

<H1>Additional Objective Questions

<H2> Single Correct Choice Type

1.(A) Work is not a state function; instead it is dependent on the path of the reaction.

2.(A) We know

$$\begin{aligned}\Delta H &= \Delta U + p\Delta V \\ \Delta U &= \Delta H - p\Delta V \\ \Delta E &= 1 \text{ kcal} - 1 \times 0.3 \text{ L atm} \\ &= 1 \text{ kcal} - 0.3 \text{ L atm} \\ &= 1 \text{ kcal} - 0.3 \times 0.024 \text{ kcal} \\ &= 1 \text{ kcal} - 0.0072 \text{ kcal} = 0.993 \text{ kcal}\end{aligned}$$

3.(C) As $\Delta G = -ve$ for spontaneous change and $\Delta G = \Delta H - T\Delta S$, we have

$$T\Delta S > \Delta H$$

$$\begin{aligned}\Rightarrow T &> \frac{\Delta H}{\Delta S} \\ \Rightarrow T &> \frac{4000}{10} \\ \Rightarrow T &> 400 \text{ K}\end{aligned}$$

4.(C) Enthalpy of hydration is the amount of enthalpy change when 1 mol of the anhydrous salt combines with the required number of moles of water so as to change into the hydrated salt.

5.(D) The heat of formation of HCl is to be calculated on per mole of HCl produced

$$\text{Heat of formation of HCl} = \frac{44}{2} = -22 \text{ kcal. (as } \Delta H = -44 \text{ kcal per 2 mol of HCl)}$$

6.(B) For an isothermal process, we have

$$\begin{aligned}w &= -nRT \ln \frac{V_2}{V_1} \\ \text{or } |w| &= nRT \ln V_2 - nRT \ln V_1\end{aligned}$$

Since, the above equation is of the form $y = mx - c$, so the slope will be positive and more for T_2 than T_1 and intercept of T_2 curve is more negative than that of T_1 .

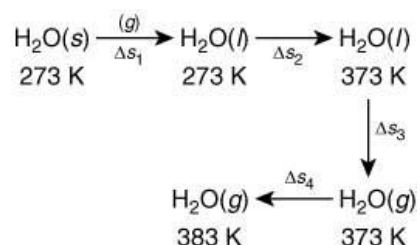
7.(B) The first reaction is exothermic and the second one is endothermic. If a mixture of steam and O₂ is passed over coke and temperature is constant, the conversion of each to CO should not show any heat change, that is, total heat evolved in I = total heat absorbed in II.

$$n_1 \times 2 \times 110 = n_2 \times 132$$

$$\frac{n_1}{n_2} = \frac{132}{200} = \frac{0.6}{1}$$

Therefore,

8.(4) For the given conversion of ice to water,



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$$\Delta S_1 = \frac{\Delta H_{\text{fusion}}}{273} = \frac{334}{273} = 1.22$$

$$\Delta S_2 = 4.2 \ln \left(\frac{363}{273} \right) = 1.19$$

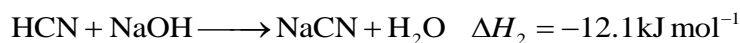
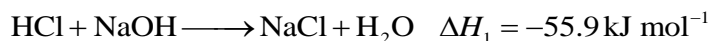
$$\Delta S_3 = \frac{\Delta H_{\text{vap}}}{373} = \left(\frac{2491}{373} \right) = 6.67$$

$$\Delta S_4 = 2 \ln \left(\frac{383}{373} \right) = 0.05$$

Since, $\Delta S_{\text{Total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

Therefore, $\Delta S_{\text{Total}} = 9.14 \text{ kJ kg}^{-1} \text{K}^{-1}$

9.(B) The reaction involved is



Enthalpy of dissociation of HCN = $\Delta H_2 - \Delta H_1 = -12.1 - (-55.9) = +43.8 \text{ kJ}$

10.(C) We know

$$\Delta G = \Delta H - T\Delta S$$

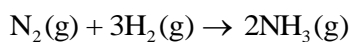
At equilibrium

$$\Delta G = 0$$

Therefore,

$$T = \frac{\Delta H}{\Delta S} = \frac{200}{40} = 5 \text{ K}$$

11.(D) In synthesis of ammonia from N_2 and H_2



$$\Delta n_g = 2 - 4 = -2$$

Therefore, entropy change of the reaction is negative.

12.(A) ΔH_f° is the enthalpy of formation; in standard state of 1 mol of a substance from its constituent elements in their standard states, for example, $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g})$.

13.(C) Work done of isothermal irreversible for ideal gas = $p_{\text{ext}} \cdot (V_2 - V_1) = 4 \times (5 - 1) = 16 \text{ Nm}$

We know

For isothermal process, $\Delta U = 0$

$$w = q = -16 \text{ J}$$

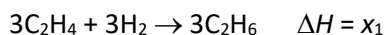
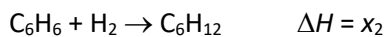
Heat used to increase temperature of 1 mol Al is

$$q = nC_m\Delta T$$

$$16 = 1 \text{ mol} \times 24 \text{ J mol}^{-1} \text{ K}^{-1} \times \Delta T$$

$$\Delta T = 2/3 \text{ K}$$

14.(C) For the given reaction,



Therefore, resonance energy of benzene (containing three double bonds) = $3x_1 - x_2$.

