

Thermodynamics 1st Law

by Tony Shing

Overview:

- Terminologies: State functions & Processes
- Review the 4 most common thermal processes $\left\{ \begin{array}{l} \text{Formula true for everything} \\ \text{Formula for ideal gas only} \end{array} \right.$
- Calculation for thermal cycle, efficiency and COP

1 Thermodynamics 1st Law

The thermodynamics 1st law is essentially energy conservation.

$$\delta Q = dU + \delta W \quad (\text{Physics convention})$$

- δQ = Heat input to the system.
- dU = Change in internal energy of the system.
- δW = Work done by the system.

Note: The convention in Chemistry books are different from Physics books.

$$dU = \delta Q + \delta W \quad (\text{Chemistry convention})$$

This is due to chemists refer δW as the work done to system, so work done by system is $-\delta W$.

1.1 Terminologies in Thermodynamics

To deep dive into thermodynamics, here are some terminologies you must understand.

1. State

We describe a system in a "specific state" if the system can be "well-distinguished" by a set of parameters.

$$\underline{\underline{\text{Different parameters} \Leftrightarrow \text{Different states}}}$$

For example,

- Ideal gas system

Every possible state of a box of gas can be described solely by 3 parameters (P, V, T).
But only 2 of them are independent, because we have ideal gas law $PV = nRT$.

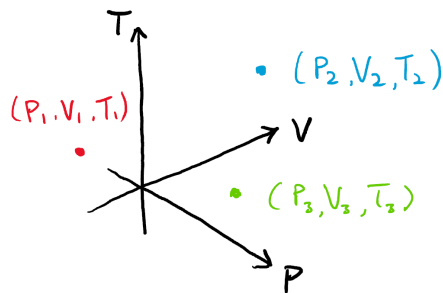
– Mechanical system

Mechanical system must satisfy Newton's 2nd law - a 2nd order ODE - which the particle's motion is completely determined after knowing its initial position (x, y, z) and velocity (v_x, v_y, v_z) , 6 parameters in total.

To describe the state of a mechanical system with N bodies, it takes $6N$ parameters.

2. State Space

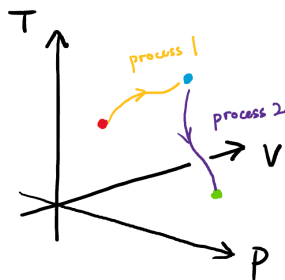
The state space is an abstract representation of the set of all possible states using state parameters.



Because ideal gas system only takes 3 parameters, we can draw it out as a 3D space, with each coordinate representing a possible state of the gas.

3. Process

It is the transition between states. If the state space can plotted out, processes are the paths connecting different states.



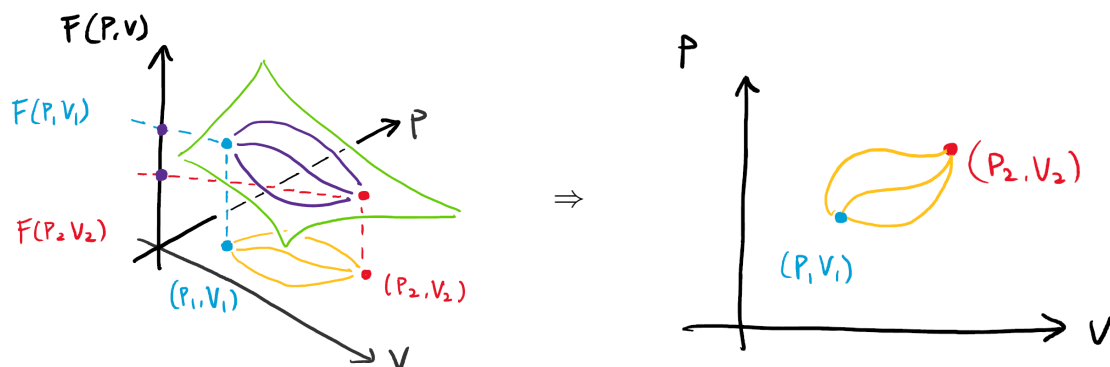
For ideal gas, because only 2 of (P, V, T) are independent, we can project the processes' path onto a 2D plane, creating the P-V diagram (or P-T/V-T diagram).

