

Thermal equilibrium: Two physical systems are in thermal equilibrium if there is no net flow of thermal energy between them when they are connected by a path ~~permeable~~ to heat. Thermal equilibrium obeys the zeroth law of thermodynamics.

Mechanical equilibrium: Mechanical equilibrium is a state where the sum of all forces acting on an object of interest is zero. For this to happen all of the forces are required to be balanced.

Chemical equilibrium: Chemical equilibrium condition in the course of a reversible chemical reaction in which no net change in the amounts of reactants and products occurs. A reversible chemical reaction is one in which the products as soon as they are formed, react to produce the original reactants.

First order phase transition: Suppose that two phases of a system is maintained at a constant temperature T and pressure p . Therefore, the condition for thermodynamic

equilibrium is that the gibb's function or Φ is a minimum. Let the two phase be labelled 1 and 2 with mass m_1 and m_2 . Then the total mass is $M = m_1 + m_2$ and the gibb's function is, $\Phi = m_1 \varphi_1 + m_2 \varphi_2$

Here, φ will be used to symbolize the gibb's function per unit mass. At equilibrium

$$d\Phi = \varphi_1 dm_1 + \varphi_2 dm_2 = 0$$

If the symbol is closed so that M is constant

$$dM = dm_1 + dm_2 = 0$$

considering these two equations,

$$\varphi_1 = \varphi_2$$

If the phase transition takes place reversibly at constant pressure, the change of enthalpy per mole is given by, $\Delta h = T(s_2 - s_1)$

The change in molar enthalpy, therefore Δg means that there is change of molar entropy.

$$dg = -SdT + vdp$$

$$\text{Then, } S = -\left(\frac{\partial g}{\partial T}\right)_P, V = -\left(\frac{\partial g}{\partial P}\right)_T$$

We may characterize the familiar phase transitions by either of the following equivalent statements

1. There are changes of molar entropy and of molar volume.
2. The first-order derivatives of the molar gibb's function change discontinuously.

Heat and thermodynamics.

SYA 2

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Seam, FW and Salinger, GL

Thermodynamics: Kinetic Theory
and Statistical Mechanism.

Thermal

thermodynamic equilibrium: When an arbitrary system is isolated and left to itself; its properties will in general change with time. If initially there are temperature difference b/w parts of the system, after a significantly sufficiently long time the temperature will become the same at all points and then the system is in thermal equilibrium.

Mechanical equilibrium: If there are variations in pressure or elastic stress within the system, parts of the system may move, or expand or contract. Eventually these motions, expansions, or contractions will cease, and when this has happened we say that the system is in mechanical equilibrium.

Chemical equilibrium: If we suppose that a system contains substances that can react chemically. After a sufficiently long time has elapsed, all possible chemical reactions will have taken place, and the system is then said to be in chemical equilibrium.

A system which is in thermal, mechanical, and chemical equilibrium is said to be in thermodynamic equilibrium.

Diffusive equilibrium: (With no flow of matter from one system to another.)
(Chemical Potential).

The steady state (with no flow of matter from one system to another) resulting from the diffusion process is called diffusive equilibrium.

Phase equilibrium: A substance is in 'phase equilibrium' when more than one phase of a substance (solid, liquid, gas) is present and the amount of material in each phase does not change.

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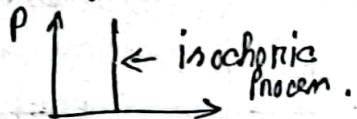
Thermodynamic process: When the system undergoes change from one thermodynamic state to final state due to change in properties like temperature, pressure, volume etc., the system is said to have undergone thermodynamic process.

Quasistatic process: If a process is carried out in such a way that at every instant the system departs only infinitesimally from an equilibrium state, the process is called quasistatic (i.e.; almost static). Thus a quasistatic process closely approximates a succession of equilibrium states. If there are finite departures from equilibrium, the process is nongeostatic.

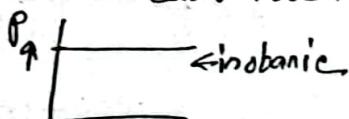
All actual processes are nongeostatic because they take place with finite differences of pressure, temperature, etc., between parts of a system.

Nevertheless, the concept of a quasistatic process is a useful and important one in thermodynamics.

