

Maharashtra State Board Class 12 Chemistry Solutions Chapter 4

Chemical Thermodynamics

1. Select the most appropriate option.

Question 1.

The correct thermodynamic conditions for the spontaneous reaction at all temperatures are

- (a) $\Delta H < 0$ and $\Delta S > 0$
- (b) $\Delta H > 0$ and $\Delta S < 0$
- (c) $\Delta H < 0$ and $\Delta S < 0$
- (d) $\Delta H < 0$ and $\Delta S = 0$

Answer:

- (a) $\Delta H < 0$ and $\Delta S > 0$

Question ii.

A gas is allowed to expand in a well-insulated container against a constant external pressure of 2.5 bar from an initial volume of 2.5 L to a final volume of 4.5 L. The change in internal energy, ΔU of the gas will be

- (a) -500 J
- (b) +500J
- (c) -1013 J
- (d) +1013 J

Answer:

- (a) -500 J

Question iii.

In which of the following, entropy of the system decreases ?

- (a) Crystallisation of liquid into solid
- (b) Temperature of crystalline solid is increased from 0 K to 115 K
- (c) $\text{H}_{2(g)} \rightarrow 2\text{H}_{(g)}$
- (d) $2\text{NaHCO}_{3(s)} \rightarrow \text{Na}_2\text{CO}_{3(s)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(g)}$

Answer:

- (a) Crystallisation of liquid into solid

Question iv.

The enthalpy of formation for all elements in their standard states is

- (a) unity
- (b) zero
- (c) less than zero
- (d) different elements

Answer:

- (b) zero

Question v.

Which of the following reactions is exothermic ?

- (a) $\text{H}_{2(g)} \rightarrow 2\text{H}_{(g)}$
- (b) $\text{C}_{(s)} \rightarrow \text{C}_{(g)}$
- (c) $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$
- (d) $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$

Answer:

- (c) $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$

Question vi.

6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat. Enthalpy of vaporization of ethanol will be

- (a) 43.4 kJ mol⁻¹
- (b) 60.2 kJ mol⁻¹
- (c) 38.9 kJ mol⁻¹
- (d) 20.4 kJ mol⁻¹

Answer:

- (a) 43.4 kJ mol⁻¹

Question vii.

If the standard enthalpy of formation of methanol is -238.9 kJ mol⁻¹ then entropy change of the surroundings will be

- (a) -801.7 JK⁻¹
- (b) 801.7 JK⁻¹
- (c) 0.8017 JK⁻¹
- (d) -0.8017 JK⁻¹

Answer:

(b) 801.7 JK⁻¹

Question viii.

Which of the following are not state functions ?

1. Q + W 2. Q 3. W 4. H-TS

(a) 1, 2 and 3

(b) 2 and 3

(c) 1 and 4

(d) 2, 3 and 4

Answer:

(b) 2 and 3

Question ix.

For vaporization of water at 1 bar, $\Delta H = 40.63 \text{ kJ mol}^{-1}$ and $\Delta S = 108.8 \text{ JK}^{-1} \text{ mol}^{-1}$. At what temperature, $\Delta G = 0$?

(a) 273.4 K

(b) 393.4 K

(c) 373.4 K

(d) 293.4 K

Answer:

(c) 373.4 K

Question x.

Bond enthalpies of H – H, Cl – Cl and H – Cl bonds are 434 kJ mol⁻¹, 242 kJ mol⁻² and 431 kJ mol⁻¹, respectively. Enthalpy of formation of HCl is

(a) 245 kJ mol⁻¹

(b) -93 kJ mol⁻¹

(c) -245 kJ mol⁻¹

(d) 93 kJ mol⁻¹

Answer:

(b) -93 kJ mol⁻¹

2. Answer the following in one or two sentences.

Question i.

Comment on the statement: No work is involved in an expansion of a gas in vacuum.

Answer:

(1) When a gas expands against an external pressure P_{ex} , changing the volume from V_1 to V_2 , the work obtained is given by

$$W = -P_{\text{ex}} (V_2 - V_1).$$

(2) Hence the work is performed by the system when it experiences the opposing force or pressure.

(3) Greater the opposing force, more is the work.

(4) In free expansion, the gas expands in vacuum where it does not experience opposing force, ($P = 0$). Since external pressure is zero, no work is obtained.

$$\therefore W = -P_{\text{ex}} (V_2 - V_1)$$

$$= -0 \times (V_2 - V_1)$$

$$= 0$$

(5) Since during expansion in vacuum no energy is expended, it is called free expansion.

Question ii.

State the first law of thermodynamics.

Answer:

The first law of thermodynamics is based on the principle of conservation of energy and can be stated in different ways as follows :

1. Energy can neither be created nor destroyed, however, it may be converted from one form into another.
2. Whenever, a quantity of one kind of energy is consumed or disappears, an equivalent amount of another kind of energy appears.
3. The total mass and energy of an isolated system remain constant, although there may be interconversion of energy from one form to another.
4. The total energy of the universe remains constant.

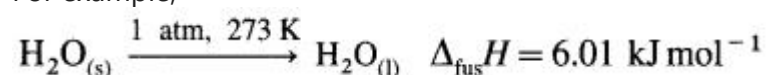
Question iii.

What is enthalpy of fusion?

Answer:

Enthalpy of fusion ($\Delta_{\text{fus}}H$) : The enthalpy change that accompanies the fusion of one mole of a solid into a liquid at constant temperature and pressure is called enthalpy of fusion.

For example,



This equation describes that when one mole of ice melts (fuses) at 0 °C (273 K) and 1 atmosphere, 6.1 kJ of heat will be absorbed.

Question iv.

What is standard state of a substance?

Answer:

The thermodynamic standard state of a substance (compound) is the most stable physical state of it at 298 K and 1 atmosphere (or 1 bar). The enthalpy of the substance in the standard state is represented as $\Delta_f H^\circ$.

Question v.

State whether ΔS is positive, negative or zero for the reaction $2H(g) \rightarrow H_2(g)$. Explain.

Answer:

(i) The given reaction, $2H(g) \rightarrow H_2(g)$ is the formation of $H_2(g)$ from free atoms.

(ii) Since two H atoms form one H_2 molecule, $\Delta n = 1 - 2 = -1$ and disorder is decreased. Hence entropy change $\Delta S < 0$ (or negative).

