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Thermodynamics 1^{st} Law

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Overview:

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

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1 Thermodynamics 1^{st} Law

The thermodynamics 1^{st} law is essentially energy conservation.

$$\delta Q = \mathrm{d}U + \delta W \qquad \text{(Physics convention)}$$

- δQ = Heat input to the system.
- $\mathrm{d}U$ = Change in internal energy of the system.
- δW = Work done by the system.

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

$$\mathrm{d}U = \delta Q + \delta W \qquad \text{(Chemistry convention)}$$

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

Before we deep dive into the world of thermodynamics, here are some terminologies you should understand.

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

   Different parameters $\Leftrightarrow$ 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 2$^{\text{nd}}$ law - a 2$^{\text{nd}}$ 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

(add figure here: state space)

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

(add figure here: process)

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:

(add figure here: height map -¿ PV diagram)

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

$$\begin{array}{c}\text{Total change}\\ \text{of } F(P,V,T)\end{array} = \int_{\substack{\text{Any process}\\ (P_1,V_1,T_1)\to(P_2,V_2,T_2)}} \mathrm{d}F = F(P_2, V_2, T_2) - F(P_1, V_1, T_1)$$

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.

(add figure here: PE)

– Entropy (Only in some situation)

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

- Work Done
  By definition,

$$\Delta(\text{W.D.}) = \underbrace{P}_{\substack{P \text{ is a state parameter} \\ \text{No problem}}} \cdot \underbrace{\Delta V}_{\substack{\Delta V = \text{Change of a state parameter} \\ \text{NOT well-defined on a given state}}}$$

  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.

$$\sum_{\text{segments } i} P_i V_i \sim \int_{\text{process}} P \, \mathrm{d}V = \text{Area under curve}$$

(add figure here: PV work done)

- Heat
  According to the 1st law,

$$\delta Q = \underbrace{\mathrm{d}U}_{\text{State function}} + \underbrace{\delta W}_{\text{Process dependent}}$$

  So heat must also be dependent of a process.

Side note:

Note the notation difference between $\mathrm{d}U$ v.s. δW , δQ:

- 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 substract the initial value from final value.

$$\int \mathrm{d}U = U_f - U_i$$

- δ $\Rightarrow$ 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 $\int_C \mathrm{d}W, \int_C \mathrm{d}Q$

2 The 4 Most Common Processes

Notations:

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

- Red boxed - True for any processes.
- 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	$T = \text{const.}$
Adiabetic	$\delta Q = 0$

It is essential to find the $\mathrm{d}U$, δW and δQ for each of the 4 process. We can even promote the derivation to find them for arbitiuary 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

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

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

$$U(P,V,T) = \frac{\overset{\overset{i\,=\,\text{degree of freedom}}{\downarrow}}{\boxed{i}}}{2}\underbrace{PV = \frac{i}{2}NkT}_{\text{By ideal gas law}}$$

Therefore,

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

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

2.2 Isovolumetric Process (const. V)

(add figure here: iso V)

1. Work Done
   By definition of the process,

$$\boxed{\int \delta W = \int_{\text{iso. } V} \mathrm{d}W = \int_{\text{iso. } V} P\underbrace{\mathrm{d}V}_{V \text{ cannot change}} = 0}$$

2. Heat

   By 1st law,

$$\delta Q = \mathrm{d}U + \cancelto{0}{\delta W} = \mathrm{d}U$$

   So we can write

$$\boxed{\int \delta Q = \int_{\text{iso. } V} \mathrm{d}Q = \int \mathrm{d}U = U_2 - U_1}$$

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

$$\boxed{\int_{\text{iso. } V} \mathrm{d}Q = \int C_V \,\mathrm{d}T \qquad \Leftrightarrow \qquad C_V(T) = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{\text{iso. } V} = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)}$$

   When the internal energy of ideal gas law is given,

$$\begin{aligned} U_2 - U_1 &= \frac{i}{2}(P_2V_2 - P_1V_1) = \frac{i}{2}Nk(T_2 - T_1) \\ &= \frac{i}{2}V(P_2 - P_1) \end{aligned}$$

   so we have

$$\boxed{\int_{\text{iso. } V} \mathrm{d}Q \equiv U_2 - U_1 = \frac{i}{2}V(P_2 - P_1) = \frac{i}{2}Nk(T_2 - T_1)}$$

   and

$$\boxed{C_V(T) \equiv \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right) = \frac{i}{2}Nk = (\text{A constant})}$$

