PHYSICAL / INORGANIC CHEMISTRY

DPP
DAILY PRACTICE PROBLEMS

DPP No. 24

Total Marks : 45

Max. Time : 49 min.

Topic : Thermodynamics (IInd Law)

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.7	(3 marks, 3 min.)	[21, 21]
Multiple choice objective ('–1' negative marking) Q.8 to Q.9	(4 marks, 4 min.)	[8, 8]
Subjective Questions ('–1' negative marking) Q.10 to Q.13	(4 marks, 5 min.)	[16, 20]

1. **(a)** Which of the following processes represent an increase in entropy of the system :

(A) Polymerisation of ethene gas forming polyethene.

(B) SO_3 gas on heating breaks up to form SO_2 gas and O_2 gas.

(C) Condensation of dew on leaves in winters.

(D) Crystallisation of $CuSO_4.5H_2O$ from solution.

(b) Which of the following reactions is associated with the most negative change in entropy ?

(A) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ (B) $C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$

(C) $C(s) + O_2 \longrightarrow CO_2(g)$ (D) $2NO_2(g) \longrightarrow N_2O_4(s)$

(c) In which of the following cases entropy decreases :

(A) Solid changing to liquid (B) Expansion of a gas

(C) Crystal dissolves (D) Polymerisation

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

(A) ΔH is +ve : ΔS in also +ve (B) ΔH is –ve; ΔS is also –ve

(C) ΔH is –ve; ΔS in +ve (D) ΔH is +ve; ΔS in –ve

3. Two moles of an ideal diatomic gas at 27ºC is made to expand reversibly and adiabatically to 4 times its initial volume. The change in entropy of the system during expansion is : (Given : R = 2 cal/K/mole, $\log_{10}2 = 0.3$, $\log_{10}3 = 0.48$)

(A) 5.6 Cal/k (B) 11.2 Cal/k (C) 2.8 Cal/k (D) None of these

4. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300ºC reversibly and isochorically is :

(A) $3\,R\,\ln\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R\,\ln\left(\frac{573}{473}\right)$ (C) $3R\,\ln\left(\frac{573}{473}\right)$ (D) $\frac{3}{2}R\,\ln\left(\frac{573}{473}\right)$

5. What is the change in entropy when 2.5 g of water is heated from 27ºC to 87ºC ? Assume that the heat capacity is constant (specific heat of water = 4.2 J/g-K, ln (1.2) = 0.18)

(A) 16.6 J/K (B) 9 J/K (C) 34.02 J/K (D) 1.89 J/K

6. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and $\Delta H = -436.8$ J mol^{-1} for the transition. Assume the surroundings to be an ice-water bath at 0ºC :

(A) – 1.09 JK^{-1} (B) 1.47 JK^{-1} (C) – 0.22 JK^{-1} (D) 0.41 JK^{-1}

7. One mole of an ideal monoatomic gas at 27ºC is subjected to a reversible isoentropic compression until final temperature reached to 327ºC. If the initial pressure was 1.0 atm, then find the value of ln P_2: (Given : ln 2 = 0.7).

(A) 1.75 atm (B) 0.176 atm (C) 1.0395 atm (D) 2.0 atm

8.* **(a)** For an isothermal free expansion of an ideal gas against vacuum, which of the following parameters have zero value :

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

(b) 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) $\Delta S_{surr} = 0$

(c) For reversible adiabatic compression of an ideal gas :

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

9.* 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) ΔG = –ve (B) $\Delta S > 0$ (C) $\Delta H > 0$ (D) $\Delta G = 0$

10. A sample of certain mass of an ideal polyatomic gas is expanded against constant pressure of 1 atm adiabatically from volume 2 L, pressure 6 atm and temperature 300 K to state where its final volume is 8L. Then calculate entropy change (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]

11. **(a)** The enthalpy of vapourisation of liquid diethyl ether is 26 kJ/mol at its boiling point (35°C). Calculate ΔS for conversion of : (i) liquid to vapour, and (ii) vapour to liquid at 35°C.

(b) Calculate the value of ΔG at 700 K for the reaction : nx $\longrightarrow$ mB. Given that the value of ΔH = –113 KJ/mol and ΔS = –145 JK^{-1} mol^{-1}.

12. **(a)** For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; ΔH = –95.4 KJ and ΔS = –198.3 JK^{-1}.

Calculate the maximum temperature at which the reaction will proceed in forward direction.

(b) A certain reaction is non-spontaneous at 298 K. The entropy change during the reaction is 121 J/K. Is the reaction endothermic or exothermic ? What is the minimum value of ΔH for the reaction ?