Question vi.

State second law of thermodynamics in terms of entropy.

Answer:

The second law of thermodynamics states that the total entropy of the system and its surroundings (universe) increases in a spontaneous process.

OR

Since all the natural processes are spontaneous, the entropy of the universe increases.

It is expressed mathematically as

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{Universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

Question vii.

If the enthalpy change of a reaction is ΔH how will you calculate entropy of surroundings?

Answer:

(i) For endothermic reaction, $\Delta H > 0$. This shows the system absorbs heat from surroundings.

$$\therefore \Delta_{\text{surr}} H < 0.$$

$$\therefore \text{Entropy change} = \Delta_{\text{surr}} S = -\frac{\Delta_{\text{surr}} H}{T}$$

There is decrease in entropy of surroundings.

(ii) For exothermic reaction, $\Delta H < 0$, hence for surroundings, $\Delta_{\text{surr}} H > 0$

$$\therefore \Delta_{\text{surr}} S > 0.$$

Question viii.

Comment on spontaneity of reactions for which ΔH is positive and ΔS is negative.

Answer:

Since ΔH is +ve and ΔS is -ve, ΔG will be +ve at all temperatures. Hence reactions will be non-spontaneous at all temperatures.

3. Answer in brief.

Question i.

Obtain the relationship between ΔG° of a reaction and the equilibrium constant.

Answer:

Consider following reversible reaction, $aA + bB \rightleftharpoons cC + dD$

The reaction quotient Q is,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The free energy change ΔG for the reaction is $\Delta G = \Delta G^\circ + RT \ln Q$

Where ΔG° is the standard free energy change.

At equilibrium

$$Q = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b} = K$$

$$\therefore \Delta G = \Delta G^\circ + RT \ln K$$

∴ at equilibrium $\Delta G = 0$

$$\therefore 0 = \Delta G^\circ + RT \ln K$$

$$\therefore \Delta G^\circ = -RT \ln K$$

$$\therefore \Delta G^\circ = -2.303 RT \log_{10} K.$$

Question ii.

What is entropy? Give its units.

Answer:

(i) Entropy : Being a state function and thermodynamic function it is defined as entropy change (ΔS) of a system in a process which is equal to the amount of heat transferred in a reversible manner (Q_{rev}) divided by the absolute temperature (T), at which the heat is absorbed. Thus,

$$\text{Entropy change} = \frac{\text{Heat transferred reversibly}}{\text{Absolute temperature of heat transfer}}$$

$$\therefore \Delta S = \frac{Q_{\text{rev}}}{T}$$

- (ii) Units of entropy are JK⁻¹ in SI unit and cal K⁻¹ in c.g.s. units. It is also expressed in terms of entropy unit (e.u.). Hence 1 e.u. = 1 JK⁻¹.
(iii) Entropy is a measure of disorder in the system. Higher the disorder, more is entropy of the system.

Question iii.

How will you calculate reaction enthalpy from data on bond enthalpies?

Answer:

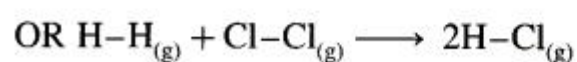
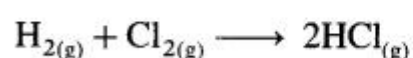
- (i) In chemical reactions, bonds are broken in the reactant molecules and bonds are formed in the product molecules.
(ii) Energy is always required to break a chemical bond while energy is always released in the formation of the bond.
(iii) The enthalpy change of a gaseous reactions ($\Delta_f H_0$) involving substances with covalent bonds can be calculated with the help of bond enthalpies of reactants and products. (In case of solids we need lattice energy or heat of sublimation while in case of liquids we need heat of evaporation.)

$$\Delta H^0(\text{reaction}) =$$

$$\left[\begin{array}{c} \text{Sum of bond enthalpies} \\ \text{of bonds broken} \\ \text{of reactants} \end{array} \right] - \left[\begin{array}{c} \text{Sum of bond} \\ \text{enthalpies of bonds} \\ \text{formed of products} \end{array} \right]$$

$$= \Sigma \Delta H^0_{\text{bonds broken}} - \Sigma \Delta H^0_{\text{bonds formed}}$$

For example for a following reaction,



$$\Delta H^0_{\text{reaction}} = [\Delta H^0_{\text{H-H}} + \Delta H^0_{\text{Cl-Cl}}] - 2[\Delta H^0_{\text{H-Cl}}]$$

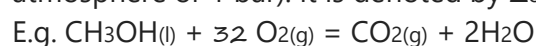
If the energy required to break the bonds of reacting molecules is more than the energy released in the bond formation of the products, then the reaction will be endothermic and ΔH_0 reaction will be positive. On the other hand if the energy released in the bond formation of the products is more than the energy required to break the bonds of reacting molecules then the reaction will be exothermic and ΔH_0 reaction will be negative.

Question iv.

What is the standard enthalpy of combustion ? Give an example.

Answer:

Standard enthalpy of combustion or standard heat of combustion : it is defined as the enthalpy change when one mole of a substance in the standard state undergoes complete combustion in a sufficient amount of oxygen at constant temperature (298 K) and pressure (1 atmosphere or 1 bar). It is denoted by $\Delta_c H_0$.



$$\Delta_c H_0 = -726 \text{ kJ mol}^{-1}$$

($\Delta_c H_0$ is always negative.)

[Note : Calorific value : It is the enthalpy change or amount of heat liberated when one gram of a substance undergoes combustion.

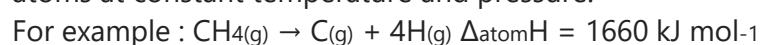
$$\therefore \text{Calorific value} = \frac{\Delta_c H^0}{\text{Molar mass}}$$

Question v.

What is the enthalpy of atomization? Give an example.

Answer:

Enthalpy of atomisation ($\Delta_{\text{atom}} H$) : it is the enthalpy change accompanying the dissociation of one mole of gaseous substance into its atoms at constant temperature and pressure.

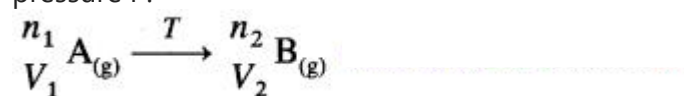


Question vi.

Obtain the expression for work done in chemical reaction.

