F.Y.BSc

Chemical Thermodynamics _Part_B

Heat capacity.

The amount of heat required to raise the temperature of a pure substance by 1^0C or 1K is called heat capacity of a substance.

If Q is the amount of heat required to raise the temperature from T_1 to T_2, then heat capacity of the substance is given by,

$$C = \frac{Q}{T_2 - T_1} = \frac{Q}{\Delta T}$$

This heat capacity is directly proportional to the amount of substance.

Heat capacity is an extensive property. Its unit is $\mathbf{JK^{-1}}$

i) Specific heat capacity ii) Molar heat capacity

i) **Specific heat capacity** : The amount of heat required to raise the temperature of 1kg of a pure substance by 1^0C or 1K is called specific heat capacity of a substance.

ii)**Molar heat capacity** : The amount of heat required to raise the temperature of one mole of a pure substance by **1^0C or 1K** is called molar heat capacity of a substance.

Relation between C_P and C_V.

C_P is heat capacity of a gas at constant pressure. It is defined as the rate of change of enthalpy with temperature at constant pressure.

$$\text{ie. } C_P = \left(\frac{dH}{dT}\right)_P$$

C_v is heat capacity of a gas at constant volume. It is defined as the rate of change of internal energy with respect to temperature at constant volume.

$$\text{ie. } C_v = \left(\frac{dU}{dT}\right)_V$$

by def^n. , H = U + PV

for one mole of an ideal gas PV = RT

therefore, H = U + RT ------------------------(i)

Differentiating equation (i) with temperature T we get,

$$\frac{dH}{dT} = \frac{dU}{dT} + R$$

i.e. $C_P = C_V + R$

For monoatomic gases, $C_V = 3/2\ R$ and $C_P = 5/2\ R$

For polyatomic gases, $C_V > 3/2\ R$ so that $C_P / C_V \approx 1$

Spontaneous process with suitable examples.

A process which occur of its own under a given set of conditions, without any external assistance is called spontaneous process.

However for some spontaneous processes, initiative is required before the process to occur of their own.

For eg. Burning of coal in air is spontaneous but will not occur unless the coal is lighted by a flame.

Characteristics of the spontaneous processes:

i. All the spontaneous processes are unidirectional and irreversible in nature.
ii. Spontaneous processes always proceed in a direction which leads to the attainment of equilibrium.
iii. They are independent of the rate ie. Spontaneous process may be fast or slow.
iv. Some spontaneous process once initiated occur of their own.

Examples of spontaneous processes:

Type I: Spontaneous process which do not required initiation:

i) Flow of water from high level to low level.
ii) Flow of heat from high temperature to low temperature.
iii) Dissolution of common salt in water.
iv) Neutralization reaction of strong acid like HCl and strong base like NaOH.

Type II) Spontaneous processes which require initiation:

i) For the combination of hydrogen and oxygen, an electric discharge is necessary without which water will not be form.

ii) Burning of LPG gas at home needs ignition.

Entropy and its relation with spontaneity.

For a process to occur spontaneously, it was assumed that the process should be exothermic in nature. However there are several processes which occur spontaneously but are endothermic in nature. For eg.

i) Melting of ice
ii) Dissociation of KCl
iii) Conversion of N_2O_4 to NO_2 above 400K

Thus exothermicity is not the sufficient criteria for the spontaneity of the process. Exothermicity favours the spontaneity but does not assure it. A spontaneous change always involves increase in randomness or disorder of the system. This disorderness was measured by a thermodynamic function called entropy, which was introduced by Clausius. Hence entropy is a measure of disorderness of a system.

