

## Chapter 5: Thermodynamics

NCERT · Class 11 · Chemistry

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### Textbook exercises

#### Question 1

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.

#### Solution

Ans: A thermodynamic state function is a quantity whose value is independent of the 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.

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#### Question 2

For the Process to Occur Under Adiabatic Conditions, the Correct Condition Is:

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

#### Solution

Ans: A system is said to be under adiabatic conditions if there is zero exchange of heat between the system and its surroundings. Hence, under adiabatic conditions,  $q = 0$ . Therefore, alternative (iii) is correct.

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### Question 3

The Enthalpies of All Elements in Their Standard States Are:

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

### Solution

Ans: The enthalpy of all elements in their standard state is zero. Therefore, alternative (ii) is correct.

### Question 4

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

- (i)  $= \Delta U^\theta$
- (ii)  $> \Delta U^\theta$
- (iii)  $< \Delta U^\theta$
- (iv)  $= 0$

### Solution

Ans: Since

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

and

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

,

$$\begin{aligned}\Delta H^\theta &= (-X) + \Delta n_g RT \\ \Rightarrow \Delta H^\theta &< \Delta U^\theta\end{aligned}$$

Therefore, alternative (iii) is correct.

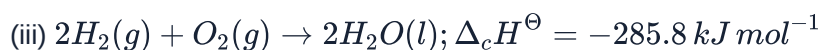
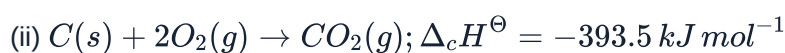
**Question 5**

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)  $+52.26 \text{ kJ mol}^{-1}$  .

**Solution**

Ans: According to the question,



Thus, the desired equation is the one that represents the formation of  $\text{CH}_4(\text{g})$  that is as follows:



Substituting the values in the above formula :

$$\text{Enthalpy of formation } \text{CH}_4(\text{g}) = (-393.5) + 2 \times (-285.8) - (-890.3) = -74.8 \text{ kJ mol}^{-1}$$

Therefore, alternative (i) is correct.

**Question 6**

A Reaction,  $\text{A} + \text{B} \rightarrow \text{C} + \text{D} + \text{q}$  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

**Solution**

Ans: 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)

That results in  $\Delta G$  = negative

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

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### Question 7

**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?**

### Solution

Ans: According to the first law of thermodynamics,

$$\Delta U = q + W \dots (i)$$

Where,

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

q = heat

W = work

Given,

q = + 701 J (Since heat is absorbed)

W = -394 J (Since work is done by the system)

Substituting the values in expression (i), we get

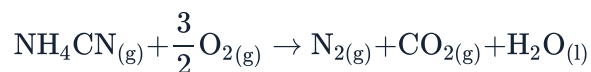
$$\Delta U = 701 J + (-394 J)$$

$$\Delta U = 307 J$$

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

**Question 8**

The reaction of cyanamide,  $\text{NH}_2\text{CN}(\text{s})$  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 the enthalpy change for the reaction at 298 K.

**Solution**

Ans: 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,

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

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

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

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

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

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

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

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

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

$$\Delta H = -741.5 \text{ kJ mol}^{-1}$$

**Question 9**

Calculate the number of kJ of heat necessary to raise the temperature of 60 g of aluminium from  $35^{\circ}\text{C}$  to  $55^{\circ}\text{C}$ .  
Molar heat capacity of Al is  $24\text{J mol}^{-1}\text{K}^{-1}$ .

**Solution**

Ans: From the expression of heat (q),

$$q = m \cdot c \cdot \Delta T$$

Where,

c = molar heat capacity

m = mass of substance

$\Delta T$  = change in temperature

Given,

m = 60 g

c =  $24\text{J mol}^{-1}\text{K}^{-1}$

$$\Delta T = (55 - 35)^{\circ}\text{C}$$

$$\Delta T = (328 - 308)\text{K} = 20\text{K}$$

Substituting the values in the expression of heat:

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

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

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

**Question 10**

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

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

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

### Solution

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

1. Energy change involved in the transformation of 1 mol of water at  $10.0^\circ\text{C}$  to 1mol of water at  $0^\circ\text{C}$ .
2. Energy change involved in the transformation of 1 mol of water at  $0^\circ\text{C}$  to 1 mol of ice at  $0^\circ\text{C}$ .
3. Energy change involved in the transformation of 1 mol of ice at  $0^\circ\text{C}$  to 1 mol of ice at  $10^\circ\text{C}$ .

