## HEAT AND WORK

As stated earlier a given system may interact with the surroundings and exchange energy with it via thermal interaction, mechanical interaction and diffusive interaction. In thermodynamics we shall confine ourselves to systems of fixed mass so as to rule out the possibility of diffusive interaction. So for such a system only two types of energy transfer occurs:
i. Heat energy vial thermal interaction
ii. Work energy by mechanical interaction.

Let us discuss these two types of energy
Heat: Heat is a form of energy which can be identified only when it is transit. It is defined as that form of energy which flows from or to a system by virtue of unbalanced temperature between the system and surrounding. Only the amount of heat flowing to or from a system can be detected and measured. But the absolute heat content of a system cannot be determined. The amount of heat flowing from or to a system depends on the process via which the heat flow occurs. So heat transferred is a path dependent function and denoted by an inexact differential $\delta \mathbf{Q}$. By convention heat transferred to a system is taken as positive and heat flowing out of a system is taken as negative with respect to the system.


Positive heat transferred w.r.to the system


Negative heat transferred w.r.to the system

A process in which no heat is transferred from or to a system is called adiabatic process
A process in which the temperature of the system remains constant is called isothermal process

Work: Work is also is a form of energy which can be identified only when it is transit. It is defined as that form of energy which flows from or to a system by virtue of unbalanced pressure between the system and surrounding. Only the amount of done on or by a system can be detected and measured. But the absolute work content of a system cannot be determined. The amount of work done on or by a system depends on the process via which the mechanical interaction occurs. So work done on or by a system is a path dependent function and denoted by an inexact differential $\delta \mathbf{W}$. By convention work done by a system is taken as positive and work done on a system is taken as negative with respect to the system.

The fig. shows a insulated piston fitted to a cylinder
 enclosing some gas and isolated from the surroundings. If the gas is compressed by pushing the piston inwards work is done on the gas and is negative. If on the other hand the
gas is allowed to expand the push the piston outwards, work is done by the system and is positive.

## Work done by a system during a quasistatic expansion:



Fig. 3.1: Work done by a system of any arbitrary shape.
Let a flexible container of arbitrary shape, enclosing some gas at pressure ' $P$ ' be considered. The walls of the container are impermeable and thermally insulated. ' $\mathrm{P}_{0}$ ' is the external uniform pressure which is very slightly less than ' $P$ '. Let ' $d A$ ' be an elementary area on the wall of the container. As ' $P$ ' is infinitesimally greater than ' $\mathrm{P}_{0}$ ', so the gas will expand and the wall of the container will be displaced by a length 'ds' in the direction making an angle ' $\theta$ ' with the normal $\hat{n}$ to dA. So the corresponding force on the section dA is:

$$
\begin{equation*}
\mathrm{F}=\mathrm{PdA} \quad(\text { in a direction } \widehat{\mathbf{n}}) \tag{3.1}
\end{equation*}
$$

So the corresponding work dine is:

$$
\begin{equation*}
\Delta \mathrm{W}=\overrightarrow{\mathrm{F}} \cdot \overrightarrow{\mathrm{ds}}=\mathrm{F} d s \operatorname{Cos} \theta=(\mathrm{PdA}) \mathrm{ds} \cdot \operatorname{Cos} \theta=\mathrm{dA} \cdot \mathrm{ds} \cdot \operatorname{Cos} \theta \cdot \mathrm{P}=\Delta \mathrm{v} \cdot \mathrm{P}=\mathrm{P} \Delta \mathrm{v} \tag{2.2}
\end{equation*}
$$

Where $\Delta v=d A . d s . \operatorname{Cos} \theta$. = volume swept out by ' dA ' in its motion through ' ds '. Summing over all the area elements of the boundary of the system the work done by it is:

$$
\begin{equation*}
\delta \mathrm{W}=\sum_{\mathrm{A}} \Delta \mathrm{~W}=\mathrm{P} \sum \Delta \mathrm{v}=\mathrm{PdV} \tag{3.2}
\end{equation*}
$$

Where $\mathrm{dV}=$ volume change of the container corresponding to ' ds '
In a finite quasistatic process in which the volume changes from ' $\mathrm{V}_{\mathrm{i}}$, to ${ }^{\prime} \mathrm{V}_{\mathrm{f}}$ ' continuously the work done by the system is given by :

$$
\begin{equation*}
W-\int_{V_{f}}^{V_{i}} P d V \tag{3.3}
\end{equation*}
$$

## Work done by a system in a process is the area under P-V curve



Fig. 3.2. P-V curve of an expanding system
$A B$ is a graph showing the variation of pressure with change of volume. The direction of the arrow shows that the system is expanding. So work is being done by the system.

