

THERMODYNAMICS (ENERGETICS)

1. Thermodynamic changes in adiabatic changes in volume of an ideal gas

$$\Delta E = q + w \quad [1st\ law]$$

$$q = 0 \text{ in adiabatic process}$$

$$\therefore \Delta E = w$$

we know that

$$\therefore \Delta E = n c_{vm} \Delta T$$

$$\therefore w = n c_{vm} \Delta T$$

$$C_{pm} - C_{vm} = R$$

$$\frac{C_{pm}}{C_{vm}} = \gamma$$

$$\gamma C_{vm} - C_{vm} = R$$

$$C_{vm} = \frac{R}{\gamma - 1}$$

$$w = n \frac{R}{\gamma - 1} \Delta T$$

$$w = \frac{nR}{\gamma - 1} [T_2 - T_1]$$

$$w = \frac{1}{\gamma - 1} [nRT_2 - nRT_1]$$

$$w = \frac{1}{\gamma - 1} [P_2 V_2 - P_1 V_1]$$

$$w = -nC_{vm} T_1 \left[1 - \frac{T_2}{T_1} \right]$$

2. Adiabatic reversible process

$$dE = dw$$

$$dE = n C_{vm} dT \text{ and } dw = -p_{ext} dv$$

$$P_{ext} \simeq P_{Int}$$

$$P_{Int} = \frac{nRT}{V}$$

$$\therefore n C_{vm} dT = -\frac{nRT}{V} dv$$

$$C_{vm} dT = -\frac{RT}{V} dv$$

$$C_{vm} \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dv}{V}$$

$$C_{vm} \ln \left(\frac{T_2}{T_1} \right) = -R \ln \left(\frac{V_2}{V_1} \right)$$

$$\ln \left(\frac{T_2}{T_1} \right)^{C_{vm}} = \ln \left(\frac{V_2}{V_1} \right)^{-R}$$

$$\left(\frac{T_2}{T_1} \right)^{C_{vm}} = \left(\frac{V_2}{V_1} \right)^{-R}$$

$$\left(\frac{T_2}{T_1} \right)^{C_{vm}} = \left(\frac{V_1}{V_2} \right)^R$$

$$\therefore T^{C_{vm}} V^R = \text{const}$$

$$TV^{R/C_{vm}} = \text{const}$$

$$TV^{r-1} = \text{const}$$

3. Relation between T and P

$$T^{C_{vm}} V^R = \text{const}$$

$$T^{C_{vm}} \left(\frac{RT}{P} \right)^R = \text{const}$$

$$T^{(C_{vm}+R)} P^{-R} = \text{const}$$

$$T^{C_{pm}} P^{-R} = \text{const}$$

$$T P^{-R/C_{pm}} = \text{const}$$

$$T P^{\frac{1-\gamma}{\gamma}} = \text{const}$$

$$\left[\begin{aligned} \frac{-R}{C_{pm}} &= -\frac{[C_{pm} - C_{vm}]}{C_{pm}} \\ &= -1 + \frac{C_{vm}}{C_{pm}} \\ &= -1 + \frac{1}{\gamma} \\ &= \frac{1-\gamma}{\gamma} \end{aligned} \right]$$

Relation between P and V

$$T^{C_{vm}} V^R = \text{const}$$

$$\left(\frac{PV}{R} \right)^{C_{vm}} V^R = \text{const}$$

$$P^{C_{vm}} V^{C_{pm}} = \text{const}$$

$$PV^{\frac{C_{pm}}{C_{vm}}} = \text{const}$$

$$PV^\gamma = \text{const}$$

4. Entropy change in terms of temperature and volume changes**1st law**

$$dU = dq + w$$

$$= dq_{rev} + (-Pdv)$$

$$dq_{rev} = dU + PdV$$

$$\frac{dq_{rev}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

$$dS = \frac{nc_{v,m} dT}{T} + \frac{nR}{v} dV$$

$$\int_{S_1}^{S_2} dS = nC_{v,m} \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

For Isothermal change $T_1 = T_2$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For Isochoric process $V_1 = V_2$

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1}$$

5. Entropy change in terms of temperature and pressure changes

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1 T_2}{P_2 T_1}$$

$$= n(C_{v,m} + R) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

For Iso baric process $P_1 = P_2$ $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$

6. Entropy changes in Isothermal process
Isothermal reversible process In Expansion
system takes q heat from surroundings

$$q_{Rev} = -w$$

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T}$$

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surrounding} = \frac{-q_{Rev}}{T}$$

$$\Delta S_{surr.} = -nR \ln \frac{V_2}{V_1}$$

$$\begin{aligned} \therefore \Delta S_{Total} (or) \Delta S_{universe} &= \Delta S_{sys} + \Delta S_{surr.} \\ &= nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} \\ &= 0 \end{aligned}$$

In compression, system gives Q heat to surroundings

$$\therefore \Delta S_{sys} = -nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surro} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{Total} = 0$$

7. Isothermal Irreversible processes

(A) Free Expansion $w = 0$ $q = 0$

since Entropy is a state function, the entropy changes of a system in going from volume V_1 to V_2 by any path will be same as that of reversible process

$$\Delta S_{\text{SYS}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surro}} = 0$$

$$\Delta S_{\text{total}} = nR \ln \frac{V_2}{V_1}$$

(B) Irreversible expansion

q_{rev} is the amount of heat the system would have absorbed. In the present case Expansion done against constant pressure

$$Q_{\text{rev}} = -w$$

$$= P_{\text{ext}}(V_2 - V_1)$$

$$\Delta S_{\text{surrounding}} = \frac{-q_{\text{Irr}}}{T} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\Delta S_{\text{Total}} = nR \ln \frac{V_2}{V_1} - \frac{P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\Delta S_{\text{SYS}} \text{ is } +ve \text{ and } \Delta S_{\text{surro}} \text{ is } -ve$$

$$\Delta S_{\text{Total}} \text{ is } +ve$$

C. Irreversible Compression

$$\Delta S_{\text{SYS}} = -nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surro}} = + \frac{P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\Delta S_{\text{SYS}} < \Delta S_{\text{surro}}$$

$$\Delta S_{\text{SYS}} \text{ is } -ve \text{ and } \Delta S_{\text{surro}} \text{ is } +ve$$

$$\therefore \Delta S_{\text{Total}} = -nR \ln \frac{V_2}{V_1} + \frac{P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\therefore \Delta S_{\text{Total}} \text{ is } +ve$$

8. Entropy changes in adiabatic process

$$q = 0 \quad \therefore \Delta S_{\text{surro}} = 0$$

(A) Reversible process

$$\Delta S_{\text{SYS}} = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$S_{\text{SYS}} = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

In Expansion, the increase entropy due to volume change just compensate the decrease in entropy due to the fall in temperature

$$\therefore S_{\text{SYS}} = 0$$

$\therefore$ The process is known as "Isoentropic process." = 0

(B) Irreversible adiabatic free Expansion

$$w = 0, \Delta T = 0 \quad [T_2 = T_1]$$

$$\Delta S_{\text{sys}} = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\therefore \Delta S_{\text{SYS}} = nR \ln \frac{P_1}{P_2}$$

(or)

$$\therefore \Delta S_{\text{SYS}} \text{ is } +ve$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{SYS}} + \Delta S_{\text{surro}}$$

$$= nR \ln \frac{V_2}{V_1} + 0$$

$$\Delta S_{\text{Total}} = nR \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{\text{Total}} \text{ is } +ve$$

(C) Intermediate Expansion

$$\Delta S_{\text{SYS}} = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

(or)

$$\Delta S_{\text{SYS}} = nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

In Expansion the increase in entropy due to volume change is larger than the decrease in entropy due to temp change

$$\therefore \Delta S_{\text{SYS}} \text{ is } +ve$$

$$\Delta S_{\text{Total}} \text{ is also } +ve$$

In compression, the decrease in entropy due to volume change is smaller than the increase in entropy due to temperature

$$\therefore \Delta S_{\text{SYS}} \text{ is } +ve$$

$$\Delta S_{\text{Total}} \text{ is also } +ve$$

9. Trouton's rule is $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$

i.e. $\Delta S_{\text{vap}} \approx 10.5R$ at boiling point

10. For $Hg_{(l)}$, $H_2O_{(l)}$, $NH_{3(l)}$ have high ΔS_{vap} and doesn't follow trouton's rule

11. $\Delta G_{\text{isothermal}}$ (in isolated gaseous system)

$$= W_{\text{max}} = -2.303nRT \log \left(\frac{V_2}{V_1} \right)$$

12. 3rd law of T.D equation is

$$S_T = 2.303nc_v \log T$$

$$S_T = \frac{C_{v,m}}{3}$$

13. Criterion of spontaneity

I.

> 0 : Spontaneous (Irreversible)

$$\Delta S_{\text{total}} \geq 0 \longrightarrow = 0: \text{Reversible Process}$$

< 0 : Non spontaneous

II.

< 0 : Spontaneous (Irreversible)

$$(\Delta G_{\text{system}})_{T,P} \leq 0 \longrightarrow = 0: \text{Reversible Process}$$

> 0 : Non spontaneous

III.

< 0 : Spontaneous (Irreversible)

$$(\Delta E_{\text{system}})_{S,V} \leq 0 \longrightarrow = 0: \text{Reversible Process}$$

> 0 : Non spontaneous

IV.

< 0 : Spontaneous (Irreversible)

$$(\Delta H_{\text{system}})_{S,P} \leq 0 \longrightarrow = 0: \text{Reversible Process}$$

> 0 : Non spontaneous

V.

< 0 : Spontaneous (Irreversible)

$$(\Delta A_{\text{system}})_{T,V} \leq 0 \longrightarrow = 0: \text{Reversible Process}$$

> 0 : Non spontaneous

VI.

> 0 : Spontaneous (Irreversible)

$$(\Delta S_{\text{system}})_{E,V} \geq 0 \longrightarrow = 0: \text{Reversible Process}$$

< 0 : Non spontaneous

SINGLE ANSWER QUESTIONS

1. The work done by a weightless piston in causing an expansion ΔV (at constant temperature), when the opposing pressure, P is variable, is given by:

(A) $W = -\int P dV$ (B) $W = 0$

(C) $W = -P\Delta V$ (D) None of these

2. No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?

(A) $\Delta U = W_{\text{ad}}$; wall is insulated

(B) $\Delta U = -q$, thermally conducting walls

(C) $\Delta U = q - w$, closed system.

(D) $\Delta U = q - w$, open system

3. Which one of the following bonds has the highest average bond energy (kcal/mol)

(A) $S = S$ (B) $C \equiv C$ (C) $C \equiv N$ (D) $N \equiv N$

4. For the reaction



We can say that

(A) ozone is more stable than oxygen

(B) ozone is less stable than oxygen and ozone decomposes forming oxygen readily

(C) oxygen is less stable than ozone and oxygen readily forms ozone

(D) none of the above

5. Which reaction either endothermic or exothermic characteristics has the greater chance of occurring spontaneously?

(A) One in which entropy change is positive

(B) One in which entropy change is negative

(C) One in which free energy change is negative

(D) One in which equilibrium has been established

6. ΔS for the reaction,

$\text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g)$ will be

(A) zero (B) -ve (C) +ve (D) ∞

7. Change in entropy is negative for:

(A) Bromine(l) $\rightarrow$ Bromine(g)

(B) $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$

(C) $\text{N}_2(g, 10\text{atm}) \rightarrow \text{N}_2(g, 1\text{atm})$

(D) $\text{Fe}(1\text{mol}, 400\text{K}) \rightarrow \text{Fe}(1\text{mol}, 300\text{K})$

8. Identify the correct statement for change of Gibb's energy for a system (ΔG_{system}) at constant temperature and pressure:

(A) if $\Delta G_{\text{system}} = 0$, the system is still moving in a particular direction

(B) if $\Delta G_{\text{system}} = -ve$, the process is not spontaneous

(C) if $\Delta G_{\text{system}} = +ve$, the process is spontaneous

(D) if $\Delta G_{\text{system}} = 0$, the system has attained equilibrium

9. The internal energy when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path. What would be the net change in internal energy?

