



ICT 1107: Physics

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ICT 1107: Physics

Chapter 2

Heat and Thermodynamics



Heat & Thermodynamics

Thermometry

&

Temperature Measurements



Chapter 2: Heat & Thermodynamics

Gas Equation in an Adiabatic Process



Chapter 2: Heat & Thermodynamics

Consider 1 gram of the working substance (ideal gas) perfectly insulated from the surroundings. Let the external work done by the gas be δW .

Applying the first law of thermodynamics

$$\delta H = dU + \delta W$$

But

$$\delta H = 0$$

and

$$\delta W = P.dV$$

where P is the pressure of the gas and dV is the change in volume.

$$\therefore 0 = dU + \frac{P.dV}{J} \quad \dots(i)$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT .

$$dU = 1 \times C_v \times dT$$
$$C_v.dT + \frac{P.dV}{J} = 0 \quad \dots(ii)$$



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For an ideal gas

$$PV = rT \quad \dots(iii)$$

Differentiating,

$$P.dV + V.dP = r.dT$$

Substituting the value of dT in equation (ii),

$$C_v \left[\frac{P.dV + V.dP}{r} \right] + \frac{P.dV}{J} = 0$$

$$C_v[P.dV + V.dP] + r \cdot \frac{P.dV}{J} = 0$$

But,

$$\frac{r}{J} = C_p - C_v$$



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$$\therefore C_v \cdot P \cdot dV + C_v \cdot V \cdot dP + C_p \cdot P \cdot dV - C_v \cdot P \cdot dV = 0$$
$$C_p \cdot P \cdot dV + C_v \cdot V \cdot dP = 0$$

Dividing by $C_v \cdot PV$,

$$\frac{C_p}{C_v} \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

But

$$\frac{C_p}{C_v} = \gamma$$

$$\therefore \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating, $\log P + \gamma \log V = \text{const.}$

$$\log PV^\gamma = \text{const.}$$

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

...(iv)

~~This is the equation connecting pressure and volume during an adiabatic process.~~



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Taking

$$PV = rT$$

or

$$P = \frac{rT}{V}$$

$$\left(\frac{rT}{V}\right) \cdot V^{\gamma} = \text{const.}$$

But r is const.

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

∴

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

...(v)

Also

$$V = \frac{rT}{P}$$

$$P\left[\frac{rT}{P}\right]^{\gamma} = \text{const.}$$

or

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

or

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

...(vi)



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Thus, during an adiabatic process

$$(i) \quad PV^\gamma = \text{const.}$$

$$(ii) \quad TV^{\gamma-1} = \text{const. and}$$

$$(iii) \quad \frac{P^{\gamma-1}}{T^\gamma} = \text{const.}$$



Chapter 2: Heat & Thermodynamics

Reversible & Irreversible Processes



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Reversible (Ideal) Process: A system process is defined as reversible if a system, after having experienced several transformations, can be returned to its original state without alteration of the system itself or the system's surroundings.

- ✓ it should occur infinitely slowly due to infinitesimal gradient
- ✓ all the changes in state occurred in the system are in thermodynamic equilibrium with each other

Remember:

In a reversible process, the entropy of the universe (i.e.,¹¹ the system plus surroundings) remains constant.



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Example of reversible processes:

A change that can go forwards or backwards,
for example melting and freezing



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Irreversible (natural) Processes:

- ✓ All processes in nature are irreversible

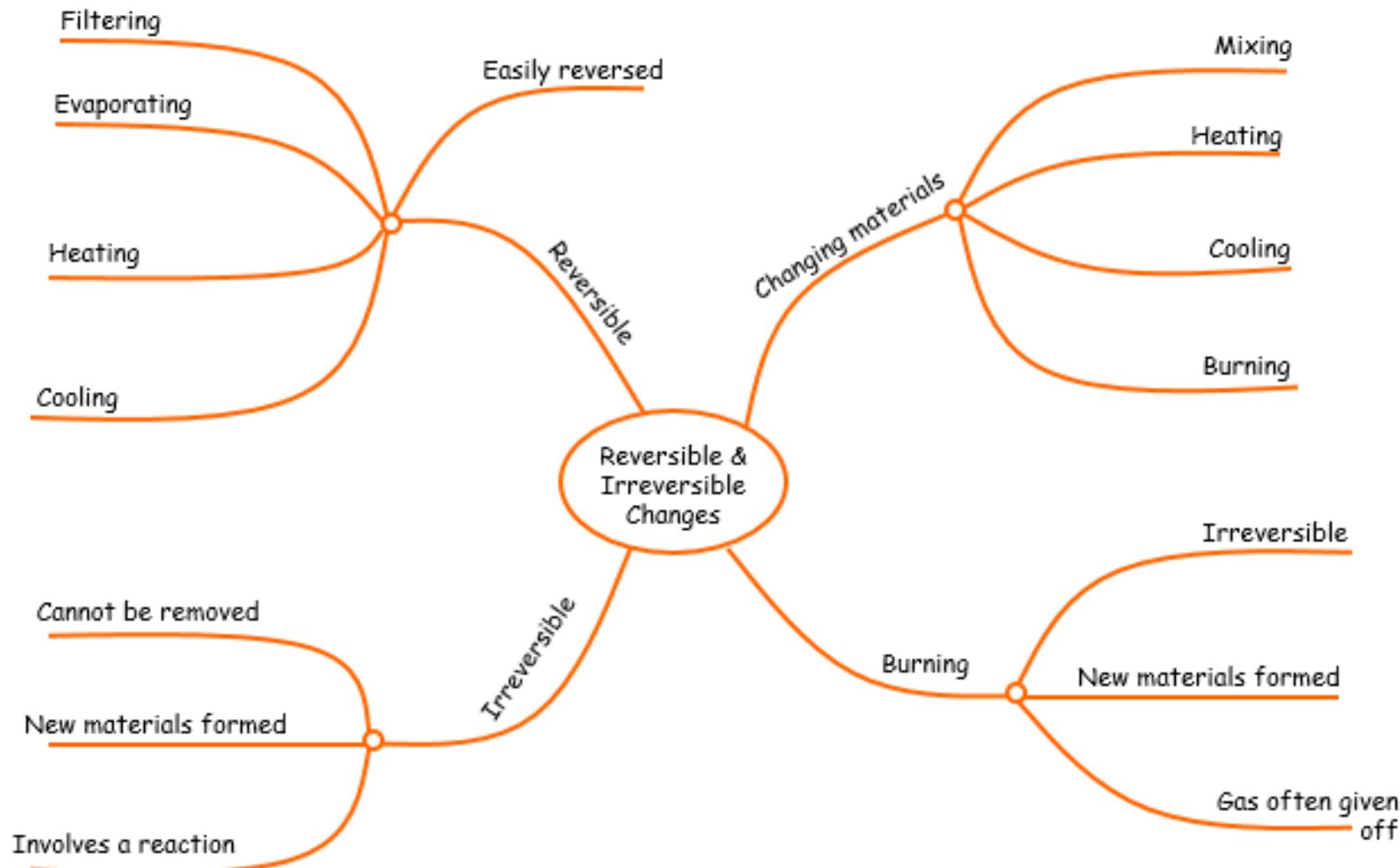
- ✓ Finite gradient between the two states of the system
 - heat flow between two bodies occurs due to temperature gradient between the two bodies;

