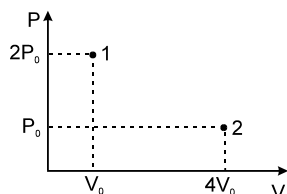
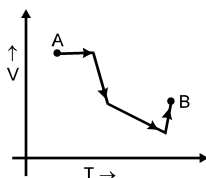


THERMODYNAMICS & THERMOCHEMISTRY

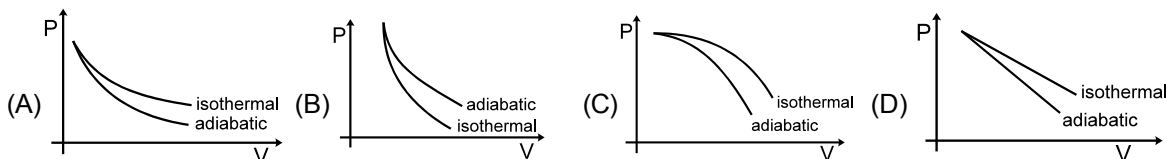
1. A liquid which is confined inside an adiabatic piston is suddenly taken from state 1 to state 2 by expanding it against constant external pressure of P_0 . If the piston comes to rest at point 2 as shown. Then the enthalpy change for the process will be :



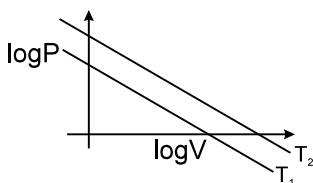
- (A) $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$ (B) $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$ (C) $\Delta H = -P_0 V_0$ (D) None of these
2. The bond dissociation energy of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol⁻¹ respectively. The enthalpy of formation for HCl gas will be
 (A) -44.0 kcal (B) -22.0 kcal (C) 22.0 kcal (D) 44.0 kcal
3. For the following V-T plot for a gas undergoing a process from state A to state B. Select the correct alternative(s).



- (A) Pressure constantly increases (B) Pressure first increases, then decreases
 (C) Final pressure is less than initial pressure (D) Pressure first decreases then increases.
4. The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is :

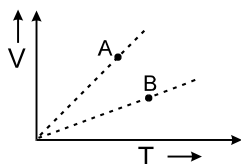


5. For the following two isotherms drawn at two different temperature T_1 and T_2 . Which of the following statements are true? (number of moles are constant)



- (A) $T_2 > T_1$ (B) $T_1 > T_2$ (C) $T_1 = T_2$ (D) Cannot be predicted

6. In the following V-T graph

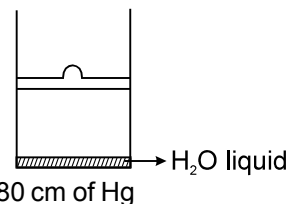


Points A and B are two states of the same gas. Then,

- (A) $P_A = P_B$
 (C) $P_A < P_B$

- (B) $P_A > P_B$
 (D) Data insufficient process must be specified

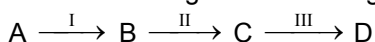
7. An ideal gas is confined inside a piston of volume 10 litres as shown. The piston contains Hydrogen gas saturated with water vapour. The piston also contains some liquid water. The total pressure is 80 cm of Hg column. If now the volume of the piston is doubled, then final total pressure will be (aq. tension of $H_2O = 20$ cm of Hg column) (Neglect volume of liquid H_2O)



- (A) 40 cm of Hg (B) 50 cm of Hg (C) 60 cm of Hg

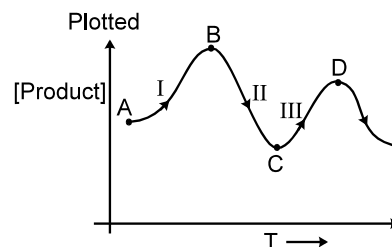
(D) 80 cm of Hg

8. For the following reaction through stages I, II, III ;

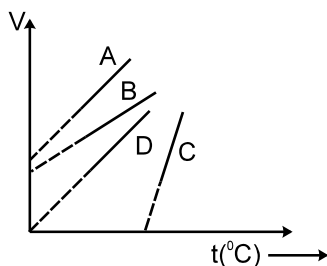


the concentration of product versus temperature was plotted
 Select the correct statement

- (A) Stages I and III are endothermic but II is exothermic
 (B) Stages I, II and III are all endothermic
 (C) Stages I, II and III are all exothermic
 (D) Stages I and II are endothermic but III is exothermic



9. Four different plots A,B,C, D were plotted for four different processes on an ideal gas.
 Which of the following statement/s may be true :



- (A) Plot A may be an isobar (constant pressure line) (B) Plot B may be an isobar
 (C) Plot D may be an isobar (D) Plot C may be an isobar

10. **Assertion** : Graphite can be converted into diamond by application of very high pressure and temperature, using a suitable catalyst.

Reason : Graphite is thermodynamically more stable and less dense than diamond.

- (A) Both A and R are true and R is the correct explanation of A.
 (B) Both A and R are true but R is not correct explanation of A
 (C) A is true but R is false
 (D) A is false but R is true
 (E) both A and R are false

11. **Assertion** : On increasing pressure, freezing point of water increases.

Reason : Density of ice is less than liquid water.

- (A) Both A and R are true and R is the correct explanation of A.
 (B) Both A and R are true but R is not correct explanation of A
 (C) A is true but R is false
 (D) A is false but R is true
 (E) both A and R are false

12. Three moles of an ideal gas [$C_p = 7/2 R$] at pressure 'P' and temperature 'T' is isothermally expanded to twice its initial volume. It is then compressed at constant pressure to its original volume. Finally the gas is brought at constant volume to its original pressure P.

(a) Sketch P–V and P–T diagrams for the processes, (b) Calculate the net work done by the gas and heat supplied to the gas during complete cycle in terms of R & T. [$\ln 2 = 0.693$]

13. Consider the following reversible changes undergone by 10 moles of an ideal, monatomic gas :
 A (10 atm, 50 ℓ) \longrightarrow B (10 atm, 100 ℓ) \longrightarrow C (5.0 atm, 100 ℓ) \longrightarrow A (10 atm, 50 ℓ). Obtain ΔE of the gas, work done and heat absorbed by the gas for each step and for the overall cycle. Express the result in litre atm. Label the different states in a P–V diagram.

14. In an isothermal expansion of a gaseous sample the correct relation is (consider w (work) with sign according to new IUPAC convention)

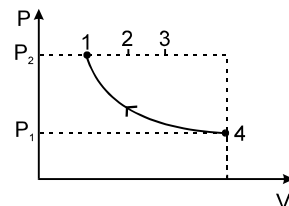
[The reversible and irreversible processes are carried out between same initial and final states.]

- (A) $w_{\text{rev}} > w_{\text{irrev}}$ (B) $w_{\text{irrev}} > w_{\text{rev}}$ (C) $q_{\text{rev}} < q_{\text{irrev}}$ (D) can not be predicted

15. A monoatomic gas ($C_V = \frac{3}{2} R$) is allowed to expand adiabatically and reversibly from initial volume of 8L at 300 K to a volume of V_2 at 250 K. V_2 is
 (A) 10.5 L (B) 23 L (C) 8.5 L (D) 50.5 L

16. An ideal gas is taken from the same initial pressure P_1 to the same final pressure P_2 by three different processes. If it is known that point 1 corresponds to a reversible adiabatic and point 2 corresponds to a single stage adiabatic then

- (A) Point 3 may be a two stage adiabatic.
 (B) the average K.E. of the gas is maximum at point 1
 (C) Work done by surrounding in reaching point number '3' will be maximum
 (D) If point 3 and point 4 lie along an isotherm, then $W_{4-3} > W_{4-2} > W_{4-1}$

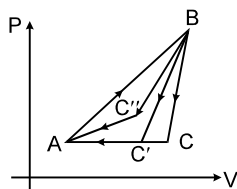


17. One mole of an ideal monoatomic gas at temperature T and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be :

- (A) $T + \frac{2}{3 \times 0.0821}$ (B) $T - \frac{2}{3 \times 0.0821}$ (C) $\frac{T}{2^{5/3-1}}$ (D) $\frac{T}{2^{5/3+1}}$

18. Three cyclic process ABCA, ABC'A and ABC''A are shown on P-V diagram. The process having maximum

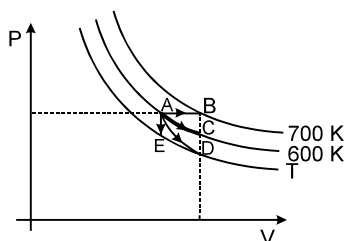
efficiency is where efficiency defined as $\eta = \text{efficiency} = \frac{\text{Total work done}}{\text{Positive heat supplied to the gas}}$ where work is net work in the complete process and heat supplied is heat given to the system, which does not include heat rejected or heat taken out from the system:



- (A) ABCA (B) ABC'A (C) ABC''A (D) can't determine

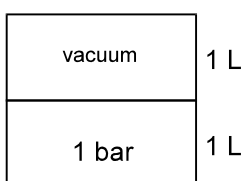
19. For an ideal gas four processes are marked as 1, 2, 3 and 4 on P-V diagram as shown in figure. The amount of heat supplied to the gas in the process 1, 2, 3 and 4 are Q_1 , Q_2 , Q_3 and Q_4 respectively, then correct order of heat supplied to the gas is :

[AB is process-1, AC is process-2, AD is adiabatic process-3 and AE is process-4]



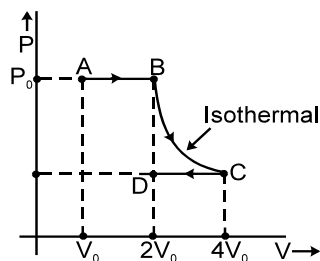
- (A) $Q_1 > Q_2 > Q_3 > Q_4$ (B) $Q_1 < Q_2 < Q_3 < Q_4$ (C) $Q_1 > Q_2 > Q_4 > Q_3$ (D) $Q_1 > Q_4 > Q_2 > Q_3$

20. The enthalpy of vaporization of water at 100°C is $40.63 \text{ kJ mol}^{-1}$. The value ΔU° for this process would be
 (A) $37.53 \text{ kJ mol}^{-1}$ (B) $39.08 \text{ kJ mol}^{-1}$ (C) $42.19 \text{ kJ mol}^{-1}$ (D) $43.73 \text{ kJ mol}^{-1}$
21. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2 . Then
 (A) $\Delta H_1 > \Delta H_2$
 (B) $\Delta H_1 < \Delta H_2$
 (C) $\Delta H_1 = \Delta H_2$, enthalpy being a state function
 (D) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.
22. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is $50 \text{ J}^{\circ}\text{C}$. Then the enthalpy change during the process is (1L atm \simeq 100 J)
23. A container of volume 2L is separated into equal compartments. In one compartment one mole of an ideal monoatomic gas is filled at 1 bar pressure and the other compartment is completely evacuated. A pinhole is made in the separator so gas expands to occupy full 2L and heat is supplied to gas so that finally pressure of gas equals 1 bar. Then



