

LESSON AT A GLANCE

- **System:** It refers to the portion of universe which is under observation.
- **Surroundings:** Everything else in the universe except system is called surroundings.
- **Open System:** In a system when there is exchange of energy and matter taking place with the surroundings is called an open system. For Example: Presence of reactants in an open beaker is an example of an open system.
- **Closed system:** A system is said to be a closed system when there is no exchange of matter but exchange of energy is possible. For example: The presence of reactants in a closed vessel made of conducting material.
- **Isolated system:** In a system when no exchange of energy or matter takes place with the surroundings, is called isolated system. For example: The presence of reactants in a thermoflask, or substance in an insulated closed vessel is an example of isolated system.
- **Homogeneous System:** A system is said to be homogeneous when all the constituent present is in the same phase and is uniform throughout the system. For example: A mixture of two miscible liquids.
- **Heterogeneous system:** A mixture is said to be heterogeneous when it consists of two or more phases and the composition is not uniform. For example: A mixture of insoluble solid in water.
- **The state of the system:** The state of a thermodynamic system means its macroscopic or bulk properties which can be described by state variables:

Pressure (P), volume (V), temperature (T) and amount (n) etc.

They are also known as state functions.

- **Isothermal process:** When the operation is carried at constant temperature the process is said to be isothermal. For isothermal process $dT = 0$

Where dT is the change in temperature.

- **Adiabatic process:** It is a process in which on transfer of heat between system and surrounding, takes place.
- **Isobaric process:** When the process is carried out at constant pressure it is said to be isobaric.
- **Isochoric process:** A process when carried out at constant volume. It is known as isochoric in nature.
- **Cyclic process:** If a system undergoes a series of changes and finally returns to its initial state it is said to be cyclic process.
- **Reversible Process:** When in a process, a change is brought in such a way that the process could, at any moment, be reversed by an infinitesimal change. The change is called reversible.
- **Internal Energy:** It is the sum of all the forms of energies that a system can process.

TEXTBOOK QUESTIONS SOLVED

Q1. 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. (ii)

Q2. For the process to occur under adiabatic conditions, the correct condition is:

- $DT = 0$
- $Dp = 0$
- $q = 0$
- $w = 0$

Ans. (iii)

Q3. The enthalpies of all elements in their standard states are:

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

Ans. (ii)

Q4. ΔU^0 of combustion of methane is $-X \text{ kJ mol}^{-1}$. The value of ΔH^0 is

- (i) $= DU^0$ (ii) $> DU^0$
 (iii) $< DU^0$ (iv) $= 0$

Ans. (iii)

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

Ans. (i)

Q6. A reaction, $A + B \longrightarrow C + D + q$ 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. (iv)

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?

Ans. We know that

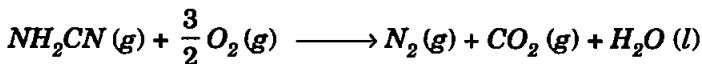
$$\Delta U = q + w$$

$$\text{Given: } q = +701 \text{ J; } w = -394 \text{ J}$$

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

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

Q8. The reaction of cyanamide, $\text{NH}_2\text{CN}(\text{s})$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K.

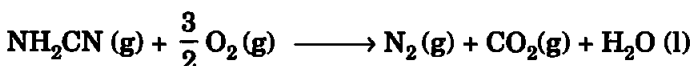


Ans. $\Delta H = \Delta U + \Delta n_g RT$

Where Δn_g = change in number of gaseous substances during the reaction

$$= n_p - n_R$$

In the reaction,



$$n_p = 1 + 1 = 2 ; n_R = \frac{3}{2}$$

$$\Delta n_g = 2 - \frac{3}{2} = +\frac{1}{2}$$

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

$$= -742.7 \text{ kJ mol}^{-1} + \frac{1}{2} \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$= -742.7 \text{ kJ} + 1238.8 \times 10^{-3} \text{ kJ mol}^{-1}$$

$$= -(742.7 + 1.2) \text{ kJ mol}^{-1}$$

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

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

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⁻¹ K⁻¹.

