

6



Thermodynamics

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Thermodynamics is **not** concerned about _____.
- energy changes involved in a chemical reaction.
 - the extent to which a chemical reaction proceeds.
 - the rate at which a reaction proceeds.
 - the feasibility of a chemical reaction.

Ans. (iii)

Explanation: Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state.

2. Which of the following statements is correct?
- The presence of reacting species in a covered beaker is an example of open system.
 - There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
 - The presence of reactants in a closed vessel made up of copper is an example of a closed system.
 - The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

Ans. (iii)

Explanation: The presence of reactants in a closed vessel made of conducting material *e.g.*, copper or steel is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between _____.
- pressure, volume, temperature
 - temperature, amount, pressure
 - amount, volume, temperature
 - pressure, volume, temperature, amount

Ans. (iv)

Explanation: Variables like p , V , T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

4. The volume of gas is reduced to half from its original volume. The specific heat will _____.

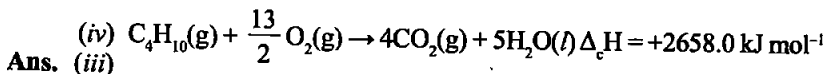
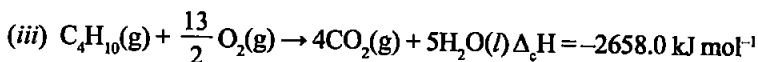
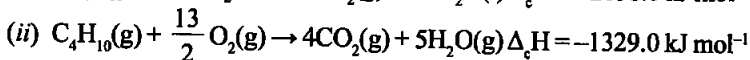
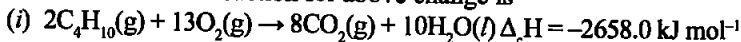
- (i) reduce to half (ii) be doubled
 (iii) remain constant (iv) increase four times

Ans. (iii)

Explanation: Specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). That is why it is an intensive property which does not depend on mass.

5. During complete combustion of one mole of butane, 2658 kJ of heat is released.

The thermochemical reaction for above change is



Explanation: Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

6. $\Delta_f U^\ominus$ of formation of $CH_4(g)$ at certain temperature is -393 kJ mol^{-1} .

The value of $\Delta_f H^\ominus$ is

- (i) zero (ii) $< \Delta_f U^\ominus$
 (iii) $> \Delta_f U^\ominus$ (iv) equal to $\Delta_f U^\ominus$

Ans. (ii)

Explanation: The reaction is $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta n_g = (n_p - n_r)_g = 1 - 3 = -2$$

$$\Delta H^\ominus = \Delta U^\ominus + \Delta n_g RT$$

$$\Delta n_g = -2$$

$$\therefore \Delta H^\ominus < \Delta_f U^\ominus$$

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

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

Ans. (iii)

Explanation: In free expansion, $w = 0$ because volume is constant, as the process is adiabatic $q = 0$ and from first law of thermodynamics $\Delta U = q + w = 0$.

8. The pressure-volume work for an ideal gas can be calculated by using

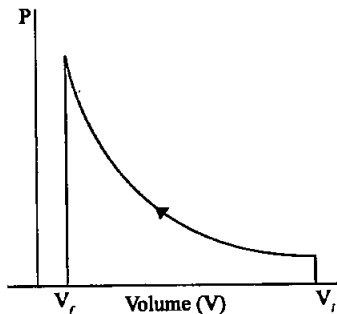
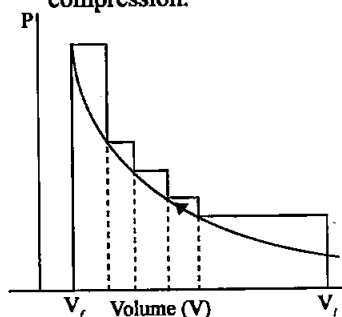
the expression $w = - \int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the

pV - plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f , choose the correct option.

- (i) w (reversible) = w (irreversible)
- (ii) w (reversible) < w (irreversible)
- (iii) w (reversible) > w (irreversible)
- (iv) w (reversible) = w (irreversible) + $p_{ex} \Delta V$

Ans. (ii)

Explanation: Area under the curve is always more in irreversible compression.



9. The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$.

When water freezes in a glass beaker, choose the correct statement amongst the following :

- (i) ΔS (system) decreases but ΔS (surroundings) remains the same.
- (ii) ΔS (system) increases but ΔS (surroundings) decreases.
- (iii) ΔS (system) decreases but ΔS (surroundings) increases.
- (iv) ΔS (system) decreases and ΔS (surroundings) also decreases.

