

# SOLUTIONS

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1.  $-w = P_{\text{Ext.}} \Delta V = 1 \times 0.5 \text{ Latm} \approx 50.65 \text{ J} \Rightarrow w = -50.65 \text{ J}$
2.  $-w = P \Delta V = P(V_g - V_\ell) \approx P V_g = nRT = 1 \times 8.314 \times 373 \Rightarrow w = -3.10 \text{ kJ}$
3.  $800 = \Delta U + 1 \times (14 - 4) \times 101.3 \Rightarrow \Delta U = 800 - 1013 = -213 \text{ J}$
4.  $\text{Zn} + \text{HCl} \longrightarrow \text{H}_2 + \text{ZnCl}_2$   
 $\Delta_r G = \Delta_r H - T \Delta_r S = -12.55 - 290 \times 5 \times 10^{-3} = -14 \text{ kJmol}^{-1}$   
 $\Delta_r G < 0$  (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 spontaneous.
6. Refer to theory
- 7.(D)  $\Delta_r G = \Delta_r H - T \Delta_r S$ ;  $\Delta_r H < 0$  and  $\Delta_r S < 0 \Rightarrow$  Reaction is spontaneous at low T and non-spontaneous at high T
- 8.(B) If an ideal gas expands in vacuum,  $\Delta S > 0$ ;  $T = \text{const.}$ ,  $\Delta U = 0$ ;  $P \downarrow$
- 9.(D)  $\Delta_r G = \Delta_r H - T \Delta_r S \Rightarrow T = \frac{20}{50} \times 1000 = 400 \text{ K}$   
 $\Rightarrow$  Above 400 K, reaction is non-spontaneous.
- 10.(A)  $\Delta_r G^\ominus = 50 = \Delta_r H^\ominus - 250 \Delta_r S^\ominus$   
 and  $30 = \Delta_r H^\ominus - 350 \Delta_r S^\ominus \Rightarrow \Delta_r S^\ominus = 200 \text{ J/K}$
- 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)  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ ; 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)  $\Delta_r S = \frac{2090}{(290)} = 7.2 \text{ J K}^{-1} \text{ mol}^{-1}$
- 16.(B)  $\Delta_r S^\ominus = 2(27.3) + 3(69.9) - (87.3) - 3 \times 130.7 = -215.1 \text{ Jmol}^{-1} \text{ K}^{-1}$
- 17.(A)  $\Delta_r S^\ominus$  has to be zero. For this change in number of moles should be zero.
- 18.(A) Use:  $\ell_n \frac{P_2}{P_1} = \frac{\Delta_r H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \ell_n \frac{0.35}{0.14} = \frac{\Delta_r H}{8.314} \left( \frac{1}{400} - \frac{1}{420} \right) \Rightarrow \Delta_r H = 64.08 \text{ kJmol}^{-1}$
- 19.(D)  $\Delta S_{A \rightarrow B} = \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} + \Delta S_{D \rightarrow B} = 50 + 30 - 20 = 60$
- 20.(B)  $-54.07 - 298 \times 10 \times 10^{-3} = -2.303 RT \log_{10} K_{\text{eq}} \Rightarrow \log_{10} K_{\text{eq}} = 10$

- 21.(B)**  $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = 177 \times 10^3 - 298 \times 285 = 177000 - 84930 = 92070 \text{ J} = 92.07 \text{ kJ}$ .  
 Since the sign of  $\Delta G$  is positive, it is non spontaneous reaction.
- 22.(B)**  $\Delta H > 0$  and  $\Delta S$  must be positive as the reaction becomes spontaneous from non-spontaneous on increasing temperature.
- 23.(B)**  $\Delta G = -2.303 RT \log K_{eq}$   
 $= -2.303 \times 8.314 \times 298 \times \log (10^{-14})$   
 $= 2.303 \times 8.314 \times 298 \times 14 \approx 8 \times 10^4 \text{ J}$
- 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  $HgO$  because value of  $\Delta G^\circ$  for formation of oxide will become less negative at higher temperature.