Example of Irreversible Processes:

All processes in nature are irreversible, a change that cannot go back, for example burning



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2nd Law of Thermodynamics



2nd Law of Thermodynamics

- ✓ The 2nd Law of thermodynamics is concerned with the maximum fraction of heat that can be converted into useful work.

The 2nd law may be stated in several different ways, such as :

1. Thermal energy will not spontaneously flow from a colder to a warmer object. (What is thermal energy?)
 2. The *entropy* (defined below) of the universe is constantly increasing.
- ✓ Thus, the 2nd law is not a conservation principle (as in the 1st law), but rather is a law defining the direction of flow of energy.



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In a system, a process that occurs will tend to increase the total entropy of the universe

1. It is impossible to make heat flow from a material at a lower temperature to a material at a higher temperature without doing external work on the working substance (**Clausius Statement**)

2. It is impossible to convert heat completely into work in a cyclic process (**Definition by Kelvin**)



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If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

$$\Delta S \geq 0 \quad (\text{second law of thermodynamics})$$

Here the greater-than sign applies to irreversible processes and the equals sign to reversible processes. This relation applies only to closed systems.



Summary

0th Law of Thermodynamics

- ✓ Definition of temperature
- ✓ Systems at different temperatures exchange energy until reaching a thermal equilibrium

1st Law of Thermodynamics

- ✓ Conservation of energy
- ✓ heat is a form of energy

2nd Law of Thermodynamics

- ✓ Entropy of an isolated system never decreases
- ✓ perpetual motions of machines is impossible



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3rd Law of Thermodynamics

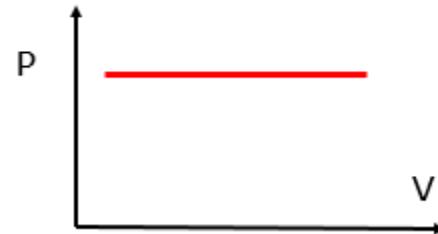
- ✓ Entropy at absolute zero temperature (0K)



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Isobaric

- $P = \text{constant}$



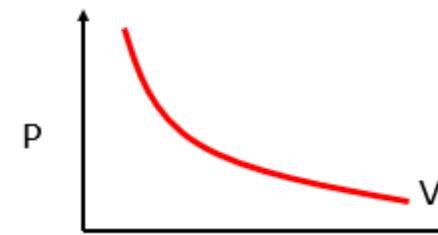
Isovolumetric/Isometric

- $V = \text{constant}$
- $W = 0$



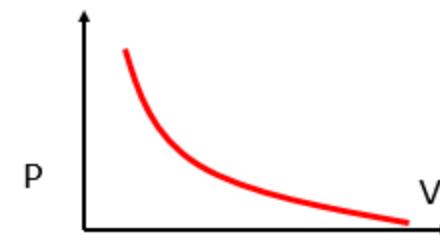
Isothermal

- $T = \text{constant}$
- $\Delta U = 0$ (ideal gas)



Adiabatic

- $Q = 0$

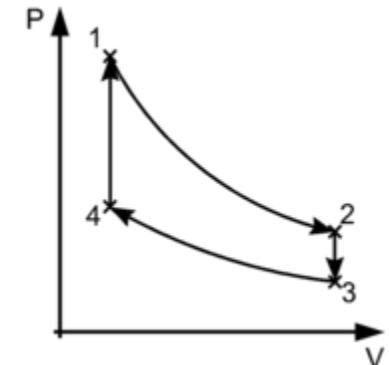




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Cyclic

- ✓ If clockwise – heat engine
- ✓ If counterclockwise – heat pump





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Carnot's Theorem

No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs

Not only there are no perfect engines and refrigerators, but also their efficiency has an upper limit!

Carnot's theorem (Alternative definition)

- (1) All reversible engines operating between two given reservoirs have the same efficiency.
- (2) No engines have an efficiency higher than that of a reversible engine.



