6

Thermodynamics

Multiple Choice Questions (MCQs)

Q. 1 Thermodynamics is not concerned about

(a) energy changes involved in a chemical reaction
(b) the extent to which a chemical reaction proceeds
(c) the rate at which a reaction proceeds
(d) the feasibility of a chemical reaction

Ans. *(c)* Thermodynamics is not concerned with the rate at which a reaction proceeds. Thermodynamics deals with the energy change, feasibility and extent of a reaction, but not with the rate and mechanism of a process.

Q. 2 Which of the following statement is correct?

(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

Ans. *(c)* For a closed vessel made of copper, no matter can exchange between the system and the surroundings but energy exchange can occur through its walls.

Presence of reaction species in a covered beaker-closed system and exchange of matter as well as energy-open-system. Presence of reactant in a closed vessel closed system and presence of reactant in thermos flask-isolated system.

Q. 3 The state of a gas can be described by quoting the relationship between

(a) pressure, volume, temperature
(b) temperature, amount, pressure
(c) amount, volume, temperature
(d) pressure, volume, temperature, amount

Ans. ***(d)*** The state of a gas can be described by quoting the relationship between pressure, volume, temperature and amount. The ideal gas equation is

$$pV = nRT$$

Thus, p, V, T and n describe the state of the system.

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

(a) reduce to half
(b) be doubled
(c) remain constant
(d) increase four times

Ans. ***(c)*** The volume of gas is reduced to half from its original volume. The specific heat will be remain constant.

Specific heat is an intensive property depending only on the nature of the gas.

Q. 5 During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l); \Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
(b) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = -1329.0 \text{ kJ mol}^{-1}$
(c) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
(d) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = +2658.0 \text{ kJ mol}^{-1}$

Ans. ***(c)*** Given that, the complete combustion of one mole of butane is represented by thermochemical reaction as

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

We have to take the combustion of one mole of C_4H_{10} and $\Delta_c H$ should be negative and have a value of 2658 kJ mol^{-1}.

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

(a) zero
(b) $< \Delta_f U^s$
(c) $> \Delta_f U^s$
(d) equal to $\Delta_f U^s$

Ans. ***(b)*** The reaction is $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

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

$$\Delta_f H^{-s} = \Delta_f U^s + \Delta n_g RT$$

As $\quad \Delta n_g = -2$

$\therefore \quad \Delta_f H^s < \Delta_f U^s$

Q. 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.

(a) $q = 0, \Delta T \neq 0, W = 0$
(b) $q \neq 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T = 0, W = 0$
(d) $q = 0, \Delta T < 0, W \neq 0$

Ans. *(c)* Free expansion, $W = 0$

Adiabatic process, $q = 0$

$\Delta U = q + W = 0$, this means that internal energy remains constant. Therefore, $\Delta T = 0$ In ideal gas there is no intermolecular attraction.

Hence, when such a gas expands under adiabatic conditions into a vacuum, no heat is absorbed or evolved since no external work is done to separate the molecules.

Q. 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.

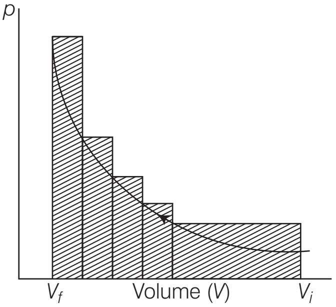
(a) W (reversible) $= W$ (irreversible)

(b) W (reversible) $< W$ (irreversible)

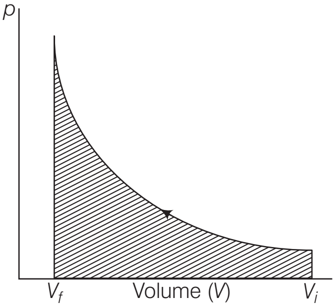
(c) W (reversible) $= W$ (irreversible)

(d) W (reversible) $= W$ (irreversible) $+ p_{ex} . \Delta V$

Ans. *(b)* The correct option is W (reversible) $< W$ (irreversible). This is because area under the curve is always more in irreversible compression as can be seen from given figure.



pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.



PV-plot when pressure is not constant and changes 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.

Q. 9 The entropy change can be calculated by using the expression $\Delta S = \frac{q_{\text{rev}}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following.

(a) ΔS (system) decreases but ΔS (surroundings) remains the same

(b) ΔS (system) increases but ΔS (surroundings) decreases

(c) ΔS (system) decreases but ΔS (surroundings) increases

(d) ΔS (system) decreases but ΔS (surroundings) also decreases

Ans. *(c)* The entropy change can be calculated by using the expression

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

When water freezes in a glass beaker, ΔS (system) decreases because molecules in solid ice are less random than in liquid water. However, when water freezes to ice, heat is released which is absorbed by the surroundings.

Hence, entropy of the surrounding increases.