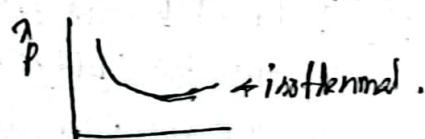
Isochoric Process: A process in which the volume of a system is constant is called isochoric or isochoric process. $dV=0$



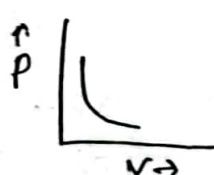
Isobaric process: If the pressure is constant, the process is called isobaric. $dP=0$



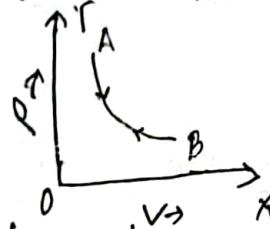
Isothermal Process: A process at constant temperature is called isothermal process. $dT=0$



Adiabatic process: A process carried out by a system enclosed by an adiabatic boundary in which there is no flow of heat across the boundary is an adiabatic process. $dQ=0$



Reversible Process: A reversible process is a process whose direction can be reversed without producing any changes in the thermodynamic properties of the universe. It is called a reversible process.



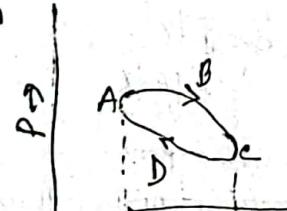
Suppose, the system has undergone a change from state A to B. If the system can be restored from state B to state A and there is no change in the universe, then the process is said to be a reversible process.

Thus, for reversible processes, it is a very slow process and all of the initial and final states of the system should be in equilibrium with each other.

Irreversible process: If a process undergoes a change in which it can not regain its initial state without doing any external effort or work is called irreversible process. It is also called natural process because all the processes occurring in nature are irreversible processes.

Cyclic Process: If a process undergoing a change in which it regains its initial state at the end of the cycle then it is called a cyclic process.

In a cyclic process the initial and final state is same and net change in internal energy ΔU is zero i.e., $\Delta U = 0$, as internal energy depends only on the state of the system.



For cyclic process, the first law of thermodynamics can be stated as,

$$\oint dQ = \oint dU + \oint dW$$

$$\text{or, } \oint dQ = \oint dW \quad \therefore [\oint dU = 0]$$

\therefore Total energy obtained = Net work done.

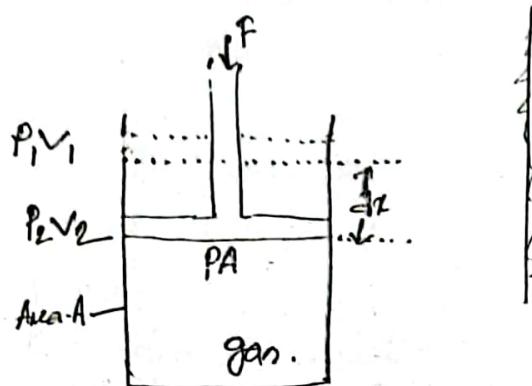
Thus, no work is obtained if no heat is supplied or work can be obtained only at the cost of energy.

From indicator diagram we can write,

$$Q = \text{Area ABCDA}$$

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Workdone in reversible isothermal Process



Suppose that gas in the initial equilibrium state (p_1v_1) is compressed to a new equilibrium state (p_2v_2) by increasing the external force on the piston and allowing it to slide in. If no frictional forces are present, all of this work goes into performing work on the gas.

Suppose that, at one of the intermediate equilibrium states during the reversible compression, the pressure is p and the balancing force on the piston is F . Then as shown in fig. $F = pA$

Where, A is the area of the piston. If the force is increased infinitesimally so that the piston moves in by dx , the workdone on the gas by surroundings applying the forces F is,

$$dw = F dx \\ = +pAdx$$

$$\Rightarrow dw = -pdv$$

④ The $-$ (ve) sign is because during compression the volume is decreased, but the workdone on the gas is positive -

The total work performed on the gas on the process is,

$$W = - \int_{V_1}^{V_2} p dv \quad p_1v_1 \rightarrow p_2v_2$$

For 1 mole gas,

$$PV = RT$$

$$\Rightarrow P = \frac{RT}{V}$$

Where, v_1 and v_2 are the initial and final volumes.