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“All the reversible engines working between the same temperature limits have the same efficiency. No engine can be more efficient than a Carnot’s reversible engine working between the same two temperatures.”

- ✓ Ideal engines = Reversible engines
- ✓ A Carnot engine is an ideal engine undergoing a Carnot cycle.



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Consider two reversible engines A and B , working between the temperature limits T_1 and T_2 (Fig. 6-15). A and B are coupled. Suppose A is more efficient than B . The engine A works as a heat engine and B as a refrigerator. The engine A absorbs an amount of heat H_1 from the source at a temperature T_1 . It does external work W and transfers it to B . The heat rejected to the sink is H_2 at a temperature T_2 . The engine B absorbs heat H_2' from the sink at temperature T_2 and W amount of work is done on the working substance. The heat given to the source at temperature T_1 is H_1' .

Suppose the engine A is more efficient than B .

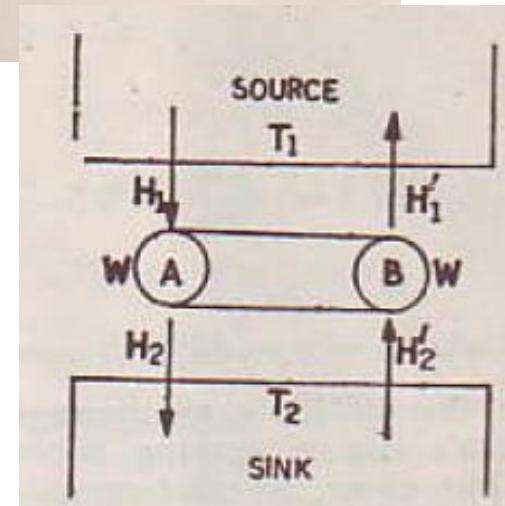


Fig. 6-15.



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Efficiency

Efficiency of the engine A

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

Efficiency of the engine B

$$= \eta' = \frac{H_1' - H_2'}{H_1'} = \frac{W}{H_1'}$$

Since $\eta > \eta'$; $H_1' > H_1$

Also, $W = H_1 - H_2 = H_1' - H_2'$

$\therefore H_2' > H_2$



Carnot's Theorem

Thus, for the two engines A and B working as a coupled system, $(H_2' - H_2)$ is the quantity of heat taken from the sink at a temperature T_2 , and $(H_1' - H_1)$ is the quantity of heat given to the source at a temperature T_1 . Both $(H_2' - H_2)$ and $(H_1' - H_1)$ are positive quantities. It means heat flows from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) i.e., heat flows from a body at a lower temperature to a body at a higher temperature. But, no external work has been done on the system. This is contrary to the second law of thermodynamics. Thus, η cannot be greater than η' . The two engines (reversible) working between the same two temperature limits have the same efficiency. Moreover, in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation (irreversible processes). Thus, the Carnot's engine has the maximum efficiency. Whatever may be the nature of the working substance, the efficiency depends only upon the two temperature limits.

In a practical engine there is always loss of energy due to friction, conduction, radiation etc. and hence its efficiency is always lower than that of a Carnot's engine.



Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites :

(1) **Source.** The source should be at a fixed high temperature T_1 from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature T_1 .

(2) **Sink.** The sink should be at a fixed lower temperature T_2 to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at T_2 .

(3) **Working Substance.** A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the *working substance*.



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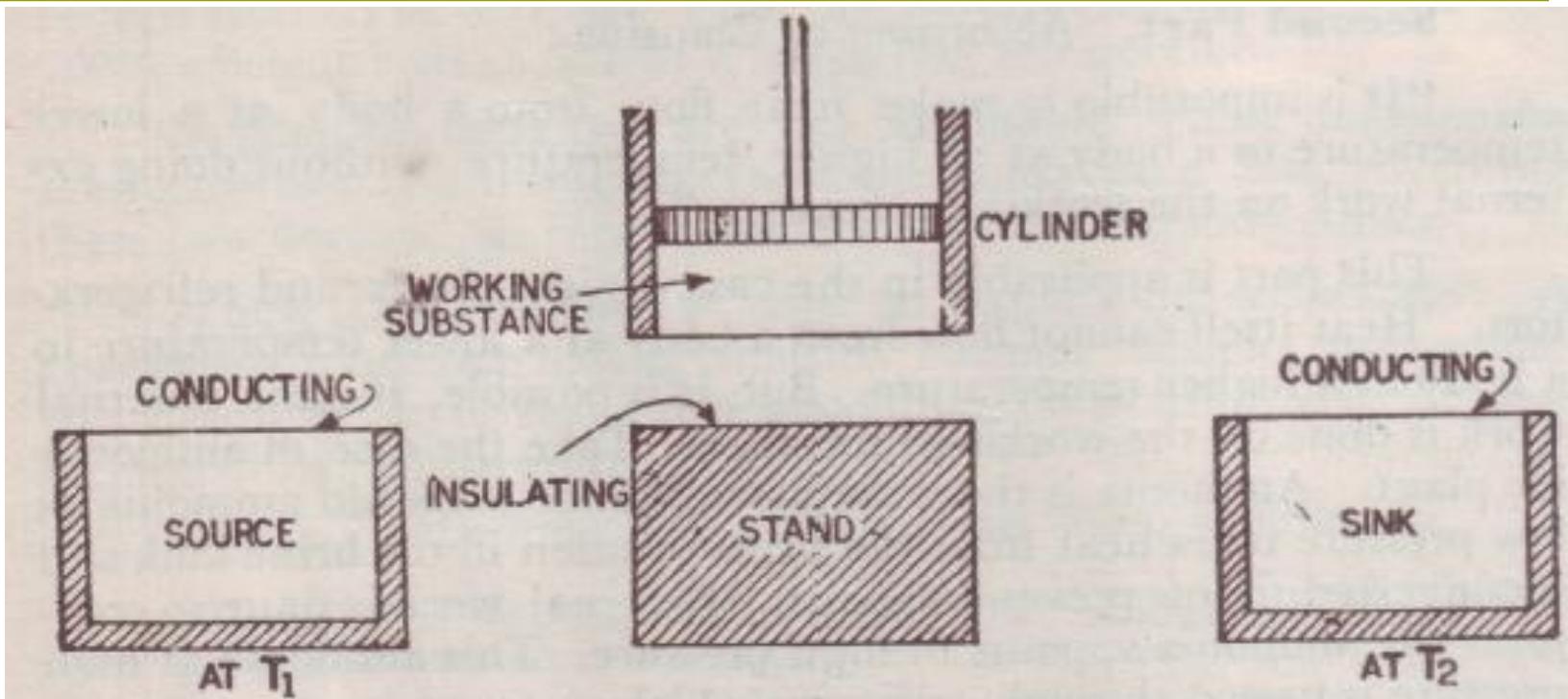


