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 (V_1) = 2.5 L = 2.5 dm^3

Final volume (V_2) = 4.5 L = 4.5 dm^3

External pressure (P_{ext}) = 2.5 bar

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

$$= - 5.0 \text{ dm}^3 \text{ bar} \times \frac{100 \text{J}}{1 \text{dm}^3 \text{bar}}$$

$= - 500 \text{ J}$

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. $H_{2(g)} \rightarrow 2H_{(g)}$
4. $2 \; NaHCO_{3(s)} \rightarrow Na2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

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. $H_{2(g)} \rightarrow 2H_{(g)}$
2. $C_{(s)} \rightarrow C_{(g)}$
3. **$2Cl_{(g)} \rightarrow Cl_{2(g)}$**
4. $H_2O_{(s)} \rightarrow H_2O_{(l)}$

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

Hint:

Bond is formed between two Cl 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}

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

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

∴ Enthalpy change for 1 mole ethanol

$$= \frac{5.89\text{kJ}}{0.1357\text{mol}}$$

= 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 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 kJ mol^{-1} then entropy change of the surroundings will be **801.7 J K^{-1}.**

Explanation:

For standard state, temperature = 298 K

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

$= + 0.8017\ kJ\ K^{-1}$

$= 801.7\ J\ K^{-1}$

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,

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

Exercises | Q 1.1 | Page 87

Select the most appropriate option.

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 _______.

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 **–93 kJ mol^{-1}**.

Explanation:

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

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

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

= -186 kJ

$\therefore H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$, $\Delta_r H°$ = -186 kJ

For enthalpy of formation of HCl, the reaction is

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)},$$

$$\Delta_r H° = \frac{-186\text{kJ}}{2 \text{ mol}} = -93 \text{ kJ mol}^{-1}$$

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:

$1\ J = 1\ kg\ m^2\ s^{-2} = 1\ Pa\ m^3$

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

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

If the pressure is expressed in bar and ΔV in dm^3, then the work has the units of bar dm^3.

$1\ bar = 10^5\ Pa = 10^5\ kg\ m^{-1}\ s^{-2}$

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

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

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

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.
2. 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); $H_{2(g)}$, $Hg_{(l)}$, $Na_{(s)}$, $C_{(graphite)}$, $C_2H_5OH_{(l)}$, $CaCO_{3(s)}$, $CO_{2(g)}$, $C_2H_5OH_{(l)}$, $H_2O_{(l)}$, $CaCO_{3(s)}$, $CO_{2(g)}$.

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 H_2 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,

$$\triangle S_{total} = \triangle S_{sys} + \triangle S_{surr} > 0.$$

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 –ΔH. The entropy change of surroundings can be calculated using the following expression:\

$$\triangle S_{surr} = -\frac{\triangle H}{T}$$

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

$\Delta G = \Delta G° + RT \ln Q$ …(1)

where, $\Delta G°$ 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),

$\Delta G = \Delta G° + RT \ln Q_C$ or $\Delta G = \Delta G° + RT \ln Q_P$

$$= \Delta G° + RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad = \Delta G° + RT \ln \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

3. When the reaction reaches equilibrium, $\Delta G° = 0$ and Q_C and Q_P become K_C and K_P, respectively.

Thus,

$\therefore 0 = \Delta G° + RT \ln K_C$ or $0 = \Delta G° + RT \ln K_P$

$\therefore \Delta G° = -RT \ln K_C$ or $\Delta G° = -RT \ln K_P$

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

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.
2. 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,

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

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

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,
   $C_2H_{2(g)} + 5/2\ O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)}$, $\Delta_r H° = - 1300$ kJ
   In the above reaction, the standard enthalpy change of the oxidation reaction, –1300 kJ is the standard enthalpy of combustion of $C_2H_{2(g)}$.

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, $Cl_{2(g)} \rightarrow Cl_{(g)} + Cl_{(g)}$; $\Delta_{atom}H = 242$ 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

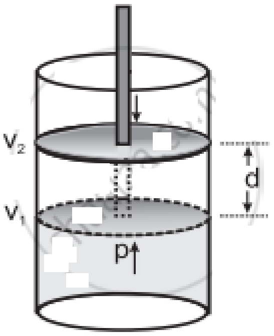
Exercises | Q 3.7 | Page 88

Answer in brief.

Derive the expression for PV work.

