

- State : State Function vs Process
 - Reviewing 4 most common processes
 - { Formula True for everything
 - vs
 - True for ideal gas only
 - Example calculation on engine (efficiency & COP)
-

Thermodynamics 1st Law

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

- δQ = Heat input to the system
- dU = Change in the system's internal energy
- δW = W.D. by the system (Chemistry prefers W.D. to system)

Chemistry book prefer
 $dU = \delta Q + \delta W$

Physics book prefer
 $\delta Q = dU + \delta W$

This is basically Energy Conservation

Terminologies in Thermodynamics

① State

A system in a "specific state"

= The system can be "well-distinguished" by a set of parameters

↳ Different numbers \Rightarrow Different states

E.g Ideal Gas System

Every state can be purely described by 3 parameters (P,V,T)

But only 2 of them are independent, because $PV = nRT$

E.g. Mechanical System

No. of parameters = $3+3+3+\dots$



We can describe the state of 1 particle by $(\vec{r}, \vec{v}, \vec{a}, \dots)$

But only \vec{r} & \vec{v} are independent, because mechanical system

are constrained by $\vec{F} = m\vec{a}$, a 2nd order ODE. We only need

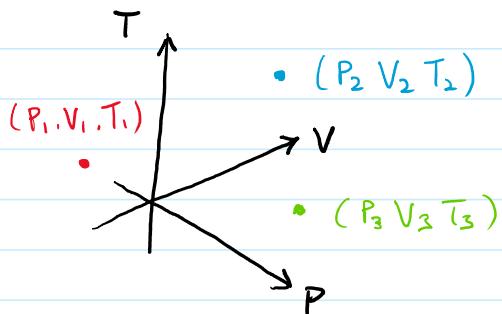
the initial position & velocity to determine subsequent motions

\Rightarrow When there are N particles, each state is described by

N sets of (\vec{r}, \vec{v}) = $6N$ parameters.

(2) State Space

\sim Graphical representation of every possible state



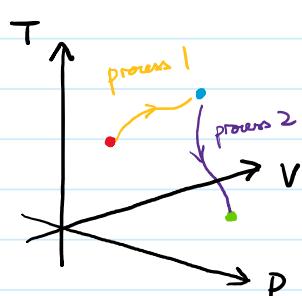
E.g. Every point in the PVT space

= A possible state of an ideal gas

(3) Process

= The transition from 1 state to another

= Paths in the state space



★ Because only 2 of (P, V, T) are independent

All ideal gas processes can be projected onto

a 2D plane \Rightarrow PV diagram

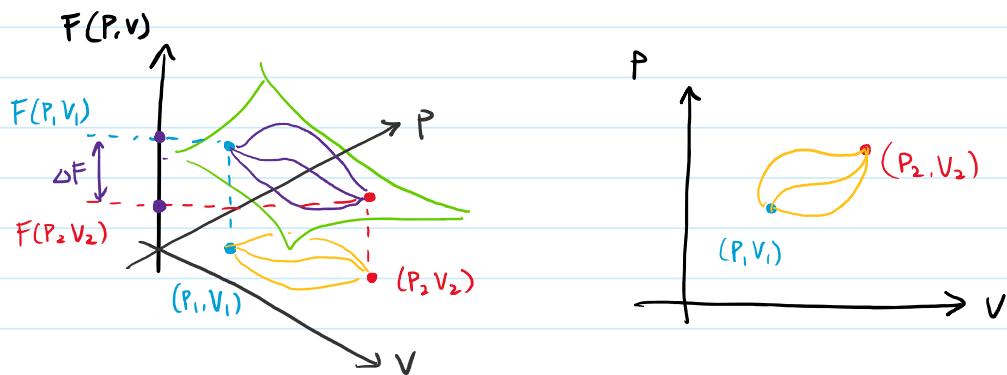
(or you can choose PT / VT plane)

