5.3.0 HEAT CAPACITY

(حرارت جذب کرنے کی صلاحیت)

"It is the amount of heat which is required to raise the temperature of the system through 1°C."

Let us supply 'q' calories of heat to a system and the temperature rises from 'T_1' to 'T_2', then heat capacity 'C' is,

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \quad \ldots\ldots (1)$$

Heat capacity is a temperature dependent function (درجہ حرارت پر انحصار کرنے والا فنگشن). So, the value of 'C' has to be considered over very narrow temperature range. It can also be defined as,

$$C = \frac{\delta q}{dT} \quad \ldots\ldots (2)$$

Heat capacity 'C' is **not a state function** because 'q' is not a state function. So, if we want to know the value of 'C' then we can fix the constant volume or constant pressure, because these two things define the **path of the reaction**.

Types of Heat Capacities:

Heat capacities are of two types.

(i) Heat capacity at constant volume (C_V).

(ii) Heat capacity at constant pressure (C_P).

5.3.1 Heat Capacity at Constant Volume (C_V) (مستقل جسامت پر گرمی جذب کرنے کی صلاحیت):

We know that, according to the definition of heat capacity,

$$C = \frac{\delta q}{dT} \quad \ldots\ldots (2)$$

According to first law of thermodynamics,

$$\delta q = dE + PdV \quad \ldots\ldots (3)$$

Putting the value of δq from equation into (2)

$$C = \frac{dE + PdV}{dT} \quad \ldots\ldots (4)$$

Equation (3) is another definition of heat capacity. When the volume is kept constant, then

$$dV = 0$$

So, equation (3) will become,

$$\boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V} \quad \ldots\ldots (5)$$

The definition of C_V is written in terms of partial differential, and according to equation (4), *"C_V is the rate of change of internal energy with respect to temperature at constant volume."* For an ideal gas equation (4) can be written in terms of differential.

چونکہ جسامت (V) ہم نے مستقل تصور کرنی ہے۔ لہٰذا dV صفر ہے۔ تو جب ایک چیز کو مستقل تصور کر لیا جائے تو دوسری چیز کے لحاظ سے تبدیلی کو Partial Differentiation سے لکھا جاتا ہے۔

$$C_V = \frac{\partial E}{\partial T} \quad \text{...... (6)}$$

5.3.2 Heat Capacity at Constant Pressure (C_P):

(دباؤ کو مستقل رکھ کر گرمی کو جذب کرنے کی صلاحیت)

This heat capacity is measured, when the pressure is kept constant. It means that the volume change is there and so $dV \neq 0$. Equation (4) can be written as,

$$C = \frac{\partial E + P\partial w}{\partial T}$$

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad \text{...... (7)}$$

It means that 'C_P' is controlled by rate of change of internal energy with respect to temperature and rate of change of volume with respect to temperature. The enthalpy is related with the internal energy as follows,

$$H = E + PV$$

Let us differentiate this equation with respect to temperature.

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad \text{...... (8)}$$

Comparing the equation (7) and (8),

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P} \quad \text{...... (9)}$$

$\left(\frac{\partial E}{\partial T}\right)_P$ کا مطلب ہے اندرونی توانائی کا درجہ حرارت کے ساتھ تبدیل ہونے کی رفتار جبکہ دباؤ کو مستقل رکھا جا رہا ہو۔

جبکہ $\left(\frac{\partial V}{\partial T}\right)_P$ جسامت کی درجہ حرارت کے ساتھ تبدیل ہونے کی رفتار کو ظاہر کرتا ہے جب دباؤ مستقل ہو۔

For an ideal gas, the equation can be simply written as,

$$C_P = \frac{dH}{dT} \quad \text{...... (10)}$$

"It means that the 'C_P' of a system is the rate of change of enthalpy with respect to temperature."

5.3.3 Relationship Between C_P and C_V:

When we measure C_V of a system, then volume is kept constant and no work is done by the system. The heat so absorbed only increases the **internal energy** of the system. On the other hand, pressure is kept constant during the supply of heat, then some work of expansion (گیس کے پھیلنے سے کام کا ہونا) is also done, in addition to the increase in internal energy. It means some extra heat is required for doing this work.

