PHYSICAL CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 59

Total Marks : 69

Max. Time : 69 min.

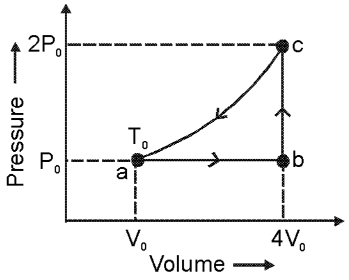
Topic : Thermodynamics & Thermochemistry

Type of Questions		**M.M., Min.**
Single choice Objective ('–1' negative marking) Q.1 to Q.14	(3 marks, 3 min.)	[42, 42]
Multiple choice objective ('–1' negative marking) Q.15 to Q.17	(4 marks, 4 min.)	[12, 12]
Assertion and Reason (no negative marking) Q.18 to Q.22	(3 marks, 3 min.)	[15, 15]

1. An isolated system is that system in which :
(A) there is exchange of energy with the surroundings.
(B) there is exchange of mass and energy with the surroundings.
(C) There is no exchange of mass and energy with the surroundings.
(D) There is exchange of mass but not energy with surroundings.

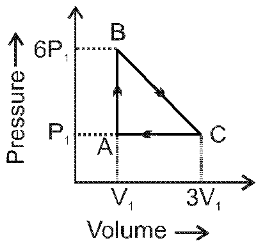
2. As per the First Law of thermodynamics, which of the following statement would be appropriate :
(A) Energy of the system remains constant.
(B) Energy of the surroundings remains constant.
(C) Entropy of the universe is always increasing in an irreversible process.
(D) Energy of the universe remains constant.

3. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then the change in the internal energy of gas from a to b and b to c is respectively :



(A) $\frac{9P_oV_o}{2}$, 6 RT$_o$ (B) $\frac{9P_oV_o}{2}$, 10 RT$_o$ (C) $\frac{15P_oV_o}{2}$, 6 RT$_o$ (D) $\frac{15P_oV_o}{2}$, 10 RT$_o$

4. An ideal gas is taken around the cycle ABCA as shown in P-V diagram. The net work done during the cycle is equal to :



(A) 7 P_1V_1 (B) –5 P_1V_1 (C) 5 P_1V_1 (D) –7 P_1V_1

5. 1 mole of SO_2 gas at 27° C is expanded in reversible adiabatic condition to make volume 8 times. Final temperature and work done respectively are: (take $2^{1.2} = 2.3$)
(A) 150 K, 900 cal   (B) 150 K, 750 cal   (C) 130.5 K, 847.5 cal   (D) 130.5 K, 508.5 cal

6. The work done in an adiabatic process on an ideal gas by a constant external pressure would be :

(A) Zero (B) ΔE (C) ΔH (D) q

7. One mole of an ideal monoatomic gas at temperature T and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions. Then final temperature of gas will be :

(A) $T + \frac{2}{3 \times 0.0821}$ (B) $T - \frac{2}{3 \times 0.0821}$ (C) $\frac{T}{2^{5/3-1}}$ (D) $\frac{T}{2^{5/3+1}}$

8. One mole of an ideal gas $\left(C_V = \frac{3}{2}R\right)$ at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is :

(A) 228 K (B) 240 K (C) 248.5 K (D) 200 K

9. The enthalpy of formation of ammonia = 46.0 kJ mol^{-1}. The enthalpy change for following reaction is :

$$2NH_3 \longrightarrow N_2 + 3H_2$$

(A) –92.0 kJ (B) 46.0 kJ (C) –46.0 kJ (D) 92.0 kJ

10. The standard enthalpy of formation of B_2O_3 is equal to :

(A) ΔH°_C (B(s)) (B) 1/2 ΔH°_C (B(s))
(C) $2\Delta H^\circ_C$ (B(s)) (D) 3/2 ΔH°_C (B(s))

11. Calculate the average O–H bond energy in H_2O with the help of following data :

(1) $H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$; $\Delta H = +\ 40.5$ KJ mol^{-1}

(2) $2H_{(g)} \longrightarrow H_{2\,(g)}$; $\Delta H = -\ 435.0$ KJ mol^{-1}

(3) $O_{2(g)} \longrightarrow 2O_{(g)}$; $\Delta H = +\ 489.5$ KJ mol^{-1}

(4) $2H_{2\,(g)} + O_{2\,(g)} \longrightarrow 2H_2O(\ell)$; $\Delta H = -\ 571.5$ KJ mol^{-1}

(A) 217.75 KJ mol^{-1} (B) 217.25 KJ mol^{-1} (C) 462.5 KJ mol^{-1} (D) 925 KJ mol^{-1}

12. For the equations :

$C(\text{diamond}) + 2H_2(g) \rightarrow CH_4(g)$; ΔH_1 and $C(g) + 4H(g) \rightarrow CH_4(g)$; ΔH_2

Select the correct option :

(A) $\Delta H_1 = \Delta H_2$ (B) $\Delta H_1 > \Delta H_2$
(C) $\Delta H_1 < \Delta H_2$ (D) Nothing can be said with certainty.

