Chapter: THERMODYNAMICS

Examples

Question 6.1: Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?

Answer: $\Delta U = \mathrm{w}_{\mathrm{ad}}$, the surface of the wall is adiabatic.

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

Answer: $\Delta U = -q$, walls that transmit heat.

(iii) w Amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Answer: $\Delta U = q - \mathrm{w}$, system that is closed.

Question 6.2: Two litres of an ideal gas at a pressure of $10\,\mathrm{atm}$ expands isothermally at $25^{\circ}\mathrm{C}$ into a vacuum until its total volume is 10 liters. How much heat is absorbed and how much work is done in the expansion?

Answer: We have $q = -\mathrm{w} = p_{ex}(10-2) = 0(8) = 0$

There is no effort done, and no heat is absorbed.

Question 6.3: Consider the same expansion, but this time against a constant external pressure of 1 atm.

Answer: $q = -\mathrm{w} = p_{\mathrm{ex}}(8) = 8 litre - atm$

Question 6.4: Consider the expansion given in Question 6.2, for $1\,\mathrm{mol}$ of an ideal gas conducted reversibly.

Answer: We have,

$$q = -w = 2.303 nRT \log \frac{V_f}{V_x}$$

$$= 2.303 \times 1 \times 0.8206 \times 298 \times \log \frac{10}{2}$$

$$= 2.303 \times 0.8206 \times 298 \times \log 5$$
$$= 2.303 \times 0.8206 \times 298 \times 0.6990$$
$$= 393.66 \, \text{L atm}$$

Question 6.5: If water vapour is assumed to be a perfect gas, molar enthalpy change for vaporization of 1mol of water at 1bar and 100°C is $41\,\text{kJ mol}^{-1}$. Calculate the internal energy change, when 1mol of water is vapourised at 1bar pressure and 100°C.

Answer: The change $H_2O(l) \rightarrow H_2O(g)$

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

or $\Delta U = \Delta H - \Delta n_g RT$,

We obtain by swapping the values,

$$\Delta U = 41.00\,\text{kJ mol}^{-1} - 1 \times 8.3\,\text{J mol}^{-1}\,\text{K}^{-1} \times 373\,\text{K}$$
$$= 41.00\,\text{kJ mol}^{-1} - 3.096\,\text{kJ mol}^{-1}$$
$$= 37.904\,\text{kJ mol}^{-1}$$

Question 6.6: 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at $298\,\text{K}$ and 1 atmospheric pressure according to the equation,

$$\text{C}(graphite) + O_2(g) \rightarrow CO_2(g)$$

During the reaction, temperature rises from $298\,\text{K}$ to $299\,\text{K}$. If the heat capacityof the bomb calorimeter is $20.7\,\text{kJ/K}$, what is the enthalpy change for the above reaction at $298\,\text{K}$ and 1atm?

Answer: If q is the amount of heat emitted by the reaction mixture and Cv is the calorimeter's heat capacity, then the amount of heat absorbed by the calorimeter $q = C_V \times \Delta T$. Because the heat lost by the system (reaction mixture) is equal to the heat acquired by the calorimeter, the amount of heat produced by the reaction will have the same magnitude but the opposite sign.

$$q = -C_V \times \Delta T$$
$$= -20.7\,\text{kJ/K} \times (299 - 298)\text{K}$$
$$= -20.7\,\text{kJ}$$

(The exothermic character of the reaction is shown by the negative sign.)

Thus, ΔU for the combustion of the 1g of graphite $= -20.7\text{kJK}^{-1}$

For combustion of 1mol of graphite,

$$= \frac{12.0\,\text{g mol}^{-1} \times (-20.7\,\text{kJ})}{1\text{g}} = -2.48 \times 10^2\ \text{kJ mol}^{-1},$$

Since $\Delta n_g = 0 \Delta H = \Delta U = -2.48 \times 10^2\ \text{kJ mol}^{-1}$

Question 6.7: A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298K? Calculate the internal energy of vaporization at 298K. $\Delta_{\text{vap}} H^{\ominus}$ For water at $298\text{K} = 44.01\text{kJ mol}^{-1}$

Answer: The evaporation process may be represented as:

$$\underset{1\text{mol}}{\text{H}_2\text{O(1)}} \xrightarrow{\text{vaporisation}} \underset{1\text{mol}}{\text{H}_2\text{O(g)}}$$

