Physical Chemistry for Energy Engineering

(6rh: 2018/09/19)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Equation of state of gas
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

Contents of today

<Last class on 9/17>

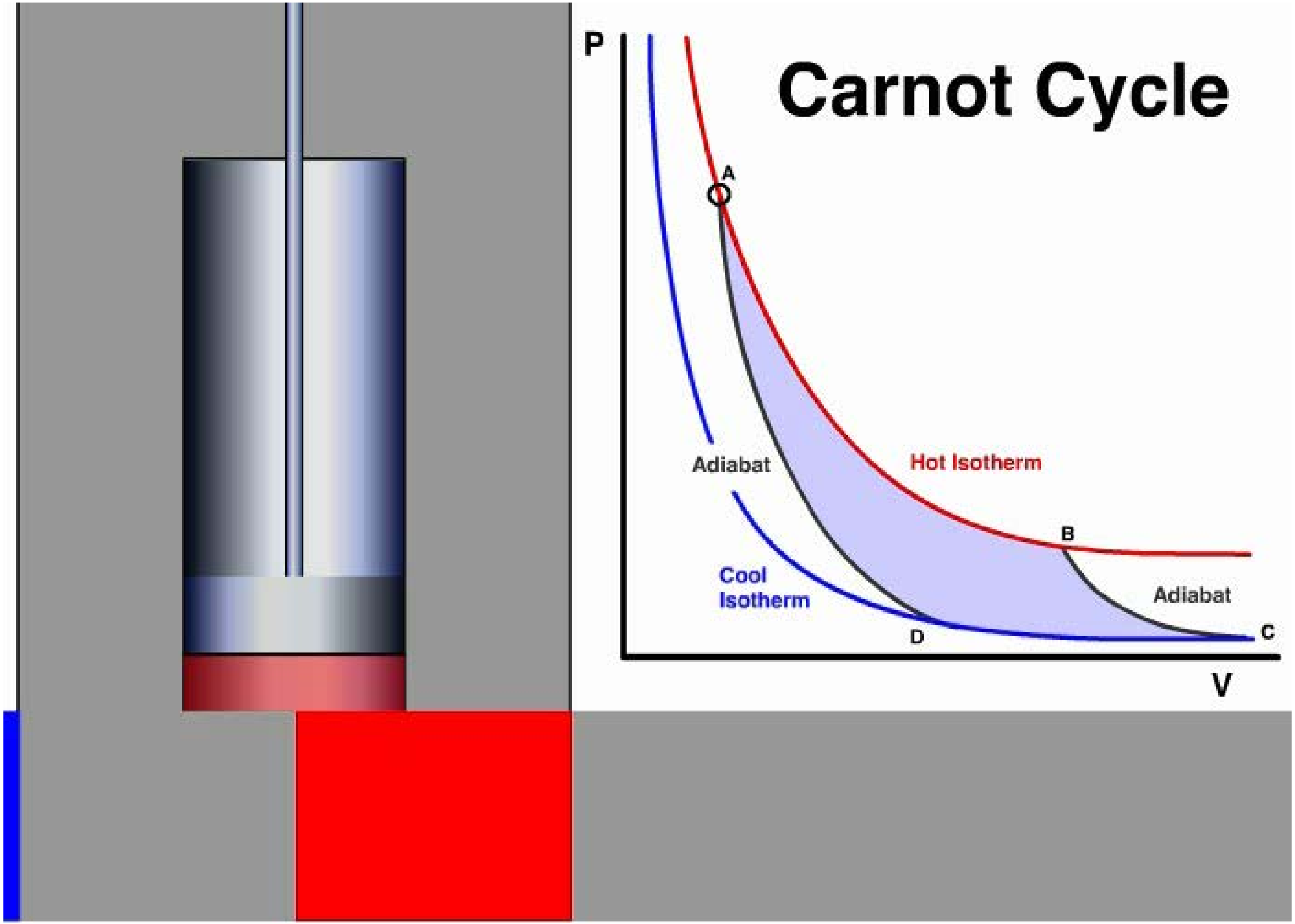
1.2.2. Thermodynamic cycle
1.3.1. The second law of thermodynamics

<Today's class on 9/19>

1.3.1. The second law of thermodynamics
1.3.2. The third law of thermodynamics

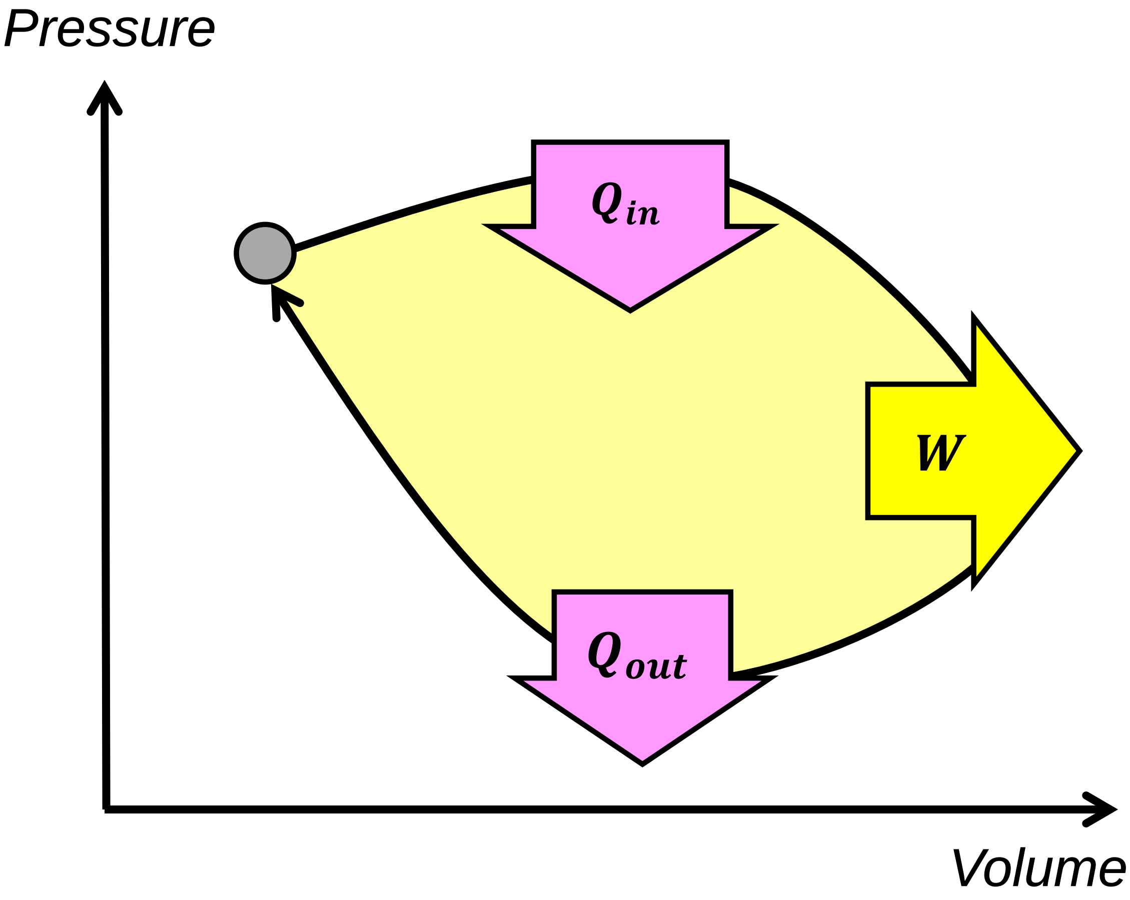
(Review) 1.3.1. The 2nd law of thermodynamics

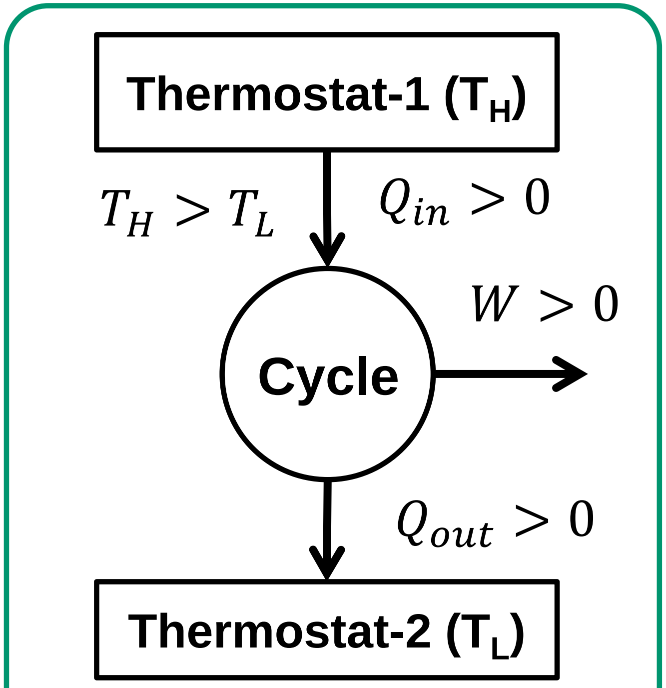
- Carnot cycle -



http://science.sbcc.edu/~physics/flash/heatengines/Carnot%20cycle.html

(Review) 1.3.1. The 2nd law of thermodynamics
- a cycle combined with 2 thermostats, more generalized-

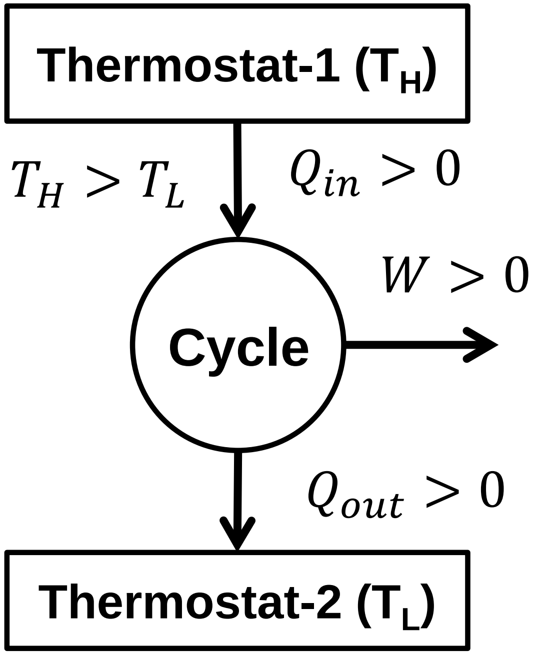




$$\Delta U = q + w$$
$$= Q_{in} - Q_{out} - W = 0$$

- ✓ The area surrounded by the cycle (P-V diagram) corresponds to the amount of work which the system makes to the surrounding by a single operation of the cycle.
- ✓ If the operation is reverse, the surroundings makes the work to the system.