Ans. (iii)

Explanation: Freezing is an exothermic process thus heat is released and entropy of the surrounding increases whereas entropy of the system decreases.

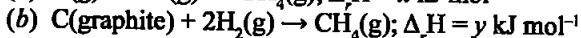
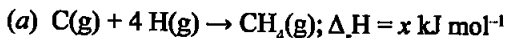
10. On the basis of thermochemical equations (a), (b) and (c), find out which of the algebraic relationships given in options (i) to (iv) is correct.

- (a) C (graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta_r H = x \text{ kJ mol}^{-1}$
 - (b) C (graphite) + $\frac{1}{2} O_2(g) \rightarrow CO(g)$; $\Delta_r H = y \text{ kJ mol}^{-1}$
 - (c) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$; $\Delta_r H = z \text{ kJ mol}^{-1}$
- (i) $z = x + y$
 - (ii) $x = y - z$
 - (iii) $x = y + z$
 - (iv) $y = 2z - x$

Ans. (iii)

Explanation: Algebraic sum of y and z will give x , $x = y + z$.

11. Consider the reactions given below. On the basis of these reactions find out which of the algebraic relations given in options (i) to (iv) is correct?



- (i) $x = y$ (ii) $x = 2y$
 (iii) $x > y$ (iv) $x < y$

Ans. (iii)

Explanation: Constituents are same in both the reactions but in eq (i) carbon and hydrogen are in atomic state.

12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

- (i) is always negative (ii) is always positive
 (iii) may be positive or negative (iv) is never negative

Ans. (iii)

Explanation: Reaction could be exothermic or endothermic.

13. Enthalpy of sublimation of a substance is equal to

- (i) enthalpy of fusion + enthalpy of vapourisation
 (ii) enthalpy of fusion
 (iii) enthalpy of vapourisation
 (iv) twice the enthalpy of vapourisation

Ans. (i)

Explanation: Enthalpy of sublimation can be shown as



14. Which of the following is **not** correct?

- (i) ΔG is zero for a reversible reaction
 (ii) ΔG is positive for a spontaneous reaction
 (iii) ΔG is negative for a spontaneous reaction
 (iv) ΔG is positive for a non-spontaneous reaction

Ans. (ii)

Explanation: ΔG is negative for a spontaneous reaction.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

In the following questions two or more options may be correct.

15. Thermodynamics mainly deals with

- (i) interrelation of various forms of energy and their transformation from one form to another.
 (ii) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.
 (iii) how and at what rate these energy transformations are carried out.
 (iv) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.

Ans. (i) and (iv)

Explanation: The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state.

16. In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. For such system

- (i) q_p will be negative (ii) $\Delta_r H$ will be negative
 (iii) q_p will be positive (iv) $\Delta_r H$ will be positive

Ans. (i) and (ii)

Explanation: In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative.

17. The spontaneity means, having the potential to proceed without the assistance of external agency. The processes which occur spontaneously are

- (i) flow of heat from colder to warmer body.
 (ii) gas in a container contracting into one corner.
 (iii) gas expanding to fill the available volume.
 (iv) burning carbon in oxygen to give carbon dioxide.

Ans. (iii) and (iv)

Explanation: In first two processes external agency is required.

18. For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression $w = -nRT \ln \frac{V_f}{V_i}$.

A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option.

- (i) Work done at 600 K is 20 times the work done at 300 K.
 (ii) Work done at 300 K is twice the work done at 600 K.
 (iii) Work done at 600 K is twice the work done at 300 K.
 (iv) $\Delta U = 0$ in both cases.

Ans. (iii) and (iv)

Explanation: For isothermal reversible change

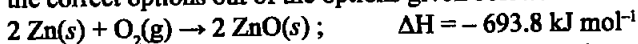
$$q = -w = nRT \ln \frac{V_f}{V_i} = 2.303 nRT \log \frac{V_f}{V_i}$$

$$\frac{W_{600\text{ K}}}{W_{300\text{ K}}} = \frac{1 \times R \times 600 \text{ K} \ln \frac{10}{1}}{1 \times R \times 300 \text{ K} \ln \frac{10}{1}} = \frac{600}{300} = 2$$

For isothermal expansion of ideal gases, $\Delta U = 0$

Since, temperature is constant this means there is no change in internal energy. Therefore, $\Delta U = 0$.

19. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below:



- (i) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

- (ii) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
- (iii) 693.8 kJ mol⁻¹ energy is evolved in the reaction.
- (iv) 693.8 kJ mol⁻¹ energy is absorbed in the reaction.

Ans. (i) and (iii)

Explanation: $\Delta_r H^\ominus = \sum_i a_i \Delta_f H^\ominus (\text{products}) - \sum_i b_i \Delta_f H^\ominus (\text{reactants})$.

Since, the above reaction is an exothermic reaction, the enthalpy of reactant is more than the enthalpy of product.

III. SHORT ANSWER TYPE

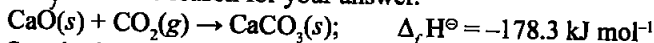
20. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol⁻¹. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

Ans. Enthalpy change for vaporizing 18g of water means 1 mol water. Given that the enthalpy change for 1 mole of water = 40.79 kJ/mol. Therefore, enthalpy change for 2 mole of water = 2 × 40.79 = + 81.58 kJ, $\Delta_{\text{vap}} H = + 40.79 \text{ kJ mol}^{-1}$.

21. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?

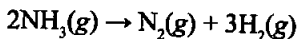
Ans. Due to weak force of attraction between molecules, acetone requires less heat to vaporise. Hence, water has higher enthalpy of vaporisation.

22. Standard molar enthalpy of formation, $\Delta_f H^\ominus$ is just a special case of enthalpy of reaction, $\Delta_r H^\ominus$. Is the $\Delta_r H^\ominus$ for the following reaction same as $\Delta_f H^\ominus$? Give reason for your answer.

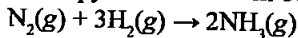


Ans. Standard molar enthalpy of formation, $\Delta_f H_1^\ominus$, is just a special case of $\Delta_r H_2^\ominus$, where one mole of a compound is formed from its constituent elements. In the above equation, enthalpy of formation and enthalpy of reaction is not same.

23. The value of $\Delta_f H^\ominus$ for NH₃ is -91.8 kJ mol⁻¹. Calculate enthalpy change for the following reaction:



Ans. Enthalpy of reaction will be +91.8 kJ/mol.



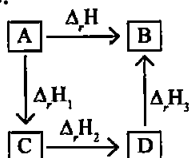
$$\Delta_f H^\ominus = -91.8 \text{ kJ/mol.}$$

When a chemical reaction is reversed, the value of $\Delta_r H^\ominus$ is reversed in sign.

24. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A → B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$ etc. for intermediate reactions?

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

It can be represented as:



25. The enthalpy of atomisation for the reaction $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ is 1665 kJ mol^{-1} . What is the bond energy of C—H bond?

Ans. $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}); \Delta_a H^\ominus = 1665 \text{ kJ mol}^{-1}$

In such cases we use mean bond enthalpy of C—H bond.

Enthalpy of atomisation of 4 moles of C—H bonds = 1665 kJ mol^{-1}

$$\therefore \text{C—H bond energy, per mole} = \frac{1665}{4} \text{ kJ mol}^{-1} = 416.2 \text{ kJ mol}^{-1}$$

26. Use the following data to calculate $\Delta_{\text{lattice}} H^\ominus$ for NaBr.

$\Delta_{\text{sub}} H^\ominus$ for sodium metal = $108.4 \text{ kJ mol}^{-1}$

Ionization enthalpy of sodium = 496 kJ mol^{-1}

Electron gain enthalpy of bromine = -325 kJ mol^{-1}

Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

$\Delta_f H^\ominus$ for NaBr(s) = $-360.1 \text{ kJ mol}^{-1}$

Ans. According to Hess's Law,

$$\Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \Delta_{\text{IE}} H^\ominus + \Delta_{\text{diss}} H^\ominus + \Delta_{\text{eg}} H^\ominus + U$$

$$\Delta_{\text{sub}} H^\ominus \text{ for Na metal} = 108.4 \text{ kJ/mol}$$

$$\text{I.E. of Na} = 496 \text{ kJ/mol}$$

$$\Delta_{\text{eg}} H^\ominus \text{ of Br} = -325 \text{ kJ/mol}$$

$$\Delta_{\text{diss}} H^\ominus \text{ of Br} = 192 \text{ kJ/mol}$$

$$\Delta_f H^\ominus \text{ for NaBr} = -360.1 \text{ kJ/mol}$$

$$\Delta_f H^\ominus = \Delta_{\text{sub}} H^\ominus + \text{I.E. of Na} + \Delta_{\text{diss}} H^\ominus + \Delta_{\text{eg}} H^\ominus + U$$

$$-360.1 = 108.4 + 496 + 96 + (-325) - U$$

$$U = +735.5 \text{ kJ/mol}$$

27. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

Ans. The greater the disorder in an isolated system, the higher is the entropy, and the process will be spontaneous.

28. Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

Ans. Entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

29. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

Ans. If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings is same as that of the system. Also, increase in enthalpy of the surroundings is equal to decrease in the enthalpy of the system.

30. At 298 K, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.

Ans. $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K$

For the process to be spontaneous ΔG should be negative.

Since $\Delta_r G^\ominus = -RT \ln K_p$

In this case, $K_p = 0.98$,

$\therefore \Delta_r G$ is -ve. Hence, the reaction is spontaneous.

31. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?

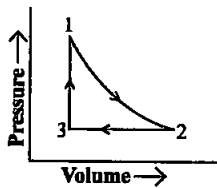


Fig. 6.1

Ans. Enthalpy change $\Delta H = 0$.

32. The standard molar entropy of $H_2O(l)$ is $70 \text{ J K}^{-1} \text{ mol}^{-1}$. Will the standard molar entropy of $H_2O(s)$ be more, or less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$?

Ans. It will be less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$ because ice is the more ordered form of water and thus, the entropy will decrease.

33. Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy.

Ans. State function: Temperature, Enthalpy, Entropy, Free energy

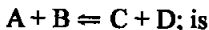
Path function: Work, Heat

34. The molar enthalpy of vapourisation of acetone is less than that of water. Why?

Ans. Due to strong intermolecular force of attraction (hydrogen bonding) in water it has high enthalpy of vaporization than acetone.

35. Which quantity out of $\Delta_r G$ and $\Delta_r G^\ominus$ will be zero at equilibrium?

Ans. The criterion for equilibrium



$$\Delta_r G = 0$$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

36. Predict the change in internal energy for an isolated system at constant volume.

Ans. If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

37. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Ans. The conditions under which heat becomes independent of path are:

(i) If volume remains constant

(ii) If pressure remains constant

At constant volume: $\Delta V = 0$. Thus $\Delta U = q + p\Delta V = q$.

ΔU is a state function $\therefore q_v$ is a state function.

At constant pressure: $\Delta U = q - p\Delta V$ (if work is done by the system)

$q = \Delta U + p\Delta V = \Delta H$ is a state function.

38. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre?

Ans. Expansion of a gas in vacuum ($p_{\text{ext}} = 0$) is called free expansion

$$(-W) = p_{\text{ext}}(V_2 - V_1) = 0 \times (5 - 1) = 0$$

For isothermal expansion $q = 0$

By first law of thermodynamics

$$q = \Delta U + (-W)$$

\Rightarrow

$$0 = \Delta U + 0$$

So

$$\Delta U = 0$$

39. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

Ans. The molar heat capacity of a , is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin).

Molar heat capacity of water = $18 \times$ specific heat

or

$$C_p = 18 \times c$$

$$\text{Specific heat } c = 4.18 \text{ Jg}^{-1} \text{ K}^{-1}$$

$$\text{Heat capacity} = C_p = 18 \times 4.18 \text{ JK}^{-1} = 75.3 \text{ JK}^{-1}$$

40. The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for 10 moles of an ideal gas.

Ans. We can write equation for heat, q at constant volume as $q_v = \Delta U = C_v \Delta T$
at constant pressure as $q_p = \Delta H = C_p \Delta T$

$$C_p - C_v = R \text{ for 1 mole of a gas}$$

For n mole of a gas

$$C_p - C_v = nR = 10 \times 4.184 \text{ J} = 41.84 \text{ J}$$

41. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

Ans. Molar enthalpy change of graphite = enthalpy change for 1 g carbon \times molar mass of carbon

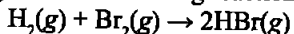
$$= -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$$

$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

The negative sign of ΔH shows that the reaction is exothermic.

42. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy

required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.