No. of moles in $18\,\text{g H}_2\text{O(l)}$ is $= \dfrac{18\,\text{g}}{18\,\text{g mol}^{-1}} = 1\text{mol}$

Heat supplied to evaporate 18g water at

$$298\text{K} = \text{n} \times \Delta_{\text{vap}} H^{\ominus}$$
$$= (1\text{mol}) \times \left(44.01\text{kJ mol}^{-1}\right)$$
$$= 44.01\text{kJ}$$

(Assumes that steam behaves like an ideal gas).

$$\Delta_{\text{vap}} U = \Delta_{\text{?ap}} H^{\ominus} - p\Delta V = \Delta_{\text{vap}} H^{\ominus} - \Delta n_g RTn$$
$$\Delta_{\text{vap}} H^{\text{v}} - \Delta\text{n}_\text{g}\text{RT} = 44.01\text{kJ} \quad -(1)\left(8.314\text{JK}^{-1}\,\text{mol}^{-1}\right)(298\,\text{K})\left(10^{-3}\,\text{kJ J}^{-1}\right)$$
$$\Delta_{\text{vap}} U^{\text{v}} = 44.01\text{kJ} - 2.48\text{kJ}$$
$$= 41.53\text{kJ}$$

Question 6.8: Assuming the water vapour to be a perfect gas, calculate the internal energy change when 1mol of water at 100°C and 1bar pressure is converted to ice at 0°C. Given the enthalpy of fusion of ice is $6.00\,\text{kJ mol}^{-1}$ heat capacity of water is $4.2\,\text{J} / \text{g}^\circ\text{C}$.

Answer: The following is how the transformation occurs:

$Step\ -1\ 1\text{molH}_2\text{O}\left(1,100^\circ\text{C}\right) \rightarrow 1mol\left(1,0^\circ\text{C}\right)$ Enthalpy Change ΔH_1

$Step - 2\backslash 1\text{molH}_2\text{O}\left(1,0^\circ\text{C}\right) \rightarrow 1\text{molH}_2\text{O}\left(\text{S},0^\circ\text{C}\right)$ Enthalpy Change ΔH_2

Total enthalpy change will be -

$$\Delta H = \Delta H_1 + \Delta H_2 \Delta H_1$$
$$= -(18 \times 4.2 \times 100) J mol^{-1}$$
$$= -7560\, J\, mol^{-1}$$
$$= -7.56 kJ mol^{-1} \Delta H_2$$
$$= -6.00\, kJ\, mol^{-1}$$

So,

$$\Delta H = -7.56\, kJ\, mol^{-1} + \left(-6.00\, kJ\, mol^{-1}\right)$$
$$= -13.56\, kJ\, mol^{-1}$$

During the transition from liquid to solid state, the volume changes very little.

So,

$$p\Delta v = \Delta ngRT = 0$$
$$\Delta H = \Delta U = -13.56\, kJ\, mol^{-1}$$

Question 6.9: The combustion of one mole of benzene takes place at $298 K$ and $1 atm$ **. After combustion,** $CO_2(g)$ **and** $H_2O(1)$ **are produced and** $3267.0 kJ$ **of heat is liberated. Calculate the standard enthalpy of formation,** $\Delta_f H^{\ominus}$ **of benzene. Standard enthalpies of formation of** $CO_2(g)$ **and** $H_2O(1)$ **are** $-393.5 kJ\, mol^{-1}$ **and** $-285.83 kJ\, mol^{-1}$ **respectively.**

Answer: The following is the benzene formation reaction:

$$6C(\text{ graphite }) + 3H_2(g) \rightarrow C_6H_6(1) \Delta_f H^{\ominus} = ? \ldots \text{ (i)}$$

The enthalpy of combustion of $1 mol$ of benzene is :

$$C_6H_6(l) + \frac{15}{2} O_2 \rightarrow 6CO_2(g) + 3H_2O(1)$$

$$\Delta_c H^{\ominus} = -3267\, kJ\, mol^{-1} \ldots \text{ (ii)}$$

The enthalpy of formation of $1 mol$ of $CO_2(g)$:

$$C(\text{ graphite }) + O_2(g) \rightarrow CO_2(g)$$

$$\Delta_f H^{\ominus} = -393.5\, kJ\, mol^{-1} \ldots \text{ (iii)}$$

The enthalpy of formation of $1 mol$ of $H_2O(l)$ is:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(1)$$

