THERMODYNAMICS

Short Answer Questions:

1. Define heat capacity .What are C_p and C_v? Show that $C_p - C_{V=R}$?

Ans. The heat required raising the temperature of the system by 1^0C or 1^0 Kelvin is called its heat capacity (C). For a small change in temperature (dT), if the heat required is (dq)

$$dC = \frac{dq}{dT}.$$

There are two types of heat capacities, at constant volume (C_v) and at constant pressure (C_p).

The heat capacity at constant volume gives the change in internal energy of the system at constant temperature, $C_v = \left(\frac{\partial E}{\partial T}\right)_v$

If a system absorbs heat at constant pressure, then heat capacity is given as,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \ or \ C_p = \left(\frac{dE}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p \qquad (\because \ H = E + PV)$$

Relationship between C_p and C_v

In case of ideal gases, H = E + PV

Differentiating with respect to temperature, $\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT}$

Ideal gas equation for one mole of gas is, PV = RT, where R is molar gas constant.

$$\therefore \frac{dH}{dT} = \frac{dE}{dT} + \frac{d(RT)}{dT} \ or \ \frac{dH}{dT} = \frac{dE}{dT} + R\left(\frac{dT}{dT}\right)$$

$$\frac{dH}{dT} - \frac{dE}{dT} = R \qquad \therefore C_p - C_v = R$$

2. What are intensive and extensive properties? Give examples?

Ans. The property of the system that depends on the total amount of the material present in the system is called an extensive property.

E.g.: Mass, volume, heat capacity, internal energy, enthalpy, entropy, Gibbs energy etc.

The property of the system that does not depend on the total amount of the material present in the system is called an intensive property.

E g: Density, viscosity, surface tension, specific heat, boiling point, freezing point, pressure, temperature,

3. What is standard enthalpy of formation? Explain it with examples?

Ans. Enthalpy of formation

At constant temperature, the amount of heat liberated or absorbed when one mole of a compound is formed from its elements is called **enthalpy of formation**. If all the reactants and the products are in the standard states, then the enthalpy of reaction is called standard enthalpy of formation. It is denoted by ΔH_f^o.

Enthalpy of formation in general may be positive or negative.

E.g.: 1) Formation of Ammonia, $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}, \Delta H_f^o = -46.35\,KJ$

2) Formation of NO (g), $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)}, \Delta H_f^o = +90.4\,KJ$

4. State and explain Hess law of constant heat summation?

Ans. Hess law of constant heat summation is stated as," the total enthalpy change during the complete course of a reaction is same whether the reaction is made in one step or in several steps".
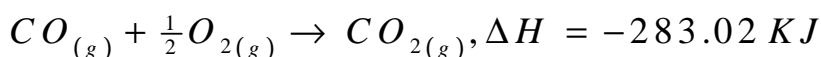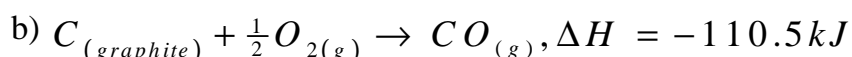
Method 1, direct formation of the product in a single step. $A \rightarrow P$; $\Delta H = Q$

Method 2, Product is formed indirectly by proceeding in several steps.

$A \rightarrow B$; $\Delta H = q_1$
$B \rightarrow C$; $\Delta H = q_2$
$C \rightarrow P$; $\Delta H = q_3$
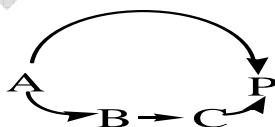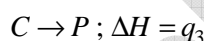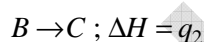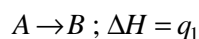
According to Hess law, $Q = q_1 + q_2 + q_3$

E.g.: $CO_{2\,(g)}$ is obtained from $C_{(graphite)}$ and $O_{2\,(g)}$ in two different ways

a) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}, \Delta H = -393.52\,KJ$

b) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \Delta H = -110.5\,kJ$

$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}, \Delta H = -283.02\,KJ$
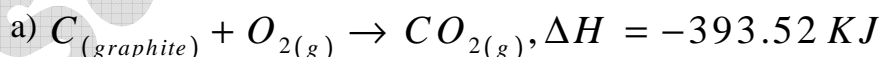
Total $\Delta H = -110.5\,kJ + (-283.02) = -393.52$.

The total enthalpy change in one step reaction is same as in two step process. Hence Hess law is proved.

5. What is entropy? Explain with examples?

Ans. The thermo dynamical quantity which measures disorder of molecules or randomness of the system is called Entropy. It is denoted by 'S'. The entropy change (ΔS) between any two states of the same substance at equilibrium is given as,

$\Delta S = q_{rev} / T$. Here q_{rev} is the heat absorbed by the system isothermally and reversibly at the equilibrium temperature (T) during the transformation. The units of ΔS are J mol^{-1} K^{-1}. Entropy is a state function and is an extensive property.

Ex: Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour .The order of entropy is $S_{(g)} > S_{(l)} > S_{(s)}$

Entropy increases in all spontaneous processes

6. State second law of Thermodynamics. What do you understand by it?

Ans. Second law of thermodynamics states that

Heat cannot flow form colder body to hotter body by its own.

(Or)

Heat cannot be converted into work completely without causing some permanent changes in the system or in the surroundings.

* It is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process, without transferring a part of it to a cold reservoir.

* A machine which transforms heat from low temperature region to high temperature region without the intervention of external agency is called perpetual motion machine of the second kind. Second law of thermodynamics rules out the existence of machine of the second kind.

