

## **PREVIOUS HSE QUESTIONS AND ANSWERS OF THE CHAPTER "THERMODYNAMICS"**

1. State Hess's law of constant heat summation. (2)

*Ans: It states that the total enthalpy change for a physical or chemical process is the same whether the reaction is taking place in a single step or in several steps.*

*Or, the total enthalpy change for a process is independent of the path followed.*

2. (i) Define extensive and intensive properties. (2)

(ii) Choose the intensive property from the following:

(A) Enthalpy (B) Molar volume (C) Heat capacity (D) Internal energy (1)

*Ans: (i) Extensive properties are properties which depend on the amount of matter present in the system.*

*E.g.: Volume (v), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity etc.*

*Intensive properties are independent of the amount of matter present in the system.*

*E.g. : Temperature (T), Pressure (P), Volume (V), density, refractive index, molar heat capacity, viscosity, surface tension etc.*

*(ii) (B) Molar volume*

3. The enthalpy and entropy changes for a reaction are  $490 \text{ kJ mol}^{-1}$  and  $198 \text{ J K}^{-1} \text{ mol}^{-1}$ . Calculate the value of Gibb's energy change ( $\Delta_r G$ ) for this reaction at 300 K. Predict whether the reaction is spontaneous at this temperature. (3) [December 2021]

*Ans: From Gibb's equation  $\Delta G = \Delta H - T\Delta S$*

*Here  $\Delta H = 490 \text{ kJ/mol} = 490 \times 10^3 \text{ J/mol}$ ,  $\Delta S = 198 \text{ J/K/mol}$  and  $T = 300 \text{ K}$*

*So  $\Delta G = 490 \times 10^3 - 300 \times 198 = 430600 \text{ J/mol} = \mathbf{430.6 \text{ kJ/mol}}$*

*Since  $\Delta G$  is positive, the reaction is not spontaneous at this temperature.*

4. Write Hess's law of constant heat summation. (2)

*Ans: Refer the answer of the question number 1*

5. (i) Name the thermodynamic system with exchange of energy and matter with surroundings. (1)

(ii) State 1<sup>st</sup> law of thermodynamics. (2)

*Ans: (i) Open system*

*(ii) It states that energy can neither be created nor be destroyed. Or, the total energy in the universe is always a constant. Or, the total energy of an isolated system is always a constant.*

6. (i) Define extensive property. (1)

(ii) Identify extensive property from the following:

density, mass, pressure, volume (2) [September 2021]

*Ans: (i) Refer the answer of the question number 2*

*(ii) Extensive properties: mass, volume*

7. Calculate the standard enthalpy of reaction:  $\text{CaCO}_3 (\text{s}) \longrightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$

Given  $\Delta_f H^\circ \text{CaCO}_3 (\text{s}) = -1206.92 \text{ kJ/mol}$ ,  $\Delta_f H^\circ \text{CaO} (\text{s}) = -635.09 \text{ kJ/mol}$  and  $\Delta_f H^\circ \text{CO}_2 (\text{g}) = -393.51 \text{ kJ/mol}$  (2)

*Ans:  $\Delta_r H^\circ = \sum \Delta_f H^\circ_{(P)} - \sum \Delta_f H^\circ_{(R)} = [\Delta_f H^\circ(\text{CaO}) + \Delta_f H^\circ(\text{CO}_2)] - [\Delta_f H^\circ(\text{CaCO}_3)]$*   
 *$= [-635.09 + -393.51] - [-1206.92] = \mathbf{178.32 \text{ kJ/mol}}$*

8. (a) State the second law of thermodynamics. (1)

(b) Define Gibbs energy. (1)

(c) How the Gibb's energy change and entropy change are related? (1) [December 2020]

Ans: (a) It states that the entropy of the universe always increases during every spontaneous process.

(b) It is defined as the maximum amount of available energy that can be converted to useful work.

(c)  $\Delta G = \Delta H - T\Delta S$

9. Define extensive and intensive properties. Give examples for each. (2)

Ans: Extensive properties are properties which depend on the amount of matter present in the system.