$$\begin{aligned} \Rightarrow W &= - \int_{V_1}^{V_2} \frac{RT}{V} dV \\ &= - RT \left[\ln V \right]_{V_1}^{V_2} \\ &= - RT \ln \frac{V_2}{V_1} \end{aligned}$$

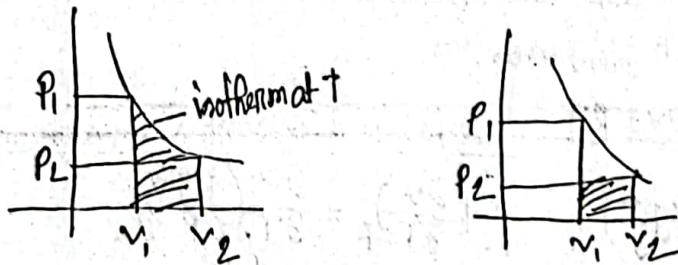
Workdone in reversible Isothermal process, (For n mole)

$$\begin{aligned} W &= -nRT \ln \frac{V_2}{V_1} & P_1 V_1 = P_2 V_2 \\ &= -nRT \ln \frac{P_1}{P_2} & \frac{V_2}{V_1} = \frac{P_1}{P_2} \end{aligned}$$

Workdone in Isothermal irreversible Process,

$$\begin{aligned} W &= - \int_{V_1}^{V_2} P_2 dV \\ &= P_2 (V_2 - V_1) \\ &= P_2 \cdot \Delta V \end{aligned}$$

Comparison of work in reversible and irreversible Process,



(i) Reversible work done

(ii) Irreversible work done.

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The differential relation between differential state variable.:

$$\text{The equation of state } P(\rho, V, T) = 0 \quad \dots \quad (1)$$

$$P = f(V, T) \quad \dots \quad (2)$$

$$\therefore dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

For isobaric process, $dP = 0$

$$\left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV = 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V dT = - \left(\frac{\partial P}{\partial V} \right)_T dV$$

$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P$$

$$\therefore \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P \cdot \left(\frac{\partial T}{\partial P} \right)_V = -1$$

* Verify the relation for ideal gas:

For one mole of ideal gas,

$$PV = RT$$

$$\therefore \left(\frac{\partial P}{\partial V} \right)_T = \frac{\partial P}{\partial V} \left(\frac{RT}{V} \right) \quad \therefore \left(\frac{\partial V}{\partial T} \right)_P = \frac{\partial V}{\partial T} \left(\frac{RT}{P} \right)$$
$$= - \frac{RT}{V^2} \quad = \frac{R}{P}$$

$$\therefore \left(\frac{\partial T}{\partial P} \right)_V = \frac{\partial T}{\partial P} \left(\frac{V}{R} \right)$$

$$= \frac{V}{R}$$

$$\therefore \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P \cdot \left(\frac{\partial T}{\partial P} \right)_V = - \frac{RT}{V^2} \cdot \frac{R}{P} \cdot \frac{V}{R}$$

$$= - \frac{RT}{PV}$$

$$= - \frac{PV}{PV}$$

$$= -1$$

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First law of thermodynamics:

Statement: The total work done in the same in all adiabatic processes between any two equilibrium states having the same kinetic and potential energy.

$$W_{\text{adiabatic}} = U_2 - U_1 = \Delta U$$

$$W_{\text{ad}} \neq \Delta U$$

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

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

$$\therefore dU = dW + dQ$$

$$dU = -pdv + dQ \quad [dW = -pdv]$$

$$\therefore dQ = dU + pdv.$$



The amount

The amount of heat Q or dQ is taken positive if heat is supplied to the system and negative if heat is removed from the system.

Similarly, the work W or dW is taken positive if the external work is done by the system in expansion and negative if the work is done on it in compression.

