Temperature :

It may be defined as that thermal property which attains the same value for all bodies placed in thermal contact with each other.

Heat Energy :

The transfer or flow of internal energy caused by the difference of temperatures between two bodies is called as Heat Energy.

Zeroth Law of thermodynamics :

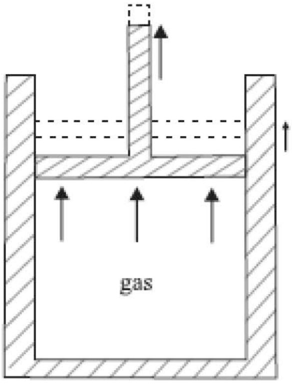
It two bodies A and B are in thermal equilibrium with another body C, then they are also in thermal equilibrium with each other.

Thermodynamical system :

It is a collection of an extremely large numbers of atoms or molecules so that they together have some pressure (P), volume (V) and temperature (T). Examples: a gas, vapour, steam, vapour in contact with the liquid.

Work Done and Internal Energy

Work Done By a Gas During Expansion



Let us consider an ideal gas enclosed in a perfectly insulated cylinder fitted with a non-conducting and frictionless piston. Let P be the pressure exerted by the gas and V be the volume of the gas at any particular instant. Let A be the area of crossection of the piston.

The force exerted by the gas on the piston = PA

If the piston moves through an infinitesimal distance dx, this force can be assumed constant, and the work done (dW) is given as :

$$dW = (PA)\,dx = P\,dV$$

($A\,dx = dV$ = infinitesimal change in volume)

$$W = \int PdV$$

(a) If volume is kept constant the piston is not displaced.

$$\Rightarrow \quad W = 0$$

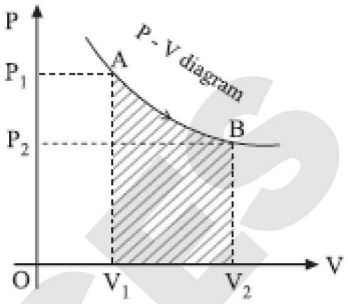
(b) If pressure is kept constant,

$$W = \int_{V_1}^{V_2} PdV = P\int_{V_1}^{V_2} dV = P(V_2 - V_1)$$

$\Rightarrow$ $W = P\Delta V$ for constant pressure and we also have $W = PV_2 - PV_1 = nRT_2 - nRT_1$

$W = nR\Delta T$ for constant pressure

Work Done From P-V Diagram



An ideal gas contained in a cylinder fitted with a massless and rictionless piston can be considered as a thermodynamical system. Its state can be represented by variables (P, V, T). If P and V are known, T can be calculated ($PV = nRT$).

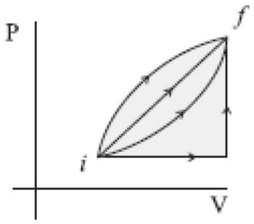
The system's state at any instant of time can be specified by two variables (P, V). The relation between pressure P and volume V can be studied on a pressure - volume (P-V) graph known as indicator diagram or a P-V diagram.

On such a graph, each equilibrium state of a thermodynamical system can be represented by a point whose x-coordinate represents volume (V) and y-coordinate represents pressure (P).

A process can be represented by a curve on the P-V diagram. If the gas goes from initial state A (P_1, V_1) to the final state B (P_2, V_2), the work done W is given by :

W = area under the curve AB above the X-axis (*shaded portion*)

Internal Energy



$\Delta U = U_f - U_i$
is same for all the four process.

Internal energy (U) of a system is the total of all kinds of energy possessed by the atoms and other particles that comprise the system. The change in internal energy ΔU depends only on the temperature difference of initial and final states and not on the process between the states.

First Law of Thermodynamics

If some heat is supplied to a system capable of doing some work, the quantity of heat absorbed by the system is the equal to the sum of external work done by the system and increase in its internal energy.

If ΔQ is the heat gained by the system, W is the work done against external pressure and ΔU is the change in internal energy, then

$$\begin{pmatrix}\text{heat energy given}\\ \text{to the system}\end{pmatrix} = \begin{pmatrix}\text{increase in}\\ \text{internal energy}\end{pmatrix} + \begin{pmatrix}\text{work done}\\ \text{by the system}\end{pmatrix}$$

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

Note : First Law of thermodynamics is a direct consequence of Law of conservation of energy.