(Review) 1.3.1. The 2nd law of thermodynamics
- a cycle combined with 2 thermostats, another drawing -



Thermostat-1 (T_H)

$T_H > T_L$

$Q_{in} > 0$

Cycle

$W > 0$

$Q_{out} > 0$

Thermostat-2 (T_L)

$$\Delta U = q + w$$
$$= Q_{in} - Q_{out} - W = 0$$

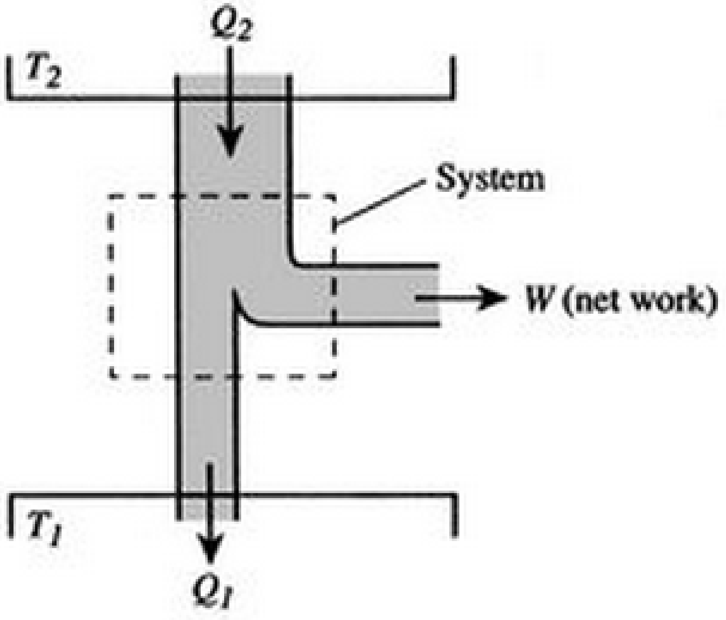


Figure 3.5: Work and heat transfers in a Carnot cycle between two heat reservoirs

http://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node24.html

(Review) 1.3.1. The 2nd law of thermodynamics

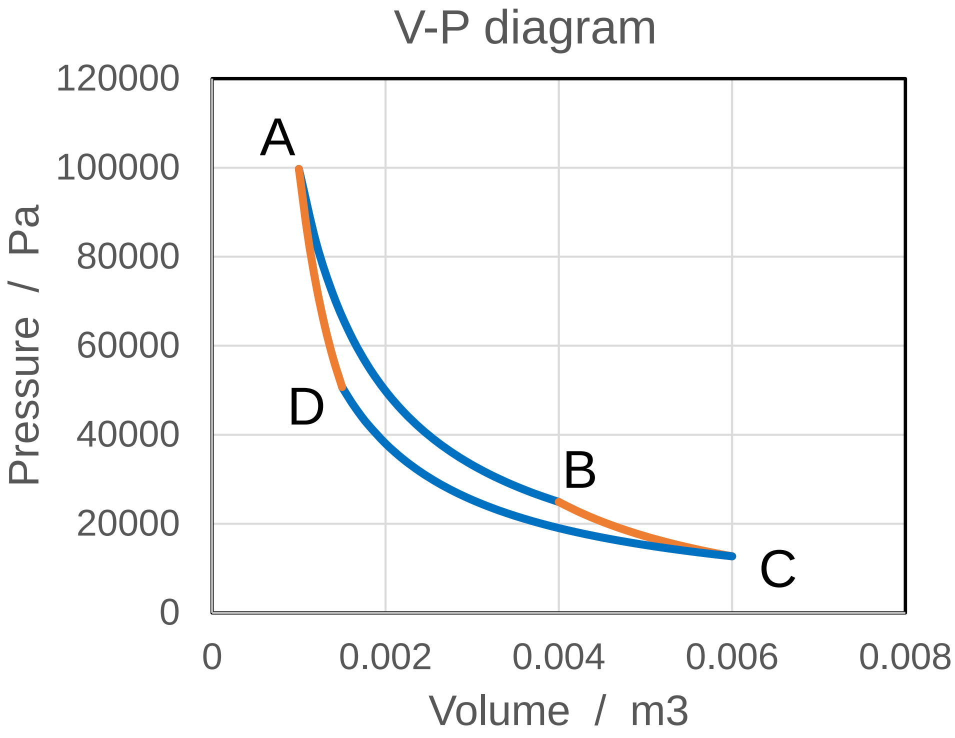
- description-

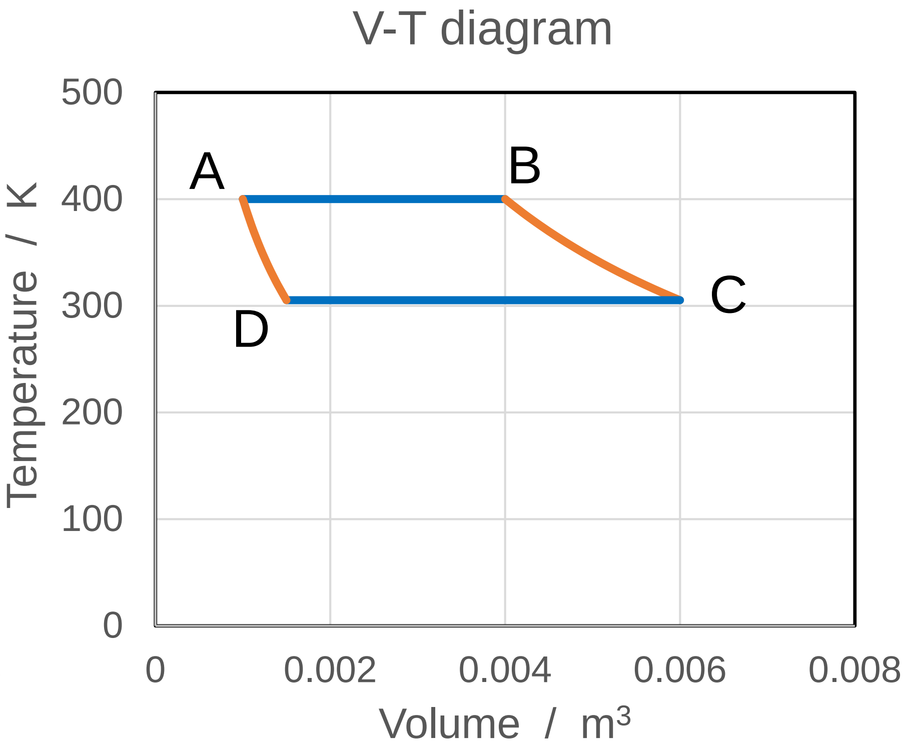
- ✓ *“The entropy of an isolated system never decreases, because isolated systems always evolve toward thermodynamic equilibrium—the state with the maximum possible entropy.” (wikipedia)*
- ✓ *“Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system.” (a version of Clausius statement)*
- ✓ *“It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.” (a version of Kelvin statement)*
- ✓ *“The efficiency of a quasi-static or reversible Carnot cycle depends only on the temperatures of the two heat reservoirs, and is independent of the working substance. A Carnot engine operated in this way is the most efficient possible heat engine using those two temperatures.” (Carnot’s principle)*
- ✓ *“There is no thermodynamic cycle that can absorb energy (>0) from a sole thermostat and then convert all the absorbed energy to a work to the surroundings.” (Thomson’s statement)*

1.3.1. The 2nd law of thermodynamics
- Carnot cycle (cont'd)-

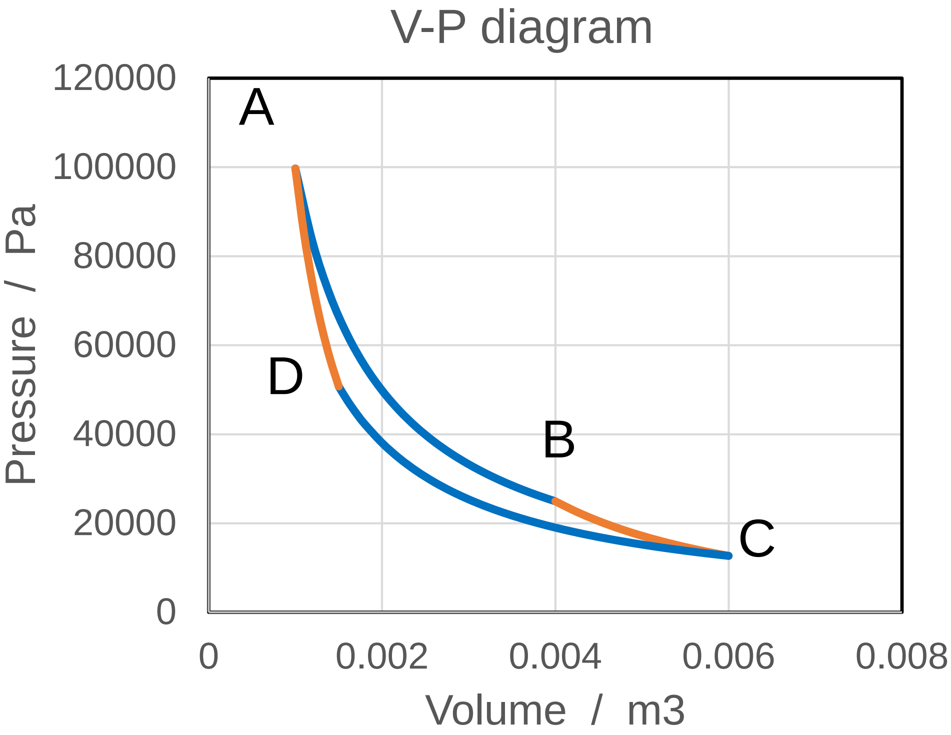
This cycle is called "Carnot cycle" composed of the following 4 processes using 2 thermostats:

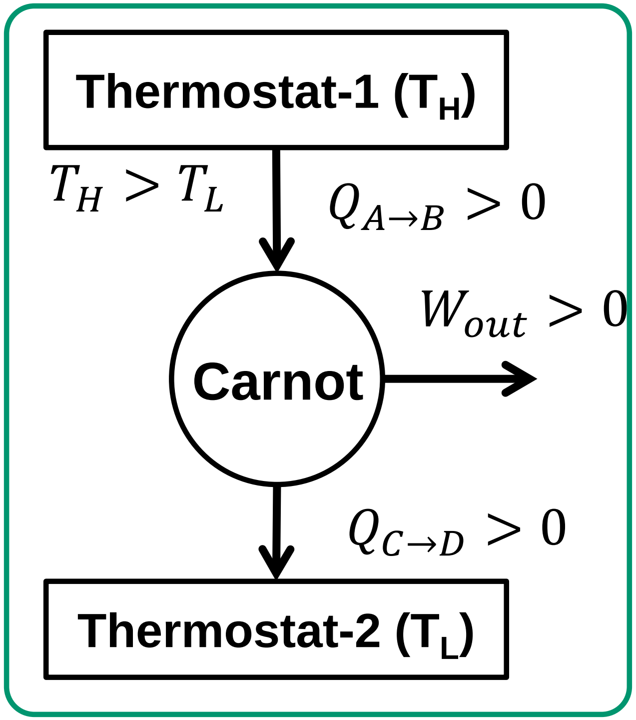
(1) [A → B] reversible isothermal expansion (T_H)
(2) [B → C] reversible adiabatic expansion
(3) [C → D] reversible isothermal compression (T_L)
(4) [D → A] reversible adiabatic compression





1.3.1. The 2nd law of thermodynamics
- Carnot cycle (A → B → C → D → A) , forward operation-





Thermostat-1 (T_H)

$T_H > T_L$

$Q_{A\to B} > 0$

Carnot

$W_{out} > 0$

$Q_{C\to D} > 0$

Thermostat-2 (T_L)

$$w = \int \delta w = w_{A\to B} + w_{B\to C} + w_{C\to D} + w_{D\to A} = -W_{A\to B} - W_{B\to C} + W_{C\to D} + W_{D\to A}$$

$$q = \int \delta q = q_{A\to B} + q_{C\to D} = Q_{A\to B} - Q_{C\to D}$$

$$\Delta U = \oint dU = w + q = 0$$

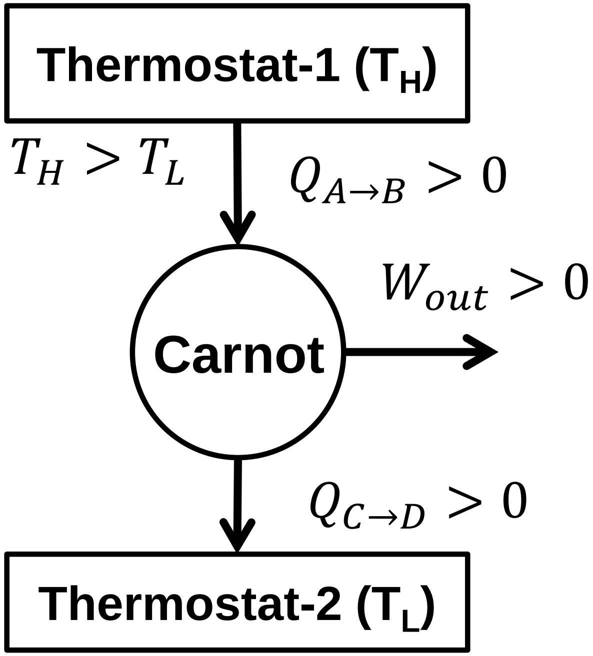
$$W_{out} = -w = q = Q_{A\to B} - Q_{C\to D}$$

1.3.1. The 2nd law of thermodynamics
- Carnot cycle and reversed Carnot cycle -

Because we consider the cycle composed of reversible (quasi-static) processes, we can reverse the cycle, so-called “reversed Carnot cycle”.