Q. 10 On the basis of theromochemical equations (1), (2) and (3), find out which of the algebraic relationships given in options (a) to (d) is correct

1. $\text{C (graphite)} + O_2\ (g) \rightarrow CO_2\ (g)\ ; \Delta_r H = x \text{ kJ mol}^{-1}$
2. $\text{C (graphite)} + \frac{1}{2} O_2\ (g) \rightarrow CO\ (g)\ ; \Delta_r H = y \text{ kJ mol}^{-1}$
3. $CO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow CO_2\ (g)\ ; \Delta_r H = z \text{ kJ mol}^{-1}$

(a) $z = x + y$ (b) $x = y - z$ (c) $x = y + z$ (d) $y = 2z - x$

Ans. *(c)* The algebraic relationships of the given reaction is

equation (a) –equation (b) = equation (c)

(a) $\text{C (graphite)} + O_2\ (g) \rightarrow CO_2\ (g)\ ; \Delta_r H = x \text{ kJ mol}^{-1}$

(b) $\text{C (graphite)} + \frac{1}{2} O_2\ (g) \rightarrow CO\ (g)\ ; \Delta_r H = y \text{ kJ mol}^{-1}$

$CO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow CO_2\ (g)\ ; \Delta_r H = z \text{ kJ mol}^{-1}$

Hence, $x - y = z$ or $x = y + z$

Q. 11 Consider the reactions given below. On the basis of these reactions find out which of the algebraic relationship given in options (a) to (d) is correct?

1. $C\ (g) + 4\ H\ (g) \rightarrow CH_4\ (g); \Delta_r H = x \text{ kJ mol}^{-1}$
2. $\text{C (graphite)} + 2H_2\ (g) \rightarrow CH_4\ (g)\ ; \Delta_r H = y \text{ kJ mol}^{-1}$

(a) $x = y$ (b) $x = 2y$ (c) $x > y$ (d) $x < y$

Ans. *(c)* Same bonds are formed in reaction (1) and (2) but no bonds are broken in reaction (1) whereas bonds in the reactant molecules are broken in reaction (2). As energy is absorbed when bonds are broken, energy released in reaction (1) is greater than that in reaction (2) hence, $x > y$

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

(a) is always negative (b) is always positive

(c) may be positive or negative (d) is never negative

Ans. *(c)* Combustion of elements to form a compound can be exothermic or endothermic. *e.g.*, $C + O_2 \rightarrow CO_2$ is exothermic.

whereas, $C + 2S \rightarrow CS_2$ is endothermic.

Hence, enthalpy of formation can be positive or negative.

Q. 13 Enthalpy of sublimation of a substance is equal to

(a) enthalpy of fusion + enthalpy of vaporisation
(b) enthalpy of fusion
(c) enthalpy of vaporisation
(d) twice the enthalpy of vaporisation

Ans. ***(a)*** Enthalpy of sublimation of a substance is equal to enthalpy of fusion + enthalpy of vaporisation.

Sublimation is, direct conversion of solid to vapour. solid → vapour

Writing in two steps, we have solid → liquid → vapour,

solid → liquid requires enthalpy of fusion

liquid → vapour requires enthalpy of vaporisation

Q. 14 Which of the following is not correct?

(a) ΔG is zero for a reversible reaction.
(b) ΔG is positive for a spontaneous reaction.
(c) ΔG is negative for a spontaneous reaction.
(d) ΔG is positive for a non-spontaneous reaction.

Ans. ***(b)*** 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.
(iii) If ΔG is zero then reaction is equilibrium.

Multiple Choice Questions (More Than One Options)

Q. 15 Thermodynamics mainly deals with

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

Ans. ***(a, d)***

Thermodynamics deals with interrelation of various forms of energy and their transformation into each other. It also deals with thermal or mechanical equilibrium. However, it does not tell anything about the rate of reaction.

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

(a) q_p will be negative
(b) $\Delta_r H$ will be negative
(c) q_p will be positive
(d) $\Delta_r H$ will be positive

Ans. ***(a, b)***

Exothermic reactions are those reactions which are accompanied by the evolution of heat.

e.g.,

$$C(s) + O_2(g) \rightarrow CO_2(g) + 393.5\ \text{kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285.8\text{kJ}$$

q_p and $\Delta_r H$ are negative for exothermic reaction.

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

(a) flow of heat from colder to warmer body
(b) gas in a container contracting into one corner
(c) gas expanding to fill the available volume
(d) burning carbon in oxygen to give carbon dioxide

Ans. ***(c, d)***

Options (a) and (b) can neither occur by themselves nor by initiation, (c) can occur by itself, (d) occur on initiation. Flowing of heat from warmer to colder body, expanding of gas and burning of carbon to give carbon dioxide, all are spontaneous process.

Q. 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 reversible 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.

(a) Work done at 600 K is 20 times the work done at 300 K
(b) Work done at 300 K is twice the work done at 600 K
(c) Work done at 600 K is twice the work done at 300 K
(d) $\Delta U = 0$ in both cases

Ans. ***(c, d)***

Given that, the work of reversible expansion under isothernal condition can be calculated by using the expression

$$W = -nRT\ln\frac{V_f}{V_i}$$

$$V_f = 10\ V_i$$

$$T_2 = 600\ \text{K}$$

$$T_1 = 300\ \text{K}$$

Putting these values in above expression

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

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

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

For isothermal expansion of ideal gases, $\Delta U = 0$. Since, temperature is constant this means there is no change in internal energy. Therefore, $\Delta U = 0$

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

$$2\text{ Zn }(s) + O_2(g) \rightarrow 2\text{ ZnO }(s); \Delta H = -693.8\text{ kJ mol}^{-1}$$

