Chapter 6. Thermodynamics

Question-1

State and explain Hess's law of constant heat summation by taking a suitable example.
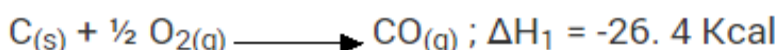
Solution:

The total heat change (ΔH) accompanying a chemical reaction is the same whether the reaction takes place in one step or more steps"

In means that the heat of a reaction depends only on the initial and final states of the system and independent of the path follwed by the system. Carbon can be converted into carbon dioxide either directly or via the formation of carbon monoxide. Formation of CO_2 directly.

$C_{(S)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H = -94$ Kcal

Formation of CO_2 via formation of carbon dioxide.

$C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}$; $\Delta H_1 = -26.4$ Kcal

$CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H_2 = 67.6$ Kcal

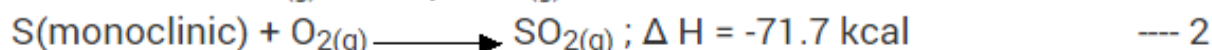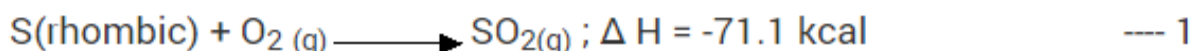According to Hess's Law : $\Delta H = \Delta H_1 + \Delta H_2$
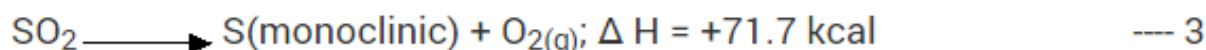
$$-94 = -26.4 + (-67.6)$$
$$-94 = -94.$$

Question-2

What is heat of enthalpy for the transition of S rhombic to S monoclinic (heat of combustion of S (rhombic) and S monoclinic are −71.1 kcal and − 71.7 k cal respectively)?
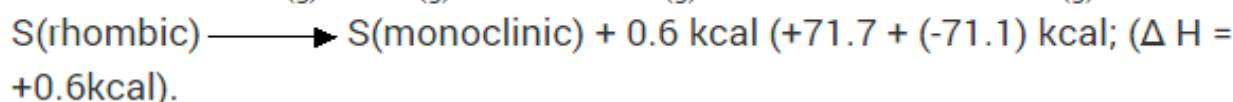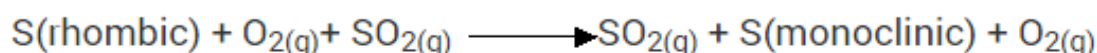
Solution:

$S(\text{rhombic}) + O_{2\ (g)} \longrightarrow SO_{2(g)}$; $\Delta H = -71.1$ kcal   ---- 1

$S(\text{monoclinic}) + O_{2(g)} \longrightarrow SO_{2(g)}$; $\Delta H = -71.7$ kcal   --- 2

Reverse equation (2),

$SO_2 \longrightarrow S(\text{monoclinic}) + O_{2(g)}$; $\Delta H = +71.7$ kcal   --- 3

On adding 1 and 3 we get

$S(\text{rhombic}) + O_{2(g)} + SO_{2(g)} \longrightarrow SO_{2(g)} + S(\text{monoclinic}) + O_{2(g)}$

$S(\text{rhombic}) \longrightarrow S(\text{monoclinic}) + 0.6$ kcal ($+71.7 + (-71.1)$ kcal; ($\Delta H = +0.6$kcal).

Question-3

Derive the mathematical formulae of first law of thermodynamics.

Solution:

Let q be the heat supplied to the system

A part of q may be used up by the system itself in increasing its internal energy by ΔE and rest is used for performing external work w.

$\therefore$ As per first law, $q = \Delta E + w$

$$\Delta E = q - w$$

If work done is the pressure - volume, then $w = p.dv$ where dv is the change in volume P is the external pressure.

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

Question-4

Show that the heat absorbed at constant volume is equal to the increase in the internal energy of the system, whereas that at constant pressure is equal to the increase in the enthalpy of the system.

