University of Salahaddin
Physics department/ Second stage

## Thrmodynamics

## Chapter Two: THE ENERGY, WORK, HEAT and the first law of thermodynamics

2.1. Energy, work and heat-energy-work and heat. 2.2. Reversible workHighlights.

## :.1. ENERGY, WORK AND HEAT

## :.1.1. Energy

Energy is a general term embracing energy in transition and stored energy. The stored energy of a substance may be in the forms of mechanical energy and internal energy (other forms of tored energy may be chemical energy and electrical energy). Part of the stored energy may ake the form of either potential energy (which is the gravitational energy due to height above ı chosen datum line) or kinetic energy due to velocity. The balance part of the energy is known is internal energy. In a non-flow process usually there is no change of potential or kinetic nergy and hence change of mechanical energy will not enter the calculations. In a flow rocess, however, there may be changes in both potential and kinetic energy and these must be aken into account while considering the changes of stored energy. Heat and work are the forms If energy in transition. These are the only forms in which energy can cross the boundaries of a ystem. Neither heat nor work can exist as stored energy.

### 2.1.2. Work and Heat

Work
Work is said to be done when a force moves through a distance. If a part of the boundary of a ystem undergoes a displacement under the action of a pressure, the work done W is the product )f the force (pressure $\times$ area), and the distance it moves in the direction of the force. Fig. 2.1 a) illustrates this with the conventional piston and cylinder arrangement, the heavy line lefining the boundary of the system. Fig. 2.1 (b) illustrates another way in which work might ee applied to a system. A force is exerted by the paddle as it changes the momentum of the luid, and since this force moves during rotation of the paddle work is done.

(a)

(b)

Nork is a transient quantity which only appears at the boundary while a change of state is aking place within a system. Work is 'something' which appears at the boundary when a ystem changes its state due to the movement of a part of the boundary under the action of a orce.

Feat
Heat (denoted by the symbol Q), may be, defined in an analogous way to work as follows : "Heat is 'something' which appears at the boundary when a system changes its state due to a difference in temperature between the system and its surroundings".

Heat, like work, is a transient quantity which only appears at the boundary while a change is taking place within the system.

It is apparent that neither $\delta \mathrm{W}$ or $\delta \mathrm{Q}$ are exact differentials and therefore any integration of the elemental quantities of work or heat which appear during a change from state 1 to state 2 must be written as
$\int_{1}^{2} \delta W=W_{1-2} \quad$ or $W \quad$ and
$\int_{1}^{2} \delta Q=Q_{1-2} \quad$ or $Q$
Sign convention :
If the heat flows into a system from the surroundings, the quantity is said to be positive and, conversely, if heat flows from the system to the surroundings it is said to be negative.
In other words :
Heat received by the system $=+\mathrm{Q}$

Heat rejected or given up by the system $=-\mathrm{Q}$.

## Comparison of Work and Heat Similarities :

(i) Both are path functions and inexact differentials.
(ii) Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
(iii) Both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
(iv) Systems possess energy, but not work or heat.

## Dissimilarities :

(i) In heat transfer temperature difference is required.
(ii) In a stable system there cannot be work transfer, however, there is no restriction for the transfer of heat.

### 2.2. REVERSIBLE WORK

Let us consider an ideal frictionless fluid contained in a cylinder above a piston as shown in fig 2.2 . Assume that the pressure and temperature of the fluid are uniform and that there is no friction between the piston and the cylinder walls.

