

## Chemical Thermodynamics

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### 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,  $\Delta U$  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,

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

$$\text{Initial volume } (V_1) = 2.5 \text{ L} = 2.5 \text{ dm}^3$$

$$\text{Final volume } (V_2) = 4.5 \text{ L} = 4.5 \text{ dm}^3$$

$$\text{External pressure } (P_{\text{ext}}) = 2.5 \text{ bar}$$

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

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

$$= - 500 \text{ J}$$

**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.  $\text{H}_{2(\text{g})} \rightarrow 2\text{H}_{(\text{g})}$
4.  $2 \text{NaHCO}_{3(\text{s})} \rightarrow \text{Na}_2\text{CO}_{3(\text{s})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$

**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.  $\text{H}_{2(\text{g})} \rightarrow 2\text{H}_{(\text{g})}$
2.  $\text{C}_{(\text{s})} \rightarrow \text{C}_{(\text{g})}$
3.  **$2\text{Cl}_{(\text{g})} \rightarrow \text{Cl}_{2(\text{g})}$**
4.  $\text{H}_2\text{O}_{(\text{s})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$

**Solution:**  $2\text{Cl}_{(\text{g})} \rightarrow \text{Cl}_{2(\text{g})}$

**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<sup>-1</sup>**
2. 60.2 kJ mol<sup>-1</sup>
3. 38.9 kJ mol<sup>-1</sup>
4. 20.4 kJ mol<sup>-1</sup>

**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<sup>-1</sup>**.

**Explanation:**

Molar mass of ethanol (C<sub>2</sub>H<sub>6</sub>O) = 46 g mol<sup>-1</sup>

$$\text{Number of moles of O}_2 = \frac{\text{Mass of ethanol}}{\text{Molar mass of ethanol}} = \frac{6.24\text{g}}{46\text{g mol}^{-1}} = 0.1357 \text{ mol}$$

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

∴ Enthalpy change for 1 mole ethanol

$$\begin{aligned} &= \frac{5.89\text{kJ}}{0.1357\text{mol}} \\ &= 43.4 \text{ kJ mol}^{-1} \end{aligned}$$

### Exercises | Q 1.07 | Page 87

**Select the most appropriate option.**

If the standard enthalpy of formation of methanol is -238.9 kJ mol<sup>-1</sup> then entropy change of the surroundings will be \_\_\_\_\_.

1. -801.7 J K<sup>-1</sup>
2. **801.7 J K<sup>-1</sup>**
3. 0.8017 J K<sup>-1</sup>
4. -0.8017 J K<sup>-1</sup>

**Solution:**

If the standard enthalpy of formation of methanol is -238.9 kJ mol<sup>-1</sup> then entropy change of the surroundings will be **801.7 J K<sup>-1</sup>**.

**Explanation:**

For standard state, temperature = 298 K

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

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

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

### 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,  $\Delta H = 40.63 \text{ kJ mol}^{-1}$  and  $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ . 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,

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

### Exercises | Q 1.1 | Page 87

Select the most appropriate option.

Bond enthalpies of H–H, Cl–Cl, and H–Cl bonds are  $434 \text{ kJ mol}^{-1}$ ,  $242 \text{ kJ mol}^{-1}$ , and  $431 \text{ kJ mol}^{-1}$ , respectively. Enthalpy of formation of HCl is \_\_\_\_\_.

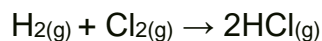
1.  $245 \text{ kJ mol}^{-1}$
2.  $-93 \text{ kJ mol}^{-1}$
3.  $-245 \text{ kJ mol}^{-1}$
4.  $93 \text{ kJ mol}^{-1}$

**Solution:**

Bond enthalpies of H–H, Cl–Cl, and H–Cl bonds are  $434 \text{ kJ mol}^{-1}$ ,  $242 \text{ kJ mol}^{-1}$ , and  $431 \text{ kJ mol}^{-1}$ , respectively. Enthalpy of formation of HCl is  $-93 \text{ kJ mol}^{-1}$ .