(A) 40 kJ (B) > 40 kJ

(C) < 40 kJ (D) zero

10. One mole of an ideal gas ($C_v = 20\text{J K}^{-1}\text{mol}^{-1}$) initially at STP is heated at constant volume to twice the initial temperature. For the process, W and q will be

(A) $W = 0$; $q = 5.46\text{ kJ}$

(B) $W = 0$; $q = 0$

(C) $W = -5.46\text{ kJ}$; $q = 5.46\text{ kJ}$

(D) $W = 5.46\text{ kJ}$; $q = 5.46\text{ kJ}$

11. Calculate Q and w for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K respectively.

(A) 5.22kJ, - 5.22kJ (B) -5.22 kJ, 5.22 kJ

(C) 27.3kJ, -27.3 kJ (D) -27.3 kJ, 27.3 kJ

12. When 1 mole of gas is heated at constant volume. Temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?

(A) $q = -W = 500\text{ J}$, $\Delta U = 0$

(B) $q = \Delta U = 500\text{ J}$, $W = 0$

(C) $q = W = 500\text{ J}$, $\Delta U = 0$

(D) $\Delta U = 0$, $q = W = -500\text{ J}$

13. A heating coil is immersed in a 100g sample of $\text{H}_2\text{O}(l)$ at 1 atm and 100°C in a closed vessel. In this heating process, 60% of the liquid is converted to the gaseous form at constant pressure of 1 atm. The densities of liquid and gaseous water under these conditions are 1000 kg/m^3 and 0.60 kg/m^3 respectively. Magnitude of the work done for the process is

A) 4997 J

B) 4970 J

C) 9994J

D) 1060J

14. What is the value of change in internal energy at 1 atm in the process?

$\text{H}_2\text{O}(l, 323\text{K}) \rightarrow \text{H}_2\text{O}(g, 423\text{K})$

Given: $C_{v,m}(\text{H}_2\text{O}, l) = 75.0\text{ J K}^{-1}\text{mol}^{-1}$;

ΔH_{vap} at $373\text{K} = 40.7\text{ KJ/mol}$

$C_{p,m}(\text{H}_2\text{O}, g) = 33.314\text{ J K}^{-1}\text{mol}^{-1}$

A) 42.91 kJ/mol B) 43086kJ/mol

C) 42.6 kJ/mol D) 49.6kJ/mol

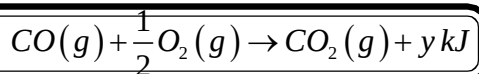
15. The standard enthalpy of formation of octane (C_8H_{18}) is -250kJ/mol. The enthalpy of combustion of C_8H_{18} . If the enthalpy of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -394 kJ/mol and -286kJ/mol respectively

A) -5200 kJ/mol B) -5726 kJ/mol

C) -5476 kJ/mol D) -5310kJ/mol

16. Consider the following reactions:

$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + x\text{kJ}$



The heat of formation of $\text{CO}(g)$ is

A) $-(x+y) \text{ kJ/mol}$ B) $(x-y) \text{ kJ/mol}$

C) $(y-x) \text{ kJ/mol}$ D) $\left(\frac{x}{2} - y\right) \text{ kJ/mol}$

The value of ΔH_f of PCl_5 is

(A) $454.5 \text{ kJ mol}^{-1}$ (B) $-454.5 \text{ kJ mol}^{-1}$

(C) -772 kJ mol^{-1} (D) -498 kJ mol^{-1}

17. The enthalpy of combustion at 25°C of H_2 , cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are -241 , -3920 and -3800 kJ/mol respectively. The heat of hydrogenation of cyclohexene is:

(A) -121 kJ mol^{-1} (B) $+121 \text{ kJ mol}^{-1}$

(C) -242 kJ mol^{-1} (D) $+242 \text{ kJ mol}^{-1}$

18. Calculate the enthalpy change when 50 mL of 0.01 M $\text{Ca}(\text{OH})_2$ reacts with 25 mL of 0.01 M HCl . Given that ΔH° neutralization of a strong acid and a strong base is $140 \text{ kcal mol}^{-1}$

(A) 14 kcal (B) 35 cal

(C) 10 cal (D) 7.5 cal

19. If $\Delta_f H^\circ(\text{C}_2\text{H}_4)$ and $\Delta_f H^\circ(\text{C}_2\text{H}_6)$ are a and $b \text{ kcal mol}^{-1}$, the heat of hydrogenation of C_2H_4 is

A) $a+b$ B) $a-b$ C) $b-a$ D) $a-2b$

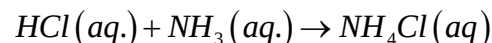
20. Stearic acid [$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$] is a fatty acid, the part of fat that stores most of the energy. 1.0 g of stearic acid was burnt in a bomb calorimeter. The bomb had a heat capacity of $652 \text{ J}^\circ\text{C}$. If the temperature of 500 g water ($c = 4.18 \text{ J/g}^\circ\text{C}$) rise from 25.0 to 39.3°C , how much heat was released when the stearic acid was burned? [Given

$C_p(\text{H}_2\text{O}) = 4.18 \text{ J/g}^\circ\text{C}$]

A) 39.21 kJ B) 29.91 kJ

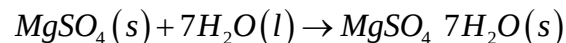
C) 108 kJ D) 9.32 kJ

21. A 0.05 L sample of 0.2 M aqueous hydrochloric acid is added to 0.05 L of 0.2 M aqueous ammonia in a calorimeter. Heat capacity of entire calorimeter system is 480 J/K . The temperature increase is 1.09 K . $\Delta_r H^\circ$ in kJ/mol for the following reaction is:



A) -52.3 B) -61.1 C) -55.8 D) -58.2

22. At 25°C , 1 mole of MgSO_4 was dissolved in water, the heat evolved was found to be 91.2 kJ . One mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.8 kJ . ΔH for the reaction



is

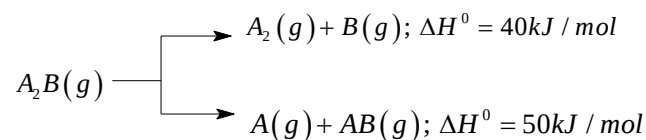
A) -105 kJ/mol B) -77.4 kJ/mol

C) 105 kJ/mol D) 77.4 kJ/mol

23. The enthalpies of neutralization AOH and a strong base BOH by HCl are -12250 cal/mol and -13000 cal/mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was -12500 cal/mol . In what ratio is the acid distributed between AOH and BOH respectively.

A) $2:1$ B) $2:3$ C) $1:2$ D) $3:2$

24. Substance $\text{A}_2\text{B}(g)$ can undergo decomposition to form two set of products



If the molar ratio of $\text{A}_2(g)$ to $\text{A}(g)$ is $5:3$ in a set of product gases, then the energy involved in the decomposition of 1 mole of $\text{A}_2\text{B}(g)$ is:

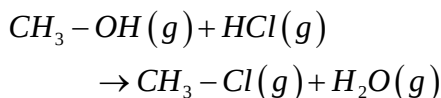
A) 48.75 kJ/mol B) 43.73 kJ/mol

C) 46.25 kJ/mol D) 64.2 kJ/mol

25. Calculate the enthalpy for the following

reaction using the given bond energies (kJ/mol)

$$\left(\begin{array}{l} C-H = 414; H-O = 463; \\ H-Cl = 431, C-Cl = 326; \\ C-O = 335 \end{array} \right)$$



- A) -23 kJ/mol B) -43 kJ/mol
C) -59 kJ/mol D) -511 kJ/mol

26. What is the bond enthalpy of $Xe-F$ bond if Ionization energy of $Xe = 279$ kcal/mol

B.E. ($F-F$) = 38 kcal/mol, electron affinity of $F = 85$ kcal/mol

- A) 24 kcal/mol B) 34 kcal/mol
C) 8.5 kcal/mol D) 16.2 kcal/mol

27. In the conversion of lime stone to lime:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ The values of ΔH° and ΔS° are $179.1 \text{ kJ mol}^{-1}$ and $160.2 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively at 298 K and 1 bar.

Assuming ΔH° and ΔS° remains constant with temperature, at which minimum temperature conversion of lime stone to lime will be spontaneous:

- (A) 1118 K (B) 1008 K
(C) 1200 K (D) 845 K

28. For an ideal gas $\frac{C_{p,m}}{C_{v,m}} = \gamma$. The molecular mass of the gas is M , its specific heat capacity at constant volume is :

- A) $\frac{R}{M(\gamma-1)}$ B) $\frac{M}{R(\gamma-1)}$
C) $\frac{\gamma RM}{\gamma-1}$ D) $\frac{\gamma R}{M(\gamma-1)}$

29. 1 mole of an ideal gas A ($C_{v,m} = 3R$) and 2

mole of an ideal gas B are ($C_{v,m} = \frac{3}{2}R$) taken in a container and expanded reversibly

and adiabatically from 1 litre to 4 litre starting from initial temperature of 320K.

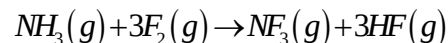
ΔE for the process is :

- A) -240R B) 240R
C) 480R D) -960R

30. When 1.0g of oxalic acid ($H_2C_2O_4$) is burnt in a bomb calorimeter whose heat capacity is 8.75 kJ/K, the temperature increases by 0.312 K. The enthalpy of combustion of oxalic acid at $27^\circ C$ is

- A) -245.7 kJ/mol B) -2.43.45 kJ/mol
C) -246.95 kJ/mol D) -122.5 kJ/mol

31. Using given standard enthalpies of formation (in kJ/mol) determine the enthalpy of the following reaction ?



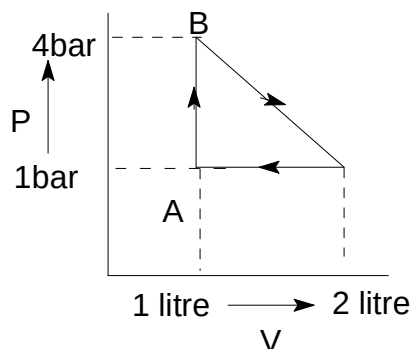
$$\Delta H_f^\circ(NH_3, g) = -46.2;$$

$$\Delta H_f^\circ(NF_3, g) = -113.0;$$

$$\Delta H_f^\circ(HF, g) = -269.0 \text{ kJ/mol}$$

- A) -335.8 kJ/mol B) -873.8 kJ/mol
C) -697.2 kJ/mol D) -890.4 kJ/mol

32. One mole of an ideal gas is subjected to a reversible cyclic process as shown in figure. the max. temperature attained by the gas during the cycle



- A) 7/6R B) 12/49R
C) 49/12R D) 12/7R

33. A gas ($C_{v,m} = \frac{5}{2}R$) behaving ideally was allowed to expand reversibly and

adiabatically from 1 litre to 32 litre. It's initial temperature was 327°C . The molar enthalpy change (in J/mol) for the process is :

- A) -1125R B) -675
C) -1575R D) 1012R

34. For polytropic process $PV^n = \text{constant}$, C_m (molar heat capacity) of an ideal gas is given by:

- A) $C_{v,m} + \frac{R}{(n-1)}$ B) $C_{v,m} + \frac{R}{(1-n)}$
C) $C_{v,m} + R$ D) $C_{p,m} + \frac{R}{(n-1)}$

35. 2 mole of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expanded from initial volume of 1L to final volume of 3L starting from initial temperature of 300K. ΔH for the process is :

- A) -600R B) -1000R
C) -3000R D) -2000R

36. The enthalpy of neutralization of a weak monoprotic acid (HA) in 1 M solution with a strong base is -55.95 kJ/mol. If the unionized acid requires 1.4 kJ/mol heat for its complete ionization and enthalpy of neutralization of the strong monobasic acid with a strong monoacidic base is -57.3 kJ/mol. What is the % ionization of the weak acid in molar solution?

