

C1 Definitions of Some Basic Terms used in Thermodynamics :

Internal Energy

It is the energy associated with a system by virtue of its molecular constitution and the motion of its molecules. The contribution of energy due to molecular constitution is known internal potential energy and the contribution of energy due to the motion of molecules is called internal energy of a system. It is given by the sum of two types of energies.

Determination of ΔE : When a reaction is carried out in such a manner that the temperature and volume of the reacting system remain constant, then the internal energy change (ΔE) of the reaction is equal to the heat exchanged with the surrounding.

Enthalpy

When we deal certain process in open vessels (at constant pressure), it becomes essential to introduce in place of internal energy, a new thermodynamics function called heat enthalpy. This new function is denoted by H.

H = E + PV

The change in enthalpy of a given system is given as follows

 $\Delta H = \Delta E + \Delta (PV),$ $\Delta H = \Delta E + P\Delta V,$ $\Delta H = \Delta E + \Delta n_R RT$

$$\Delta n_{\rm p} = n_{\rm p}(g) - n_{\rm p}(g)$$

Practice Problems :

- 1. For the reaction, $Fe_2O_3(s) + 3CO_2(g) \rightarrow 3CO_2(g) + 2Fe(s)$. Which of the following is correct ?
 - (a) $\Delta H^0 = \Delta E^0 + 3RT$

| $\Delta \mathbf{H}^0 = \Delta \mathbf{E}^0$ | (d) $\Delta H^0 = \Delta E^0 - RT$ |
|---|--|
| $\Delta \mathbf{H} = \Delta \mathbf{E}$ | $(\mathbf{u}) = \Delta \mathbf{H} = \Delta \mathbf{E} = \mathbf{K} \mathbf{I}$ |

2. The difference between the heats of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ is

(b) $\Delta H^0 = \Delta E^0 + RT$

(a) -7.43 (b) 3.72 (c) -3.72 (d) 7.43 [Answers : (1) c (2) a]

Heat Capacity

(c)

The heat capacity of a system is defined as the quantity of heat required for increasing the temperature of

one mole of a system through 1°C. Heat capacity may be given as follows : $C = \frac{dq}{dT}$

Temperature Dependence of ΔH and ΔE (Kirchoff's Equation)

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_{P,} \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$$

Where ΔC_p and ΔC_v are change of molar heat capacities at constant pressure and at constant volume respectively.

C2 <u>CALORIMETRY</u>

An object undergoing a temperature change without a chemical reaction or change of state absorbs or discharge an amount of heat equal to its heat capacity times the temperature change.

Heat exchange = (heat capacity) \times (temperature change)

C3 Calculation of Enthalpy of Reaction :

1. On the basis of enthalpy of formation value

$$\Delta H = \sum \Delta H_{f} (product) - \sum \Delta H_{f} (Reactant)$$

2. On the basis of bond energies of reactants

 $\Delta H = \{$ sum of bond energies of reactants – sum of bond energies of products $\}$

C4 HESS'S LAW

The total enthalpy change of a reaction is the same regardless of whether the reaction is completed in one step or in several steps.

$$A \xrightarrow{\Delta H} D$$

$$\Delta H_1 \longrightarrow D$$

$$A \xrightarrow{\Delta H_2} C$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

C5 <u>Physical Meaning of Enthalpy</u>

From the above discussions, it is clear that Enthalpy is the total heat stored with the system and it is an extensive property i.e, it depends upon the nature as well as on the amount of the substance. Like internal energy, its absolute value can not be calculated. We can only determine the change in enthalpy through the heat of reaction. If H_p and H_p are enthalpies of reactants and products then

$$H_{p} - H_{p} = \Delta H = heat of reaction$$

Hence, enthalpy is a state function.

Exothermic and Endothermic reactions

Depending upon the nature of heat exchanged, the chemical reactions are of two types.



C6 Bond Energy : Origin of Enthalpy change in a Reaction

It is known that a chemical reaction involves the breaking of one or more bonds in the reactants and the formation of one or more bonds in the products. The bond breaking process is purely endothermic and the bond formation is an exothermic process. Therefore, the net heat change during any chemical reaction (enthalpy change) is given as :

$$\Delta H = \sum (B.E.)_{Reactants} - \sum (B.E.)_{Products}$$

Calculation of Resonance Energy :

If a compound undergo resonance its experimental heat of formation and theoretical heat of formation will be different. Subtraction of $\Delta H_{f(exp)}$ and $\Delta H_{f(th)}$ is equal to resonance energy.

