PHYSICAL CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 55

Total Marks : 37

Max. Time : 42 min.

Topic : Thermodynamics & Thermochemistry

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.6 to Q.8	(3 marks, 3 min.)	[9, 9]
Subjective Questions ('–1' negative marking) Q.1, 2, 5, 9, 10	(4 marks, 5 min.)	[20, 25]
Multiple choice objective ('–1' negative marking) Q.3 to Q.4	(4 marks, 4 min.)	[8, 8]

1. A sample of certain mass of an ideal polyatomic non-linear gas is expanded against constant pressure of 1 atm adiabatically from volume 2 L, pressure 6 atm and temperature 300 K to a state, where its final volume is 8 L. Then calculate entropy change of system (in J / K) in the process : (Neglect vibrational degrees of freedom) [1L atm = 100 J, log 2 = 0.3, log 3 = 0.48, log e = 2.3]

2. 2 moles of an ideal monoatomic gas undergo a reversible process for which P^2V = constant. The gas sample is made to expand from initial volume of 1L to final volume of 4L starting from initial temperature of 300K. Find the value of ΔS_{sys} for the above process. Report your answer as 'X' where $\Delta S_{sys} = XR\ell n2$.

3.* For Isothermal expansion against constant external pressure of an ideal gas :

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

4.* For an adiabatic free expansion of an ideal gas against vacuum, which of the following parameters has/ have zero value :

(A) q
(B) ΔH
(C) $\Delta S_{surr.}$
(D) $\Delta S_{sys.}$

5. How many of the given statements are correct :

I : Molar entropy of a substance follows the order $(S_m)_{Solid} < (S_m)_{liquid} < (S_m)_{gas}$
II: Entropy change of system for the reaction $H_2(g) \longrightarrow 2H(g)$ is +ve.
III: Molar entropy of a non-crystalline solid will be zero at absolute zero.
IV: If the path of an irreversible process is reversed, then both system and surroundings shall be restored to their orginal states.
V : Refractive index and molarity are intensive properties.

6. The spontaneous nature of a reaction is impossible if :

(A) ΔH is +ve and ΔS is also +ve
(B) ΔH is – ve and ΔS is also – ve
(C) ΔH is – ve ; ΔS is + ve
(D) ΔH is + ve ; ΔS is – ve

7. If a chemical reaction is non-spontaneous at high temperatures and spontaneous at low temperatures, then:

(A) $\Delta H > 0$ and $\Delta S > 0$
(B) $\Delta H > 0$ and$\Delta S < 0$
(C) $\Delta H < 0$ and $\Delta S > 0$
(D) $\Delta H < 0$ and $\Delta S < 0$

8. For the process $H_2O(\ell)$ (1 bar, 373 K) $\rightleftharpoons$ $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is:

(A) $\Delta G = 0$
(B) $\Delta S > 0$
(C) $\Delta H > 0$
(D) $\Delta G = -ve$

9. For a perfectly crystalline solid, $(C_P)_m = aT^3$, where a is a constant. If $(C_P)_m$ at 10K is 0.375 J/K-mol, then find the value of molar entropy at 20K (in J/K-mol).

10. What is the free energy change (ΔG) in KCal, when 144 g of water at 100ºC and 1 atm pressure in converted into steam at 100ºC and 4 atm pressure ? (Take R = 2 Cal/K/mole, ℓn 2 = 0.7).
Give your answer rounding it off to the nearest whole number.

Answer Key

DPP No. # 55

1.	3.312 J/K	**2.**	7	**3.***	(A,B,C)	**4.***	(A,B,C)	**5.**	3
6.	(D)	**7.**	(D)	**8.**	(A,B,C)	**9.**	1	**10.**	8

Hints & Solutions

DPP No. # 55

1. $W = -P_{ext}(V_f - V_i) = -(1\text{ atm})(8-2)\text{ L} = -6\text{ L atm}$

as $q = 0$ so

$$\Delta E = W = n\left(\frac{6}{2}R\right)\left(\frac{P_fV_f}{nR} - \frac{P_iV_i}{nR}\right)$$

Here $\Delta E = nC_V\Delta T$

$$3\,(8\,P_f - 12) = -6$$

therefore, $8\,P_f = 12 - \frac{6}{3} = 10 \quad \Rightarrow \quad P_f = \frac{5}{4}$ atm

$$\text{so,} \quad \frac{T_f}{T_i} = \frac{\frac{5}{4}\times 8}{6\times 2} = \frac{10}{12}$$

$$\text{so} \quad \Delta S = 3\,\frac{12}{300}\ln\left(\frac{10}{12}\right) + \frac{12}{300}\ln 4 = 3.312\text{ J/K}$$

2. $P^2V = \text{constant} \;\therefore\; \left(\frac{nRT}{V}\right)^2 V = \text{constant} \;\therefore\; \frac{T^2}{V} = \text{constant}$

$$\therefore \quad \frac{T_1^2}{V_1} = \frac{T_2^2}{V_2} \;\therefore\; \frac{(300)^2}{1} = \frac{T_2^2}{4} \;\therefore\; T_2 = 600\text{K}$$

$$\Delta S_{sys} = nC_V\ell n\,\frac{T_2}{T_1} + nR\ell n\,\frac{V_2}{V_1} = 2\times\frac{3R}{2}\,\ell n\left(\frac{600}{300}\right) + 2\times R\ell n\left(\frac{4}{1}\right) = 7R\ell n\,2$$

$\therefore \quad X = 7$

4.* For isothermal free expansion of an ideal gas,

$\Delta T = 0$ Therefore, $\Delta H = \Delta E = 0$

Also, $W = 0$ (since $P_{ext} = 0$)

Therefore, from first law, $q = 0$. Therefore, $\Delta S_{surr.} = 0$.

Since gas is expanding, $\Delta S_{sys.} > 0$.

5. **I.** Molar entropy of gas is much greater than that of solid and liquid.

II. Entropy change is positive if Δn_g is positive.

III. Molar entropy of a crystalline solid will be zero at absolute zero.

IV. In irreversible process both system and surroundings are not restored if path is reversed.

V. Refractive index and molarity are intensive properties.

7. If $\Delta H < 0$ and $\Delta S < 0$, then reaction is non-spontaneous at high temperatures and spontaneous at low temperatures.

8. $H_2O(\ell, 1\text{bar}, 373K) \longrightarrow H_2O(g, 1\text{bar}, 373\ K)$

$\Delta S > 0$
$\Delta H > 0$
$\Delta G = 0$

9. $(C_p)_m = aT^3 \therefore 0.375 = a\,(10)^3 \therefore a = \frac{3}{8} \times 10^{-3}$

$$S_m = \int_0^{20} \frac{(C_P)_m dT}{T} = \int_0^{20} aT^2 dT = \left.\frac{aT^3}{3}\right|_0^{20} = \frac{8000a}{3} = \frac{8000}{3} \times \frac{3}{8} \times 10^{-3} = 1\text{J/K–mol}$$

10. $\Delta G = nRT\ \ell n \left(\frac{P_f}{P_i}\right) = \left(\frac{144}{18}\right) \times \frac{2}{1000} \times 373 \ell n \left(\frac{4}{1}\right) \approx 8\text{Kcal.}$