- A) 1% B) 3.57% C) 35.7% D) 10%

37. Consider the following data:

$$\Delta_f H^0(N_2H_4, l) = 50 \text{ kJ/mol},$$

$$\Delta_f H^0(NH_3, g) = -46 \text{ kJ/mol}$$

$$B.E.(H-H) = 436 \text{ kJ/mol}$$

$$\Delta_{vap} H(N_2H_4, l) = 18 \text{ kJ/mol}$$

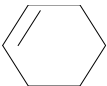
$$B.E.(N-H) = 393 \text{ kJ/mol}$$

The N-N bond energy in N_2H_4 is

- A) 226 kJ/mol B) 154 kJ/mol

- C) 190 kJ/mol D) 182 kJ/mol

38. If enthalpy of hydrogenation of $C_6H_6(l)$ into $C_6H_{12}(l)$ is -205 kJ and resonance energy of $C_6H_6(l)$ is -152 kJ/mol then enthalpy of

hydrogenation of  is Assume

ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ are equal

- A) -535.5 kJ/mol B) -238 kJ/mol
C) -357 kJ/mol D) -119 kJ/mol

39. 3 mole of a diatomic ideal gas which is heated and compressed from 298 K and 1 bar to 596 K and 4 bar ΔS is

$$[\text{Given: } C_{v,m}(\text{gas}) = \frac{5}{2} R;$$

$$\ln(2) = 0.70; R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}]$$

- A) -14.7 cal K^{-1} B) $+14.7 \text{ cal K}^{-1}$
C) -4.9 cal K^{-1} D) 6.3 cal K^{-1}

40. One mole of an ideal monoatomic gas at 27°C is subjected to a reversible isentropic compression until final temperature reached to 327°C . If the initial pressure was 1.0 atm then find the value of $\ln P_2$: (Given : $\ln 2 = 0.7$)

- A) 1.75 atm B) 0.176 atm
C) 1.0395 atm D) 0 atm

41. For a perfectly crystalline solid $C_{p,m} = aT^3 + bT$, where a and b are constant, If $C_{p,m}$ is 0.40 J/K mol at 10 K and 0.92 J/K mol at 20 K, the molar entropy at 20 K is

- A) 0.92 J/K mol B) 8.66 J/K mol
C) 0.813 J/K mol D) 8.314 J/K mol

42. Calculate $\Delta_f G^0$ for (NH_4Cl, s) at 310 K.

$$\Delta_f H^0(NH_4Cl, s) = -314.5 \text{ kJ/mol};$$

$$\Delta_r C_p = 0$$

$$S^0_{N_{2(g)}} = 192 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S^0_{H_2(g)} = 130.5 JK^{-1} mol^{-1}$$

$$S^0_{Cl_{2(g)}} = 233 JK^{-1} mol^{-1}$$

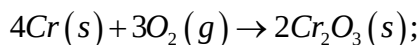
$$S^0_{NH_4Cl(s)} = 99.5 JK^{-1} mol^{-1}$$

All given data at 300 K.

A) $-198.56 kJ / mol$ B) $-426.7 kJ / mol$

C) $-202.3 kJ / mol$ D) $-84.5 kJ / mol$

43. Calculate $\Delta_f H^0$ (in kJ / mol) for Cr_2O_3 from the $\Delta_f G^0$ and the S^0 values provided at $27^0 C$



$$\Delta_f G^0 = -2093 kJ / mol$$

$$S^0 (J / K mol) : S^0 (Cr, s) = 24;$$

$$S^0 (O_2, g) = 205; S^0 (Cr_2O_3, s) = 81$$

$$J K^{-1} mol^{-1}$$

A) $-2258.1 kJ / mol$ B) $-1129.05 kJ / mol$
C) $-964.35 kJ / mol$ D) $3462 kJ / mol$

MULTIANSWER QUESTIONS

44. In an isothermal ideal gas expansion

A) $w = 0$

B) $U_1 = U_2$

C) $H_1 = H_2$

D) $q = nRT \ln \frac{V_2}{V_1}$

45. In an adiabatic process, the work involved during expansion or compression of an ideal gas is given by

A) $nC_V \Delta T$

B) $\frac{nR}{\gamma - 1} (T_2 - T_1)$

C) $-nR P_{ext} \left[\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right]$

D) $-2.303 RT \log \frac{V_2}{V_1}$

46. The value of $\Delta H_{transition}$ of $C(\text{graphite}) \rightarrow C(\text{diamond})$ is $1.9 kJ / mol$ at $25^0 C$ entropy of graphite

is higher than entropy of diamond. This implies that

A) C (diamond) is more thermodynamically stable than C (graphite) at $25^0 C$

B) C (graphite) is more thermodynamically stable than C (diamond) at $25^0 C$

C) diamond will provide more heat on complete combustion at $25^0 C$

$\Delta G_{transition}$ of $C(\text{diamond}) \rightarrow C(\text{graphite})$ is -ve

47. Select the correct statements:

(A) temperature can be raised in an insulated system by doing electrical or mechanical work
(B) temperature can be lowered in an insulated system by doing electrical or mechanical work
(C) temperature cannot be lowered in an insulated system by doing electrical or mechanical work
(D) temperature cannot be raised in an insulated system by doing electrical or mechanical work

48. Which statements are correct?

(A) A spontaneous chemical reaction has maximum total entropy
(B) The entropy increases in an irreversible adiabatic process
(C) The entropy decreases in a reversible adiabatic process
(D) The entropy does not change in a reversible adiabatic process

49. The enthalpy of reaction depend upon:

(A) The manner by which the reaction is carried out
(B) Temperature at which the reaction is carried out
(C) Physical state of reactants and products
(D) Whether the reaction is carried out at constant pressure or at constant volume

50. Select the correct statements:

(A) State of a system is assumed to be in internal equilibrium and the temperature and pressure are uniform throughout the system
(B) Thermal drift in a system with time is more in Dewar flask than in insulated system.
(C) Thermal drift in a system with time is more in non-insulated system than in insulated system.

(D) Thermal drift in a system with time is more in insulated system than in non-insulated system

51. Which are not correct representation at equilibrium:

(A) $\frac{V_1}{V_2} = e^{-\Delta S/R}$ (B) $K = e^{-\Delta G^\circ/RT}$

(C) $\frac{V_2}{V_1} = e^{-\Delta S/RT}$ (D) $\frac{P_2}{P_1} = e^{\Delta H/RT}$

52. Select the correct statements:

(A) Dissolution of KCl in water shows an increase in entropy

(B) Acetic acid in benzene shows a decrease in entropy

(C) The benzene solution containing acetic acid is more ordered than molecular acetic acid.

(D) The solution containing ionised acetic acid is less ordered than molecular acetic acid.

53. Which of the following expression may be represents for the spontaneous reaction

(A) $(\partial G)_{T,P} = -ve$ (B) $(\partial G)_{T,P} = +ve$

(C) $(\partial H)_{P,T} = -ve$ (D) $(\partial S)_{E,V} = +ve$

54. Choose the correct statements:

(A) There is net reduction in energy when a large number of gas phase K^+ and Cl^- ions come together to form a bulk ionic solid

(B) There is a net increase in energy when a large number of gas phase K^+ and Cl^- ions come together to form a bulk ionic solid

(C) The net effect of all the ion interactions in the solid KCl lattice, is attraction, because the cation or anion is the closest to ions of opposite charge

(D) The net effect of all the ion interactions in the solid KCl lattice, is repulsion, because the anion and cation is the closest to ions of same charge.

55. Choose the correct statements:

(A) The enthalpy change for the reverse of any process is the negative of the enthalpy change for the original process

(B) The enthalpy change for the reverse of any process is not the negative of the enthalpy change for the original process and depends on the path taken from the initial state of the final state

(C) Generally, the higher the freezing point, the higher the enthalpy of melting

(D) Generally, the higher the freezing point, the lower the enthalpy of melting

56. During the formation of an ion pair, say between a gaseous K atom and a gaseous Cl atom, as they approach each other, one contribution to energy is the energy.

(A) Needed to form the K^+ ions from a K atom in the gas phase, which is the electron affinity of potassium

(B) Needed to form the K^+ ions from a K atom in the gas phase, which is the ionisation energy of potassium

(C) Released when the Cl^- ion forms from a Cl atom in the gas phase which is the electron affinity of chlorine

(D) Needed to form the Cl^- ion from a Cl atom in the gas phase which is the ionisation energy of chloride

57. Which of the following statements is/are correct for bond enthalpies in case of general diatomic molecules?

(A) Bond enthalpy increases with the increase in the number of bonds between the atoms

(B) Bond enthalpy decreases with the increase in the number of bonds between the atoms

(C) Bond enthalpy increases with the increase in the size of the neighbouring atoms

(D) Bond enthalpy decreases with the increase in the size of the neighbouring atoms

58. Which of the following statements is/are correct

(A) Absolute value of internal energy cannot be determined

(B) Absolute value of heat content can be determined

(C) Absolute value of entropy can be determined

(D) All the three E, H and S are extensive properties

59. In the reaction, $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$\Delta H = -x \text{ kJ}$

(A) $x \text{ kJ}$ is the heat of formation of H_2O

(B) $x \text{ kJ}$ is the heat of reaction

(C) $x \text{ kJ}$ is the heat of combustion of H_2

(D) $x/2 \text{ kJ}$ is the heat of formation of H_2O

60. Predict in which of the following, entropy increases/decreases:

- (A) A liquid crystallizes into a solid.
- (B) Temperature of a crystalline solid is raised from 0 K to 115 K.
- (C) $2\text{NaHCO}_3(\text{s}) \longrightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- (D) $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$

61. The vapour pressure of solid benzoic acid has been found to obey the relationship (in the neighbourhood of 298 K) as:

$$\ln \frac{P}{P^\circ} = a - \frac{b}{T} \quad ; \text{ where } a = 22.88 \text{ and } b =$$

$1.07 \times 10^4 \text{ K}$ Which of the following values are correct at 298 K for the sublimation of benzoic acid?

- (A) $\Delta G^\circ = 32.34 \text{ kJ mol}^{-1}$
- (B) $\Delta H^\circ = 88.96 \text{ kJ mol}^{-1}$
- (C) $\Delta S^\circ = 190 \text{ JK}^{-1} \text{ mol}^{-1}$
- (D) $\Delta H^\circ = -88.96 \text{ kJ mol}^{-1}$

62. Select the incorrect statements about the plots of $\ln K$ vs $1/T$

- (A) Linear with slope equal to $\frac{\Delta G^\circ}{R}$ and intercept ΔH
- (B) Curve
- (C) Linear with slope $-\frac{\Delta H^\circ}{R}$ and intercept $\frac{\Delta S^\circ}{R}$
- (D) none of these

63. A 250 W electric heater raised the temperature of a calorimeter by 4.22°C in 55s. When the oxidation of a methanol sample was carried out in the same calorimeter, the temperature rose from 22.49°C to 26.77°C . Then,

- (A) The amount of heat supplied by the electric heater is 13.75 kJ
- (B) The amount of heat supplied by the electric heater is 4.6 kJ
- (C) The enthalpy of change for the oxidation is 1.39 kJ
- (D) The enthalpy of change for the oxidation is 13.9 kJ

64. Choose the correct statements:

- (A) The enthalpy of combustion of a fuel per gram (expressed without a negative sign) is called its specific enthalpy
- (B) The enthalpy of combustion of a fuel per gram (expressed without a negative sign) is called its enthalpy density
- (C) The enthalpy of combustion of fuel per litre (expressed without a negative sign) is called its specific enthalpy
- (D) The enthalpy of combustion of fuel per litre (expressed without a negative sign) is called its enthalpy density

65. 200 g of water is contained in a beaker of mass 150 g at 20°C . The temperature of water is required to be raised to 80°C . It is given that the specific heat of water is $4.184 \text{ J/(g}^\circ\text{C)}$ and of glass is $0.78 \text{ J/(g}^\circ\text{C)}$. Then

- (A) Heat required by water is 50.2 kJ
- (B) Heat required by glass is 7.0 kJ
- (C) Heat required by glass 9.4 kJ
- (D) Total heat required is 57.2 kJ

66. Which statements are correct?

- (A) A spontaneous chemical reaction which starts far from equilibrium always gives irreversible process.
- (B) The entropy increases in an irreversible adiabatic process
- (C) The entropy decreases in reversible adiabatic process
- (D) The entropy does not change in a reversible adiabatic process

67. Select the correct statements:

- (A) Gibbs energy plays the same role for a chemical system as the gravitational energy plays for a purely mechanical systems
- (B) Gibbs energy is minimum at definite pressure and temperature for a chemical system at equilibrium
- (C) A positive value of ΔG° does not mean that the reaction does not occur spontaneously.
- (D) A negative value of ΔG° means for the spontaneous conversion of reactants into products, if both are in standard states

68. Point out the correct statements:

(A) Oxides of nitrogen are thermodynamically unstable with respect to decomposition into elements

(B) A spontaneous process does not necessarily reduce internal energy or enthalpy of a system

(C) For thermodynamic equilibrium $\Delta S_{\text{total}} = 0$

(D) Entropy can not decrease in an isolated system

69. Which of the following statements are correct?

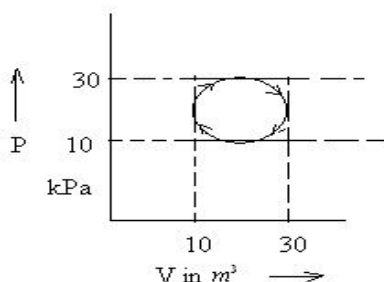
(A) The entropy of an isolated system increases in an irreversible process

