

SOLUTIONS

1.
$$-w = P_{Ext} \Delta V = 1 \times 0.5 Latm \approx 50.65 J \implies w = -50.65 J$$

2.
$$-w = P\Delta V = P(V_g - V_\ell) \approx PV_g = nRT = 1 \times 8.314 \times 373 \implies w = -3.10 \text{ kJ}$$

3.
$$800 = \Delta U + 1 \times (14 - 4) \times 101.3$$
 \Rightarrow $\Delta U = 800 - 1013 = -213 J$

4.
$$Zn + HCl \longrightarrow H_2 + ZnCl_2$$

 $\Delta_rG = \Delta_rH - T\Delta_rS = -12.55 - 290 \times 5 \times 10^{-3} = -14 \text{ kJmol}^{-1}$
 $\Delta_rG < 0 \text{ (spontaneous)}$

5.
$$\Delta G = 40.64 - T \times 108.8 \times 10^{-3}$$
 \Rightarrow $T = 373.53 \text{ K}$
At $T > 373.5 \text{ K}$; reaction will become sponteneous.

- **6.** Refer to theory
- **7.(D)** $\Delta_{x}G = \Delta_{x}H T\Delta_{x}S$; $\Delta_{x}H < 0$ and $\Delta_{x}S < 0$ \Rightarrow Reaction is spontaneous at low T and non-spontaneous at high T
- **8.(B)** If an ideal gas expands in vaccum, $\Delta S > 0$; T = const., $\Delta U = 0$; $P \downarrow$

9.(D)
$$\Delta_r G = \Delta_r H - T \Delta_r S \implies T = \frac{20}{50} \times 1000 = 400 \text{ K}$$

⇒ Above 400 K, reaction is non-spontaneous.

10.(A)
$$\Delta_r G^{\Theta} = 50 = \Delta_r H^{\Theta} - 250 \Delta_r S^{\Theta}$$
 and
$$30 = \Delta_r H^{\Theta} - 350 \Delta_r S^{\Theta}$$
 $\Rightarrow \Delta_r S^{\Theta} = 200 \text{ J/K}$

11.(C)
$$q = \Delta U + (-w) = -52 \text{ kJ} + 1.5 (30) \text{ Latm} = -57 \text{kJ} + 4.559 \text{kJ} = -47.4 \text{kJ}$$

- 12.(A) $H_2O(\ell) \rightleftharpoons H_2O(g)$; Reversible process at equilibrium: $\Delta G = 0$; $\Delta S > 0$
- 13.(CD) Check for increase in the number of gaseous moles.
- **14.(C)** $\Delta_r G$ always be negative, if $\Delta_r H < 0$ and $\Delta_r S > 0$

15.(C)
$$\Delta_{\rm r} S = \frac{2090}{(290)} = 7.2 \text{J K}^{-1} \text{mol}^{-1}$$

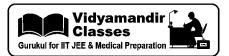
16.(B)
$$\Delta_r S^{\Theta} = 2(27.3) + 3(69.9) - (87.3) - 3 \times 130.7 = -215.1 \text{ Jmol}^{-1} \text{K}^{-1}$$

17.(A) $\Delta_r S^{\Theta}$ has to be zero. For this change in number of moles should be zero.

18.(A) Use:
$$\ln \frac{P_2}{P_1} = \frac{\Delta_r H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \implies \ln \frac{0.35}{0.14} = \frac{\Delta_r H}{8.314} \left(\frac{1}{400} - \frac{1}{420} \right) \implies \Delta_r H = 64.08 \text{ kJmol}^{-1}$$

19.(D)
$$\Delta S_{A \to B} = \Delta S_{A \to C} + \Delta S_{C \to D} + \Delta S_{D \to B} = 50 + 30 - 20 = 60$$

20.B)
$$-54.07 - 298 \times 10 \times 10^{-3} = -2.303 \text{ RT } \log_{10} \text{K}_{\text{eq}} \implies \log_{10} \text{K}_{\text{eq}} = 10$$



21.(B)
$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = 177 \times 10^3 - 298 \times 285 = 177000 - 84930 = 92070 J = 92.07 kJ.$$

Since the sign of ΔG is positive, it is non spontaneous reaction.

22.(B) $\Delta H > 0$ and ΔS must be positive as the reaction becomes spontaneous from non-spontaneous on increasing temperature.

23.(B)
$$\Delta G = -2.303 \text{ RT log K}_{eq}$$

$$=-2.303 \times 8.314 \times 298 \times \log (10^{-14})$$

$$= 2.303 \times 8.314 \times 298 \times 14 \approx 8 \times 10^4 \,\mathrm{J}$$

- **24.(A)** If $\Delta H < 0$ and $\Delta S < 0$ (decrease in number of moles of gas) then reaction will be spontaneous at low temperature and non-spontaneous at high temperature because $\Delta G > 0$ at high temperature.
- **25.(B)** C_6H_6 is in liquid state.

 $\Delta H < 0$ for combustion reactions.

 $\Delta S > 0$ more gaseous substances

 $\Delta G < 0$ spontaneous reaction

- **26.(D)** When $\Delta H > 0$, and $\Delta S < 0$ then $\Delta G > 0$ at all temperature hence reaction will be non-spontaneous and impossible to occur.
- 27.(C) From $\Delta G = \Delta H T \cdot \Delta S$

For an ideal gas at isothermal condition, $\Delta T = 0$ and $\Delta H = 0$

$$\Rightarrow \Delta G = T - \Delta S$$
?

28.(C) Most easily decomposed metal oxide will be HgO becasue value of ΔG° for formation of oxide will becomes less negative at higher temperature.