In Thermodynamics :

1. Work done by a system is taken as positive (+). Work done on the system is taken as negative (–).
2. Heat gained by a system is taken as positive (+) and the heat lost by the system is taken as negative (–).
3. Increase in internal energy is taken as positive (+) and decrease in internal energy is taken as negative (–).

Specific Heat of a Gas

The specific heat of gas is defined as the amount of heat required to raise the temperature of unit mass of substance through 1*K*. Its unit in *S.I.* system is *J*/*Kg*/*K*. When the unit mass is 1 mole, the specific heat is known as *molar specific heat* and its units are *J*/*mol*/*K* or *cal*/*mol*/*K*.

Molar specific heat = molecular weight (*specific heat in J/gm/K*)

In gases, on giving heat to the gas, besides temperature, its pressure and the volume may also change. Thus specific heat of a gas depends upon the conditions under which the heat is given to the gas. Hence we will define two principal types of specific heats of a gas.

Specific Heat at constant volume (C_v) :

C_v of a gas is defined as the amount of heat required to raise the temperature of 1 mole of that gas through 1*K*, provided that the volume of the gas remains constant. It is also known as *molar specific heat at constant volume.*

In general, if n moles of a gas are heated at constant volume to increase the temperature by ΔT,

Heat required = $\Delta Q = n\, C_v\, \Delta T$

Specific Heat at constant pressure (C_p) :

C_p of a gas is defined as the amount of heat required to raise the temperature of 1 mole of that gas through 1°*K*, provided that the pressure of the gas remains constant. It is also known as *molar specific heat at constant pressure.*

In general, if n moles of a gas are heated at constant pressure resulting in a temperature rise by ΔT,

Heat required = $\Delta Q = n\, C_p\, \Delta T$

Note : C_p is greater than C_v ($C_p > C_v$).

When we heat the gas at constant volume, the heat is supplied to raise the temperature of gas only. When we heat the gas at constant pressure, the volume of the gas apart from temperature of the gas rises. When the gas expands, it does some external work for increasing the volume. So in this case, the heat is supplied :

(a) *to raise the temperature of the gas* (b) *to do the mechanical work for expansion*

As a result more amount of heat is required to increase the temperature of the gas through the same amount when the pressure is kept constant. Hence C_p is always greater than the value of C_v.

The ratio of $\frac{C_p}{C_v}$ is denoted by γ i.e. $\boxed{\gamma = \frac{C_p}{C_v}}$ $(\gamma > 1)$

Specific Heat Relation :

Consider n moles of an ideal gas. If its temperature is raised by ΔT at constant volume, then the heat transferred is $n\,C_v\,\Delta T$, where C_v is the specific heat at constant volume.

$W = 0$ (as no volume change is there)

By first law of thermodynamics :

$$\Delta Q = \Delta U + 0 \quad \Rightarrow \quad n\,C_v\,\Delta T = \Delta U \qquad \text{. . . . (i)}$$

Next, let us heat the same gas at constant pressure. The heat ΔQ required to change the temperature by ΔT will be $n\,C_p\,\Delta T$, where C_p is the specific heat at constant pressure.

$W = P\,\Delta V$ where ΔV is the change in volume.

By first law of thermodynamics :

$$\Delta Q = \Delta U + P\,\Delta V \quad \Rightarrow \quad n\,C_p\,\Delta T = \Delta U + P\,\Delta V \qquad \text{. . . . (ii)}$$

From (i) and (ii), we get :

$$n\,C_p\,\Delta T = n\,C_v\,\Delta T + P\,\Delta V$$

From gas equation :

$$P\Delta V = nR\,\Delta T \quad \Rightarrow \quad n\,C_p\,\Delta T = n\,C_v\,\Delta T + nR\,\Delta T$$

$$\Rightarrow \quad C_p = C_v + R \quad \Rightarrow \quad \boxed{C_p - C_v = R}$$

Combining $C_p - C_V = R$ and $C_p/C_v = \gamma$, we set :

$$\boxed{C_V = \frac{R}{\gamma - 1} \quad \text{and} \quad C_V = \frac{\gamma R}{\gamma - 1}}$$

C_p and C_v for Gases :

Consider 1 mole of a gas heated to raise the temperature by 1°C. When the gas is heated at constant volume, all heat is converted to increase in internal energy. The work done is zero, i.e. $C_v = \Delta U$ for 1°C (or 1 K) rise in temperature for 1 mole of a gas.

