

Chemical Thermodynamics

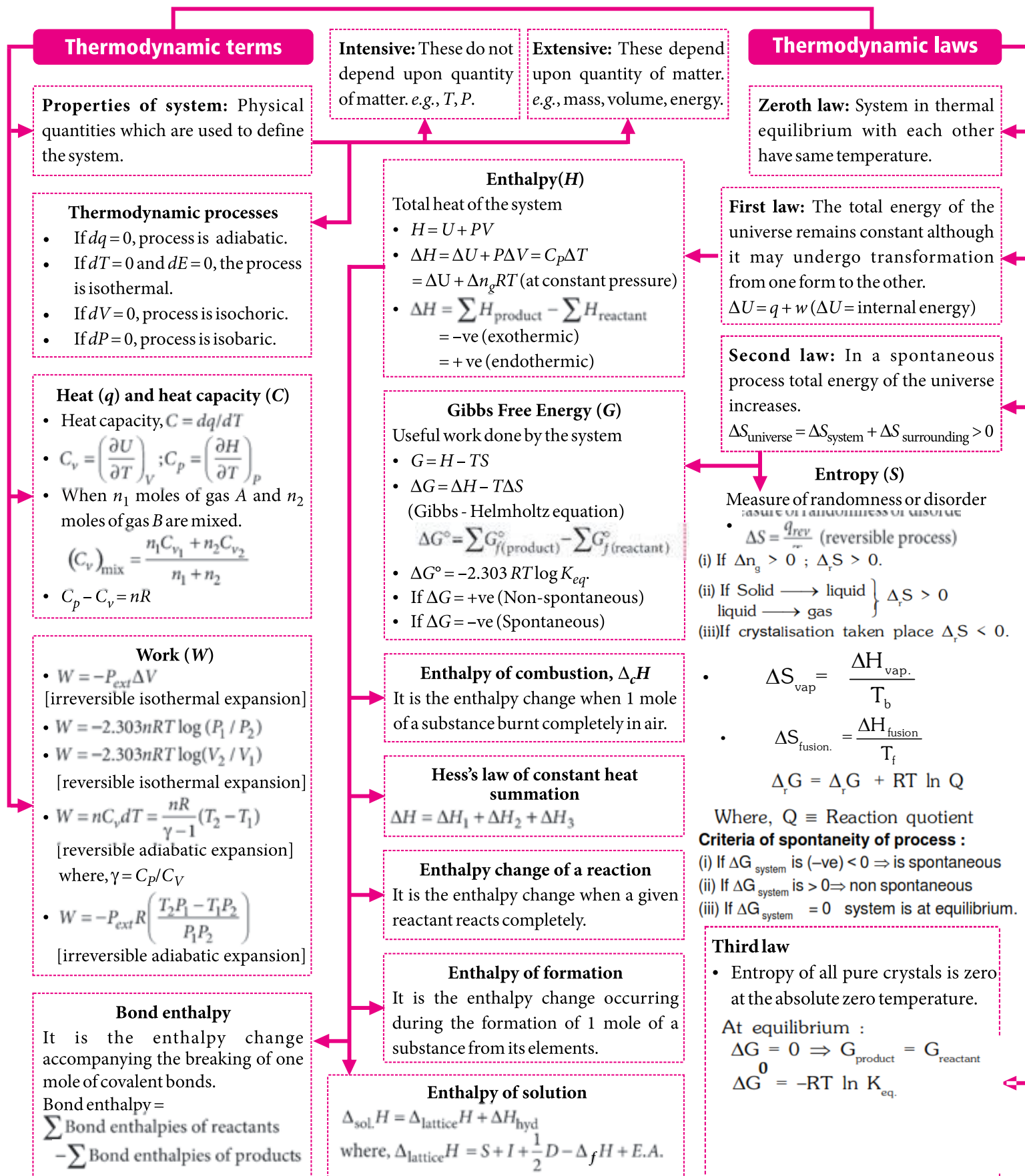
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THERMODYNAMICS

Important definitions

- Thermodynamics is the branch of science that deals with quantitative aspects of interconversion of various forms of energy and the conversion of energy into work and vice versa.
- **System**—Part of universe selected for investigation.
- **Surrounding**—Part of universe other than the investigation.
- **System can be classified as—**
 - Open system** can exchange matter and energy both with its surroundings.
 - Closed system** can exchange only energy with its surroundings but not the matter.
 - Isolated system** can neither exchange matter nor energy with surroundings.
- **State of system**—The conditions of existence of a system when its macroscopic properties have a definite value.
- Properties of a system can be classified into state and paths function.
- **State Functions**—The thermodynamic quantities which depend only on initial and final state of the system. *e.g.*, pressure, volume and temperature are the variables which are used to describe the state of the system and are state functions. A **path function** depends upon the path taken by the system during a change in state, *e.g.*, heat and work.
- Thermal process is the one which is carried out at a constant temperature.
- Isobaric process is the one which is carried out at a constant pressure.
- Isochoric process is the one during which the volume remains constant.
- Adiabatic process is the one during which no heat is gained or lost by the system.
- A reversible process takes place in a manner that system never deviates significantly from equilibrium state. It occurs infinitely slowly. All real processes are irreversible in nature.
- A cyclic process is the one that after undergoing a change in state returns back to its initial state.
- An extensive property is a property whose value depends on the quantity or size of matter present in the system, *e.g.*, mass, volume, internal energy, enthalpy, heat capacity, etc.
- An intensive property is that property which is independent of the mass or quantity or size of matter present in the system *e.g.*, temperature, density, pressure etc.
- A substance (solid, liquid or gas) is said to be in standard state when it is pure, under 1 bar pressure and at any specified temperature.
- Heat and work are the two common forms of energy which are exchanged between a system and surroundings. Both are path functions and appear only during a change in state.
- **Heat (q)**—It is random form of energy.
- **Work (w)**—It is organised form of energy.
- Heat is positive if it is gained by the system (*i.e.*, heat is transferred from the surroundings to the system) and heat is negative if it is lost by the system (*i.e.*, heat is transferred from system to the surroundings.)
- Work is positive when it is done on the system and negative when done by the system.
- **Internal energy (U)**—The all types of energy associated with the system at particular conditions of temperature and pressure.