Solution:

As per mathematical form of first law of thermodynamics, $\Delta E = q - P\Delta V.$

At constant volume,

$\Delta V = 0$; (ie) $\Delta E = q - o = \Delta E = q$; That is heat absorbed at constant volume is equal to the increase in the internal energy of the system.

From definition,

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

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

At constant pressure, $\Delta p = o$;

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

substitution $\Delta H = q_p - P\Delta V$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p.$$

Question-5

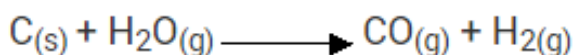**What is the relation between enthalpy of reaction and enthalpies of formation?**

Solution:

Enthalpy of reaction

ΔH = [Sum of the standard enthalpies of formation of products] - [sum of the standard enthalpies of formation of the reactants]

= $\Sigma \Delta H^0f$ products - $\Sigma \Delta H^0f$ reactants.

Question-6

Given the standard enthalpies of formation of $CO_{(g)}$ and $H_2O_{(g)}$ as −110.5 kJ and −241.8 KJ mol^{-1} respectively. Calculate ΔH^0 and ΔE^0 for the reaction.

Solution:

$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$

$\Delta H^0 = \Sigma \Delta H^0_f$ products - $\Sigma \Delta H^0_f$ reactants

= - 110.5 - (-241.8)

ΔH^0 = +131.3 ;

Δn = 2-1 = 1;

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

$\Delta E^0 = \Delta H^0 - (\Delta n) RT$

= +131.3 - (1) (8.314 ×^{3} k Jk$^-$)(298 k)

= +131.3 - 2.478 KJ

= 128.82 kJ.

Question-7

(a) What is the relationship between enthalpy of reaction and bond energies of reactants and products?

(b) Calculate the enthalpy change (ΔH) of the following reaction:
$2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$, **given average bond energies of various bonds**
(i.e.) C – H, C $\equiv$ C, O = O, O – H as 414, 810,499, 724 and 460 kJ mole^{-1} respectively.
One C_2H_2 contains two C – H bonds and one C $\equiv$ C bond
One O_2 contains one O=O bonds
One CO_2 contains, two C=C bonds
One H_2O contains two O – H bonds.

Solution:

(a) Enthalpy of reaction = [Sum of bond energies of reactants] - [sum of bond energies products]

(b) Bond energy due to one C_2H_2 molecule	= (2 × C - H bond energy) + (1 × C $\equiv$ C bond energy)
	= (2 × 414) + (1 × 810) kJmol^{-1}
B. E of one O_2	= (1 × 0 = 0 bond energy) = 499 kJmol^{-1}
B. E of one CO_2	= (2 × 724 kJmol^{-1})
B. E of one H_2O	= 1 × 460 kJ mole^{-1}

ΔH = [Total energy required to break the bonds in reactants] - [Energy given out in forming the bonds in products]
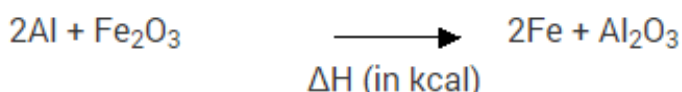$\Delta H = (4\ \Delta H_{C-H} + 2\Delta H_{C \equiv C} + 5\ \Delta H_{O=O}) - [8\ \Delta_{C=O} + 4\ \Delta H_{O-H}]$
$= (4 × 414 + 2 × 810 + 5 × 499) - (8 × 724 + 4 × 460)$
$= 5771 - 7632 = -1861$ KJ.

Question-8

Calculate the heat of reaction for the reduction of ferric oxide by aluminium (thermite reaction) at 25^0C. The heat of formation of Fe_2O_3 and Al_2O_3 are − 197.3 and 400.5 kcal respectively.

Solution:

The thermite reaction is as below,

$$2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3$$

$$\Delta H \text{ (in kcal)}$$

2(0) - 197.3   2(O) - 400.5

ΔHf^0 for any element in its standard state is zero.