(B) The entropy of an isolated system remains unchanged in a reversible process

(C) Entropy can never decrease

(D) $\Delta S(\text{system})$ as well as $\Delta S(\text{surroundings})$ are negative quantities

70. Which one of the following is not correct for a cyclic process as shown in figure?



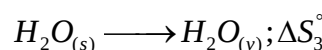
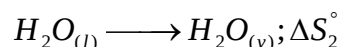
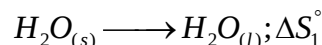
A) $dU = 0$

B) $q = -w$

C) $W = 314 \text{ J}$

D) $W = 31.4 \text{ J}$

71. Select the correct statements for the equilibrium under standard conditions



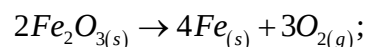
A) $\Delta S_1^\circ > \Delta S_2^\circ$

B) $\Delta S_2^\circ \gg \Delta S_1^\circ$

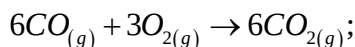
C) $\Delta S_3^\circ > \Delta S_2^\circ$

D) $\Delta S_3^\circ > \Delta S_1^\circ$

72. Given



$$\Delta G_1^\circ = +1487 \text{ kJ mol}^{-1}$$



$$\Delta_r G_2^\circ = -1543.2 \text{ kJ mol}^{-1}$$

correct statement is:

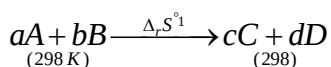
A) $\Delta_r G^\circ$ for reduction of iron oxide by CO is $+56.2 \text{ kJ mol}^{-1}$

B) Fe_2O_3 can be reduced by CO spontaneously

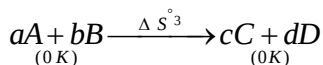
C) Fe_2O_3 cannot be reduced by CO spontaneously

D) The reduction of Fe_2O_3 takes part in higher part of blast furnace

73. Which of the following is incorrect for the change shown below?



$$\Delta_r S_2^\circ \downarrow \quad \uparrow \Delta_r S_4^\circ$$



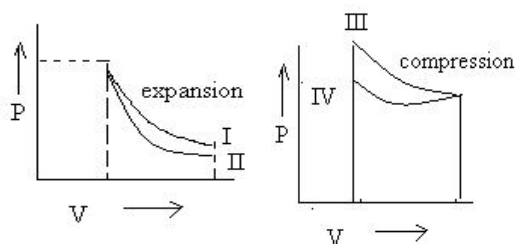
A) $\Delta_r S_1^\circ = cS_C^\circ + dS_D^\circ - (aS_A^\circ + bS_B^\circ)$

B) $\Delta_r S_2^\circ = -[aS_A^\circ + bS_B^\circ]$

C) $\Delta_r S_3^\circ = 0$

D) $\Delta_r S_4^\circ = -[cS_C^\circ + dS_D^\circ]$

74. Which of the following figures given below shows adiabatic process;



A) II, III

B) I, III

C) II, IV

D) I, IV

75. He, N_2 and O_3 are expanded adiabatically and their expansion curves between P and V are plotted under similar conditions. About the ratio of the slopes,

which one is not correct;

- A) the ratio of slopes of P-V curves for He and O_3 is 1.25
 B) the ratio of slopes of P-V curves for He and N_2 is 1.20
 C) the ratio of slopes of P-V curves for N_2 and O_3 is 1.05.
 D) the slope of He is least steeper and for O_3 is most steeper.

76. Heat of neutralisation of strong acid and strong base under 1 atm and $25^\circ C$ is -13.7 kcal. If standard Gibbs energy change for dissociation of water to

H^+ and OH^- is -19.14 kcal, the change is standard entropy for dissociation of water in $cal\ K^{-1}\ mol^{-1}$ is;

- A) 18.25 B) 110.2
 C) -18.25 D) none of these.

77. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature, which of the following statement is correct?

- A) $(T_f)_{irrev} > (T_f)^{rev}$
 B) $(T_f > T_i)$ for reversible process but $T_f = T_i$ for irreversible process.
 C) $(T_f)_{rev} = (T_f)_{irrev}$
 D) $T_f = T_i$ for both reversible and irreversible process

78. One mole of CH_3COOH undergo dimerization in vapour state at $127^\circ C$ as $2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$ if dimer formation is due to two H-bonds involved in dimer, each of 33 kJ strength and the degree of dimerisation of acetic acid 98.2% which is correct

- A) ΔS° for dimerization is negative
 B) ΔS° for dimerization is positive
 C) ΔS° for dimerization is -104.1 J/mol
 D) ΔS° for dimerization is +1.04 J/mol

79. Work done in expansion of an gas from 4 litre to 6 litre against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is $4.184\ J\ g^{-1}\ K^{-1}$, the final temperature of water is nearly ?

A) 300K B) 456K C) 278K D) 600K

80. 2 mole of a perfect gas at $27^\circ C$ is compressed reversibly and isothermally from a pressure of

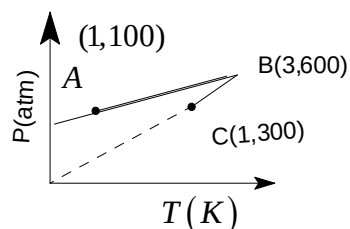
$1.01 \times 10^5\ Nm^{-2}$ to $5.05 \times 10^6\ Nm^{-2}$ which is correct among the following

- A) work done on the gas is $1.9518 \times 10^4\ J$
 B) Free energy change for the process is $1.9518 \times 10^4\ J$
 C) work done on the gas is $1.19 \times 10^7\ J$
 D) Free energy change for the process is $-1.19 \times 10^7\ J$

81. If one mole of an ideal gas with $C_v = \frac{3}{2} R$ is heated at a constant pressure of 1 atm $25^\circ C$ to $100^\circ C$. Which is correct

- A) ΔU during the process is 223.51 cal
 B) ΔH during the process is 372.56 cal
 C) entropy change during the process is $1.122\ cal\ K^{-1}\ mol^{-1}$
 D) $\Delta U, \Delta H$ are same for the process

82. One mole of an ideal gas is subjected to a two step reversible process as shown in figure. ($A \rightarrow B$ and $B \rightarrow C$) the pressure at A and C is same. The correct statement(s) is/are



- A) Work involved in the path AB is zero

B) In the path AB work will be done on the gas by the surroundings

C) Volume of gas at C = $3 \times$ volume of gas at A

D) Volume of gas at B is 16.42 litres

83. For a process to be spontaneous

A) $(\Delta G_{\text{system}})_{T,P} = 0$

B) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

C) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$

D) $(\Delta G_{\text{system}})_{T,P} < 0$

84. The normal boiling point of a liquid 'X' is 400K. Which of the following statement is true about the process $X(l) \rightarrow X(g)$?

A) At 400 K and 1 atm pressure $\Delta G = 0$

B) At 400K and 2 atm pressure $\Delta G = +ve$

C) at 400K and 0.1 atm pressure $\Delta G = -ve$

D) at 410 K and 1 atm pressure $\Delta G = +ve$

85. Which of the following statements (s) is/are false?

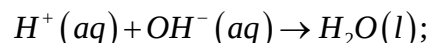
A) all adiabatic process are isentropic (or isentropic) processes

B) When $(\Delta G_{\text{system}})_{T,P} < 0$; the reaction must be exothermic

C) $dG = VdP - SdT$ is applicable for closed system, both PV and non-PV work

D) The heat of vaporisation of water at 100°C is 40.6 kJ/mol. When 9gm of water vapour condenses to liquid at 100°C of 1 atm, then $\Delta S_{\text{system}} = 54.42 \text{ J / K}$

86. From the following data, mark the option (s) where ΔH is correctly written for the given reaction. Given



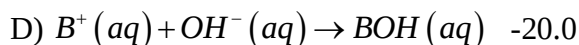
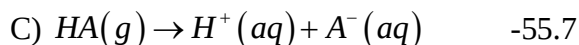
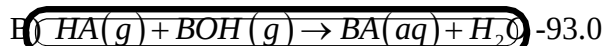
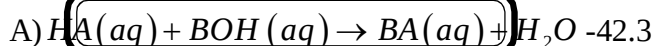
$$\Delta H = -57.3 \text{ kJ}$$

$$\Delta H_{\text{solution}} \text{ of } HA(g) = -70.7 \text{ kJ / mol}$$

$$\Delta H_{\text{solution}} \text{ of } BOH(g) = 20 \text{ kJ / mol}$$

$$\Delta H_{\text{ionization}} \text{ of } HA = 15 \text{ kJ / mol and } BOH \text{ is a}$$

strong base Reaction ΔH_r (kJ / mol)



COMPREHENSION TYPE QUESTIONS

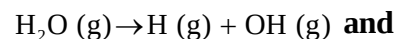
Comprehension-1

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present.

The bond energy of N — H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 because there are three N-H bonds and those of C — H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4 .

Heat of a reaction = Bond energy of reactants - Bond energy of products

87. The enthalpy changes for the reaction



$OH(g) \rightarrow O(g) + H(g)$ are $501.87 \text{ kJ mol}^{-1}$ and $423.38 \text{ kJ mol}^{-1}$. The bond enthalpy of O-H bond is

(A) $-462.625 \text{ kJ mol}^{-1}$ (B) $462.625 \text{ kJ mol}^{-1}$

(C) $-713.54 \text{ kJ mol}^{-1}$ (D) $713.54 \text{ kJ mol}^{-1}$

88. In which of the following, the bond enthalpy and bond dissociation enthalpy are identical?

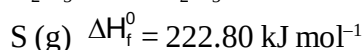
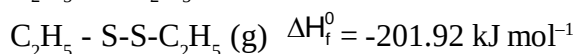
(A) H- H bond enthalpy in $\text{H}_2(g)$

(B) O-H bond enthalpy in $\text{H}_2\text{O}(g)$

(C) C- H bond enthalpy in $\text{CH}_4(g)$

(D) N- H bond enthalpy in $\text{NH}_3(g)$

89. Find the bond enthalpy of S-S bond from the following data.



(A) $-277.49 \text{ kJ mol}^{-1}$ (B) $277.49 \text{ kJ mol}^{-1}$

(C) $-349.15 \text{ kJ mol}^{-1}$ (D) $349.15 \text{ kJ mol}^{-1}$

COMPREHENSION -2

Two vessels A and B are connected via a stopcock. The vessel A is filled with a gas at a certain pressure and the vessel B is completely evacuated. The entire assembly is immersed in a large vat of water and is allowed to come to thermal equilibrium with the water. The stopcock is opened and the gas is allowed to expand till both the vessels are uniformly occupied. After sometime when the vessel has again come to thermal equilibrium, temperature of the water is recorded. The result shows that the temperature of water after the experiment is the same as that before.

90. For the expansion referred to above, which of the following is true?

(A) $du = 0$ (B) $du > 0$ (C) $du < 0$ (D) $dq > 0$

91. Taking 'U' as a function of T and V, under the given conditions of the experiment. Choose the correct statement.

(A) The change in energy of a gas with change of volume at constant temperature is a positive quantity.

(B) The energy of the gas is a function of temperature only.

(C) The change in energy of a gas with change of volume at constant temperature is a negative quantity.

(D) The result is applicable to both ideal and real gases.

92. The expansion that occurred is

(A) isothermal reversible expansion

(B) isothermal irreversible expansion

(C) adiabatic reversible expansion

(D) isothermal free expansion

Comprehension-3

The first law of thermodynamics gives as $q = \Delta U + (-w)$; where q is heat given to a system and ΔU represents increase in internal energy and $-w$ is work done by the system. Various processes such as isothermal, adiabatic, cyclic, isobaric and isochoric process in terms of first law of thermodynamics leads for important results. The molar heat capacity for 1 mole of monoatomic gas is $3/2R$ at constant volume and $5/2R$ at constant pressure.

1. Increase in internal energy from state A to state B is 50 J.

93. Which of the following statements are correct :

(1) Both work and heat appears at the boundaries of system.

(2) Heat given to a system is given +ve sign.

(3) Heat given to a system is equal to increase in internal energy under isothermal conditions

(4) Heat given to a system is used to increase internal energy under isochoric conditions

(5) Both work and heat are not state functions but their sum ($q + w$) is state function.