Given that Bond energy of H_2 , Br_2 and HBr is 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

Ans. $\Delta_r H^\ominus = \sum \text{bond enthalpies}_{\text{reactants}} = -\sum \text{bond enthalpies}_{\text{products}}$
 $\Delta_r H^\ominus = \text{Bond energy of } \text{H}_2 + \text{Bond energy of } \text{Br}_2 - 2 \times \text{Bond energy of } \text{HBr}$
 $= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$
 $\Delta_r H^\ominus = -109 \text{ kJ mol}^{-1}$

43. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1} . Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of $\text{CCl}_4 = 154 \text{ g mol}^{-1}$).

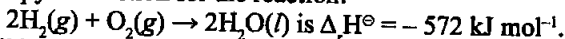
Ans. Given that enthalpy of vaporization of 1 mole of $\text{CCl}_4 = 30.5 \text{ kJ/mol}$.
 It means 1 mole of $\text{CCl}_4 = 154 \text{ g}$.

154 g requires heat of vaporization = 30.5 kJ/mol .

\therefore Heat required for vapourisation of 284 g of CCl_4

$$= \frac{284 \text{ g}}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ mol}^{-1} = 56.2 \text{ kJ}$$

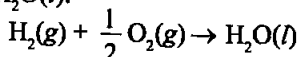
44. The enthalpy of reaction for the reaction:



What will be standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$?

Ans. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^\ominus$.

According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$.



or the standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ will be half of the enthalpy of the given equation i.e., $\Delta_r H^\ominus$ is also halved.

$$\Delta_f H_{\text{H}_2\text{O}}^\ominus(\text{l}) = \frac{1}{2} \times \Delta_r H^\ominus = \frac{-572 \text{ kJ mol}^{-1}}{2} = -286 \text{ kJ/mol}$$

45. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 6.2. Explain graphically.

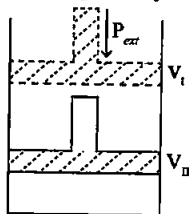
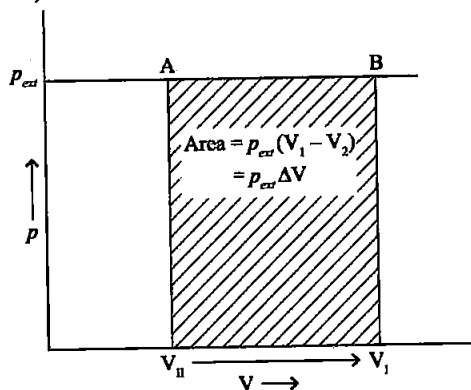


Fig. 6.2

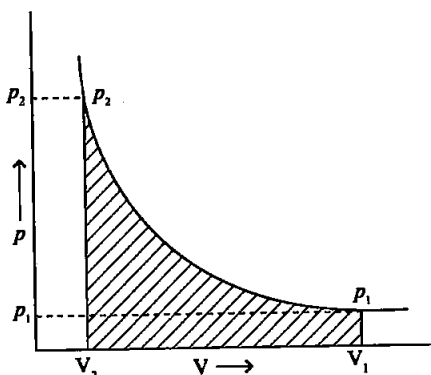
Ans. Let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p . If external pressure is p_{ext} which is greater than p , piston is moved inward till the pressure inside becomes equal to p_{ext} . Let this change be achieved in a single step and the final volume be V_f .
 $W = P_{ext} (\Delta V)$.



46. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

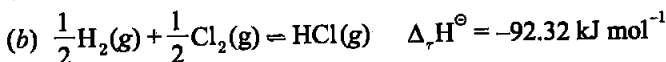
Ans. A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change.

Work done can be calculated from pV -plot when pressure is not constant and changes are in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f . Work done on the gas is represented by the shaded area.



47. Represent the potential energy/enthalpy change in the following processes graphically.

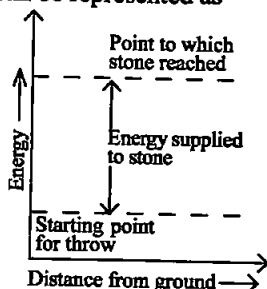
(a) Throwing a stone from the ground to roof.



In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?

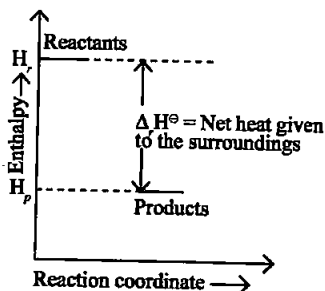
Ans. (a) On throwing stone from ground to the roof we need to supply energy to the stone.

