

ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iii) 2. (iii) 3. (iv) 4. (iii) 5. (iii) 6. (ii)
7. (iii)

Justification : free expansion $w = 0$
adiabatic process $q = 0$
 $\Delta U = q + w = 0$, this means that internal energy remains constant. Therefore, $\Delta T = 0$.

In ideal gas there is no intermolecular attraction. Hence when such a gas expands under adiabatic conditions into a vacuum no heat is absorbed or evolved since no external work is done to separate the molecules.

8. (ii) w (reversible) < w (irreversible)

Justification : Area under the curve is always more in irreversible compression as can be seen from Fig. 6.5 (a) and (b).

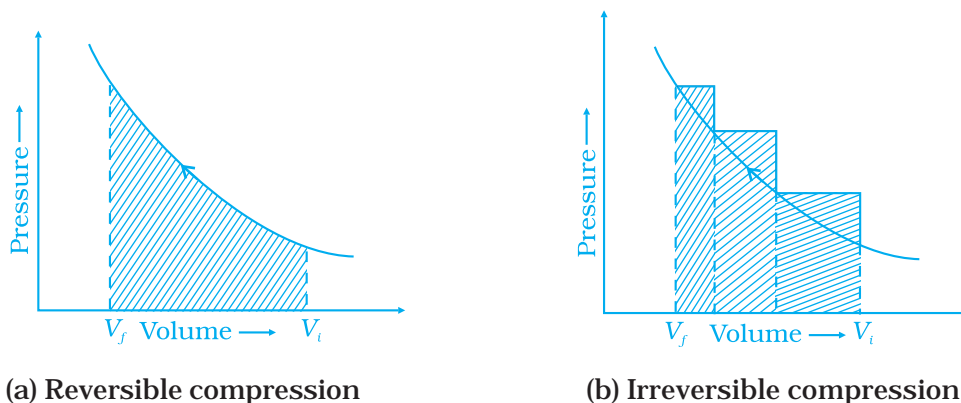


Fig. : 6.5

9. (iii)

Justification : Freezing is exothermic process. The heat released increases the entropy of surrounding.

10. (iii)

11. (iii)

Justification : Same bonds are formed in reaction (a) and (b) but bonds between reactant molecules are broken only in reaction (b).

12. (iii) 13. (i) 14. (ii)

II. Multiple Choice Questions (Type-II)

15. (i), (iv)

16. (i), (ii)

17. (iii), (iv)

18. (iii), (iv)

$$\text{Justification : } \frac{w_{600K}}{w_{300K}} = \frac{1 \times R \times 600 K \ln \frac{10}{1}}{1 \times R \times 300 K \ln \frac{10}{1}} = \frac{600}{300} = 2$$

For isothermal expansion of ideal gases, $\Delta U = 0$

since temperature is constant this means there is no change in internal energy.
Therefore, $\Delta U = 0$

19. (i), (iii)

III. Short Answer Type

20. + 81.58 kJ, $\Delta_{\text{vap}} H^\ominus = + 40.79 \text{ kJ mol}^{-1}$ 21.
Water 22.

No, since CaCO_3 has been formed from other compounds and not from its constituent elements.

23. $\Delta_r H^\ominus = +91.8 \text{ kJ mol}^{-1}$

24. $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \dots$

25. $\frac{1665}{4} \text{ kJ mol}^{-1} = 416.2 \text{ kJ mol}^{-1}$

26. +735.5 kJ mol⁻¹

27. It is spontaneous process. Although enthalpy change is zero but randomness or disorder (i.e., ΔS) increases. Therefore, in equation $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. Hence, ΔG will be negative.

28. $\Delta S = \frac{q_{\text{rev}}}{T}$

29. Yes

30. The reaction is spontaneous

$$\Delta_r G^\ominus = -RT \ln K_p$$

31. $\Delta H(\text{cycle}) = 0$

32. Less, because ice is more ordered than $\text{H}_2\text{O}(l)$.

33. State Functions : Enthalpy, Entropy, Temperature, Free energy
Path Functions : Heat, Work

34. Because of strong hydrogen bonding in water, its enthalpy of vapourisation is more.

35. $\Delta_r G$ will always be zero.

