Thermodynamics

Thermal Equilibrium and Zeroth Law of Thermodynamics

- Thermodynamics deals with heat and temperature, and the inter-conversion of heat and other energy forms.

- Thermodynamics is a macroscopic science. It deals with bulk system, and does not go into the molecular constitution of matter.

- Thermal equilibrium: State of a system is an equilibrium state if the macroscopic variables that characterise the system do not change. Two systems at the same temperature are said to be in thermal equilibrium with each other.

- Adiabatic wall: It is an insulating wall that does not allow flow of heat

- Diathermic wall: It is a conducting wall that allows flow of heat. In this case, thermal equilibrium can be attained.

Zeroth Law of Thermodynamics

- When two systems are separately in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.

- The physical quantity which is required to be in thermal equilibrium is temperature

- Consider three systems, *X*, *Y* and *Z*.

  X and *Y* are separately in thermal equilibrium with *Z*.

  $\therefore T_X = T_Z \text{ and } T_Y = T_Z$

  Where,

  T_X = Temperature of *X*

  T_Y = Temperature of *Y*

  T_Z = Temperature of *Z*

  Hence,

  $T_X = T_Y$

The systems *X* and *Y* are also in thermal equilibrium with each other.

Heat, Internal Energy and Work

Heat

- It is a form of energy.
- Heat is a transfer of energy due to the temperature difference between a system and its surroundings.
- The flow of heat between two bodies stops when their temperatures equalise; the two bodies are then in thermal equilibrium.

Internal Energy

- Work is transfer of energy brought about by other means, such as moving the piston of a cylinder containing gas.
- Internal energy of a system is the sum of the kinetic and potential energies of the molecular constituents of the system.
- It includes the energy associated with the random motion of molecules of the system.
- Internal energy (as a state variable) depends on the given state of the system, and not on the path taken to reach the state.
- Internal energy and work are equivalent.

Difference between heat and internal energy

In thermodynamics, heat and work are not state variables; however, internal energy is a state variable.

First Law of Thermodynamics:

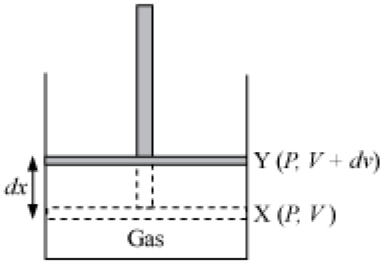
- The first law of thermodynamics is based on the law of conservation of energy.
- According to the first law of thermodynamics, the energy(ΔQ) supplied to a system is partly spent to increase the internal energy of the system (ΔU) and the rest is spent in doing work on the surroundings (W).
- The equation for the first law of thermodynamics is

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

First Law of Thermodynamics and Specific Heat Capacity

- According to first law of thermodynamics, when an amount of heat ΔQ is added to a system, a part of it increases its internal energy by ΔU and the remaining part is used up as the external ΔW done by the system.

  $\therefore \Delta Q = \Delta U + \Delta W \ldots (1)$

  A gas is enclosed in a cylinder provided with mass-less and frictionless piston.

  Initial state − X

  Final state − Y

  Here,

  P − Pressure

  V − Volume

  a − Area of cross-section of piston

  dx − Distance moved by the piston

  dV − Increase in volume

  Work done, dW = Force on piston × dx

  $\Delta W = Pa \times dx$

  $= P\,(adx)$

  Since $dV = adx$,

  $\therefore \Delta W = PdV \ldots (2)$

From equations (1) and (2),

$$\Delta Q = \Delta U + PdV$$

Specific Heat Capacity (s):

- Heat capacity, $S = \frac{\Delta Q}{\Delta T}$

Where, ΔQ − Heat supplied

ΔT − Change in temperature

- Specific heat capacity, $s = \frac{1}{m}\frac{\Delta Q}{\Delta T}$

m − Mass of the substance

Unit − $\mathrm{Jkg^{-1}K^{-1}}$

- Molar specific heat capacity, $C = \frac{S}{\mu}$

$$= \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$$

μ − Number of moles

Let us consider a solid of N atoms, each vibrating about its mean position.