Fig. 6.12

A perfect non-conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6.12).

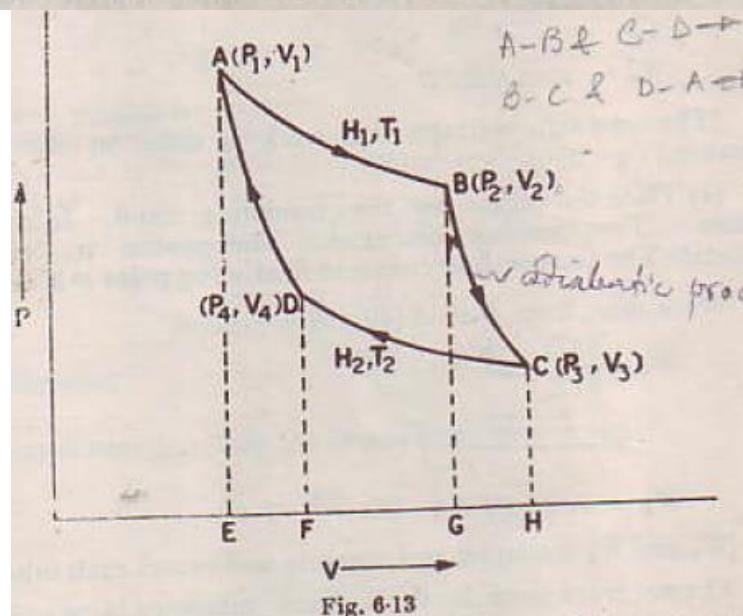
A perfectly non-conducting stand is also provided so that the working substance can undergo adiabatic operation.



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Carnot's Cycle

(1) Place the engine containing the working substance over the source at temperature T_1 . The working substance is also at a temperature T_1 . Its pressure is P_1 and volume is V_1 , as shown by the point A in Fig. 6-13. Decrease the pressure. The volume of the working substance increases. Work is done by the working substance. As the bottom is perfectly conducting to the source at temperature T_1 , it absorbs heat. The process is completely isothermal. The temperature remains constant. Let the amount of heat





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absorbed by the working substance be H_1 at the temperature T_1 .
The point B is obtained.

Consider one gram molecule of the working substance.

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P_1 dV = RT_1 \log \frac{V_2}{V_1} \quad [P_1 V_1 =$$

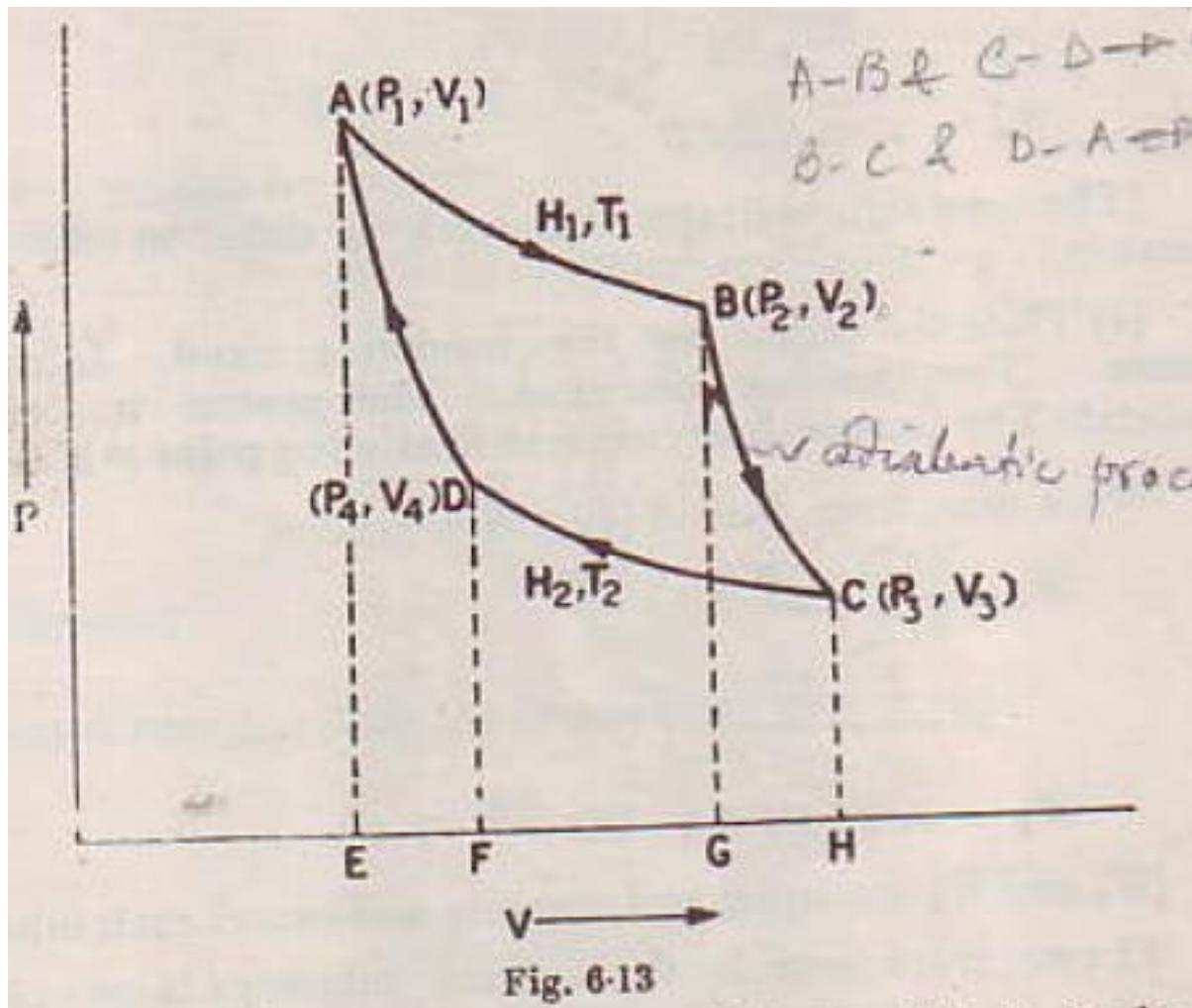
... (i)