- ✓ Carnot cycle: A → B → C → D → A
- ✓ Reversed Carnot cycle: A → D → C → B → A

Carnot cycle



Thermostat-1 (T_H)

$T_H > T_L$

$Q_{A\to B} > 0$

Carnot

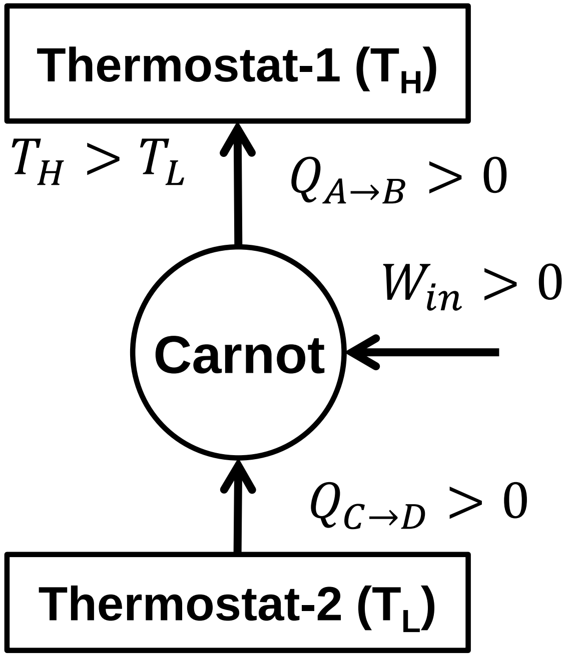
$W_{out} > 0$

$Q_{C\to D} > 0$

Thermostat-2 (T_L)

$$\Delta U = Q_{A\to B} - W_{out} - Q_{C\to D} = 0$$

Reversed Carnot cycle



Thermostat-1 (T_H)

$T_H > T_L$

$Q_{A\to B} > 0$

Carnot

$W_{in} > 0$

$Q_{C\to D} > 0$

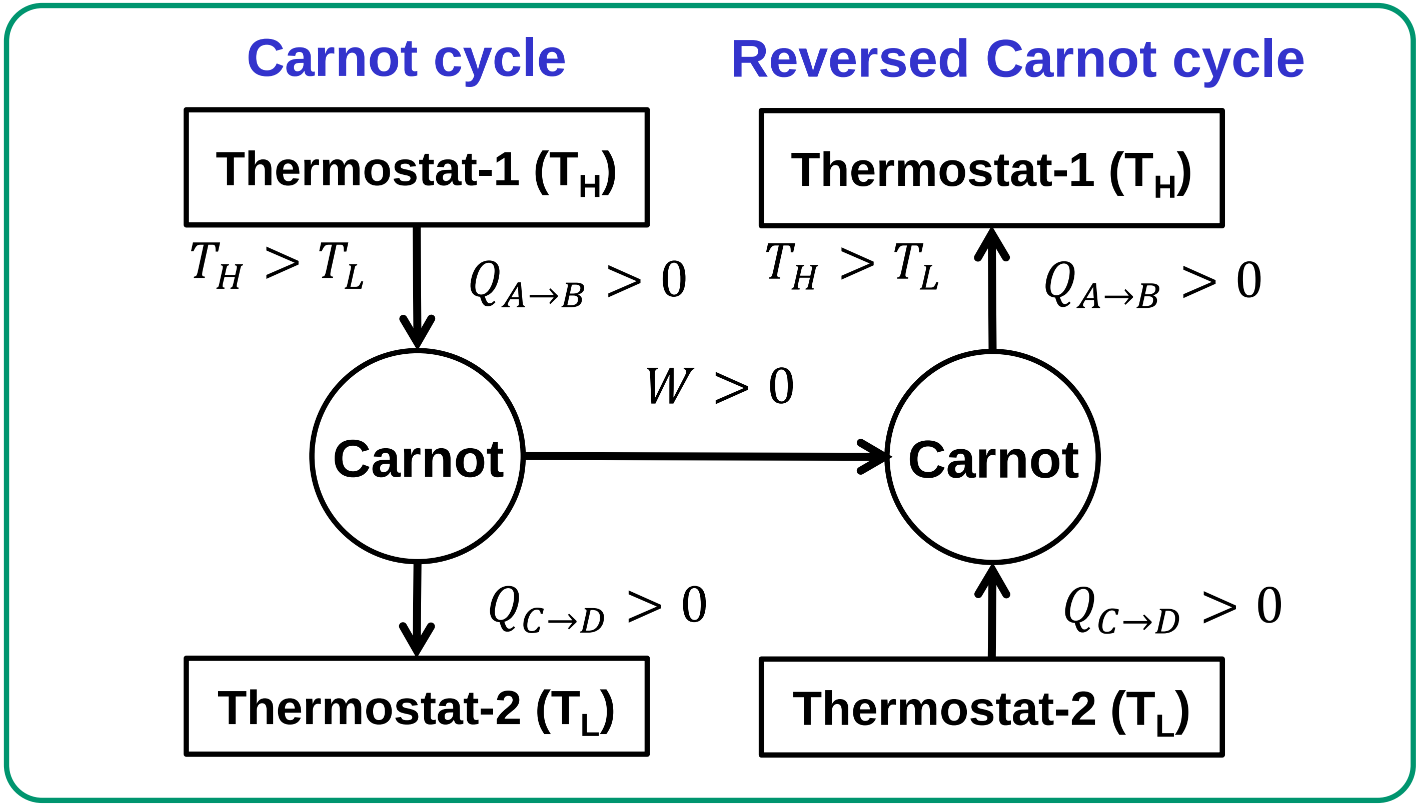
Thermostat-2 (T_L)

$$\Delta U = -Q_{A\to B} + W_{in} + Q_{C\to D} = 0$$

1.3.1. The 2nd law of thermodynamics
- Carnot cycle and reversed Carnot cycle (cont'd)-

Indeed, if we combine Carnot cycle and reversed Carnot cycle, both the system (engine) and the surroundings (thermostats + something on which a work is made) do not change throughout the combined operation of Carnot cycle and reversed Carnot cycle.

- ✓ This means a combined cycle is also reversible as Carnot cycle and reversed Carnot cycle are reversible.



Carnot cycle

Reversed Carnot cycle

Thermostat-1 (T_H)

Thermostat-1 (T_H)

$T_H > T_L$

$Q_{A\to B} > 0$

$T_H > T_L$

$Q_{A\to B} > 0$

$W > 0$

Carnot

Carnot

$Q_{C\to D} > 0$

$Q_{C\to D} > 0$

Thermostat-2 (T_L)

Thermostat-2 (T_L)

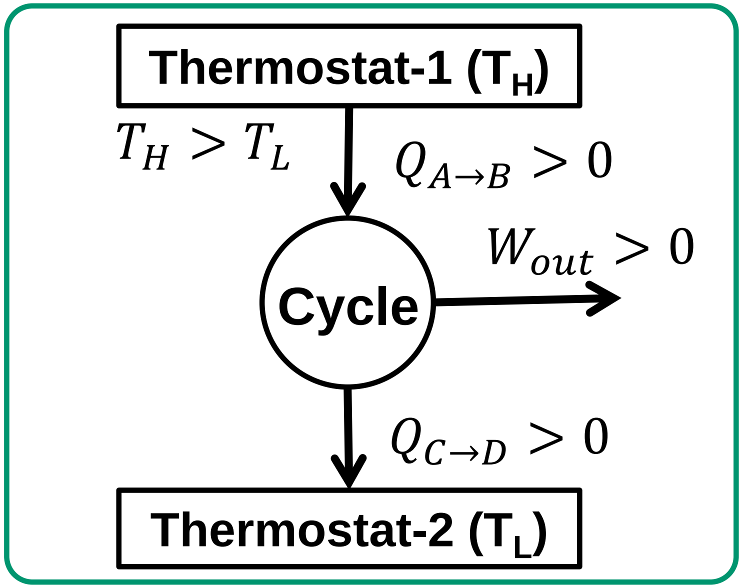
1.3.1. The 2nd law of thermodynamics

- Constraints in work of Carnot cycle -

<Theorem>
When operating a Carnot cycle (not reverse), the following condition is achieved:

$$W_{out} = Q_{A\to B} - Q_{C\to D} > 0$$

It means the engine always does a work to the surroudings.



(1) Check whether $W_{out} = 0$ is achievable or not.

(2) Check whether $W_{out} < 0$ is achievable or not.