Average energy of an oscillator in one-dimension

$$= 2 \times \frac{1}{2} k_B T = k_B T$$

∴ Average energy in three-dimension = $3k_BT$

Where, k_B − Boltzmann constant

T − Temperature

∴ Total energy, $U = 3k_BT \times N_A$

= 3RT

Where R − Gas constant

At constant pressure,

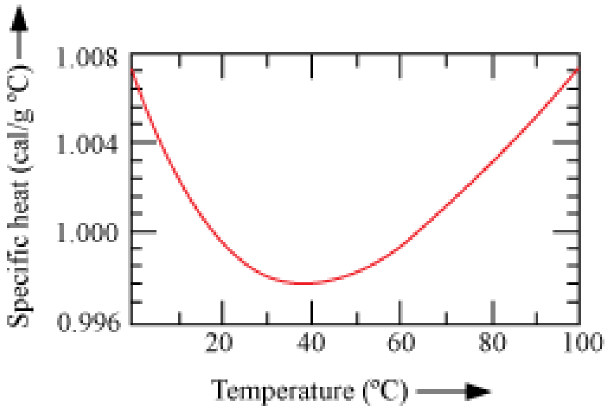
$\Delta Q = \Delta U + P\Delta V \cong \Delta U$ (For a solid, ΔV is negligible)

$$\therefore C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3\text{R}$$

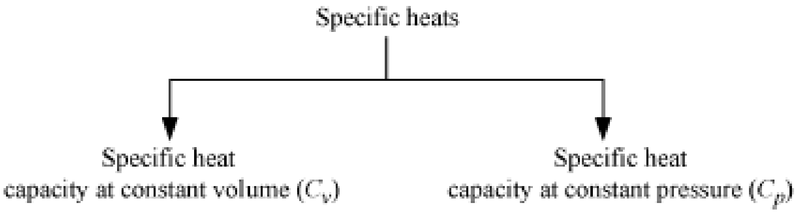
∴ Molar specific heat, C = 3R

Specific Heat Capacity of Water

- Specific heat of water varies slightly with temperature.



- 1 calorie − Amount of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C
- Specific heat capacity of water is 4186 $\text{Jkg}^{-1}\text{K}^{-1}$ (in SI units).
- For gases, we can define two specific heats:



For 1 mole of a gas,

$$\Delta Q = \Delta U + P\Delta V$$

$$C = \frac{\Delta Q}{\Delta T}$$

At constant volume,

$\Delta V = 0$

$$\therefore C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right) \qquad ...(3)$$

At constant pressure,

$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P = \left(\frac{\Delta U}{\Delta T}\right)_P + P\left(\frac{\Delta V}{\Delta T}\right)_P$$

$$= \left(\frac{\Delta U}{\Delta T}\right)_P + P\left(\frac{\Delta V}{\Delta T}\right)_P \qquad ...(4)$$

For 1 mole of an ideal gas,

$$PV = \mathrm{R}T$$

$$P\left(\frac{\Delta V}{\Delta T}\right)_P = \mathrm{R} \qquad ...(5)$$

From equations (4) and (5),

$$C_P = \left(\frac{\Delta U}{\Delta T}\right) + \mathrm{R} \qquad ...(6)$$

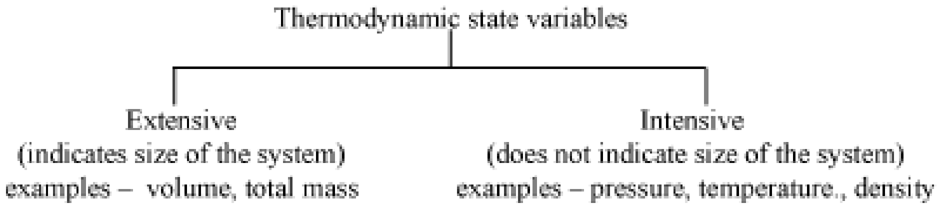
From equations (3) and (6),

$$\boxed{C_P - C_V = \mathrm{R}}$$

Thermodynamic State Variables and Equation of State

State Variables

- Macroscopic variables (such as pressure, volume, temperature, mass) used for describing the equilibrium state of a thermo-dynamic system completely are called state variables. The values of state variables depend only on the given state of a system.



Equation of State

- The relation between the state variables of a system is called the equation of state.