$P_1 V_1 = RT_1$

(2) Place the engine on the stand having an insulated top.
Decrease the pressure on the working substance. The volume



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increases. The process is completely adiabatic. Work is done by the working substance at the cost of its internal energy. The temperature falls. The working substance undergoes adiabatic change from B to C . At C the temperature is T_2 (Fig. 6.13).

Work done from B to C (adiabatic process)

$$\begin{aligned}
 W_2 &= \int_{V_2}^{V_3} P \cdot dV \\
 &= K \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \\
 &= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma} \\
 &= \frac{P_3V_3 - P_2V_2}{1-\gamma} \\
 &= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma-1} \\
 W_2 &= \text{Area } BOHG
 \end{aligned}$$

But $PV^\gamma = \text{constant} = K$
 $P_2V_2 = RT_1$

$P_3V_3 = RT_2$ ✓

$P_3V_3^\gamma = P_2V_2^\gamma = K$

... (ii)



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(3) Place the engine on the sink at temperature T_3 . Increase the pressure. The work is done on the working substance. As the base is conducting to the sink, the process is isothermal. A quantity of heat H_2 is rejected to the sink at temperature T_3 . Finally the point D is reached.

Work done from C to D (isothermal process)

$$\begin{aligned} W_3 &= \int_{V_3}^{V_4} P dV \\ &= RT_3 \log \frac{V_4}{V_3} \\ &= -RT_3 \log \frac{V_3}{V_4} \end{aligned} \quad \dots(iii)$$

$$W_3 = \text{area } CHFD$$

(The -ve sign indicates that work is done on the working substance.)



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(4) Place the engine on the insulating stand. Increase the pressure. The volume decreases. The process is completely adiabatic. The temperature rises and finally the point *A* is reached.

Work done from *D* to *A* (adiabatic process).

$$W_4 = \int_{V_4}^{V_1} P dV$$
$$= - \frac{R(T_1 - T_4)}{\gamma - 1}$$

$$W_4 = \text{Area } DFEA \quad \dots(iv)$$

[W_2 and W_4 are equal and opposite and cancel each other.]

The net work done by the working substance in one complete cycle

$$\begin{aligned} &= \text{Area } ABGE + \text{Area } BCHG - \text{Area } CHFD \\ &\quad - \text{Area } DFEA \\ &= \text{Area } ABCD \end{aligned}$$



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The net amount of heat absorbed by the working substance

$$= H_1 - H_2$$

Net work = $W_1 + W_2 + W_3 + W_4$

$$= RT_1 \log \frac{V_2}{V_1} + \frac{R(T_1 - T_2)}{\gamma - 1} - RT_2 \log \frac{V_3}{V_4} - \frac{R(T_1 - T_2)}{\gamma - 1}$$

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \quad \dots(v)$$

The points A and D are on the same adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad \dots(vi)$$



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The points B and C are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$
$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1} \quad \dots(vii)$$

From (vi) and (viii)

$$\left(\frac{V_1}{V_4} \right)^{\gamma-1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1}$$

or

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

or

$$\frac{V_3}{V_1} = \frac{V_2}{V_4}$$

From equation (v)

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_1}$$

$$W = R \left[\log \frac{V_2}{V_1} \right] [T_1 - T_2]$$

$$W = H_1 - H_2$$



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Efficiency

$$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from A to B only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$$\therefore \eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1 - T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)}$$

$$\eta = 1 - \frac{H_2}{H_1}$$

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

....(viii)



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The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat H_2 is taken from the sink and external work is done on the working substance and heat H_1 is given to the source at a higher temperature.

The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

All practical engines have an efficiency less than the Carnot's engine.



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Problem

Imagine a Carnot engine that operates between the temperatures $T_H = 850\text{ K}$ and $T_L = 300\text{ K}$. The engine performs 1200 J of work each cycle, which takes 0.25 s.

- (a) What is the efficiency of this engine?