④ State Function

= Any function that depends on the state parameters only

= Function's value is well-defined for every state

E.g. For a scalar state function, we can draw it as a smooth height map



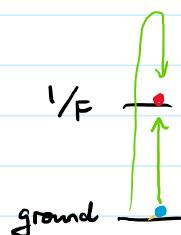
★ You can describe a state function like a conservative field

$$\text{Total change} = \int_{\text{g } F(P, V)}^{\text{any process}} dF = F(P_2, V_2) - F(P_1, V_1)$$

$(P_1, V_1) \rightarrow (P_2, V_2)$

Example of State Function

- Internal Energy, E.g. PE, KE



state parameter = height

The net change in PE is independent of the path

The thermodynamics internal energy U is similar

- All state parameters themselves are state function

E.g. You can always write sth. like $F(P, V, T) = P$

- Entropy (only in some situations)

Example of NOT a state function

① Work Done

$$\Delta W.D. = P \cdot \Delta V$$

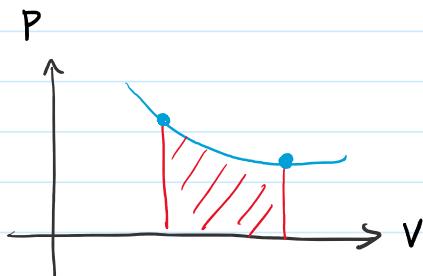
P is a state parameter
no problem

ΔV = Change of state parameter
NOT well-defined on a given state

You cannot define W.D. with one state

W.D. is a property of a process.

From its definition



W.D. is a weighted sum along a process

$$\sum_{\text{segment}} P_i \Delta V_i \sim \int_{\text{process}} p dV$$

= area under curve

② Heat

From 1st Law $\delta Q = dU + \delta W$

dU state function δW process dependent

$\therefore \delta Q$ must also be process dependent

As a comparison :

- dU along a close path always = 0
- $\delta W, \delta Q$ along a close path may not be 0

★ Notation :

- Change in state function \Rightarrow use d e.g. dU
- Change in path dependent function \Rightarrow use δ e.g. $\delta W, \delta Q$

When appearing in an integral =

d \Rightarrow Independent of path, simply substitute initial & final value

δ \Rightarrow Have to do line integral explicitly

- Without the given path, we write $\int \delta W, \int \delta Q$

- After given the path C , we can write $\int_C dW, \int_C dQ$

Reviewing the 4 main processes

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

We are interested in finding $dU, \delta W, \delta Q$ for all 4 processes.

(In general, we can promote to any arbitrary process)

Here I split the formula into 2 kinds

Red Bounding box \Rightarrow True for all materials

Blue font \Rightarrow For ideal gas only
∴ Require kinetic theory / Ideal gas law

① Internal Energy

$U = \text{State function} = \text{Path independent}$

$$\Delta U = U(P_2, V_2, T_2) - U(P_1, V_1, T_1) \quad \text{for any process}$$

For ideal gas only:

Deriving from kinetic theory of a box of free particle

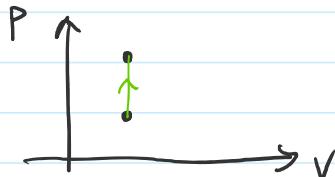
$$U(P, V) = \frac{i}{2} PV = \frac{i}{2} NkT$$

$i = \text{degree of freedom.}$

$$\therefore \Delta U = \frac{i}{2} (P_2 V_2 - P_1 V_1) = \frac{i}{2} Nk (T_2 - T_1)$$

Therefore U of ideal gas is a state function of T only

② Isovolumetric Process



W.D.