$\Delta H^0 = \Delta H_p - \Delta H_R$

$= -400.5 - (-197.3)$

$\Delta H^0 = -203.2 kcal = -850 kJ$

(1kcal = 4.18 J).

Question-9

Calculate the difference between heats of reaction at constant pressure and constant volume for the reaction at 25^0C in kJ.

Solution:

$$2C_6H_6(l) + 15 \, O_{2(g)} \longrightarrow 12 \, CO_{2(g)} + 6H_2O(l)$$

$\Delta n = 12 - 15 = -3;$

$\Delta H = \Delta E + \Delta nRT; \Delta H - \Delta E = \Delta nRT$

$= (-)3 \times 8.314 \, JK^{-1}mole^{-1}$

$= (-3) \times 8.314 \times 10^{-3} \times 298 \, KJ \, mole^{-1}$

$= -7.443 \, kJ \, mole^{-1}.$

Question-10

The heat liberated on complete combustion of 7.8g benzene is 327kJ. This heat has been measured at constant volume and at 27^0C. Calculate the heat of combustion of benzene at constant pressure. ($R = 8.3J$ mole^{-1} I_e^{-1}).

Solution:

$C_6H_{6(R)} + 71/2\ O_{2\ (g)} \longrightarrow 6\ CO_{2(g)} + 3H_2O_{(l)}$

Heat liberated on complete combustion of 7.8 g or benzene = 327 kJ

∴Heat liberated on complete combustion of 78 g (1mol) of benzene = 327 kJ

$\Delta n = 6-7\ ½ = -1.5$

$R = 8.3 \times 10^{-3}$ kJ mole^{-1} K^{-1}

$T = 300$ K

$\Delta H = \Delta E + \Delta ngRT;$

$= -327kJ + (-1.5)\ (8.314 \times 10^{-3})\ (300)$ kJ mole^{-1}

$-327 -3.7413 = 330.7413$ KJ

CBSE Class 11 Chemistry
Important Questions
Chapter 6
Thermodynamics

1 Marks Questions

1.Define a system.

Ans. A system in thermodynamics refers to that part of the universe in which observations are made.

2.Define surroundings.

Ans. The rest of the universe which might be in a position to exchange energy and matter with the system is called its surroundings.

3.State the first law of thermodynamics.

Ans. The first law of thermodynamics stales that 'the energy of an isolated system is constant'.

4.What kind of system is the coffee held in a cup?

Ans . Coffee held in a cup is an open system because it can exchange matter (water vapors) and energy (heat) with the surroundings.

5.Give an example of an isolated system.

Ans. Coffee held in a thermos flask is an isolated system because it can neither exchange energy nor matter with the surroundings.

6.Name the different types of the system.

Ans. There are three types of system –

(i) Open system

(ii) Closed system

(iii) Isolated system.

7.What will happen to internal energy if work is done by the system?

Ans. The internal energy of the system will decrease if work is done by the system.

8.From thermodynamic point of view, to which system the animals and plants belong?

Ans. Open system.

9.How may the state of thermodynamic system be defined?

Ans. The state of thermodynamic system may be defined by specifying values of state variables like temperature, pressure, volume.

10.Define enthalpy.

Ans. It is defined as total heat content of the system.

11.Give the mathematical expression of enthalpy.

Ans. Mathematically,

H = U + pv where U is internal energy.

12.When is enthalpy change $\left(\Delta H \right)$ -

(i) positive

(ii) negative.

Ans. (i) ΔH is positive for endothermic reaction which absorbs heat from the surroundings.

(ii) ΔH is negative for exothermic reactions which evolve heat to the surroundings.

13.Give the expression for

(i)isothermal irreversible change, and

isothermal reversible change.