$\Delta_r G^\ominus$ is zero for $K = 1$ because $\Delta G^\ominus = -RT \ln K$, ΔG^\ominus will be non zero for other values of K .

36. For isolated system, there is no transfer of energy as heat or as work i.e., $w=0$ and $q=0$. According to the first law of thermodynamics.

$$\begin{aligned}\Delta U &= q + w \\ &= 0 + 0 = 0\end{aligned}$$

$$\therefore \Delta U = 0$$

37. **At constant volume**

By first law of thermodynamics:

$$q = \Delta U + (-w)$$

$$(-w) = p\Delta V$$

$$\therefore q = \Delta U + p\Delta V$$

$$\Delta V = 0, \text{ since volume is constant.}$$

$$\therefore q_v = \Delta U + 0$$

$$\Rightarrow q_v = \Delta U = \text{change in internal energy}$$

At constant pressure

$$q_p = \Delta U + p\Delta V$$

$$\text{But, } \Delta U + p\Delta V = \Delta H$$

$$\therefore q_p = \Delta H = \text{change in enthalpy.}$$

So, at a constant volume and at constant pressure heat change is a state function because it is equal to change in internal energy and change in enthalpy respectively which are state functions.

38. $(-w) = p_{\text{ext}}(V_2 - V_1) = 0 \times (5 - 1) = 0$

For isothermal expansion $q = 0$

By first law of thermodynamics

$$q = \Delta U + (-w)$$

$$\Rightarrow 0 = \Delta U + 0 \text{ so } \Delta U = 0$$

39. For water, heat capacity = $18 \times$ specific heat

$$\text{or } C_p = 18 \times c$$

$$\text{Specific heat} = c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{Heat capacity} = C_p = 18 \times 4.18 \text{ J K}^{-1} = 75.3 \text{ J K}^{-1}$$

40. $C_p - C_v = nR$

$$= 10 \times 4.184 \text{ J}$$

41. Molar enthalpy change of graphite = enthalpy change for 1 g carbon \times molar mass of carbon
 $= -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$
 $\therefore \Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$

Negative value of $\Delta H \Rightarrow$ exothermic reaction.

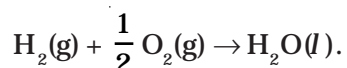
42. $\Delta_r H^\ominus = \text{Bond energy of H}_2 + \text{Bond energy of Br}_2 - 2 \times \text{Bond energy of HBr}$
 $= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$
 $\Rightarrow \Delta_r H^\ominus = -109 \text{ kJ mol}^{-1}$

43. $q_p = \Delta H = 30.5 \text{ kJ mol}^{-1}$

$$\therefore \text{Heat required for vapourisation of 284 g of CCl}_4 = \frac{284 \text{ g}}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ mol}^{-1}$$

$$= 56.2 \text{ kJ}$$

44. According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $\text{H}_2\text{O}(l)$



or the standard enthalpy of formation of $\text{H}_2\text{O}(l)$ will be half of the enthalpy of the given equation i.e., $\Delta_r H^\ominus$ is also halved.

$$\Delta_f H_{\text{H}_2\text{O}}^\ominus(l) = \frac{1}{2} \times \Delta_r H^\ominus = \frac{-572 \text{ kJ mol}^{-1}}{2} = -286 \text{ kJ/mol.}$$

45. Work done on an ideal gas can be calculated from p - V graph shown in Fig. 6.6. Work done is equal to the shaded area ABV_1V_2 .

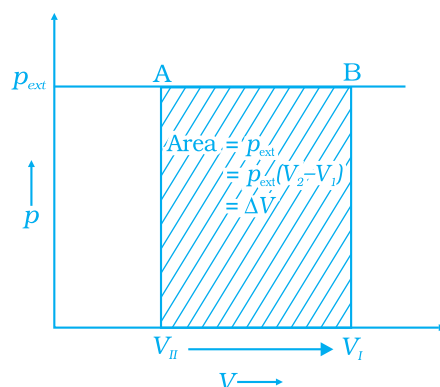


Fig. : 6.6

46. The work done can be calculated with the help of p - V plot. A p - V plot of the work of compression which is carried out by change in pressure in infinite steps, is given in Fig. 6.7. Shaded area represents the work done on the gas.