- (b) What is the average power of this engine?

- (c) How much energy $|Q_H|$ is extracted as heat from the high-temperature reservoir every cycle?

- (e) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?



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Solution

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300 \text{ K}}{850 \text{ K}} = 0.647 \approx 65\%. \text{ (Answer)}$$

$$P = \frac{W}{t} = \frac{1200 \text{ J}}{0.25 \text{ s}} = 4800 \text{ W} = 4.8 \text{ kW}. \text{ (Answer)}$$

$$|Q_H| = \frac{W}{\varepsilon} = \frac{1200 \text{ J}}{0.647} = 1855 \text{ J}. \text{ (Answer)}$$
$$|Q_L| = |Q_H| - W \\ = 1855 \text{ J} - 1200 \text{ J} = 655 \text{ J}. \text{ (Answer)}$$

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855 \text{ J}}{850 \text{ K}} = +2.18 \text{ J/K}. \text{ (Answer)}$$

Similarly, for the *negative* transfer of energy Q_L to the low-temperature reservoir at T_L , we have

$$\Delta S_L = \frac{Q_L}{T_L} = \frac{-655 \text{ J}}{300 \text{ K}} = -2.18 \text{ J/K}. \text{ (Answer)}$$

Note that the net entropy change of the working substance for one cycle is zero, as we discussed in deriving Eq. 20-10.



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Entropy

If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad (\text{change in entropy defined}).$$

Here Q is the energy transferred as heat to or from the system during the (reversible) process, and T is the temperature of the system in kelvins.



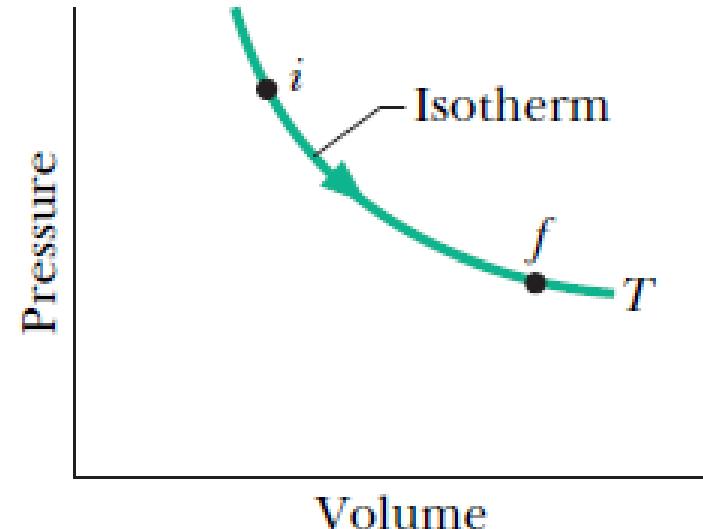
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Entropy of an Isothermal Process

$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

$$\int dQ = Q,$$

$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}).$$





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Entropy & 2nd Law of Thermodynamics



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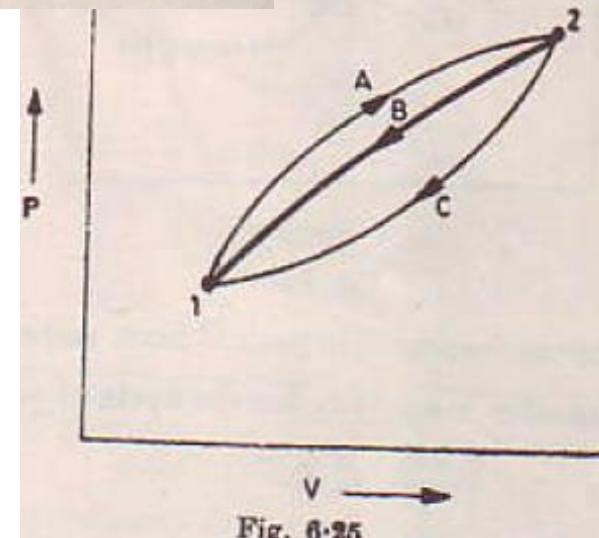
Entropy and 2nd Law of Thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B (Fig. 6.25). As this is a reversible cyclic process

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0$$

... (i)





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Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C .

For this reversible cyclic process

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \quad \dots(iii)$$

From equations (i) and (iii)

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \quad \dots(iv)$$



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This shows that $\int \frac{\delta H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\int \frac{\delta H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called entropy. Entropy is a thermodynamical property and is defined by the relation

$$dS = \frac{\delta H}{T} \quad \dots(iv)$$

or $S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \quad \dots(v)$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.



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Change of Entropy in an Irreversible Process



Consider a reversible cycle where the state is changed from 1 to 2 along the path A and 2 to 1 along the path B (Fig. 6.26).
For a reversible cyclic process

$$\oint \delta H = 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \quad \dots(i)$$

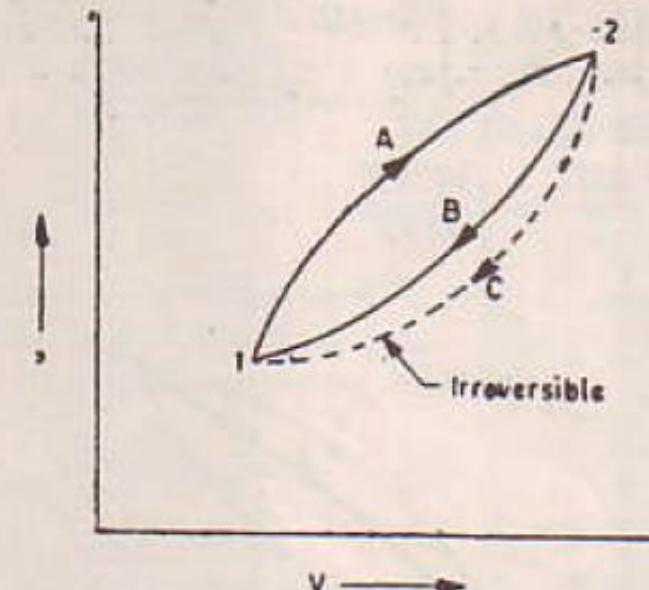


Fig. 6.26



Now consider an irreversible path C from state 2 to state 1.

