MIND MAP

Thermodynamics

Thermo Dynamics

Thermodynamics is the study of energy changes accompanying physical and chemical changes.

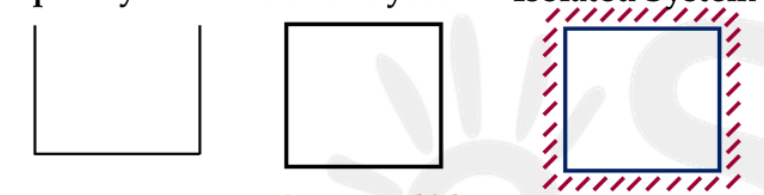
System

Part of universe under investigation is called system.

Surrounding

Anything out side the system is called surrounding.

Open System | Closed System | Isolated System



A system which can exchange both energy and matter with surrounding.

A system which can exchange only energy with surrounding.

A system which cannot exchange matter or energy with surrounding.

Boundary

The interface between system and surrounding is called boundary.

Extensive Properties

Properties which depend on the amount of the e.g. Mass, volume, heat capacity etc.

Intensive Properties

Properties which are independent of the amount of substance e.g. pressure, density, temperature, etc.

State variables

A state variable is one of the set of variables that are used to describe thermodynamic state of a system.

State of a system

A system is said to be in a certain definite state when all of its properties have definite values.

Any system can go from state 1 to state 2 trough two ways

(1) State Function

(2) Path Function

State function

The value of a function of state (or state variable) depends upon the current definite state of a system. The important properties of state functions are

(1) $\Delta X_I = \Delta X_{II}$ irrespective of path or process.

(2) $\oint dX = 0$

(iii) If $\phi = f(x,y)$ is a state function, Euler's reciprocity theorem must be satisfied.

Path function

The value of path function depends upon path connecting two states .

Heat and Work are two important path dependent quantities.

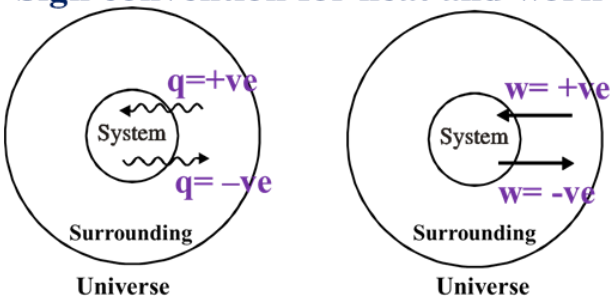
Heat

Heat is the amount of energy flowing from one body of matter to another spontaneously due to their temperature difference.

Work (W)

$$W = -\int P_{ext} \cdot dV$$

Sign convention for heat and work



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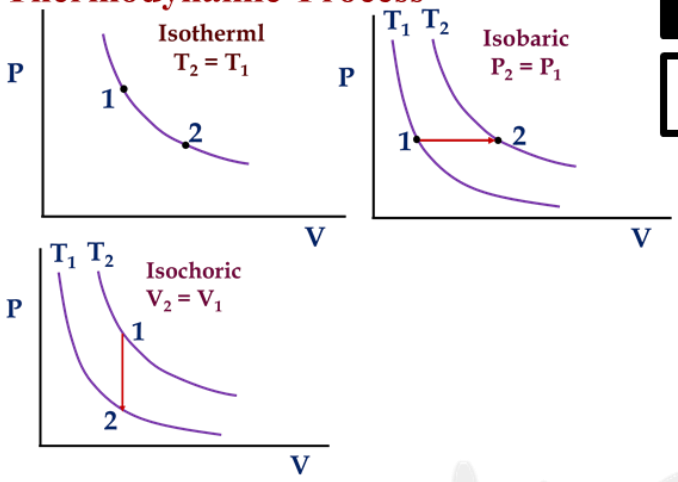
Thermodynamics

Thermodynamic Process



Cyclic Process

If a system after completing a series of different process returns to its initial state then overall process is called cyclic process.

Irreversible Process

When difference between driving force and the opposing force is quite large, the process is called an irreversible process.

Reversible Process

When the difference between driving force and opposing force is very small and the process is carried out infinitesimally slowly, then the process is called reversible process.

Heat Capacity

The amount of heat required to raise the temperature of the system by one degree.

$$C_m = \frac{dq}{dT}$$

Types of Heat Capacity

Specific Heat Capacity: the amount of heat required to raise the temperature of 1 gm of the system by 1 degree.

$$C_S = \frac{dq}{mdT}$$

Molar Heat Capacity:

the amount of heat required to raise the temperature of 1 mol of the system by 1 degree.

$$C_m = \frac{dq}{ndT}$$

Heat capacity at constant volume(C_v)

$$C_V = \frac{dq_v}{ndT}$$

$$q_v = nC_{v,m}dT$$
$$q_p = nC_{p,m}dT$$

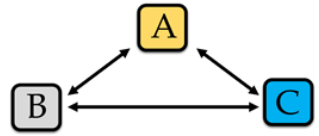
Heat capacity at constant Pressure (C_p)

$$C_p = \frac{dq_p}{ndT}$$

For Ideal Gas

$$C_p = C_v + R$$

Zeroth Law of Thermodynamics



When a body 'A' is in thermal equilibrium with another body 'B', and also separately in thermal equilibrium with a body 'C', then body 'B' and 'C' will also be in thermal equilibrium with each other.