Graphically, it can be represented as



(b) In the reaction heat is evolved it means the process is followed by decrease in energy.

It can be represented as



Energy increases in (a) part and decreases in (b). Hence, in process (b), the enthalpy change is the contributing factor to the spontaneity.

48. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide spontaneity of a reaction from given diagram. Explain.

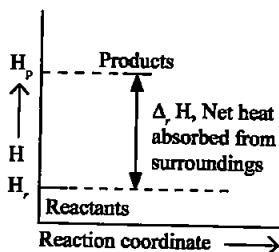


Fig 6.3

Ans. No, enthalpy is not the only criteria for spontaneity we need to consider enthalpy and entropy both.

49. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

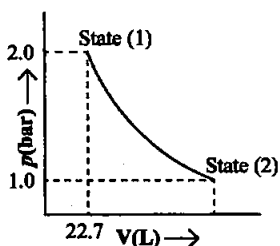


Fig 6.4

Ans. From the given diagram it is very clear that it is a reversible change because the process is

$$w = -2.303 nRT \log \frac{V_2}{V_1}$$

$$\text{But, } p_1 V_1 = p_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$$

carried out in infinite no. of steps

$$\begin{aligned} \therefore w &= -2.303 nRT \log \frac{p_1}{p_2} \\ &= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}^{-1} \times \log 2 \\ &= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J} = -1717.46 \text{ J} \end{aligned}$$

50. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?

(Given that 1 L bar = 100 J)

Ans. Work done in the process can be calculated as

$$w = -P_{\text{ex}} (V_f - V_i) = -2 \times 40 = -80 \text{ bar} = -8 \text{ kJ}$$

The negative sign shows that work is done by the system on the surroundings. Work done will be more in the reversible expansion because internal pressure and external pressure are almost same at every step.

IV. MATCHING TYPE

In the following questions more than one correlation is possible between options of both columns.

51. Match the followings:

A	B
(i) Adiabatic process	(a) Heat
(ii) Isolated system	(b) At constant volume
(iii) Isothermal change	(c) First law of thermodynamics
(iv) Path function	(d) No exchange of energy and matter
(v) State function	(e) No transfer of heat
(vi) $\Delta U = q$	(f) Constant temperature
(vii) Law of conservation of energy	(g) Internal energy

(viii) Reversible process	(h) $p_{ext} = 0$
(ix) Free expansion	(i) At constant pressure
(x) $\Delta H = q$	(j) Infinitely slow process which proceeds through a series of equilibrium states.
(xi) Intensive property	(k) Entropy
(xii) Extensive property	(l) Pressure
	(k) Specific heat

Ans. (i) \rightarrow (e); (ii) \rightarrow (d); (iii) \rightarrow (f); (iv) \rightarrow (a); (v) \rightarrow (g); (vi) \rightarrow (b); (vii) \rightarrow (c); (viii) \rightarrow (j); (ix) \rightarrow (h); (x) \rightarrow (i); (xi) \rightarrow (l), (m); (xii) \rightarrow (g), (k)

52. Match the following processes with entropy change:

Reaction	Entropy change
(i) A liquid vapourises	(a) $\Delta S = 0$
(ii) Reaction is non-spontaneous at all temperatures and ΔH is positive.	(b) $\Delta S = \text{positive}$
(iii) Reversible expansion of an ideal gas	(c) $\Delta S = \text{negative}$

Ans. (i) \rightarrow (b); (ii) \rightarrow (c); (iii) \rightarrow (a)

Explanation:

Reaction	Entropy change
(i) A liquid vapourises	When liquid changes into vapour, randomness of the molecules increases thus entropy increases.
(ii) Reaction is non-spontaneous at all temperatures and ΔH is positive.	When ΔH is positive, Energy factor opposes. ΔG is positive because the process is non-spontaneous so, $\Delta S = -ve$.
(iii) Reversible expansion of an ideal gas	The process remains in equilibrium at every stage.

53. Match the following parameters with description for spontaneity :

Δ (Parameters)	Description
$\Delta_r H^\ominus$ $\Delta_r S^\ominus$ $\Delta_r G^\ominus$	
(i) + - +	(a) Non-spontaneous at high temperature.
(ii) - - + at high T	(b) Spontaneous at all temperatures.
(iii) - + -	(c) Non-spontaneous at all temperatures.

