

# Thermodynamics

## 5 Chapter

### Exercise

1. Choose the correct answer. A thermodynamic state function is a quantity
- used to determine heat changes
  - whose value is independent of path
  - used to determine pressure volume work
  - whose value depends on temperature only.

**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 (b) is correct.

2. For the process to occur under adiabatic conditions, the correct condition is:
- $\Delta T=0$
  - $\Delta p=0$
  - $q=0$
  - $w=0$

**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 (c) is correct.

3. The enthalpies of all elements in their standard states are:
- unity
  - zero
  - $< 0$
  - different for each element

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

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)  $= 0$

**Ans:** Since  $\Delta H^\theta = \Delta U^\theta + \Delta n_g RT$  and  $\Delta U^\theta = -X \text{ kJ mol}^{-1}$ ,

$$\Delta H^\theta = (-X) + \Delta n_g RT$$

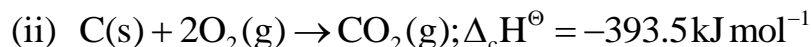
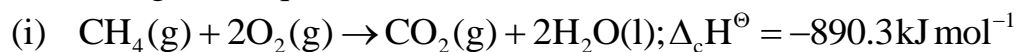
$$\Rightarrow \Delta H^\theta < \Delta U^\theta$$

Therefore, alternative (iii) is correct.

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

**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.

6. 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

**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,  
 $\Delta S = \text{positive}$   
 $\Delta H = \text{negative}$  (since heat is evolved)  
 That results in  $\Delta G = \text{negative}$   
 Therefore, the reaction is spontaneous at any temperature.  
 Hence, alternative (iv) is correct.

**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?**

**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,

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

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

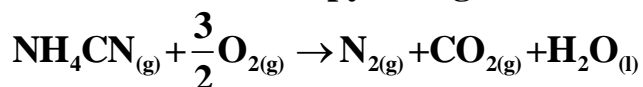
Substituting the values in expression (i), we get

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

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

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

**8. 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 the enthalpy change for the reaction at 298 K.**



**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  $\Delta H$

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

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

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

- 9. Calculate the number of kJ of heat necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24J mol<sup>-1</sup>K<sup>-1</sup>.**

**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,

$$m = 60 \text{ g}$$

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

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

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

Substituting the values in the expression of heat:

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

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

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

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

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

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

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

- Energy change involved in the transformation of 1 mol of water at 10.0°C to 1 mol of water at 0°C.
- Energy change involved in the transformation of 1 mol of water at 0°C to 1 mol of ice at 0°C.
- Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at 10°C.

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

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

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

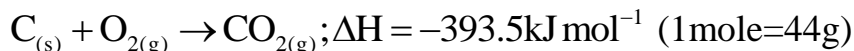
$$\Delta H = -7151 \text{ J mol}^{-1}$$

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

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

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.

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



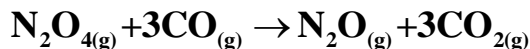
Heat released in the formation of 44 g of  $\text{CO}_2 = 393.5 \text{ kJ mol}^{-1}$

Heat released in the formation of 35.2 g of

$$\text{CO}_2 = (393.5 \text{ kJ}) \times \frac{(35.2 \text{ g})}{(44 \text{ g})} = 314.8 \text{ kJ}$$

So, heat released upon formation of 35.2 g of  $\text{CO}_2$  from carbon and dioxygen gas is 314.8 kJ.

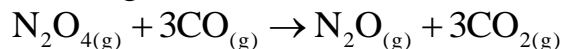
- 12. Enthalpies of formation of CO (g), CO<sub>2</sub>(g), N<sub>2</sub>O(g) and N<sub>2</sub>O<sub>4</sub>(g) are -110 , -393, 81 kJ and 9.7 kJ mol<sup>-1</sup> respectively. Find the value of Δ<sub>r</sub>H for the reaction:**



**Ans:** Δ H for a reaction is defined as the difference between Δ H value of products and Δ<sub>r</sub>H value of reactants.

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

For the given reaction,



$$\Delta_r H = \left[ \{ \Delta_f H(\text{NO}_2) + 3\Delta_f H(\text{CO}_2) \} - \{ \Delta_f H(\text{N}_2\text{O}) + 3\Delta_f H(\text{CO}) \} \right]$$

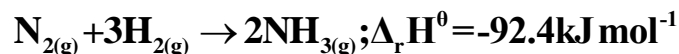
Substituting the values of Δ<sub>r</sub>H for CO (g), CO<sub>2</sub>(g), N<sub>2</sub>O(g) and N<sub>2</sub>O<sub>4</sub>(g) from the question, we get:

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

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

Hence, the value of Δ<sub>r</sub>H for the reaction is -777.7 kJ mol<sup>-1</sup>