$\Delta_c H^{\ominus} = -285.83\,\text{kJ mol}^{-1} \ldots \text{(iv)}$

Multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

$$6\text{C(graphite)} + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g})$$

$$\Delta_f H^{\ominus} = -2361\,\text{kJ mol}^{-1}$$

$$3\text{H}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow 3\text{H}_2\text{O(l)}$$

$$\Delta_f H^{\ominus} = -857.49\,\text{kJ mol}^{-1}$$

Combining the two equations above, we get:

$$6\text{C(graphite)} + 3\text{H}_2(\text{g}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(1)}$$

$$\Delta_5 H^{\ominus} = -3218.49\,\text{kJ mol}^{-1} \ldots \text{(v)}$$

Reversing equation (ii);

$$6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)} \rightarrow \text{C}_6\text{H}_6\text{(1)} + \frac{15}{2}\text{O}_2$$

$$\Delta_f H^{\ominus} = -3267.0\,\text{kJ mol}^{-1} \ldots \text{(vi)}$$

Combining the two equations (v) and (vi) above, we get:

$$6\text{C(graphite)} + 3\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6\text{(l)}$$

$$\Delta_f H^{\ominus} = -48.51\,\text{kJ mol}^{-1} \ldots (iv)$$

Question 6.10: Predict in which of the following, entropy increases/decreases:

(i) A liquid crystallizes into a solid.

Answer: The molecules achieve an ordered state after freezing, and hence the entropy reduces.

(ii) Temperature of a crystalline solid is raised from $0\,\text{K}\ to 115\,\text{K}$.

Answer: The constituent particles are static and entropy is minimal at $0\,K$.

When the temperature is raised to $115\,K$,

They begin to move and oscillate about their equilibrium locations in the lattice, causing the system to become more disordered and entropy to rise.

(iii) $2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(g)}$

Answer: Reactant $NaHCO_3$ is a solid with a low entropy value.

One solid and two gases are among the products. As a result, the products reflect a greater entropy state.

(iv) $H_2(g) \rightarrow 2H(g)$

Answer:
One molecule produces two atoms, resulting in an increase in the number of particles and a more disordered state. The entropy of two moles of H atoms is larger than that of one mole of dihydrogen molecule.

Question 6.11: For oxidation of iron,

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ **Entropy change is** $-549.4 JK^{-1} mol^{-1} at 298 K$ **. In spite of negative entropy change of this reaction, why is the reaction spontaneous?**

$\left(\Delta_r H^{\ominus} \text{ for this} -1648\times10^3 \, J\,mol^{-1}\right)$ **is** $-1648\times10^3 \, J\,mol^{-1}\,J$ **.**

Answer: When determining the spontaneity of a reaction, one must consider the following factors.

$\Delta S_{total} \left(\Delta S_{sys} + \Delta S_{surr}\right)$.

For calculating ΔS_{surr} ,

We must take into account the heat absorbed by the environment, which is equivalent to $-\Delta_r H^{\ominus}$. At temperature T , The environment's entropy is changing.

$$\Delta S_{sur} = -\frac{\Delta_r H^{\ominus}}{T} (\text{ at constant pressure })$$

$$= -\frac{\left(-1648\times10^3 \, J\,mol^{-1}\right)}{298\,K}$$

$$= 5530 JK^{-1} \, mol^{-1}$$

Thus, total entropy change for this reaction

$$r\Delta_r S_{total} = 5530 JK^{-1} \, mol^{-1} + \left(-549.4 JK^{-1} \, mol^{-1}\right)$$

$$= 4980.6 JK^{-1} \, mol^{-1}$$

This proves that the reaction described above is unintentional.

Question 6.12: Calculate $\Delta_r G^{\ominus}$ **for conversion of oxygen to ozone,** $3/2O_2(g) \rightarrow O_3(g)$

At $298\,K$ **. If** K_p **for this conversion is** 2.47×10^{-29} **.**

Answer: We are aware that,

$\Delta_r G^{\ominus} = -2.303\text{RT}\log K_p$ *and*

$\text{R} = 8.314\text{JK}^{-1}\,\text{mol}^{-1}$

Therefore,

$$\Delta_r G^{\ominus} = -2.303\left(8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\right)\times(298\,\text{K})\left(\log 2.47\times10^{-29}\right)$$

$$=163000\,\text{J}\,\text{mol}^{-1}$$

$$=163\,\text{kJ}\,\text{mol}^{-1}$$

Question 6.13: Find out the value of equilibrium constant for the following reaction at $298\,\text{K}$.

$$2\text{NH}_3(g)+\text{CO}_2(g)\rightleftharpoons \text{NH}_2\text{CONH}_2(\text{aq}) \ +\text{H}_2\text{O(l)}$$

Standard Gibbs energy change, $\Delta_r G^{\ominus}$ at the given temperature is $-13.6\,\text{kJ}\,\text{mol}^{-1}$.