Solution:

Pressure-volume work



1. 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 V_1 at temperature T. This is shown in the adjacent diagram.
2. 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,
   $f = - P_{ext} \times A$ .....(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.
   $W = f \times d$ .....(2)

Substituting equation (1) in (2) gives
$W = - P_{ext} \times A \times d$ .....(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 V_2 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 NO_2? The reaction is:

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

Solution:

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

To find: Heat evolved when 12g of CO reacts with NO_2

Calculation:

According to the given reaction, 1200 kJ of heat is evolved when 4 moles of CO react with NO_2. So heat evolved per mole is 1200kJ/4 mol = 300 kJ mol^{-1}

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

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

So, heat evolved when 0.4286 moles of CO reacts

= 0.4286 mol × 300 kJ mol^{-1} = 128.58 kJ

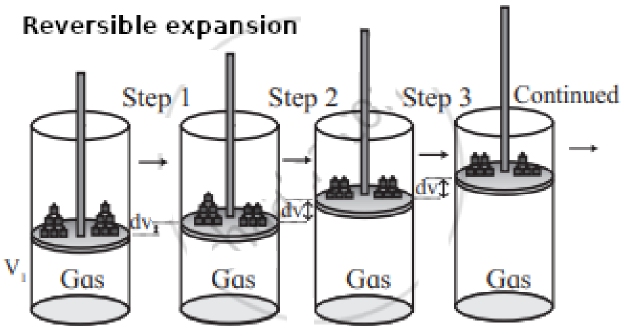
The heat evolved when 12 g of CO reacts with NO_2 is 128.58 kJ.

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 ....(1)

3. As the expansion is reversible, P is greater by a very small quantity dp than P_{ext}.

Thus P - Pext = dP or Pext = P - dP ....(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,

$$\int_{initial}^{final} dW = -\int_{V_2}^{V_1} PdV$$

Hence,

$$Wmax = -\int_{V_2}^{V_1} PdV \quad .....(4)$$

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

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

$$= -nRT\int_{V_2}^{V_1} \frac{dV}{V} \quad ...(\because T \text{ is constant.})$$

$$= -nRT \ln (V)_{V_1}^{V_2}$$

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

$$= -nRt \ln \frac{V_2}{V_1}$$

$$= -2.303\ nRT \log 10 \frac{V_2}{V_1} \quad ....(5)$$

6. At constant temperature, $P_1V_1 = P_2V_2$ or $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

Replacing $\frac{V_2}{V_1}$ in in equation (5) by $\frac{P_1}{P_2}$, we get,

$$Wmax = -2.303\ nRT \log \frac{P_1}{P_2} \quad ....(6)$$

Equations (5) and (6) are expressions for work done in reversible isothermal process.

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

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

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

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

$= \Delta H + P(V_2 – V_1)$

$\Delta H = \Delta U + PV_2 – PV_1$ …(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

$\Delta H = \Delta U + n_2RT – n_1RT$

$= \Delta U + (n_2 – n_1) RT$

$= \Delta U + \Delta n_g RT$ ....(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 NH_3,

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

2. $N_2H_{4(g)} + H_{2(g)} \rightarrow 2NH_{3(g)}, \triangle_r H_2^0 = -187.6$ kJ

$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}, \Delta_r H° = -92.2$ 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 H_2 and O_2 is -327 J K^{-1}, it is spontaneous. Explain.

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

Solution:

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

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,

$$\triangle S_{surr} = \frac{Q_{rev}}{T} = \frac{572 \times 10^3 J}{298K} = +1919 \text{ J K}^{-1}$$

4. The total enthalpy change is,

$$\triangle S_{total} = \triangle S_{sys} + \triangle S_{surr}$$

$= -327 \text{ J K}^{-1} + 1919 \text{ J K}^{-1}$

$= +1592 \text{ J K}^{-1}$

5. Since $\triangle S_{total} > 0$, 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 $\triangle S_{total}$. Comment on the spontaneity of the reaction.

Solution:

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

$\triangle S_{total} = \triangle S_{sys} + \triangle S_{surr}$

OR

$\triangle S_{total} = \triangle S + \triangle S_{surr}$ ....(1)

2) According to second law of thermodynamics for a process to be spontaneous, $\triangle S_{total} > 0$.

3) If ΔH is the enthalpy change accompanying a reaction (system), the enthalpy change of the surroundings is −ΔH. Thus,

$$\triangle S_{surr} = -\frac{\triangle H}{T} \quad ....(2)$$

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

$$\triangle S_{total} = \triangle S - \frac{\triangle H}{T}$$

Rearranging above expression, we get,

$T \triangle S_{total} = T \triangle S - \triangle H$

or

$-T \triangle S_{total} = \triangle H - T \triangle S$ .....(3)

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

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

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

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

7) For a spontaneous reaction, S_{total} > 0 and hence, ΔG < 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 ΔG < 0, the process is spontaneous.