E.g.: Volume (v), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity etc.

Intensive properties are independent of the amount of matter present in the system.

E.g. : Temperature (T), Pressure (P), Volume (V), density, refractive index, molar heat capacity, viscosity, surface tension etc.

10. (a) Write the mathematical expression of First Law of thermodynamics. (1)

(b) Define standard enthalpy of formation. (1)

(c) Write the condition of temperature for a process to be spontaneous whose  $\Delta H$  and  $\Delta S$  values are positive. [Hint :  $\Delta G = \Delta H - T\Delta S$ ] (1) [March 2020]

Ans: (a)  $\Delta U = q + w$

(b) It is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation (reference state).

(c) When  $\Delta H$  and  $\Delta S$  values are positive, the process will be spontaneous at higher temperatures.

11. In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system. The change in internal energy for the process is ..... (1)

Ans: 307 J [Here  $q = 701$  J and  $w = -394$  J.  $\Delta U = q + w = 701 + -394 = 307$  J]

12. The std. enthalpies of formation of  $\text{CH}_4$  (g),  $\text{CO}_2$  (g) and  $\text{H}_2\text{O}$  (l) at 298K are  $-74.81 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively. Calculate the std. enthalpy of the reaction:



Ans:  $\Delta_r H^\circ = \sum \Delta_f H^\circ_{(P)} - \sum \Delta_f H^\circ_{(R)} = [\Delta_f H^\circ(\text{CO}_2) + 2 \times \Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{CH}_4) + 2 \times \Delta_f H^\circ(\text{O}_2)]$   
 $= [-393.5 + 2 \times -285.8] - [-74.81 + 2 \times 0] = -890.29 \text{ kJ mol}^{-1}$

13. (a) What is a spontaneous process? (1)

(b) For the reaction,  $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2 \text{Fe}_2\text{O}_3(\text{s})$ , the entropy change is  $-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K.

In spite of the negative entropy change, why is the reaction spontaneous? Given  $\Delta H^\circ = -1648 \text{ kJ mol}^{-1}$ . (3) [July 2019]

Ans: (a) It is a process that takes place without the help of any external agency.

(b) Spontaneity of a reaction is mainly determined by  $\Delta G$  not by  $\Delta S$ .

Here  $\Delta H^\circ = -1648 \text{ kJ mol}^{-1} = -1648 \times 10^3 \text{ J/mol}$ .  $\Delta S^\circ = -549.4 \text{ J K mol}^{-1}$  and  $T = 298 \text{ K}$

We know that  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -1648 \times 10^3 - 298 \times -549.4 = -1811.72 \times 10^3 \text{ J/mol}$$

Since  $\Delta G^\circ$  is negative, the process is spontaneous.

14. According to the first law of thermodynamics, for an isolated system,  $\Delta U = \dots\dots\dots$  (1)

Ans: Zero

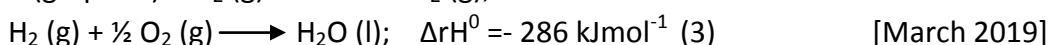
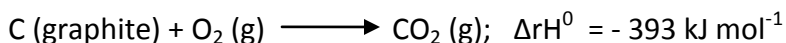
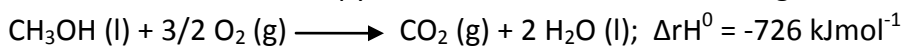
15. What is meant by spontaneous processes? Give the criterion of spontaneity in terms of  $\Delta G$  for a process taking place at constant temperature and pressure. (2)

Ans: A process that takes place without the help of any external agency is called a spontaneous process. Or, it is a process that has a natural tendency to occur.

