

## NCERT Solutions for Class 11 Chemistry Chapter 6

### Thermodynamics Class 11

#### Chapter 6 Thermodynamics Exercise Solutions

Exercise : Solutions of Questions on Page Number : 182

Q1 :

Choose the correct answer. A thermodynamic state function is a quantity

- (i) used to determine heat changes
- (ii) whose value is independent of path
- (iii) used to determine pressure volume work
- (iv) whose value depends on temperature only.

Answer :

A thermodynamic state function is a quantity whose value is independent of a path.

Functions like  $p$ ,  $V$ ,  $T$  etc. depend only on the state of a system and not on the path.

Hence, alternative (ii) is correct.

Q2 :

For the process to occur under adiabatic conditions, the correct condition is:

- (i)  $\Delta T = 0$
- (ii)  $\Delta p = 0$
- (iii)  $q = 0$
- (iv)  $w = 0$

Answer :

A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions,  $q = 0$ .

Therefore, alternative (iii) is correct.

Q3 :

The enthalpies of all elements in their standard states are:

- (i) unity
- (ii) zero
- (iii)  $< 0$
- (iv) different for each element

**Answer :**

The enthalpy of all elements in their standard state is zero.

Therefore, alternative (ii) is correct.

**Q4 :**

$\Delta U^{\text{AZA}}$  of combustion of methane is  $-X \text{ kJ mol}^{-1}$ . The value of  $\Delta H^{\text{AZA}}$  is

- (i)  $= \Delta U^{\text{AZA}}$
- (ii)  $> \Delta U^{\text{AZA}}$
- (iii)  $< \Delta U^{\text{AZA}}$
- (iv)  $= 0$

**Answer :**

Since  $\Delta H^{\text{AZA}} = \Delta U^{\text{AZA}} + \Delta n_g RT$  and  $\Delta U^{\text{AZA}} = -X \text{ kJ mol}^{-1}$ ,  $\Delta H^{\text{AZA}} =$   
 $(-X) + \Delta n_g RT$ .

$$\Rightarrow \Delta H^{\text{AZA}} < \Delta U^{\text{AZA}}$$

Therefore, alternative (iii) is correct.

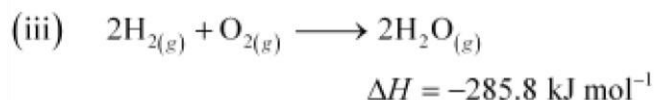
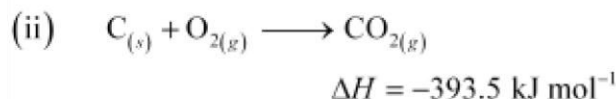
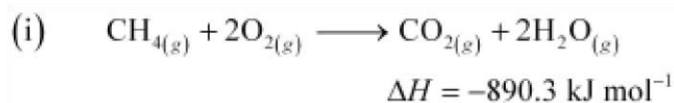
**Q5 :**

The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are,  $-890.3 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$ , and  $-285.8 \text{ kJ mol}^{-1}$  respectively. Enthalpy of formation of  $\text{CH}_4(\text{g})$  will be

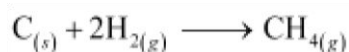
- (i)  $-74.8 \text{ kJ mol}^{-1}$       (ii)  $-52.27 \text{ kJ mol}^{-1}$
- (iii)  $+74.8 \text{ kJ mol}^{-1}$       (iv)  $+52.26 \text{ kJ mol}^{-1}$

**Answer :**

According to the question,



Thus, the desired equation is the one that represents the formation of  $\text{CH}_{4(g)}$  i.e.,



$$\begin{aligned} \Delta_f H_{\text{CH}_4} &= \Delta_c H_c + 2\Delta_c H_{\text{H}_2} - \Delta_c H_{\text{CO}_2} \\ &= [-393.5 + 2(-285.8) - (-890.3)] \text{ kJ mol}^{-1} \\ &= -74.8 \text{ kJ mol}^{-1} \end{aligned}$$

∴ Enthalpy of formation of  $\text{CH}_{4(g)} = -74.8 \text{ kJ mol}^{-1}$

Hence, alternative (i) is correct.