Ans. (i) \rightarrow (c); (ii) \rightarrow (a); (iii) \rightarrow (b)

Explanation:

Δ (Parameters)	Description
$\Delta_r H^\ominus$ $\Delta_r S^\ominus$ $\Delta_r G^\ominus$	
(i) + - +	When enthalpy change is positive, ΔG is positive and ΔS is negative, then the process is non-spontaneous at all temperatures.

(ii) - - + at high T	When enthalpy change is -ve and ΔG is +ve, then the process will be non-spontaneous at very high temperature. $T\Delta S > \Delta H$.
(iii) - + -	When $\Delta H = -ve$, $\Delta S = +ve$ then $\Delta G = -ve$ and the process will be spontaneous at all temperatures.

54. Match the following:

Column I	Column II
(i) Entropy of vapourisation	(a) decreases
(ii) K for spontaneous process	(b) is always positive
(iii) Crystalline solid state	(c) lowest entropy
(iv) ΔU in adiabatic expansion of ideal gas	(d) $\frac{\Delta H_{\text{vap}}}{T_b}$

Ans. (i) \rightarrow (d); (ii) \rightarrow (b); (iii) \rightarrow (c); (iv) \rightarrow (a)

Explanation:

Column I	Column II
(i) Entropy of vaporisation	$\frac{\Delta H_{\text{vap}}}{T_b}$
(ii) K for spontaneous process	since $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K$
(iii) Crystalline solid state	Always has the lowest entropy because the molecules in solid crystal are in most ordered form.
(iv) ΔU in adiabatic expansion of ideal gas	Since $\Delta U = q - w$ in case of expansion because work is done by the system and $q = 0$ and $\Delta U = -w$

V. ASSERTION AND REASON TYPE

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.

55. 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.

Ans. (ii)

Explanation: In combustion reaction, enthalpy of the reactants is always greater than the enthalpy of the product.

56. **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.

Ans. (ii)

Explanation: For spontaneous process energy factor should be favourable means $\Delta H = -ve$ and randomness should be positive.

57. **Assertion (A):** A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R): In crystals, molecules organise in an ordered manner.

(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.

Ans. (i)

Explanation: When a liquid crystallizes, its entropy decreases since, in crystalline form, the molecules are more ordered.

VI. LONG ANSWER TYPE

58. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Ans. We know that the heat absorbed at constant volume is equal to change in the internal energy *i.e.*, $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2.

We can rewrite the above equation as

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \quad \dots(1)$$

Now, we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as :

$$H = U + pV \quad \dots(2)$$

So, equation (1) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although, q is a path dependent function, H is a state function because it depends on U , p and V , all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path. For finite changes at constant pressure, we can write equation (2) as

$$\Delta H = \Delta U + p\Delta V$$

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \quad \dots(3)$$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

At constant volume ($\Delta V = 0$), $\Delta U = q_v$, therefore, equation (3) becomes

$$\Delta H = \Delta U = q_v$$

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$\begin{aligned} pV_A &= n_A RT \\ \text{and} \quad pV_B &= n_B RT \\ \text{Thus,} \quad pV_B - pV_A &= n_B RT - n_A RT = (n_B - n_A)RT \\ \text{or} \quad p(V_B - V_A) &= (n_B - n_A)RT \\ \text{or} \quad p\Delta V &= \Delta n_g RT \quad \dots(4) \end{aligned}$$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation (4) in equation (3), we get

$$\Delta H = \Delta U + \Delta n_g RT \quad \dots(5)$$

59. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Ans. In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

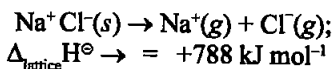
Those properties which do not depend on the quantity or size of matter present, are known as intensive properties. For example, temperature, density, pressure etc. are intensive properties. A molar property, χ_m , is the value of an extensive property χ of the system for 1 mol of the

substance. If n is the amount of matter, $\chi_m = \frac{\chi}{n}$, is independent of the amount of matter. The ratio of two extensive properties is always an intensive property.