C7 <u>Different types of Heat of Reactions</u>

(a) (i) <u>Heat of Formation or Enthalpy of Formation</u>

It is the amount of heat evolved or absorbed when one g mole of a substance is formed from its constituent element e.g.

Formation of CH₄

$$C(s) + O_{\gamma}(g) \rightarrow CO_{\gamma}(g) + Q_{1}$$

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(ii) <u>Standard Heat of Formation (Q.)</u>

A substance is said to be in its standard state when it is present at 298 K (i.e. 25°C) under one atmospheric pressure.

Standard heat of formation is the amount of heat evolved or absorbed when one mole of substance is formed from its elements in their standard states i.e., at 298 K and 1 atm.

"Conventionally, the heat of formation of element in its elemental state is zero".

(b) <u>Heat of Combustion</u>

It is the amount of heat evolved when one mole of a compound (or any substance) is completely oxidised (or burnt) in the presence of oxygen.

The heat of combustion is represented by an equation which refers the one mole of substance used in combustion e.g.

(i)
$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l) + Q_1$$

(ii)
$$C_2H_5OH(l) + 3O_2(g) = 2CO_2(g) + 3H_2O(l) + Q_3$$

Calorific Value of a fuel

It is the amount of heat or energy released when one gram of a fuel is completely burnt in oxygen.

(c) <u>Heat of Neutralisation</u>

It is the amount of heat change (evolved) when 1 g equivalent of an acid in its aqueous and dilute solution is completely neutralised by a base through its dilute solution* and vice versa. Various examples are :

- (i) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l), \qquad \Delta H = -13.6 \text{ K cal/eq or } -57.1 \text{ kJ/eq}.$
- (ii) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4 + 2H_2O$, $\Delta H = -27.2 \text{ K cal/}$

But if in this process, either a weak acid or a weak base is involved, the heat of neutralisation is always less than 13.6 kcal/eq.

(d) <u>Heat of Hydrogenation</u>

It is the amount of heat change (evolved) when one mole of an unsaturated organic compound is completely hydrogenated.

$$CH_2 = CH_2(g) + H_2(g) \rightarrow CH_3 - CH_3(g)$$

(e) <u>Heat of Hydration</u>

It is the amount of heat change when one mole of an anhydrous salt combines with the required number of moles of water to form its hydrate. e.g.

 $\begin{array}{c} CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s) + Q(78.55kJ) \\ anhydrous \\ (Colourless) \end{array}$

 $\Delta H_{\rm hydration~(Anhydrous~salt)} = \Delta H_{\rm solu.(anhydrous~salt)} - \Delta H_{\rm solu.~(Hydrated~salt)}$

(f) <u>Heat of Solution</u>

It is the amount of heat change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change e.g.,

 $NH_4Cl(s) + aq \rightarrow NH_4Cl(aq) - Q$

 $NaOH(s) + aq \rightarrow NaOH(aq) + Q$

(g) Born Haber Cycle

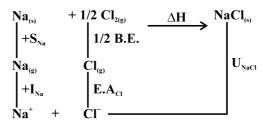
Lattice energies are calculated by employing energies involved in the various steps leading to the formation of an ionic compound. These steps can be shown graphically as a cycle hence the name Born - Haber cycle.

Let us take an example of formation of an ionic compound NaCl, by the reaction of solid Na and gaseous chlorine at 25°C and 1 atm. This process evolves 410.9 kJ/mole

 $Na_{(s)} + \frac{1}{2}Cl_{2(s)} \rightarrow NaCl(s), \quad \Delta H = -410.9 \text{ kJ/mole}$

This reaction consists of no. of steps. According to the principle of conservation of energy, the algebraic sum of the individual energy changes during various steps must be same as that of the overall change in energy.