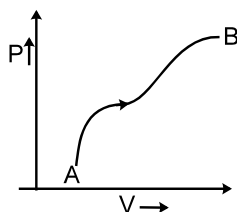
- (A) $\Delta E = \Delta H = 150 \text{ J}$ (B) $\Delta H = 250 \text{ J}$ (C) $\Delta E = 100 \text{ J}$ (D) $\Delta E = \Delta H = 0$

24. q , w , ΔE and ΔH for the following process ABCD on a monoatomic gas are :



- (A) $w = -2 P_0 V_0 \ln 2$, $q = 2 P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$
 (B) $w = -2 P_0 V_0 \ln 2$, $q = 2 P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 2 P_0 V_0 \ln 2$
 (C) $w = -P_0 V_0 (1 + \ln 2)$, $q = P_0 V_0 (1 + \ln 2)$, $\Delta E = 0$, $\Delta H = 0$
 (D) $w = -P_0 V_0 \ln 2$, $q = P_0 V_0 \ln 2$, $\Delta E = 0$, $\Delta H = 0$

25. The graph given below shows the P-V plot for a process on an ideal gas. Select the correct statement.

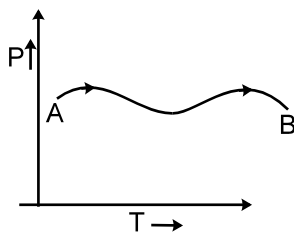


- (A) Enthalpy content of the gas is constantly increasing and the process is carried out slowly.
 (B) Enthalpy content of the gas first increases then decreases and the process is quasistatically.
 (C) Enthalpy content of the gas is constant and the process takes infinite amount of time for completion
 (D) Enthalpy content first decreases then increases and the process is reversible.

26. A vessel contains 100 litres of a liquid x. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]

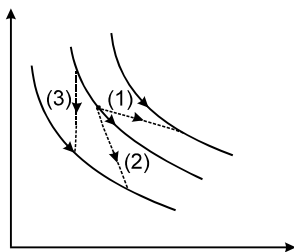
(A) $\Delta U = 0$, $\Delta H = 0$ (B) $\Delta U = +202.6\text{ J}$, $\Delta H = +202.6\text{ J}$
 (C) $\Delta U = -202.6\text{ J}$, $\Delta H = -202.6\text{ J}$ (D) $\Delta U = 0$, $\Delta H = +202.6\text{ J}$

27. The P-T graph as given below was observed for a process on an ideal gas, which of the following statement is true.



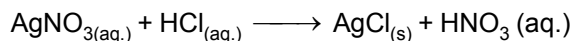
(A) $w = +ve$, $\Delta H = +ve$ (B) $w = -ve$, $\Delta H = -ve$
 (C) $w = -ve$, $\Delta H = +ve$ (D) $w = +ve$, $\Delta H = -ve$

28. A student plotted different isothermal process as shown but forgot to label the axes. He then also draw process (1), (2) and (3) as shown by the dotted lines. If it is known that in none of the processes, the heat given equalled the change in enthalpy, then identify the correct statement



(A) (2) – rev. adiabatic (3) rev. isobar (B) (1) – rev. adiabatic (3) rev. isochore
 (C) (1) – irrev. adiabatic (3) rev. isochore (D) (2) – rev. adiabatic (3) rev. isochore

29. If ΔH_f° for Ag^+ (∞ diluted), NO_3^- (∞ diluted), Cl^- (∞ diluted) and $\text{AgCl}_{(s)}$ are 105.579, -207.36 , -167.159 and -127.068 respectively. Calculate the enthalpy change for the reaction



(A) 21.471 KJ/mol (B) 145.688 KJ/mol (C) 65.488 KJ/mol (D) None

30. Given $\Delta_{\text{ioniz}} H^\circ$ (HCN) = 45.2 kJ mol^{-1} and $\Delta_{\text{ioniz}} H^\circ$ (CH_3COOH) = 2.1 kJ mol^{-1} . Which one of the following facts is true ?

(A) pK_a (HCN) = pK_a (CH_3COOH) (B) pK_a (HCN) > pK_a (CH_3COOH)
 (C) pK_a (HCN) < pK_a (CH_3COOH) (D) pK_a (HCN) = $(45.17/2.07)\text{pK}_a$ (CH_3COOH)

31. The standard enthalpes of formation of FeO and Fe_2O_3 are -65 kcal mol^{-1} and $-197\text{ kcal mol}^{-1}$ respectively. A mixture of two oxides contains FeO and Fe_2O_3 in the mole ratio 2 : 1. If, by oxidation, the mixture is changed into 1 : 2 mole ratio, how much thermal energy is released per mole from the initial mixture?

32. With the help of following data construct Born-Haber cycle for $\text{CaF}_2(s)$ and $\text{CaF}(s)$ and prove that CaF cannot exist, rather it will undergo disproportionation into CaF_2 and Ca .

Data (all in Kcal mol^{-1})

Sublimation energy for $\text{Ca}(s)$ = 48

First and second ionisation energy for Ca = 141 and 274 respectively

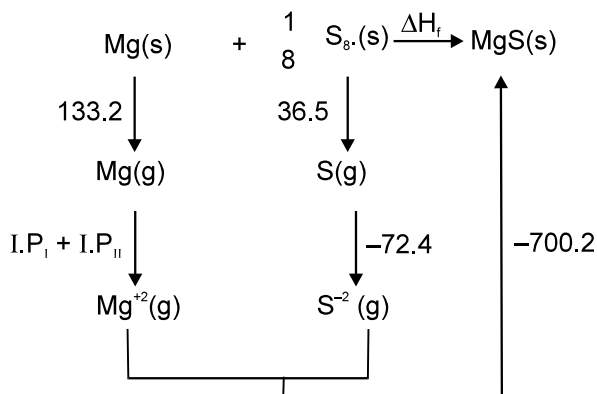
Dissociation energy for $\text{F}_{2(g)}$ = 34

$\Delta H_{E.A.(F)} = -83.0$; $\Delta H_{L.E.(CaF_2)} = -627$; $\Delta H_{L.E.(CaF)} = -190$

33. Calculate the fuel efficiency in $\frac{\text{kJ}}{\text{gram}}$ of C_2H_4 and C_4H_{10} . The heats of formation of C_2H_4 , C_4H_{10} , CO_2 and

H_2O are 52.3, -126.1 , -393.5 and $-285.8\text{ kJ mol}^{-1}$ respectively.

34. Calculate ΔH_f for the formation of MgS from the Born-Haber cycle given below



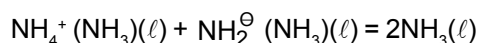
All the values are in Kcal/mol. ΔH_f is the enthalpy of formation of MgS(s). IP_I and I.P_{II} are first and second I.E. Given $3(\text{I.P}_I + \text{I.P}_{II}) = -19\Delta H_f$.

35. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.

- 18 gm of graphite on complete combustion evolve 590 KJ heat
- 15889 KJ heat is required to dissociate all the molecules of 1 litre water in to H_2 and O_2 .
- The heat of formation of liquid benzene is 50 kJ/mol
- Density of C_6H_6 (ℓ) = 0.87 gm/ml

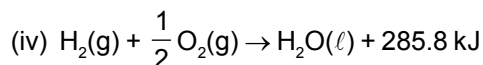
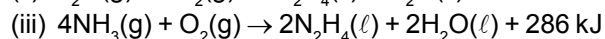
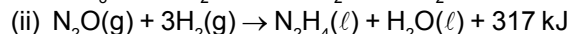
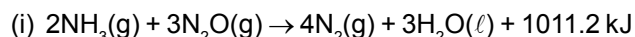
36. The thermal effect of reaction in liquid NH_3 at -33°C were measured by observing the quantity of liquid NH_3 vaporised by the process of intersect. The heat of vaporisation of NH_3 at -33°C is 327 cal g^{-1} . When 0.835 g of NH_4Br was dissolved in 20 g of liquid NH_3 , 0.221 g of NH_3 was vaporised. (a) Find the molar heat of solution of NH_4Br in liquid NH_3 at this concentration. (b) When 0.948 g of NH_4Br was dissolved in 20 g of liquid NH_3 containing an equimolar amount of KNH_2 , 0.845g of ammonia was vaporised.

Find ΔH at 240 K for the reaction



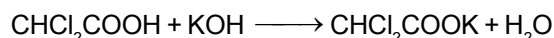
37. Only gases remain after 16 g of carbon is treated with 25 lit. of air at 27°C & 6 atm pressure. (Assume 20% by volume oxygen, 79.0% nitrogen, 1% CO_2). Determine the heat evolved under constant pressure. The heats of formation per mole at 27°C are -26 & -94 kcal for CO & CO_2 respectively. (At. wt. C = 12)

38. Set up the Hess' law cycle to find the standard enthalpy of combustion of hydrazine using the following thermochemical reactions.



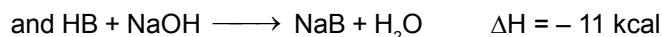
Also find ΔH_f (N_2H_4). Is N_2H_4 an endothermic compound?

