

Chemical Themodynamics

EXERCISES [PAGES 86 - 89]

Exercises | Q 1.01 | Page 86

Select the most appropriate option.

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

- 1. $\Delta H < 0$ and $\Delta S > 0$
- 2. $\Delta H > 0$ and $\Delta S < 0$
- 3. $\Delta H < 0$ and $\Delta S < 0$
- 4. $\Delta H < 0$ and $\Delta S = 0$

Solution: The correct thermodynamic conditions for the spontaneous reaction at all temperatures are $\Delta H < 0$ and $\Delta S > 0$.

Exercises | Q 1.02 | Page 86

Select the most appropriate option.

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 _____.

- 1. –500 J
- 2. + 500 J
- 3. –1013 J
- 4. + 1013 J

Solution:

- 500 J

Explanation:

Since the container is insulated, this is an adiabatic process. For adiabatic process,

 $\Delta U = +W = -P_{ext} \Delta V = -P_{ext} (V_2 - V_1)$ Initial volume (V₁) = 2.5 L = 2.5 dm³ Final volume (V₂) = 4.5 L = 4.5 dm³ External pressure (P_{ext}) = 2.5 bar



$$\Delta U = W = -2.5 \text{ bar} \times (4.5 \text{ dm}^3 - 2.5 \text{ dm}^3)$$

= - 5.0 dm³ bar ×
$$\frac{100J}{1 dm^3 bar}$$

= - 500 J

Exercises | Q 1.03 | Page 86

Select the most appropriate option.

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

- 1. Crystallization of liquid into solid
- 2. Temperature of crystalline solid is increased from 0 K to 115 K
- $3. \hspace{0.2cm} H_{2(g)} \rightarrow 2H_{(g)}$
- 4. 2 NaHCO_{3(s)} \rightarrow Na2CO_{3(s)} + CO_{2(g)} + H₂O_(g)

Solution: Crystallization of liquid into solid

Exercises | Q 1.04 | Page 87

Select the most appropriate option.

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

- 1. unity
- 2. zero
- 3. less than zero
- 4. different elements

Solution: The enthalpy of formation for all elements in their standard states is zero.

Exercises | Q 1.05 | Page 87

Select the most appropriate option.

Which of the following reactions is exothermic?

- $1. \hspace{.1in} H_{2(g)} \hspace{.1in} \rightarrow \hspace{.1in} 2H_{(g)}$
- $2. \ C_{(s)} \ \rightarrow \ C_{(g)}$
- 3. $2CI_{(g)} \rightarrow CI_{2(g)}$
- $4. \hspace{.1in} H_2O(s) \hspace{.1in} \rightarrow \hspace{.1in} H_2O(l)$

Solution: $2CI_{(g)} \rightarrow CI_{2(g)}$

Hint:

Bond is formed between two CI atoms and hence, energy is released.

Exercises | Q 1.06 | Page 87



Select the most appropriate option.

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

- 1. 43.4 kJ mol⁻¹
- 2. 60.2 kJ mol⁻¹
- 3. 38.9 kJ mol⁻¹
- 4. 20.4 kJ mol⁻¹

Solution: 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat. Enthalpy of vaporization of ethanol will be 43.4 kJ mol^{-1} .

Explanation:

Molar mass of ethanol (C_2H_6O) = 46 g mol⁻¹

Number of moles of $O_2 = \frac{\text{Mass of ethanol}}{\text{Molar mass of ethanol}} = \frac{6.24\text{g}}{46\text{g mol}^{-1}} = 0.1357 \text{ mol}$

The enthalpy change when 0.1357 mol of ethanol vapourize is 5.89 kJ.

- .: Enthalpy change for 1 mole ethanol
 - 5.89kJ

0.1357 mol

= 43.4 kJ mol⁻¹

Exercises | Q 1.07 | Page 87

Select the most appropriate option.

If the standard enthalpy of formation of methanol is $-238.9 \text{ kJ mol}^{-1}$ then entropy

change of the surroundings will be _____.

- 1. –801.7 J K⁻¹
- 2. 801.7 J K⁻¹
- 3. 0.8017 J K⁻¹
- 4. –0.8017 J K⁻¹

Solution:

If the standard enthalpy of formation of methanol is $-238.9 \text{ kJ mol}^{-1}$ then entropy change of the surroundings will be <u>801.7 J K⁻¹</u>.

Explanation:

For standard state, temperature = 298 K



$$\bigtriangleup S_{surr} = -\frac{\bigtriangleup H}{T} = -\frac{(-238.9 \text{ kJ})}{298 \text{k}}$$

= + 0.8017 kJ K⁻¹

= 801.7 J K⁻¹

Exercises | Q 1.08 | Page 87

Select the most appropriate option.

Which of the following are not state functions?

Q + W

Q

w

H - TS

- 1. 1, 2 and 3
- 2. 2 and 3
- 3. 1 and 4
- 4. 2, 3 and 4

Solution: 2 and 3 i.e., Q and W

Exercises | Q 1.09 | Page 87

Select the most appropriate option.

For vaporization of water at 1 bar, $\Delta H = 40.63$ kJ mol⁻¹ and $\Delta S = 108.8$ J K⁻¹ mol⁻¹. At what temperature, $\Delta G = 0$?

- 1. 273.4 K
- 2. 393.4 K
- 3. 373.4 K
- 4. 293.4 K

Solution: 373.4 K

Explanation:

Temperature at which reaction is at equilibrium ($\Delta G = 0$) is,

$$T = \frac{\triangle H}{\triangle S} = \frac{40.63 \text{ kJ mol}^{-1}}{108.8 \times 10^{-3} \text{kJ K}^{-1}} = 373.4 \text{ K}$$



Exercises | Q 1.1 | Page 87

Select the most appropriate option.

Bond enthalpies of H–H, CI–CI, and H–CI bonds are 434 kJ mol⁻¹, 242 kJ mol^{-1,} and

431 kJ mol⁻¹, respectively. Enthalpy of formation of HCl is _____.

- 1. 245 kJ mol⁻¹
- 2. –93 kJ mol⁻¹
- 3. –245 kJ mol⁻¹
- 4. 93 kJ mol⁻¹

Solution:

Bond enthalpies of H–H, Cl–Cl, and H–Cl bonds are 434 kJ mol⁻¹, 242 kJ mol^{-1,} and 431 kJ mol⁻¹, respectively. Enthalpy of formation of HCl is <u>–93 kJ mol⁻¹</u>.