CONCEPT MAP



Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal process	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$	0	0	
Irreversible isothermal process	$w = -P_{ext} (V_2 - V_1)$ $= -P_{ext} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{ext} (V_2 - V_1)$	0	0	
Isobaric process	$w = -P_{ext} (V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p\Delta T$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_v\Delta T$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	
Reversible adiabatic process	$w = nC_v(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	

Thermodynamic processes :

- Isothermal process :** $T = \text{constant}$
 $dT = 0$
 $\Delta T = 0$
- Isochoric process :** $V = \text{constant}$
 $dV = 0$
 $\Delta V = 0$

- Isobaric process :** $P = \text{constant}$
 $dP = 0$
 $\Delta P = 0$
- Adiabatic process :** $q = 0$

or heat exchange with the surrounding = 0(zero)

 5 Free expansion – Always going to be irreversible and since $P_{ext} =$
◆ Relationship between $\Delta_r H$ and $\Delta_r U$ for a reaction

$$\Delta_r H = \Delta_r U + \Delta n_g RT \quad (\text{for ideal gas})$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \quad (\text{for non ideal conditions})$$

◆ The stoichiometric coefficient of solids and liquids is not considered in calculation of Δn_g (because $V_s \sim V_L \ll V_g$)

Estimation of Enthalpy of a reaction from bond Enthalpies : $\Delta H = \left(\begin{array}{l} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gaseous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gaseous atoms} \end{array} \right)$

Or

Internal energy is the quantity that represents all the form of the energy of the system, i.e., kinetic and potential energies of the system.

- **Internal energy change (ΔU)**—It is a measure of heat change occur during the process at constant temperature and constant volume.

$$\Delta U = qv$$

- **Enthalpy (H)**—It is the sum total of internal energy and PV energy of the system at particular conditions of temperature and pressure. It is also called heat content of the system.

$$H = U + PV.$$

- **Enthalpy change (ΔH)**—It is the measure of heat change taking place during the process at constant temperature and constant pressure.

$$\Delta H = qp$$

ΔH is negative for exothermic reactions and is positive for endothermic reactions.

- **Law of conservation of energy**—It is also called first law of thermodynamics and states that energy of universe always remain constant during physical or chemical changes

Or

Energy can neither be created nor be destroyed. Mathematically, it can be written as :

$$\Delta U = q + w.$$

- **Relation between ΔH and ΔU** —

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

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

- The magnitude of temperature change during heat transfer depends upon the heat capacity of the system according to the relation

$$q = m \times c \times \Delta t$$

- Specific heat or 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).

- Q. 1. In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system ? What is the change in internal energy for the process ?**

$$\begin{aligned} &= n_2 - n_1 \\ &= 2 - \frac{3}{2} = \frac{1}{2} \end{aligned}$$

$\frac{1}{2}$

$$[T = 298 \text{ K}, R = 0.0083 \text{ kJ mol}^{-1} \text{ K}^{-1}]$$

$$\Delta H = -742.7 + \frac{1}{2} (0.0083) \times 298$$

\therefore

$$= (-742.7 + 1.24) \text{ kJ}$$

$$= -741.5 \text{ kJ mol}^{-1} \quad 1$$

\therefore Enthalpy change for the reaction is $-741.5 \text{ kJ mol}^{-1}$.

- Ans.** $\Delta E = q + w$, where ΔE is the change in internal energy $\frac{1}{2}$

Given $q = +701 \text{ J}$

Since the work is done by the system; w is -ve $\frac{1}{2}$

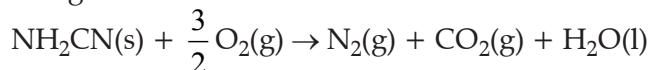
$$\therefore \Delta E = q - w = (701 - 394) \text{ J} = 307 \text{ J}$$

$$\therefore \text{Change in internal energy} = 307 \text{ J.} \quad 1$$

- Q. 2. The reaction of cyanamide $\text{NH}_2\text{CN(s)}$ with O_2 was carried out in a bomb calorimeter and ΔU was found to be -742.7 kJ/mol at 298 K . Calculate enthalpy change for the reaction at 298 K .**



- Ans.** The given reaction is



$$\Delta U = -742.7 \text{ kJ mol}^{-1}$$

$$\text{Enthalpy change } \Delta H = \Delta U + \Delta n_g RT \quad \frac{1}{2}$$

where Δn_g = change in the no. of moles (gaseous)

- Q. 3. Calculate the number of kJ necessary to raise the temperature of 60 g of Aluminium from 35 to 55°C. Molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$. [Imp.]**

- Ans.** Mass of Al given is 60 g

$$\Delta T = \text{rise in temp.} = 55 - 35 = 20^\circ\text{C} \quad \frac{1}{2}$$

$$\text{No. of moles of Aluminium} = \frac{60}{27} \quad \frac{1}{2}$$

$$\text{Molar heat capacity} = 24 \text{ J/mol K}$$

$$= \text{Moles} \times \Delta T \times \text{Molar heat capacity}$$

$$\text{Total heat required i.e., } T = \frac{60}{27} \times 20 \times 24 \text{ J} \quad 1$$

$$= 1067 \text{ J} = 1.067 \text{ kJ.}$$

- **Enthalpy of Reaction**—The enthalpy change accompanying the chemical reaction in which number of moles of reactants consumed and those of products formed are the same as the stoichiometric coefficients.
- **Enthalpy of Neutralisation ($\Delta_n H$)**—It is the enthalpy change taking place during neutralisation of 1 gm equivalent of acid with 1 gm equivalent of a base in dilute aqueous solution.
- **Standard Enthalpy of Fusion ($\Delta_{\text{fusion}} H^\circ$)**—It is the enthalpy taking place during the fusion of one mole solid at its melting point.
- **Standard Enthalpy of Vaporisation ($\Delta_{\text{vap}} H^\circ$)**—It is the enthalpy change taking place during the vaporisation of 1 mole of liquid at its boiling point and under standard pressure (1 bar).
- **Standard Enthalpy of Sublimation, ($\Delta_{\text{sub}} H^\circ$)**—It is the change in the enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1 bar).
- **Standard Enthalpy of Formation ($\Delta_f H^\circ$)**—It is enthalpy change accompanying the formation of 1 mole of the substance from its constituent elements in their standard state.
 $\Delta_f H^\circ$ can be > 0 or < 0 .
- **Hess's law**—The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps.
- **Standard Enthalpy of Combustion ($\Delta_c H^\circ$)**—It is the enthalpy change occurring during the combustion of the mole of the substances in excess of oxygen. $\Delta_c H^\circ$ is always less than zero.
- **Enthalpy of Atomisation**—It is the enthalpy change accompanying the dissociation of 1 mole of substance into gaseous atoms.
- **Bond Enthalpy ($\Delta_{\text{bond}} H^\circ$)**—The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.
- **Enthalpy of Solution ($\Delta_{\text{sol}} H^\circ$)**—It is the enthalpy change taking place when 1 mole of the solute is dissolved in large excess of solvent so that on further dilution no enthalpy occurs.
- **Enthalpy of Hydration**—It is the enthalpy change occurring during the hydration of 1 mole of anhydrous salt by combining with specific number of moles of water.
- 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.

