

11

THERMOCHEMISTRY

Q1: Define the following terms: Thermochemistry, joule, calorie, exothermic reactions, endothermic reactions, system surrounding and boundaries of the system.

Ans: Thermochemistry: (ETEA: 2005)

"The branch of chemistry which deals with the study of amount of heat evolved or absorbed during a chemical reaction is called thermochemistry."

Joule:

The SI unit of energy is joule. "The energy expended when one Newton force, displaces a body through one meter is called one joule energy."

Calorie:

One calorie is the amount of heat, energy needed to raise the temperature of one gram of water from 14.5°C – 15.5°C.

$$1 \text{ Cal} = 4.18 \text{ joule}$$

$$1 \text{ K-Cal} = 1000 \text{ Cal}$$

Thermochemical Reactions:

"Chemical reactions during which heat is either evolved or absorbed are called thermochemical reactions." Thermochemical reactions are of two types:

1. Exothermic reactions
2. Endothermic reactions

1. Exothermic Reaction:

"Exo = outside, therm = heat"

"Chemical reactions during which heat is given out are called exothermic reactions." The released energy is represented by negative sign.

Examples:

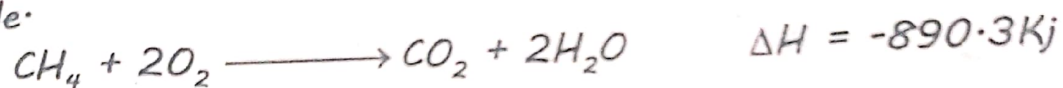


$$\Delta H = -296.6 \text{ KJ}$$



$$\Delta H = -92.3 \text{ KJ}$$

During exothermic reactions energy is released because the bonds in reactant molecules are broken and new bonds between atoms are formed to form product molecules. For example; burning of methane gas $[CH_4]$ in the presence of oxygen, produces water, carbon dioxide and energy. During this reaction old existing bonds in CH_4 and O_2 molecules are broken which needs energy [endothermic reaction] and new bonds are formed between hydrogen and oxygen to make water, and between carbon and oxygen to make carbon dioxide. This is exothermic reaction. In exothermic reactions the total energy of the products is less than the total energy of the reactants so products formed are stable.



Endothermic Reactions:

"Endo" mean "inside" and "therm" means "heat".

"Chemical reactions during which heat is absorbed from the surrounding are called endothermic reactions." The absorbed heat is represented by positive sign, $\Delta H = +ive$.

Examples:



$$\Delta H = 285.5KJ$$



$$\Delta H = 530KJ$$

System:

"A material or collection of materials which is under study is called a system." (OR)

"Any part of the universe which is under study is called system."

Surrounding:

"Everything outside the system is called surrounding."

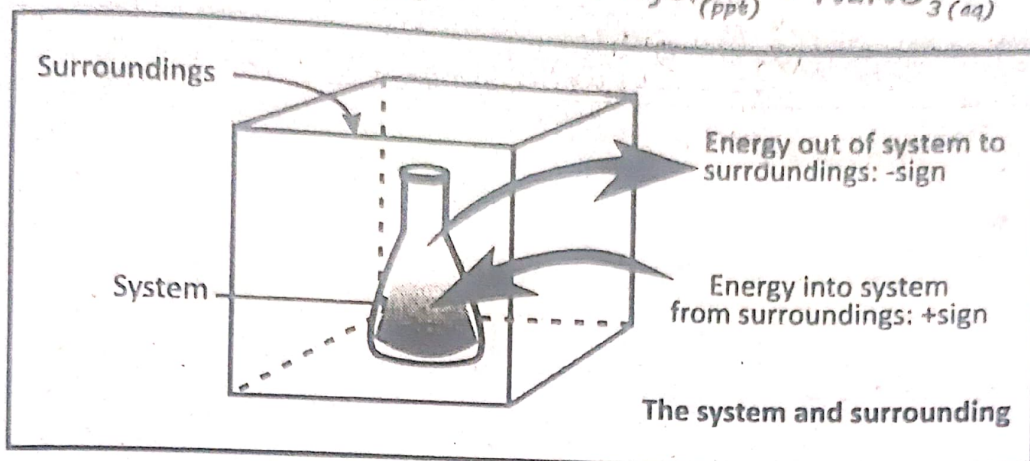
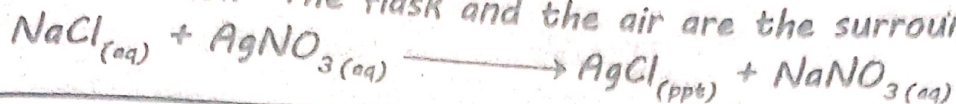
Boundary of the System:

"The surface which separate, the system from surrounding is called boundary of the system."

For Example:

If boiling water in a beaker is under observations, then boiling water is the system, beaker and the heat source is surrounding. Consider the reaction between $NaCl$ and $AgNO_3$ solution, which can be called a sys-

tem under observation. The flask and the air are the surroundings.



Thermodynamics:

"The study of flow of heat or any other form of energy into or out of the system is called thermodynamics."

Q2: Explain the following terms: state of the system, state function, path function and internal energy of the system.

Ans: State of the System:

(ETEA: 2013,17,19, BISE Mardan + Bannu 2018)

"The condition of a system is called state of a system." For example: the properties such as temperature, pressure and volume describe the state of a system. There are two types of state;

1. Initial state

2. Final state

1. Initial State: "The state of a system before a change has taken place is called initial state."

2. Final State: "The state of a system after it undergoes any change is called final state of the system."

The difference between the initial and final state of a system is called change in state and is denoted / represented by delta $[\Delta]$.

Change in state = Final state - Initial state

Change in temperature = $\Delta T = T_2 - T_1$

Change in volume = $\Delta V = V_2 - V_1$

Change in pressure = $\Delta P = P_2 - P_1$

State Function: (BISE Bannu 2018)

"A macroscopic property of the system which depends upon initial and

final states of a system and is independent of the path followed by the system is called state function." For example; temperature, pressure, volume and enthalpy.

$$\text{Change in temperature} = \Delta T = T_2 - T_1$$

$$\text{Change in pressure} = \Delta P = P_2 - P_1$$

$$\text{Change in volume} = \Delta V = V_2 - V_1$$

$$\text{Change in enthalpy} = \Delta H = H_2 - H_1$$

$$\text{Change in energy} = \Delta E = E_2 - E_1$$

Path Function / Exact Function:

"Properties of the system which depends upon the path followed by the system are called path functions / exact functions." Example are: heat and work done.

Actually these are not the properties of a system but simply represent mode of transfer of heat from the system to the surrounding and vice versa. Thus heat and work depend on the manner in which their change is brought about and are not state functions.

Internal Energy:

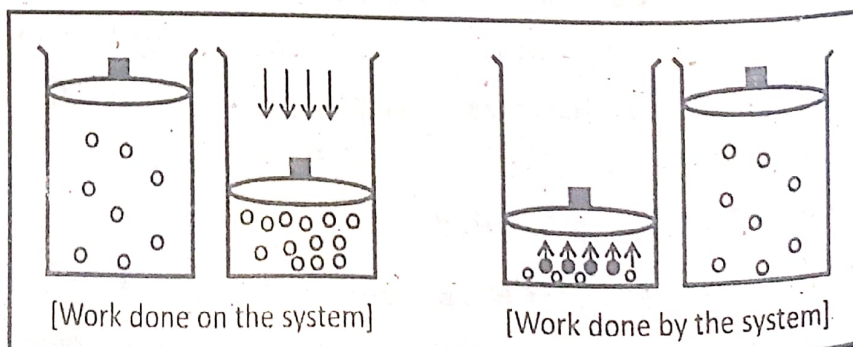
Internal energy is a definite energy contained by a system. Internal energy is the sum of kinetic energy and potential energy of all the particles of a system. Internal energy depends on the motion of the molecules such as translational, vibrational and rotational, their inter-molecular and intra-molecular forces. Energy of the system changes because energy is transferred into or out of the system.

Internal Energy of the System Increases when:

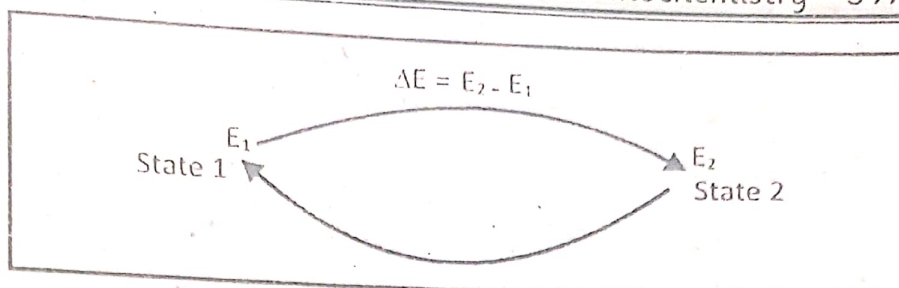
1. Heat is added to the system
2. Work is done on the system by the surrounding

Internal Energy of the System Decreases when:

1. When a system loses heat to the surrounding
2. System do work on the surrounding



The two ways of transferring energy from the system to the surroundings and from the surrounding



to the system are heat and work. We cannot determine / measure the exact internal energy (E) of the system but change in internal energy (ΔE) can be determined experimentally. Internal energy is a state function and depends on, initial and final states of the system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$\Delta E = E_2 - E_1$$

An increase in internal energy of a chemical system has three possible results:

1. Increase in internal energy of a system can increase the temperature of the system by increasing the kinetic energy of molecules.
2. Increase in internal energy can result in a chemical reaction. When increase in internal energy is sufficient to break the bonds, a chemical reaction takes place.
3. Increase in internal energy of a system can result in phase change of a system. For example melting and evaporation can occurs.