For a spontaneous process  $\Delta G_{(T,P)}$  or  $\Delta G$  should be -ve. (Or,  $\Delta G < 0$ )

16. (a) State Hess' law of constant heat summation. (1)

(b) Calculate the standard enthalpy of formation from the following:

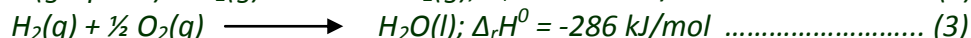
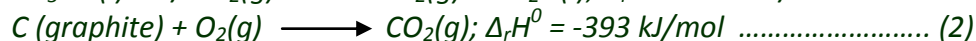
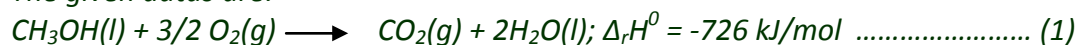


Ans: (a) **Hess's Law:** It states that the total enthalpy change for a physical or chemical process is the same whether the reaction is taking place in a single step or in several steps.

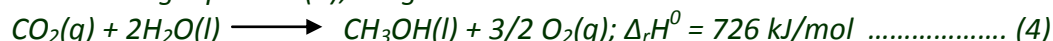
Or, the total enthalpy change for a process is independent of the path followed.

(b) The required equation is:  $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l})$

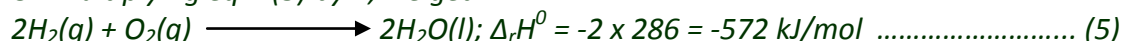
The given data are:



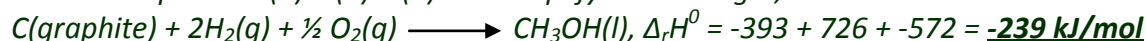
On reversing equation (1), we get



On multiplying eqn. (3) by 2, we get



Now add equations (2) + (4) + (5) and simplify. Then we get,



17. Differentiate state functions from path functions and give one example for each. (2)

Ans: A function or a property that depends only on the initial and final state of a system and not on the path followed is called a state function.

E.g. for state functions: T, P, V, U, H, S, G etc.

**Path functions:** These are properties which depend on the path followed also.

E.g. heat (q) and work (w)

18. First law of thermodynamics can be stated as  $\Delta U = q + w$ . How can this equation be expressed for :

a) An isothermal reversible change?

b) A process carried out at constant volume? (2)

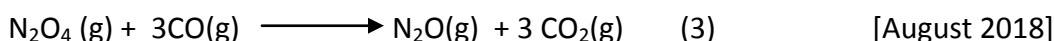
Ans: (a) For an isothermal reversible change,  $\Delta U = 0$ . So  $q = -w$

(b) For a process taking place at constant volume,  $\Delta V = 0$ . So  $\Delta U = q_v$

19. Enthalpies of formation of some compounds are given below :

Compound	CO	CO <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub> O <sub>4</sub>
Enthalpy of formation (kJ/mol)	-110.0	-393.0	81.0	9.7

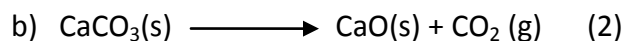
Using these data, calculate the enthalpy of reaction for



$$\begin{aligned} \text{Ans: } \Delta_r H^\circ &= \sum \Delta_f H^\circ_{(P)} - \sum \Delta_f H^\circ_{(R)} = [\Delta_f H^\circ(\text{N}_2\text{O}) + 3 \times \Delta_f H^\circ(\text{CO}_2)] - [\Delta_f H^\circ(\text{N}_2\text{O}_4) + 3 \times \Delta_f H^\circ(\text{CO})] \\ &= [81.0 + 3 \times -393.0] - [9.7 + 3 \times -110.0] = \underline{\underline{-777.7 \text{ kJ/mol}}} \end{aligned}$$

20. What is meant by entropy of a system? What happens to the entropy during the following changes?

a) A gas condenses into liquid.

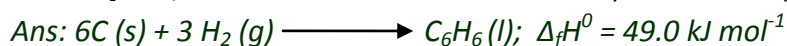
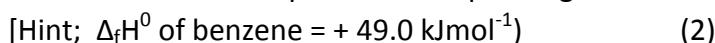


Ans: It is a measure of degree of disorderness or randomness of a system.