Answer:

Consider n_1 moles of gaseous reactants A of volume V_1 change to n_2 moles of gaseous products B of volume V_2 at temperature T and pressure P.



In the initial state, $PV_1 = n_1 RT$

In the final state, $PV_2 = n_2 RT$

$$PV_2 - PV_1 = n_2 RT - n_1 RT = (n_2 - n_1) RT = \Delta n RT$$

where Δn is the change in number of moles of gaseous products and gaseous reactants.

Due to net changes in gaseous moles, there arises change in volume against constant pressure resulting in mechanical work, $-P\Delta V$.

$$\therefore W = -P\Delta V = -P(V_2 - V_1) = -\Delta nRT$$

(i) If $n_1 = n_2$, $\Delta n = 0$, $W = 0$. No work is performed.

(ii) If $n_2 > n_1$, $\Delta n > 0$, there is a work of expansion by the system and W is negative.

(iii) If $n_2 < n_1$, $\Delta n < 0$, there is a work of compression, hence work is done on the system and W is positive.

Question vii.

Derive the expression for PV work.

Answer:

Consider a certain amount of an ideal gas enclosed in an ideal cylinder fitted with massless, frictionless rigid movable piston at pressure P , occupying volume V_1 at temperature T .

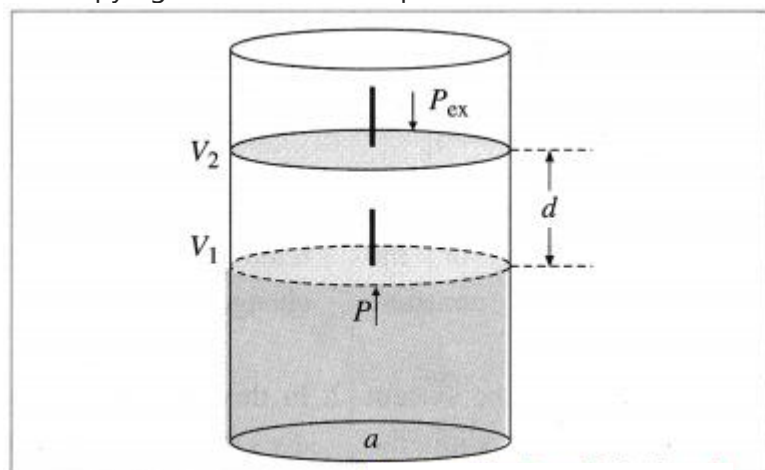


Fig. 4.8 : Work of expansion

As the gas expands, it pushes the piston upward through a distance d against external force F , pushing the surroundings.

The work done by the gas is,

$$W = \text{opposing force} \times \text{distance} = -F \times d$$

-ve sign indicates the lowering of energy of the system during expansion.

If a is the cross section area of the cylinder or piston, then,

$$W = -Fa \times d \times a$$

Now the pressure is $P_{\text{ex}} = Fa$

while volume change is, $\Delta V = d \times a$

$$\therefore W = -P_{\text{ex}} \times \Delta V$$

If during the expansion, the volume changes from V_1 and V_2 then, $\Delta V = V_2 - V_1$

$$\therefore W = -P_{\text{ex}}(V_2 - V_1)$$

During compression, the work W is +ve, since the energy of the system is increased,

$$W = +P_{\text{ex}}(V_2 - V_1)$$

Question viii.

What are intensive properties? Explain why density is intensive property.

Answer:

(A) Intensive property : It is defined as a property of a system whose magnitude is independent of the amount of matter present in the system.

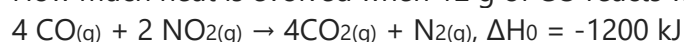
Explanation :

1. Intensive property is characteristic of the system, e.g., refractive index, density, viscosity, temperature, pressure, boiling point, melting point, freezing point of a pure liquid, surface tension, etc.
2. The intensive properties are not additive.

(B) Density is a ratio of two extensive properties namely, mass and volume. Since the ratio of two extensive properties represents an intensive property, density is an intensive property. It does not depend on the amount of a substance.

Question ix.

How much heat is evolved when 12 g of CO reacts with NO_2 ? The reaction is :

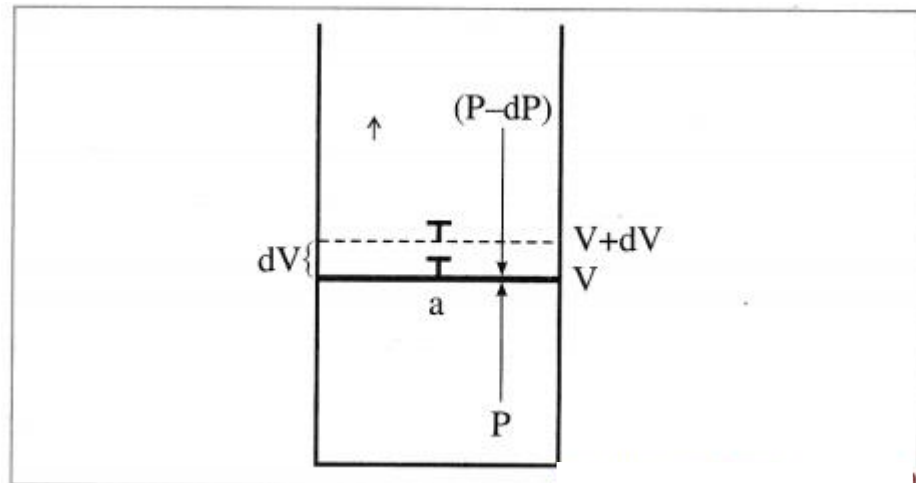


4. Answer the following questions.

Question i.

Derive the expression for the maximum work.

Answer:



Consider n moles of an ideal gas enclosed in an ideal cylinder fitted with a massless and frictionless movable rigid piston. Let V be the volume of the gas at a pressure P and a temperature T .

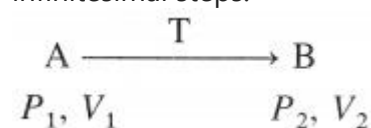
If in an infinitesimal change pressure changes from P to $P - dP$ and volume increases from V to $V + dV$. Then the work obtained is, $dW = -(P-dP) dV$

$$= -PdV + dPdV$$

Since $dP \cdot dV$ is negligibly small relative to PdV

$$dW = -PdV$$

Let the state of the system change from $A(P_1, V_1)$ to $B(P_2, V_2)$ isothermally and reversibly, at temperature T involving number of infinitesimal steps.