Explanation:

 $\Delta_r H^\circ = \sum \Delta H^\circ$ (reactant bonds) - $\sum \Delta H^\circ$ (products bonds)

 $H_{2(g)} + CI_{2(g)} \rightarrow 2HCI_{(g)}$

 $\therefore \Delta_r H^\circ = [1 \text{ mol} \times 434 \text{ kJ mol}^{-1} + 1 \text{ mol} \times 242 \text{ kJ mol}^{-1}] - [2 \text{ mol} \times 431 \text{ kJ mol}^{-1}]$

= -186 kJ

 $\therefore H_{2(g)} + CI_{2(g)} \rightarrow 2HCI_{(g)}, \Delta_r H^\circ = -186 \text{ kJ}$

For enthalpy of formation of HCI, the reaction is

$$\begin{aligned} &\frac{1}{2}\mathrm{H}_{2(\mathrm{g})} + \frac{1}{2}\mathrm{Cl}_{2(\mathrm{g})} \to \mathrm{HCl}_{(\mathrm{g})}, \\ &\Delta_{\mathrm{r}}\mathrm{H}^{\circ} = \frac{-186\mathrm{kJ}}{2\mathrm{\ mol}} = -93\mathrm{\ kJ\ mol}^{-1} \end{aligned}$$

Exercises | Q 2.1 | Page 87

Answer the following in one or two sentences.

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

Solution:

- 1. A free expansion means expansion against zero opposing force. Such expansion occurs in a vacuum.
- 2. When the gas expands in a vacuum, there is no opposing force, that is, $P_{ext} = 0$. The work done by a system during such expansion is W = - $P_{ext} \Delta V = 0$

Thus, no work is done when the gas expands freely in a vacuum.

Note: Units of energy and work:



 $1 J = 1 kg m^2 s^2 = 1 Pa m^3$

$$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

From the equation, $W = - P_{ext} \Delta V$

If the pressure is expressed in bar and ΔV in dm³, then the work has the units of bar dm³.

1 bar = 10^5 Pa = 10^5 kg m⁻¹ s⁻²

 $1 \text{ dm}^3 \text{ bar} = \text{dm}^3 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$

 $= m^3 \times 10^{-3} \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$

 $= 100 \text{ kg m}^2 \text{ s}^{-2} = 100 \text{ J}$

Exercises | Q 2.2 | Page 87

Answer the following in one or two sentences.

State the first law of thermodynamics.

Solution:

According to the first law of thermodynamics, "the total energy of a system and surroundings remains constant when the system changes from an initial state to final state."

Exercises | Q 2.3 | Page 87

Answer the following in one or two sentences.

What is enthalpy of fusion?

Solution:

Enthalpy change that occurs when one mole of a solid is converted into liquid without a change in temperature at constant pressure is the enthalpy of fusion.

Exercises | Q 2.4 | Page 87

Answer the following in one or two sentences.

What is standard state of a substance?

Solution:

- 1. The standard state of a substance is the form in which the substance is most stable at a pressure of 1 bar and at temperature 298 K.
- If the reaction involves species in solution its standard state refers to 1 M concentration.
 e.g. Standard states of certain elements and compounds are (at 1 bar and 25 °C); H_{2(g)}, Hg(I), Na(s), C(graphite), C₂H₅OH(I), CaCO_{3(s)}, CO_{2(g)}, C₂H₅OH(I), H₂O(I), CaCO_{3(s)}, CO_{2(g)}.

Exercises | Q 2.5 | Page 87

Answer the following in one or two sentences.



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

Solution:

 ΔS is negative. Two moles of gaseous H atoms are converted into 1 mole H₂ gas. Thus,

a disorder of the system decreases, and hence, entropy increases or ΔS is positive.

Exercises | Q 2.6 | Page 87

Answer the following in one or two sentences.

State second law of thermodynamics in terms of entropy.

Solution:

Statement: "The second law of thermodynamics states that total entropy of a system and its surroundings increases in a spontaneous process."

For the process to be spontaneous,

 $\triangle \mathbf{S}_{\text{total}} = \triangle \mathbf{S}_{\text{sys}} + \triangle \mathbf{S}_{\text{surr}} > \mathbf{0}.$

Exercises | Q 2.7 | Page 87

Answer the following in one or two sentences.

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

surroundings?

Solution:

If ΔH is the enthalpy change accompanying a reaction (system) the enthalpy change of the surroundings is then $-\Delta H$. The entropy change of surroundings can be calculated using the following expression:

$$\bigtriangleup \mathbf{S}_{surr} = -\frac{\bigtriangleup \mathbf{H}}{\mathbf{T}}$$

Exercises | Q 2.8 | Page 87

Answer the following in one or two sentences.

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

Solution:

When ΔH positive and ΔS is negative, then ΔG is positive regardless of temperature. Such reactions are nonspontaneous at all temperatures.

Exercises | Q 3.1 | Page 87

Answer in brief.

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



1. Gibbs energy change for a chemical reaction is given by

 $\Delta G = \Delta G^{\circ} + RT \ln Q \qquad \dots (1)$

where, ΔG° is standard Gibbs energy change that is, the Gibbs energy change when the reactants and products in a reaction are in their standard states. Q is called reaction quotient. Q is analogous to that of the equilibrium constant and involves nonequilibrium concentrations or partial pressures in case of a gaseous reaction.

2. Consider the reaction, $aA + bB \rightarrow cC + dD$

From equation (1),

 $\Delta G = \Delta G^{\circ} + RT \ln Q_{C} \quad \text{or} \quad \Delta G = \Delta G^{\circ} + RT \ln Q_{P}$ $= \Delta G^{\circ} + RT \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad \text{or} \quad = \Delta G^{\circ} + RT \ln \frac{P_{C}^{c} \times P_{D}^{d}}{P_{A}^{a} \times P_{B}^{b}}$

3. When the reaction reaches equilibrium, $\Delta G^{\circ} = 0$ and Q_{C} and Q_{P} become K_C and K_P, respectively.

Thus,

- $\therefore 0 = \Delta G^{\circ} + RT \ln K_{C}$ or $0 = \Delta G^{\circ} + RT \ln K_{P}$
- $\therefore \Delta G^{\circ} = -RT \ln K_{C}$ or $\Delta G^{\circ} = -RT \ln K_{P}$

 $\therefore \Delta G^{\circ} = -2.303 \text{ RT} \log_{10} K_C \text{ or } \Delta G^{\circ} = -2.303 \text{ RT} \log_{10} K_P$

Exercises | Q 3.2 | Page 87

Answer in brief.

What is entropy? Give its units.

Solution:

- 1. Entropy is a measure of molecular disorder or randomness.
- An entropy change of a system is equal to the amount of heat transferred (Q_{rev}) to it in a reversible manner divided by the temperature (T) in Kelvin at which the transfer takes place. Thus,

$$riangle \mathbf{S} = rac{\mathbf{Q}_{\mathrm{rev}}}{\mathrm{T}}$$

3. Units of entropy: J K-1

Note: Entropy or its change ΔS is a state function and depends on the initial and final states of the system and not on the path connecting two states

Exercises | Q 3.3 | Page 87

Answer in brief.

