

Plus One Chemistry Chapter Wise Important Questions

Chapter 5 Thermodynamics

Question 1.

a) State Hess's Law of constant heat summation. (March – 2009)

b) The equilibrium constant for a reaction is 5. What will be the value of ΔG° .

Given that $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

Answer:

a) Hess's law : Enthalpy change in a chemical reaction is same whether it takes place in one step or more than one step,

$$\Delta G = -2.303RT \log K$$

$$\Delta G = -2.303 \times 8.314 \times 300 \times \log 5$$

$$= -2.30 \times 8.314 \times 300 \times 0.6989$$

$$= -4014.581 \text{ J/mol}$$

Question 2.

A system in thermodynamics refers to that part of the universe in which observation are made. (March – 2010)

a) What do you mean by an isolated system? Given an example.

b) Distinguish between intensive and extensive properties. Give two examples for each.

Answer:

a) A system which can neither exchange matter nor energy with the surrounding. It is called as isolated system.

Eg: Thermo flask

b) Extensive property : The properties of the system which depend upon the quantity of the matter contained in the system.

Eg: mass, volume.

Intensive property : The properties of the system whose values are independent of the quantity of substance present in the system.

Eg: Temperature, pressure.

Question 3.

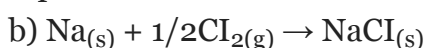
Lattice enthalpy of an ionic salt is a factor that determine its stability. (Say – 2010)

a) Define the lattice enthalpy.

b) Draw the Born-Haber cycle for the calculation of lattice enthalpy of the ionic crystal NaCl.

Answer:

a) The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of the ionic compound into gaseous constituent ions.



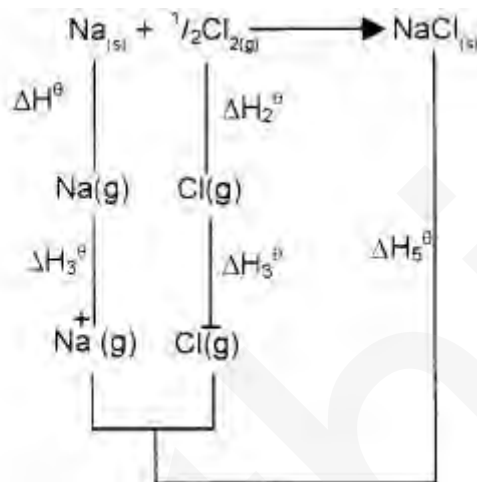
Question 4.

The spontaneity of a process is expressed in terms of a change in Gibbs energy. (March – 2011)

- What is meant by a change in Gibbs energy of a system?
- How is it related to the enthalpy and entropy of a system?
- How is it useful in predicting the feasibility of a process?

Answer:

- Free energy is the energy available to a system that can be converted into useful work.
- $\Delta G = \Delta H - T\Delta S$
- For a spontaneous process, $\Delta G = -ve$
For Non-Spontaneous process $\Delta G = +ve$
If the system is at equilibrium $\Delta G = 0$



Question 5.

A spontaneous process is an irreversible process and may only be reversed by some external agency. (Say – 2012)

- Decrease in enthalpy is the only criterion for spontaneity. Do you agree? Why?
- Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at 27°C, from a volume of 10 dm³ to a volume of 20 dm³.

Answer:

- No. Decrease in enthalpy ($\Delta H = -ve$) is not the only criterion for spontaneity. There are many endothermic processes which are also spontaneous like the evaporation of water placed in an open vessel. A process takes place spontaneously not only in the direction in which enthalpy of the system is reduced but also in the direction in which disorder or randomness increases ($\Delta S = +ve$). Thus, a resultant of the tendencies to decrease enthalpy and increase entropy determines the spontaneity of a process.

Question 6.

Thermodynamics deals with energy changes of macroscopic systems. (March – 2012)

- Consider a chemical reaction taking place in a closed insulated vessel. To which type of thermodynamic system does it belong?
- State the first law of thermodynamics.
- 3 mol of an ideal gas at 1.5 atm and 25°C expands isothermally in a reversible manner to twice its original volume against an external pressure of 1 atm. Calculate the work done. [R = 8.314 JK⁻¹ mol⁻¹]

$$\begin{aligned}
 \text{b) } W_{\text{rev}} &= -2.303nRT \log \frac{V_f}{V_i} \\
 &= -2.303 \times 1 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{20}{10} \\
 &= -2.303 \times 1 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times 0.3010 \\
 &= -1729 \text{ J} = -1.729 \text{ kJ}
 \end{aligned}$$

Answer:

a) Isolated system

b) 1st law of thermodynamics states that 'the energy of an isolated system is Constant'.