For mono-atomic gas :

Internal energy per mole $=\frac{3}{2}RT$

$$C_v = \Delta V = \frac{3}{2}R(T+1) - \frac{3}{2}RT = \frac{3}{2}R$$

$\Rightarrow \quad C_v = \frac{3}{2}R$ and $\quad C_p = \frac{5}{2}R$ (as $C_p - C_v = R$) $\quad \Rightarrow \gamma = \frac{C_p}{C_v} = \frac{5}{3}$

For di-atomic gas :

Internal energy per mole $=\frac{5}{2}RT$

$$C_v = \Delta U = \frac{5}{2}R(T+1) - \frac{5}{2}RT = \frac{5}{2}R$$

$\Rightarrow \quad C_v = \frac{5}{2}R$

$\Rightarrow \quad C_p = \frac{7}{2}R \qquad$ (as $C_p - C_v = R$) $\qquad \Rightarrow \gamma = \frac{C_p}{C_v} = \frac{7}{2}$

Illustration - 13 *One mole of oxygen is heated at constant pressure from 0°C. What must be the quantity of heat that should be supplied to the gas for the temperature to be doubled ? If the same heat is supplied to the gas at constant volume, what will be the final temperature ?*

SOLUTION :

$T_1 = 0 + 273 = 273\ K$

Temperature is to be doubled

$\Rightarrow \quad T_2 = 2T_1 = 546\ K$

ΔQ at constant pressure $= n\,C_p\,\Delta T$

Hence $\Delta Q = n\,C_p\,\Delta T = n\left(\frac{7}{2}R\right)\Delta T$

$\Rightarrow \quad \Delta Q = 1 \times \frac{7}{2} \times 8.3 \times (546 - 273)$

$= 7930.6$ J

If heating is done at constant volume :

$$\Delta Q = n\,C_v\,\Delta T$$

$$\Delta Q = \frac{nR}{\gamma - 1}\Delta T$$

$\Rightarrow \quad 7930.6 = \frac{1 \times 8.3}{1.4 - 1}(273)$

$\Rightarrow \quad T = 655\ K$

Illustration - 14 *When water is boiled under a pressure of 2 atm., the heat of vapourisation is* 2.20×10^6 *J/Kg and the boiling point is* $120°C$*. At this pressure 1 Kg of water has a volume of* 10^{-3} m^3 *and 1 Kg of steam has a volume of* 0.824 m^3*.*

(a) *Compute the work done when 1 Kg of steam is formed at this temperature.*

(b) *Compute the increase in the internal energy.*

SOLUTION :

(a) Work done = $P(\Delta V)$ (at constant pressure)

$\Rightarrow \quad W = 2\ atm \times (0.824 - 0.001)\ m^3$

$\Rightarrow \quad W = 2 \times 1.013 \times 10^5\ N/m^2 \times 0.823\ m^3$

$= 166.74\ kJ$

(b) $U = \Delta Q - W$

$\Delta U = m\,L - W$

$\Rightarrow \Delta U = 1\ kg \times 2.20 \times 10^6\ J/kg - 166.74\ kJ$

$= (2200 - 166.74) = 2033.26\ kJ$

Illustration - 15 *The temperature of 3 kg of krypton gas is raised from* $-20°C$ *to* $80°C$*.*

(a) *If this is done at constant volume, compute the heat added, the work done and the change in internal energy.*

(b) *Repeat if the heating process is at constant pressure.*

(*for mono-atomic gas Kr,* $C_v = 0.0357\ cal/g/K$, $C_p = 0.0595\ cal/g/K$)

SOLUTION :

(a) **At constant volume :**

$W = 0$

$\Delta Q = m\,C_v\,\Delta T = 3000 \times 0.0357 \times 100$;

$\Delta T = 80 - (-20) = 100°C$

$\Delta Q = 10.7\ kcal$

$\Delta U = \Delta Q - 0 = 10.7 \times 10^3 \times 4.18\ \text{J}$

$= 44.8\ kJ$

(b) **At constant pressure :**

$\Delta Q = m\,C_p\,\Delta T = 3000 \times 0.0595 \times 100$

$= 17.85\ kcal$

$W = P(V_2 - V_1) = nR(T_2 - T_1)$

$W = \left(\dfrac{3000}{83.8}\right) \times 8.3 \times 100\ J = 30\ kJ$

$\Delta U = n\,C_v\,\Delta T = 44.8\ kJ$

[*Note* : ΔU is same for both processes as it is a State Function]

Note : (i) It can be verified that $\Delta Q = \Delta U + W$.