4. State Function

State functions are functions that only take state parameters as inputs.

A state function's values are well-defined for every state.

For example, for a scalar state function, we can draw it as a smooth height map:



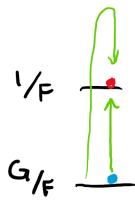
You can think of a state function like some potential function.

$$\text{Total change of } F(P, V, T) = \int_{(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)}^{\text{Any process}} dF = F(P_2, V_2, T_2) - F(P_1, V_1, T_1)$$

1.2 State Functions v.s. Non-State Functions

Here are some examples of state function in thermodynamics:

- The state parameters themselves - you can always write something like $F(P, V, T) = P$.
- Internal energy - such as potential energy and kinetic energy.



Here the state parameter is the height.
Change in PE only depends on initial and final height,
independent of the path we take.

- Entropy (Only in some situation)

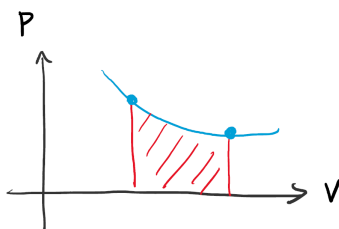
And here are some examples that are NOT state function in thermodynamics:

- Work Done
By definition,

$$\Delta(\text{W.D.}) = \underline{P} \cdot \underline{\Delta V}$$

P is a state parameter
No problem
ΔV = Change of a state parameter
NOT well-defined on a given state

Because you cannot define work done with only one state, it cannot be a state function. In fact, we always visualize W.D. as the area under curve (= process!) in the P-V diagram, indicating that it is a property of a process.



$$\sum_{\text{segments } i} P_i V_i \sim \int_{\text{process}} P dV = \text{Area under curve}$$

- Heat
According to the 1st law,

$$\delta Q = \underline{dU} + \delta W$$

State function
Process dependent

So heat must also depend on the process.

Side note:

Note the notation difference between dU v.s. $\delta W, \delta Q$:

- Change in state function \Rightarrow Use d
- Change in path dependent function \Rightarrow Use δ

This is significant when doing (line) integral:

- $d \Rightarrow$ Independent of path. Simply subtract the initial value from final value.

$$\int dU = U_f - U_i$$

- $\delta \Rightarrow$ Path dependent. Must do the integral explicitly.
 - Without knowing the given path, we must write $\int \delta W, \int \delta Q$
 - After the path is known, we can write $\int_C dW, \int_C dQ$

2 The 4 Most Common Processes

Notations:

In the following section, I will stick to the colour scheme:

- Red boxed - True for any material.
- Blue boxed - Only true for ideal gas. Derivation requires ideal gas' properties.

Normally, thermodynamics texts only concern these 4 processes:

Isovolumetric (Isochoric)	$V = \text{const.}$
Isobaric	$P = \text{const.}$
Isothermal	$T = \text{const.}$
Adiabatic	$\delta Q = 0$

It is essential to find the $dU, \delta W$ and δQ for each of the 4 process. But using similar logic, we can also promote the derivations to find $dU, \delta W$ and δQ for arbitrary kind of processes.

2.1 Internal Energy

As mentioned, internal energy is a state function - **change in internal energy is independent of process**. So if the function form of U is not known, we can only write

$$\Delta U = U(P_2, V_2, T_2) - U(P_1, V_1, T_1)$$

In case of ideal gas, the function form of U is derived using kinetic theory:

$$U(P, V, T) = \frac{i}{2} PV = \frac{i}{2} nRT$$

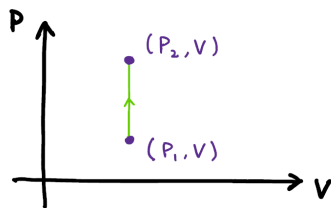
$i = \text{degree of freedom}$
↓
By ideal gas law

Therefore,

$$\Delta U = \frac{i}{2}(P_2V_2 - P_1V_1) = \frac{i}{2}nR(T_2 - T_1)$$

U of ideal gas can be written as a function of only T !