The various steps can be represented by Born Haber Cycle as,



Hence the overall change in the reaction is

$$\Delta \mathbf{H} = \mathbf{S} + \mathbf{I} + \frac{\mathbf{B}.\mathbf{E}.}{2} + \mathbf{E}.\mathbf{A}. + \mathbf{U} \qquad [\text{EA and } \mathbf{U} \text{ is } -\text{ve}]$$

Practice Problems :

1. ΔH_{f}^{0} for CO₂(g), CO(g) and H₂O(g) are respectively -339.5, -110.5 and -240.8 kJ, Mol⁻¹. The standard enthalpy change in (kJ) for the reaction CO₂(g) + H₂(g) \rightarrow CO(g) + H₂O(g) is

(a) 524.1 (b)
$$-11.8$$
 (c) -262.5 (d) -41.2

2. Given that

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 $C + O_2 \rightarrow CO_2; \quad \Delta H^0 = -x \text{ kJ}$ $2CO + O_2 \rightarrow 2CO_2; \quad \Delta H^0 = -y \text{ kJ}$ then enthalpy of formation of CO(g) is (a) y - 2x (b) (2x - y)/2 (c) (y - 2x)/2 (d) (x - y)/2

3. Let us study the formation of NaCl then ΔH_{t} of NaCl is

$$Na(s) + 1/2 Cl_{2}(g) \xrightarrow{\Delta H_{r}} NaCl$$

$$\downarrow S(+) \qquad \downarrow \frac{D}{2}(+)$$

$$Na(g) \qquad Cl(g)$$

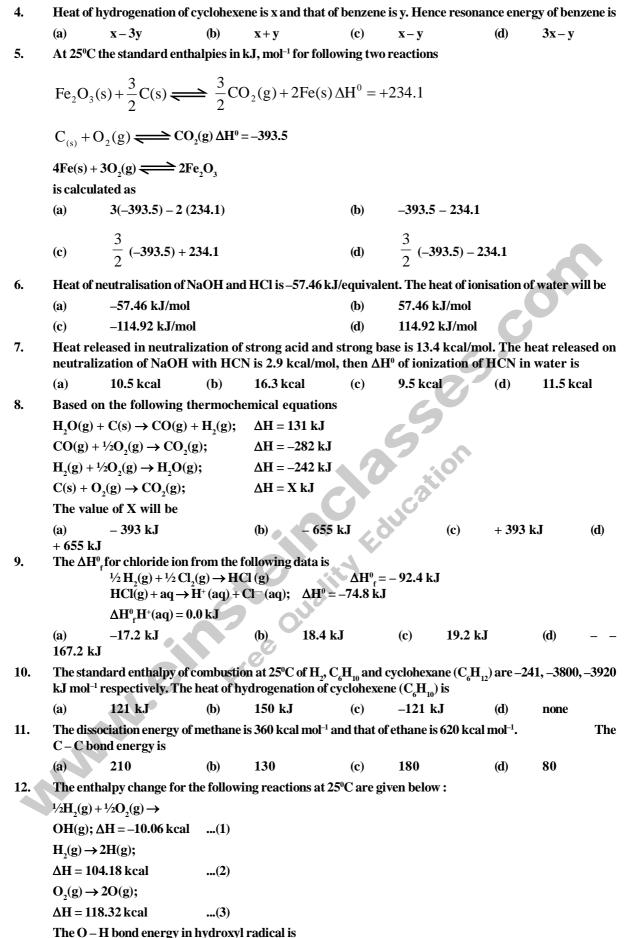
$$\downarrow IE(+) \qquad \downarrow EA(-)$$

$$Na_{(g)}^{+} \qquad Cl_{(g)}^{-}$$

$$(a) \qquad S + \frac{1}{2}D + IE + EA + U \qquad (b) \qquad S + \frac{1}{2}D + IE - EA + U$$

$$(c) \qquad S + \frac{1}{2}D - IE + EA + U \qquad (d) \qquad S + \frac{1}{2}D + IE - EA - U$$

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(c)

110.11 kcal

(**d**)

111.23 kcal

116.15 kcal

(a)

121.31 kcal

(b)

C8 <u>First law of Thermodynamics</u>

Energy may be converted from one form to another, but it is impossible to create or destroy it. There are various ways of enhancing the first law of thermodynamics. Some of the selected statements are given below :

C9 Mathematical Formulation of the First Law

Suppose a system absorbs a quantity of heat q and its state change from A to B. This heat is used up.

- i) In increasing the internal energy of the system i.e., $\Delta E = E_{B} E_{A}$
- ii) To do some external work 'w' by the system on its surroundings.

From the first law, we get.

Heat obsorbed by the system = its internal energy + work done by the system.

 \therefore $q = \Delta E + w$...1

The sign convention : According to latest S.I. convention, w is taken as negative if work is done by the system whereas it is taken as positive if work is done on the system. When heat is given by the system to surrounding it is given as negative sign. When heat is absorbed by the system from the surrounding then positive sign is given

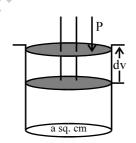
- iii) q and w are not state function because changes in their magnitude is dependent on the path by which the change is accomplished. Mathematically q & w are not exact differential and we always write the inexact differential by δq , δ w etc.
- iv) For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition.

