

Unit 5: Energetics of a Chemical Reactions

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$6 \text{C}(\text{s}) + 6 \text{H}_2(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}), \Delta H = -1169 \text{ kJ mol}^{-1}$	46

Unit 5: Energetics of a Chemical Reactions

Syllabus

- ☐ Introduction, unit of energy
- ☐ Some thermodynamical terms: system, surrounding, boundary, universe
different types of system, state function, state variables and internal energy
- ☐ Exchange of energy between the system and surrounding
- ☐ Different types of thermodynamic process
- ☐ The first law of thermodynamics
- ☐ Sign convention of heat and work
- ☐ Enthalpy, enthalpy change in chemical reactions
- ☐ Hess's law of constant heat summation
- ☐ Heat of neutralization, heat of solution, heat of combustion, heat of vapourization, heat of formation and bond energy (Solving related numerical problems)

Some important terms, concepts and formulae

1. Properties of a thermodynamic system that is independent of the quantity of the matter is called intensive property e.g. Density, Temperature etc.
2. Properties of a system that depends upon quantity of matter present in the system is called extensive property. e.g. Enthalpy, entropy.
3. The sum of all kinds of energy associated with a system is called it's internal energy (E).
4. The total heat content of a system is called it's enthalpy (H).
5. Enthalpy is related to internal energy.
$$\Delta H = \Delta E + P\Delta V \dots \dots \dots (i) \text{ and}$$
$$\Delta H = \Delta E + \Delta nRT \dots \dots \dots (ii)$$
6. Hess's law of constant heat summation states that the total amount of heat evolved or absorbed during a chemical change is same whether the reaction is carried out in a single step or in a multiple steps.
7. According to first law of thermodynamics, "Energy can neither be created nor destroyed."
8. Those thermodynamic functions that depends only upon the state of a system and are independent of the path followed are called state functions. e.g. Enthalpy, Entropy.
9. Thermodynamic functions that depends only upon the state of the system are called state functions.
10. Enthalpy of reaction (ΔH) = Sum of enthalpies of products – Sum of enthalpies of reactants = $\Sigma \Delta H$ (Products) – $\Sigma \Delta H$ (Reactants)

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

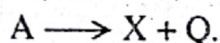
Subject Matter

Very Short Questions-Answers

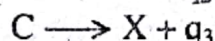
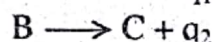
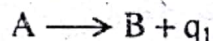
Q.1. State Hess's law of constant heat summation.

Ans: This law was stated by G.H. Hess in 1840. It states that "the amount of heat evolved or absorbed in a given chemical reaction, is always the same, regardless of whether the process takes place in a single step or in a series of steps."

Suppose, Q amount of heat is evolved when the reactant A changed to product X , i.e.



Again, the same product X was obtained from the same reactant A , but this time the reaction was completed in three different steps, i.e.



Where, q_1 , q_2 and q_3 are heat evolved in each elementary steps. Then according to Hess's law,

$$Q = q_1 + q_2 + q_3$$

Q.2. Define First law of thermodynamics.

Ans: First law of thermodynamics is also called the law of conservation of energy. It states that "total energy of the universe remains constant". or "Energy can neither be created nor be destroyed but can be transferred from one form to another form".

Mathematically,

$$q = \Delta E + W$$

Where,

q = amount of heat supplied to the system

ΔE = change in its internal energy

W = Work done on the system

Q.3. Point out the limitations of 1st law of thermodynamics?

Ans: The limitations of First law of thermodynamics are as follows:

- (a) The first law of thermodynamics does not explain the direction of flow of heat.
- (b) It also fails to tell us anything about the efficiency of the process, i.e. it does not explain the extent of conversion of heat into work.
- (c) It does not explain the feasibility of a process.

Q.4. Define enthalpy.

Ans: Enthalpy is defined as total energy content of a system and is given as sum total of the internal energy and pressure volume work, i.e.

$$H = E + PV$$

or, $\Delta H = \Delta E + P \Delta V$ at constant pressure

Where, ΔH = change in enthalpy

ΔE = change in Internal energy

$P \Delta V$ = pressure volume work.