Q. 1. The enthalpies of all elements in their standard states are : [NCERT]

- (i) Unity (ii) zero
 (iii) < 0 (iv) different for each element

Ans. zero. 1

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

$$\Delta H = -2878 \text{ kJ}$$

ΔH is the heat of of butane gas.

(ii) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$;

$$\Delta H = -57.1 \text{ kJ}$$

In real terms

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq)$
 $\rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$

ΔH is the heat of of hydrochloric acid and sodium hydroxide solutions.

(iii) $C(s) \rightarrow C(g)$; $\Delta H = 716.7 \text{ kJ}$

(graphite)

ΔH is the heat of of graphite.

(iv) $C(s) \rightarrow C(g)$; $\Delta H = 714.8 \text{ kJ}$

(diamond)

ΔH is the heat of of diamond.

(v) $H_2O(s) \rightarrow H_2O(l)$; $\Delta H = 6.01 \text{ kJ}$

ΔH is the heat of of ice.

(vi) $H_2O(l) \rightarrow H_2O(s)$; $\Delta H = -6.01 \text{ kJ}$

ΔH is the heat of of water.

(vii) $H_2O(l) \rightarrow H_2O(g)$; $\Delta H = 40.7$

ΔH is the heat of of water.

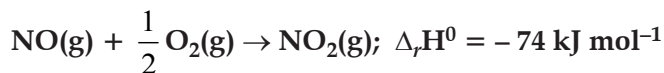
(viii) $H_2O(g) \rightarrow H_2O(l)$; $\Delta H = -40.7$

ΔH is the heat of of steam.

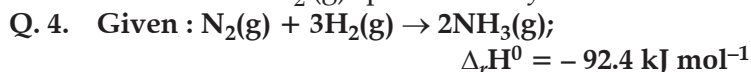
(1 mark each)

- Ans. (i) Combustion (v) Fusion
 (ii) Neutralization (vi) Solidification
 (iii) Sublimation (vii) Vaporization
 (iv) Sublimation (viii) Condensation.

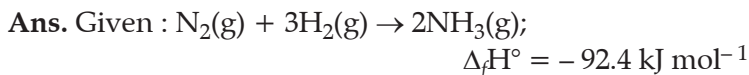
Q. 3. Comment on the thermodynamic stability of $NO(g)$, given :



Ans. As can be seen from the first reaction, formation of NO is endothermic process and will take only when 90 K mol⁻¹ energy is available. However, the second reaction involving the oxidation of NO to NO₂ is an exothermic process and energetically more feasible. Therefore NO(g) is unstable and it would get converted into NO₂(g) spontaneously. 1



What is the standard enthalpy of formation of NH₃ gas ?



This is the heat evolved for 2 moles of NH₃(g)
 \therefore Heat evolved for 1 mole of NH₃(g)

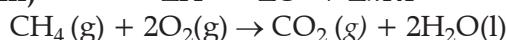
$$= \frac{-92.4}{2} = -46.2 \text{ kJ}$$

Hence ΔH° of NH₃ gas = -46.2 kJ mol⁻¹. 1

Q. 5. ΔU° of combustion of methane is -X kJ mol⁻¹. The value of ΔH° is :

(i) = ΔU° (ii) > ΔU°

(iii) < ΔU° (iv) = 0



$$\Delta n = n_P - n_R$$

$$= 1 - 3 = -2$$

$$\Delta H = \Delta U - 2RT$$

$$\Delta H^\circ = \Delta U^\circ$$

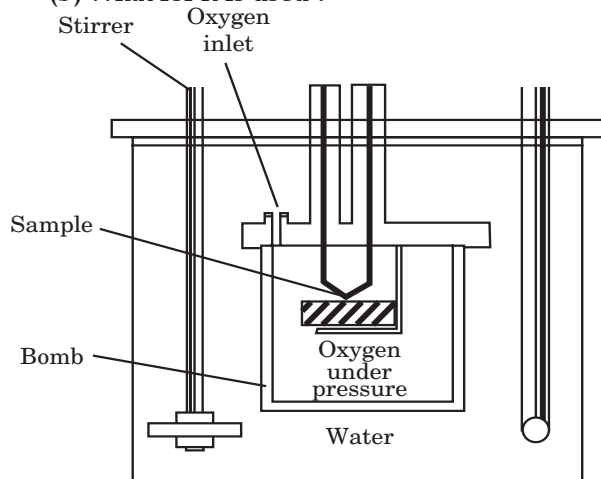
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SHORT ANSWER TYPE QUESTIONS-I

(2 marks each)

Q. 1. (a) What does the following diagram indicate?

(b) What for it is used ?



Ans. (a) Bomb calorimeter 1

(b) Bomb calorimeter is used for the measurement of ΔU . 1

Q. 2. Enthalpy of combustion of carbon to CO₂ is -393.5 kJ/mol. Calculate heat released upon

formation of 35.2g of CO₂ from carbon and O gas ?



1 mole 1 mole 1 mole

$$\Delta H = -393.5 \text{ kJ/mol} \quad \frac{1}{2}$$

For formation of 44 g of CO₂ heat released is -393.5 kJ mol⁻¹ 1/2

For formation of 35.2 g of CO₂ heat released is

$$= \frac{-393.5}{44} \times 35.2$$

$$= -314.8 \text{ kJ mol}^{-1}. \quad 1$$

Q. 3. Enthalpies of formation of CO(g), CO₂(g), N₂O(g) and N₂O₄(g) are -110, -393, 81 and 9.7 kJ mol⁻¹. Find the value of $\Delta_r H$ for the reaction.



$\Delta_r H = ?$

$$\Delta_r H = \sum \Delta_f H_{(\text{Product})} - \sum \Delta_f H_{(\text{reactants})} \quad \frac{1}{2}$$

$$= [\Delta_f H(\text{N}_2\text{O}) + 3 \times \Delta_f H_{\text{CO}_2}]$$

$$- [\Delta_f H(\text{N}_2\text{O}_4) + 3 \times \Delta_f H_{\text{CO}}]$$

$$= [81 + 3 \times (-393)] - [9.7 + 3(-110)] \quad \frac{1}{2}$$

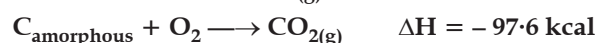
$$= -777.8 \text{ kJ}. \quad \frac{1}{2}$$

SHORT ANSWER TYPE QUESTIONS-II

(3 marks each)

Q. 1. (a) What is enthalpy change at constant volume. Explain.

(b) Calculate the enthalpy of transition for carbon from the following :



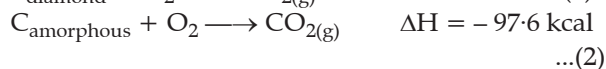
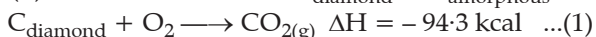
Also calculate the heat required to change.