Let the entire curve $A B$ be assumed to be split into a ' $n$ ' number of portions of equal width $\Delta \mathrm{V}$ along the volume ( $\mathrm{n} \rightarrow \infty$ as the curve is continuous). $\Delta \mathrm{V}$ is so small that the pressure does not change appreciably within that small change of volume. For the first strip the pressure is practically constant at $P_{1}$. For the seconds strip the pressure is practically constant at $P_{2}$ and so on. Hence the strips can be considered as more or rectangles. So the work done by the system in the process represented by the part of the graph within the first strip is

$$
W_{1}=P_{1} . \Delta V \approx \text { area under the first strip(Shaded part) }
$$

Similarly $\quad W_{2}=P_{2} \Delta V \approx$ area under the second strip

$$
\mathrm{W}_{3}=\mathrm{P}_{3} \Delta \mathrm{~V} \approx \text { area under the third strip }
$$

$$
W_{n}=P_{n} \Delta V \approx \text { area under the } \mathrm{n}^{\text {th }} \text { strip }
$$

Adding all of them strip by strip the total work done by the system is hence equal to the sum of the area of all strips i.e. the area under the $\mathrm{P}-\mathrm{V}$ curve. This proves that the work done by a system in a process is the area under corresponding P-V curve.

$$
\begin{equation*}
\mathrm{W}=\lim _{\mathrm{n} \rightarrow \infty, \Delta \mathrm{~V} \rightarrow 0}\left\{\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{P}_{\mathrm{i}} \Delta \mathrm{~V}\right\}=\int_{\mathrm{V}_{\mathrm{I}}}^{\mathrm{V}_{\mathrm{f}}} \mathrm{PdV} \text { (as process is continuous) } \tag{3.4}
\end{equation*}
$$

This work is positive work. If the arrow in $A B$ had been along $B A$, the system would have been compressed and work would have been done on the system which is negative work.


Positive work


Negative work

Corollary I: If the system takes a different path to go from $A$ to $B$, the area under that curve will be different from the previous one and amount of work done will be different as is evident from the fig. below. Thus work done by a system is path dependent.


Fig: 3.3: $P$-V curves of a system along three different paths ' $I$ ', 'II' and 'III' connecting teo terminal states $A$ and $B$

Corollary II: Work done by a system in a cyclic process is equal to the area enclosed by the cycle


Fig. 3.4: P-V diagram of a system undergoing a cyclic process
$A$ system goes from state $A$ to $B$ via path $I$. The work done by it is the area $A Q B V_{f} V_{i} A$. This work is positive as the system expands. While returning from the state $B$ to initial state $A$ the system follows a different path II. The work done is the area $B R A V_{f} V_{i} B$. This work is negaitive as the system is compressed. So the total work done by the system in the cycle is:

$$
\mathrm{W}=\operatorname{area} A Q B V_{f} V_{i} \mathrm{~A}-\mathrm{BRAV}_{\mathrm{f}} \mathrm{~V}_{\mathrm{i}} \mathrm{~B}=\text { area } \mathrm{AQBRA}=\text { Area enclosed by the cycle }
$$

## Work Done In Other Processes

## i) Work in changing the Length of a wire under tension



Let the wire of initial length ' $L_{i}$ ' be suspended from a fixed point O on a rigid support. The Other end is subjected to an external stretching force ' $\mathrm{F}_{\mathrm{e}}$ '. The work done on the wire due to a small elongation dL is : $\quad \delta \mathrm{W}=-\mathrm{F}_{\mathrm{e}} \mathrm{dL}$