Then the total work or maximum work in the process is obtained by integrating above equation.

$$W_{\max} = \int_A^B dW$$

$$= \int_A^B -PdV \quad \because PV = nRT$$

$$\therefore P = \frac{nRT}{V}$$

$$W_{\max} = \int_{V_1}^{V_2} -nRT \frac{dV}{V}$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT (\ln V_2 - \ln V_1)$$

$$= -nRT \log_e \frac{V_2}{V_1}$$

$$\therefore W_{\max} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

At constant temperature,

$$\therefore P_1 \times V_1 = P_2 \times V_2$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore W_{\max} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

where n , P , V and T represent number of moles, pressure, volume and temperature respectively. For the process, $\Delta U = 0$, $\Delta H = 0$.

The heat absorbed in reversible manner

Q_{rev} , is completely converted into work.

$$Q_{\text{rev}} = -W_{\max}$$

Hence work obtained is maximum.

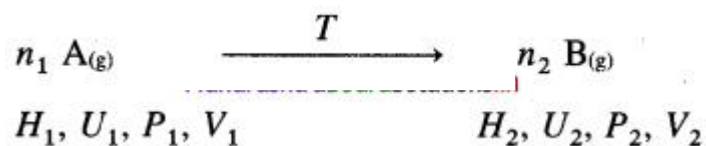
Question ii.

Obtain the relationship between ΔH and ΔU for gas phase reactions.

Answer:

Consider a reaction in which n_1 moles of gaseous reactant in initial state change to n_2 moles of gaseous product in the final state.

Let H_1 , U_1 , P_1 , V_1 and H_2 , U_2 , P_2 , V_2 represent enthalpies, internal energies, pressures and volumes in the initial and final states respectively then,



The heat of reaction is given by enthalpy change ΔH as,

$$\Delta H = H_2 - H_1$$

By definition, $H = U + PV$

$$\therefore H_1 = U_1 + P_1V_1 \text{ and } H_2 = U_2 + P_2V_2$$

$$\therefore \Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$\text{Now, } \Delta U = U_2 - U_1$$

Since $PV = nRT$,

For initial state, $P_1V_1 = n_1RT$

For final state, $P_2V_2 = n_2RT$

$$\therefore P_2V_2 - P_1V_1 = n_2RT - n_1RT$$

$$= (n_2 - n_1) RT$$

$$= \Delta nRT$$

where Δn

$$= \left[\begin{array}{c} \text{Number of moles} \\ \text{of gaseous products} \end{array} \right] - \left[\begin{array}{c} \text{Number of moles of} \\ \text{gaseous reactants} \end{array} \right]$$

$$\therefore \Delta H = \Delta U + \Delta nRT$$

If Q_P and Q_V are the heats involved in the reaction at constant pressure and constant volume respectively, then since $Q_P = \Delta H$ and $Q_V = \Delta U$.

$$\therefore Q_P = Q_V = \Delta nRT$$

Question iii.

State Hess's law of constant heat summation. Illustrate with an example. State its applications.

Answer:

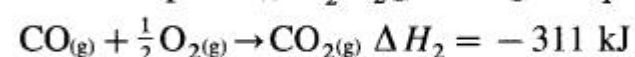
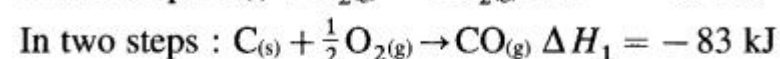
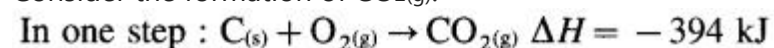
Statement of law of constant heat summation : It states that, the heat of a reaction or the enthalpy change in a chemical reaction depends upon initial state of reactants and final state of products and independent of the path by which the reaction is brought about (i.e. in single step or in series of steps).

OR

Heat of reaction is same whether it is carried out in one step or in several steps.

Explanation :

Consider the formation of $CO_{2(g)}$.



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

$$-394 \text{ kJ} = -83 \text{ kJ} + (-311) \text{ kJ}$$

Hess's law treats thermochemical equations mathematically i.e., they can be added, subtracted or multiplied by numerical factors like algebraic equations.

Applications : Hess's law is used for :

1. To calculate heat of formation, combustion, neutralisation, ionization, etc.
2. To calculate the heat of reactions which may not take place normally or directly.
3. To calculate heats of extremely slow or fast reactions.
4. To calculate enthalpies of reactants and products.

Question iv.

Although ΔS for the formation of two moles of water from H_2 and O_2 is -327 JK^{-1} , it is spontaneous. Explain. (Given ΔH for the reaction is -572 kJ).

Answer:

$$\text{Given : } \Delta S = -327 \text{ JK}^{-1}; \Delta H = -572 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S, \text{ and } \Delta H < T\Delta S$$

$$\therefore \Delta G < 0, \text{ and hence the formation of } H_2O_{(l)} \text{ is spontaneous.}$$

Question v.

Obtain the relation between ΔG and ΔS_{Total} . Comment on spontaneity of the reaction.

Answer:

(i) Gibbs free energy, G is defined as,

$$G = H - TS$$

where H is the enthalpy, S is the entropy of the system at absolute temperature T .

Since H , T and S are state functions, G is a state function and a thermodynamic function.

(ii) At constant temperature and pressure, change in free energy ΔG for the system is represented as, $\Delta G = \Delta H - T\Delta S$

$$\text{Free energy change} = \text{Total enthalpy change} - \text{Temperature} \times \text{Entropy change}$$

This is called Gibbs free energy equation for ΔG . In this ΔS is total entropy change, i.e., ΔS_{Total} .

(iii) The SI units of ΔG are J or kJ (or J mol^{-1} or kJ mol^{-1}).

The c.g.s. units of ΔG are cal or kcal (or cal mol^{-1} or kcal mol^{-1} .)

The second law explains the conditions of spontaneity as below :

(i) $\Delta S_{\text{Total}} > 0$ and $\Delta G < 0$, the process is spontaneous.

(ii) $\Delta S_{\text{Total}} < 0$ and $\Delta G > 0$, the process is nonspontaneous.