Internal Energy (U)

Internal Energy is the sum of molecular kinetic and potential energies of the system when the system is at rest.

Factors affecting U

Amount of substance ↑ U ↑

Solid < Liquid < Gas

First Law of Thermodynamics

$$\Delta U = Q + W$$

Total energy of universe remain constant.

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Thermodynamics

Enthalpy

Enthalpy is equal to internal energy of the system plus product of Pressure & Volume

$H = U + PV$

Change In Enthalpy

$\Delta H = \Delta U + P\Delta V$ at constant pressure

$\Delta H = \Delta U + V\Delta P$ at constant volume

$\Delta_r H = \Delta_r U + \Delta n_g RT$ for chemical reactions

Calculation of work done in various process

Isothermal process :

(A) Irreversible process : $w = -PdV$

(B) Reversible process :

$$W = -nRT \ln \frac{V_2}{V_1}$$

Isochoric process :

since $dV = 0 \Rightarrow W = 0$

from 1st law $\Delta U = q$

Adiabatic process :

$q = 0$,

$$W = nC_V(T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

Free expansion of ideal gas :

$W = 0$ for free expansion.

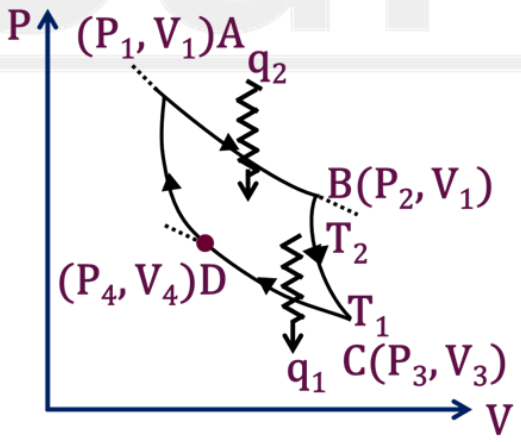
Carnot Cycle

AB – Isothermal reversible expansion

$$q_2 = -wAB = nRT_2 \ln \frac{V_2}{V_1}$$

BC – adiabatic reversible expansion

$$w_{BC} = nC_V(T_1 - T_2)$$



CD – Isothermal reversible compression

$$q_1 = -wCD = nRT_1 \ln\left(\frac{V_4}{V_3}\right)$$

DA – adiabatic reversible compression

$$w_{DA} = nC_V(T_2 - T_1)$$

Carnot efficiency

$$\eta = \frac{-w_{Total}}{q_2} = \frac{q_1 + q_2}{q_2} = \frac{T_2 - T_1}{T_2}$$

Spontaneous Process:

A process which can take place by itself or has a tendency to take place is called spontaneous process.

Second Law of Thermodynamics

Entropy of the entire universe, as an isolated system will always increase over time.

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Thermodynamics

Entropy (S)

Entropy - a measure of the unavailability of a system's energy to do work; also a measure of disorder; the higher the entropy the greater the disorder.

$$dS = \frac{dq_{rev}}{T}$$

Change in entropy can be calculated as:

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$\Delta S_{sys} = 0$

for reversible adiabatic compression and expansion

(E) Entropy changes for the reactions :

$$\Delta S_r = \sum S(\text{products}) - \sum S(\text{reactants})$$

(F) Entropy change during phase change :

$$\Delta S = \frac{\Delta H}{T}$$

Gibbs Free Energy (G) and Spontaneity

Gibbs free energy is a thermodynamics potential that measures the "useful" work obtainable from a thermodynamic system at a constant temperature and pressure.

$G = H - TS$

At constant temperature and pressure

$\Delta G = \Delta H - T\Delta S$

If $(\Delta G)_{T.P.} < 0$ process is irreversible (spontaneous)

$(\Delta G)_{T.P.} = 0$ process is reversible

$(\Delta G)_{T.P.} > 0$ process is impossible (non spontaneous)

Free Energy and Equilibrium Constant

When $\Delta G = 0$, a reaction is at equilibrium.

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

Spontaneous $\Delta G^\circ < 0$ & $K > 1$

Non-Spontaneous $\Delta G^\circ > 0$ & $K < 1$

Relation between ΔG & useful work done

$W_{nonexpansion} = -\Delta G$

$W_{useful} = -\Delta G$

Third Law of Thermodynamics

The entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.