The negative sign denotes that work is done on the wire during elongation. If the external force $F_{e}$ is maintained only slight different from the tension ' $\tau$ ' all the time, the stretching is quasitatic, and : $\delta \mathrm{W}=-\tau \mathrm{dL}$

The total work done in elongating the wire from length ' $\mathrm{L}_{\mathrm{i}}$ ' to ' $\mathrm{L}_{\mathrm{f}}$ ' is :

$$
\begin{equation*}
\mathrm{W}=-\int_{\mathrm{L}_{\mathrm{i}}}^{\mathrm{L}_{\mathrm{f}}} \tau \mathrm{dL} \tag{3.6}
\end{equation*}
$$

ii) Work done in changing the area of a surface film


Let a soap film be considered to be formed on a rectangular wire frame $A B C D$, having a sliding crossbar BC. The film has two free surfaces. Inward forces due to surface tension are exerted by the film at its boundary. The inward force exerted by a film surface per unit length of its boundary is called the surface tension $\sigma$.

The cross bar is kept in equilibrium by an external force ' $F_{\mathrm{e}}$ ' pointing outwards.
If ' L ' be the length of the cross bar then the total inward force is : $\mathrm{F}_{\mathrm{i}}=2 \sigma \mathrm{~L}$, considering both the free surfaces. When the cross bar moves through a distance ' $d x$ ' under the effect of ' $F_{e}$ ', the work done on the film against $F_{i}$ is:
$\delta W=-F_{e} d x$ $\qquad$
The negative sign indicates that work is done on the film against ' $F_{i}$
For a quasistatic process: $\mathrm{F}_{\mathrm{e}} \approx \mathrm{F}_{\mathrm{i}}=2 \sigma \mathrm{~L}$. This gives: $\delta \mathrm{W}=-2 \sigma \mathrm{~L} d x=-\sigma d \mathrm{~A}$
Where $d A=2 L d x=$ increase in surface area of the film. The total work done in increasing the surface area of the film from ' $A_{i}$ ' to $A_{f}$ ' is:

$$
\begin{equation*}
\mathrm{W}=-\int_{\mathrm{A}_{\mathrm{i}}}^{\mathrm{A}_{\mathrm{f}}} \tau \mathrm{dL} \tag{3.8}
\end{equation*}
$$

iii) Work done in charging and discharging a reversible cell.


A reversible cell is one in which the direction of chemical reaction accompanying the current is reversed when the current is reversed. If $a$ reversible cell operates at constant atmospheric pressure and does not release any gas, then the pressure and volume of the chemicals inside the cell are constant. The thermodynamic coordinates of the cell are its emf ' $E$ ', charge ' $Q$ ' and temperature ' $T$ '. During charging or discharging the change in charge content(dQ) is numerically equal to the quantity of electricity transferred during the chemical reaction.
dQ is negative while charging positive while discharging. Let the internal resistance of the cell be negligible. One terminal of such a cell is connected to one end of a resistance and the other terminal to a sliding contact ' $b$ '. The resistance ' $a$ ' $^{\prime}$ is connected across a second cell of emf ' E ' such that ' $E$ ' $>$ ' $E$ '. If the position of the sliding contact is adjusted such that the external potential difference ' $\mathrm{V}_{\mathrm{cb}}$ ' is equal to ' E ' then net emf in the primary circuit is zero and no current flows in the cell. But if ' $V_{c b}$ ' is slightly greater than ' $E$ ', there is a quasistatic transfer of charge 'dQ' through the primary circuit to the cell thus charging it. Work is done on the cell. If on the contrary ' $\mathrm{V}_{\mathrm{cb}}$ ' is slightly less than ' $E$ ', there is a quasistatic transfer of charge ' dQ ' in the opposite direction thus discharging it. Work is hence done by the cell on the external circuit. The work done in time ' dt ' is

$$
\begin{equation*}
\delta \mathrm{W}=-\mathrm{EdQ}=- \text { Eidt } \tag{3.9}
\end{equation*}
$$

The negative sign denotes that the cell does work when dQ is negative.
iv) Work done in changing the magnetization of a paramagnetic material

Let $M \rightarrow$ Magnetic moment of a paramagnetic material
The material is subjected to an external magnetic field with intensity of magnetization ' H '. If the magnetic moment changes by a small amount ' dM ' then the corresponding work done is:

$$
\begin{equation*}
\delta \mathrm{W}=-\mu_{0} \mathrm{HdM} \tag{3.10}
\end{equation*}
$$

Where, $\mu_{0}$ is the permeability of free space. The negative sign indicates that work is done on the paramagnetic substance during magnetization.
v) Work done in changing the polarization of a dielectric slab.