Let $\mathrm{A}=$ Cross-sectional area of the piston,
$\mathrm{p}=$ Pressure of the fluid at any instant, ( $p-d p) A=$ Restraining force exerted by the surroundings on the piston, and $d l=$ The distance moved by the piston under the action of the force exerted. Then work done by the fluid on the piston is given by force times the distance moved, Work done by the fluid $\mathrm{p}=(\mathrm{pA}) \times \mathrm{dl}=\mathrm{pdV}$
(where $\mathrm{dV}=$ a small increase in volume) Or considering unit mass Work done $=\mathrm{pdv}$ (where $\mathrm{v}=$ specific volume)

This is only true when (a) the process is frictionless and (b) the difference in pressure between the fluid and its surroundings during the process is infinitely small. Hence when a reversible process takes place between state 1 and state 2, we have

Fig. 2.2
Work done by the unit mass of fluid $==$
 $\int_{1}^{2} p d v$
2.1

When a fluid undergoes a reversible process a series of state points can be joined up to form a line on a diagram of properties. The work done by the fluid during any reversible process is therefore given by the area under the line of process plotted on a p-v diagram (Fig. 2.3).
$=\int_{1}^{2} p d v$
i.e., Work done $=$ Shaded area on Fig. 2.3

When p can be expressed in terms of v then the integral, $\int_{1}^{2} p d v$, can be evaluated.

Fig 2.3


### 2.3. INTERNAL ENERGY

It is the heat energy stored in a gas. If a certain amount of heat is supplied to a gas the result is that temperature of gas may increase or volume of gas may increase thereby doing some external work.
Joule's law of internal energy states that internal energy of a perfect gas is a function of temperature only. In other words, internal energy of a gas is dependent on the temperature change only and is not affected by the change in pressure and volume. We do not know how to find the absolute quantity of internal energy in any substance ; however, what is needed in engineering is the change of internal energy $(\Delta U)$.

### 2.4. LAW OF CONSERVATION OF ENERGY

In the early part of nineteenth century the scientists developed the concept of energy and hypothesis that it can be neither created nor destroyed ; this came to be known as the law of the conservation of energy. The first law of thermodynamics is merely one statement of this general law.

### 2.5. FIRST LAW OF THERMODYNAMICS

The First Law of Thermodynamics can, therefore, be stated as follows :
"When a system undergoes a thermodynamic cycle then the net heat supplied to the system from the surroundings is equal to net work done by the system on its surroundings.

## WORK HEAT

- Work: $\quad w=F \cdot \ell$


Expansion work

$$
F=p_{e x t} A
$$



$$
w=-\left(p_{\text {ext }} A\right) \ell=-p_{\text {ext }} \Delta V
$$

convention:
Having a "-" sign here implies w>0 if $\Delta \mathrm{V}<0$, that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings $(\Delta V>0)$ then $w<0$.

- $\partial w=-p_{\text {ext }} d V$
- If p ext is not constant, then we have to look at infinitesimal changes
- $\partial$ means this is not an exact differential
- Integral depends on the path!!!

$$
W=-\int_{1}^{2} P_{e x t} d V
$$

-     - Path dependence of w
- Example: assume a reversible process so that $\mathrm{p}_{\mathrm{ext}}=\mathrm{p}=$ Compression
- $\operatorname{Ar}\left(\mathrm{g}, \mathrm{p}_{1}, \mathrm{~V}_{1}\right)=\operatorname{Ar}\left(\mathrm{g}, \mathrm{P}_{2}, \mathrm{~V}_{2}\right)$
- Compression $\quad \mathrm{V}_{1}>\mathrm{V}_{2}, \quad \mathrm{P}_{1}<\mathrm{P}_{2}$


Two paths: (1) First $\mathrm{V} 1 \rightarrow \mathrm{~V} 2$ at $\mathrm{p}=\mathrm{p} 1$
then $\mathrm{p} 1 \rightarrow \mathrm{p} 2$ at $\mathrm{V}=\mathrm{V} 2$
(2) First $\mathrm{p} 1 \rightarrow \mathrm{p} 2$ at $\mathrm{V}=\mathrm{V} 1$
then $\mathrm{V} 1 \rightarrow \mathrm{~V} 2$ at $\mathrm{p}=\mathrm{p} 2$
$\operatorname{Ar}(\mathrm{g}, \mathrm{p} 1, \mathrm{~V} 1)=\operatorname{Ar}(\mathrm{g}, \mathrm{p} 1, \mathrm{~V} 2)=\operatorname{Ar}(\mathrm{g}, \mathrm{p} 2, \mathrm{~V} 2)$
$\operatorname{Ar}(\mathrm{g}, \mathrm{p} 1, \mathrm{~V} 1)=\operatorname{Ar}(\mathrm{g}, \mathrm{p} 2, \mathrm{~V} 1)=\operatorname{Ar}(\mathrm{g}, \mathrm{p} 2, \mathrm{~V} 2)$