Q3: State and explain 1st law of thermodynamics.

Ans. 1st Law of Thermodynamics: (ETEA: 2013,15,18)

Josiah Willard Gibbs in 1873, on the basis of experimental work, stated the 1st law of thermodynamics. It is simply the law of conservation of energy, and can be stated in a number of ways.

1. Energy of the universe remains constant.
2. Total energy of the system and surrounding always remains constant.
3. Energy can neither be created nor destroyed, although it can be changed from one form to another form [universe = system + surrounding].

Explanation:

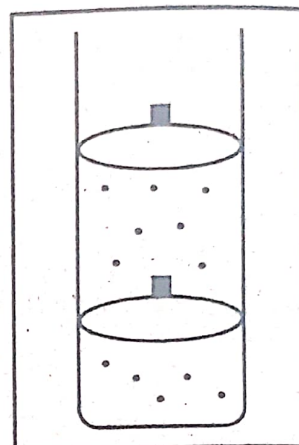
An electric bulb converts electric energy into light energy. The potential energy of the falling ball is converted into kinetic energy.

Energy is exchanged between the system and surroundings in the form of heat and work. A system may lose energy to the surroundings in

the form of heat and at the same time, the same amount of energy is absorbed by the surroundings. Hence the amount of energy lost by the system is equal to the energy gained by the surroundings.

Lets consider the gaseous system, having gas in a cylinder. The cylinder has a moveable piston. The internal energy of the system is " E_1 ". The heat " q " is supplied to the system / gas. The internal energy of the system becomes " E_2 " change in internal energy is given as,

$$\Delta E = E_2 - E_1$$



Consider an amount of heat " q " is gained by a system. This heat changes the internal energy and also performs some work (w), against the surroundings. Mathematically;

The 1st law of thermodynamics can be written as,

$$q = \Delta E + w \quad \text{--- (i)}$$

$$\text{OR } \Delta E = q - w \quad \text{--- (ii)}$$

Equation (i) shows that, change in internal energy of a system is the sum of the heat exchanged " q " between the system and the surrounding and the work done " w " on / by the system.

Sign Conventions for Work and Heat:

Process	Sign
Work done by the system on the surrounding	$w = -\text{ive}$
Work done on the system by the surrounding	$w = +\text{ive}$
Heat absorbed by the system from the surrounding	$q = +\text{ive}$
Heat absorbed by the surrounding from the system	$q = -\text{ive}$

(OR)

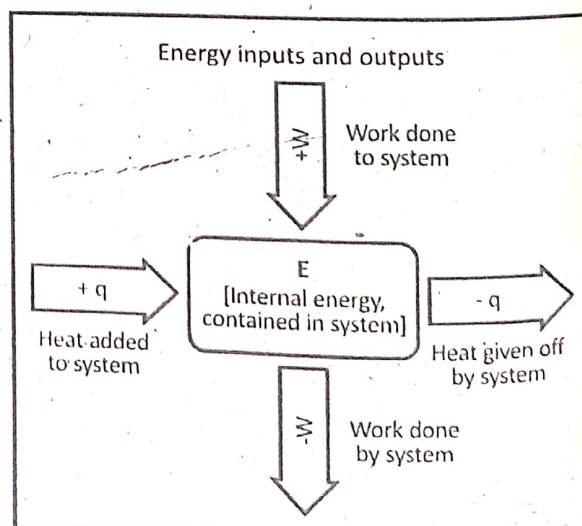
$w = \text{ive}$ when work is done by the system

$w = +\text{ive}$ when work is done on the system

$q = -\text{ive}$ when system evolve heat

$q = +\text{ive}$ when heat is added to the system.

The 1st law of thermodynamic states



that, the change in internal energy for the system (ΔE) is equal to the amount of heat (q) provided to the system minus the amount of work done (w) by the system.

Q4: Explain pressure - volume work or prove that $w = P\Delta V$

Ans: Pressure - Volume Work: (ETEA: 2010)

"The only type of work in thermodynamics is the work of expansion or pressure - volume work. This is the work done when a system expands against an opposing pressure. Consider a gas is enclosed in a cylinder of cross sectional area " A " having frictionless, light and moveable piston. The pressure on the piston is equal to " P ".

We know that,

$$P = \frac{F}{A} \quad \text{_____ (i)}$$

$$F = PA \quad \text{_____ (ii)}$$

When the system do some work, it will push the piston against the external pressure " P ". Its volume will increases from V_1 to V_2 i.e. volume will change. We know that,

Work = force $\times$ distance

$$W = F \times \Delta l \quad \text{_____ (iii)}$$

Putting the value of " F " from equation (ii) into equation (iii)

$$W = PA\Delta L \quad \text{_____ (iv)}$$

$$\text{As } V = l \times l \times l$$

$$V = A \times l$$

$$\text{As } A = l \times l$$

$$\Delta V = A\Delta L$$

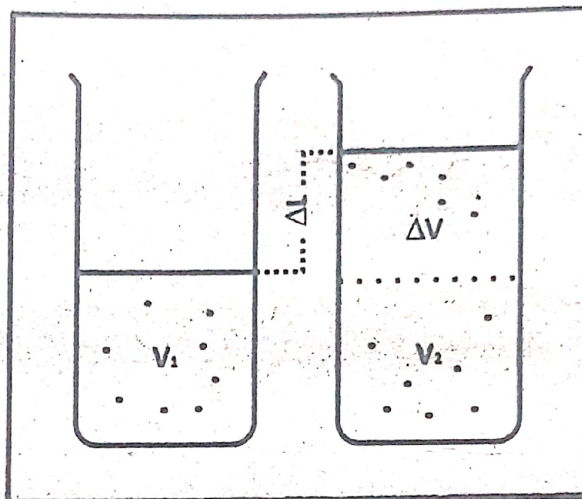
Now putting the value of $A\Delta L = \Delta V$ in equation (iv)

$$W = P\Delta V \quad \text{_____ (v) (hence proved)}$$

This is called pressure - volume work / work of expansion. Work done will be positive when it is done on the system and will be negative when it is done by the system.

$$W = P\Delta V \rightarrow \text{work done on the system}$$

$$W = -P\Delta V \rightarrow \text{work done by the system}$$



Putting the value of work done in 1st law of thermodynamics i.e.

$$\Delta E = q - W$$

$$\Delta E = q - (P\Delta V)$$

$$\Delta E = q - P\Delta V$$

Process at Constant Volume, Prove that $\Delta E = q_v$:

Consider a gas is enclosed in a cylinder having a fixed piston. When heat is added to the system, its volume will remain constant ($\Delta V=0$), 1st law of thermodynamics become as;

$$q = \Delta E + W$$

$$q_v = \Delta E + P\Delta V$$

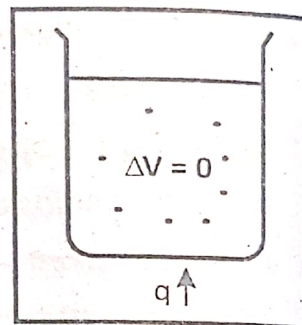
$$q_v = \Delta E + P(0)$$

$$q_v = \Delta E + 0$$

$$q_v = \Delta E$$

$$\text{As } W = P\Delta V$$

$$\text{As } \Delta V = 0$$



The above equation shows that heat supplied to a system will only increase the internal energy of the system and work done will be zero.

EXAMPLE 11-1: Calculate the work done when one mole of an ideal gas expands from 15dm^3 to 20dm^3 against a constant external pressure of 2-atmosphere.

Solution:

$$\text{Work done} = W = ?$$

$$\text{Pressure} = P = 2\text{atm}$$

$$\text{Initial volume} = V_1 = 15\text{dm}^3$$

$$\text{Final volume} = V_2 = 20\text{dm}^3$$

$$\text{Change in volume} = \Delta V = V_2 - V_1 = 20 - 15 = 5\text{dm}^3$$

Using the equation,

$$W = P\Delta V$$

$$W = 2\text{atm} \times 5\text{dm}^3$$

$$[W = 10\text{atm}\cdot\text{dm}^3]$$

Q5: Define and explain enthalpy. Explain process carried out at constant pressure.

Ans: Enthalpy:

"Enthalpy" is a Greek word which means "to worm in". "The total heat content of a system is called enthalpy." It is denoted by "H". Its unit is joule. It is a state function. Mathematically, enthalpy is

equal to the internal energy plus the product of pressure and volume.

$$H = E + PV$$

$$H_1 = E_1 + PV_1$$

$$H_2 = E_2 + PV_2$$

As energy (E), pressure (P) and volume are state functions so its product enthalpy is also a state function and its change can be measured.