By definition

$$\delta W = P \underline{dV} = 0$$

V cannot change

2 Heat

By 1st Law, $\delta Q = dU + \delta W = dU$

So we can write $\int \delta Q = \int_{\text{iso } V \text{ path}} dQ = \int dU = U_2 - U_1$

The heat capacity under constant V can be defined as

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

i.e. Rate of heat input per temperature change

(given that volume cannot change during heat transfer)

For ideal gas only

$$\text{Because } \Delta U = \frac{i}{2} (P_2 V_2 - P_1 V_1) = \frac{i}{2} V (P_2 - P_1)$$

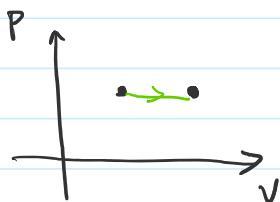
$$= \frac{i}{2} N k (T_2 - T_1)$$

$V = \text{const.}$

$$\Rightarrow \left[\int_{\text{iso. } V} dQ = \Delta U = \frac{i}{2} V (P_2 - P_1) = \frac{i}{2} N k (T_2 - T_1) \right]$$

$$\Rightarrow \left[C_v(T) = \left(\frac{dQ}{dT} \right)_{\text{iso. } V} = \frac{dU}{dT} = \frac{i}{2} N k = \text{const.} \right]$$

② Isobaric Process (const. P)



W.D.

$$\text{By } \int_{\text{iso. } P} P dV = P \int dV$$

$$= P(V_2 - V_1)$$

$\downarrow P = \text{const.}$

$= Nk(T_2 - T_1)$ for ideal gas

③ Heat

$$\text{By 1st Law: } \delta Q = dU + \delta W$$

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

The heat capacity under constant P can be defined as

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

For ideal gas only:

$$\left[\int_{\text{iso. } P} dQ \right] = \frac{i}{2} (P_2 V_2 - P_1 V_1) + P(V_2 - V_1)$$

$P_2 = P_1$

$$= \frac{i+2}{2} P(V_2 - V_1) = \frac{i+2}{2} Nk(T_2 - T_1)$$

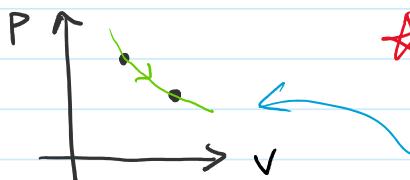
$$\left[C_p(T) \right] = \frac{d}{dT} \left(\frac{i}{2} NkT \right) + P \cdot \frac{dV}{dT}$$

$$= \frac{i}{2} Nk + P \cdot \frac{d}{dT} \left(\frac{NkT}{P} \right)$$

$$= \frac{i}{2} Nk + NK$$

$$= \frac{i+2}{2} Nk = \text{const.}$$

③ Isothermal Process (const. T)



* Iso. T curve on PV diagram depends on the material

This shape of curve is only true for ideal gas

W.D.

The form $\left[\int P dV \right]$ cannot be further simplified unless you know the relation between (i.e. knowing the material's property)

For ideal gas only:

The relation of P, V, T is well known : $P = \frac{NkT}{V}$

Under constant T , this is enough for computing the integral

$$\left[\int P dV = \int \frac{NkT}{V} dV = NkT \ln \left(\frac{V_2}{V_1} \right) \right]$$

2] Heat

Again, if relation of P, V, T is unknown

We cannot do any simplification. $\boxed{\int \delta Q = U_2 - U_1 + \int pdV}$

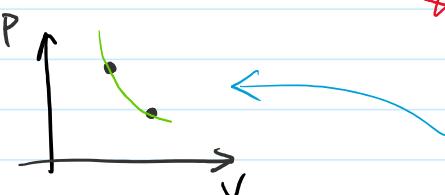
For ideal gas only:

Because ideal gas's internal energy solely depends on T

$$\Delta U = \frac{1}{2} Nk(T_2 - T_1) = 0 \text{ if } T \text{ is fixed}$$

$$\Rightarrow \boxed{\int_{\text{iso-T}} \delta Q = \int PdV = NkT \ln\left(\frac{V_2}{V_1}\right)}$$

④ Adiabatic ($\delta Q = 0$)



* Again, the shape of the curve depends on the material

This shape is for ideal gas only

1] Heat : $\boxed{\delta Q = 0}$ By definition

2] W.D. : By 1st Law $\delta Q = dU + dW$

$$\boxed{dW = -dU}$$

★★★ If we know the relation of U with P, V,

we can derive the adiabatic relation

For ideal gas only:

The adiabatic relation is derived as follows :

\therefore We know $U = \frac{1}{2}PV$ for ideal gas $\Rightarrow dU = \frac{1}{2}(pdV + VdP)$

Substitute into $-dU = \delta W$

$$-\frac{i}{2}(pdV + Vdp) = pdV$$

$$\frac{-i}{2} Vdp = \frac{i+2}{2} pdV$$

$$\frac{1}{p} dp = -\left(\frac{i+2}{2}\right) \frac{1}{V} dV$$

$$\int \frac{1}{p} dp = -\left(\frac{i+2}{2}\right) \int \frac{1}{V} dV$$

$$\ln P = -\left(\frac{i+2}{2}\right) \ln V + \text{const.}$$

$$\ln(PV^{\frac{i+2}{2}}) = \text{const.}$$

$$\boxed{PV^{\frac{i+2}{2}} = \text{const.}}$$

Adiabatic relation
of ideal gas

★ In general, the adiabatic relation of most material

look like $\boxed{PV^\gamma = \text{const.}}$

The index γ is called adiabatic constant

For ideal gas, $\gamma = \frac{i+2}{i} = \frac{C_p}{C_v} = \text{const.}$

which is a numerical coincidence

However this is NOT correct for other materials

(The adiabatic "constant" may not even be a constant)

Summary in a table

red underline = always True

blue = ideal gas only

	dU is a state function	δW by definition: $\int pdV$	δQ by 1 st law: $\delta Q = dU + \delta W$
Iso. V	$\underline{U(P_2V_2T_2) - U(P_1V_1T_1)}$ $= \frac{i}{2}(P_2V_2 - P_1V_1)$ $= \frac{i}{2}NK(T_2 - T_1)$	0	$\underline{\Delta U + 0}$ $= \underline{\int C_V(T) dT}$ $= \frac{i}{2} \underline{NK(T_2 - T_1)}_{C_V}$
Iso. P	(Same as iso. V)	$P(V_2 - V_1)$ $= NK(T_2 - T_1)$	$\underline{\Delta U + P(V_2 - V_1)}$ $= \underline{\int C_P(T) dT}$ $= \frac{i+2}{2} \underline{NK(T_2 - T_1)}_{C_P}$
Iso. T	(Same as iso. V) $= 0$ for ideal gas	$\int pdV$ (<u>no further reduction</u>) $= NKT \ln\left(\frac{V_2}{V_1}\right)$	$\underline{\Delta U + \int pdV}$ $= NKT \ln\left(\frac{V_2}{V_1}\right)$
Adiabatic	(Same as iso. V)	$\underline{\delta W = -dU}$ $= -\frac{i}{2}(P_2V_2 - P_1V_1)$ $= -\frac{i}{2}NK(T_2 - T_1)$	$\underline{0}$ (By definition)

Standard thermal cycle practice problem



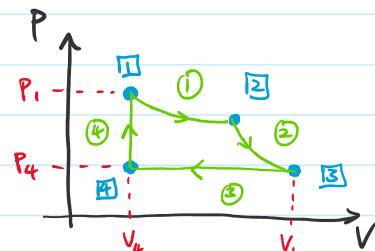
The most common question to ask :
What is the engine efficiency? COP?

Some general steps to follow :

- ① Write down the relation of parameters at different states
(Depends on the process that connects them)
- ② Write down the dU , dW , dQ of each process
- ③ Identify if the dQ of each process is an input or output
- ④ Calculate the efficiency / COP by formula

Example 1 : A cycle with all 4 kinds of processes

1. Iso T (expand)



2. Adiabatic (expand)

3. Iso P (contract)

4. Iso V

(Assume running on ideal gas)