$$
\begin{aligned}
W_{(1)} & =-\int_{V_{1}}^{V_{2}} p_{\text {ext }} d V-\int_{V_{2}}^{V_{2}} p_{e x t} d V \\
& =-\int_{V_{1}}^{V_{2}} p_{1} d V=-p_{1}\left(V_{2}-V_{1}\right) \\
& =w_{(1)}=p_{1}\left(V_{1}-V_{2}\right)
\end{aligned}
$$

$$
w_{(2)}=-\int_{H_{1}}^{V_{1}} p_{e x t} d V-\int_{V_{1}}^{V_{2}} p_{e x t} d V
$$

$$
=-\int_{V_{1}}^{V_{2}} p_{2} d V=-p_{2}\left(V_{2}-V_{1}\right)
$$

$$
w_{(2)}=p_{2}\left(V_{1}-V_{2}\right)
$$

- (Note w $>0$, work done to system to compress it)
- w (1) $=$ w (2)!!!
- Note for the closed cycle [path (1)] - [path (2)], $\int d-w \neq 0$
- closed cycle
- $\underline{w}$ is not a state function
- cannot write $w=f(p, V)$


## Work

- Work (w) is not a function of state. For a cyclic process, it is possible for



## Heat

- That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.
- Sign convention:
- sf heat enters the system, then it is positive.
- Heat (q), like w, is a function of path. Not
- a state function
- It is possible to have a change of state
- $(\mathrm{p} 1, \mathrm{~V} 1, \mathrm{~T} 1)=(\mathrm{p} 2, \mathrm{~V} 2, \mathrm{~T} 2)$
- adiabatically (without heat transferred) nonadiabatically.
- or
- Historically measured in calories
- $\left[1 \mathrm{cal}=\right.$ heat needed to raise $1 \mathrm{~g} \mathrm{H} 2 \mathrm{O} 1^{\circ} \mathrm{C}$,
- from $14.5^{\circ} \mathrm{C}$ to $\left.15.5^{\circ} \mathrm{C}\right]$
- The modern unit of heat (and work) is the Joule.
- $1 \mathrm{cal}=4.184 \mathrm{~J}$


## Heat Capacity

$$
\begin{aligned}
& \underline{\underline{C}} \quad \text { - connects heat with temperature } \\
& \mathrm{d} q=C_{\text {path }} \mathrm{d} T \quad \text { or } \quad C_{\text {path }}=\left(\frac{\mathrm{d} q}{d T}\right)_{\text {path }} \\
& \text { heat capacity is path dependent }
\end{aligned}
$$

Constant volume: $\quad C_{V}$
Constant volume: $\quad C_{p}$

$$
\therefore \quad q=\int_{\text {path }} C_{p a t h} d T
$$

- Equivalence of work and heat [Joule (1840's)]
- Joule showed that it's possible to raise the temperature of H 2 O


# (a) with only heat 



$$
T_{1} \rightarrow T_{2}
$$

(b) with only work (weight falls \&
 churns propeller)

- Experimentally it was found that
- $\int(\partial w+\partial q)=0$
- $\Rightarrow$ The sum $(\mathrm{w}+\mathrm{q})$ is independent of path
- $\Rightarrow$ This implies that there is a state function whose differential is
- $\partial \mathrm{w}+\partial \mathrm{q}$
- We define it as U, the "internal energy" or just "energy"
- $\therefore \mathrm{dU}=\partial \mathrm{w}+\partial \mathrm{q}$
- For a cyclic process $\int \mathrm{d} U=0$
- For a change from state 1 to state 2,
- does not depend on path
- $\Delta U=\int_{1}^{2} d U=U_{2}-U_{1}=q+W$
- each depends on path individually, but not the sum
- For fixed n, we just need to know 2 properties, e.g. (T, V), to fully describe the system
- $\mathrm{So} \mathrm{U}=\mathrm{U}(\mathrm{T}, \mathrm{V})$ is an extensive function (scales with system size).
- $U^{-}=\frac{U}{N}$ is molar energy (intensive function)