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

$$\Delta H = \Delta E + \Delta(PV)$$

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

Since external pressure remains constant so $V\Delta P = 0$ then,

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

ΔH is positive, when heat is absorbed and is negative when heat is released by the system.

Note: Process involving solids and liquids have their $\Delta H = \Delta E$, since the change in volume $[\Delta V]$ is very small and the term " $P\Delta V$ " in the above equation can be neglected.

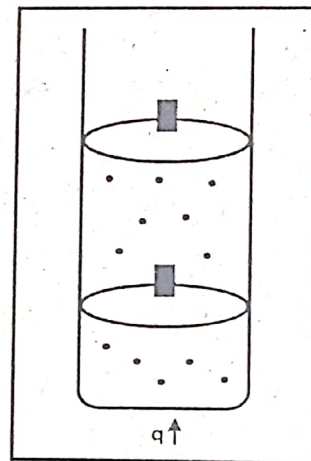
$$\Delta H = \Delta E + P\Delta V$$

$[P\Delta V \rightarrow \text{neglected term}]$

$$\Delta H = \Delta E$$

Process at Constant External Pressure:

Let we have a system, in which gas is enclosed in a cylinder, having moveable and frictionless piston. If " q " amount of heat is supplied to the system at constant pressure. The system will do some work on the surrounding because it will push the atmosphere back and the volume will increase from V_1 - V_2 . According to 1st law of thermodynamics,



$$q = \Delta E + W$$

$$q_p = \Delta E + P\Delta V$$

$[As W = P\Delta V]$

$$q_p = \Delta E + P(V_2 - V_1)$$

$$q_p = E_2 - E_1 + PV_2 - PV_1$$

$$q_p = E_2 + PV_2 - E_1 - PV_1$$

$[Re-arranging]$

$$q_p = (E_2 + PV_2) - (E_1 + PV_1)$$

$[Taking -ive sign as common]$

$$q_p = H_2 - H_1$$

$$E_2 + PV_2 = H_2$$

$$q_p = \Delta H$$

$$E_1 + PV_1 = H_1$$

$$H_2 - H_1 = \Delta H$$

It means that heat evolved or absorbed at constant pressure is equal to the change in enthalpy " ΔH " of the system.

From the above discussion it is concluded that,

1. Since " E ", " P " and " V " are state functions, so according to the equation ($H = E + PV$) enthalpy is also a state function.
2. ΔH is positive when heat is absorbed and it is negative when heat is released by the system.
3. Process involving solids and liquids have their $\Delta H = \Delta E$, since the change in volume (ΔV) is very small and closed to zero, hence the term $P\Delta V$ can be neglected.

EXAMPLE 11-2: When one mole of ice melts at 0°C and constant pressure of 1-atmosphere, 6025 joule of heat is absorbed by the system. The molar volume of ice and water are 0.020 and 0.018dm^3 respectively. Calculate ΔH and ΔE .

Solution:

$$(a) \Delta H = q_p = 6025 \text{ joule}$$

$$\text{Pressure (P)} = 1\text{atm}$$

$$P\Delta V = P(V_2 - V_1)$$

$$P\Delta V = 1\text{atm} (0.018\text{dm}^3 - 0.020\text{dm}^3)$$

$$P\Delta V = (-0.002 \text{ atm} \cdot \text{dm}^3)$$

$$\text{Since } 1\text{dm}^3 \text{ atm} = 101.25\text{J}$$

$$\text{So, } P\Delta V = -0.002 \times 101.25\text{J} = (-0.2025\text{J})$$

$$(b) \Delta H = \Delta E + P\Delta V$$

$$\Delta E = \Delta H - P\Delta V$$

$$\Delta E = 6025\text{J} - (-0.2025\text{J})$$

$$\Delta E = 6025 + 0.2025\text{J}$$

$$[\Delta E = 6025.2025\text{J}]$$

Q6: Define and explain enthalpy change (ΔH) and standard enthalpy change (ΔH°). (BISE Bannu 2017, Kohat 2018, Swat + Abtd)

Ans: Enthalpy Change " ΔH ": (ETEA: 2009,13).

Definition: "The amount of heat evolved or absorbed during a physical or chemical process is called enthalpy change." It is denoted by ΔH .

Standard Enthalpy Change " ΔH° ": (BISE Malakand 2018)

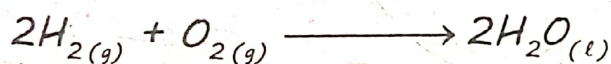
Definition: "The change in enthalpy measured at room temperature

[25°C] and 1-atmospheric pressure when the reactants and products are in their standard [natural] states are called the standard enthalpy change."

Explanation: The standard states are 25°C and 1atm. It is represented by ΔH° . Here the superscript shows standard state.

There is no way to measure absolute value of enthalpy of a substance. Relative enthalpy change can be measured. The arbitrary (♾️) reference point is the set of conditions of temperature and pressure. These conditions of temperature and pressure, for thermo-chemical measurements are 25°C and 1-atm respectively.

The enthalpy change measured under the above conditions [25°C and 1-atm] is known as standard enthalpy change and denoted by ΔH° . It means that all the substances involved in the reaction are in their normal and natural state at 25°C and 1-atm. This state is called the standard state. Thus ΔH_{298}° for reaction corresponds to gaseous hydrogen, oxygen and liquid water [not steam], which are their most stable and normal state or standard states.



Q7: Explain the following terms:

- (i) Standard enthalpy of formation (ΔH_f°)
- (ii) Standard enthalpy of reaction ($\Delta H_{\text{reaction}}^\circ$)
- (iii) Standard enthalpy of combustion (ΔH_c°)
- (iv) Standard enthalpy of neutralization ($\Delta H_{\text{neu}}^\circ$)
- (v) Bond dissociation energy (BDE)

Ans: (i) Standard Enthalpy of Formation " ΔH_f° ":

Definition: "The heat change that occurs, when 1-mole of a compound is formed from its elements under standard conditions is called standard enthalpy of formation."

Explanation: The standard enthalpy of formation of all the elements in their most stable form is arbitrary taken as zero. For example, molecular oxygen is more stable than its allotropic form ozone, under standard conditions. The standard heat of formation of CO_2 and SO_2 are given below:



Standard enthalpy of formation of elements and compounds are helpful to calculate standard enthalpies of reactions and are given below:

Standard Enthalpies of Formation at 25°C:

Substance	ΔH_f°	Substance	ΔH_f°
All elements in their standard states	0.00	$\text{CaC}_2(s)$	-62.5
C [Graphite]	0.00	$\text{CS}_2(l)$	+89.7
C [Diamond]	+1.90	$\text{HCl}(g)$	-92.31
P [White]	0.00	$\text{NaCl}(s)$	-411.00
P [Red]	-17.60	$\text{HBr}(g)$	-36.40
$\text{H}_2\text{O}(l)$	-285.84	$\text{HI}(g)$	+26.48
$\text{SO}_2(g)$	-296.83	$\text{NH}_3(g)$	-46.11
$\text{CO}(g)$	-110.53	$\text{H}_2\text{S}(g)$	-20.63
$\text{CO}_2(g)$	-393.51	$\text{CH}_4(g)$	-74.81
$\text{Fe}_2\text{O}_3(s)$	-824.2	$\text{C}_2\text{H}_2(g)$	+226.73
$\text{Fe}_3\text{O}_4(s)$	-1118.2	$\text{H}_2\text{SO}_4(l)$	-814
$\text{CaO}(s)$	-635.5	$\text{HNO}_3(l)$	-174

(ii) Standard Enthalpy of Reaction " $\Delta H_{\text{reaction}}^\circ$ ": (ETEA: 2012,16)

The standard enthalpy of reaction (ΔH_r°) is the change occurs in enthalpy for a given reaction calculated from the standard enthalpies of formation for all reactants and products. It can be calculated from the difference between the total enthalpies of formation of products and reactants as follow:

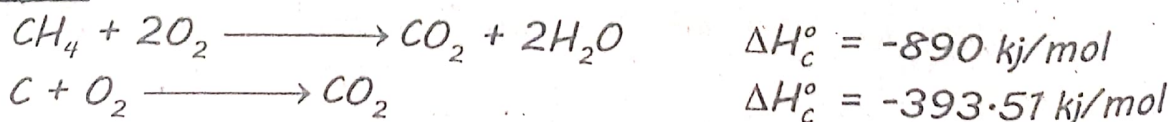
$$\Delta H_{\text{reaction}}^\circ = \sum \Delta H_{(\text{products})}^\circ - \sum \Delta H_{(\text{reactants})}^\circ$$

For example: $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} \quad \Delta H_r^\circ = -572 \text{ KJ}\cdot\text{mol}^{-1}$

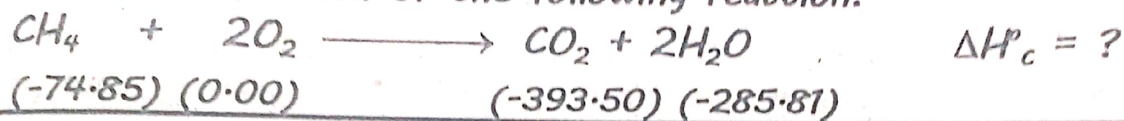
(iii) Standard Enthalpy of Combustion " ΔH_c° ":

"The enthalpy change that occurs when one mole of a substance is completely burnt in an excess of oxygen under standard conditions is called standard enthalpy or combustion." It is denoted (باحتراق) by ΔH_c° . Its unit is kJ/mol.