**Explanation:**

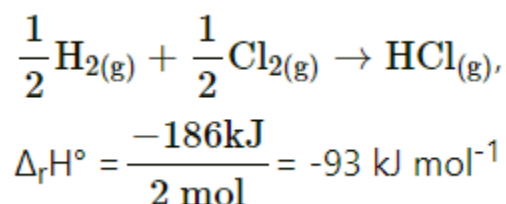
$$\Delta_r H^\circ = \sum \Delta H^\circ (\text{reactant bonds}) - \sum \Delta H^\circ (\text{products bonds})$$



$$\therefore \Delta_r H^\circ = [1 \text{ mol} \times 434 \text{ kJ mol}^{-1} + 1 \text{ mol} \times 242 \text{ kJ mol}^{-1}] - [2 \text{ mol} \times 431 \text{ kJ mol}^{-1}]$$
$$= -186 \text{ kJ}$$

$$\therefore \text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)}, \Delta_r H^\circ = -186 \text{ kJ}$$

For enthalpy of formation of HCl, the reaction is



### 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,  $P_{\text{ext}} = 0$ . The work done by a system during such expansion is  $W = -P_{\text{ext}} \Delta V = 0$   
Thus, no work is done when the gas expands freely in a vacuum.

**Note:** Units of energy and work:

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

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

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

If the pressure is expressed in bar and  $\Delta V$  in  $\text{dm}^3$ , then the work has the units of  $\text{bar dm}^3$ .

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

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

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

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

### 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.
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);  $\text{H}_2(\text{g})$ ,  $\text{Hg}(\text{l})$ ,  $\text{Na}(\text{s})$ ,  $\text{C}(\text{graphite})$ ,  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ ,  $\text{CaCO}_3(\text{s})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{CaCO}_3(\text{s})$ ,  $\text{CO}_2(\text{g})$ .

### Exercises | Q 2.5 | Page 87

**Answer the following in one or two sentences.**

State whether  $\Delta S$  is positive, negative or zero for the reaction  $2\text{H}_{(g)} \rightarrow \text{H}_{2(g)}$ . Explain.

**Solution:**

$\Delta S$  is negative. Two moles of gaseous H atoms are converted into 1 mole  $\text{H}_2$  gas. Thus, a disorder of the system decreases, and hence, entropy increases or  $\Delta S$  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,

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

**Exercises | Q 2.7 | Page 87**

**Answer the following in one or two sentences.**

If the enthalpy change of a reaction is  $\Delta H$  how will you calculate the entropy of surroundings?

**Solution:**

If  $\Delta H$  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:\

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

**Exercises | Q 2.8 | Page 87**

**Answer the following in one or two sentences.**

Comment on the spontaneity of reactions for which  $\Delta H$  is positive and  $\Delta S$  is negative.

**Solution:**

When  $\Delta H$  positive and  $\Delta S$  is negative, then  $\Delta G$  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  $\Delta G^\circ$  of a reaction and the equilibrium constant.

**Solution:**

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

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots(1)$$

where,  $\Delta G^\circ$  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,

$$\therefore 0 = \Delta G^\circ + RT \ln K_C \quad \text{or} \quad 0 = \Delta G^\circ + RT \ln K_P$$

$$\therefore \Delta G^\circ = -RT \ln K_C \quad \text{or} \quad \Delta G^\circ = -RT \ln K_P$$

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

### 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 ( $Q_{\text{rev}}$ ) to it in a reversible manner divided by the temperature ( $T$ ) in Kelvin at which the transfer takes place. Thus,

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

3. Units of entropy:  $\text{J K}^{-1}$

**Note:** Entropy or its change  $\Delta S$  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:

$$\Delta_r H^\circ = \sum \Delta H^\circ (\text{reactant bonds}) - \sum \Delta H^\circ (\text{product bonds})$$

e.g. Consider the reaction,  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)}$

The enthalpy is given by

$$\Delta_r H^\circ = [\Delta H^\circ (\text{H} - \text{H}) + \Delta H^\circ (\text{I} - \text{I})] - [2\Delta H^\circ (\text{H} - \text{I})]$$

**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,  
 $\text{C}_2\text{H}_{2(g)} + 5/2 \text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$ ,  $\Delta_r H^\circ = -1300 \text{ kJ}$   
In the above reaction, the standard enthalpy change of the oxidation reaction,  $-1300 \text{ kJ}$  is the standard enthalpy of combustion of  $\text{C}_2\text{H}_{2(g)}$ .