Ans.(i) For isothermal irreversible change $Q = -w = pex\ (v_f - v_i)$

(ii) For isothermal reversible change$q = -w = nRT\ \ln \dfrac{v_f}{v_i}$

$= 2.303\ nRT\ \log \dfrac{v_f}{v_i}$

14.Define Heat capacity

Ans. The heat capacity for one mole of the substance is the quantity of heat needed fo raise the temperature of one mole by one degree Celsius.

15.Define specific heat.

Ans. Specific heat /specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree Celsius (or one Kelvin).

16.Give the mathematical expression of heat capacity.

Ans. The mathematical expression of heat capacity

$q = c\ x\ m\ x\ \Delta T$ (c = heat capacity) when m = 1

$= C\Delta T$

where C = specific heat

m = mass

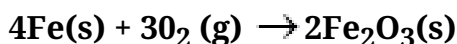ΔT = temperature change.

17. Define reaction enthalpy.

Ans. The enthalpy change accompanying a reaction is called the reaction enthalpy (ΔrH).

18. Define standard enthalpy.

Ans. The standard enthalpy of reaction is the enthalpy change for a reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

19. The standard heat of formation of Fe_2O_3 (s) is 824.2kJ mol^{-1} Calculate heat change for the reaction.

$4Fe(s) + 3O_2 (g) \longrightarrow 2Fe_2O_3(s)$

Ans. $\Delta H^° = \sum \Delta H_f^°(products) - \sum \Delta H_f^°(reac \tan ts)$

= [2 X ΔH_f^O $Fe_2O_3(s)$] – [4 ΔH_f $^O Fe$ (s) + 3 ΔH_f $^O O_2(g)$]

= 2(-824.2kJ) – [4 x 0 + 3 x 0]

= $-1648.4kJ$

20. Define spontaneous process.

Ans. A spontaneous process is an irreversible process and may only be reversed by some external agency.
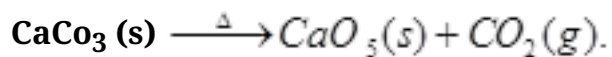
21. Define non-spontaneres process.

Ans. A process is said to be non-spontaneous if it does not occur of its own under given condition and occur only when an external force is continuously applied.

22.What is the sign of enthalpy of formation of a highly stable compound?

Ans. Negative.

23.Predict the sign of ΔS **for the following reaction**

CaCo$_3$ (s) $\xrightarrow{\Delta} CaO_5(s) + CO_2(g).$

Ans. ΔS is positive.

24.Two ideal gases under same pressure and temperature are allowed to mix in an isolated system – what will be sign of entropy change?

Ans. Entropy change is positive. It is because disorder or degree of freedom increase on mixing.

CBSE Class 12 Chemistry
Important Questions
Chapter 6
Thermodynamics

2 Marks Questions

1.Change in internal energy is a state function while work is not, why?

Ans. The change in internal energy during a process depends only upon the initial and final state of the system. Therefore it is a state function. But the work is related the path followed. Therefore, it is not a state function.

2.With the help of first law of thermodynamics and H = U + pv, prove $\Delta H = q_p$

Ans. The enthalpy is defined as

H = U + pv

For a change in the stales of system,

$$\Delta H = \Delta \left(U + pv\right)$$

$$= \Delta U + \Delta\left(pv\right)$$

$$= \Delta U + p\Delta v + v\Delta p \ldots\ldots\ldots\ldots(i)$$

The first law of thermodynamics states that –

$$\Delta U = q + w$$

$$= q - \Delta v \ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

From (i) and (ii),

$$\Delta H = q - \cancel{\Delta v} + p\cancel{\Delta v} + v\Delta p$$

$= q + V\Delta p$

When the pressure is constant,

$\Delta p = 0,$ then $v\Delta p = 0,$

$\therefore \Delta H = q \,(at \text{ constant pressure})$

$\Delta H = qp$

3.Why is the difference between ΔH and ΔU not significant for solids or liquids?

Ans. The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids because they do not suffer any significant volume changes upon heating.

4.What is an extensive and intensive property?

Ans. Extensive property is a property whose value depends on the quantity or size of matter present in the system.