(a) 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

(b) 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

(c) 693.8 kJ mol^{-1} energy is evolved in the reaction

(d) 693.8 kJ mol^{-1} energy is absorbed in the reaction

Ans. ***(a, c)***

For the reaction,

$$2\text{ Zn }(s) + O_2\ (g) \rightarrow 2\text{ ZnO }(s); \Delta H = -693.8\text{ kJ mol}^{-1}$$

As we know that, $\Delta H = H_p - H_R$

A negative value of ΔH shows that $H_R > H_P$ or $H_P < H_R$, *i.e.*, enthalpy of two moles of ZnO is less than the enthalpy of two moles of zinc and one mole of oxygen by 693.8kJ. As $H_R > H_P$, 693.8kJ $\text{mol}^{-1}$of energy is evolved in the reaction.

Short Answer Type Questions

Q. 20 18.0 g of water completely vaporises 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 vaporising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?

Ans. Given that, quantity of water = 18.0 g, pressure = 1 bar

As we know that, 18.0 gH_2O = 1 mole H_2O

Enthalpy change for vaporising 1 mole of H_2O = 40.79 kJ mol^{-1}

$\therefore$ Enthalpy change for vaporising 2 moles of $H_2O = 2 \times 40.79$ kJ = 81.358kJ

Standard enthalpy of vaporisation at 100°C and 1 bar pressure, $\Delta_{\text{vap}}H^\circ = +\ 40.79\text{ kJ mol}^{-1}$

Q. 21 One mole of acetone requires less heat to vaporise than 1 mole of water. Which of the two liquids has higher enthalpy of vaporisation?

Ans. One mole of acetone requires less heat to vaporise than 1 mole of water. Hence, acetone has less enthalpy of vaporisation and water has higher enthalpy of vaporisation. It can be represented as (ΔH_V)water $>$ (ΔH_V)acetone.

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

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s); \Delta_f H^s = -178.3 \text{ kJ mol}^{-1}$$

Ans. No, the $\Delta_r H^s$ for the given reaction is not same as $\Delta_r H^s$. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states (reference states) is called standard molar enthalpy of formation, $\Delta_f H^s$.

$$Ca(s) + C(s) + \frac{3}{2} O_2(g) \rightarrow CaCO_3(s); \Delta_f H^s$$

This reaction is different from the given reaction.

Hence, $\Delta_r H° \neq \Delta_f H°$

Q. 23 The value of $\Delta_f H^s$ for NH_3 is –91.8kJ mol^{-1}. Calculate enthalpy change for the following reaction.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

Ans. Given, $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightarrow NH_3(g); \Delta_f H^s = -91.8 \text{ kJ mol}^{-1}$

($\Delta_f H^s$ means enthalpy of formation of 1 mole of NH_3)

∴ Enthalpy change for the formation of 2 moles of NH_3

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta_f H^s = 2 \times -91.8 = -183.6 \text{ kJ mol}^{-1}$$

And for the reverse reaction,

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g); \Delta_f H^s = +183.6 \text{ kJ mol}^{-1}$$

Hence, the value of $\Delta_f H^s$ for NH_3 is + 183.6 kJ mol^{-1}

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

Ans. In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3 \ldots$ representing enthalpies of reaction leading to same product B along another route, then we have

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

Note *For a general reaction Hess's law of constant heat summation can be represented as*

$$\begin{tikzcd}
\boxed{A} \arrow[r, "\Delta_r H"] \arrow[d, "\Delta_r H_1"'] & \boxed{B} \\
\boxed{C} \arrow[r, "\Delta_r H_2"'] & \boxed{D} \arrow[u, "\Delta_r H_3"']
\end{tikzcd}$$

Q. 25 The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H\,(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond?

Thinking Process

To solve this problem, keep in mind that in methane all the four C–H *bonds are identical in bond length and energy. However, the energies required to break the individual* C – H *bonds in each successive step differ. In such cases, we use mean bond enthalpy of* C – H *bond i.e.,* $\Delta_{C-H} H^s = \frac{1}{4} (\Delta_a H^s)$

Ans. In CH_4, there are four C — H bonds. The enthalpy of atomisation of 1 mole of CH_4 means dissociation of four moles of C — H bond.

$$\therefore \qquad \text{C – H bond energy per mol} = \frac{1665 \text{ kJ}}{4 \text{ mol}}$$
$$= 416.\,25 \text{ kJ mol}^{-1}$$

Q. 26 Use the following data to calculate $\Delta_{\text{lattice}} H^s$ for NaBr. $\Delta_{\text{sub}} H^s$ for sodium metal $= 108.4$ kJ mol^{-1}, ionisation 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}, $\Delta_f H^s$ for $NaBr(s) = -\,360.\,1$ kJ mol^{-1}

Thinking Process

This question is based upon the concept of Born-Haber cycle as well as Hess's law. Following steps are used to solve this problem.