2.2 Isovolumetric Process (const. V)



Always vertical line in PV diagram.

1. Work Done

By definition of the process,

$$\int \delta W = \int_{\text{iso. } V} dW = \int_{\text{iso. } V} P dV = 0$$

V cannot change

2. Heat

By 1st law,

$$\delta Q = dU + \cancel{\delta W}^0 = dU$$

So we can write

$$\int \delta Q = \int_{\text{iso. } V} dQ = \int dU = U_2 - U_1$$

We can also define C_V , the **heat capacity under constant volume**:

$$\int_{\text{iso. } V} dQ = \int C_V dT \quad \Leftrightarrow \quad C_V(T) = \left(\frac{dQ}{dT} \right)_{\text{iso. } V} = \left(\frac{dU}{dT} \right)$$

When the internal energy of ideal gas law is given,

$$U_2 - U_1 = \frac{i}{2}(P_2V_2 - P_1V_1) = \frac{i}{2}nR(T_2 - T_1) \\ = \frac{i}{2}V(P_2 - P_1)$$

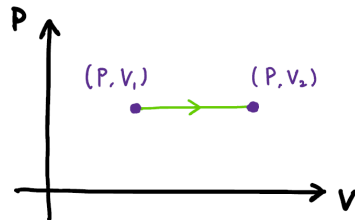
so we have

$$\int_{\text{iso. } V} dQ \equiv U_2 - U_1 = \frac{i}{2}V(P_2 - P_1) = \frac{i}{2}nR(T_2 - T_1)$$

and

$$C_{V(T)} \equiv \left(\frac{dU}{dT} \right) = \frac{i}{2}nR = (\text{Constant})$$

2.3 Isobaric Process (const. P)



Always horizontal line in PV diagram.

1. Work Done

By definition of work done,

$$\int \delta W = \int_{\text{iso. } P} dW = \int P dV = \underset{\substack{\uparrow \\ P=\text{constant}}}{P} \int dV = P(V_2 - V_1)$$

Substituting ideal gas law, we can also write

$$\int_{\text{iso. } P} dW = nR(T_2 - T_1)$$

2. Heat

By 1st law,

$$\delta Q = dU + \delta W$$

$$\int_{\text{iso. } P} dQ = (U_2 - U_1) + P(V_2 - V_1)$$

We can also define C_P , the **heat capacity under constant pressure**:

$$\int_{\text{iso. } P} dQ = \int C_P dT \quad \Leftrightarrow \quad C_P(T) = \left(\frac{dQ}{dT} \right)_{\text{iso. } P} = \left(\frac{dU}{dT} \right) + P \left(\frac{dV}{dT} \right)$$

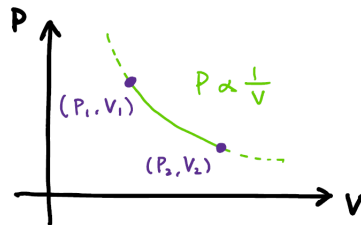
Then for ideal gas,

$$\begin{aligned}\int_{\text{iso. } P} dQ &\equiv (U_2 - U_1) + P(V_2 - V_1) \\ &= \frac{i}{2}P(V_2 - V_1) + P(V_2 - V_1) \\ \int_{\text{iso. } P} dQ &= \frac{i+2}{2}P(V_2 - V_1) = \frac{i+2}{2}nR(T_2 - T_1)\end{aligned}$$

and

$$C_P(T) \equiv \left(\frac{dU}{dT}\right) + P\left(\frac{dP}{dT}\right) = \frac{i+2}{2}nR = (\text{Constant})$$

2.4 Isothermal Process (const. T)



They look like this **only for ideal gas!**

1. Work Done

We are unable to reduce the form $\int_{\text{iso. } T} \delta W = \int P dV$ unless we know what is the relation between P and V of the material.

For ideal gas, this relation is already known: $P = \frac{nRT}{V}$. Then the integral becomes

$$\int_{\text{iso. } T} \delta W = \int \frac{nRT}{V} dV = nRT \int \frac{dV}{V} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

\uparrow
 $T = \text{constant}$

2. Heat

Even with 1st law, again, we cannot reduce the form $\int_{\text{iso. } T} \delta Q = (U_2 - U_1) + \int P dV$ unless we know what is the relation between P and V of the material.