  For an ideal gas, the relation of the equation of state is $PV = \mu RT$

  μ = Number of moles (is fixed)

Thermodynamic Processes

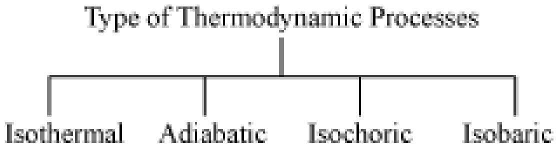
Quasi-Static Process

- An idealised process in which at every stage the system is in an equilibrium state.

  Such a process is infinitely slow and hence, named quasi-static (i.e., nearly static).

  Changes in the system are so slow that it remains in thermal and mechanical equilibrium with its surroundings.

Types of Thermodynamic Processes



Isothermal Process

- Occurs at a constant temperature; PV = Constant

  Isothermal changes take place in an ideal gas (at temperature T)

  Initially,

  Pressure = P_1

  Volume = V_1

Finally,

Pressure = P_2

Volume = V_2

At the intermediate stage,

Pressure = P

Work done for the entire process

$$W = \int_{V_1}^{V_2} P\,dV \qquad (PV = \mu RT)$$

$$\therefore\ W = \mu RT \int_{V_1}^{V_2} \frac{dV}{V} = \mu RT\ \ln \frac{V_2}{V_1}$$

- There is no change in the internal energy of an ideal gas in isothermal process.
- In isothermal expansion ($V_2 > V_1$), the gas absorbs heat and does work ($W > 0$)
- In isothermal compression ($V_2 < V_1$), work is done on the gas by the environment and heat is released.

Adiabatic Process

- During this process, no heat enters or leaves the thermodynamic system during the change.
- System is insulated from its surroundings.

PV^{γ} = Constant(1)

γ = Ratio of specific heats

$$\left(\gamma = \frac{C_P}{C_V}\right)$$

- If an ideal gas undergoes a change adiabatically,

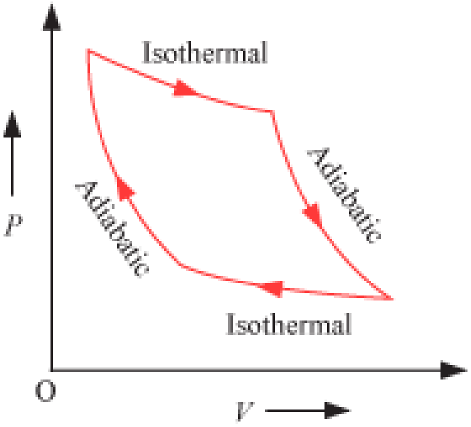
Initial state = P_1, V_1

Final state = P_2, V_2

Then,

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad (2)$$

The following graph shows the *P*-*V* curves of an ideal gas for two adiabatic processes connecting two isotherms.



Work done, $W = \int_{V_1}^{V_2} P\,dV$

From equation (1), we get

= Constant × $\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$

= Constant × $\left|\frac{V^{-\gamma+1}}{1-\gamma}\right|_{V_1}^{V_2}$

= Constant $\times \frac{1}{1-\gamma}\left[\frac{P_2\ V_2{}^{\gamma}}{V_2{}^{\gamma-1}} - \frac{PV}{V}\right]$

$P_1V_1^{\gamma}$ or $P_2V_2^{\gamma}$ is a constant

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}[P_2V_2 - P_1V_1] = \frac{\mu R(T_1 - T_2)}{\gamma - 1}$$

- Work done by the gas ($W > 0$); so $T_2 < T_1$
- Work done on the gas ($W < 0$); so $T_2 > T_1$

Isochoric Process

- Occurs at constant volume.
- No work is done on or by the gas.
- Heat absorbed by the gas is used for changing the internal energy and temperature of the gas.

Isobaric Process

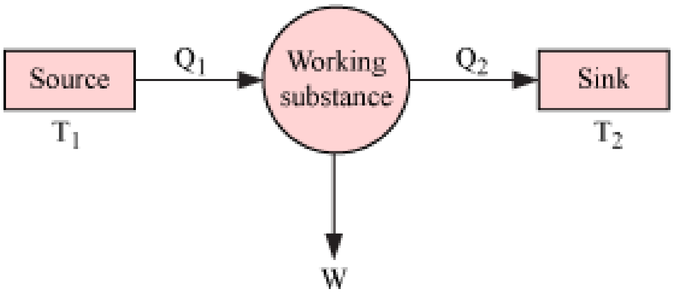
- Occurs at constant pressure.
- Work done, $W = P(V_2 - V_1) = \mu R(T_2 - T_1)$
- Change in temperature also changes the internal energy.
- Heat absorbed is used partly for increasing internal energy and partly for doing work.