2.3 Isobaric Process (const. P)

(add figure here: iso P)

1. Work Done

   By definition of work done,

$$\boxed{\int \delta W = \int_{\text{iso. } P} \mathrm{d}W = \int P \,\mathrm{d}V = \underset{P=\text{constant}}{\underline{P}} \int \mathrm{d}V = P(V_2 - V_1)}$$

   Substituting ideal gas law, we can also write

$$\boxed{\int_{\text{iso. } P} \mathrm{d}W = Nk(T_2 - T_1)}$$

2. Heat

   By 1st law,

$$\delta Q = \mathrm{d}U + \delta W$$

$$\boxed{\int_{\text{iso. } P} \mathrm{d}Q = (U_2 - U_1) + P(V_2 - V_1)}$$

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

$$\boxed{\int_{\text{iso. } P} \mathrm{d}Q = \int C_P \, \mathrm{d}T \qquad \Leftrightarrow \qquad C_P(T) = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{\text{iso. } P} = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right) + P\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)}$$

   Then for ideal gas,

$$\begin{aligned} \int_{\text{iso. } P} \mathrm{d}Q &\equiv (U_2 - U_1) + P(V_2 - V_1) \\ &= \frac{i}{2} P(V_2 - V_1) + P(V_2 - V_1) \end{aligned}$$

$$\boxed{\int_{\text{iso. } P} \mathrm{d}Q = \frac{i+2}{2} P(V_2 - V_1) = \frac{i+2}{2} Nk(T_2 - T_1)}$$

   and

$$\boxed{C_P(T) \equiv \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right) + P\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right) = \frac{i+2}{2} Nk = (\text{A constant})}$$

2.4 Isothermal Process (const. T)

(add figure here: iso T)

1. Work Done

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

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

$$\boxed{\int_{\text{iso. } T} \delta W = \int \frac{NkT}{V} \mathrm{d}V = Nk\underbrace{T}_{T\,=\,\text{constant}} \int \frac{\mathrm{d}V}{V} = NkT \ln\left(\frac{V_2}{V_1}\right)}$$

2. Heat

   Even with 1st law, again, we cannot reduce the form $\boxed{\int_{\text{iso. } T} \delta Q = (U_2 - U_1) + \int P \, \mathrm{d}V}$ 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,

$$\int \mathrm{d}U = \frac{i}{2}Nk(T_2 - T_1) = 0$$

Then

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

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

(add figure here: adiabetic)

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

$$\boxed{\delta Q = 0}$$

2. Work Done
   By 1st law,

$$\delta Q = \mathrm{d}U + \delta W$$
$$\boxed{\delta W = -\,\mathrm{d}U}$$

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

   The relation depends on the function form of $U(P, V)$. Although we can always start the derivation from

$$\boxed{-\,\mathrm{d}U = \delta W = P\,\mathrm{d}V}$$

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

$$\begin{aligned}
-\frac{i}{2}(P\,\mathrm{d}V + V\,\mathrm{d}P) &= P\,\mathrm{d}V \\
-\frac{i}{2}V\,\mathrm{d}P &= \frac{i+2}{2}P\,\mathrm{d}V \\
\frac{1}{P}\,\mathrm{d}P &= -\frac{i+2}{i}\frac{1}{V}\,\mathrm{d}V \\
\int \frac{1}{P}\,\mathrm{d}P &= -\frac{i+2}{i}\int \frac{1}{V}\,\mathrm{d}V \\
\ln P &= -\frac{i+2}{i}\ln V + (\text{Constant}) \\
\ln\left(PV^{\frac{i+2}{i}}\right) &= (\text{Constant}) \\
\boxed{PV^{\frac{i+2}{i}} = (\text{Constant})}
\end{aligned}$$