Question 7.

a) i) Construct an enthalpy diagram for the determination of lattice enthalpy of sodium chloride. (Say – 2012)

ii) Enthalpy and entropy changes of a reaction are 40.63 kJ/mol and 108.8 J K⁻¹ mol⁻¹. Predict the feasibility of the reaction at 27°C.

OR

b) i) Explain the Hess's law of constant heat summation, with an example.

ii) Draw the enthalpy diagram for an exothermic and endothermic reaction.

Answer:

Since ΔG is +ve, the reaction is not feasible at 27°C.

OR

b) i) Hess's law states that the enthalpy change during a process is the same whether it takes place in one step or in several steps.

Then according to Hess's law

Question 8.

Most of the naturally occurring processes are spontaneous. (March – 2013)

a) Give the criteria for spontaneity of a process in terms of free energy change (ΔG)

b) Exothermic reactions associated with a decrease in entropy are spontaneous at lower temperatures. Justify on the basis of Gibbs equation.

c) Find the temperature above which the reaction

Answer:

a) Free energy change (ΔG) is negative for a spontaneous process.

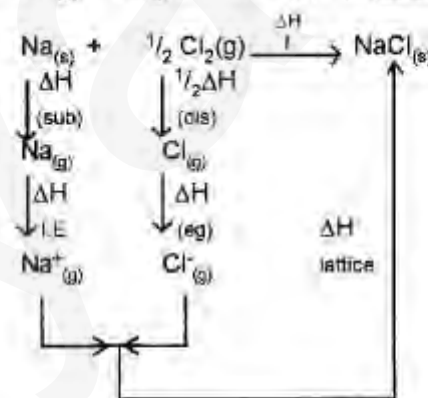
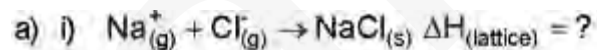
b) For a process to be spontaneous ΔG should be -ve. But ΔG = ΔH - T ΔS (1)

For Exothermic reaction ΔH = -ve

and decrease in entropy ΔS = -ve.

Substitute the value of ΔH and ΔS in (1) ΔG become -ve only when ΔH > T ΔS. Such

$$\begin{aligned}
 \text{c) } W_{\text{rev}} &= -nRT \ln \frac{V_2}{V_1} \quad n = 3 \\
 &= -2.303 n RT \log \frac{V_2}{V_1} \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\
 &= -2.303 \times 3 \times 8.314 \times 298 \log \frac{(2)}{(1)} \quad T = 298\text{K} \\
 &= -2.303 \times 8.314 \times 298 \times 0.3010 \quad V_1=1, V_2=2 \\
 &= -5152.38 \text{ kJ}
 \end{aligned}$$



$$\begin{aligned}
 \text{ii) } \Delta H &= 40.63 \text{ kJ/mol} \quad \Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1} \\
 T &= 27^\circ\text{C} = 300\text{K} \\
 \Delta G &= \Delta H - T\Delta S = 40630 - (108.8 \times 300) \\
 &= 7990 \text{ J/mol}
 \end{aligned}$$

reactions are spontaneous only at low temperatures.

At 2474.7K and above this temperature the reaction become spontaneous.

Question 9.

- a) The enthalpy of combustion of $\text{CH}_4(\text{g})$, $\text{C}_{(\text{Graphite})}$ and $\text{H}_2(\text{g})$ at 298 K are $-890.3 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively. Calculate the enthalpy of formation of $\text{CH}_4(\text{g})$. (Say – 2013)
- b) Match the following:

Answer:

Question 10.

- a) For the oxidation of iron $4 \text{ Fe}_{(\text{s})} + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ Fe}_2\text{O}_3(\text{s})$, entropy change is $-549.4 \text{ JK}^{-1} \text{ mol}^{-1}$ at 298 K. In spite of the negative entropy change of this reaction, why is the reaction spontaneous? (ΔH°_r for the reaction is $-1648 \times 10^3 \text{ J mol}^{-1}$). (March – 2014)
- b) Write the difference between extensive and intensive properties. Give one example of each.