Q.5. Derive the relationship between enthalpy change and entropy change on the basis of first law of thermodynamics.

Ans: According to first law of thermodynamics,

$$H = E + PV$$

Where,

H = Enthalpy of the system

E = Internal energy

PV = Work

Now, if the enthalpy of the system is changed to H_2 at constant pressure then,

$$\Delta H = H_2 - H_1$$

If H_1 and H_2 are initial and final enthalpy of a system with E_1 and V_1 initial internal energy and volume while E_2 and V_2 final internal energy and volume, then,

$$\begin{aligned}\Delta H &= (E_2 + PV_2) - (E_1 + PV_1) \\ &= E_2 + PV_2 - E_1 - PV_1 \\ &= E_2 - E_1 + PV_2 - PV_1 \\ &= (E_2 - E_1) + P(V_2 - V_1)\end{aligned}$$

$$\therefore \Delta H = \Delta E + P \Delta V$$

Q.6. Differentiate between enthalpy and internal energy.

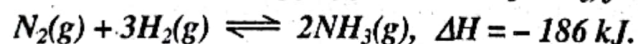
Ans: Two differences between enthalpy and internal energy are as follows:

Enthalpy	Internal energy
1. The energy stored within a system that is available for conversion into heat is called enthalpy of the system.	1. Every system has some definite amount of energy stored in it, called the internal energy.
2. Enthalpy change of a system is heat evolved or absorbed by the system at constant pressure.	2. Internal energy change is the heat evolved or absorbed by a system at constant volume.

Q.7. What are meant exothermic and endothermic reaction?

Ans: When heat is evolved during a chemical reaction, the reaction is said to be exothermic. Similarly, if heat is absorbed during a chemical reaction, it is said to be endothermic. For exothermic reaction, enthalpy of product is less than that of reactant and for endothermic reaction, enthalpy of product is greater than that of reactant.

Q.8. Calculate the enthalpy of formation of NH_3 , from the following equation.

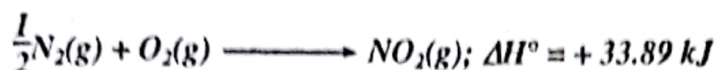
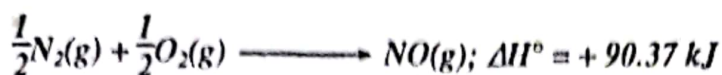


Ans: The enthalpy of formation of a compound is defined as the enthalpy change that takes place when one mole of that compound is formed from its constituent elements. In the given reaction of formation of ammonia, the enthalpy change given is for two moles of ammonia gas. Thus, the enthalpy of formation of ammonia is calculated as:

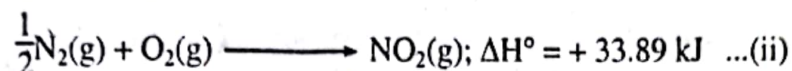
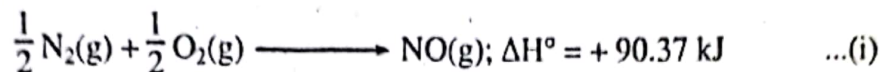
$$\begin{aligned}\Delta H_f(NH_3) &= \frac{1}{2} \times -186 \text{ kJ} \\ &= -93 \text{ kJ.}\end{aligned}$$

i.e. Enthalpy of formation of NH_3 is -93 kJmol^{-1} .

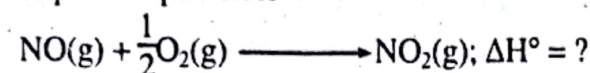
Q.9. Calculate the enthalpy of combustion of nitric oxide from the following data:



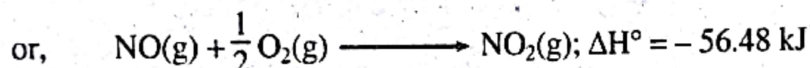
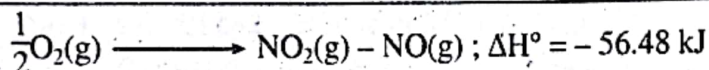
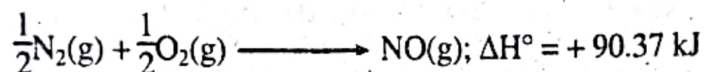
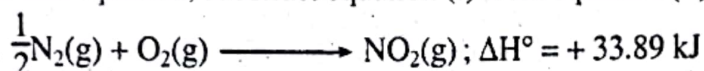
Soln: Given,



and the required equation is

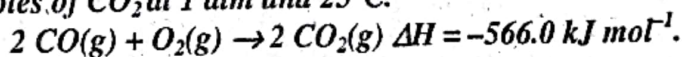


To get this equation, subtract equation (i) from equation (ii), we get,

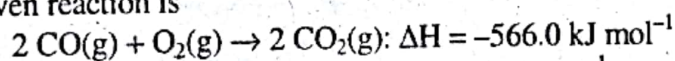


Hence, standard enthalpy of combustion of nitric oxide is -56.48 kJ .

Q.10. Calculate the change in internal energy. When 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C .



Soln: The given reaction is



Change in enthalpy of reaction (ΔH) = $-566.0 \text{ kJ mol}^{-1}$

Temperature (T) = 25°C

$$= -25 + 273 = 298 \text{ K}$$

Change in no. of moles (Δn) = $(2 - 3) = -1$

Universal gas constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Change in internal energy (ΔE) = ?

We know that,

$$\Delta H = \Delta E + \Delta n RT$$

or, $\Delta E = \Delta H - \Delta n RT$

$$= (-566.0 \times 1000) \text{ J mol}^{-1} - (-1) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= (-566000 + 2477.6) \text{ J mol}^{-1}$$

$$= -563522.43 \text{ J mol}^{-1}$$

$$= -563.53 \text{ kJ mol}^{-1}$$

\therefore The change in internal energy $\Delta E = -563.53 \text{ kJ mol}^{-1}$

Q.11. For the decomposition $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ at 950°C , ΔH is 176 kJ mol^{-1} . Assuming that the volume of the solid phase changes very little, calculate ΔE for the decomposition.

Soln: Given, $\Delta H = 176 \text{ kJ mol}^{-1}$

$$T = 950^\circ\text{C} = 950 + 273 = 1223 \text{ K}$$

$$\Delta n(\text{g}) = 1$$

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

We know,

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$\begin{aligned}\therefore \Delta E &= \Delta H - \Delta n_{(g)} RT \\ &= (176 - 1 \times 8.314 \times 10^{-3} \times 1223) \text{ kJ mol}^{-1} \\ &= 165.832 \text{ kJ mol}^{-1}\end{aligned}$$

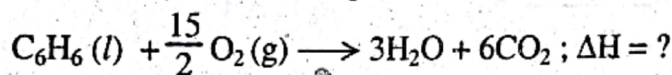
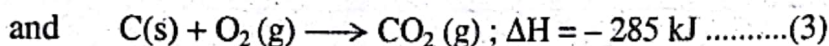
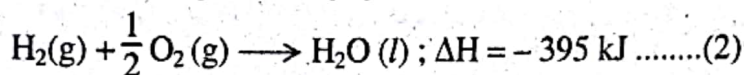
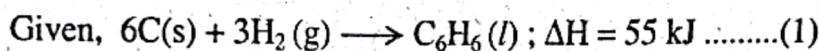
Hence, ΔE for the decomposition of $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is $165.832 \text{ kJ mol}^{-1}$.

Short Questions-Answers

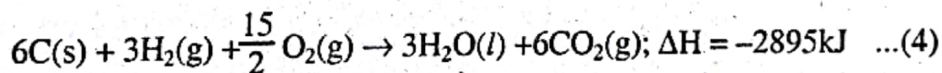
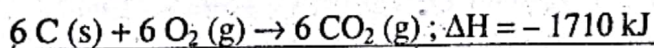
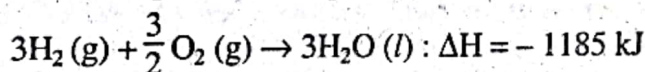
Q.12. Define enthalpy of combustion. Enthalpy of formation of benzene is 55 kJ , enthalpy of formation of water and carbondioxide are -395 kJ and -285 kJ respectively. Calculate the enthalpy of combustion of benzene.