 $\oint d\mathbf{q} = \oint d\mathbf{w}$ i.e. the total work obtained is equal to the net heat supplied.

- v) In an isolated system, there is no heat exchange with the surrounding i.e. dQ = 0
 - \therefore dE + dW = 0
 - or dw = -dE

C10 <u>Work in Reversible Process :</u>

a) Expansion of a gas



Suppose n moles of a perfect gas is enclosed in a cylinder by a friction less piston. The whole cylinder is kept in large constant temperature bath at TK. Any change that would occur to the system would be isothermal.

 \therefore w = P . dV

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Let the gas expand from initial volume V_1 to the final volume V_2 , then the total work done $(\mathbf{w}) = -\int_{\mathbf{v}_1}^{\mathbf{v}_2} \mathbf{P} d\mathbf{V}$

(b) Work done in isothermal reversible expansion of an ideal gas: The small amount of work done, dw when the gas expands through, a small volume dV, against the external pressure, P is given by

$$dw = -PdV$$

 \therefore Total work done when the gas expands from initial volume V, to final volume V, will be

$$\mathbf{W} = \int_{\mathbf{v}_1}^{\mathbf{v}_2} \mathbf{P} \mathbf{d} \mathbf{V} , \quad \mathbf{W} = \int_{\mathbf{v}_1}^{\mathbf{v}_2} \frac{\mathbf{n} \mathbf{R} \mathbf{T}}{\mathbf{V}} \mathbf{d} \mathbf{V} \quad [\because \mathbf{T} = \text{constant}],$$

W = -nRT ln
$$\frac{V_2}{V_1}$$
 = -2.303 nRT log $\frac{V_2}{V_1}$ = -2.303 nRT log $\frac{P_1}{P_2}$

The -ve sign indicates work of expansion.

Note : Work in the reversible process is the maximum and is greater than that in the irreversible process.

Practice Problems :

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- 1. 2.5 mol of ideal gas at 2 atm and 300k expands isothermally to 2.5 times of its original volume against the external pressure of 1 atm. The calculated value of q, w and ΔE are
 - (a)
 -4.7 kJ, 0 and + 4.7 kJ
 (b)
 + 4.7 kJ, 0 and 4.7 kJ

 (c)
 -4.7 kJ, 0 and 0
 (d)
 0, 0 and + 4.7 kJ

 [Answers : (1) a]
 (d)
 (e)
 (f)

(c) Adiabatic Process (Reversible) :

An adiabatic change by definition, is one which does not allow any transfer of heat, i.e., q = 0, it follows from the 1st law,

$$\Delta U = -W$$
$$dU = -dW$$

Let only mechanical work of expansion or contraction is involved, dW = PdV. Moreover,

$$dU = C_v dT$$
$$C_v dT = -PdV$$

 $PV^{\gamma} = constant$

Similarly
$$\mathbf{T}\mathbf{V}^{\gamma-1} = \mathbf{T}\left(\frac{\mathbf{R}\mathbf{T}}{\mathbf{P}}\right)^{\gamma-1} = \text{constant}$$

 $T^{\gamma}P^{1-\gamma} = constant$

(d) Adiabatic work :

 $dW = -C_v dT = -C_v (T_2 - T_1) = C_v (T_1 - T_2)$ Where T₁, T₂ are initial and final temperatures. For 1 mole of gas T = PV/R Hence adiabatic work

$$W = C_{V} \left(\frac{P_{1}V_{1}}{R} - \frac{P_{2}V_{2}}{R} \right) = \frac{C_{V}}{R} (P_{1}V_{1} - P_{1}V_{2})$$

 $W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$ or

(e) Isochoric Process : dW = 0

Limitations of first Law of Thermodynamics

- 1. This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into the other.
- 2. The first law fails to contradict the non-existence of a 100% efficient heat engine or a regrigerator.

C11 Second law of thermodynamics

It has been stated in several forms as follows.

- i) All the spontaneous process are irreversible in nature.
- The entropy of universe is always increasing in the course of every spontaneous process. ii)
- asing in asin asing in asing in asing in asing in asing in asing in asing i Spontaneous or natural process are always accompanied with an increasing in entropy. iii)