39. If heat of dissociation of CHCl_2COOH is 0.7 kcal/mole then ΔH for the reaction :



- (A) -13 kcal (B) $+13$ kcal (C) -14.4 kcal (D) -13.7 kcal

40. If $\text{HA} + \text{NaOH} \longrightarrow \text{NaA} + \text{H}_2\text{O}$ $\Delta H = -12$ kcal



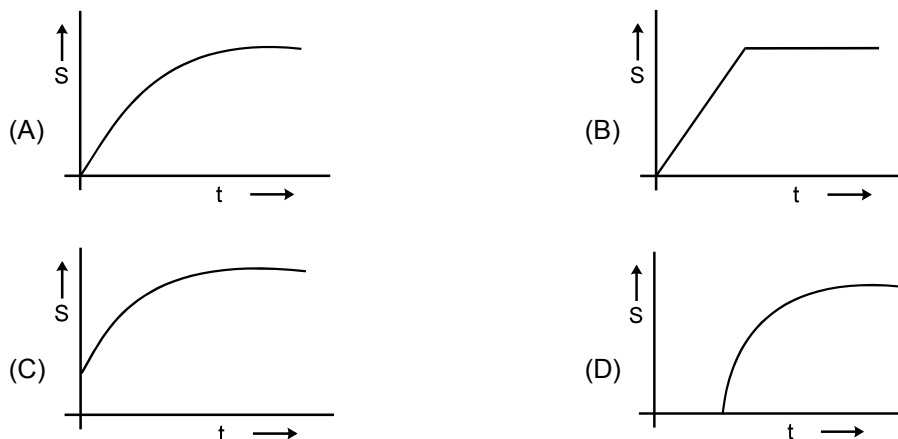
then equimolar solution of which acid has higher pH -

- (A) HA (B) HB (C) both have same pH (D) information insufficient

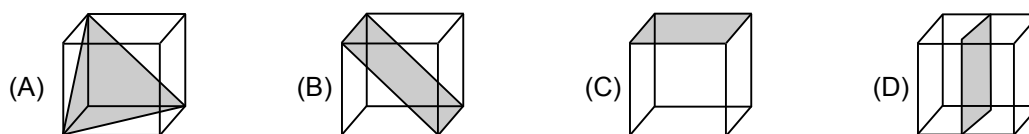
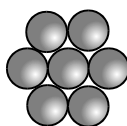
41. $C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -94.3 \text{ kcal/mol}$
 $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \quad \Delta H = -67.4 \text{ kcal/mol}$
 $O_2(g) \rightarrow 2O(g); \quad \Delta H = 117.4 \text{ kcal/mol}$
 $CO(g) \rightarrow C(g) + O(g); \quad \Delta H = 230.6 \text{ kcal/mol}$
 Calculate ΔH for $C(s) \rightarrow C(g)$ in kcal/mol.
 (A) 171 (B) 154 (C) 117 (D) 145
42. The enthalpy of neutralization of HNO_3 by $NaOH = -13680 \text{ cal/eq}$. When one equivalent of $NaOH$ is added to a dilute solution containing one equivalent of HNO_3 and one equivalent of a certain monoprotic weak acid, 13960 cal are evolved. Assume that the base is distributed between HNO_3 and the weak acid in the ratio 3 : 1 and the weak acid is practically nonionized. Calculate the enthalpy of ionization of the weak acid.
 (A) -1120 cal (B) -2110 cal (C) -1210 cal (D) +1210 cal
43. The difference between ΔH and ΔE on a molar basis for the combustion of n-octane at $25^\circ C$ would be :
 (A) -13.6 kJ (B) -1.14 kJ (C) -11.15 kJ (D) +11.15 kJ
44. Calculate the ΔH_c° for diborane B_2H_6 using
 (i) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s) \quad \Delta H = -1273 \text{ kJ}$
 (ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ}$
 (iii) $H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = 44 \text{ kJ}$
 (iv) $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g) \quad \Delta H = 36 \text{ kJ}$
 (A) -2035 kJ/mol (B) -1991 kJ/mol (C) -2079 kJ/mol (D) -1273 kJ/mol
45. A gas mixture 3.67 L in volume contain C_2H_4 and CH_4 in proportion of 2 : 1 by moles and is at $25^\circ C$ and 1 atm. If the $\Delta H_c(C_2H_4)$ and $\Delta H_c(CH_4)$ are -1400 and -900 kJ/mol find heat evolved on burning this mixture.
 (A) 20.91 kJ (B) 50.88 kJ (C) 185 kJ (D) 160 kJ
46. In the reaction $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad \Delta H = -265 \text{ kcal}$
 The enthalpies of formation of CO_2 and SO_2 are both negative and are in the ratio 4 : 3. The enthalpy of formation of CS_2 is +26 kcal/mol. Calculate the enthalpy of formation of SO_2 .
 $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad \Delta H = -265 \text{ kcal}$
 (A) -90 kcal/mol (B) -52 kcal/mol (C) -78 kcal/mol (D) -71.7 kcal/mol
47. Reaction of gaseous fluorine (F_2) with compound X yields a single product Y, whose mass percent composition is 61.7% F and 38.3% Cl.
 Calculate $\Delta_f H^\circ$ (in kJ/mol) for the synthesis of Y using following information and fill in the magnitude only in your answer sheet
 $2ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g) \quad \Delta H^\circ = 205.6 \text{ kJ}$
 $2ClF_3(g) + 2O_2(g) \longrightarrow Cl_2O(g) + 3OF_2(g) \quad \Delta H^\circ = 533.0 \text{ kJ}$
 $\Delta_f H^\circ(OF_2, g) = 24.7 \text{ kJ/mol}$
48. The two liquids CH_3COOCH_3 and $CHCl_3$ combine in such a way that they form a single H-bond between each pair of molecules. In an experiment to determine the approximate strength of this bond, samples of the two liquids were mixed in an insulated glass beaker and the temperature was found to rise by $1^\circ C$. Other data are given in the table below
- | | mass(gm) | Amt. in moles | sp. heat J/gm-K |
|---------------|----------|---------------|-----------------|
| CH_3COOCH_3 | 3.71 | 0.05 | 2.0 |
| $CHCl_3$ | 1.195 | 0.01 | 1.0 |
| Beaker | 66 | - | 0.5 |
- The approximate strength of the H-bond according to the above experiment (in KJ/mole) will be
 (A) 0.73 (B) 3.6 (C) 4.9 (D) 2.8

49. The heat of combustion of ethene gas is $330 \text{ Kcal mol}^{-1}$ calculate >C=C< bond energy assuming that bond energy of C–H bond is $93.6 \text{ KCal mol}^{-1}$
Given : ΔH_f° for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ are -94.2 and $-61 \text{ Kcal mol}^{-1}$ respectively. Heat of atomisation of carbon and hydrogen are 150 and $51.5 \text{ Kcal mol}^{-1}$ respectively.
50. A gaseous mixture of propane, acetylene and CO_2 is burnt in excess of air. The mixture evolved 4800 kJ of heat. The heat evolved is used in two separate processes :
(i) Vapourising 87.5% water obtained in the process.
(ii) Forming C_2H_4 (3808 litres at stp)
The volume of CO_2 obtained on burning was 224 L (stp). Using the information above and additionally (in kJ/mole)
 $\epsilon_{\text{H-H}} = 435$, $\epsilon_{\text{C-H}} = 416$, $\epsilon_{\text{C=C}} = 615$, $\epsilon_{\text{C-C}} = 347$, $\epsilon_{\text{C=O}} = 812$, $\Delta H_{\text{sub}}(\text{gr}) = 718$, $\Delta H_f^\circ \text{CO}_2 = -394$,
 $\Delta H_f^\circ(\text{H}_2\text{O}(\ell)) = -286$, $\Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) = -246$
find the moles of each constituent of the gaseous mixture.
51. The average energy required to break a P–P bond in $\text{P}_4(\text{s})$ into gaseous atoms is $53.2 \text{ kcal mol}^{-1}$. The bond dissociation energy of $\text{H}_2(\text{g})$ is $104.2 \text{ kcal mol}^{-1}$; ΔH_f° of $\text{PH}_3(\text{g})$ from $\text{P}_4(\text{s})$ is $5.5 \text{ kcal mol}^{-1}$. The P-H bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in $\text{P}_4(\text{s})$]
(A) 85.2 (B) 57.6 (C) 76.9 (D) 63.3
52. The average, S–F bond energy in SF_6 if the ΔH_f° value are -1100 , $+275$ and $+80 \text{ kJ/mol}$ respectively for $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$ and $\text{F}(\text{g})$ is
(A) $390.1 \frac{\text{kJ}}{\text{mol}}$ (B) $103.9 \frac{\text{kJ}}{\text{mol}}$ (C) $903.1 \frac{\text{kJ}}{\text{mol}}$ (D) $309.1 \frac{\text{kJ}}{\text{mol}}$
53. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is **correct**, for the above process?
(A) The randomness of the universe decreases
(B) The randomness of the surroundings decreases
(C) Increase in randomness of surroundings equals the decrease in randomness of system
(D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.
54. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state, is $\Delta H = -401.7 \text{ J mol}^{-1}$ for the transition. Assume the surroundings to be an ice-water both at 0°C :
(A) -1.09 JK^{-1} (B) 1.47 JK^{-1} (C) 0.38 JK^{-1} (D) None of these
55. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in $\text{J K}^{-1} \text{ mol}^{-1}$)
(A) 19.15 (B) -19.15 (C) 4.7 (D) zero
56. 1 Kg of boiling water at 100°C is dropped into Indian ocean, the temperature of which is 27°C . Calculate entropy change of the universe.
[specific heat of water = $4.2 \times 10^3 \text{ J Kg}^{-1}$, $\log\left(\frac{298}{373}\right) = 0.0975$]
57. One mole of an ideal diatomic gas ($C_v = 5 \text{ cal}$) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L . The entropy change of the process can be expressed as ($R = 2 \text{ calories/mol/K}$)
(A) $3 \ln \frac{298}{373} + 2 \ln 10$ (B) $5 \ln \frac{373}{298} + 2 \ln 10$
(C) $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$ (D) $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$
58. The entropy of mixing of $100 \text{ g N}_2\text{O}$ at 120°C and 1.5 bar with 100 g CO_2 at 120°C and 1.5 bar is ($\log 2 = 0.300$)
(A) $18.4 \frac{\text{J}}{\text{K}}$ (B) $26.19 \frac{\text{J}}{\text{K}}$ (C) $41.8 \frac{\text{J}}{\text{K}}$ (D) $14.8 \frac{\text{J}}{\text{K}}$

59. A copper block of mass 'm' at temperature ' T_1 ' is kept in the open atmosphere at temperature ' T_2 ' where $T_2 > T_1$. The variation of entropy of the copper block with time is best illustrated by



60. In an f.c.c. crystal, which of the following shaded planes contains the following type of arrangement of atoms?



61. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is : [R = 0.082 L atm mol⁻¹ K⁻¹ = 8.3 J mol⁻¹K⁻¹].

