

# Physical Chemistry for Energy Engineering (5<sup>th</sup>: 2018/09/17)

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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	No lecture

# Contents of today

## <Last class on 9/12>

1.2.1. Thermodynamic process

## <Today's class on 9/17>

**1.2.2. Thermodynamic cycle**

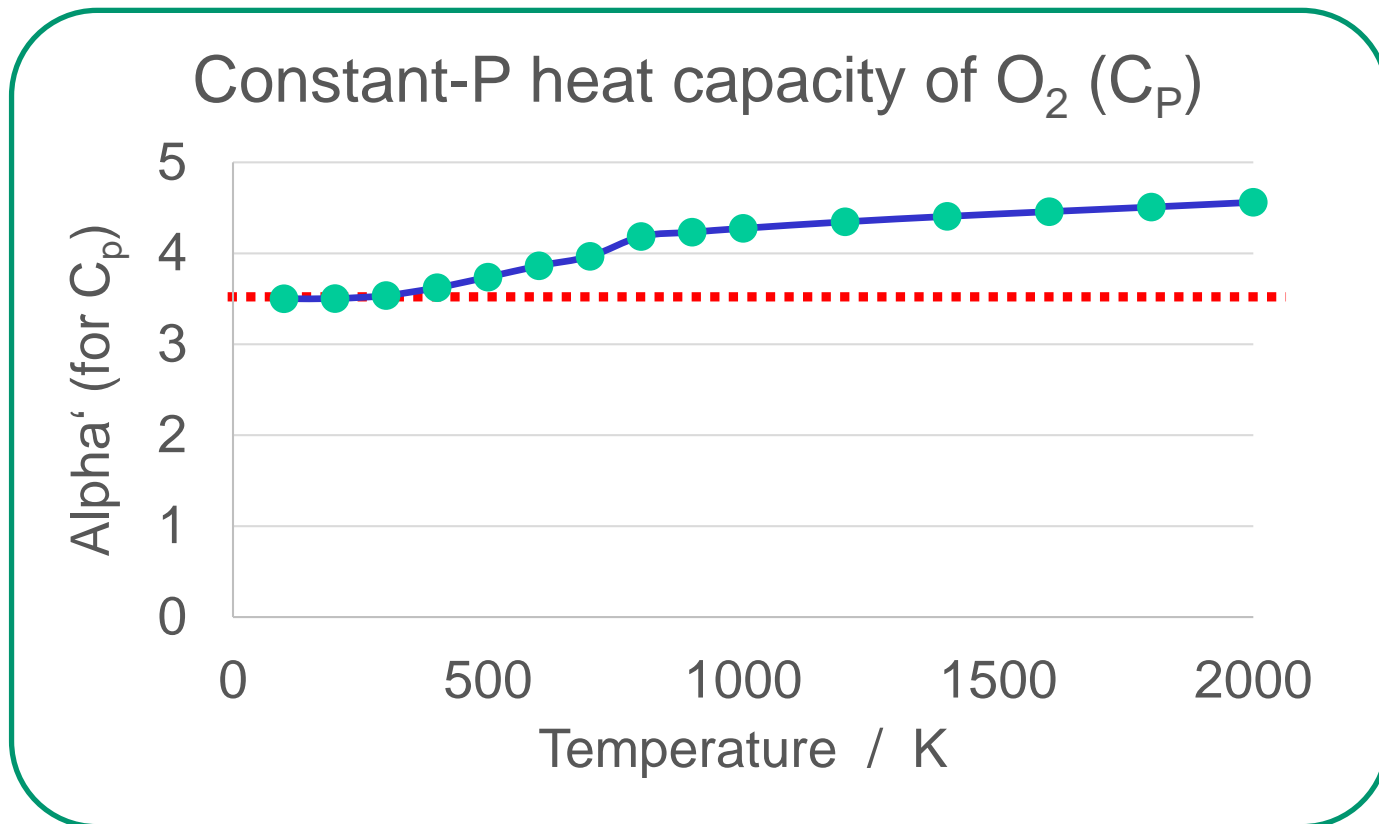
1.3.1. The second law of thermodynamics

# (in the last class) 1.2.1. Thermodynamic process

## - Heat capacity of real gas-

For ideal gas, " $C_V = \alpha nR$  [J K<sup>-1</sup>],  
where  $\alpha = 3/2$  for He (monoatomic gas),  $\alpha = 5/2$  for O<sub>2</sub> (diatomic gas).

$C_P - C_V = nR$  thus  $C_p = \frac{7}{2}nR$  for O<sub>2</sub> in ideal gas approximation

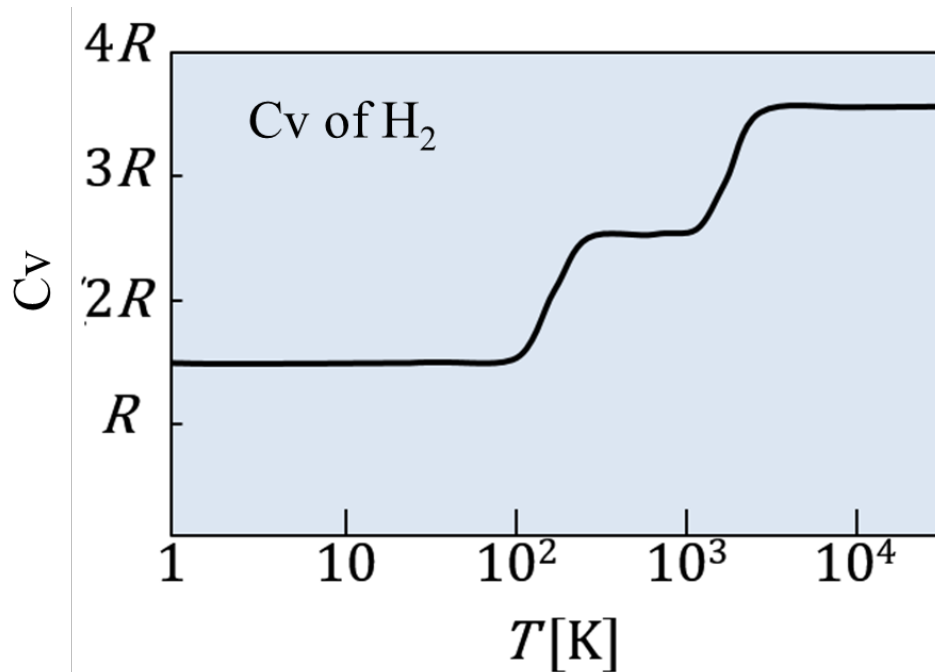


# (in the last class) 1.2.1. Thermodynamic process

## - Heat capacity of real gas-

For each vibrational mode, there are two degrees of freedom: (i) kinetic energy and (ii) potential energy.

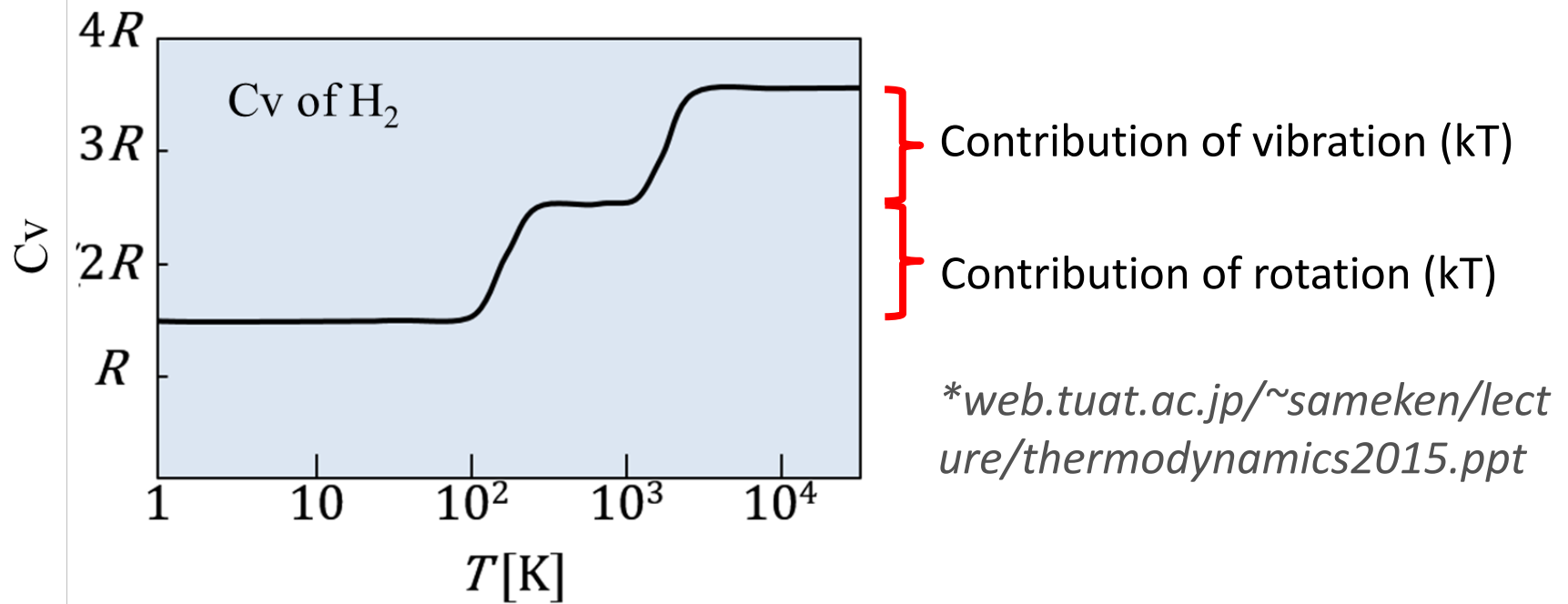
$$E_{vib} = \left\langle \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2 \right\rangle = \left\langle \frac{1}{2}mv_x^2 \right\rangle + \left\langle \frac{1}{2}kx^2 \right\rangle = \frac{1}{2}kT + \frac{1}{2}kT = kT$$



*\*web.tuat.ac.jp/~sameken/lecture/thermodynamics2015.ppt*

# (addition) 1.2.1. Thermodynamic process

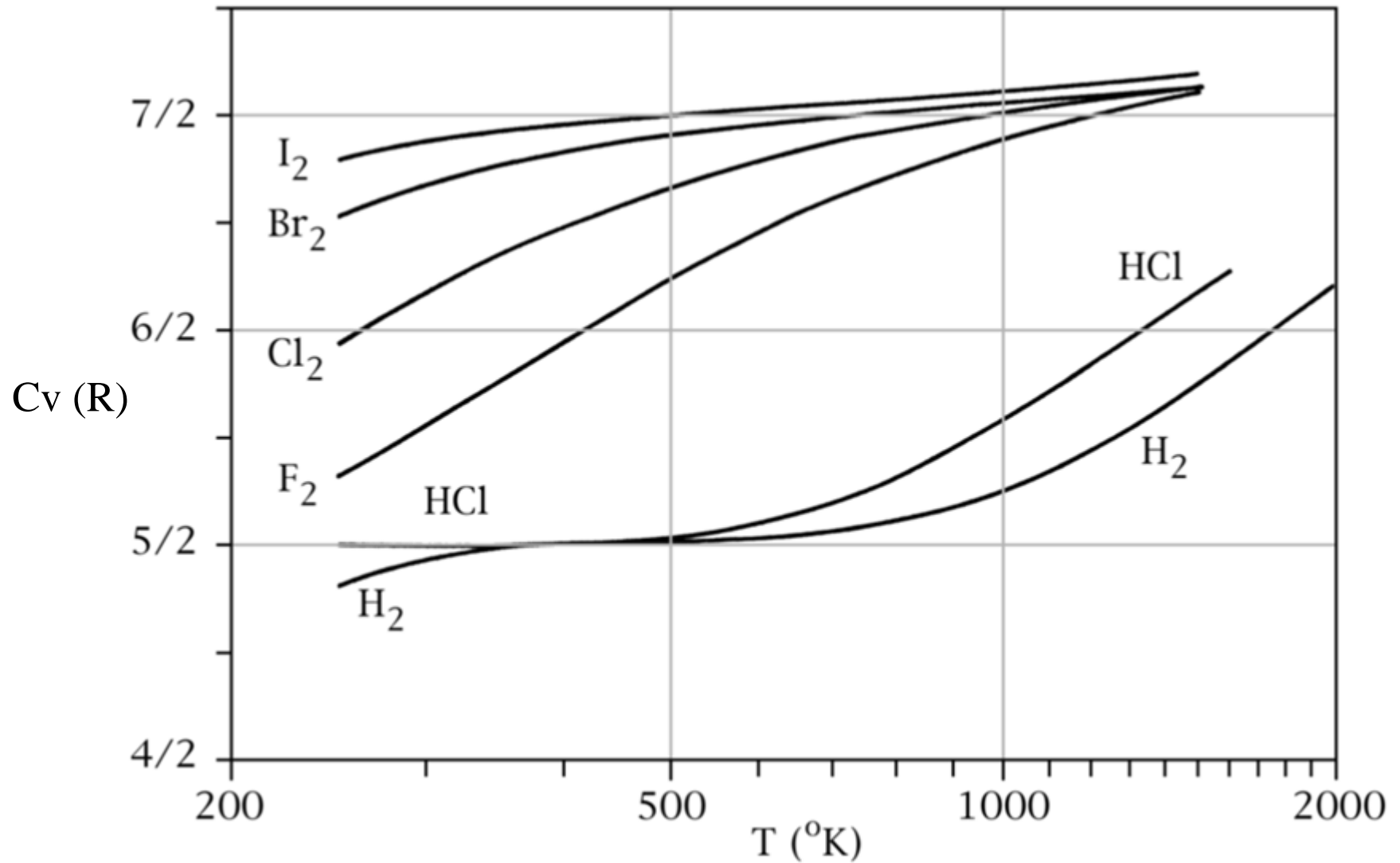
## - Comparison between real and ideal gasses-



- ✓ For both real H<sub>2</sub> gas and diatomic ideal gas, the translational degrees of freedom (of the center of mass) always contribute to the heat capacity ( $3/2$  kT)
- ✓ In real H<sub>2</sub> gas, the rotational and vibrational degrees of freedom do not contribute to the heat capacity below  $\sim 100$  K and  $\sim 1000$  K respectively, due to the quantum effects. This makes the heat capacity of real H<sub>2</sub> gas as in the figure above.
- ✓ In ideal diatomic gas, the rotational contribution happens from 0 K, while no vibrational contribution. Because ideal gas is classical (not quantum), and there is no interaction between atoms/molecules. (we imagine a fixed H-H structure, where H-H distance never changes. Even in this case, the rotation can occur. As a result,  $C_v$  becomes  $(5/2)kT$  for diatomic molecule independent of the temperature.