13. For oxidation of iron,

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

entropy change is –549.4 JK^{-1} mol^{-1} at 298 K. Inspite of negative entropy change of this reaction. The reaction is spontaneous, why ? Justify your answer (Given : $\Delta_r H°$ = –1648 KJ/mol).

Answer Key

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1.	**(a)** (B)	**(b)** (D)	**(c)** (D)	**2.**	(D)	**3.**	(D)		
4.	(C)	**5.**	(D)	**6.**	(D)	**7.**	(A)		
8.	**(a)** (A,B,C)	**(b)** (A,B,C)	**(c)** (C,D)			**9.**	(B,C,D)	**10.**	6 J/K
11.	**(a)** (i) 84.41 JK^{-1} mol^{-1} ; (ii) –84.14 JK^{-1} mol^{-1}				**(b)** –11.50 KJ/mol.				
12.	**(a)** 481 K.	**(b)** $\Delta H_{min} = T\Delta S = 36.06$ KJ.				**13.**	$\Delta S_{total} = 4980.6\ JK^{-1}\ mol^{-1} > 0$		

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

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1. **(a)** In polymerisation of ethene gas forming polyethene and condensation of dew on leaves in winters, entropy of the system decreases.

(b) Δn_g is most – ve

(c) Polymerisation leads to more ordered structure.

3. For a reversible adiabatic process, $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$

4. $\Delta S_{gas} = n\, C_{V,m} \ln \frac{T_2}{T_1} = 2 \times \frac{3}{2} R \ln \frac{573}{473} = 3R \ln \left(\frac{573}{473}\right)$.

5. $\Delta S = mS \ln \frac{T_2}{T_1} = 2.5 \times 4.2 \ln \left(\frac{360}{300}\right) = 1.89$ J/K

6. $\Delta S_{(system)} = \frac{1 \times -436.8}{368} = -1.19\ JK^{-1}$

The ice-water bath absorbs the 436.8 J mol^{-1} at temperature 273 K.

$\therefore \quad \Delta S_{surrounding} = \frac{1 \times 436.8}{273} = 1.6\ JK^{-1}$ and $\Delta S_{(universe)} = -1.19 + 1.6 = 0.41\ JK^{-1}$

7. (A) For isoentropic process $\Delta S_{system} = 0$

$$\therefore nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 \Rightarrow \ln (P_2) = \frac{5}{2} \times \ln \left(\frac{600}{300}\right)$$

$$= 1.75 \text{ atm.}$$

8. **(a)** 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, $\Delta S_{sys.} > 0$.

9.* $H_2O(\ell, 1\text{bar}, 373K) \longrightarrow H_2O(g, 1\text{bar}, 373\ K)$
$\Delta S > 0$
$\Delta H > 0$
$\Delta G = 0$

10. $W = -P_{ext}(V_f - V_i) = -(1 \text{ atm})(8-2)\ L$
$= -6$ L atm
as $q = 0$ so

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

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

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

$$\text{so,} \quad \frac{T_f}{T_i} = \frac{\frac{5}{4} \times 3}{6 \times 2} = \frac{10}{12}$$

$$\text{so} \quad \Delta S = 3\ \frac{12}{300} \ln \left(\frac{10}{12}\right) + \frac{12}{300} \ln 8$$

$$= \frac{3 \times 12}{300} \ln \left(\frac{5}{6} \times 2\right) = \frac{12}{100} \ln \left(\frac{5}{3}\right) \times 100 \text{ J}$$

$$= 12 (\ln 5 - \ln 3) = 12 \times 2.3 \times (0.7 - 0.48)$$
$$= 12 \times 2.3 \times 0.22 = 6.072 \text{ J/K}$$

Ans. 6 J/K

11. **(a) (i)** $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26 \times 10^3}{308} = 84.41\ JK^{-1}\ mol^{-1}.$

(ii) $\Delta S_{cond.} = \frac{\Delta H_{cond}}{T} = -84.41\ JK^{-1}\ mol^{-1}.$

(b) Using $\Delta G = \Delta H - T\Delta S = -11.50$ KJ/mol.

12. **(a)** $T < \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 10^3}{-198.3} = 481.0$ K. (Since ΔS and ΔH both are negative)

(b) For $\Delta H_{min.}$, $\Delta G = 0$

$\therefore$ $\Delta H_{min} = T\Delta S = 36.06$ KJ.

13. Spontaneity of a reaction is decideded by

$$\Delta S_{total} = (\Delta S_{Sys} + \Delta S_{surr.}) > 0$$

$$\Delta S_{surr} = \frac{-1648 \times 10^3\ J/mol}{298} = 5530\ JK^{-1}\ mol^{-1}$$

$\therefore$ $\Delta S_{total} = 4980.6\ JK^{-1}\ mol^{-1} > 0$ (Hence, spontaneous).