Significance of the first law of thermodynamics:

The first law of thermodynamics is important because -

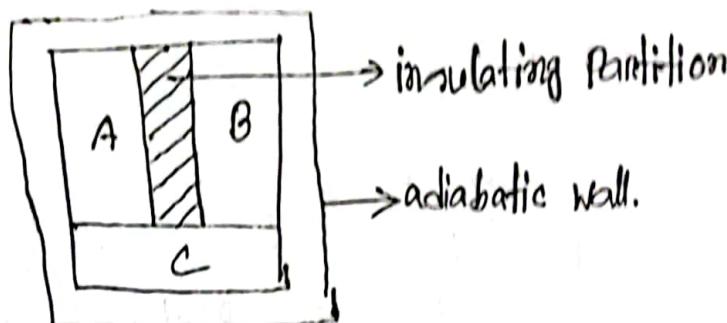
- It is applicable to any process by which a system undergoes a physical or chemical change.
- It introduces the concept of internal energy.
- It provides the method for determining the change in internal energy.

Limitations: The first law of thermodynamics is based on the principle of conservation of energy of a system. Though it is applicable to every process in nature between the equilibrium states, it does not specify the condition under which a system can use its heat energy to produce a supply of mechanical work. It does not say how much of heat energy can be converted into work.

Zeroth law of thermodynamics:

It states that if two bodies each are separately in thermal equilibrium with a third body then the two bodies are also in thermal equilibrium with each other.

Explanation:



Suppose, two systems A and B are insulated from each other and good contact with a common system C.

Systems A and B attain thermal equilibrium with system C. Now, if the insulating partition is removed and brought system A and B into thermal contact. We find that there is no further change.

This means the system A and B are also in thermal equilibrium with each other. This is known as zeroth law of thermodynamics.

Adiabatic expansion of ideal gas:

Consider, 1 gm of working substance (ideal gas) perfectly isolated from the system and let the external work done by the gas is $dW = PdV$.

Applying the first law of thermodynamics,

$$dQ = dU + PdV \quad \text{--- (1)}$$

Heat capacity at constant volume for that system;

$$C_V = \frac{dU}{dT}$$

$$\therefore dU = C_V dT$$

$$\therefore \text{from eqn (1); } dQ = C_V dT + PdV \quad \text{--- (2)}$$

For ideal gas, $PV = RT$

$$PdV + Vdp = RdT$$

$$\therefore PdV = RdT - Vdp \quad \text{--- (3)}$$

Substituting eqn. (3) in eqn. (2);

$$dQ = C_V dT + RdT - Vdp$$

$$= (C_V + R) dT - Vdp$$

$$= C_p dT - Vdp \quad \left[\begin{array}{l} \because C_p - C_V = R \\ \therefore C_p = C_V + R \end{array} \right] \quad \text{--- (4)}$$

For adiabatic process,

$$dQ = 0$$

Thus, from eqn. (4) and (1);

$$C_V dT = -PdV \quad \text{--- (5)}$$

$$C_p dT = Vdp \quad \text{--- (6)}$$

(6) \div (5);

$$\therefore \gamma = \frac{C_p}{C_V} = -\frac{Vdp}{PdV}$$

$$\int \frac{dp}{P} = -\gamma \int \frac{dv}{V}$$

$$\therefore \ln P = -\gamma \ln V + \ln k.$$

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$$\Rightarrow \ln p + \gamma \ln v = \ln k$$

$$\Rightarrow \ln(pv^\gamma) = \ln k$$

$\therefore pv^\gamma = \text{constant.}$

(C) Prove, $TV^{\gamma-1} = \text{constant.}$

B For ideal gas, $PV = RT$

$$\Rightarrow P = \frac{RT}{V}$$

We know, $PV^\gamma = \text{constant.}$

$$\therefore \frac{RT}{V} \cdot V^\gamma = \text{constant}$$

$$\Rightarrow RT \cdot V^{\gamma-1} = \text{constant}$$

$$\therefore TV^{\gamma-1} = \text{constant} [\because R \text{ is constant}]$$

(D) Prove $\frac{dP}{dT} = T P^{\frac{1-\gamma}{\gamma}}$ = constant.