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



Solution:

Reaction and bond enthalpies:

- 1. In a chemical reaction, bonds are broken and formed.
- 2. The enthalpies of reactions involving substances having covalent bonds are calculated by knowing the bond enthalpies of reactants and those in products.
- 3. The calculations assume all the bonds of a given type are identical.
- 4. Enthalpy change of a reaction can be calculated using the following expression:

 $\begin{array}{l} \Delta_r H^\circ = \sum \Delta H^\circ \mbox{ (reactant bonds)} - \sum \Delta H^\circ \mbox{ (product bonds)} \\ e.g. \mbox{ Consider the reaction, } H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)} \\ The enthalpy is given by \\ \Delta_r H^\circ = [\Delta H^\circ \mbox{ (H - H)} + \Delta H^\circ \mbox{ (I - I)}] - [2\Delta H^\circ \mbox{ (H - I)}] \end{array}$

Note:

i. If reactants and products are diatomic molecules, the above equation gives accurate results. The bond enthalpies are known accurately.

ii. For reactions involving polyatomic molecules, the reaction enthalpies calculated using above equation would be approximate and refer to average bond enthalpies.

Exercises | Q 3.4 | Page 87

Answer in brief.

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

Solution:

- 1. The standard enthalpy of combustion of a substance is the standard enthalpy change accompanying a reaction in which one mole of the substance in its standard state is completely oxidised.
- 2. Consider the reaction,

 $C_2H_{2(g)} + 5/2 \ O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)}, \Delta_r \ H^\circ = -1300 \ kJ$

In the above reaction, the standard enthalpy change of the oxidation reaction, -1300 kJ is the standard enthalpy of combustion of C₂H_{2(g)}.

Exercises | Q 3.5 | Page 87

Answer in brief.

What is the enthalpy of atomization? Give an example.

Solution:

- 1. The enthalpy change accompanying the dissociation of one mole of gaseous substance into atoms is called enthalpy of atomization.
- 2. For example, $Cl_{2(g)} \rightarrow Cl_{(g)} + Cl_{(g)}$; $\Delta_{atom}H = 242 \text{ kJ mol}^{-1}$

Exercises | Q 3.6 | Page 87

Answer in brief.

Obtain the expression for work done in chemical reaction.



Solution:

- 1. The work done by a system at constant temperature and pressure is given by $W = P_{ext} \Delta V$ (1)
- 2. Assuming $P_{ext} = P$, $W = -P\Delta V$ $= -P(V_2 - V_1)$ $W = -PV_2 + PV_1$ (2)
- 3. If the gases were ideal, at constant temperature and pressure., $PV_1 = n_1RT$ and $PV_2 = n_2RT$ (3) Substitution of equation (3) into equation (2) yields $W = -n_2RT + n_1RT$ $= -(n_2 - n_1) RT$ $= -\Delta n_g RT$ (4)
- 4. The equation (4) gives the work done by the system in chemical reactions

Exercises | Q 3.7 | Page 88

Answer in brief.

Derive the expression for PV work.

Solution:

Pressure-volume work



- Consider a certain amount of gas at constant pressure P is enclosed in a cylinder fitted with a frictionless, rigid movable piston of area A. Let the volume of the gas be V₁ at temperature T. This is shown in the adjacent diagram.
- On expansion, the force exerted by a gas is equal to area of the piston multiplied by pressure with which the gas pushes against piston. This pressure is equal in magnitude and opposite in sign to the external atmospheric pressure that opposes the movement and has its value - P_{ext}.

Thus,

 $f = - P_{ext} \times A \qquad \dots (1)$

where, P_{ext} is the external atmospheric pressure.

3. If the piston moves out a distance d, then the amount of work done is equal to the force multiplied by distance.

 $W = f \times d \qquad \dots (2)$



Substituting equation (1) in (2) gives

 $W = - P_{ext} \times A \times d \qquad \dots (3)$

4. The product of area of the piston and distance it moves is the volume change (ΔV) in the system.

 $\Delta V = A \times d$ (4) Combining equation (3) and (4), we get $W = -P_{ext} \Delta V$ $W = -P_{ext} (V_2 - V_1)$ Where V₂ is the final volume of the gas.

Exercises | Q 3.8 | Page 88

Answer in brief.

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

Solution:

- 1. A property which is independent of the amount of matter in a system is called intensive property.
- 2. Density is a ratio of mass to volume. Mass and volume are extensive properties. Since density is a ratio of two extensive properties, it is an intensive property. Thus, density is independent of the amount of matter present.

Exercises | Q 3.9 | Page 88

Answer in brief.

How much heat is evolved when 12 g of CO reacts with NO₂? The reaction is:

 $4CO_{(g)}\ 2NO_{2(g)} \rightarrow 4CO_{2(g)} + N_{2(g)}, \ \Delta_r H^\circ = \text{-} \ 1200 \ \text{kJ}$

Solution:

Given: $\Delta_r H^\circ$ = - 1200 kJ, Mass of CO = 12 g

To find: Heat evolved when 12g of CO reacts with NO2

Calculation:

According to the given reaction, 1200 kJ of heat is evolved when 4 moles of CO react with NO₂. So heat evolved per mole is 1200kJ/4 mol = 300 kJ mol⁻¹

Molar mass of CO = $12 + 16 = 28 \text{ g mol}^{-1}$

Number of moles of CO =
$$\frac{\text{Mass of CO}}{\text{Molar mass of CO}} = \frac{12\text{g}}{28\text{g mol}^{-1}} = 0.4286 \text{ mol}$$

So, heat evolved when 0.4286 moles of CO reacts

= 0.4286 mol × 300 kJ mol⁻¹ = 128.58 kJ

The heat evolved when 12 g of CO reacts with NO₂ is 128.58 kJ.

Exercises | Q 4.01 | Page 88



Answer the following question.

Derive the expression for the maximum work.

Solution:



1. Consider n moles of an ideal gas enclosed in a cylinder fitted with a frictionless movable rigid piston. It expands isothermally and reversibly from the initial volume V_1 to final volume V_2 at temperature T. The expansion takes place in a number of steps as shown in the figure.

2. When the volume of a gas increases by an infinitesimal amount dV in a single step, the small quantity of work done

 $dW = -Pext dV \dots(1)$

3. As the expansion is reversible, P is greater by a very small quantity dp than Pext.

Thus P - Pext = dP or Pext = P - dP $\dots(2)$

Combining equations (1) and (2),

dW = - (P - dP)dV = - PdV + dP.dV

Neglecting the product dP.dV which is very small, we get

dW = -PdV(3)

4. The total amount of work done during the entire expansion from volume V_1 to V_2 would be the sum of the infinitesimal contributions of all the steps. The total work is obtained by integration of Equation (3) between the limits of initial and final states. This is the maximum work, the expansion being reversible.