Cyclic Process

- In a cyclic process, the system returns to its initial state.
- Internal energy ($\Delta U = 0$); so the total heat absorbed equals the work done by the system.

Heat Engines & Refrigerators

Heat engine is a device which converts heat energy into mechanical energy.



Efficiency (η) of a Heat Engine

Q_1 → Heat taken from a hot reservoir

T_1 → Temperature of hot reservoir

Q_2 → Heat released to cold reservoir

T_2 → Temperature of cold reservoir

W → Work done by the system

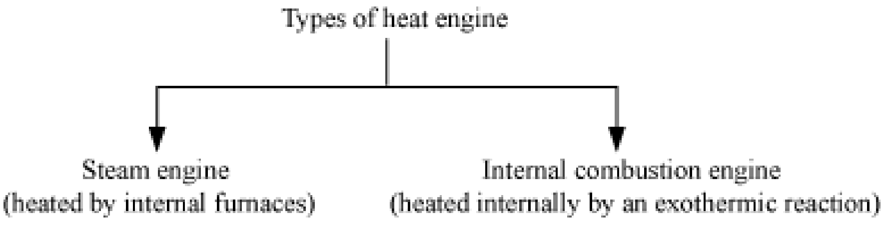
$$\eta = \frac{W}{Q_1}$$

$$W = Q_1 - Q_2$$

$$\therefore \eta = 1 - \frac{Q_2}{Q_1}$$

η = 1 (Not possible)

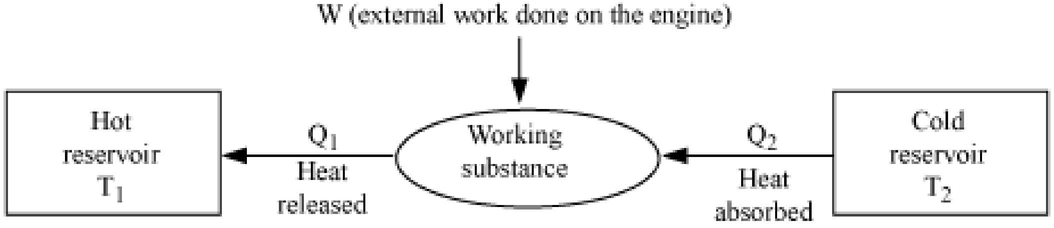
Types of heat engine



Refrigerators or Heat Pumps

- Reverse of heat engine

W (external work done on the engine)



Refrigerator − Its purpose is to cool a portion of space.

Heat pump − Its purpose is to pump heat into a space.

Steps followed by the working substance of a refrigerator:

- Expansion of the gas suddenly from high to low pressure cools it and converts it into a vapour liquid mixture.
- Cold fluid of heat is absorbed from the region to be cooled and coverts it into vapour.
- External work done on the system heats up the vapour.
- Release of heat by the vapour to the surroundings brings the working substance to its initial state and the cycle is complete.
- Coefficient of performance (α),

$$\alpha = \frac{Q_2}{W}$$

$$W = Q_1 - Q_2$$

$$\therefore \alpha = \frac{Q_2}{Q_1 - Q_2}$$

α can be greater than 1.

- Heat is never fully converted to work and refrigerator cannot work without some external work done on the system. Therefore, co-efficient of performance cannot be infinite.

Second Law of Thermodynamics & Reversible and Irreversible Processes

Limitation of the First Law of Thermodynamics

- It does not indicate the direction of heat transfer.

- It does not tell anything about the conditions under which heat can be transformed into work

- It does not indicate as to why the entire heat energy cannot be converted into mechanical work continuously.

These limitations were taken into consideration by the second law of thermodynamics.

Second law of Thermodynamics can be stated as follows:

Kelvin−Planck Statement

It is not possible to design a heat engine which works in cyclic process and whose only result is to take heat from a body at a single temperature and convert it completely into mechanical work.

Clausius Statement

It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at lower temperature to another at higher temperature.

Reversible and Irreversible Processes

- **Reversible process**: Any process which can be made to proceed in reverse direction with equal ease, by variations in its conditions, so that all changes occurring in the direct process are exactly reversed in the reverse process.

