

Important Questions

Multiple Choice questions-

Question 1. Hesss law is an application of

- (a) 1st law of Thermodynamics
- (b) 2nd law of Thermodynamics
- (c) Entropy change
- (d) $\Delta H = \Delta U + P \Delta V$.

Question 2. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. Wirr at 300 K is:

- (a) -15.921 kJ
- (b) -11.224 kJ
- (c) -110.83 kJ
- (d) None of these

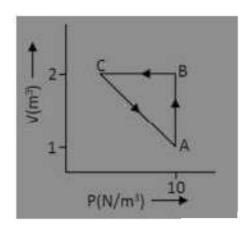
Question 3. At absolute zero the entropy of a perfect crystal is zero. This statement corresponds to which law of thermodynamics?

- (a) Zeroth Law
- (b) First Law
- (c) Second Law
- (d) Third Law

Question 4. Which of the following has the highest entropy?

- (a) Mercury
- (b) Hydrogen
- (c) Water
- (d) Graphite

Question 5. An ideal gas is taken through the cycle $A \rightarrow B \rightarrow C \rightarrow A$ as shown in figure. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process $C \rightarrow A$.

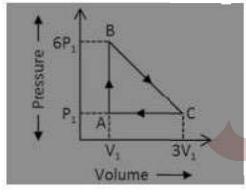


- (a) -5 J
- (b) -15 J
- (c) -10 J
- (d) -20 J

Question 6. One mole of which of the following has the highest entropy?

- (a) Liquid Nitrogen
- (b) Hydrogen Gas
- (c) Mercury
- (d) Diamond

Question 7. An ideal gas is taken around the cycle ABCA as shown in P-V diagram The next work done by the gas during the cycle is equal to:





- (a) 12P₁V₁
- (b) 6P₁V₁
- (c) $5P_1V_1$
- (d) P_1V_1

Question 8. Third law of thermodynamics provides a method to evaluate which property?

(a) Absolute Energy

- (b) Absolute Enthalpy
- (c) Absolute Entropy
- (d) Absolute Free Energy

Question 9. Which of the following is/are a reason that water is a desirable heat sink for use in calorimeters?

- I) Waters heat specific capacity is very precisely known.
- II) Water is readily available.
- III) Water has an unusually large specific heat capacity.
- (a) I only
- (b) I and II
- (c) I, II and III
- (d) II only

Question 10. In a chemical reaction the bond energy of reactants is more than the bond energy of the products. Therefore, the reaction is

- (a) Exothermic
- (b) Athermic
- (c) Endothermic
- (d) Endergonic

Question 11. In a reversible process the system absorbs 600 kJ heat and performs 250 kJ work on the surroundings. What is the increase in the internal energy of the system?

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- (a) 850 kJ
- (b) 600 kJ
- (c) 350 kJ
- (d) 250 kJ

Question 12. Which of the following neutralization reactions is most exothermic?

- (a) HCl and NaOH
- (b) HCN and NaOH
- (c) HCl and NH4OH
- (d) CH3COOH and NH4OH

Question 13. A student runs a reaction in a closed system. In the course of the reaction, 64.7 kJ of heat is released to the surroundings and 14.3 kJ of work is done on the system. What is the change in internal energy (ΔU) of the reaction?

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- (a) -79.0 kJ
- (b) 50.4 kJ
- (c) 79.0 kJ
- (d) -50.4 kJ

Question 14. Identify the correct statement from the following in a chemical reaction.

- (a) The entropy always increases
- (b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction
- (c) The enthalpy always decreases
- (d) Both the enthalpy and the entropy remain constant

Question 15. 2 mole of an ideal gas at 27° C expands isothermally and reversibly from a volume of 4 litters to 40 litre. The work done (in kJ) is:

- (a) w = -28.72 kJ
- (b) w = -11.488 kJ
- (c) w = -5.736 kJ
- (d) w = -4.988 kJ

Very Short:

- 1. Under what conditions the heat evolved or absorbed is equal to the internal energy change?
- 2. What is the sign of AH for endothermic reactions and why?
- 3. What is the relationship between the standard enthalpy of formation and the enthalpy of a compound?
- 4. Why enthalpy of neutralization of HF is greater than 57.1 kJ mol⁻¹?
- 5. What are the specific heat capacity and molar heat capacity for water?
- 6. Why enthalpy of neutralization is less if either the acid or the base or both are weak?
- 7. What do you mean by a system?