Ans. Heat required to raise the temperature can be calculated from the formula.

$$q = n \times c \times \Delta T$$

Given: Mass of Al = 60.0 g

$$n = \frac{\text{Mass}}{\text{Molar mass}} = \frac{60.0 \text{ g}}{27 \text{ g mol}^{-1}}$$

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

$$\Delta T = T_f - T_i = (55 + 273 - 35 - 273) \text{ K}$$

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

Putting the values in the above relation,

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

$$= 1066.7 \text{ J} = 1.07 \text{ kJ}$$

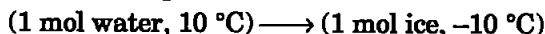
Heat required in kJ = 1.07 kJ.

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.

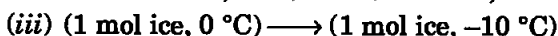
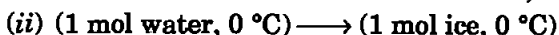
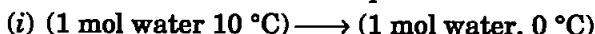
$$C_p[H_2O(l)] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

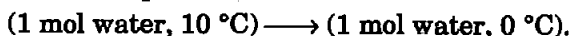
Ans. The process given



It can be divided into three steps



For the (i) process



For 1 mol water

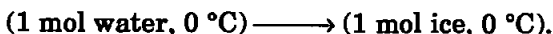
$$q(i) = C_{p,m}(H_2O, l) \times \Delta T$$

$$\text{Given: } C_{p,m}[H_2O, l] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta T = 273 \text{ K} - 283 \text{ K} = -10 \text{ K}$$

$$\begin{aligned} \therefore q(i) &= (75.3 \text{ J mol}^{-1} \text{ K}^{-1})(-10 \text{ K}) \\ &= -753 \text{ J mol}^{-1} = -0.75 \text{ kJ mol}^{-1}. \end{aligned}$$

For (ii) process



For 1 mol water,

$$\begin{aligned} q(ii) &= -\Delta_{fus}H \\ &= -6.03 \text{ kJ mol}^{-1} \end{aligned}$$

$$q(ii) = -6.03 \text{ kJ mol}^{-1}.$$

For (iii) process



For 1 mol ice $q(iii) = C_{p,m}(H_2O, s)\Delta T$

$$\text{Given: } C_{p,m}(H_2O, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta T = 263 \text{ K} - 273 \text{ K} = -10 \text{ K}$$

$$\begin{aligned} \therefore q(iii) &= (36.8 \text{ J mol}^{-1} \text{ K}^{-1}) \times (-10 \text{ K}) \\ &= -368 \text{ J mol}^{-1} = -0.37 \text{ kJ mol}^{-1} \end{aligned}$$

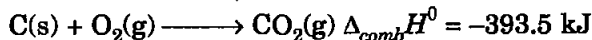
$$\begin{aligned} q &= q(i) + q(ii) + q(iii) \\ &= (-0.75 \text{ kJ mol}^{-1}) + (-6.03 \text{ kJ mol}^{-1}) \\ &\quad + (-0.37 \text{ kJ mol}^{-1}) \\ &= -7.15 \text{ kJ mol}^{-1}. \end{aligned}$$

Since the process is carried out at constant pressure

$$\Delta H = q = -7.15 \text{ kJ mol}^{-1}.$$

Q11. Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans. Given that enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$ i.e.,

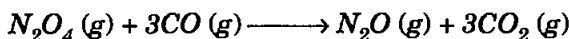


$$\begin{aligned} \text{Heat released when 1 mol (44 g) CO}_2 \text{ is formed} \\ = 393.5 \text{ kJ} \end{aligned}$$

\therefore Heat released when 35.2 g of CO_2 is formed

$$= \frac{393.5 \times 35.2}{44} = 314.8 \text{ kJ.}$$

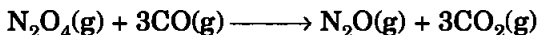
Q12. Enthalpies of formation of $\text{CO}(\text{g})$, $\text{CO}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are -110 , -393 , 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:



Ans. Given that enthalpies of formation of $\text{CO}(\text{g})$, $\text{CO}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are -110 , -393 , 81 and 9.7 kJ mol^{-1} respectively.