First Law of Thermodynamics

- Mathematical statement
- $d U=\partial q+\partial W$
- $\operatorname{Or} \Delta U=q+W \quad$ or $-\oint \partial q=\oint \partial W$
- Consequence: Conservation of energy

$$
\begin{gathered}
\Delta U_{\text {system }}=q+w \quad \Delta U_{\text {surroundings }}=-q-w \\
\Rightarrow \quad \Delta U_{\text {universe }}=\Delta U_{\text {system }}+\Delta U_{\text {surroundings }}=0
\end{gathered}
$$

- Clausius statement of 1 stLaw:

The energy of the universe is conserved

Example 2.1. The specific heat capacity of the system during a certain process is given by:
$\mathrm{Cn}=(0.4+0.004 \mathrm{~T}) \mathrm{kJ} / \mathrm{kg}^{\circ} \mathrm{C}$.
If the mass of the gas is 6 kg and its temperature changes from $25^{\circ} \mathrm{C}$ to $125^{\circ} \mathrm{C}$ find :
(i) Heat transferred;
(ii) Mean specific heat of the gas.

Solution. Mass of the gas, $m=6 \mathrm{~kg}$
Change in temperature of the gas $=25^{\circ} \mathrm{C}$ to $125^{\circ} \mathrm{C}$
(i) Heat transferred, Q:

We know that heat transferred is given by,
$Q=\int m C_{n} d T=6 \int_{25}^{125}(0.4+0.004 T) d T$
$=6\left[0.4 T+0.004\left(\frac{T^{2}}{2}\right)\right]_{25}^{125}$
$=6\left[0.4(125-25)+0.002\left(125^{2}-25^{2}\right)\right]$
$=6(40+30)=420 \mathrm{~kJ}$.
(ii) Mean specific heat of the gas, $\mathrm{C}_{\mathrm{n}}$ :

$$
Q=m C_{n} d T
$$

$$
420=6 \times C_{n} \times(125-25)
$$

$$
C_{n}=\frac{420}{6 \times 100}=0.7 \mathrm{KJ} \cdot \mathrm{~kg} \cdot \mathrm{C}
$$

$=0.7 \mathrm{~kJ} / \mathrm{kg}^{\circ}$. C .

## EXAMPLE 2.2

A 0.5 mole of gas at temperature 300 K expands isothermally from an initial volume of 2 L to 6 L
(a) What is the work done by the gas?
(b) Estimate the heat added to the gas?
(c) What is the final pressure of the gas? (The value of gas constant,
$\left.\mathrm{R}=8.31 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)$

## Solution

(a) We know that work done by the gas in an isothermal expansion

Since $\mathrm{n}=0.5$

$$
\begin{aligned}
& W=-\int_{V_{1}}^{V_{2}} p d V \\
& p=\frac{n R T}{V} \\
& W=-\int_{V_{1}}^{V_{2}} \frac{n R T}{V} d V \\
& W=-0.5 \operatorname{mol} x \frac{8.3 J}{m o l . K} x 300 \mathrm{~K} \ln \left(\frac{6 L}{2 L}\right) \\
& W=-1.369 \mathrm{~kJ}
\end{aligned}
$$

Note that W is negative since the work is done by the gas.

This is because work is defined as the energy transferred from one system to another due to a change in volume. In this case, the gas is doing work on the surroundings by pushing back the external pressure as it expands, which results in a transfer of energy from the gas to the surroundings. Since the surroundings gain energy, the work done by the system (the gas) is negative.
(b) From the First law of thermodynamics, in an isothermal process the heat supplied is spent to do work.