Short Questions:

- 1. Ice is lighter than water, but the entropy of ice is less than that of water. Explain.
- 2. Define spontaneity or-feasibility of a process.
- 3. Enthalpy of neutralization of CH₃COOH and NaOH is 55.9 kJ. What is the value of ΔH for ionization of CH₃COOH?

- 4. When 1 gm of liquid naphthalene (C10H8) solidifies, 150 J of heat is evolved. What is the enthalpy of fusion of $C_{10}H_8$?
- 5. Why most of the exothermic processes (reactions) are spontaneous?
- 6. What is meant by the term state function? Give examples.

Long Questions:

- 1. Define
 - (i) Standard enthalpy of formation.
 - (ii) Standard enthalpy of combustion
 - (iii) Enthalpy of atomization
 - (iv) Enthalpy of solution
 - (v) Lattice enthalpy
 - (vi) Thermochemical equation.
- 2. For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K_c = 1.8 \times 10^{-7}$. What is ΔG° for the reaction? (R = 8.314 JK⁻¹ mol⁻¹).
- 3. Calculate the equilibrium constant, K, for the following reaction at 400 K?

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2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)
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Given that $\Delta_r H^\circ = 80.0 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 120 \text{ JK}^{-1} \text{ mol}^{-1}$.

4. Calculate the standard entropy change for the reaction $X \rightleftharpoons Y$ if the value of $\Delta H^\circ = 28.40$ kJ and equilibrium constant is 1.8×10^{-7} at 298 K and $\Delta_r G^\circ = 38.484$ kJ.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): Combustion of all organic compounds is an exothermic reaction.

Reason (R): The enthalpies of all elements in their standard state are zero.

- (i) Both A and R are true and R is the correct explanation of A.
- (ii) Both A and R are true but R is not the correct explanation of A.
- (iii) A is true but R is false.
- (iv) A is false but R is true
- 2. In the following questions, a statement of Assertion (A) followed by a statement of Reason

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(R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): Spontaneous process is an irreversible process and may be reversed by some external agency.

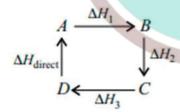
Reason (R): Decrease in enthalpy is a contributory factor for spontaneity.

- (i) Both A and R are true and R is the correct explanation of A.
- (ii) Both A and R are true but R is not the correct explanation of A.
- (iii) A is true but R is false.
- (iv) A is false but R is true.

Case Study Based Question:

1. This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.



Total enthalpy change from A to D,

$$\Delta H_{\rm total} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_{\rm total} + \Delta H_{\rm direct} = 0$$

$$i.e.$$
, $\Delta H_{\text{total}} = -\Delta H_{\text{direct}}$

For example, formation of CO2 from C in two

different manners involves a total heat change of -393.5 kJ/mol

Single step process:

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \, \to \, \mathrm{CO}_{2(g)}$$
 ; $\Delta H = -393.5 \text{ kJ/mol}$

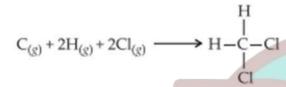
Two step process :

(i)
$$C(s) + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$$
; $\Delta H = -110.5 \text{ kJ/mol}$

(ii)
$$CO(g) + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$
; $\Delta H = -283.0 \text{ kJ/mol}$

$$\Delta H_{\text{Total}} = -110.5 + (-283.0) = -393.5 \text{ kJ/mol}$$

- (1) In which of the enlisted cases, Hess's law is not applicable?
 - (a) Determination of lattice energy
 - (b) Determination of resonance energy
 - (c) Determination of enthalpy of transformation of one allotropic form to another
 - (d) Determination of entropy
- (2) Use the bond energy data and calculate the enthalpy change for



The Bond energies of C — H and C — Cl are 413 and 328 kJ mol⁻¹ respectively.