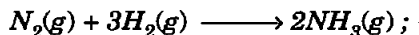
$$\Delta_r H = \sum_f a_i \Delta_f H_{(\text{Products})} - \sum_f b_i \Delta_f H_{(\text{Reactants})}$$

For the reaction



$$\begin{aligned} \Delta_r H &= [\Delta_f H(\text{N}_2\text{O}, \text{g}) + 3\Delta_f H(\text{CO}_2, \text{g})] \\ &\quad - [\Delta_f H(\text{N}_2\text{O}_4, \text{g}) + 3\Delta_f H(\text{CO}, \text{g})] \\ &= [81 + 3 \times (-393)] - [9.7 + 3 \times (-110)] \text{ kJ mol}^{-1} \\ &= (81 - 1179) - (9.7 - 330) \text{ kJ mol}^{-1} \\ &= 81 - 1179 - 9.7 + 330 = -777.7 \text{ kJ mol}^{-1}. \end{aligned}$$

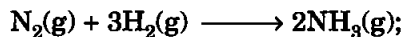
Q13. Given:



$$\Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

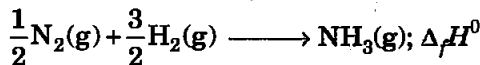
What is the standard enthalpy of formation of NH_3 gas?

Ans. Given:



$$\Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

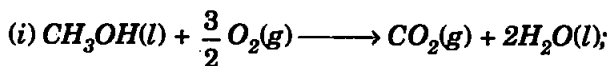
The formation reaction of $\text{NH}_3(\text{g})$ is



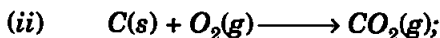
Comparing the two equations,

$$\begin{aligned}\Delta_f H^0(\text{NH}_3, \text{g}) &= \frac{1}{2} \Delta_r H^0 = \frac{1}{2} \times (-92.4) \\ &= -46.2 \text{ kJ mol}^{-1}.\end{aligned}$$

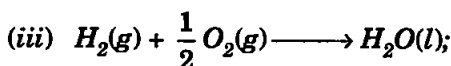
Q14. Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH}(\text{l})$ from the following data:



$$\Delta_r H^0 = -726 \text{ kJ mol}^{-1}$$

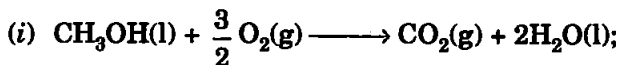


$$\Delta_c H^0 = -393 \text{ kJ mol}^{-1}$$

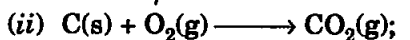


$$\Delta_f H^0 = -286 \text{ kJ mol}^{-1}.$$

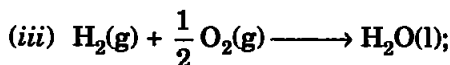
Ans. Given:



$$\Delta_r H^0 = -726 \text{ kJ mol}^{-1}$$

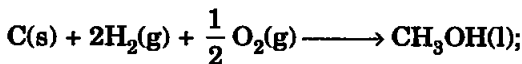


$$\Delta_c H^0 = -393 \text{ kJ mol}^{-1}$$



$$\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$$

Formation reaction of $\text{CH}_3\text{OH}(\text{l})$,

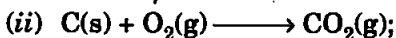


$$\Delta_f H^0 = x$$

Reversing (i) reaction

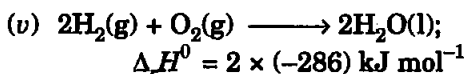


$$\Delta_r H^0 = 726 \text{ kJ mol}^{-1}$$

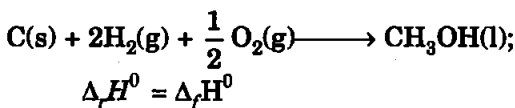


$$\Delta_c H^0 = -393 \text{ kJ mol}^{-1}$$

Multiplying (iii) by 2,



Adding (iv), (ii) and (v), we get



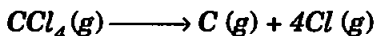
which is the formation reaction of $\text{CH}_3\text{OH}(\text{l})$.