(i) $Na\,(s) \rightarrow Na\,(g);\ \Delta_{\text{sub}} H^s$

(ii) $Na\,(g) \rightarrow Na^+\,(g) + e^-\,(g);\ IE$

(iii) $\frac{1}{2} Br_2\,(g) \rightarrow Br\,(g);\ \Delta_{\text{diss}} H^s$

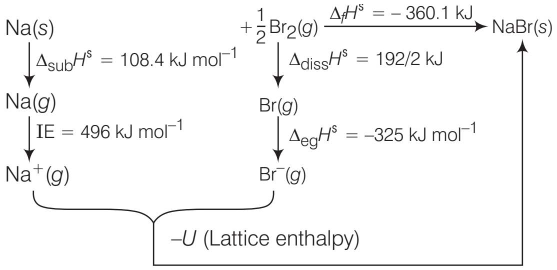
(iv) $Br\,(g) + e^-(g) \rightarrow Br^-(g);\ \Delta_{eg} H^s$

(v) Applying Hess's law $\Delta_f H^s = \Delta_{\text{sub}} H^s + IE + \Delta_{\text{diss}} H^s + \Delta_{eg} H^s + U$

Ans. Given that, $\Delta_{\text{sub}} H^s$ for Na metal = 108.4 k J mol^{-1}

IE of Na = 496 k J mol^{-1}, $\Delta_{eg} H^s$ of Br = – 325 k J mol^{-1}, $\Delta_{\text{diss}} H^s$ of Br = 192 k J mol^{-1}, $\Delta_f H^s$ for NaBr = – 360.1 kJ mol^{-1}

Born-Haber cycle for the formation of NaBr is as



By applying Hess's law,

$$\Delta_f H^s = \Delta_{sub} H^s + IE + \Delta_{diss} H^s + \Delta_{eg} H^s + U$$
$$-360.1 = 108.4 + 496 + 96 + (-325) - U$$
$$U = +735.5 \text{kJ mol}^{-1}$$

Q. 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 mixing of two gases have ΔH equal to zero. Therefore, it is spontaneous process because energy factor has no role to play but randomness increases *i.e.*, randomness factor favours the process.

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

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

Here, ΔS = change in entropy
q_{rev} = heat of reversible reaction
T = temperature

Q. 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. *Yes*, the temperature of system and surroundings be the same when they are in thermal equilibrium.

Note *Thermal equilibrium is defined as when two physical systems are brought into a connection that does not allow transfer of matter between them, and does not allow transfer of energy between them, such a connection is said to permit transfer of energy as heat, and is called diathermal.*

If a diathermal connection is made between two physical systems and the making of the connection is followed by no change of state of either, then the two systems are said to be in relation of thermal equilibrium. It obeys zeroth law of thermodynamics.

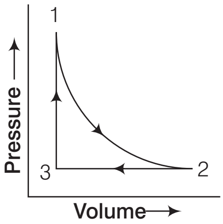
Q. 30 **At 298 K, K_p for reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.**

Ans. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = 0.98$

As we know that $\Delta_r G^s = -2.303 \text{ RT} \log K_p$

Here, $K_p = 0.98$ *i.e.*, $K_p < 1$ therefore, $\Delta_r G^\circ$ is positive, hence the reaction is non-spontaneous.

Q. 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 figure. What will be the value of ΔH for the cycle as a whole?



Ans. The net enthalpy change, ΔH for a cyclic process is zero as enthalpy change is a state function, *i.e.,* ΔH (cycle) = 0

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

Ans. The standard molar entropy of H_2O (l) is 70 JK^{-1} mol^{-1}. The solid form of H_2O is ice. In ice, molecules of H_2O are less random than in liquid water.

Thus, molar entropy of H_2O $(s) <$ molar entropy of H_2O (l). The standard molar entropy of H_2O (s) is less than 70 J K^{-1} mol^{-1}.

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

Ans. State functions are those values which depend only on the state of the system and not on how it is reached *e.g.,* enthalpy, entropy, temperature and free energy. Path functions are those values which depend on the path of the system. *e. g*, heat and work .

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

Ans. Amount of heat required to vaporise one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its **molar enthalpy of vaporisation** $\Delta_{\text{vap}}H^s$. Molar enthalpy of vaporisation of water is more than that of acetone because there is strong hydrogen bonding in H_2O molecule.

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

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

$$\Delta_r G = \Delta_r G^s + RT \ln K$$

At equilibrium, $$0 = \Delta_r G^\circ + RT \ln K \qquad (\because \Delta_r G = 0)$$

or $$\Delta_r G^s = -RT \ln K$$

$$\Delta_r G^s = 0 \text{ when } K = 1$$

For all other values of K, $\Delta_r G^s$ will be non-zero.

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

Ans. For isolated system there is no transfer of energy as heat, *i.e.,* $q = 0$ and there is no transfer of energy as work. *i.e.*, $W = 0$. According to the first law of thermodynamics

$$\Delta U = q + W$$
$$\Delta U = 0 + 0 = 0$$

Q. 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 two conditions under which heat becomes independent of path are*

(i) when volume remains constant
(ii) when pressure remains constant

Explanation

(i) **At constant volume** By first law of thermodynamics, $\Delta U = q + W$ or $q = \Delta U - W$. But $W = -p\Delta V$ Hence, $q = \Delta U + p\Delta V$. But as volume remains constant $\Delta V = 0$

$\therefore$ $q_v = \Delta V$ but ΔU is a state function.

Hence, q_V is a state function.