Examples:



EXAMPLE 11.3: The heats of formation of CH_4 , CO_2 and H_2O are; $-74.85 \text{ kJ/mol}^\circ$, $-393.50 \text{ kJ/mol}^\circ$ and $-285.81 \text{ kJ/mol}^\circ$ respectively. Calculate the heat of combustion of the following reaction:



Solution:

$$\text{Heat of reaction} = \Delta H_r^\circ = \sum [\Delta H_{f, \text{products}}^\circ] - \sum [\Delta H_{f, \text{react}}^\circ]$$

$$\Delta H_c^\circ = [\Delta H_f^\circ \text{CO}_2 + 2\Delta H_{f, (\text{H}_2\text{O})}^\circ] - [\Delta H_{f, (\text{CH}_4)}^\circ + 2\Delta H_{f, \text{O}_2}^\circ]$$

$$\Delta H_c^\circ = [-393.50 + 2(-285.81)] - [-74.85 + 2(0)] \text{ kJ/mol}^\circ$$

$$\Delta H_c^\circ = [-393.50 - 571.62] - [-74.85 + 0] \text{ kJ/mol}^\circ$$

$$\Delta H_c^\circ = [-965.12 + 74.85] \text{ kJ/mol}^\circ$$

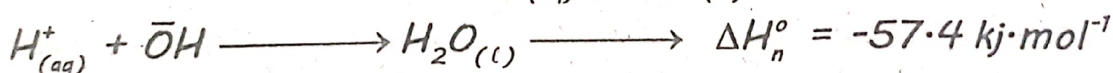
$$(\Delta H_c^\circ = -890.27 \text{ kJ/mol}^\circ)$$

(iv) Standard Enthalpy of Neutralization " $\Delta H_{\text{neu}}^\circ$ ":

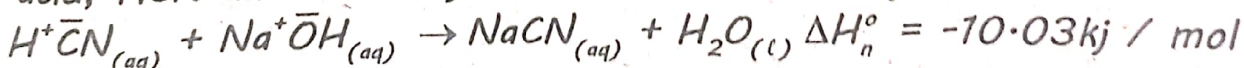
(ETEA: 2018-19)

Definition: "The amount of heat evolved when one mole of hydrogen ion $[\text{H}^+]$ from an acid react with one mole of hydroxide ions $[\text{OH}^-]$ from a base to form one mole of water under standard conditions is called standard heat / enthalpy of neutralization." It is denoted by " $\Delta H_{\text{neu}}^\circ$ "

Examples:



The heat of neutralization of a strong acid with a strong base is approximately equal to -57.4 kJ/mol . The heat of neutralization of a weak acid, HCN and a strong base NaOH is -10.03 kJ/mol .



(v) Bond Energy: (BISE Swat 2017)

Definition: "The enthalpy change occurs when one mole of bonds are broken down in a stable molecule under standard conditions is called bond energy." It is also called bond dissociation energy.

Examples:



Actually bond dissociation energy is a measure of the bond strength. The above values show that double covalent bond in oxygen molecule $[O = O]$ is stronger than a single covalent bond in hydrogen molecule $[H_2]$.

Q8: Explain the terms, heat capacity, specific heat capacity and molar heat capacity.

Ans: Heat Capacity $[C]$: (BISE Malakand 2018)

Definition: "The capacity of a substance to absorb heat is called heat capacity."

Explanation: The heat capacity $[C]$ of a substance is the amount of heat required to raise the temperature of the given amount of substance by $1^\circ C$. It is an extensive property and depends on the amount of the substance. The SI units of heat capacity is $J \cdot ^\circ C^{-1}$ / $J \cdot K^{-1}$.

Extensive Property is a property that depends on the amount of matter in a sample. Mass and volume are the examples of extensive properties.

Specific Heat Capacity:

Definition: "The specific heat $[S]$ of a substance is the amount of heat required to raise the temperature of one gram of a substance by $1^\circ C / 1K$. It is also called the specific heat capacity."

Explanation: It is an intensive property which does not depend on the quantity of substance. The SI unit of specific heat capacity is $J \cdot g^{-1} \cdot K^{-1}$. The relationship between heat capacity $[C]$ and specific heat capacity $[S]$ is given below:

$$C = ms$$

Intensive Properties are those properties which do not depend on the amount of the substance such as density and colour. These properties do not change as the size of an object changes.

Example: Calculate the heat capacity of 50 grams of water. Specific heat of water is $4.18 J \cdot g^{-1} \cdot ^\circ C^{-1}$.

Solution: As we know that,

$$C = ms$$

$$C = 50g \times 4.184 J \cdot g^{-1} \cdot K^{-1} = [209.2 J \cdot K^{-1}]$$

If we know the specific heat and amount of substance, then the change in temperature of the substance [sample] " ΔT " will tell us the

amount of heat $[q]$ that has been absorbed or released in a particular process. Equation used for calculating the heat change is,

$$q = ms\Delta T$$

OR $q = C\Delta T$

As $ms = C$

Molar Heat Capacity:

"The amount of heat required to raise the temperature of one mole of a substance through $1^\circ\text{C}/1\text{K}$ is called molar heat capacity." Unit for molar heat capacity is $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Molar heat capacity of water = $75.312\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

Specific heat of 1g of water = $4.184\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

Specific heat of 1-mole (18g) = $18 \times 4.184\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
 $= [75.312\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$

Q9: How enthalpy change can be measured? (ETEA: 2018)

Ans: Measurement of Enthalpy Change " ΔH ":

Definition: "Calorimeter is the instrument used to measure the enthalpy change during chemical or physical process."

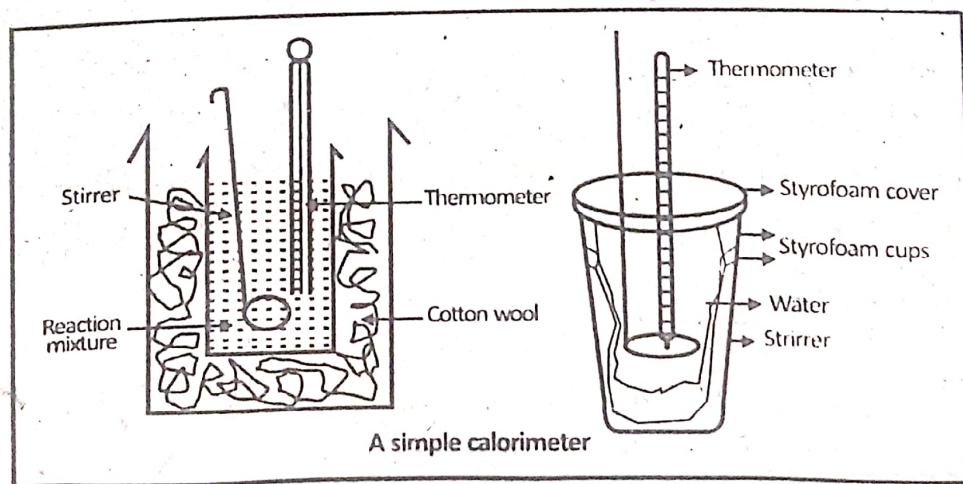
Calorimetry:

"The process of measurement of enthalpy change during chemical reaction or a physical change by using calorimeter is called calorimetry." In enthalpy changes occurring in chemical process may be measured by two main methods:

1. Direct calorimetry
2. Indirect calorimetry

1. Direct Calorimetry:

In a calorimeter, heat changes $[\Delta H]$ of those reactions are measured which go to completion without side reactions. For example the heat of neutralization, of aqueous solutions of a strong acid



by a strong base can be measured by a calorimeter.

A sample calorimeter consists of an insulated container in which a reaction vessel is placed. The reaction vessel contains a stirrer (دک) and thermometer. There is cotton wool in between the reaction vessel and outer beaker. The cotton wool acts as an insulator. When the reaction starts, heat will either evolve or absorb. In case of exothermic reaction, the released heat will raise the temperature of water, which is measured by a thermometer.

Heat given out by reactants = heat gained by water. From the specific heat of the system $[C]$, the temperature change $[\Delta T]$, the amount of heat evolved or absorbed $[Q]$ can be calculated by using the equation,
 $Q = nC\Delta T$

Q = amount of heat evolved or absorbed

n = number of moles of reactants

C = molar heat capacity

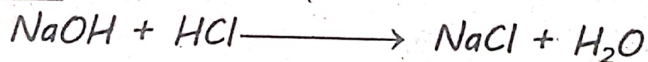
ΔT = change in temperature i.e. $(T_2 - T_1)$

If we take mass of the reaction mixture instead of number of moles, the given equation becomes,

$$Q = mC\Delta T$$

EXAMPLE 11-4: When 50cm^3 of $2\text{mol}\cdot\text{dm}^{-3}$ HCl is added to 50cm^3 of $2\text{mol}\cdot\text{dm}^{-3}$ NaOH solution. The temperature rise is 13.6°C . Calculate the heat of neutralization per mole, where the specific heat of water is $4.2\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$.