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

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

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

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

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

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

### Question 11

Enthalpy of combustion of carbon to carbon dioxide 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.

### Solution

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



(1mole=44g)

Heat released in the formation of 44 g of  $CO_2 = 393.5 \text{ kJ mol}^{-1}$

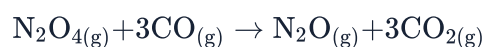
Heat released in the formation of 35.2 g of

$$CO_2 = (393.5 \text{ kJ}) \times \frac{(35.2 \text{ g})}{(44 \text{ g})} = 314.8 \text{ kJ}$$

So, heat released upon formation of 35.2 g of  $CO_2$  from carbon and dioxygen gas is 314.8 kJ.

### Question 12

Enthalpies of formation of  $CO(g)$ ,  $CO_2(g)$ ,  $N_2O(g)$  and  $N_2O_4(g)$  are -110, -393, 81 kJ and 9.7 kJ  $\text{mol}^{-1}$  respectively. Find the value of  $\Delta_r H$  for the reaction:

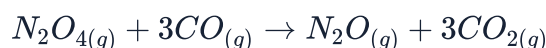


### Solution

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

$$\Delta_r H = \sum \Delta_f H (\text{product}) - \sum \Delta_f H (\text{reactant})$$

For the given reaction,



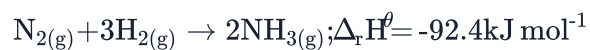
$$\Delta_r H = [\{\Delta_f H(NO_2) + 3\Delta_f H(CO_2)\} - \{\Delta_f H(N_2O) + 3\Delta_f H(CO)\}]$$

Substituting the values of  $\Delta_f H$  for  $CO(g)$ ,  $CO_2(g)$ ,  $N_2O(g)$  and  $N_2O_4(g)$  from the question, we get:

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

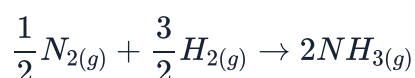
$$\Delta_r H = -777.7 \text{ kJ mol}^{-1}$$

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

**Question 13****Given****What is the standard enthalpy of formation of  $\text{NH}_3$  gas?****Solution**

Ans: 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  $\text{NH}_3(g)$  is as follows:



Therefore, standard enthalpy of formation of  $\text{NH}_3(g)$

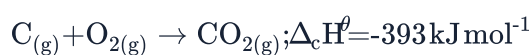
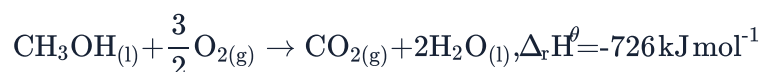
$$= \frac{1}{2} \Delta_r H^\theta$$

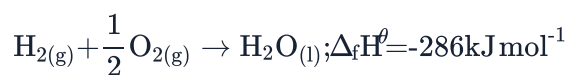
$$\frac{1}{2} \left( -92.4 \text{ kJ mol}^{-1} \right)$$

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

**Question 14**

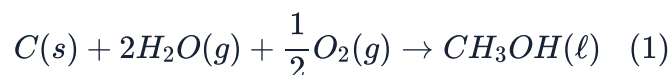
**Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}(\ell)$  from the following data:**





### Solution

Ans: The reaction that takes place during the formation of  $\text{CH}_3\text{OH}(\ell)$  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)

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

Therefore,  $\Delta_f H^\theta [\text{CH}_3\text{OH}(\ell)] = -239 \text{ kJ mol}^{-1}$

### Question 15

**Calculate the Enthalpy Change for the Process**



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

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

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

$$\Delta_a H^\theta(\text{C}) = 715.0 \text{ kJ mol}^{-1}$$

where,  $\Delta_a H^\theta$  is enthalpy of atomization

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

### Solution

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

1.  $CCl_{4(l)} \rightarrow CCl_{4(g)} \Delta_{vap} H^\theta = 30.5 kJ mol^{-1}$
2.  $C_{(s)} \rightarrow C_{(g)} \Delta_a H^\theta = 715.0 kJ mol^{-1}$
3.  $Cl_{2(g)} \rightarrow 2Cl_{(g)} \Delta_a H^\theta = 242 kJ mol^{-1}$
4.  $C_{(g)} + 4Cl_{(g)} \rightarrow CCl_{4(g)} \Delta_f H = -135.5 kJ mol^{-1}$