13. Enthalpy of polymerisation of ethylene, as represented by the reaction, $nCH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$ is –100 kJ per mole of ethylene. Given that bond enthalpy of C=C bond is 600 kJ mol^{-1}. Enthalpy of C–C bond (in kJ mol) will be :

(A) 500 (B) 350 (C) 400 (D) indeterminate

14. 1 mole of a diatomic ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy of gas during expansion (in JK^{-1} mol^{-1}) :

(A) R ln 10 (B) 1.5 R ln 10 (C) 2.5 R ln 10 (D) None of these

15.* If a process is both endothermic and spontaneous, then :

(A) $\Delta S_{sys} > 0$ (B) $\Delta S_{sys} < 0$ (C) $\Delta S_{univ} > 0$ (D) $\Delta S_{univ} < 0$

16.* The enthalpy change for a given reaction at 298 K is – x J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature :

(A) can be negative but numerically larger than x/298.
(B) can be negative but numerically smaller than x/298.
(C) cannot be negative.
(D) can be positive.

17.* The value of $\Delta H_{transition}$ of C (graphite) $\longrightarrow$ C (diamond) is 1.9 kJ/mol at 25°C entropy of graphite is higher than entropy of diamond. This implies that :
(A) C (diamond) is more thermodynamically stable than C (graphite) at 25°C.
(B) C (graphite) is more thermodynamically stable than C (diamond) at 25°C.
(C) Diamond will provide more heat on complete combustion at 25°C.
(D) $\Delta G_{transition}$ of C (diamond) $\longrightarrow$ C (graphite) is –ve.

Assertion / Reason

DIRECTIONS :

The following questions consist of two statements one labelled ASSERTION and the another labelled REASON . Select the correct answers to these questions from the codes given below :
(A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
(B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion.
(C) Assertion is true but Reason is false.
(D) Assertion is false but Reason is true.

18. **Assertion :** The increases in internal energy (ΔE) for the vaporisation of one mole of water at 1 atm and 373 K is zero.
Reason : For all isothermal processes on perfect gases, $\Delta E = 0$.

19. **Assertion :** The enthalpy of formation of $H_2O(\ell)$ is greater than that of H_2O (g) in magnitude.
Reason : Enthalpy change is negative for the condensation reaction :

$$H_2O\,(g) \longrightarrow H_2O(\ell)$$

20. **Assertion :** Enthalpy of neutralisation of $HClO_4$ with NaOH is same as that of HCl with NaOH.
Reason : Both HCl and $HClO_4$ are strong acids.

21. **Assertion :** Decrease of free energy during a process under constant temperature and pressure provides a criteria of its spontaneity.
Reason : A spontaneous change must have positive sign of ΔS_{system}.

22. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25° C are –156 and + 49 KJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° is –119 kJ mol^{-1}. Use these data to estimate the resonance energy of benzene.

Answer Key

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1.	(C)	**2.**	(D)	**3.**	(A)	**4.**	(C)	**5.**	(A)
6.	(B)	**7.**	(B)	**8.**	(A)	**9.**	(D)	**10.**	(C)
11.	(C)	**12.**	(B)	**13.**	(B)	**14.**	(D)	**15.**	(AC)
16.	(BD)	**17.**	(BCD)	**18.**	(D)	**19.**	(A)	**20.**	(A)
21.	(C)	**22.**	–152 kJ mole^{-1}						

Hints & Solutions

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2. First law of thermodynamics is the law of conservation of energy.

4. Work done by the gas in the cyclic process = Area bounded (ABCA) = $5P_1V_1$

6. From I law of thermodynamics $\Delta E = Q + W$
where Q = 0 for adiabatic process.

7. $\Delta U = W$

$$nCv\,(T_2 - T) = -P \times (V_2 - V_1)$$

$$\frac{3}{2}\,R\,(T_2 - T) = -1 \qquad \Rightarrow \qquad \therefore \qquad T_2 = T - \frac{2}{3 \times 0.0821}$$

8. $q = 0 \qquad \therefore \qquad \Delta U = w$

$$\Rightarrow nC_{v,m}\,(T`_2 - T_1) = -P_{ext}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$\therefore\; C_{v,m}\,[T_2 - T_1] = P_{ext}\,.\,R\left[\frac{T_1}{P_1} - \frac{T_2}{P_2}\right] \qquad \Rightarrow \frac{3}{2}\,R\,[T_2 - 300] = 2 \times R\left[\frac{300}{5} - \frac{T_2}{2}\right] \qquad \Rightarrow \qquad T_2 = 228\text{ K}$$

9. When one mole of NH_3 is formed from its constituent elements the enthalpy change = – 46.0 kJ
Therefore when one mole of NH_3 decompose to give its constituent elements enthalpy change = 46.0 kJ
$\Rightarrow$ When 2 mole NH_3 decompose, enthalpy change = 2 × 46 = 92.0 kJ

10. Combustion reaction of solid boron

$$B(s) + \frac{3}{4}O_2(g) \longrightarrow \frac{1}{2}B_2O_3$$

$$\Delta H^\circ_r = \Delta H^\circ_c = \frac{1}{2}\Delta H^\circ_f\,(B_2O_3,\,s) - \Delta H^\circ_f\,(B,\,s) - \frac{3}{4}\Delta H^\circ_f\,(O_2,\,g)$$