(ii) **At constant pressure** As we know, $q_p = \Delta U + p\Delta V$. But $\Delta U + p\Delta V = \Delta H$.

$\therefore q_p = \Delta H$. As ΔH is a state function therefore, q_p is a state function.

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

Ans. Work done of a gas in vacuum, $W = -p_{ext}\ (V_2 - V_1)$. As $p_{\text{ext}} = 0$ so $W = -0\,(5-1) = 0$ As internal energy of an ideal gas depends only on temperature, therefore, for isothermal expansion of an ideal gas, internal energy remains constant,

i.e., $\Delta U = 0$.

It is to be remember that as $H = U + pV$, $\Delta H = \Delta(U + pV) = \Delta U + p\Delta V = \Delta U + nR\,(\Delta T)$. For isothermal process, $\Delta T = 0$ and also $\Delta U = 0$, as stated above, therefore, $\Delta H = 0$.

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

Ans. For water, molar heat capacity, $C_p = 18 \times$ Specific heat, c

$C_p = 18 \times c$ Specific heat

$c = 4.18\ \text{Jg}^{-1}\text{K}^{-1}$ (for water)

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

$= 75.3\ \text{JK}^{-1}\text{mol}^{-1}$

Q. 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. Given that, C_v = heat capacity at constant volume,

C_p = heat capacity at constant pressure

Difference between C_p and C_v is equal to gas constant (R).

$$\therefore \quad C_p - C_v = nR \qquad \text{(where, } n = \text{no. of moles)}$$
$$= 10 \times 4.184 \text{ J}$$
$$= 41.84 \text{ J}$$

Q. 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. Given that, enthalpy of combustion of 1g graphite = 20.7 kJ

Molar enthalpy change for the combustion of graphite, ΔH = enthalpy of combustion of 1 g graphite × molar mass

$$\Delta H = -20.7 \text{ kJg}^{-1} \times 12 \text{ g mol}^{-1}$$
$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Negative sign in the value of ΔH indicates that the reaction is exothermic.

Q. 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? $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. 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.

Thinking Process

To, calculate the enthalpy change, use the following formula when the reactants, and products are in gas phase as

$$\Delta_r H^s = \Sigma \text{ bond energy (reactants)} - \Sigma \text{ bond energy (products)}$$

Ans. Given that, bond energy of H_2 = 435 kJ mol^{-1}

bond energy of Br_2 = 192 kJ mol^{-1}

bond energy of HBr = 368 kJ mol^{-1}

For the reaction

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$
$$\Delta_r H^s = \Sigma\text{BE (Reactants)} - \Sigma\text{BE (Products)}$$
$$= \text{BE }(H_2) + \text{BE}(Br_2) - 2\text{BE (HBr)}$$
$$= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$$
$$= -109 \text{ kJ mol}^{-1}$$

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

Ans. Given that, 1 mol of CCl_4 = 154 g

$\Delta_{vap}\,H$ for 154 g CCl_4 = 30. 5 kJ

$$\therefore \quad \Delta_{vap}\,H \text{ for } 284 \text{ g } CCl_4 = \frac{30.\ 5 \times 284}{154} \text{ kJ} = 56.\ 25 \text{ kJ}$$

Q. 44 The enthalpy of reaction for the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \text{ is } \Delta_r\ H^{s} = -572 \text{ kJ mol}^{-1}$$

What will be standard enthalpy of formation of $H_2O\ (l)$?

Ans. Given that,

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l),\ \Delta_r H^\circ = -\ 572 \text{ kJ mol}^{-1}$$

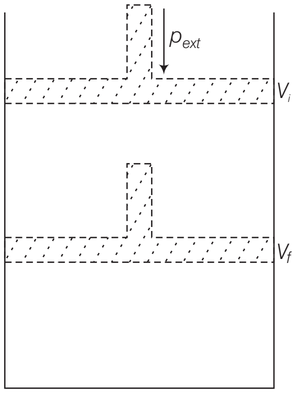
Enthalpy of formation is the enthalpy change of the reaction when 1 mole of the compound is formed from its elements then

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l),\ \Delta_r H^\circ = ?$$

This can be obtained by dividing the given equation by 2.

Therefore, $$\Delta_f H^\circ\ (H_2O) = -\frac{572 \text{ kJmol}^{-1}}{2} = -\ 286 \text{ kJ mol}^{-1}$$

Q. 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 figure? Explain graphically.



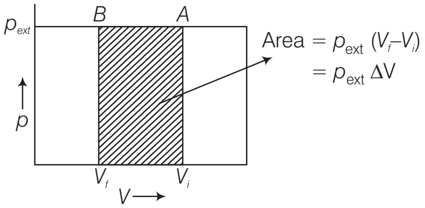
Ans. Suppose total volume of the gas is V_i and pressure of the gas inside cylinder is p. After compression by constant external pressure, (p_{ext}) in a single step, final volume of the gas becomes V_f.