Ans: Enthalpy of combustion is defined as the enthalpy change that takes place when one mole of a substance is completely burnt in sufficient amount of oxygen.

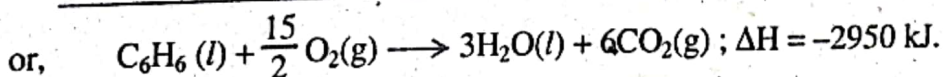
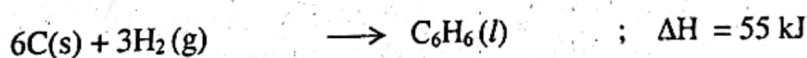
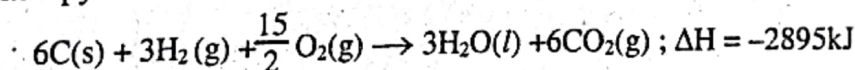
Numerical:



At first multiply equation (2) by 3, equation (3) by 6 and then add them together. We will get another equation (4) as



Now, Subtract equation (1) from equation (4) to get the desired equation and the enthalpy of combustion of $\text{C}_6\text{H}_6(\text{l})$. i.e.



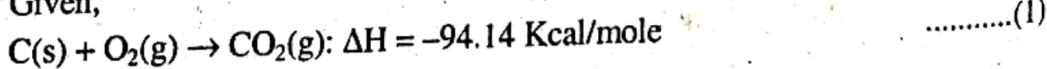
Hence, from the data given above, enthalpy of combustion of benzene is found to be $-2950 \text{ kJ mol}^{-1}$.

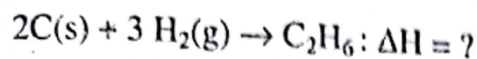
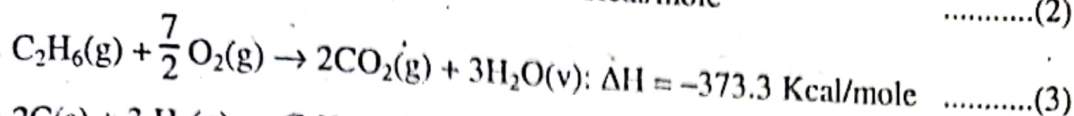
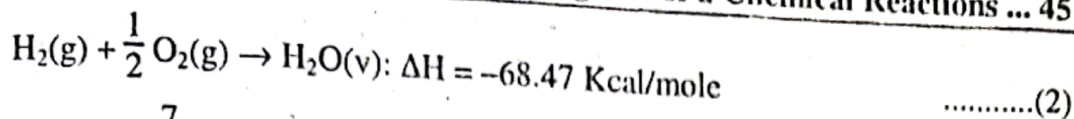
Q.13. What is meant by standard enthalpy of formation? Calculate the enthalpy of Formation of ethane at 25°C , if the enthalpies of combustion of C , H and C_2H_6 are -94.14 , -68.47 and -373.3 Kcal/mol respectively.

Ans: The standard enthalpy of formation is defined as the enthalpy change taking place during the formation of one mole of a substance from its constituent elements, all the substances being in their standard state.

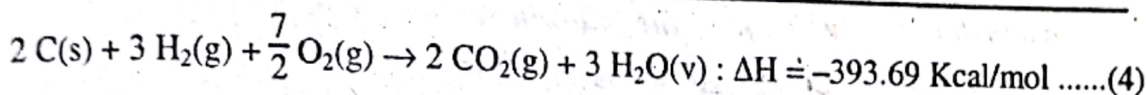
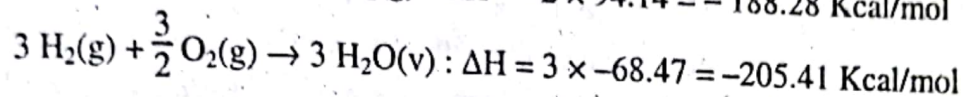
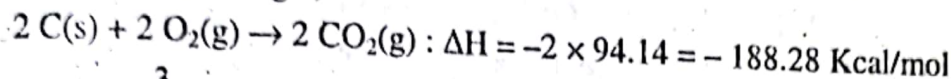
Numerical