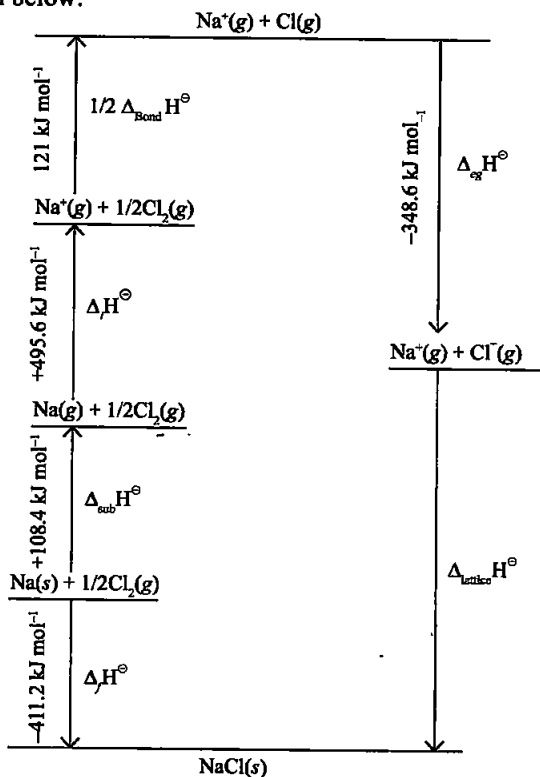
$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

e.g., Mole fraction = $\frac{\text{Moles}}{\text{Total number of moles}} = \frac{(\text{Extensive})}{(\text{Extensive})}$

60. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of $\text{NaCl}(s)$.
- Ans. The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.



Let us now calculate the lattice enthalpy of $\text{Na}^+ \text{Cl}^-(s)$ by following steps given below:



Enthalpy diagram for lattice enthalpy of NaCl

1. $\text{Na}(s) \rightarrow \text{Na}(g)$, sublimation of sodium metal, $\Delta_{\text{sub}} H^\ominus = 108.4 \text{ kJ mol}^{-1}$.
2. $\text{Na}(g) \rightarrow \text{Na}^+(g) + e^-(g)$, the ionization of sodium atoms, ionization enthalpy

$$\Delta_i H^\ominus = 496 \text{ kJ mol}^{-1}$$

3. $\frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl}^\ominus(g)$, the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy.

$$\frac{1}{2} \Delta_{\text{bond}} H^\ominus = 121 \text{ kJ mol}^{-1}.$$

4. $\text{Cl}(g) + e^-(g) \rightarrow \text{Cl}^\ominus(g)$ electron gained by chlorine atoms. The electron gain enthalpy,

$$\Delta_{\text{eg}} H^\ominus = -348.6 \text{ kJ mol}^{-1}$$

5. $\text{Na}^+(g) + \text{Cl}^\ominus(g) \rightarrow \text{Na}^+\text{Cl}^\ominus(s)$

61. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG . If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?

Ans. We know,

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

If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings is same as that of the system. Also, increase in enthalpy of the surroundings is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \left(-\frac{\Delta H_{\text{sys}}}{T} \right)$$

Rearranging the above equation:

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}}$$

For spontaneous process,

$$\Delta S_{\text{total}} > 0, \text{ so}$$

$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$\Rightarrow -(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}) > 0$$

The above equation can be written as

$$-\Delta G > 0$$

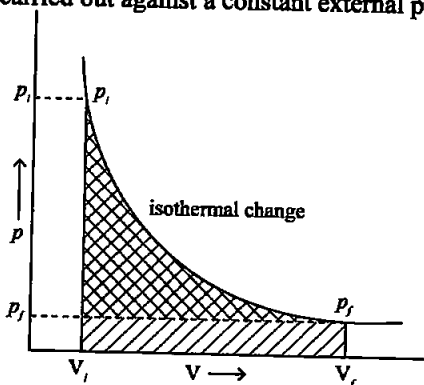
$$\Delta G = \Delta H - T\Delta S < 0$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{\text{sys}}$ is the energy which is not available to do useful work. So, ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.




ΔG gives a criteria for spontaneity at constant pressure and temperature.

- (i) If ΔG is negative (< 0), the process is spontaneous.
- (ii) If ΔG is positive (> 0), the process is non-spontaneous.
 - Unit of ΔG is Joule.
 - The reaction will be spontaneous at high temperature.

62. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f, V_f) . With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_f .



Ans.

- (i) Reversible work is represented by the combined areas  and 
- (ii) Work against constant pressure, p_f is represented by the area .
Work (i) > Work (ii).

□□□