Then volume change, $\Delta v = (V_f - V_i)$

If W is the work done on the system by movement of the piston, then

$$W = p_{ext}\ (-\ \Delta V)$$
$$W = -\ p_{ext}\ (V_f - V_i)$$

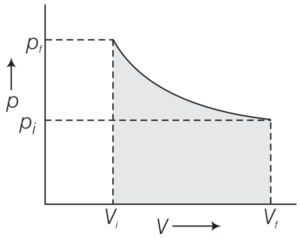
This can be calculated from $p - V$ graph as shown in the figure. Work done is equal to the shaded area ABV_fV_i



The negative sign in this expression is required to obtain conventional sign for W which will be positive. Because in case of compression work is done on the system, so ΔV will be negative.

Q. 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. When compression is carried out in infinite steps with change in pressure, it is a reversible process. The work done can be calculated from $p - V$ plot as shown in the given figure. Shaded area under the curve represents the work done on the gas.



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

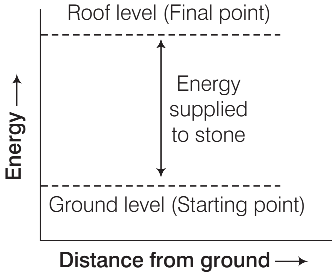
(a) Throwing a stone from the ground to roof.

(b) $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightleftharpoons HCl(g) \; \Delta_r H^s = -92.32 \text{ kJ mol}^{-1}$

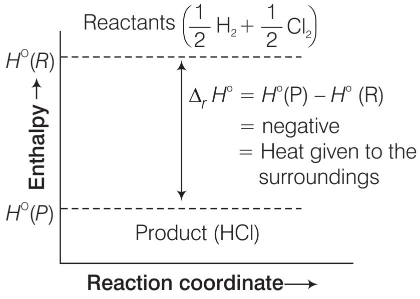
In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?

Ans. *Representation of potential energy/enthalpy change in the following processes*

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

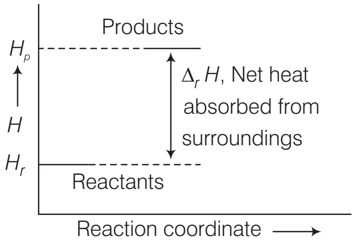


(b) $\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)\,;\ \Delta_r H^{s} = -92.32\ \text{kJ mol}^{-1}$



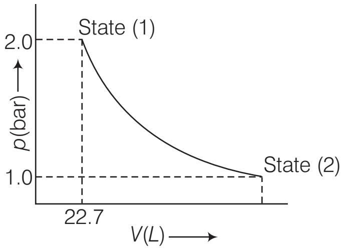
Energy increases in (a) and it decreases in (b) process. Hence, in process (b), enthalpy change is the contributing factor to the spontaneity.

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



Ans. *No*, enthalpy is one of the contributing factors in deciding spontaneity but it is not the only factor. Another contributory factor, entropy factor has also to be taken into consideration.

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



Ans. The given diagram represent that the process is carried out in infinite steps, hence it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm 298 K.

$$W = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$W = -2.303 \times 1\,\text{mol} \times 8.314\ \text{JK}^{-1}\text{mol}^{-1} \times 298\ \text{K} \log 2 \qquad \left(\because \frac{p_1}{p_2} = \frac{2}{1}\right)$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010\ \text{J}$$

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

Q. 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. In the first case, as the expansion is against constant external pressure

$$W = -p_{\text{ext}}\,(V_2 - V_1) = -2\,\text{bar} \times (50 - 10)\ \text{L}$$
$$= -80\ \text{L bar} \qquad (1\ \text{L bar} = 100\ \text{J})$$
$$= -80 \times 100\ \text{J}$$
$$= -8\ \text{kJ}$$

If the given expansion was carried out reversibly, the internal pressure of the gas should be greater than the external pressure at every stage. Hence, the work done will be more.

Matching The Columns

Q. 51 Match the following.

	List I		**List II**
A.	Adiabatic process	1.	Heat
B.	Isolated system	2.	At constant volume
C.	Isothermal change	3.	First law of thermodynamics
D.	Path function	4.	No exchange of energy and matter
E.	State function	5.	No transfer of heat
F.	$\Delta U = q$	6.	Constant temperature
G.	Law of conservation of energy	7.	Internal energy
H.	Reversible process	8.	$p_{\text{ext} = 0}$
I.	Free expansion	9.	At constant pressure
J.	$\Delta H = q$	10.	Infinitely slow process which proceeds through a series of equilibrium states.
K.	Intensive property	11.	Entropy
L.	Extensive property	12.	Pressure
		13.	Specific heat

Ans. **A.** → (5) **B.** → (4) **C.** → (6) **D.** → (1) **E.** → (7, 11, 12) **F.** → (2) **G.** → (3) **H.** → (10)
I. → (8) **J.** → (9) **K.** → (1, 12, 13) **L.** → (7,11)

Correct Matching can be done as

A.	Adiabatic process	No transfer of heat
B.	Isolated system	No exchange of energy and matter
C.	Isothermal change	Constant temperature
D.	Path function	Heat
E.	State function	Internal energy Entropy Pressure
F.	$\Delta U = q$	At constant volume
G.	Law of conservation of energy	First law of thermodynamics
H.	Reversible process	Infinitely slow process which proceeds through a series of equilibrium states
I.	Free expansion	$p_{ext} = 0$
J.	$\Delta H = q$	At constant pressure
K.	Intensive property	Heat Pressure Specific heat
L.	Extensive property	Internal energy Entropy