(ii) ΔQ is usually measured in calories and ΔU and W are measured in Joules.

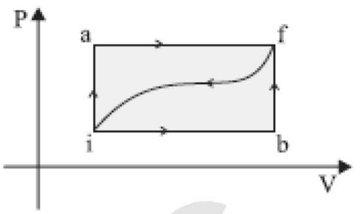
Illustration - 16 *A system is taken from state i to the state f (refer to the fig.). Along path "i a f", it is found that $\Delta Q = 50$ cal, $\Delta W = 20$ cal. Along the path "i b f", $\Delta Q = 36$ cal. Calculate :*

(a) *ΔW along the path "i b f"*

(b) *If $\Delta W = -13$ cal for curved path " f i ", what is ΔQ for this path ?*

(c) *Taking $U_i = 10$ cal, what is U_f ?*

(d) *If $U_b = 22$ cal, what is ΔQ for the process " i b" and for the process "b f" ?*



SOLUTION :

Path " i a f "

$\Delta Q = 50\ cal$; $\Delta W = 20\ cal$

$\Rightarrow \quad \Delta U = \Delta Q - \Delta W$

$\Delta U = 50 - 20 = 30\ cal$

$\Rightarrow \quad U_f - U_i = 30\ cal.$

As internal energy change is a State function, ΔU will be same for any path from i to f.

(a) **Path " i b f "**

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

$\Delta W = 36 - (U_f - U_i) = 36 - (30) = 6\ cal$

(b) **Path " f i "**

$\Delta Q = \Delta U + \Delta W = (U_i - U_f) + \Delta W$

$= (-30) + (-13) = -43\ cal.$

(c) $U_f - U_i = 30\ cal$

$\Rightarrow \quad U_f = U_i + 30 = 40\ cal$

(d) **Process "i b"**

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

$\Delta Q = (U_b - U_i) + (\Delta W)_{ibf}$

$\{(\Delta W)_{ib} = (\Delta W)_{ibf}$ because $(\Delta W)_{bf} = 0\}$

$\Delta Q = (22 - 10) + 6 = 18\ cal$

(d) **Process "b f "**

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

$\Delta Q = (U_f - U_b) + 0 = 40 - 22 = 18\ cal.$

THERMODYNAMIC PROCESSES

In a thermodynamic process, the initial and final states are important, but the manner in which the system is taken from initial to final state must also be taken into account. Hence it is important to distinguish between the following processes.

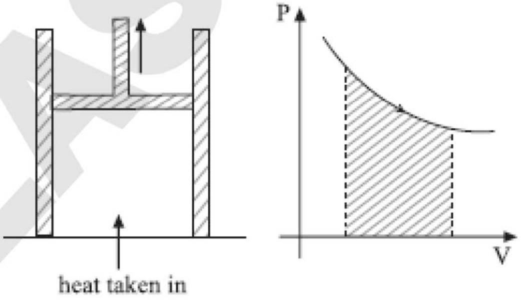
Isothermal process :

An isothermal process is one in which the temperature remains constant.
A gas under going an isothermal process should remain in perfect thermal contact with a constant temperature heat reservoir. The gas obeys *Boyle's Law*, during an isothermal process, i.e. $PV = constant$

As the temperature remains constant internal energy of the system remains constant.
i.e., $\Delta U = 0$ (for isothermal process)
From Ist Law : $\Delta Q = W$

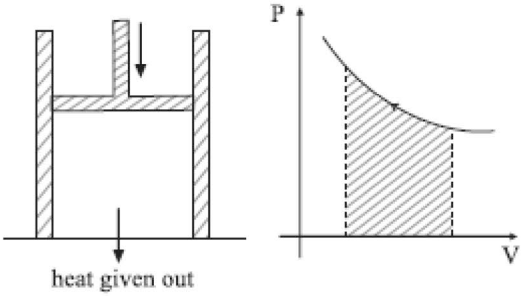
(a) Isothermal Expansion :

- If the gas expands, it takes heat from the heat reservoir and does positive work, i.e. in equation $\Delta Q = W$, both ΔQ and W are positive.
- The process takes place slowly. As the pressure on the piston is reduced, the gas tries to expand.
- In expansion, it tends to cool down, but the heat reservoir gives heat input to keep temperature constant.