A volatile liquid in an open vessel vapourises at any temperature without intervention of any external agency. Therefore vapourisation of a liquid is spontaneous as per second law of thermodynamics. All natural processes are spontaneous and are thermodynamically irreversible.

7.What are the criteria for the spontaneity of chemical reaction?

Ans. Spontaneity: 1. An exothermic reaction is believed to occur readily and spontaneously. Therefore, negative enthalpy change is one of the criteria for the spontaneity of the reaction.

But there are reactions which are endothermic by nature, but still they are spontaneous. Hence, negative enthalpy change is a required condition for the spontaneity of the reaction, but it is not necessary and sufficient condition.

2. The reactions with positive entropy change take place spontaneously. Therefore positive entropy change is one of the criteria for the spontaneity of a reaction. But there are reactions with negative entropy change, but still they are spontaneous.

3. In order to explain the spontaneous nature of a process, Gibb introduced a new thermodynamic parameter called Gibbs energy (or) Gibbs function (G) that accounts for both exothermicity and entropy.

G = H – TS.

G is state function and extensive property.

For a process $\Delta G_{(sys)} = \Delta H_{(sys)} - T\Delta S_{(sys)}$, $\Delta G_{sys} = -T\Delta S_{Total}$

If ∆G = –ve, the process is spontaneous.

∆G = +ve, the process is non spontaneous

∆G = 0, the system is in equilibrium state

$\triangle H$	$\triangle S$	$\triangle G$	Nature of reation
$-ve$	$+ve$	$-ve$ at all temperature	spontaneous at all temperatures
$+ve$	$-ve$	$+ve$ at all temperature	Non spontaneous at all temperatures
$-ve$	$-ve$	$-ve$ at low temperature $+ve$ at high temperature	spontaneous at low temperature, non spontaneous at high temperature.
$+ve$	$+ve$	$+ve$ at low temperature $-ve$ at high temperature	non spontaneous at low temperature, spontaneous at high temperature.

8. State and explain the third law of thermodynamics?

Ans. Third law of thermodynamics

At the absolute zero temperature, the entropy of a pure and perfectly crystalline substance is zero.

This is known as third law of thermodynamics and has not much significance, except that imposes a limitation on the absolute value of entropy.

$$S_{T \to O} = 0 \quad \text{(or)} \quad S_T = \int_0^T \frac{C_p}{T} \, dT$$

Very Short Answer Questions

1. What is a thermo chemical equation? Give example?

Ans. The balanced chemical equation accompanied with the enthalpy changes of the process and the physical states of the reactants and the products is called thermo chemical equation.

Example: $C_{(graphite)} + O_{2\ (g)}\ CO_{2(g)}$; $\Delta H = -393.5$ kJ

2. State the first law of thermodynamics?

Ans. First law of thermodynamics is also known as law of conservation of energy. It states that

The energy in a process may be transformed from one form into the other form, but it is neither created nor destroyed. (OR) In any process the sum of energies of the system and surroundings is constant. The total energy is conserved in a given process.

(OR) A machine which operates in cycles and produce work without any expenditure of energy on it is called perpetual machine of the first kind. First law of thermodynamics rules out the existence of motion machine of the first kind.

3). How are ΔU and ΔH are related for a gaseous equilibrium reaction?

Ans. $\Delta H = \Delta U + \Delta nRT$, Where ΔU Heat of reaction at constant volume, ΔH Heat of reaction at constant pressure and $\Delta n = n_P - n_R$

n_P = no. of moles of Gaseous Products, n_R = no. of moles of Gaseous Reactants.

4. What is heat of a reaction?

Ans. The amount of heat evolved or absorbed when the chemical reaction takes place between the reactants as indicated in the stoichiometric equation is called the heat of reaction

The heat of a reaction ΔH may be +ve or –Ve

5. What is heat of combustion? How is it determined using bomb calorimeter?

Ans. The change in enthalpy when one mole of the substance is completely burnt (oxidised) in oxygen is called the heat of combustion or the enthalpy of combustion.

Eg. i) $H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)}$, ΔH =–286KJ

Here, ΔH represents enthalpy of combustion of H_2.

6. Define heat of formation. Write suitable examples?

Ans. The change in heat content when one mole of a compound in the standard state is formed from its constituent elements in their standard state is called the Standard heat of formation.

E g. *i) $H_{2\ (g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)}$, ΔH =–286KJ* Here, ΔH represents Standard heat of formation of H_2O.

ii) $C_{(graphite)} + O_{2\ (g)} \rightarrow CO_{2(g)}$, ΔH =– 393 KJ Here, ΔH represents Standard heat of formation of $C_{(graphite)}$

7. Define heat of neutralization. Write the basic equation?

Ans. The change in enthalpy when one gram equivalent weight of an acid is completely neutralised by one gram-equivalent weight of a base in dilute solution is called the heat of neutralisation or enthalpy of neutralization The heat of neutralisation of any strong acid by any strong base is equal to -13.7K cal or -57.3K.J.

Net reaction is given by $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}; \Delta H = -13.7 K.Cal$

8. Define Heat of solution. Give an example?

Ans. The change in enthalpy when 1 mole of the solute is dissolved in a large quantity (infinite quantity) of the solvent is known as heat of solution.

E.g. $MgSO_4(s) \xrightarrow{\ H_2O(excess)\ } MgSO_4(aq), \Delta H = -84.42 KJ/ mole$