1.3.1. The 2nd law of thermodynamics

- Constraints in work of Carnot cycle -

<Theorem>
When operating a Carnot cycle (not reverse), the following condition is achieved:

$$W_{out} = Q_{A\to B} - Q_{C\to D} > 0$$

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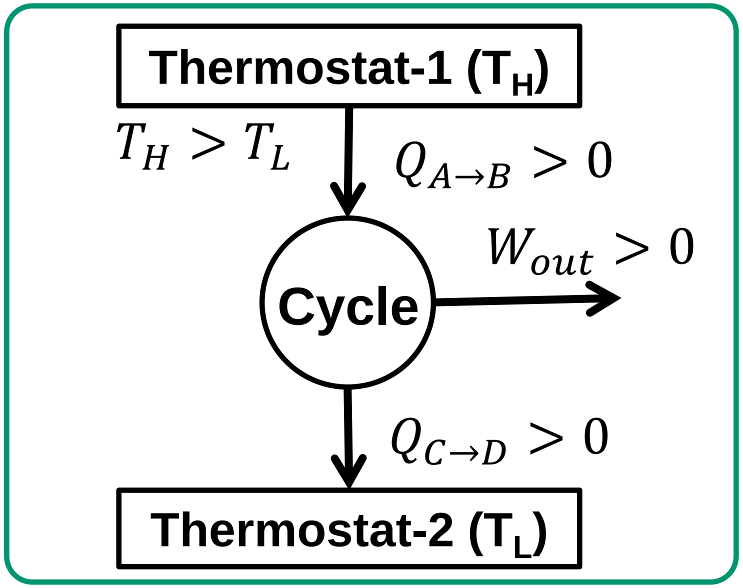


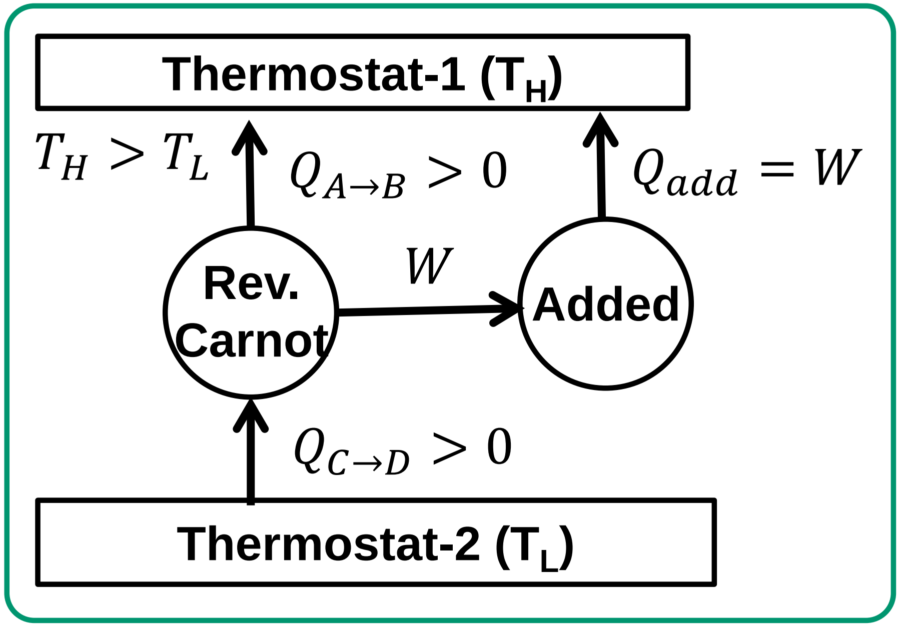
(1) Check whether $W_{out} = 0$ is achievable or not.

- ✓ Here we assume $W_{out} = 0$. In this case, when the engine is reversibly operated (= reverse Carnot cycle), $W_{in} = 0$ is achieved.
- ✓ In this case, this reversed Carnot cycle absorbs energy (as heat) from the lower-temperature thermostat and release it to the hither-temperature thermostat, which violates the 2nd law (of Clausius description).
- ✓ Hence, the assumption of $W_{out} = 0$ is inappropriate..

1.3.1. The 2nd law of thermodynamics
- Constraints in work of Carnot cycle (cont'd)-

(2) Check whether $W_{out} < 0$ is achievable or not.

- ✓ Here we assume $W_{out} < 0$. In this case, when the engine is reversibly operated (= reversed Carnot cycle), $W_{in} < 0$ is achieved, which means this reverse Carnot cycle can do a work to the surroundings.
- ✓ Because a work can be fully converted to a heat, we add another cycle to convert this work to a heat and then release the heat to the higher-temperature thermostat.



Thermostat-1 (T_H)

$T_H > T_L$

$Q_{A\rightarrow B} > 0$

$Q_{add} = W$

Rev. Carnot

W

Added

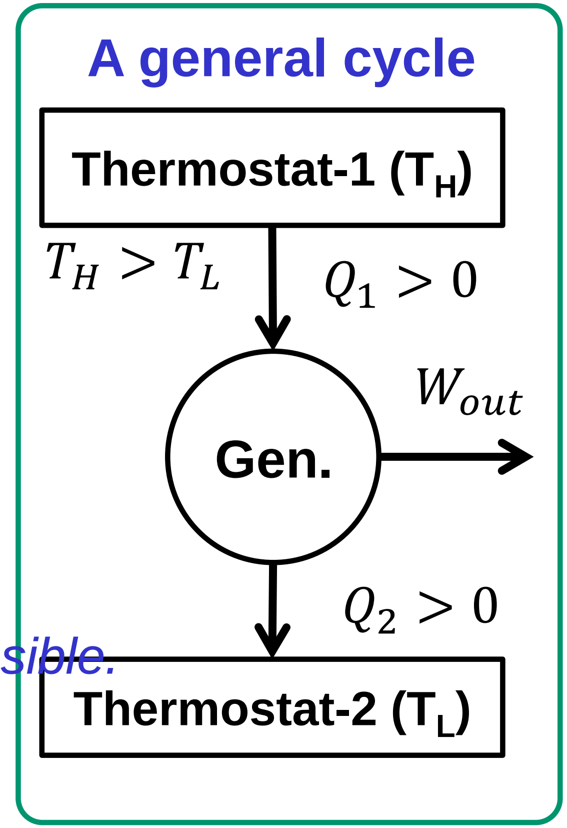
$Q_{C\rightarrow D} > 0$

Thermostat-2 (T_L)

- ✓ We can consider the combined cycle as a new cycle. For this cycle, an energy (as heat) is absorbed from the lower-temperature thermostat and then is released to the hither-temperature thermostat, which violates the 2nd law (of Clausius description).
- ✓ Hence, the assumption of $W_{out} < 0$ is inappropriate.

1.3.1. The 2nd law of thermodynamics
- Definition of efficiency of a general cycle -

Here, we consider an engine of a general cycle using two thermostats.



A general cycle

Thermostat-1 (T_H)

$T_H > T_L$

$Q_1 > 0$

Gen.

W_{out}

$Q_2 > 0$

Thermostat-2 (T_L)

The 1st law gives:

$$\Delta U = Q_1 - W_{out} - Q_2 = 0$$

$$W_{out} = Q_1 - Q_2$$

We define the ratio of heats as:

$$f = \frac{Q_2}{Q_1}$$

** Note that $Q_2 \neq 0$ thus $f \neq 0$, as $Q_2 = 0$ means all heat changes to work, which violates the 2nd law. $Q_1 = 0$ is also impossible.*

Then, the efficiency (η) of this cycle (engine) can be written as:

$$\eta = \frac{W_{out}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - f$$

We have the following constraints:

$$0 < f \leq 1 \qquad\qquad 0 \leq \eta < 1$$

**For engineering, it is very important to maximize η.*

1.3.1. The 2nd law of thermodynamics
- Efficiency of Carnot cycle -

$$\boxed{f = \frac{Q_2}{Q_1}} \quad \boxed{\eta = \frac{W_{out}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - f}$$

- ✓ In Carnot cycle, we just assume that it is composed of reversible isothermal and adiabatic processes. It means any gas can be used as the system to make a Carnot cycle.
- ✓ Hence, as far as we use a Carnot cycle, the efficiency of cycle does not depend on the gas sort, but only depends on $f = \frac{Q_2}{Q_1}$.

- ✓ In addition, we have another important result on Carnot cycle (a simplified demonstration with an ideal gas is given in the next slide):

$$\boxed{f = \frac{Q_2}{Q_1} = \frac{T_L}{T_H} \qquad \text{thus} \qquad \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_L}{T_H} \quad \textit{(for Carnot cycle)}}$$

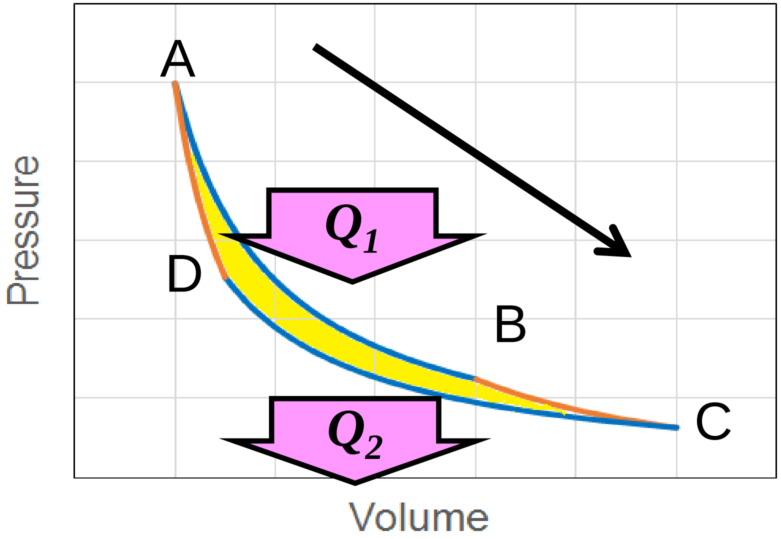
*This can be used as a version of temperature definition.

1.3.1. The 2nd law of thermodynamics

- A simplified demonstration of “$Q_2/Q_1 = T_L/T_H$” with an ideal gas-

Here, we demonstrate $\frac{Q_2}{Q_1} = \frac{T_L}{T_H}$ for Carnot cycle (with ideal gas, for simplicity).

(1) [A → B] Isothermal expansion (T_H)
(2) [B → C] Adiabatic expansion
(3) [C → D] Isothermal compression (T_L)
(4) [D → A] Adiabatic compression
*Assuming that all processes are reversible.



The first law of reversible isothermal process ($dT = 0$) for ideal gas ($U = U(T)$) is:

$$Q_1 = q_{A\to B} = -w_{A\to B} = \int PdV = nRT_H \ln\frac{V_B}{V_A},\ Q_2 = -q_{B\to C} = nRT_L \ln\frac{V_C}{V_D}$$

For reversible adiabatic processes, we can use the relationship between T and V as:

$\left(\frac{T_{fin}}{T_{ini}}\right)^{\alpha} = \left(\frac{V_{ini}}{V_{fin}}\right)$ where $\alpha = const.$ (e.g. $\alpha = \frac{3}{2}$ for He). Using this equation gives $\left(\frac{T_C}{T_B}\right)^{\alpha} = \left(\frac{T_L}{T_H}\right)^{\alpha} = \left(\frac{V_B}{V_C}\right)$ and $\left(\frac{T_A}{T_D}\right)^{\alpha} = \left(\frac{T_H}{T_L}\right)^{\alpha} = \left(\frac{V_D}{V_A}\right)$. Comparing these 2 equations gives $\left(\frac{V_B}{V_C}\right) = \left(\frac{V_A}{V_D}\right)$ then $\left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$. Thus, $\frac{Q_2}{Q_1} = \frac{nRT_L \ln\frac{V_C}{V_D}}{nRT_H \ln\frac{V_B}{V_A}} = \frac{T_L}{T_H}$