- **Irreversible process**: Any process which cannot be made to proceed in reverse direction.

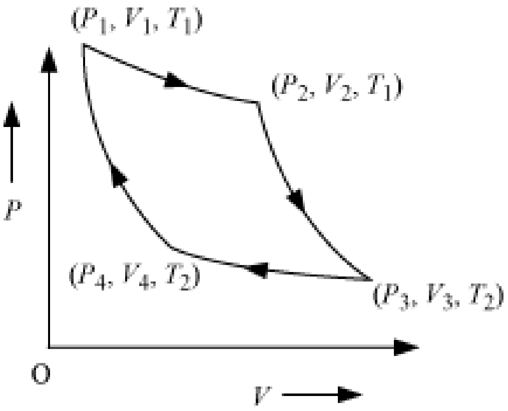
- For a reversible process, the following conditions must be obeyed:

1. The process must take place very slowly.

2. The system must be free from dissipative forces like friction, viscosity, etc.

Carnot Engine

- A reversible heat engine operating between two temperatures is called a Carnot engine.



- The sequence of steps constituting one cycle of a Carnot engine is called a Carnot cycle.

  Steps Undergone By a Carnot Engine:

- **Step 1 → 2**

  Isothermal expansion of gas

  Heat absorbed (Q_1) by the gas from the reservoir is the work done.

  ($W_{1\rightarrow 2}$) by the gas,

  $$\text{Initial state } (P_1, V_1, T_1) \longrightarrow \text{Final state } (P_2, V_2, T_1)$$

  $$\therefore W_{1\rightarrow 2} = Q_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) \qquad ...(1)$$

- **Step 2 → 2**

  Adiabatic expansion of gas

  $$\text{Initial state } (P_2, V_2, T_1) \longrightarrow \text{Final state } (P_3, V_3, T_2)$$

  Work done by the gas,

  $$W_{2\rightarrow 3} = \frac{\mu R(T_1 - T_2)}{\gamma - 1} \qquad ...(2)$$

- **Step 3 → 4**

  Isothermal compression

$$\text{Initial state } (P_3, V_3, T_2) \longrightarrow \text{Final state } (P_4, V_4, T_2)$$

Heat released (Q_2) by the gas to the reservoir is the work done ($W_{3\rightarrow 4}$) on the gas by the environment.

$$W_{3\rightarrow 4} = Q_2 = \mu R T_2 \ln \frac{V_3}{V_4} \qquad \text{...(3)}$$

- **Step 4 → 1**

  Adiabatic compression

  $$\text{Initial state } (P_4, V_4, T_2) \longrightarrow \text{Final state } (P_1, V_1, T_1)$$

  Work done on the gas,

  $$W_{4\rightarrow 1} = -\mu R\left(\frac{T_1 - T_2}{\gamma - 1}\right) \qquad \text{...(4)}$$

- Total work done, *W*

  $$= \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) + \frac{\mu R (T_1 - T_2)}{\gamma - 1} - \mu R T_2 \ln\left(\frac{V_3}{V_4}\right) - \frac{\mu R (T_1 - T_2)}{\gamma - 1}$$

  $$W = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) - \mu R T_2 \ln\left(\frac{V_3}{V_4}\right)$$

  $$W = Q_1 - Q_2$$

- Efficiency (η) of a Carnot engine,

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$= \frac{\mu R T_1 \ln\left(\frac{V_2}{V_1}\right) - \mu R T_2 \ln\left(\frac{V_3}{V_4}\right)}{\mu R T_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$$= 1 - \frac{T_2 \ln\left(\frac{V_3}{V_4}\right)}{T_1 \ln\left(\frac{V_2}{V_1}\right)} \qquad \ldots(5)$$

From the adiabatic processes in equations (2) and (4), we get

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \qquad \ldots(6)$$

On putting the values of equation (6) in equation (5), we get

$$\eta = 1 - \frac{T_2}{T_1}$$

- Carnot’s Theorem:
- Working between the two given temperatures of the hot (T_1) and cold (T_2) reservoirs, efficiency of no engine can be more than that of a Carnot engine.
- Efficiency of the Carnot engine is independent of the nature of the working substance
- For a Carnot cycle

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

It is independent of the nature of the system.