Let ' $P$ ' be the dipole moment of a dielectric slab. Let the slab be subjected to an external electric field of intensity ' $E$ '. This changes the dipole moment of the slab. If ' $d M$ ' be a small change in the dipole moment, then the corresponding work done is:

$$
\delta \mathrm{W}=-\mathrm{Ed} \mathrm{P}
$$

$\qquad$
The negative sign indicates that work is done on the slab by the external field when the dipole moment increases.

Configurational Work In all the expressions of work in different modes, it is seen that work is always expressed in the form:

$$
\delta \mathrm{W}=\text { An intensive variable } \times \text { Change in an extensive variable } .
$$

By analogy with work in mechanics, the intensive variables can be designated as generalized force ( Y ) and the change in the corresponding extensive variables generalized displacement(dX). Of course ' $Y$ ' and ' $X$ ' may not have the dimensions of force and displacement respectively, but ' YdX ' has the dimension of work. If more than one work mode is possible in the same system with generalized forces ' $Y_{1}{ }^{\prime},{ }^{\prime} Y_{2}{ }^{\prime},{ }^{\prime} Y_{3}{ }^{\prime}$....... ' $Y_{n}$ ' with corresponding generalized displacements ' $d X_{1}$ ', ' $d X_{2}$ ', ' $d X_{3}$ '....... Then the total work done by the system is :

$$
\begin{equation*}
\delta \mathrm{W}=\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{Y}_{\mathrm{i}} \mathrm{~d} \mathrm{X}_{\mathrm{i}} \tag{3.12}
\end{equation*}
$$

Where each product is to be taken with proper sign. ' YdX ' or $\sum \mathrm{YdX}$ is called configurational work.

## Some Mathematical formulations required in Thermodynamics

Let the equation of state of any system be represented by:

$$
\begin{equation*}
F(x, y, z)=0 \tag{i}
\end{equation*}
$$

Where, ' $x$ ', ' $y$ ', ' $z$ ' are any three thermodynamic coordinates and hence state functions. Since there are three variables connected by a single equation hence any two of them can be taken as independent and the third one is dependent on the other two. Let it be assumed that ' $x$ ' and ' $y$ ' are the two independent variables and ' $z$ ' is the dependent one. So ' $z$ ' can be expressed as a function of ' $x$ ' and ' $y$ '.

$$
z=f(x, y)
$$

Hence

$$
\begin{equation*}
\mathrm{dz}=\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \mathrm{dx}+\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \mathrm{dy} \tag{ii}
\end{equation*}
$$

Again considering ' $y$ ' and ' $z$ ' as the two independent variables and ' $x$ ' being dependent on them we can write: $\quad d x=\left(\frac{\partial x}{\partial y}\right)_{z} d y+\left(\frac{\partial x}{\partial z}\right)_{y} d z$

Substituting (iii) in (ii)

$$
\begin{equation*}
\mathrm{dz}=\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left\{\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \mathrm{dy}+\left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}} \mathrm{dz}\right\}+\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \mathrm{dy} \tag{iv}
\end{equation*}
$$

or

$$
\begin{equation*}
\mathrm{dz}=\left\{\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}}+\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}}\right\} \mathrm{dy}+\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}} \mathrm{dz} \tag{v}
\end{equation*}
$$

Equating the coefficient of dz on either side of equation ( v )

$$
1=\left(\frac{\partial z}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}}
$$

Or

$$
\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}=\frac{1}{\left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}}}
$$