- (a) 1465 kJ/mol
- (b) 1465 kJ/mol
- (c) 1482 kJ/mol
- (d) 1482 kJ/mol
- (3) A hypothetical reaction, A 2B, proceeds through the following sequence of steps:

$$\begin{array}{ll} A & \longrightarrow C; \Delta H = q_1 \\ C & \longrightarrow D; \Delta H = q_2 \\ \hline \frac{1}{2}D & \longrightarrow B; \Delta H = q_3 \end{array}$$

The heat of reaction is

- (a) $q_1 q_2 + 2q_3$
- (b) $q_1 + q_2 2q_3$
- (c) $q_1 + q_2 + 2q_3$
- (d) $q_1 2q_2 + 2q_3$
- 2. The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

$$H = U + PV$$

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = qp, \Delta H = \Delta U + P\Delta V$$

(1) Which of the following is not correct about enthalpy?

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- (a) It is an extensive property
- (b) It is not a state function
- (c) Its absolute value cannot be determined
- (d) Enthalpy of a compound is equal to the enthalpy of formation of that compound.
- (2) Lattice enthalpies are determined by:
 - (a) Born-Haber cycle
 - (b) Hess's law
 - (c) lattice cycle
 - (d) None of these
- (3) In which of the following thermochemical changes ΔH is always negative?
 - (a) Enthalpy of solution
 - (b) Enthalpy of hydrogenation
 - (c) Enthalpy of reaction
 - (d) Enthalpy of transition

Answer Key:

MCQ

- 1. (d) 1st law of Thermodynamics
- 2. (b) -11.224 kJ
- 3. (d) Third Law
- 4. (b) Hydrogen
- 5. (a) -5 J
- 6. (b) Hydrogen Gas
- 7. (c) $5P_1V_1$
- 8. (c) Absolute Entropy
- 9. (c) I, II and III
- 10.(c) Endothermic



- 11.(c) 350 kJ
- 12.(a) HCl and NaOH
- 13.(d) -50.4 kJ
- 14.(b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction
- 15.(b) w = -11.488 k

Very Short Answer:

- 1. At constant volume.
- 2. AH is positive as $\Delta H = H_p H_r$ and $H_r < Hp$.
- 3. They are equal.
- 4. This is due to the high hydration energy of fluoride ions.
- 5. Specific heat capacity for $H_2O = 4.18 \text{ JK}^{-1} \text{ g}^{-1}$

Molar heat capacity for $H_2O = 4.18 \times 18 = 75.24 \text{ JK}^{-1} \text{ mol}^{-1}$.

- 6. A part of the heat is used up for dissociation of the weak acid or weak base or both
- 7. A specified part of the universe that is under thermodynamic observation is called a system.

Short Answer:

Ans: 1. Water is the liquid form while ice is its solid form. Molecular motion in ice is restricted than in water, i.e., a disorder in ice is restricted than water, i.e., a disorder in ice is less than in water.

Ans: 2. Spontaneity or feasibility of a process means its inherent tendency to occur on its own in a particular direction under a given set of conditions.

Ans: 3. The heat of neutralization of strong acid and strong base + ΔH of ionization of CH₃COOH

- = Enthalpy of neutralization of CH₃COOH and NaOH
- \therefore − 57.1 kJ + Δ H of ionization of CH3COOH = − 55.9 kJ
- \therefore ∆H of ionization of CH₃COOH = (- 55.9 + 57.1) kJ
- = 1.2 kJ.

Ans: 4. Δ Hsolidification = $-150 \times 128 = -19200 \text{ J} = -19.2 \text{ kJ}$

[: M.wt.of
$$C_{10}H_8 = 128$$
]

Ans: 5. $\Delta G = \Delta H - T\Delta S$; For exothermic reactions,

 ΔH is -ve For a spontaneous process ΔG is to be -ve.

Thus decrease in enthalpy (- AH) contributes significantly to the driving force (To make ΔG negative).