Solution:



$$n_{\text{HCl}} = \frac{50}{1000} \times 2 = (0.1 \text{ mol})$$

$$n_{\text{NaOH}} = \frac{50}{1000} \times 2 = (0.1 \text{ mol})$$

$$\text{Total volume of solution} = 50 + 50 = 100\text{cm}^3$$

Since the solution is dilute so we can use the density of water instead of density of solution.

$$\text{Density of water} = 1\text{g}/\text{cm}^3 \text{ at } 4^\circ\text{C}$$

$$\text{Mass of solution } dv = 1 \times 100 = 100\text{gram}$$

Conversion of cm^3 into dm^3
 we divide 50 by 1000
 As $1\text{dm}^3 = 1000\text{cm}^3$

$$d = \frac{m}{v} \quad \text{and} \\ m = dv$$

$$\text{Heat of neutralization} = mC_w T_c$$

$$\begin{aligned}\text{Heat of neutralization} &= 100 \times 4.2 \times 13.6 \\ &= -5712 \text{ J} / 0.1 \text{ mol}\end{aligned}$$

0.1 mol of acid and 0.1 mol of base gives $\Delta H_{\text{neu}} = -5712 \text{ J}$

1 mole of acid and 1-mol of base give heat of neutralization

$$= \frac{-5712}{0.1} = -57120 \text{ J}$$

$$\text{OR heat of neutralization} = \frac{-57120}{1000} = [-57.12 \text{ kJ} / \text{mol}]$$

Q10: Explain indirect calorimetry (OR) explain Hess law of constant heat summation. (BISE Mardan 2018)

Ans: Hess's Law [Enthalpy Change Calculation]:

[Graham Hess, a Swiss born Russian chemist]

Statement:

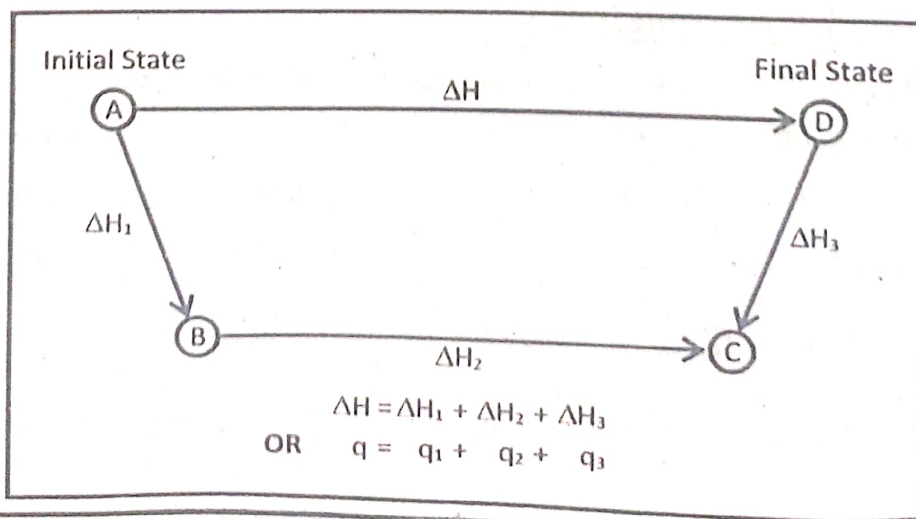
"The amount of heat evolved or absorbed during a chemical reaction is the same whether the reaction takes place in a single step or in several steps."

Explanation:

In certain chemical reactions enthalpy of formation $[\Delta H_f^\circ]$ cannot be determined directly due to the following reasons:

1. Some compounds cannot be directly synthesized from their elements.
2. The rate of some reactions are very slow to be subjected for enthalpy measurement.
3. In some cases side reactions takes place and produce products other than the desired one.

In such cases ΔH_f° can be determined by an indirect method, which is based on Hess law of constant heat summation. From the statement of Hess law it is clear that



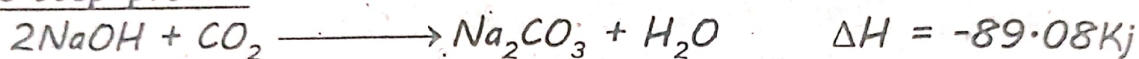
the net heat of reaction depends only on the initial and final states and not on intermediate steps.

Let a system changes from initial state "A" to final state "D". There are two possibilities:

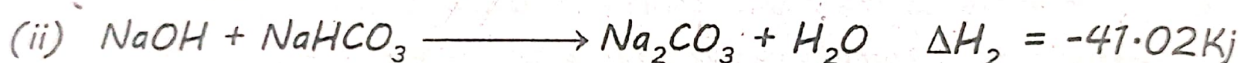
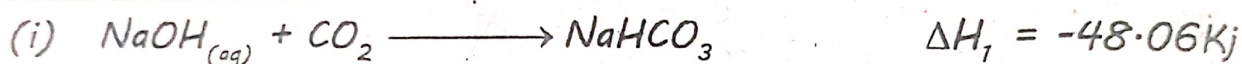
1. When it changes directly, change in enthalpy during this process is ΔH .
2. When the system 1st changes to state "B", the enthalpy change is ΔH_1 . Then goes from B - C, with enthalpy change ΔH_2 and finally from C - D with enthalpy change ΔH_3 .

Example: [Formation of Na_2CO_3]

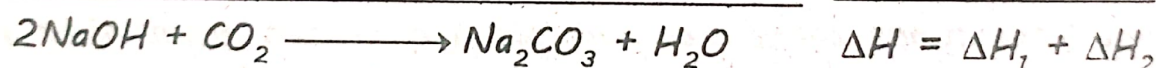
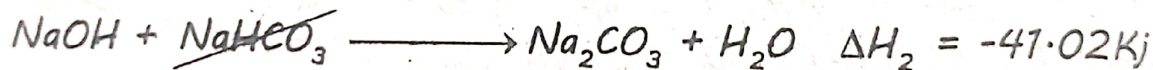
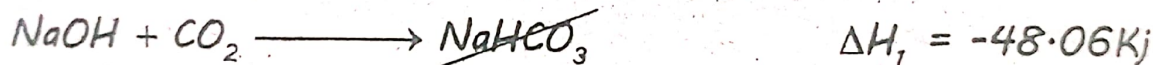
Single step process:



Two step process:



Adding the two equations,



$$\Delta H = -48.06 + (-41.02)$$

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2$$

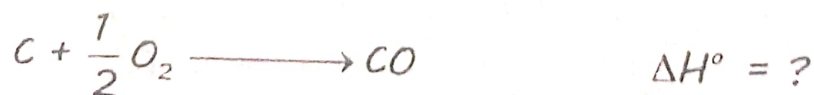
$$\Delta H = -48.06 - 41.02$$

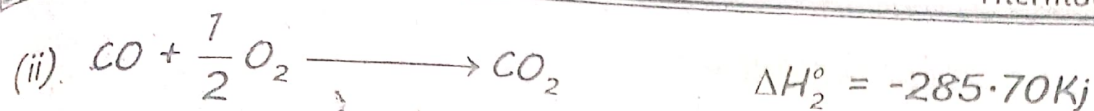
$$(\Delta H = -89.08\text{Kj})$$

$$-89.08\text{Kj}$$

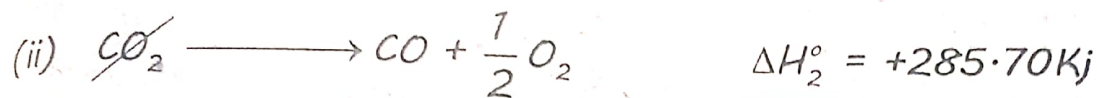
Heat of Formation:

Carbon monoxide is prepared by reacting carbon with oxygen, but along with carbon monoxide, carbon dioxide is also formed. So to determine the heat of reaction of "CO" formation an indirect method is used as follow:





Invert (i) equation (ii) and then add with equation (i) we will find out enthalpy change for the formation of CO indirectly.



$$\Delta H_f^\circ = -393.50 + (285.70)$$

$$(\Delta H_f^\circ = -107.80 \text{ KJ})$$

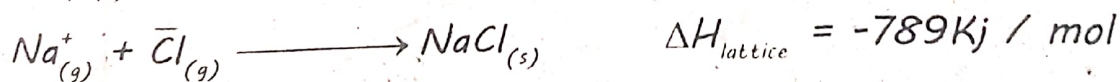
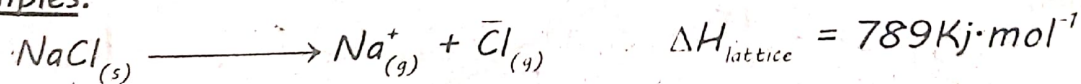
Q11: What is lattice energy? Explain Born-Haber cycle by giving examples.

Ans: Lattice Energy:

Definition: "The amount of heat energy required to break one mole of an ionic compound into its oppositely charged ions is called lattice energy."

