

THERMODYNAMICS

Topic: 3

Thermo chemical equations and Hess's law, its applications

VERY SHORT ANSWER QUESTIONS

1. Explain enthalpy?

Enthalpy (H): "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature"

Enthalpy is state function. Thus, the magnitude to enthalpy change depends only upon the enthalpies in the initial and final states.

$$\Delta H = [H_{\text{products}} - H_{\text{reactants}}]$$

2. What is heat capacity? Explain.

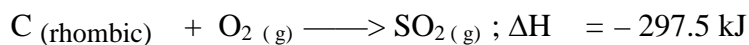
Ans. Heat capacity (C): "Heat capacity of a substance is defined as the amount of heat required to raise its temperature through one degree"

Heat capacity (C) is a state function. Hence to evaluate 'C' the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

- i) Heat capacity at constant volume (C_v)
- ii) Heat capacity at constant pressure (C_p).

3. What is thermo chemical equation? Give one example.

Ans: Thermo chemical equation: The chemical equation in which heat change accompanying a reaction is also numerically specified with proper sign by ΔH (or) ΔE by the side of the equation are known as thermo chemical equation.



4. State Hess's law?

Ans. Hess's law: The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps.

5. What is Gibbs energy?

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

SHORT ANSWER QUESTIONS

1. State second law of thermodynamics.

Ans. II law of thermodynamics:

Statements:

- i) "It is impossible for a self acting machine unaided by any external agency to convert heat from a body at low temperature to a body at higher temperature".
- ii) " All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes."
- iii) "For any spontaneous process taking place in an isolated system, the change in entropy (ΔS) is positive".

2. What is entropy?

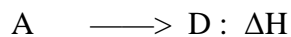
Ans. Entropy: is taken as a measure of disorder of molecules (or) randomness of system. Greater the disorder of molecules in a system, the higher is the entropy.
Entropy is a state function. It depends on the temperature, pressure of the system.
For a spontaneous process in an isolated system the entropy change is positive.

LONG ANSWER QUESTIONS

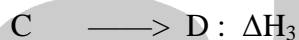
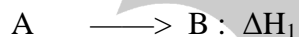
1. State Hess's law of constant heat summation and explain it with an example.

Ans: Hess's law states that the total amount of heat evolved or absorbed in a chemical reaction is always same whether the reaction is carried out in one step (or) in several steps.

Illustration: This means that the heat of reaction depends only on the initial and final stages and not on the intermediate stages through which the reaction is carried out. Let us consider a reaction in which A gives D. The reaction is brought out in one step and let the heat of reaction be ΔH .



Suppose the same reaction is brought out in three stages as follows –



The net heat of reaction is $\Delta H_1 + \Delta H_2 + \Delta H_3$.

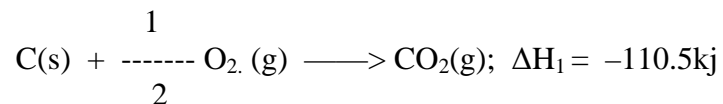
According to Hess law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

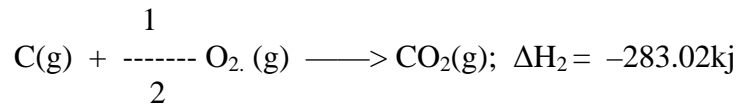
Ex: Consider the formation of CO_2 . It can be prepared in two ways.

1) **Direct method:** By heating carbon in excess of O_2 .



2) **Indirect method:** Carbon can be converted into CO_2 in the following two steps.





$$\text{Total } \Delta H = -393.52\text{kJ}$$

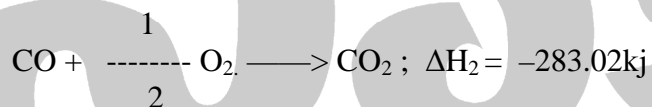
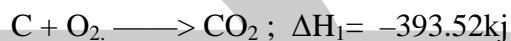
The two ΔH values are same.

2. Give the applications of Hess's law of constant heat summation with examples.

Ans: Applications of Hess's law:

1) It is used in the indirect determination of heat of formation of intermediate compounds which are unstable (or) which cannot be isolated.

Ex: Heat of formation (ΔH) of CO, cannot be directly determined but it is obtained indirectly using Hess's law from the following reactions.



$$\Delta H \text{ of CO formation} = (\Delta H_1 - \Delta H_2) = -393.52 - (-283.02)$$

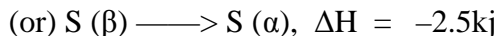
$$\Delta H = -110.50 \text{ kJ}$$

3) Heat of reactions which are slow can be easily calculated.

Ex: Transformation of α -sulphur to β - sulphur is slow and the heat change of the transformation cannot be measured experimentally easily. But it can be calculated from the heats of combustion of α -sulphur and β - sulphur as shown below.