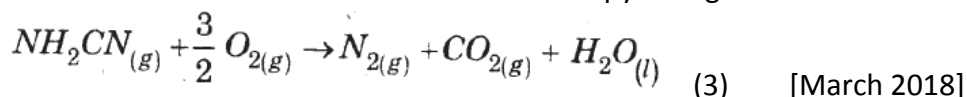
a) Entropy decreases

b) Entropy increases.

21. Write the thermochemical equation corresponding to the standard enthalpy of formation of benzene.



22. The reaction of cyanamide ( $\text{NH}_2\text{CN}$ ) with dioxygen was carried out in a bomb calorimeter and  $\Delta U$  was found to be -742.7 kJ mol<sup>-1</sup> at 298K. Calculate enthalpy change for the reaction at 298 K.



Ans:

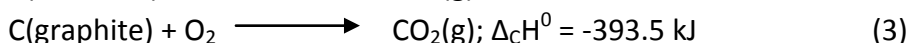
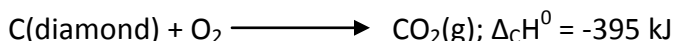
Here  $\Delta U = -742.7 \text{ kJ/mol} = -742.7 \times 10^3 \text{ J/mol}$ ,  $\Delta n = n_{P(\text{g})} - n_{R(\text{g})} = 2 - 5/2 = -1/2$ ,  $T = 298 \text{ K}$ ,  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$\Delta H = \Delta U + \Delta nRT$

$$= -742.7 \times 10^3 + -1/2 \times 8.314 \times 298 = \underline{\underline{-743.938 \times 10^3 \text{ J/mol}}}$$

23. a) i) State Hess's law.

ii) Calculate  $\Delta_f H^\circ$  when diamond is formed from graphite.



b) An extensive property is.....

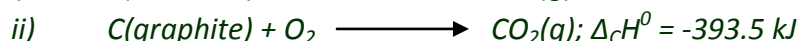
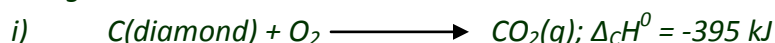
- i) density    ii) pressure    iii) temperature    iv) mass    (1)    [July 2017]

Ans: a) (i) It states that the total enthalpy change for a physical or chemical process is the same whether the reaction is taking place in a single step or in several steps.

Or, the total enthalpy change for a process is independent of the path followed.

(ii) The required equation is:  $\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{diamond})$

The given datas are:



b) Mass

24. a) Some macroscopic properties are given below. Help Reena to classify them into two groups under suitable titles.

[Heat capacity, Entropy, Refractive index, Surface tension] (2)

b) For the reaction  $2\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow 2\text{D}(\text{g})$ ,  $\Delta U^\circ = -10.5 \text{ kJ/mol}$ ,  $\Delta S^\circ = -44.1 \text{ J/K/mol}$  at 298K.

Calculate  $\Delta G^\circ$  for the reaction. (2) [March 2017]

Ans: a) Extensive properties: Heat capacity, Entropy

Intensive properties: Refractive index, Surface tension

b) Given  $\Delta U^\circ = -10.5 \text{ kJ/mol} = -10.5 \times 10^3 \text{ J/mol}$ ,  $\Delta S^\circ = -44.1 \text{ J/K/mol}$ ,  $R = 8.314 \text{ J/K/mol}$  and  $T = 298 \text{ K}$ .

$$\Delta n = n_{P(\text{g})} - n_{R(\text{g})} = 2 - 3 = -1$$

We know that  $\Delta H^0 = \Delta U^0 + \Delta nRT = -10.5 \times 10^3 + -1 \times 8.314 \times 298 = -12977.6 \text{ J/mol}$

Also  $\Delta G^0 = \Delta H^0 - T\Delta S^0$

$$= -12977.6 - 298 \times -44.1 = \underline{-26.119 \times 10^3 \text{ J/mol}}$$

25. a) Which of the following is a process taking place with increase in entropy?