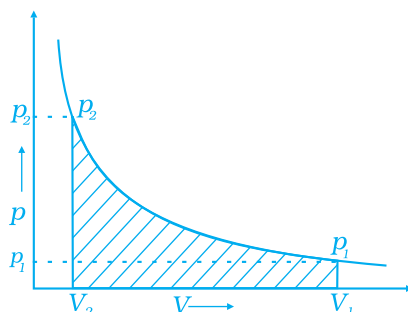


Fig. : 6.7

- 47.

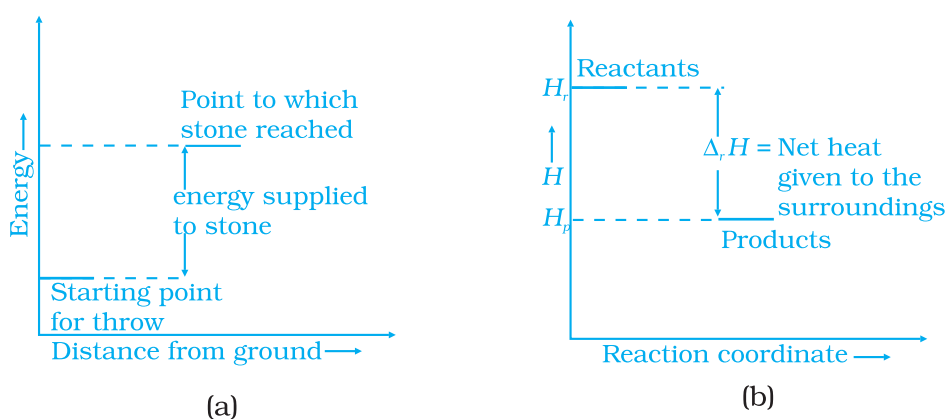


Fig. : 6.8 Enthalpy change in processes (a) and (b)

48. No.

Enthalpy is one of the contributory factors in deciding spontaneity but it is not the only factor. One must look for contribution of another factor i.e., entropy also, for getting the correct result.

49. It is clear from the figure that the process has been carried out in infinite steps, hence it is isothermal reversible expansion.

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

$$\text{But, } p_1 V_1 = p_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$$

$$\begin{aligned} \therefore w &= -2.303 nRT \log \frac{p_1}{p_2} \\ &= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}^{-1} \times \log 2 \\ &= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J} = -1717.46 \text{ J} \end{aligned}$$

$$50. \quad w = -p_{\text{ex}}(V_f - V_i) = -2 \times 40 = -80 \text{ L bar} = -8 \text{ kJ}$$

The negative sign shows that work is done by the system on the surrounding. Work done will be more in the reversible expansion because internal pressure and external pressure are almost same at every step.

IV. Matching Type

51. (i) → (e) (ii) → (d) (iii) → (f) (iv) → (a)
 (v) → (g), (k), (l) (vi) → (b) (vii) → (c) (viii) → (j)
 (ix) → (h) (x) → (i) (xi) → (a), (l), (m) (xii) → (g), (k)
52. (i) → (b) (ii) → (c) (iii) → (a)
53. (i) → (c) (ii) → (a) (iii) → (b)
54. (i) → (b), (d) (ii) → (b) (iii) → (c) (iv) → (a)

V. Assertion and Reason Type

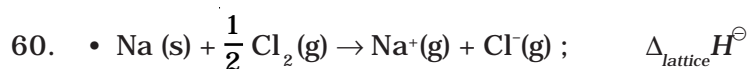
55. (ii) 56. (ii) 57. (i)

VI. Long Answer Type

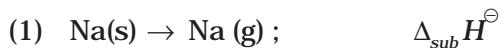
59. **Hint :** Ratio of two extensive properties is always intensive