1.3.1. The 2nd law of thermodynamics

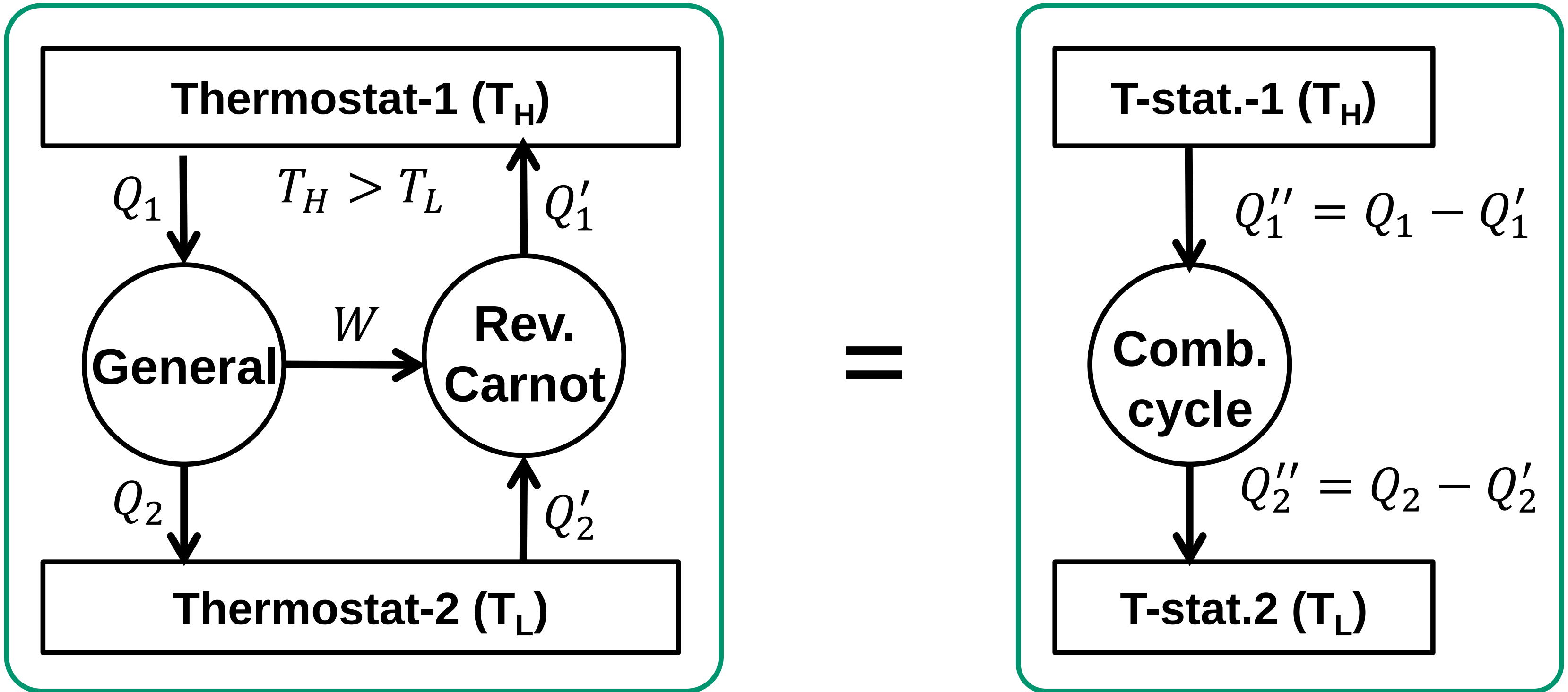
- Comparison of efficiency with Carnot cycle -

<Theorem> The efficiency of a (general) cycle using 2 thermostats is less than the efficiency of Carnot cycle.

$$\eta \leq \eta_c = 1 - \frac{T_L}{T_H}$$

The equal sign is achieved when the cycle is reversible.

To demonstrate this theorem, we connect reversed Carnot cycle to a general cycle and also consider these combined cycle.



1.3.1. The 2nd law of thermodynamics
- Comparison of efficiency with Carnot cycle (cont'd)-

<Theorem> The efficiency of a (general) cycle using 2 thermostats is less than the efficiency of Carnot cycle.

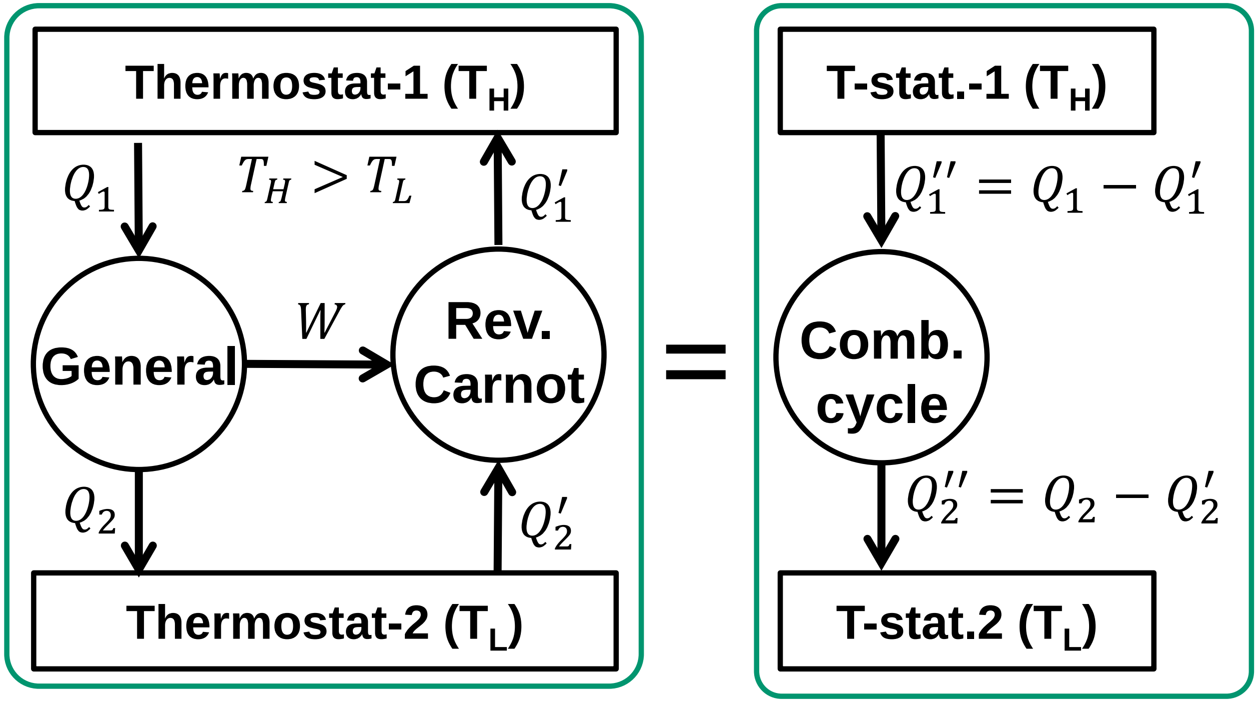
$$\eta \leq \eta_c = 1 - \frac{T_L}{T_H} \qquad \left(\eta = 1 - \frac{Q_2}{Q_1}\right)$$

The equal sign is achieved when the cycle is reversible.

The combined cycle does no work, thus

$$Q_1'' = Q_1 - Q_1' \geq 0$$

to avoid energy flow as a heat from the lower-temp. thermostat to the higher-temp. thermostat.



Thermostat-1 (T_H)

Q_1

$T_H > T_L$

Q_1'

General

W

Rev. Carnot

Q_2

Q_2'

Thermostat-2 (T_L)

=

T-stat.-1 (T_H)

$Q_1'' = Q_1 - Q_1'$

Comb. cycle

$Q_2'' = Q_2 - Q_2'$

T-stat.2 (T_L)

Thus,

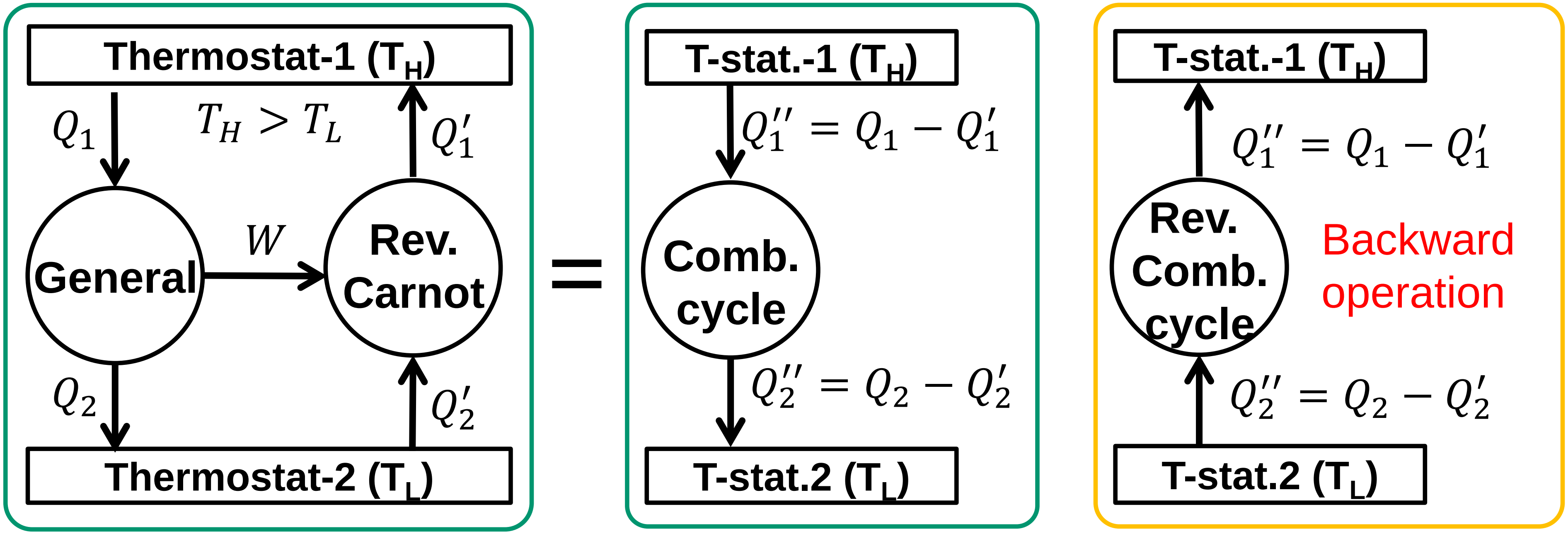
$$\eta_{gen} = \frac{W}{Q_1} \leq \frac{W}{Q_1'}$$

Here, the last term W/Q_1' is equal to the efficiency of Carnot cycle. Then,

$$\eta_{gen} = \frac{W}{Q_1} \leq \frac{W}{Q_1'} = \eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

1.3.1. The 2nd law of thermodynamics

- Comparison of efficiency with Carnot cycle (cont'd) -



- ✓ Here we assume the general cycle is reversible. In this case as (reversed) Carnot cycle is reversible, the combined cycle is also reversible.
- ✓ Then, we consider a backward operations of the combined cycle. For this, $Q_1'' = Q_2'' = 0$ thus $Q_1 = Q_1'$ is required to avoid a heat transfer from lower-temp. side to higher-temp. side without any work. (This conditions does not appear if the cycle is irreversible, because backward operation is not allowed.)
- ✓ Hence, $\eta_{gen} = {}^{W}/_{Q_1} = {}^{W}/_{Q_1'} = \eta_{Carnot}$, which demonstrates that the equal sign is achieved when the cycle is reversible.

1.3.1. The 2nd law of thermodynamics
- Comparison of efficiency with Carnot cycle (cont'd) -

So, what we demonstrated is:

<Theorem> The efficiency of a (general) cycle using 2 thermostats is less than the efficiency of Carnot cycle.

$$\eta = 1 - \frac{Q_2}{Q_1} \leq \eta_c = 1 - \frac{T_L}{T_H}$$

The equal sign is achieved when the cycle is reversible.

