

**ESO201A**  
**Lecture#13**  
**(Class Lecture)**

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By

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## Clarifications regarding the Example Problem in Lecture #12

van der Waals Eq.

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$v_{cr} = 3b$$

$$T_{cr} = \frac{8a}{27bR}$$

$$P_{cr} = \frac{a}{27b^2}$$

These expressions can be used when 'a' and 'b' are known from the experimental data fit. Thus,  $v_{cr}$ ,  $P_{cr}$  and  $T_{cr}$  can be calculated.

$$a = \frac{27 R^2 T_{cr}^2}{64 P_{cr}}$$

$$b = \frac{R T_{cr}}{8 P_{cr}}$$

These expressions are used to obtain 'a' and 'b' when the experimental values of  $P_{cr}$  and  $T_{cr}$  are known.

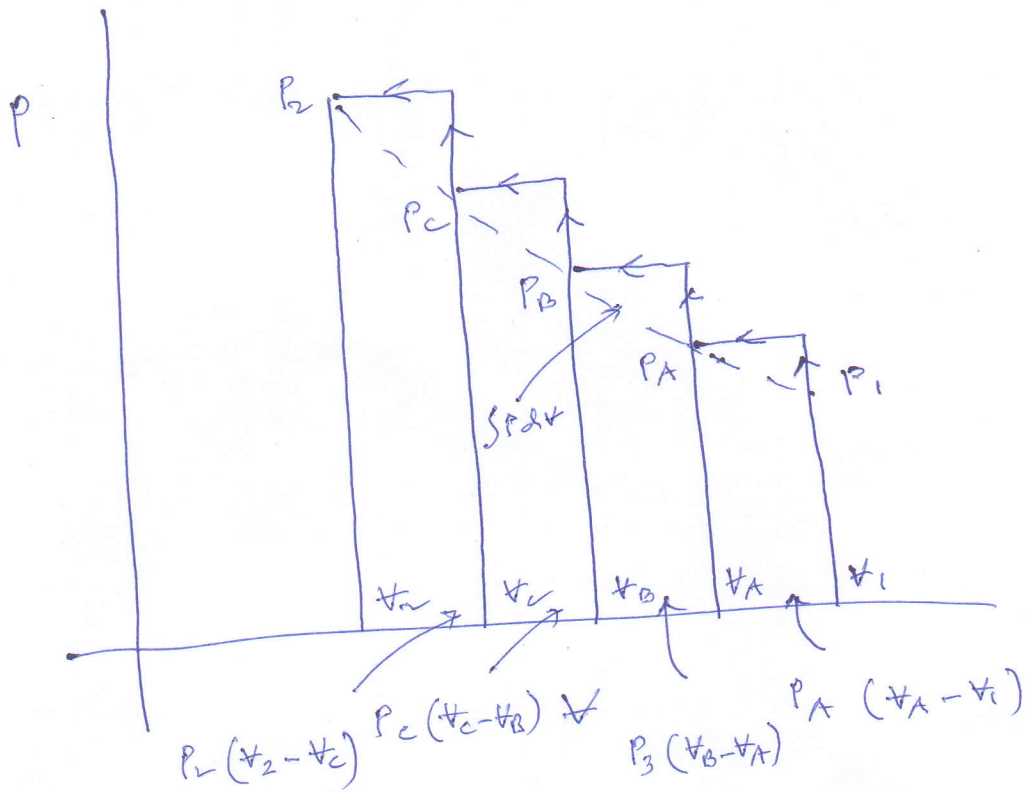
## Conditions for Reversibility

Reversible processes are always quasi-equilibrium processes and irreversible processes are always nonquasi-equilibrium processes.

However, quasi-equilibrium processes are not necessarily reversible.

A reversible process is defined as a process that can be reversed without leaving any trace on the surroundings. That is, both the system and the surroundings are returned to their initial states at the end of the reverse process. This is possible only if the net heat and net work exchange between the system and the surroundings is zero for the combined (original and reverse process).