1g of C_{diamond} to C_{amorphous} [KVS-2014]

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

then $q_p = q_v = \Delta V$ or $\Delta H = \Delta U$. 1

(b) Heat of transition of C_{diamond} to C_{amorphous}



Subtraction equation (2) from (1)



$$= 3.3 \text{ kcal}. \quad 1$$

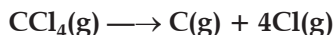
This heat represents the transformation of 1 mole

C_{diamond} to C_{amorphous}

Therefore, heat of transformation for 1 g of C_{diamond} to 1 g C_{amorphous} = 3.3 kcal/12

$$= 0.275 \text{ kcal.} \quad 1$$

Q. 2. Calculate the enthalpy change for the process.



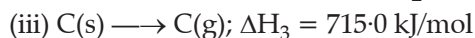
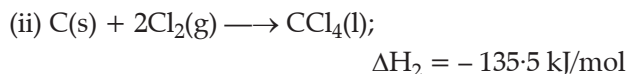
and calculate bond enthalpy of C - Cl in $\text{CCl}_4(\text{g})$

Given :

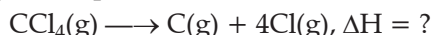
$$\begin{aligned} \Delta_{\text{vap}}H^0 (\text{CCl}_4) &= 30.5 \text{ kJ/mol} \\ \Delta_f H^0 (\text{CCl}_4) &= -135.5 \text{ kJ/mol} \\ \Delta_a H^0 (\text{C}) &= 715.0 \text{ kJ/mol} \end{aligned}$$

where $\Delta_a H^0$ is enthalpy of atomisation.

$$\Delta_a H (\text{Cl}_2) = 242 \text{ kJ/mol.}$$



Required equation



Now carry out the following operations to get the required equation.

$$\text{Eq. (iii)} + 2 \times \text{Eq. (iv)} - \text{Eq. (i)} - \text{Eq. (ii)}$$

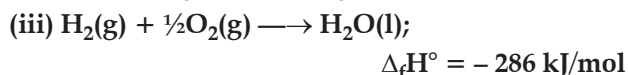
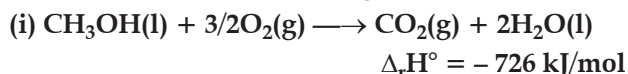
$$\therefore \Delta H = \Delta H_3 + 2\Delta H_4 - \Delta H_1 - \Delta H_2 \quad 1$$

$$\begin{aligned} \Delta H &= 715 + 2 \times 242 - 30.5 - (-135.50 \text{ kJ/mol}) \\ &= 1304 \text{ kJ/mol} \end{aligned}$$

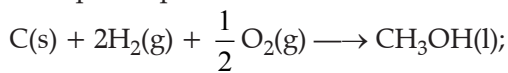
Since during this reaction, 4C-Cl bonds are broken bond enthalpy of C - Cl in CCl_4 (average value)

$$= \frac{\Delta H}{4} = \frac{1304}{4} = 326 \text{ kJ/mol.} \quad 1$$

Q. 3. Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH}(\text{l})$ from the following data.

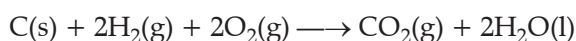


Ans. The require equation is



$$\Delta_f H^0 = \pm ? \frac{1}{2}$$

Multiply eq. (iii) by 2 and add to eq. (ii)

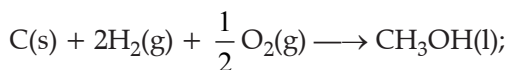


$$\Delta H = (2 \times -286) + (-393)$$

$$= -572 - 393$$

$$= -965 \text{ kJ/mol}$$

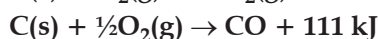
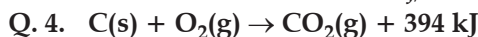
Subtract eq. (i) and eq. (iv)



$$\Delta H = -965 - (-726)$$

$$= -239 \text{ kJ/mol}$$

$$\Delta H = -239 \text{ kJ/mol}$$



(i) In an oven using coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% carbon is converted to CO. Find out the heat generated when 10 kg of coal is burnt in this fashion.

(ii) Calculate the heat generated if a more efficient oven is used so that only CO_2 is formed.

(iii) Calculate the percentage loss in heating value for the inefficient oven.

Ans. (i) Wt. of pure coal = $\frac{80}{100} \times 10 = 8.0 \text{ kg}$

$$\text{Wt. of coal converted into } \text{CO}_2 = 8 \times \frac{60}{100}$$

$$= 4.8 \text{ kg}$$

$$\text{Wt. of coal converted in to CO} = 8 - 4.8$$

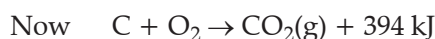
$$= 3.2 \text{ kg}$$

Moles of C in 4.8 kg coal

$$= \frac{4800}{12} = 400 \text{ moles}$$

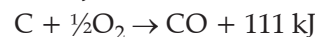
Moles of C in 3.2 kg coal

$$= \frac{3200}{12} = 266.67 \text{ moles}$$



1 mole of C gives heat = 394 kJ

$$\therefore 400 \text{ moles give heat} = 400 \times 394 = 157600 \text{ kJ } \frac{1}{2}$$



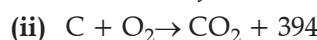
1 mole of C gives heat = 111 kJ

$$\therefore \frac{3200}{12} \text{ mole of C gives heat}$$

$$= 111 \times \frac{3200}{12} = 29600 \text{ kJ}$$

Total heat generated = 157600 + 29600

$$= 187200 \text{ kJ}$$



1 mole of C gives heat = 394 kJ

$$\frac{8000}{12} \text{ mole of C gives heat}$$

$$= 394 \times \frac{8000}{12} = 262667 \text{ kJ}$$

(iii) Heat lost due to inefficient oven

$$= 262667 - 187200 = 75467 \text{ kJ}$$

$$\therefore \% \text{ loss} = \frac{75467}{262667} \times 100 = 28.8\%$$

Q. 5. If a man submits to a diet of 9500 kJ per day and expands energy in all forms to a total of 12000 kJ per day. What is the change in internal energy per day? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg? (Ignore water loss for this problem).