Let us deduce this fact logically.

We know that

$$H = E + PV$$

For one mole of gas

$$PV = RT$$

So, $H = E + RT$ ...... (11)

Let us differentiate equation (11) with respect to temperature.

$$\frac{dH}{dT} = \frac{dE}{dT} + R\frac{dT}{dT} = \frac{dE}{dT} + R \quad \text{...... (12)}$$

According to the definitions,

$$\frac{dH}{dT} = C_P, \qquad \frac{dE}{dT} = C_V$$

So, $C_P = C_V + R$

$$\boxed{C_p - C_V = R} \quad \text{...... (13)}$$

جذب کرنے کی صلاحیتوں کا فرق R کے برابر ہے۔ R جنرل گیس کانسٹنٹ ہے جس کی قیمت 31 JK^{-1} mol.

$$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$$

Putting the values,

$$\Delta H_2 = -152.5 + 2.36 \times 10^{-3} (400 - 300)$$

$$\Delta H_2 = -152.5 + 0.236$$

$$\Delta H_2 = \boxed{-152.264 \text{ kcal}}$$

5.5.0 ISOTHERMAL EXPANSION OF A GAS

(گیس کا درجہ حرارت کو مستقل رکھ کر پھیلنا)

In isothermal process, the temperature is kept constant. We know that the work done du expansion of a gas is 'PdV'.

If we have reasonable charlge of volume of a gas from 'V_1' to 'V_2', then the work done can calculated by doing the integration of 'PdV' from 'V_1' to 'V_2'.

$$W = \int_{V_1}^{V_2} PdV \quad \ldots\ldots (1)$$

If we have 'n' mole of a gas, behaving ideally, then

$$PV = nRT$$

Rearranging it

$$\text{or} \quad P = \frac{nRT}{V} \quad \ldots\ldots (2)$$

Putting the value of pressure from equation (2) into (1),

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

For an isothermal process, temperature is constant, so nRT in above equation is constant. I will not undergo integration and it should be taken outside the integration sign.

We should know that

$$\int \frac{dx}{x} = \ln x \qquad \int \frac{dy}{y} = \ln y \qquad \int \frac{dA}{A} = \ln A$$

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Performing integration of R.H.S

$$W = nRT \left[\ln V\right]_{V_1}^{V_2}$$

Putting limits, first V_2 minus V_1.

$$W = nRT (\ln V_2 - \ln V_1)$$

Using the formula of ln

$$W = nRT \ln\left(\frac{V_2}{V_1}\right) \quad \ldots\ldots (3)$$

This equation can be converted into common logarithmic system, so

$$\boxed{W = 2.303\ nRT \log\left(\frac{V_2}{V_1}\right)} \quad \ldots\ldots (4)$$

So, if we know the two volumes i.e. initial (V_1) and final (V_2) and the temperature (T) at which this change is being studied, then work done by the expansion of the gas can be calculated.

This equation (4) convinces us that greater the number of moles of gas (n), and greater the difference of V_1 and V_2, greater the work done due to isothermal expansion.

Sample Problem (5.3)

So, $\boxed{\Delta H = \Delta E}$

5.5.3 Adiabatic Expansion of an Ideal Gas

(Adiabatic Process میں حرارت کی تبدیلی صفر ہوتی ہے)

In adiabatic process, no heat enters or leaves the system, so for every infinitesimal change in a process.

$$\delta q = 0 \qquad \cdots\cdots (1)$$

The mathematical shape of the first law of thermodynamics is,

$$dE = \delta q - \delta W \qquad \cdots\cdots (2)$$

Putting equation (1) in (2)

$$dE = -\delta W \qquad \cdots\cdots (3)$$

یعنی اگر Work ہو گا تو اندرونی انرجی dE کم ہو جائے گی۔ اس کا مطلب ہے کہ اندرونی انرجی کی قربانی کے بدلے گیس کام کرے گی۔ اسی وجہ سے مساوات (3) کے ہاں منفی کا اشارہ جو موجود ہے۔