Therefore, $Q=W=1.369 \mathrm{~kJ}$. Thus Q is positive which implies that heat flows in to the system.
(c) For an isothermal process
$P_{\mathrm{i}} V_{\mathrm{i}}=P_{\mathrm{f}} \mathrm{V}_{\mathrm{f}}=\mathrm{n} R T$
$P_{f}=\frac{n R T}{V_{f}}=0.5 \mathrm{~mol} X \frac{8.31 \mathrm{~J}}{\text { mol. } K} X \frac{300 \mathrm{~K}}{6 \times 10^{-3} \mathrm{~m}^{3}} \quad=207.75 \mathrm{kPa}$

## EXAMPLE 2.3

500 g of water is heated from $30^{\circ} \mathrm{C}$ to $60^{\circ} \mathrm{C}$. Ignoring the slight expansion of water, calculate the change in internal energy of the water? (specific heat of water 4184 J/kg.K)

## Solution:

When the water is heated from $30^{\circ} \mathrm{C}$ to $60^{\circ} \mathrm{C}$,there is only a slight change in its volume. So we can treat this process as isochoric. In an isochoric process the work done by the system is zero. The given heat supplied is used to increase only the internal energy.
$\Delta \mathrm{U}=\mathrm{Q}=\mathrm{m} \operatorname{Cv} \Delta \mathrm{T}$

The mass of water $=500 \mathrm{~g}=0.5 \mathrm{~kg}$

The change in temperature $=30 \mathrm{~K}$
The heat $\mathrm{Q}=0.5 \times 4184 \times 30=62.76 \mathrm{~kJ}$

## EXAMPLE 2.4

The PV diagrams for a thermodynamical system is given in the figure below. Calculate the total work done in each of the cyclic processes shown.


## Solution

In the case (a) the closed curve is anticlockwise. So the net work done is negative, implying that the work done on the system is greater than the work done by the system. The area under the curve BC will give work done on the gas (isobaric compression) and area under the curve DA (work done by the system) will give the total work done by the system.

Area under the curve $\mathrm{BC}=$ Area of rectangle $\mathrm{BC} 12=1 \times 4=-4 J$

Area under the curve $\mathrm{DA}=1 \times 2=+2 J$

Net work done in cyclic process $=-4+2=-2 \mathrm{~J}$

## EXMPALE 2.5

One mole of an ideal gas initially kept in a cylinder at pressure 1 MPa and temperature $27^{\circ} \mathrm{C}$ is made to expand until its volume is doubled.
(a) How much work is done if the expansion is (i) adiabatic (ii) isobaric (iii) isothermal?
(b) Identify the processes in which change in internal energy is least and is maximum.
(c) Show each process on a PV diagram.
(d) Name the processes in which the heat
(Take $\gamma=5 / 3$ and $\mathrm{R}=8.3 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ )

## Solution

(a) (i) In an adiabatic process the work done by the system is

$$
W_{\text {adia }}=\frac{n R}{\gamma-1}\left[T_{i}-T_{f}\right]
$$

To find the final temperature $\mathrm{T}_{\mathrm{f}}$, we can use adiabatic equation of state.

$$
\begin{aligned}
& T_{f} V_{f}^{\gamma-1}=T_{i} V_{i}^{\gamma-1}, \quad T_{f}=T_{i}\left(\frac{V_{i}}{V_{f}}\right)^{\gamma-1}=300 X\left(\frac{1}{2}\right)^{\frac{2}{3}} \\
& =0.63 \times 300 \mathrm{~K}=189.8 \mathrm{~K} \\
& \mathrm{~W}=1 \times 8.3 \times 3 / 2(300-189.8)=1.37 \mathrm{~kJ}
\end{aligned}
$$

(ii) In an isobaric process the work done by the system

$$
W=P \Delta V=P\left(V_{\mathrm{f}}-V_{\mathrm{i}}\right) \quad \text { and } V_{\mathrm{f}}=2 V \mathrm{i} \quad \text { so } W=2 P V_{\mathrm{i}}
$$