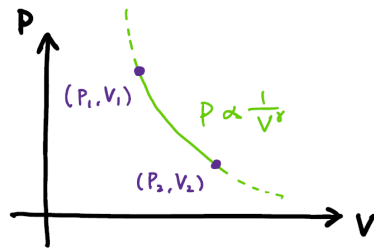
For ideal gas, because its internal energy can be written in a form that only has T ,

$$\int dU = \frac{i}{2}nR(T_2 - T_1) = 0$$

Then

$$\int_{\text{iso. } T} \delta Q = 0 + \int_{\text{iso. } T} \delta W = nRT \ln \left(\frac{V_2}{V_1} \right)$$

2.5 Adiabatic Process ($\delta Q = 0$)



1. Heat

By definition of the process, there must be no energy exchange in the form of heat.

$$\delta Q = 0$$

2. Work Done

By 1st law,

$$\delta Q = dU + \delta W$$

$$\delta W = -dU$$

3. Adiabatic Relation

Because all P, V, T of initial and final states in an adiabatic process are different, we need to derive the equation of the line connecting the two states. The set of equations of the lines is called **adiabatic relation**.

The relation depends on the form of $U(P, V, T)$. We always start the derivation from

$$-dU = \delta W = P dV$$

For ideal gas, $U = \frac{i}{2}PV$, so $dU = \frac{i}{2}(P dV + V dP)$. Substitute to above,

$$-\frac{i}{2}(P dV + V dP) = P dV$$

$$-\frac{i}{2}V dP = \frac{i+2}{2}P dV$$

$$\frac{1}{P} dP = -\frac{i+2}{i} \frac{1}{V} dV$$

$$\int \frac{1}{P} dP = -\frac{i+2}{i} \int \frac{1}{V} dV$$

$$\ln P = -\frac{i+2}{i} \ln V + (\text{Constant})$$

$$\ln \left(PV^{\frac{i+2}{i}} \right) = (\text{Constant})$$

$$PV^{\frac{i+2}{i}} = (\text{Constant})$$

In general, adiabatic relation of common materials would have the form $PV^\gamma = (\text{constant})$, where the index γ is called **adiabatic constant**.

For ideal gas, $\gamma = \frac{i+2}{i} = \frac{C_P}{C_V}$. However this value does NOT apply to every material.

To some material, its adiabatic "constant" may not even be a constant.

2.6 Summary

Summarizing all useful formula under a table:

	U is a state function	W derive from definition: $\delta W = P dV$	Q derive by 1 st law: $\delta Q = dU + \delta W$
Iso. V	$U(P_2, V, T_2) - U(P_1, V, T_1)$ $= \frac{i}{2} V (P_2 - P_1)$ $= \frac{i}{2} n R (T_2 - T_1)$	0	$= \int dU + 0$ $= \int C_V dT$ $= \underbrace{\frac{i}{2} n R (T_2 - T_1)}_{C_V}$
Iso. P	$U(P, V_2, T_2) - U(P, V_2, T_1)$ $= \frac{i}{2} P (V_2 - V_1)$ $= \frac{i}{2} n R (T_2 - T_1)$	$P (V_2 - V_1)$ $= n R (T_2 - T_1)$	$= \int dU + \int \delta W$ $= \int C_P dT$ $= \underbrace{\frac{i+2}{2} n R (T_2 - T_1)}_{C_P}$
Iso. T	$U(P_1, V_2, T) - U(P_1, V_2, T)$ $= 0$	$\int P dV$ $= n R T \ln \left(\frac{V_2}{V_1} \right)$	$= \int dU + \int \delta W$ $= n R T \ln \left(\frac{V_2}{V_1} \right)$
Adiabatic	$U(P_2, V_2, T_2) - U(P_1, V_1, T_1)$ $= \frac{i}{2} (P_2 V_2 - P_1 V_1)$ $= \frac{i}{2} n R (T_2 - T_1)$	$= -dU$ $= -\frac{i}{2} (P_2 V_2 - P_1 V_1)$ $= -\frac{i}{2} n R (T_2 - T_1)$	0

3 Solving Thermal Cycle

In this section, we will deal with one of the basic but extremely common problem in thermodynamics - given an arbitrary thermal cycle, derive the formula of efficiency / coefficient of performance (COP).