(OR) "The amount of energy released when one mole of an ionic compound is formed from one mole of positive and one mole of negative gaseous ions is called lattice energy."

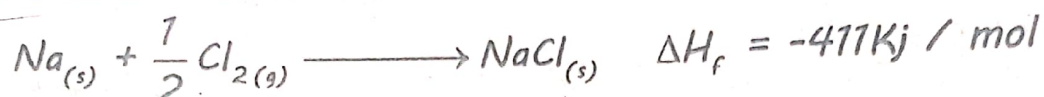
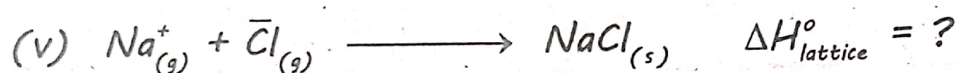
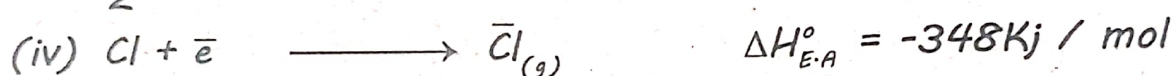
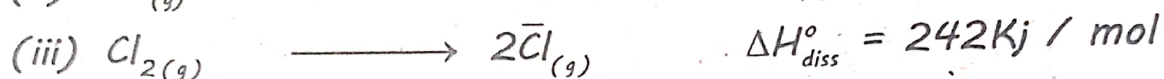
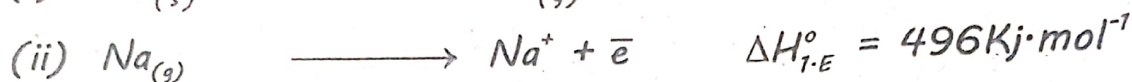
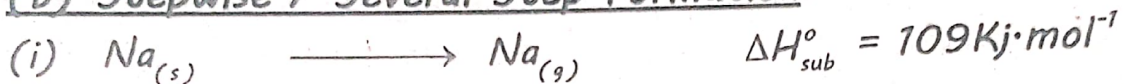
Examples:



Born-Haber Cycle:

Definition: "The cyclic process used for the determination of lattice energy was proposed by Born and Haber so it is called Born-Haber process."

Explanation: Lattice energy cannot be measured directly. It can be measured indirectly by Born-Haber cycle which is the application of Hess law. It can be explained by taking the example of NaCl formation.

(a) Direct or One Step Formation:(b) Stepwise / Several Step Formation:

According to Hess law, enthalpy change in one step process is equal to the sum of enthalpy change for the all five steps.

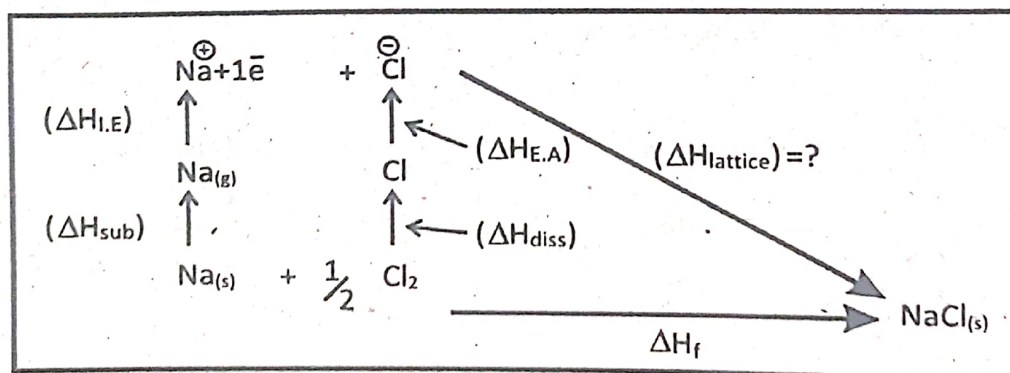
$$\Delta H_f^{\circ} = \Delta H_{\text{sub}} + \Delta H_{\text{I.E}} + \Delta H_{\text{diss}}^{\circ} + \Delta H_{\text{E.A}} + \Delta H_{\text{lattice}}^{\circ}$$

$$\Delta H_{\text{lattice}}^{\circ} = \Delta H_f^{\circ} - \Delta H_{\text{sub}}^{\circ} - \Delta H_{\text{I.E}}^{\circ} - \Delta H_{\text{diss}}^{\circ} - \Delta H_{\text{E.A}}^{\circ}$$

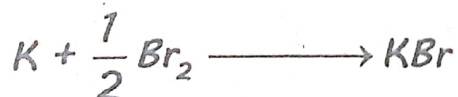
$$\Delta H_{\text{lattice}}^{\circ} = -411 - 109 - 496 - 121 - (-348)$$

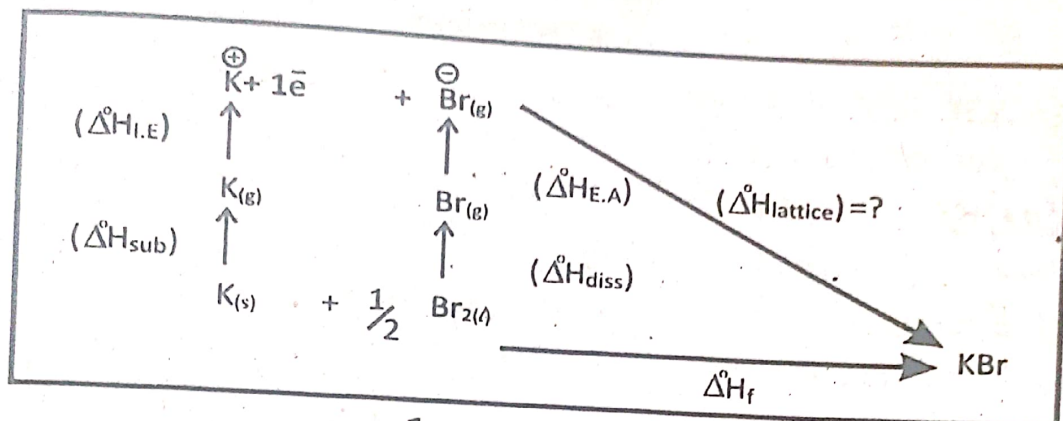
$$\Delta H_{\text{lattice}}^{\circ} = -1137 + 348 = [-789 \text{Kj / mol}]$$

These changes can be shown in cyclic way as follow:



EXAMPLE 11-5: Calculate the lattice energy of KBr. The heat of sublimation of potassium is 88Kj/mole, the heat of dissociation of bromine gas is 192.5kj/mol. The ionization energy of "K" is 414Kj/mol, the electron affinity for "Br" is -334.7Kj/mol and the heat of formation of KBr is -405.8Kj/mol.



Solution:

$$\Delta H_f^{\circ} = \Delta H_{sub}^{\circ} + \Delta H_{I.E}^{\circ} + \frac{1}{2} \Delta H_{diss}^{\circ} + \Delta H_{E.A}^{\circ} + \Delta H_{lattice}^{\circ}$$

$$\Delta H_{lattice}^{\circ} = \Delta H_f^{\circ} - \Delta H_{sub}^{\circ} - \Delta H_{I.E}^{\circ} - \Delta H_{\left(\frac{1}{2}diss\right)}^{\circ} - \Delta H_{E.A}^{\circ}$$

$$\Delta H_{lattice}^{\circ} = -405.8 - 88 - 414 - \left(\frac{192.5}{2}\right) - (-334.7)$$

$$\Delta H_{lattice}^{\circ} = -1004.05 + 334.7$$

$$\Delta H_{lattice}^{\circ} = [-669.35 \text{ KJ / mol}]$$

Exercise

1: Choose the correct option from the given options:

1. ΔH per mol is expressed in the units of:
☒ (a) KJ (b) F^o (c) C^o (d) K
2. Which of the following is not state function?
(a) Enthalpy ☒ (b) Heat
(c) Temperature (d) Pressure
3. For solids and liquids:
☒ (a) $\Delta H = \Delta E$ (b) $\Delta H > \Delta E$
(c) $\Delta H < \Delta E$ (d) $\Delta E = 0$
4. 1Kcal is equal to:
(a) $41.8 \times 10^3 J$ (b) $418 \times 10^3 J$
☒ (c) $4.18 \times 10^3 J$ (d) $0.418 \times 10^3 J$
5. Standard enthalpy [ΔH°] for 1-mole of a substance, which exists in its natural state at 1-atm pressure is measure at:
(a) 0K ☒ (b) 298K (c) 273K (d) 0C^o
6. ΔH can be measured indirectly by applying:
(a) Avogadro's law (b) Gas laws
☒ (c) Hess law (d) Faraday laws
7. Enthalpy means:
(a) Disorder (b) Transition state
(c) Rate constant ☒ (d) Heat content
8. No work is done at constant:
(a) Pressure ☒ (b) Volume
(c) Temperature (d) Mass
9. Heat capacity depends on:
(a) Pressure (b) Volume
(c) Composition ☒ (d) Mass
10. Which one of the following reaction is spontaneous?
(a) Endothermic (b) Exothermic
(c) Reversible ☒ (d) Irreversible
11. Energy possessed by water in a dam is:
☒ (a) Potential energy (b) Heat energy
(c) Electric energy (d) Heat energy
12. When heat is absorbed from the surrounding the process is:

- (a) Reversible (b) Mechanical
(c) Exothermic ✓ (d) Endothermic
13. The sum of all the energies of all the molecules or atoms of a substance is called its:
(a) Specific heat (b) Heat capacity
(c) Latent heat ✓ (d) Internal energy
14. Which one of the following process has ΔH , +ive.
✓ (a) Ionization energy (b) Electron affinity
(c) Combustion (d) Exothermic reaction

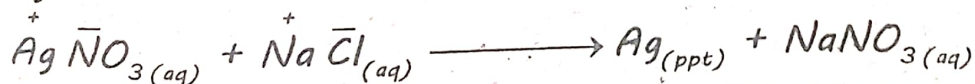
Short Questions

Q1: Total energy of the system and its surroundings remain constant.