(b) Isothermal Compression :

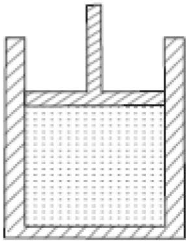
- If the gas is compressed isothermally, it gives heat to the reservoir and the work done is negative, i.e., in the equation $\Delta Q = W$, both ΔQ and W are negative.
- To do a perfectly isothermal process, pressure is increased in very small steps. As the gas is compressed slowly, its temperature tends to rise, but the reservoir extracts the heat from the system to keep the temperature constant.



Adiabatic process :

In an adiabatic process, no heat enters or leaves the system. Such a situation is achieved by heavily insulating the system.

From Ist Law of thermodynamics : $\Delta Q = \Delta U + W$



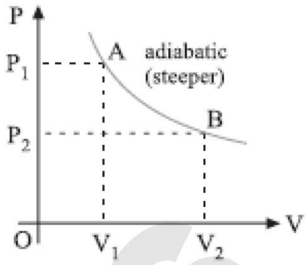
In adiabatic process $\Delta Q = 0$

$\Rightarrow \quad U + W = 0$

The gas in this process obeys the relation :

$$PV^{\gamma} = \text{constant} \qquad (\gamma = C_p/C_v)$$

$\Rightarrow \quad P_1V_1^{\gamma} = P_2V_2^{\gamma}$



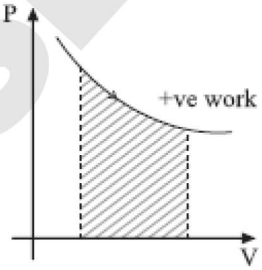
Note : *The adiabatic curve in P-V diagram is much steeper than the isothermal curve.*

(a) Adiabatic Expansion :

As the pressure on the piston is reduced, the gas pushes the piston upwards. Due to the expansion, the temperature of the system falls down. The molecules of the gas lose speed after colliding with a receding (moving away) piston. The loss in the speed causes a fall in the temperature. The gas does positive work and its internal energy decreases. In the equation of Ist law :

$\Delta U + W = 0$, ΔU is negative and W is positive.

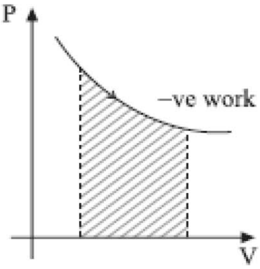
(internal energy of the gas is being converted into work done)



(b) Adiabatic Compression :

As the pressure on the piston is increased, it moves downwards compressing the gas. Due to compression, the temperature of the gas rises. The molecules of the gas gain speed after colliding with an incoming piston. The gain in speed causes a rise in temperature. Work is done on the gas and its internal energy increases.

In the equation : $\Delta U + W = 0$, ΔU is positive and W is negative.



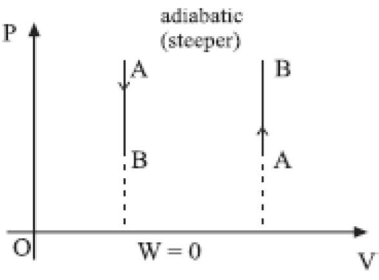
Isochoric process :

A process in which the volume remains constant is known as isochoric process.

For an isochoric process, an ideal gas is taken in a container with rigid walls so that neither expansion nor compression occurs.

The gas obeys the relation : $P \propto T$

In isochoric process, $\Delta W = 0$. So from Ist Law of thermodynamics : $\Delta Q = \Delta U$.

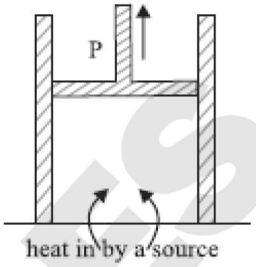


(a) If heat is given to the gas, its temperature and pressure rise. Its internal energy also rises. ΔU and ΔQ are both positive.