Q. 6. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are $-890.3 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively. Calculate Enthalpy of formation of $\text{CH}_4(\text{g})$.

Ans. Given : (i) $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

$$\Delta H = -890.3 \text{ kJ mol}^{-1}$$

(ii) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}), \Delta H = -395.5 \text{ kJ mol}^{-1}$

(iii) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}),$

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

Aim : $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}), \Delta H = ?$

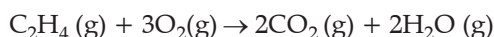
Eqn. (ii) + 2 × Eqn. (iii) – Eqn. (i) gives the required equation with

$$\begin{aligned} \Delta H &= -395.5 + 2(-285.8) - (-890.3) \text{ kJ mol}^{-1} \\ &= -76.8 \text{ kJ mol}^{-1} \end{aligned}$$

Q. 6. Calculate the enthalpy of combustion of ethylene (gas) to form $\text{CO}_2(\text{gas})$ and $\text{H}_2\text{O}(\text{gas})$ at 298 K and 1 atmospheric pressure. The enthalpies of formation of $\text{CO}_2, \text{H}_2\text{O}$ and C_2H_4 are $-393.7, -241.8 + 52.3 \text{ kJ}$

per mole respectively.

Ans. We aim at :



We are given :

$$\Delta H_f(\text{CO}_2) = -393.7 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}_2\text{O}) = -241.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{C}_2\text{H}_4) = +52.3 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H_{\text{Reaction}} &= (\text{Sum of } \Delta H_f^\circ \text{ values of Products}) \\ &\quad - (\text{Sum of } \Delta H_f^\circ \text{ values of Reactants}) \end{aligned}$$

$$= [2 \times \Delta H_f^\circ(\text{CO}_2) + 2 \times \Delta H_f^\circ(\text{H}_2\text{O})]$$

$$- [\Delta H_f^\circ(\text{C}_2\text{H}_4) + 3 \times \Delta H_f^\circ(\text{O}_2)]$$

$$= [2 \times (-393.7) + 2 \times (-241.8)] - [(52.3) + 0]$$

($\because \Delta H_f^\circ$ for elementary substance = 0)

$$= [-787.4 - 483.6] - 52.3$$

$$= -1323.3 \text{ kJ mol}^{-1}$$

Q. 6. Neither q nor w is a state function, yet $q + w$ is a state function. Explain why.

Ans. $q + w = \Delta E$ and ΔE is a state function.

Q. 7 When $\text{NH}_4\text{NO}_2(\text{s})$ decomposes at 373 K, it forms (g) and $\text{H}_2\text{O}(\text{g})$. The ΔH for the reaction at one atmospheric pressure and 373 K is $-223.6 \text{ kJ mol}^{-1}$. What is the value of ΔE for the reaction under the same conditions ?

(Given $R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$)

Ans. $\text{NH}_4\text{NO}_2(\text{s}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}),$

$$\Delta n_g = 3 - 0 = 3$$

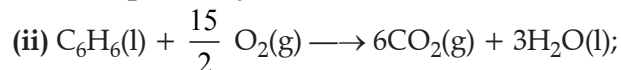
$$\Delta U = \Delta H - \Delta n_g RT$$

$$= -223.6 \text{ kJ mol}^{-1} - (3 \text{ mol})$$

$$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K})$$

$$= -232.9 \text{ kJ mol}^{-1}.$$

(ii) The combustion of 1 mole benzene takes place at 298 K and 1 atm. After combustion $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are produced and 3267.0 kJ of heat is liberated. Calculate standard enthalpy of formation ($\Delta_f H^\circ$) of Benzene. Standard enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 kJ/mol and $-285.83 \text{ kJ mol}^{-1}$ respectively. [NCT-2007, NCT-2011]



$$\Delta H = -3267.0 \text{ kJ}$$

$$\begin{aligned} \text{Now, } \Delta_r H^\circ &= \sum \Delta_f H^\circ(\text{P}) - \sum \Delta_f H^\circ(\text{R}) \\ &= 6 \times \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) \\ &\quad - \Delta_f H^\circ(\text{C}_6\text{H}_6) - \frac{15}{2} \Delta_f H^\circ(\text{O}_2) \end{aligned}$$

$$\begin{aligned} \text{or } -3267.0 &= 6 \times (-393.5) + 3(-285.83) \\ &\quad - \Delta_f H^\circ(\text{C}_6\text{H}_6) - \frac{15}{2} (0) \end{aligned}$$

(for elements enthalpy of formation is zero)

$$\Delta_f H^\circ(\text{C}_6\text{H}_6) = 3267 - 6(393.5) - 3(285.83)$$

$$\Delta_f H^\circ(\text{C}_6\text{H}_6) = 3267 - 2361 - 857.49$$

$$= 48.51 \text{ kJ/mol.}$$

Q. 8. What are heat capacities at constant volume and constant pressure ? What is the relationship between them ?

Ans. Heat capacity at constant volume (C_V) : Heat supplied to a system to raise its temperature by 1°C , keeping the volume of the system constant is called its heat capacity at constant volume (C_V).

Heat capacity at constant pressure (C_P) : Heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called its heat capacity at constant pressure. (C_P).

Relationship between C_P and C_V :

$$C_P - C_V = R.$$

- **Spontaneous process**—A process which has an urge or a natural tendency to occur in a particular direction either of its own or after proper initiation under a given set of conditions.
- Entropy is a thermodynamic property which is a measure of disorder. It is related to heat absorbed at a constant temperature by the system in a reversible process as : $\frac{-q_{rev}}{T}$
For a spontaneous change, total entropy change is positive.
- **Second law of Thermodynamics** : The entropy of universe always tends to increase during any spontaneous process.
- **Third law of Thermodynamics** : At absolute zero, the entropy of a perfectly crystalline substance is zero.
- Gibbs energy is another thermodynamic property which is a measure of energy stored in a system or a substance that is available for doing useful work. It is related to changes in enthalpy and entropy of the system during a process as :

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

For a spontaneous change, $\Delta G_{sys} < 0$, for a non-spontaneous change, $\Delta G_{sys} > 0$, and $\Delta G_{sys} = 0$ shows equilibrium.