Step 1 : Write down the relation of parameters at different states

① P_1, V_1, T_1

② P_2, V_2, T_2

③ P_3, V_3, T_3

④ P_4, V_4, T_4

$$\boxed{1} \rightarrow \boxed{2} = \text{iso } T \Rightarrow T_1 = T_2$$

You can also use ideal gas law to get more relation

$$\boxed{2} \rightarrow \boxed{3} = \text{adiabatic} \Rightarrow P_2 V_2^\gamma = P_3 V_3^\gamma$$

$$\boxed{3} \rightarrow \boxed{4} = \text{iso } P \Rightarrow P_3 = P_4$$

But do it only if you really need (Don't waste time)

$$\boxed{4} \rightarrow \boxed{1} = \text{iso } V \Rightarrow V_4 = V_1$$

Step 2 : Write down the dU , SW , SO of each process

$$\boxed{1} \rightarrow \boxed{2} = \text{iso. T} \quad \left\{ \begin{array}{l} \Delta U = 0 \\ \int SW = NkT_1 \ln\left(\frac{V_2}{V_1}\right) \\ \int SO = NkT_1 \ln\left(\frac{V_2}{V_1}\right) > 0 \end{array} \right.$$

$$\boxed{2} \rightarrow \boxed{3} = \text{adiabatic} \quad \left\{ \begin{array}{l} \Delta U = \frac{i}{2}(P_3V_3 - P_2V_2) = \frac{i}{2}Nk(T_3 - T_2) \\ \int SW = \frac{i}{2}(P_3V_3 - P_2V_2) = \frac{i}{2}Nk(T_3 - T_2) \\ \int SO = 0 \end{array} \right.$$

$$\boxed{3} \rightarrow \boxed{4} = \text{iso. P} \quad \left\{ \begin{array}{l} \Delta U = \frac{i}{2}P(V_4 - V_3) = \frac{i}{2}Nk(T_4 - T_3) \\ \int SW = P(V_4 - V_3) = Nk(T_4 - T_3) \\ \int SO = \frac{i+2}{2}P(V_4 - V_3) = \frac{i+2}{2}Nk(T_4 - T_3) < 0 \end{array} \right.$$

$$\boxed{4} \rightarrow \boxed{1} = \text{iso. V} \quad \left\{ \begin{array}{l} \Delta U = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}Nk(T_1 - T_4) \\ \int SW = 0 \\ \int SO = \frac{i}{2}V_4(P_1 - P_4) = \frac{i}{2}Nk(T_1 - T_4) > 0 \end{array} \right.$$

Step 3 : Identify whether each SO is an input or output

★★ Recall in the Physics convention of 1st law

$$SO = dU + SW$$

↑ heat input to the system ↑ change in U of the system ↑ W.D. by the system

⇒ Any $SO > 0$ is input
 $SO < 0$ is output

⇒ Path with heat input : $\boxed{1} \rightarrow \boxed{2}$, $\boxed{4} \rightarrow \boxed{1}$

heat output : $\boxed{3} \rightarrow \boxed{4}$

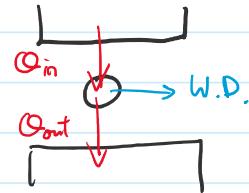
Step 4 : Calculate efficiency / COP by formulae

By definition :

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

i.e. What is the portion of heat input

can the engine convert into W.D.?



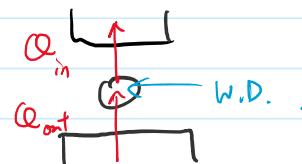
Eg. Efficiency of the above engine , by formulae

$$= 1 - \left| \frac{\frac{i+2}{2} Nk(T_4 - T_3)}{\frac{i}{2} Nk(T_1 - T_4) + NkT_1 \ln\left(\frac{V_2}{V_1}\right)} \right|$$

* You may further simplify the expression by the state parameter relations from step 1 .