Answer:

b) Extensive properties – properties whose values depend on the quantity or size of matter present in the system. e.g., Mass, Volume. Internal energy. Enthalpy, Heat capacity etc.

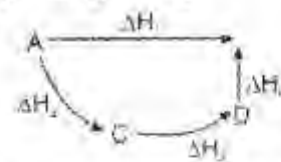
Intensive properties- properties which do not depend on the quantity or size of matter present in the system. e.g., Temperature, Density, Pressure etc.

Question 11.

- a) ΔG gives a criteria for spontaneity of reactions at a constant pressure and temperature. How is ΔG helpful in predicting the spontaneity of the reaction? (August – 2014)
- b) State and explain Hess's law of constant heat summation.

Answer:

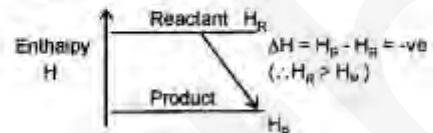
$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$



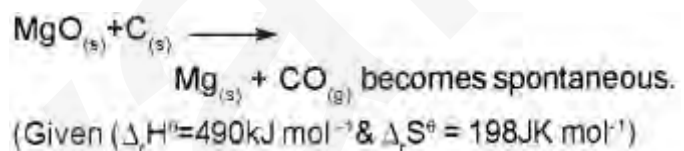
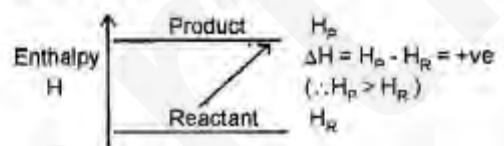
ie. reaction go into backward direction.

ii) Enthalpy Diagram

a) Exothermic reaction



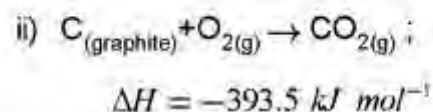
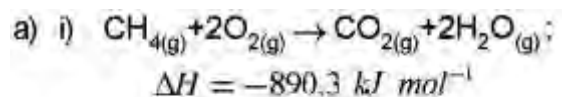
b) Endothermic reaction.



c) $\Delta_r H^\circ = 490 \text{ kJ mol}^{-1} = 490000 \text{ J/mol}$
 $\Delta_r S^\circ = 198 \text{ JK}^{-1} \text{ mol}^{-1}$

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{490000}{198} = \underline{\underline{2474.7\text{K}}}$$

$W = -\Delta u$	- Enthalpy change
$\Delta u = 0$	- Universal gas constant
$C_p - C_v$	- Adiabatic process
q_p	- Isothermal process
	- Cyclic process



a) If ΔG is negative (<0), the process is spontaneous. If ΔG is positive (>0), the process is non-spontaneous.

b) Hess's law states that the enthalpy change during a process is the same whether it takes place in one step or in several steps.

Then according to Hess's law

Question 12.

a) Classify the following into intensive and extensive properties.

(March – 2015)

i) Internal energy

ii) Density

iii) Heat Capacity

iv) Temperature

b) Calculate the standard free energy change (ΔG°) for the conversion of oxygen to ozone $3/2 O_{2(g)} \rightarrow O_{3(g)}$ at 298 K if the equilibrium constant for the conversion is 2.47×10^{-29} . (Given $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Answer:

a) Intensive properties –

ii) Density and

iv) Temperature

Extensive properties-

i) Internal energy

iii) Heat capacity

Question 13.

Expansion of a gas in vacuum is called free expansion. (Say – 2015)

a) Which one of the following represents free expansion of an ideal gas under adiabatic conditions?

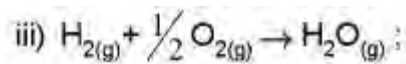
i) $q = 0, \Delta T \neq 0, w = 0$

ii) $q \neq 0, \Delta T = 0, w = 0$

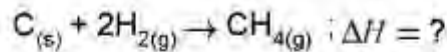
iii) $q = 0, \Delta T = 0, w = 0$

iv) $q = 0, \Delta T < 0, w = 0$

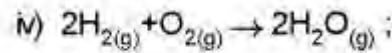
b) The enthalpy change for the reaction.



