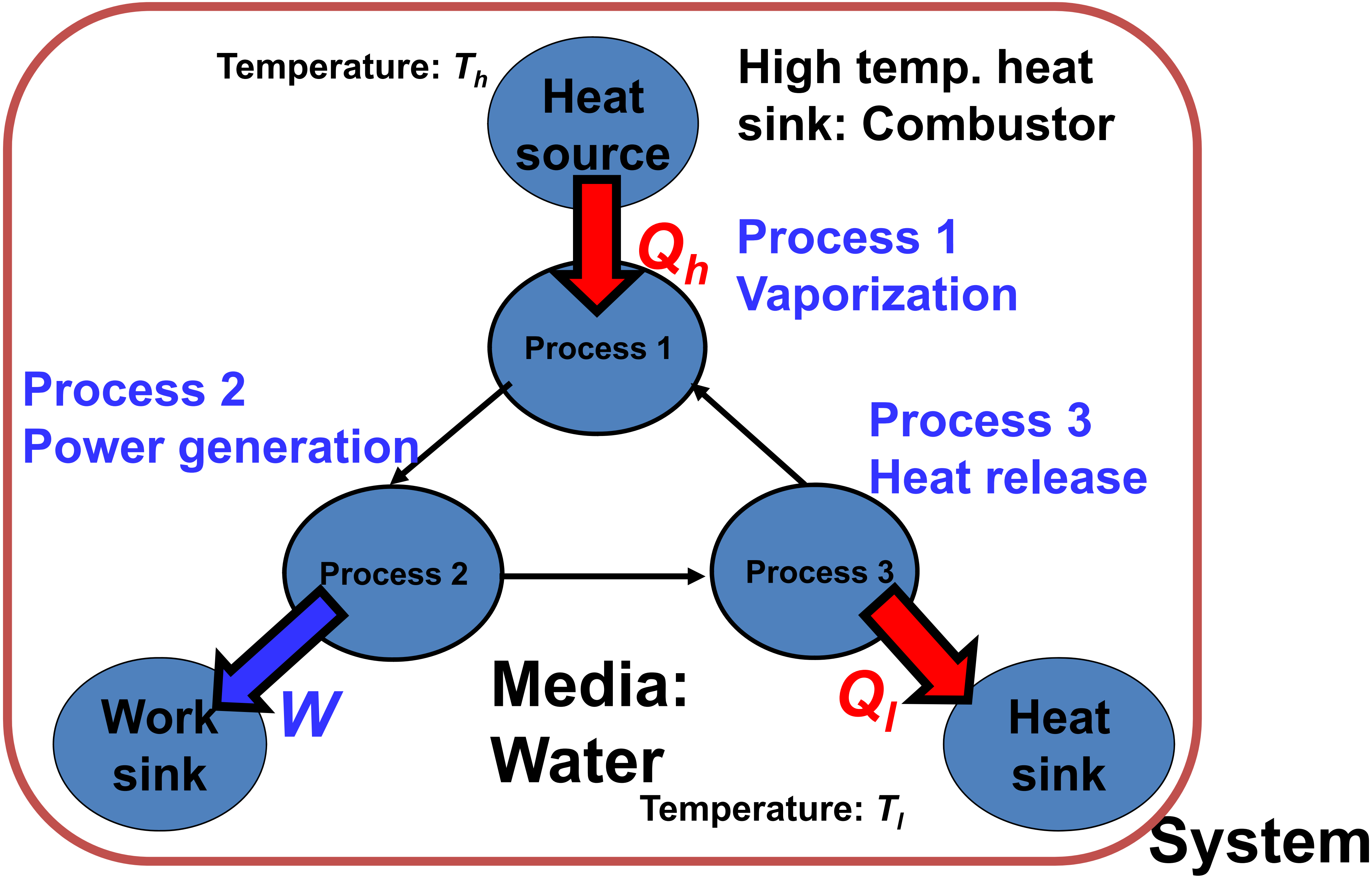
Heating rate＝1kW＝（1kJ/s）＝Q_h

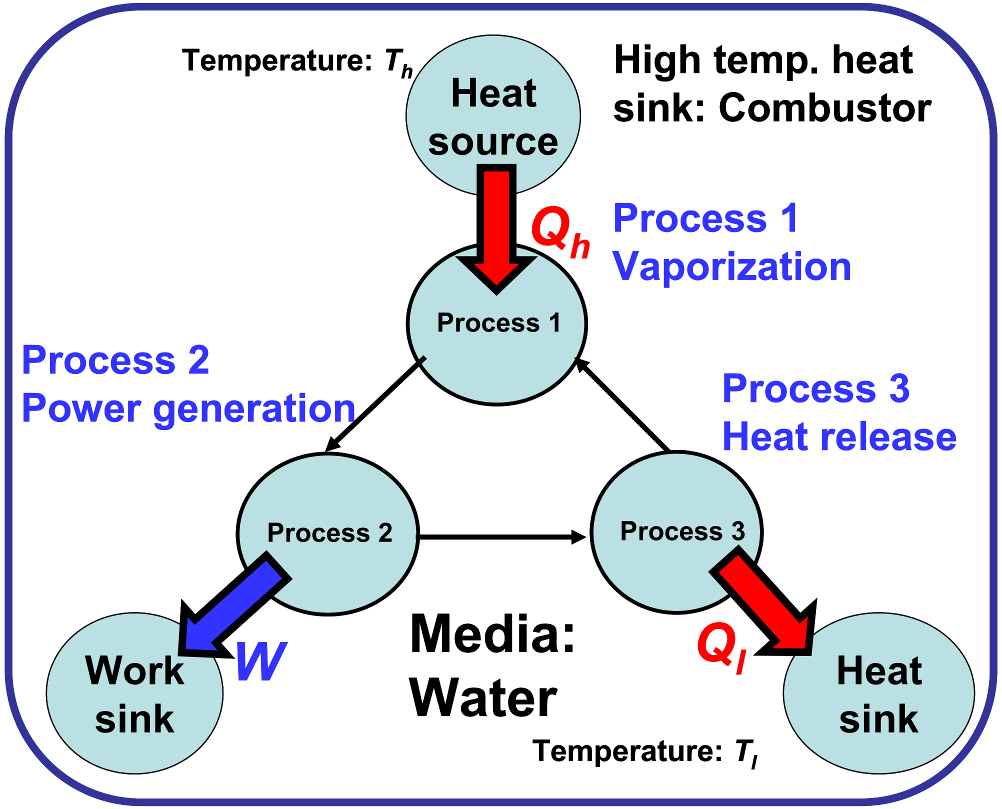
$$W \geq \frac{T_h - T_l}{T_h} Q_h = \frac{[(300)-(270)]}{(300)}(1) = 0.1[\mathrm{kW}]$$