# (addition) 1.2.1. Thermodynamic process

## - Comparison between real and ideal gasses-



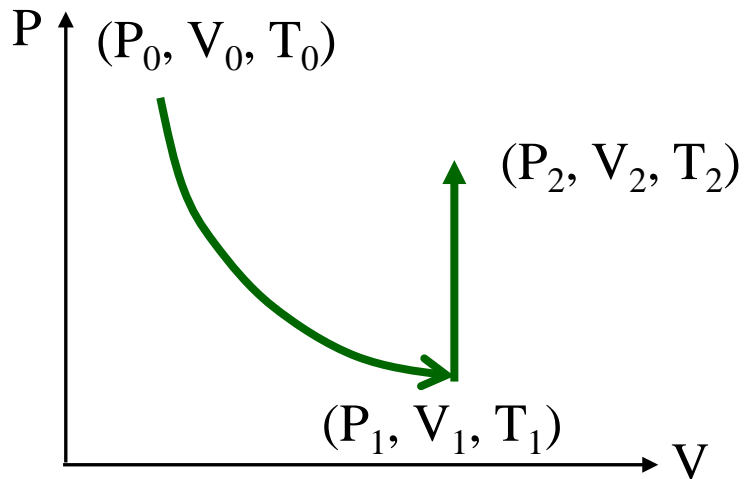
## 1.2.2. Thermodynamic cycle

- definition -

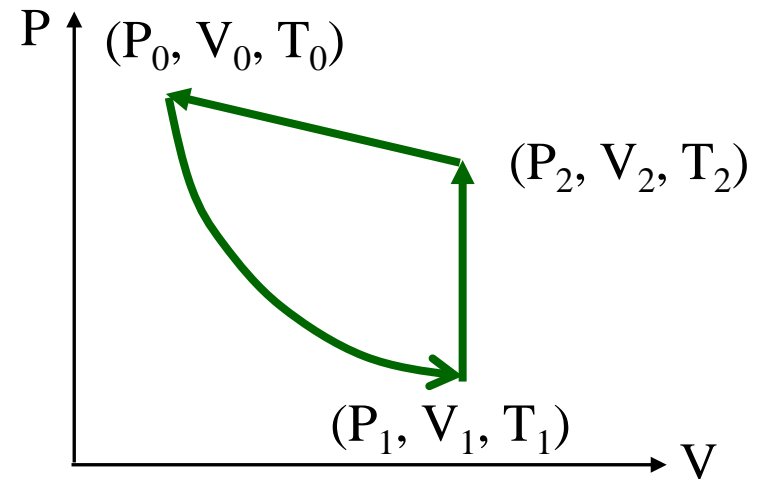
*“A thermodynamic cycle consists of a linked sequence of thermodynamic processes that involve the transference of heat and work into and out of the system, while varying pressure, temperature, and other state variables within the system, and that **eventually returns the system to its initial state.**”*

(\*wikipedia)

This is not a cycle because the system does not come back to the initial state.



This is a cycle because the system comes back to the initial state.



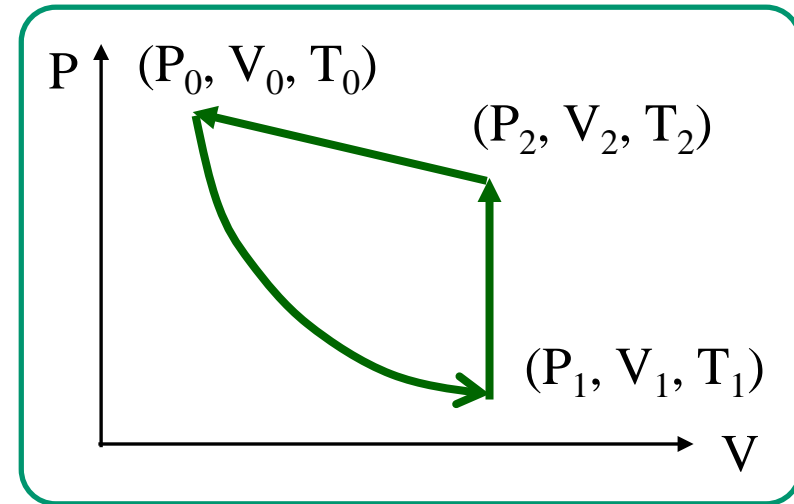


## 1.2.2. Thermodynamic cycle

- what do we do with a cycle? -

We usually calculate

- (1) energy transfer (heat & work),
  - (2) variation of state functions
- along processes involved in the cycle.



In a cycle, because the initial and the final states are identical, there are several constraints in state functions, for examples:

$$P_{ini} = P_{fin} \quad \Delta U_{cycle} = \oint dU = U_{fin} - U_{ini} = 0$$

Be careful about the difference between state functions and path functions.

$$q_{cycle} = \oint \delta q \neq 0 \quad w_{cycle} = \oint \delta w \neq 0$$

$$q_{cycle} + w_{cycle} = \oint \delta q + \oint \delta w = \Delta U_{cycle} = 0$$

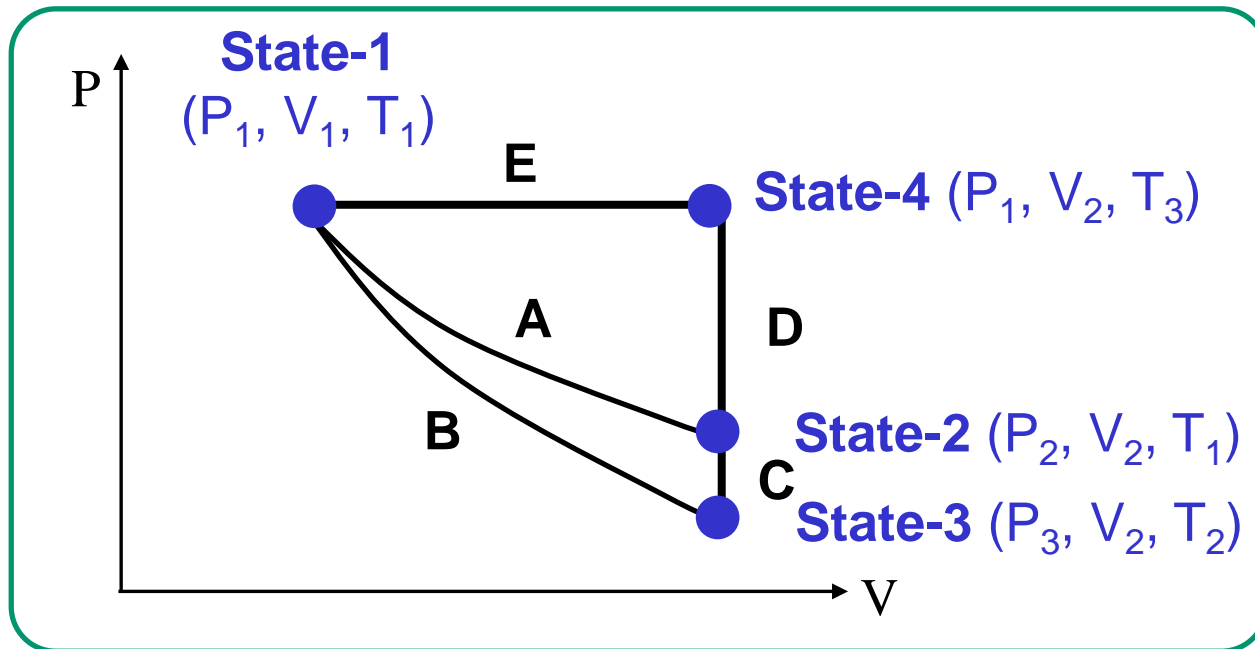
*\*Of course,  $q_{cycle}$  and  $w_{cycle}$  may be 0 accidentally, but not necessarily.*

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise -

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

- ✓ [Path-A] Reversible isothermal expansion: s-1 ( $P_1, V_1, T_1$ )  $\rightarrow$  s-2 ( $P_2, V_2, T_1$ )
- ✓ [Path-B] Reversible adiabatic expansion: s-1 ( $P_1, V_1, T_1$ )  $\rightarrow$  s-3 ( $P_3, V_2, T_2$ )
- ✓ [Path-C] Reversible constant-V heating: s-3 ( $P_3, V_2, T_2$ )  $\rightarrow$  s-2 ( $P_2, V_2, T_1$ )
- ✓ [Path-D] Reversible constant-V heating: s-2 ( $P_2, V_2, T_1$ )  $\rightarrow$  s-4 ( $P_1, V_2, T_3$ )
- ✓ [Path-E] Reversible constant-P cooling: s-4 ( $P_1, V_2, T_3$ )  $\rightarrow$  s-1 ( $P_1, V_1, T_1$ )



1<sup>st</sup> law: [derivative form]  $dU = \delta q + \delta w$  ; [integral form]  $\Delta U = q + w$

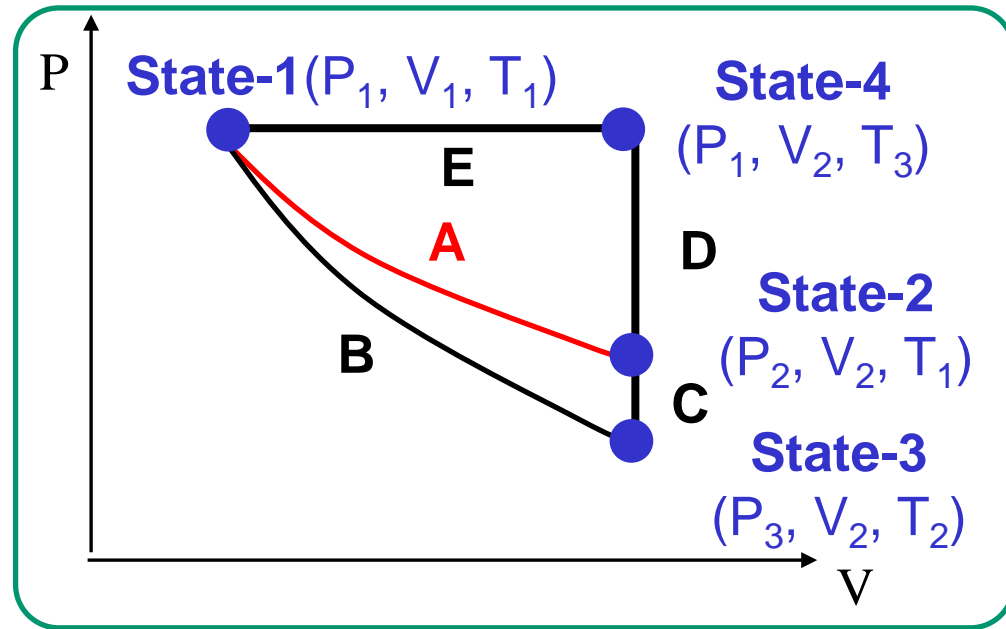
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-A)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-A] Reversible isothermal expansion:

$$\begin{aligned} & \text{s-1 } (P_1, V_1, T_1) \rightarrow \\ & \text{s-2 } (P_2, V_2, T_1) \end{aligned}$$