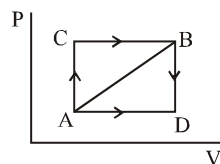
(A) 1, 2, 4, 5 (B) 1, 3, 4, 5

(C) 1, 2, 3, 4 (D) 2, 3, 4, 5

94. A system is allowed to move from state A to B following path ACB by absorbing 80 J of heat energy. The work done by the system is 30 J. The work done by the system in reaching state B from A is 10 J through path ADB which statements are correct:

1. Increase in internal energy from state A to state B is 50 J.

2. If path ADB is followed to reach state B, $\Delta U = 50 J$



3. If work done by the system in path AB is 20 J, the heat absorbed during path AB = 70 J.

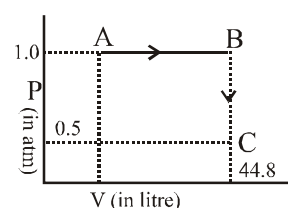
4. The value $U_C - U_A$ is equal to $U_D - U_B$.

5. Heat absorbed by the system to reach B from A through path ADB is 60 J.

(A) 1, 5 (B) 1, 3, 5

(C) 1, 2, 3, 5 (D) 1, 4, 5

95. 1 mole of a monoatomic gas is expanded through path ABC as shown in figure.

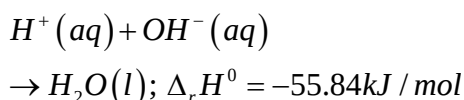


Select the correct statements :

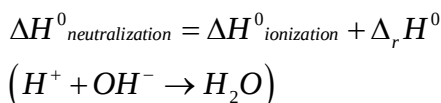
- (1) If specific heat of gas are 0.125 and 0.075 cal/g, the mol. wt. of gas = 40.
 (2) Temperature at point A, B, C are 273, 546 and 273 K respectively.
 (3) ΔU for the process A to B is 2.27 kJ.
 (4) ΔU for the process B to C is 3.44 kJ.
 (5) ΔU for the overall cycle $A \rightarrow B \rightarrow C \rightarrow A$ is 3.4 kJ.
 (A) 1, 2, 3, 4 (B) 3, 4, 5
 (C) 1, 3, 4 (D) 1, 2, 5

Comprehension-4

Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution. For strong acid and strong base neutralization net chemical change is



$\Delta H^\circ_{\text{ionization}}$ of aqueous solution of strong acid and strong base is zero. When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base for weak acid /base



96. If enthalpy of neutralization of CH_3COOH by HCl is -49.86 kJ/mol then enthalpy of ionization of CH_3COOH is
 (A) 5.98 kJ/mol (B) -5.98 kJ/mol
 (C) 105.7 kJ/mol (D) 10.57 kJ/mol
97. What is ΔH° for complete neutralization of strong diacidic base $A(OH)_2$ by HNO_3
 (A) -55.84 kJ (B) -111.68 kJ
 (C) 55.84 kJ/mol (D) -49.86 kJ/mol
98. Under the same conditions how many mL of 0.1 M NaOH and $0.05 \text{ M } H_2A$ (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature

- A) 25: 75 (B) 50:50
 C) 75: 25 (D) 66.66:33.33

Comprehension-5

Work done by the system in isothermal reversible

process is : $w_{\text{rev.}} = -2.303 nRT \log \frac{V_2}{V_1}$. Also in case of adiabatic reversible process work done

by the sytem is given by : $w_{\text{rev.}} = \frac{nR}{\gamma-1} [T_2 - T_1]$.

During expansion disorder increases and the increase in disorder is expressed in terms of

change in entropy $\Delta S = \frac{q_{\text{rev.}}}{T}$. The entropy changes also occurs during transformation of one

state to other and expressed as $\Delta T = \frac{\Delta H}{T}$. Both

entropy and enthalpy changes obtained for a process were taken as a measure of spontaneity of process but finally it was recommended that decrease in free energy is responsible for spontaneity and $\Delta G = \Delta H - T\Delta S$.

99. **Which of the following statements are correct:**

- (1) The expansion work for a gas into vacuum is equal to zero.
 (2) 1 mole of a gas occupying 3 litre volume on expanding to 15 litre at constant pressure of 1 atm does expansion work 1.215 kJ.
 (3) The maximum work done during expansion of 16 g O_2 at 300 K from 5 dm^3 to 25 dm^3 is 2.01 kJ .
 (4) The ΔS for $S \rightarrow L$ is almost negligible in comparison to ΔS for $L \rightarrow G$.

(5) $\Delta S = 2.303 nR \log \frac{V_2}{V_1}$. (at constant T)

- (A) 2, 3, 4, 5 (B) 1, 2, 3, 4, 5
 (C) 1, 2 (D) 4, 5

100. **The heat of vaporisation and heat of fusion of H_2O are 540 cal/g and 80 cal/g . The ratio**

of $\frac{\Delta S_{\text{vap.}}}{\Delta S_{\text{fusion}}}$ for water is:

- (A) 6.75 (B) 9.23 (C) 4.94 (D) 0.2

101. $\text{Ag}_2\text{O}(\text{S}) \longrightarrow 2\text{Ag}(\text{S}) + \frac{1}{2}\text{O}_2(\text{g})$; attains

equilibrium at temperature ... K is:

(The ΔH and ΔS for the reaction are 30.5 kJ/mol and 66 J/mol/K)

- (A) 462.12 (B) 237
(C) 373 (D) 273

102. A chemical change will definitely be spontaneous if :

- (A) $\Delta H = -ve$, $\Delta S = -ve$ and low temperature
(B) $\Delta H = +ve$, $\Delta S = -ve$ and high temperature
(C) $\Delta H = -ve$, $\Delta S = +ve$ and any temperature
(D) $\Delta H = +ve$, $\Delta S = +ve$ and $T\Delta S < \Delta H$

MATRIX MATCHING

103. Match the following

Column - I

- A) Free energy change ΔG of a reaction
B) Enthalpy change of a reaction in standard state ΔH^0
C) Entropy change ΔS of a reaction
D) Free energy change of a reaction in standard state

Column - II

P) $-RT\ln K$

Q) $RT^2 \left(\frac{d \ln K}{dT} \right)_P$

R) $-nFE$

S) $-\left(\frac{d\Delta G}{dT} \right)_P$

104. Match the following

Column - I

- A) ΔG
B) ΔG^0
C) W or $W_{\max}$
D) ΔS^0

Column - II

P) $-nFE$ or $-nFE^0$

Q) $\Delta H - T\Delta S$

R) $-RT \log_e K$

S) $2.303 nR \log_{10} \left[\frac{V_2}{V_1} \right]$

105. Match the list - I with list - II

List - I (Thermodynamic properties)

- A) Free energy change of a reaction (ΔG)
B) Enthalpy change of a reaction in a standard state (ΔH^0)
C) Entropy change (ΔS^0)
D) Free energy change of a reaction in a standard state (ΔG^0)

List - II (Equation)

P) $-RT\ln K$

Q) $RT^2 \left[\frac{d \ln K}{dT} \right]_P$

R) $-nFE$

S) $-\left[\frac{d\Delta G}{dT} \right]_P$

106. Match the column:

Column - I

- A) Joule Thomson coefficient for ideal gas
B) $\Delta S_{\text{vap}, m}$ for liquids which does not undergo association and dissociation
C) Work done in adiabatic irreversible expansion of an ideal gas
D) Work done in adiabatic reversible expansion of an ideal gas

Column - II

P) $88 \text{ J mol}^{-1} \text{ K}^{-1}$

Q) $nC_v m (T_2 - T_1)$

R) 0

S) $nRT_1 \left(\frac{T_2}{T_1} - \frac{P_2}{P_1} \right)$

107. Column - I

(A) $(DG_{\text{system}})_{T,P} = 0$

(B) $DS_{\text{system}} + DS_{\text{surrounding}} > 0$

(C) $DS_{\text{system}} + DS_{\text{surrounding}} < 0$

(D) $(DG_{\text{system}})_{T,P} > 0$

Column - II

(P) Process is in equilibrium

(Q) Process is nonspontaneous

(R) Process is spontaneous

(S) System is unable to do useful work

108. Column - I

(A) $(DG_{\text{system}})_{T,P}$

(B) Work done in reversible isothermal ideal gas expansion

(C) DG for reversible isothermal expansion of an ideal gas(D) DS_{gas} for isothermal expansion of an ideal gas**Column - II**(P) $nR \ln \left(\frac{V_2}{V_1} \right)$ (Q) $nRT \ln \left(\frac{P_2}{P_1} \right)$ (R) $-nFE$ (S) $nR \ln \left(\frac{P_1}{P_2} \right)$ **109. Column - I**

(A) Heating of an ideal gas at constant pressure

(B) Compression of liquid at constant temperature

(C) Reversible process for an ideal gas at constant temperature

(D) Adiabatic free expansion of an ideal gas

Column - II(P) $DH = nC_{p,m} DT \neq 0$ (Q) $DU = 0$ (R) $DG = V DP$ (S) $DG = nRT \ln \left(\frac{P_2}{P_1} \right)$ **110. Column - I**

(A) Reversible adiabatic compression

(B) Reversible vaporisation of liquid

(C) $2N(g) \rightleftharpoons N_2(g)$ (D) $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$ **Column - II**(P) $DS_{\text{system}} > 0$ (Q) $DS_{\text{system}} < 0$ (R) $DS_{\text{surrounding}} < 0$ (S) $DS_{\text{surrounding}} = 0$ **111. Column - I**(A) $H^+(aq)$ (B) $H(g)$ (C) $H_2(g)$ (D) $C(s, \text{diamond})$ **Column - II**(P) $D_f H^\circ = 0$ (Q) $D_f H^\circ \neq 0$ (R) $D_f G^\circ = 0$ (S) $D_f S^\circ < 0$ **112. Column - I**

(A) An ideal gas

(B) A real gas at inversion temperature

(C) H_2 gas at STP(D) NH_3 gas at STP**Column - II [Under adiabatic free expansion]**

(p) Temperature increases

(q) Temperature decreases

(r) Temperature remains constant

(s) Temperature first increases and then decreases

113. The feasibility of a chemical reaction can be explained based on DH , DS and DG , so answer the following :**Column-I**(A) $2O_3(g) \longrightarrow 3O_2(g)$ (B) $3O_2(g) \longrightarrow 2O_3(g)$ (C) $NH_2COONH_4(s) \xrightarrow{\text{Low temp.}} 2NH_3(g) + CO_2(g)$ (D) $\text{Ice} \rightleftharpoons H_2O(l)$ at room temperature $25^\circ C$ **Column-II**(p) $DH = +ve$, $DS = -ve$ (q) $DH = -ve$, $DS = +ve$ (r) $DG = +ve$ (s) $DH = -ve$ (t) $DG = -ve$ **114. Match the following :****Column-I**(A) $H_2(g)$ (B) $H_2O(l)$ (C) $C(\text{diamond})$ (D) $NO(g)$ **Column-II**

- (p) $\Delta H_f^\circ = 0$
 (q) $\Delta G_f^\circ = 0$
 (r) Entropy at absolute zero = 0
 (s) Entropy at absolute zero $\neq 0$
 (T) $\Delta G_F^\circ \neq 0$
 (u) $\Delta S_f^\circ = 0$

STATEMENT TYPE QUESTIONS

115. **Statement – 1:** For a process to be spontaneous, ΔG as well as ΔS has to be less than zero.
Statement – 2: For spontaneous change, $\Delta S_{total} > 0$
 a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for statement-1
 b) Statement-1 is true, Statement-2 is true, Statement-2 is not a correct explanation for statement-1
 c) Statement-1 is true, Statement-2 is false
 d) Statement-1 is false, Statement-2 is true
116. **Statement – 1:** Phase transition involves change in internal energy only.
Statement – 2: Phase transition occurs at constant pressure.
117. **Statement – 1:** The work done in an open container at 300 K, when 112 g of iron reacts with dil. HCl is 1200 cal.
Statement – 2: Work done = $P_{ext} (V_2 - V_1)$, where V_1 and V_2 are initial and final volume of reaction mixture & P_{ext} is external applied pressure.
118. **Statement – I:** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperatures.
Statement – II : Energy of the system increases with increase in temperature.
119. **Statement – 1:** In the case of an ideal gas the change in Gibbs free energy and Helmholtz free energies are equal to each other

($\Delta G = \Delta A$) for isothermal reversible process.