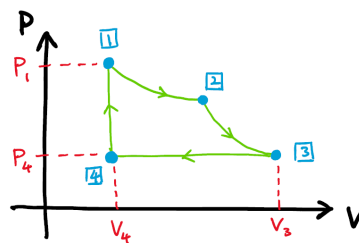


In general, you can follow these steps:

1. Write down the relation of P, V, T between initial/final states of each process.
2. Write down the $dU, \delta W, \delta Q$ for each process.
3. Identify if the δQ of each process is an input or output.
4. Calculate efficiency / COP according to the signs of δQ .

Example 3.1. A thermal cycle of ideal gas with all 4 kinds processes.

1. Iso. T (expansion)
2. Adiabatic (expansion)
3. Iso. P (contraction)
4. Iso. V



1. Write down the relations of P, V, T between initial/final states of each process.

	Process	Relation
1 → 2	Iso. T	$T_1 = T_2$
2 → 3	Adiabatic	$P_2 V_2^\gamma = P_3 V_3^\gamma$
3 → 4	Iso. P	$P_3 = P_4$
4 → 1	Iso. V	$V_4 = V_1$

You can use ideal gas law
to get more relations.
But do it later.

2. Write down the $dU, \delta W, \delta Q$ for each process.

Process		$dU, \delta Q, \delta W$
$\boxed{1} \rightarrow \boxed{2}$	Iso. T	$\begin{cases} \Delta U = 0 \\ \int \delta W = nRT_1 \ln \left(\frac{V_2}{V_1} \right) \\ \int \delta Q = nRT_1 \ln \left(\frac{V_2}{V_1} \right) > 0 \end{cases}$
$\boxed{2} \rightarrow \boxed{3}$	Adiabatic	$\begin{cases} \Delta U = \frac{i}{2}(P_3V_3 - P_2V_2) = \frac{i}{2}nR(T_3 - T_2) \\ \int \delta W = -\frac{i}{2}(P_3V_3 - P_2V_2) = -\frac{i}{2}nR(T_3 - T_2) \\ \int \delta Q = 0 \end{cases}$
$\boxed{3} \rightarrow \boxed{4}$	Iso. P	$\begin{cases} \Delta U = \frac{i}{2}P_3(V_4 - V_3) = \frac{i}{2}nR(T_4 - T_3) \\ \int \delta W = P_3(V_4 - V_3) = nR(T_4 - T_3) \\ \int \delta Q = \frac{i+2}{2}P_3(V_4 - V_3) = \frac{i+2}{2}nR(T_4 - T_3) < 0 \end{cases}$
$\boxed{4} \rightarrow \boxed{1}$	Iso. V	$\begin{cases} \Delta U = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}(T_1 - T_4) \\ \int \delta W = 0 \\ \int \delta Q = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}(T_1 - T_4) > 0 \end{cases}$

3. Identify if the δQ of each process is an input or output. Recall in the 1st law's convention,

$$\delta Q = dU + \delta W$$

Heat input to the system ↑ Increase in U of the system ← W.D. by the system

If $\delta Q > 0$, it is a heat input, otherwise it is a heat output. We can check for each process,

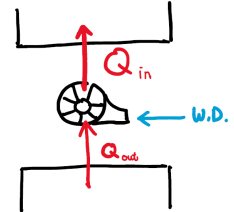
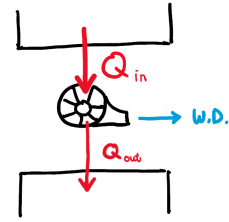
- With heat input: $\boxed{1} \rightarrow \boxed{2}, \boxed{4} \rightarrow \boxed{1}$
- With heat output: $\boxed{3} \rightarrow \boxed{4}$

