Chemical Energetics

Q. 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.

Ans. 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.

Q. 2. For the process to occur under adiabatic conditions, the correct condition is: (i) $\Delta T = 0$ (ii) $\Delta p = 0$ (iii) $\Delta q = 0$ (iv) $w = 0$.

Ans. A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions, $q = 0$.Therefore, alternative (iii) is correct.

Q. 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.

Q. 4. 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,

$$\text{(i)}\quad CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$
$$\Delta H = -890.3 \text{ kJ mol}^{-1}$$

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

$$\text{(iii)}\quad 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$
$$\Delta H = -285.8 \text{ kJ mol}^{-1}$$

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

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$
$$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_c H_{H_2} - \Delta_c H_{CO_2}$$

$$= \left[-393.5 + 2(-285.8) - (-890.3)\right] \text{ kJ mol}^{-1}$$
$$= -74.8 \text{ kJ mol}^{-1}$$

Enthalpy of formation of $CH_4(g)$ = – 74.8 kJ mol^{-1}
Hence, alternative (i) is correct.

Q. 5. 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

Ans. For a reaction to be spontaneous, ΔG should be negative. ΔG = ΔH – TΔS According to the question, for the given reaction, ΔS = positive ΔH = negative (since heat is evolved). Therefore ΔG = negative Hence, the reaction is spontaneous at any temperature. So, alternative (iv) is correct.

Q. 6. 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,
ΔE = q + W (i)

Where,ΔE = 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
ΔE = 701 J + (–394 J)
ΔE = 307 J
Hence, the change in internal energy for the given process is 307 J.

Q. 7. The reaction of cyanamide, $NH_22CN_{(s)}$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$$NH_2CN_{(g)} + \frac{3}{2}O_{2(g)} \longrightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

Ans. Enthalpy change for a reaction (ΔH) is given by the expression,
ΔH = ΔE + Δn_gRT, where, ΔE = change in internal energy Δn_g = change in number of moles.
For the given reaction,
Δng = Σn_g (products) – Σn_g (reactants) = (2 – 2.5) moles
Δng = –0.5 moles And, ΔE = –742.7 kJ mol^{-1} T = 298 K R = 8.314 × 10–3 kJ mol^{-1} K^{-1}
Substituting the values in the expression of ΔH:
ΔH = (–742.7 kJ mol^{-1}) + (–0.5 mol) (298 K) (8.314 × 10^{-3} kJ mol^{-1} K^{-1}) = –742.7 – 1.2
ΔH = –743.9 kJ mol^{-1}

Q. 8. 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. 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

Q. 9. 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}

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

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

= (75.3 J mol^{-1} K^{-1}) (0 – 10)K + (–6.03 × 10^3 J mol^{-1}) + (36.8 J mol^{-1} K^{-1}) (–10 – 0)K
= –753 J mol^{-1} – 6030 J mol– 368 J mol^{-1}
= –7151 J mol^{-1}
= –7.151 kJ mol^{-1}
Hence, the enthalpy change involved in the transformation is –7.151 kJ mol^{-1}.

Q. 10. 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.

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

$$\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)} \qquad \Delta_f H = -393.5\text{ kJ mol}^{-1}$$

(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

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

= –314.8 kJ mol^{-1}

Q. 11. Enthalpies of formation of $CO_{(g)}$, $CO_{2(g)}$, $N_2O(g)$ and $N_2O4_{(g)}$ are -110 kJ mol^{-1}, $-$ 393 kJ mol^{-1}, 81 kJ mol^{-1} and 9.7 kJ mol^{-1} respectively. Find the value of ΔrH for the reaction:

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

Ans. ΔrH for a reaction is defined as the difference between ΔfH value of products and ΔfH value of reactants.

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

For the given reaction,

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

$$\Delta_r H = \left[\left\{\Delta_f H(N_2O) + 3\Delta_f H(CO_2)\right\} - \left\{\Delta_f H(N_2O_4) + 3\Delta_f H(CO)\right\}\right]$$

Substituting the values of $\Delta_f H$ for N_2O, CO_2, N_2O_4 and CO from the question, we get:

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

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

Hence, the value of $\Delta_r H$ for the reaction is.

Q. 12. Given

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ $\Delta rH^\theta = -92.4$ 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 $NH_{3(g)}$,

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

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

$= \frac{1}{2} \Delta rH^\theta$

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

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

Q. 13. Calculate the standard enthalpy of formation of $CH_3OH_{(i)}$ from the following data:

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

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

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

Ans. The reaction that takes place during the formation of $CH_3OH_{(i)}$ can be written as:

$$C_{(s)} + 2H_2O_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CH_3OH_{(l)} \ (1)$$

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

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

$$\Delta_f H^\theta [CH_3OH_{(l)}] = \Delta_c H^\theta + 2\Delta_f H^\theta [H_2O_{(l)}] - \Delta_r H^\theta$$

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

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

$$\therefore \Delta_f H^\theta [CH_3OH_{(l)}] = -239 \text{ kJ mol}^{-1}$$

Q. 14. Calculate the enthalpy change for the process

$CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ and calculate bond enthalpy of C–Cl in $CCl_{4(g)}$

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

.