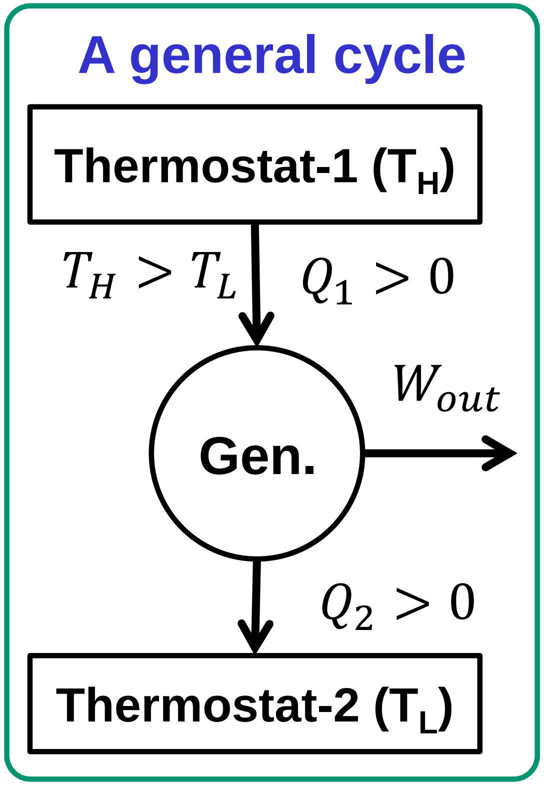
Here, we focus on the correlation between heat and temperature:

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_L}{T_H} \quad \text{then} \quad \frac{Q_2}{Q_1} \geq \frac{T_L}{T_H}$$

By replacing T_H with T_1 and T_L with T_2:

$$\frac{Q_2}{Q_1} \geq \frac{T_2}{T_1} \quad \text{then} \quad \frac{Q_1}{T_1} + \frac{-Q_2}{T_2} = \frac{q_1}{T_1} + \frac{q_2}{T_2} \leq 0$$

The equal sign is achieved when the cycle is reversible.



A general cycle

Thermostat-1 (T_H)

$T_H > T_L$

$Q_1 > 0$

Gen.

W_{out}

$Q_2 > 0$

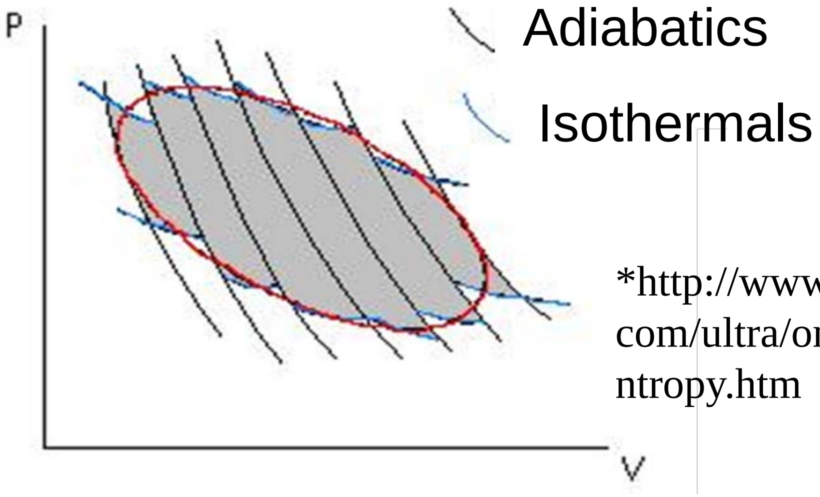
Thermostat-2 (T_L)

1.3.1. The 2nd law of thermodynamics

- Extension to infinite number of thermostats, then Clausius theorem -

Then, we extend the number of thermostats from 2 to n.

For this aim, we replace a general cycle with multiple Carnot cycles as given in the right figure.



*http://www.angelfire.com/ultra/omshome/entropy.htm

For a cycle composed by 2 thermostats, we have $\frac{Q_1}{T_1}+\frac{-Q_2}{T_2}=\frac{q_1}{T_1}+\frac{q_2}{T_2}\leq 0$ where the equal sign is achieved when the cycle is reversible.

For each Carnot cycle in the multiple Carnot cycles, this equation can be applied:

$$\left(\frac{q_{1,1}}{T_{1,1}}+\frac{q_{1,2}}{T_{1,2}}\right)+\left(\frac{q_{2,1}}{T_{2,1}}+\frac{q_{2,2}}{T_{2,2}}\right)+..+\left(\frac{q_{n,1}}{T_{n,1}}+\frac{q_{n,2}}{T_{n,2}}\right)\leq 0 \qquad \text{then} \qquad \sum_i^{2n}\frac{q_i}{T_i}\leq 0$$

To generalize this concept, we need to consider infinite number of thermostats, which gives an integral form as $\oint\frac{\delta q}{T}\leq 0$, where the equal sign is for reversible process and unequal sign is for irreversible process. This equation is called “Clausius theorem” or “Clausius inequality”.

1.3.1. The 2^{nd} law of thermodynamics

- Definition of entropy -

The efficiency (η) of a general cycle (engine) can be defined as

$$\eta = \frac{W_{out}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

For Carnot cycle, the efficiency is rewritten as

$$\eta_C = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_L}{T_H}$$

The efficiency of a (general) cycle using 2 thermostats is less than the efficiency of Carnot cycle.

$$\eta \leq \eta_c = 1 - \frac{T_L}{T_H} \qquad \left(\eta = 1 - \frac{Q_2}{Q_1}\right)$$

The equal sign is achieved when the cycle is reversible.

We derived the following equation which is applicable for any cycle in a closed system, based on the 2^{nd} law statement:

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

where equal sign is for reversible process and the unequal is for irreversible.

1.3.1. The 2nd law of thermodynamics

- Definition of entropy(cont'd) -

We derived the following equation which is applicable for any cycle in a closed system, based on the 2nd law statement: $\oint \frac{\delta q}{T} \leq 0$
where the equal sign is for reversible process and unequal sign is for irreversible process

- ✓ Focusing on reversible process, the equation is written as $\oint \frac{\delta q_{rev}}{T} = 0$ where δq_{rev} explicitly indicates that the cycle is composed only by reversible processes.
- ✓ This implies that S is a state function if $dS = \frac{\delta q_{rev}}{T}$ is defined, although $\frac{\delta q_{non-rev}}{T}$ and δq are not state functions.
- ✓ Then, here we define a new state function called entropy (S [J/K]) as:

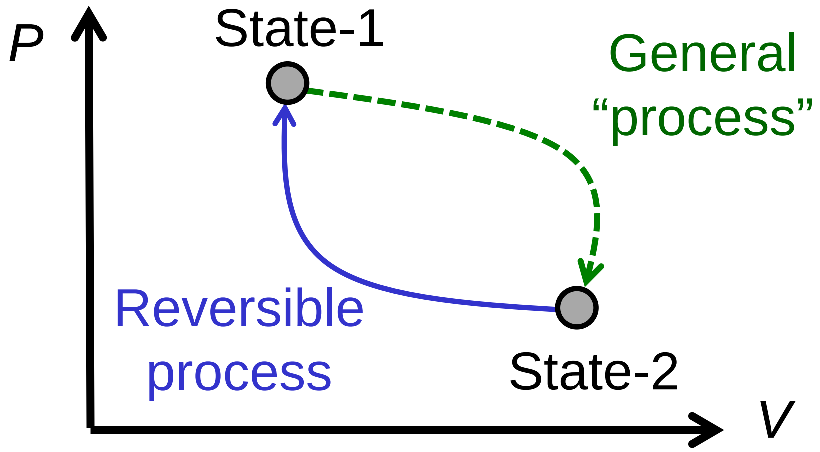
$$dS = \frac{\delta q_{rev}}{T}$$

- ✓ As entropy is a state functions, its difference between two states (1 and 2) can be calculated as follows:

$$\Delta S = S_2 - S_1 = \int_{state-1}^{state-2} \frac{\delta q_{rev}}{T}$$

1.3.1. The 2nd law of thermodynamics
- Entropy change in a process (not in a cycle) -

So far, we considered a cycle and defined entropy.
Here, we discuss the response of entropy in a process.



- ✓ For this cycle composed of 2 processes Clausius theorem gives:

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^1 \frac{\delta q_{rev}}{T} \leq 0 \quad \text{then} \quad \int_1^2 \frac{\delta q}{T} \leq \int_1^2 \frac{\delta q_{rev}}{T} = \int_1^2 dS = S_2 - S_1 = \Delta S$$

where the equal sign is achieved when the general process is reversible and the unequal sign is achieved when the general process is irreversible.

- ✓ The last equation can be re-written as $dS \geq \frac{\delta q}{T}$, where, again, the equal sign is for reversible process and unequal sign is for irreversible process. This equation is applicable for any process of a (closed) system.

1.3.1. The 2nd law of thermodynamics
- then, the 2nd law statement using entropy -

<a statement of the Second Law of Thermodynamics>
There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the (closed) system,

$$dS \geq \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

Be sure that

- dS can be less than 0 if $\delta q < 0$.
- However, if we consider the system is isolated (or thermally isolated), $dS \geq 0$ is achieved as $\delta q = 0$. In addition, the entropy is conserved (namely $dS = 0$) if the process is reversible.

<The summary of the 1st and 2nd laws of thermodynamics by Clausius>

- ✓ *The energy of the universe is constant.*
- ✓ *The entropy is tending to a maximum.*

1.3.1. The 2^{nd} law of thermodynamics
- Comparison with other statements -

<a statement of the Second Law of Thermodynamics>
There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the (closed) system,

$$dS \geq \frac{\delta q}{T}$$

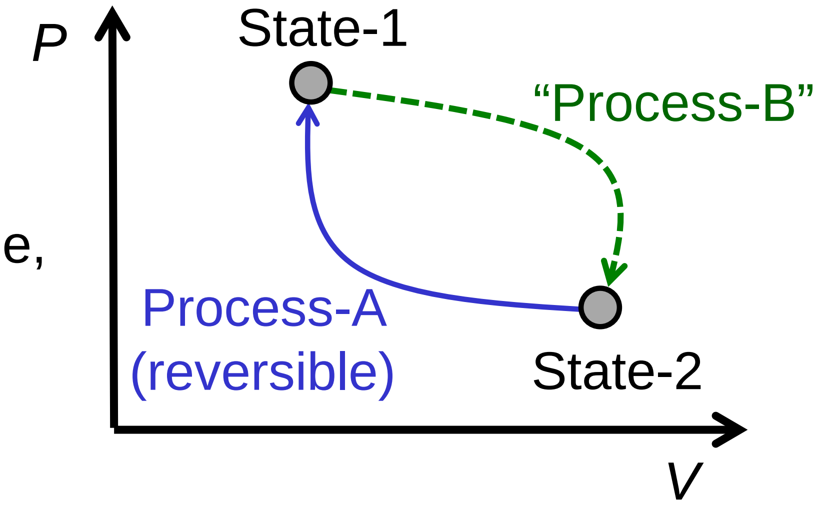
where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

- ✓ There are several other statements corresponding to the 2^{nd} law:
  - ✓ [#1: Thomson, Lord Kelvin] It is impossible to devise an engine/cycle that only absorb heat from one reservoir and produce the same amount of work. (100% efficiency is impossible.)
  - ➢ [#2: Clausius] An engine cannot move heat q from low T_1 to high T_2 without other effects.
  - ➢ [#3] All reversible Carnot cycle operating between T_H and T_L ($T_H > T_L$) must have the same efficiency as $\eta_c = 1 - \frac{T_L}{T_H}$.

*As definition, the efficiency is $\eta = 1 - \frac{Q_2}{Q_1}$

(Appendix) Why *S* is a state function?