B For ideal gas, $PV = RT$

$$\Rightarrow V = \frac{RT}{P}$$

We know, $PV^\gamma = \text{constant}$

$$\Rightarrow P \left(\frac{RT}{P} \right)^\gamma = \text{constant.}$$

$$\Rightarrow \frac{R^\gamma T^\gamma}{P^{1-\gamma}} = \text{constant}$$

$$\Rightarrow \frac{T^\gamma}{P^{\gamma-1}} = \text{constant}$$

$$\Rightarrow \frac{P^{\gamma-1}}{T^\gamma} = \text{constant}$$

$$\Rightarrow T^{-\gamma} P^{\gamma-1} = \text{constant.}$$

$$\Rightarrow -\gamma \ln T + (\gamma - 1) \ln P = \text{constant}$$

$$\Rightarrow \frac{-\gamma}{\gamma} \ln T - \left(\frac{\gamma-1}{\gamma}\right) \ln P = \text{constant.}$$

$$\Rightarrow \ln T - \ln P \frac{\gamma-1}{\gamma} = \text{constant.}$$

$$\Rightarrow \ln T + \ln P \frac{1-\gamma}{\gamma} = \text{constant.}$$

$$\Rightarrow \ln TP^{\frac{1-\gamma}{\gamma}} = \text{constant.}$$

$$\therefore TP^{\frac{1-\gamma}{\gamma}} = \text{constant.}$$

(*) Heat Capacity: Heat capacity of a body is defined by as the amount of heat absorbed or rejected to change the temperature by one unit.

$$S = \frac{dQ}{dT}.$$

(*) Molar specific heat: Molar specific heat of a gaseous substance is defined as the amount of heat absorbed or rejected to change the temperature of one mole of it by one unit.

$$C = \frac{S}{m} = \frac{1}{m} \cdot \frac{dQ}{dT} \text{ where, } m = \text{mole.}$$

Molar specific heat - Molar specific heat at constant pressure, C_p
Molar specific heat at constant volume, C_v

Molar specific heat at constant pressure, C_p : If we want to increase one degree temperature of a system by keeping the pressure constant, the required amount of heat is called heat capacity at constant pressure. If we restrict the increase in pressure, the supplied heat will increase the temperature and volume.

$$C_p = \frac{1}{m} \frac{dQ_p}{dT}$$

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Molar specific heat at constant volume, C_V : If we want to increase one degree temperature of a system by keeping the volume constant, the required amount of heat is called heat capacity at constant volume. If we restrict the increase in volume, the supplied heat will increase the temperature and pressure of the system.

$$C_V = \frac{1}{m} \cdot \frac{dQ_V}{dT}$$

Q Why $C_P > C_V$?

Soln: According to first law of thermodynamics,

$$dQ = dU + dW$$

From the definition of C_P and C_V in a constant pressure (isobaric) and constant volume (isochoric) Process respectively,

$$\therefore dQ_P = m \cdot C_P \cdot dT$$

$$\therefore dQ_V = m \cdot C_V \cdot dT$$

In a constant volume (isochoric) process, $dW = 0$. Where in a constant pressure (isobaric) process, work is done. Hence,

$$dQ_P > dQ_V$$

Since C_P and C_V are proportional to dQ_P and dQ_V respectively then we can say that, $C_P > C_V$.

③ When gas is heated at constant pressure (C_P) it receives more heat energy as there is a change in internal energy and external work done.

But, in case of constant volume (C_V) there is no external work done, so that the given heat has to increase only internal energy.

Therefore, C_P is always greater than C_V .

Difference between different heat capacities for one mole of ideal gas:

from first law of thermodynamics,

$$dQ = dU + PdV \quad \text{--- (1)}$$

Internal energy,

$$U = U(T, V) \quad \text{--- (2)}$$

$$\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{--- (3)}$$

Putting eqn (3) in eqn (1) we get,

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

$$\Rightarrow \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT} \quad \text{--- (4)}$$

For

isochoric process, $dV = 0$

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{--- (5)}$$

For isobaric process, $dP = 0$

$$C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (6)}$$

$$= C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P \quad \boxed{C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T P}$$

$$\therefore C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

For ideal gas,

$$\text{Internal energy, } U = \frac{3}{2} k_B T$$

$$U = U(T)$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$$

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∴ In case of ideal gas,

$$C_p - C_v = P \left(\frac{\partial V}{\partial T} \right)_P$$

We know, for one mole of ideal gas,

$$PV = RT$$

$$\Rightarrow V = \frac{RT}{P}$$

$$\begin{aligned}\therefore \left(\frac{\partial V}{\partial T} \right)_P &= \frac{\partial}{\partial T} \left\{ \frac{RT}{P} \right\} \\ &= \frac{R}{P}.\end{aligned}$$

$$\therefore C_p - C_v = P \cdot \frac{R}{P}$$

$$\therefore C_p - C_v = R$$

Calculation of C_p and C_v for monoatomic ideal gas;

for ideal gas internal energy,

$$U = \frac{3}{2}RT$$

Molar specific heat at constant volume,

$$\begin{aligned}C_v &= \frac{du}{dT} \\ &= \frac{d}{dT} \left(\frac{3}{2}RT \right) \\ &= \frac{3}{2}R.\end{aligned}$$

