NCERT Solutions for Class XI Chemistry

Chapter-6

NCERT Chemistry Class 11

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.

1. A thermodynamic state function is a quantity whose value is independent of a 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.

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) $w = 0$

2. Adiabatic process is processes that take place without any transfer of heat between the system and surrounding. i.e, in adiabatic process $q = 0$.
Thus answer is (iii) $q = 0$
[Option (i) $\Delta T = 0$ is an isothermal process. In the isothermal process, the temperature of the system remains constant.
Option (ii) $\Delta p = 0$ is for isobaric process; where pressure of system is kept constant.]

3. The enthalpies of all elements in their standard states are:
(i) unity
(ii) zero
(iii) < 0
(iv) different for each element

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

4. ΔU^θ of combustion of methane is $-X\ \text{kJ mol}^{-1}$. The value of ΔH^θ is
(i) $= \Delta U^\theta$
(ii) $> \Delta U^\theta$
(iii) $< \Delta U^\theta$
(iv) $= 0$

4. We know,
$\Delta H = \Delta U + \Delta n_g RT$
Where,

ΔH is change in enthalpy

ΔU is change in Internal energy

Δn_g is difference in number of moles of gaseous substance on both side of equation

The chemical equation for combustion of methane is

$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

In the reactant side, there are 3 mole of gases (1 mole CH_4 and 2 mole O_2)

On product side there is only one mole of gaseous substance (CO_2)

$\therefore \quad \Delta n_g = 1 - 3 = -2$

i.e, $\Delta H = \Delta U - 2RT$

$\therefore \Delta H > \Delta U$

Answer is (ii).

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}.

5. According to the question,

(i) $CH_4(g) + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

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

(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta H = -393.5\ kJ\ \text{mol}^{-1}$

(iii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$

$\Delta H = -285.8\ kJ\ \text{mol}^{-1}$

Thus, the desired equation is the one that represents the formation of CH_4 (g) i.e.,

$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$

$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_c H_{H_2} - \Delta_c H_{CO_2}$

= [–393.5 + 2(–285.8) – (–890.3)] kJ mol^{-1}

= –74.8 kJ mol^{-1}

$\therefore$ Enthalpy of formation of $CH_{4(g)}$ = –74.8 kJ mol^{-1} Hence,

Alternative (i) is correct.

6. A reaction, A + B → 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

6. A reaction is said to be feasible of possible when change in Gibbs free energy for that reaction at particular temperature is negative.

We know, change in Gibbs free energy,

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

Where
ΔH is change in enthalpy
ΔS is change in entropy
T is temperature at which reaction occurs.
Given Energy is released when a forward reaction occurs (since q is on product side), therefore ΔH is negative.
It is also given that entropy change for the reaction is positive.
Thus $-T\Delta S$ would be negative for all temperatures.
Therefore,
$\Delta G = \Delta H - T\Delta S$ would always be negative.
Thus (iv) possible at any temperature is the right answer.

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?

7. 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
$\Delta U = 701\text{ J} + (-394\text{ J})$
$\Delta U = 307\text{ J}$
Hence, the change in internal energy for the given process is 307 J.

8. The reaction of cyanamide, $NH_2CN(s)$, 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.

8. We know that,
$\Delta U = \Delta H - \Delta n_g RT$
The balanced chemical equation of reaction is,
$NH_2CN(s) + 3/2O_2(g) \rightleftharpoons N_2(g) + CO_2(g) + H_2O(l)$
Number of moles of gaseous particles in product side is 2 (one N_2 and one CO_2)
Number of moles of gaseous particles on reactant side is 3/2 (O_2)
Thus, change in number of moles of gaseous particle,
$\Delta n_g = 2 - 3/2 = 1/2$
$\therefore \quad \Delta U = \Delta H - \Delta n_g RT$
Given,
$\Delta H = -742.7\text{ kJ}$
$R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$
$= 8.414 \times 10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}$
$\Delta n_g = 1/2$
T = 298 K
Thus,
$\Delta U = (-742.7\text{ kJ mol}^{-1}) - (\frac{1}{2}\text{mol}) \times (8.314 \times 10^{-3}\text{ kJ K}^{-1}\text{mol}^{-1}) \times 298$
$= -742.7 + 1.239$

= –741.46 kJ

9. 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}.