Given,

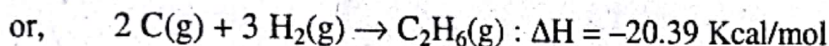
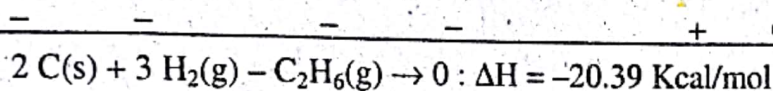
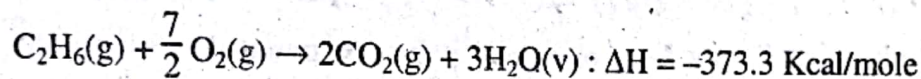
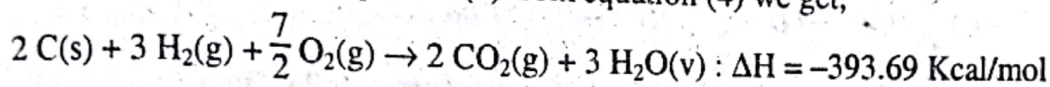




To get this equation, Multiply equation (1) by 2 and (2) by 3 and then add them together, we get,



Now, subtract equation (3) from equation (4) we get,



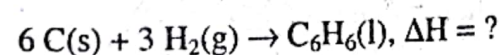
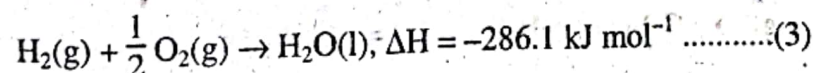
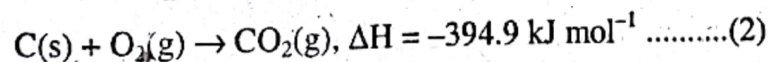
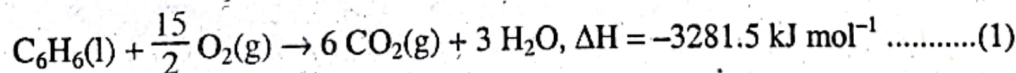
\therefore Heat of formation of ethane is -20.39 Kcal/mol .

Q.14. State and explain Hess's Law of constant heat summation. Define enthalpy of formation. Calculate the enthalpy of Formation of Benzene. The enthalpies of combustion of benzene, carbon, and hydrogen -3281.5 kJ , -394.9 kJ and -286.1 kJ per mole respectively.

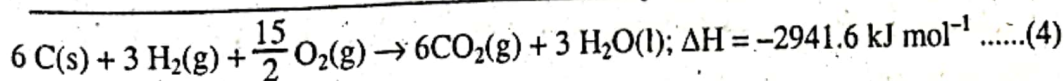
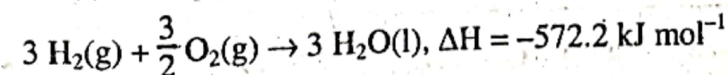
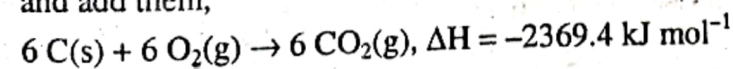
Ans: 1st part: See answer to Q.No. 1, Page No. 41.

The standard enthalpy of formation is defined as the enthalpy change taking place during the formation of one mole of a substance from its constituent elements, all the substances being in their standard state.

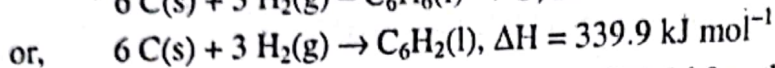
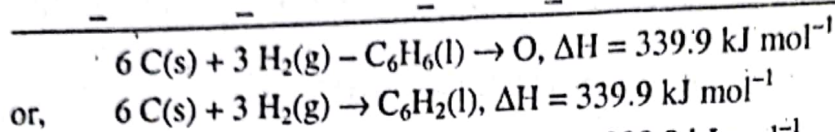
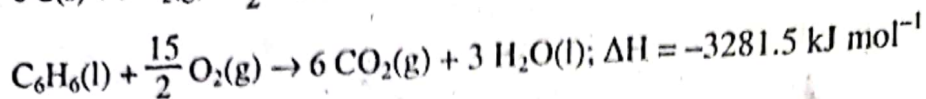
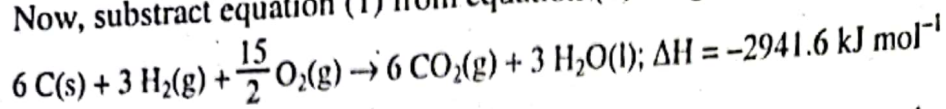
Numerical