Answer: We are aware that, $\log K = \dfrac{-\Delta_r G^{\ominus}}{2.303RT}$

$$=\frac{\left(-13.6\times10^{3}\,\text{J}\,\text{mol}^{-1}\right)}{2.303\left(8.314\text{JK}^{-1}\,\text{mol}^{-1}\right)(298\,\text{K})}=2.38$$

Hence $K = \textit{antilog}\,2.38 = 2.4\times10^{2}$.

Question 6.14: At 60°C, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Answer: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

If N_2O_4 is 50% dissociated, the mole fraction of both chemicals is calculated as follows:

$$x_{\text{N}_2\text{O}_4} = \frac{1-0.5}{1+0.5} : x_{\text{NO}_2} = \frac{2\times0.5}{1+0.5}$$

$$p_{\text{N}_2\text{O}_4} = \frac{0.5}{1.5}\times1\text{atm},\ p_{\text{NO}_2} = \frac{1}{1.5}\times1\text{atm}.$$

The equilibrium constant K_p is,

$$K_p = \frac{\left(p_{\text{NO}_2}\right)^2}{p_{\text{N}_2\text{O}_4}} = \frac{1.5}{(1.5)^2(0.5)} = 1.33\,\text{atm}$$

As, $\Delta_r G^{\ominus} = -\text{R}T\ln K_p$

$$\Delta_r G^\ominus = \left(-8.314\,\text{JK}^{-1}\,\text{mol}^{-1}\right)\times(333\,\text{K}) \quad \times(2.303)\times(0.1239)$$

$$= -763.8\,\text{kJ mol}^{-1}$$

Exercises

6.1Choose 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 unaffected by the route it follows.

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

So, option (ii) is accurate.

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

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

Answer: If there is no heat exchange between the system and its surroundings, it is considered to be under adiabatic circumstances. As a result, $q = 0$ under adiabatic circumstances.

So, option (iii) is accurate.

6.3 The enthalpies of all elements in their standard states are:

(i) Unity

(ii) Zero

(iii) < 0

(iv) Different for each element

Answer: All elements have zero enthalpy in their standard state.

As a result, option (ii) is accurate.

6.4 ΔU^{θ} **of combustion of methane is** $-X\ \text{kJ mol}^{-1}$**. The value of** ΔH^{θ} **is**

(i) $=\Delta U^{\theta}$

(ii) $>\Delta U^{\theta}$

(iii) $<\Delta U^{\theta}$

(iv) $=0$

Answer: Option (iii) is accurate because

$$\Delta H^{\theta}=\Delta U^{\theta}+\Delta n_g \mathrm{R}T and \Delta U^{\theta}=-X\ \text{kJ mol}^{-1},$$

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

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

6.5 The enthalpy of combustion of methane, graphite and dihydrogen at $298\,\mathrm{K}$ **are,** $-890.3\,\text{kJmol}^{-1}$ $-393.5\,\text{kJ mol}^{-1}$**, and** $-285.8\,\text{kJ mol}^{-1}$ **respectively. Enthalpy of formation of** $\mathrm{CH}_{4(g)}$ **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: Option (i) is accurate. Because

$$\mathrm{CH}_{4(z)}+2\mathrm{O}_{2(g)}\rightarrow \mathrm{CO}_{2(g)}+2\mathrm{H}_2\mathrm{O}_{(g)}$$

$$\Delta H=-890.3\,\text{kJ mol}^{-1}$$

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

6.6 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

Answer: In order for a reaction to be spontaneous, ΔG should be negative.

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

For the provided reaction, according to the question,

$\Delta S=$ positive

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

$n\Rightarrow\Delta G=\{\ negative\ \}$

As a result, the reaction can occur at any temperature.

Hence, option (iv) is accurate.