Ans: According to the law of conservation of energy "energy can neither be created nor destroyed during a chemical reaction, although it can be changed from one form to another form." It means that total energy of universe remains constant. A system may lose energy to the surroundings in the form of heat but at the same time, the same amount of energy is absorbed by the surroundings. Hence the amount of energy lost by the system is equal to the amount of energy gained by the surroundings. Thus the total energy of the system and its surrounding remains constant.

Q2: Ionic reactions are very fast.

Ans: Ionic reactions are very fast as in aqueous medium ions are only exchanged which are already separated [dissociated] in aqueous solution.



Q3: The work done has positive and negative values. (BISE Swat 2017)

Ans: In gaseous system two types of work done can take place:

1. When work is done on the system i.e. atmosphere pushes the piston downward and compression of the system occurs. It is taken as positive [$W = +ive$].
2. When work is done by the system i.e. system pushes the surrounding against the external pressure and expansion of the sys-

tem occurs. It will be taken as negative i.e. $[W = -ive]$.

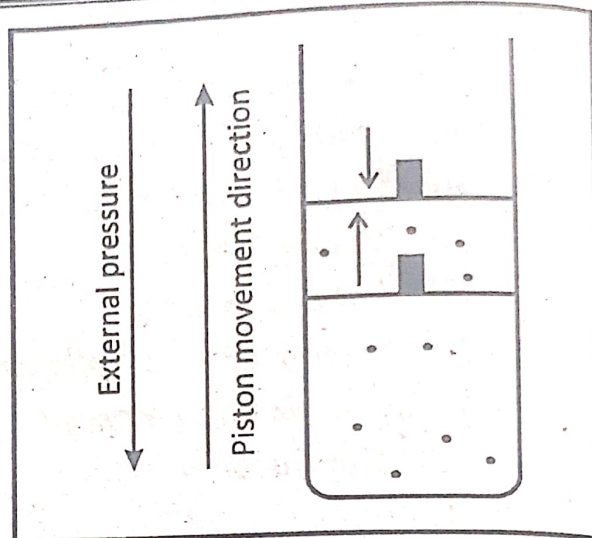
During expansion, external pressure and work done [piston movement] are in opposite direction and the angle is 180° .

$$W = F \cdot d \cos \theta$$

$$W = F \cdot d \cos 180^\circ$$

$$W = F \cdot d \times -1$$

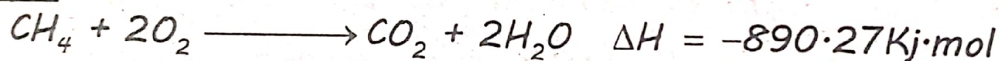
$$W = -(\text{negative value})$$



Q4: Heat of combustion is always negative.

Ans: We know that during combustion, of oil, coal, paper, wood or natural gas, heat is always released to the surrounding. It means that the total heat in for old bonds breaking is less than the total heat out during new bonds formation in products, so net result is negative value. So combustion process is always exothermic.

Example:



Q5: Enthalpy change is a state function but heat is not.
(BISE Mardan 2018)

Ans: As enthalpy change only depends upon the initial and final states so it is a state function and its change can be find out $[\Delta H = H_2 - H_1]$. Heat depends on the manner in which its change is brought about and do not depends upon the initial and final states so it is not a state function but it is exact / path function.

Q6: ΔH for solids and liquids becomes equal to ΔE .

Ans: We know that solids and liquids are almost incompressible [very little compressible]. As compared to gases its expansion is negligible so $\Delta V = 0$. It means that no change occurs in volume of solids and liquids with change in pressure so the " $P\Delta V$ " term is neglected and ΔH becomes equal to ΔE . According to the 1st law of thermodynamics;

$$q = \Delta E + W$$

$$\text{OR } \Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P(0)$$

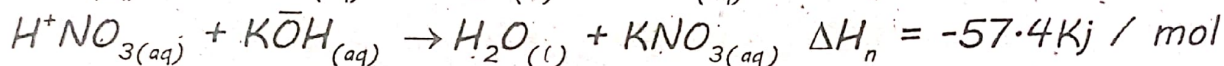
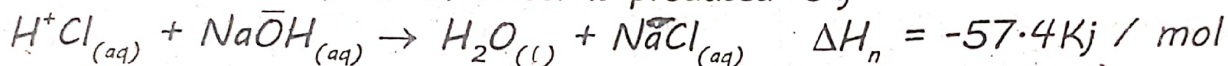
$$\text{As } W = P\Delta V$$

$$\Delta H = \Delta E + 0$$

$$(\Delta H = \Delta E)$$

Q7: Enthalpy of neutralization of strong acids, and strong bases has always the same value.

Ans: We know that all strong acids and all strong bases ionizes completely in water. The aqueous solutions of all strong acids have the same concentrations of hydrogen ions $[H^+]$. Similarly the aqueous solutions of all strong bases contain the same amount of hydroxide ions, $[OH^-]$. It means that 1-molar solution of any strong acid and 1-molar solution of any one strong base, by mixing release the same amount of heat. It is because in all cases 1-mole of water is produced. e.g.



In both the cases one moles of H^+ ions of an acid combine with one mole of OH^- ions of a base to form one mole of water so, the same enthalpy change occurs.

Q8: What do you mean by state of a system? What are state functions?

Ans: The condition of a system is called state of the system. Macroscopic properties of the system which depends upon initial and final states of a system and independent of the path followed by the system are called state functions.

Examples of state functions: Temperature, pressure and volume.

Long Questions

Q1: State and explain Hess's law of constant heat summation. Show that it is a direct consequence of the 1st law of thermodynamics.

Ans: Please see question number 10.

Q2: How does Born-Haber cycle help in calculating the lattice energy?

Ans: Please see question number 11.

Q3: What is meant by heat of reaction? Explain how the heat of reaction at constant volume differs from the heat of reaction at constant pressure?

Ans: Heat of reaction: Please see question number 7.

Heat of reaction at constant volume differ from heat of reaction at constant external pressure because heat supplied to a system at constant volume will only increase the internal energy of the system and work done will be zero i.e.

$$q_v \text{ or } \Delta H = \Delta E$$

On the other hand, heat supplied to a system at constant external pressure will only change the enthalpy of the system. i.e.

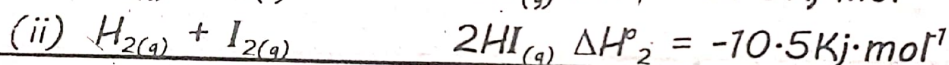
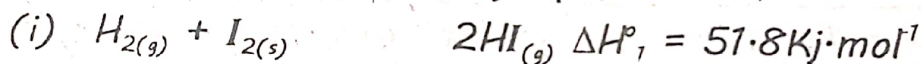
$$q_p = \Delta H$$

Q4: What is meant by pressure - volume work? How it is related to the 1st law of thermodynamics?

 Please see question number 4.