Statement – 2: There is no change in internal energies and enthalpies for ideal gas at constant temperature.

120. **Statement – I:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Statement – II : The volume occupied by the molecules of an ideal gas is zero.
121. **Statement – 1:** For a reaction at equilibrium, the free energy for the reaction is minimum.
Statement – 2: The free energy for both reactants and products decreases and become equal.
122. **Statement – I:** $C_p - C_v = R$ for ideal gas.

Statement – II : $\left(\frac{dU}{dV}\right)_T = 0$ for ideal gas

$C_p - C_v = R$ is correct statement

$\left(\frac{dU}{dV}\right)_T = 0$ is also correct

But because $\left(\frac{dU}{dV}\right)_T = 0$

Therefore, to say $C_p - C_v = R$ is not a correct reasoning.

123. **Statement – 1:** The amount of heat change during the isothermal free expansion of an ideal gas is zero.
Statement – 2: There are no intermolecular forces of attraction among the gas molecules, in case of real gas at a given pressure.
124. **Statement – 1 :** The enthalpy of formation of $H_2O(l)$ is greater than of $H_2O(g)$.
Statement – 2: Enthalpy change is negative for the condensation reaction
 $H_2O(g) \longrightarrow H_2O(l)$
125. **Statement – 1 :** Heat of neutralisation of H_3PO_4 with NaOH is more than that of HCl with NaOH.

Statement – 2 : H_3PO_4 is a triprotic acid and hence releases more heat on complete neutralization, while HCl is a monoprotic acid.

126. Statement – 1: Work done by the surrounding on the system of an ideal gas to do a particular isothermal compression reversibly is less than that done irreversibly.

Statement – 2: Isothermal reversible compression takes place through infinite number of infinitesimally small steps.

127. Statement – 1 : The magnitude of the work involved in an isothermal reversible expansion is greater than that involved in an adiabatic reversible expansion.

Statement – 2 : Adiabatic expansion is associated with fall in temperature of the system which in turn decreases the pressure of the system to a lower value than that in isothermal process.

128. Statement – 1 : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

and

Statement – 2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

129. Statement – 1 : There is a natural asymmetry between converting work to heat and converting heat to work.

and

Statement – 2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

130. Statement – 1 : Entropy change in reversible adiabatic expansion of an ideal gas is zero.

Statement – 2: The increase in entropy due to volume increase just compensates the decrease in entropy due to fall in temperature.

131. Statement – 1 : The standard free energy changes of all spontaneously occurring

reactions are negative.

Statement – 2: The standard free energies of the elements in their standard states at 1 bar and 298 K are taken as zero.

132. Statement – 1 : Enthalpy and entropy of any elementary substance in the standard states are taken as zero.

Statement – 2 : At absolute zero, particles of the perfectly crystalline substance become completely motionless.

133. Statement – 1: A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

Statement – 2: All exothermic reactions are accompanied by decrease of randomness.

134. Statement – 1 : Many endothermic reactions that are not spontaneous at room temperatures become spontaneous at high temperature.

Statement – 2 : ΔH° of the endothermic reaction increases with increase in temperature.

135. Statement – 1 : Decrease of free energy during the process under constant temperature and pressure provides a measure of its spontaneity.

Statement – 2 : A spontaneous change must have +ve sign of ΔS_{system} .

136. Statement – 1 : All combustion reactions are exothermic.

Statement – 2 : Enthalpies of products greater than enthalpies of reactants ($\sum \nu_p \Delta_f H(P) > \sum \nu_R \Delta_f H(R)$)

137. Statement – 1 : Due to adiabatic free expansion temperature of real gas may increase

Statement – 2 : In adiabatic free expansion, temperature is always constant irrespective of real or ideal gas

138. Statement – 1: Under adiabatic free expansion,

$\left(\frac{dU}{dV}\right)_T$ is +ve when attractive forces

are dominant between gas molecules [U, V, T represent internal energy, volume and temperature of gas respectively]

Statement – 2 : Internal energy is a state function.

139. Statement – 1 : At low temperatures, ΔH is the dominant factor for spontaneity of a reaction.

Statement – 2: At low temperatures, the opposing factor $T\Delta S$ remains very small.

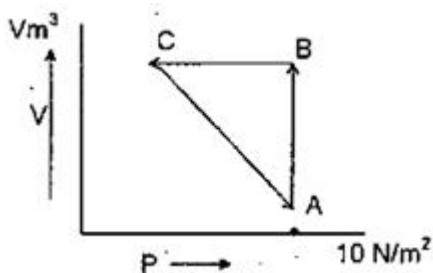
140. Statement – 1 : A reaction which is spontaneous and accompanied by decrease of randomness must exothermic.

Statement – 2 : All exothermic reactions are accompanied by decrease of randomness.

INTEGER TYPE QUESTIONS

141. Temperature of one mole of helium gas is increased by 1°C , find the increase in internal energy in cal.

142. An ideal gas is taken through the cycle $A \rightarrow B \rightarrow C \rightarrow A$ as shown in figure. If net heat supplied to the gas in the cycle is 5 J . Find the work done by the gas in the process $C \rightarrow A$ in Joule (taken mole value)



143. If 2 kcal heat is given to a system and 6 kcal work is done on the system then the internal energy of system will increase by how many kcal?

144. The constant volume molar heat capacity of an ideal gas is expressed by

$$C_{v,m} = 16.5 + 10^{-2}T \quad (\text{All values are in SI units})$$

If 2.5 mol of this gas at constant volume is heated from 27°C to 127°C , the internal energy increases by “x” kJ. Hence, x is

145. Molar enthalpy of vaporization of a liquid is 2.6 kJ . If boiling point of this liquid is 177°C , the molar entropy of vaporization (in JK^{-1}) unit is

146. The chemical reaction

$A \rightarrow P$ $\Delta H = 2.8\text{ kJ}$ is spontaneous only above 400 K . Therefore, ΔS of reaction must be at least (JK^{-1})

KEY

LEVEL (V)

SINGLE ANSWER QUESTIONS

- | | | | |
|-------|-------|-------|-------|
| 1. A | 2. A. | 3. D | 4. B |
| 5. C | 6. C | 7. D | 8. D |
| 9. D | 10. A | 11. A | 12. B |
| 3. C | 14. C | 15. C | 16. C |
| 17. A | 18. B | 19. C | 20. A |
| 21. A | 22. A | 23. A | 24. B |
| 25. B | 26. B | 27. A | 28. A |
| 29. D | 30. D | 31. B | 32. C |
| 33. C | 34. B | 35. B | 36. B |
| 37. C | 38. D | 39. D | 40. A |
| 41. C | 42. A | 43. B | |

ONE OR MORE ANSWER QUESTIONS

- | | |
|------------------|---------------|
| 44. (B, C, D) | 45. (A, B, C) |
| 46. B | 47. (A, C) |
| 48. (A, B, D) | 49. (B, C, D) |
| 50. (A, C) | 51. (A, C, D) |
| 52. (A, B, C) | 53. (A, C, D) |
| 54. (A, C) | 55. (A, C) |
| 56. (B, C) | 57. (A, D) |
| 58. (A, D) | 59. (B, D) |
| 60. (A, B, C, D) | 61. (A, B, C) |
| 62. (A, B) | 63. (A, D) |
| 64. (A, D) | 65. (A, B) |
| 66. (A, B, D) | 67. (A, B, D) |
| 68. (A, B, C, D) | 69. (A, B) |
| 70. (a, b, c) | 71. (b, c, d) |
| 72. B | 73. (d) |
| 74. (a) | 75. (d) |
| 76. (b) | 77. (a) |
| 78. (c) | 79. (a) |
| 80. A, B | 81. (a, b, c) |
| 82. (c, d) | 83. (B, D) |
| 85. (A, B, C, D) | 84. (A, B, C) |
| | 86. (A, B, C) |

COMPREHENSION TYPE QUESTIONS

- 87.(B) 88.(A) 89.(B) 90.(A)
 91.(A) 92.(D) 93.(A) 94.(C)
 95.(A) 96.(A) 97.(B) 98.(B)
 99.(B) 100.(C) 101.(A) 102.(C)

MATRIX MATCHING

103. A-R, B-Q, C-S, D-P
 104. A - P, Q ; B - P, R ; C - P ; D - S
 105. A - R ; B - Q ; C - S ; D - P
 106. A - R ; B - P ; C - S ; D - Q
 107. A - P, S ; B - R ; C - Q, S ; D - Q, S ;
 108. A - R ; B - Q ; C - Q ; D - P, S
 109. A - P ; B - R ; C - Q, S ; D - Q, S ;
 110. A - S ; B - P, R ; C - Q ; D - P, R ;
 111. A - P, R ; B - Q ; C - P, R ; D - Q, S
 112. (A - r) ; (B - r) ; (C - p) ; (D - q).
 113. (A - q, t) ; (B - p, r) ; (C - r) ; (D - t)
 114. A - p, q, s, u, B - s, t, u, C - r, t, D - s, t

STATEMENT TYPE QUESTIONS

- 115.(D) 116. (D) 117. (A) 118 (C)
 119 (A) 120 (B) 121 (A) 122 (B)
 123 (C) 124 (A) 125 (D) 126 (A)
 127 (A) 128 (D) 129 (A) 130 (A)
 131 (B) 132 (D) 133 (C) 134 (C)
 135 (C) 136 (C) 137 (C) 138 (B)
 139 (A) 140 (C)

INTEGER TYPE QUESTIONS

- 141 (3) 142 (5) 143 (8) 144 (5)
 145 (8) 146 (7)

LEVEL(V)

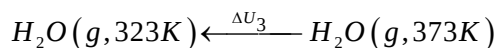
HINTS & SOLUTIONS

SINGLE ANSWER QUESTIONS

1. (A)
 $W_{\text{rev}} = -\int PdV$ or $-\int P\Delta V$; note that opposing pressure is not constant throughout.
 2. This is possible for adiabatic wall and thus $\Delta U = W_{\text{adiabatic}}$
 3. (D)
 B.E. of S = S, C $\equiv$ C, C $\equiv$ N and N $\equiv$ N are 523, 839, 891 and 941 kJ mol⁻¹ respectively.

4. (B)
 O₃ possesses more energy than O₂
 5. (C)
 If $\Delta G = -ve$, process is spontaneous.
 6. (C)
 $\Delta n = +1$ and thus, entropy increases.
 7. (D)
 The gaseous phase have more entropy and thus, ΔS is +ve in (A) and (B). Also decrease in pressure increases disorder and thus, ΔS is +ve in (C). In (D) the disorder decreases in liquid state due to decrease in temperature. Thus, $\Delta S = -ve$.
 8. (D)
 $\Delta G_{\text{system}} = -ve$, the system is spontaneous process, $\Delta G_{\text{system}} = 0$, the system has attained equilibrium $\Delta G_{\text{system}} = +ve$, the system is non spontaneous.
 9. (D)
 In a cyclic process $\Delta E = 0$
 10. (A) $W = P\Delta V = P \times 0 = 0$
 $Q = C_v (\Delta T) = 20 \times 273 = 5460 \text{ J} = 5.46 \text{ kJ}$
 11. (A) $DU = 0$; $-q = w$
 vapour equilibrium $\Delta n = 3 - 0 = 3$ than
 $\Delta U = 30000 - 3 \times 2 \times 500 = 27 \text{ kcal}$.
 12. (B)
 At constant volume $P\Delta V = 0$, $\therefore Q = \Delta U$
 13. (c)
 $w = -P_{\text{ext}} (V_f - V_i)$
 $= -10^5 \left(\frac{60 \times 10^{-3}}{0.60} + \frac{40 \times 10^{-3}}{1000} - \frac{100 \times 10^{-3}}{1000} \right)$
 $= -10^5 (100 \times 10^{-3} + 0.04 \times 10^{-3} - 0.1 \times 10^{-3})$
 $; |w| = 9994 \text{ J}$
 14. (c)
 $H_2O(l, 323 \text{ K}) \xrightarrow{\Delta U_1} H_2O(l, 373 \text{ K})$

$$\updownarrow \Delta U_2$$



$$C_{v,m}(H_2O, g) = 33.314 - 8.314$$

$$= 25 J / K \text{ mol}$$

$$\Delta U_2 = \Delta H_2 - \Delta n_g RT = 37.6;$$

$$\Delta U_{total} = \Delta U_1 + \Delta U_2 + U_3$$

$$= C_{v,m}(l) \Delta T + \Delta U_{vap} + C_{vap} + C_{vm}(g) \Delta T$$

$$= \frac{75 \times 50}{1000} + 37.6 + \frac{25 \times 50}{1000};$$

$$= 42.6 \text{ kJ / mol}$$

15. (c)

$$\Delta_r H^0 = 8 \times (-394) + 9 \times (-286) - (-250)$$

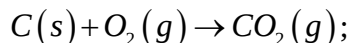
$$= -5476 \text{ kJ / mol}$$

$$(C - H)_6 = 6 \times 90 = 540 \quad ;$$

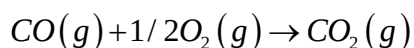
$$620 = 540 + C - C$$

$$C - C = 80.$$

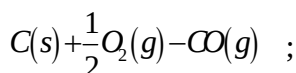
16. (c)



$$\Delta_r H_1 = -x \text{ kJ / mol} \quad \dots (1)$$

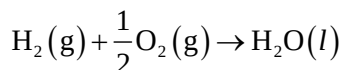


$$\Delta_r H_2 = -y \text{ kJ / mol} \quad \text{Equation (1) - (2)}$$

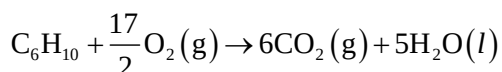


$$\Delta_r H = (y - x) \text{ kJ / mol}$$

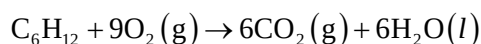
17. (A)



$$(\Delta H = -241 \text{ kJ}) \quad \dots (i)$$



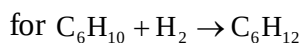
$$(\Delta H = -3800 \text{ kJ}) \quad \dots (ii)$$



$$(\Delta H = -3920 \text{ kJ}) \quad \dots (iii)$$

Eq. (i) + eq. (ii) - eq. (iii) gives

$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ}$$



18. (B)