15.(C) $\Delta_r G^\circ$ is given by relation

$$\Delta_r G^\circ (\text{in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

At equilibrium $\Delta G^\circ = 0$

At $T = 315 \text{ K}$

$$\Delta_r G^\circ = 120 - \frac{3}{8}T$$

$$\Delta_r G^\circ = 120 - \frac{3}{8} \times 315 = 1.875 \text{ kJmol}^{-1}$$

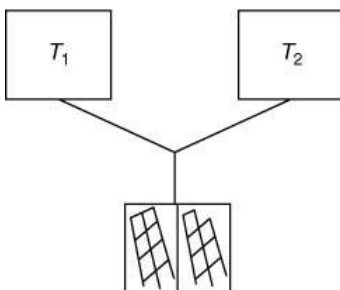
$\Delta_r G^\circ = +1.875 \text{ kJ mol}^{-1}$, so, reaction is non-spontaneous at this temperature, therefore, X will be the major product.

16.(A) The heat of neutralization of strong acid and strong base = $-13.7 \text{ kcal equiv}^{-1}$.
Therefore, $-13.7 \times 2 = -27.4 \text{ kcal}$ should be evolved but evolved actually is -25.4 kcal .
Therefore, $\Delta_{\text{diss}}H = -25.4 - (-27.4) = +2 \text{ kcal}$

17.(A) We know

$$\Delta S = \frac{\Delta H}{T} \Rightarrow T = \frac{30 \times 10^3}{75} = 400 \text{ K}$$

18.(B)



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$$T_t = \frac{T_1 + T_2}{2}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T}$$

$$= nC_p \int \frac{dT}{T}$$

$$\Delta S_I = nC_p \int_{T_1}^{T_t} \frac{dT}{T}$$

$$\Delta S_I = nC_p \ln \frac{T_t}{T_1} \quad (1)$$

$$\Delta S_{II} = nC_p \int_{T_2}^{T_t} \frac{dT}{T}$$

$$\Delta S_{II} = nC_p \ln \frac{T_t}{T_2} \quad (2)$$

Adding Eq. (1) and Eq. (2), we get

$$\Delta S_I + \Delta S_{II} = nC_P \ln \frac{T_f^2}{T_1 T_2}$$

$$\Delta S_{\text{total}} = nC_P \ln \frac{\left(\frac{T_1 + T_2}{2}\right)^2}{(T_1 T_2)}$$

$$\Delta S_{\text{total}} = C_P \ln \left[\frac{\left(\frac{T_1 + T_2}{2}\right)^2}{(T_1 T_2)} \right]$$

19.(C) We know

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

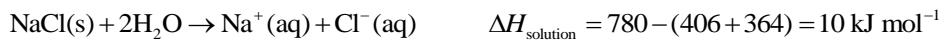
$$\Delta H = 30 + (4 \times 5) - (2 \times 3) = 44 \text{ L atm}$$

20.(B) $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad \Delta H = +780 \text{ kJ (Lattice energy)}$

$\text{Na}^+(\text{g}) + \text{aq} \rightarrow \text{Na}^+(\text{aq}) \quad \Delta H = -406 \text{ kJ (Hydration)}$

$\text{Cl}^-(\text{g}) + \text{aq} \rightarrow \text{Cl}^-(\text{aq}) \quad \Delta H = -364 \text{ kJ (Hydration)}$

The net reaction is dissolution of NaCl(s)



21.(C) Given,

$$\Delta_r H^\circ = 491.1 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$$

from relation

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (1)$$

At equilibrium. $\Delta_r G^\circ = 0$

from Eq. (1)

$$\Delta_r H^\circ = T\Delta_r S^\circ$$

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{491.1 \times 10^3 \text{ J mol}^{-1}}{198.0 \text{ JK}^{-1} \text{ mol}^{-1}}$$

$$T = 2480.3 \text{ K}$$

Therefore, given reaction is feasible above 2480.3 K temperature.

22.(D) Internal energy and volume depend on initial and final states.

23.(C) In a reversible process, the driving force and opposing force of that process are nearly equal, and hence, the system and the surrounding always remain in equilibrium with each other.

24.(A) We know

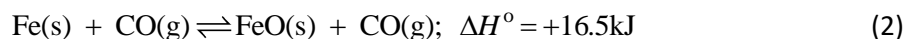
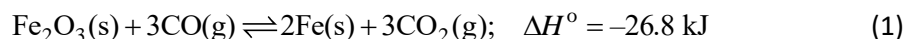
$$\Delta_r G^\circ = A - BT \quad (1)$$

At absolute temperature (*i.e.* 0 K) Eq. (1) reduced to

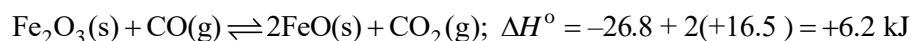
$$\Delta_r G^\circ = A$$

Therefore, if $A > 0$, reaction is endothermic.