Also , if we operate the engine reversely , it becomes a refrigerator

i.e. Remove heat by applying work



$$\text{COP} \quad (\text{Coefficient of Performance}) = \frac{\text{Heat remove}}{\text{W.D.}} = \left| \frac{\text{Heat output}}{\text{Heat input} - \text{Heat output}} \right|$$

$$= \frac{1-\eta}{\eta} \quad (\text{After some algebra derivation})$$

Example 2 : System of Photon gas

Photon's internal energy & pressure are given by

$$\left\{ \begin{array}{l} U = 3PV = aVT^4 \\ P = \frac{1}{3}aT^4 \end{array} \right. \quad \text{with } a = \text{some const.}$$

↑ substitute to get

For comparison,
the formulae for ideal gas are

$$\left\{ \begin{array}{l} U = \frac{i}{2}PV = \frac{i}{2}NkT \\ P = \frac{NkT}{V} \end{array} \right. \quad \text{which we cannot use.}$$

* Photon is NOT ideal gas. We cannot use any formulae that are derived from kinetic theory or ideal gas law.

(Any blue formulae on the table)

We must re-derive the dU , dW , dQ of 4 processes.

* Remember U is always a state function. ΔU is independent of process

$$\Delta U = \underline{U(P_2, V_2, T_2) - U(P_1, V_1, T_1)} \quad \text{true for all system.}$$

$$\begin{aligned} &= \underline{3(P_2V_2 - P_1V_1)} \\ &= \underline{a(V_2T_2^4 - V_1T_1^4)} \end{aligned} \quad \begin{aligned} &\text{Using photon gas's formulae} \\ &U = 3PV = aVT^4 \end{aligned}$$

II Iso V.

$$-\Delta U = 3V(P_2 - P_1) = aV(T_2^4 - T_1^4)$$

$$-\int dW = \int pdV = \underline{0} \quad (\text{always true, by definition})$$

$$-\int dQ = \underline{\Delta U + 0} = 3V(P_2 - P_1) = \boxed{aV(T_2^4 - T_1^4)}$$

$$= \int C_V(T) dT$$

$$\Rightarrow C_V(T) = \left(\frac{dQ}{dT} \right)_{\text{Iso } V} = \frac{dU}{dT} = \boxed{4aVT^3}$$

2 Iso P (Note that for photon gas, $\text{iso P} = \text{iso T}$)

* Note : For photon gas, $\underline{\text{iso P}} = \underline{\text{iso T}}$.

\because By $P = \frac{1}{3}aT^4$, if P is fixed, then T is fixed!

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

$$-\int \delta W = \underline{\int P dV} = P(V_2 - V_1) = \boxed{\underline{\frac{1}{3}aT^4(V_2 - V_1)}}$$

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

$$\text{BUT } C_p(T) = \left(\frac{dQ}{dT} \right)_{\text{iso P}} = \boxed{\underline{\text{undefined.}}}$$

\therefore Under constant pressure, no matter how much Q is input to the system the temperature cannot change!

$$\int_{\text{iso P}} dQ = \int C_p(T) dT = \int (\text{undefined}) \cdot (0)$$

3 Adiabatic

$$-\int \delta Q = 0 \quad (\text{always true, by definition})$$

$$-\underline{\delta W} = -dU$$

$$P dV = -d(3PV)$$

$$= -3(PdV + VdP)$$

$$4PdV = 3VdP$$

$$\frac{4}{3} \int \frac{1}{V} dV = - \int \frac{1}{P} dP$$

$$\ln(V^{\frac{4}{3}}) = \ln(P^{-1}) + \text{const.}$$

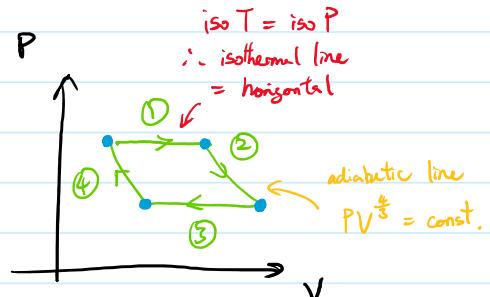
$$\boxed{PV^{\frac{4}{3}} = \text{const}}$$

\therefore Adiabatic const. for photon gas = $\frac{4}{3}$ and obviously $\neq \frac{C_V}{C_P}$

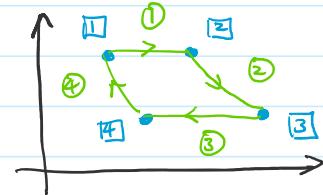
Example 3 Carnot cycle by photon gas.