Number of moles of HCl

$$= \frac{MV}{1000} = \frac{0.01 \times 25}{1000} = 25 \times 10^{-5}$$



Number of moles of $Ca(OH)_2$

$$= \frac{MV}{1000} = \frac{0.01 \times 50}{1000} = 50 \times 10^{-5}$$

$$n_{OH^-} = 2 \times 50 \times 10^{-5} = 10^{-3}$$

In the process of neutralisation 25×10^{-5} mole H^+ will be completely neutralised

$\therefore$

$$\Delta H = 140 \times 25 \times 10^{-5} \text{ kcal} = 0.035 \text{ kcal} = 35 \text{ cal}$$

19. Conceptual

$$20. (a) \quad -q_{reaction} = q_{bomb} + q_{water}$$

$$-q_{reaction} = [C(bomb) + (m_{water} \times c)] \Delta T$$

$$= (652 + 500 \times 4.18) \times 14.3$$

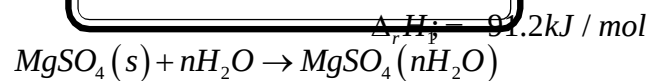
$$= 39210 \text{ J or } 39.21 \text{ kJ}$$

$$21. (a) \text{ m mole of acid} = 0.05 \times 0.2 = 0.01$$

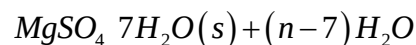
$$\Delta_r H^0 = \frac{480 \times 1.09}{0.01 \times 1000} = -52.32 \text{ kJ / mol}$$

22. (a)

Given that



.....(i)



$$\Delta_r H_2 = 13.8 \text{ kJ / mol} \quad \dots (ii)$$

$$\text{Equation (i) - (ii) or } \Delta H_{hyd} = \Delta_r H_1 - \Delta_r H_2$$

$$= -91.2 \text{ kJ / mol} - 13.8 \text{ kJ / mol}$$

$$= -105 \text{ kJ / mol}$$

23. (a) $-12250x - 13000(1-x) = -12500$
 $750x = 500 \Rightarrow x = 2/3$ and $y = 1/3$ So ,

$$\frac{x}{y} = \frac{2}{1}$$

24. (b)

$$\Delta_r H = \frac{5}{8} \times 40 + \frac{3}{8} \times 50 = 43.75 \text{ kJ/mol}$$

25. Conceptual

26. (b)

$$\Delta_r H = [\text{Heat supplied}] - [\text{Heat evolved}]$$

$$292 = [4x + 279] - [38 + 85]$$

$$\Rightarrow x = 34 \text{ kcal/mol}$$

27. (A)

For spontaneous reaction $\Delta G^\circ = -ve$

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

$$\therefore \Delta H^\circ < T\Delta S^\circ$$

$$\text{or } T > \frac{\Delta H^\circ}{\Delta S^\circ} > \frac{179.10 \times 10^3}{160.2} > 1118 \text{ K}$$

28. (a)

$$\therefore \frac{C_{pm}}{C_{vm}} = \gamma \text{ and } C_{p,m} - C_{v,m} = R$$

$$\therefore C_{v,m} = \frac{R}{\gamma - 1}$$

$$C_{v,m} = \frac{C_v}{n} \text{ and } C_v = m.c_v$$

$$\therefore \frac{R}{\gamma - 1} = \frac{m.c_v}{m} \times M \text{ and}$$

$$\therefore C_v = \frac{R}{(\gamma - 1)M}$$

29. (d)

$$\text{Aev. } C_{v,m} = \frac{n_1 C_{v,m_1} + n_2 C_{v,m_2}}{n_1 + n_2} = 2R \quad \text{For}$$

adiabatic process $dU = dW$

$$\frac{dT}{T} = -\frac{R}{C_{v,m}} \left(\frac{dV}{V} \right)$$

$$n_1 C_{v,m_1} dT + n_2 C_{v,m_2} dT$$

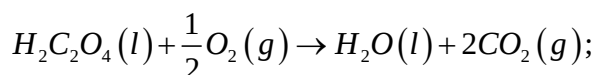
$$= -(n_1 RT + n_2 RT) \times \frac{dV}{V} ;$$

$$\ln \frac{T_2}{T_1} = -\frac{1}{2} \ln \left(\frac{V_2}{V_1} \right) \Rightarrow T_2 = 320 \times \left(\frac{1}{4} \right)^{1/2}$$

$$= 160 \text{ K}$$

$$\Delta U = (n_1 C_{v,m_1} + n_2 C_{v,m_2}) \Delta T = -960R$$

30. (d)



$$\Delta n_g = 3/2$$

$$\Delta U_c = -\frac{0.312 \times 8.75}{1} \times 90$$

$$= -245.7 \text{ kJ/mol}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -245.7 + \frac{3}{2} \times \frac{8.314 \times 300}{1000}$$

$$= -246.95 \text{ KJ/mol}$$

31. (B) Conceptual

32. (c)

Max temp attained by gas in between B to C
 According to equation of straight line

$$\frac{P-4}{1-4} = \frac{V-1}{2-1} \Rightarrow P-4 = -3V+3$$

$$\Rightarrow P = 7 - 3V \quad \text{For 1 mole gas}$$

$$\frac{RT}{V} = 7 - 3V; RT = 7V - 3V^2;$$

$$R \frac{dT}{dV} = 7 - 6V = 0; \quad V = \frac{7}{6}$$

$$\text{substituting in eq (1)} RT = \left(7 - 3 \times \frac{7}{6} \right) \times \frac{7}{6}$$

$$\Rightarrow T = \frac{49}{12R}$$

33. (c) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$; $T_2 = T_1 \left(\frac{1}{32}\right)^{\frac{7}{5}-1} =$

$$600 \left(\frac{1}{2^5}\right)^{2/5}$$

$$= 600(0.5)^2 = 150K ;$$

$$\Delta H_m = \frac{7}{2} R \times (150 - 600) = -1575R$$

34. (b) $dU = dp + dw$
 $nC_{v,m}dT = nC_m dT - P.dV ;$

$$C_m = C_{v,m} + \frac{P.dV}{n.dT} \quad \dots\dots (1)$$

$$PV^n = K \text{ and } PV = nRT$$

$$\therefore KV^{1-n} = nRT$$

$$K(1-n)V^{-n}.dV = nRdT$$

$$\frac{dV}{dT} = \frac{nR}{K(1-n)V^{-n}} \quad \dots\dots\dots (2) \quad ; \text{ From}$$

Eqs (1) and (2)

$$C_m = C_{v,m} + \frac{R}{(1-n)}$$

35. (b) $P_2V_2^2 = P_1V_1^2$
 $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^2$ Now, $\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{V_1}{V_2} = \frac{1}{3}$

$$\therefore T_2 = \frac{300}{3} = 100K ; \Delta H = nC_{p,m}\Delta T$$

$$= 2 \times \frac{5}{2} R \times (-200K) = 1000R$$

36. (b) $HA \rightarrow H^+ + A^- ; \Delta_r H = 1.4kJ / mol$

$$\Delta H_{\text{neutralization}} = \Delta H_{\text{ionization}} (H^+ + OH^- \rightarrow H_2O)$$

$$-55.95 = \Delta H_{\text{ionization}} - 57.3$$

$$\Delta H_{\text{ionization}} \text{ for } 1M \text{ HA} = 1.35 \text{ kJ/mol}$$

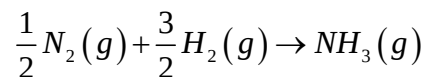
% heat utilized by 1M acid for ionization

$$= \frac{1.35}{1.4} \times 100 = 96.43\%$$

so, acid is $100 - 96.3 = 3.57\%$ ionized

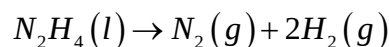
37.

(c)



Let B.E of $N \equiv N$ is x

$$-46 = \frac{x}{2} + \frac{3}{2} \times 436 - 3 \times 393 \Rightarrow x = 958$$



$$\Delta_r H = -50 \text{ kJ / mol}$$

$$\Delta_r H = [\Delta_{\text{vap}} H(N_2H_4, l) + 4 \times \text{B.E.}(N-H) + \text{B.E.}, (N-N)]$$

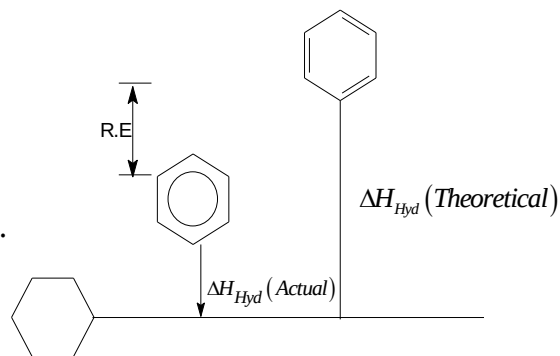
$$-(\text{B.E.}(N \equiv N) + 2 \times \text{B.E.}(H-H))$$

$$-50 = (18 + 4 \times 393 + y) - (958 + 2 \times 436)$$

$$-50 = (1590 + y) - (1830)$$

$$\text{B.E.}(N-N) \text{ or } y = 190 \text{ kJ / mol}$$

38.



$$= -205 - 152 = -357$$

Enthalpy of hydrogenation of

$$\frac{-357}{3} = -119 \text{ kJ / mol}$$

39. (d)

$$\Delta S = nC_{pm} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= 3 \times \frac{7}{2} R \ln \left(\frac{596}{298} \right) + 3R \ln \frac{1}{4}$$

$$= -6.3 \text{ cal K}^{-1}$$

40. (a)

For isentropic process $\Delta S_{\text{system}} = 0$

$$\therefore nC_{pm} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0$$

$$\Rightarrow \ln(P_2) = \frac{5}{2} \times \ln \left(\frac{600}{300} \right); \quad = 1.75 \text{ atm}$$