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

For ideal gas, $\boxed{\gamma = \frac{i+2}{i} = \frac{C_P}{C_V}}$. However this value does NOT apply to every material. To some material, its adiabetic "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: $\delta W = P\,\mathrm{d}V$	Q derive by 1st law: $\delta Q = \mathrm{d}U + \delta W$
Iso. V	$\boxed{U(P_2, V, T_2) - U(P_1, V, T_1)}$ $= \boxed{\frac{i}{2} V(P_2 - P_1)}$ $= \boxed{\frac{i}{2} Nk(T_2 - T_1)}$	0	$= \boxed{\int \mathrm{d}U + 0}$ $= \boxed{\int C_V\,\mathrm{d}T}$ $= \boxed{\underbrace{\frac{i}{2}}_{C_V} Nk(T_2 - T_1)}$
Iso. P	$\boxed{U(P, V_2, T_2) - U(P, V_2, T_1)}$ $= \boxed{\frac{i}{2} P(V_2 - V_1)}$ $= \boxed{\frac{i}{2} Nk(T_2 - T_1)}$	$\boxed{P(V_2 - V_1)}$ $= \boxed{Nk(T_2 - T_1)}$	$= \boxed{\int \mathrm{d}U + \int \delta W}$ $= \boxed{\int C_P\,\mathrm{d}T}$ $= \boxed{\underbrace{\frac{i+2}{2}}_{C_P} Nk(T_2 - T_1)}$
Iso. T	$\boxed{U(P_1, V_2, T) - U(P_1, V_2, T)}$ $= \boxed{0}$	$\boxed{\int P\,\mathrm{d}V}$ $= \boxed{NkT \ln\left(\frac{V_2}{V_1}\right)}$	$= \boxed{\int \mathrm{d}U + \int \delta W}$ $= \boxed{NkT \ln\left(\frac{V_2}{V_1}\right)}$
Adiabetic	$\boxed{U(P_2, V_2, T_2) - U(P_1, V_1, T_1)}$ $= \boxed{\frac{i}{2}(P_2 V_2 - P_1 V_2)}$ $= \boxed{\frac{i}{2} Nk(T_2 - T_1)}$	$= \boxed{-\mathrm{d}U}$ $= \boxed{-\frac{i}{2}(P_2 V_2 - P_1 V_2)}$ $= \boxed{-\frac{i}{2} Nk(T_2 - T_1)}$	0

3 Solving Thermal Cycle

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

(add figure here: random cycle)

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 $\mathrm{d}U$, δW , δQ 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. Adiabetic (expansion)
3. Iso. P (contraction)
4. Iso. V

(add figure here: cycle of 4 process)

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

	Process	Relation
$\boxed{1} \to \boxed{2}$	iso. T	$T_1 = T_2$
$\boxed{2} \to \boxed{3}$	Adiabetic	$P_2 V_2^\gamma = P_3 V_3^\gamma$
$\boxed{3} \to \boxed{4}$	iso. P	$P_3 = T_4$
$\boxed{4} \to \boxed{1}$	iso. V	$V_4 = V_1$

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

2. Write down the $\mathrm{d}U$, δW , δQ for each process.

	Process	$\mathrm{d}U\,,\delta Q\,,\delta W$
$\boxed{1} \to \boxed{2}$	iso. T	$\begin{cases} \Delta U = 0 \\ \int \delta W = NkT_1 \ln\left(\frac{V_2}{V_1}\right) \\ \int \delta Q = NkT_1 \ln\left(\frac{V_2}{V_1}\right) \quad > 0 \end{cases}$
$\boxed{2} \to \boxed{3}$	Adiabetic	$\begin{cases} \Delta U = \frac{i}{2}(P_3V_3 - P_2V_2) = \frac{i}{2}Nk(T_3 - T_2) \\ \int \delta W = -\frac{i}{2}(P_3V_3 - P_2V_2) = -\frac{i}{2}Nk(T_3 - T_2) \\ \int \delta Q = 0 \end{cases}$
$\boxed{3} \to \boxed{4}$	iso. P	$\begin{cases} \Delta U = \frac{i}{2}P_3(V_4 - V_3) = \frac{i}{2}Nk(T_4 - T_3) \\ \int \delta W = P_3(V_4 - V_3) = Nk(T_4 - T_3) \\ \int \delta Q = \frac{i+2}{2}P_3(V_4 - V_3) = \frac{i+2}{2}Nk(T_4 - T_3) \quad < 0 \end{cases}$
$\boxed{4} \to \boxed{1}$	iso. V	$\begin{cases} \Delta U = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}(T_1 - T_4) \\ \int \delta W = 0 \\ \int \delta Q = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}(T_1 - T_4) \quad > 0 \end{cases}$

