HEAT CAPACITY AND HEAT OF REACTION

Kumud Bala

Heat capacity: The heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1°C.

Thus, if q is the amount of heat supplied to a system and as a result, if the temperature of system rises from T_1 to T_2 then the heat capacity (C) of the system is given by

$$C = \frac{q}{T2-T1} = \frac{q}{\Delta T} \qquad (i)$$

However, since the heat capacity varies with temperature, therefore, the value of C has to be considered over a very narrow temperature range. Thus, if δq is small amount of heat absorbed by a system which raises the temperature of the system by a small amount dT (say from T to T+dT) , then the heat capacity of the system will be given by

$$C = \frac{\delta q}{dT} \qquad (ii)$$

The specific heat capacity, C_s, of a substance is defined as the amount of heat required to raise the temperature of 1 gram of the substance through 1°C. If instead of 1g, 1 mole of the substance is taken, the term used is called molar heat capacity, C_m. Thus, Molar heat capacity of a substance is defined as the amount of heat required to raise the temperature of one mole of the substance through 1°C. i.e., $C_m = \frac{C}{n}$ where n is number of moles.

Example – To understand the difference between heat capacity, specific heat capacity and molar heat capacity, let us take the following example: A piece of Al metal weighing 3g requires 5.4 J of heat to raise the temperature from 298K to 300K.

Solution – Heat capacity of the piece of Al $= \frac{5.4\ J}{2K} = 2.7$ JK^{-1}

Specific heat capacity of Al $= \frac{5.4\ J}{3g \times 2K} = 0.9$Jg^{-1}K^{-1}

Molar heat capacity of Al $= \frac{5.4J}{3g \times 2K} \times 27 = 24.3$Jmol^{-1}K^{-1} (1 mole of Al =27g)

Evidently , the amount of heat, q, required to raise the temperature from T_1 to T_2 of mass m gram of a sample and having specific heat c, can be calculated from the expression q =m×c×(T_2-T_1) = m×c×ΔT

Or using the heat capacity(C), we have q=C×ΔT It is useful to remember that the specific heat capacity of water is 1cal g^{-1} K^{-1}

Types of heat capacities or molar heat capacities: Since q is not a state function and depends upon the path followed; therefore C is also not a state function. Hence, to know the value of C, the condition such as constant volume or constant pressure have to be specified which define the path. Thus, there are two types of heat capacities: (i) heat capacity at constant volume (represented by C_v), (ii) heat capacity at constant pressure (represented by C_p). The heat supplied to a system to raise its temperature through 1°C keeping the volume of the system constant is called heat capacity at constant volume. Similarly, the heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called heat capacity at constant pressure. Now, according to first law of thermodynamic,

we know that $\delta q = dU + PdV$ \qquad (iii)

$$C = \frac{dU+PdV}{dT} \qquad (iv)$$

When the volume is kept constant dV=0 and therefore equation (iv) becomes

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad (v)$$

Or for an ideal gas, this equation may simply be written as

$$C_v = \frac{dU}{dT} \qquad (vi)$$

Thus, the heat capacity at constant volume may be defined as the rate of change of internal energy with temperature at constant volume.

When pressure is constant during the absorption of heat, equation (iv) becomes

$$C_p = (\frac{\partial U}{\partial T})_p + P(\frac{\partial V}{\partial T})_p \qquad \text{(vii)}$$

Also, we know that the heat content or enthalpy of a system is given by H=U+PV. Differentiating w.r.t T at constant P, we get

$$(\frac{\partial H}{\partial T})_P = (\frac{\partial U}{\partial T})_p + P(\frac{\partial V}{\partial T})_p \qquad \text{(viii)}$$

Combining equation (vii) and (viii), we get

$$C_p = (\frac{\partial H}{\partial T})_p \qquad \text{(ix)}$$

Or for an ideal gas, the equation may simply be put in the form

$$C_p = \frac{dH}{dT} \qquad \text{(x)}$$

Thus, the heat capacity at constant pressure may be defined as rate of change of enthalpy with temperature at constant pressure.