Q. 52 Match the following processes with entropy change

Reaction	Entropy change
A. A liquid vaporises	1. $\Delta S = 0$
B. Reaction is non-spontaneous at all temperatures and ΔH is positive	2. ΔS =positive
C. Reversible expansion of an ideal gas	3. ΔS = negative

Ans. **A.** → (2) **B.** → (3) **C.** → (1)

A. When a liquid vaporises, *i.e.*, liquid → vapour, entropy increase *i.e.*, ΔS = positive

B. When ΔH = positive, *i.e.*, energy factor opposes. The process is non-spontaneous at all temperatures if entropy factor also opposes the process, *i.e.*, ΔS = negative

C. In the reversible expansion of an ideal gas, the system remains in equilibrium at every stage. Hence, $\Delta S = 0$

Q. 53 Match the following parameters with description for spontaneity.

Δ (Parameters) $\Delta_r H^S$ $\Delta_r S^S$ $\Delta_r G^S$	**Description**
A. + − +	1. Non-spontaneous at high temperature
B. − − + at high T	2. Spontaneous at all temperatures
C. − + −	3. Non-spontaneous at all temperatures

Ans. **A.** → (3) **B.** → (1) **C.** → (2)

A. When $\Delta_r G^s$ is positive, reaction is non-spontaneous at all temperatures

B. When $\Delta_r G^s$ is positive at high temperature means the reaction is non-spontaneous at high temperature.

C. When $\Delta_r H^s$ = negative means it favours, $\Delta_r S^s$ = positive means it also favours. $\Delta_r G^\circ$ = negative means reaction is spontaneous at all temperatures.

Q. 54 Match the following

A.	Entropy of vaporisation	1.	decreases
B.	K for spontaneous process	2.	is always positive
C.	Crystalline solid state	3.	lowest entropy
D.	ΔU in adiabatic expansion of ideal gas	4.	$\dfrac{\Delta H_{\text{vap}}}{T_b}$

Ans. **A.** → (2, 4) **B.** → (2) **C.** → (3) **D.** → (1)

A. Entropy of vaporisation is always positive. It is equal to $\Delta H_{\text{vap}} / T_b$

B. $\Delta_r G^\circ = -RT \ln K$

If K is positive, $\Delta_r G^\circ$ = negative and reaction is spontaneous.

C. Crystalline solid state has lowest entropy.

D. During adiabatic expansion of an ideal gas, $q = 0$. Hence, $\Delta U = q + W$ gives $\Delta U = W$, *i.e.,* work done is at the cost of internal energy which decreases.

Assertion and Reason

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 in each question.*

Q. 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.

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

Ans. ***(b)*** Both assertion and reason are true but reason is not the correct explanation of assertion.

Correct explanation In a combustion reaction, sum of enthalpies of reactants is greater than the sum of the enthalpies of products.

Q. 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.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

Ans. *(b)* Both assertion and reason are true but reason is not the correct explanation of assertion.

Spontaneous processes are accompanied by decrease in energy and increase in randomness.

Q. 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.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

Ans. *(a)* Both assertion and reason are true and reason is the correct explanation of assertion.

When a liquid crystallises, entropy decreases because in crystalline form the molecules are more ordered as compared to the liquid.

Long Answer Type Questions

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

Ans. From the first law of thermodynamics, $q = \Delta U + p\Delta V$

If the process carried out at constant volume, $\Delta V = 0$

Hence, $q_v = \Delta U$

[Here, q_v = Heat absorbed at constant volume, ΔU = change in internal energy]

Similarly, $q_p = \Delta H$

Here, q_p = heat absorbed at constant pressure

ΔH = enthalpy change of the system.

Enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

As we know that at constant pressure, $\Delta H = \Delta U + p\Delta V$

where, ΔV is the change in volume.

This equation can be rewritten as $\Delta H = \Delta U + p(V_f - V_i) = \Delta U + (pV_f - pV_i)$ ...(i)

where, V_i = initial volume of the system V_f = final volume of the system

But for the ideal gases, $pV = nRT$

So that $pV_1 = n_1RT$

and $pV_2 = n_2RT$

where, n_1 = number of moles of the gaseous reactants

n_2 = number of moles of the gaseous products.

Substituting these values in Eq. (i), we get

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$

$$\Delta H = \Delta U + (n_2 - n_1)RT$$

or $$\Delta H = \Delta U + \Delta n_g RT$$

where, $\Delta n_g = n_2 - n_1$ is the difference between the number of moles of the gaseous products and gaseous reactants.

Putting the values of ΔH and ΔU we get

$$q_p = q_v + \Delta n_g RT$$

Note *Conditions under which $q_p = q_v$ or $\Delta H = \Delta U$*

(i) When reaction is carried out in a closed vessel so that volume remains constant i.e., $\Delta V = 0$

(ii) When reaction involves only solids or liquids or solutions but no gaseous reactant or product. This is because the volume changes of the solids and liquids during a chemical reaction are negligible.

(iii) When reaction involves gaseous reactants and products but their number of moles are equal (i.e., $n_p = n_r$) e.g.,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

Since, q_p is different from q_v only in those reactions which involves gaseous reactants and products and (n_p) gaseous $\neq (n_r)$ gaseous.