**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,  $\text{Cl}_{2(g)} \rightarrow \text{Cl}_{(g)} + \text{Cl}_{(g)}$ ;  $\Delta_{\text{atom}} H = 242 \text{ kJ mol}^{-1}$

**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

$$W = P_{\text{ext}} \Delta V \quad \dots(1)$$

2. Assuming  $P_{\text{ext}} = P$ ,

$$W = - P \Delta V$$

$$= - P (V_2 - V_1)$$

$$W = - P V_2 + P V_1 \quad \dots(2)$$

3. If the gases were ideal, at constant temperature and pressure.,

$$P V_1 = n_1 R T \text{ and } P V_2 = n_2 R T \quad \dots(3)$$

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

$$W = - n_2 R T + n_1 R T$$

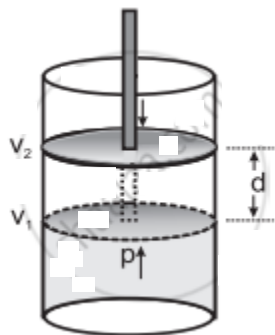
$$= - (n_2 - n_1) R T$$

$$= - \Delta n_g R T \quad \dots(4)$$

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  $- P_{\text{ext}}$ .

Thus,

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

where,  $P_{\text{ext}}$  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.

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

Substituting equation (1) in (2) gives

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

4. The product of area of the piston and distance it moves is the volume change ( $\Delta V$ ) in the system.

$$\Delta V = A \times d \quad \dots\dots(4)$$

Combining equation (3) and (4), we get

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

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

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.

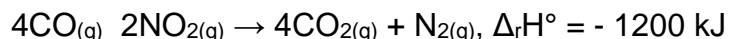
#### Solution:

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  $\text{NO}_2$ ? The reaction is:



#### Solution:

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

**To find:** Heat evolved when 12g of CO reacts with  $\text{NO}_2$

#### Calculation:

According to the given reaction, 1200 kJ of heat is evolved when 4 moles of CO react with  $\text{NO}_2$ . So heat evolved per mole is  $1200\text{kJ}/4 \text{ mol} = 300 \text{ kJ mol}^{-1}$

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

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

So, heat evolved when 0.4286 moles of CO reacts

$$= 0.4286 \text{ mol} \times 300 \text{ kJ mol}^{-1} = 128.58 \text{ kJ}$$

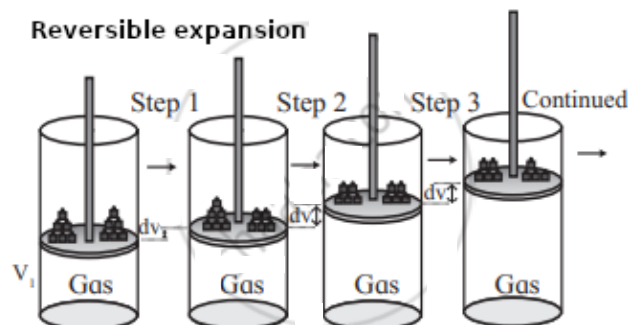
The heat evolved when 12 g of CO reacts with  $\text{NO}_2$  is 128.58 kJ.

### 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

$$dW = -P_{\text{ext}} dV \quad \dots(1)$$

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

$$\text{Thus } P - P_{\text{ext}} = dP \text{ or } P_{\text{ext}} = P - dP \quad \dots(2)$$

Combining equations (1) and (2),

$$dW = - (P - dP)dV = - PdV + dP \cdot dV$$

Neglecting the product  $dP \cdot dV$  which is very small, we get

$$dW = - PdV \quad \dots(3)$$

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,

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

Hence,

$$W_{\text{max}} = - \int_{V_2}^{V_1} PdV \quad \dots(4)$$

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

$$\begin{aligned} W_{\text{max}} &= - \int_{V_2}^{V_1} nRT \frac{dV}{V} \\ &= -nRT \int_{V_2}^{V_1} \frac{dV}{V} \quad \dots(\because T \text{ is constant.}) \\ &= -nRT \ln(V) \Big|_{V_1}^{V_2} \\ &= -nRT (\ln V_2 - \ln V_1) \\ &= -nRT \ln \frac{V_2}{V_1} \\ &= -2.303 nRT \log_{10} \frac{V_2}{V_1} \quad \dots(5) \end{aligned}$$

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 equation (5) by  $\frac{P_1}{P_2}$ , we get,

$$W_{\text{max}} = -2.303 nRT \log \frac{P_1}{P_2} \quad \dots(6)$$

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

### Exercises | Q 4.02 | Page 88

Obtain the relationship between  $\Delta H$  and  $\Delta U$  for gas phase reactions.

**Solution:**

1. At constant pressure,  $\Delta H$  and  $\Delta U$  are related as

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

2. For reactions involving gases,  $\Delta V$  cannot be neglected. Therefore,

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

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

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

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,

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT \quad \dots(3)$$

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

$$\Delta H = \Delta U + n_2RT - n_1RT$$

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

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

where,  $\Delta n_g$  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.