ΔH_f° of element in stable state of aggregation is assumed to be zero.

$$\boldsymbol{\Delta H^\circ_c = \frac{1}{2}\Delta H^\circ_f\,(B_2O_3)}$$

11. (1) $H_2O(\ell) \longrightarrow H_2O(g)$ $\qquad \Delta H = 40.6$ KJ/mole

(2) $2H(g) \longrightarrow H(g)$ $\qquad \Delta H = -435.0$ KJ/mole

(3) $O_2(g) \longrightarrow 2\,O_2(g)$ $\qquad \Delta H = -49836$ KJ/mole

(4) $\Delta H = -571.6$ KJ/mole

$$\begin{tikzcd} 2H_2(g) + \arrow[d] & O_2(g) \arrow[r] \arrow[d] & H_2O(\ell) \\ 4H(g) + & 2O(g) \arrow[ur] & \end{tikzcd}$$

(1) Calculation of $\Delta H^\circ_f(H_2O,\ell)$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)\ \Delta H = -571.6\ \text{KJ/mole}$$

$$\Delta H^\circ_r = 2\Delta H^\circ_F(H_2O,\ell) - 2\underset{\text{Zero}}{\underset{\downarrow}{\Delta H^\circ_F\{H_2,(g)\}}} - \underset{\text{Zero}}{\underset{\downarrow}{\Delta H^\circ_F(O_2, g)}}$$

$-571.6 = 2\Delta H^\circ_F(H_2O,\ell)$ so $\Delta H^\circ_F(H_2O,\ell) = -285.5$

(2) Calculation of $\Delta H^\circ_F(H_2O, g)$

$H_2O(\ell) \longrightarrow H_2O(g)$ $\Delta H = 40.6$

$\Delta H_r = \Delta H^\circ_F(H_2O, g) - \Delta H^\circ(H_2O,\ell)$

$\Delta H^\circ_F(H_2O, g) = \Delta H^\circ_F(H_2O,\ell) + \Delta H_r$

$= -285.8 + 40 = -245.8$

(3)

$$\begin{tikzcd}
H_2(g) \arrow[d] & + & \frac{1}{2}O_2(g) \arrow[d] \arrow[r] & H_2O(g) \\
2H(g) & + & O(g) \arrow[ru] &
\end{tikzcd}$$

$\Delta H = -245.8$

$\Delta Hr = \epsilon_{H-H} + \frac{1}{2}\epsilon_{O-O} - 2\epsilon_{O-H} \Rightarrow -245.8 = +435 + \frac{1}{2}(489.6) - 2 \times \epsilon_{O-H}$

$2\epsilon_{O-H} = 435 + 244.8 + 245.8 \Rightarrow 2\epsilon_{O-H} = 925.6$

$\epsilon_{O-H} = \mathbf{462.5}$

13. $nCH_2 = CH_2 \longrightarrow (-CH_2-CH_2-)_n$ $\Delta H = -100$ KJ/mole

$n[C=C] + n[C-H]4 - n[C-H]4 - n[C-C] \times 2 = -100$

$n[C=C] - 2n[C-C] = -100 \Rightarrow [C=C] - 2[C-C] = -100$

$\Rightarrow +600 - 2[C-C] = -100 \Rightarrow -2[C-C] = -700$ KJ/mole $\Rightarrow (C-C) = -350$

14. Process is Reversible and adiabatic (Q = 0)

So, $\Delta S = 0$

15.* Process is endothermic i.e., $\Delta H = +$ ve and process is also spontaneous i.e., $\Delta G = -$ ve

Hence, from Gibbs-Helmholtz equation

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

ΔS must be positive so that ΔG may be negative.

16.* It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0. If ΔH is – ve, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has to be less than $\frac{\Delta H}{T}$ i.e., $\frac{x}{298}$.

18. The assertion that the increase in internal energy for vaporisation of one mole of water at 1 atm and 373 K is zero is true because for all isothermal process change in internal energy is zero.

19. $H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(g)$; $\Delta H_f = -\varepsilon_1$, ...(i)

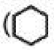
$H_2O(g) \longrightarrow H_2O(l)$; $\Delta H_f = -\varepsilon_2$, ...(ii)

and (i) and (ii).

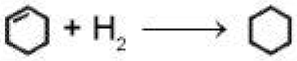
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$. ; $\Delta H = -(\varepsilon_1 + \varepsilon_2)$.

20. Heat of neutralisation for strong acid and strong base combination is constant is equal to – 13.7 Kcal or – 57.1 KJ.

22. Enthalpy of formation of 3 carbon-carbon double bonds

$= \Delta H_F$ () $- \Delta H_f$ ()

$= -156 - (+49)$ kJ $= -205$ kJ.

Given that,  $\Delta H = 119$ kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

$= 3 \times (-119)$ kJ $= -357$ kJ.

$\therefore$ resonance energy of benzene $= -357 - (-205)$ kJ $= -152$ kJ mole^{-1} ®