25.(C) From the given equation,



Multiplying Eq. (2) by 2 and adding to Eq. (1), we get



26.(A) We know $C_p = \frac{7}{2}R$ (independent of p). Therefore, Graph (1) does not represent the correct variation of C_p vs p .

Also, $C_v = \frac{5}{2}R$ (independent of V)

27.(C) We know

$$\Delta S = \frac{\Delta H}{T(\text{K})}$$

$$\Rightarrow 14.4 = \frac{\Delta H}{391}$$

$$\Rightarrow \Delta H = 391 \times 14.4 = 5630 \text{ cal mol}^{-1} = \frac{5630}{60} = 93.8 \text{ cal g}^{-1}$$

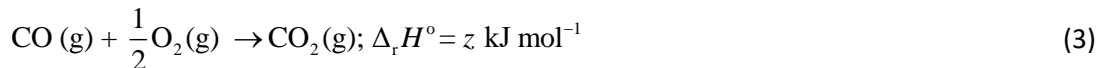
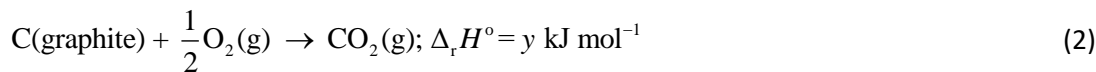
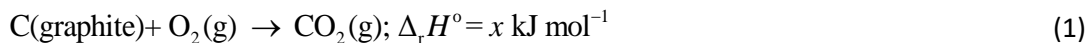
28.(A) For isothermal expansion $pV = \text{constant}$ that is, graph (I) and $p = \frac{\text{const.}}{V}$ that is, graph (III) are correct.

29.(C) Enthalpy of reaction = Σ Bond energies of Reactants – Σ Bond energies of Products

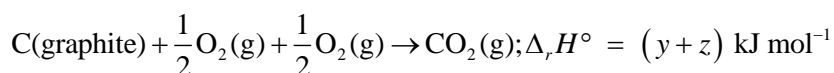
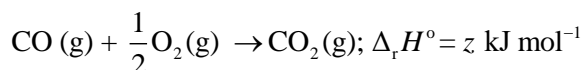
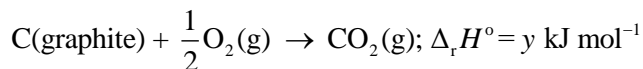
Therefore,

$$\begin{aligned} \Delta H &= [2(\text{C}-\text{H}) + (\text{C} \equiv \text{C}) + (\text{H}-\text{H})] - [4(\text{C}-\text{H}) + (\text{C}=\text{C})] \\ &= [2(98) + 198 + 103] - [4(98) + 145] = -40 \text{ kcal} \end{aligned}$$

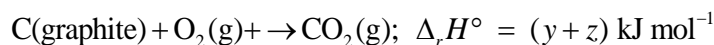
30.(A) From the given equation, we have



Adding Eq. (2) and (3), we get



Or



31.(D) We know

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}; \frac{T_2}{T_1} = \frac{6}{3}$$

$$\Delta S = 2.303 \times n \left\{ C_p \log_{10} \frac{T_2}{T_1} + R \log_{10} \frac{p_1}{p_2} \right\} = 2.303 \times 1 \left\{ 30.96 \log_{10} \frac{6}{3} + R \log_{10} \frac{20}{10} \right\} = 27.22 \text{ J K}^{-1} \text{ mol}^{-1}$$

32.(A) At constant pressure

$$\Delta H = \int_{T_1}^{T_2} n C_p dT$$

$$\Delta H = \int_{300 \text{ K}}^{1000 \text{ K}} 3 \times (23 + 0.01T) dT \quad [\text{Given; } C_p = 23 + 0.01T \text{ JK}^{-1} \text{ mol}^{-1}]$$

$$= 3 \left[23T + \frac{0.01T^2}{2} \right]_{300}^{1000}$$

$$= 3 \left[\left(23 \times 1000 + \frac{0.01(1000)^2}{2} \right) - \left(23 \times 300 + \frac{0.01 \times (300)^2}{2} \right) \right]$$

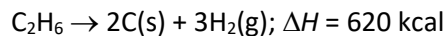
$$= 3[(23000 + 5000) - (6900 + 450)]$$

$$= 3[28000 - 7350]$$

$$= 3 \times 20650$$

$$= 61.950 \text{ J} \approx 62 \text{ kJ}$$

33.(D) $\text{CH}_4 \rightarrow \text{C}(\text{s}) + 2\text{H}_2(\text{g}); \Delta H = 360 \text{ kcal}$



$$\text{The average C-H bond energy} = \frac{360}{4} = 90 \text{ kcal}$$

$$\text{Therefore, C-C bond energy} = 620 - 90 \times 6 = 620 - 540 = 80 \text{ kcal}$$