Thus,



$$\int\limits_{initial}^{final} dW = - \int\limits_{V_2}^{V_1} P dV$$

Hence,

Wmax =
$$-\int_{V_2}^{V_1} P dV$$
(4)

5. Using the ideal gas law, PV = nRT,

$$\begin{split} & \mathsf{Wmax} = - \int_{V_2}^{V_1} n \mathbf{RT} \frac{d\mathbf{V}}{\mathbf{V}} \\ &= -n \mathbf{RT} \int_{V_2}^{V_1} \frac{d\mathbf{V}}{\mathbf{V}} \quad ...(\because \mathsf{T} \text{ is constant.}) \\ &= -n \mathbf{RT} \ln (\mathbf{V})_{V_1}^{V_2} \\ &= -n \mathbf{RT} \ln (\mathbf{V}_2 - \ln \mathsf{V}_1) \\ &= -n \mathbf{Rt} \ln \frac{V_2}{V_1} \\ &= -2.303 \text{ nRT} \log 10 \frac{V_2}{V_1} \quad(5) \\ & \text{6. At constant temperature, } \mathsf{P}_1 \mathsf{V}_1 = \mathsf{P}_2 \mathsf{V}_2 \text{ or } \frac{V_2}{V_1} = \frac{\mathsf{P}_1}{\mathsf{P}_2} \\ & \text{Replacing } \frac{V_2}{V_1} \text{ in in equation (5) by } \frac{\mathsf{P}_1}{\mathsf{P}_2}, \text{ we get,} \\ & \text{Wmax} = -2.303 \text{ nRT} \log \frac{\mathsf{P}_1}{\mathsf{P}_2} \quad(6) \\ & \text{Equations (5) and (6) are expressions for work done in reversible isothermal process.} \end{split}$$

Exercises | Q 4.02 | Page 88

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



Solution:

1. At constant pressure, ΔH and ΔU are related as

 $\Delta H = \Delta U + P \Delta V \qquad \dots (1)$

2. For reactions involving gases, ΔV cannot be neglected. Therefore,

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

 $= \Delta H + P(V_2 - V_1)$

 $\Delta H = \Delta U + PV_2 - PV_1 \qquad \dots (2)$

where, V_1 is the volume of gas-phase reactants and V_2 that of the gaseous products.

3. We assume reactant and product behave ideally. Applying an ideal gas equation, PV = nRT. Suppose that n_1 moles of gaseous reactants produce n_2 moles of gaseous products. Then,

 $PV_1 = n_1RT$ and $PV_2 = n_2RT$...(3)

4. Substitution of equation (3) into equation (2) yields

 $\Delta H = \Delta U + n_2 RT - n_1 RT$

 $= \Delta U + (n_2 - n_1) RT$

 $= \Delta U + \Delta n_g RT$ (4)

where, Δn_g is the difference between the number of moles of products and those of reactants.

Exercises | Q 4.03 | Page 88

Answer the following question.

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

applications.

Solution:

1. Hess's law of constant heat summation:

Hess's law of constant heat summation states that, "Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction".

2. Illustration:

- The enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs. Hess's law is a direct consequence of the fact that enthalpy is state function. The enthalpy change of a reaction depends only on the initial and final states and not on the path by which the reaction occurs.
- To determine the overall equation of reaction, reactants and products in the individual steps are added or subtracted like algebraic entities.



• Consider the synthesis of NH₃,

1.
$$2H_{2(g)} + N_{2(g)} \rightarrow N_2H_{4(g)}$$
, $\triangle_r H_1^0 = + 95.4$ kJ

2. $\underline{N_2H_{4(g)} + H_{2(g)} \rightarrow 2NH_{3(g)'}} \bigtriangleup_r H_2^0 = -187.6 \text{ kJ}$

 $3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}, \Delta_r H^\circ = -92.2 \text{ kJ}$

The sum of the enthalpy changes for steps (1) and (2) is equal to enthalpy change for the overall reaction.

3. Application of Hess's law:

The Hess's law has been useful to calculate the enthalpy changes for the reactions with their enthalpies being not known experimentally.

Exercises | Q 4.04 | Page 88

Answer the following question.

Although ΔS for the formation of two moles of water from H₂ and O₂ is –327J K⁻¹, it is

spontaneous. Explain.

(Given ΔH for the reaction is -572 kJ).

Solution:

1. For the process to be spontaneous, $\triangle S_{tota} = \triangle S_{sys} + \triangle S_{surr} > 0$.

2. For the reaction, $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$, when 2 moles of H_2 and 1 mole of O_2 gas combine to form 2 moles of liquid water, 572 kJ of heat is released which is received by surroundings at constant pressure (and 298 K).

3. The entropy change of the surroundings is,

$$\label{eq:surr} \bigtriangleup \mathbf{S}_{surr} = \frac{\mathbf{Q}_{rev}}{T} = \frac{572 \times 10^3 \mathrm{J}}{298 \mathrm{K}} \texttt{=} \texttt{+} \texttt{1919} \texttt{J} \texttt{K}^{\texttt{-1}}$$

4. The total enthalpy change is,

 $\triangle \mathbf{S}_{total} = \triangle \mathbf{S}_{sys} + \triangle \mathbf{S}_{surr}$

5. Since $\triangle S_{\text{total}} > 0$, the reaction is spontaneous at 25 °C.

6. It follows that to decide spontaneity of reactions, we need to consider the entropy of system and its surroundings.

Exercises | Q 4.05 | Page 88



Answer the following question.

Obtain the relation between ΔG and $\bigtriangleup S_{total}.$ Comment on the spontaneity of the reaction.

Solution:

1) The total entropy change that accompanies a process is given by,

$$\begin{split} \triangle \mathbf{S}_{total} &= \triangle \mathbf{S}_{sys} + \triangle \mathbf{S}_{surr} \\ \text{OR} \\ \triangle \mathbf{S}_{total} &= \triangle \mathbf{S} + \triangle \mathbf{S}_{surr} \quad(1) \end{split}$$

2) According to second law of thermodynamics for a process to be spontaneous,

 $\triangle \mathbf{S}_{\text{total}} > 0.$

3) If Δ H is the enthalpy change accompanying a reaction (system), the enthalpy change of the surroundings is – Δ H. Thus,

$$riangle \mathbf{S}_{\mathrm{surr}} = -rac{ riangle \mathbf{H}}{\mathbf{T}}$$
(2)

4) Substituting equation (2) in equation (1), we get,

$$riangle \mathbf{S}_{\text{total}} = riangle \mathbf{S} - rac{ riangle \mathbf{H}}{\mathbf{T}}$$

Rearranging above expression, we get,

$$\begin{split} \mathbf{T} & \bigtriangleup \mathbf{S}_{total} = \mathbf{T} \bigtriangleup \mathbf{S} - \bigtriangleup \mathbf{H} \\ \text{or} \\ -\mathbf{T} & \bigtriangleup \mathbf{S}_{total} = \bigtriangleup \mathbf{H} - \mathbf{T} \bigtriangleup \mathbf{S} \qquad \text{.....(3)} \end{split}$$

5) The change in Gibbs energy at constant temperature and constant pressure is given by,

$$\Delta G = \Delta H - T \Delta S \dots (4)$$

6) Substituting equation (3) in equation (4), we get,

 $\Delta G = -T \bigtriangleup S_{total}$



7) For a spontaneous reaction, $S_{total} > 0$ and hence, $\Delta G < 0$. At constant temperature and pressure Gibbs energy of the system decreases in a spontaneous process.