(b) If heat is taken out from the gas, its temperature and pressure fall. Its internal energy also decreases. ΔQ and ΔU are both negative.

Isobaric process :

A process in which the pressure is kept constant is called as isobaric process.



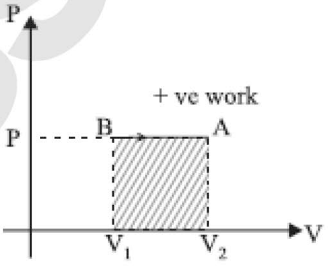
For isobaric process, the external pressure on the piston is kept constant.

The gas obeys Charles' Law : $V \propto T$

The work done : $W = P\,(V_2 - V_1)$

$= n\,R\,(T_2 - T_1)$

(a) Isobaric Expansion :



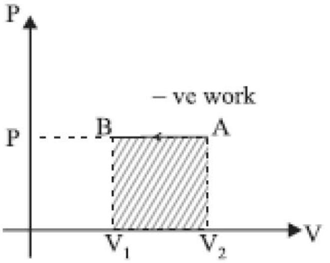
If heat is given to the gas, isobaric expansion occurs. The volume and the temperature both rise. The gas expands doing positive work.

In equation :

$\Delta Q = \Delta U + W$, all the three terms :

ΔQ, ΔU and W are positive in the isobaric expansion.

(b) Isobaric Compression :



If heat is taken out of the gas, isobaric compression occurs. The temperature falls and the gas contracts causing negative work.

In the equation :

$\Delta Q = \Delta U + W$, all three terms :

ΔQ, ΔU and W are negative in the isobaric compression.

Expressions for ΔU, W, and ΔQ for Different Processes

Internal Energy Change : (ΔU)

$\Delta U = nC_v\,\Delta T$ for every process.

It is state function and depends only on the difference of initial and final temperatures.

$$\Delta U = n\,C_v\,\Delta\mathrm{T} = \frac{n\,R}{\gamma - 1}\Delta T$$

Process	Work Done : (W)	Heat Exchange : (ΔQ)
Isothermal Process :	$W = 2.303\ nRT\ \log_{10}\dfrac{V_2}{V_1}$	$\Delta Q = 2.303\ nRT\ \ell og_{10}\dfrac{V_2}{V_1}$
Adiabatic Process :	$W = \dfrac{P_1V_1 - P_2V_2}{\gamma - 1} = \dfrac{nR(T_1 - T_2)}{\gamma - 1}$	$\Delta Q = 0$
Isochoric Process :	$W = 0$	$\Delta Q = n\,C_v\,\Delta T$ (use definition of C_v)
Isobaric Process :	$W = P\,\Delta V = P\,(V_2 - V_1)$ $W = nR\,(T_2 - T_1)$	$\Delta Q = n\,C_p\,\Delta T$ (use definition of C_p)

Relations for Thermodynamic Processes (State Variables P, V, T)

Isochoric process :

Volume remains constant. $\Rightarrow$ $P \propto T$ $\Rightarrow$ $\dfrac{P_1}{T_2} = \dfrac{P_2}{T_2}$

Isothermal process :

Temperature remains constant $\Rightarrow$ $P \propto 1/V$ $\Rightarrow$ $P_1V_1 = P_2V_2$

Isobaric process :

Pressure remains constant. $\Rightarrow$ $V \propto T$ $\Rightarrow$ $\dfrac{V_1}{T_2} = \dfrac{V_2}{T_2}$

Adiabatic process :

No heat transfer takes place.

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \qquad T_1^{\gamma}P_1^{1-\gamma} = T_2^{\gamma}P_2^{1-\gamma}$$

Illustration - 17 *An ideal gas undergoes an isothermal expansion at* $0°C$ *from* $0.010\ m^3$ *to* $0.200\ m^3$*. For 5 moles of gas, compute the work done, the heat added, and the change in internal energy.*

SOLUTION :

Let $V_1 = 0.01\ m^3$; $V_2 = 0.2\ m^3$;

$T_1 = T_2 = 273\ K$; $n = 5$ moles

$$W = 2.303\ nRT_1\ \log_{10}\frac{V_2}{V_1}$$

$$W = 2.303 \times 5 \times 8.3 \times 273\ \log_{10} 20 = 33.946\ J.$$

As $\Delta U = 0$ for isothermal process, $\Delta Q = W = 33946\ J.$