- (A) 0 (B) $R \ln(24.6)$ (C) $R \ln(2490)$ (D) $\frac{3}{2} R \ln(24.6)$

62. The enthalpy change for a given reaction at 298 K is $-x$ J mol⁻¹ (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature

- (A) can be negative but numerically larger than $x/298$
 (B) can be negative but numerically smaller than $x/298$
 (C) cannot be negative
 (D) cannot be positive

63. For a perfectly crystalline solid $C_{p.m.} = aT^3$, where a is constant. If $C_{p.m.}$ is 0.42 J/K-mol at 10 K, molar entropy at 10 K is

- (A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero

64. For a perfectly crystalline solid $C_{p.m.} = aT^3$, where a is constant. If $C_{p.m.}$ is 0.84 J/K-mol at 10 K, molar entropy at 10 K is

- (A) 0.42 J/K-mol (B) 0.28 J/K-mol (C) 4.2 J/K-mol (D) 2.8 J/K-mol

65. What is ΔG° at 1000°C for the following reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; is this reaction spontaneous at 1000°C and 1 atm? What is the value of K_p at 1000°C for this reaction? What is partial pressure of CO_2 ? Use the following data : (anti log 0.987 = 9.75)

	$\text{CaCO}_3(\text{s})$	$\text{CaO}(\text{s})$	$\text{CO}_2(\text{g})$
ΔH_f°	-1206.9	-635.1	-393.5 kJ
S°	92.9	38.2	213.7 J/K

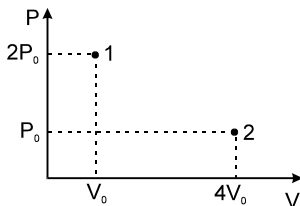
66. Find ΔE , ΔH , ΔS and ΔG in expanding reversibly one litre of one mole of an ideal gas to 100 ℓ at a constant temperature of 27°C.

67. Calculate free energy when 1 mole of an ionic salt MX (s) is dissolved in water at 25°C. Given
 Lattice energy of MX = 780 kJ mol⁻¹
 Hydration energy of MX = - 775.0 kJ mol⁻¹
 Entropy change of dissolution at 25°C = 45 J mol⁻¹ K⁻¹
68. A reaction has $\Delta H = -33 \text{ kJ}$ and $\Delta S = -58 \frac{\text{J}}{\text{K}}$. This reaction would be :
 (A) spontaneous at all temperature (B) non-spontaneous at all temperatures
 (C) spontaneous above a certain temperature only (D) spontaneous below a certain temperature only
69. Consider the reaction
 $\text{HgS(s)} + \text{O}_2(\text{g}) \rightarrow \text{Hg}(\ell) + \text{SO}_2(\text{g})$
 for which the $\Delta S^\circ = +36.7 \text{ J/K}$
 Given ΔH° data
 $\text{HgS} \Rightarrow -58.2 \text{ kJ}$, $\text{SO}_2 \Rightarrow -296.8 \text{ kJ}$
 Indicate whether the reaction is spontaneous at 25°C or not? How does heating facilitate the reaction ?
70. Given that : $\Delta G_f^\circ (\text{CuO}) = -30.4 \text{ kcal/mole}$
 $\Delta G_f^\circ (\text{Cu}_2\text{O}) = -34.98 \text{ kcal/mole}$ T = 298 K
 Now on the basis of above data which of the following predictions will be most appropriate under the standard conditions and reversible reaction.
 (A) Finely divided form of CuO kept in excess O₂ would be completely converted to Cu₂O
 (B) Finely divided form of Cu₂O kept in excess O₂ would be completely converted to CuO
 (C) Finely divided form of CuO kept in excess O₂ would be converted to a mixture of CuO and Cu₂O (having more of CuO)
 (D) Finely divided form of CuO kept in excess O₂ would be converted to a mixture of CuO and Cu₂O (having more of Cu₂O)
71. If $\Delta G = -177 \text{ K cal}$ for (1) $2 \text{ Fe(s)} + \frac{3}{2} \text{ O}_2(\text{g}) \longrightarrow \text{Fe}_2\text{O}_3(\text{s})$
 and $\Delta G = -19 \text{ K cal}$ for (2) $4 \text{ Fe}_2\text{O}_3(\text{s}) + \text{Fe(s)} \longrightarrow 3 \text{ Fe}_3\text{O}_4(\text{s})$
 What is the Gibbs free energy of formation of Fe₃O₄ ?
 (A) $+229.6 \frac{\text{kcal}}{\text{mol}}$ (B) $-242.3 \frac{\text{kcal}}{\text{mol}}$ (C) $-727 \frac{\text{kcal}}{\text{mol}}$ (D) $-229.6 \frac{\text{kcal}}{\text{mol}}$
72. One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. Then for this process (R = 2 calories/mol/K) (take calories as unit of energy and kelvin for temp)
 (A) $\Delta H = 525$ (B) $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$
 (C) $\Delta E = 525$ (D) ΔG of the process can not be calculated using given information.
73. If a certain mass of gas is made to undergo separately adiabatic and isothermal expansions to the same pressure, starting from the same initial conditions of temperature and pressure, then as compared to that of isothermal expansion, in the case of adiabatic expansion, the final :
 (A) volume and temperature will be higher
 (B) volume and temperature will be lower
 (C) temperature will be lower but the final volume will be higher
 (D) volume will be lower but the final temperature will be higher
74. The molar entropy content of 1 mole of oxygen (O₂) gas at 300 K and 1 atm is 300 J mole⁻¹ K⁻¹. Calculate ΔG when 2 moles of oxygen is expanded reversibly and isothermally from 300 K, 1 atm to double its volume (Take R = 8.3 J mole⁻¹ K⁻¹, ln 2 = 0.7)
 (R = 8.3 J mole⁻¹ K⁻¹, ln 2 = 0.7)
 (A) -3.486 KJ mole⁻¹ K⁻¹ (B) 0
 (C) -1.728 KJ mole⁻¹ K⁻¹ (D) 0.75 KJ mole⁻¹ K⁻¹
75. 2 mole of an ideal gas at 27°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J k⁻¹ mol⁻¹)
 (A) 19.15 (B) -19.15 (C) 4.7 (D) zero

76. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is :
 (Given : $\Delta_r H_{298K}^\circ = -54.07 \text{ kJ mol}^{-1}$, $\Delta_r S_{298K}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $2.303 \times 8.314 \times 298 = 5705$)
 (A) 5 (B) 10 (C) 95 (D) 100

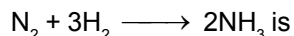
77. For the process $\text{H}_2\text{O}(l) (1 \text{ bar}, 373 \text{ K}) \rightleftharpoons \text{H}_2\text{O}(g) (1 \text{ bar}, 373 \text{ K})$, the correct set of thermodynamic parameters is:
 (A) $\Delta G = 0$, (B) $\Delta S > 0$ (C) $\Delta H > 0$ (D) $\Delta G = -ve$

78. A liquid which is confined inside an adiabatic piston is suddenly taken from state 1 to state 2 by a single stage process. If the piston comes to rest at point 2 as shown. Then the enthalpy change for the process will be :



- (A) $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$ (B) $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$ (C) $\Delta H = -P_0 V_0$ (D) None of these

79. Bond energy of N – H, H – H and N \equiv N bonds are q_1 , q_2 and q_3 . ΔH of :



- (A) $q_3 + 3q_2 - 2q_1$ (B) $2q_1 - q_3 - 2q_2$ (C) $q_3 + 3q_2 - 6q_1$ (D) $q_1 + q_2 - q_3$

80. A gas absorbs 100 J of heat and is simultaneously compressed by a constant external pressure of 1.50 atm from 8.00 to 2.00 L in volume. What is ΔE in joules for the gas ?

- (A) -812 (B) +812 (C) -912 (D) 1012

81. Calculate the final temperature of a sample of a monoatomic gas that is expanded reversibly and adiabatically from 500 mL at 300 K to 2.00 L [$(4)^{0.66} = 2.521$]

- (A) 119 K (B) 150 K (C) 300 K (D) 20 K

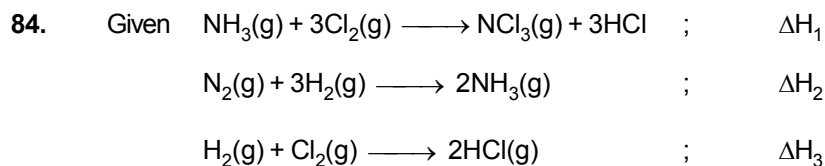
82. The heat capacities of A, B and C are in the ratio 1 : 2 : 3. The enthalpy change for the reaction,

$A + B \longrightarrow C$, at temperature T_1 is ΔH_1 . Assuming the heat capacities do not change with temperature, the enthalpy change ΔH_2 at temperature T_2 will be :

- (A) greater than ΔH_1
 (B) equal to ΔH_1
 (C) less than ΔH_1
 (D) greater than or less than ΔH_1 depending on whether T_2 is greater or lesser than T_1

83. The melting point of a solid is 300 K and its latent heat of fusion is 600 cal mol^{-1} . The entropy change for the fusion of 1 mole of the solid (in cal K^{-1}) at the same temperature would be :

- (A) 200 (B) 2 (C) 0.2 (D) 20



express the enthalpy of formation $\{\Delta H_1^\circ(\text{NCl}_3)\}$ in terms of ΔH_1 , ΔH_2 and ΔH_3 .

- (A) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \Delta H_1 + \frac{\Delta H_2}{2} + \frac{3}{2} \Delta H_3$
 (C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$ (D) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} + \frac{\Delta H_3}{2}$

85. One mole of an ideal gas (not necessarily monatomic) is subjected to the following sequence of steps

- (a) It is heated at constant volume from 298 K to 373 K
 (b) It is expanded freely into a vacuum to double volume
 (c) It is cooled reversibly at constant pressure to 298 K

Calculate w for the overall process. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Report the answer by writing value only e.g. 101.23 should be written as 10123.

86. The heat evolved in neutralizing a solution of HCN with a strong alkali is 3.0 kcal. The enthalpy of dissociation of HCN is

- (A) 10.2 kcal (B) 13.7 kcal (C) 10.7 kcal (D) 16.7 kcal

87. 0.5 mole each of two ideal gas A ($C_v = \frac{3}{2} R$) and B ($C_v = \frac{5}{2} R$) are taken in a container and expanded reversibly and adiabatically from $V = 1$ litre to $V = 4$ litre starting from initial temperature $T = 300$ K. ΔH for the process (in cal/mol) is.