# Irreversible Compression



$$W_{\text{irrev, comp}} > \int P dV$$

$$P_1 \rightarrow P_A \rightarrow P_B \rightarrow P_C \rightarrow P_2$$

## Polytropic Processes

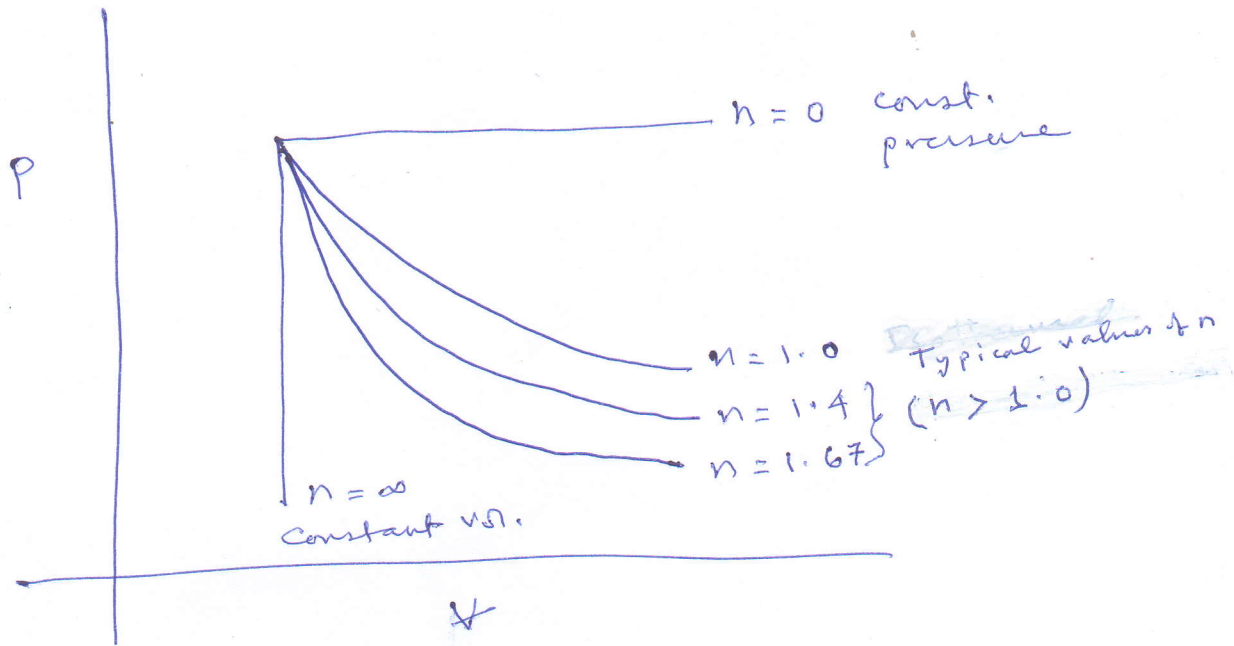
The  $P-v$  curves obtained in real engines can be analyzed accurately, and it is found that actual curves (of irreversible compressions and expansions) fit, with reasonable accuracy, curves of the form:

$$Pv^n = C$$

where  $C$  is a constant and  $n$  is chosen to allow this equation to fit an actual curve. ' $P$ ' is absolute pressure.

The index  $n$  can have a considerable range of values leading to a 'family' of processes, which are called polytropic, meaning many paths.

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$$W_b = \int_1^2 P dV = c \int_1^2 \frac{dV}{V^n}$$

since

$$P = \frac{c}{V^n}$$

$$= c \left( \frac{V^{-n+1}}{-n+1} \right)_1^2$$

$$= \frac{c}{1-n} \left( V_2^{1-n} - V_1^{1-n} \right)$$

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

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

Substituting  $c = PV^n$  at both states

For an ideal gas ( $PV = nRT$ )  
 $W_b = \frac{nR(T_2 - T_1)}{1-n}$   
 $n \neq 1$



Note that

$$n = 0 \quad P = \text{const.}$$

$$W_b = 0 \quad \text{when } n = \infty \leftarrow \text{const. vol. process.}$$

$$n = 1.0$$

$$P \propto \text{const.}$$

$$n = \begin{Bmatrix} 1.4 \\ 1.67 \\ 1.8 \end{Bmatrix}$$

Typical values of  $n$  ( $n > 1$ )For  $n = 1$ 

$$W = \frac{0}{0} \text{ since}$$

$$W = \frac{P_2 V_2 - P_1 V_1}{1-n} = \frac{c - c}{1-1} = \frac{0}{0}$$

For  $n = 1$ 

$$\begin{aligned} W_b &= \int_1^2 P dV = \int_1^2 c V^{-1} dV \\ &= c \int_1^2 \frac{dV}{V} = c \left| \ln V \right|_1^2 \\ &= P V \ln \left( \frac{V_2}{V_1} \right) \end{aligned}$$