(iii) $\Delta S_{\text{Total}} = 0$ and $\Delta G = 0$, the process is at equilibrium.

Question vi.

One mole of an ideal gas is compressed from 500 cm^3 against a constant external pressure of $1.2 \times 10^5 \text{ Pa}$. The work involved in the process is 36.0 J . Calculate the final volume.

Answer:

Given : $V_1 = 500 \text{ cm}^3 = 0.5 \text{ dm}^3$;

$P_{\text{ex}} = 1.2 \times 10^5 \text{ Pa} = 1.2 \text{ bar}$; $W = 36 \text{ J}$;

$1 \text{ dm}^3 \text{ bar} = 100 \text{ J}$; $V_2 = ?$

$W = -P_{\text{ex}} (V_2 - V_1)$

$36 \text{ J} = -1.2 (V_2 - 0.5) \text{ dm}^3 \text{ bar}$

$= -1.2 \times 100 (V_2 - 0.5) \text{ J}$

$\therefore V_2 - 0.5 = \frac{-36}{1.2 \times 100} = -0.3$

$\therefore V_2 = 0.5 - 0.3 = 0.2 \text{ dm}^3 = 200 \text{ cm}^3$

Ans. Final volume = 200 cm^3 .

Question vii.

Calculate the maximum work when 24 g of O_2 are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K .

Answer:

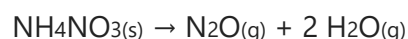
Given : $W_{\text{O}_2} = 24 \text{ g}$, $P_1 = 1.6 \text{ bar}$, $P_2 = 1 \text{ bar}$

$T = 298 \text{ K}$, $W_{\text{max}} = ?$

$$\begin{aligned} W_{\text{max}} &= -2.303 nRT \log_{10} \frac{P_1}{P_2} \\ &= -2.303 \times \frac{W_{\text{O}_2}}{M_{\text{O}_2}} \times 8.314 \times 298 \times \log_{10} \frac{1.6}{1} \\ &= -2.303 \times \frac{24}{32} \times 8.314 \times 298 \times 0.2041 \\ &= -873.4 \text{ J} \\ \text{Ans. } W_{\text{max}} &= -873.4 \text{ J} \end{aligned}$$

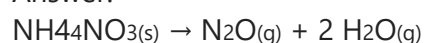
Question viii.

Calculate the work done in the decomposition of 132 g of NH_4NO_3 at 100°C .



State whether work is done on the system or by the system.

Answer:



$m_{\text{NH}_4\text{NO}_3} = 132 \text{ g}$; $M_{\text{NH}_4\text{NO}_3} = 80 \text{ g mol}^{-1}$

$T = 273 + 100 = 373 \text{ K}$; $\Delta n = ?$

For the reaction,

$$\Delta n = \sum n_2 \text{ gaseous products} - \sum n_1 \text{ gaseous reactants}$$

$$= 3 - 0 = 3 \text{ mol}$$

Since there is an increase in number of gaseous moles, the work is done by the system.

$$n_{\text{NH}_4\text{NO}_3} = \frac{m_{\text{NH}_4\text{NO}_3}}{M_{\text{NH}_4\text{NO}_3}}$$

$$= \frac{132}{80}$$

$$= 1.65 \text{ mol}$$

For $1 \text{ mol NH}_4\text{NO}_3(\text{s})$ $\Delta n = 3 \text{ mol}$

\therefore For $1.65 \text{ mol NH}_4\text{NO}_3(\text{s})$ $\Delta n = 3 \times 1.65 = 4.95 \text{ mol}$

$$W = -\Delta nRT = -4.95 \times 8.314 \times 373$$

$$= -15350 \text{ J}$$

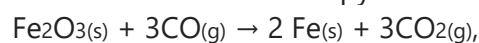
$$= -15.35 \text{ kJ}$$

Ans. Work is done by the system.

Work done = -15.35 kJ

Question ix.

Calculate standard enthalpy of reaction,



from the following data.

$$\Delta_f H_0(\text{Fe}_2\text{O}_3) = -824 \text{ kJ/mol},$$

$$\Delta_f H_0(\text{CO}) = -110 \text{ kJ/mol},$$

$$\Delta_f H_0(\text{CO}_2) = -393 \text{ kJ/mol}$$

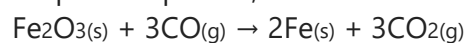
Answer:

$$\text{Given : } \Delta_f H_0 \text{Fe}_2\text{O}_3 = -824 \text{ kJ/mol-1};$$

$$\Delta_f H_0(\text{CO}) = -110 \text{ kJ mol-1}$$

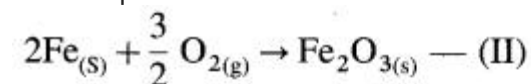
$$\Delta_f H_0(\text{CO}_2) = -393 \text{ kJ/mol-1}; \Delta_f H_0 = ?$$

Required equation,

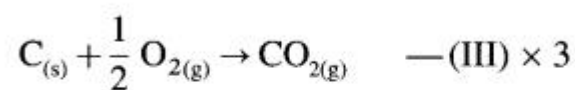


$$\Delta H_1 = ? - (\text{I})$$

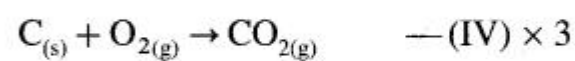
Given equations :



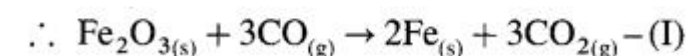
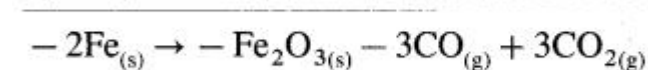
— — —



— — —



+ + +



$$\text{eq. (I)} = - \text{eq. (II)} - 3 \text{ eq. (III)} + 3 \text{ eq. (IV)}$$

$$\therefore \Delta H_1^0 = -\Delta H_2^0 - 3\Delta H_3^0 + 3\Delta H_4^0$$

$$= -(-824) - 3(-110) + 3(-393)$$

$$= 824 + 330 - 1179$$

$$\Delta_f H_0 = -25 \text{ kJ}$$

$$\text{Ans. } \Delta_f H_0 = -25 \text{ kJ}$$

Question x.

For a certain reaction $\Delta H_0 = 219 \text{ kJ}$ and $\Delta S_0 = -21 \text{ J/K}$. Determine whether the reaction is spontaneous or nonspontaneous.

