

THERMODYNAMICS

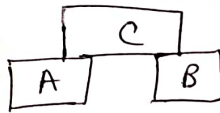
thermodynamic system: A collection of large no. of molecules of matter which are so arranged that these possess certain values of P, V & T .

• P, V, T, U , etc are thermodynamic state variables.

thermal equilibrium: Variables like P, V, T, n , etc. do not change with time.

Two systems in contact with each other come to thermal equilibrium when their temp is same.

0th LAW of thermodynamic:



If, $A \rightleftharpoons C$ as well as $B \rightleftharpoons C$ are in thermal equilibrium, then $A \rightleftharpoons B$ will also be in thermal equilibrium.

Heat, Work, Internal energy:

Heat energy: Transferred to or from the system because of the difference in temperature by conduction, convection or radiation.

Work: Energy i.e. transferred from one sys. to another by force moving its point of application in its own direction is called work.

$$\begin{aligned}\text{Work done} &= \int F dx \\ &= \int P A dx\end{aligned}$$

$$W = \int P dV$$

Heat & Work \rightarrow Path functions

Internal Energy \rightarrow State functions

Important terms:

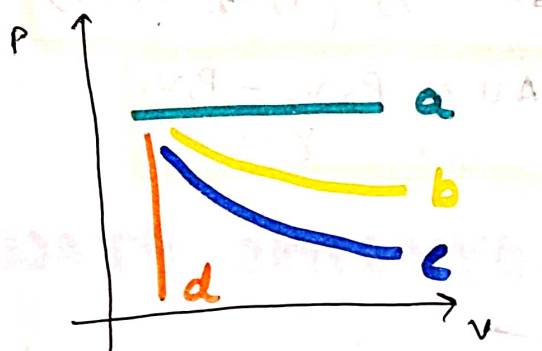
1 Eq. of state: the eq. that connects the P, V, T of a gas.

2 Thermodynamic Process: Process when some changes occur in the state of thermodynamic system.

3 Quasi static process: A thermodynamic process which is infinitely slow.

all processes are assumed quasistatic unless stated.

4 Indicator or P-V-diagram:



a → isobaric
b → isothermal
c → adiabatic
d → isochoric

* Area under graph is work done.

First Law of thermodynamics:

→ Basically law of conservation of energy.

$$\Delta Q = \Delta W + \Delta U$$

Q = heat

W = work done

U = internal energy

SIGN convention:

Q supplied +ve
 taken -ve

W expansion, by system +ve
 compression, on system -ve

U increase +ve
 decrease -ve

Different formulas for internal energy:

$$\star U = \frac{f}{2} n R T \quad \Rightarrow \quad \Delta U = \frac{f}{2} n R \Delta T$$

$$\star C_V = \frac{f R}{2} \quad \Rightarrow \quad \Delta U = n C_V \Delta T$$

$$\star \gamma = 1 + \frac{2}{f} \quad \Rightarrow \quad \Delta U = \frac{1}{\gamma - 1} n R \Delta T$$

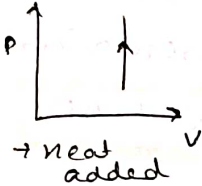
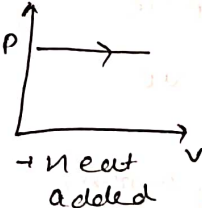
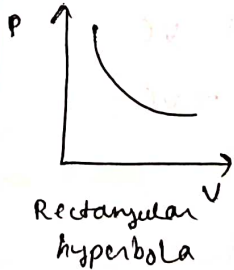
$$f/2 = \frac{1}{\gamma - 1}$$

$$\star P V = n R T$$

$$P_2 V_2 - P_1 V_1 = n R \Delta T \quad \Rightarrow \quad \Delta U = \frac{f}{2} (P_2 V_2 - P_1 V_1)$$

$$\Delta U = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

Different thermodynamic processes:

Process	Constant	P-V graph	Work Done	1st Law	Heat transfer
ISOCORIC	Volume (Gay Lussac law) $\frac{P}{T} = \text{constant}$		$W = 0$	$\Delta Q = \Delta U$	$Q = n C_V \Delta T$
ISOBARIC	Pressure (Charles law) $\frac{V}{T} = \text{constant}$		$W = \int P dV$ \downarrow $W = P(V_2 - V_1)$	$\Delta Q = \Delta W + \Delta U$	$Q = n C_P \Delta T$
ISOTHERMAL	Temperature (Boyle's law) $P V = \text{constant}$ (Ideal gas only)		$W = n R T \ln\left(\frac{V_2}{V_1}\right)$ OR $n R T \ln\left(\frac{P_1}{P_2}\right)$ $\star \ln \downarrow \text{natural log.}$	$\Delta U = 0$ $\Delta Q = \Delta W$	$Q = W$

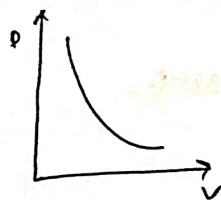
ADIABATIC

$$PV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{const.}$$

$$T^\gamma P^{1-\gamma} = \text{const.}$$

$$Q = 0$$



$$W = -\Delta U$$

$$W = -\left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1}\right)$$

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

$$\Delta W = -\Delta U$$

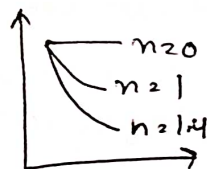
$$0$$

POLY-TROPIC

$$PV^n = \text{const.}$$

or

$$PV^n = \text{const.}$$



$$W = \frac{P_1 V_1 - P_2 V_2}{n - 1}$$

$$\Delta Q = \Delta W + \Delta U$$

$$\Delta Q$$

$$PV^0 = C$$

$$P = C \text{] Isothermal}$$

$$PV^1 = C$$

$$PV = C \text{] -Thermo$$

$$PV^{1.4} = C$$

$$PV^\gamma = C \text{] Adia.$$

$$PV^\alpha = C$$

$$V = C$$

$$P = C$$

$$V = C$$

$$\text{Choric}$$

Free expansion in vacuum

$$\Delta U = 0$$

$$U, T \propto$$

$$PV = \text{constant}$$

$$0$$

$$0$$

$$0$$

CYCLE PROCESS

$$(P_1, V_1, T_1)$$

equals to

$$(P_2, V_2, T_2)$$

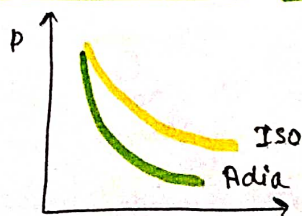
$$W_{\text{net}} = \text{area below cycle on P-V graph}$$

$$\Delta U = 0$$

$$\Delta Q = \Delta W$$

$$Q_{\text{net}} = W_{\text{net}}$$

Comparing adiabatic & isothermic graph:



Slope of adiabatic

>

Slope of isothermic

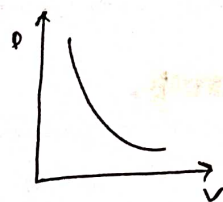
ADIABATIC

$$PV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{const.}$$

$$TP^{\frac{1}{1-\gamma}} = \text{const.}$$

$$Q = 0$$



$$W = -\Delta U$$

$$W = -\left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1}\right)$$

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$\Delta W = -\Delta U$$

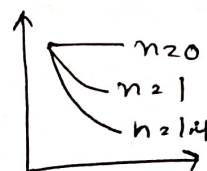
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POLY-TROPIC

$$PV^n = \text{const.}$$

or

$$PV^n = \text{const.}$$



$$W = \frac{P_1 V_1 - P_2 V_2}{n - 1}$$

$$\Delta Q = \Delta W + \Delta U$$

0

$$PV^0 = C$$

$$P = C \text{] Iso baric$$

$$PV^1 = C$$

$$PV = C \text{] -Thermo$$

$$PV^{1.4} = C$$

$$PV^\gamma = C \text{] Adia.$$

$$PV^\alpha = C$$

$$\left. \begin{array}{l} V = C \\ \text{or} \\ P = C \end{array} \right\} \text{Choric}$$