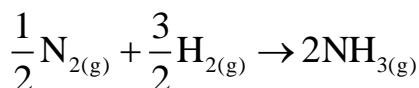
- 13. Given**



**What is the standard enthalpy of formation of NH<sub>3</sub> gas?**

**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 NH<sub>3</sub>(g) is as follows:



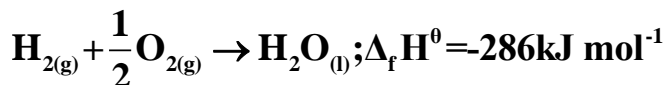
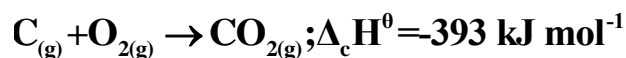
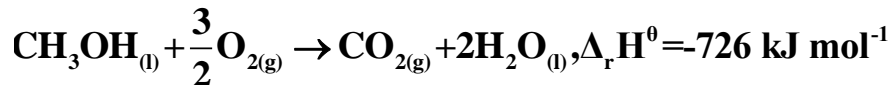
Therefore, standard enthalpy of formation of NH<sub>3</sub>(g)

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

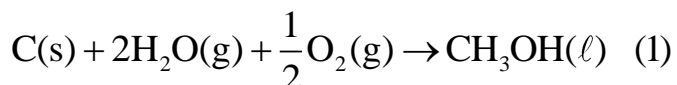
$$= \frac{1}{2} (-92.4 \text{ kJ mol}^{-1})$$

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

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



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



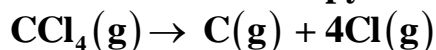
The reaction (1) can be obtained from the given reactions by following the algebraic calculations as:

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

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

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

- 15. Calculate the enthalpy change for the process**



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

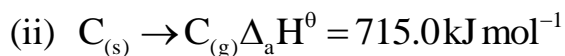
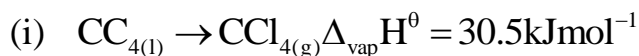
$$\Delta_{\text{vap}} H^\theta (\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}$$

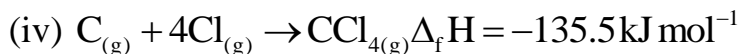
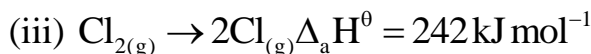
$$\Delta_f H^\theta (\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$$

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

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

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





Enthalpy change for the given process  $\text{CCl}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{Cl}_{(g)}$  can be calculated using the following algebraic calculations as:

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

$$\Delta H = \Delta_a H^\theta(\text{C}) + 2\Delta_a H^\theta(\text{Cl}_2) - \Delta_{\text{vap}} H^\theta - \Delta_f H$$

$$= (715.0 \text{ kJ mol}^{-1}) + 2(242 \text{ kJ mol}^{-1}) - (30.5 \text{ kJ mol}^{-1}) - (-135.5 \text{ kJ mol}^{-1}) \text{ Therefore,}$$

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

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

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

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

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

**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.

**17. For the reaction at 298 K,**



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

**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)

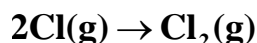


$$= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

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

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.

**18. For the reaction,**



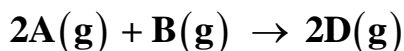
**What are the signs of  $\Delta H$  and  $\Delta S$  ?**

**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.

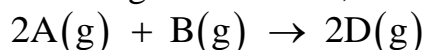
**19. For the reaction**



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

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

**Ans:** For the given reaction,



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

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

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

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

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

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

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.

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

**Ans:** From the expression,

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

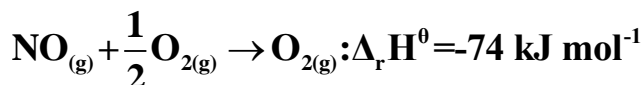
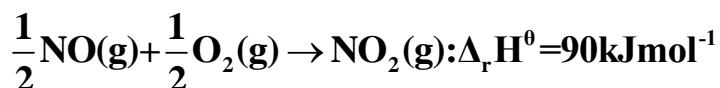
$\Delta G^\theta$  for the reaction,

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

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

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

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



**Ans:** The positive value of  $\Delta_r H$  indicates that heat is absorbed during the formation of  $\text{NO}(\text{g})$ . This means that  $\text{NO}(\text{g})$  has higher energy than the reactants ( $\text{N}_2$  and  $\text{O}_2$ ). Hence,  $\text{NO}(\text{g})$  is unstable. The negative value of  $\Delta_r H$  indicates that heat is evolved during the formation of  $\text{NO}_2(\text{g})$  from  $\text{NO}(\text{g})$  and  $\text{O}_2(\text{g})$ . The product,  $\text{NO}_2(\text{g})$  is stabilized with minimum energy. Hence, unstable  $\text{NO}(\text{g})$  changes to unstable  $\text{NO}_2(\text{g})$ .

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

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

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

Entropy change ( $\Delta S_{\text{surr}}$ ) for the surroundings  $= \frac{q_{\text{surr}}}{7}$

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

Therefore, ( $\Delta S_{\text{surr}}$ ) =  $959.73 \text{ J mol}^{-1} \text{ K}^{-1}$ .