(Question) Why $\oint \frac{\delta q_{rev}}{T} = 0$ indicates "S is a state function if $dS = \frac{\delta q_{rev}}{T}$ is defined" ?



✓ In the right figure, if process-B is reversible,

$$\oint \frac{\delta q_{rev}}{T} = \oint dS =$$

$$\int_{s-2\,(path-A)}^{s-1\,(path-A)} dS + \int_{s-1\,(path-B)}^{s-2\,(path-B)} dS = 0$$

$$\int_{s-1\,(path-A)}^{s-2\,(path-A)} dS = \int_{s-1\,(path-B)}^{s-2\,(path-B)} dS$$

Hence, $\Delta S \left(= \int_{s-1}^{s-2} dS = S_2 - S_1\right)$ is determined by the initial and final states, and does not depend on the path, which meant it is a state function.

*Even If the process-B is irreversible process, ΔS_B should be equal to $S_2 - S_1$ to make $\oint dS = 0$, which is required as a state function. However, in this case, we cannot calculate the entropy change by the process-B using $\Delta S = \int \frac{\delta q_{rev}}{T}$ because the $\delta q \neq \delta q_{rev}$. How can we evaluate it?

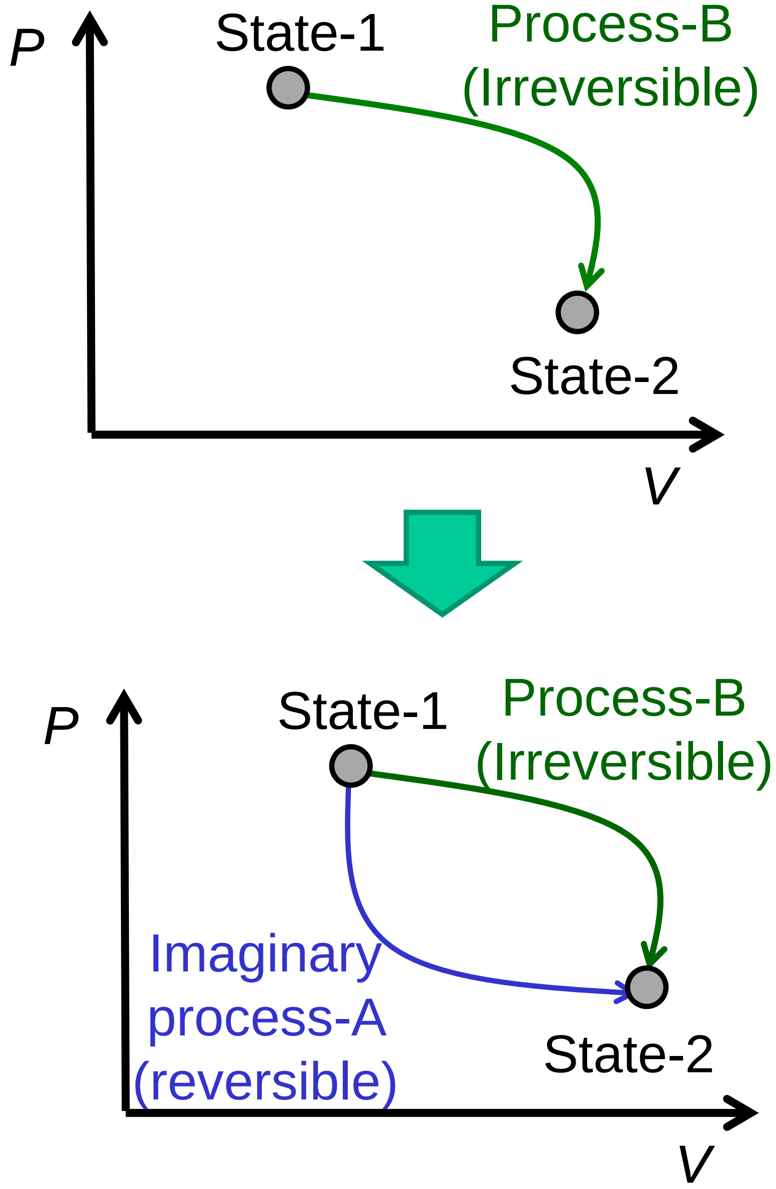
(Appendix) How to calculate ΔS for irreversible process?

(Question) We consider process-B, which is irreversible. Please evaluate the corresponding entropy change.

- ✓ For this problem, we cannot use $\Delta S = \int_{s-1}^{s-2} dS = \int_{s-1}^{s-2} \frac{\delta q_{rev}}{T}$, because $\delta q \neq \delta q_{rev}$ for the process-B. Note that $dS = {}^{\delta q_{rev}}/_{T}$, but $dS > {}^{\delta q_{irr}}/_{T}$.

- ✓ In this case, we should use the character of state function: we can calculate ΔS_{B-irr} using an imaginary path-A (reversible) which has the same initial and final states with path-B (irreversible):

$$\Delta S_{B-irr} = S_2 - S_1 = \Delta S_{A-rev}$$
$$= \int_{s-1\ (path-A)}^{s-2\ (path-A)} dS = \int_{s-1\ (path-A)}^{s-2\ (path-A)} \frac{\delta q_{rev}}{T}$$



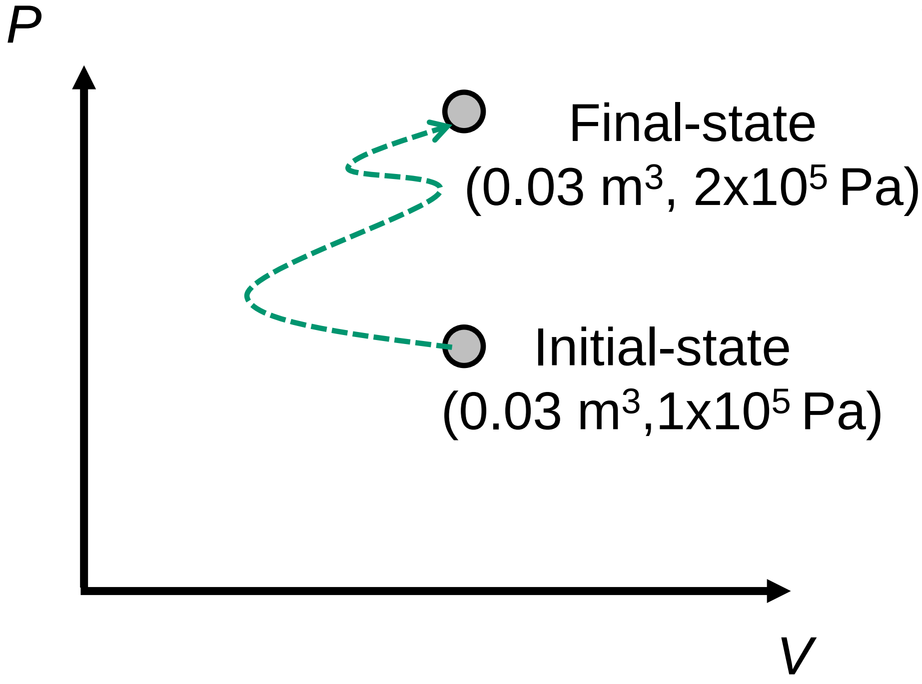
(Example) evaluation of entropy change

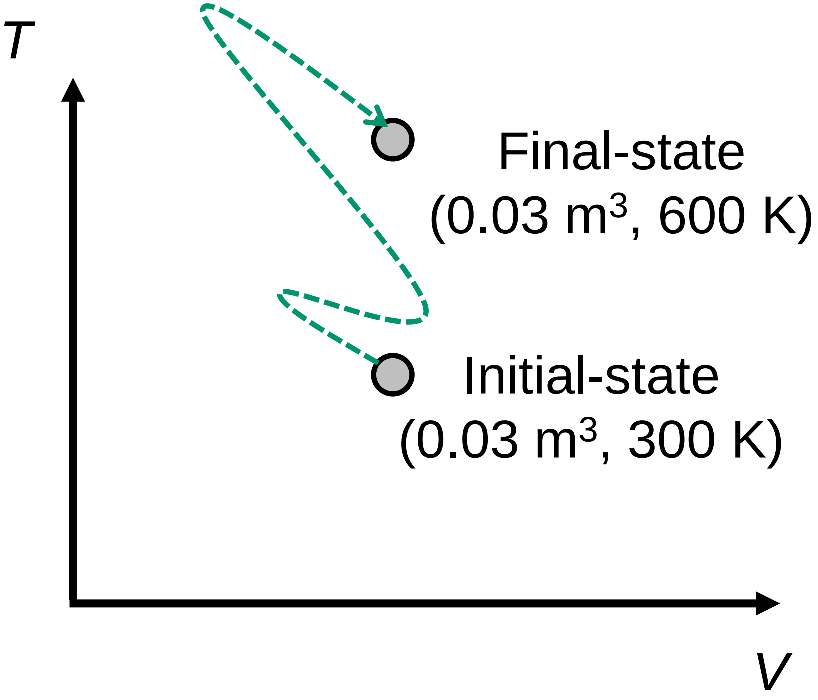
- ✓ [Quiz-1] The system of ideal gas changed its state from (1.0×10^5 Pa, 0.030 m^3, 300 K) to (2.0×10^5 Pa, 0.030 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.
  - (1) Evaluate the entropy change by reversible constant-volume heating process from 300 K to 600 K. Then, this is the answer.

- ✓ [Quiz-2] The system of ideal gas changed its state from (1.0×10^5 Pa, 0.030 m^3, 300 K) to (4.0×10^5 Pa, 0.015 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.
  - (1) Evaluate the entropy change by reversible constant-volume heating process from 300 K to 600 K. Thus, the system is now (2.0×10^5 Pa, 0.030 m^3, 600 K)
  - (2) Then, evaluate the entropy change by reversible constant-temperature compression process from 0.030 m^3 to 0.015 m^3.
  - (3) The summation of (1) and (2) is the answer.

(Example) evaluation of entropy change

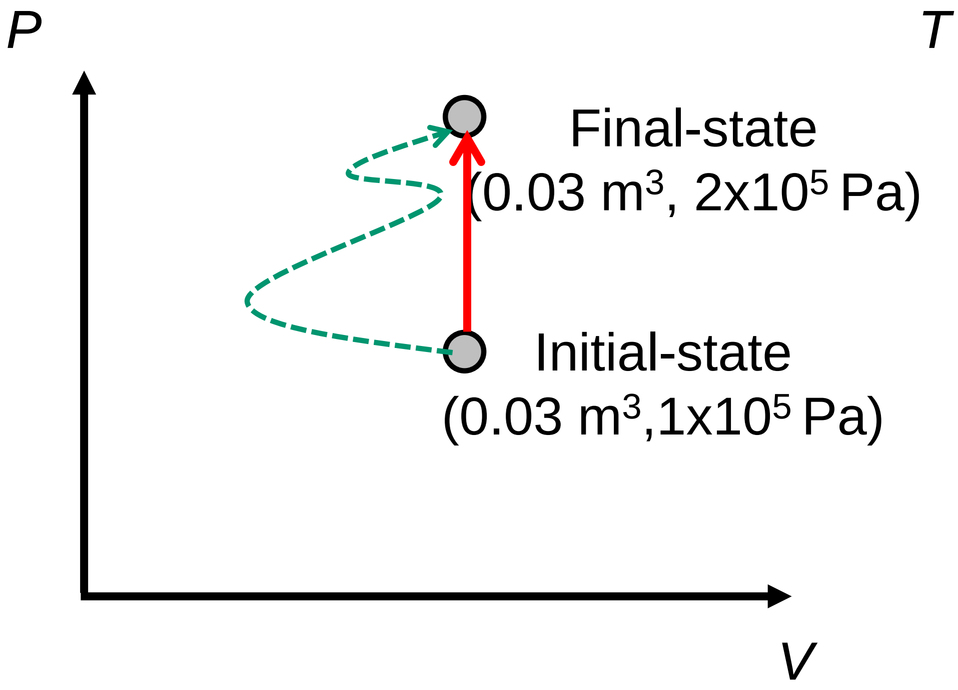
- ✓ [Example] The system of ideal gas changed its state from (1×10^5 Pa, 0.03 m^3, 300 K) to (2×10^5 Pa, 0.03 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.