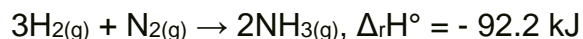
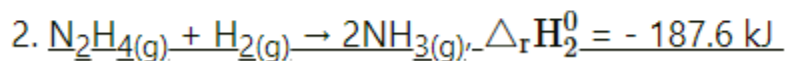
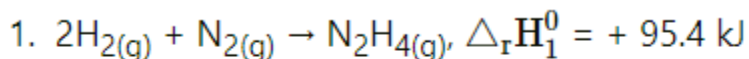
**Solution:****1. Hess's law of constant heat summation:**

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  $\text{NH}_3$ ,



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  $\Delta S$  for the formation of two moles of water from  $\text{H}_2$  and  $\text{O}_2$  is  $-327 \text{ J K}^{-1}$ , it is spontaneous. Explain.

(Given  $\Delta H$  for the reaction is  $-572 \text{ kJ}$ ).

**Solution:**

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

2. For the reaction,  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(l)}$ , when 2 moles of  $\text{H}_2$  and 1 mole of  $\text{O}_2$  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,

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

4. The total enthalpy change is,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

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

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

5. Since  $\Delta S_{\text{total}} > 0$ , 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  $\Delta G$  and  $\Delta S_{\text{total}}$ . Comment on the spontaneity of the reaction.

**Solution:**

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

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

OR

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surr}} \quad \dots(1)$$

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

$$\Delta S_{\text{total}} > 0.$$

3) If  $\Delta H$  is the enthalpy change accompanying a reaction (system), the enthalpy change of the surroundings is  $-\Delta H$ . Thus,

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T} \quad \dots(2)$$

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

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

Rearranging above expression, we get,

$$T \Delta S_{\text{total}} = T \Delta S - \Delta H$$

or

$$-T \Delta S_{\text{total}} = \Delta H - T \Delta S \quad \dots(3)$$

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

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

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

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



7) For a spontaneous reaction,  $S_{\text{total}} > 0$  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)  $\Delta S_{\text{total}} > 0$  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.

### Exercises | Q 4.06 | Page 88

**Answer the following question.**

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

**Solution:**

**Given:**

Initial volume ( $V_1$ ) = 500 cm<sup>3</sup>

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

Work ( $W$ ) = 36.0 J

**To find:** Final volume ( $V_2$ )

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

**Calculation:** Initial volume ( $V_1$ ) = 500 cm<sup>3</sup> = 0.5 dm<sup>3</sup>

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

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

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

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

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

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

The final volume ( $V_2$ ) = 200 cm<sup>3</sup>.

### Exercises | Q 4.07 | Page 88

**Answer the following question.**

Calculate the maximum work when 24 g of O<sub>2</sub> are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K.

**Solution:**

**Given:**

Mass of O<sub>2</sub> = 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:**

$$\text{Number of moles of O}_2 = n = \frac{24\text{g}}{32\text{g mol}^{-1}} = 0.75 \text{ mol}$$

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

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

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

$$= -2.303 \times 0.75 \times 8.314 \text{ J} \times 298 \times 0.2041$$

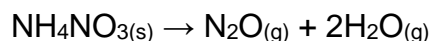
$$= -873.4 \text{ J}$$

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  $\text{NH}_4\text{NO}_3$  at  $100^\circ\text{C}$ .



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

**Solution:**

**Given:**

Decomposition of 1 mole of  $\text{NH}_4\text{NO}_3$

Temperature =  $T = 100^\circ\text{C} = 373\text{ K}$

**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  $\text{NH}_4\text{NO}_3 = (2 \times 14) + (3 \times 16) + (4 \times 1) = 80\text{ g mol}^{-1}$

$$\text{Moles of } \text{NH}_4\text{NO}_3 = n = \frac{132\text{g}}{80\text{g mol}^{-1}} = 1.65\text{ mol}$$

The given reaction is for 1 mole of  $\text{NH}_4\text{NO}_3$ . For 1.65 moles of  $\text{NH}_4\text{NO}_3$ , the reaction is given as follows:



Now,

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

$$\Delta n_g = (1.65 + 3.30) - 0 = +4.95\text{ mol } (\because \text{NH}_4\text{NO}_3 \text{ is in solid state})$$

Hence,

$$W = -\Delta n_g RT$$

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

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

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

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

The work done is  $-15.35\text{ kJ}$ . The work is done by the system.