**Q6 :**

**A reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + q$  is found to have a positive entropy change. The reaction will be**

- (i) possible at high temperature
- (ii) possible only at low temperature
- (iii) not possible at any temperature
- (iv) possible at any temperature

**Answer :**

For a reaction to be spontaneous,  $\Delta G$  should be negative.

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

According to the question, for the given reaction,

$\Delta S =$  positive

$\Delta H =$  negative (since heat is evolved)

$\Rightarrow \Delta G =$  negative

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

Q7 :

In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

**Answer :**

According to the first law of thermodynamics,

$$\Delta U = q + W \text{ (i)}$$

Where,

$\Delta U$  = change in internal energy for a process  $q$  = heat

$W$  = work Given,

$q = +701 \text{ J}$  (Since heat is absorbed)

$W = -394 \text{ J}$  (Since work is done by the system)

Substituting the values in expression (i), we get

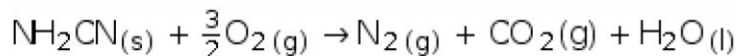
$$\Delta U = 701 \text{ J} + (-394 \text{ J})$$

$$\Delta U = 307 \text{ J}$$

Hence, the change in internal energy for the given process is 307 J.

Q8 :

The reaction of cyanamide,  $\text{NH}_2\text{CN}_{(s)}$ , with dioxygen was carried out in a bomb calorimeter, and  $\Delta U$  was found to be  $-742.7 \text{ kJ mol}^{-1}$  at 298 K. Calculate enthalpy change for the reaction at 298 K.



**Answer :**

Enthalpy change for a reaction ( $\Delta H$ ) is given by the expression,

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

Where,

$\Delta U$  = change in internal energy

$\Delta n_g$  = change in number of moles

For the given reaction,



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$$\Delta n_g = \sum n_g (\text{products}) - \sum n_g (\text{reactants})$$

$$= (2 - 1.5) \text{ moles}$$

$$\Delta n_g = 0.5 \text{ moles}$$

And,

$$\Delta U = -742.7 \text{ kJ mol}^{-1}$$

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

$$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Substituting the values in the expression of  $\Delta H$ :

$$\Delta H = (-742.7 \text{ kJ mol}^{-1}) + (0.5 \text{ mol}) (298 \text{ K}) (8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$= -742.7 + 1.2 \Delta H =$$

$$-741.5 \text{ kJ mol}^{-1}$$

**Q9 :**

Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol<sup>-1</sup> K<sup>-1</sup>.

**Answer :**

From the expression of heat ( $q$ ),

$$q = m \cdot c \cdot \Delta T \text{ Where,}$$

$c$  = molar heat capacity

$m$  = mass of substance

$\Delta T$  = change in temperature

Substituting the values in the expression of  $q$ :

$$q = \left( \frac{60}{27} \text{ mol} \right) (24 \text{ J mol}^{-1} \text{ K}^{-1}) (20 \text{ K})$$

$$q = 1066.7 \text{ J}$$

$$q = 1.07 \text{ kJ}$$

**Q10 :**

Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C.  $\Delta_{fus}H = 6.03 \text{ kJ mol}^{-1}$  at 0°C.

$$C_p[\text{H}_2\text{O}(l)] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p[\text{H}_2\text{O}(s)] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

**Answer :**

Total enthalpy change involved in the transformation is the sum of the following changes:

(a) Energy change involved in the transformation of 1 mol of water at 10°C to 1 mol of water at 0°C.

(b) Energy change involved in the transformation of 1 mol of water at 0° to 1 mol of ice at 0°C.

(c) Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at -10°C.

$$\text{Total } \Delta H = C_p [\text{H}_2\text{O}(l)] \Delta T + \Delta H_{\text{freezing}} + C_p [\text{H}_2\text{O}(s)] \Delta T$$

$$= (75.3 \text{ J mol}^{-1} \text{ K}^{-1}) (0 - 10) \text{ K} + (-6.03 \times 10^3 \text{ J mol}^{-1}) + (36.8 \text{ J mol}^{-1} \text{ K}^{-1}) (-10 - 0) \text{ K}$$

$$= -753 \text{ J mol}^{-1} - 6030 \text{ J mol}^{-1} - 368 \text{ J mol}^{-1}$$

$$= -7151 \text{ J mol}^{-1}$$

$$= -7.151 \text{ kJ mol}^{-1}$$

Hence, the enthalpy change involved in the transformation is  $-7.151 \text{ kJ mol}^{-1}$ .