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

Answer: The first law of thermodynamics states that

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

Where,

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

$q=$ Heat

$W=$ Work

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

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

Putting the values in (i), we get

$\Delta U=701\,\text{J}+(-394\,\text{J})\Delta U$
$=307\,\text{J}$

As a result, the internal energy change for the given process is $307\,J$.

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

$$\text{NH}_2\text{CN}_{(g)}+\frac{3}{2}\text{O}_{2(g)}\rightarrow \text{N}_{2(g)}+\text{CO}_{2(g)}+\text{H}_2\text{O}_{(0)}$$

Answer: Enthalpy change for a reaction (ΔH) is, $\Delta H=\Delta U+\Delta n_g\text{R}T$

Where,

$\Delta U=$ Change in internal energy

Δn_g = Change in number of moles

For the given reaction,

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

$$= (2 - 2.5) \text{ moles}$$

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

And,

$$\Delta U = -742.7\,\text{kJ mol}^{-1}$$
$$T = 298\,\text{K}$$

$$\text{R} = 8.314\times10^{-3}\,\text{kJ mol}^{-1}\,\text{K}^{-1}$$

Putting the values in ΔH :

$$\Delta H = \left(-742.7\,\text{kJ mol}^{-1}\right) + (-0.5\,\text{mol})(298\,\text{K})\left(8.314\times10^{-3}\,\text{kJ mol}^{-1}\,\text{K}^{-1}\right)$$
$$= -742.7 - 1.2\Delta H$$
$$= -743.9\,\text{kJ mol}^{-1}$$

6.9 Calculate the number of kJ of heat necessary to raise the temperature of $60.0\,\text{g}$ of aluminum from 35°C to 55°C. Molar heat capacity of Al is $24\,\text{J mol}^{-1}\,\text{K}^{-1}$.

Answer: From the expression of heat (q),

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

Where,

c = Molar heat capacity

m = Mass of substance

ΔT = Change in temperature

Putting the values in q :

$$q = \left(\frac{60}{27}\text{mol}\right)\left(24\,\text{J mol}^{-1}\,\text{K}^{-1}\right)(20\,\text{K})$$
$$q = 1066.7\,\text{J}q$$
$$= 1.07\,\text{kJ}$$

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

$C_p[H_2O(I)] = 75.3\,J\,mol^{-1}\,K^{-1}$

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

Answer:

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

(a) Energy change involved in the transformation of $1\,mol$ of water at $10^{\circ}C$ to $1\,mol$ of water at $0^{\circ}C$. (b) Energy change involved in the transformation of $1\,mol$ of water at 0° to $1\,mol$ of ice at $0^{\circ}C$.

(c) Energy change involved in the transformation of $1\,mol$ of ice at $0^{\circ}C$ to $1\,mol$ of ice at $-10^{\circ}C$.

$$\text{Total } \Delta H = C_p[H_2OCl]\Delta T + \Delta H_{freenng} + C_p[H_2O_{(s)}]\Delta T$$

$$= (75.3\,J\,mol^{-1}\,K^{-1})(0-10)K + (-6.03\times10^3\,J\,mol^{-1}) + (36.8\,J\,mol^{-1}\,K^{-1})(-10-0)K$$

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

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

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

As a result, the transformation's enthalpy change is $-7.151\,kJ\,mol^{-1}$.

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

Answer: Formation of CO_2 from carbon and dioxygen gas is:

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

Heat released on formation of $44\,g\,CO_2 = -393.5\,kJ\,mol^{-1}$

Heat released on formation of $35.2\,g\ CO_2$

$$= \frac{-393.5\,kJ\,mol^{-1}}{44\,g} \times 35.2\,g = -314.8\,kJ\,mol^{-1}$$

6.12 Enthalpies of formation of $CO_{(g)}, CO_{2(g)}, N_2O_{(g)}$ and $N_2O_{4(g)}$ are $-110\,kJ\,mol^{-1}, -393\,kJ\,mol^{-}1, 81\,kJ\,mol^{-1}$ and $9.7\,kJ\,mol^{-1}$ respectively. Find the value of $\Delta_r H$ for the reaction:

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

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

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

For the given reaction,

$$\mathrm{N_2O}_{4(g)} + 3\mathrm{CO}_{(g)} \rightarrow \mathrm{N_2O}_{(g)} + 3\mathrm{CO}_{2(g)}$$

$$\Delta_r H = \left\{\Delta_f H\left(\mathrm{N_2O}\right) + 3\Delta_f H\left(\mathrm{CO_2}\right)\right\} - \left\{\Delta_f H\left(N_2\mathrm{O}_4\right) + 3\Delta_f H(\mathrm{CO})\right\}$$