Enthalpy change for the given process  $CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$  can be calculated using the following algebraic calculations as:

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

$$\Delta H = \Delta_a H^\theta(C) + 2\Delta_a H^\theta(Cl_2) - \Delta_{vap} H^\theta - \Delta_f H$$

$$(715.0 kJ mol^{-1}) + 2(242 kJ mol^{-1}) - (30.5 kJ mol^{-1}) - (-135.5 kJ mol^{-1})$$

Therefore,  $\Delta H = 1304 kJ mol^{-1}$

Bond enthalpy of C-Cl bond in  $CCl_4(g)$

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

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

### Question 16

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

#### Solution

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

Since for an isolated system,  $\Delta U = 0$ , hence  $\Delta S$  will be positive and the reaction will be spontaneous.

### Question 17

For the reaction at 298 K,  $2A + B \rightarrow C$

$\Delta H = 400 \text{ kJ mol}^{-1}$  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?

### Solution

Ans: From the expression,

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

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

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

$$= \frac{\Delta H}{\Delta S}$$

( $\Delta G = 0$  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.

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### Question 18

For the reaction,  $2\text{Cl(g)} \rightarrow \text{Cl}_2\text{(g)}$  What are the signs of  $\Delta H$  and  $\Delta S$  ?

### Solution

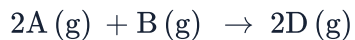
Ans:  $\Delta H$  and  $\Delta S$  are negative.

The given reaction represents the formation of chlorine molecules from chlorine atoms. Here, bond formation is occurring. 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.

**Question 19**

For the reaction

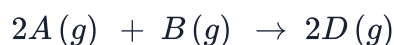


$$\Delta U^\theta = -10.5 \text{ kJ and } \Delta S^\theta = -44.1 \text{ J K}^{-1}.$$

Calculate  $\Delta G^\theta$  for the reaction, and predict whether the reaction may occur spontaneously.

**Solution**

Ans: For the given reaction,



$$\Delta n_g = 2 - (3) = -1 \text{ mole}$$

Substituting the value of  $\Delta U^\theta$  in the expression of  $\Delta H^\theta$ :

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

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

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

$$\Delta H^\theta = -12.98 \text{ kJ}$$

Substituting the values of  $\Delta H^\theta$  and  $\Delta S^\theta$  in the expression of  $\Delta G^\theta$ :

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

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

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

$$\Delta G^\theta = + 0.16 \text{ kJ}$$

Since  $\Delta G^\theta$  for the reaction is positive, the reaction will not occur spontaneously.

### Question 20

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

### Solution

Ans: From the expression,

$$\Delta G^\theta = - 2.303 RT \log K_{eq}$$

$\Delta G^\theta$  for the reaction,

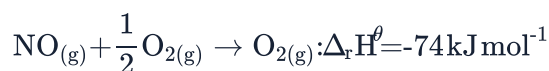
$$= (2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \log 10$$

$$= -5744.14 \text{ J mol}^{-1}$$

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

### Question 21

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



### Solution

Ans: 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  $NO_2(g)$  from  $NO(g)$  and  $O_2(g)$ . The product,  $NO_2(g)$  is stabilized with minimum energy.

Hence, unstable  $NO(g)$  changes to unstable  $NO_2(g)$ .

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### Question 22

Calculate the entropy change in surroundings when 1.00 mol of  $H_2O(l)$  is formed under standard conditions.  $\Delta_f H^\theta = -286 \text{ kJ mol}^{-1}$ .

### Solution

Ans: It is given that  $286 \text{ kJ mol}^{-1}$  of heat is evolved on the formation of 1 mol of  $H_2O(l)$ . 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,  $(\Delta S_{surr}) = 959.73 \text{ J mol}^{-1} \text{ K}^{-1}$ .