Intensive property is a property which do not depend upon the quantity or size of matter present.

5.Show that for an ideal gas Cp- Cv = R

Ans. When a gas is heated under constant pressure, the heat is required for raising the temperature of the gas and also for doing mechanical work against the external pressure during expansion.

At constant volume, the heat capacity, C is written as Cv and at constant pressure this is denoted by Cp.

we write heat q

at constant volume as qv = Cv $\Delta T = \Delta U$

at constant pressure as qp = $Cp\Delta T = \Delta H$

The difference between Cp and Cv can be derived for an ideal gas as :

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pv)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$\therefore \quad \Delta H = \Delta U + R\Delta T$ _ _ _ _ _ _ _ (i)

On putting the values of ΔH and ΔU, we have;

$$Cp\Delta T = Cv\Delta T + R\Delta T$$

Cp = Cv +R

$$Cp - Cv = R$$

6.Show that for an ideal gas, the molar heat capacity under constant volume conditions is equal to 3/2 R.

Ans. For an ideal gas, from kinetic theory of gases, the average kinetic energy per mole (Ek) of the gas at any temperature T_k is given by $Ek = \frac{3}{2}RT$

At (T+1)k, the kinetic energy per mole (Ek^1) is Ek^1 = $\frac{3}{2}R(T+1)$

Therefore increase in the average kinetic energy of the gas for 1^{0}C (or 1K) rise in temperature is $\Delta \overline{E}_k = \frac{3}{2}R(T+1) - \frac{3}{2}RT = \frac{3}{2}R$

$\overline{E}_k$ by definition is to the molar heat capacity of a gas at constant volume, Cv.

$$\therefore Cv = \frac{3}{2}R$$

7.A 1.25g sample of octane ($C_{18}H_{18}$) is burnt in excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rises from 294.05 to 300.78K. If heat capacity of the calorimeter is 8.93 KJ/K. find the heat transferred to calorimeter.

Ans .Mass of octane,

M = 1.250g.

= 0.00125.

Heat capacity, c = 8.93 kJ/k
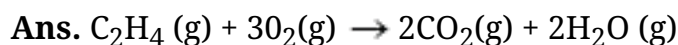
Rise in temp, $\Delta T = 300.78 - 294.05$

= 6.73K

Heat transferred to calorimeter

$= m$ x c x ΔT

= 0.00125 x 8.93 x 6.73

= 0.075 kJ

8.Calculate the heat of combustion of ethylene (gas) to from CO_2 (gas) and H_2O (gas) at 298k and 1 atmospheric pressure. The heats of formation of CO_2, H_2O and C_2H_4 are – 393.7, - 241.8, + 52.3 kJ per mole respectively.

Ans. C_2H_4 (g) + $3O_2$(g) $\rightarrow$ $2CO_2$(g) + $2H_2O$ (g)

$\Delta H_f(CO_2) = -393.7kJ$

$\Delta H_f(H_2O) = -241.8kJ$

$\Delta H_f(C_2H_4) = +52.3kJ$

$$\Delta Hreaction = \sum \Delta H_f^\circ products - \sum \Delta H_f^\circ reactants$$

$$= [2 \times \Delta H_f^{O}(CO_2) + 2 \times \Delta H_f^{O}(H_2O)] - \left[\Delta H_f^{O}(C_2H_4) + 3 \times \Delta H_f^{O}(O_2)\right]$$

= 2 x[(-393.7)m+2x (-241.8)] – [(523.0) + 0)]

$$\left[\therefore \Delta H_f^{O} \text{ fot elementary substance} = 0\right]$$
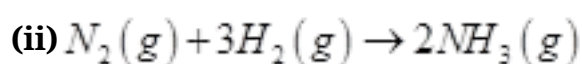
= [-787.4 – 483.6] -53.3

= - 1323.3 kJ.

9.Give two examples of reactions which are driven by enthalpy change.