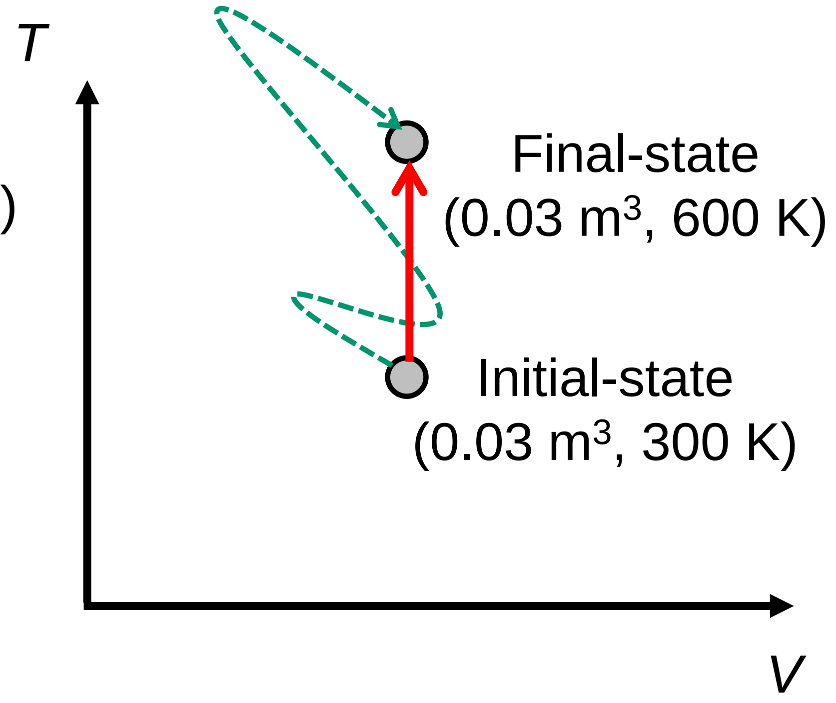




(Example) evaluation of entropy change

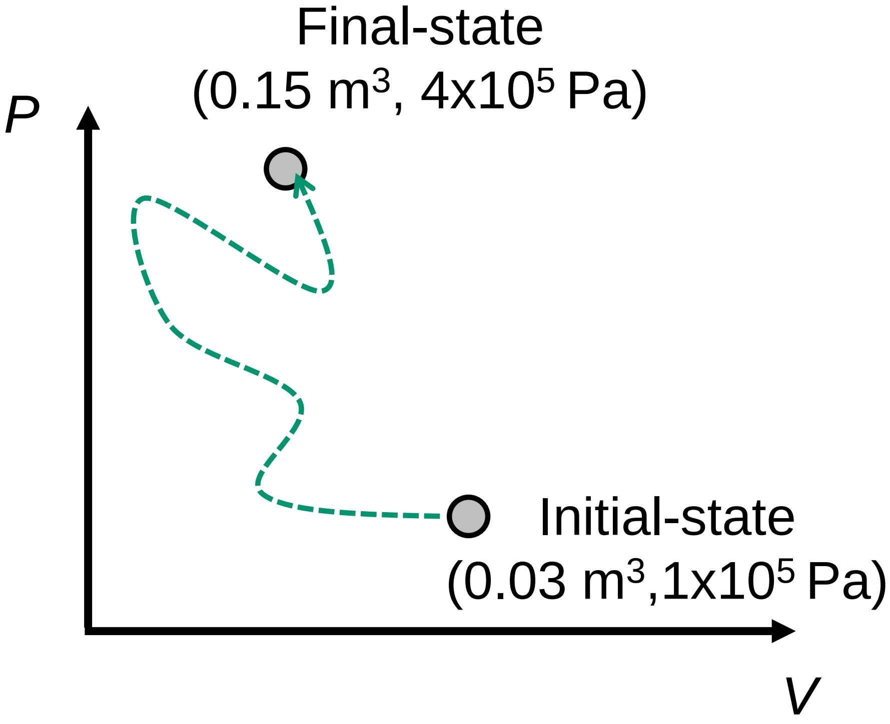
- ✓ [Example] The system of ideal gas changed its state from (1×10^5 Pa, 0.03 m^3, 300 K) to (2×10^5 Pa, 0.03 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.
  - (1) Evaluate the entropy change by reversible constant-volume heating process from 300 K to 600 K. Then, this is the answer.

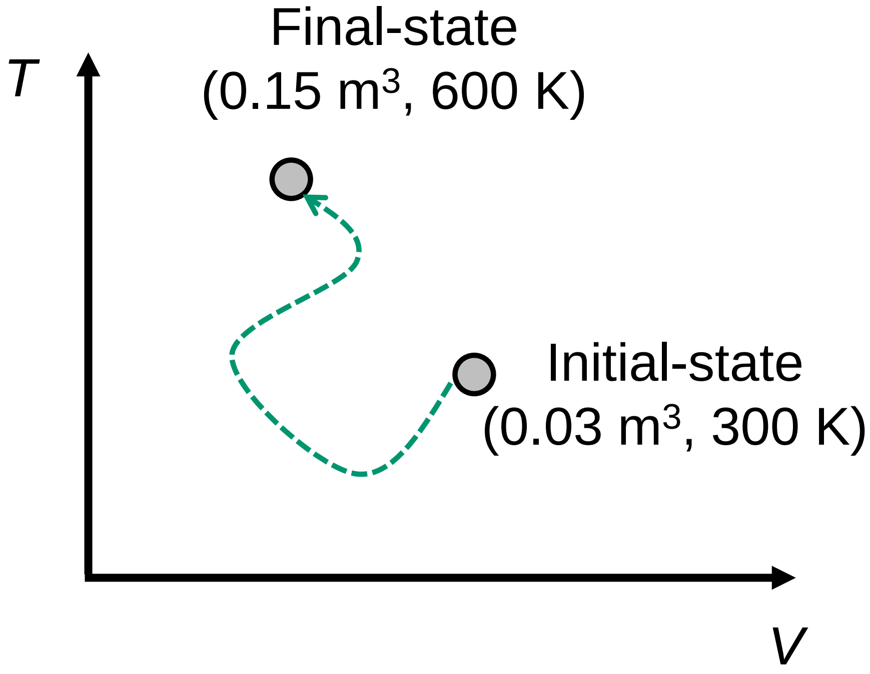




(Quiz) evaluation of entropy change

✓ [Quiz] The system of ideal gas changed its state from (1.0x10^5 Pa, 0.030 m^3, 300 K) to (4.0x10^5 Pa, 0.015 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.





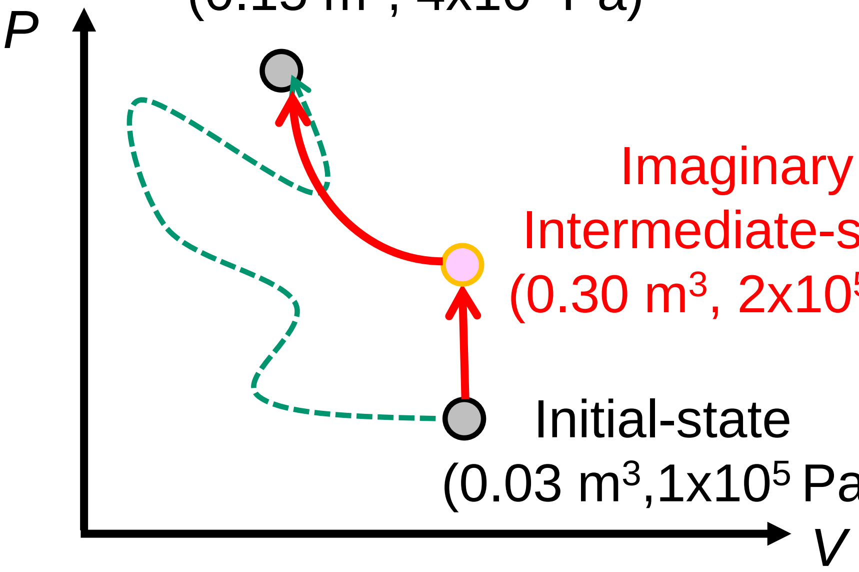
(Quiz) evaluation of entropy change

✓ [Quiz] The system of ideal gas changed its state from (1.0×10^5 Pa, 0.030 m^3, 300 K) to (4.0×10^5 Pa, 0.015 m^3, 600 K) by an irreversible process. Please evaluate the entropy change by this process.

(1) Evaluate the entropy change by reversible constant-volume heating process from 300 K to 600 K. Thus, the system is now (2.0×10^5 Pa, 0.030 m^3, 600 K)

(2) Then, evaluate the entropy change by reversible constant-temperature compression process from 0.030 m^3 to 0.015 m^3.

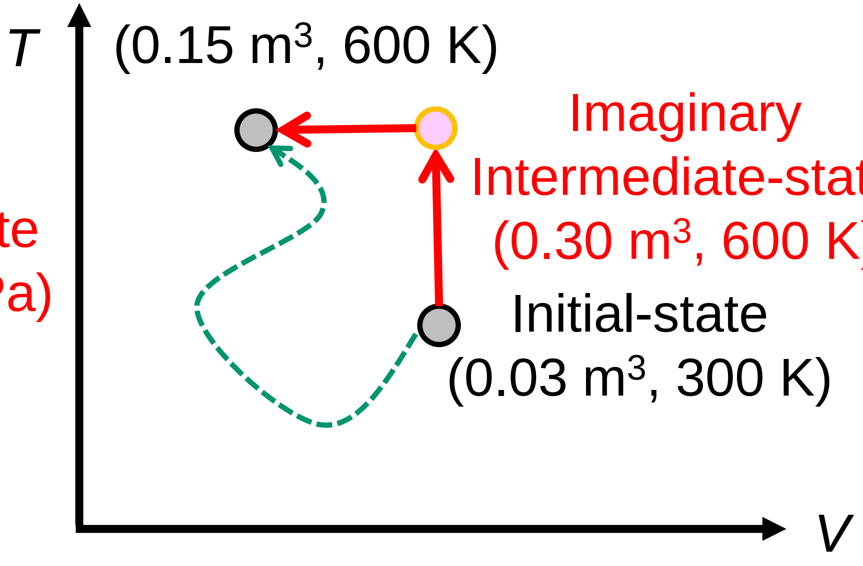
(3) The summation of (1) and (2) is the answer.



Final-state
(0.15 m^3, 4×10^5 Pa)

Imaginary
Intermediate-state
(0.30 m^3, 2×10^5 Pa)

Initial-state
(0.03 m^3,1×10^5 Pa)



Final-state
(0.15 m^3, 600 K)

Imaginary
Intermediate-state
(0.30 m^3, 600 K)

Initial-state
(0.03 m^3, 300 K)