By definition, Carnot cycle is made of :

- ① Iso T. expansion
- ② Adiabatic expansion
- ③ Iso. T. contraction
- ④ Adiabatic contraction



Step 1 : Write out the relation between state parameter of different states.



$$\boxed{1} \rightarrow \boxed{2} = \text{iso. P/T} \Rightarrow P_1 = P_2, T_1 = T_2$$

$$\boxed{2} \rightarrow \boxed{3} = \text{adiabatic} \Rightarrow P_2 V_2^{4/3} = P_3 V_3^{4/3}$$

$$\boxed{3} \rightarrow \boxed{4} = \text{iso P/T} \Rightarrow P_3 = P_4, T_3 = T_4$$

$$\boxed{4} \rightarrow \boxed{1} = \text{adiabatic} \Rightarrow P_4 V_4^{4/3} = P_1 V_1^{4/3}$$

Step 2 : Write down ΔU , δW , δQ of each process

and Step 3 : Identify whether each δQ is an input or output

$$\boxed{1} \rightarrow \boxed{2} = \text{iso P/T} \quad \left\{ \begin{array}{l} \Delta U = a T_1^4 (V_2 - V_1) \\ \int \delta W = \frac{1}{3} a T_1^4 (V_2 - V_1) \\ \int \delta Q = \frac{4}{3} a T_1^4 (V_2 - V_1) > 0 \end{array} \right.$$

$$\boxed{2} \rightarrow \boxed{3} = \text{adiabatic} \quad \left\{ \begin{array}{l} \Delta U = a (V_3 T_3^4 - V_2 T_2^4) \\ \int \delta W = -a (V_3 T_3^4 - V_2 T_2^4) \\ \int \delta Q = 0 \end{array} \right.$$

$$[3] \rightarrow [4] = \text{iso P/T}$$

$$\left\{ \begin{array}{l} \Delta U = a T_3^4 (V_4 - V_3) \\ \int \delta Q = \frac{1}{3} a T_3^4 (V_4 - V_3) \\ \int \delta Q = \frac{4}{3} a T_3^4 (V_4 - V_3) < 0 \end{array} \right.$$

$$[4] \rightarrow [1] = \text{adiabatic}$$

$$\left\{ \begin{array}{l} \Delta U = a (V_1 T_1^4 - V_4 T_4^4) \\ \int \delta Q = -a (V_1 T_1^4 - V_4 T_4^4) \\ \int \delta Q = 0 \end{array} \right.$$

Step 4 : Compute engine efficiency

$$\eta = 1 - \left| \frac{\text{Heat output}}{\text{Heat input}} \right| = 1 - \left| \frac{\frac{4}{3} a T_3^4 (V_4 - V_3)}{\frac{4}{3} a T_1^4 (V_2 - V_1)} \right|$$

The expression can be simplified using relations in step 1

By adiabatic relation

$$PV^{\frac{4}{3}} = \text{const}$$

$$\frac{1}{3} a T^4 V^{\frac{4}{3}} = \text{const}$$

$$T V^{\frac{1}{3}} = \text{const} \Rightarrow \underline{T^3 V = \text{const}}$$

From the relations between state parameters :

$$\left\{ \begin{array}{l} T_1 = T_2 , T_3 = T_4 \\ T_2^3 V_2 = T_3^3 V_3 , T_4^3 V_4 = T_1^3 V_1 \end{array} \right.$$

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

∴ $T_3 = T_4$
 $T_2 = T_1$

$\frac{T_4^3 V_4}{T_2^3 V_2} = T_1^3 V_1$
 $\frac{T_3^3 V_3}{T_1^3 V_1} = T_2^3 V_2$

which is the same as Carnot cycle of ideal gas !