Comparison **Joule heating**

W＝1kW

Ex.3 Thermodynamic analysis of power generation





$$W - Q_h + Q_l = 0$$

$$-\frac{Q_h}{T_h} + \frac{Q_l}{T_l} \geq 0$$

$$W \leq \frac{T_h - T_l}{T_h} Q_h$$

High temp. heat source: 600℃（＝873K）

Low temp. heat sink: 50℃（＝323K）

$$W \leq \frac{T_h - T_l}{T_h} Q_h = \frac{[(873)-(323)]}{(873)} Q_h = 0.63 Q_h$$

Temp. of heat source → **Conversion efficiency to electricity**

$$W - Q_h + Q_l = 0$$

$$-\frac{Q_h}{T_h} + \frac{Q_l}{T_l} \geq 0$$

$$\longrightarrow \quad Q_l = Q_h - W \geq \frac{T_l}{T_h} Q_h$$

Heat from high temp. heat source: Q_h

$\geq$

Converted electric energy: W

$$W \leq \frac{T_h - T_l}{T_h} Q_h \quad \longrightarrow \quad \frac{W}{Q_h} \leq \frac{T_h - T_l}{T_h}$$

=

Carnot efficiency ⇨ **Ratio of the max. work energy taken to thermal energy taken to**

Change of Gibbs free energy

$$\Delta G = \Delta H - T \Delta S$$

Temperature: T ⇨ **Ambient temp.** T_0 **(=298K)**

$$\Delta \varepsilon = \Delta H - T_0 \Delta S$$

$\Delta \varepsilon$ **: Change of exergy [J], [J/s]**

The 2nd law $\sum_j \Delta S_j \geq 0$

$$\sum_j \Delta \varepsilon_j = \sum_j \left(\Delta H_j - T_0 \Delta S_j \right) = -T_0 \sum_j \Delta S_j \leq 0$$

Decreasing law of exergy

Quality of energy

Degree of low level *d*

$$d = \frac{\Delta S}{\Delta H} \quad \text{[1/K]}$$

$$\frac{\Delta \varepsilon}{\Delta H} \equiv A$$

Energy level

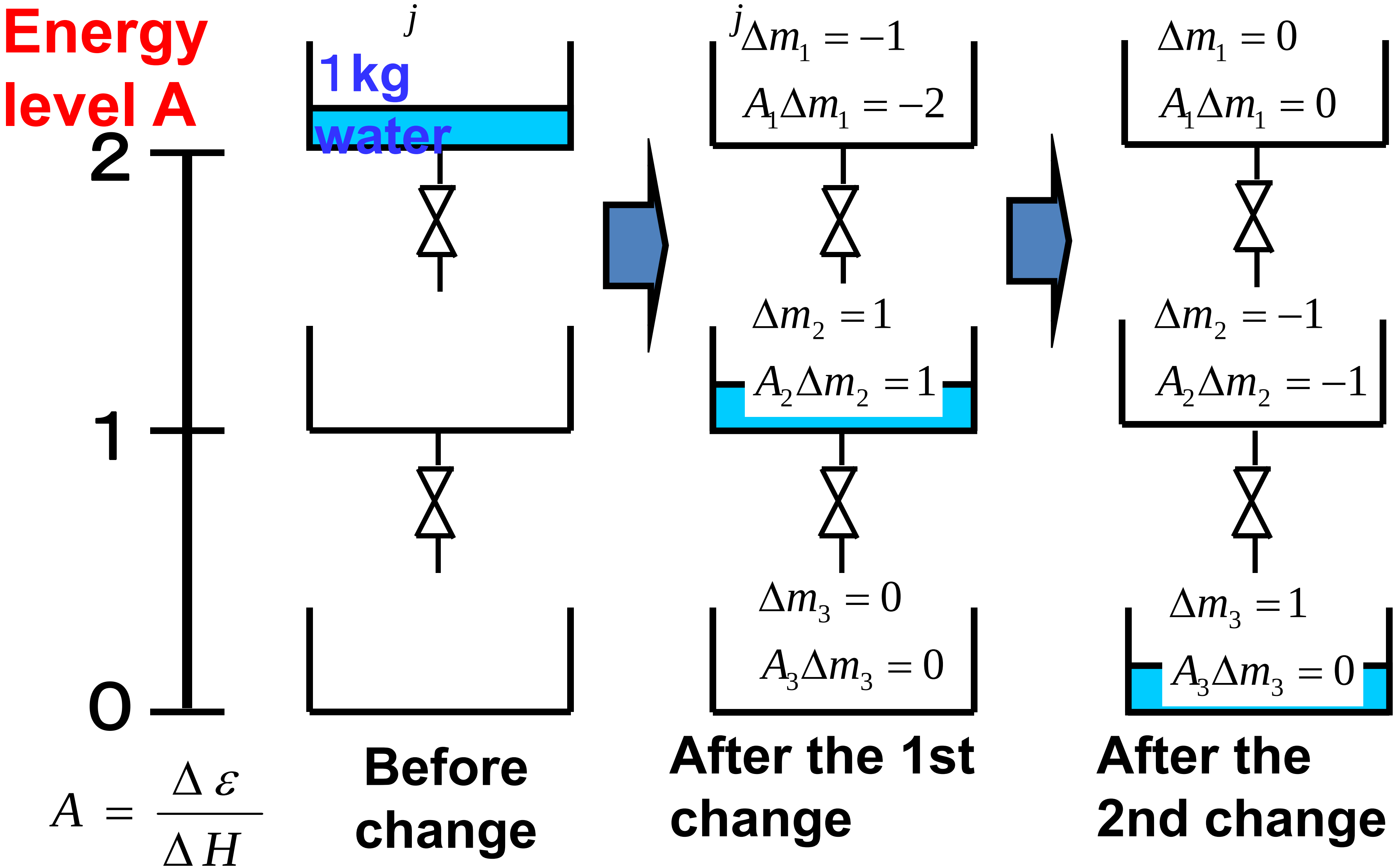
$$A = \frac{\Delta \varepsilon}{\Delta H} = \frac{\Delta H - T_0 \Delta S}{\Delta H} = 1 - T_0 \frac{\Delta S}{\Delta H} = 1 - T_0 d$$