$$\Delta H = -285.8 \text{ kJ mol}^{-1}$$

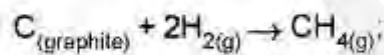


$$\text{Eq. (iii)} \times 2 \Rightarrow$$



$$\Delta H = -571.6 \text{ kJ mol}^{-1}$$

$$\text{Eq. (ii)} + \text{Eq. (iv)} - \text{Eq. (i)} \Rightarrow$$



$$\Delta H = -393.5 + -571.6 - (-890.3) \text{ kJ mol}^{-1}$$

$$= -74.8 \text{ kJ mol}^{-1}$$

b) $W = -\Delta u$ - Adiabatic process

$\Delta u = 0$ - Cyclic process

$C_p - C_v$ - Universal gas constant

q_p - Enthalpy change

$$\text{a) } \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{surr} = -\frac{\Delta_r H^\circ}{T} \text{ (at constant pressure)}$$

$$= -\frac{(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} = 5530 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S_{total} = 5530 \text{ J K}^{-1} \text{ mol}^{-1} + (-549.4 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= 4980.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer:

Question 14.

The enthalpy change in a process is the same, whether the process is carried out in a single step or in several steps. (March – 2016)

- Identify the law stated here.
- Calculate the enthalpy of formation of CH_4 from the following data:

Answer:

- Hess's law
- The required equation is

The given data are:

Question 15.

- Which of the following is a process taking place with increase in entropy? (Say – 2016)
 - Freezing of water
 - Condensation of steam
 - Cooling of a liquid
 - Dissolution of a solute

- State and illustrate Hess's law.

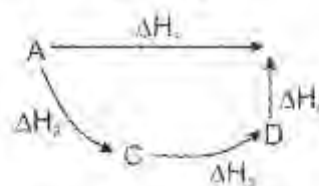
Answer:

- iv) Dissolution of a solute
- Hess's law states that if a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature. Illustration:

Consider the formation of CO_2 from carbon and oxygen. There are two ways by which the change can be brought about.

In general, if enthalpy of an overall reaction $\text{A} \rightarrow \text{B}$ along one route is $\Delta_1 H$ and $\Delta_1 H_1, \Delta_2 H_2, \Delta_3 H_3 \dots$ representing enthalpies of reactions leading to same product, B along another route, then according to Hess's law,

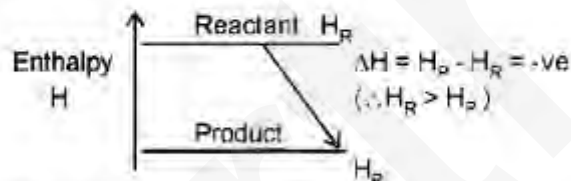
$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$



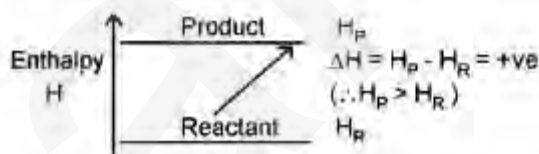
ie. reaction go into backward direction.

Enthalpy Diagram

- Exothermic reaction



- Endothermic reaction.

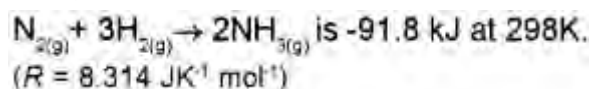


$$\text{b) } \Delta_r G^\ominus = -2.303 RT \log K_p$$

$$= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log (2.47 \times 10^{-28})$$

$$= 163000 \text{ J mol}^{-1}$$

$$= 163 \text{ kJ mol}^{-1}$$



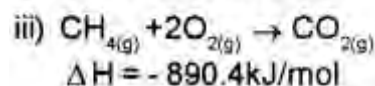
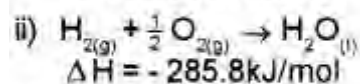
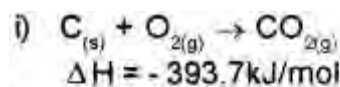
$$\text{a) iii) } q = 0, \Delta T = 0, w = 0$$

$$\text{b) } \Delta H = \Delta U + \Delta n_g RT$$

$$\therefore \Delta U = \Delta H - \Delta n_g RT$$

$$= -91.8 \times 10^3 \text{ J mol}^{-1} - (1 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= -94277.57 \text{ J mol}^{-1} = 94.3 \text{ kJ mol}^{-1}$$



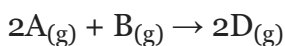
Question 16.

a) Some macroscopic properties are given below.