Equating the coefficient of $d y$ on either side of equation (v)

$$
\begin{array}{ll} 
& 0=\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}}+\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \\
\text { Or } & \left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}}=-\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \\
\text { Or } & \frac{\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}}}{\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}}}=-1
\end{array}
$$

Using relation (vi) in (vii):

$$
\left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}}\left(\frac{\partial \mathrm{y}}{\partial \mathrm{z}}\right)_{\mathrm{x}}\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{v}}=-1
$$

.(viii) $\{$ Cyclic relation\}

Equations (vi) and (viii) are two fundamental relations often used in thermodynamic If: $\mathrm{x}=$ Presseure $\mathrm{P}, \mathrm{y}=$ volume $\mathrm{V}, \mathrm{z}=$ temperature T , then

$$
\begin{align*}
& \left(\frac{\partial \mathrm{P}}{\partial \mathrm{~V}}\right)_{\mathrm{T}}=\frac{1}{\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}}  \tag{IXA}\\
& \left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}=\frac{1}{\left(\frac{\partial \mathrm{~T}}{\partial \mathrm{~V}}\right)_{\mathrm{P}}}  \tag{IXB}\\
& \left(\frac{\partial \mathrm{~T}}{\partial \mathrm{P}}\right)_{\mathrm{V}}=\frac{1}{\left(\frac{\partial \mathrm{P}}{\partial \mathrm{~T}}\right)_{\mathrm{V}}} \\
& \left(\frac{\partial \mathrm{P}}{\partial \mathrm{~V}}\right)_{\mathrm{T}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}\left(\frac{\partial \mathrm{~T}}{\partial \mathrm{P}}\right)_{\mathrm{V}}=-1
\end{align*}
$$

Coefficient of volume expansion of a system =

$$
\begin{equation*}
\beta_{P}=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P} \tag{x}
\end{equation*}
$$

Isothermal bulk modulus of a system =


Isothermal compressibility of a system =

$\qquad$

## Some Solved Problems on Work

Q1. The figures below shows the P-V diagrams of some systems. Find the work done on or by the system
(A)


Ans. Work done is area under P-V curve. So the work done will be area under the trapezium OMNRO $=\frac{1}{2}(\mathrm{MN}+\mathrm{OR}) \times \mathrm{OM}=\frac{1}{2}(50+75) \times 20=1250$ Joules. Work is done by the system as it expands and hence is positive.
(B)


Ans. Work done is area under P-V curve. So the work done will be = Area of the trapezium OABEO + Area of the rectangle BCDEB
$=\frac{1}{2}(E B+O A) \times O E+E B \times E D=\frac{1}{2}(10+15) \times 12+10 \times(30-12)=150+180=330$ ergs. Work is done by the system as it expands and hence is positive.
(C)


Ans. Work done is area under P-V curve. So the work done will be = area of the rectangle $A B C D A=A B \times B C=(45-15) \times(55-30)=30 \times 25=750$ Joules.

Work is done by the system in the expansion process $A B$ and is equal to area under $A B$. Work is done on the system in the compression process $C D$ and is equal to area under $C D$ which is greater than area under AB. So net work is done on the system which is negative. So work done $=-750$ Joules.
(D)


Ans. Work done is area under P-V curve. So the work done will be = Area of the trapezium EABCE + Area of the rectangle ECDOE
$=\frac{1}{2}(E C+A B) \times E A+O E \times E C=\frac{1}{2}(60+40) \times(45-25)+(25-5) \times 60=1000+1200=2200$ ergs. Work is done on the system as it is compressed and hence is negative. So the work done is -2200ergs.