Free expansion in vacuum

$$\Delta U = 0$$

$$U, T \propto$$

$$pV = \text{constant}$$

0

0

0

CYCLE PROCESS

$$(P_1, V_1, T_1)$$

equals to

$$(P_2, V_2, T_2)$$

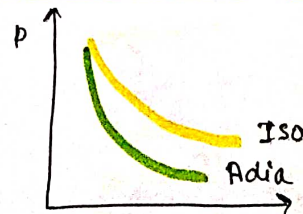
$$W_{\text{net}} = \text{area b/w cycle on P-V graph}$$

$$\Delta U = 0$$

$$\Delta Q = \Delta W$$

$$Q_{\text{net}} = W_{\text{net}}$$

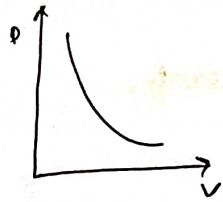
Comparing adiabatic & isothermic graph:



slope of adiabatic > slope of isothermic

ADIABATIC

$PV^\gamma = \text{constant}$
 $TV^{\gamma-1} = \text{const.}$
 $T^\gamma P^{1-\gamma} = \text{const.}$
 $Q = 0$



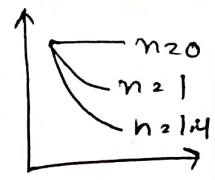
$W = -\Delta U$
 $W = -\left(\frac{P_2 V_2 - P_1 V_1}{\gamma - 1}\right)$
 $W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$

$\Delta W = -\Delta U$

0

POLY-TROPIC

$PV^n = \text{const.}$
 or
 $PV^m = \text{const.}$



$W = \frac{P_1 V_1 - P_2 V_2}{n - 1}$

$\Delta Q = \Delta W + \Delta U$

ΔQ

- $PV^0 = C$
 $P = C$ } Isobaric
- $PV^1 = C$
 $PV = C$ } Thermo
- $PV^{1.4} = C$
 $PV^\gamma = C$ } Adia.
- $PV^\alpha = C$
 $V = C$ or $P = C$
 $V = C$ } Choric

Free expansion in vacuum

$\Delta U = 0$
 $U, T \propto$
 $PV = \text{constant}$

0

0

0

CYCLE PROCESS

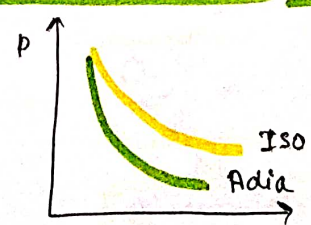
(P_1, V_1, T_1)
 equals to
 (P_2, V_2, T_2)

$W_{\text{net}} = \text{area b/w cycle on P-V graph}$

$\Delta U = 0$
 $\Delta Q = \Delta W$

$Q_{\text{net}} = W_{\text{net}}$

Comparing adiabatic & isothermic graph:



slope of adiabatic > slope of isothermic

$PV^\gamma = \text{constant}$

Imp.

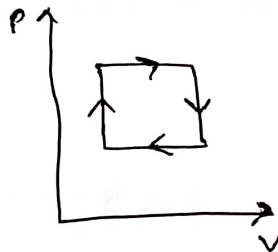
$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

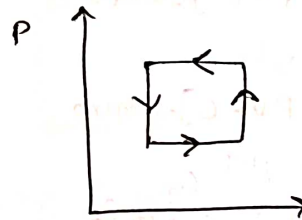
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

→ CYCLIC PROCESS:

$W_{\text{net}} = \text{Area enclosed}$



→ Clockwise
 $W = +ve$

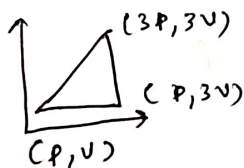


→ Anticlockwise
 $W = -ve$

$\Delta U = 0$ (Because U is state function)