Mathematically entropy is defined in terms of entropy change ΔS and is given by the expression:
$\mathbf{\Delta S = \frac{q_{rev}}{T}}$

Where q_{rev} – amount of heat absorbed by a system under reversible conditions

T - temperature at which the heat is absorbed

A spontaneous process is always accompanied by increase in entropy of the system. Hence the sign of ΔS is useful to discuss with the spontaneity of the process. For this purpose, let us consider two types of system:

i) Isolated System and ii) Open and closed system

i) **Isolated System**: In this system, no exchange of matter nor energy occur. With the surroundings. Therefore, a spontaneous process such as mixing of two gases, spreading of milk drop in water etc. are involve increase in disorder and hence increase in entropy. For such process occurring in an isolated system, ΔS is always positive.

ii) **Open and closed system**: In these system, there is exchange of energy with the surroundings. Any spontaneous process occurring in this system brings about entropy change in system as well as that of surroundings. Hence the total entropy change (ΔS_{total}) is given by
$\boldsymbol{\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}}$

for a spontaneous process $\Delta S_{total} > 0$

Since system and surroundings together contribute the universe, therefore, the total entropy change is equal to change in entropy universe.

$\boldsymbol{\Delta S_{total} = \Delta S_{universe} > 0}$

Thus the entropy of the universe always increases during a spontaneous change and tends towards a maximum value.

On the basis of above discussion, the criterion for spontaneity of a process in terms of entropy can be summarized as follows:

i) If $\boldsymbol{\Delta S_{total}}$ **is +ve ie.>0**, the process is always spontaneous.

ii) If $\boldsymbol{\Delta S_{total}}$ **is –ve ie.<0**, the process is always non-spontaneous.

iii) If $\boldsymbol{\Delta S = 0}$, the process is at equilibrium.

Physical significance of entropy.

Entropy is a measure of disorderness of a system. Larger the disorderness in the system, more is the entropy of the system. This can be illustrated with the following example.

In solid state, the atoms or molecules are closely packed. There is a strong intermolecular force of attraction. Therefore there is a definite arrangement of atoms or molecules in a solid. As a result, its entropy is less.

During transformation of a solid to liquid, the ordered state changes into disorder state which leads to increase in entropy. Similarly , the vapour state of a substance has more disordered arrangement compare to its solid and liquid state.

Thus in general,

$$\Delta \mathbf{S}_{vap} > \Delta \mathbf{S}_{liq.} > \Delta \mathbf{S}_{solid}$$

The process of mixing of gases, melting of ice, evaporation of water etc. Are spontaneous in nature and are accompanied by increase in disorderness of the system. Hence, entropy ia a measure of disorderness of the system.

Characteristics of entropy.

i) Entropy is a measure of disorderness of a system.

ii) Entropy is a state function.

iii) The SI unit of entropy is JK^{-1}

iv)Mathematically entropy is defined as

$$\Delta \mathbf{S} = \frac{\mathbf{q_{rev}}}{\mathbf{T}}$$

Where q_{rev} – amount of heat absorbed by a system

For a small change, entropy change dS is given by $dS = \frac{dq_{rev}}{T}$

v) in a reversible adiabatic change, $dq_{rev}=0$ and hence dS = 0 . Such changes are referred as isoentronpic changes.

vi) Entropy is an extensive property.

vii) Absorption of heat increases the entropy of the system. Therefore $\Delta \mathbf{S} > 0$ while rejection of heat, decreases the entropy of the system hence $\Delta \mathbf{S} < 0$.

Entropy in terms of second law of thermodynamics.

Entropy is a measure of disorderness in a system. All naturally occurring processes are thermodynamically irreversible in nature and irreversible processes are accompanied by increase in entropy. Hence the second law of thermodynamics can be expressed in terms of entropy as follows:

‘**All naturally occurring processes tend to occur with increase in**

entropy and the direction of changes is such that it always leads to an entropy increase'.

Thus entropy of the universe is continuously increasing. But 1st law of thermodynamics lay down the fact that energy of the universe is constant. These two facts lead Clausius to come to the following conclusion.

'**The energy of the universe is constant, the entropy of the universe tends to a maximum'**.

Entropy and probability.

Entropy measure disorderness in a system, while thermodynamic probability represents the total number of different ways in which the given system, in the specified thermodynamic state, can be realised.