It means that, there is work done at the expense of internal energy. Suppose that, this work done is due to expansion of a gas. Let dV be very small change at constant pressure, then

$$\delta W = PdV \qquad \cdots\cdots (4)$$

Putting equation (4) into (3),

$$dE = -PdV \qquad \cdots\cdots (4)$$

According to the definition of 'C_V' it is the rate of change of internal energy with respect to temperature, i.e., $\frac{dE}{dT}$, so

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

Separating variables

$$dE = C_V\, dT \qquad \cdots\cdots (5)$$

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Comparing equation (4) and (5)

$$C_V\,dT = -PdV \qquad \cdots\cdots (6)$$

Now, for one mole of an ideal gas,

$$PV = RT$$

or

$$P = \frac{RT}{V} \qquad \cdots\cdots (7)$$

Putting this value of 'P' in equation (6),

$$C_V\,dT = -\frac{RT}{V}\,dV \qquad \cdots\cdots (8)$$

Equation (8) has two variables i.e., temperature (T) and volume (V). Let us separate the variables in this equation and rearrange as follows.

$$\frac{C_V\,dT}{T} = -R\frac{dV}{V} \qquad \cdots\cdots (9)$$

Suppose, the volume of the gas changes from 'V_1' to 'V_2', when the temperature is changed from 'T_1' to 'T_2', then above equation (8) can be integrated within limits. 'C_V' and 'R' are constants and remain outside the integration sign.

$$C_V\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V}$$

Doing the integration. Integration of $\frac{dT}{T}$ in 'ln T' and of $\frac{dV}{V}$ in 'ln V'.

$$C_V\left[\ln T\right]_{T_1}^{T_2} = -R\left[\ln V\right]_{V_1}^{V_2}$$

Putting limits $C_V(\ln T_2 - \ln T_1) = -R(\ln V_2 - \ln V_1)$

Using formula of ln

or

$$C_V \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

Inverting the R.H.S to change its sign

$$C_V \ln\frac{T_2}{T_1} = R\ln\frac{V_1}{V_2} \qquad \cdots\cdots (10)$$

This equation (10) is for one mole of an ideal gas,

Putting the value of 'R' as $(C_P - C_V)$ in equation (10),

$$C_V \ln\frac{T_2}{T_1} = (C_P - C_V)\ln\frac{V_1}{V_2}$$

Dividing this equation by 'C_V' on both sides.

$$\ln\frac{T_2}{T_1} = \left(\frac{C_P - C_V}{C_V}\right)\ln\frac{V_1}{V_2}$$

or

$$\ln\frac{T_2}{T_1} = \left(\frac{C_P}{C_V} - 1\right)\ln\frac{V_1}{V_2}$$

$\frac{'C_P'}{C_V}$ is the ratio of two heat capacities and that is represented by γ.

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2}$$

Rearranging the equation, keeping in view the rule of ln.

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \boxed{x \ln y = \ln y^x}$$

When we take the antiln of this equation on both sides, then ln vanishes on both sides.

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = \frac{V_1^{\gamma - 1}}{V_2^{\gamma - 1}} \qquad \ldots\ldots \quad (11)$$

Cross-multiplication

$$T_1V_1^{\gamma - 1} = T_2V_2^{\gamma - 1}$$

Just as you did in Boyle's law. (That $P_1V_1 = P_2V_2$ So, PV = constt.)

So, $\boxed{TV^{\gamma - 1} = \text{constant}}$

It means that, when the temperature is multiplied with '$V^{\gamma - 1}$', at constant pressure, then factor '$TV^{\gamma - 1}$' is constant.

SAMPLE PROBLEM (5.4)

process is that, which can take place without the help of an external agency. All the natural processes are spontaneous. Some of the definitions of second law of thermodynamics are as follows.