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

iii) $\triangle S_{total}$ = 0 and ΔG = 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 (V_1) = 500 cm^3
External pressure (P_{ext}) = 1.2×10^5 Pa
Work (W) = 36.0 J

To find: Final volume (V_2)

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

Calculation: Initial volume (V_1) = 500 cm^3 = 0.5 dm^3

External pressure (P_{ext}) = 1.2×10^5 Pa = 1.2 bar

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

Now, from formula,

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

$$\therefore 0.360 \text{ dm}^3 \text{ bar} = - 1.2 \text{ bar} \times (V_2 - 0.5 \text{ dm}^3)$$

$$\therefore \frac{0.360 \text{ dm}^3 \text{ bar}}{1.2 \text{bar}} = - (V_2 - 0.5 \text{ dm}^3)$$

$\therefore 0.3\ dm^3 = -V_2 + 0.5\ dm^3$

$\therefore V_2 = 0.2\ dm^3 = 200\ cm^3$

The final volume (V_2) = 200 cm^3.

Exercises | Q 4.07 | Page 88

Answer the following question.

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.

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 (W_{max})

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

Calculation:

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

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

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

$= -2.303 \times 0.75\ mol \times 8.314\ J\ K^{-1} mol^{-1} \times 298\ K \times \log_{10} \frac{1.6}{1}$

$= -2.303 \times 0.75 \times 8.314\ J \times 298 \times 0.2041$

$= -873.4\ J$

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 NH_4NO_3 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 NH_4NO_3

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 × 14) + (3 × 16) + (4 × 1) = 80 g mol^{-1}

$$\text{Moles of } NH_4NO_3 = n = \frac{132\text{g}}{80\text{g mol}^{-1}} = 1.65 \text{ mol}$$

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:

$1.65\ NH_4NO_{3(s)} \rightarrow 1.65\ N_2O_{(g)} + 3.30\ H_2O_{(g)}$

Now,

Δn_g = (moles of product gases) – (moles of reactant gases)

Δn_g = (1.65 + 3.30) – 0 = +4.95 mol (∵ NH_4NO_3 is in solid state)

Hence,

$W = -\Delta n_g RT$

$= -(+4.95 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 373 \text{ K}$

= - 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,

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$, from the following data.

$\Delta_f H°(Fe_2O_3)$ = - 824 kJ/mol,

$\Delta_f H°(CO)$ = - 110 kJ/mol,

$\Delta_f H°(CO_2)$ = - 393 kJ/mol

Solution:

Given:

$\Delta_f H°(Fe_2O_3)$ = - 824 kJ/mol,

$\Delta_f H°(CO)$ = - 110 kJ/mol,

$\Delta_f H°(CO_2)$ = - 393 kJ/mol

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

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

Calculation:

The reaction is

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$

$\Delta_r H° = \sum \Delta_f H° \text{ (products)} - \sum \Delta_f H° \text{ (reactants)}$

$= [2\ \Delta_f H° (Fe) + 3\ \Delta_f H° (CO_2)] - [\Delta_f H° (Fe_2O_3) + 3\ \Delta_f H° (CO)]$

$= [0 + 3 \text{ mol} \times (- 393 \text{ kJ mol}^{-1})] - [1 \text{ mol} \times (- 824 \text{ kJ mol}^{-1}) + 3 \text{ mol} \times (- 110 \text{ kJ mol}^{-1})]$

= - 1179 + 824 + 330

= - 25 kJ

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 ΔH° = 196 kJ, ΔS° = –126 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 cross-over temperature.

Exercises | Q 4.12 | Page 88

Answer the following question.

Calculate ΔU at 298 K for the reaction,

$C_2H_{4(g)} + HCl_{(g)} \rightarrow C_2H_5Cl_{(g)}$, ΔH = - 72.3 kJ

How much PV work is done?

Solution:

Given:
Enthalpy change = ΔH = –72.3 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:

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

$\Delta n_g = 1 – 2 = –1$ mol

Using formula (i)

$W = - \Delta n_g RT$

$= - (- 1 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$

= 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.

∴ 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 NH_3 in which volume changes from 8.0 dm^3 to 4.0 dm3 at a constant external pressure of 43 bar. In what direction the work-energy flows?