$\Delta U_A =$
$q_A =$
$w_A =$

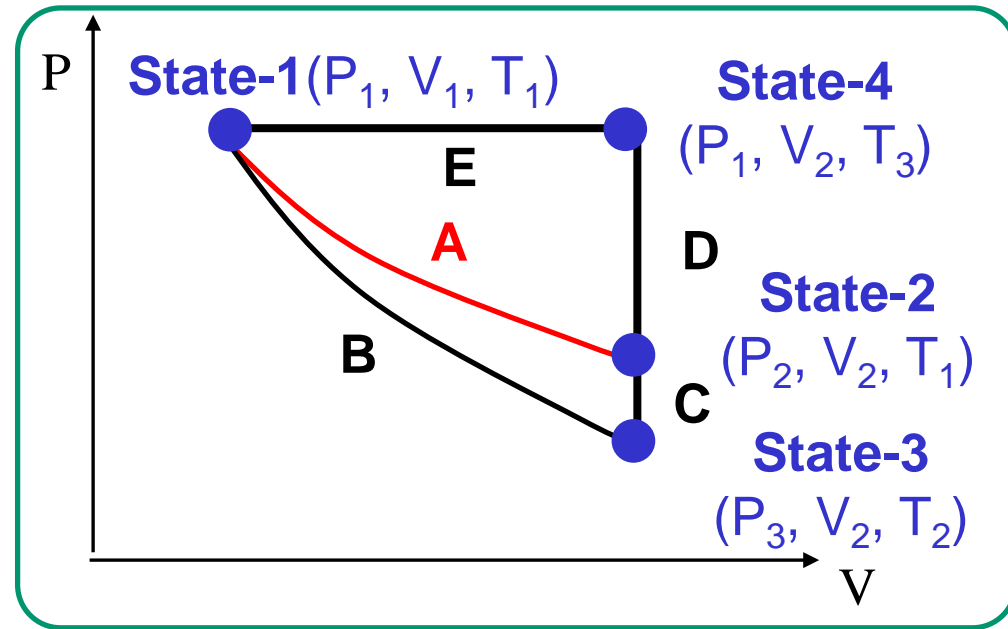
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-A)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-A] Reversible isothermal expansion:

$$\begin{aligned} & \text{s-1 } (P_1, V_1, T_1) \rightarrow \\ & \text{s-2 } (P_2, V_2, T_1) \end{aligned}$$



As the energy of ideal gas only depends on temperature and  $dT = 0$ ,

$$\Delta U_A = U(T_1) - U(T_1) = 0$$

The first law can be re-written:  $w_A = -q_A$

As a reversible process (as  $P = P_{ext}$ )

$$w_A = - \int_{V_1}^{V_2} P dV = -nRT_1 \int_{V_1}^{V_2} \frac{dV}{V} = -nRT_1 \times \ln \frac{V_2}{V_1}$$

$$\Delta U_A = 0$$

$$q_A = nRT_1 \times \ln \frac{V_2}{V_1}$$

$$w_A = -nRT_1 \times \ln \frac{V_2}{V_1}$$

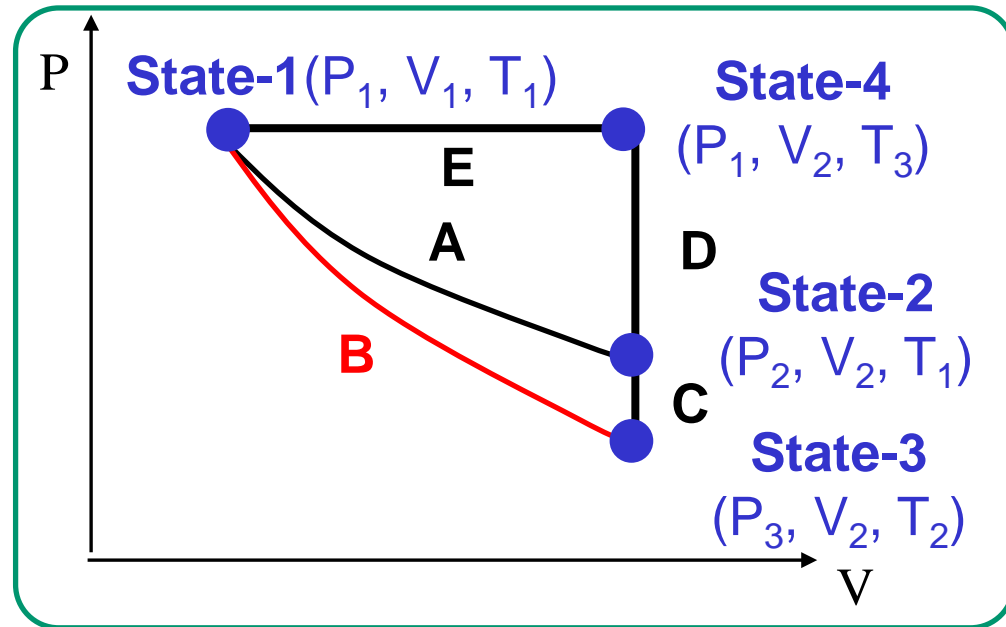
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-B)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-B] Reversible  
adiabatic expansion:

$$s-1 (P_1, V_1, T_1) \rightarrow \\ s-3 (P_3, V_2, T_2)$$



$$\Delta U_B =$$

$$q_B =$$

$$w_B =$$

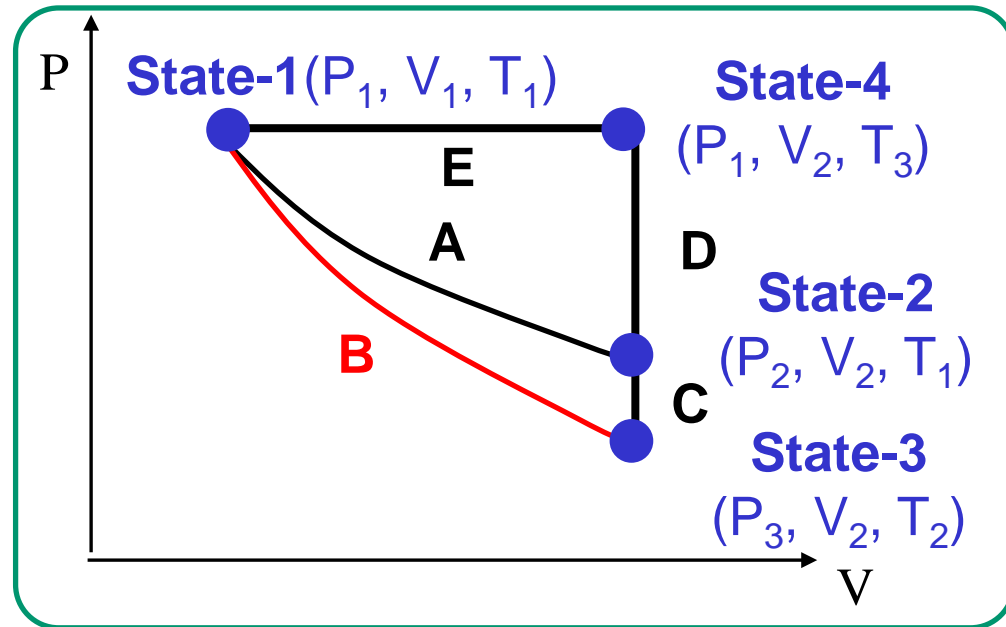
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-B)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-B] Reversible  
adiabatic expansion:

$$s-1 (P_1, V_1, T_1) \rightarrow s-3 (P_3, V_2, T_2)$$



As adiabatic process ( $\delta q = 0$  and then  $q = 0$ ), the first law is:  $dU_B = \delta w_B$

As we assume the system is of an ideal gas:

$$\Delta U_B = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1)$$

$$\Delta U_B = C_V(T_2 - T_1)$$

$$q_B = 0$$

$$w_B = C_V(T_2 - T_1)$$

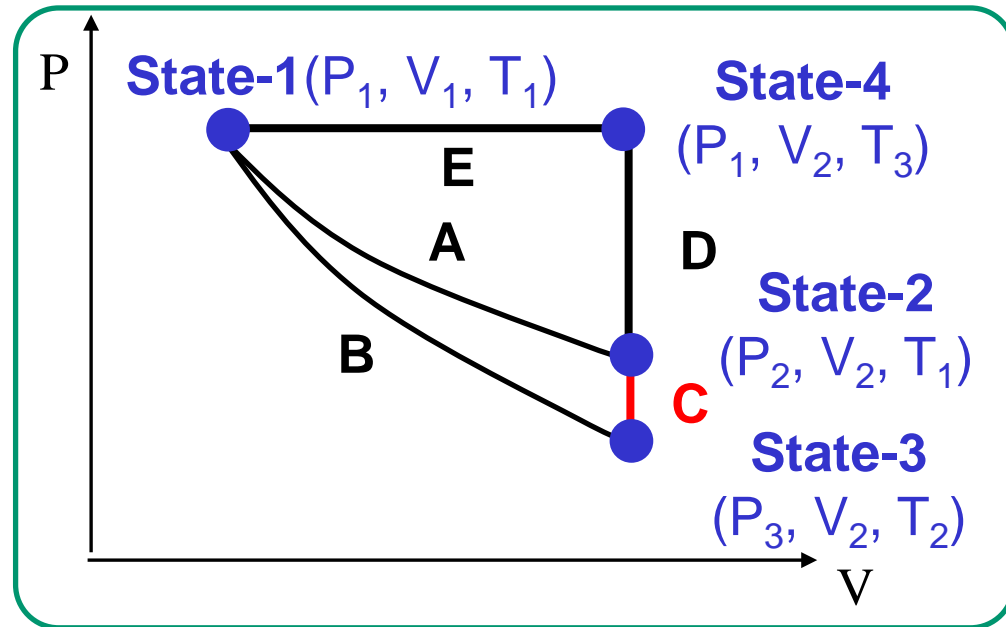
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-C)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-C] Reversible constant-V heating:

s-3 ( $P_3, V_2, T_2$ )  $\rightarrow$   
s-2 ( $P_2, V_2, T_1$ )



$$\Delta U_C =$$

$$q_C =$$

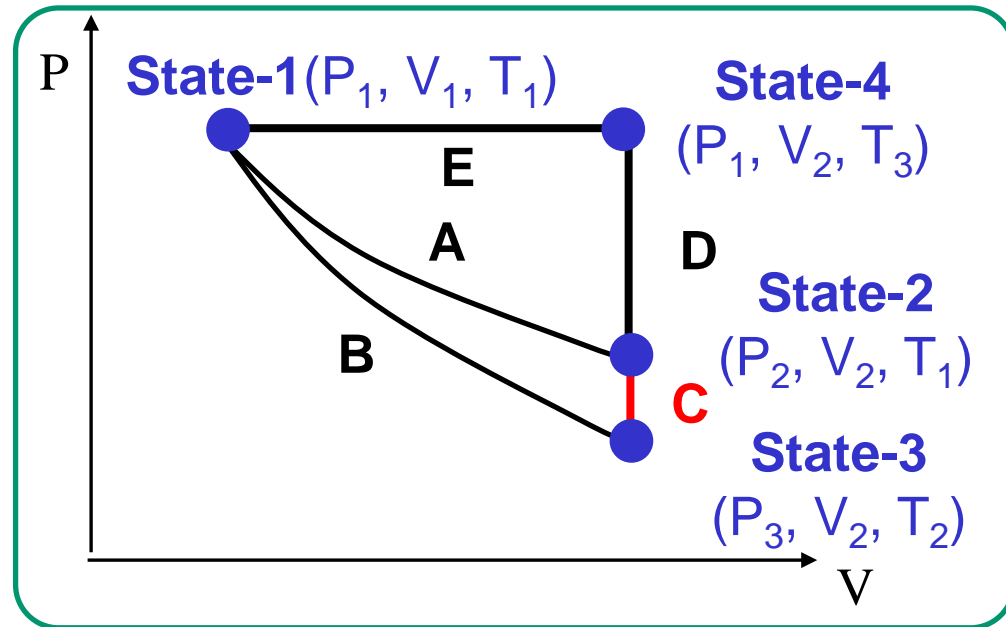
$$w_C =$$

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-C)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-C] Reversible constant-V heating:  
s-3 ( $P_3, V_2, T_2$ )  $\rightarrow$   
s-2 ( $P_2, V_2, T_1$ )



As constant-V process ( $dV = 0$ ),  $\delta w_C = -P_{ext}dV = 0$ .

Then, the first law is:  $dU_C = \delta q_C$

As we assume the system is of an ideal gas:

$$\Delta U_C = \int_{T_2}^{T_1} C_V dT = C_V(T_1 - T_2)$$

$$\Delta U_C = C_V(T_1 - T_2)$$

$$q_C = C_V(T_1 - T_2)$$

$$w_C = 0$$



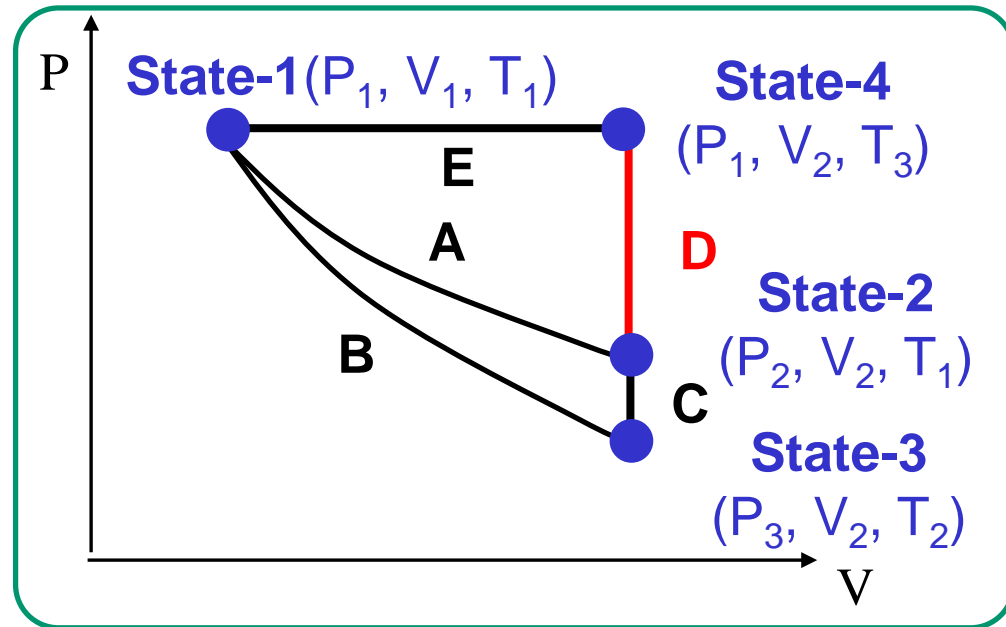
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-D)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-D] Reversible constant-V heating:

s-2 ( $P_2, V_2, T_1$ )  $\rightarrow$   
s-4 ( $P_1, V_2, T_3$ )



$$\Delta U_D =$$

$$q_D =$$

$$w_D =$$

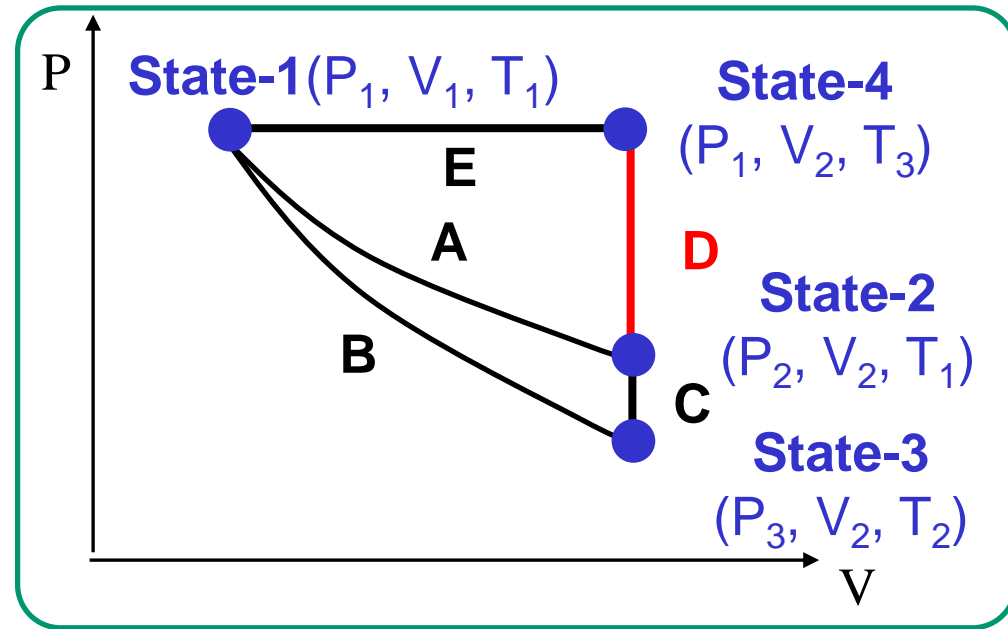
## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-D)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-D] Reversible constant-V heating:

$$s-2 (P_2, V_2, T_1) \rightarrow s-4 (P_1, V_2, T_3)$$



As constant-V process ( $dV = 0$ ),  $\delta w_D = -P_{ext}dV = 0$ .

Then, the first law is:  $dU_D = \delta q_D$

As we assume the system is of an ideal gas:

$$\Delta U_D = \int_{T_1}^{T_3} C_V dT = C_V(T_3 - T_1)$$

$$\Delta U_D = C_V(T_3 - T_1)$$

$$q_D = C_V(T_3 - T_1)$$

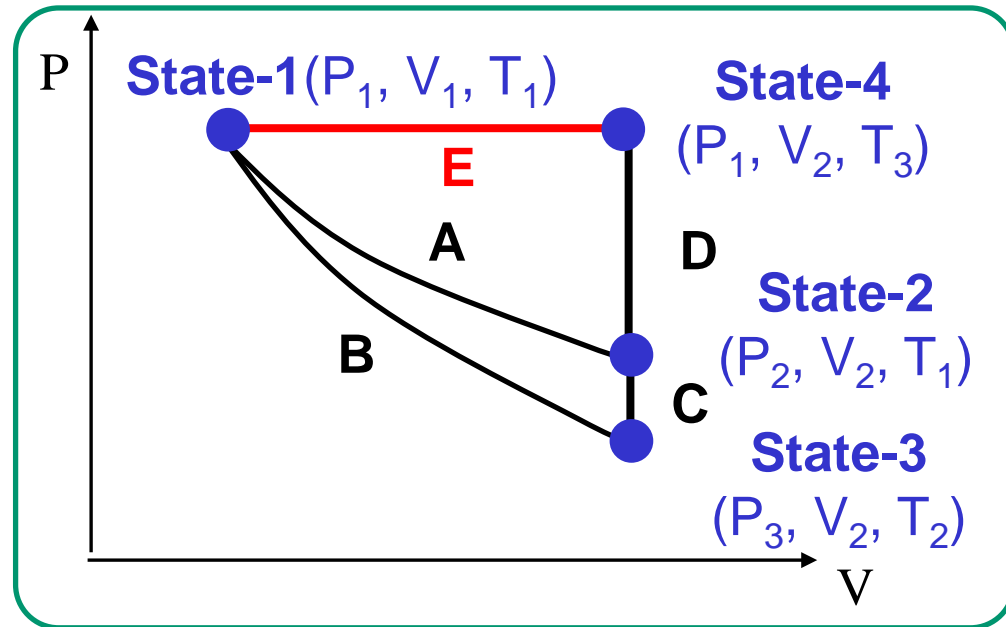
$$w_D = 0$$

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (path-E)-

Assuming  $n$  mole of idea gas ( $PV = nRT$ ,  $U = U(T)$ ,  $dU = C_V dT$  and  $C_V = \alpha nR = \text{const.}$ ), please evaluate (1)  $\Delta U$ , (2)  $q$ , (3)  $w$ , for each process.

[Path-E] Reversible constant-P cooling:  
s-4 ( $P_1, V_2, T_3$ )  $\rightarrow$   
s-1 ( $P_1, V_1, T_1$ )



As reversible constant-P process ( $P = P_{ext}$  and  $dP = 0$ ),

$$w_E = - \int P dV = -P_1 \int dV = -P_1(V_1 - V_2).$$

As we assume the system is of an ideal gas:

$$\Delta U_E = \int_{T_3}^{T_1} C_V dT = C_V(T_1 - T_3)$$

Then, using the first law:

$$q_E = \Delta U_E - w_E = C_V(T_1 - T_3) + P_1(V_1 - V_2)$$

$$\Delta U_E = C_V(T_1 - T_3)$$

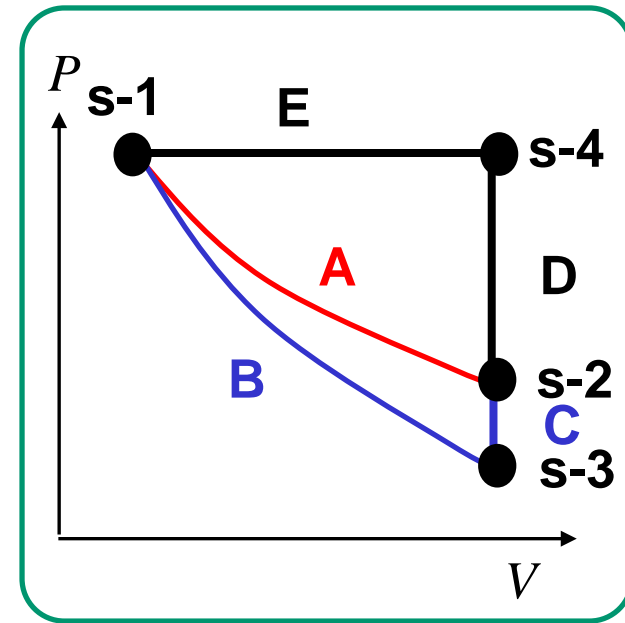
$$q_E = C_V(T_1 - T_3) + P_1(V_1 - V_2)$$

$$w_E = -P_1(V_1 - V_2)$$

# 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (summary)-

Path	$\Delta U$	$q$	$w$
<b>A</b>	0	$nRT_1 \times \ln \frac{V_2}{V_1}$	$-nRT_1 \times \ln \frac{V_2}{V_1}$
<b>B</b>	$C_V(T_2 - T_1)$	0	$C_V(T_2 - T_1)$
<b>C</b>	$C_V(T_1 - T_2)$	$C_V(T_1 - T_2)$	0
<b>D</b>	$C_V(T_3 - T_1)$	$C_V(T_3 - T_1)$	0
<b>E</b>	$C_V(T_1 - T_3)$	$C_V(T_1 - T_3) + P_1(V_1 - V_2)$	$-P_1(V_1 - V_2)$



## (1) [Path-A] v.s. [Path-B+C]

$$\Delta U_{B+C} = C_V(T_2 - T_1) + C_V(T_1 - T_2) = 0 = \Delta U_A$$

$$q_{B+C} = 0 + C_V(T_1 - T_2) = C_V(T_1 - T_2) \neq q_A$$

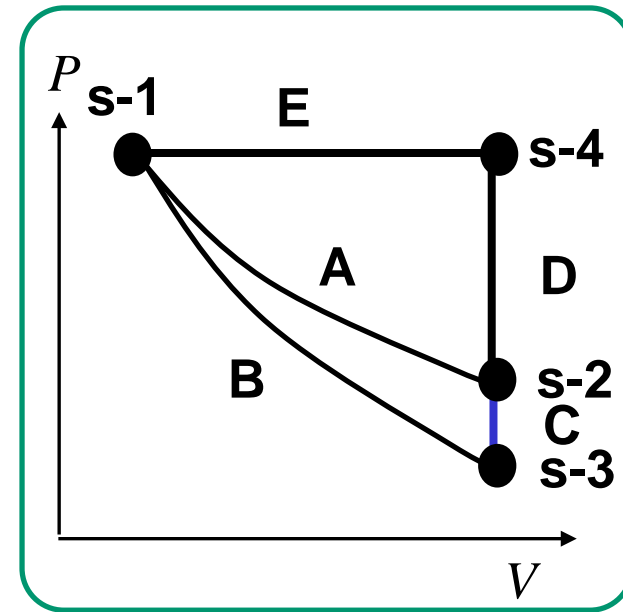
$$w_{B+C} = C_V(T_2 - T_1) + 0 = C_V(T_2 - T_1) \neq w_A$$

- ✓ As the initial and final states are identical in two paths, the change in state functions (e.g.  $U$ ) is identical.
- ✓ However, path functions (e.g.  $q$  and  $w$ ) depend on the path.

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (summary)-

Path	$\Delta U$	$q$	$w$
<b>A</b>	0	$nRT_1 \times \ln \frac{V_2}{V_1}$	$-nRT_1 \times \ln \frac{V_2}{V_1}$
<b>B</b>	$C_V(T_2 - T_1)$	0	$C_V(T_2 - T_1)$
<b>C</b>	$C_V(T_1 - T_2)$	$C_V(T_1 - T_2)$	0
<b>D</b>	$C_V(T_3 - T_1)$	$C_V(T_3 - T_1)$	0
<b>E</b>	$C_V(T_1 - T_3)$	$C_V(T_1 - T_3) + P_1(V_1 - V_2)$	$-P_1(V_1 - V_2)$



**(2) [Cycle-a: 1 → 2 → 4 → 1] v.s. [Cycle-b: 1 → 3 (→ 2) → 4 → 1]**

$$\Delta U_a = \Delta U_A + \Delta U_D + \Delta U_E = 0$$

$$\begin{aligned} q_a &= q_A + q_D + q_E \\ &= nRT_1 \times \ln \frac{V_2}{V_1} + P_1(V_1 - V_2) \end{aligned}$$

$$\begin{aligned} w_a &= w_A + w_D + w_E \\ &= -nRT_1 \times \ln \frac{V_2}{V_1} - P_1(V_1 - V_2) \end{aligned}$$

$$\Delta U_b = \Delta U_B + \Delta U_C + \Delta U_D + \Delta U_E = 0$$

$$\begin{aligned} q_b &= q_B + q_C + q_D + q_E \\ &= C_V(T_1 - T_2) + P_1(V_1 - V_2) \end{aligned}$$

$$\begin{aligned} w_b &= w_B + w_C + w_D + w_E \\ &= C_V(T_2 - T_1) - P_1(V_1 - V_2) \end{aligned}$$

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (summary) -

**(2) [Cycle-a: 1 → 2 → 4 → 1] v.s. [Cycle-b: 1 → 3 (→ 2) → 4 → 1]**

$$\Delta U_a = \Delta U_A + \Delta U_D + \Delta U_E = 0$$

$$\begin{aligned} q_a &= q_A + q_D + q_E \\ &= nRT_1 \times \ln \frac{V_2}{V_1} + P_1(V_1 - V_2) \end{aligned}$$

$$\begin{aligned} w_a &= w_A + w_D + w_E \\ &= -nRT_1 \times \ln \frac{V_2}{V_1} - P_1(V_1 - V_2) \end{aligned}$$

$$\Delta U_b = \Delta U_B + \Delta U_C + \Delta U_D + \Delta U_E = 0$$

$$\begin{aligned} q_b &= q_B + q_C + q_D + q_E \\ &= C_V(T_1 - T_2) + P_1(V_1 - V_2) \end{aligned}$$

$$\begin{aligned} w_b &= w_B + w_C + w_D + w_E \\ &= C_V(T_2 - T_1) - P_1(V_1 - V_2) \end{aligned}$$