$$\Delta G^\circ = -RT \ln K = 2.303 RT \log K$$

Important Formulae

- | | | | |
|--|--|---|--|
| (i) $\Delta U = q + w$ | | (vi) For process to be spontaneous | |
| (ii) $\Delta H = \Delta U + P\Delta V$ | | $\Delta S_{system} + \Delta S_{surr} > 0$ | |
| (iii) $\Delta H^\circ = \sum \Delta_f H^\circ (\text{Products}) - \sum \Delta_f H^\circ (\text{Reactants})$ | | | |
| (iv) $\Delta H^\circ = [\text{Sum of } H \text{ bond of reactants}] - [\text{Sum of } H \text{ bond of products}]$ | | (vii) $\Delta G = \Delta H - T\Delta S$ | |
| | | (viii) $\Delta G_{sys} = -T\Delta S_{total}$ | |
| (v) $\Delta S = \frac{q_{(rev)}}{T}$ | | (ix) $\Delta_r G^\circ = \sum \Delta_f G^\circ (\text{Products}) - \sum G^\circ (\text{Reactants})$ | |
| $\Delta S_f = \Delta H_f / T_f$ and $\Delta S_{vap} = \Delta H_{vap} / T_b$. | | (x) $\Delta G_{T,P} < 0$ refers to spontaneous process. | |

VERY SHORT ANSWER TYPE QUESTIONS

(1 mark each)

Q. 1. Predict the sign of entropy change in each of the following :

- (i) A liquid crystallises into solid.
- (ii) Temperature of perfectly crystalline solid is raised from 0 K to 115 K.
- (iii) $2\text{NaHCO}_3 (\text{s}) \longrightarrow \text{Na}_2\text{CO}_3 (\text{s}) + \text{H}_2\text{O} (\text{g})$
- (iv) $\text{H}_2 (\text{g}) \longrightarrow 2\text{H} (\text{g})$.

- Ans. (i) -ve
(ii) +ve
(iii) +ve because gaseous product is formed
(iv) +ve.

Q. 2. Predict the sign of entropy change for each of the following changes of state :

- (1) $\text{Hg} (\text{l}) \longrightarrow \text{Hg} (\text{g})$
- (2) $\text{AgNO}_3 (\text{s}) \longrightarrow \text{AgNO}_3 (\text{aq})$
- (3) $\text{I}_2 (\text{g}) \longrightarrow \text{I}_2 (\text{s})$
- (4) $\text{C} (\text{graphite}) \longrightarrow \text{C} (\text{Diamond})$. (1 mark each)

- Ans. (i) +ve (iii) -ve
(ii) +ve (iv) -ve.

Q. 3. A reaction $\text{A} + \text{B} \longrightarrow \text{C} + \text{D} + q$ is found to have entropy change. The reaction will be :

- (1) Possible at high temperature
- (2) Possible only at low temperature
- (3) Not possible at any temperature
- (4) Possible at any temperature. [NCERT]

- Ans. (4) Since the reaction is Exothermic ($\Delta H < 0$) and has $\Delta S > 0$, therefore, it is feasible at all temperatures because both the factors favour spontaneity. 1

Q. 4. In the following changes, state whether order has

increased or decreased and consequently the direction of changes of entropy of the system.

- (i) Stretched rubber band \rightarrow Loose rubber band.
- (ii) $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{O} (\text{s})$
- (iii) Dry ice (solid carbon dioxide) $\rightarrow \text{CO}_2 (\text{g})$
- (iv) Steam \rightarrow Water
- (v) $\text{Cr}^{3+} + 6\text{H}_2\text{O} (\text{aq}) \rightarrow \text{Cr} (\text{H}_2\text{O})_6^{3+}$
- (vi) $\text{CO}_2 + \text{H}_2\text{O} \xrightarrow[\text{Photosynthesis}]{\text{light}}$

Carbohydrates + O₂

(vii) Proteins (helical form)

$\xrightarrow[\text{Denaturation}]{\text{light}}$ Proteins

(random coil form)

(viii) Normal egg \rightarrow hard boiled egg.

- Ans. (i) Order increases, entropy decreases.
(ii) Order increases, entropy decreases.
(iii) Disorder increases, entropy increases
(iv) Order increases, entropy decreases.
(v) Order increases, entropy decreases.
(vi) Order increases, entropy decreases.
(vii) Disorder increases, entropy increases.
(viii) Order increases, entropy decreases.

Q. 5. For an isolated system $\Delta U = 0$, what will be ΔS ?

- Ans. For an isolated system with $\Delta U = 0$, the spontaneous change will occur if $\Delta S > 0$. 1

SHORT ANSWER TYPE QUESTIONS-I

(2 marks each)

Q. 1. For the reaction at 298 K



$$\Delta H = 400 \text{ kJ mol}^{-1} \text{ and } \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

At what temperature will reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range? [NCERT] [KVS-2013]

Ans. For the reaction $2A + B \rightarrow C$;

$$\Delta H = 400 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{and } \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S \quad \frac{1}{2}$$

For a spontaneous reaction ΔG has to be negative

ΔH is 400 kJ mol^{-1} (positive)

$\therefore T\Delta S$ has to be $> \Delta H$

$$\text{or } T > \frac{\Delta H}{\Delta S} > \frac{400}{0.2} \quad \frac{1}{2}$$

$$\text{or } T > 2000 \text{ K}$$

For the reaction to be spontaneous $T > 2000 \text{ K}$. 1

Q. 2. The equilibrium constant for a reaction is 10. What will be the value of ΔG° ? $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$. [NCERT]

Ans. The equilibrium constant given for a reaction is 10.

$$\text{i.e., } K = 10$$

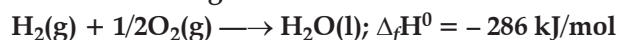
$$\Delta G^\circ = -2.303 RT \log K \quad \frac{1}{2}$$

$$= -2.303 \times 8.314 \times 300 \log 10 \quad 1$$

$$= -2.303 \times 8.314 \times 300 \times 1 \quad [\text{as } \log 10 = 1]$$

$$= -5744.142 \text{ J mol}^{-1} = -5.744 \text{ kJ mol}^{-1}. \quad \frac{1}{2}$$

Q. 3. For the following reaction



Temperature = 298 K

Calculate ΔS in surroundings? [NCERT]

Ans. Since heat (enthalpy) is evolved in the above reaction.

\therefore It is absorbed by the surroundings.