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

$$\underbrace{\delta Q}_{\substack{\text{Heat input} \\ \text{to the system}}} = \underbrace{\mathrm{d}U}_{\substack{\text{Increase in } U \\ \text{of the system}}} + \underbrace{\delta W}_{\substack{\text{W.D. by} \\ \text{the system}}}$$

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

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

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

$$\boxed{\text{Efficiency} = \eta \overset{\text{def}}{=} \frac{\text{W.D.}}{\text{Heat input}} = 1 - \left|\frac{\text{Heat output}}{\text{Heat intput}}\right|}$$

(add figure here: engine eff)

and

$$\boxed{\begin{array}{c}\text{Coefficienty of}\\ \text{Performance}\\ \text{(COP)}\end{array} \overset{\text{def}}{=} \frac{\text{Heat remove}}{\text{Work done}} = \left|\frac{\text{Heat output}}{\text{Heat intput - Heat output}}\right| = \frac{1-\eta}{\eta}}$$

(add figure here: engine cop)

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

$$\eta = 1 - \left| \frac{\frac{i+2}{2}Nk(T_4 - T_3)}{\frac{i}{2}Nk(T_1 - T_4) + NT_1 \ln\left(\frac{V_2}{V_1}\right)} \right|$$

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

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

Substitute to get

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

We have to re-derive $\mathrm{d}U$, 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.

$$\Delta U = U(P_2, V_2, T_2) - U(P_1, V_1, T_1)$$
$$\boxed{\Delta U = 3(P_2V_2 - P_1V_1) = a(V_2T_2^4 - V_1T_1^4)}$$

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

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

   The heat capacity under constant volume is then

$$\boxed{\int C_V \,\mathrm{d}T = \frac{\mathrm{d}U}{\mathrm{d}T} = 4aVT^3 = \text{(NOT a constant)}}$$

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!

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

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

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

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

$$\boxed{\int_{\text{iso. } P} \delta Q = \int C_P \, \mathrm{d}T = \int (\text{undefined}) \cdot (0)}$$

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

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

The adiabetic 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 definitoin, a Carnot cycle is made of 4 processes:

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

(add figure here: cycle of photon carnot)

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

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

2. Write down the $\mathrm{d}U$, δW , δQ for each process.

	Process	$\mathrm{d}U$, δQ , δW
$\boxed{1} \to \boxed{2}$	iso. P & T	$\begin{cases} \Delta U = a T_1^4 (V_2 - V_1) \\ \int \delta W = \frac{1}{3} a T_1^4 (V_2 - V_1) \\ \int \delta Q = \frac{4}{3} a T_1^4 (V_2 - V_1) \quad {\color{red} > 0} \end{cases}$
$\boxed{2} \to \boxed{3}$	Adiabetic	$\begin{cases} \Delta U = a (V_3 T_3^4 - V_2 T_2^4) \\ \int \delta W = -a (V_3 T_3^4 - V_2 T_2^4) \\ \int \delta Q = 0 \end{cases}$
$\boxed{3} \to \boxed{4}$	iso. P	$\begin{cases} \Delta U = a T_3^4 (V_4 - V_3) \\ \int \delta W = \frac{1}{3} a T_3^4 (V_4 - V_3) \\ \int \delta Q = \frac{4}{3} a T_3^4 (V_4 - V_3) \quad {\color{red} < 0} \end{cases}$
$\boxed{4} \to \boxed{1}$	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: $\boxed{1} \to \boxed{2}$
- With heat output: $\boxed{3} \to \boxed{4}$

4. Calculate efficiency according to the signs of δQ.

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

To simplify, we can use the adiabetic relation:

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

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

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

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

— The End —