Relationship between C_p and C_v : If the volume of the system is kept constant and heat is added to a system, then no work is done by the system. Thus, the heat absorbed by the system is used up completely to increase the internal energy of the system. Again if the pressure of the system is kept constant and heat is supplied to the system, then some work of expansion is also done by the system in addition to the increase in internal energy. Thus, if at constant pressure, the temperature of the system is to be raised through the same value as at constant volume, then some extra heat is required for doing the work of expansion. Hence $C_p > C_v$. The difference between the heat capacities of an ideal gas can be obtained by subtracting equation (vi) from (x) so we have

$$C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT} \qquad \text{(xi)}$$

But H=U+PV (by definition)

And PV= RT (for 1 mole of an ideal gas) $\therefore$ H = U + RT differentiating this equation w.r.t T, we get

$$\frac{dH}{dT} = \frac{dU}{dT} + R \qquad \text{(xii) \quad or}$$

$$\frac{dH}{dT} - \frac{dU}{dT} = R \qquad \text{(xiii)}$$

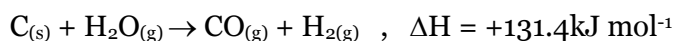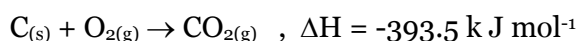Combining equation (xi) and (xiii)

$C_p - C_v = R$ (for 1 mole of an ideal gas)

Thus, C_p is greater than C_v by the gas constant R i.e., approximately 2 calories or 8.314 joules.

$C_p - C_v = nR$ (for n mole of an ideal gas)

Thermo Chemical Equation : In a thermo chemical equation, the physical states of reactants and products along with heat energy evolved or absorbed are indicated. For example-

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O (l)$, ΔH= -286kJ
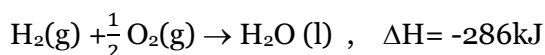
Heat of Reaction or Enthalpy of Reaction: "The amount of heat evolved or absorbed in a chemical reaction when the number of moles of the reactants as represented by the chemical equation have completely reacted is called the heat of reaction." For example:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$, ΔH = -393.5 k J mol^{-1}

$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$, ΔH = +131.4kJ mol^{-1}

Different Types of the Enthalpies of Reaction:

Enthalpy of Formation is - "The enthalpy of formation of a substance is defined as the heat change i.e., heat evolved or absorbed when 1 mole of the substance is formed from its elements under given conditions of temperature and pressure." It is usually represented by $\Delta_f H$

For example, $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta_f H$ = -74.8 kJ mol^{-1}
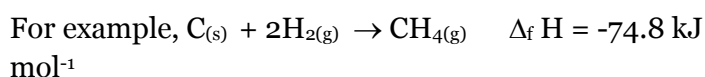
Standard enthalpy of formation of a substance is defined as the enthalpy change accompanying the formation of 1 mole of the substance in the standard state form its elements, also taken in the standard state (i.e., 298K and 1 bar pressure). It is usually
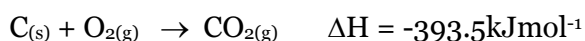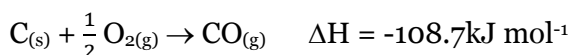
represented by $\Delta_f H^\circ$ (enthalpies of formation of all free elements in their standard state taken to be zero)

Standard enthalpy of reaction = standard enthalpies of formation of products – standard enthalpies of formation of reactants

Enthalpy of Combustion is - "The enthalpy of combustion of a substance is defined as the heat change (usually the heat evolved) when 1 mole of substance is completely burnt or oxidized in oxygen." For example

$$CH_4 + 2O_2 \rightarrow CO_{2(g)} + H_2O_{(l)} \quad \Delta H = -890.3 kJ\ mol^{-1}$$
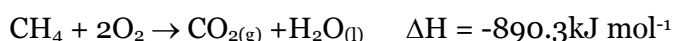
Combustion is always an exothermic reaction. Therefore $\Delta_c H$ must be negative for the combustion reactions. If the combustion of a substance is incomplete or is carried in the limited supply of air or oxygen, then the energy evolved does not represent enthalpy of combustion. For example,

$$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \quad \Delta H = -108.7 kJ\ mol^{-1}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -393.5 kJmol^{-1}$$

Complete oxidation means oxidation to CO_2 and not to CO. Hence, heat of combustion of carbon is $393.5 KJ\ mol^{-1}$. Standard enthalpy of combustion is the amount of heat evolved when one mole of the substance under standard condition (298K, 1 bar pressure) is completely burnt to form the products also under standard condition. It is represented by $\Delta_c H^\circ$