- i) Freezing of water ii) Condensation of steam iii) Cooling of a liquid iv) Dissolution of a solute (1)

b) State and illustrate Hess's law. (3) [September 2016]

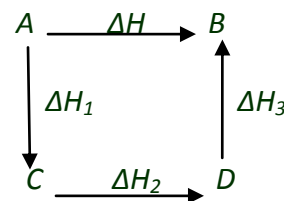
Ans: (a) Dissolution of a solute

(b) The law states that the total enthalpy change for a physical or chemical process is the same whether the reaction taking place in a single step or in several steps. Or, the total enthalpy change for a process is independent of the path followed.

Illustration:

Consider a process in which the reactant A is converted to product B in a single step by involving heat change  $\Delta H$ . Let the same reactant A is first converted to C, then to D and finally to B involving heat changes  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  respectively.

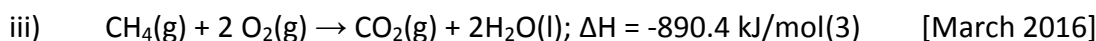
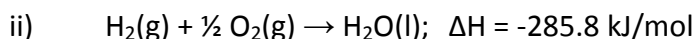
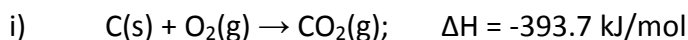
Then according to Hess's law:  $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$



26. The enthalpy change in a process is the same, whether the process is carried out in a single step or in several steps.

a) Identify the law stated here. (1)

b) Calculate the enthalpy of formation of  $\text{CH}_4$  from the following data:



Ans: (a) Hess's Law

(b) The required equation is:  $\text{C(s)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$

Given:  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = -393.7 \text{ kJ/mol}$

Multiply equation (ii)  $\times 2$ ;  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O(l)}; \Delta H = -285.8 \times 2 = -571.6 \text{ kJ/mol}$

Reverse equation (iii)  $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)} \rightarrow \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}); \Delta H = 890.4 \text{ kJ/mol}$

Now add the above three equations we get  $\text{C(s)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g}); \Delta H = -393.7 + -571.6 + 890.4 = \underline{-74.9 \text{ kJ/mol}}$

27. Expansion of a gas in vacuum is called free expansion.

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)  $q = 0, \Delta T < 0, w \neq 0$  (1)

b) The enthalpy change for the reaction  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$  is  $-91.8 \text{ kJ}$  at  $298 \text{ K}$ . Calculate the value of internal energy change. ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) (3) [Oct. 2015]

Ans: (a) i)  $q = 0, \Delta T = 0, w = 0$  [For adiabatic process  $q = 0$ . For free expansion no work is done. So  $w = 0$ . On applying these values to the mathematical form 1<sup>st</sup> law,  $\Delta U = q + w = 0$ . Also since  $\Delta U = q \cdot \Delta T, \Delta T = 0$ ]

(b)  $\Delta H = \Delta U + \Delta nRT$

Given  $\Delta H = -91.8 \text{ kJ} = -91.8 \times 10^3 \text{ J}$ ,  $\Delta n = 2 - 4 = -2$ ,  $R = 8.314 \text{ J/K/mol}$ ,  $T = 298 \text{ K}$

$\Delta U = \Delta H - \Delta nRT = -91800 - -2 \times 8.314 \times 298 = \underline{-86844.86 \text{ J/mol}}$

28. a) Classify the following into intensive and extensive properties.

i) Internal energy      ii) Density      iii) Heat capacity      iv) Temperature      (2)

b) Calculate the standard free energy ( $\Delta G^0$ ) for the conversion of oxygen to ozone  $3/2 \text{ O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$  at 298K, if the equilibrium constant for the conversion is  $2.47 \times 10^{-29}$ . (Given  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ). (2)  
[March 2015]

*Ans: (a) Intensive properties: Density, Temperature*

*Extensive properties: Internal energy, Heat capacity*

*(b) Here  $K = 2.47 \times 10^{-29}$ ,  $R = 8.314 \text{ J/K/mol}$  and  $T = 298\text{K}$*

$$\Delta G^0 = -2.303RT \log K$$

$$= -2.303 \times 8.314 \times 298 \times \log (2.47 \times 10^{-29}) = 163000 \text{ J/mol} = \underline{163 \text{ kJ/mol}}$$