The 1st law $\sum_j \Delta H_j = 0$

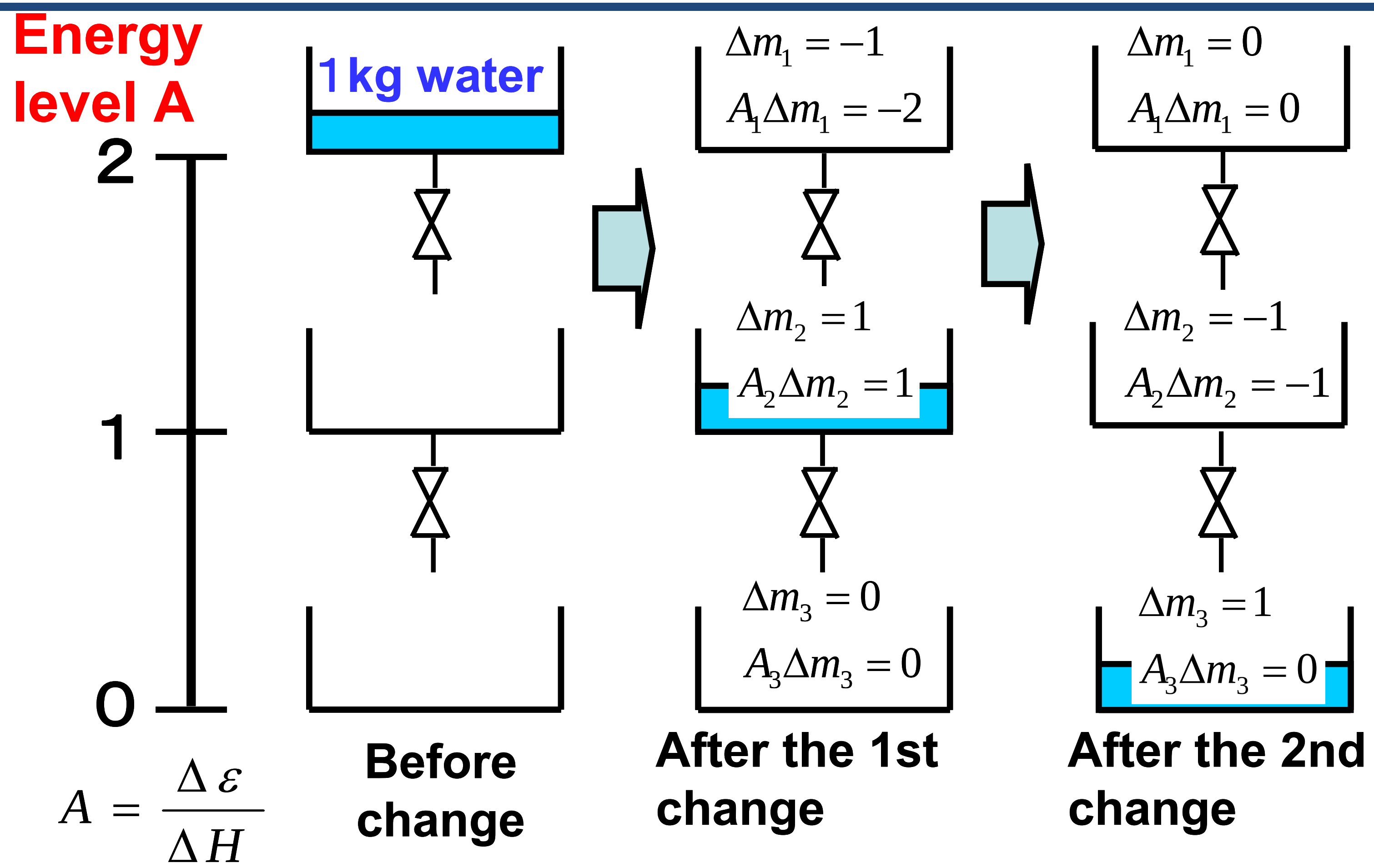
The 2nd law $\sum_j A_j \Delta H_j \leq 0$