To get this equation, at first multiply equation (2) by 6 and equation (3) by 3 and add them,

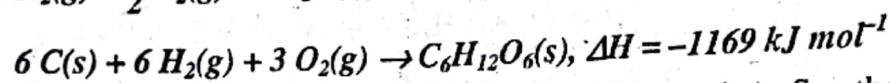
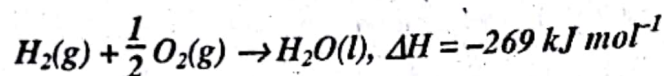
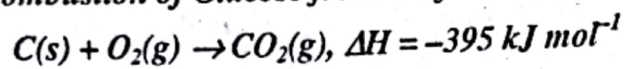


Now, subtract equation (1) from equation (4) we get,



\therefore Enthalpy of formation of benzene is $339.9 \text{ kJ mol}^{-1}$.

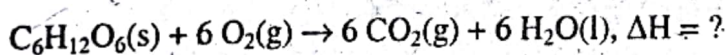
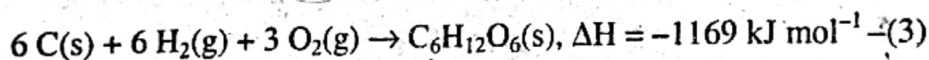
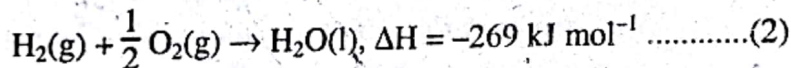
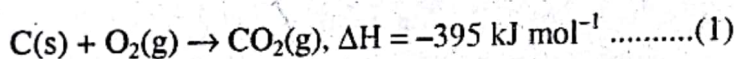
Q.15. Define Hess Law of constant heat summation. Calculate the heat of combustion of Glucose from the following data:



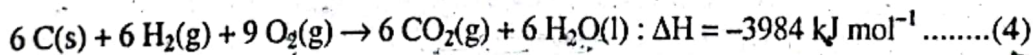
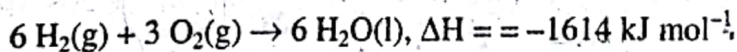
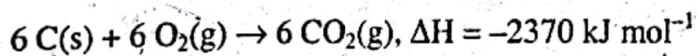
Ans: Definition of Hess's Law of constant heat summation: See the answer to Q.No. 1, Page No. 41.

Numerical

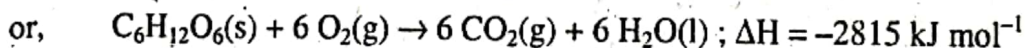
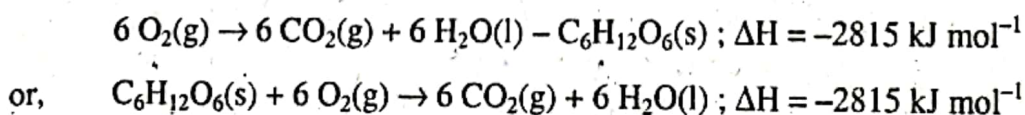
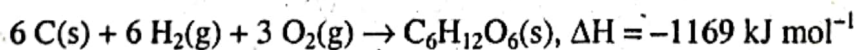
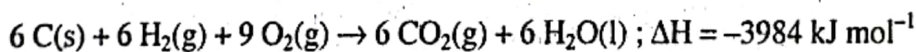
Given,



To get this equation, multiply equations (1) and (2) by 6 and then add them together.



Now, subtract equation (4) from equation (3), we get,



\therefore The heat of combustion of Glucose is $-2815 \text{ kJ mol}^{-1}$