**Q11 :**

**Enthalpy of combustion of carbon to  $\text{CO}_2$  is  $-393.5 \text{ kJ mol}^{-1}$ . Calculate the heat released upon formation of 35.2 g of  $\text{CO}_2$  from carbon and dioxygen gas.**

**Answer :**

Formation of  $\text{CO}_2$  from carbon and dioxygen gas can be represented as:



(1 mole = 44 g)

Heat released on formation of 44 g  $\text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$

∴ Heat released on formation of 35.2 g  $\text{CO}_2$

$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{ g}} \times 35.2 \text{ g}$$

$$= -314.8 \text{ kJ mol}^{-1}$$

**Q12 :**

**Enthalpies of formation of  $\text{CO}_{(g)}$ ,  $\text{CO}_{2(g)}$ ,  $\text{N}_2\text{O}_{(g)}$  and  $\text{N}_2\text{O}_{4(g)}$  are  $-110 \text{ kJ mol}^{-1}$ ,  $-393 \text{ kJ mol}^{-1}$ ,  $81 \text{ kJ mol}^{-1}$  and  $9.7 \text{ kJ mol}^{-1}$  respectively. Find the value of  $\Delta_r H$  for the reaction:**



**Answer :**

$\Delta_r H$  for a reaction is defined as the difference between  $\Delta_f H$  value of products and  $\Delta_f H$  value of reactants.

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

For the given reaction,



$$\Delta_r H = \left[ \left\{ \Delta_f H (\text{N}_2\text{O}) + 3\Delta_f H (\text{CO}_2) \right\} - \left\{ \Delta_f H (\text{N}_2\text{O}_4) + 3\Delta_f H (\text{CO}) \right\} \right]$$

Substituting the values of  $\Delta_f H$  for  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_4$  and  $\text{CO}$  from the question, we get:

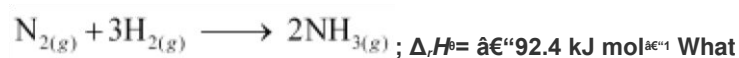
$$\Delta_r H = \left[ \left\{ 81 \text{ kJ mol}^{-1} + 3(-393) \text{ kJ mol}^{-1} \right\} - \left\{ 9.7 \text{ kJ mol}^{-1} + 3(-110) \text{ kJ mol}^{-1} \right\} \right]$$

$$\Delta_r H = -777.7 \text{ kJ mol}^{-1}$$

Hence, the value of  $\Delta_r H$  for the reaction is  $-777.7 \text{ kJ mol}^{-1}$ .

**Q13 :**

**Given**

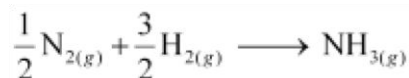


What is the standard enthalpy of formation of  $\text{NH}_3$  gas?

**Answer :**

Standard enthalpy of formation of a compound is the change in enthalpy that takes place during the formation of 1 mole of a substance in its standard form from its constituent elements in their standard state.

Re-writing the given equation for 1 mole of  $\text{NH}_{3(g)}$ .



∴ Standard enthalpy of formation of  $\text{NH}_{3(g)}$

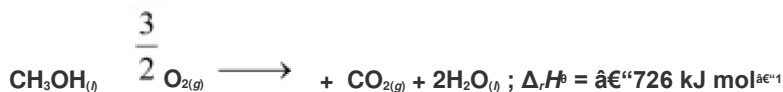
$$= \frac{1}{2} \Delta_r H^\ominus$$

$$= \frac{1}{2} (-92.4 \text{ kJ mol}^{-1})$$

$$= -46.2 \text{ kJ mol}^{-1}$$

**Q14 :**

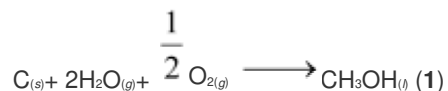
Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}(l)$  from the following data:



**Answer :**



The reaction that takes place during the formation of  $\text{CH}_3\text{OH}_{(l)}$  can be written as:



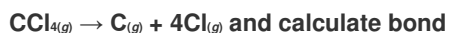
The reaction (1) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) + equation (i)

$$\begin{aligned} \Delta_f H^\ominus[\text{CH}_3\text{OH}_{(l)}] &= \Delta_c H^\ominus + 2\Delta_f H^\ominus[\text{H}_2\text{O}_{(l)}] + \Delta_f H^\ominus \\ &= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) + (-726 \text{ kJ mol}^{-1}) \\ &= (-393 - 572 - 726) \text{ kJ mol}^{-1} \\ \therefore \Delta_f H^\ominus[\text{CH}_3\text{OH}_{(l)}] &= -239 \text{ kJ mol}^{-1} \end{aligned}$$

**Q15 :**

**Calculate the enthalpy change for the process**



**enthalpy of C-Cl in  $\text{CCl}_{4(g)}$ .**

$$\Delta_{\text{vap}} H^\ominus(\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}.$$

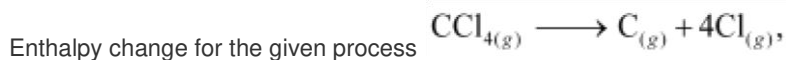
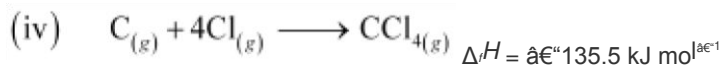
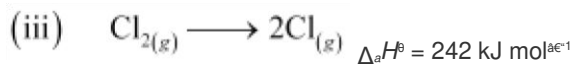
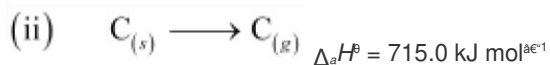
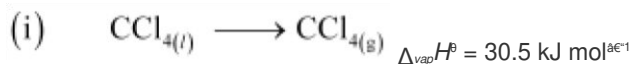
$$\Delta_f H^\ominus(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}.$$

$$\Delta_a H^\ominus(\text{C}) = 715.0 \text{ kJ mol}^{-1}, \text{ where } \Delta_a H^\ominus \text{ is enthalpy of atomisation } \Delta_a H^\ominus.$$

$$(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$$

**Answer :**

The chemical equations implying to the given values of enthalpies are:



Enthalpy change for the given process algebraic calculations as:

can be calculated using the following

Equation (ii) + 2 × Equation (iii) + Equation (i) + Equation (iv)

$$\begin{aligned} \Delta H &= \Delta_a H^\ominus(\text{C}) + 2\Delta_a H^\ominus(\text{Cl}_2) + \Delta_{\text{vap}} H^\ominus + \Delta_f H^\ominus \\ &= (715.0 \text{ kJ mol}^{-1}) + 2(242 \text{ kJ mol}^{-1}) + (30.5 \text{ kJ mol}^{-1}) + (-135.5 \text{ kJ mol}^{-1}) \end{aligned}$$

$$\therefore \Delta H = 1304 \text{ kJ mol}^{-1}$$

Bond enthalpy of C-Cl bond in  $\text{CCl}_4(g)$

$$= \frac{1304}{4} \text{ kJ mol}^{-1}$$

$$= 326 \text{ kJ mol}^{-1}$$

**Q16 :**

**For an isolated system,  $\Delta U = 0$ , what will be  $\Delta S$ ?**

**Answer :**

$\Delta S$  will be positive i.e., greater than zero

Since  $\Delta U = 0$ ,  $\Delta S$  will be positive and the reaction will be spontaneous.

**Q17 :**

**For the reaction at 298 K,**



$$\Delta H = 400 \text{ kJ mol}^{-1} \text{ and } \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

**At what temperature will the reaction become spontaneous considering  $\Delta H$  and  $\Delta S$  to be constant over the temperature range?**

**Answer :**

From the expression,

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

Assuming the reaction at equilibrium,  $\Delta G$  for the reaction would be:

$$T = (\Delta H - \Delta G) \frac{1}{\Delta S}$$

$$= \frac{\Delta H}{\Delta S} \quad (\Delta G = 0 \text{ at equilibrium})$$

$$= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

$$T = 2000 \text{ K}$$

For the reaction to be spontaneous,  $\Delta G$  must be negative. Hence, for the given reaction to be spontaneous,  $T$  should be greater than 2000 K.

