Thermodynamics

5
Chapter

Exercise

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

a. used to determine heat changes
b. whose value is independent of path
c. used to determine pressure volume work
d. 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:

a. $\Delta T=0$
b. $\Delta p=0$
c. $q=0$
d. $w=0$

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:

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

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

4. **ΔU^{θ} of combustion of methane is $-X$ kJ mol^{-1}. The value of ΔH^{θ} 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 $\Delta U^{\theta} = -X$ 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 kJ mol^{-1}, -393.5 kJ mol^{-1}, and -285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be**

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

Ans: According to the question,

(i) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta_c H^{\ominus} = -890.3 \text{kJ mol}^{-1}$

(ii) $C(s) + 2O_2(g) \rightarrow CO_2(g); \Delta_c H^{\ominus} = -393.5 \text{kJ mol}^{-1}$

(iii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \Delta_c H^{\ominus} = -285.8 \text{kJ mol}^{-1}$

Thus, the desired equation is the one that represents the formation of $CH_4(g)$ that is as follows:

$C(s) + 2H_2(g) \rightarrow CH_4(g); \Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_c H_{H_2} - \Delta_c H_{CO_2}$

Substituting the values in the above formula :

Enthalpy of formation $CH_4(g) = (-393.5) + 2 \times (-285.8) - (-890.3) = -74.8 \text{kJmol}^{-1}$

Therefore, alternative (i) is correct.

6. **A reaction, $A + B \rightarrow C + D + q$ 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, ΔG 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,

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

Where,

ΔU = 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.

8. The reaction of cyanamide, $NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742.7 $KJ\ mol^{-1}$ at 298 K. Calculate the enthalpy change for the reaction at 298 K.

$$NH_4CN_{(g)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

Ans: Enthalpy change for a reaction ΔH (is given by the expression,

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

Where,

ΔU = change in internal energy

Δn_g = change in number of moles

For the given reaction,

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

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

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

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

T = 298 K

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

Substituting the values in the expression of ΔH

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

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

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

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^{-1}K^{-1}.

Ans: From the expression of heat (q),

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

Where,

c = molar heat capacity

m = mass of substance

ΔT = change in temperature

Given,

m = 60 g

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

$$\Delta T = \left(55-35\right)°\text{C}$$

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

Substituting the values in the expression of heat:

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

q = 1066.7 J

q = 1.07 kJ

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

$C_p\left[H_2O(l)\right]$ = 75.3 J mol^{-1} K^{-1} ;

$C_p\left[H_2O(s)\right]$ = 36.8 J mol^{-1} K^{-1} .

Ans: 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 $10.0°C$ to 1mol of water at $0°C$.

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

Total $\Delta H = C_p\left[H_2O(l)\right]\Delta T + \Delta H_{freezing} + C_p\left[H_2O(s)\right]\Delta T$

$\Delta H = \left(75.3\ Jmol^{-1}K^{-1}\right)\left(0-10\right)K + \left(-6.03\times10^{3}Jmol^{-1}\right) + \left(36.8\ Jmol^{-1}K^{-1}\right)\left(-10-0\right)K$

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

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

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

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

11. Enthalpy of combustion of carbon to carbon dioxide is -393.5 kJ mol^{-1} Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans: Formation of CO_2 from carbon and dioxygen gas can be represented as

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}; \Delta H = -393.5 kJ\,mol^{-1}$ (1mole=44g)

Heat released in the formation of 44 g of CO_2 = 393.5 $kJmol^{-1}$

Heat released in the formation of 35.2 g of

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

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

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 mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$N_2O_{4(g)} + 3CO_{(g)} \rightarrow N_2O_{(g)} + 3CO_{2(g)}$

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,

$$N_2O_{4(g)} + 3CO_{(g)} \rightarrow N_2O_{(g)} + 3CO_{2(g)}$$

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

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:

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

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

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

13. Given

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}; \Delta_r H^{\theta} = -92.4 kJ\,mol^{-1}$

What is the standard enthalpy of formation of NH_3 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 $NH_3(g)$ is as follows:

$$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow 2NH_{3(g)}$$

Therefore, standard enthalpy of formation of $NH_3(g)$

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

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

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

14. Calculate the standard enthalpy of formation of $CH_3OH(\ell)$ from the following data:

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

$$\mathbf{C_{(g)}+O_{2(g)} \rightarrow CO_{2(g)}; \Delta_c H^{\theta}=-393\ kJ\ mol^{-1}}$$

$$\mathbf{H_{2(g)}+\frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; \Delta_f H^{\theta}=-286 kJ\ mol^{-1}}$$