9. From the expression of heat (q),
q = m. c. ΔT Where,
c = molar heat capacity m
= mass of substance
ΔT = change in temperature
Substituting the values in the expression of q:

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

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.
$C_p[H_2O(l)] = 75.3$ J mol^{-1} K^{-1}
$C_p[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}

10. Given: $\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0° C
C_p $[H_2O(l)] = 75.3$ J mol^{-1} K^{-1}
C_p $[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}
To calculate the enthalpy change, we use Hess's Law
Total $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$
Where $\Delta H = C_p\Delta T$
ΔC_p = Heat capacity at constant pressure
$\Delta T = T_2 - T_1$
∴ Total ΔH = (1 mol water at 10° C → 1 mol water at 0° C) +
(1 mol water at 0° C → 1 mol water at 0° C) +
(1 mol water at 0° C → 1 mol water at -10° C)
∴ Total ΔH = $C_p[H_2O\ (l)] \times \Delta T + \Delta H_{freezing} + C_p\ [H_2O\ (s)] \times \Delta T$
By substituting the given values, we get
Total ΔH = 75.3 J mol^{-1} K^{-1} × (0 -10) K +(–6.03 kJ mol^{-1}) + 36.8 J mol^{-1} K^{-1} × (–10) K
Total ΔH = –753 Jmol^{-1} -6.03 kJ mol^{-1} – 368 Jmol^{-1}
Total ΔH = –0.753 kJmol^{-1} – 6.03 kJ mol^{-1} – 0.368 kJmol^{-1} (1J = $\frac{1}{1000}$ kJ)
Total ΔH = –7.151 kJmol^{-1}
Thus, the enthalpy change involved in the process is –7.151 kJ/mol.
Note: Hess's Law states that "if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e., the total enthalpy change is independent of intermediate steps involved in the change. The enthalpy depends on the initial and final stages only.

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.

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

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta_f H = -393.5\ kJ\ \text{mol}^{-1}$$

(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

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

= –314.8 kJ mol^{-1}

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 Δ_rH for the reaction:

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

12. Given: For the given reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

Enthalpy of formation ($\Delta H_{f\,(CO)}$) = –110 kJ mol^{-1}

$\Delta H_{f\,(CO2)}$ = –393 kJ mol^{-1}

$\Delta H_{f\,(N2O)}$ = 81kJ mol^{-1}

$\Delta H_{f\,(N2O4)}$ = 9.7 kJ mol^{-1}

Now, to calculate Δ_rH for the reaction, we apply the formula given below:

Δ_rH = (Sum of enthalpy of formation of products) – (sum of enthalpy of reactants)

or, $\Delta_rH = \sum \Delta_fH$ (Products) – $\sum \Delta_fH$ (Reactants)

In the given reaction,

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

Products are N_2O and CO_2

Reactants are N_2O_4 and CO

∴ $\Delta_rH = [\Delta_fH\ (N_2O) + 3\Delta_fH\ (CO_2)] - [\Delta_fH(N_2O_4) + 3\Delta_fH\ (CO)]$

By substituting the values given, we get

⇒ Δ_rH = [81 kJ/mol + 3 × (–393 kJ/mol)] – [9.7 kJ/mol + 3 × (–110 kJ/mol)]

⇒ Δ_rH = –777.7 kJ/mol

Thus, the value of Δ_rH for the reaction is –777.7 kJ/mol.

Note: Enthalpy of reaction (Δ_rH) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted.

13. Given

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)};\ \Delta_rH^\theta = -92.4\ kJ\ \text{mol}^{-1}$$

What is the standard enthalpy of formation of NH_3 gas?

13. 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),

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

∴ Standard enthalpy of formation of $NH_{3(g)}$

= ½ Δ_rH^θ

= ½ (–92.4 kJ mol^{-1})

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

14. Calculate the standard enthalpy of formation of $CH_3OH_{(l)}$ from the following data:

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)};\ \Delta_r H^\theta = -7.26\ kJ\ \text{mol}^{-1}$$

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

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

14. Given:

$CH_3OH\ (I) + \frac{3}{2}\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)\ ;\ \Delta_rH^\circ = -726\ \text{kJ mol}^{-1}$ (1)

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta_cH^\circ = -393\ \text{kJ mol}^{-1}$ (2)

$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l)\ ;\ \Delta_fH^\circ = -286\ \text{kJ mol}^{-1}$ (3)

To calculate the standard enthalpy of formation of $CH_3OH(l)$, first we will make the formation reaction of CH_3OH by using carbon, hydrogen, oxygen.

$C\ (s) + 2H_2\ (g) + ½\ O_2\ (g) \longrightarrow CH_3OH\ (l)$

This is the required reaction

Now, we make the required reaction from the given data

Step 1: Add the reaction (2) and reaction (3)

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta_cH^\circ = -393\ \text{kJ mol}^{-1}$

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)\ ;\ \Delta_fH^\circ = -572\ \text{kJ mol}^{-1}$. [2 × reaction (2)]

$C + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta_fH^\circ = -965\ \text{kJ mol}^{-1}$

Step 2: Subtract reaction (1) from the above reaction, we get

$C + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta_fH^\circ = -965\ \text{kJ mol}^{-1}$

$CO_2(g) + 2H_2O(l) \longrightarrow CH_3OH\ (l) + \frac{3}{2}\ O_2(g);\ \Delta_rH^\circ = -726\ \text{kJ mol}^{-1}$

$C\ (s) + 2H_2\ (g) + ½\ O_2\ (g) \longrightarrow CH_3OH\ (l)\ ;\ \Delta_rH^\circ = -239\ \text{kJ mol}^{-1}$

(formation of required reaction)

Thus, the standard enthalpy of formation of $CH_3OH(l)$ is $-239\ \text{kJ mol}^{-1}$.

15. Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4Cl(g)$ and calculate bond

enthalpy of C–Cl in $CCl_4(g)$.

$\Delta_{vap}H^\theta\ (CCl_4) = 30.5\ \text{kJ mol}^{-1}$.

$\Delta_fH^\theta\ (CCl_4) = -135.5\ \text{kJ mol}^{-1}$.

$\Delta_aH^\theta\ (C) = 715.0\ \text{kJ mol}^{-1}$, where Δ_aH^θ is enthalpy of atomisation

$\Delta_aH^\theta\ (Cl_2) = 242\ \text{kJ mol}^{-1}$

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

$(\mathrm{i})\ CCl_{4(l)} \longrightarrow CCl_{4(g)_{\Delta vap}} \qquad H^{\theta} = 30.5\ kJ\ \mathrm{mol}^{-1}$

$(\mathrm{ii})\ C_{(s)} \longrightarrow C_{(g)}{}_{a}^{\theta} \qquad \Delta H = 715.0\ kJ\ \mathrm{mol}^{-1}$

$(\mathrm{iii})\ Cl_{2(g)} \longrightarrow 2Cl_{(g)}{}_{a}^{\theta} \qquad \Delta H = 242\ kJ\ \mathrm{mol}^{-1}$

$(\mathrm{iv})\ \mathrm{C}_{(g)} + 4\mathrm{Cl}_{(g)} \longrightarrow \mathrm{CCl}_{4(g)} \qquad \Delta_r H = -135.5\ kJ\ \mathrm{mol}^{-1}$

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

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

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

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

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

Bond enthalpy of C–Cl bond in CCl_4 (g)

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

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

16. For an isolated system ΔU = 0, what will be ΔS?

16. An isolated system is the one in which neither energy nor matter can enter/leave the system.

ΔS is the change in entropy. Entropy is a measure of randomness or disorder in a system. More the randomness, more is the entropy of a system.

According to the second law of thermodynamics the total entropy can never decrease over time for an isolated system.

The total entropy is constant in ideal cases where the system is in equilibrium, or undergoing a reversible process and approaches 0 at absolute zero only.

In all spontaneous processes, the total entropy always increases and the process is irreversible.

Therefore, ΔS is always greater than 0, ΔS > 0.

17. For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = 0.2\ \mathrm{kJ\ K^{-1}\ mol^{-1}}$

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

17. 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)

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

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?

18. In the reaction, chlorine molecule is being formed from chlorine atoms. Hence, bond formation takes place, leading to release of energy. As it is exothermic reaction, ΔH is negative (-ve).
In the reaction, 2 moles of atoms having higher randomness combine to form 1 mole of molecules, having lesser randomness.
Therefore, ΔS is negative (–ve), which is represented as $S_{products} - S_{reactants}$.

19. For the reaction
$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$
$\Delta U^\theta = -10.5$ kJ and $\Delta S^\theta = -44.1$ JK^{-1}.
Calculate ΔG^θ for the reaction, and predict whether the reaction may occur spontaneously.

19. For the given reaction,
$2\ A(g) + B(g) \rightarrow 2D(g)$
$\Delta n_g = 2 - (3)$
$= -1$ mole
Substituting the value of ΔU^θ in the expression of ΔH:
$\Delta H^\theta = \Delta U^\theta + \Delta n_g RT$
$= (-10.5\ \text{kJ}) - (-1)\ (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\ (298\ \text{K})$
$= -10.5\ \text{kJ} - 2.48\ \text{kJ}$
$\Delta H^\theta = -12.98\ \text{kJ}$
Substituting the values of 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^θ? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

20. Using,
$\Delta G = -RT\ln K$
$\Rightarrow \Delta G = -2.303RT\log K$
ΔG = change in Gibbs energy
$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1} – constant
T = temperature; given as 300K
K = equilibrium constant
Substituting the above values
$\Delta G = -2.303 \times 8.314 \times 10^{-3} \times 300 \times \log 10$

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

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

$$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{(g)}; \Delta_r H^\theta = 90 \text{ kJ mol}^{-1}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)} : \Delta_r H_\theta = -74 \text{ kJ mol}^{-1}$$

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

22. It is given that a energy of 286 kJ is released per mole, when water is formed under standard conditions. This means 286 kJ of energy is absorbed by the surroundings in this process. So,

$q = - \Delta H = 286 \text{ kJ mol}^{-1}$

$\Delta S = q/T$

$\Rightarrow \Delta S = 286 \text{ kJ}/ 298 \text{ K}$

$\Rightarrow \Delta S = 959.73 \text{ J mol}^{-1}\text{K}^{-1}$

T = Temperature = 298K.