29. a)  $\Delta G$  gives a criterion for spontaneity of reactions at a constant pressure and temperature. How is  $\Delta G$  helpful in predicting the spontaneity of the reaction? (2)

b) State and explain Hess's law of constant heat summation. (2) [August 2014]

*Ans: (a) For a spontaneous process  $\Delta G$  is negative. If  $\Delta G^0$  is +ve, the process is non-spontaneous and if it is zero, the process is at equilibrium.*

*(b) Ref. the ans. of the qn. No. 25 (b)*

30. 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  $\Delta S$  is  $-549.4 \text{ J/K/mol}$  at 298K. In spite of the negative entropy change of this reaction, why is the reaction spontaneous? ( $\Delta_r H^0$  for the reaction is  $-1648 \times 10^3 \text{ J/mol}^{-1}$ ). (2)

b) Write the differences between extensive and intensive properties. Give one example of each. (2)  
[March 2014]

*Ans: (a) Spontaneity of a reaction is mainly determined by  $\Delta G$  not by  $\Delta S$ .*

*Here  $\Delta H^0 = -1648 \times 10^3 \text{ J/mol}$ .  $\Delta S^0 = -549.4 \text{ J K mol}^{-1}$  and  $T = 298 \text{ K}$*

*We know that  $\Delta G^0 = \Delta H^0 - T\Delta S^0$*

$$= -1648 \times 10^3 - 298 \times -549.4 = -1811.72 \times 10^3 \text{ J/mol}$$

*Since  $\Delta G^0$  is negative, the process is spontaneous.*

*(b) Extensive properties depend on the amount of matter present in the system. Or, these are the properties which change when a system is divided. E.g.: Volume (v), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity etc.*

*Intensive properties are independent of the amount of matter present in the system. Or, these are the properties which do not change when a system is divided. E.g. : Temperature (T), Pressure (P), Volume (V), density, refractive index, molar heat capacity, viscosity, surface tension etc.*

31. a) The enthalpy of combustion of  $\text{CH}_{4(\text{g})}$ , C(graphite) and  $\text{H}_{2(\text{g})}$  at 298K 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  $\text{CH}_{4(\text{g})}$ . (2)

b) Match the following:

1. $W = -\Delta U$	a) Enthalpy change
2. $\Delta U = 0$	b) Universal gas constant
3. $C_p - C_v$	c) Adiabatic process
4. $q_p$	d) Isothermal process
	e) Cyclic process

Ans: (a) Ref. the answer of the qn. No. 26(b)

(b)

1. $W = -\Delta U$	c) Adiabatic process
2. $\Delta U = 0$	d) Isothermal process
3. $C_p - C_v$	b) Universal gas constant
4. $q_p$	a) Enthalpy change

32. Most of the naturally occurring processes are spontaneous.

- Give the criteria for spontaneity of a process in terms of free energy change ( $\Delta G$ ). (1)
- Exothermic reactions associated with a decrease in entropy are spontaneous at lower temperatures. Justify on the basis of Gibbs equation. (1)
- Find the temperature above which the reaction  $\text{MgO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Mg}_{(s)} + \text{CO}_{(g)}$  becomes spontaneous. (Given  $\Delta_r H^\circ = 490 \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ = 198 \text{ JKmol}^{-1}$ ). (2) [March 2013]

Ans: a) For a spontaneous process  $\Delta G$  is negative.

b) Here  $\Delta H$  is -ve and  $\Delta S$  is also -ve. So according to Gibb's eqn,  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  becomes -ve only when  $T\Delta S < \Delta H$ . This is possible at low temperature.

c) At equilibrium,  $\Delta_r G^\circ = 0$

So the Gibb's equation,  $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$  becomes:

$$0 = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$\text{Or, } \Delta_r H^\circ = T\Delta_r S^\circ$$

$$\text{So, } T = \Delta_r H^\circ / \Delta_r S^\circ = 490 \times 10^3 / 198 = 2474.74 \text{ K.}$$