34.(B) From first law of thermodynamics

$$\Delta U = q + w;$$

For cyclic process, $\Delta U = 0$

\Rightarrow

$$q = -w$$

For Adiabatic process, $q = 0$

\Rightarrow

$$\Delta U = w$$

For isochoric process, $\Delta V = 0$ or $w = -p\Delta V = 0$

\Rightarrow

$$\Delta U = q$$

For isothermal process, $\Delta T = 0$ or $\Delta U = 0$

\Rightarrow

$$q = -w$$

$$\mathbf{35.(B)} \Delta_r H = 6\Delta H_{f(\text{NaCl})}^\circ - \Delta H_{f(\text{Al}_2\text{Cl}_6)}^\circ$$

where $\Delta H_{f(\text{NaCl})}^\circ$ and $\Delta H_{f(\text{Al}_2\text{Cl}_6)}^\circ$ are the heats of formation of NaCl and Al_2Cl_6 . For Al(s) and Na(s), $\Delta H_f^\circ = 0$.

Therefore, $\Delta H_{f(\text{Al}_2\text{Cl}_6)}^\circ = -331 \text{ kcal}$.

36.(A) Algebraic sum of two path function is a state function, that is, $q + w$ and $H - TS$ are state function internal energy (U) and Gibbs free energy (G) respectively.

37.(B) The heat of neutralization = -55.9 kJ . Now,

the heat of neutralization of HCN by NaOH = the heat released on neutralization + the energy of dissociation of HCN = -12.1 kJ

So, the energy of dissociation of HCN = $+55.9 - 12.1 = 43.8 \text{ kJ}$

This is because HCN is a weak acid.

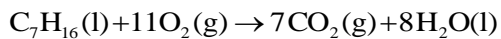
38.(C) From the relation

$$\Delta G = \Delta H - T\Delta S$$

for spontaneous process $\Delta G < 0$ and at all temperatures it is possible when $\Delta H < 0$ and $\Delta S > 0$.

39.(B) For a reaction at equilibrium $\Delta G = 0$ and not ΔG° . $\Delta G = \Delta G^\circ$, $\Delta G = \Delta G^\circ + RT \ln Q$ at equilibrium, $\Delta G = 0$ and $\Delta G^\circ = -RT \ln K_{\text{eq}}$.

40.(A) The combustion reaction of heptane is



We know

$$\begin{aligned}\Delta n_{\text{g}} &= n_{\text{p}} - n_{\text{R}} \\ &= 7 - 11 \\ &= -4\end{aligned}$$

Also,

$$\Delta H = \Delta U + \Delta n_{\text{g}} RT$$

$$\Delta H - \Delta U = -4RT$$

41.(B) When $\Delta n = 0$, $\Delta H = \Delta U$ because $\Delta H = \Delta U + \Delta n_{\text{g}} RT$. In the other three cases, $\Delta n_{\text{g}} \neq 0$.

42.(C) Work done against a constant external pressure

$$\begin{aligned}w &= -p_{\text{ext.}} (V_2 - V_1) \\ w &= -1 \text{ bar} \times (10 - 1) \text{ lit.} \\ w &= -9 \text{ bar lit.} \\ w &= -900 \text{ J}\end{aligned}$$

43.(B) Lower is heat of neutralization, more is dissociation energy, weaker is acid. As some of the neutralization energy is spend in making that weak acid dissociated.

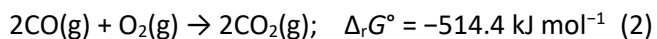
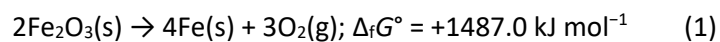
$$w = -0.9 \text{ kJ}$$

44.(C) We know

$$\Delta G^\circ = -RT \ln K$$

If $K < 1$, then $\Delta G^\circ > 0$

45.(B) We have



$\Delta_{\text{r}}G^\circ$ for the reaction $2\text{Fe}_2\text{O}_3(\text{s}) + 6\text{CO}(\text{g}) \rightarrow 4\text{Fe}(\text{s}) + 6\text{CO}_2(\text{g})$ can be obtained by Eq. (1) + 3 Eq. (2)

$$\begin{aligned}\Delta G^\circ &= 1487.0 + 3 \times (-514.4) \\ &= 1487 - 1543.2 \\ &= -56.2 \text{ kJ mol}^{-1}\end{aligned}$$

46.(C) The reaction involved is $\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

We know that

$$\Delta H = \Delta U + \Delta n_g RT \quad (1)$$

where

$$\begin{aligned}\Delta n_g &= \Delta n_p - \Delta n_r \\ &= 6 - \frac{15}{2} = -1.5\end{aligned}$$

Substituting $\Delta U = -3263.9 \text{ kJ}$, $R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$ and $\Delta n_g = -1.5$ in Eq. (1), we get

$$\begin{aligned}\Delta H &= -3263.9 + (-1.5) \times 8.314 \times 10^{-3} \times 298 \\ &= -3267.6 \text{ kJ}\end{aligned}$$