Explanation of energy level by Water model

$$\sum_j \Delta m_j = 0, \ \sum_j A_j \Delta m_j \le 0$$



$$A = \frac{\Delta \varepsilon}{\Delta H}$$



The 2nd law (Decreasing law of exergy)

$$\sum_j \Delta \varepsilon_j = \sum_j A_j \Delta m_j = A_1 \Delta m_1 + A_2 \Delta m_2 + A_3 \Delta m_3 = -1 \le 0$$

Process	Quantity of energy	Tempera-ture	ΔH	⊗ε	A
Heat source	Output Q	T	$-Q$	$-\frac{T-T_0}{T}Q$	$\frac{T-T_0}{T}$
Heat sink	Input Q	T	Q	$\frac{T-T_0}{T}Q$	$\frac{T-T_0}{T}$
Work source	Output W	—	$-W$	$-W$	1
Work sink	Input W	—	W	W	1

$$\Delta\varepsilon=\Delta H - T_0 \Delta S$$

$$A = \frac{\Delta \varepsilon}{\Delta H}$$

Energy level of work source and sink = 1

Energy level of heat source and sink ⇒ Carnot efficiency at $T_l = T_0$

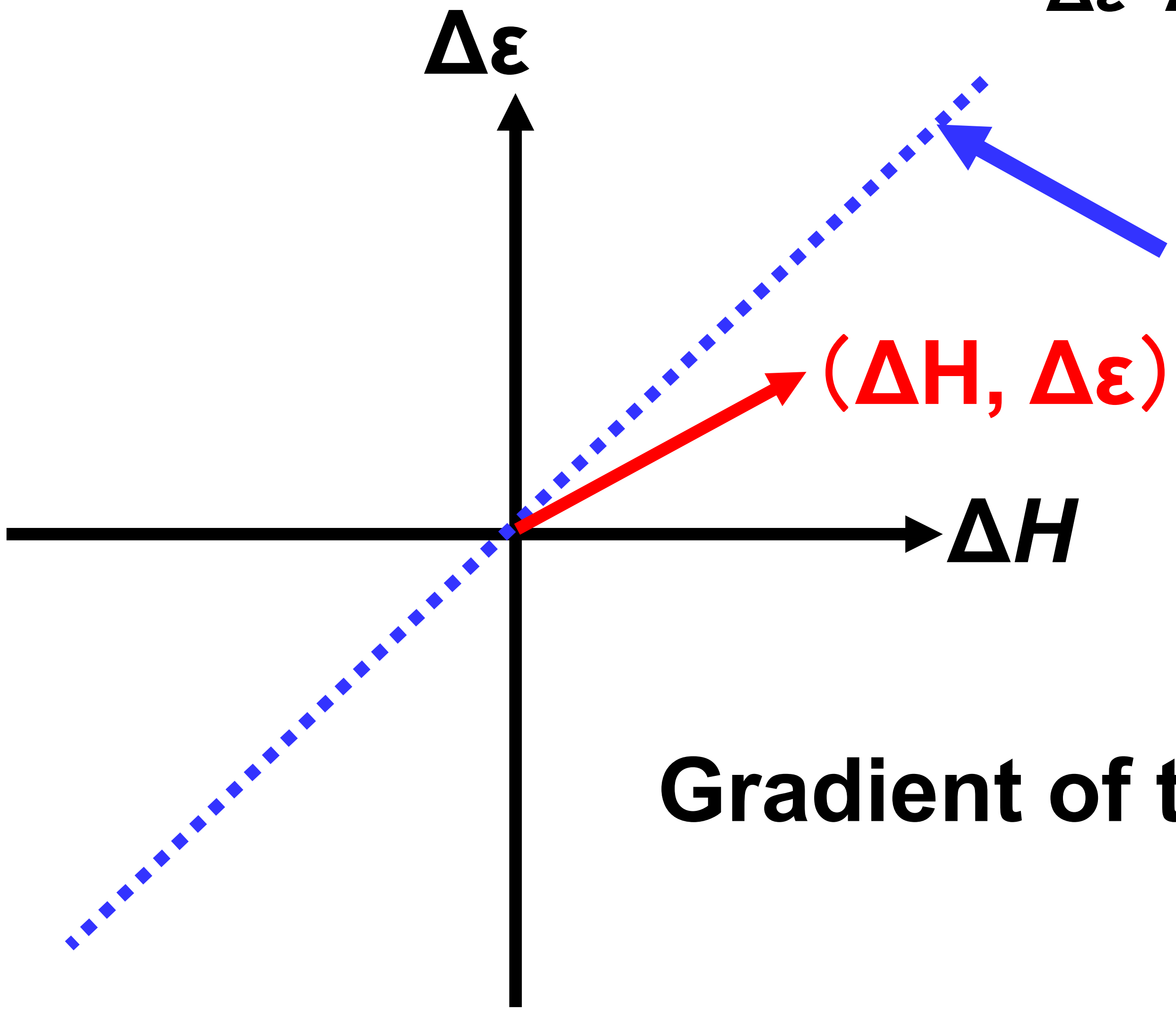
Temp. of heat source and sink = T_0 $A=0$

Temp. of heat source and sink = ∞ $A=1$

⇐ Corresponding to work source and sink

Thermodynamic compass?