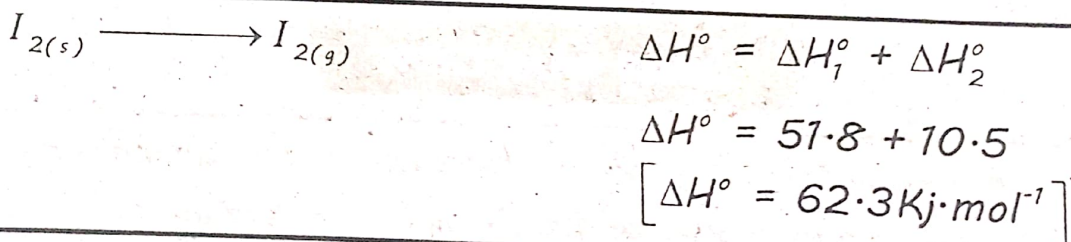
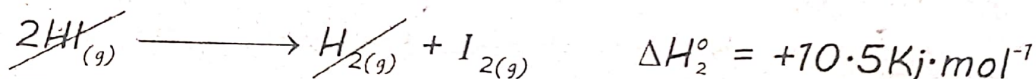
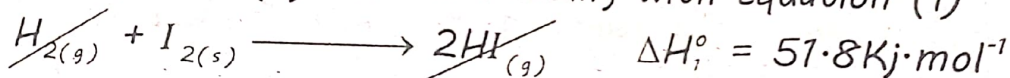
Numerical Questions

Q1: Apply Hess's law to calculate ΔH° for the sublimation of one mole of iodine from the following equations:

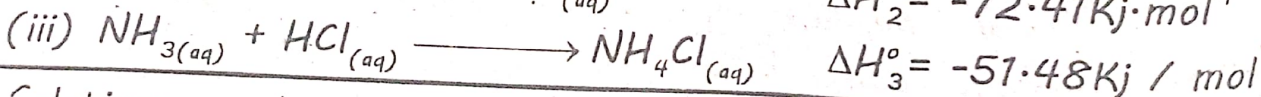
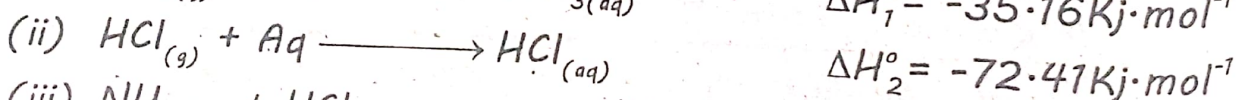
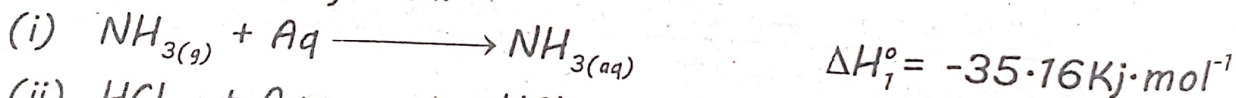


Solution:

Inverting equation (ii) and then adding with equation (i)

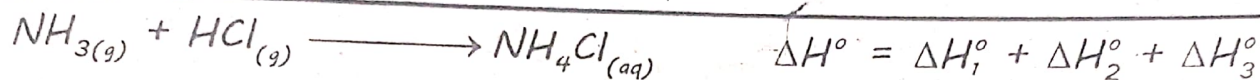
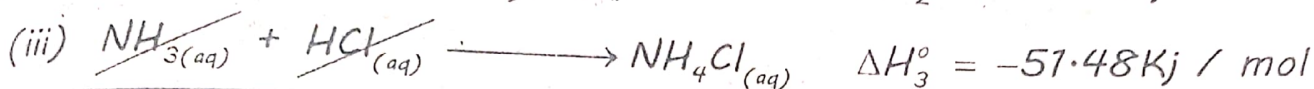
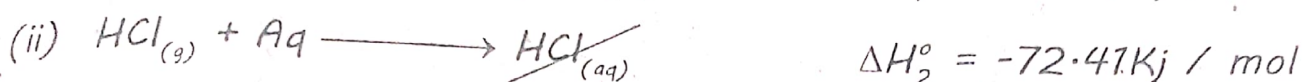
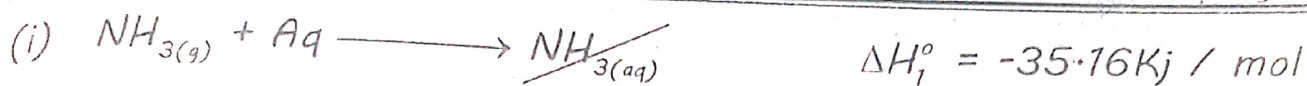


Q2: Calculate the heat of formation of an aqueous solution of NH_4Cl from the following data:



Solution:

Adding all three equations

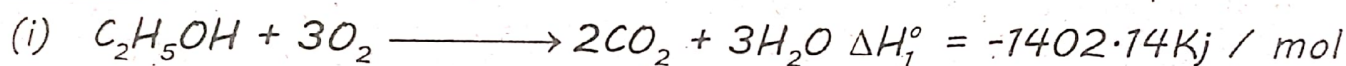


$$\Delta H^\circ = -35.16 - 72.41 - 51.48$$

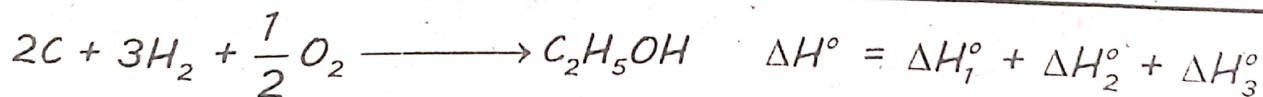
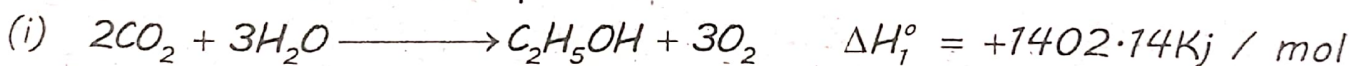
$$[\Delta H^\circ = -159.05 \text{Kj / mol}]$$

Q3: Liquid ethanol when burnt in oxygen at 25°C liberates heat i.e. $\Delta H = -1402.14 \text{Kj/mol}$. The heats of formation of CO_2 and H_2O are $-393.50 \text{Kj/mol}^\circ$ and $285.81 \text{Kj/mol}^\circ$ respectively at the same temperature. Calculate the heat of formation of ethanol at 25°C.

Solution:



Invert equation (i), multiply equation (ii) by (2) and equation (iii) by (3), then add all the equations



$$\Delta H = +1402.14 - 787 - 857.43$$

$$[\Delta H^\circ = -242.29 \text{Kj / mol}]$$

Q4: A chemical reaction takes place in a container of cross sectional area of 0.01m^2 , fitted with a weightless and frictionless piston. The piston is moved up through 0.01m against an external pressure of 101325 pascals as a result of the reaction. Calculate the work done by the system.

Solution:

$$\text{Area of the container} = A = 0.01\text{m}^2$$

$$\text{Distance covered by the piston} = l = 0.01\text{m}$$

$$\text{External pressure} = P = 101325\text{Pa} = 101325\text{Nm}^{-2}$$

$$\text{Work done} = W = ?$$

$$\begin{aligned}\text{Change in volume} &= \text{Area} \times \text{Length} \\ &= A \times l = 0.01\text{m}^2 \times 0.01\text{m} = 0.0001\text{m}^3\end{aligned}$$

Formula used,

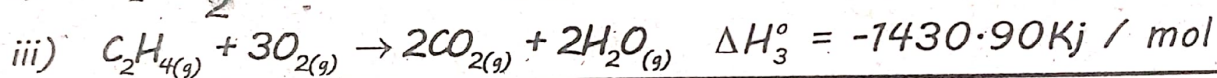
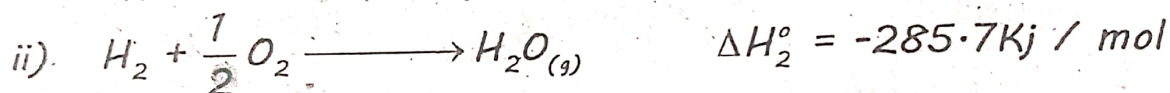
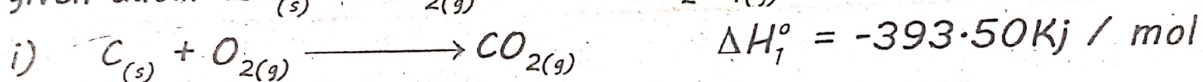
$$W = P\Delta V$$

$$W = 101325\text{Nm}^{-2} \times 0.0001\text{m}^3$$

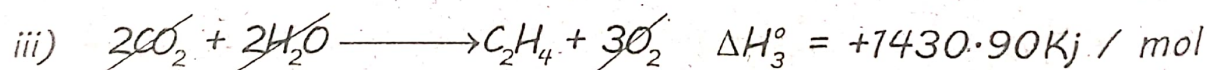
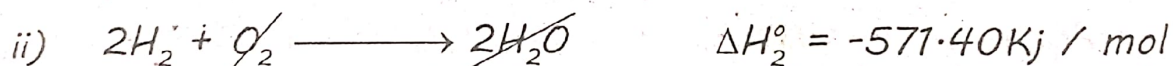
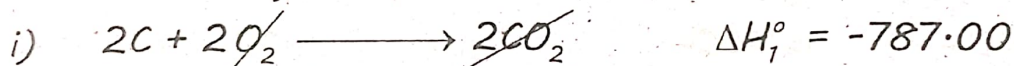
$$W = 10.1325\text{Nm}$$

$$[W = 10.1325\text{J}] \quad \text{As Nm} = \text{Joul}$$

Q5: Determine ΔH° for the following reaction with the help of the given data: $2\text{C}_{(s)} + 2\text{H}_{2(g)} \longrightarrow \text{C}_2\text{H}_{4(g)}$ $\Delta H^\circ = ?$

Solution:

Multiply equation (i) and equation (ii) by (2), inverting equation (iii) and then adding all the three equations,



$$\Delta H^\circ = -787 - 571.40 + 1430.90$$

$$\Delta H^\circ = -1358.40 + 1430.90$$

$$[\Delta H^\circ = 72.50\text{Kj / mol}]$$



Life is a book of three pages; 1st page is birth & the last page is death. Central page is empty, it depends on you, how do you fill your page.