Putting the values of $\Delta H for \mathrm{N_2O}, \mathrm{CO_2}, \mathrm{N_2O_4}$, and CO , we receive:

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

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

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

6.13 Given $\mathrm{N}_{2(g)} + 3\mathrm{H}_{2(g)} \rightarrow 2\mathrm{NH}_{3(g)}; \Delta r H^{\theta} = -92.4\,\mathrm{kJ\,mol^{-1}}$. What is the standard enthalpy of formation of $\mathrm{NH_3}$ gas?

Answer:
The change in enthalpy that occurs during the creation of 1 mole of a material in its standard form from its component constituents in their standard condition is known as the standard enthalpy of formation.

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

$$\frac{1}{2}\mathrm{N}_{2(g)} + \frac{3}{2}\mathrm{H}_{2(g)} \rightarrow \mathrm{NH}_{3(g)}$$

Standard enthalpy of formation of $\mathrm{NH}_{3(g)}$,

$$= 1/2\Delta_r H^{\theta}$$
$$= 1/2\left(-92.4\,\mathrm{kJ\,mol^{-1}}\right)$$
$$= -46.2\,\mathrm{kJ\,mol^{-1}}$$

6.14 Calculate the standard enthalpy of formation of $\mathrm{CH_3OH}_{(l)}$ from the following data:

$$\mathrm{CH_3OH}_{(l)} +^{\frac{3}{2}} \mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)} + 2\mathrm{H_2O}_{(t)}; \Delta_r H^{\theta} = -726\,\mathrm{kJ\,mol^{-1}}$$

$$\mathrm{C}_{(g)} + \mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)}; \Delta_c \mathrm{H}_{\theta} = -393\,\mathrm{kJ\,mol}_{-1}$$

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

Answer: During the formation of $CH_3OH_{(l)}$ the equation is,

$C_{(s)} + 2H_2O_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CH_3OH(t)(\mathbf{1})$

The reaction (1) can be calculated from the given reactions using algebraic calculations as follows:

Equation (ii) $+2\times$ equation (iii) $-$ equation (i)

$\Delta tH_\theta\left[CH_3OH(t)\right] = \Delta_c H_\theta + 2\Delta tH_\theta\left[H_2O_{(f)}\right] - \Delta_r H_\theta$

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

$= (-393 - 572 + 726)\mathrm{kJmol^{-1}}$

$\therefore \Delta H^\theta\left[CH_3OH_{(l)}\right] = -239\,\mathrm{kJ\,mol^{-1}}$

6.15 Calculate the enthalpy change for the process $CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ and calculate bond enthalpy of $C-Cl$ in $CCl_{4(g)}$.

$\Delta_{vap} H^\theta\left(CCl_4\right) = 30.5\,\mathrm{kJ\,mol^{-1}}$

$\Delta_H H^\theta\left(CCl_4\right) = -135.5\,\mathrm{kJ\,mol^{-1}}$.

$\Delta_a H^\theta(C) = 715.0\,\mathrm{kJ\,mol^{-1}}$, **Where $\Delta_a H^\theta$ is enthalpy of atomization?**

$\Delta_a H^\theta\left(Cl_2\right) = 242\,\mathrm{kJ\,mol^{-1}}$

Answer: The chemical equations indicating the provided enthalpies are as follows:

$(i)CCl_{4(l)} \rightarrow CCl_{4(g)}\Delta_{vap}\ H^\theta\ 30.5\,\mathrm{kJ\,mol^{-1}}$

$(ii)C_{(s)} \rightarrow C_{(g)}\ \theta_a \quad \Delta H = 715.0\,\mathrm{kJ\,mol^{-1}}$

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

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

Enthalpy change for the given process $CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$, is,

Equation $(ii) + 2\times$ *Equation* (iii) $-$ *Equation* (i) $-$ *Equation* (iv)

$\Delta H = \Delta_a H^{\ominus}(C) + 2\Delta_a H^\theta\left(Cl_2\right) - \Delta_{vap} H^{\ominus} - \Delta_H H$

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

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

Bond enthalpy of $\text{C}-\text{C}$ bond in $\text{CCl}_4(g) = \dfrac{1304}{4}\,\text{kJ mol}^{-1}$

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

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

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

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

6.17 For the reaction at $298\,\text{K}$,

$$2\text{A} + \text{B} \rightarrow \text{C}$$
$$\Delta H = 400\,\text{kJ mol}^{-1} \text{ and } \Delta S = 0.2\,\text{kJ K}^{-1}\,\text{mol}^{-1}$$

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Answer:

According to the phrase,

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

Let, the reaction at equilibrium, ΔT for the reaction is:

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

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

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

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

$DeltaG$ must be negative for the reaction to be spontaneous.
As a result, T should be more than $2000K$ for the given response to be spontaneous.