Ans: The reaction that takes place during the formation of $CH_3OH(\ )$ canℓbe written as:

$$C(s)+2H_2O(g)+\frac{1}{2}O_2(g) \rightarrow CH_3OH(\ell) \quad (1)$$

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

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

$$\Delta_f H^{\theta}\left[CH_3OH(\ell)\right]=\Delta_c H^{\theta}+2\Delta_f H^{\theta}[H_2O(l)]-\Delta_r H^{\theta}$$

$$= (-393\,kJ\,mol^{-1}) + 2(-286\ kJ\,mol^{-1}) - (-726\ kJ\,mol^{-1})$$

$$= (-393 - 572 + 726)\ kJ\,mol^{-1}$$

Therefore, $\Delta_f H^{\theta}\left[CH_3OH(\ell)\right]=-239\,kJmol^{-1}$

15. Calculate the enthalpy change for the process

$$\mathbf{CCl_4(g) \rightarrow C(g) + 4Cl(g)}$$

and calculate bond enthalpy of C-Cl in $CCl_4(g)$.

$\mathbf{\Delta_{vap}\ H^{\theta}(CCl_4)=30.5\ kJmol^{-1}}$

$\mathbf{\Delta_f H^{\theta}(CCl_4)=-135.5\ kJmol^{-1}}$

$\mathbf{\Delta_a H^{\theta}(C)=715.0\ kJmol^{-1}}$ **where, $\Delta_a H^{\theta}$ is enthalpy of atomization**

$\mathbf{\Delta_a H^{\theta}(Cl_2)=242\ kJmol^{-1}}$

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

(i) $CC_{4(l)} \rightarrow CCl_{4(g)} \Delta_{vap} H^{\theta}=30.5 kJmol^{-1}$

(ii) $C_{(s)} \rightarrow C_{(g)} \Delta_a H^{\theta}=715.0\,kJ\,mol^{-1}$

(iii) $Cl_{2(g)} \rightarrow 2Cl_{(g)} \Delta_a H^\theta = 242\,kJ\,mol^{-1}$

(iv) $C_{(g)} + 4Cl_{(g)} \rightarrow CCl_{4(g)} \Delta_f H = -135.5\,kJ\,mol^{-1}$

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)

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

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

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

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

$= \frac{1304}{4} kJmol^{-1}$

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

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

Ans: ΔS will be positive i.e., greater than zero.

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

17. For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400\ kJ\ mol^{-1}$ and $\Delta S = 0.2\ kJ\ K^{-1}\ mol^{-1}$ At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Ans: From the expression,

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

Assuming the reaction at equilibrium, ΔT for the reaction would be:

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

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

(ΔG = 0 at equilibrium)

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

T = 2000 K

For the reaction to be spontaneous, ΔG must be negative. Hence, for the given reaction to be spontaneous, T should be greater than 2000 K.

18. For the reaction,

$2Cl(g) \rightarrow Cl_2(g)$

What are the signs of ΔH and ΔS ?

Ans: ΔH and ΔS 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, ΔH is negative.

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

19. For the reaction

$2A(g) + B(g) \rightarrow 2D(g)$

ΔU^θ = -10.5 kJ and ΔS^θ = -44.1 JK^{-1} .

Calculate ΔG^θ for the reaction, and predict whether their action may occur spontaneously.

Ans: For the given reaction,

$2A(g) + B(g) \rightarrow 2D(g)$

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

Substituting the value of ΔU^θ in the expression of ΔH:

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

$= (-10.5\,\text{kJ}) - (-1)\left(8.314\times10^{-3}\,\text{kJ K}^{-1}\text{mol}^{-1}\right)(298\,\text{K})$

=-10.5 kJ - 2.48kJ

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

Substituting the values of ΔH^θ and ΔS^θ in the expression of ΔG^θ:

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

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

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

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

Since ΔG^{θ} 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 ΔG^{0}? $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 300\ K$.**

Ans: From the expression,

$\Delta G^{\theta} = -2.303\ \text{RTlogKeq}$

ΔG^{θ} for the reaction,

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

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

$= -5.744\ \text{kJmol}^{-1}$

21. **Comment on the thermodynamic stability of NO(g), given**

$$\frac{1}{2}NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) : \Delta_r H^{0} = 90 kJmol^{-1}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow O_{2(g)} : \Delta_r H^{0} = -74\ kJ\ mol^{-1}$$

Ans: The positive value of $\Delta_r H$ indicates that heat is absorbed during the formation of NO(g). This means that NO(g) has higher energy than the reactants (N_2 and O_2). Hence, 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 $NO_2(g)$.

22. **Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta H^{0}_{f} = -286\ kJ\ mol^{-1}$.**

Ans: It is given that 286 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.

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

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

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

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