Solution:

Given:
Initial volume (V_1) = 8.0 dm 3
Final volume (V_2) = 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,

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

∴ $W = - 43 \text{ bar} \times (4.0 \text{ dm}^3 - 8.0 \text{ dm}^3) = 172 \text{ dm}^3 \text{ bar}$

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

Hence, $172 \text{ dm}^3 \times \dfrac{100\text{J}}{1\text{dm}^3\text{bar}} = 17200 \text{ J} = 17.2 \text{ kJ}$

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

∴ 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 $HCl_{(g)}$ at 200 °C according to reaction.

$4HCl_{(g)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + 2H_2O_{(g)}$

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 $HCl_{(g)}$
Temperature = T = 200 °C = 473 K

2) Decomposition of one mole of NO
Temperature = T = 300 °C = 573 K

To find: Work done

Formula: $W = -\Delta n_g RT$

Calculation:

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

$$HCl_{(g)} + \frac{1}{4} O_{2(g)} \rightarrow \frac{1}{2} Cl_{2(g)} + \frac{1}{2} H_2O_{(g)}$$

Now,

Δn_g = (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,

$W = -\Delta n_g RT$

$= -(-0.25 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 473 \text{ K}$

= + 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_g = (moles of product gases) - (moles of reactant gases)

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

Hence,

$W = - \Delta n_g RT$

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

= 0 kJ

No work is done (since W = 0).

∴ The work done is +983 J. The work is done on the system.

∴ 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 O_2 reacts with ClF as per

$2ClF_{(g)} + O_{2(g)} \rightarrow Cl_2O_{(g)} + OF_{2(g)}$

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction? ($\Delta_r H° = 205.6$ kJ)

Solution:

Given:

Enthalpy change for a given mass = 38.55 kJ
Mass of O_2 = 6.0 g

To find: Standard enthalpy of the given reaction

Calculation:

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

The enthalpy change when 0.1875 mol of O_2 react with ClF is 28.55 kJ.

∴ Enthalpy change for 1 mole O_2 = $\frac{38.55}{0.1875} = 205.6$ kJ

From the reaction, 2 moles of ClF react with 1 mole of O_2.

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 $CH_3OH_{(l)}$ from the following data:

$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$; $\Delta_rH° = -726\ kJ\ mol^{-1}$

$C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_rH° = -393\ kJ\ mol^{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta_rH° = -286\ kJ\ mol^{-1}$

Solution:

Given: Given equations are,

$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$; $\Delta_rH° = -726\ kJ\ mol^{-1}$ ....(i)

$C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_rH° = -393\ kJ\ mol^{-1}$ ....(ii)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta_rH° = -286\ kJ\ mol^{-1}$ ....(iii)

To find: The standard enthalpy of formation ($\Delta_f H°$) of $CH_3OH_{(l)}$

Calculation:

Required equation is, $C_{graphite} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}$

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

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$, $\Delta_r H°$ = - 575 kJ mol^{-1}

$C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta_c H°$ = - 393 kJ mol^{-1}

$C_{graphite} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

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

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

$CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_3OH_{(l)} + \frac{3}{2}O_{2(g)}$, $\Delta_r H°$ = 726 kJ mol^{-1}

$C_{graphite} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$, $\Delta_r H°$ = - 965 kJ mol^{-1}

$C_{graphite} + 2H_{2(g)} + \frac{1}{2}2O_{2(g)} \rightarrow CH_3OH_{(l)}$

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

The standard enthalpy of formation ($\Delta_f H°$) of $CH_3OH_{(l)}$ from the given data is – 239 kJ mol^{-1}

Exercises | Q 4.17 | Page 89

Answer the following question.

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

1) $2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)}$, $\Delta_r H°$ = + 14.4 kJ

2) $H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)}$, $\Delta_r H°$ = - 0.02 kJ

3) $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}$, $\Delta_rH° = + 17.3$ kJ

Solution:

Given: Given equations are,

$2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)}$, $\Delta_rH° = + 14.4$ kJ ...(i)

$H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)}$, $\Delta_rH° = - 0.02$ kJ ....(ii)

$H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}$, $\Delta_rH° = + 17.3$ kJ .....(iii)

To find: The standard enthalpy of the given reaction ($\Delta_rH°$)

Calculation:

Reverse equation (i) and multiply by 2,

$2B_2O_{3(s)} + 6H_2O_{(l)} \rightarrow 4H_3BO_{3(aq)}$, $\Delta_rH° = - 28.8$ kJ ......(iv)