Ans. Examples of reactions driven by enthalpy change:

The process which is highly exothermic, i.e. enthalpy change is negative and has large value but entropy change is negative is said to be driven by enthalpy change, eg.
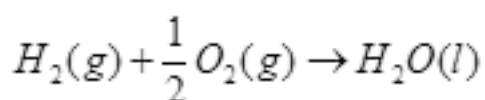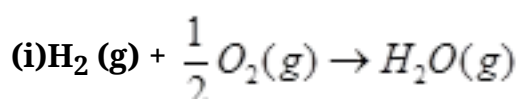
(i) $H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)$

$\Delta H_f^{O} = -285.8kJ \, mol^{-1}$

(ii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
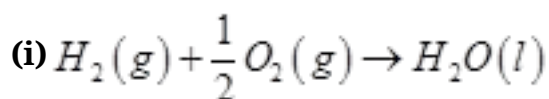
$\Delta H^{O} = -92k \, J \, mol^{-1}$.

10.Will the heat released in the following two reactions be equal? Give reasons in support of your answer.

(i)H$_2$ (g) + $\dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)$

Ans. No, the heats released in the two reactions are not equal. The heat released in any reaction depends upon the reactants, products and their physical states. Here in reaction (i), the water produced is in the gaseous state whereas in reaction (ii) liquid is formed. As we know, that when water vapors condensed to from water, heat equal to the latent heat of vaporization is released. Thus, more heat is released in reaction (ii).

11. What is the relation between the enthalpy of reaction and bond enthalpy?

Ans .A chemical reaction involves the breaking of bonds in reactants and formation of new bonds in products. The heat of reaction (enthalpy change) depends on the values of the heat needed to break the bond formation .Thus

(Heat of reaction = (Heat needed to break the bonds in reactants – Heat liberated to from bonds in products).

ΔH^O = Bond energy in (to break the bonds) - Bond energy out (to form the bonds)

= Bond energy of reactants – Bond energy of products.

12. The reaction C (graphite) + O_2 (g) $\rightarrow$ CO_2(g) + 393.5 kJ mol^{-1} represents the formation of CO_2 and also combustion of carbon. Write the ΔH^O values of the two processes.

Ans.(i) The standard enthalpy of formation of CO_2 is -393.5 kJ per mole of CO_2.

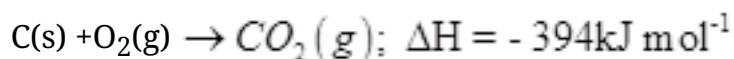That is $\Delta H_f^O \left(CO_2, g \right) = -393.5 kJ \ \text{mol}^{-1}$.

(ii) The standard enthalpy of combustion of carbon is - 393.5 kJ per mole of carbon i.e. $\Delta H^O comb(c) = -393.5 \ \text{kJ mol}^{-1}$.
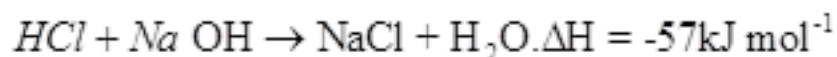
13. Explain how is enthalpy related to spontaneity of a reaction?

Ans. Majority of the exothermic reactions are spontaneous because there is decrease in energy.

Burning of a substance is a spontaneous process.

C(s) $+O_2$(g) $\rightarrow CO_2(g)$; $\Delta H = -394$kJ mol^{-1}

Neutralisation of an acid with a base is a spontaneous reaction.

$HCl + Na\ OH \rightarrow NaCl + H_2O.\Delta H = -57$kJ mol^{-1}

Many spontaneous reactions proceed with the absorption of heat. Conversion of water into water vapour is an endothermic spontaneous change. Therefore change in enthalpy is not the only criterion for deciding the spontaneity of a reaction.

14.The ΔH and ΔS for $2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$ are given + 61.17kJ mol^{-1} and + 132 Jk^{-1}mol^{-1} respectively. Above what temperature will the reaction be spontaneous?