$$\therefore \Delta_f H^\circ = [726 + (-393) + 2(-286)] \text{ kJ mol}^{-1}$$

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

$$= -239 \text{ kJ mol}^{-1}.$$

Q15. Calculate the enthalpy change for the process



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

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

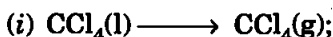
$$\Delta_f H^\circ (\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$$

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

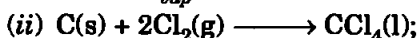
where $\Delta_a H^\circ$ is enthalpy of atomisation

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

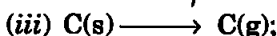
Ans. Given:



$$\Delta_{\text{vap}} H^\circ = 30.5 \text{ kJ mol}^{-1}$$



$$\Delta_f H^\circ = -135.5 \text{ kJ mol}^{-1}$$

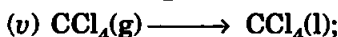


$$\Delta_a H^\circ = 715.0 \text{ kJ mol}^{-1}$$



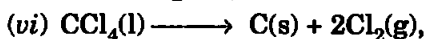
$$\Delta_a H^\circ = 242 \text{ kJ mol}^{-1}$$

Reversing (i),

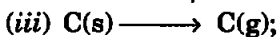


$$\Delta_r H^\circ = -30.5 \text{ kJ mol}^{-1}$$

Reversing (ii),

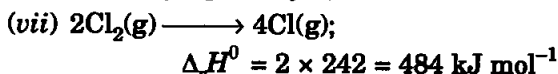


$$\Delta_r H^\circ = 135.5 \text{ kJ mol}^{-1}$$

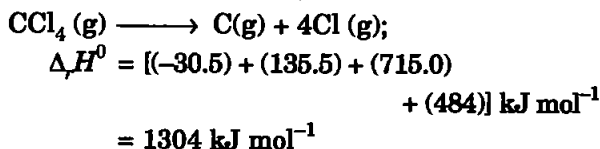


$$\Delta_a H^\circ = 715.0 \text{ kJ mol}^{-1}$$

Multiplying (iv) by 2,



Adding (v), (vi), (vii) and (iii),



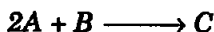
Bond enthalpy of C-Cl in $\text{CCl}_4(\text{g}) = \frac{1}{4} \times \Delta_r H^\circ$, since 4 C-Cl bonds are broken in this reaction.

$$\therefore \text{Bond Enthalpy} = \frac{1}{4} \times 1304 = 326 \text{ kJ mol}^{-1}.$$

Q16. For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans. In an isolated system if a process occurs in which $\Delta U = 0$, i.e., in which there is no change in interactions between molecules of the substances present (like mixing of two ideal gases in which there are no intermolecular forces), the driving force would be the increase in disorder which would increase the entropy of the system. Hence $\Delta S > 0$.

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 ΔH and ΔS to be constant over the temperature range.

Ans. Given that for the reaction, $\Delta H = 400 \text{ kJ mol}^{-1}$ and $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 298 K. Since both the quantities do not change with temperature, let us first calculate the temperature at which the reaction would be at equilibrium, i.e.,

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\text{or } \Delta H = T\Delta S$$

$$\text{and } T = \frac{\Delta H}{\Delta S}$$

$$= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 2000 \text{ K}$$

Since $\Delta H = +ve$ and $\Delta S = +ve$, the reaction would be spontaneous when

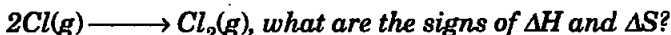
$$\Delta G = \Delta H - T\Delta S = -ve$$

or when $|T\Delta S| > |\Delta H|$

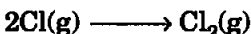
The $T\Delta S$ term would increase with rise in temperature beyond the equilibrium temperature of 2000 K.

Thus, the reaction would be spontaneous at $T > 2000 \text{ K}$.

Q18. For the reaction

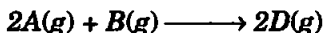


Ans. For the reaction



- (i) Since bonds are formed during the reaction, energy would be released, i.e., $\Delta H = -ve$.
- (ii) Since two moles of gas are reduced to 1 mole of gas during the reaction, there would be decrease in entropy, i.e., $\Delta S = -ve$.