Q2. Prove that: $\frac{\beta_{\mathrm{P}}}{\kappa_{T}}=\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$
LHS $=\frac{\beta_{P}}{\kappa_{T}}=\frac{\frac{1}{v}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}}{-\frac{1}{\mathrm{~V}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}}=-\left(\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{T}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$ .....................(using reciprocal relation)

$$
=\frac{1}{\left(\frac{\partial \mathrm{~T}}{\partial \mathrm{P}}\right)_{\mathrm{V}}}
$$

$\qquad$ .(using cyclic relation)
$=\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$ $\qquad$ .(using reciprocal relation)
$=$ RHS

Q2. Prove that the work done by an ideal gas in an arbitrary process is

$$
\begin{array}{rl}
\delta W=P & V \beta_{P} d T-P \kappa_{T} V d P=n R d T-n R T \frac{d P}{P} \\
L H S=\delta W=P d V & =P\left\{\left(\frac{\partial V}{\partial T}\right)_{P} d T+\left(\frac{\partial V}{\partial P}\right)_{T} d P\right\} \\
& =P\left\{V \beta_{P} d T-V \kappa_{T} d P\right\} \quad \text { For ideal gas } P V=n R T \text {. hence }\left(\frac{\partial V}{\partial P}\right)_{T}=-\frac{n R T}{P^{2}} \\
& =P V \beta_{P} d T-P \kappa_{T} V d P \text { (proved) ........................................... (1) } \tag{1}
\end{array}
$$

For ideal gas $\mathrm{PV}=\mathrm{nRT}$. hence $\kappa_{\mathrm{T}}=-\frac{1}{\mathrm{~V}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}=\frac{\mathrm{nRT}}{\mathrm{VP}^{2}}=\frac{1}{\mathrm{P}} \quad$ and $\quad \beta_{\mathrm{P}}=\frac{1}{\mathrm{~V}}\left(\frac{\partial \quad \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}=\frac{\mathrm{nR}}{\mathrm{PV}}=\frac{1}{T}$
Which gives from (1) $\delta W=\frac{P V}{T} d T-\frac{P V}{P} d P==n R d T-V d P=n R d T-n R T \frac{d P}{P}=R H S$.

Q3. Find the work done by 1 mole of a gas in expanding from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$ (a) at constant temperature and (b) at constant pressure if the equation of state is: $\left.\left(P+\frac{a}{V^{2}}\right)(V-b)\right)=R T$ Ans. $\delta \mathrm{W}=\mathrm{PdV}$. In expanding from a volume $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$ the total work done is :

$$
W=\int_{V_{I}}^{V_{f}} P d V=\int_{V_{1}}^{V_{2}}\left(\frac{R T}{V-b}-\frac{a}{V^{2}}\right) d V
$$

a) At constant temperature:
$W=R T \int_{V_{I}}^{V_{f}} \frac{1}{V-b} d V-\int_{V_{1}}^{V_{2}}\left(\frac{a}{V^{2}}\right) d V=\left\{R T \ln (V-b)+\frac{a}{V}\right\}_{V_{1}}^{V_{2}}=R T \ln \left(\frac{V_{2}-b}{V_{1}-b}\right)+a\left(\frac{1}{V_{2}}-\frac{1}{V_{1}}\right)$
b) At constant pressure:

$$
\left(P+\frac{a}{V^{2}}\right)(V-b)=R T
$$

Or $\quad \mathrm{PV}-\mathrm{Pb}+\frac{a}{V}-\frac{\mathrm{ab}}{\mathrm{V}^{2}}=\mathrm{RT}$
Or $\quad P d V-\frac{a}{V^{2}} d V+\frac{2 a b}{V^{3}} d V=R d T$
Or $\quad P d V=R d T+\frac{a}{V^{2}} d V-\frac{2 a b}{V^{3}} d V$
So $\quad W=\int_{V_{I}}^{V_{f}} P d V=R \int_{T_{i}}^{T_{f}} d T+\int_{V_{1}}^{V_{2}}\left(\frac{a}{V^{2}}\right) d V-\int_{V_{1}}^{V_{2}}\left(\frac{2 a b}{V^{3}}\right) d V \quad$ where $T_{i}$ and $T_{f}$ are the temperatures corresponding to the volumes $\mathrm{V}_{1}$ and $\mathrm{V}_{2}$

Or $\quad \mathrm{W}=\left\{R T-\frac{a}{V}+\frac{a b}{V^{2}}\right\}_{\left(V_{1}, T_{1}\right)}^{\left(V_{2}, T_{2}\right)}=\mathrm{R}\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)-a\left(\frac{1}{V_{2}}-\frac{1}{\mathrm{~V}_{1}}\right)+a b\left(\frac{1}{V_{2}^{2}}-\frac{1}{V_{1}^{2}}\right)$