Ans. The reaction

$2Ag_2O$ (s) $\rightarrow 4Ag(s) + O_2(g)$

Will be spontaneous when ΔG is negative.

Since ΔH is +ve and ΔS is also +ve, the relation

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

Shows that ΔG would be –ve when,

$\Delta H < T\Delta S$

Or T > $\dfrac{\Delta H}{\Delta S}$ = $\dfrac{61170 \text{ mol}^{-1}}{132 Jk^{-1}mol^{-1}}$ = $463.4K$

$\therefore$ The process will be spontaneous above a temperature of $463.4K$.

CBSE Class 12 Chemistry
Important Questions
Chapter 6
Thermodynamics

3 Marks Questions

1.Give the relationship between ΔU and ΔH for gases.

Ans. For gases the volume change is appreciable.

let V_A be the total volume of gaseous reactants, and

V_B be the total volume of gaseous product.

n_A be the number of moles of the reactant and

n_B be the number of moles of the product,

Then at constant pressure and temperature,

p V_A = n_A RT

p V_B = n_B RT

or p V_B - pV_A = (n_B - n_A) RT

or p $\Delta V = \left(\Delta n \right)_g RT$

where $\left(\Delta n \right)_g = n_B n_A$ and is equal to the difference between the number of moles of gaseous products and gaseous reactants.

Substituting the value of p ΔV awe get.

$$\Delta H = \Delta U + \left(\Delta n \right)_g RT$$

∴ $\Delta H = qp$ (heat change under constant pressure)

$\Delta U = qv$ (heat change under constant volume)

∴ for gaseous system.

$$qp = qv + (\Delta n)_g RT$$

2. It has been found that 221.4J is needed to heat 30g of ethanol from 15^0C to 18^0C. calculate (a) specific heat capacity, and (b) molar heat capacity of ethanol.

Ans.(a) Specific heat capacity

$$\frac{Heat \text{ absorbed by the substance}}{Mass \text{ of the substance x Rise in temp.}}$$

$$C = \frac{221.4j}{30g \left(18^0c - 15^0c\right)} = \frac{221.4}{30 \times 3} Jg^{-1} \, {}^0c^{-1}$$

$$= \underline{2.46J \, g^{-1} \, {}^0c^{-1}}$$

Since 1^0C is equal to 1k, the specific heat capacity of ethanol = 2.46Jg^{-1} ^{0}c^{-1}.

(b) Molar heat capacity, Cm = specific heat x molar mass.

Therefore, Cm (ethanol) = 2.46 x 46

= 113.2 Jmol^{-1} ^{0}c^{-1}

The molar heat capacity of ethanol is 113.2 J mol^{-1} ^{0}c^{-1}.

Chemical Thermodynamics

Short Answer Type Questions

1. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalphy of vapourisation for water?

2. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?

3. 22. Standard molar enthalpy of formation, $\Delta_f H^{\ominus}$ is just a special case of enthalpy of reaction, $\Delta_r H^{\ominus}$. Is the $\Delta_r H^{\ominus}$ for the following reaction same as $\Delta_f H^{\ominus}$? Give reason for your answer.

   $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$; $\Delta_f H^{\ominus} = -178.3$ kJ mol^{-1}
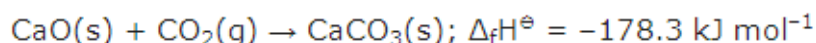
4. The value of $\Delta_f H^{\ominus}$ for NH_3 is -91.8 kJ mol^{-1}. Calculate enthalpy change for the following reaction :

   $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

5. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$..... etc. for intermediate reactions.

6. The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond?

7. 26. Use the following data to calculate $\Delta_{lattice} H^{\ominus}$ for NaBr.