Q. 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. **Extensive properties** Those properties whose value depends on the quantity or size of matter present in the system is known as extensive properties.

e.g., mass, internal energy, heat capacity.

Intensive properties Those properties which do not depend on the quantity or size of matter present are known as intensive properties. *e.g.,* pressure, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Mole fraction or molarity of a solution is same whether we take a small amount of the solution or large amount of the solution.

Ratio of two extensive properties is always intensive.

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

So, mole fraction and molarity are intensive properties.

e.g., $$\text{mole fraction} = \frac{\text{Moles of the component}}{\text{Total no. of moles}} = \frac{\text{Extensive}}{\text{Extensive}}$$

and $$\text{molarity} = \frac{\text{Mole}}{\text{Volume}} = \frac{\text{Extensive}}{\text{Extensive}}$$

Q. 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 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. For the reaction

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g);\ \Delta_{lattice}\ H^S = +\ 788\ k\ J\ mol^{-1}$$

Since, it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber cycle.

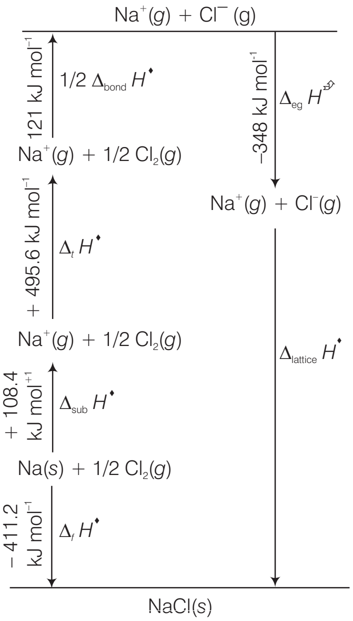
Let us now calculate the lattice enthalpy of Na^+Cl^- *(s) by following steps given below*

(i) $Na^+\ (s) \rightarrow Na(g)$; Sublimation of sodium metal, $\Delta_{sub}\ H^S = 108.4\ kJ\ mol^{-1}$

(ii) $Na\ (g) \rightarrow Na^+(g) + e^-\ (g)$; The ionisation of sodium atoms, ionisation enthalpy $\Delta_i\ H^S = 496\ kJ\ mol^{-1}$

(iii) $\frac{1}{2}\ Cl_2\ (g) \rightarrow Cl\ (g)$; The dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy $\frac{1}{2}\ \Delta_{bond}\ H^S = 121\ kJ\ mol^{-1}$

(iv) $Cl\ (g) + e^-(g) \rightarrow Cl^-(g)$; electron gained by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H^S = -\ 348.6\ kJ\ mol^{-1}$



Enthalply diagram for lattice enthalpy of NaCl

(v) $Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$

The sequence of steps is shown in given figure and is known as Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

Applying Hess's law, we get

$$\Delta_{lattice}H^S = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{lattice}\ H^s = +\ 788\ kJ$$

Q. 61 **ΔG is 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. Gibbs free energy is that thermodynamic quantity of a system, the decrease in whose value during a process is equal to the maximum possible useful work that can be obtained from the system.

Mathematically,this results may be derived as follows

The relationship between heat absorbed by a system q , the change in its internal energy, ΔU and the work done by the system is given by the equation of the first law of thermodynamics, therefore,

$$q = \Delta U + W_{\text{expansion}} + W_{\text{non-expansion}} \quad \text{...(i)}$$

Under constant pressure condition, the expansion work is given by $p\Delta V$.

$$\therefore \quad q = \Delta U + p\Delta V + W_{\text{non-expansion}} \quad (\because \Delta U + p\Delta V = \Delta H)$$

$$= \Delta H + W_{\text{non-expansion}} \quad \text{...(ii)}$$

For a reversible change taking place at constant temperature,

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ or } q_{\text{rev}} = T\Delta S \quad \text{...(iii)}$$

Substituting the value of q from Eq. (iii) in Eq. (ii), we get

$$T\Delta S = \Delta H + W_{\text{non-expansion}}$$

$$\text{or} \quad \Delta H - T\Delta S = -W_{\text{non-expansion}} \quad \text{... (iv)}$$

For a change taking place under conditions of constant temperature and pressure,

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

Substituting this value in equation (iv), we get

$$\Delta G = -W_{\text{non-expansion}} \quad \text{...(v)}$$

Thus, free energy change can be taken as a measure of work other than the work of expansion. For most changes, the work of expansion can not be converted to other useful work, whereas the non-expansion work is convertible to useful work.

Rearranging equation (v), it may write as

$$-\Delta G = W_{\text{non-expansion}} = W_{\text{useful}}$$

As $-\Delta G = W_{\text{useful}}$ therefore, ΔG has the same units as those of work *i.e.*, joule

$$\Delta G = \Delta H - T\Delta S.$$

If $\Delta H =$ positive and $\Delta S =$ positive, then

ΔG will be negative *i.e.*, process will be spontaneous only when $T\Delta S > \Delta H$ in magnitude, which will be so when temperature is high.

Q. 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 pressure p_f.**

Ans. **(i)** 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). Reversible work is represented by the combined areas ABC and BCV_iV_f.

(ii) Work against constant pressure, p_f is represented by the area BCV_iV_f. Work (i) > work (ii)