### PHYSICAL CHEMISTRY



### DPP No. 54

**Total Marks: 32** 

Max. Time: 33 min.

**Topic: Thermodynamics & Thermochemistry** 

#### Type of Questions M.M., Min.

Single choice Objective ('-1' negative marking) Q.1 to Q.4, 6, 7, 9, 10 (8 marks, 8 min.) [24, 24]

Multiple choice objective ('-1' negative marking) Q.5 (4 marks, 4 min.) [4, 4]

Subjective Questions ('-1' negative marking) Q.8 (4 marks, 5 min.) [4, 5]

- 1. In which of the following cases, generally entropy decreases :
  - (A) Solid changing to liquid

(B) Expansion of a gas

(C) Crystal dissolves

- (D) Polymerisation
- 2. Predict which of the following reaction(s) have a positive entropy change?

I. 
$$Ba^{2+}$$
 (aq) +  $SO_4^{2-}$  (aq)  $\longrightarrow$   $BaSO_4$  (s)

II. 
$$CaCO_{2}(s) \longrightarrow CaO(s) + CO_{2}(g)$$

III. 
$$2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)$$

- (A) I and II
- (B) III
- (C) II and III
- (D) II
- 3. Which of the following reactions is expected to have 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)
- **4.** Which statement regarding entropy is correct?
  - (A) A completely ordered deck of cards has more entropy than a shuffled deck in which cards are arranged randomly.
  - (B) A perfect ordered crystal of solid nitrous oxide has more entropy than a disordered crystal in which the molecules are oriented randomly.
  - (C) 1 mole N<sub>2</sub> gas at STP has more entropy than 1 mole N<sub>2</sub> gas at 273 K in a volume of 11.2 litre.
  - (D) 1 mole  $N_2$  gas at STP has more entropy than 1 mole  $N_2$  gas at 273 K and 0.25 atm.
- **5\*.** Select the correct option(s):
  - (A) Specific volume and molar heat capacity are intensive parameters.
  - (B) For an irreversible adiabatic compression process, entropy change of surrounding will be equal to zero.
  - (C) Change in internal energy for an ideal gas for an isobaric process is expressed as  $\Delta U = nC_V (T_2 T_1)$ , where the terms used have their usual meaning.
  - (D) Free expansion is a reversible process.
- **6.** Two moles of an ideal gas ( $\gamma$  = 4/3) 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



7. Two moles of an ideal monoatomic gas expands isothermally against a constant external pressure of 2 atm from an initial volume of 22.4 L to a state where its final pressure becomes equal to external pressure. If the initial temperature of gas is 273°C, then the entropy change of system in the above process is :

[Given: 1 mole of an ideal gas occupies 22.4 L at STP conditions]

- (A) R In 16
- (B) R In 4
- (C) R In 8
- (D) Zero
- 8. The enthalpy of vapourisation of liquid diethyl ether is 26 kJ/mol at its boiling point (52°C). Calculate  $\Delta$ S for conversion of : (a) liquid to vapour, and (b) vapour to liquid at 52°C.
- 9. When two equal sized pieces of the same metal, each of mass m at different temperatures T<sub>b</sub> (hot piece) and  $T_c$  (cold piece) are brought into contact and isolated from surrounding, the total change in entropy of system is given by : (Specific heat capacity of metal = s)
- (A) ms ln  $\frac{T_C + T_h}{2T_C}$  (B) ms ln  $\frac{T_h}{T_C}$  (C) ms ln  $\frac{(T_C + T_h)^2}{2T_hT_C}$  (D) ms ln  $\frac{(T_C + T_h)^2}{4T_hT_C}$
- One mole of an ideal monoatomic gas at 27°C is subjected to a reversible isoentropic compression until 10. final temperature reached to 327°C. If the initial pressure was 1.0 atm, then find the value of In P<sub>2</sub>: (Given:  $\ln 2 = 0.7$ ).
  - (A) 1.75 atm
- (B) 0.176 atm
- (C) 1.0395 atm
- (D) 2.0 atm

# Answer Key

DPP No. # 54

- 1. (D)
- 2.
- (C)
- (D)
- 4. (C)

- 5.\* (ABC)
- (D)

3.

(B)

- (a) 80 JK-1 mol-1 8.
- (b) 80 JK-1 mol-1

- 9. (D)
- 10.

(A)



## Hints & Solutions

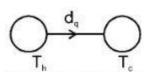
#### DPP No. # 54

- 1. Polymerisation leads to more ordered structure.
- 2. Δn is + ve
- 3. Δn is most - ve
- 4. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.
- 6. For a reversible adiabatic process,  $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$
- For initinal state  $P_i \times 22.4 = 2 \times R \times 546$ 7. ∴ P<sub>i</sub> = 4 atm Now,  $P_i V_i = P_f V_f$  (... process is Isothermal)  $4 \times 22.4 = 2 \times V_{f}$

$$\therefore \Delta S_{\text{sys}} = \text{nR In} \left( \frac{V_f}{V_i} \right) = 2 \text{ R In} \left( \frac{44.8}{22.4} \right) = 2 \text{ R In } 2 = \text{R In } 4$$

- (a)  $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{325} = 80 \text{ JK}^{-1} \text{ mol}^{-1}.$ 8.
  - **(b)**  $\Delta S_{cond.} = \frac{\Delta H_{cond.}}{T} = -80 \text{ JK}^{-1} \text{ mol}^{-1}.$

9.



For a small exchange in heat at time 't'

change entropy for hot piece =  $\frac{dq}{T_1^1}$ 

where T<sub>h</sub><sup>1</sup> is temp of hot piece at time 't'

change of entropy by cold piece =  $\frac{dq}{T_1^1}$ .

As heat capacities of the pieces is same.

$$T_c + T_h = T_c^1 + T_h^1 = 2T_f$$

 $T_c + T_h = T_c^{-1} + T_h^{-1} = 2T_t$ where  $T_t$  is final temperature of each piece.



$$\Delta \text{S for hot piece} = \int\!\!\frac{\text{dq}}{\text{T}_h^{-1}} = \text{mS} \int\limits_{\text{T}_h}^{\text{T}_f} \!\!\frac{\text{dT}}{\text{T}_h^{-1}} \qquad = \text{mS In } \frac{\text{T}_f}{\text{T}_h}$$

 $\Delta$ S for cold piece = mS In  $\frac{T_f}{T_c}$  .

$$\therefore \qquad \text{Total } \Delta S = \text{ mS In } \frac{T_f^2}{T_h T_c} \qquad = \text{ ms In } \frac{(T_C + T_h)^2}{4T_h T_C}$$

10. For isoentropic process  $\Delta S_{\text{system}} = 0$ 

:. 
$$nC_{p, m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0$$

$$\Rightarrow \ln (P_2) = \frac{5}{2} \times \ln \left( \frac{600}{300} \right) = 1.75 \text{ atm}$$