Q19. For the reaction

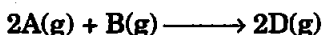


$$\Delta U^0 = -10.5 \text{ kJ and } \Delta S^0 = -44.1 \text{ J K}^{-1}.$$

Calculate ΔG^0 for the reaction, and predict whether the reaction may occur spontaneously.

Ans. For calculating ΔG^0 , ΔH^0 for the reaction is required and can be calculated from ΔU^0 which is $-10.5 \text{ kJ mol}^{-1}$. Temperature is not given and can be taken as 298 K.

The reaction is:



$$\begin{aligned} \Delta n_g &= n_g(\text{Products}) - n_g(\text{Reactants}) \\ &= [2 - (2 + 1)] \text{ mol} = -1 \text{ mol} \end{aligned}$$

$$\Delta H^0 = \Delta U^0 + \Delta n_g RT$$

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

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

$$= -10.5 \text{ kJ} - 2.48 \text{ kJ} = -12.98 \text{ kJ}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$= -12.98 \text{ kJ} - (298 \text{ K})(-44.1 \times 10^{-3} \text{ kJ K}^{-1})$$

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

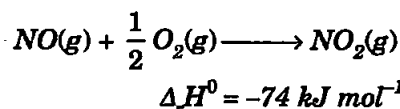
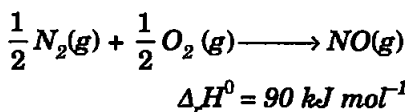
$$= + 0.16 \text{ kJ}.$$

Since ΔG^0 is positive, the reaction cannot occur spontaneously.

Q20. The equilibrium constant for a reaction is 10. What will be the value of ΔG^0 ? $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.

Ans. $\Delta G^0 = -2.303 RT \log K$
 $= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log 10$
 $= (-2.303 \times 8.314 \times 300 \times 1) \text{ J mol}^{-1}$
 $= -5744.1 \text{ J mol}^{-1}$
 $= -5.744 \text{ kJ mol}^{-1}$.

Q21. Comment on the thermodynamic stability of $\text{NO}(\text{g})$, given



Ans. Since formation reaction of $\text{NO}(\text{g})$ is endothermic, its energy is greater than that of its constituent elements and, therefore, it is unstable. Further, since its oxidation to $\text{NO}_2(\text{g})$ is an exothermic process, energetically, $\text{NO}_2(\text{g})$ is more stable and $\text{NO}(\text{g})$ would spontaneously get converted into $\text{NO}_2(\text{g})$.

Q22. Calculate the entropy change in surroundings when 1.00 mol of $\text{H}_2\text{O}(\text{l})$ is formed under standard conditions. $\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$.

Ans. Since standard enthalpy of formation of water is $\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$ this much heat is evolved in the surroundings.

$$\therefore q_{\text{surr}} = -\Delta_f H^0 = 286 \text{ kJ mol}^{-1}$$

$T = 298$ (since standard values of all thermo-dynamics are tabulated at 298 unless a different temperature is mentioned)

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$

$$= 0.9597 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= 959.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

TEXTBOOK PROBLEMS SOLVED

Problem 1. *State Second Law of Thermodynamics.*

Solution. The second law of thermodynamics states that in any spontaneous process, the entropy of the universe (system and surroundings) always increases.

Problem 2. *Write the conditions in terms of ΔH and ΔS when a reaction would be always spontaneous.*

Solution. A reaction would always be spontaneous if $\Delta H = -ve$ (or $\Delta H < 0$) and $\Delta S = +ve$ (or $\Delta S > 0$). (See table 6.5)

Problem 3. *When $\Delta H > 0$ and $\Delta S < 0$, a reaction is never spontaneous. Explain.*

Solution. When $\Delta H > 0$ (+ve) and $\Delta S < 0$ (-ve) ($T = +ve$ always)

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

$$= (+) - (-)$$

$$= +$$

In such a case, Gibbs energy would always increase and the reaction would never be spontaneous.

□□□

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