Since

$$P_1 V_1 = P_2 V_2$$

$$W_b = P_1 V_1 \ln \frac{V_2}{V_1}$$

$$= P_2 V_2 \ln \frac{V_2}{V_1}$$

$$= P_1 V_1 \ln \frac{P_1}{P_2}$$

$$= P_2 V_2 \ln \frac{P_1}{P_2}$$

$$\Rightarrow \boxed{W_b = P V \ln \left( \frac{V_2}{V_1} \right)}$$

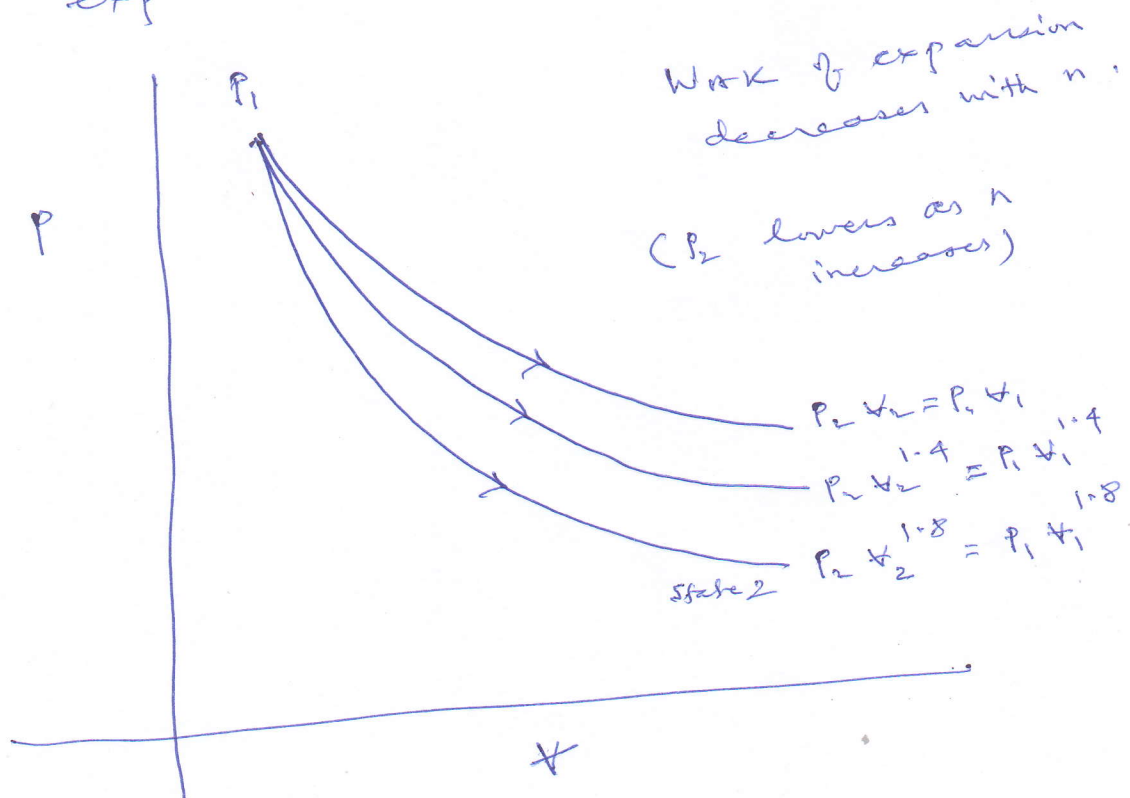
$$W_b = m R T \ln \left( \frac{V_2}{V_1} \right)$$

Holds good  
for an ideal  
gas boundary  
work for an  
isothermal  
process.

The work of an expansion for  $n$  greater than 1 is less than it is when  $n$  is equal to 1.

So what controls the value of  $n$  and the amount of work we shall get in a particular expansion?

We will see later that  $n$  is dependent on a second interaction of heat taking place simultaneously with the work interaction during an expansion or compression.





## First Law of Thermodynamics

A series of experiments carried out by Joule between 1843 and 1848 form the basis for the first law of thermodynamics.

In Joule's paddle wheel experiment (Fig. 1), a known amount of water was taken in a rigid and insulated vessel. The vessel was provided with a paddle wheel driven by mass  $m$  through a distance  $(Z_1 - Z_2)$ . The work done on the system was computed in terms of the change in the potential energy of the mass  $m$ .