✓ As cycle is closed, “[initial state] = [final state]” is required. Then:

$$\Delta U_{cycle} = \oint dU = U_{fin} - U_{ini} = 0$$

This is also applicable for other (extensive) state functions like enthalpy

✓ On the other hands, path functions do not have such result as:

$$w_{cycle} = \oint \delta w \neq 0 \quad q_{cycle} = \oint \delta q \neq 0$$

## 1.2.2. Thermodynamic cycle (\$19.4)

- a case of thermodynamic cycle: exercise (summary) -

(2) [Cycle-a: 1 → 2 → 4 → 1] v.s. [Cycle-b: 1 → 3 (→ 2) → 4 → 1]

$$\Delta U_a = \Delta U_A + \Delta U_D + \Delta U_E = \oint dU = 0$$

$$\Delta U_b = \Delta U_B + \Delta U_C + \Delta U_D + \Delta U_E = \oint dU = 0$$

- ✓ Using this character of state function in a cycle (i.e.  $\oint dU = 0$ , for example), we can sometimes easily determine the change of a state function in a certain path.
  - ✓ For example, here assuming the cycle is composed by 4 processes.

$$\Delta U_{cycle} = \Delta U_{path-1} + \Delta U_{path-2} + \Delta U_{path-3} + \Delta U_{path-4} = 0$$

- ✓ If  $\Delta U_{path-4}$  is difficult to be directly calculated but we know the contour integral is 0, we can determine it as:

$$\Delta U_{path-4} = -\Delta U_{path-1} - \Delta U_{path-2} - \Delta U_{path-3}$$

# Contents of today

## <Last class>

1.2.1. Thermodynamic process

## <Today's class>

1.2.2. Thermodynamic cycle

**1.3.1. The second law of thermodynamics**



## 1.3.1. The 2<sup>nd</sup> 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**)

## 1.3.1. The 2<sup>nd</sup> law of thermodynamics - perpetual motion (machines) -

### **(1) Perpetual motion machine of the 1<sup>st</sup> kind:**

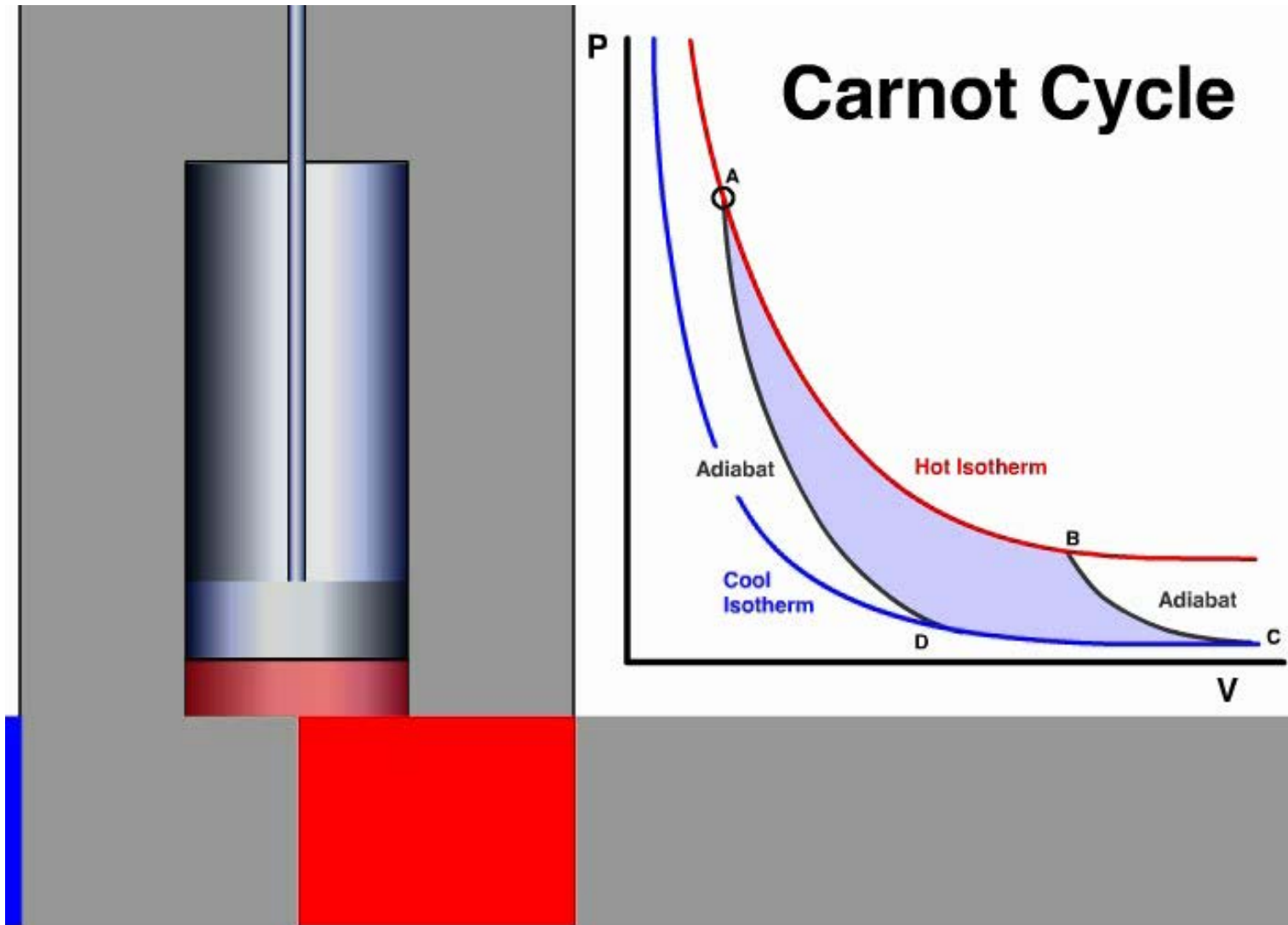
- ✓ “a machine that can do work to the surroundings without obtaining any inputs from the surroundings.”
- ✓ This motion violates the 1<sup>st</sup> law of thermodynamics, thus unfeasible.

### **(2) Perpetual motion machine of the 2<sup>nd</sup> kind:**

- ✓ “a machine/cycle that receives a heat from a thermostat (surroundings) and do equivalent amount of work to the surroundings.”
- ✓ This motion violates the 2<sup>nd</sup> law of thermodynamics, thus unfeasible.

# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

- a cycle combined with 2 thermostats -



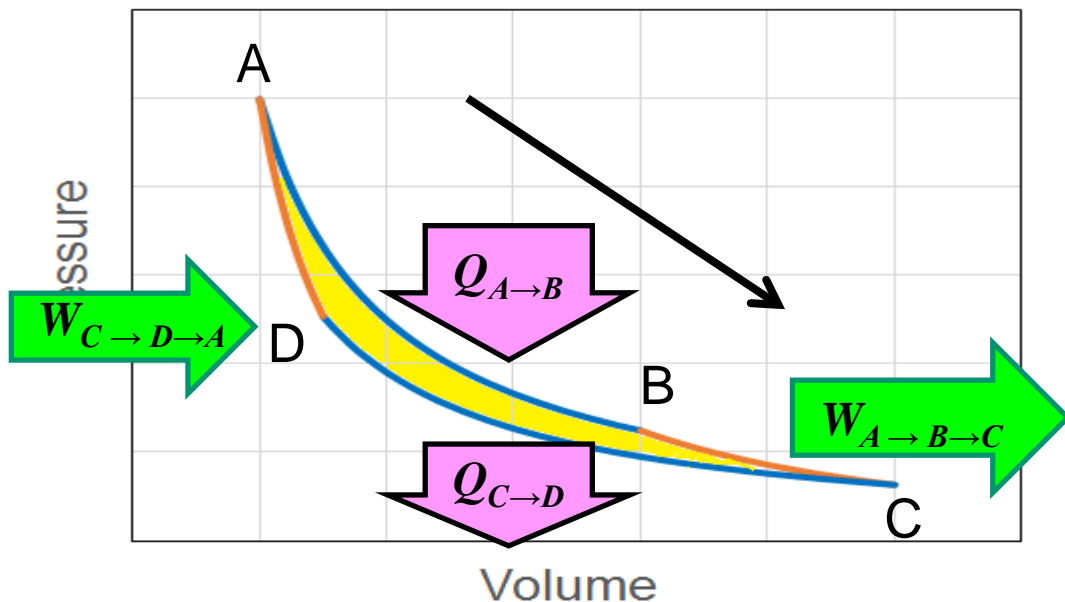
# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

## - a cycle combined with 2 thermostats (cont'd)-

We consider a cycle combined with 2 thermostats:

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

where  $T_H > T_L$  and assuming all processes are reversible.



**\*Hereafter,  
we define**

$$Q = |q|$$

$$W = |w|$$

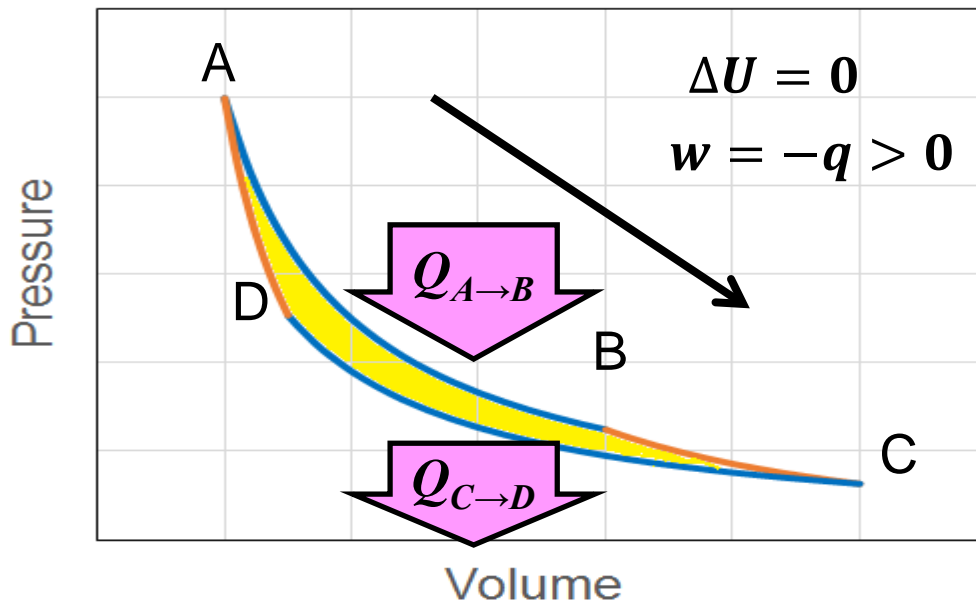
$$\begin{aligned}\Delta U &= q + w \\ &= Q_{A \rightarrow B} - Q_{C \rightarrow D} \\ &\quad - W_{A \rightarrow B} - W_{B \rightarrow C} \\ &\quad + W_{C \rightarrow D} + W_{D \rightarrow A} = 0\end{aligned}$$

The yellow area corresponds to “the work that the system did to the surroundings by a single operation of the cycle”

# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

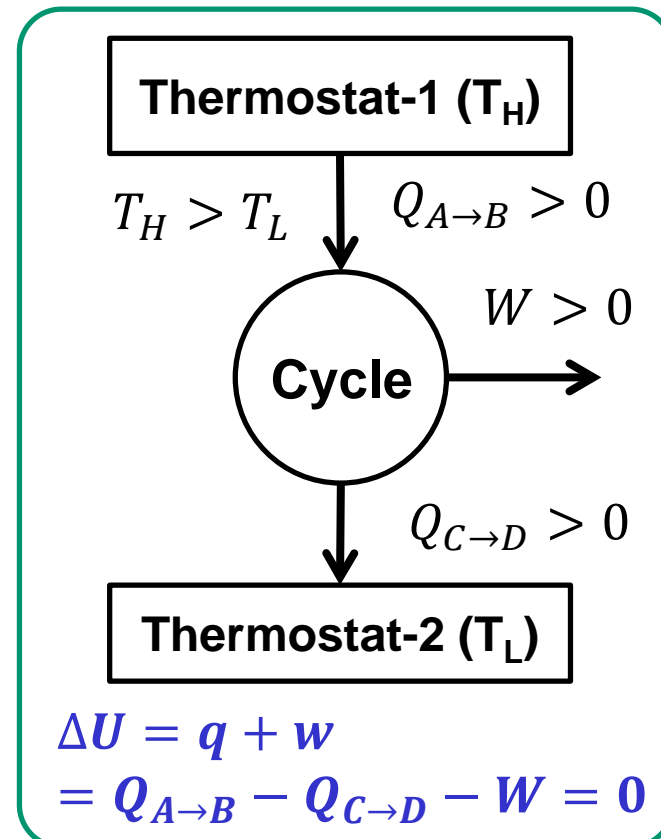
## - a cycle combined with 2 thermostats: forward operation -

- ✓ A single operation of this cycle (“A → B → C → D → A”) is conceptually re-drawn as in the right figure, which indicates that the cycle “outputs work  $W$  by absorbing heat  $Q_{A \rightarrow B}$  from the higher-temperature thermostat and discarding heat  $Q_{C \rightarrow D}$  to the lower-temperature thermostat.”
- ✓ This kind of devices include engines and turbines.