**Exercises | Q 4.09 | Page 88**

**Answer the following question.**

Calculate standard enthalpy of reaction,

$\text{Fe}_2\text{O}_{3(s)} + 3\text{CO}_{(g)} \rightarrow 2\text{Fe}_{(s)} + 3\text{CO}_{2(g)}$ , from the following data.

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

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

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

**Solution:**

**Given:**

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

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

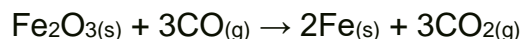
$\Delta_f H^\circ(\text{CO}_2) = -393 \text{ kJ/mol}$

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

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

**Calculation:**

The reaction is



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

$$= [2 \Delta_f H^\circ (\text{Fe}) + 3 \Delta_f H^\circ (\text{CO}_2)] - [\Delta_f H^\circ (\text{Fe}_2\text{O}_3) + 3 \Delta_f H^\circ (\text{CO})]$$

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

$$= -1179 + 824 + 330$$

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

The standard enthalpy of the given reaction is  $-25 \text{ kJ}$ .

### Exercises | Q 4.1 | Page 88

**Answer the following question.**

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

**Solution:**

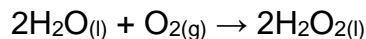
When  $\Delta H$  positive and  $\Delta S$  is negative, then  $\Delta G$  is positive regardless of temperature.

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.



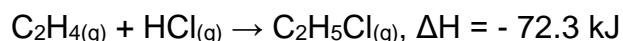
if  $\Delta H^\circ = 196 \text{ kJ}$ ,  $\Delta S^\circ = -126 \text{ J/K}$ , does it have a cross-over temperature?

**Solution:**

When  $\Delta H$  positive and  $\Delta S$  is negative, then  $\Delta G$  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  $\Delta U$  at 298 K for the reaction,



How much PV work is done?

**Solution:****Given:**

Enthalpy change =  $\Delta H = -72.3 \text{ kJ}$

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

**To find:**

PV work done and internal energy change ( $\Delta U$ )

**Formulae:**

1.  $W = -\Delta n_g RT$

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

**Calculations:**

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

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

Using formula (i)

$$W = -\Delta n_g RT$$

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

$$= 2477.57 \text{ J} = 2.48 \text{ kJ}$$

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 ( $\Delta U$ ) is  $-69.8 \text{ kJ}$ .

### Exercises | Q 4.13 | Page 88

**Answer the following question.**

Calculate the work done during the synthesis of  $\text{NH}_3$  in which volume changes from  $8.0 \text{ dm}^3$  to  $4.0 \text{ dm}^3$  at a constant external pressure of 43 bar. In what direction the work-energy flows?

**Solution:**

**Given:**

Initial volume ( $V_1$ ) =  $8.0 \text{ dm}^3$

Final volume ( $V_2$ ) =  $4.0 \text{ dm}^3$

External pressure ( $P_{\text{ext}}$ ) = 43 bar

**To find:**

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

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

**Calculations:**

From formula,

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

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

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

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

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

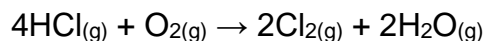
∴ The work done ( $W$ ) = 17.2 kJ

∴ Work energy flows into the system.

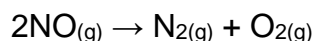
### Exercises | Q 4.14 | Page 88

Calculate the amount of work done in the

1) Oxidation of 1 mole  $\text{HCl}_{(\text{g})}$  at  $200^\circ \text{C}$  according to reaction.



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



**Solution:**

**Given:**

1) Oxidation of 1 mole  $\text{HCl}_{(g)}$

Temperature =  $T = 200\text{ }^{\circ}\text{C} = 473\text{ K}$

2) Decomposition of one mole of NO

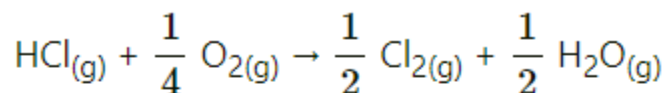
Temperature =  $T = 300\text{ }^{\circ}\text{C} = 573\text{ K}$

**To find:** Work done

**Formula:**  $W = -\Delta n_g RT$

**Calculation:**

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



Now,

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

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

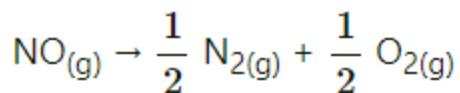
Hence,

$$W = -\Delta n_g RT$$

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

$$= +983 \text{ J}$$

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



Now,

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

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

Hence,

$$W = - \Delta n_g RT$$

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

$$= 0 \text{ kJ}$$

No work is done (since  $W = 0$ ).