Spontaneous processes are irreversible in nature and leads to increasing disorderness in a system. Hence the disordered state is more probable than partially order or completely ordered state. Therefore once can conclude that all spontaneous process represent chnages from less probable to more probable state. An entropy and probability both increases in a spontaneous process, a corelation between the two was given by L.Boltzmann in 1896.

Thus if S is the actual entropy and W represent thermodynamic probability, then,

$\mathbf{S = k\ln W + constant}$ ------(i)

The constant 'k' in the equation (i) represents Boltzmann constant ie. Gas constant per single molecule.

Max Plank showed that the constant in equation (i) has zero value

Therefore, $\mathbf{S = k\ln W}$

Expression for entropy changes in isothermal isobaric and isochoric change.

Consider **n moles** of an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. Let dq_{rev} be heat absorbed by the gas. If dU is the internal energy change occurred due to absorption of heat and dW is the work of expansion, then from 1st law of thermodynamics,

$\mathbf{dU = dq_{rev} + dW}$

$\mathbf{dU = dq_{rev} - PdV}$

therefore, $dq_{rev} = \mathbf{dU - PdV}$ ----------(i)

dividing equation (i) by T we get,

$\frac{\mathbf{q_{rev}}}{\mathbf{T}} = \frac{\mathbf{dU}}{\mathbf{T}} + \frac{\mathbf{PdV}}{\mathbf{T}}$ ----------(ii)

But, **dS =** $\frac{\mathbf{q_{rev}}}{\mathbf{T}}$---------(iii) , **dU = nC$_V$.dT** -----(iv) (for n moles of an ideal gas)

and **P =** $\frac{\mathbf{nRT}}{\mathbf{V}}$ ------(v)

Substituting (iii) , (iv) and (v) in equation (ii) we get,

dS = $\frac{\mathbf{nC_VdT}}{\mathbf{T}} + \frac{\mathbf{nRT}}{\mathbf{V}} . \frac{\mathbf{dV}}{\mathbf{T}}$

ie. dS = $\frac{\mathbf{nC_VdT}}{\mathbf{T}} + \mathbf{nR}\frac{\mathbf{dV}}{\mathbf{V}}$**-------(**vi)

Assuming C$_V$ to remain constant over the temperature change T$_1$ and T$_2$ on integrating equation (vi) we get,

$$\int_{S_1}^{S_2} \mathbf{ds} = \mathbf{nC_V}\int_{T_1}^{T_2}\frac{\mathbf{dT}}{\mathbf{T}} + \mathbf{nR}\int_{V_1}^{V_2}\frac{\mathbf{dV}}{\mathbf{V}}$$

$$[S]_{S_1}^{S_2} = \mathbf{nC_V}[\boldsymbol{ln}\mathbf{T}]_{T_1}^{T_2} + \mathbf{nR}[\boldsymbol{ln}\mathbf{V}]_{V_1}^{V_2}$$

$$\mathbf{S_2} - \mathbf{S_1} = \mathbf{nC_V}[\boldsymbol{ln}\mathbf{T_2} - \boldsymbol{ln}\mathbf{T_1}] + \mathbf{nR}[\boldsymbol{ln}\mathbf{V_2} - \boldsymbol{ln}\mathbf{V_1}]$$

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

Converting to log$_{10}$, we get,

$\Delta\mathbf{S} = \mathbf{2.303nC_V}\boldsymbol{log}\frac{\mathbf{T_2}}{\mathbf{T_1}} + \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{V_2}}{\mathbf{V_1}}$ ---------------(vii)

For an ideal gas,

$$\frac{P_1\mathrm{V}_1}{\mathrm{T}_1} = \frac{P_2\mathrm{V}_2}{\mathrm{T}_2}$$

$\therefore \frac{\mathrm{V}_2}{\mathrm{V}_1} = \frac{\mathrm{P}_1}{\mathrm{P}_2} = \frac{\mathrm{T}_2}{\mathrm{T}_1}$- ----------------(viii)