The thermometer, immersed in water, was used to determine the change in the state of the system. The temperature of the water was found to increase after the work had been performed on the system. Once the system has come to 'rest', it was brought into contact with a water bath and the system was allowed to come to the initial state.

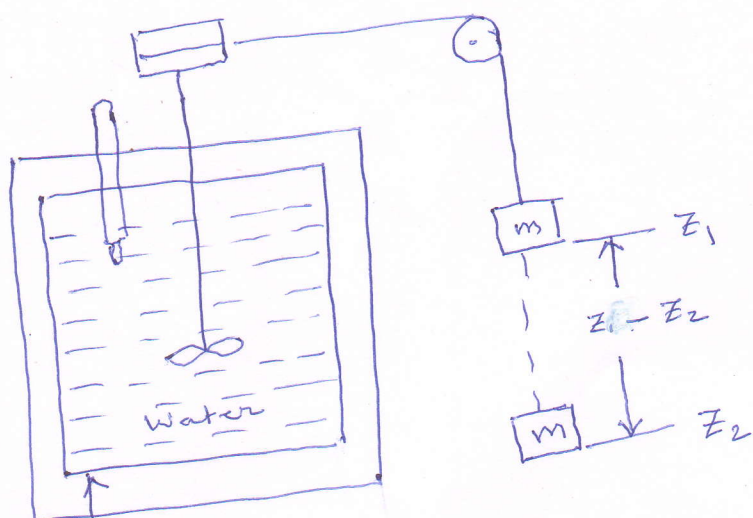


Fig. 1(a)  
Rigid and insulated container

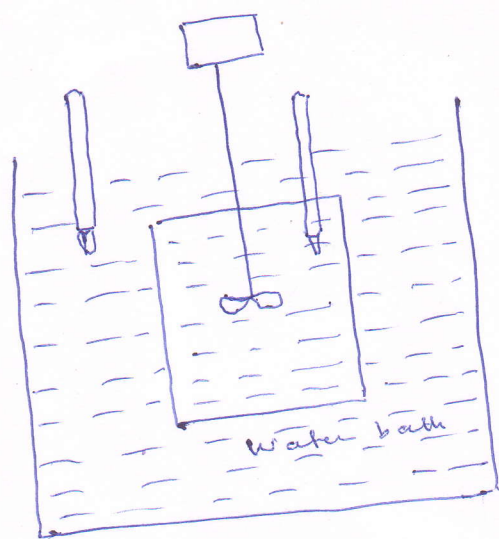


Fig. 1(b)

Fig. 1 Schematic diagram of  
Joule's paddle wheel experiment

The amount of energy transferred as heat from the system to the bath was estimated in terms of temperature rise of the bath. Thus, the system went through a cyclic change.

Joule carried out many experiments involving different types of work interactions. In some experiment, the water was heated electrically (electrical work converted to heat).

Joule found that the net work done on the system was always equal to the net energy removed from the system as heat irrespective of the type of work interaction, the rate at which work was done on the system and the method employed for transferring the energy in the form of work into heat.

(4)

It can be noted that each of Joule's experiments involved an irreversible process through which the system underwent a change of state. It is obvious that the temperature of the system cannot be reduced adiabatically.

The following observations can be made from Joule's experiments.

1. State 2 can be reached from state 1 following an adiabatic process.
2. But state 1 cannot be reached from state 2 following an adiabatic process.
3. However, state 1 can be reached from state 2 by following an entirely different process.



It is possible for the system to follow  $1 \rightarrow 2$  or  $2 \rightarrow 1$  adiabatically, but not both.

Also, when a system is taken from state 1 to state 2, the work done on the system is independent of the process followed by the system.

It is observed that

$$\oint \delta Q = \oint \delta W$$

(from system)                      (on system)

$$\text{or } \oint \delta Q - \oint \delta W = 0$$

(from system)                      (on system)

where  $\oint$  denotes the integral over a cycle.

Therefore, the first law of thermodynamics can be stated as:

Whenever a system undergoes a cyclic change, however complex the cycle may be, the algebraic sum of the work transfer is equal to the algebraic sum of energy transfers as heat.

⑥

It may be noted that there is no restriction on the type of process the system has undergone. Therefore, the first law of thermodynamics is applicable to reversible as well as irreversible processes.