Multiply equation (ii) by 4

$4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(l)}$, $\Delta_rH° = - 0.08$ kJ ....(v)

Add equations (iv), (v) and (iii),

$2B_2O_{3(s)} + 6H_2O_{(l)} \rightarrow 4H_3BO_{3(aq)}$, $\Delta_rH° = - 28.8$ kJ

$4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(l)}$, $\Delta_rH° = - 0.08$ kJ

$H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}$, $\Delta_rH° = + 17.3$ kJ

$H_2B_4O_{7(s)} + H_2O_{(l)} \rightarrow 4HBO_{2(aq)}$ $\Delta_rH° = - 28.8 + (- 0.08) + 17.3 = - 11.58$ kJ

The standard enthalpy ($\Delta_rH°$) 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: $\Delta_{fus}H°$ (ice) = 6.01 kJ mol^{-1} at 0 °C, $\Delta_{vap}H°$ (H_2O) = 40.7 kJ mol^{-1} at 100 °C, Specific heat of water is 4.18 J g^{-1} K^{-1}]

Solution:

Given:

$\Delta_{fus}H°$ (ice) = 6.01 kJ mol^{-1} at 0 °C,
$\Delta_{vap}H°$ (H_2O) = 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:

$$\underset{\text{(ice at 0 °C)}}{H_2O_{(s)}} \xrightarrow[\text{of fusion 0°C}]{\text{Latent heat}} \underset{\text{(water at 0 °C)}}{H_2O_{(l)}} \xrightarrow{\text{Heating}} \underset{\text{(water at 100 °C)}}{H_2O_{(l)}} \xrightarrow[\text{haeat of vaporization 100°C}]{\text{Latent}} \underset{\text{(Stream at 100 °C)}}{H_2O_{(g)}}$$

a) $H_2O_{(s)} \rightarrow H_2O_{(l)}$

0 °C 0 °C

Heat required = Latent heat for 180 g.

1 mol of H_2O = 6.01 kJ

1 mol of H_2O = 18 g

$\therefore$ 180 g of H2O = $\dfrac{180\text{g}}{18\text{g mol}^{-1}}$ = 10 moles of H_2O

$\therefore$ 10 mol of H_2O requires = 60.1 kJ

$\therefore$ Heat required = 60.1 kJ …(i)

b) $H_2O_{(l)} \rightarrow H_2O_{(s)}$

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) $H_2O_{(l)} \rightarrow H_2O_{(g)}$

100 °C 100 °C

Heat required = Latent heat of vaporization

1 mol of H_2O requires = 40.7 kJ

$\therefore$ 1 mol of H_2O = 18 g

$\therefore$ 180 g of H_2O = 10 moles of H_2O

∴ 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 H_2 react at 1 bar pressure. Calculate the pressure-volume type of work and ΔU for the reaction.

Solution:

Given:

Enthalpy change (ΔH) = - 620 J

Volumes of reactants; C_2H_4 = 100 mL, H_2 = 100 mL

Pressure (P_{ext}) = 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 mL + 100 mL = 200 mL = 0.2 dm^3

V_2 = 100 mL = 0.1 dm^3

From formula (i),

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

= -1 bar (0.1 dm^3 - 0.2 dm^3)

$= 0.10\ dm^3\ bar$

$$= 0.10\ dm^3\ bar \times 100\ \frac{J}{dm^3 bar} = +\ 10.00\ J$$

$\therefore -P_{ext} = \Delta V = 10.00\ J$

$\therefore P_{ext} = \Delta V = -\ 10.00\ J$

From formula (ii),

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

$\therefore \Delta U = \Delta H - P_{ext}\Delta V$

$= -\ 620 - (-\ 10.00\ J) = -\ 610\ J$

Pressure-volume work (W) = +10.00 J and $\Delta U = -\ 610\ J$

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 NH_4NO_3 at 100 °C

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

Solution:

Given:

Decomposition of 1 mole of NH_4NO_3

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: $W = -\ \Delta n_gRT$

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:

$2NH_4NO_{3(s)} \rightarrow 2N_2O_{(g)} + 4H_2O_{(g)}$

Now,
Δn_g = (moles of product gases) - (moles of reactant gases)

$\Delta n_g = 6 - 0 = +\ 6$ mol   ($\because$ NH_4NO_3 is in solid state)

Hence,

$W = -\ \Delta n_gRT$

$= - (+ 6\ mol) \times 8.314\ J\ K^{-1}\ mol^{-1} \times 373\ K$

$= - 18606.75\ J$

$= - 18.61\ kJ$

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

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