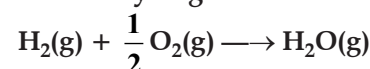
$$\text{i.e., } q_{\text{surr}} = +286 \text{ kJ/mol} \quad \frac{1}{2}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{286000}{298} \text{ J} \quad \frac{1}{2}$$

$$\Delta S = 959.73 \text{ JK}^{-1}. \quad 1$$

Q. 4. Calculate the entropy change ΔS per mole for following reaction.

Combustion of Hydrogen in a fuel cell at 298 K.



$$\Delta H = 241.60 \text{ kJ}$$

$$\Delta G = 288.40 \text{ kJ}. \quad \text{[NCERT]}$$

Ans. $\Delta G = \Delta H - T\Delta S \quad \frac{1}{2}$

Putting in the values,

$$-288.40 = -241.6 - 298 \times \Delta S$$

$$\therefore \Delta S = \frac{-288.4 + 241.6}{-298} \quad 1$$

$$= 0.157 \text{ kJ K}^{-1} \text{ mol}^{-1} \quad \frac{1}{2}$$

SHORT ANSWER TYPE QUESTIONS-II

(3 marks each)

Q. 1. (a) Under what conditions is the heat absorbed by a system is equal to the work done by the system.

(b) Under what conditions the following reaction will be spontaneous:

(i) Reaction with both ΔH and ΔS positive.

(ii) Reaction with both ΔH and ΔS negative.

[KVS-2014]

Ans. (a) For an ideal gas undergoing an isothermal change, $\Delta U = 0$. Hence,

$$q = -w$$

i.e., the heat absorbed by the system is equal to work done by the system. $\frac{1}{2}$

(b) (i) $\Delta G = \Delta H - T\Delta S = -ve$, then reaction is spontaneous if both ΔH and ΔS are +ve.

Then, the reaction will be spontaneous, if $T\Delta S > \Delta H$.

Therefore, the reaction with both ΔH and ΔS are positive will be spontaneous at sufficiently high temperature.

(ii) Now if both ΔH and ΔS are -ve.

That means $-T\Delta S$ will become positive and the reaction will be spontaneous at low temperature. where, ΔG will be negative.

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

at low temperature.

$$\Delta G = -ve \quad \frac{1}{2}$$

Q. 2. For a reaction $2A(\text{g}) + B(\text{g}) \longrightarrow 2D(\text{g})$.

$$\Delta U^\circ = -10.5 \text{ kJ}, \Delta S^\circ = -44.1 \text{ JK}^{-1}$$

Calculate ΔG° for the reaction and predict whether the reaction is spontaneous or not?

[NCERT]

Ans. $\Delta H^\circ = \Delta U^\circ + \Delta n(\text{g})RT \quad \frac{1}{2}$

$$\Delta U^\circ = -10.5 \text{ kJ} \quad \frac{1}{2}$$

$$\Delta n(\text{g}) = 2 - 3 = -1 \text{ mol}$$

$$T = 298 \text{ K}$$

(Room temperature 25°C is taken)

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta H^\circ = -10.5(\text{kJ}) + [-1(\text{mol}) \times 8.314 \times 10^{-3} (\text{kJ K}^{-1}\text{mol}^{-1}) \times 298 \text{ K}]$$

$$= -12.978 \text{ kJ} \quad 1$$

According to Gibbs Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \frac{1}{2}$$

$$= -12.978 (\text{kJ}) - 298 (\text{K})$$

$$\times -0.0441 (\text{kJK}^{-1}) \quad \frac{1}{2}$$

$$= -12.978 + 13.1418$$

$$= +0.1638 \text{ kJ}$$

Since ΔG° is positive, the reaction is non spontaneous.

Q. 3. Calculate the standard Gibbs energy change for the formation of propane $\text{C}_3\text{H}_8(\text{g})$ at 298 K. Given that

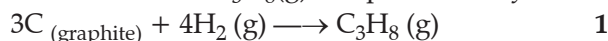
$$\Delta_f H^\circ \text{ for propane} = -103.85 \text{ kJ/mol}$$

$$S^0_M \text{C}_3\text{H}_8(\text{g}) = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^0_M \text{H}_2(\text{g}) = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^0_M \text{C}_{(\text{graphite})} = 5.74 \text{ J K}^{-1}. \quad [\text{NCERT}]$$

Ans. The formation of $\text{C}_3\text{H}_8(\text{g})$ is represented by



$$\Delta S^0 = S^0(\text{C}_3\text{H}_8) - 4S^0(\text{H}_2) - 3S^0(\text{C})$$

$$= 270.2 - [4 \times 130.68] - [3 \times 5.74]$$

$$= -269.74 \text{ J K}^{-1} \quad 1$$

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

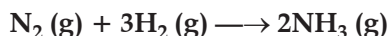
$$= -103.85 \times 10^3 (\text{J}) - 298 (\text{K})$$

$$\times (-269.74 \text{ J K}^{-1})$$

$$= -23470.48 \text{ J}$$

$$= 23.47 \text{ kJ}. \quad 1$$

Q. 4. For the reaction :



$$\Delta H = -95.4 \text{ kJ and } \Delta S = -198.3 \text{ J K}^{-1}$$

Calculate the temperature at which Gibbs energy change (ΔG) is equal to zero. Predict the nature of the reaction at this temperature and above it ?

[*BSM 2011-12]

$$\text{Ans.} \quad \Delta G = \Delta H - T\Delta S \quad \frac{1}{2}$$

$$\text{when } \Delta G = 0 \quad \frac{1}{2}$$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

* BSM : (Board Supplementary Material)

$$= \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ J K}^{-1}} \quad 1$$

$$= 481 \text{ K}$$

At this temperature the reaction would be in equilibrium. With increase in temperature the opposing factor $T\Delta S$ would become more and hence ΔG would become positive and the reaction would become non-spontaneous. The reaction would be spontane-

ous at the temperature below 481 K. 1

Q. 5. Fill up the blanks in the following table related to $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}_{(\text{steam})}$ at standard atmospheric pressure. [NCERT]