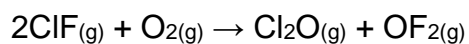
∴ The work done is +983 J. The work is done on the system.

∴ 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  $\text{O}_2$  reacts with ClF as per



The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction? ( $\Delta_r H^\circ = 205.6 \text{ kJ}$ )

**Solution:**

**Given:**

Enthalpy change for a given mass = 38.55 kJ

Mass of  $\text{O}_2 = 6.0 \text{ g}$

**To find:** Standard enthalpy of the given reaction

**Calculation:**



$$\text{Number of moles of O}_2 = \frac{\text{Mass of O}_2}{\text{Molar mass of O}_2} = \frac{6\text{g}}{32\text{g mol}^{-1}} = 0.1875 \text{ mol}$$

The enthalpy change when 0.1875 mol of O<sub>2</sub> react with ClF is 28.55 kJ.

$$\therefore \text{Enthalpy change for 1 mole O}_2 = \frac{38.55}{0.1875} = 205.6 \text{ kJ}$$

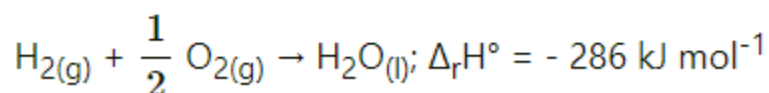
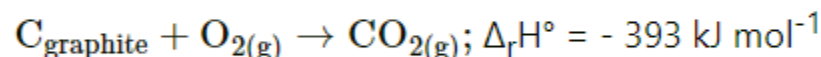
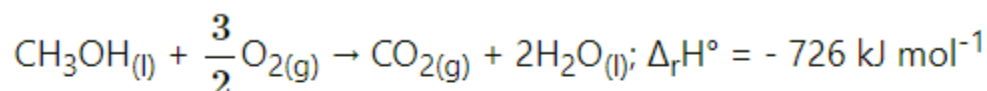
From the reaction, 2 moles of ClF react with 1 mole of O<sub>2</sub>.

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

### Exercises | Q 4.16 | Page 89

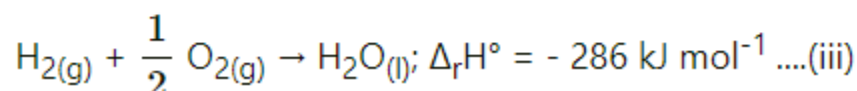
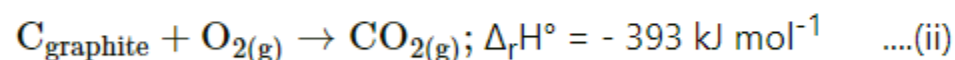
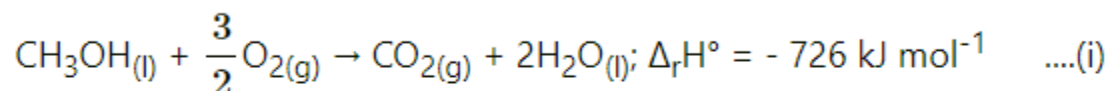
**Answer the following question.**

Calculate the standard enthalpy of formation of CH<sub>3</sub>OH<sub>(l)</sub> from the following data:



**Solution:**

**Given:** Given equations are,

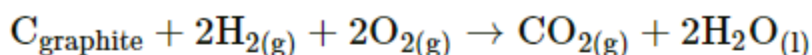
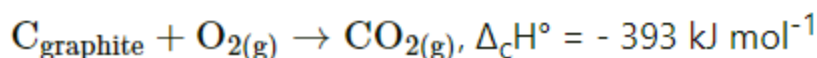
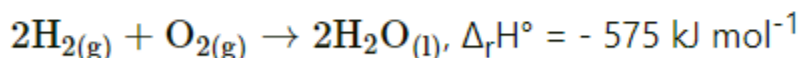