47.(B) We know

$$\Delta S = \frac{\Delta H}{T}$$

\Rightarrow

$$T = \frac{\Delta H}{\Delta S} = \frac{1435 \text{ cal}}{5.26} = 273 \text{ K} = 0^\circ\text{C}$$

48.(C) For the reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$, the enthalpy of reaction will be given by

$$\begin{aligned}\Delta H_{(\text{g})} &= \sum \text{BE}_{(\text{Reactants})} - \sum \text{BE}_{(\text{Products})} \\ &= \left[\text{BE}(\text{H}-\text{H}) + \frac{1}{2} \text{BE}(\text{O}-\text{O}) \right] - [2\text{BE}(\text{O}-\text{H})] \\ \Delta H_{(\text{g})} &= x_1 + \frac{x_2}{2} - 2x_3\end{aligned}$$

For formation of liquid water, the heat of latent heat for conversion of water vapor into liquid water needs to be added. This value is equal to $-(\text{latent heat of vaporization})$, so enthalpy of formation of liquid water is

$$\Delta H_{(\text{l})} = x_1 + \frac{x_2}{2} - 2x_3 - x_4$$

49.(B) We have

$$\begin{aligned}\Delta U_{\text{AB}} &= q_{\text{AB}} + w_{\text{AB}} \\ &= 2 + (-5) = -3 \text{ kJ mol}^{-1}\end{aligned}$$

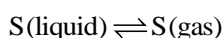
For a cyclic process, $\Delta U = 0$. Therefore, $\Delta U = \Delta U_{\text{AB}} + \Delta U_{\text{BC}} + \Delta U_{\text{CA}}$

$$\begin{aligned}\Delta U_{CA} &= -\Delta U_{AB} - \Delta U_{BC} \\ &= -(-3) - (-5) = 8 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{CA} &= q_{CA} + w_{CA} \\ 8 &= q_{CA} + 3 \Rightarrow q_{CA} = 5 \text{ kJ mol}^{-1}\end{aligned}$$

50.(B) The higher the pressure, the lower is the entropy. When pressure increase on the gases, the kinetic energy of the particles decreases along with the pressure. This causes the particles to come closer and intermolecular distance decreases thus the entropy decreases.

51.(A) We have



$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ} &= \Delta_f G^{\circ}(\text{vapor}) - \Delta_f G^{\circ}(\text{liquid}) \\ &= 103 - 100.7 \\ &= 2.3 \text{ kcal mol}^{-1}\end{aligned}$$

We know

$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ} &= -RT \ln K \\ 2.3 \times 10^3 &= -2 \times 500 \times \ln K_p \\ \ln K_p &= -2.3 \Rightarrow K_p = 0.1 \Rightarrow \text{vapour pressure} = 0.1 \text{ atm}\end{aligned}$$

52.(D) We know that

$$\Delta H = \Delta E + \Delta(pV) \quad \Delta H = \Delta U + \Delta(pV)$$

Using ideal gas equation, we have

$$\Delta H = \Delta U + nR\Delta T$$

For an ideal gas undergoing reversible isothermal expansion, $\Delta T = 0$ and $\Delta U = 0$. Therefore, the enthalpy change (ΔH) = 0.

53.(D) We know

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium $\Delta G = 0$; therefore,

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3 \text{ J mol}^{-1}}{75 \text{ J mol}^{-1}\text{K}^{-1}} = 400 \text{ K}$$

54.(A) At 100 °C, H₂O in liquid state is in equilibrium with H₂O in vapor phase; therefore, $\Delta G = 0$ Also the liquid molecules are converting into gaseous phase and we know that the randomness of system increases from liquid to gaseous phase so, $\Delta S = +ve$.

55.(B) Cl₂ is a gas at 298 K while Br₂ is a liquid.

<H2> Multiple Correct Choice Type

1.(A, B, D) Here only option (C) is incorrect that plot of $\log p$ versus $1/T$ is linear at constant volume.

Rather, at constant volume, $\frac{P}{T} = \text{constant}$.

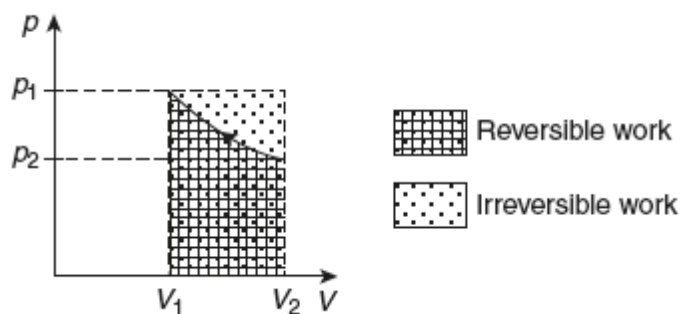
2.(B, C, D) From the given options only combustion of methane is not an endothermic reaction.