(March – 2017)

Help Reena to classify them into two groups under suitable titles [Heat capacity, Entropy, Refractive index, Surface tension] (2)

b) For the reaction



$$\Delta U^\circ = -10.5 \text{ kJ/mol}$$

$$\Delta S^\circ = -44.1 \text{ J/k/mol at } 298 \text{ K}$$

Calculate ΔG° for the reaction

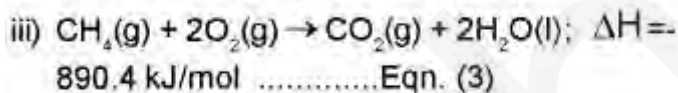
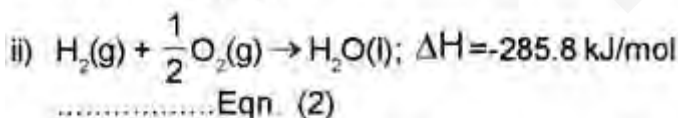
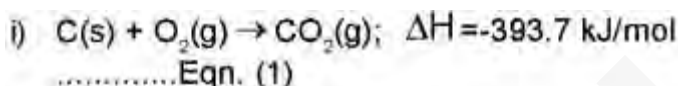
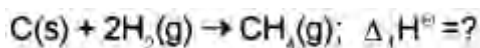
Answer:

a) Extensive properties: Heat capacity,

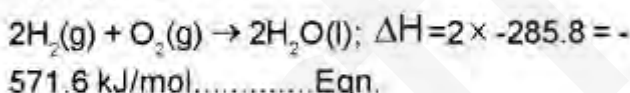
Entropy Intensive properties:

Refractive index, Surface tension

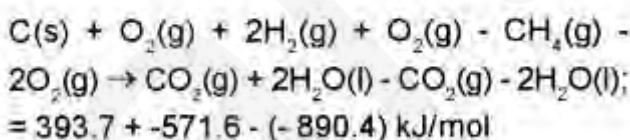
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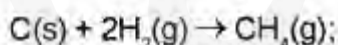
$$\text{Eqn. (2)} \times 2 \Rightarrow$$



$$\text{Eqn. (1)} + \text{Eqn. (4)} - \text{Eqn. (3)} \Rightarrow$$

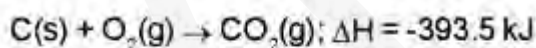


On simplifying we get,

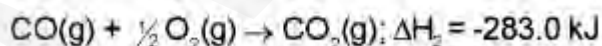
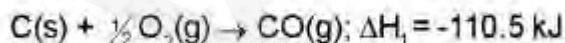


$$\Delta_r H^\circ = 712.5 \text{ kJ/mol}$$

1) Conversion of C to CO_2



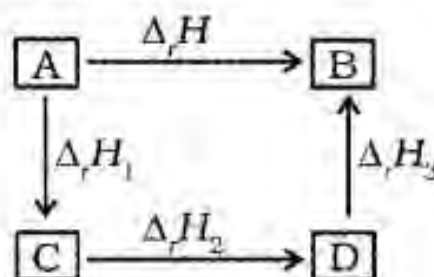
2) Conversion of C to CO and subsequent oxidation of CO to CO_2 .



According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2$

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \dots$$

It can be represented as,



b) Given that, $\Delta U^\ominus = -10.5 \text{ kJ/mol} = -10.5 \times 10^3 \text{ J/mol}$

$\Delta S^\ominus = -44.1 \text{ J/K/mol}$ and $T = 298 \text{ K}$

We have, $\Delta H^\ominus = \Delta U^\ominus + \Delta n_g RT$

For the reaction, $2A(g) + B(g) \rightarrow 2D(g)$,

$\Delta n_g = 2 - 3 = -1$ and $R = 8.314 \text{ J/K/mol}$

$\therefore \Delta H^\ominus = -10.5 \times 10^3 \text{ J/mol} + (-1) \times 8.314 \text{ J/K/mol} \times 298 \text{ K} = -12977.57 \text{ J/mol}$

Also we have, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

i.e., $\Delta G^\ominus = -12977.57 \text{ J/mol} - (298 \text{ K} \times -44.1 \text{ J/K/mol})$
 $= 164.23 \text{ J/mol} = 0.16423 \text{ kJ/mol}$