**To find:** The standard enthalpy of formation ( $\Delta_f H^\circ$ ) of  $\text{CH}_3\text{OH}_{(l)}$

**Calculation:**

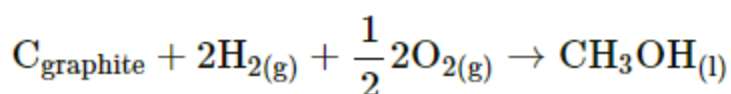
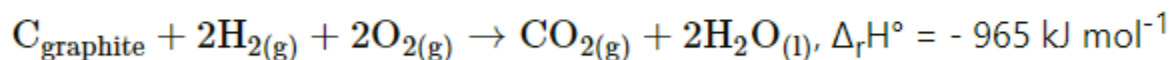
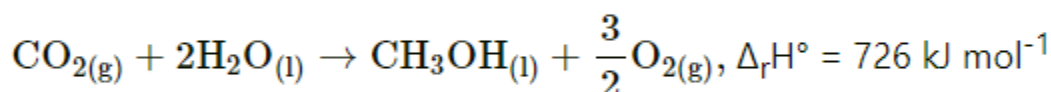
Required equation is,  $\text{C}_{\text{graphite}} + 2\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CH}_3\text{OH}_{(l)}$

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



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

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



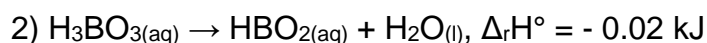
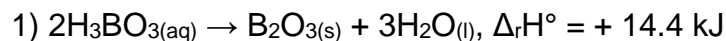
$$\Delta_f H^\circ = \Delta_r H^\circ = 726 - 965 = -239 \text{ kJ mol}^{-1}$$

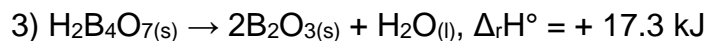
The standard enthalpy of formation ( $\Delta_f H^\circ$ ) of  $\text{CH}_3\text{OH}_{(l)}$  from the given data is  $-239 \text{ kJ mol}^{-1}$

### Exercises | Q 4.17 | Page 89

**Answer the following question.**

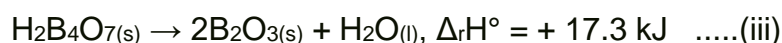
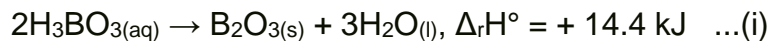
Calculate  $\Delta_r H^\circ$  for the following reaction at 298 K:





**Solution:**

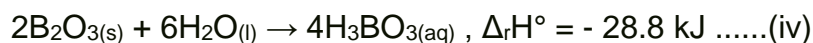
**Given:** Given equations are,



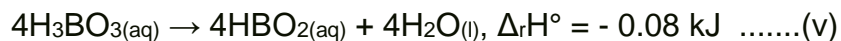
**To find:** The standard enthalpy of the given reaction ( $\Delta_r H^\circ$ )

**Calculation:**

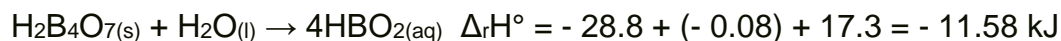
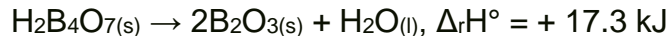
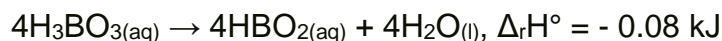
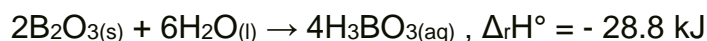
Reverse equation (i) and multiply by 2,



Multiply equation (ii) by 4



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



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:  $\Delta_{\text{fus}} H^\circ$  (ice) = 6.01 kJ mol<sup>-1</sup> at 0 °C,  $\Delta_{\text{vap}} H^\circ$  (H<sub>2</sub>O) = 40.7 kJ mol<sup>-1</sup> at 100 °C,

Specific heat of water is 4.18 J g<sup>-1</sup> K<sup>-1</sup>]

**Solution:**

**Given:**

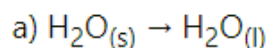
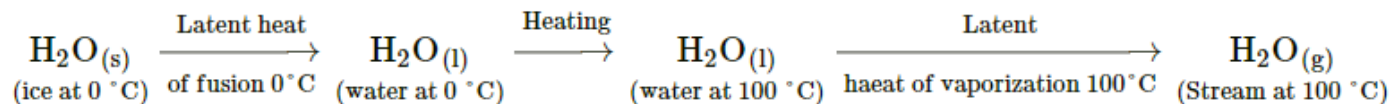
$\Delta_{\text{fus}} H^\circ$  (ice) = 6.01 kJ mol<sup>-1</sup> at 0 °C,

$\Delta_{\text{vap}} H^\circ$  (H<sub>2</sub>O) = 40.7 kJ mol<sup>-1</sup> at 100 °C,

Specific heat of water is 4.18 J g<sup>-1</sup> K<sup>-1</sup>

**To find:**

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

**Calculation:**

Heat required = Latent heat for 180 g.