8) The second law leads to the conditions of spontaneity as follows:

i) $\triangle S_{total} > 0$ and $\Delta G < 0$, the process is spontaneous.

ii) $\triangle S_{total} < 0$ and $\Delta G > 0$, the process is nonspontaneous.

iii) $\triangle S_{total} = 0$ and $\Delta G = 0$, the process is at equilibrium.

Exercises | Q 4.06 | Page 88

Answer the following question.

One mole of an ideal gas is compressed from 500 cm3 against a constant pressure of 1.2×10^5 Pa. The work involved in the process is 36.0 J. Calculate the final volume.

Solution:

Given:

Initial volume (V₁) = 500 cm³ External pressure (P_{ext}) = 1.2×10^5 Pa Work (W) = 36.0 J

To find: Final volume (V₂) **Formula:** W = - $P_{ext} \Delta V = - P_{ext} (V_2 - V_1)$

Calculation: Initial volume (V₁) = $500 \text{ cm}^3 = 0.5 \text{ dm}^3$

External pressure $(P_{ext}) = 1.2 \times 10^5 Pa = 1.2 bar$

Work (W) = 36.0 J = 36.0 J × $\frac{1 \text{dm}^3 \text{bar}}{100 \text{J}}$ = 0.360 dm³ bar

Now, from formula,

W = - P_{ext} △ V = - P_{ext} (V₂ - V₁)
∴ 0.360 dm³ bar = - 1.2 bar × (V₂ - 0.5 dm³)
∴
$$\frac{0.360 \text{ dm}^3 \text{ bar}}{1.2 \text{ bar}}$$
 = - (V₂ - 0.5 dm³)



 $\therefore 0.3 \text{ dm}^3 = - \text{V}_2 + 0.5 \text{ dm}^3$

 \therefore V₂ = 0.2 dm³ = 200 cm³

The final volume $(V_2) = 200 \text{ cm}^3$.

Exercises | Q 4.07 | Page 88

Answer the following question.

Calculate the maximum work when 24 g of O₂ are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K.

Solution:

Given: Mass of $O_2 = 24$ g Initial pressure = $P_1 = 1.6$ bar Final pressure = $P_2 = 1$ bar Temperature = T = 298 K

To find: Maximum work (Wmax)

Formula:
$$W_{max} = -2.303 \text{ nRT } \log_{10} \frac{P_1}{P_2}$$

Calculation:

Number of moles of $O_2 = n = \frac{24g}{32g \text{ mol}^{-1}} = 0.75 \text{ mol}$

Gas constant = $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\begin{split} W_{max} &= -2.303 \text{ nRT } \log_{10} \frac{P_1}{P_2} \\ &= -2.303 \times 0.75 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 298 \text{ K} \times \log_{10} \frac{1.6}{1} \\ &= -2.303 \times 0.75 \times 8.314 \text{ J} \times 298 \times 0.2041 \\ &= -873.4 \text{ J} \end{split}$$

The maximum work done is - 873.4 J.

Exercises | Q 4.08 | Page 88



Answer the following question.

Calculate the work done in the decomposition of 132 g of NH₄NO₃ at 100 °C.

 $NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)}$

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

Solution:

Given:

Decomposition of 1 mole of NH₄NO₃

Temperature = T = 100 °C = 373 K

To find: Work done and to determine whether work is done on the system or by the system.

Formula: $W = -\Delta n_g RT$

Calculation:

Molar mass of $NH_4NO_3 = (2 \times 14) + (3 \times 16) + (4 \times 1) = 80 \text{ g mol}^{-1}$

Moles of NH₄NO₃ = n =
$$\frac{132g}{80g \text{ mol}^{-1}}$$
 = 1.65 mol

The given reaction is for 1 mole of NH_4NO_3 . For 1.65 moles of NH_4NO_3 , the reaction is given as follows:

 $1.65 \ NH_4 NO_{3(s)} \rightarrow 1.65 \ N_2 O_{(g)} + 3.30 \ H_2 O_{(g)}$

Now,

 $\Delta n_g = (moles of product gases) - (moles of reactant gases)$

 $\Delta n_g = (1.65 + 3.30) - 0 = +4.95 \text{ mol} (:: NH_4NO_3 \text{ is in solid state})$

Hence,

```
W = -\Delta n_g RT
```

= - (+ 4.95 mol) × 8.314 J K⁻¹ mol⁻¹ × 373 K

= - 15350 J

```
= - 15.35 kJ
```

Work is done by the system (since W < 0).

The work done is -15.35 kJ. The work is done by the system.

Exercises | Q 4.09 | Page 88

Answer the following question.



Calculate standard enthalpy of reaction,

 $\begin{aligned} & \mathsf{Fe}_2\mathsf{O}_{3(s)} + 3\mathsf{CO}_{(g)} \rightarrow 2\mathsf{Fe}_{(s)} + 3\mathsf{CO}_{2(g)}, \text{ from the following data.} \\ & \Delta_f \ \mathsf{H}^\circ(\mathsf{Fe}_2\mathsf{O}_3) = -824 \ \mathsf{kJ/mol}, \\ & \Delta_f \ \mathsf{H}^\circ(\mathsf{CO}) = -110 \ \mathsf{kJ/mol}, \\ & \Delta_f \ \mathsf{H}^\circ(\mathsf{CO}_2) = -393 \ \mathsf{kJ/mol} \end{aligned}$

Solution:

Given:

 $\Delta_{\rm f} \, \mathrm{H}^{\circ}(\mathrm{Fe}_2\mathrm{O}_3) = - \, 824 \, \mathrm{kJ/mol},$

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

 $\Delta_{\rm f} \, {\rm H^o(CO_2)} = - \, 393 \, {\rm kJ/mol}$

To find: Standard enthalpy of the given reaction ($\Delta_r H^\circ$)