- (A) -500 cal (B) -900 cal (C) -450 cal (D) -600 cal

ANSWER AND SOLUTIONS

1. (C)

Sol. Since liquid is expanding against external pressure P_0 hence work done

$$w = -P_0(4V_0 - V_0) = -3P_0V_0$$

$$\Delta U = w = -3P_0V_0$$

$$\Rightarrow \Delta H = \Delta U + P_2V_2 - P_1V_1 \\ = -3P_0V_0 + 4P_0V_0 - 2P_0V_0.$$

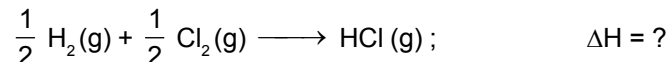
2. (B)

Sol. Given $\text{H}_2(\text{g}) \longrightarrow \text{HCl}(\text{g}); \quad \Delta H = 104 \text{ kcal} \quad \dots(1)$

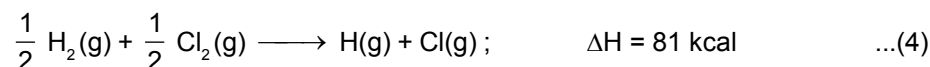
$\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g}); \quad \Delta H = 58 \text{ kcal} \quad \dots(2)$

$\text{HCl}(\text{g}) \longrightarrow \text{H}(\text{g}) + \text{Cl}(\text{g}); \quad \Delta H = 103 \text{ kcal} \quad \dots(3)$

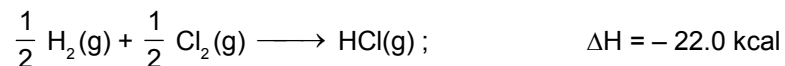
Heat of formation for HCl



Divide equation (1) and (2) by 2, and then add



Subtracting equation (3) from equation (4)



\therefore Enthalpy of formation of HCl gas = -22.0 kcal

3. (B)

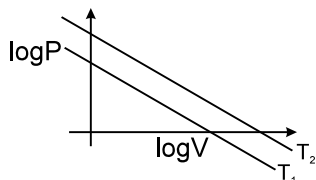
Sol. Can be seen by drawing isochore lines in the PV graph, greater the volume in isochoric process smaller will be the slope of that isochoric line. Hence the result can be obtained.

4. (A)

Sol. Slope of adiabatic curve is greater than isothermal curve

5. (A)

Sol.



$$PV = \text{const} = K$$

$$\log P + \log V = \log K$$

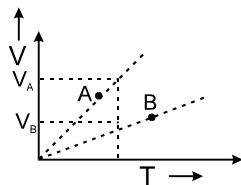
$$\Rightarrow y + x = K_1 \quad \text{as} \quad T \uparrow \quad K_1 \uparrow$$

Hence intercept on co-ordinate axes will increase

$$\Rightarrow T_2 > T_1$$

6. (C)

Sol.



$$\Rightarrow P_A < P_B$$

7. (B)

Sol. Total pressure is = 80 cm of Hg

V. P. of H₂O is = 20 cm of Hg

∴ Pressure of H₂ gas = 80 – 20 = 60 cm of Hg

Now if the volume of the piston is doubled then V.P. of water won't change since there is water in the container to maintain the equilibrium. Pressure of H₂ will become half

⇒ P_{H₂} = 30 cm of Hg

V. P_{H₂O} = 20 cm of Ag

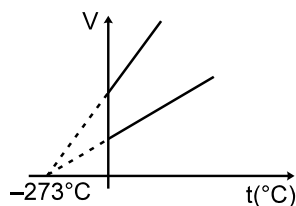
Total pressure = 20 + 30 = 50 cm of Ag

8. (A)

Sol. Plot shows that incase of I and III concentration of product increases with the increase in temperature hence reaction is endo thermic but incase of II conc. of product decreases with the increase in temperature hence it is an axo thermic process.

9. (A)

Sol.



At 0°C $V = V_0 + \frac{V_0 t}{273}$

$V = at + b$

Hence, plots A, B can be isobars.

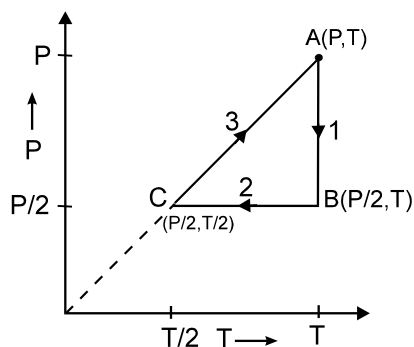
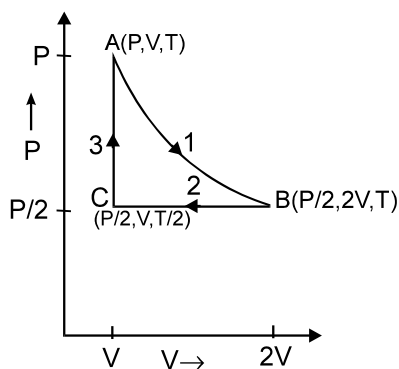
10. (A)

Sol. both assertion and reason are correct

11. (D)

Ans. On increasing pressure freezing point of water decreases. (D) is correct option.

12. (a)



(b) Work done in various process will be

for Isothermal process = - 2.08RT

for Isobaric process = 1.5 RT

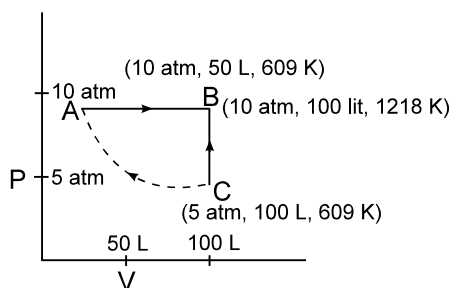
for Isochoric process = 0

∴ W_{Net} = - 0.58 RT Ans.

& Net heat supplied to the gas will be

Q_{net} = W_T = 0.58RT Ans.

13.



Total number of moles = 10

State A $10 \text{ atm} \times 50 \text{ lit.} = 10 \text{ mole} \times 0.0821 \text{ lit atm K}^{-1} \text{ mol}^{-1} \times T$

$$T = \frac{500}{10 \times 0.0821} = 609 \text{ K}$$

Step 1 A (10 atm, 50 lit, 609 K) \longrightarrow B (10 atm, 100 lit, 1218 K) $C_p = \frac{5}{2} R$ for a monatomic gas. The quantity of heat absorbed by the gas,

$$Q = nC_p \cdot \Delta T = 10 \times 2.5 \times 0.0821 \times 609 = 1250 \text{ lit atm.}$$

$$\text{Workdone by the gas} = P \cdot \Delta V = 10 \times 50 = 500 \text{ lit atm.}$$

$$\therefore \Delta E = 1250 - 500 = 750 \text{ lit atm.}$$

Step 2 B(10 atm, 100 L, 1218 K) \longrightarrow C (5 atm, 100 L, 609 K)

$$W = 0; C_v = \frac{3}{2} R \text{ and } Q = \Delta E = n \cdot C_v \cdot \Delta T = 10 \times 1.5 \times 0.0821 \times (-609)$$

$$= -750 \text{ lit atm (i.e., Quantity of heat given out by the gas} = 750 \text{ lit atm)}$$

Step 3 C(5 atm, 100 L, 609 K) \longrightarrow A (10 atm, 50 L, 609 K) $\Delta E = 0$ for an isothermal process for an ideal gas.

$$Q = W = n \cdot RT \ln \frac{V_2}{V_1} = 10 \times 0.0821 \times 609 \ln \frac{50}{100} = -346.5 \text{ L atm}$$

(i.e., heat given out by the gas = work done on the gas = + 346.5 L atm)

14. (B)

Sol. From 1st Law

15. (A)

Sol. $TV^{\gamma-1} = \text{constant}$

$$\gamma = \frac{5}{3} \quad \therefore \gamma - 1 = \frac{2}{3}$$

$$\therefore 300 \times (8)^{2/3} = 250 \times (V_2)^{2/3} \quad \Rightarrow \quad (V_2)^{2/3} = 4.8$$

$$\Rightarrow V_2 = (4.8)^{3/2} \cong 4.8 \times 2.2 = 10.5 \text{ L}$$

16. (D)

Sol. Since work done on the system, is maximum in single stage compression hence all other adiabatic points will fall between 1 and 2.

For the same pressure difference isothermal work is more than adiabatic work.

17. (B)

Sol. $\Delta U = \Delta W$

$$n C_v (T_2 - T) = -P \times (V_2 - V_1)$$

$$\frac{3}{2} R (T_2 - T) = -1$$

$$\therefore T_2 = T - \frac{2}{3 \times 0.0821}$$

18. (A)

Sol. Heat is supplied to the gas in process AB only.

$$\eta = \text{efficiency} = \frac{\text{work done}}{\text{heat supplied to the gas}}$$

work done is area under PV curve.

Area is maximum in the case of process ABCA

so work done is maximum in ABCA process

$$\eta = \frac{\text{work done}}{\text{heat supplied}}$$

efficiency maximum in process ABCA.

19. (A)

Sol. In process-1 heat supplied = area under AB curve + $n \times c_v \times 100$ (isobaric process)
In process-2 heat supplied = area under AC curve (isothermal process)
In process-3 heat supplied = 0 (adiabatic process)
In process-4 heat supplied = $n \times c_v (T - 600)$ = negative (isochoric process)

20. (A)

Sol. We have

$$\begin{aligned} \text{H}_2\text{O}(l) &\rightarrow \text{H}_2\text{O}(g) & \Delta H^\circ &= 40.63 \text{ kJ mol}^{-1} \\ \Delta U^\circ &= \Delta H^\circ - (\Delta n_g) RT = 40.63 \text{ kJ mol}^{-1} - (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) (373 \text{ K}) \\ &= (40.73 - 3.10) \text{ kJ mol}^{-1} = 37.53 \text{ kJ mol}^{-1} \end{aligned}$$

21. (B)

Sol. $\Delta H = nC_p \Delta T$.

Now for expansions

$(\Delta T)_{\text{rev}} > (\Delta T)_{\text{irreversible}}$. Hence the result.

22. $\Delta H = \Delta E + \Delta(PV)$ & $\Delta E = q + W = (50 \times 300 - 3 \times 100) \text{ J}$ [as $T_f = 2 \times 300 \text{ K} = 600 \text{ K}$]
= 14.7 kJ
 $\Delta H = 14700 + 10 \times 100 = 15700 \text{ J} = 15.7 \text{ kJ}$.