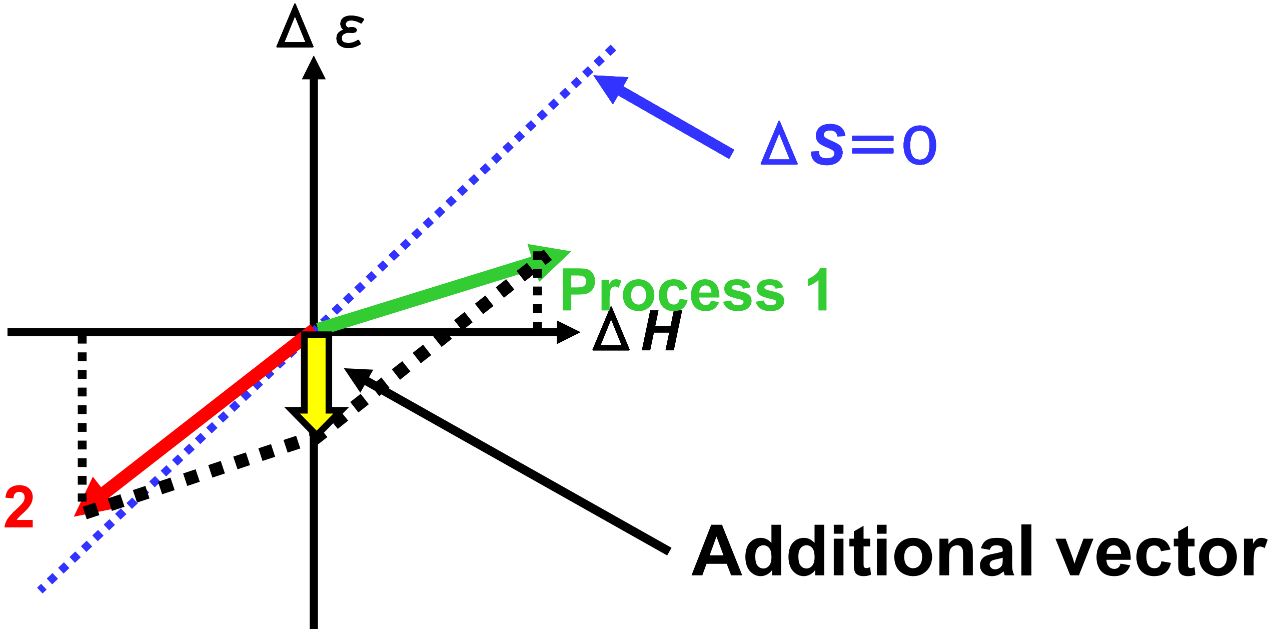
$$\Delta\varepsilon = \Delta H - T_0 \Delta S$$