3.(A, D) Internal energy (E) and molar enthalpy (H) are state functions. The quantities ΔE and ΔH are path independent and definite quantities in a given change of states.

4.(B, C, D) For an ideal solution formed by benzene and naphthalene:

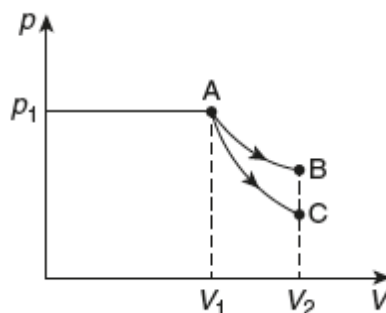
$$\Delta H_{\text{mixing}} = 0, \Delta S_{\text{system}} > 0 \text{ and } \Delta S_{\text{surroundings}} = 0$$

5.(A, B, C) **Option (A):** Correct. For compression of gas, $V_2 < V_1$, thus, from $w = -p\Delta V$, work done on the gas will be positive. Below graph shows the pressure-volume curve for work done during reversible and irreversible compression process. Area under curve during irreversible process is greater than the area under curve during reversible process. Therefore, work done on the gas in irreversible process is greater than in reversible process, that is, $w_{\text{irr}} > w_{\text{rev}}$.



Option (B): Correct. For work done in free expansion, $p_{\text{ext}} = 0$, therefore, $w = 0$. For an adiabatic process, $q = 0$ and for isothermal process, $\Delta T = 0$. Therefore, from first law of thermodynamics, $\Delta U = q + w = 0$.

Option (C): Correct. Below graph represents the expansion under adiabatic (AC) and isothermal condition (AB). Therefore, $|w_{\text{AB}}| > |w_{\text{AC}}|$



6.(B, D) The relationship between the concentration of the reactants and products is described by equilibrium constant expression (K). Increasing value of K implies that the concentration of the product is higher than the concentration of the reactant or reaction is moving more towards forward direction and vice versa.

Option (B): Correct. An increase in temperature favors the forward reaction in the case of endothermic process ($\Delta H > 0$); therefore the value of K will increase as $\Delta S_{\text{surr}} < 0$ (Surrounding is unfavourable).

Option (D): Correct. An increase in temperature favors the backward reaction in the case of exothermic process ($\Delta H < 0$); therefore the value of K will decrease as $\Delta S_{\text{surr}} > 0$ (Surrounding is favourable)

7.(A, B, D) For a spontaneous process in an isolated system, $\Delta S_{U,V} > 0$. For a reversible adiabatic process, $\Delta S_{U,V} = 0$.

$$\mathbf{8.(A, B)} \quad \Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) = 5 \ln\left(\frac{373}{298}\right) + 2 \ln 10$$

Also, $C_p - C_V = R \Rightarrow C_p = 7$. Now,

$$\Delta H = nC_p \Delta T = 1 \times 7 \times 75 = 525 \text{ cal}$$

and

$$\Delta U = nC_V \Delta T = 1 \times 5 \times 75 = 375 \text{ cal}$$

9.(C, D) According to the properties of ideal gases

$$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$$

10.(A, B) Melting is an endothermic process.

11. **(A, B, C)** All the above forms are different ways of expressing Kirchhoff's equation.

12. **(B, C, D)** $\Delta H = \Delta U + \Delta w$. If $\Delta H = 0$, $\Delta w = -\Delta U$. Thus, internal energy decreases. The temperature of the reversible adiabatic process always decreases and is also known as isentropic process.

13. **(A, C)** If the stability of products is lesser than that of reactants, then reactions will be endothermic and ΔH will be positive (as $\Delta H = \sum H_P - \sum H_R$).

14. **(C, D)** Heat of combustion is the amount of heat released when 1 mol of that substance burns in excess of air. Here, statement **(C)** and **(D)** are correct.

15. **(A, B, C)** Adiabatic means no exchange of heat energy from the surrounding.

$\Delta U = q + w$. When $q = 0$, $\Delta U = w$.

16. **(C, D)** $\Delta H_{PR} = \Delta H_{PQ} + \Delta H_{QS} + \Delta H_{SR} = (-134) + 92 - (-75) = +33 \text{ kJ mol}^{-1}$

$\Delta H_{RQ} = \Delta H_{RS} + \Delta H_{SQ} = (-750) - (+92) = -167 \text{ kJ mol}^{-1} \Rightarrow \Delta H_{RQ} < 0$, so exothermic.

$\Delta H_{SP} = \Delta H_{SQ} + \Delta H_{QP} = -(+92) - (-134) = +42 \text{ kJ mol}^{-1}$

17. **(A, C)** In both reactions, large number of molecules combine together to form lesser number of molecules.

18. **(B, C)**

ΔH	ΔS	Temperature (T)	Spontaneity
(B) -	-	Low T	Spontaneous
(C) +	+	Low T	Non-spontaneous

19. **(A, D)** The overall process is cyclic.