(i) ***"All the spontaneous processes (اپنے آپ ہونے والا پراسیس) are thermodynamically irreversible (حرکیات کے حوالے سے پلٹانہ کھانے والا)."*** Clacius statement Q → W

(ii) ***"It is impossible to have a complete conversion (تبدیلی) of heat into work without leaving some effects elsewhere."*** Kelvin statement

(iii) ***"It is not possible to construct a machine which is functioning (کام کرنا) in cycle (دائرے میں), which can convert heat completely into equivalent (برابر) amount of work without producing changes elsewhere."***

(iv) ***"Heat can not pass from colder to hotter body without the use of an external agency (باہر کی ایجنسی)."***

5.6.2 Spontaneous Processes (خود بخود ہونے والا پراسیس):

All the natural processes (قدرتی عملیات) are spontaneous and they happen without the help of an external energy. Some of the spontaneous and irreversible process are as follows.

(i) Heat flows from a hot reservoir (حرارت کا ذخیرہ) to cold reservoir. For the reverse process, energy has to be supplied from outside.

(ii) Electricity can flow from a higher potential (زیادہ طاقت) to a lower potential. If we want to reverse the direction of the current, then an external field (بیرونی میدان) has to be applied in opposite direction.

(iii) Water flows from higher level to the lower level. We can not reverse the direction of the flow without some external help.

(iv) Heat can not flow from colder to the hotter end of the metal bar (دھات کا ٹکڑا).

(v) A gas expands (پھیلتی ہے) spontaneously from a region (علاقہ) of high pressure to low pressure.

Spontaneous processes proceed at a definite (خاص) and measurable rates (قابل پیمائش رفتار میں). They all lead to a change in a direction which reaches the equilibrium stage. These processes are unidirectional (یک سمتی). They do not reverse themselves.

5.6.3 Efficiency of an Engine:

"Entropy is the quantitative measurement** (مقدار کے حوالے سے پیمائش) **of randomness** (بے ترتیبی) **of the system." When system moves from ordered state to disordered state, then we say that the entropy of the system has increased. For example,

(i) When a solid is melted, there happens a net increase of entropy. The atoms, molecules or ions find more places to be accommodated (جگہیں جن میں چیزیں رہ سکتی ہیں) in the same volume occupied as compared to when the substances is in the solid state. In the solid state, the particle are fixed in their positions. So, we say that the entropy or the randomness of the system is less.

(ii) When the liquid is evaporized, there happens increase of entropy. In the vapour state, the atoms, ions or molecules are more disordered as compared to the liquid state. It means that the molecules of the gaseous substances can roam about in a better way.

5.7.7 Entropy Change for an Ideal Gas in Terms of Temperature and Volume (درجِ حرارت اور جسامت کی شکل میں آئیڈیل گیس کی انٹروپی کی تبدیلی):

In order to have a relationship between entropy change and the change of temperature and volume we take the help of fundamental definition (بنیادی تعریف) of entropy change and first law of thermodynamics.

Consider one mole of an ideal gas, enclosed in a cylinder. There is frictionless piston (ایسا پسٹن جس میں رگڑ نہ ہو) in the cylinder. Now, supply a small amount of heat δq reversibly and isothermally at temperature 'T', then the entropy change is given by the following equation.

$$dS = \frac{\delta q_{rev}}{T} \quad \ldots\ldots (1)$$

The expression for δq, according to first law of thermodynamics is

$$\delta q = dE + \delta w \quad \ldots\ldots (2)$$

If first law of thermodynamics is applied under the reversible conditions, then

$$\delta q_{rev} = dE + \delta w \quad \ldots\ldots (3)$$

Let the work done is due to the expansion of the gas, then

$$\delta w = PdV$$

Hence, equation (3) can be written as

$$\delta q_{rev} = dE + PdV \quad \ldots\ldots (4)$$

Now, put equation (4) in (1), to get the value of change of entropy.