Combustion of Foods and Fuels: We know that a fuel such as wood, petrol and kerosene etc., undergoes combustion in a machine or furnace to produce heat energy for the running of machines. Similarly for the working of human machines, we eat carbohydrates, fats etc. in the form of food. The carbohydrates are first decomposed in our body by the enzymes to form glucose which then undergoes oxidation by the oxygen that we inhale to produce energy.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)} \quad \Delta H^\circ = -2802.0 kJmol^{-1}$$
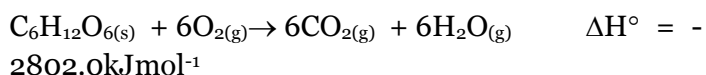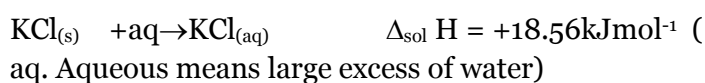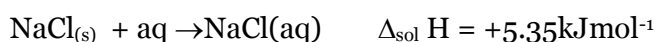
This oxidation reaction is usually called combustion of food. Different fuels and foods produce different amounts of heat on combustion. These are usually expressed in terms of their calorific values. These are defined as "the calorific value of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food". Thus, according to the above reaction, 1 mole of glucose, i.e., 180g of glucose produce heat = $2802 kJmol^{-1}$. Hence, calorific value of glucose $= \frac{2802}{180}$ $= 15.56 kJg^{-1}$ A normal person needs about 3000kcal (about 12000 – 13000 kJ) per day. S.I. unit is kJg^{-1}

Calorific Values of Food and Fuel

Food	Calorific value (kJg⁻¹)	Fuel	Calorific value (kJg⁻¹)
Curd	2.5	Wood	17
Milk	3.2	Charcoal	33
Egg	7.3	Kerosene oil	48
Meat	12.0	Fuel oil	45
Honey	13.3	Butane (LPG)	55
Ghee	37.6	Hydrogen	150

Enthalpy of solution: It may be define as "The change in enthalpy or heat energy when one mole of a substance is dissolved in such a large excess of the solvent at a given temperature that the further addition of the solvent does not produce any more heat energy change." For example,

$$NaCl_{(s)} + aq \rightarrow NaCl(aq) \quad \Delta_{sol} H = +5.35 kJmol^{-1}$$

$$KCl_{(s)} + aq \rightarrow KCl_{(aq)} \quad \Delta_{sol} H = +18.56 kJmol^{-1}$$ (aq. Aqueous means large excess of water)

Enthalpy of Hydration: "The change in enthalpy or heat energy when one mole of anhydrous salt changes to a hydrated salt by combining with specified number of moles of water." For example,
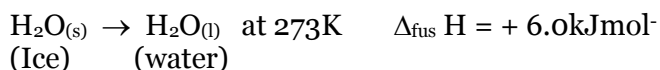
$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4.5H_2O \quad \Delta_{hyd} H = -78.2 kJmol^{-1}$$
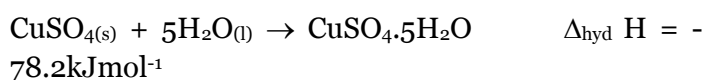
Phase Transition: Solid, liquid and gas are the three phase of a substance. When substance changes from one phase to another phase, it evolves or

absorbs energy due to inter particle forces of attraction. For example, Solid→liquid→gas

Enthalpy Changes of the Different Phases :

Enthalpy of fusion: "The change in enthalpy or heat energy when one mole of a solid at its melting point change to its liquid state." For example,

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ at 273K $\quad \Delta_{fus} H = + 6.0kJmol^-$
(Ice) (water)

$NaCl_{(s)} \rightarrow NaCl_{(l)}$ $\quad\quad \Delta_{fus} H = + 29.0kJ\ mol^{-1}$

Enthalpy of fusion of NaCl is more than $\Delta_{fus} H$ of ice due to more attractive forces in $NaCl_{(s)}$

Enthalpy of Vaporization: "The change in enthalpy or heat energy when one mole of a liquid at its boiling point changes to its gaseous state." For example,

$H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\quad\quad \Delta_{vap} H = +40.7kJ\ mol^{-1}$

As condensation is reverse of vaporization, the enthalpy of condensation has the same value as the enthalpy of vaporization but has opposite sign. Thus,

$H_2O_{(g)} \rightarrow H_2O_{(l)}$, $\quad\quad \Delta_{cond} H = -40.7kJ\ mol^{-1}$

Enthalpy of Sublimation: Enthalpy of sublimation of a substance is the enthalpy change accompanying the conversion of one mole of a solid directly into vapour phase at a given temperature below its melting point. For example,

$I_{2(s)} \rightarrow I_{2(g)}$, $\quad\quad \Delta_{sub} H = + 62.39kJ\ mol^{-1}$