Applying Clausius inequality for the cycle of processes A and C

$$\int \frac{\delta H}{T} < 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} < 0 \quad \dots(iii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} > 0$$

Since path B is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore dS > \frac{\delta H}{T} \quad \dots(iv)$$

or $S_2 - S_1 > \int_1^2 \delta H$ 0 $\dots(iv)$



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To conclude,

For a reversible process

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T}$$

and for an irreversible process

$$S_2 - S_1 > \int_1^2 \frac{\delta H}{T}$$

Equation (4) clearly states that the irreversible process always tends to enhance the entropy of a system.



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Change of Entropy in a Reversible Process



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Consider a complete reversible process [Carnot's cycle] $ABCD A$ (Fig. 6.28). From A to B , heat energy H_1 is absorbed by the work-

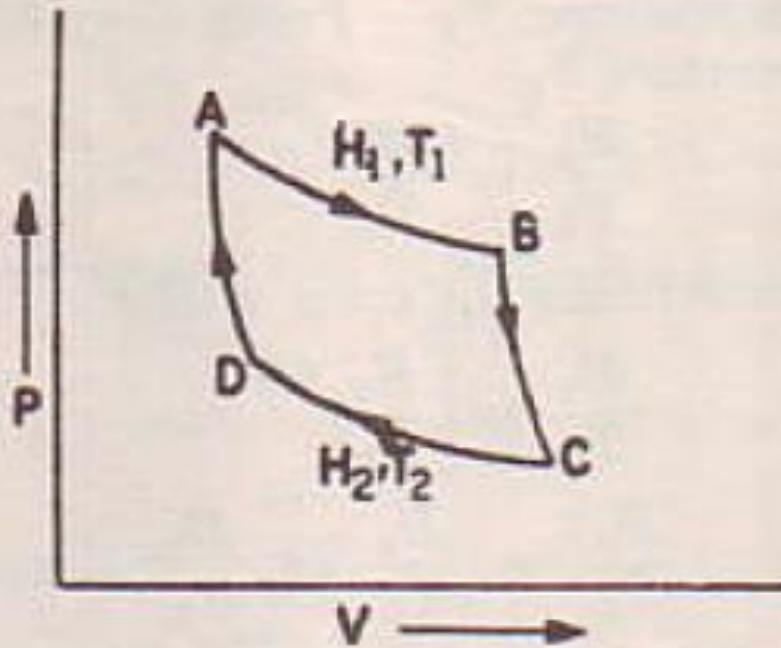


Fig. 6.28



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ing substance at temperature T_1 . The gain in entropy of the working substance from A to $B = H_1/T_1$. (H_1/T_1 is the decrease in entropy of the source from which the amount of heat H_1 is drawn at a temperature T_1). From B to C there is no change in entropy because BC is an adiabatic. From C to D , heat energy H_2 is rejected by the working substance at a temperature T_2 . The loss in entropy of the working substance from C to $D = H_2/T_2$. (H_2/T_2 is also the gain in entropy of the sink to which the amount of heat H_2 is rejected at a temperature T_2). From D to A there is no change in entropy. Thus



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the total gain in entropy by the working substance in the cycle *ABCDA*

$$= \frac{H_1}{T_1} - \frac{H_2}{T_2}$$

But for a complete reversible process

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Hence the total change in entropy of the working substance in a complete reversible process

$$= \oint dS = \frac{H_1}{T_1} - \frac{H_1}{T_2} = 0.$$



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Maxwell's Thermodynamic Relations



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From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities viz. pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\delta H = dU + PdV$$

$$dU = \delta H - PdV$$

or

From the second law of thermodynamics,

$$dS = \frac{\delta H}{T}$$

$$\delta H = TdS$$

or



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Substituting this value of δH in the first equation

$$dU = TdS - PdV \quad \dots(1)$$

Considering S , U and V to be functions of two independent variables x and y [here x and y can be any two variables out of P , V , T and S],

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$



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Substituting these values in equation (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \right] dx + \left[T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \right] dy$$

Comparing the coefficients of dx and dy , we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \quad \dots(ii)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \quad \dots(iii)$$



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Differentiating equation (ii) with respect to y and equation (iii) with respect to x

$$\begin{aligned}\frac{\partial^2 U}{\partial y \cdot \partial x} = & \left(\frac{\partial T}{\partial y} \right)_x \left(\frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} \\ & - \left(\frac{\partial P}{\partial y} \right)_x \left(\frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial^2 U}{\partial x \partial y} = & \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} \\ & - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_x - P \frac{\partial^2 V}{\partial x \partial y}\end{aligned}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or vice versa is the same.



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It means dU is a perfect differential

$$\therefore \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x} \text{ and}$$

$$\begin{aligned} & \left(\frac{\partial T}{\partial y} \right)_z \left(\frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y} \right)_z \left(\frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x} \\ &= \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} \\ & \quad - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_x - P \frac{\partial^2 V}{\partial x \partial y} \end{aligned}$$

Simplifying,

$$\begin{aligned} & \left(\frac{\partial T}{\partial y} \right)_z \left(\frac{\partial S}{\partial x} \right)_y - \left(\frac{\partial P}{\partial y} \right)_z \left(\frac{\partial V}{\partial x} \right)_y \\ &= \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_x \quad ... (iv) \end{aligned}$$

Here x and y can be any two variables out of P, V, T and S .