Thus, $\Delta U = 0$, $\Delta H = 0$, $\Delta S = 0$.

Now, $\Delta U = q + w \Rightarrow 0 = q + w \Rightarrow q = -w$

Total work = $w_{AB} + w_{BC} + w_{CA}$

$$w = -p(V_B - V_A) + 0 + 2.303 \times nRT \log \frac{V_C}{V_A}$$

$$w = -1 \times (40 - 20) + 0 + 2.303 \times p_A V_A \log \frac{V_C}{V_A}$$

$$w = -6.13 \text{ L atm} = -621.1 \text{ J}$$

$$(\text{as } 1 \text{ L atm} = 101.325 \text{ J})$$

20.(A, B, C, D) $\Delta G = 0$ indicates that the system is at equilibrium and ΔG is negative for all spontaneous processes. Exergonic process will occur spontaneously and is thermodynamically favorable. Endergonic processes are not spontaneous at standard conditions of pressure, temperature.

<H2> Assertion–Reasoning Type

- 1.(A)** As the disorder increases by changing the state from solid to vapor, the entropy increases.

- 2.(A)** Entropy of all elements and compounds decreases with decrease of temperature and becomes zero at 0 K.

- 3. (A)** Concept based.

- 4.(C)** Slope of isothermal process curve = slope of adiabatic process curve.

- 5.(D)** During an adiabatic expansion of a real gas, the temperature of the gas changes and the internal energy of the gas falls.

- 6.(A)** Concept based.

- 7.(D)** Gibbs free energy is negative for spontaneous process.

- 8.(A)** Since, internal energy is a state function, therefore, it depends upon only the initial and final position and does not depend on path followed.

- 9. (A)** Since, condensation involved decrease in temperature, therefore, the enthalpy change is negative for this process.

- 10.(C)** The entropy of formation of gaseous oxygen molecules is not zero.

- 11.(D)** Work done against vacuum is zero but heat absorbed may not be zero. The volume occupied by molecules of an ideal gas is negligible but not zero.

- 12.(C)** For isothermal expansion of ideal gas $\Delta U = 0$ and hence $q = -w$.

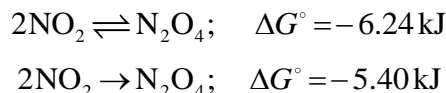
<H2>Comprehension Type

1.(C) We know

$$\Delta G^\circ = \Delta G_1 + \Delta G_2$$
$$\Delta G^\circ = (-5.40) + (-0.84) = -6.24 \text{ kJ.}$$

2.(C) From the given graph, $\Delta G^\circ = -0.84 \text{ kJ.}$

3.(D) For the given reaction,



One reaction is in equilibrium other is not.

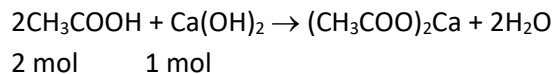
4.(B) The reaction involved is

	$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$			
Initial equivalent.	0.33	1	0	0
Equivalent at equilibrium	0	0.67	0.33	0.33
Equivalent added	0.66	0.01	0.66	0.66

$\Delta H = -4.6 \text{ cal.}$ On further addition $\Delta H = -9.2 \text{ cal.}$

5.(B) The observed value of heat of neutralization of HF is more due to extensive solvation of F^- ion because of its small size. Hydration reactions are exothermic also in nature.

6.(D) For the reaction,



Therefore, $\Delta_{\text{diss}} H$ of $\text{CH}_3\text{COOH} = 0.005 \text{ kcal g}^{-1} \times 60 = 0.3 \text{ kcal mol}^{-1}$

7.(A) For the reaction

$$\Delta_r H = \sum H_f^\circ (\text{Product}) - \sum H_f^\circ (\text{Reactants})$$
$$-890.4 = [-393.7 + 2(-285.8)] - [\Delta H_f^\circ (\text{CH}_4) + 2(0)]$$

Therefore, $\Delta H_f^\circ (\text{CH}_4) = -965.3 + 890.4 - 74.9 \text{ kJ mol}^{-1}$

8.(C) We know

$$\Delta H_{\text{reaction}} = \sum H_f^\circ (\text{Products}) - \sum H_f^\circ (\text{Reactants}) = -285.8 \text{ kJ mol}^{-1}$$
$$[11 \times (-285.8) + 12(-394.5)] - [12 \times 0 + \Delta H_f^\circ (\text{Sucrose})] = -5200.7$$

Therefore, $(-3143.8 - 4734) - \Delta H_f^\circ(\text{Sucrose}) = -5200.7$

or $\Delta H_f^\circ = -2677.1 \text{ kJ mol}^{-1}$

9.(D) $\text{C}_6\text{H}_6(\text{l}) + 12\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 12 \text{H}_2\text{O}(\text{l})$

$$\begin{aligned}\Delta H_{\text{reaction}} &= \sum \Delta H_f^\circ(\text{Products}) - \sum \Delta H_f^\circ(\text{Reactants}) \\ &= [6 \times (-398.3) + 12(-285.8)] - [49 + 12 \times 0] \\ &= -3242.2 \text{ kJ mol}^{-1}\end{aligned}$$

<H2> Integer Answer Type

The answer is a **non-negative integer**.