S. No.	t°C	TK	ΔH (Enthalpy change) kJ mol ⁻¹	ΔS (Entropy change) J mol ⁻¹ K ⁻¹ (TΔS kJ	ΔG (Free energy) kJ
1	90	363.0	41.1	—	—	+1.193
2	110	373.0	40.7	109	—	—
3	110	383.0	40.1	—	—	-0.979

$$\begin{aligned} \text{Ans. (1)} \quad \Delta G &= \Delta H - T\Delta S \\ &+ 1.193 = 41.1 - 363 \times \Delta S \\ 363 \times \Delta S &= 41.1 - 1.193 = 39.907 \quad 1 \end{aligned}$$

$$\therefore \Delta S = \frac{39.907}{363}$$

$$= 0.1099 \text{ kJ mol}^{-1}\text{K}^{-1}$$

$$= 110 \text{ J mol}^{-1}\text{K}^{-1}$$

$$(2) \quad \therefore T\Delta S = 383 \times 109$$

$$= 41747 = 41.75 \text{ kJ mol}^{-1}$$

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

$$= 40.7 - 41.75$$

$$= -1.05 \text{ kJ mol}^{-1} \quad 1$$

$$(3) \quad \Delta G = \Delta H - T\Delta S$$

$$-0.979 = 40.1 - T\Delta S$$

$$\therefore T\Delta S = 40.1 + 0.979$$

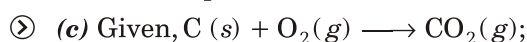
$$= 41.079 \text{ kJ mol}^{-1}$$

$$\Delta S = \frac{T\Delta S}{T} = \frac{41.079}{383}$$

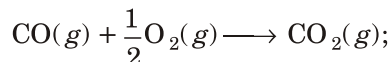
$$= 0.1072 \text{ kJ mol}^{-1}\text{K}^{-1}$$

$$= 107.2 \text{ J mol}^{-1}\text{K}^{-1}. \quad 1$$

6 The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is

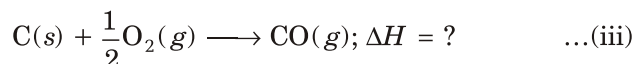


$$\Delta H_1 = -393.5 \text{ kJ mol}^{-1} \dots(\text{i})$$



$$\Delta H_2 = -283.5 \text{ kJ mol}^{-1} \dots(\text{ii})$$

We have to find enthalpy of formation of $\text{CO}(\text{g})$



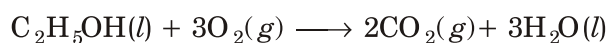
By subtracting Eq. (ii) from Eq. (i), we get the required equation, i.e. Eq. (iii)

$$\begin{aligned} \therefore \Delta H &= \Delta H_1 - \Delta H_2 = (-393.5 + 283.5) \text{ kJ mol}^{-1} \\ &= -110 \text{ kJ mol}^{-1} \end{aligned}$$

7 For the complete combustion of ethanol,

$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$, the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

a) For the given reaction,



$$\Delta U = -1364.47 \text{ kJ mol}^{-1}$$

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

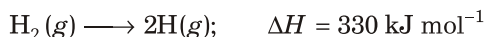
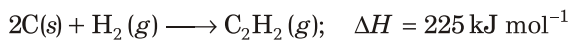
$$\Delta n_g = 2 - 3 = -1$$

$$\therefore \Delta H = -1364.47 + (-1) \times 0.008314 \times 298$$

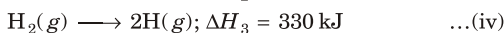
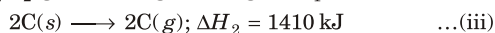
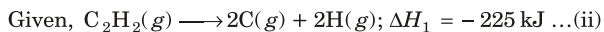
$$= (-1364.47 - 2.4776) \text{ kJ mol}^{-1}$$

$$= -1366.95 \text{ kJ mol}^{-1}$$

- 8 . Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $\text{C}\equiv\text{C}$ bond in C_2H_2 . That energy is (take the bond energy of a $\text{C}-\text{H}$ bond as 350 kJ mol^{-1})



- ⊙ (d) **Key concept** For calculation of $\text{C}\equiv\text{C}$ bond energy, first calculate dissociation energy of C_2H_2 .



Addition of Eqs. (ii), (iii) and (iv) gives Eq. (i)

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -225 + 1410 + 330 = 1515 \text{ kJ} \end{aligned}$$

$$\Delta H = 2\text{BE}_{(\text{C}-\text{H})} + \text{BE}_{(\text{C}\equiv\text{C})}$$

$$1515 = 2 \times 350 + \text{BE}_{(\text{C}\equiv\text{C})}$$

$$\text{BE}_{(\text{C}\equiv\text{C})} = 1515 - 700 = 815 \text{ kJ mol}^{-1}$$

9.1

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25°C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = -w = p_{\text{ex}}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

9.2

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{\text{ex}}(8) = 8 \text{ litre-atm}$

9.3

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solution

$$\begin{aligned} \text{We have } q &= -w = 2.303 \text{ nRT} \log \frac{V_f}{V_s} \\ &= 2.303 \times 1 \times 0.8206 \times 298 \times \log \frac{10}{2} \\ &= 2.303 \times 0.8206 \times 298 \times \log 5 \\ &= 2.303 \times 0.8206 \times 298 \times 0.6990 \\ &= 393.66 \text{ L atm} \end{aligned}$$

- 10 If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1} . Calculate the internal energy change, when

1 mol of water is vapourised at 1 bar pressure and 100°C .

- (i) The change $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

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

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$$\begin{aligned} \Delta U &= 41.00 \text{ kJ mol}^{-1} - 1 \\ &\quad \times 8.3 \text{ J mol}^{-1}\text{K}^{-1} \times 373 \text{ K} \\ &= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1} \\ &= 37.904 \text{ kJ mol}^{-1} \end{aligned}$$

- 11 A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K.

$$\Delta_{\text{vap}} H^\ominus \text{ for water}$$

$$\text{at } 298\text{K} = 44.01 \text{ kJ mol}^{-1}$$

We can represent the process of evaporation as



No. of moles in 18 g $\text{H}_2\text{O}(l)$ is

$$= \frac{18 \text{ g}}{18 \text{ g mol}^{-1}} = 1 \text{ mol}$$

$$\begin{aligned} \text{Heat supplied to evaporate 18g water at } \\ 298 \text{ K} &= n \times \Delta_{\text{vap}} H^\ominus \\ &= (1 \text{ mol}) \times (44.01 \text{ kJ mol}^{-1}) \\ &= 44.01 \text{ kJ} \end{aligned}$$

(assuming steam behaving as an ideal gas).

$$\Delta_{\text{vap}} U = \Delta_{\text{vap}} H^\ominus - p\Delta V = \Delta_{\text{vap}} H^\ominus - \Delta n_g RT$$

$$\begin{aligned} \Delta_{\text{vap}} H^\ominus - \Delta n_g RT &= 44.01 \text{ kJ} \\ &\quad - (1)(8.314 \text{ JK}^{-1}\text{mol}^{-1})(298\text{K})(10^{-3} \text{ kJ J}^{-1}) \end{aligned}$$

$$\begin{aligned} \Delta_{\text{vap}} U^\ominus &= 44.01 \text{ kJ} - 2.48 \text{ kJ} \\ &= 41.53 \text{ kJ} \end{aligned}$$