:Process vector

$$A = \frac{\Delta\varepsilon}{\Delta H}$$

Gradient of the vector＝*A*



Expression of the 1st and 2nd laws on the coordinate

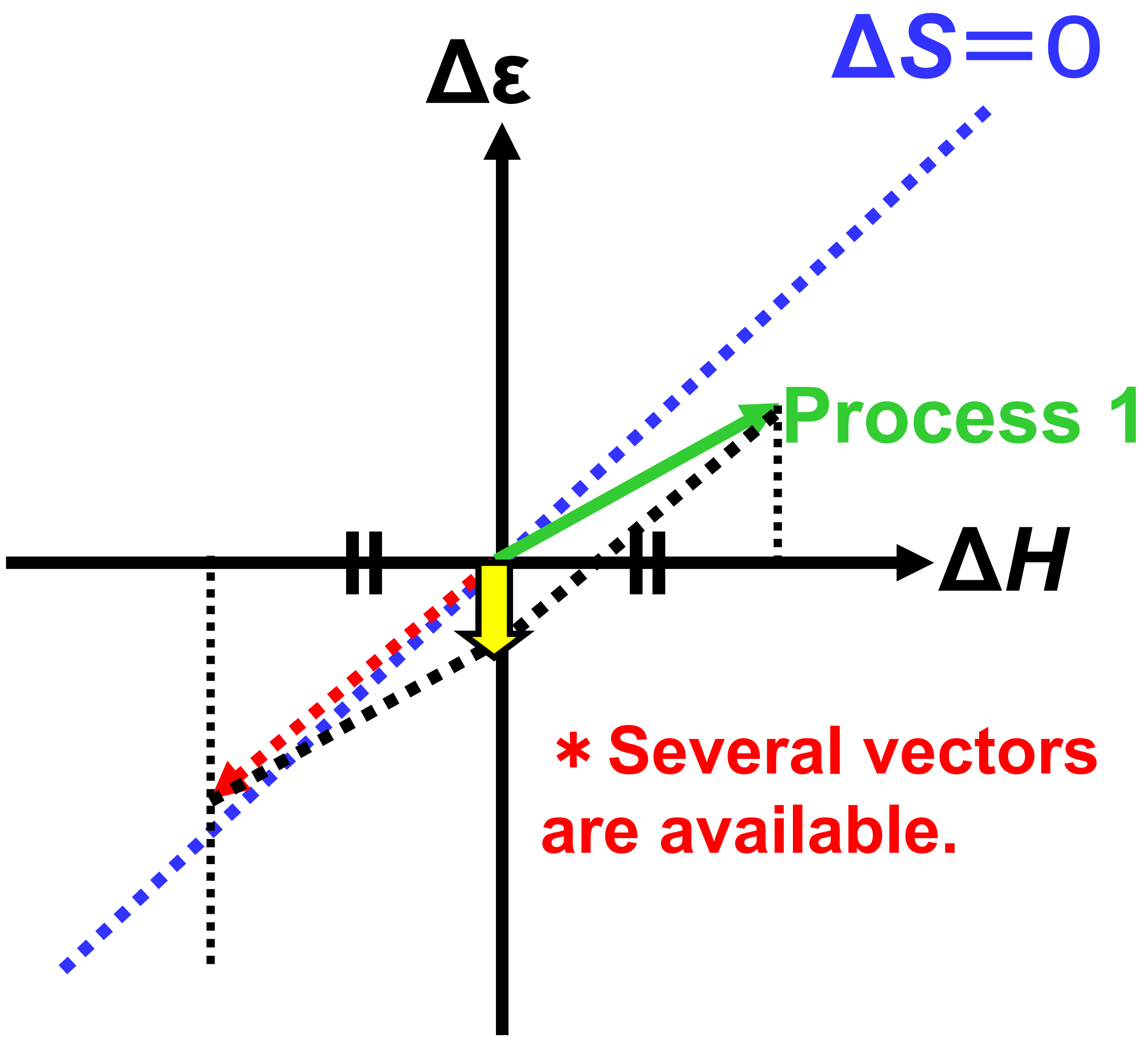
System: Addition of two process vectors

The additional vector must be negative or 0 on the Δε axis

Reasons **The 1st law** $\sum_j \Delta H_j = 0$

The 2nd law $\sum_j \Delta \varepsilon_j \leq 0$

How to use the thermodynamic vector



Determination of Process 1

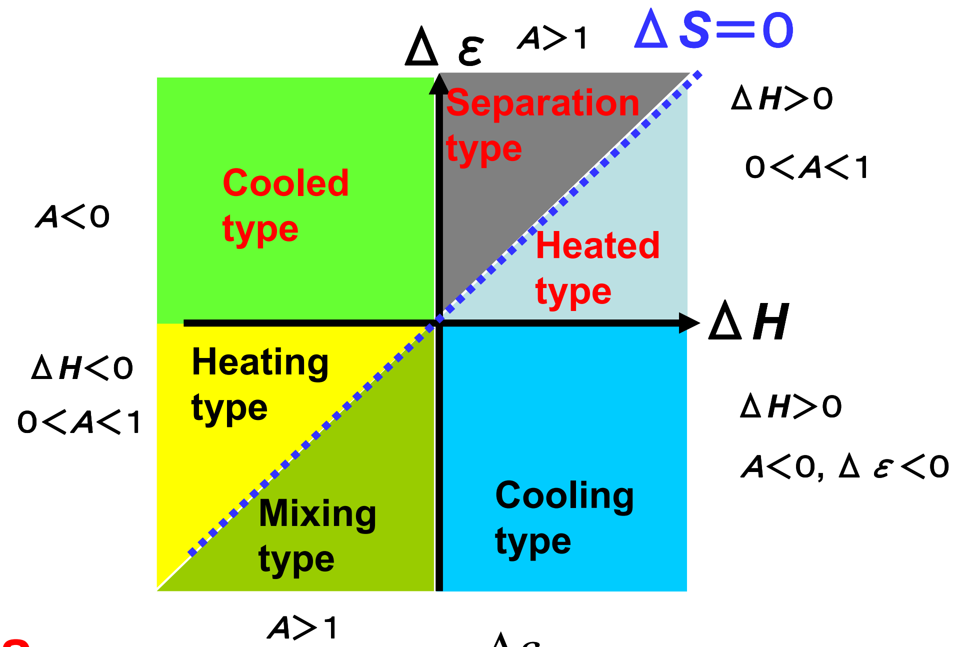
Finding the vector to satisfy that the additional vector must be negative on the Δε axis

