Chemical Thermodynamics

Short Answer Type Questions

1. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?
2. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?
3. 22. Standard molar enthalpy of formation, $\Delta_f H^\ominus$ is just a special case of enthalpy of reaction, $\Delta_r H^\ominus$. Is the $\Delta_r H^\ominus$ for the following reaction same as $\Delta_f H^\ominus$? Give reason for your answer.
   $CaO(s) + CO_2(g) \rightarrow CaCO_3(s); \Delta_f H^\ominus = -178.3$ kJ mol^{-1}
4. The value of $\Delta_f H^\ominus$ for NH_3 is – 91.8 kJ mol^{-1}. Calculate enthalpy change for the following reaction :
   $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
5. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$..... etc. for intermediate reactions.
6. The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H(g)$ is 1665 kJ mol^{-1}. What is the bond energy of C–H bond?
7. 26. Use the following data to calculate $\Delta_{lattice} H^\ominus$ for NaBr.
   $\Delta_{sub} H^\ominus$ for sodium metal = 108.4 kJ mol^{-1}
   Ionization enthalpy of sodium = 496 kJ mol^{-1}
   Electron gain enthalpy of bromine = – 325 kJ mol^{-1}
   Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}
   $\Delta_f H^\ominus$ for NaBr (s) = – 360.1 kJ mol^{-1}
8. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?
9. Heat has randomising influence on a system and temperature is the measure of average

chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

10. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?
11. At 298 K. K_p for the reaction $N_2O4(g) \rightleftharpoons 2NO\ 2\ (g)$ is 0.98. Predict whether the reaction is spontaneous or not.
12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?

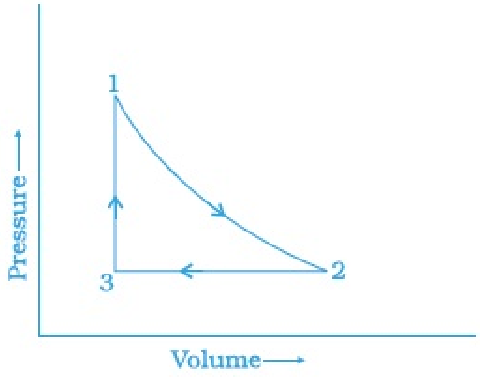

Fig. : 6.1

13. The standard molar entropy of $H_O(l)$ is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more, or less than 70 J K^{-1} mol^{-1}?
14. Identify the state functions and path functions out of the following :
    enthalpy, entropy, heat, temperature, work, free energy.
15. The molar enthalpy of vapourisation of acetone is less than that of water. Why?
16. Which quantity out of Δ_rG and $\Delta_rG^\ominus$ will be zero at equilibrium?
17. Predict the change in internal energy for an isolated system at constant volume.
18. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.
19. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the

change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre?

20. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?
21. The difference between C_P and C_V can be derived using the empirical relation H = U + pV. Calculate the difference between C_P and C_V for 10 moles of an ideal gas.
22. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.
23. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction.
    $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
    Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.
24. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol^{-1} . Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1}).
25. The enthalpy of reaction for the reaction :
    $2H_2 (g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta_R H^{\ominus} = - 572$ kJ mol^{-1}. What will be standard enthalpy of formation of $H_2O(l)$?
26. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Fig. 6.2. Explain graphically.

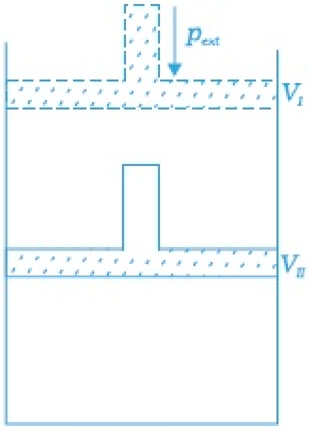

Fig. : 6.2

27. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?
28. Represent the potential energy/enthalpy change in the following processes graphically.
    - (a) Throwing a stone from the ground to roof.
    - (b) $(1/2)H_2(g) + (1/2)Cl_2(g) \Leftrightarrow HCL(g)\ \Delta_r H^{\ominus} = -92.32\ kJ\ mol^{-1}$

29. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide spontaneity of a reaction from given diagram. Explain.

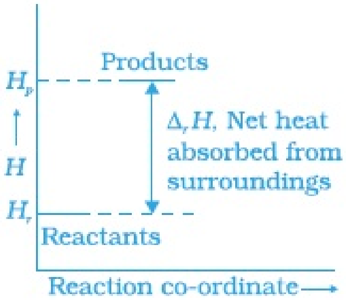

Fig. : 6.3

30. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.

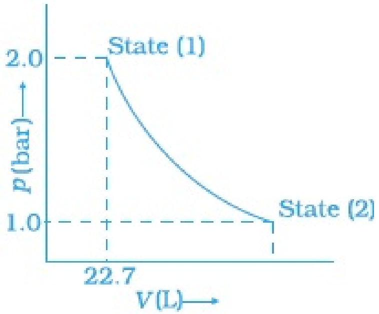

Fig. : 6.4

31. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step.

    Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?

    (Given that 1 L bar = 100 J)

Long Answer Type Questions

1. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.
2. Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

   Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.
3. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s).
4. ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?
5. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_F ,V_F). With the help of a pV plot compare the work done in the above case with that carried out against a constant external pressure p_F.