To find $V \mathrm{i}$, we can use the ideal gas law for initial state. $P \mathrm{i} V \mathrm{i}=R T \mathrm{i}$
$V_{i}=\frac{R T_{i}}{P_{i}}=8.3 \times \frac{300}{1} \times 10^{-6}=24.9 \times 10^{-14} \mathrm{~m}^{3}$
The work done during isobaric process,
$W=2 \times 10^{6} \times 24.9 \times 10^{-4}=4.9 \mathrm{~kJ}$
(iii) In an isothermal process the work done by the system,
$W=\mu R T \ln \left(\frac{V_{f}}{V_{i}}\right)$
In an isothermal process the initial room temperature is constant.

$$
W=1 \times 8.3 \times 300 \times \ln (2)=1.7 \mathrm{~kJ}
$$

(b) Comparing all three processes, we see that the work done in the isobaric process is the greatest, and work done in the adiabatic process is the least.
(c) The PV diagram is shown in the Figure.


The area under the curve $\mathrm{AB}=$ Work done during the isobaric process

The area under the curve $\mathrm{AC}=$ Work done during the isothermal process

The area under the curve $\mathrm{AD}=$ Work done during the adiabatic process
From the PV diagram the area under the curve AB is more, implying that the work done in isobaric process is highest and work done in adiabatic process is least.
(d) In an adiabatic process no heat enters into the system or leaves from the system. In an isobaric process the work done is more so heat supplied should be more compared to an isothermal process.

## Example 2.6

A liquid is compressed isothermally inside a chamber.
Obtain an expression for the total amount of work required if the compression process is quasistatic and is given by the equation

$$
\text { In }\left(V / V_{0}\right)=-A\left(p-p_{0}\right) \quad \text { where } A, V_{0} \text { and } p_{0} \text { are constants. }
$$

- Since the process is quasi-static, the work done is
- $\mathrm{W}={ }^{2} \int_{1} \mathrm{pdV}$
- $\quad$ Since $\operatorname{In}\left(\mathrm{V} / \mathrm{V}_{0}\right)=-\mathrm{A}\left(\mathrm{p}-\mathrm{p}_{0}\right)$,
- $d V=-A V d p$,
- Therefore,

$$
W=-A V \int_{1}^{2} V P d P
$$

- To perform the integration, the expression for V has to be a function of p .
- In general, the volume of a liquid is not sensitive to a change in pressure.

Hence, assuming constant V in the integration,

$$
W=-A V \int_{1}^{2} P d P=-\left(\frac{A V}{2}\right)\left(P_{2}^{2}-P_{1}^{2}\right)
$$

Since A and V are positive quantities, W will be negative if $\mathrm{p}_{2}$ is greater than $\mathrm{p}_{1}$. This is consistent with the convention that work is done to a system in a compression process. The values for A and V will be different for different substances.

## Example 2.7

How many joules are equivalent to one lit-atm of work?

- Solution:
- For $76.00-\mathrm{cm}$ column of mercury (density $=13.596 \mathrm{gm} / \mathrm{cm}^{3}$ ) supported by the atmosphere,

$$
\mathrm{M} / \mathrm{A}=(76 \mathrm{~cm})\left(13.6 \mathrm{gm} / \mathrm{cm}^{3}\right)=1033 \mathrm{gm} / \mathrm{cm}^{2}=1.033 \mathrm{kgm} / \mathrm{cm}^{2} .
$$

- Hence

$$
\mathrm{P}_{\mathrm{X}}=\mathrm{Mg} / \mathrm{A}=\left(1.033 \mathrm{kgm} / \mathrm{cm}^{2}\right)\left(9.81 \mathrm{~meter} / \mathrm{sec}^{2}\right)
$$

$$
=10.13 \mathrm{kgm}-\mathrm{meter} / \mathrm{sec}^{2}-\mathrm{cm}^{2}=10.13 \text { newton } / \mathrm{cm}^{2} ;
$$

and one lit-atm will represent

$$
P_{x} \Delta V=\left(10.13 \text { newton } / \mathrm{cm}^{2}\right)\left(1000 \mathrm{~cm}^{3}\right)=
$$

10130 newton- $\mathrm{cm}=101.3$ newton-meter $=101.3$ joule.