Q4. If the equation of state of a real gas is $P V=R T\left(1+\frac{B}{V}\right)$, where $R$ is a constant and $B$ is a function of temperature (T) only, Show that
a) $\beta=\frac{1}{T}\left(\frac{v+B+T \frac{d B}{d T}}{v+2 B}\right)$
b) $\kappa=\frac{1}{P}\left(\frac{1}{1+\frac{\mathrm{BRT}}{\mathrm{PV}^{3}}}\right)$

Ans. a) For 1 mole of gas $P V=R T+\frac{R T B}{V}$
Differentiating with respect to T at constant P :
$P\left(\frac{\partial V}{\partial T}\right)_{P}=R+\frac{R B}{V}+\frac{R T}{V} \frac{d B}{d T}-\frac{R T B}{V^{2}}\left(\frac{\partial V}{\partial T}\right)_{P}$
$\operatorname{Or}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{P}\left(\mathrm{P}+\frac{\mathrm{RTB}}{\mathrm{V}^{2}}\right)=\mathrm{R}+\frac{\mathrm{RB}}{\mathrm{V}}+\frac{\mathrm{RT}}{\mathrm{V}} \frac{\mathrm{dB}}{\mathrm{dT}}$
Or $\left(\frac{\partial V}{\partial T}\right)_{P}\left(P+\frac{R T B}{V^{2}}\right)=R+\frac{R B}{V}+\frac{R T}{V} \frac{d B}{d T}$
Or $\left(\frac{\partial V}{\partial T}\right)_{P}=\frac{R+\frac{R B}{V}+\frac{R T d B}{V d T}}{P+\frac{R T B}{V^{2}}}=\frac{R\left(1+\frac{B}{V}+\frac{T d B}{V d T}\right)}{\frac{R T}{V}+\frac{R T B}{V^{2}}+\frac{R T B}{V^{2}}}=\frac{R\left(1+\frac{B}{V}+\frac{T d B}{V d T}\right)}{\frac{R T}{V}+\frac{R T B}{V^{2}}+\frac{R T B}{V^{2}}}=\frac{R\left(1+\frac{B}{V}+\frac{T d B}{V d T}\right)}{\frac{R T}{V}+\frac{R T B}{V^{2}}+\frac{R T B}{V^{2}}}=\frac{\left(V+B+\frac{d B}{d T}\right)}{T\left(1+\frac{2 B}{V}\right)}$
$\left.\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P}=\frac{1}{V} \frac{\left(V+B+T^{d B}\right.}{T\left(1+\frac{2 T B}{V}\right)}=\frac{1}{T} \frac{(V+B+T \mathrm{~dB}}{(\mathrm{dT}}\right)$
.....(Proved)
b) For 1 mole of gas PV $=R T+\frac{R T B}{V}$

Differentiating with respect to $P$ at constant $T$
$\mathrm{V}+\mathrm{P}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}=-\frac{\mathrm{RTB}}{\mathrm{V}^{2}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$
Or $\left(P+\frac{\mathrm{RTB}}{\mathrm{V}^{2}}\right)\left(\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}=-\mathrm{V}$
Or $\quad\left(\frac{\partial V}{\partial \mathrm{P}}\right)_{\mathrm{T}}=-\frac{\mathrm{V}}{\mathrm{P}+\frac{\mathrm{RTB}}{\mathrm{V}^{2}}}=-\frac{\mathrm{V}}{\mathrm{P}\left(1+\frac{\mathrm{RTB}}{\mathrm{PV}^{2}}\right)}$
$K=-\frac{1}{\mathrm{~V}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}=\frac{1}{\mathrm{P}\left(1+\frac{\mathrm{RTB}}{\mathrm{PV}^{2}}\right)} \ldots \ldots . .$. (Proved)