$$dS = \frac{dE + PdV}{T}$$

Rearranging this equation

$$TdS = dE + PdV \quad \ldots\ldots (5)$$

According to the definition of heat capacity at constant value (C_V), we have

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

$$dE = C_V\,dT \quad \ldots\ldots (6)$$

The general gas equation for one mole of an ideal gas is

$$PV = RT$$

$$P = \frac{RT}{V} \quad \ldots\ldots (7)$$

Now, put equation (6) and (7) is equation (5)

$$TdS = C_V\,dT + \frac{RT}{V}dV$$

Dividing this equation by 'T'

$$dS = C_V\frac{dT}{T} + R\frac{dV}{V} \quad \ldots\ldots (8)$$

This equation is very important because we are calculating the value of small change of entropy '**dS**', in terms of small change of temperature 'dT' and small change of volume '**dV**'. If we want to calculate the appreciable changes of entropy that is 'ΔS', in terms of appreciable changes of temperature and volume, then we should proceed as follows.

Suppose that volume changes from 'V_1' to 'V_2' when the temperature change from 'T_1' to 'T_2', then the equation (8) should be integrated between these limits to get the change of entropy 'ΔS' from S_1 to S_2.

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_V\frac{dT}{T} + \int_{V_1}^{V_2} R\frac{dV}{V}$$

$$\int_{S_1}^{S_2} dS = C_V\int_{T_1}^{T_2}\frac{dT}{T} + R\int_{V_1}^{V_2}\frac{dV}{V}$$

Keep it in mind that 'C_V' is thought to be constant when the temperature change takes pl... from 'T_1' to 'T_2'. **Actually 'C_v' is not constant for appreciable change of temperature.**

Performing integration

$$[S]_{S_1}^{S_2} = C_V[\ln T]_{T_1}^{T_2} + R[\ln V]_{V_1}^{V_2}$$

Putting the limits

$$S_2 - S_1 = C_V(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1)$$

Applying the formula of ln

$$\boxed{\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)} \quad \cdots\cdots (9)$$

With the help of equation (9), we can calculate the entropy change (انٹروپی کی تبدیلی کا حساب کرکے) when the temperature of one mole of an ideal gas is increased from 'T_1' to 'T_2' and consequently the volume changes from 'V_1' To 'V_2'. It is clear from this equation (7), that if $T_2 > T_1$ and $V_2 > V_1$ then 'ΔS' is positive.

5.7.8 Entropy Change in Terms of Temperature and Pressure:

(درجہ حرارت اور گیس پر دباؤ انٹروپی کو بدلتا ہے)

We can use the general gas equation and substitute the term $\frac{'V_2'}{V_1}$ in equation (9) of 5.7.7. For one mole of an ideal gas,

$$P_1V_1 = RT_1$$

$$P_2V_2 = RT_2$$

Divide these two equations

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$$

or $$\frac{V_2}{V_1} = \frac{T_2P_1}{T_1P_2} \quad \ldots\ldots (10)$$

Put equation (10) in (9) of 5.7.7

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_2P_1}{T_1P_2}\right) \quad \ldots\ldots (11)$$

In order to make the two terms $\ln\frac{T_2}{T_1}$ together, from two separate factors from R.H.S. of equation (11) we take the help of C_P and C_V.

Since, $C_p - C_V = R$ so, $C_V = C_p - R$

Put this value of C_V in equation (11)

$$\Delta S = (C_P - R) \ln\frac{T_2}{T_1} + R \ln\frac{T_2P_1}{T_1P_2}$$

Opening the brackets and using the formula of log system, we get

$$\Delta S = C_P \ln\frac{T_2}{T_1} - R \ln\frac{T_2}{T_1} + R \ln\frac{T_2}{T_1} + R \ln\frac{P_1}{P_2}$$

$$\boxed{\Delta S = C_P \ln\frac{T_2}{T_1} + R \ln\frac{P_1}{P_2}} \quad \ldots\ldots (12)$$

Equation (12) tells us the change of entropy for one mole of an ideal gas when the temperature changes from 'T_1' to 'T_2', and the pressure change from 'P_1' to 'P_2'.