23. (B)

Sol. Final temperature of gas must be double of the initial temperature

$$\begin{aligned} \Delta H &= \Delta E + \Delta(PV) = nC_v \Delta T + \Delta(PV) & (\Delta T = T_f - T_i = 2T_i) \\ &= \frac{nR}{(\gamma - 1)} T_i + \Delta(PV) = \frac{3}{2} \times 100 + 100 = 250 \text{ J}. \end{aligned}$$

24. (A)

Sol. At A and D the temperatures of the gas will be equal, so

$$\Delta E = 0, \quad \Delta H = 0$$

$$\text{Now } w = w_{AB} + w_{BC} + w_{CD} = -P_0 V_0 - 2P_0 V_0 \ln 2 + P_0 V_0 = -2P_0 V_0 \ln 2$$

$$\text{and } q = -w = 2P_0 V_0 \ln 2$$

25. (A)

Sol. The product PV is increasing so temperature will keep on increasing in the process, hence $\Delta H = \Delta E + \Delta(PV)$ will increase constantly

26. (D)

Sol. $\Delta H =$ heat given so process is isobaric.

$$w = p_{\text{ext}} (\Delta V) = -1 \times 2 \text{ litre.atm} = -202.6 \text{ J}$$

$$\text{Hence } q = 202.6 \text{ J} = \Delta H. \text{ and } \Delta E = q + w = 0.$$

27. (C)

Sol. From graph we know that $V_B > V_A$, so expansion has taken place so w will be with -ve sign and ΔH will be +ve as both ΔE and $\Delta(PV)$ have increased.

28. (D)

Sol. As heat added is not equal to change in enthalpy hence process can never be isobar. clearly from the sketch. (2) is reversible adiabatic and (3) will be isochore.

29. (C)

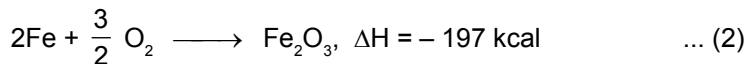
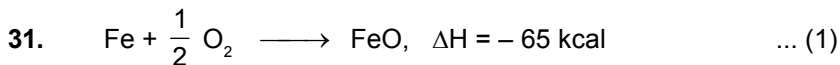
Sol.
$$\Delta H^\circ_{\text{reaction}} = [\Delta H_f(\text{AgCl}) + \Delta H_f(\text{H}^+) + \Delta H_f(\text{NO}_3^-)] - [\Delta H_f(\text{Ag}^+) + \Delta H_f(\text{NO}_3^-) + \Delta H_f(\text{Cl}^-) + \Delta H_f(\text{H}^+)]$$

$$= -127.068 - [105.579 - 167.159]$$

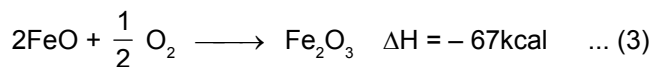
$$= 65.488 \text{ KJ / mol.}$$

30. (B)

Sol. Larger the value of $\Delta_{\text{ioniz}} H^\circ$, weaker the acid and larger the value of pK_a . Hence, $pK_a(\text{HCN}) > pK_a(\text{CH}_3\text{COOH})$



\therefore equation (2) – 2 × eq (1) we get



Let initially the total moles of FeO and Fe_2O_3 be 'a'

Then $\text{FeO} = \frac{2a}{3}$ and $\text{Fe}_2\text{O}_3 = \frac{a}{3}$

Let 'b' mole of FeO are converted in to Fe_2O_3 , then mole of FeO left = $\frac{2a}{3} - b$, mole of Fe_2O_3 formed = $\frac{b}{2}$

$\therefore \text{Fe}_2\text{O}_3 \text{ total} = \frac{a}{3} + \frac{b}{2}$

given $\frac{\text{FeO}}{\text{Fe}_2\text{O}_3} \text{ after oxidation} = \frac{1}{2}$

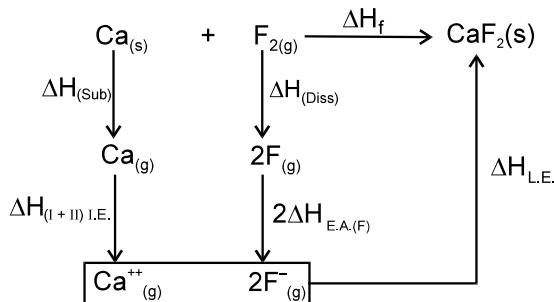
$$\therefore \frac{\frac{2a}{3} - b}{\frac{a}{3} + \frac{b}{2}} = \frac{1}{2} \quad \text{or} \quad a = \frac{5b}{2}, \quad \therefore b = \frac{2}{3} a$$

\therefore 2 mole of FeO released heat = – 67kcal

\therefore heat produced by 'b' mole of FeO = $\frac{-67 \times b}{2} = \frac{-67 \times 2 \times a}{2 \times 3} = -13.4a$

\therefore Heat liberated per mole of mixt = $\frac{-13.4a}{a} = -13.4 \text{ kcal / mol. Ans.}$

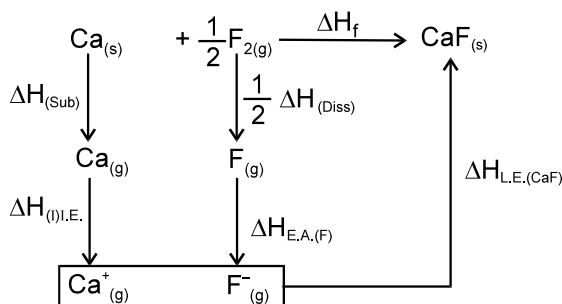
32. B – H cycle for CaF_2



$$\therefore \Delta H_f(\text{CaF}_2) = +48 + (141 + 274) + 34 - (83 \times 2) - 627$$

$$= -296 \text{ Kcal mol}^{-1}$$

B-H cycle for CaF



$$\therefore \Delta H_f(\text{CaF}) = +48 + 141 + 17 - 83 - 190$$

$$= -67.0 \text{ Kcal mol}^{-1}$$

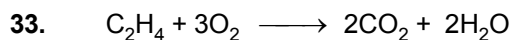
\therefore L.E. of CaF_2 is larger than L.E. of CaF , hence CaF_2 is more stable
Now consider the reaction



$$\therefore \Delta H_{\text{reaction}} = -296 - (-134)$$

$$= -162 \text{ Kcal mol}^{-1}$$

\therefore Even if CaF is formed, it will disproportionate into CaF_2 and Ca , because this reaction is energetically more favourable than the formation of CaF .



$$\Delta H_{\text{comb.}} = [2 \times (-393.5) + 2 \times (-285.8)] - [0 + 52.3] = -1410.9 \text{ kJ / mol}$$

$$\therefore \text{fuel eff.} = \frac{1410.9}{28} = 50.39 \frac{\text{kJ}}{\text{gram}}$$

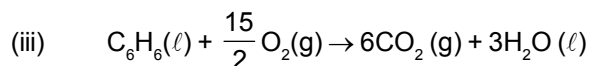
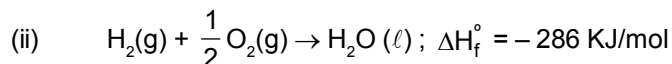
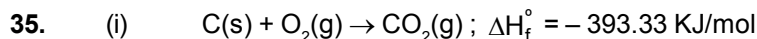
Similarly for C_4H_{10} ,

$$\Delta H_{\text{comb}} = [4 \times (-393.5) + 5 \times (-285.8)] - [0 + (-126.1)] = -2876.9 \text{ kJ / mol.}$$

34. For Born – Harber cycle of Mgs

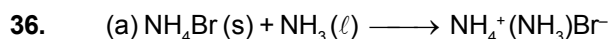
$$\Delta H_f = 133.2 + \left(-\frac{19}{3} \Delta H_f\right) + \frac{36.5}{8} - 72.4 - 700.2$$

$$\therefore \Delta H_f = -86.6 \text{ Kcal Ans.}$$



$$\therefore \Delta H^\circ = [6(-393.33) + 3(-286)] - 50 = -3268 \text{ KJ}$$

$$\therefore \text{Heat evolved from 87 gm benzene} = 3645 \text{ KJ Ans.}$$



$$\begin{array}{ccc} \downarrow & & \downarrow \\ \frac{0.835}{98} \text{ mole} & \frac{20}{17} \text{ mole} & = 0.00852 \text{ mole} \end{array}$$

under these conditions, $\text{NH}_3(\ell)$ vaporised = 0.221 gm.

That is, heat of vaporisation = $0.221 \times 327 \text{ cal} = 72.27 \text{ cal}$.

This is for the dissolution of 0.00852 mole of NH_4Br . So the molar heat of solution (ΔH) of NH_4Br is

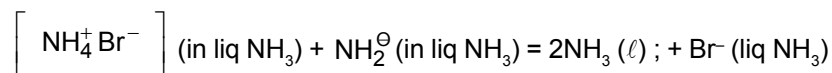
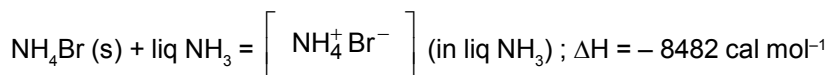
$$- \frac{72.27}{0.00852} = -8482 \text{ cal mol}^{-1} = -8.482 \text{ kcal mol}^{-1}$$

For the dissolution of 0.948 g of NH_4Br (s) in 20 g of NH_3 (ℓ) containing NH_2^\ominus , heat of vaporisation of NH_3 (ℓ)

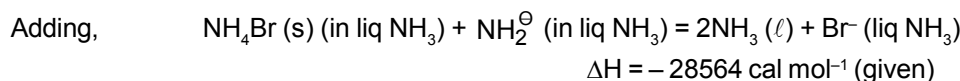
$= 0.845 \times 327 \text{ cal} = 276.3 \text{ cal}$. This is for $\frac{0.948}{98} \text{ mol}$ i.e., 0.009673 mole of NH_4Br . Therefore, the molar heat

of solution of NH_4Br in NH_2^\ominus /liq NH_3 , is $-\frac{276.3}{0.009673} = -28564 \text{ cal mol}^{-1}$. We now proceed to determine ΔH

of the reaction of NH_4^+ (liq NH_3) with NH_2^\ominus (in liq NH_3), using Hess' law.



$$\Delta H = x \text{ cal mol}^{-1}$$



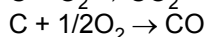
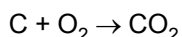
$$-8482 + x = -28564$$

$$\therefore x = -28564 + 8482 = -20,082 \text{ cal mol}^{-1}$$

Thus ΔH of the reaction of NH_4^+ with NH_2^\ominus in liq NH_3 is $-20.08 \text{ kcal mol}^{-1}$.