Formula: $\Delta H^{\circ} = \sum \Delta_f H^{\circ}$ (products) - $\sum \Delta_f H^{\circ}$ (reactants)

Calculation:

The reaction is

$$\begin{split} &\mathsf{Fe}_2\mathsf{O}_{3(s)} + 3\mathsf{CO}_{(g)} \to 2\mathsf{Fe}_{(s)} + 3\mathsf{CO}_{2(g)} \\ &\Delta_r\mathsf{H}^\circ = \sum \Delta_f \,\mathsf{H}^\circ \,(\text{products}) - \sum \Delta_f \,\mathsf{H}^\circ \,(\text{reactants}) \\ &= [2 \,\Delta_f \,\mathsf{H}^\circ \,(\mathsf{Fe}) + 3 \,\Delta_f \,\mathsf{H}^\circ \,(\mathsf{CO}_2)] - [\Delta_f \,\mathsf{H}^\circ \,(\mathsf{Fe}_2\mathsf{O}_3) + 3 \,\Delta_f \,\mathsf{H}^\circ \,(\mathsf{CO})] \\ &= [0 + 3 \,\operatorname{mol}\,\times \,(\text{-} \,393 \,\text{kJ} \,\operatorname{mol}^{-1})] - [1 \,\operatorname{mol}\,\times \,(\text{-} \,824 \,\text{kJ} \,\operatorname{mol}^{-1}) + 3 \,\operatorname{mol}\,\times \,(\text{-} \,110 \,\text{kJ} \,\operatorname{mol}^{-1})] \\ &= -1179 + 824 + 330 \\ &= -25 \,\text{kJ} \end{split}$$

The standard enthalpy of the given reaction is -25 kJ.

Exercises | Q 4.1 | Page 88

Answer the following question.

For a certain reaction ΔH° = 219 kJ and ΔS° = -21 J/K. Determine whether the reaction is spontaneous or nonspontaneous.

Solution:

When ΔH positive and ΔS is negative, then ΔG is positive regardless of temperature. Hence, the reaction is nonspontaneous at all temperatures.

Exercises | Q 4.11 | Page 88



Answer the following question.

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

 $2H_2O_{(l)} + O_{2(g)} \rightarrow 2H_2O_{2(l)}$ if $\Delta H^\circ = 196 \text{ kJ}$, $\Delta S^\circ = -126 \text{ J/K}$, does it have a cross-over temperature?

Solution:

When ΔH positive and ΔS is negative, then ΔG is positive regardless of temperature. Hence, the reaction is nonspontaneous at all temperatures. It does NOT have a crossover temperature.

Exercises | Q 4.12 | Page 88

Answer the following question.

Calculate ΔU at 298 K for the reaction,

 $C_2H_{4(g)} + HCI_{(g)} \rightarrow C_2H_5CI_{(g)}, \Delta H = -72.3 \text{ kJ}$

How much PV work is done?

Solution:

Given: Enthalpy change = $\Delta H = -72.3 \text{ kJ}$ Temperature = T = 298 K

To find: PV work done and internal energy change (ΔU)

Formulae: 1. W = - $\Delta n_g RT$

2. $\Delta H = \Delta U + \Delta n_g RT$

Calculations:

 $\Delta n_g = (moles of product gases) - (moles of reactant gases)$

 $\Delta n_g = 1 - 2 = -1 \text{ mol}$

Using formula (i)

 $W = -\Delta n_g RT$

= - (- 1 mol) × 8.314 J K⁻¹ mol⁻¹ × 298 K

= 2477.57 J = 2.48 kJ

Now, using formula (ii) and rearranging,



 $\Delta U = \Delta H - \Delta n_g RT = \Delta H + W = -72.3 \text{ kJ} + 2.48 \text{ kJ} = -69.8 \text{ kJ}$

- ∴ The PV work done is 2.48 kJ.
- \therefore The internal energy change (ΔU) is –69.8 kJ.

Exercises | Q 4.13 | Page 88

Answer the following question.

Calculate the work done during the synthesis of NH₃ in which volume changes from 8.0 dm³ to 4.0 dm3 at a constant external pressure of 43 bar. In what direction the work-energy flows?

Solution:

Given:

Initial volume (V₁) = 8.0 dm 3 Final volume (V₂) = 4.0 dm 3 External pressure (P_{ext}) = 43 bar

To find:

The work done (W) and direction of the work energy flow.

Formulae: $W = -P_{ext} \Delta V = -P_{ext} (V_2 - V_1)$

Calculations:

From formula,

W = - P_{ext} Δ V = - P_{ext} (V₂ - V₁) ∴ W = - 43 bar × (4.0 dm³ - 8.0 dm³) = 172 dm³ bar

Now, $1 \text{ dm}^3 \text{ bar} = 100 \text{ J}$

Hence, 172 dm³ ×
$$\frac{100J}{1 dm^3 bar}$$
 = 17200 J = 17.2 kJ

Since, the work is done on the system, work-energy flows into the system from surroundings.

 \therefore The work done (W) = 17.2 kJ

: Work energy flows into the system.

Exercises | Q 4.14 | Page 88

Calculate the amount of work done in the

1) Oxidation of 1 mole $HCI_{(g)}$ at 200 °C according to reaction.



 $4HCI_{(g)} + O_{2(g)} \rightarrow 2CI_{2(g)} + 2H_2O_{(g)}$

2) Decomposition of one mole of NO at 300 °C for the reaction

 $2NO_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$

Solution:

Given:

1) Oxidation of 1 mole $HCI_{(g)}$ Temperature = T = 200 °C = 473 K

2) Decomposition of one mole of NO Temperature = T = $300 \text{ }^{\circ}\text{C} = 573 \text{ K}$

To find: Work done

Formula: $W = -\Delta n_g RT$

Calculation:

1) The given reaction is for 4 moles of HCI. For 1 mole of HCI, the reaction is given as follows:

$$\mathsf{HCl}_{(g)} + \frac{1}{4} \mathsf{O}_{2(g)} \rightarrow \frac{1}{2} \mathsf{Cl}_{2(g)} + \frac{1}{2} \mathsf{H}_2 \mathsf{O}_{(g)}$$

Now,

 Δn_q = (moles of product gases) - (moles of reactant gases)

$$\Delta n_{g} = \left(\frac{1}{2} + \frac{1}{2}\right) - \left(1 + \frac{1}{4}\right) = -0.25 \text{ mol}$$

Hence,

 $W = - \Delta n_g RT$

= -(- 0.25 mol) × 8.314 J K⁻¹ mol⁻¹ × 473 K

= + 983 J

2) The given reaction is for 2 moles of NO. For 1 mole of NO, the reaction is given as follows:



$$NO_{(g)} \rightarrow \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$$

Now,

 Δn_q = (moles of product gases) - (moles of reactant gases)

$$\Delta n_{g} = = \left(\frac{1}{2} + \frac{1}{2}\right) - 1 = 0 \text{ mol}$$

Hence,

W = $-\Delta n_g RT$ = $-0 \text{ mol} \times 8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} \times 573 \text{ K}$

= 0 kJ

No work is done (since W = 0).