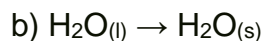
$$1 \text{ mol of H}_2\text{O} = 6.01 \text{ kJ}$$

$$1 \text{ mol of H}_2\text{O} = 18 \text{ g}$$

$$\therefore 180 \text{ g of H}_2\text{O} = \frac{180\text{g}}{18\text{g mol}^{-1}} = 10 \text{ moles of H}_2\text{O}$$

$$\therefore 10 \text{ mol of H}_2\text{O requires} = 60.1 \text{ kJ}$$

$$\therefore \text{Heat required} = 60.1 \text{ kJ} \dots(\text{i})$$

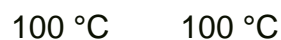
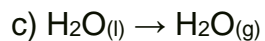


$$\text{Heat required} = \text{Mass} \times \text{Specific heat} \times \Delta T$$

$$= 180 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 100 \text{ K}$$

$$= 75240 \text{ J}$$

$$= 75.240 \text{ kJ} \dots(\text{ii})$$



$$\text{Heat required} = \text{Latent heat of vaporization}$$

$$1 \text{ mol of H}_2\text{O requires} = 40.7 \text{ kJ}$$

$$\therefore 1 \text{ mol of H}_2\text{O} = 18 \text{ g}$$

$$\therefore 180 \text{ g of H}_2\text{O} = 10 \text{ moles of H}_2\text{O}$$

∴ 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

$$= 60.1 \text{ kJ} + 75.240 \text{ kJ} + 407 \text{ kJ} = + 542.34 \text{ kJ}$$

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,

$\text{C}_2\text{H}_{4(g)} + \text{H}_{2(g)} \rightarrow \text{C}_2\text{H}_{6(g)}$  is - 620 J when 100 mL of ethylene and 100 mL of  $\text{H}_2$  react at 1 bar pressure. Calculate the pressure-volume type of work and  $\Delta U$  for the reaction.

**Solution:**

**Given:**

Enthalpy change ( $\Delta H$ ) = - 620 J

Volumes of reactants;  $\text{C}_2\text{H}_4$  = 100 mL,  $\text{H}_2$  = 100 mL

Pressure ( $P_{\text{ext}}$ ) = 1 bar

**To find:**

Pressure-volume work (W) and change in internal energy ( $\Delta U$ ) for the given reaction

**Formulae:**

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

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

**Calculation:**

According to the equation of reaction 1 mole of  $\text{C}_2\text{H}_4$  reacts with 1 mole of  $\text{H}_2$  to produce 1 mole of  $\text{C}_2\text{H}_6$ . Hence, 100 mL of  $\text{C}_2\text{H}_4$  would react with 100 mL of  $\text{H}_2$  to produce 100 mL of  $\text{C}_2\text{H}_6$ .

$$V_1 = 100 \text{ mL} + 100 \text{ mL} = 200 \text{ mL} = 0.2 \text{ dm}^3$$

$$V_2 = 100 \text{ mL} = 0.1 \text{ dm}^3$$

From formula (i),

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

$$= -1 \text{ bar} (0.1 \text{ dm}^3 - 0.2 \text{ dm}^3)$$

$$= 0.10 \text{ dm}^3 \text{ bar}$$

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

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

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

From formula (ii),

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

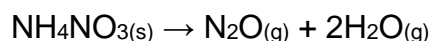
$$\therefore \Delta U = \Delta H - P_{\text{ext}} \Delta V$$

$$= - 620 - (- 10.00 \text{ J}) = - 610 \text{ J}$$

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

### 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  $\text{NH}_4\text{NO}_3$  at  $100^\circ\text{C}$



**Solution:**

**Given:**

Decomposition of 1 mole of  $\text{NH}_4\text{NO}_3$

Temperature =  $T = 100^\circ\text{C} = 373 \text{ K}$

**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  $\text{NH}_4\text{NO}_3$ . For 2 moles of  $\text{NH}_4\text{NO}_3$ , the reaction is given as follows:



Now,

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

$$\Delta n_g = 6 - 0 = + 6 \text{ mol} \quad (\because \text{NH}_4\text{NO}_3 \text{ is in solid state})$$

Hence,

$$W = - \Delta n_g RT$$

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

$$= - 18606.75 \text{ J}$$

$$= - 18.61 \text{ kJ}$$

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

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