The yellow area corresponds to “the work that the system does to the surroundings by a single operation of the cycle”

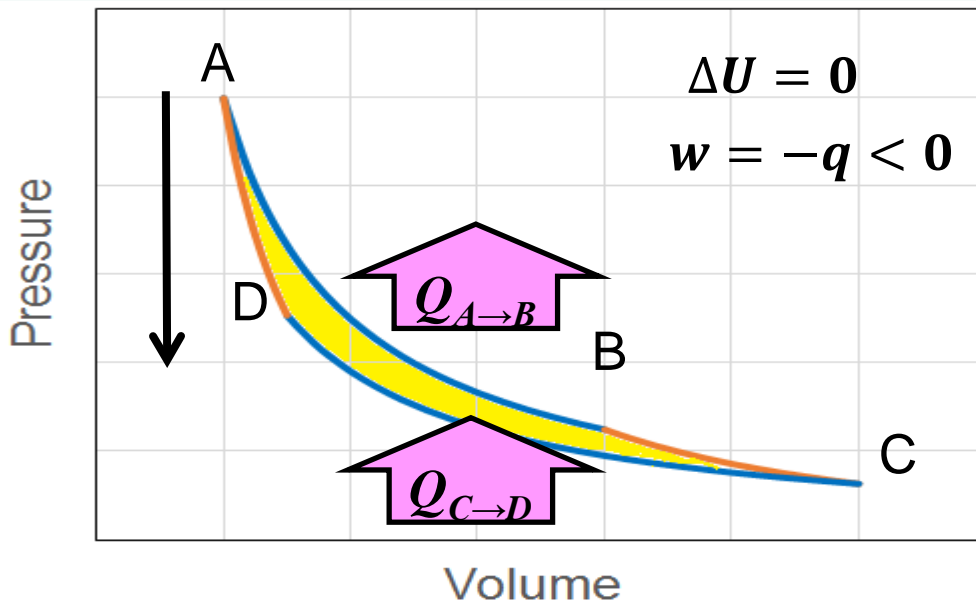
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# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

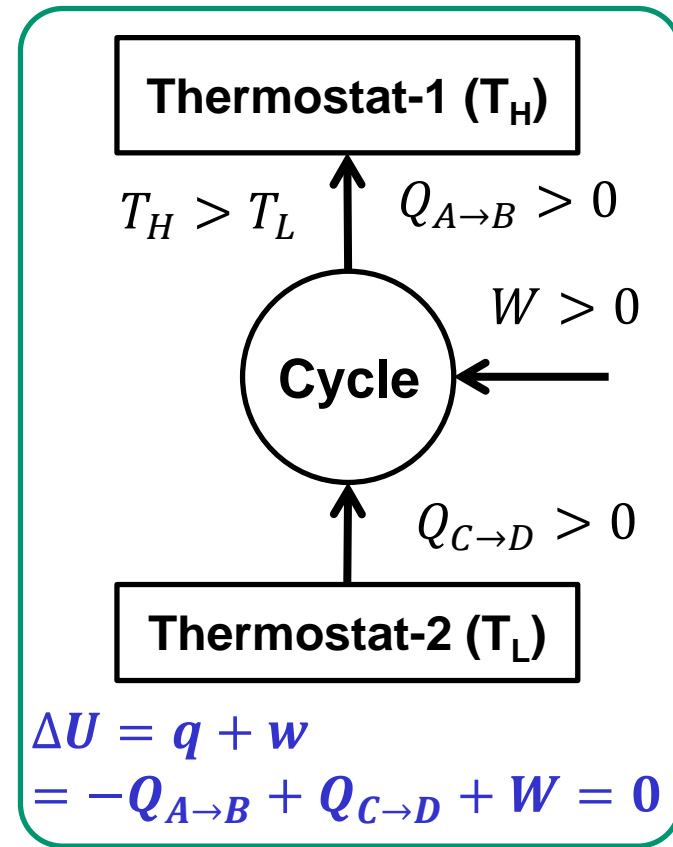
## - a cycle combined with 2 thermostats: backward operation -

- ✓ If all processes are **reversible**, we can reversely operate the cycle as “**A → D → C → B → A**”.
- ✓ This reverse operation makes a device that “absorbs heat  $Q_{C \rightarrow D}$  from the lower-temperature thermostat and discards heat  $Q_{A \rightarrow B}$  to the higher-temperature thermostat by receiving work  $W$  from the surroundings”.
- ✓ A cooler uses this kind of cycle, for example.



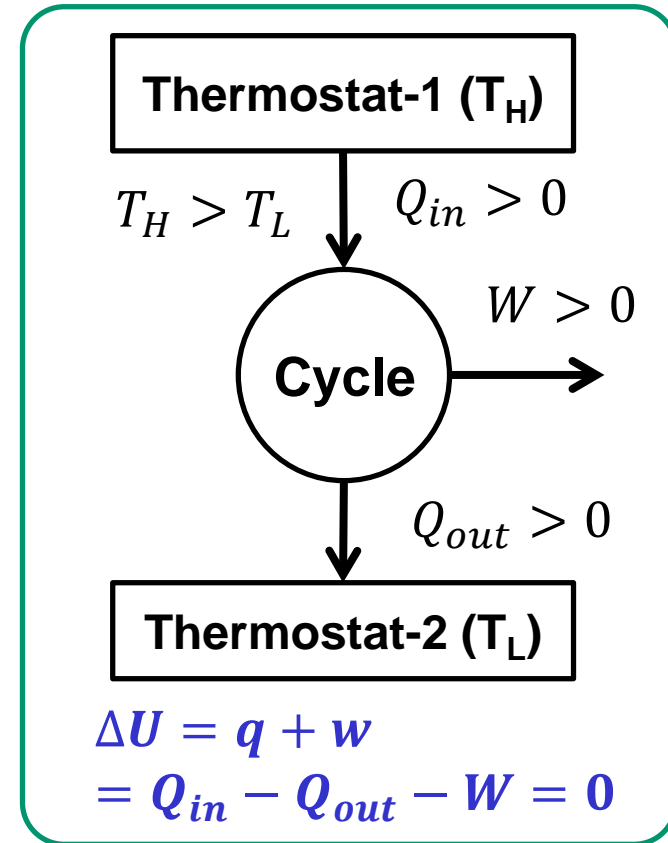
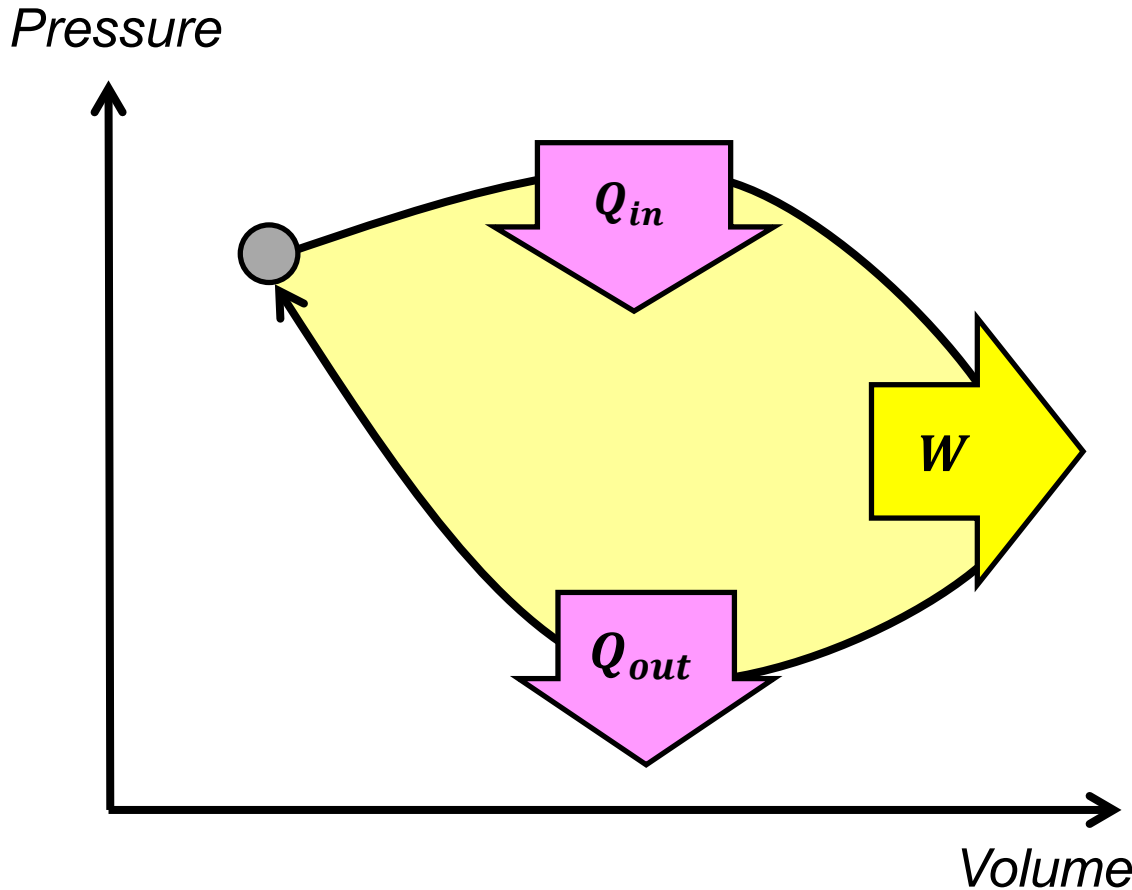
The yellow area corresponds to “the work that the surroundings did to the system by a single reverse operation of the cycle”

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# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

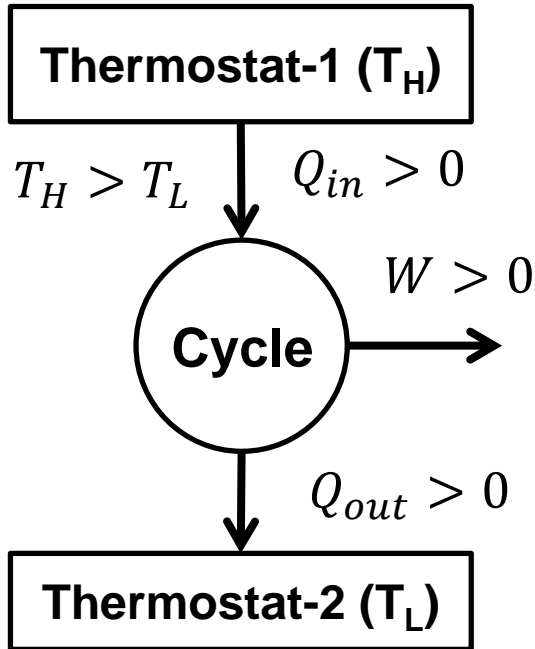
- a cycle combined with 2 thermostats, more generalized-



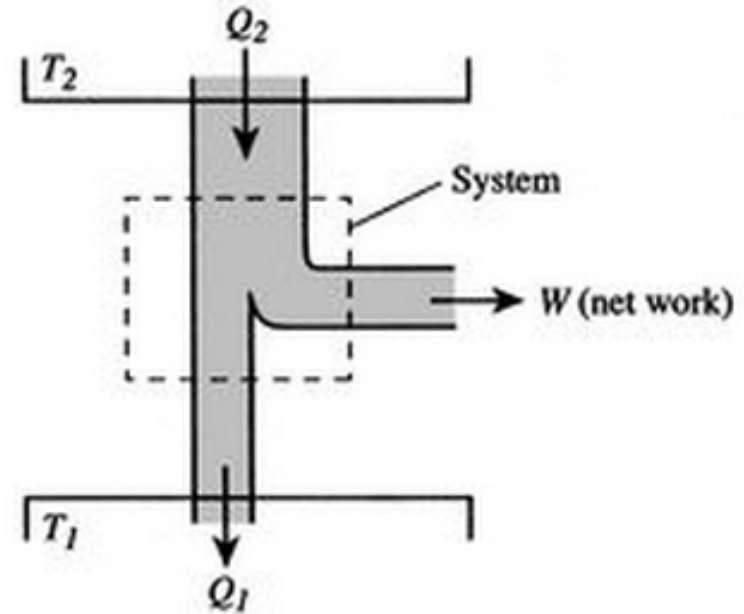
- ✓ The area surrounded by the cycle (P-V diagram) corresponds to the amount of work which the system makes to the surrounding by a single operation of the cycle.
- ✓ If the operation is reverse, the surroundings makes the work to the system.

# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

- a cycle combined with 2 thermostats, another drawing -



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



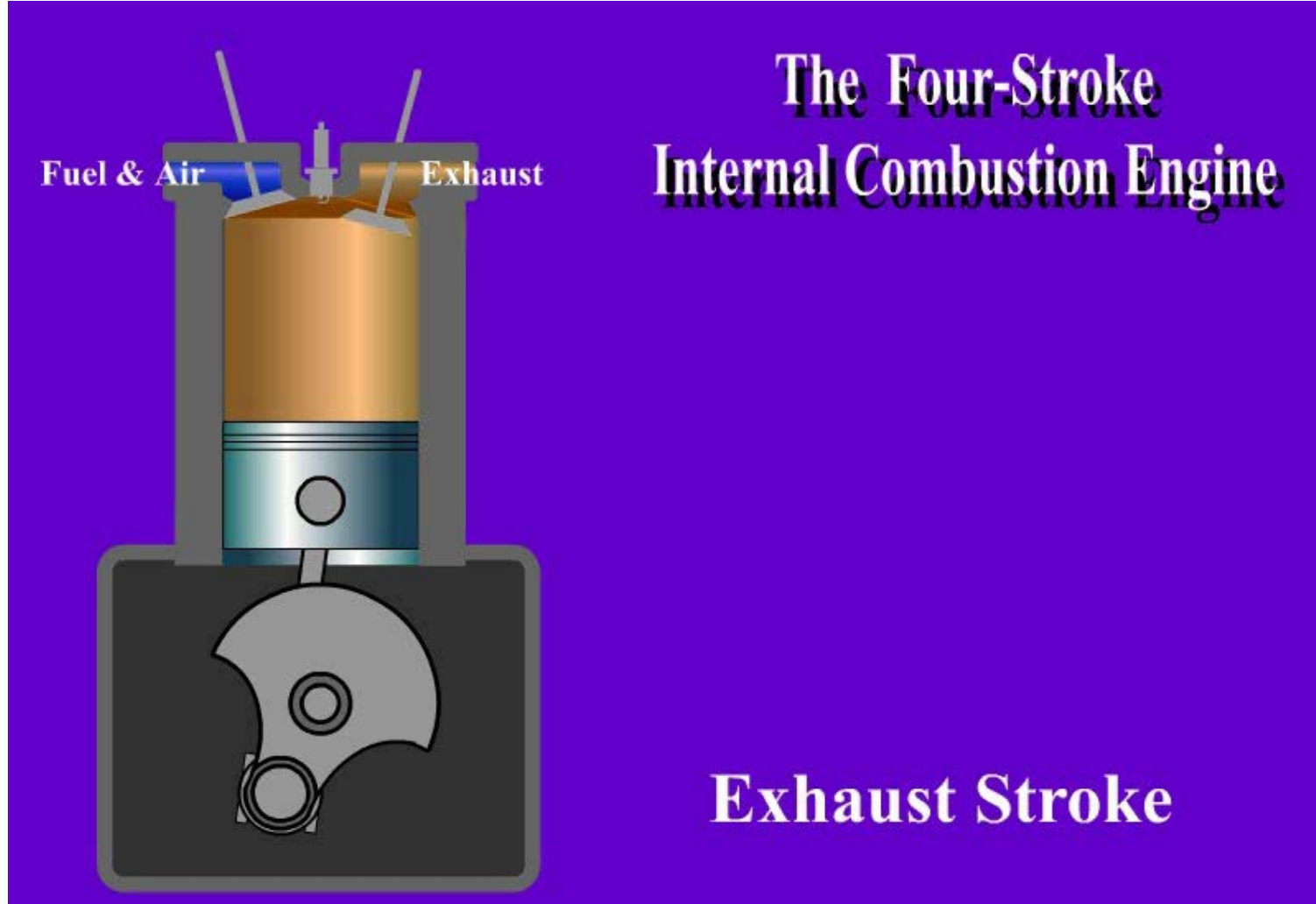
**Figure 3.5:** Work and heat transfers in a Carnot cycle between two heat reservoirs

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



## 1.3.1. The 2<sup>nd</sup> law of thermodynamics

- application of cycle: an internal combustion engine (2/2) -



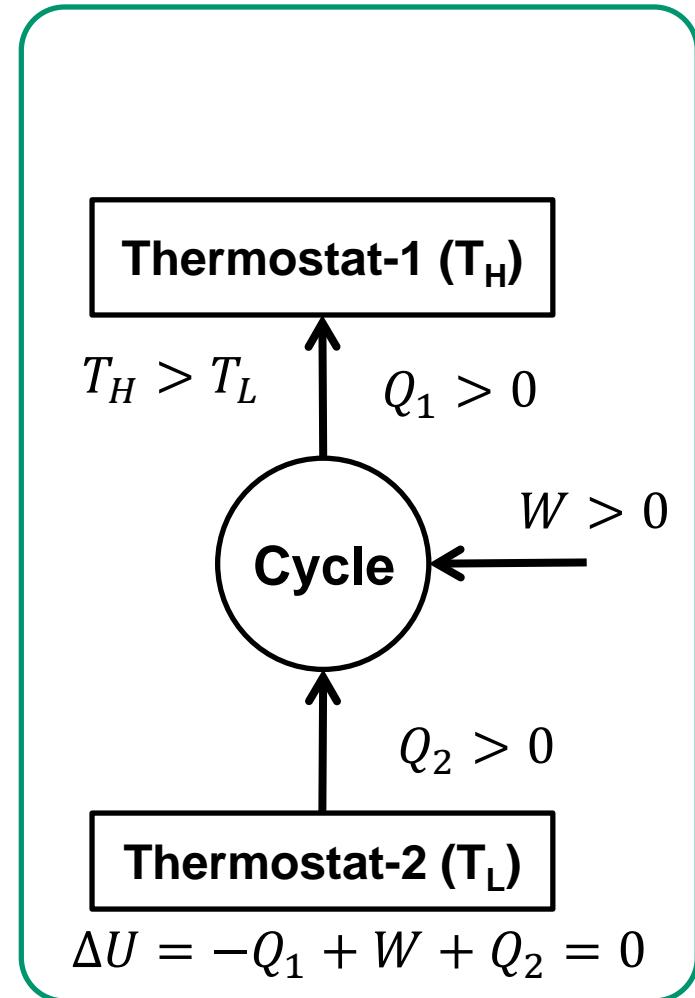
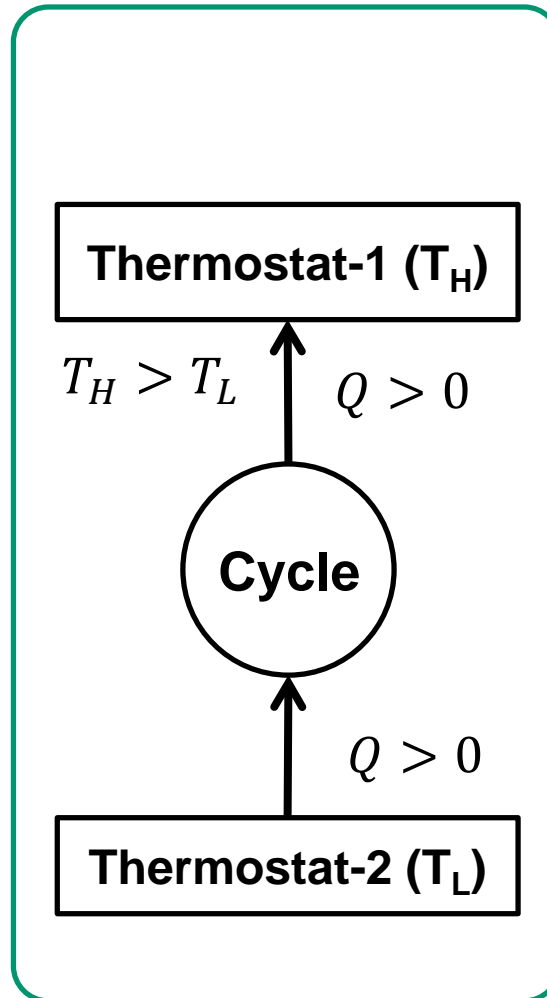
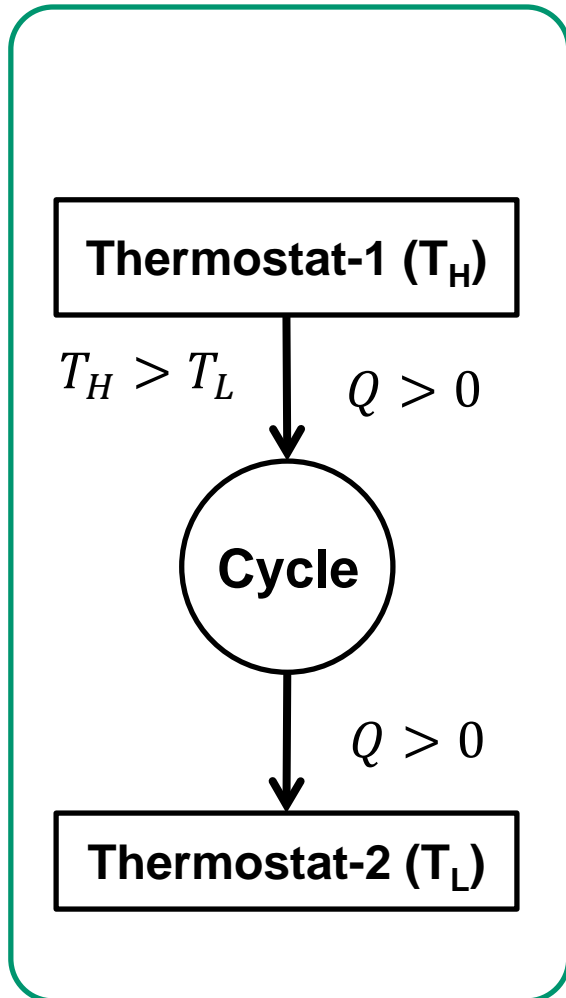
<http://www.phy.ntnu.edu.tw/ntnujava/index.php?topic=23>

\*This is a kind of **Otto cycle**.

# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

## - 2<sup>nd</sup> law description by Clausius -

*“There is no thermodynamic cycle that can absorb energy ( $>0$ ) from lower-temperature thermostat and release energy ( $>0$ ) to higher-temperature thermostat, without making any change other than these energy transfers.”*

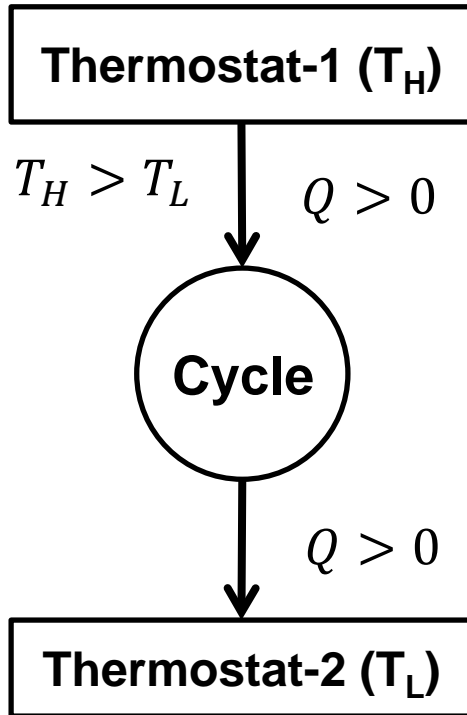


# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

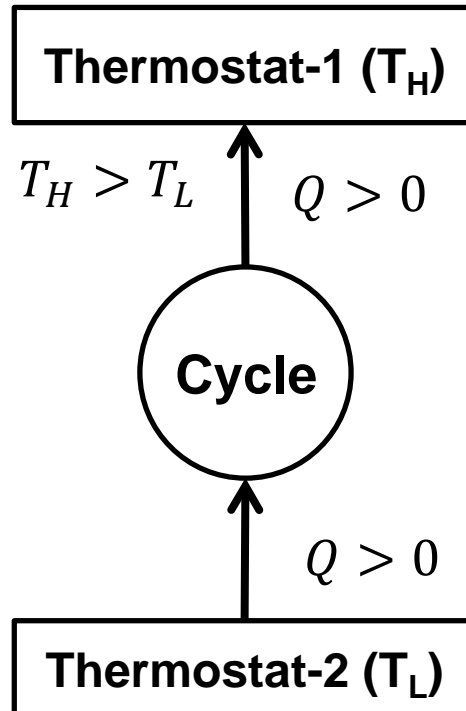
## - 2<sup>nd</sup> law description by Clausius -

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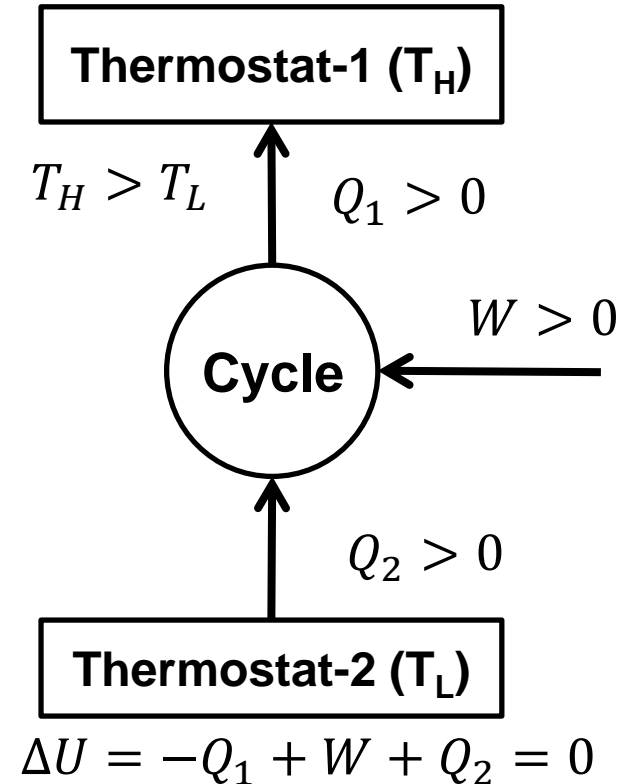
**Feasible**



**Unfeasible**



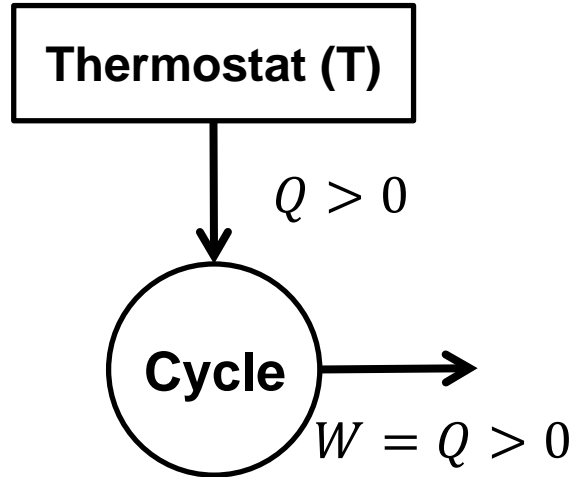
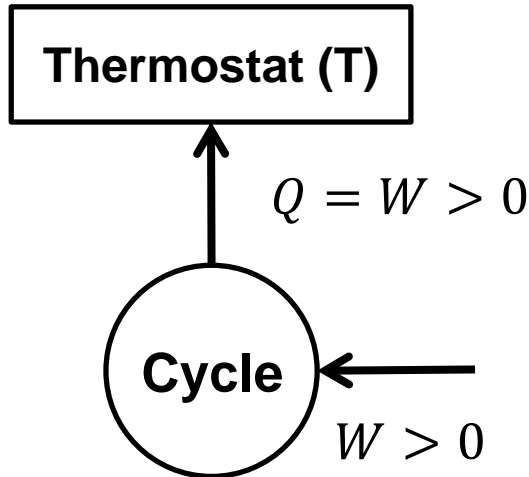
**Feasible**  
(e.g. cooler, fridge, etc)