   $\Delta_{sub} H^{\ominus}$ for sodium metal = 108.4 kJ mol^{-1}

   Ionization enthalpy of sodium = 496 kJ mol^{-1}

   Electron gain enthalpy of bromine = -325 kJ mol^{-1}

   Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

   $\Delta_f H^{\ominus}$ for NaBr (s) = -360.1 kJ mol^{-1}

8. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

9. Heat has randomising influence on a system and temperature is the measure of average

chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

10. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

11. At 298 K. K_p for the reaction $N_2O4(g) \rightleftharpoons 2NO_2 (g)$ is 0.98. Predict whether the reaction is spontaneous or not.

12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?
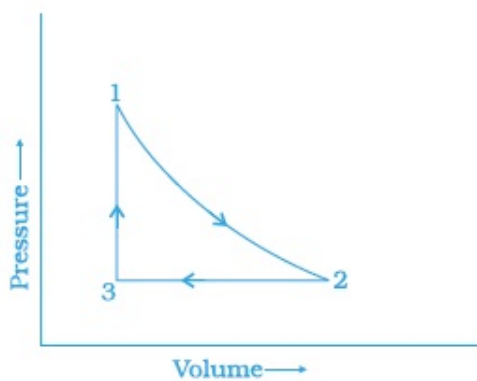

Fig. : 6.1

13. The standard molar entropy of $H_O(l)$ is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more, or less than 70 J K^{-1} mol^{-1}?

14. Identify the state functions and path functions out of the following :
    enthalpy, entropy, heat, temperature, work, free energy.

15. The molar enthalpy of vapourisation of acetone is less than that of water. Why?

16. Which quantity out of Δ_rG and $\Delta_rG^{\ominus}$ will be zero at equilibrium?

17. Predict the change in internal energy for an isolated system at constant volume.

18. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

19. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the

change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre?

20. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

21. The difference between C_P and C_V can be derived using the empirical relation H = U + pV. Calculate the difference between C_P and C_V for 10 moles of an ideal gas.

22. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

23. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

24. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1} . Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1}).

25. The enthalpy of reaction for the reaction :

$2H_2 (g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta_R H^{\ominus}$ = $-$ 572 kJ mol^{-1}. What will be standard enthalpy of formation of $H_2O(l)$?

26. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 6.2. Explain graphically.
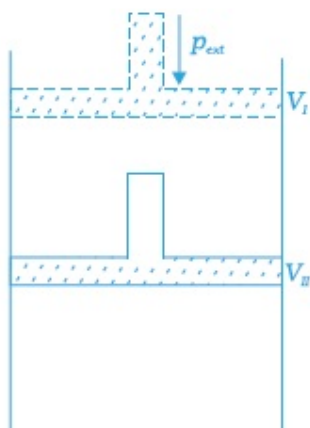
Fig. : 6.2

27. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

28. Represent the potential energy/enthalpy change in the following processes graphically.
    ○ (a) Throwing a stone from the ground to roof.
    ○ (b) $(1/2)H_2(g) + (1/2)Cl_2(g) \rightleftharpoons HCL(g)$ $\Delta_r H^\ominus = -92.32$ kJ mol^{-1}

29. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide spontaneity of a reaction from given diagram. Explain.
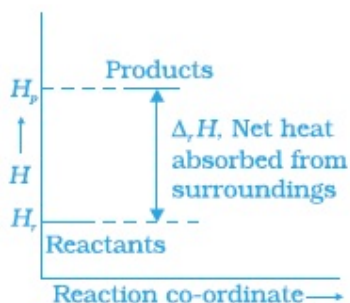

Fig. : 6.3

30. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.
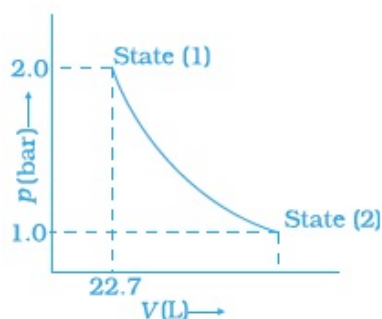
Fig. : 6.4

31. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step.
Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?
(Given that 1 L bar = 100 J)

Long Answer Type Questions

1. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

2. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.
Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

3. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s).

4. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?

5. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_F, V_F). With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_F.