37. 16 gm carbon = 1.33 mol carbon

$$n(\text{O}_2) = \frac{PV}{RT} = \frac{6 \times 0.2 \times 25}{0.0821 \times 300} = 1.218 \text{ mol O}_2$$



Let x = number of moles carbon converted to CO_2

$$\therefore 1.33 - x = \text{number of moles CO formed}$$

The number of moles of oxygen atoms is the same before and after the reaction

$$2x + (1.33 - x) = 2 \times 1.218$$

$$x = 1.106 \text{ mol CO}_2$$

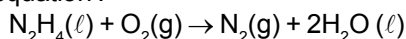
and $1.33 - 1.106 = 0.224 \text{ mol CO}$

$$\therefore \text{Heat evolved is } 1.106 \times (-94) = 103.96 \text{ Kcal (for CO}_2)$$

$$0.224 \times (-26) = -5.8 \text{ Kcal (for CO)}$$

$$\therefore \text{Total heat evolved is } -(5.8 + 103.96) = -109.78 \text{ Kcal}$$

38. Target equation :



which can be obtained by the given manipulation.

$$\frac{1}{4} \times (\text{i}) - \frac{3}{4} (\text{ii}) + \frac{9}{4} (\text{iv}) - \frac{1}{8} (\text{iii})$$

Hence ΔH for target equation is

$$\frac{1}{4} (-1011.2) - \frac{3}{4} (-317) + \frac{9}{4} (-285.8) - \frac{1}{8} (-286)$$

$$= \frac{1}{4} [-1011.2 + 3 \times 317 - 9 \times 285.8 + 0.5 \times 286]$$

$$= -622.35 \text{ kJ/mole hydrazine}$$

$$\text{Now } -622.35 = 2 \times (-285.8) - \Delta H_f (\text{N}_2\text{H}_4)$$

$$\Rightarrow \Delta H_f (\text{N}_2\text{H}_4) = +50.75 \text{ kJ/mol}$$

Yes it is an endothermic compound.

39. (A)

Sol. The required heat released will be $(13.7 - \text{heat required to dissociate } \text{CHCl}_2\text{COOH})$
 $= 13.0 \text{ kcal}$

40. (B)
Sol. HA will be stronger acid, so its solution will have lower pH.

41. (D)
Sol. $C(s) \longrightarrow C(g)$

Can be obtained as $\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta H_4$

42. (A)

Sol. $-13960 = -13680 \times \frac{3}{4} - 13680 \times \frac{1}{4} + \frac{1}{4} x$
where x is enthalpy of dissociation/ ionisation of weak acid.
so $x = -1120$ calories.

43. (C)

Sol. $\Delta H - \Delta E = -4.5 \times 8.315 \times 298 \text{ J} = -11.15 \text{ kJ}$

44. (A)

Sol. The equation $B_2H_6(g) + 3 O_2(g) \longrightarrow B_2O_3(s) + 3 H_2O(l)$ can be obtained by taking
 $-(4) + (1) + 3 \times (2) + 3 \times (3)$
Hence $\Delta H_c^\ominus = -36 - 1273 + 3 \times (-286) + 3 \times 44 = -2035 \text{ kJ}$

45. (C)

Sol. Easy

There is 2.44 L $C_2H_4 \longrightarrow n = \frac{1 \times 2.44}{0.082 \times 298} = 0.1 \text{ mol}$

there is 1.22 L $CH_4 \longrightarrow n = \frac{1 \times 1.22}{0.082 \times 298} = 0.05 \text{ mol}$

\therefore Heat evolved
 $= 0.1 \times 1400 + 0.05 \times 900 = 185 \text{ kJ}$.

46. (D)

Sol. $CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \Delta H =$
Let $\Delta H_f(CO_2, g) = 4x$
and $\Delta H_f(SO_2, g) = 3x$
 $\Delta H_{\text{reaction}} = \Delta H_f(CO_2, g) + 2\Delta H_f(SO_2, g) - \Delta H_f(CS_2, l)$
 $-265 = 4x + 6x - 26$
 $x = -23.9$
 $\therefore \Delta H_f(SO_2, g) = 3x = 71.7 \text{ kcal/mol}$.

47. 139

Sol.

	Cl	F
no. of moles	$\frac{38.7}{35.5} = 1.09$	$\frac{61.7}{19} = 3.42$

Simplest relative ratio 1 : 3

So, product Y is ClF_3 & compound X is ClF

For the synthesis of Y reaction is $F_2(g) + ClF(g) \rightarrow ClF_3(g)$

$1/2Cl_2O(g) + 3/2OF_2(g) \longrightarrow ClF_3(g) + O_2(g) \quad \Delta H^\ominus = -533.0/2 \text{ kJ} \quad \Rightarrow \quad -266.5 \text{ kJ}$

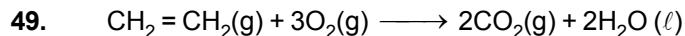
$ClF(g) + 1/2O_2(g) \longrightarrow 1/2Cl_2O(g) + 1/2OF_2(g) \quad \Delta H^\ominus = 205.6/2 \text{ kJ} \quad \Rightarrow \quad 102.8 \text{ kJ}$

$F_2(g) + \frac{1}{2} O_2(g) \rightarrow F_2O(g) \Delta H^\ominus = 24.7 \text{ kJ}$

$ClF(g) + F_2(g) \rightarrow ClF_3(g) \quad \Delta_f H^\ominus = -139 \text{ kJ/mol}$

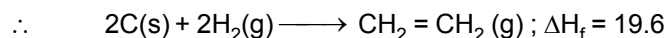
48. (B)

Sol. $\Delta H = 0.742 \times 2 \times 1 + 1.195 \times 1 \times 1 + 66 \times 0.5 \times 1$
 $\approx 36 \text{ J from } 0.01 \text{ mole } \text{CHCl}_3$
 $\therefore H_{\text{BE}} = 3.6 \text{ KJ mol}^{-1}$



$$\therefore -330 = [2 \times (-94.2) + 2(-61)] - \left[\Delta H_f^\circ \text{C}_2\text{H}_4 \right]$$

$$\therefore \Delta H_f^\circ (\text{C}_2\text{H}_4) = 19.6 \text{ Kcal mol}^{-1}$$

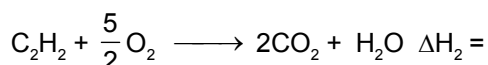
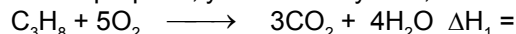


$$\therefore \Delta H_{\text{Reaction}} = \sum \text{B.E.}_{(\text{Reactants})} - \sum \text{B.E.}_{(\text{Products})}$$

on substituting the value in above relation we get $\text{B.E.}_{(\text{C}=\text{C})} = 122 \text{ Kcal / mol Ans.}$

50. 1 mole propane, 2 moles acetylene, 3 moles CO_2

Sol. Let x moles be propane, y moles acetylene, z moles CO_2

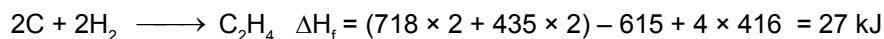


Moles of CO_2 formed = $3x + 2y$

Moles of CO_2 available = $3x + 2y + z$

Moles of H_2O formed = $4x + y$

$$\text{Heat used in (i) is } \frac{87.5}{100} \times (4x + y) \times 40 \text{ kJ}$$



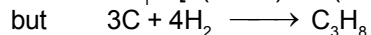
$$\text{Heat used in (ii) } \frac{3808}{22.4} \times 424 \text{ kJ}$$

$$4800 = 0.875 \times 40(4x + y) + 170 \times 27$$

$$\Rightarrow 4x + y = 6 \quad \dots (1)$$

$$3x + 2y + z = 10 \quad \dots (2)$$

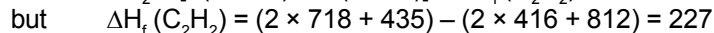
$$\Delta H_1 = [3(-394) + 4(-286)] - \Delta H_f(\text{C}_3\text{H}_8)$$



$$\Delta H_f(\text{C}_3\text{H}_8) = (3 \times 718 + 4 \times 435) - (2 \times 347 + 8 \times 416) = -128$$

$$\therefore \Delta H_1 = -2198 \text{ kJ}$$

$$\Delta H_2 = [2(-394) + 1(-286)] - \Delta H_f(\text{C}_2\text{H}_2)$$



$$\therefore \Delta H_2 = -1301 \text{ kJ}$$

$$\therefore 2198x + 1301y = 4800$$

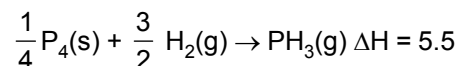
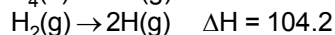
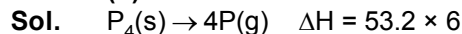
$$\Rightarrow 1.689x + y = 3.689 \quad \dots (3)$$

From (1) and (3) $2.311x = 2.311$

$$\Rightarrow x = 1$$

$$\therefore y = 2 \text{ and } z = 3$$

51. (C)



$$\frac{1}{4} \times 6 \times 53.2 + \frac{3}{2} \times 104.2 - 3\epsilon_{\text{P-H}} = 5.5$$

$$\Rightarrow \epsilon_{\text{P-H}} = 76.866 \text{ i.e. } 76.9 \text{ kcal mol}^{-1}$$

52. (D)



$$6 E_{\text{S-F}} = [275 + 6 \times 80] - [-1100]$$

$$\Rightarrow E_{\text{S-F}} = 309.1$$

53. (D)

Sol. As dew formation is spontaneous process therefore entropy or randomness of the universe will increase. As randomness of the system has decreased but randomness of the surrounding will increase larger so that change is positive.

54. (C)

Sol.
$$\Delta S_{(\text{system})} = \frac{1 \times -401.7}{368} = -1.09 \text{ JK}^{-1}$$

The ice-water both absorbs the 401.7 J mol⁻¹ at temperature 273 K

$$\therefore \Delta S_{\text{surrounding}} = \frac{1 \times 401.7}{273} = 1.47 \text{ JK}^{-1}$$
$$\Delta S_{(\text{universe})} = -1.09 + 1.47 = 0.38 \text{ JK}^{-1}$$

55. (D)

Sol.
$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

For adiabatic process (Q = 0)

$$\Delta E = W$$

$$nC_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S = 0$$

56. Amount of heat lost by 1 kg H₂O = m s ΔT = 315000 Joule

$$\therefore \text{This heat is absorbed by ocean hence entropy of ocean increases} = \frac{dq}{T} = 1050 \text{ JK}^{-1}$$

And entropy decrease of 1 Kg of boiled H₂O = -941.85 J

$$\therefore \Delta S_{\text{universe}} = 108.15 \text{ JK}^{-1} \text{ Ans.}$$

57. (B)

Sol.
$$\Delta S = nC_v \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right)$$

58. (B)

Sol.
$$\Delta S_{\text{mixing}} = -[n_1 R \ln X_1 + n_2 R \ln X_2]$$

$$= - \left[\frac{100}{44} \times 8.315 \ln \frac{1}{2} + \frac{100}{44} \times 8.315 \ln \frac{1}{2} \right]$$

$$= + \frac{100}{44} \times 8.135 \times 2.303 \log 2 = 26.19 \frac{\text{J}}{\text{K}}$$

59. (C)

Sol. There is some finite value of entropy at t = 0. It increases constantly till the temperature of the copper block and surrounding is equal. This will be the equilibrium situation hence further change in entropy is restricted ΔS = 0 at equilibrium.