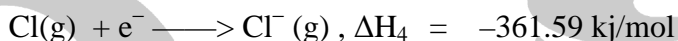
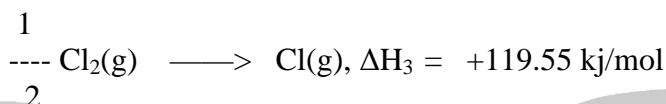
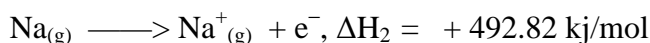
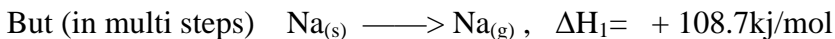
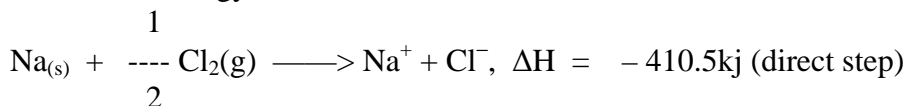


$$\therefore \text{S} (\alpha) \longrightarrow \text{S} (\beta), \Delta H = (\Delta H_1 - \Delta H_2) = -297.5 - (-300) = + 2.5\text{kJ}$$



4) Determination of lattice energy (U) of NaCl (Born – Haber Cycle):

The lattice energy is calculated from the thermo chemical data as follows:



But (from Hess's law) $\Delta H = (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - U)$

$$-410.5 = 108.7 + 492.82 + 119.55 - 361.59 - U$$

$$U = -769.96 (\approx 770) \text{ kJ/mol}$$

5. How are thermodynamic systems classified?

Ans: For the purpose of thermodynamic study, we divide the entire universe mainly in to two parts. They are –

System: A small part of the universe chosen for thermodynamic study is called system.

Surroundings: The remaining part of the universe in contact with the system is known as surroundings

Types of systems: The systems are classified into three types. These are:

a) Open system: A system which can exchange matter as well as energy with the surroundings is called an open system.

Ex: Evaporation of water from a beaker presents as open system.

Here vapours of water (matter) go into the atmosphere and heat (energy) required is absorbed by water from the surroundings.

b) Closed system: A system which may exchange energy but not matter with surroundings is called a closed system.

Ex: Consider boiling of water in a closed metallic vessel. Here, heat is transferred from the burner (surroundings) to the system. Steam remains inside the vessel. Thus, matter is not exchanged.

c) Isolated system: A system which can neither exchange matter nor energy with the surroundings is called an isolated system.

Ex: Take some water in an insulated vessel and put a small piece of sodium metal in it. An exothermic reaction takes place. Neither hydrogen gas (matter) nor heat (energy) is transferred to the surroundings.

6. What are C_p and C_v ?

Ans: Heat capacity (C): Heat capacity (C) of a substance is defined as the amount of heat required to raise its temperature through one degree.

(or)

It is the ratio of heat absorbed (q) to the resulting increase in temperature (dT).

$$\therefore C = \frac{q}{dT}$$

Heat capacity (C) is a state function. Hence to evaluate 'C', the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are :

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p)

From first law of thermodynamics,

$$q = dE + W = dE + P \cdot dV \quad (\because W = PV)$$

$$\therefore C \frac{q}{dT} = \frac{dE + P \cdot dV}{dT}$$

If the absorption of heat takes place at constant volume, C_v (i.e.,) $dV = 0$

$$\therefore C_v = \frac{q_v}{dT} = \frac{\partial E + 0}{\partial T} = \frac{[\partial E]}{[\partial T]_v}$$

$$\therefore C_v = \frac{[\partial E]}{[\partial T]_v}$$

Definition for “ C_v ”: Heat capacity of a system at constant volume (C_v) may be defined as rate of change of internal energy with temperature at constant volume.

If heat is absorbed by the system at constant pressure, heat capacity is denoted by “ C_p ” and is called heat capacity at constant pressure.

$$C_p = \frac{q_p}{dT} = \frac{[\partial E]}{[\partial T]_p} + P \frac{[\partial v]}{[\partial T]_p} \quad \text{-----(1)}$$

But $H = E + PV$

Differentiating this equation w.r.to T at constant pressure, we get

$$\frac{[\partial H]}{[\partial T]_p} = \frac{[\partial E]}{[\partial T]_p} + \frac{[\partial v]}{[\partial T]_p} \quad \text{-----(2)}$$

From equations (1) and (2) , we get

$$C_p = \frac{[\partial H]}{[\partial T]_p}$$

Definition for C_p : Heat capacity of a system at constant pressure (C_p) may be defined as rate of change of enthalpy with temperature at constant pressure.

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