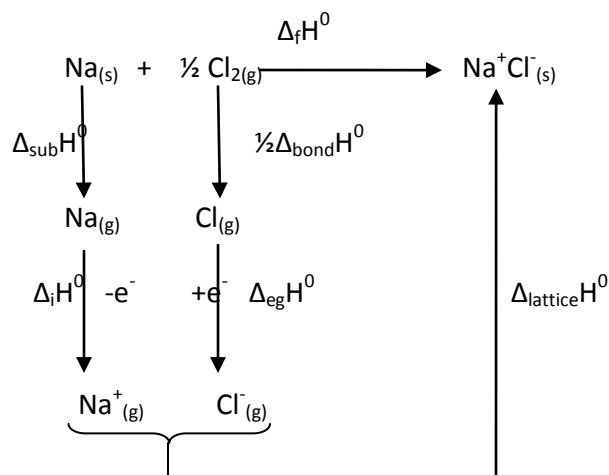
So at 2474.74K, the reaction is at equilibrium.

Above this temperature, the reaction becomes spontaneous. [Here both  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are +ve. So  $\Delta_r G^\circ$  becomes -ve only when  $T\Delta_r S^\circ > \Delta_r H^\circ$ . This is possible at high temperature.]

33. a) Construct an enthalpy diagram for the determination of lattice enthalpy of sodium chloride. (2)

b) Enthalpy and entropy changes of a reaction are 40.63 kJ/mol and 108.8 J/K/mol. Predict the feasibility of the reaction at 27°C. (2) [September 2012]

Ans: a)



b) Given  $\Delta H = 40.63 \text{ kJ/mol} = 40630 \text{ J/mol}$ ,  $\Delta S = 108.8 \text{ J/K/mol}$  and  $T = 27 + 273 = 300 \text{ K}$ .



From Gibb's equation,  $\Delta G = \Delta H - T\Delta S$

$$= 40630 - 300 \times 108.8 = \underline{7990 \text{ J/mol}}$$

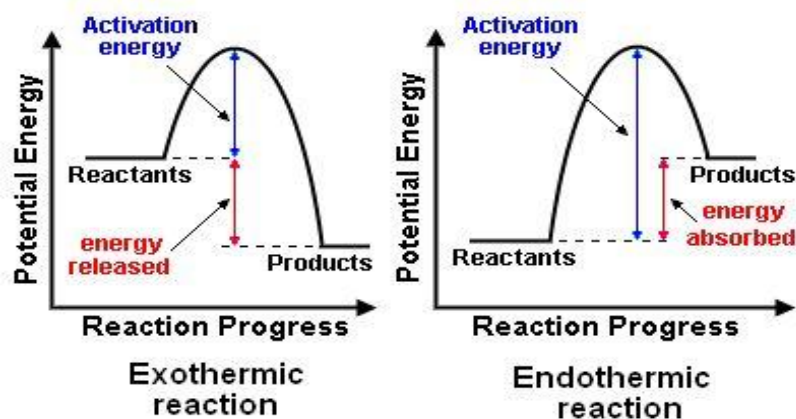
Since  $\Delta G^0$  is positive, the process is non-spontaneous at this temperature.

34. a) Explain the Hess's law of constant heat summation, with an example. (2)

b) Draw the enthalpy diagram for exothermic and endothermic reactions. (2) [September 2012]

Ans: (a) Ref. the answer of the qn. No. 15(b)

(b)



35. Thermodynamics deals with energy changes of macroscopic systems.

a) Consider a chemical reaction taking place in a closed insulated vessel. To which type of thermodynamic system does it belong? (1)

b) State the first law of thermodynamics. (1)

c) 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. ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) (2) [March 2012]

Ans: (a) Adiabatic system

(b) It states that energy can neither be created nor be destroyed. Or, the total energy in the universe is always a constant. Or, the total energy of an isolated system is always a constant.