Ans: 6. A state function is a thermodynamic property that depends upon the state of the system and is independent of the path followed to bring about the change. Internal energy change (ΔU), enthalpy change (ΔH) entropy change (ΔS), and free energy change (ΔG) are examples.

Long Answer:

Ans: 1. Standard enthalpy of formation: The heat change accompanying the formation of 1 mole df a substance from its elements in their most stable state of aggregation is called its standard enthalpy of formation.

$$H_2(g) + \frac{1}{2} O_2(g) H_2O(I)$$
; $\Delta f He = 285.8 \text{ kJ mol}^{-1}$

(ii) Standard enthalpy of combustion: It is the heat change accompanying the complete combustion or burning of one mole of a substance in its standard state in excess of air or oxygen.

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(1); \Delta H\theta = -2658.0 \text{ kJ mol}^{-1}.$$

(iii) Enthalpy of atomization: It is defined as the enthalpy change accompanying the breaking of one mole of a substance completely into its atoms in the gas phase.

$$H_2(g) \rightarrow 2H(g) \Delta_c He = 435.0 \text{ kJ mol}^{-1}$$

- (iv) Enthalpy of solution: It is defined as the heat change when one mole of a substance dissolves in a specified amount of the solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving 2 moles of the substance in an infinite amount of the solvent.
- (v) Lattice Enthalpy: The lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of an ionic compound dissociates into its ions in a gaseous state.

Na⁺Cl⁻(s)
$$\longrightarrow$$
 Na⁺(g) + Cl⁻(g); Δ_{lattice} H⁰ = + 788 kJ mol⁻¹ 1 mole

(vi) Thermochemical Equation: A balanced chemical equation together with the value of its A^H is called a thermochemical equation.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \Delta_rH^0 = -1367 \text{ kJ}$$

 mol^{-1}

The above equation describes the combustion of liquid ethanol. The negative sign indicates that tills are an exothermic reaction. We specify the physical state along with the allotropic state of the substance in a thermochemical equation.

Ans: 2.

$$K_p = K_C(RT)^{\Delta n}$$

 $\Delta n = n_p - n_r = 2 - 1 = 1.$
 $T = 298 \text{ K}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} [Given]$
 $\therefore K_p = 1.8 \times 10^{-7} \times 8.314 \times 298 = 4.46 \times 10^{-4}$
Now $\Delta_r G^0 = -2.303 \text{ RT log } K_p$
 $= -2.303 \times 8.314 \times 298 \times \log (4.46 \times 10^{-4})$
 $= 19111.86 \text{ J mol}^{-1} = 19.12 \text{ kJ mol}^{-1}.$

Ans: 3.

$$\Delta_{r}G^{0} = \Delta_{r}H^{0} - T\Delta_{r}S^{0}$$

$$= 80.0 - 400 \times 0.12 = 32.0 \text{ kJ}$$

$$\Delta_{r}G^{0} = -2.303 \text{ RT log K}$$

$$32.0 = -2.303 \times 0.0831 \times 400 \text{ log K}$$
or
$$\log K = -4.1782 = \overline{5}.8218$$
or
$$K = \text{Antilog } \overline{5}.8218 = 6.634 \times 10^{-5}.$$

Ans: 4.

$$\Delta_r G^0 = -2.303 \text{ RT log K} = 38484 \text{ J (given)}$$

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

$$\Delta_r S^0 = \frac{\Delta_r H^0 - \Delta_r G^0}{T} = \frac{28400 - 38484}{298}$$

 $= -33.8 \, \text{JK}^{-1} \, \text{mol}^{-1}$

Assertion Reason Answer:

- 1. (ii) Both A and R are true but R is not the correct explanation of A.
- 2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. Answer:

- (1) (d) Determination of entropy
- (2) (c) 1482 kJ/mol
- (3) (c) $q_1 + q_2 + 2q_3$

2. Answer:

- (1) (b) It is not a state function
- (2) (a) Born-Haber cycle
- (3) (b) Enthalpy of hydrogenation