1st law: $\Delta Q = \Delta W + \Delta U$
 $\Delta Q = \Delta W$

Ques:



$W = ?$

Sol: Area = W_{net}

$$\text{Area} = \frac{1}{2} \times B \times H$$

$$= \frac{1}{2} \times 2P \times 2V$$

$$= \underline{\underline{2PV}}$$

Ques:



Sol

$$W_{\text{net}} = \pi r^2$$

$$= \frac{22}{7} \times \left(\frac{4V}{2}\right)^2$$

$$= \frac{22}{7} \times 4V^2$$

$$= \underline{\underline{4\pi V^2}}$$

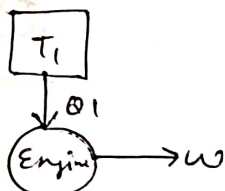
→ kelvin - Planck's statement:

↳ Based on the fact that the efficiency of the heat engine cycle is never 100%. i.e. some heat is always rejected.

→ CLAUSIUS statement:

↳ To transfer the heat from low temperature to higher temperature reservoir some external work should be done on the cycle.

1



Not possible

Because, here.

entropy of system = 0 (cyclic)

entropy of surrounding = $-\frac{dQ}{T}$ [-ve cuz heat is rejected]

$\Delta S_{\text{universe}} = \text{(-ve)}$ which is never possible.

ENTROPY:

↳ Randomness

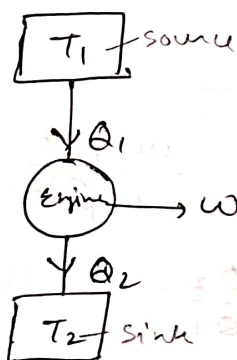
$$dS = \frac{dQ}{T}$$

$$\Delta S_{\text{universe}} > 0 \text{ (always)}$$

$$\Delta S_{\text{uni.}} = 0 \text{ (Ideal, reversible process)}$$

$$\Delta S_{\text{uni}} < 0 \text{ (Never)}$$

2



$$\Delta S_{\text{uni.}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding 1}} + \Delta S_{\text{surrounding 2}}$$

$$\Delta S_{\text{uni.}} = 0 + \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

$$\Delta S_{\text{uni.}} = (+ve) \text{ (possible)}$$

CARNOT CYCLE:

→ Ideal & Reversible but only hypothetical process.

→ $\Delta S_{\text{universe}} = 0$

Formula:

$$\Delta S_{\text{uni}} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

$$\star W = Q_{\text{in}} - Q_{\text{out}} \quad 0 = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

$$\star \eta = \frac{W}{Q_{\text{in}}}$$

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

OR

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

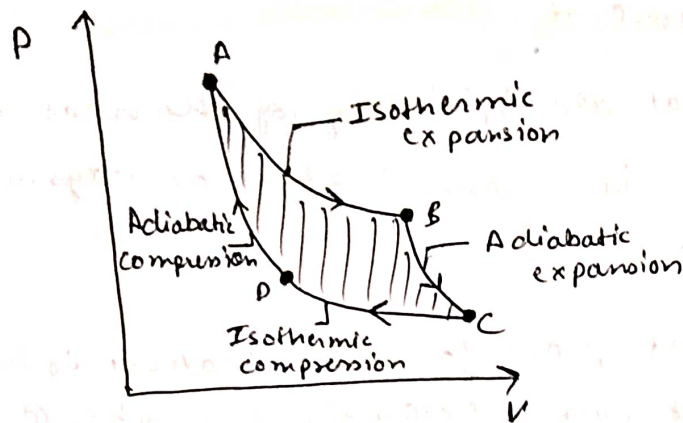
Isothermal expansion

↓
Adiabatic expansion

↓
Isothermal compression

↓
Adiabatic compression

Processes in Carnot Cycle:



Process	Name	Q	ΔU	W
AB	Isothermal expansion $T_1 = \text{constant}$	$Q = W$ $= +ve$	0	+ve
BC	Adiabatic expansion	0	-ve	+ve
CD	Isothermal compression $T_2 = \text{constant}$	$Q = W$ $= -ve$	0	-ve
DA	Adiabatic compression	0	+ve	-ve

Efficiency for Carnot cycle $\Rightarrow \eta = \frac{\text{Work done}}{\text{Energy supplied}} = \frac{\text{Output}}{\text{Input}}$

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

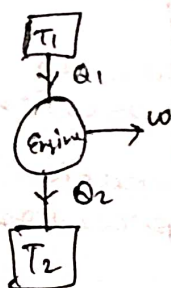
OR

$$\eta = 1 - \frac{T_2}{T_1} \quad \text{For Carnot only.}$$

Efficiency of Carnot cycle is maximum (not 100%).

Entropy in universe is always increasing.

Efficiency of Heat Engine:



According to 1st Law:

$$\delta Q = \delta W + \delta U$$

$$\delta Q = \delta W \quad (\text{Cyclic})$$

$$Q_1 - Q_2 = W \quad \text{--- (1)}$$

$$\eta = \frac{\text{output}}{\text{input}} = \frac{Q_1 - Q_2}{Q_1}$$

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

→ For any heat engine.

Q: Inventor claim to have ~~an engine of~~ efficiency 55% for following engine:



Sol: $\eta = 1 - \frac{T_2}{T_1}$

$$\eta = 1 - \frac{300}{500}$$

$$= \frac{200}{500} \times 100$$

$$= 40\%$$

So the claim of inventor is false.

Only true is:

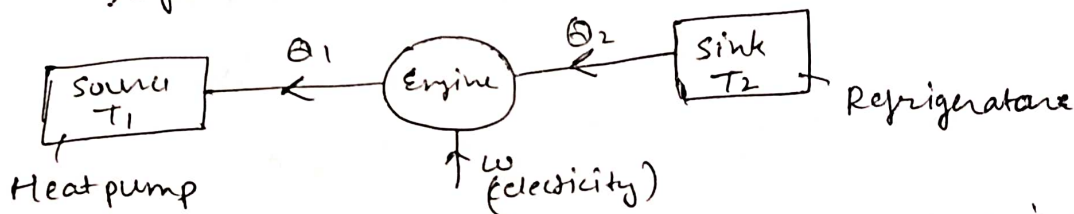
$$\eta_c > \eta \quad \checkmark$$

$$\eta_c \leq \eta \quad \times$$

Since, efficiency of Carnot at given temp is 40%, the engine must have lesser than this.

Refrigerator & Heat Pump:

↳ takes heat from a cold body, work is done on it & the work done together w/ heat absorbed is rejected to the source.



It can be regarded as Carnot ideal heat engine working in reverse direction.

→ Coefficient of performance:

C.O.P → ratio of qty of heat removed per cycle (Q_2) to the work done on working substance per cycle.

$$COP = \frac{\text{Desired effect}}{\text{work input}}$$

$$COP = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

$$COP \propto \frac{1}{W}$$

$COP_{\text{heat pump}} - COP_{\text{refrigerator}}$

$$\Rightarrow \frac{Q_1}{Q_1 - Q_2} - \frac{Q_2}{Q_1 - Q_2} \Rightarrow \frac{Q_1 - Q_2}{Q_1 - Q_2} = \underline{\underline{1}}$$

* heating is easier.
COP of heat pump

more than

COP of refrigerator

i.e. heat pump will consume less electricity.

Ques: If a refrigerator door is left open, will the room get hot or cold?

Sol The room will be get hot, because heat pump is also present in the same room. And the COP of heat pump is more thus it will heat up the room more in same electricity provided.

$$\eta = \frac{W}{Q_1}$$

$$\eta = \frac{1}{COP_{\text{heat pump}}}$$



Heat pump

COP of heat pump

$$COP = \frac{Q_2}{W}$$

$$COP = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$