1.(1) We know

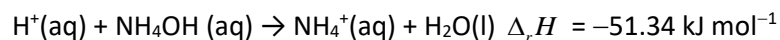
$$K = e^{-\Delta G^\circ/RT}$$

For $\Delta G^\circ = 0$

$$K = e^0 = 1$$

2.(1) Enthalpy of neutralization of a strong acid and a strong base is -57.54 kJ . It is the heat evolved when one-gram equivalent of strong acid (HCl) is mixed with strong base (NaOH). Since 100 ml of 1 g-equiv solution evolves 5.71 kJ of heat, so the molarity of the solution is 1.

3.(6) Given that



We may consider neutralization in two steps:

(i) Ionization: $\text{NH}_4\text{OH}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta_r H_1$

(ii) Neutralization: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta_r H_2 = -57.32 \text{ kJ mol}^{-1}$

Now,

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

Therefore, $\Delta_r H_1 = \Delta_r H - \Delta_r H_2 = -51.34 - (-57.32) = 5.98 \text{ kJ mol}^{-1} \cong 6$

4.(0) For a monoatomic perfect gas $C_v = \frac{3}{2}R$

The change in internal energy, $\Delta U = C_v \Delta T$

$$\Delta U = \frac{3}{2} \times 8.314 \times 100 = 1247.1 \text{ J} = 1.247 \text{ kJ}$$

Since the volume remains constant, $w = 0$

5.(26) Given, $T_1 = 0^\circ\text{C}; T_2 = 40^\circ\text{C}$

We know

$$Q = mC\Delta T \quad (1)$$

Substituting the values in Eq. (1), we get

$$Q = 52 \times 1 \times (40 - 0) \quad \left[\text{Since, } C = 1 \text{ cal g}^{-1} \right]$$

$$\Rightarrow Q = 2080 \text{ cal}$$

Since, by adding 52 g of ice to 100 g of water at 40°C, ice gain 2080 cal to change its states to water.

Now, from latent heat, we have

$$Q = mL$$

$$\Rightarrow 2080 = m \times 80 \quad \left[\text{Since, } L = 80 \text{ cal g}^{-1} \right]$$

$$\Rightarrow m = 26 \text{ g}$$

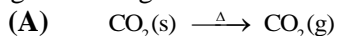
$$6.(6) 1 \text{ atm L} = 101.325 \text{ J. Therefore, } 607.8 \text{ J} = \frac{1}{101.325} \times 607.8 = 5.99 \cong 6 \text{ L atm.}$$

7.(0) $\Delta G = 0$ at equilibrium.

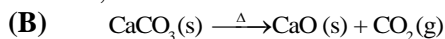
<H2> Matrix–Match Type

1.(A)→(p), (r), (s); (B)→(r), (s); (C)→(t); (D)→(q), (r), (t)

For the given changes:



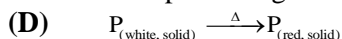
Phase transition, $\Delta H = +\text{ve}$ and $\Delta S = +\text{ve}$



No phase transition, $\Delta H = +\text{ve}$ and $\Delta S = +\text{ve}$



Two particles give one gaseous particle, so $\Delta S = -\text{ve}$



This is an allotropic change. ΔH is positive, as white phosphorus converts to red phosphorus on heating. ΔS is negative, as red phosphorus is a polymeric solid, less reactive than white phosphorus.

2.(A)→(r), (t); (B)→(p), (q), (s); (C)→(p), (q), (s); (D)→(p), (q), (s), (t)

(A) During freezing of water entropy decreases, $\Delta S_{\text{sys}} < 0$, $\Delta G = 0$.

(B) In vacuum, free expansion work done = 0. So, $q = 0$ and $\Delta U = 0$.

(C) For an ideal gas in isolated condition $q = 0$, $\Delta U = 0$, so as per first law $w = 0$.

(D) The process is cyclic through unique reversible path, hence, $\Delta U = 0$ (cyclic), $\Delta G = 0$. $w = 0$ (positive and negative work are same and opposite) and $q = 0$.

3. A \rightarrow (p), B \rightarrow (r), C \rightarrow (q), D \rightarrow (s)

Using the equation $\Delta G = \Delta H - T\Delta S$

4. A \rightarrow (s), B \rightarrow (r), C \rightarrow (q), D \rightarrow (p)

5. A \rightarrow (r); B \rightarrow (s); C \rightarrow (p, s); D \rightarrow (q, s)

(A) For constant volume, that is, $\Delta V = 0$.

As $w = -p\Delta V$

Therefore, $w = 0$

(B) From Gay Lussac's law, at constant pressure, the change in temperature is zero, that is, $\Delta T = 0$.

(C) At constant temperature, $\Delta T = 0$.

(D) For adiabatic process, the heat change is zero, and also, the change in temperature is zero.