(c) Here  $n = 3 \text{ mol}$ ,  $R = 8.314 \text{ J/K/mol}$ ,  $V_1 = z$ ,  $V_2 = 2z$  and  $T = 25 + 273 = 298 \text{ K}$

For isothermal reversible expansion, work done,  $W_{\text{exp}} = -2.303nRT \log(V_2/V_1)$

$$= -2.303 \times 3 \times 8.314 \times 298 \times \log(2z/z)$$

$$= \underline{\underline{-5152.38 \text{ J}}}$$

36. A spontaneous process is an irreversible process and may only be reversed by some external agency.

a) Decrease in entropy is the only criterion for spontaneity. Do you agree? Why? (2)

b) Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at 27°C, from a volume of 10 dm<sup>3</sup> to a volume of 20 dm<sup>3</sup>. (2) [October 2011]

Ans: (a) No. Decrease in entropy alone can't predict the spontaneity of a process. If during a process, the enthalpy of the system decreases and entropy increases, the process is spontaneous. Or decrease in Gibb's energy determines spontaneity.

(b) Here  $n = 1 \text{ mol}$ ,  $R = 8.314 \text{ J/K/mol}$ ,  $V_1 = 10 \text{ dm}^3$ ,  $V_2 = 20 \text{ dm}^3$  and  $T = 25 + 273 = 298 \text{ K}$

For isothermal reversible expansion, work done,  $W_{\text{exp}} = -2.303nRT \log(V_2/V_1)$

$$= -2.303 \times 1 \times 8.314 \times 298 \times \log(20/10)$$



$$= \underline{-1717.46 \text{ J}}$$

37. The spontaneity of a process is expressed in terms of a change in Gibbs energy.

- What is meant by change in Gibbs energy of a system? (1)
- How is it related to the enthalpy and entropy of a system? (1)
- How is it useful in predicting the feasibility of a process? (2) [March 2011]

*Ans: (a) It is defined as the maximum amount of available energy that can be converted to useful work.*

*The change in Gibbs energy ( $\Delta G$ ) =  $G_2 - G_1$*

*(b)  $G = H - TS$  Or,  $\Delta G = \Delta H - T\Delta S$*

*(c) For a spontaneous process  $\Delta G$  should be negative.*

38. Lattice enthalpy of an ionic salt is a factor that determines its stability.

- Define the lattice enthalpy. (1)
- Draw the Born-Haber cycle for the calculation of lattice enthalpy of the ionic crystal NaCl. (3) [September 2010]

*Ans: (a) The lattice enthalpy of an ionic compound is the enthalpy change when one mole of an ionic compound dissociates into gaseous ions.*

*(b) Ref. answer of the Qn. No. 33 (a)*

39. A system in thermodynamics refers to that part of the universe in which observations are made.

- What do you mean by an isolated system? Give an example. (1)
- Distinguish between intensive and extensive properties. Give two examples for each. (3) [March 2010]

*Ans: (a) It is a system that cannot exchange both energy and matter with the surroundings.*

*E.g.: Hot water taken in a thermoflask.*

*(b) Ref. answer of the Qn. No. 30 (b)*

40. a) State Hess's law of constant heat summation. (2)

- The equilibrium constant for a reaction is 5. What will be the value of  $\Delta G^0$ ? Given that  $R = 8.314 \text{ J/K/mol}$ ,  $T = 300\text{K}$ . (2) [March 2009]

*Ans: (a) Ref. answer of the Qn. No. 1*

*(b)  $\Delta G^0 = -2.303RT \log K$*

*$= -2.303 \times 8.314 \times 300 \times \log 5 = \underline{-4014.58 \text{ J/mol}}$*

41. Some properties are "state functions".

- $q$  and  $w$  are not state functions, but  $(q+w)$  is a state function. Why? (1)
- What do you mean by saying that pressure is an intensive property? (1)
- What is the difference in internal energy of a system, if 100 kJ of energy is radiated out without doing any work? (1) [February 2008]

*Ans: (a)  $q + w = \Delta U$ . Internal energy is a state function.*

*(b) Pressure of a system does not change when the system is divided. So it is an intensive property.*

*(c) From first law of Thermodynamics,  $\Delta U = q + w = -100 + 0 = \underline{-100 \text{ kJ}}$  (Since energy is radiated  $q$  is -ve)*