The 1st law

$$\sum_j \Delta H_j = 0$$

The 2nd law

$$\sum_j \Delta \varepsilon_j \le 0$$



$$A = \frac{\Delta\varepsilon}{\Delta H}$$

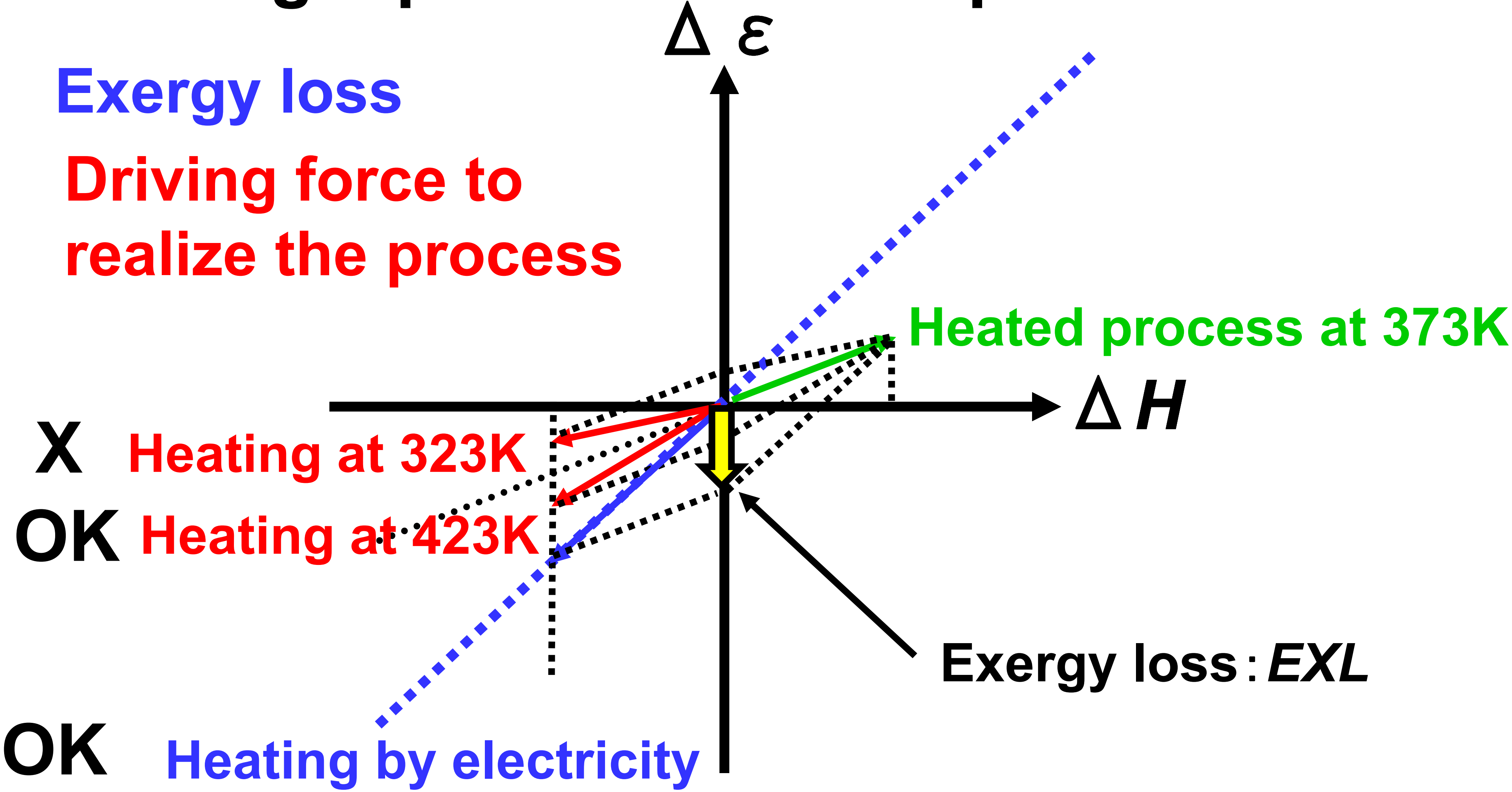
Red processes: Depending on process

Process examples

Heated type	**Temp. increase from 100℃ to 200℃**
Heating type	**Temp. decrease from 200℃ to 100℃**
Cooling type	**Temp. increase from -50℃ to -30℃**
Cooled type	**Temp. decrease from -30℃ to -50℃**
Separation type	**Separation of air to N_2 and O_2**
Mixing type	**Mixing of N_2 with O_2**

Process selection against target process

Ex. Target process: Heated process at 373K



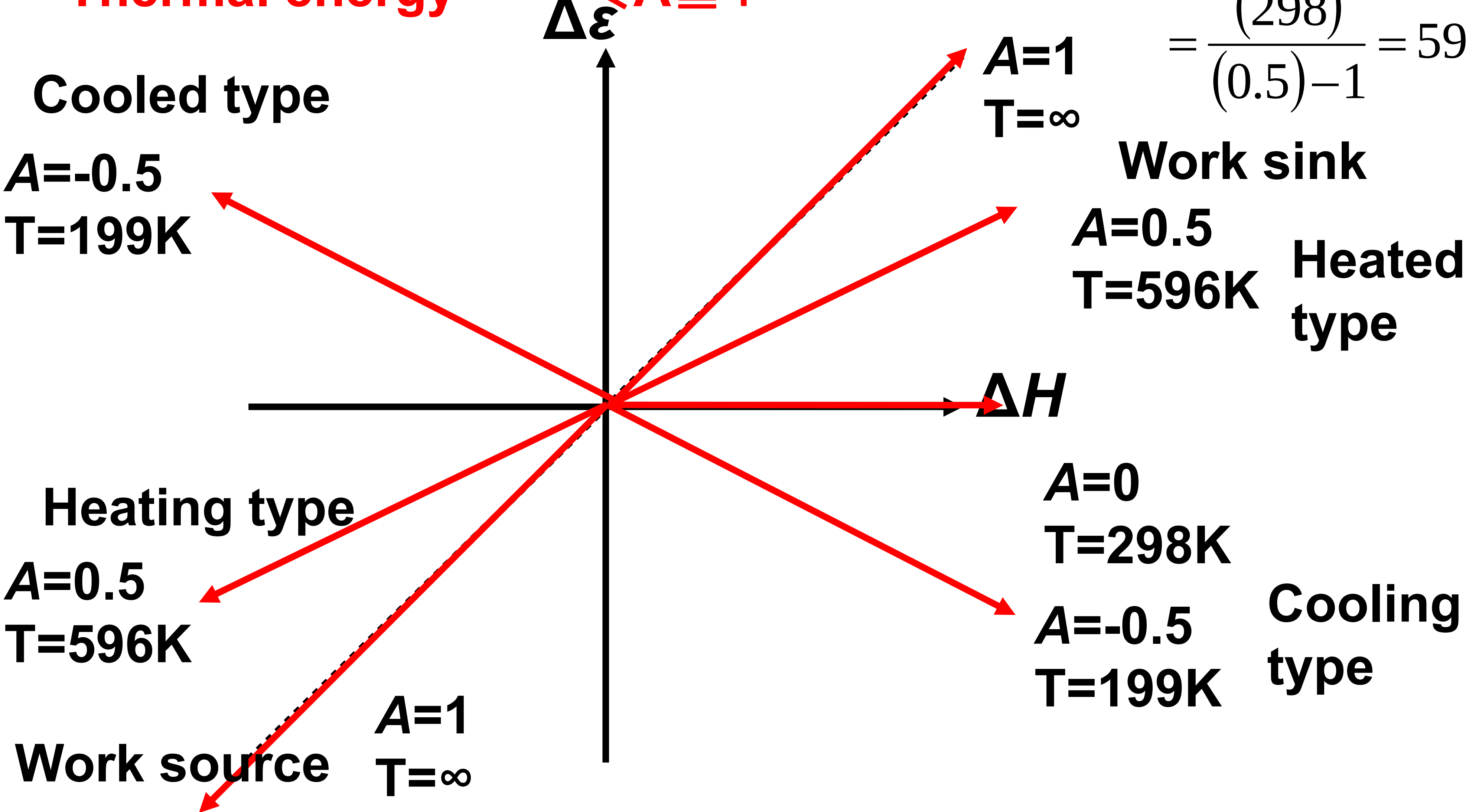
Max. exergy loss: Utilization of electricity