It may be pointed out that sublimation is nothing but fusion and vaporization carried out in one step, i.e., $\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap}H$

Enthalpy of Atomization (bond enthalpies): When a bond is formed between two atoms, a certain amount of energy is needed to break the bond. This is known as bond dissociation energy or bond enthalpy or enthalpy of atomization. It may be defined as the amount of energy required to break one mole bonds of a particular type between two atoms in the gaseous state of a substance. For example,
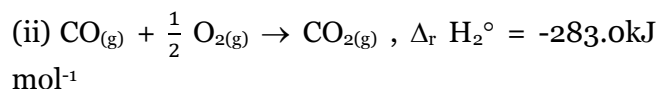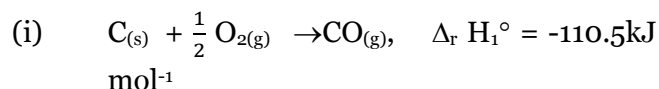
$H_{2(g)} \rightarrow 2H_{(g)}$, $\Delta_a H= 435.0kJ\ mol^{-1}$

Hess's Law of Heat Summation: G.H. Hess, a Russian chemist, in1840, gave a law about the heat of reaction on the basis of experimental observation. This law is known after his name as Hess's law. It states as the total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place in one step or in a number of steps.

Basis of Hess's law: Hess's law follows from the fact that enthalpy is a state function, i.e., enthalpy change depends only on the initial state (i.e., enthalpy of the reactants) and the final state (i.e., enthalpy of the products) and does not depend upon the path followed. For example, when carbon(graphite) burns to carbon dioxide directly in one step, 393.5kJ mol^{-1} of heat produced, i.e.,

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$, $\quad \Delta_r H° = -393.5kJ\ mol^{-1}$

If carbon burns to form carbon monoxide first which then burns to form carbon dioxide, the heats evolved in the two steps are as follows:-

(i) $C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$, $\quad \Delta_r H_1° = -110.5kJ\ mol^{-1}$

(ii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta_r H_2° = -283.0kJ\ mol^{-1}$

Thus, the total heat evolved in the two steps will be $\Delta H° = (- 110.5) + (-283.0) = -393.5kJ\ mol^{-1}$ which is the same when the reaction takes place directly in one step.

Theoretical Proof of Hess's law : Consider the general reaction A→D. Suppose the heat evolved in this reaction is Q joules. Now, if the same reaction takes place in three steps as follows :- A → B → C→ D, and the heats evolved in these three steps are q_1 , q_2 , q_3 joules respectively. Then, the total heat evolved = $q_1 + q_2 + q_3 = Q'$ joules (say). According to Hess's law, we must have Q =Q'. If Hess's law were not correct, then either Q' < Q or Q' > Q . Suppose Q' > Q, this means that if we go from A to D in a number of steps, the heat evolved is more than the heat absorbed when we return from D to A directly in one step. Thus, when the cyclic process is completed, Q-

Q' joules of heat is produced. Thus, by repeating the cyclic process a number of times, a large amount of heat can be created. This is, however, against the law of conservation of energy. Hence, Q must be equal to Q', i.e., Hess's law must be correct.

Application of Hess's law: The most important application of Hess's Law is in the calculation of heat changes for those reactions for which experimental determination is not possible. The calculations are based upon the following consequence of Hess's law:-

The thermo chemical equation can be treated as algebraic equations which can be added, subtracted, multiplied or divided. A few important applications of Hess's law are given below:-

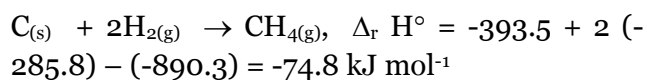**1 .Calculation of Enthalpy of Formation:-** the enthalpies of formation of many compounds cannot be determined experimentally. These are calculated by the application of Hess's law.

Example – Calculate the enthalpy of formation of methane (CH_4) from the following data:

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta_r H° = -393.5kJ$ mol^{-1}

(ii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta_r H° = -285.8kJ\ mol^{-1}$

(iii) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta_r H° = -890.3kJ$ mol^{-1}

Solution : we aim at $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta_f H° = ?$

Multiplying equation (ii) with 2, adding to (i) and then subtracting equation (iii) from the sum, we get

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$, $\Delta_r H° = -393.5 + 2 (-285.8) - (-890.3) = -74.8$ kJ mol^{-1}

Hence , enthalpy of formation of methane is $\Delta_f H° = -74.8kJ\ mol^{-1}$

2. Calculation of Enthalpy of Allotropic Transformation: Elements like carbon and sulphur exit in   different allotropic forms. The change of one form to the other involves a very small amount of heat and is a very slow process.