Molar specific heat at constant pressure,

We know,

$$C_p - C_v = R$$

$$\Rightarrow C_p = R + C_v$$

$$= R + \frac{3}{2}R$$

$$= \frac{2PAQ}{2}$$

$$\rightarrow \frac{P}{2}Q$$

We know,

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

$$= \frac{\frac{5}{2}R}{\frac{3}{2}R}$$

$$= \frac{5}{3}$$

Workdone in adiabatic process:

$$dU = dW + dQ$$

$$\Rightarrow dW = dU - dQ$$

In adiabatic process, $dQ = 0$

$$\therefore dW = dU$$

$$\Rightarrow dW = -PdV$$

\therefore Workdone in adiabatic Process,

$$W = - \int_{V_1}^{V_2} PdV$$

$$= - \int_{V_1}^{V_2} \frac{RK}{\sqrt{\gamma}} dV \quad [PV^{\gamma} = RK \Rightarrow P = \frac{RK}{V^{\gamma}}]$$

$$= - \int_{V_1}^{V_2} KRV^{\gamma} dV$$

$$= -K \int_{V_1}^{V_2} V^{\gamma} dV$$

$$= -K \left[\frac{V^{\gamma+1}}{\gamma+1} \right]_{V_1}^{V_2}$$

$$= -K \left[\frac{V_2^{\gamma+1}}{\gamma+1} - \frac{V_1^{\gamma+1}}{\gamma+1} \right]$$

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$$\begin{aligned}
 &= -\frac{k}{\gamma-1} \cdot (v_2 - v_1)^{-\gamma+1} \\
 &= \frac{-k}{-(\gamma-1)} (v_2^{1-\gamma} - v_1^{1-\gamma}) \\
 &= \frac{k}{\gamma-1} (v_2^{1-\gamma} - v_1^{1-\gamma}) \\
 &= \frac{P_2 v_2^{\gamma} v_2 - P_1 v_1^{\gamma} v_1}{(\gamma-1)(v_2^{\gamma} - v_1^{\gamma})} \\
 &= \frac{(v_2^{\gamma} - v_1^{\gamma}) P_2 v_2^{\gamma} (P_2 v_2 - P_1 v_1)}{(\gamma-1) (v_2^{\gamma} - v_1^{\gamma})} \\
 &= \frac{1}{\gamma-1} (P_2 v_2 - P_1 v_1)
 \end{aligned}$$

We know that;

$$P_1 v_1^{\gamma} = P_2 v_2^{\gamma} = k$$

$$\begin{aligned}
 \therefore W &= \frac{1}{\gamma-1} \left[\frac{k}{v_2^{\gamma-1}} - \frac{k}{v_1^{\gamma-1}} \right] \\
 &= \frac{1}{\gamma-1} \left[\frac{P_2 v_2^{\gamma}}{v_2^{\gamma-1}} - \frac{P_1 v_1^{\gamma}}{v_1^{\gamma-1}} \right] \\
 &= \frac{1}{\gamma-1} [P_2 v_2 - P_1 v_1] \quad \text{--- (1)}
 \end{aligned}$$

We know that;

$$P_1 T_1 = R T_1 \quad \text{and} \quad P_2 T_2 = R T_2$$

Substituting these values in Eq.(1);

$$W = \frac{1}{\gamma-1} [R T_2 - R T_1]$$

$$\Rightarrow W = \frac{R}{\gamma-1} [T_2 - T_1]$$

$$= \frac{R}{\gamma-1} [T_1 - T_2]$$

Thus, the workdone in adiabatic process depends only upon the initial and final temperature T_1 and T_2 .

Method of finding work done
at constant pressure