4. Calculate efficiency / COP according to the signs of δQ . By definition,

$$\text{Efficiency} = \eta \stackrel{\text{def}}{=} \frac{\text{W.D.}}{\text{Heat input}} = 1 - \left| \frac{Q_{\text{out}}}{Q_{\text{in}}} \right|$$

and

$$\text{Coefficient of Performance (COP)} \stackrel{\text{def}}{=} \frac{\text{Heat remove}}{\text{W.D.}} = \left| \frac{Q_{\text{out}}}{Q_{\text{in}} - Q_{\text{out}}} \right| = \frac{1 - \eta}{\eta}$$



For example in the cycle with 4 processes, we can compute the efficiency as

$$\eta = 1 - \left| \frac{\frac{i+2}{2}nR(T_4 - T_3)}{\frac{i}{2}nR(T_1 - T_4) + nRT_1 \ln\left(\frac{V_2}{V_1}\right)} \right|$$

Example 3.2. Thermal processes of photon gas

This time we are dealing with a non-ideal gas material. Photon gas' internal energy and pressure relation are given by

$$\begin{cases} U = 3PV = aVT^4 \\ P = \frac{1}{3}aT^4 \end{cases} \quad \text{with } a = \text{some constant}$$

$\xrightarrow{\text{Substitute to get}}$

In comparison, we cannot use any properties of ideal gas, i.e. $\begin{cases} U = \frac{i}{2}PV = \frac{i}{2}nRT \\ P = \frac{nRT}{V} \end{cases}$

We have to re-derive dU , δW and δQ before we can proceed to solve any thermal cycle.

1. Internal Energy

Remember that U is always a state function. Its change is independent of process.

$$\Delta U = U(P_2, V_2, T_2) - U(P_1, V_1, T_1)$$

$$\Delta U = 3(P_2V_2 - P_1V_1) = a(V_2T_2^4 - V_1T_1^4)$$

2. Iso V.

By definition of the process, $\int \delta W$ is always 0. Then for heat,

$$\int_{\text{iso. V}} dQ = \Delta U = 3V(P_2 - P_1) = aV(T_2^4 - T_1^4)$$

The heat capacity under constant volume is then

$$\int C_V dT = \frac{dU}{dT} = 4aVT^3 = (\text{NOT a constant})$$

3. Iso P. and Iso T.

Note that in the pressure relation, $P = \frac{1}{3}aT^4$, if P is fixed, then T is also fixed!

$$\Delta U = 3P(V_2 - V_1) = aT^4(V_2 - V_1)$$

$$\int_{\text{iso. } P} \delta W = P(V_2 - V_1) = \frac{1}{3}aT^4(V_2 - V_1)$$

$$\int_{\text{iso. } P} \delta Q = \Delta U + \int \delta W = 4P(V_2 - V_1) = \frac{4}{3}aT^4(V_2 - V_1)$$

However, it is impossible to define the heat capacity under constant pressure, because you cannot change temperature under constant pressure.

$$\int_{\text{iso. } P} \delta Q = \int C_P dT = \int (\text{undefined}) \cdot (0)$$

4. Adiabatic

By definition of the process, $\int \delta Q$ is always 0. Then we can derive the adiabatic relation:

$$\begin{aligned} P dV &= -dU \\ &= -d(3PV) = -3(P dV + V dP) \\ 4P dV &= -3V dP \\ \frac{4}{3} \int \frac{dV}{V} &= - \int \frac{dP}{P} \\ \ln\left(V^{\frac{4}{3}}\right) &= -\ln P + (\text{constant}) \end{aligned}$$

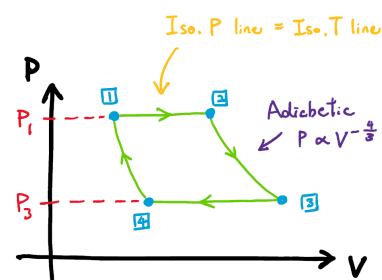
$$PV^{\frac{4}{3}} = (\text{constant})$$

The adiabatic constant for photon gas is $\gamma = \frac{4}{3} \neq \frac{C_V}{C_P}$, obviously.