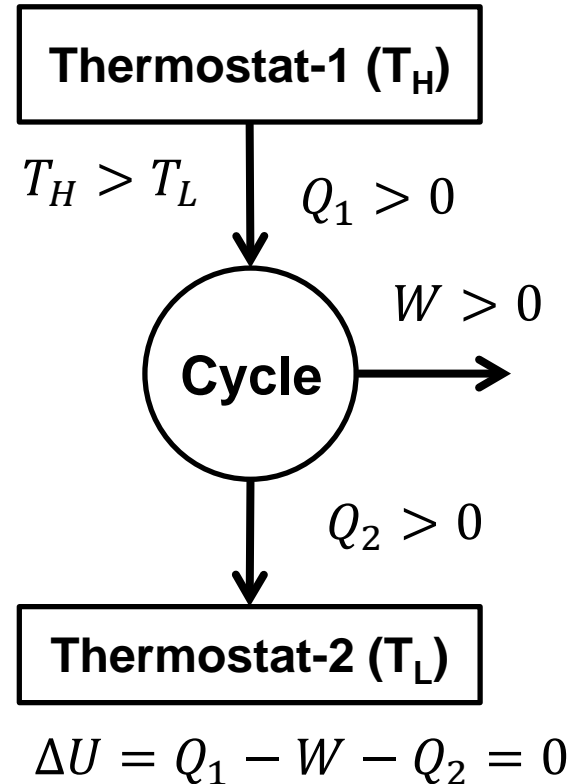
# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

## - 2<sup>nd</sup> law description by Thomson -

“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.”



*\*This is so-called  
“perpetual motion of  
the 2<sup>nd</sup> kind”.*

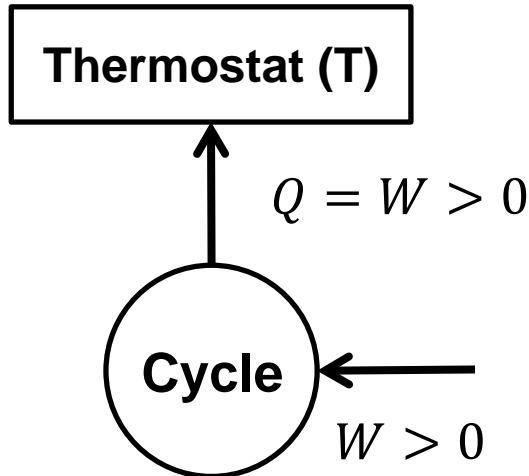


# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

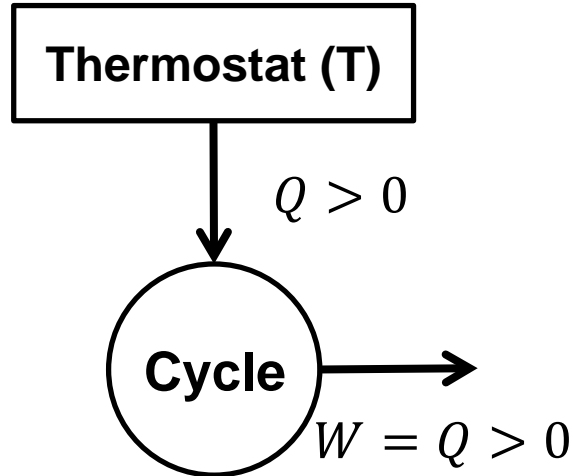
## - 2<sup>nd</sup> law description by Thomson -

“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.”

**Feasible**  
(full conversion  
of work to heat)

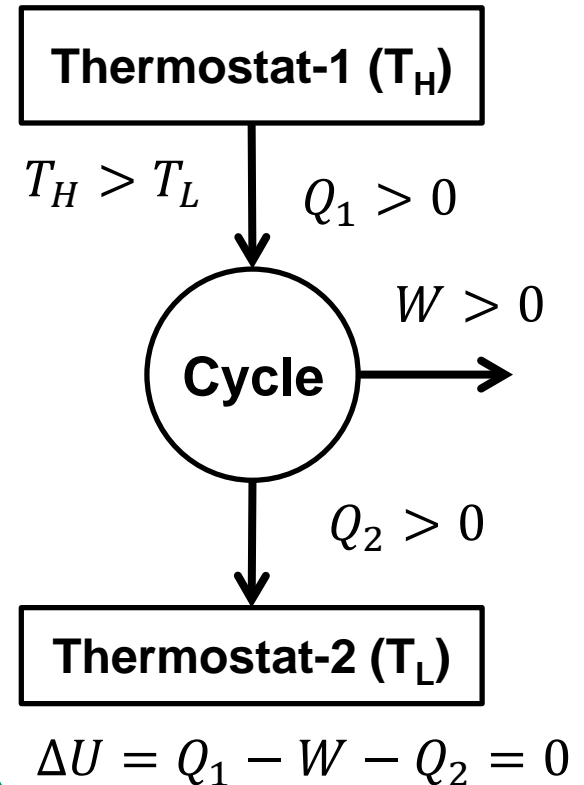


**Unfeasible**  
(full conversion  
of heat to work)



*\*This is so-called  
“perpetual motion of  
the 2<sup>nd</sup> kind”.*

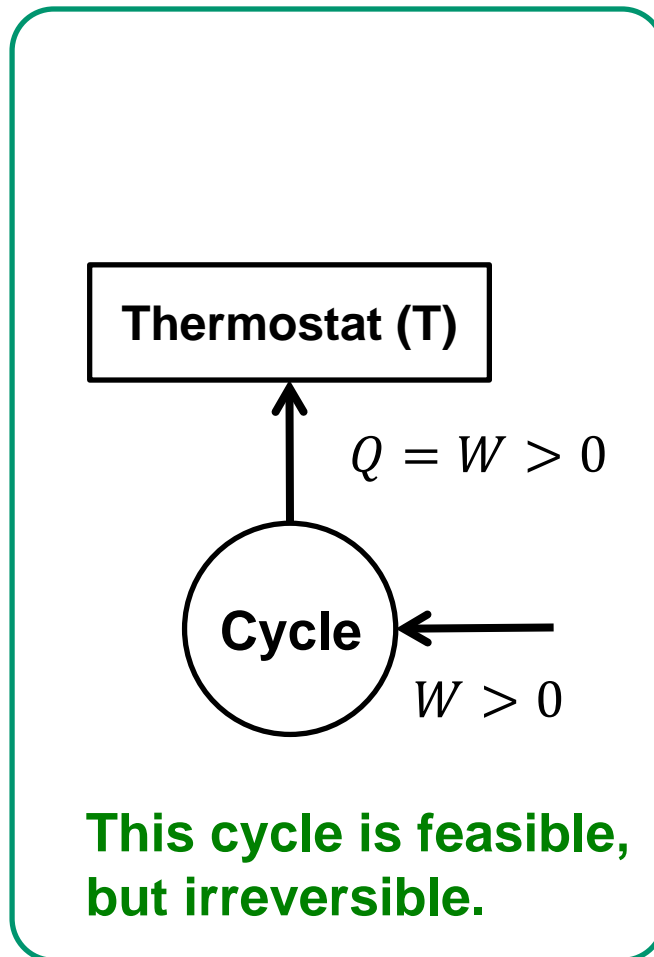
**Feasible**  
(e.g. normal engine)



## 1.3.1. The 2<sup>nd</sup> law of thermodynamics

### - 2<sup>nd</sup> law description by Thomson -

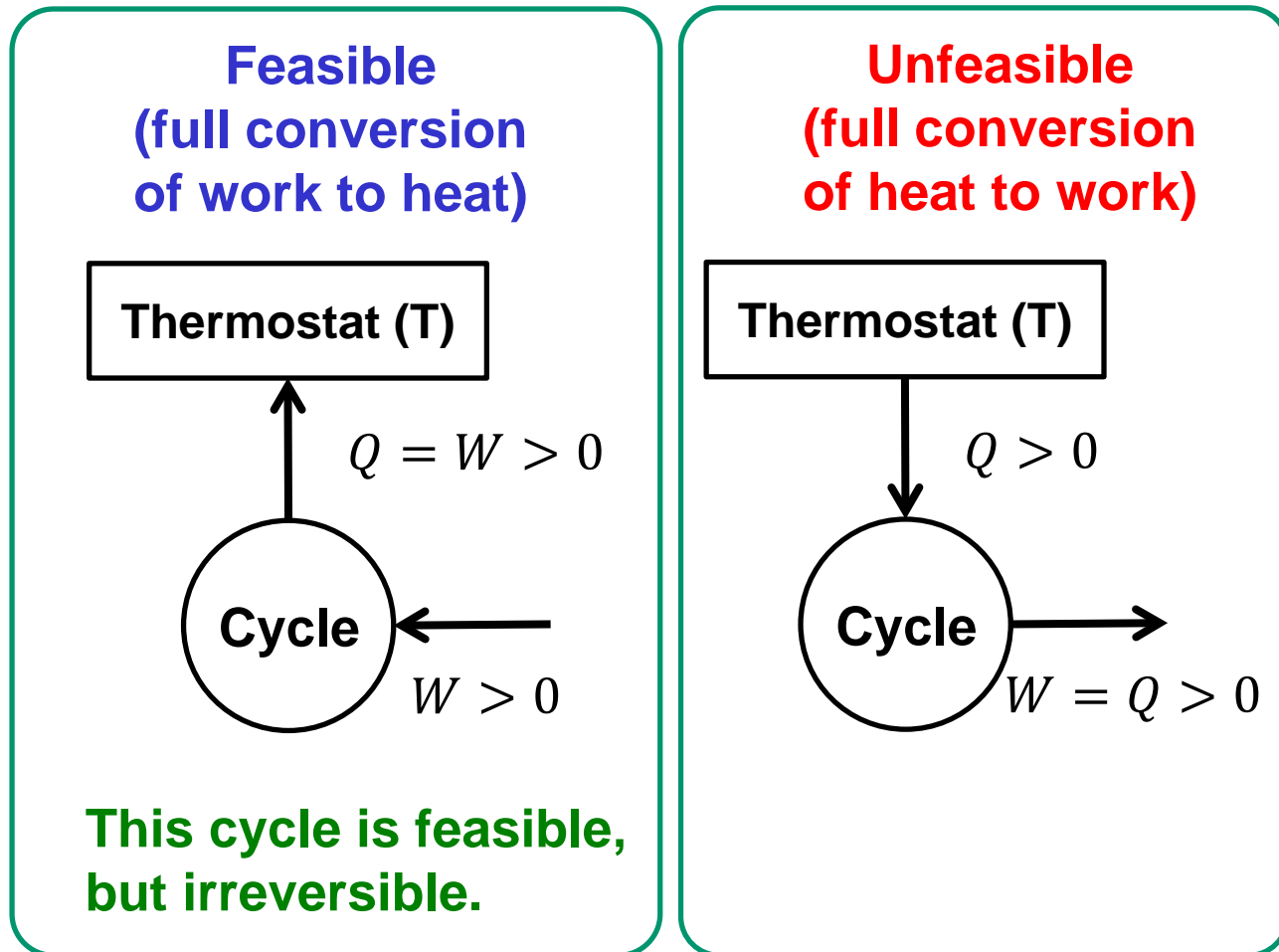
Thomson's statement also indicate that "a cycle that convert all work to heat (as left figure) is irreversible". Why?



# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

## - 2<sup>nd</sup> law description by Thomson -

Thomson's statement also indicate that "a cycle that convert all work to heat (as left figure) is irreversible", because to make it reversible, we need to make a backward operation of it, which is forbidden (right figure).



# Review of the last class

## -quasi-static/reversible/irreversible process>

< Definition of quasi-static process (in this course, we use definition (1)!) >

- 1) Very (infinitesimally) slow process so that we consider the system is always at some equilibrium state.
- 2) Very (infinitesimally) slow process and the process takes place with adhering the system to some equilibrium state and keeping concerned thermodynamic quantities of the system and the surroundings equal.
  - >> for this definition, “quasi-static” is equivalent with “reversible”
  - >> In this course, this is the definition of reversible process.

- ✓ “A **reversible process** is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings.” (\*wikipedia)
- ✓ If some change remains, the process is an **irreversible process**.



# 1.3.1. The 2<sup>nd</sup> law of thermodynamics

## - 2<sup>nd</sup> law description by Thomson (cont'd)-

- ✓ Even if the left engine is impossible, if  $Q_2$  in the right engine can be extremely minimized, we may approximately consider  $W \sim Q_1$ , which means all absorbed heat is almost converted to a work.
- ✓ However, it is impossible to “extremely minimize  $Q_2$ ”. There is a principle to restrict it. (to be given latter)