Q5) In a quasistatic isothermal process the tension in a wire of initial length $L$ is increased from $\tau_{1}$ to $\tau_{2}$. If the length $L$, cross sectional area $A$ and the isothermal Young's modulus $Y_{T}$ remain practically constant, show that the work done is: $\mathrm{W}=-\frac{\mathrm{L}}{2 \mathrm{AY}_{\mathrm{T}}}\left(\tau_{2}^{2}-\tau_{1}^{2}\right)$

Ans. The work done on the wire due to a small elongation dL is : $\delta \mathrm{W}=-\tau \mathrm{dL}$
Stress on the wire due to a small change of tension $\mathrm{d} \tau=\frac{\text { Change in Tension }}{\text { cross sectional area }}=\frac{\mathrm{d} \tau}{\mathrm{A}}$
Strain produced $=\frac{\text { Change in length }}{\text { initial length }}=\frac{\mathrm{dL}}{\mathrm{L}}$
Isothermal Young's modulus $=Y_{T}=\frac{\text { Stress }}{\text { Strain }}=\frac{\text { Ld } \tau}{\text { AdL }}$
Hence $d L=\frac{L d \tau}{\mathrm{AY}_{\mathrm{T}}} . \quad$ Substituting in the expression for work done:

$$
\delta \mathrm{W}=-\tau \mathrm{dL}=-\frac{\mathrm{L} \tau \mathrm{~d} \tau}{\mathrm{AY}_{\mathrm{T}}}
$$

So the total work done in increasing the tension from $\tau_{1}$ to $\tau_{2}$ is:

$$
\mathrm{W}=-\int_{\tau_{1}}^{\tau_{2}} \frac{\mathrm{~L} \tau \mathrm{~d} \tau}{\mathrm{AY}_{\mathrm{T}}}=-\frac{\mathrm{L}}{\mathrm{AY}_{T}} \int_{\tau_{1}}^{\tau_{2}} \tau \mathrm{~d} \tau=-\frac{\mathrm{L}}{2 \mathrm{AY}_{\mathrm{T}}}\left(\tau^{2}\right)_{\tau_{1}}^{\tau_{2}}=-\frac{\mathrm{L}}{2 \mathrm{AY}_{\mathrm{T}}}\left(\tau_{2}^{2}-\tau_{1}^{2}\right) \quad \text { (Proved) }
$$

## Problem Sheet

Q1. The figures below shows the P-V diagrams of some systems. Find the work done on or by the system
i) $P\left(N / m^{2}\right)$

ii)


Q2. The figure below shows the P-V diagrams of a system. Find the work done by it in each of the five steps. Hence find the total work done by the body.


Q3. Find the work done when 1 mole of a Vander waal gas expands quasistatically and isothermally from a volume of 10 litres to 20 litres at $0^{\circ} \mathrm{C}$ if ' $a$ ' $=0.14 \mathrm{Nm}^{4} \mathrm{~mole}^{-2}$ and ' $\mathrm{b}^{\prime}=$ $4.1 \times 10^{-5} \mathrm{~m}^{3} . \mathrm{mole}^{-1}$ Ans. (1570J)

Q4. Find the work done by 1 mole of a gas in expanding from $V_{1}$ to $V_{2}$ (a) at constant temperature and (b) at constant pressure if the equation of state is :
i) $P V=R T$
ii) $P(V-b)=R T$
iii) $\left(P+\frac{a}{V^{2}}\right) V=R T$

Ans: (a)
i) $\mathrm{RT} \ln \frac{V_{2}}{V_{1}}$
ii) $\operatorname{RT} \ln \left(\frac{V_{2}-b}{V_{1}-b}\right)$
iii) $\operatorname{RT} \ln \frac{V_{2}}{V_{1}}+\mathrm{a}\left(\frac{1}{\mathrm{~V}_{2}}-\frac{1}{\mathrm{~V}_{1}}\right)$
(b)
i) $R\left(T_{2}-T_{1}\right)$
ii) $R\left(T_{2}-T_{1}\right)$
iii) $R\left(T_{2}-T_{1}\right)-a\left(\frac{1}{v_{2}}-\frac{1}{V_{1}}\right)$

Please solve and post in my email id: phalguni.dac@gmail.com by 22.09.2020. After receiving the solution sheet from you , I will post the next part of the syllabus.