 \therefore The work done is +983 J. The work is done on the system.

 \therefore The work done is 0 kJ. There is no work done.

Exercises | Q 4.15 | Page 89

Answer the following question.

When 6.0 g of O2 reacts with CIF as per

 $2CIF_{(g)} + O_{2(g)} \rightarrow CI_2O_{(g)} + OF_{2(g)}$

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction? ($\Delta_r H^\circ =$

205.6 kJ)

Solution:

Given:

Enthalpy change for a given mass = 38.55 kJMass of $O_2 = 6.0 \text{ g}$

To find: Standard enthalpy of the given reaction

Calculation:



Number of moles of $O_2 = \frac{\text{Mass of } O_2}{\text{Molar mass of } O_2} = \frac{6\text{g}}{32\text{g mol}^{-1}} = 0.1875 \text{ mol}$

The enthalpy change when 0.1875 mol of O₂ react with CIF is 28.55 kJ.

: Enthalpy change for 1 mole O₂ = $rac{38.55}{0.1875} = 205.6$ kJ

From the reaction, 2 moles of CIF react with 1 mole of O₂.

So, the standard enthalpy of reaction is + 205.6 kJ.

Exercises | Q 4.16 | Page 89

Answer the following question.

Calculate the standard enthalpy of formation of CH₃OH_(I) from the following data:

CH₃OH_(I) +
$$\frac{3}{2}$$
O_{2(g)} → CO_{2(g)} + 2H₂O_(I); Δ_r H° = - 726 kJ mol⁻¹

 $\mathrm{C}_{\mathrm{graphite}} + \mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CO}_{2(\mathrm{g})}; \Delta_r \mathrm{H}^\circ$ = - 393 kJ mol⁻¹

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}; \Delta_r H^\circ = -286 \text{ kJ mol}^{-1}$$

Solution:

Given: Given equations are,

$$CH_3OH_{(I)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(I)}; \Delta_r H^\circ = -726 \text{ kJ mol}^{-1}(i)$$

 $\mathrm{C}_{\mathrm{graphite}} + \mathrm{O}_{2(g)}
ightarrow \mathrm{CO}_{2(g)}; \Delta_r \mathrm{H}^\circ$ = - 393 kJ mol⁻¹(ii)

$$H_{2(g)} + \frac{1}{2} O_{2(g)} → H_2O_{(I)}; Δ_r H^\circ = -286 \text{ kJ mol}^{-1}(iii)$$



To find: The standard enthalpy of formation ($\Delta_{f}H^{\circ}$) of CH₃OH_(I)

Calculation:

Required equation is, $\mathrm{C}_{\mathrm{graphite}} + 2\mathrm{H}_{2(\mathrm{g})} + rac{1}{2}\mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CH}_{3}\mathrm{OH}_{(\mathrm{l})}$

Multiply equation (iii) by 2 and add to equation (ii),

$$2\mathrm{H}_{2(\mathrm{g})} + \mathrm{O}_{2(\mathrm{g})}
ightarrow 2\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$$
, $\Delta_{\mathrm{r}}\mathsf{H}^{\circ}$ = - 575 kJ mol⁻¹

 $\mathrm{C}_{\mathrm{graphite}} + \mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CO}_{2(\mathrm{g})}$, $\Delta_{\mathrm{c}}\mathrm{H}^{\circ}$ = - 393 kJ mol⁻¹

$$\mathrm{C}_{\mathrm{graphite}} + 2\mathrm{H}_{2(\mathrm{g})} + 2\mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CO}_{2(\mathrm{g})} + 2\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$$

$$\Delta_r H^\circ = -572 - 393 = -965 \text{ kJ mol}^{-1}$$

Reverse equation (i) and add to equation (iv),

$$\mathrm{CO}_{2(\mathrm{g})} + 2\mathrm{H}_2\mathrm{O}_{(\mathrm{l})}
ightarrow \mathrm{CH}_3\mathrm{OH}_{(\mathrm{l})} + rac{3}{2}\mathrm{O}_{2(\mathrm{g})}, \Delta_{\mathrm{r}}\mathrm{H}^\circ$$
 = 726 kJ mol⁻¹

 $\mathrm{C_{graphite}} + 2\mathrm{H}_{2(\mathrm{g})} + 2\mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CO}_{2(\mathrm{g})} + 2\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})'} \Delta_{\mathrm{r}}\mathrm{H}^{\circ}$ = - 965 kJ mol⁻¹

$$\mathrm{C}_{\mathrm{graphite}} + 2\mathrm{H}_{2(\mathrm{g})} + rac{1}{2}2\mathrm{O}_{2(\mathrm{g})}
ightarrow \mathrm{CH}_{3}\mathrm{OH}_{(\mathrm{l})}$$

 $\Delta_f H^\circ = \Delta_r H^\circ = 726 - 965 = -239 \text{ kJ mol}^{-1}$

The standard enthalpy of formation ($\Delta_f H^\circ$) of CH₃OH_(I) from the given data is – 239 kJ mol⁻¹

Exercises | Q 4.17 | Page 89

Answer the following question.

Calculate $\Delta_r H^\circ$ for the following reaction at 298 K:

- 1) $2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)}, \Delta_r H^\circ = + 14.4 \text{ kJ}$
- 2) $H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)}, \Delta_r H^\circ = -0.02 \text{ kJ}$



3) $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}, \Delta_r H^\circ = + 17.3 \text{ kJ}$

Solution:

Given: Given equations are,

 $2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(I)}, \Delta_r H^\circ = + 14.4 \text{ kJ} \dots(i)$

 $H_{3}BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_{2}O_{(I)}, \Delta_{r}H^{\circ} = -0.02 \text{ kJ} \quad(ii)$

 $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}, \Delta_r H^\circ = + 17.3 \text{ kJ} \dots (iii)$

To find: The standard enthalpy of the given reaction ($\Delta_r H^\circ$)

Calculation:

Reverse equation (i) and multiply by 2, $2B_2O_{3(s)} + 6H_2O_{(1)} \rightarrow 4H_3BO_{3(aq)}$, $\Delta_r H^\circ = -28.8 \text{ kJ}$ (iv) Multiply equation (ii) by 4 $4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(1)}$, $\Delta_r H^\circ = -0.08 \text{ kJ}$ (v) Add equations (iv), (v) and (iii), $2B_2O_{3(s)} + 6H_2O_{(1)} \rightarrow 4H_3BO_{3(aq)}$, $\Delta_r H^\circ = -28.8 \text{ kJ}$ $4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(1)}$, $\Delta_r H^\circ = -0.08 \text{ kJ}$ $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(1)}$, $\Delta_r H^\circ = +17.3 \text{ kJ}$

 $H_2B_4O_{7(s)} + H_2O_{(I)} \rightarrow 4HBO_{2(aq)} \Delta_r H^\circ = -28.8 + (-0.08) + 17.3 = -11.58 \text{ kJ}$

The standard enthalpy ($\Delta_r H^\circ$) of the given reaction is -11.58 kJ.