## Example 2.8

A refrigerator is a common device used in every home.
Examine the following systems regarding the direction of heat transfer.
(a) The refrigerator alone
(b) The room the refrigerator is located in.

- (a) In order to keep the products stored inside the refrigerator at a lower temperature, heat must be absorbed from the products stored (through the evaporator) and rejected to the atmosphere. In fact this is
the principle for a refrigeration cycle. Therefore, as far as heat transfer is concerned, heat is transferred from the refrigerator (the system)and thus

$$
\mathrm{Q}=-\mathrm{Q} .
$$

- (b) From the statement made in part (a), heat is rejected from the refrigerator to the room. The heat transfer is done through the condenser which is so arranged that the air in the room flows past the condenser by natural convection. As a result of that, heat is added to the room and the heat transfer is positive $(\mathrm{Q}=+\mathrm{Q})$ for the system under consideration. This explains why the room where the refrigerator is usually located, is always warmer than the other rooms.


## Example 2.9

Calculate the heat transferred when 100J of work is done on a system consisting of 1 mole of an ideal gas. At constant temperature, $\Delta \mathrm{E}=0$ for the expansion of an ideal gas.

A statement of the first law of thermodynamics is expressed as

$$
\Delta \mathrm{E}=\mathrm{q}-\mathrm{w}
$$

where $\Delta \mathrm{E}=$ change in internal energy of the system

$$
\begin{gathered}
q=\text { quantity of heat } \\
\text { w = work done }
\end{gathered}
$$

In this problem, work is done on the system and so w is negative.
(Note that we are adopting the convention that work done on the system is negative.) Since $\Delta \mathrm{E}=0$ for an isothermal expansion of an ideal gas,

$$
\begin{gathered}
\Delta \mathrm{E}=0=\mathrm{q}-\mathrm{w} \\
\therefore \mathrm{q}=\mathrm{w} \\
\mathrm{q}=-100 \mathrm{~J}
\end{gathered}
$$

or

As a result, 100J of heat must be transferred from the system to maintain isothermal conditions

## Example 2.10

What can you say about the following statements if one has an adiabatic process in which there is no heat transfer between the system and the surroundings, either because the system is well insulated or because the process occurs very rapidly?

$$
\begin{array}{lll}
\text { 1. } \mathrm{q}=+\mathrm{w} & \text { 2. } \mathrm{q}=0 & \text { 3. } \Delta \mathrm{E}=\mathrm{q}
\end{array}
$$

4. $\Delta \mathrm{E}=\mathrm{w}$
5. $\mathrm{P} \Delta \mathrm{V}=0$

In an adiabatic system there is no heat flow into or out of the system, thus $q=0$

1. This statement gives $q$ to be $+w$ but this can only happen when $\Delta \mathrm{E}=0$ since for instance $\Delta \mathrm{E}=\mathrm{q}-\mathrm{w}$ for isothermal expansion of an ideal gas.
2. Statement (2) is correct since $\mathrm{q}=0$ for the process.
3. This statement indicates $\Delta \mathrm{E}=\mathrm{q}$, but this can only happen, as in the case when one expands a gas into a vacuum, when $\mathrm{w}=0$.
4. Since $\Delta E=q-w, \Delta E$ will be equal to $w$ only when $q=2 w$ so that

$$
\Delta \mathrm{E}=2 \mathrm{w}-\mathrm{w}=\mathrm{w}
$$

5. $\Delta \mathrm{E}=\mathrm{q}-\mathrm{w}$

$$
=\mathrm{q}-\mathrm{P} \Delta \mathrm{~V}
$$

Thus for $\mathrm{P} \Delta \mathrm{V}$ to be zero, $\Delta \mathrm{E}$ must be equal to q such that $\Delta \mathrm{E}=\Delta \mathrm{E}-\mathrm{P} \Delta \mathrm{V}$

$$
\therefore \mathrm{P} \Delta \mathrm{~V}=0
$$

## Example 2.11

When 100 kJ of work is done on a closed system during a process, the total energy of the system increases by 55.0 kJ .
Calculate how much heat is either added or removed from the system?