Hence, the experimental determination of heat changes for such transformations is very difficult. These are calculated by the application of Hess's law as illustrated by the example given below:-

Example Calculate the enthalpy change accompanying the transformation of C (graphite) to C (diamond). Given that the enthalpies of combustion of graphite and diamond are 393.5 and 395.4kJmol^{-1} respectively.

Solution: We are given

(i) $C(graphite) + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_c H° = -393.5kJ\ mol^{-1}$

(ii) $C(diamond) + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_c H° = -395.4kJ\ mol^{-1}$

We aim at C(graphite) $\rightarrow$ C(diamond), $\Delta_{trans} H° = ?$

Subtracting equation (ii) from (i), we get C(graphite) – C(diamond) $\rightarrow$ 0;

$\Delta_r H° = -393.5 - (-395.4) = +1.9kJ\ mol^{-1}$ or

C(graphite) $\rightarrow$ C(diamond); $\Delta_{trans} H° = +1.9kJ\ mol^{-1}$

3.   Calculation of the Enthalpy of Hydration: The experimental determination of the enthalpy of hydration is almost impossible. However, it can be easily calculated using Hess's law as illustrated by the following example:
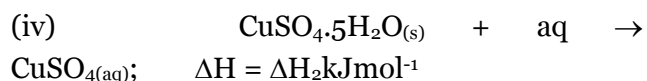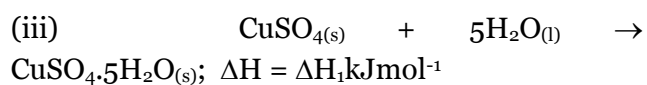
Example: Calculate the enthalpy of hydration of anhydrous copper sulphate ($CuSO_4$) into hydrated copper sulphate ($CuSO_4.5H_2O$). Given that the enthalpies of solutions of anhydrous copper sulphate and hydrated copper sulphate are -66.5 and +11.7kJ mol^{-1} respectively.

Solution: We are given

(i) $CuSO_4(s) + aq \rightarrow CuSO_4(aq)$; $\Delta_{sol} H = -66.5kJ\ mol^{-1}$

(ii) $CuSO_4.5H_2O_{(s)} + aq \rightarrow CuSO_4(aq)$; $\Delta_{sol} H = +11.7kJ\ mol^{-1}$

We aim at $CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4.5H_2O_{(s)}$; $\Delta_{hyd} H$ = ?

Equation (i) can be written in two steps as

(iii) $CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4.5H_2O_{(s)}$; $\Delta H = \Delta H_1 kJmol^{-1}$

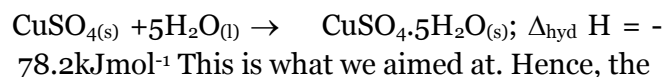(iv) $CuSO_4.5H_2O_{(s)} + aq \rightarrow CuSO_{4(aq)}$; $\Delta H = \Delta H_2 kJmol^{-1}$

According to Hess's law $\Delta H_1 + \Delta H_2 = -66.5$ kJmol^{-1}

Further, equation (ii) and (iv) are same. $\therefore$ $\Delta H_2 = + 11.7$ kJmol^{-1}

Putting this value above, we get $\Delta H_1 + 11.7 = -66.5$kJmol^{-1} or

$\Delta H_1 = -66.5 - 11.7 = -78.2$kJ mol^{-1} Thus, equation (iii) may be written as

$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow$ $CuSO_4.5H_2O_{(s)}$; $\Delta_{hyd} H = -78.2$kJmol^{-1} This is what we aimed at. Hence, the

required value of the enthalpy of hydration is $\Delta_{hyd} H = -78.2$ kJ mol^{-1}.

1. **Predicting the Enthalpy Change for any Reaction**: Hess's law can be applied to predict the enthalpy change for any reaction from the enthalpy changes of certain other reactions.

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Answers to Science Quiz in June'17

Kumud Bala

1. (A)   2. (C)   3. (B)   4. (C)   5. (A)   6. (A)   7 (A)   8. (B)   9. (C)   10. (A)
11 (A)   12. (B) 13. (C)   14. (D)   15. (C)   16. (C)   17. (A)   18. (D)   19. (C)

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I am impressed with the urgency of doing. Knowing is not enough, use it; being willing is not enough, do it.

- **Leonardo da Vinci**