Exercises | Q 4.18 | Page 89

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: $\Delta_{fus}H^{\circ}$ (ice) = 6.01 kJ mol⁻¹ at 0 °C, $\Delta_{vap}H^{\circ}$ (H₂O) = 40.7 kJ mol⁻¹ at 100 °C, Specific heat of water is 4.18 J g⁻¹ K⁻¹] Solution: Given: $\Delta_{fus}H^{\circ}$ (ice) = 6.01 kJ mol⁻¹ at 0 °C,

 Δ_{fus} H° (H₂O) = 6.01 kJ mol⁻¹ at 0 °C, Δ_{vap} H° (H₂O) = 40.7 kJ mol⁻¹ at 100 °C, Specific heat of water is 4.18 J g⁻¹ K⁻¹



To find:

The total heat required to carry out the given reaction using 180 g of ice.

Calculation:

 $\begin{array}{c} H_2O_{(s)} & \xrightarrow{\text{Latent heat}} & H_2O_{(l)} & \xrightarrow{\text{Heating}} & H_2O_{(l)} & \xrightarrow{\text{Heating}} & H_2O_{(l)} & \xrightarrow{\text{Latent}} & H_2O_{(g)} & \xrightarrow{\text{Latent}} & \xrightarrow{\text{Latent}} & H_2O_{(g)} & \xrightarrow{\text{Latent}} & \xrightarrow{\text{Latent}}$ a) $H_2O_{(s)} \rightarrow H_2O_{(l)}$ 0°C 0°C Heat required = Latent heat for 180 g. $1 \text{ mol of H}_2\text{O} = 6.01 \text{ kJ}$ $1 \text{ mol of H}_2\text{O} = 18 \text{ g}$ $\therefore 180 \text{ g of H2O} = \frac{180 \text{g}}{18 \text{g mol}^{-1}} = 10 \text{ moles of H}_2\text{O}$ \therefore 10 mol of H₂O requires = 60.1 kJ \therefore Heat required = 60.1 kJ ...(i) b) $H_2O_{(I)} \rightarrow H_2O_{(s)}$ 0°C 100 °C Heat required = Mass × Specific heat × ΔT = 180 g × 4.18 J g⁻¹ K⁻¹ × 100 K = 75240 J = 75.240 kJ(ii) c) $H_2O(I) \rightarrow H_2O(g)$ 100 °C 100 °C Heat required = Latent heat of vaporization 1 mol of H_2O requires = 40.7 kJ \therefore 1 mol of H₂O = 18 g \therefore 180 g of H₂O = 10 moles of H₂O



: Heat required by 10 moles of water = 407 kJ(iii)

From (i), (ii) and (iii),

Total heat required to carry out the given reaction using 180 g of ice

= 60.1 kJ + 75.240 kJ + 407 kJ = + 542.34 kJ

The total heat required to melt 180 g of ice at 0 °C, heat it to 100 °C and then vaporize it at that temperature is + 542.34 kJ.

Exercises | Q 4.19 | Page 89

The enthalpy change for the reaction,

 $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$ is - 620 J when 100 mL of ethylene and 100 mL of H₂ react at 1 bar pressure. Calculate the pressure-volume type of work and ΔU for the reaction.

Solution:

Given:

Enthalpy change (Δ H) = - 620 J

Volumes of reactants; $C_2H_4 = 100 \text{ mL}$, $H_2 = 100 \text{ mL}$

Pressure (Pext) = 1 bar

To find:

Pressure-volume work (W) and change in internal energy (ΔU) for the given reaction

Formulae:

1) W = - $P_{ext} = \Delta V$

2) $\Delta H = \Delta U + P_{ext} \Delta V$

Calculation:

According to the equation of reaction 1 mole of C_2H_4 reacts with 1 mole of H_2 to produce 1 mole of C_2H_6 . Hence, 100 mL of C_2H_4 would react with 100 mL of H_2 to produce 100 mL of C_2H_6 .

 $V_1 = 100 \text{ mL} + 100 \text{ mL} = 200 \text{ mL} = 0.2 \text{ dm}^3$ $V_2 = 100 \text{ mL} = 0.1 \text{ dm}^3$ From formula (i), $W = -P_{ext} = \Delta V$ $= -1 \text{ bar } (0.1 \text{ dm}^3 - 0.2 \text{ dm}^3)$



= 0.10 dm³ bar = 0.10 dm³ bar × 100 $\frac{J}{dm^{3}bar}$ = + 10.00 J \therefore - P_{ext} = ΔV = 10.00 J \therefore P_{ext} = ΔV = - 10.00 J From formula (ii), $\Delta H = \Delta U$ + P_{ext} ΔV $\therefore \Delta U = \Delta H$ - P_{ext} ΔV = - 620 - (- 10.00 J) = - 610 J Pressure-volume work (W) = +10.00 J and ΔU = - 610 J

Exercises | Q 4.2 | Page 89

Calculate the work done and comment on whether work is done on or by the system for the decomposition of 2 moles of NH₄NO₃ at 100 °C

 $NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)}$

Solution:

Given:

Decomposition of 1 mole of NH₄NO₃

Temperature = T = 100 °C = 373 K

To find:

Work done and to determine whether work is done on the system or by the system

Formula: $W = -\Delta n_g RT$

Calculation:

The given reaction is for 1 mole of NH_4NO_3 . For 2 moles of NH_4NO_3 , the reaction is given as follows:

$$\begin{split} 2NH_4NO_{3(s)} &\rightarrow 2N_2O_{(g)} + 4H_2O_{(g)} \\ Now, \\ \Delta n_g &= (moles \mbox{ of product gases}) - (moles \mbox{ of reactant gases}) \\ \end{split}$$

 $\Delta n_g = 6 - 0 = + 6 \text{ mol}$ (:: NH₄NO₃ is in solid state)

Hence,

 $W = -\Delta n_g RT$



= - (+ 6 mol) × 8.314 J K⁻¹ mol⁻¹ × 373 K

= - 18606.75 J

= - 18.61 kJ

Work is done by the system (since W < 0).

The work done is - 18.61 kJ. The work is done by the system.