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

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

$\Delta aH^\theta (Cl_2) = 242$ kJ mol−1

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

(i) $CCl_{4(l)} \longrightarrow CCl_{4(g)}$ $\Delta_{Vap} H^\theta = 30.5 \text{ kJ mol}^{-1}$

(ii) $C_{(s)} \longrightarrow C_{(g)}$ $\Delta aH^\theta = 715.0 \text{ kJ mol}^{-1}$

(iii) $Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ $\Delta aH^\theta = 242 \text{ kJ mol}^{-1}$

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

Enthalpy change for the given process $CCl_{4(g)} \longrightarrow C_{(g)} + 4Cl_{(g)}$, can be calculated using the following algebraic calculations as:

Equation (ii) + 2 × Equation (iii) – Equation (i) – Equation (iv)
$\Delta H = \Delta aH^{\theta}(C) + 2\Delta aH^{\theta}(Cl2) - \Delta_{Vap} H^{\theta} - \Delta_f H$
$= (715.0\ kJ\ mol^{-1}) + 2(242\ kJ\ mol^{-1}) - (30.5\ kJ\ mol^{-1}) - (-135.5\ kJ\ mol^{-1})$

$\Delta H = 1304\ kJ\ mol^{-1}$
Bond enthalpy of C–Cl bond in $CCl_{4(g)}$

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

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

Q. 15. For an isolated system, $\Delta U = 0$, what will be ΔS?

Ans. ΔS will be positive i.e., greater than zero.
Since $\Delta E = 0$, ΔS will be positive and the reaction will be spontaneous.

Q. 16. 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:

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

$$= \frac{\Delta H}{\Delta S}$$ ($\Delta G = 0$ 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.

Q. 17. For the reaction, $2Cl_{(g)} \rightarrow Cl2_{(g)}$, what are the signs of ΔH and ΔS ?

Ans. ΔH and ΔS are negative’ The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. 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.

Q. 18. For the reaction
$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

$\Delta E^\theta = -10.5$ kJ and $\Delta S^\theta = -44.1\ JK^{-1}$.Calculate ΔG^θ for the reaction, and predict whether the reaction may occur spontaneously.

Ans. For the given reaction, $2\ A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$
$\Delta ng = 2 - (3) = -1$ mole
Substituting the value of ΔEθ in the expression of ΔH:
$\Delta H^\theta = \Delta E^\theta + \Delta ngRT$
$= (-10.5\ kJ) - (-1)\ (8.314 \times 10-3\ kJ\ K^{-1}\ mol^{-1})\ (298\ K)$
$= -10.5\ kJ - 2.48\ kJ$
$\Delta H^\theta = -12.98\ kJ$
Substituting the values of ΔH^θ and ΔS^θ in the expression of
ΔG^θ: $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
$= -12.98\ kJ - (298\ K)\ (-44.1\ J\ K^{-1})$
$= -12.98\ kJ + 13.14\ kJ$
$\Delta G^\theta = +\ 0.16\ kJ$
Since ΔG^θ for the reaction is positive, the reaction will not occur spontaneously.

Q. 19. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ? $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 300\ K$.

Ans. From the expression, $\Delta G^\theta = -2.303\ RT\ logKeq$ ΔG^θ for the reaction,
$= (2.303)\ (8.314\ JK^{-1}\ mol^{-1})\ (300\ K)\ log10$
$= -5744.14\ Jmol^{-1}$
$= -5.744\ kJ\ mol^{-1}$

Q. 20. Comment on the thermodynamic stability of $NO_{(g)}$, given.

$\frac{1}{2}\ N2_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)}$; $\Delta rH^\theta = 90\ kJ\ mol^{-1}$

$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g)}$: $\Delta rH^\theta = -74\ kJ\ mol^{-1}$

Ans. The positive value of ΔrH 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 ΔrH 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 $NO_{2(g)}$.

Q. 21. Calculate the entropy change in surroundings when 1.00 mol of $H_2O_{(i)}$. is formed under standard conditions. $\Delta_f H^\theta = -286\ kJ\ mol^{-1}$.