$$A = \frac{T - T_0}{T}$$

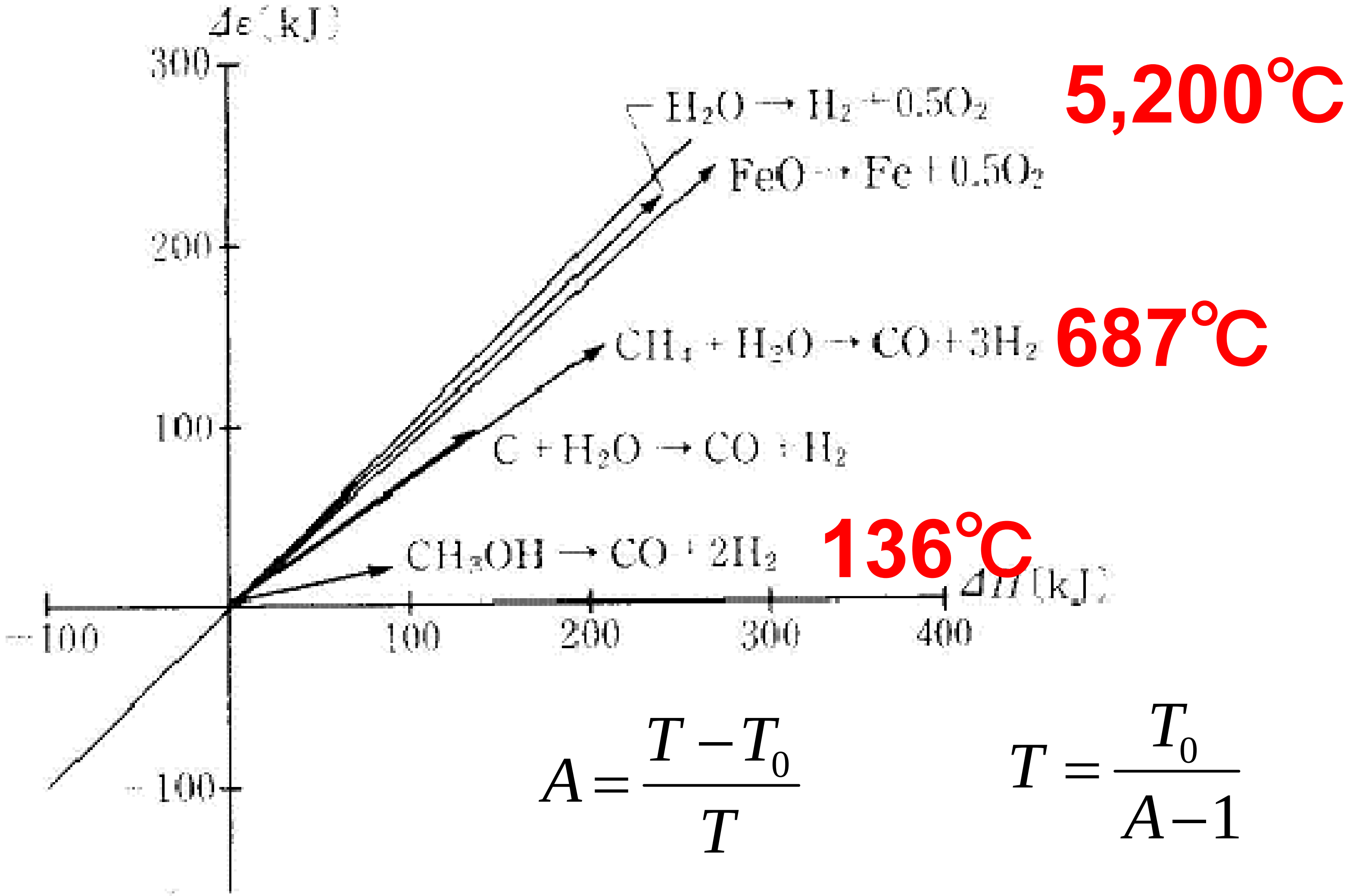
T_0=298 [K] *A*=0.5

$$T = \frac{T_0}{A-1} = \frac{(298)}{(0.5)-1} = 596[\mathrm{K}]$$

Thermal energy −∞<A≦1



Example of vectors of endothermic reaction



$$A = \frac{T - T_0}{T}$$

$$T = \frac{T_0}{A - 1}$$

Example of vectors of exothermic reaction