6.18 For the reaction,

$2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$**, what are the signs of** ΔH and ΔS **?**

Answer: ΔH and ΔS are negative.

The synthesis of a chlorine molecule from chlorine atoms is represented by the given process.

The building of bonds is going place here. As a result, energy is released. As a result, ΔH is negative. Furthermore, two moles of atoms are more random than one mole of a molecule.
For the given response, ΔS is negative since spontaneity is reduced.

6.19 For the reaction,

$$2\,\mathrm{A}_{(g)}+\mathrm{B}_{(g)}\rightarrow 2\mathrm{D}_{(g)}$$
$$\Delta U^{\theta}=-10.5\,\mathrm{kJ}\text{ and }\Delta S^{\theta}=-44.1\mathrm{JK}^{-1}$$

Calculate ΔG^{θ} for the reaction, and predict whether the reaction may occur spontaneously.

Answer: For the reaction in question,

$$2\,\mathrm{A}_{(g)}+\mathrm{B}_{(g)}\rightarrow 2\mathrm{D}(g)$$
$$\Delta n_{g}=2-(3)$$
$$=-1\text{ mole}$$

Putting the value of ΔU^{θ} in the expression of ΔH :

$$\Delta H^{\theta}=\Delta U^{\theta}+\Delta n_{g}RT$$
$$=(-10.5\,\mathrm{kJ})-(-1)\left(8.314\times10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}\right)(298\,\mathrm{K})$$
$$=-10.5\,\mathrm{kJ}-2.48\,\mathrm{kJ}$$
$$\Delta H^{\theta}=-12.98\,\mathrm{kJ}$$

Putting the values of $\Delta H^{\theta} and \Delta S^{\theta}$ in the expression of ΔG^{θ} :

$$\Delta G^{\theta}=\Delta H^{\theta}-T\Delta S^{\theta}$$
$$=-12.98\,\mathrm{kJ}-(298\,\mathrm{K})\left(-44.1\,\mathrm{J\,K^{-1}}\right)$$
$$=-12.98\,\mathrm{kJ}+13.14\,\mathrm{kJ}\Delta G^{\theta}$$
$$=+0.16\,\mathrm{kJ}$$

If the response for ΔG^{θ} is positive, the reaction will not happen on its own.

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

Answer:

According to the phrase,

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

ΔG^{θ} for the reaction,

$$= (2.303)\left(8.314\text{JK}^{-1}\ \text{mol}^{-1}\right)(300\,\text{K})\log 10$$
$$= -5744.14\text{Jmol}^{-1}$$
$$= -5.744\,\text{kJ mol}^{-1}$$

6.21 Comment on the thermodynamic stability of $NO_{(g)}$, given

$$\frac{1}{2}\text{N}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{NO}_{(g)}; \Delta H_\theta = 90\,\text{kJ mol} - 1$$

$$\text{NO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{NO}_{2(g)} : \Delta_r H_\theta = -74\,\text{kJ mol} - 1$$

Answer: When the value of $\triangle_r H$ is positive, it means that heat is absorbed during the creation of $\text{NO}_{(g)}$. It means that $\text{NO}_{(g)}$ has higher energy than the reactants $\left(\text{N}_2 \text{ and } \text{O}_2\right)$.

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 unstable $\text{NO}_{2(g)}$.

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

Answer: It is given that $286\,\text{kJ mol}^{-1}$ of heat is evolved on the formation of $1\,\text{mol}$ of $\text{H}_2\text{O}_{(l)}$.

As a result, the surroundings will absorb an equivalent quantity of heat.

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

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

$$= \frac{286\,\text{kJ mol}^{-1}}{298\text{k}}$$
$$\therefore \Delta S_{\text{surr}} = 959.73\,\text{J mol}^{-1}\,\text{K}^{-1}$$