Answer:

$$\text{Given : } \Delta H_0 = 219 \text{ kJ}; \Delta S_0 = -21 \text{ J/K}, \Delta G_0 = ?$$

For standard state, $T = 298 \text{ K}$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0$$

$$= 219 - 298 \times (-21) \times 10^{-3}$$

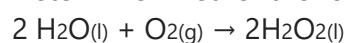
$$= 219 + 6.258$$

$$= 225.3 \text{ kJ}$$

Since $\Delta S < 0$ and $\Delta G_0 > 0$, the reaction is non-spontaneous.

Question xi.

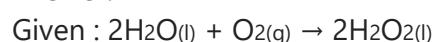
Determine whether the following reaction is spontaneous under standard state conditions.



$$\text{if } \Delta H_0 = 196 \text{ kJ}, \Delta S_0 = -126 \text{ J/K}$$

Does it have a cross-over temperature?

Answer:



$$\Delta H_0 = +196 \text{ kJ}$$

$$\Delta S_0 = -126 \text{ JK}^{-1} = 0.126 \text{ kJ K}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta G_0 = ?$$

$$\text{Cross over temperature} = T = ?$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0$$

$$= 196 - 298(-0.126)$$

$$= 196 + 37.55$$

$$= +233.55 \text{ kJ}$$

∴ $\Delta G_0 > 0$, the reaction is non-spontaneous.

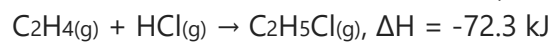
$$\Delta H_0 > 0, \Delta S_0 < 0,$$

Since at all temperatures, $\Delta G_0 > 0$, there is no cross over temperature.

Ans. The reaction is non-spontaneous.

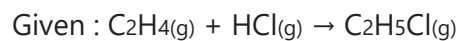
There is no cross-over temperature for the reaction.

Question xii.

Calculate ΔU at 298 K for the reaction,

How much PV work is done?

Answer:



$$T = 298 \text{ K}; \Delta H = -72.3 \text{ kJ}; PV = ?;$$

$$\Delta U = ?$$

$$\Delta n = \sum n_{\text{gaseous products}} - \sum n_{\text{gaseous reactants}}$$

$$= 1 - (1 + 1) = -1 \text{ mol}$$

For PV work :

$$W = -\Delta nRT$$

$$= -(-1) \times 8.314 \times 298$$

$$= 2478 \text{ J} = 2.478 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\therefore \Delta U = \Delta H - \Delta nRT$$

$$= -72.3 - (-2.478)$$

$$= -69.82 \text{ kJ}$$

$$\text{Ans. PV work} = 2.478 \text{ kJ}$$

$$\Delta U = -69.82 \text{ kJ}$$

Question xiii.

Calculate the work done during synthesis of NH_3 in which volume changes from 8.0 dm^3 to 4.0 dm^3 at a constant external pressure of 43 bar. In what direction the work energy flows?

Answer:

$$\text{Given : } V_1 = 8.0 \text{ dm}^3; V_2 = 4.0 \text{ dm}^3; P_{\text{ex}} = 43 \text{ bar}$$

$$W = ? \text{ What direction work energy flows ?}$$

$$W = -P_{\text{ex}}(V_2 - V_1)$$

$$= -43 (4 - 8)$$

$$= 172 \text{ dm}^3 \text{ bar}$$

$$= 172 \times 100 \text{ J}$$

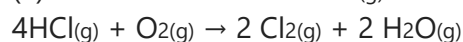
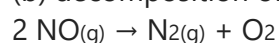
$$= 17200 \text{ J}$$

$$= 17.2 \text{ kJ}$$

In this compression process, the work is done on the system and work energy flows into the system.

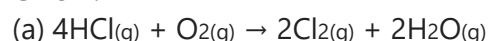
Question xiv.

Calculate the amount of work done in the

(a) oxidation of 1 mole $\text{HCl}(\text{g})$ at 200°C according to reaction.(b) decomposition of one mole of NO at 300°C for the reaction

Answer:

Given :



$$n_{\text{HCl}} = 1 \text{ mol}; T = 273 + 200 = 473 \text{ K}, W = ?$$

$$\text{For 4 mol HCl } \Delta n = (2 + 2) - (4 + 1) = -1 \text{ mol}$$

$$\therefore \text{For 1 mol HCl } \Delta n = -1/4 = -0.25 \text{ mol}$$

$$W = -\Delta nRT = -(-0.25) \times 8.314 \times 473 = 983.11$$

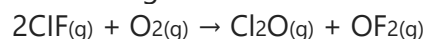
$$\text{(b) } \Delta n = (1 + 1) - 2 = 0 \text{ mol}$$

$$W = -\Delta nRT = -(0) \times 8.314 \times 473 = 0$$

$$\text{Ans. (a) } W = 983.1 \text{ J}$$

$$\text{(b) } W = 0.0 \text{ J}$$

Question xv.

When 6.0 g of O_2 reacts with ClF as per

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction ?

Answer:

Given : The given reaction is for 1 mol O_2 or 32 g O_2 .

$$\therefore \text{For 6.0 g } \text{O}_2$$

$$\Delta H_0 = 38.55 \text{ kJ}$$

$$\therefore \text{For 32 g } \text{O}_2$$

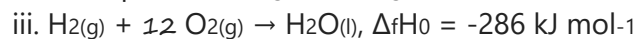
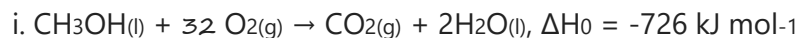
$$\Delta H_0 = 32 \times 38.556$$

$$= 205.6 \text{ kJ}$$

$$\text{Ans. } \Delta H_0 = 205.6 \text{ kJ}$$

Question xvi.

Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH}(\text{l})$ from the following data:



Answer:

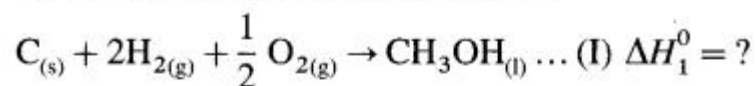
Given : $\Delta_c H_{\text{CH}_3\text{OH}}^0 = -726 \text{ kJ mol}^{-1};$

$\Delta_f H_{\text{CO}_2}^0 = -393 \text{ kJ mol}^{-1}$

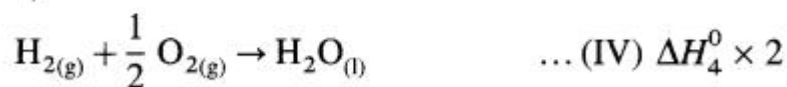
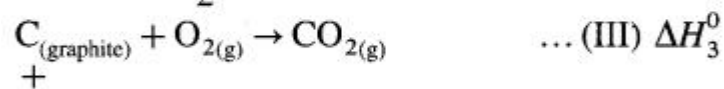
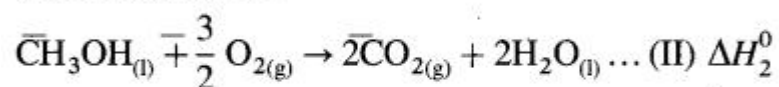
$\Delta_f H_{\text{H}_2\text{O}}^0 = -286 \text{ kJ mol}^{-1};$

$\Delta_f H_{\text{CH}_3\text{OH}}^0 = ?$

Required thermochemical equation :



Given equations :



+

Eq. (I) = - eq. (II) + eq. (III) + 2 eq. (IV)

$\therefore \Delta H_0$

$= -\Delta H_{02} + \Delta H_{03} + 2\Delta H_{04}$

$= -(-726) + (-393) + 2(-286)$

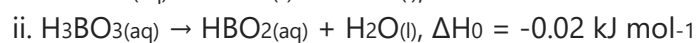
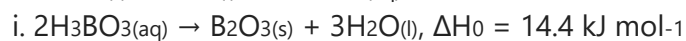
$= 726 - 393 - 572$

$= -239 \text{ kJ mol}^{-1}$

Ans. Standard enthalpy of formation = $\Delta_f H_0 = -239 \text{ kJ mol}^{-1}$

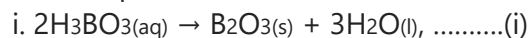
Question xvii.

Calculate ΔH_0 for the following reaction at 298 K

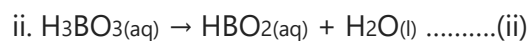


Answer:

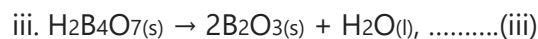
Given equations :



$\Delta H_0 = 14.4 \text{ kJ mol}^{-1}$

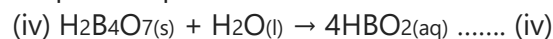


$\Delta H_0 = -0.02 \text{ kJ mol}^{-1}$



$\Delta H_0 = 17.3 \text{ kJ mol}^{-1}$

Required equation :



$\Delta H_{04} = ?$

To obtain eq. (iv) add 4 times equation (ii) and eq.

(iii) and subtract 2 times equation (i).

$\therefore \text{eq. (iv)} = 4 \text{ eq. (ii)} + \text{eq. (iii)} - 2 \text{ eq. (i)}$

$\therefore \Delta H_{04} = 4\Delta H_{02} + \Delta H_{03} - 2\Delta H_{01}$

$= 4(-0.02) + 17.3 - 2(14.4)$

$= -0.08 + 17.3 - 28.8$

$= -11.58 \text{ kJ}$

\therefore Enthalpy change for the reaction

$= \Delta_r H_0 = -11.58 \text{ kJ}$

Ans. $\Delta_r H_0$ for the given reaction = -11.58 kJ

Question xviii.

Calculate the total heat required (a) to melt 180 g of ice at 0 °C, (b) heat it to 100 °C and then (c) vapourise it at that temperature. Given

$\Delta_{\text{fus}} H_{(\text{ice})} = 6.01 \text{ kJ mol}^{-1}$ at 0 °C, $\Delta_{\text{vap}} H_{(\text{H}_2\text{O})} = 40.7 \text{ kJ mol}^{-1}$ at 100 °C specific heat of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

Answer:

Given : Mass of ice = m = 180 g

$T_1 = 273 + 0 \text{ °C} = 273 \text{ K}$

$T_2 = 273 + 100 \text{ °C} = 373 \text{ K}$

$$\Delta_{\text{fus}}H(\text{ice}) = \Delta_{\text{fus}}H(\text{H}_2\text{O})(\text{s}) = 6.01 \text{ kJ mol}^{-1}$$

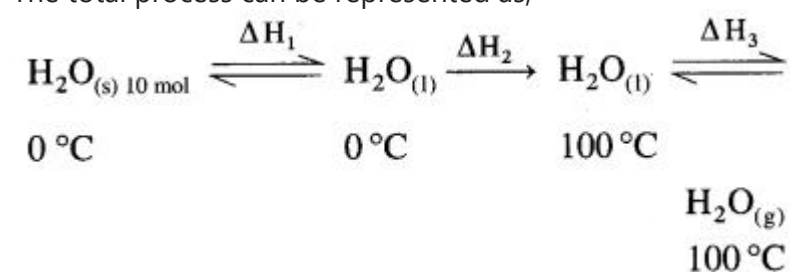
$$\Delta_{\text{vap}}H(\text{H}_2\text{O})(\text{l}) = 40.7 \text{ kJ mol}^{-1}$$

$$\text{Specific heat of water} = C = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

For converting 180 g ice into vapour, $\Delta H_{\text{Total}} = ?$

$$\text{Number of moles of H}_2\text{O} = \frac{180}{18} = 10 \text{ mol}$$

The total process can be represented as,



$$(i) \Delta H_1 = \Delta_{\text{fus}}H = 10 \text{ mol} \times 6.01 \text{ kJ mol}^{-1}$$

$$= 60.1 \text{ kJ}$$

(ii) When the temperature of water is raised from 0°C to 100°C (i.e., 273 K to 373 K), then

$$\Delta H_2 = m \times C \times \Delta T$$

$$= m \times C \times (T_2 - T_1)$$

$$= 180 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times (373 - 273) \times 10^{-3} \text{ kJ} = 75.24 \text{ kJ}$$

$$\Delta H_3 = \Delta_{\text{vap}}H = 10 \text{ mol} \times 40.7 \text{ kJ mol}^{-1} = 407 \text{ kJ}$$

Hence total enthalpy change,

$$\Delta H_{\text{Total}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

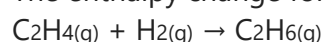
$$= 60.1 + 75.24 + 407$$

$$= 542.34 \text{ kJ}$$

Ans. Total heat required = 542.34 kJ

Question xix.