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(1) Taking T and V as independent variables and

$$x = T$$

and

$$y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \text{...}(v)$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \left(\frac{\partial H}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{...}(vi)$$



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✓ (2) Taking T and P as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad | \quad \dots \text{(vii)}$$

or

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P \quad | \quad \dots \text{(viii)}$$



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(3) Taking S and V as independent variables and

$$x = S$$

and

$$y = V$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \cancel{\text{Eq}}$$

or

$$\left(\frac{\partial T}{\partial V} \right)_S = -T \left(\frac{\partial P}{\partial H} \right)_V \quad ... (x)$$



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✓ (4) Taking S and P as independent variables and

$$x = S$$

and

$$y = P$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \text{ |||} \quad \dots(iv)$$

or

$$\left(\frac{\partial T}{\partial P} \right)_S = T \left(\frac{\partial V}{\partial H} \right)_P \quad \dots(vii)$$



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(5) Taking P and V as independent variables and

$$x = P \quad \text{and} \quad y = V$$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial S}{\partial V} \right)_P - \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial P} \right)_V = 1 \quad \dots \text{(xiii)}$$



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(6) Taking T and S as independent variables and
 $x = T$ and $y = S$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0, \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1 \quad \dots(iv)$$



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Sample Questions

8. Outline the essential features of the kinetic theory of gases.

9. Derive an expression for the pressure of an ideal gas on the basis of the kinetic theory of gases. Prove that the pressure of a gas is equal to $\frac{2}{3}$ of the translational kinetic energy of the molecules in a unit volume of gas.



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Sample Questions

10. Apply the kinetic theory of gases to account for the simple gas laws.
11. Find an expression for the energy of a gas on the kinetic theory of gases. Give the kinetic interpretation of the temperature.
12. What is meant by mean free path of a gas molecule? Applying the assumptions of the kinetic theory of gases show that the mean free path is equal to $\lambda = \frac{kT}{\sqrt{2.\pi p d^2}}$, where the symbols carry their standard meanings.



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Sample Questions

13. Show that the mean free path of a gas molecule is directly proportional to its absolute temperature, inversely proportional to its pressure, and inversely proportional to its density.
14. Explain the essential features of the Brownian motion.
15. Explain the terms ‘degrees of freedom’ and ‘the law of equipartition of energy’.
16. Applying the kinetic theory of gases, find the ratio of the two specific heats (is given by $1 + \frac{2}{f}$, where f is the degrees of freedom of the gas) for a monatomic, diatomic, and triatomic gases.



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Sample Questions

17. Briefly discuss the considerations which led Van der Waal's to modify the gas equations. Derive the Van der Waal's equation of state and hence find the expressions for the critical constants in terms of Van der Waal's constants a and b .
18. Derive the Van der Waal's equation of state and hence find the expressions for the Van der Waal's constants a and b .
19. What are meant by critical constants of a gas? Calculate the values of these constants.



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Sample Questions

20. Explain the corrections introduced by Van der Waal's in the gas equation. Show that for a gas obeying Van der Waal's equation: $\frac{RT_c}{P_c V_c} = \frac{8}{3}$, where the symbols carry their standard meanings.
21. Derive the adiabatic gas equation: $PV^\gamma = \text{constant}$, where the symbols carry their standard meanings.
22. Define entropy. Write up its physical significance. Show that the entropy of a perfect gas remains constant in a reversible process but increases in an irreversible process.



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Sample Questions

23. Discuss the second law of thermodynamics and the principle of increase of entropy.
24. Define entropy. Show that the change of entropy of a substance in a cyclic process is zero.
25. State and prove Carnot's theorem.
26. Define entropy. State and prove the principle of increase of entropy.



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Sample Questions

25. What is meant by a reversible process? Define the Carnot's theorem, and show that all reversible engines working between the same two temperatures have the same efficiency.
26. State the first law of thermodynamics. Express it mathematically and explain its physical significance.
27. Prove that the efficiency of a Carnot engine using an ideal gas as a working substance is $\eta = \frac{T_1 - T_2}{T_1}$, where the symbols carry their standard meanings.



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Sample Questions

28. State and explain third law of thermodynamics.
29. State and explain the second law of thermodynamics.
30. Define adiabatic, isothermal, isobaric, and isochronic processes.
31. Derive a relation between the volume and temperature for a perfect gas during an adiabatic transformation ($TV^{\gamma-1} = \text{Constant}$).



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Sample Questions

32. For a perfect gas during an adiabatic transformation, derive the relationship between the pressure and temperature ($T^\gamma P^{1-\gamma} = \text{Constant}$).

33. Derive the following Maxwell's thermodynamic relations:

$$(i) \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_P$$

$$(ii) \left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

$$(iii) \left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P$$



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Sample Questions

$$(IV) \left(\frac{\partial T}{\partial V} \right)_S = -T \left(\frac{\partial P}{\partial H} \right)_V$$

$$(V) \left(\frac{\partial T}{\partial P} \right)_S = T \left(\frac{\partial V}{\partial H} \right)_P$$

$$(VI) \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial S}{\partial V} \right)_P - \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial P} \right)_V = 1$$

$$(VII) \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial V}{\partial S} \right)_T - \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial V}{\partial T} \right)_S = 1$$



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Home Work

Solve a few problems related to the theory we have studied in this chapter



Thank You for Listening



Physics is hopefully simple but Physicists are not