Substituting (viii) in equation (vii) we get,

$\Delta\mathbf{S} = \mathbf{2.303nC_V}\boldsymbol{log}\frac{\mathbf{T_2}}{\mathbf{T_1}} + \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{P_1}}{\mathbf{P_2}} + \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{T_2}}{\mathbf{T_1}}$

$\Delta\mathbf{S} = \mathbf{2.303n(C_V} + \boldsymbol{R})\boldsymbol{log}\frac{\mathbf{T_2}}{\mathbf{T_1}} + \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{P_1}}{\mathbf{P_2}}$

$\Delta\mathbf{S} = \mathbf{2.303nC_P}\boldsymbol{log}\frac{\mathbf{T_2}}{\mathbf{T_1}} + \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{P_1}}{\mathbf{P_2}} - - - -$**(ix) since C$_P$ – C$_V$ = R**

For isothermal process, T$_1$ = T$_2$

$\Delta\mathbf{S} = \mathbf{2.303nR}\boldsymbol{log}\frac{\mathbf{P_1}}{\mathbf{P_2}}$ **from equation (**ix) and $\Delta S = 2.303nR\,log\frac{V_2}{V_1}$ from equation (vii)

for isobaric process , $P_1 = P_2$

$\Delta S = 2.303nC_P\,log\frac{T_2}{T_1}$ from equation (ix)

for isochoric process , $V_1 = V_2$

$\Delta S = 2.303nC_V\,log\frac{T_2}{T_1}$

i) Heat engine ii) Mechanical efficiency of a heat engine.

i) **Heat engine** is a device or a machine , which converts heat energy to work.

ii) **Mechanical efficiency of heat engine**: The fraction of heat absorbed by a machine that it can transform into work is called mechanical efficiency of a heat engine.

steps in Carnot's cycle with a PV diagram.

Carnot's cycle is a cyclic process , which demonstrate the maximum conversion of heat into work. Carnot showed that the maximum work in the cycle can be obtained only when every step in the cycle is carried out in a reversible manner. The Carnot cycle has the following steps:

i) **Isothermal and reversible expansion** of an ideal gas from initial volume V_1 to volume V_2 at source temperature T_2.

ii) **Adiabatic expansion** from volume V_2 to volume V_3 till the temperature reaches T_1 of the sink.

iii) **Isothermal and adiabatic compression** from volume V_3 to volume V_4 at temperature T_1.

iv)**Adiabatic compression** from V_4 to V_1 till the temperature T_2 of the source is attained.

The Carnot cycle employs an imaginary heat engine which absorbs heat energy q_2 from a heat source kept at temperature T_2.The engine converts fraction of the heat absorbed into work and reject q_1 heat to the sink kept at temperature T_1.

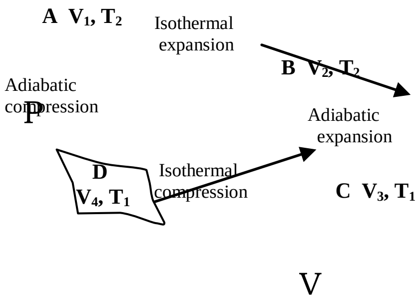
The efficiency of the engine is then given by,

$$\epsilon = \frac{\text{work done}}{\text{heat absorbed}}$$

$$= \frac{q_1 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

The efficiency of the engine depends upon the difference in temperature of the source and the sink and is independent of the nature of working substance.

P – V Diagram:



Carnot's theorem

Carnot's theorem: All Carnot engines operates between same source and same sink will have same efficiency.

Or

All reversible heat engines operating between two given temperatures have same efficiency.

The efficiency of Carnot's heat engine is given by,

$$\epsilon = \frac{\mathbf{T_2 - T_1}}{\mathbf{T_2}}$$

Where, T_2 – is temperature of the source

T_1 – is temperature of the sink

Carnot theorem suggest that no other engine operating between same two temperatures can have greater efficiency. It is therefore impossible to make an engine having efficiency more than the Carnot engine. For this reason, Carnot's efficiency is called thermodynamic efficiency.