**Q18 :**

For the reaction,



Answer :

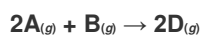
$\Delta H$  and  $\Delta S$  are negative

The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy is being released. Hence,  $\Delta H$  is negative.

Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased,  $\Delta S$  is negative for the given reaction.

Q19 :

For the reaction



$$\Delta U_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = -10.5 \text{ kJ and } \Delta S_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = -44.1 \text{ JK}^{-1}.$$

Calculate  $\Delta G_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$  for the reaction, and predict whether the reaction may occur spontaneously.

Answer :

For the given reaction,



$$\Delta n_g = 2 - (3)$$

$$= -1 \text{ mole}$$

Substituting the value of  $\Delta U_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$  in the expression of  $\Delta H$ :

$$\Delta H_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = \Delta U_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} + \Delta n_g R T$$

$$= (-10.5 \text{ kJ}) - (-1) (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$$

$$\Delta H_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = -12.98 \text{ kJ}$$

Substituting the values of  $\Delta H_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$  and  $\Delta S_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$  in the expression of  $\Delta G_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$ :

$$\Delta G_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = \Delta H_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} - T \Delta S_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$$

$$= -12.98 \text{ kJ} - (298 \text{ K}) (-44.1 \text{ J K}^{-1})$$

$$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$$

$$\Delta G_{\text{A}\ddot{\text{A}}\ddot{\text{A}}} = +0.16 \text{ kJ}$$

Since  $\Delta G_{\text{A}\ddot{\text{A}}\ddot{\text{A}}}$  for the reaction is positive, the reaction will not occur spontaneously.

Q20 :

The equilibrium constant for a reaction is 10. What will be the value of  $\Delta G^{\circ}$ ?  $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $T = 300 \text{ K}$ .

Answer :

From the expression,

$$\Delta G^{\circ} = -2.303 R T \log K_{eq}$$

$\Delta G^{\circ}$  for the reaction,

$$= (2.303) (8.314 \text{ JK}^{-1}\text{mol}^{-1}) (300 \text{ K}) \log 10$$

$$= -5744.14 \text{ Jmol}^{-1}$$

$$= -5.744 \text{ kJ mol}^{-1}$$

Q21 :

Comment on the thermodynamic stability of  $\text{NO}_{(g)}$ , given



Answer :

The positive value of  $\Delta_r H$  indicates that heat is absorbed during the formation of  $\text{NO}_{(g)}$ . This means that  $\text{NO}_{(g)}$  has higher energy than the reactants ( $\text{N}_2$  and  $\text{O}_2$ ). Hence,  $\text{NO}_{(g)}$  is unstable.

The negative value of  $\Delta_r H$  indicates that heat is evolved during the formation of  $\text{NO}_{2(g)}$  from  $\text{NO}_{(g)}$  and  $\text{O}_{2(g)}$ . The product,  $\text{NO}_{2(g)}$  is stabilized with minimum energy.

Hence, unstable  $\text{NO}_{(g)}$  changes to stable  $\text{NO}_{2(g)}$ .

Q22 :

Calculate the entropy change in surroundings when 1.00 mol of  $\text{H}_2\text{O}_{(l)}$  is formed under standard conditions.  $\Delta_r H^{\circ} = -286 \text{ kJ mol}^{-1}$ .

Answer :

It is given that 286  $\text{kJ mol}^{-1}$  of heat is evolved on the formation of 1 mol of  $\text{H}_2\text{O}_{(l)}$ . Thus, an equal amount of heat will be absorbed by the surroundings.

$$q_{surr} = +286 \text{ kJ mol}^{-1}$$

Entropy change ( $\Delta S_{surr}$ ) for the surroundings =  $\frac{q_{surr}}{T}$

$$= \frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$

$$\therefore \Delta S_{surr} = 959.73 \text{ J mol}^{-1} \text{ K}^{-1}$$