$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

$$\text{e.g., Mole fraction} = \frac{\text{Moles}}{\text{Total number of moles}} = \frac{(\text{Extensive})}{(\text{Extensive})}$$



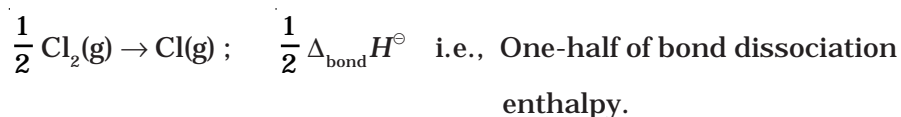
- Born - Haber Cycle
- Steps to measure lattice enthalpy from Born - Haber cycle
- Sublimation of sodium metal



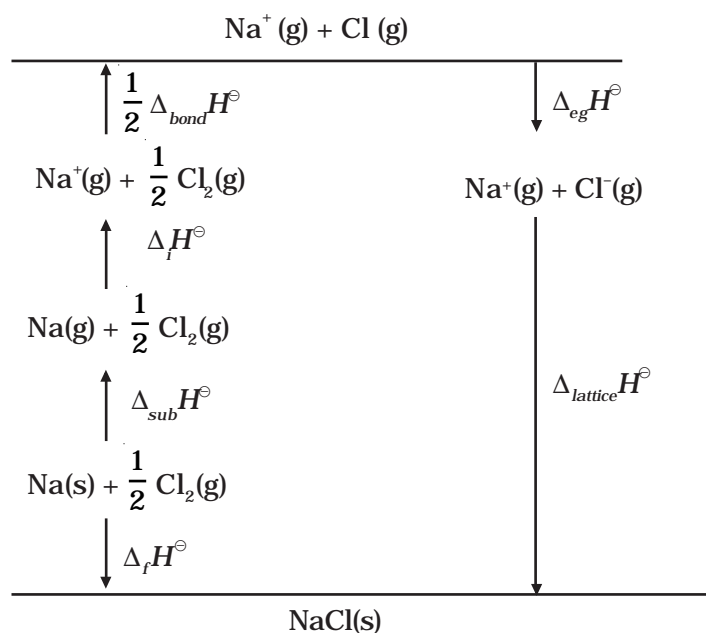
- (2) Ionisation of sodium atoms



- (3) Dissociation of chlorine molecule



- (4) $\text{Cl}(\text{g}) + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g}) ; \quad \Delta_{\text{eg}} H^\ominus$ i.e., electron gain enthalpy.



61. $\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \left(\frac{-\Delta H_{\text{sys}}}{T} \right)$$

$$T \Delta S_{\text{Total}} = T \Delta S_{\text{sys}} - \Delta H_{\text{sys}}$$

For spontaneous change, $\Delta S_{\text{total}} > 0$

$$\therefore T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$\Rightarrow -(\Delta H_{\text{sys}} - T \Delta S_{\text{sys}}) > 0$$

But, $\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}}$

$\therefore -\Delta G_{\text{sys}} > 0$

$\Rightarrow \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0$

ΔH_{sys} = Enthalpy change of a reaction.

$T \Delta S_{\text{sys}}$ = Energy which is not available to do useful work.

ΔG_{sys} = Energy available for doing useful work.

- Unit of ΔG is Joule
- The reaction will be spontaneous at high temperature.

62.

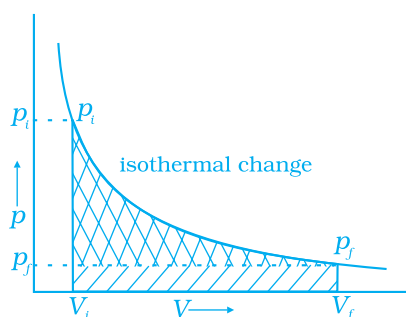




Fig. : 6.9

- Reversible Work is represented by the combined areas  and .
- Work against constant pressure, p_f is represented by the area . Work (i) > Work (ii)