Example 3.3. Carnot cycle by photon gas

By definition, a Carnot cycle is made of 4 processes:

1. Iso. T (expansion)
2. Adiabatic (expansion)
3. Iso. T (contraction)
4. Adiabatic (contraction)



1. Write down the relations of P, V, T between initial/final states of each process.

	Process	Relation
$\boxed{1} \rightarrow \boxed{2}$	Iso. P & T	$P_1 = P_2, T_1 = T_2$
$\boxed{2} \rightarrow \boxed{3}$	Adiabatic	$P_2 V_2^\gamma = P_3 V_3^\gamma$
$\boxed{3} \rightarrow \boxed{4}$	Iso. P & T	$P_3 = P_4, T_3 = T_4$
$\boxed{4} \rightarrow \boxed{1}$	Adiabatic	$P_4 V_4^\gamma = P_1 V_1^\gamma$

2. Write down the $dU, \delta W, \delta Q$ for each process.

	Process	$dU, \delta Q, \delta W$
$\boxed{1} \rightarrow \boxed{2}$	Iso. P & T	$\begin{cases} \Delta U = aT_1^4(V_2 - V_1) \\ \int \delta W = \frac{1}{3}aT_1^4(V_2 - V_1) \\ \int \delta Q = \frac{4}{3}aT_1^4(V_2 - V_1) > 0 \end{cases}$
$\boxed{2} \rightarrow \boxed{3}$	Adiabatic	$\begin{cases} \Delta U = a(V_3 T_3^4 - V_2 T_2^4) \\ \int \delta W = -a(V_3 T_3^4 - V_2 T_2^4) \\ \int \delta Q = 0 \end{cases}$
$\boxed{3} \rightarrow \boxed{4}$	Iso. P	$\begin{cases} \Delta U = aT_3^4(V_4 - V_3) \\ \int \delta W = \frac{1}{3}aT_3^4(V_4 - V_3) \\ \int \delta Q = \frac{4}{3}aT_3^4(V_4 - V_3) < 0 \end{cases}$
$\boxed{4} \rightarrow \boxed{1}$	Iso. V	$\begin{cases} \Delta U = a(V_1 T_1^4 - V_4 T_4^4) \\ \int \delta W = -a(V_1 T_1^4 - V_4 T_4^4) \\ \int \delta Q = 0 \end{cases}$

3. Identify if the δQ of each process is an input or output. We can check for each process,

- With heat input: $\boxed{1} \rightarrow \boxed{2}$
- With heat output: $\boxed{3} \rightarrow \boxed{4}$

4. Calculate efficiency according to the signs of δQ .

$$\eta = 1 - \left| \frac{\text{Heat output}}{\text{Heat input}} \right| = 1 - \left| \frac{\cancel{\frac{4}{3}}aT_3^4(V_4 - V_3)}{\cancel{\frac{4}{3}}aT_1^4(V_2 - V_1)} \right|$$

To simplify, we can use the adiabatic relation:

$$\begin{aligned} PV^{\frac{4}{3}} &= (\text{const.}) \\ \Rightarrow \frac{1}{3}aT^4V^{\frac{4}{3}} &= (\text{const.}) \\ \Rightarrow T^3V &= (\text{const.}) \end{aligned}$$

And the relations between state parameters that we derived in step 1:

$$\begin{cases} T_1 = T_2, & T_3 = T_4 \\ T_2^3V_2 = T_3^3V_3, & T_4^3V_4 = T_1^3V_1 \end{cases}$$

The efficiency is now

$$\begin{aligned} \eta &= 1 - \left| \frac{T_3^4(V_4 - V_3)}{T_1^4(V_2 - V_1)} \right| \\ &= 1 - \frac{T_3}{T_1} \left| \frac{T_3^3V_4 - T_3^3V_3}{T_1^3V_2 - T_1^3V_1} \right| \\ &= 1 - \frac{T_3}{T_1} \left| \frac{\cancel{T_4}^3V_4 - T_3^3V_3}{\cancel{T_2}^3V_2 - T_1^3V_1} \right| \\ &= 1 - \frac{T_3}{T_1} \end{aligned}$$

which is exactly the same as Carnot cycle with ideal gas!

— The End —