Ans. It is given that 286 kJ mol^{-1} of heat is evolved on the formation of 1 mol of $H_2O_{(i)}$. Thus, an equal amount of heat will be absorbed by the surroundings.

qsurr = +286 kJ mol^{-1}

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

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

ΔSsurr = 959.73 J mol^{-1} K^{-1}

Q. 22. Calculate the entropy change in surroundings when 1.00 mol of $H_2O_{(i)}$ is formed under standard conditions. $\Delta_f H^{\theta} = -286$ kJ mol^{-1}.

Ans. It is given that 286 kJ mol^{-1} of heat is evolved on the formation of 1 mol of $H_2O_{(i)}$. Thus, an equal amount of heat will be absorbed by the surroundings.

qsurr = +286 kJ mol^{-1} Entropy change (ΔSsurr) for the surroundings = $\frac{q_{surr}}{7}$

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

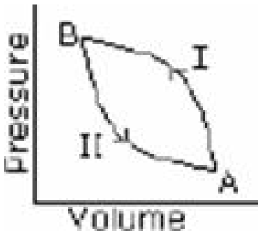
ΔSsurr = 959.73 J mol^{-1} K^{-1}

Q. 23. Describe the Ist law of thermodynamics.

Ans. This law is a corollary of law of conservation of energy. This law is based on experience. There is no theoretical proof of this law. Mathematical form of the first law of thermodynamics is ΔE = q + w.

Q. 24. How can you justify that though q and w are not state functions, yet (q + w) is a state function.

Ans.



Let the internal energies at A and B be EA and EB. If internal energy is a state function, the difference in internal energy from A to B or B to A should be same. If not, suppose the internal energy increases by an amount ΔE while going from A to B. Now suppose the internal energy decreases by an amount ΔE' while returning from B to A. Let ΔE >ΔE', that means after returning to A, an amount of energy equal to (ΔE - ΔE') has been created which is against the law of conservation of energy.

Q. 25. Derive the relationship between heat of reaction at constant temperature qp and heat of reaction at constant volume qv.

Ans- $\Delta H = \Delta E + P\Delta V$.
or $\Delta H = \Delta E + P(V_2 - V_1) = \Delta E + (PV_2 - PV_1)$ ......(1)
For ideal gas
$PV= nRT$
$PV_1 = n1RT$
$PV_2 = n_2RT$
Substituting in equation (1), we get
$\Delta H = \Delta E + (n_2RT - n_1RT)$
$= \Delta E + (n_2 - n_1)RT$.
or $\Delta H = \Delta E + \Delta n_gRT$.

Q. 26. Define the following terms: (i) System. (ii) State variables. (iii) State functions. (iv) Extensive and intensive properties. (v) Isothermal process. (vi) Adiabatic process.

Ans. (i) **System :** Part of the universe which is under investigation is called system.
(ii) **State variables:** Variables like temperature, pressure and volume etc. of a system which determines the state of a system are called state variables.
(iii) **State functions :** Properties which depend upon the state of a system are called state functions.
(iv) **Extensive and intensive properties :** Properties which depend upon the quantity of a substance in a system are extensive properties and those which depend upon the nature of the substance are called intensive properties.
(v) **Isothermal process :** A process which takes place keeping the temperature of the system constant is called isothermal process.
(vi) **Adiabatic process :** A process, which takes place in such a manner that flow of heat from one to another part of the system does not take place, is called adiabatic process.

Q. 27. What are the limitations of first law of thermodynamics? State second law of thermodynamics in as many ways as you can.

Ans. First law of thermodynamics has the limitation that it merely indicates that in any process there is an exact equivalence between various forms of energy. It provides no information concerning the spontaneity or feasibility of the process. Various statements of second law of thermodynamics are:
(i) All spontaneous processes (or naturally occurring processes) are thermodynamically irreversible.
(ii) Without the help of an external agency, a spontaneous process cannot be reversed.
(iii) The complete conversion of heat into work is impossible without leaving some effect elsewhere.
(iv) The entropy of the universe is continuously increasing.

Q. 28. Explain what is meant by Gibb's free energy change. "The sign of free energy is very important". Justify.

Ans. Gibb's free energy change which is represented by ΔG is related to enthalpy and entropy changes by the following equations - $\Delta G = \Delta H - T\Delta S$
(i) If ΔG is -ve, the forward reaction is spontaneous.
(ii) If ΔG is zero, the reaction is in equilibrium.
(iii) If ΔG is +ve, the forward process is non-spontaneous.

Q. 29. Define entropy. Why is it a state function? Explain the effect of increased temperature on the entropy of a substance.

Ans. Entropy is the measure of disorder of a system. Its value depends upon the state of the system, hence it is a state function. On increasing the temperature, the molecular motion increases. Hence, entropy will increase with increase of temperature.