- In accordance with the principle of energy conservation, a net energy transfer to a system results in an equal increase of internal energy stored in the system. This may be written as
- $\quad \mathrm{Q}=\Delta \mathrm{E}+\mathrm{W}$
- where Q is the heat transferred to the system during the process.

W is the work transferred from the system during the process. $\Delta \mathrm{E}$ is the change in the internal energy of the system during the process, and all these terms are expressed in the same units.

Eq. (1) is the usual statement of the First Law. It says that in any change of state the heat supplied to a system is equal to the increase of internal energy in the system plus the work done by the system.

Considering work done on a system as positive, from Eq. (1)

$$
\begin{aligned}
& \mathrm{Q}+(+100.0)=+55.0 \\
& \mathrm{Q}=+55.0-100.0 \\
& =-45.0 \mathrm{Kj}
\end{aligned}
$$

From the result, due to the negative sign, 45.0 kJ of energy in the form of heat is removed from the system during the process.

Example 2.12. Comment whether the following quantities can be called as properties or not:
(i) $\int p d V$,
(ii) $\int V d p$,
(iii) $\int p d V+\int V d p$

Solution: (i) $\int p d V$
p is a function of V and integral can only be evaluated if relation between p and V is known. It is thus an inexact differential and hence not a property.

## (ii) $\int V d p$

It is not a property for the same reason as mentioned in (i).
(iii) $\int P D V+\int V D P$
(iii) $\int P D V+\int V D P=\int P d V+V d p=\int d(p V)=p V$

Thus the integral can be evaluated without knowing the relation between p and V. It is an exact differential and hence it is a property.

Example 2.13. Gas from a cylinder of compressed helium is used to inflate an inelastic flexible balloon, originally folded completely flat, to a volume 0.6 m 3 . If the barometer reads 760 mm Hg , what is the amount of work done upon the atmosphere by the balloon ? Sketch the system before and after the process.

Solution. Refer Figure below. The firm line B 1 shows the boundary of the system before the process, and dotted line B 2 shows the boundary after the process.


The displacement work,
$W_{d}=\int_{\text {cylinder }} p d V+\int_{\text {ballon }} p d V=0+\int_{\text {ballon }} p d V$
$=101.325 \times 0.6$
$=60.795 \mathrm{~kJ}$

This is a positive work, because the work is done by the system. Work done by the atmosphere is -60.795 kJ . Since the wall of the cylinder is rigid there is no pdV-work involved in it.

It is assumed that the pressure in the balloon is atmospheric at all times, since the balloon fabric is light, inelastic and unstressed. If the balloon were elastic and stressed during the filling process, the work done by the gas would be greater than 60.795 kJ by an amount equal to the work done in stretching the balloon, although the displacement work done by atmosphere is still 60.795 kJ . However, if the system includes both the gas and the balloon, the displacement work should be 60.795 kJ , as estimated above.

Example 2.14. Determine the work done by the air which enters into an evacuated vessel from atmosphere when the valve is opened. The atmospheric pressure is 1.013 bar and 1.5 m 3 of air at atmospheric condition enters into the vessel.

Solution. Figure below shows the initial and final condition of the system.


No work is done by the boundary in contact with the vessel as the boundary does not move. Work is done by the external boundary at constant pressure.
$W=\int_{V_{1}}^{V_{2}} p d V=\int_{1.5}^{0} p d V \quad V 1=1.5 m^{3}$ and $V 2=0$
$=\mathrm{p}(0-1.5)=1.013 \times 10^{5} \times(-1.5)$
$=-1.5195 \times 10^{5} \mathrm{~J}=151.95 \mathrm{~kJ}$
Since the free air boundary is contracting, the work done by the system is negative, and the surroundings do positive work upon the system.