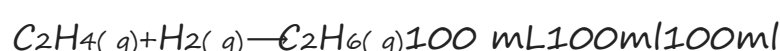
The enthalpy change for the reaction,



is -620 J when 100 ml of ethylene and 100 mL of H_2 react at 1 bar pressure. Calculate the pressure volume type of work and ΔU for the reaction.

Answer:

Given :



$$\Delta H = -620 \text{ J}; V_{\text{C}_2\text{H}_4} = 100 \text{ mL}; V_{\text{H}_2} = 100 \text{ mL}$$

$$P_{\text{ex}} = 1 \text{ bar}; W = ?; \Delta U = ?$$

$$\Delta V = 100 - (100 + 100) = -100 \text{ mL} = -0.1 \text{ dm}^3$$

$$W = -P_{\text{ex}}(V_2 - V_1)$$

$$= -P_{\text{ex}} \times \Delta V$$

$$= -1 \times (-0.1)$$

$$= 0.1 \text{ dm}^3 \text{ bar}$$

$$= 0.1 \times 100 \text{ J}$$

$$= +10 \text{ J}$$

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

$$\therefore \Delta U = \Delta H - P\Delta V = -620 - (+10) = -610 \text{ J}$$

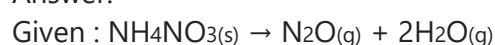
$$\text{Ans. } W = +10 \text{ J}; \Delta U = -610 \text{ J}$$

Question xx.

Calculate the work done and comment on whether work is done on or by the system for the decomposition of 2 moles of NH_4NO_3 at 100°C



Answer:



$$n_{\text{NH}_4\text{NO}_3} = 2 \text{ mol}; T = 273 + 100 = 373 \text{ K}$$

$$W = ? \text{ Comment on work} = ?$$

$$\Delta n_{\text{reaction}} = (1 + 2) - 0 = 3 \text{ mol}$$

$$\therefore \text{For 1 mol of } \text{NH}_4\text{NO}_3 \Delta n_{\text{reaction}} = 3 \text{ mol}$$

$$\therefore \text{For 2 mol of } \text{NH}_4\text{NO}_3 \Delta n_{\text{reaction}} = 6 \text{ mol}$$

Due to 6 moles of gaseous products from 2 mol NH_4NO_3 , there is work of expansion, hence work is done by the system.

$$W = -\Delta nRT$$

$$= -6 \times 8.314 \times 373 = -18606 \text{ J}$$

$$= -18.606 \text{ kJ}$$

Ans. Work is done by the system.

$$W = -18.606 \text{ kJ}$$

12th Chemistry Digest Chapter 4 Chemical Thermodynamics Intext Questions and Answers

(Textbook page No. 73)

Question 1.

Under what conditions $\Delta H = \Delta U$?

Answer:

(a) $\Delta H = \Delta U + P\Delta V$

when $\Delta V = 0$, $\Delta H = \Delta U$

(b) $\Delta H = \Delta U + \Delta nRT$

when $\Delta n = 0$, $\Delta H = \Delta U$ [Try this... \(Textbook page No. 71\)](#)

Question 1.

25 kJ of work is done on the system and it releases 10 kJ of heat. What is ΔU ?

Answer:

$W = 25 \text{ kJ}; Q = -10 \text{ kJ}$

$\Delta U = Q + W = -10 + 25$

$\Delta U = +15 \text{ kJ}$

[Try this... \(Textbook page No. 75\)](#)

Question 1.

For KCl, $\Delta_L H = 699 \text{ kJ/mol}^{-1}$ and $\Delta_{\text{hyd}} H = -681.8 \text{ kJ/mol}^{-1}$. What will be its enthalpy of solution?

Answer:

Enthalpy of solution :

$\Delta_{\text{soln}} H = \Delta_L H + \Delta_{\text{hyd}} H$

$= 699 + (-681.8)$

$\Delta_{\text{soln}} H = +17.2 \text{ kJ mol}^{-1}$

[Try this... \(Textbook page No. 76\)](#)

Question 1.

Given the thermochemical equation,

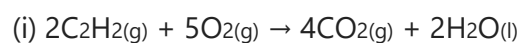


Write thermochemical equations when

i. Coefficients of substances are multiplied by 2.

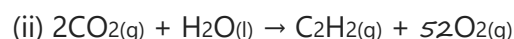
ii. equation is reversed.

Answer:



$\Delta_r H_0 = -2 \times 1300 \text{ kJ}$

$= -2600 \text{ kJ}$



$\Delta_r H_0 = +1300 \text{ kJ}$

[Try this... \(Textbook page No. 78\)](#)

Question 1.

(i) Write thermochemical equation for complete oxidation of one mole of $\text{H}_2(\text{g})$. Standard enthalpy change of the reaction is -286 kJ.

(ii) Is the value -286 kJ, enthalpy of formation or enthalpy of combustion or both? Explain.

Answer:

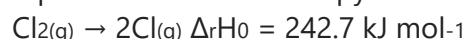
(ii) The value -286 kJ is the standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ or standard enthalpy of combustion of $\text{H}_2(\text{g})$.

Question 2.

Write equation for bond enthalpy of Cl-Cl bond in Cl_2 molecule $\Delta_r H_0$ for dissociation of Cl_2 molecule is 242.7 kJ.

Answer:

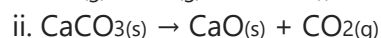
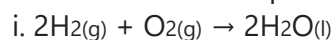
Equation for bond enthalpy :



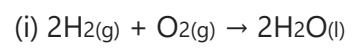
$\therefore \text{Bond enthalpy of } \text{Cl}_2 = 242.7 \text{ kJ mol}^{-1}$

[Try this... \(Textbook page No. 82\)](#)

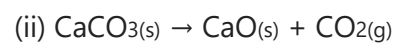
Question 1.

State whether ΔS is positive, negative or zero for the following reactions.

Answer:



Since the system is converted from gaseous state to a liquid state, the disorder is decreased, hence $\Delta S < 0$ (negative).



Since molecules of solid CaCO_3 break giving gaseous CO_2 , disorder is increased hence $\Delta S > 0$ (positive).

Allguidesite