60. (A)

Sol. Shown arrangement is hexagonally closed pack plane & these type of planes are arranged perpendicular to body diagonal of fcc unit cell as shown.

61. (B)

Sol.
$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = R \ln \left(\frac{P_i}{P_f} \right) = R \ln \left(\frac{300R}{1L \times 1 \text{ atm}} \right) = R \ln (24.6)$$

62. (B)

Sol. It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0 . If ΔS is $-ve$, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has to be less than

$$\frac{\Delta H}{T} \text{ i.e., } \frac{x}{298}.$$

63. (B)

Sol. $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$

$$S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K - mol}$$

64. (B)

Sol. $0.84 = a(10)^3 \Rightarrow a = 0.84 \times 10^{-3}$

$$S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.84}{3} = 0.28 \text{ J/K - mol}$$

65. For the given reaction,

$$\Delta H^\circ = (-635.1) + (-393.5) - (-1206.9) = 178.3 \text{ kJ}$$

$$\Delta S^\circ = (38.2) + (213.7) - (92.9) = 159.0 \text{ J/K}$$

To determine whether the reaction is spontaneous in the forward direction, let us calculate ΔG° .

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

$$\Delta G^\circ = 178.3 - 1273 \times (159.0 \times 10^{-3}) = -24.1 \text{ kJ.}$$

The negative sign of ΔG° suggests that the reaction is spontaneous at 1273 K and 1 atm.

$$\text{Further, } \log K = - \frac{(-24.1)}{2.303 \times (8.314 \times 10^{-3}) \times 1273}$$
$$= 0.987$$

$$K = K_p = 9.75$$

$$\therefore K_p = p_{\text{CO}_2} = 9.75 \text{ atm.}$$

66. For an ideal gas, at constant temperature, $\Delta E = 0$ and $\Delta H = 0$;

$$\Delta S_T = R \ln \frac{V_2}{V_1} = 2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \log 100$$
$$= 9.15 \text{ cal K}^{-1} \text{ mol}^{-1}$$

At constant temperature,

$$\Delta G = \Delta H - T\Delta S = 0 - 298.2 \times 9.15 = -2729 \text{ cal mol}^{-1}$$

$$\left(\text{Aliter : } \Delta G_T = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \right)$$

$$67. \Delta H_{\text{dissolution}} = \Delta H_{\text{(ionisation)}} + \Delta H_{\text{(hydration)}}$$
$$= 780 - 775$$
$$= 5 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{dissolution}} = \Delta H_{\text{dissolution}} - T\Delta S_{\text{dissolution}}$$
$$= 5000 - 298 \times 45 = -8410 \text{ J}$$
$$= 8.41 \text{ kJ mol}^{-1}$$

68. (D)

$$\text{Sol. } \Delta G = (\Delta H) - T(\Delta S)$$
$$\begin{array}{ccc} & \downarrow & \downarrow \\ & -ve & -ve \end{array}$$

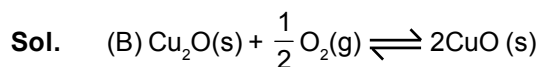
since both are $-ve$, the reaction would have a $-ve \Delta G$ below a temperature of $\frac{33000}{58} \text{ K} (= 569\text{K})$

69. $\Delta H_{\text{reaction}}^{\circ} = (-296.8) - (-58.2)$
 $= -238.6 \text{ kJ}$

Hence $\Delta G^{\circ} = -238.6 - 298 \times (36.7) \times 10^{-3}$
 $= -249.536$

The reaction is spontaneous even at 25°C but heating speeds up the reaction thereby liberating mercury faster from cinnabar (HgS).

70. (B)



$\Delta G_{\text{reaction}}^{\circ} = [2 \times (-30.4)] - [-34.98] = -25.82 \text{ kcal}$
and $-25.82 \times 10^3 = 2.303 \times 2 \times 298 \log K$

$\therefore K \approx 10^{19}$, a very high value, hence reaction will be almost complete with a trace of Cu_2O .

71. (B)

Sol. ΔG for $3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) \longrightarrow \text{Fe}_3\text{O}_4(\text{s})$ can be obtained by taking

$[(2) + 4 \times (1)] \times \frac{1}{3}$

Hence we get $\Delta G_f = [-19 + 4 \times (-177)] \times \frac{1}{3}$
 $= -242.3 \text{ kcal for 1 mole Fe}_3\text{O}_4$

72. (A)

Sol. $\Delta S = nC_v \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right)$

$\Delta H = nC_p \Delta T$
 $\Delta E = nC_v \Delta T$
 $\Delta G = \Delta H - \Delta(TS)$

73. (B)

Sol. Work done in isothermal expansion is maximum. Hence, in adiabatic volume and temperature will be lower.

74. (A)

Sol. $\Delta G = \Delta H - \Delta(TS)$
 $= \Delta H - T\Delta S$ (isothermal)

$= 0 - T\Delta S = -T \left(\int \frac{dq_{\text{rev}}}{T} \right)$

$= - \int dq_{\text{rev}} = -q_{\text{rev}} = W_{\text{rev}}$

as process is isothermal so $\Delta E = 0 = q_{\text{rev}} + W_{\text{rev}}$

so $\Delta G = -nRT \ln \left(\frac{V_f}{V_i} \right)$

$= -RT \ln 2 = -2 \times 8.3 \times 300 \times 0.7 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1}$
 $= -3.486 \text{ KJ mol}^{-1} \text{ K}^{-1}$

75. (D)

Sol. $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

For adiabatic process ($Q = 0$)
 $\Delta E = W$

$nC_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$

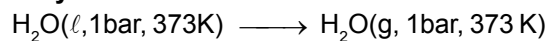
$\therefore \Delta S = 0$

76. (B)

Sol.
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -54.07 \times 1000 - 298 \times 10 \\ &= -54070 - 2980 = -57050 \\ \Delta G^\circ &= -2.303 RT \log_{10} K \\ -57050 &= -2.303 \times 298 \times 8.314 \log_{10} K \\ &= -5705 \log_{10} K \\ \log_{10} K &= 10\end{aligned}$$

77. (A)

Sol. Easy



$$\Delta S > 0$$

$$\Delta H > 0$$

$$\Delta G = 0$$

78. (C)

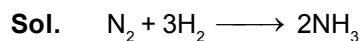
Sol. Since liquid is expanding against external pressure P_0 hence work done

$$w = -P_0(4V_0 - V_0) = -3P_0V_0$$

$$\Delta U = w = -3P_0V_0$$

$$\Rightarrow \Delta H = \Delta U + P_2V_2 - P_1V_1 = -3P_0V_0 + 4P_0V_0 - 2P_0V_0$$

79. (C)



$$\Delta H = q_3 + 3q_2 - 6q_1$$

80. (D)

Sol.
$$w = -P_{\text{ext}}(v_2 - v_1) = -1.5(2 - 8) = 9 \text{ atm} \times \text{Ltr} = 9 \times 101.3 \text{ Joul}$$

$$\Delta E = q + w = 100 + 911.7 = 1011.7$$

81. (A)

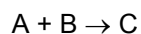
Sol.
$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\frac{300}{T_2} = (4)^{\gamma-1}$$

$$T_2 = 119 \text{ K}$$

82. (B)

Sol.
$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$



$$x \quad 2x \quad 3x$$

$$\therefore \Delta C_p = 3x - 3x = 0$$

$$\therefore \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = 0$$

$$\Delta H_2 - \Delta H_1 = 0 \text{ or } \Delta H_2 = \Delta H_1$$

83. (B)

Sol.
$$\Delta S = \frac{\Delta H_f}{T_f} = \frac{600}{300} = 2$$

84. (A)

Sol. $\Delta H_1 = \{\Delta H_f^0(\text{NCl}_3) + 3\Delta H_f^0(\text{HCl})\} - \Delta H_f^0(\text{NH}_3)$

$$\Delta H_f^0(\text{NH}_3) = \frac{\Delta H_2}{2} ; \Delta H_f^0(\text{HCl}) = \frac{\Delta H_3}{2}$$

$$\Delta H_1 = \left\{ \Delta H_f^0(\text{NCl}_3) + \frac{3}{2}\Delta H_3 \right\} - \frac{\Delta H_2}{2}$$

$$\Delta H_f^0(\text{NCl}_3) = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$$

85. 62355

Sol. Step (a) : $w = 0$

Step (b) : $w = 0$

Step (c) : $w = -\int pdV = -R\Delta T = (75\text{K}) R$
 $= 75 \times 8.314$
 $= 623.55 \text{ Jmol}^{-1}$

86. (C)

Sol. enthalpy of dissociation = $(13.7 - 3) \text{ Kcal} = 10.7 \text{ Kcal}$

87. (B)

Sol. $n_1 C_{V1} dT + n_2 C_{V2} dT = -(n_1 RT + n_2 RT) \frac{dV}{V}$

$$= \frac{dT}{T} = -\left(\frac{1}{2}\right) \frac{dV}{V}$$

$$= \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{1}{2}}$$

$$\Delta T = T_2 - T_1 = \frac{T_1}{2} - T_1 = -\frac{T_1}{2}$$

$$\Delta T = -150 \text{ K}$$

$$\Delta H = \frac{1}{2} \left[\left(\frac{3}{2}R + R\right) + \left(\frac{5}{2}R + R\right) \right] \Delta T$$

$$= \frac{1}{2} (6R) \Delta T = -3 \times 2 \times 150 = -900 \text{ cal}$$

Although many substances are known to have more than one solid phase, one usually finds only one liquid phase for a substance. Helium is one interesting substance which exists in two different kinds of liquid forms, helium I and helium II with characteristic properties. The phase diagram of helium is shown in Fig.2 There are two triple points, one between the solid, liquid helium I and liquid helium II, and the other between the two liquids and the vapour. We see that there is no contact between the solid and vapour regions. The phase diagram also indicates that liquid helium II is the most stable form even at 0 K and ordinary pressures. Only by applying high pressure can solid helium be obtained. One of the fascinating properties of helium II is its very low viscosity.

The phase diagram of carbon shown in Fig.3 clearly shows that graphite is the stable form at ordinary temperatures and pressures. In order to form diamond from graphite, application of high pressures is essential. In nature,