41. (c)

$$0.40 = aT_1^3 + bT_1$$

$$0.40 = a \times (1000) + b \times 10$$

$$0.4 = 1000a + 10b \dots\dots(1)$$

$$0.92 = aT_2^3 + bT_2$$

$$\Rightarrow 0.92 = a \times 8000 + 20b \dots\dots(2) \quad \text{from}$$

Eqs (1) and (2)

$$a = 2 \times 10^{-5}, b = 0.038$$

$$S_m = \int \frac{aT^3 + bT}{T} \cdot dT$$

$$= \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

$$= 0.813 \text{ J / K - mol}$$

42. (a)

$$\Delta_f S^0 (\text{NH}_4\text{Cl}, s) \text{ at } 300\text{K}$$

$$= S_{\text{NH}_4\text{Cl}(s)}^0 - \left[\frac{1}{2} S_{\text{N}_2}^0 + 2S_{\text{H}_2}^0 + \frac{1}{2} S_{\text{Cl}_2}^0 \right]$$

$$= -374 \text{ JK}^{-1} \text{ mol}^{-1} \quad \because \Delta_r C_p = 0$$

$$\therefore \Delta_f S_{310}^0 = \Delta_f S_{300}^0 = -374 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta_f H_{310}^0 = \Delta_f H_{300}^0 = -314.5$$

$$\Delta_f G_{310}^0 = \Delta_f H^0 - 310 \Delta S^0$$

$$= -314.5 - \frac{310(-374)}{1000} = -198.56 \text{ kJ / mol}$$

43. (b)

$$\Delta_r G^0 = \Delta_r H^0 - T \times \Delta_r S^0$$

$$\Delta_r S^0 = 2 \times 81 - 4 \times 24 - 3 \times 205 \text{ J / mol}$$

$$\therefore \Delta_r H^0 = -2258.1 \text{ kJ / mol}$$

$$\Delta_r H^0 = 2 \times \Delta_f H^0 (\text{Cr}_2\text{O}_3, s)$$

$$\therefore \Delta_f H^0 (\text{Cr}_2\text{O}_3, s) = -\frac{2258.1}{2}$$

$$= -1129.05 \text{ kJ / mol}.$$

MULTI ANSWER QUESTIONS

44. (b,c,d)

$$\Delta U = 0 \therefore U_2 - U_1 = 0$$

$$\text{similary, } \Delta H = 0$$

$$q = -w = nRT \ln \frac{V_2}{V_1}$$

45. (A,B,C) Conceptual

51. (A, C, D); defined at equilibrium

52. (A, B, C); conceptual

53. (A, C, D); For spontaneous process,

$$(\partial G)_{T,P} = -ve; \quad (\partial S)_{E,V} = +ve \quad \text{and}$$

$$(\partial H)_{P,T} = -ve$$

54. (A, C); factual

55. (A, C); factual

56. (B, C); defined

57. (A, D)

58. (A, D) $\Rightarrow$ Internal energy depends upon large no. of factors, $U = E_{\text{tra}} + E_{\text{rot}} + E_{\text{nuclear}} + E_{\text{vib}} \dots\dots$
The exact calculation is not possible.

59. (B, D); defined

60. (A, B, C, D); Increase in randomness increases the entropy.

61. (A, B, C)

62. (A, B)

63. (A, D)

Heat supplied by electric heater is = 250 J/sec

x 55 sec = 13.75 kJ

64. (A, D); defined

65. (A, B)

 $q = ms\Delta T$ for water and glass

66. (A, B, D); factual

67. (A, B, D); factual

70. (a,b,c)

For a cyclic process $dU=0$

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

Also, $w =$ area covered by sphere

$$= \pi r^2 = \pi \times \left[\frac{(V_2 - V_1)}{2} \right]^2 = \frac{\pi \times (20)^2}{2^2} = 100 \times 3.14 = 314 \text{ J}$$

71. (b,c,d) $H_2O_{(s)}$ has more ordered arrangement. Also

$$\Delta S_2^\circ = S_{H_2O_{(v)}}^\circ - S_{H_2O_{(l)}}^\circ \quad ;$$

$$\Delta S_0^\circ = S_{H_2O_{(l)}}^\circ - S_{H_2O_{(s)}}^\circ$$

 $\therefore S_{H_2O_{(v)}}^\circ$ is maximum and thus $\Delta S_2^\circ \gg \Delta S_1^\circ$

72.

$$\Delta G^\circ \text{ for } 2Fe_2O_3 + 600 \rightarrow 4Fe + 6CO_2 = \Delta_r G_1^\circ + \Delta_r G_2^\circ$$

$$= +1487 - 1543.2 = -56.2 \text{ kJmol}^{-1}$$

The reduction occurs spontaneously in lower part of blast furnace.

73.

$$(d) \Delta_r S_4^\circ = \sum S_p^\circ - \sum S_R^\circ = CS_c^\circ + dS_D^\circ - 0 - 0$$

74. (a) Adiabatic slope are more steeper than isothermal.

Slope of adiabatic process $= \gamma \times$ slope of isothermal process75. (d) Ratio of slope $= \frac{\gamma \text{ for gas I}}{\gamma \text{ for gas II}}$; slope forHe, N_2 and O_3 are 7/5, 5/4 and 4/3 respectively.

76.

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

b) for $H_2O \rightleftharpoons H^+ + OH^-$ is +13.7 kcal

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{+13.7 + 19.14}{298} = 0.1102$$

$$\text{kcal mol}^{-1}$$

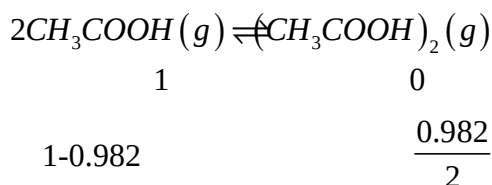
$$= 11.2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

77. (a) Work done in (-ve) reversible process is maximum. Thus, in reversible process

$$T_{f \text{ rev}} < T_{f \text{ irrev}}$$

78. C.

Sol:



$$K^0 = \frac{(CH_3COOH)_2}{(CH_3COOH)^2} = \frac{0.982}{2 \times (0.018)^2} = 1515.4$$

$$\text{Now, } \Delta H^0 \text{ for dimerization} = -2 \times 33 \text{ kJ} = -66 \text{ kJ}$$

$$\text{Thus, } \Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$-2.303 RT \log K^0 = \Delta H^0 - T\Delta S^0$$

$$-2.303 \times 8.314 \times 400 \times \log(1515.4) = -66 \times 10^3 - 400 \times \Delta S^0$$

$$-24359.2 = -66000 - 400\Delta S^0$$

$$\Delta S^0 = -\frac{41640.8}{400} = -104.102 \text{ J/mol}$$

79. .Ans (A)

Solution: Since, work is done against constant pressure process is irreversible.

Given, $\Delta V = (6 - 4) = 2$ litre, $p = 2.5$ atm

$$w = -p_{\text{ext}} \times \Delta V = -2.5 \times 2 = -5 \text{ litre-atm}$$

$$= -\frac{5 \times 1.987}{0.0821} \text{ cal} = -\frac{5 \times 1.987 \times 4.187}{0.0821} \text{ J} = -506.31 \text{ J}$$

$$C = 4.184 \text{ J/g/K or } 4.184 \text{ J/mol}$$

Now this work is used in heating 1 mole water

$$W = n \times C \times \Delta T = 506.31$$

$$= 1 \times 4.184 \times \Delta T \therefore \Delta T = 6.723$$

$\therefore$ Final temperature

$$= T_1 + \Delta T = 293 + 6.723 = 299.723 K$$

80. Ans (A,B) reversible process:

$$W_{rev} = -2.303nRT \log_{10} \frac{p_1}{p_2}$$

$$= -2.303 \times 2 \times 8.314 \times 300 \log_{10} \frac{1.01 \times 10^5}{5.05 \times 10^6}$$

$$= +1.9518 \times 10^4 \text{ joule}$$

Since $W_{reversible}$ is a measure of free change

$$-\Delta G = -W_{rev} = -W_{max} = 1.9518 \times 10^4 J$$

81. Ans A,B,C

$$\therefore C_v = \frac{3}{2}R \therefore C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\therefore \text{Heat given at constant pressure} = m \cdot C_p \cdot \Delta T$$

or

$$\text{Now work done in the process} = -P\Delta V$$

$$\Delta H \text{ or } q_p = 1 \times \frac{5}{2} \times R \times (373 - 298) \text{ or } \Delta H = 1 \times \frac{5}{2} \times 1.987 \times 75 = 372.56 \text{ cal}$$

$$w = -p(V_2 - V_1) = -p \left(\frac{nRT_2}{p} - \frac{nRT_1}{p} \right)$$

$$(\because pv = nRT)$$

$$= -nR(T_2 - T_1) = -1 \times 1.987 \times (373 - 298)$$

$$= -149.225 \text{ cal}$$

$\therefore$ from I law of thermodynamics

$$\Delta U = q + W = 372.56 - 149.05$$

$$\therefore \Delta U = 223.51 \text{ cal}$$

$$\text{Also, } dq_{rev} = nC_p \cdot dt$$

$$ds = \frac{dq_{rev}}{T} \therefore ds = \frac{nC_p \cdot dt}{T}$$

$$\text{or } \Delta S = \int_{T_1}^{T_2} \frac{nC_p \cdot dT}{T} = nC_p \log_e \frac{T_2}{T_1}$$

$$\therefore \Delta S = 2.303 nC_p \log_{10} \frac{T_2}{T_1}$$

$$= 2.303 \times 1 \times \frac{5}{2} R \times \log_{10} \frac{373}{298} = 1.122 \text{ cal } K^{-1} \text{ mol}^{-1}$$

$$82 \quad (c,d) \quad \text{At } V_A = \frac{1 \times R \times 100}{1} = 100R$$

$$V_B = \frac{1 \times R \times 600}{3} = 200R$$

$\therefore V_B > V_A$ so expansion of gas takes place

$$V_B = 200 \times 0.0821 = 16.42 L$$

83 (B,D)

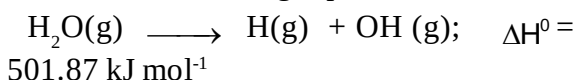
84 (A,B,C)

85 (A,B,C,D)

86 (A,B,C)

COMPREHENSION TYPE QUESTIONS

87. (B) The enthalpy of dissociation of the O-H bond depends on the molecular species from which H-atom is being separated.



However to break O-H bond in hydroxyl a different quantity of heat ($423.38 \text{ kJ mol}^{-1}$) is
BE (O - H) =

$$\frac{501.87 \text{ kJ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625$$

kJ mol^{-1}

88 (A)

In case of diatomic molecules, bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction
 $H_2(g) \longrightarrow 2H(g); \text{BE}(H-H) = 433.93 \text{ kJ mol}^{-1}$

89. (B)

BE (S - S)

$$\Delta H_{vap}(S) - \{\Delta H_f^0(C_2H_5S - SC_2H_5)\}$$

$$= \Delta H_{vap}(S) - \Delta H_f^0$$

$$\begin{aligned}
 &= -\Delta H_f^\circ(\text{C}_2\text{H}_5 - \text{S} - \text{C}_2\text{H}_5) \\
 &= 222.80 - \{-201.92 - (-147.23)\} \\
 &= 277.49 \text{ kJ mol}^{-1}
 \end{aligned}$$

90. (A) The gas expands against a zero opposing pressure. Since $dw = -P_{\text{opp}} dv$, it is obvious that the work involved in the expansion is zero.
- $$du = dq + dw$$
- Hence $du = dq$
- Since there is no change in temperature $dq = 0$
- Hence $du = 0$

91. (A) $u = f(T, V)$

$$du = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV$$

$$\text{Since } dT = 0; \quad du = 0$$

$$\left(\frac{\partial u}{\partial V}\right)_T dV = 0$$

Since $dV \neq 0$, follows that

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

since it is a free expansion, it is applicable to only ideal gases.

92. (D)

If the external pressure is only infinitesimally smaller than the pressure of the gas, the expansion is said to take place reversibly. If, however, the external pressure is much smaller than the gas pressure, the expansion occurs irreversibly. If the external pressure is zero, the expansion is known as free expansion.

93. (A) $q = \Delta U + P\Delta V$

$$\text{at } T = \text{constant} \quad q = P\Delta V$$

94. (C) $ACB = AC + BC$ $ADB = AD + B$

$$\begin{array}{lcl} \text{Heat absorbed} & 80 \text{ J} & \text{Work done by the} \\ \text{system} & = & 10 \text{ J} \end{array} \quad \therefore w = -10 \text{ J}$$

$$\therefore w = -30 \text{ J} \quad \text{Also } w = -10 \text{ J}$$

$$\therefore UB - UA = 50 \text{ J} \quad \therefore q = 50 + 10 = 60 \text{ J}$$

95. (A) $C_p - C_v = \frac{R}{M}$ At A, $P = 1 \text{ atm}$. $V = 22.4 \text{ L}$

$$\therefore 0.125 - 0.075 = \frac{2}{M} \times 273$$

$$\therefore M = 40 \quad \text{At B, } P = 1 \text{ atm. } V = 44.8 \text{ L}$$

$$\therefore T = 546 \text{ K}$$

$$\text{At C, } P = 0.5 \text{ atm., } V = 44.8 \text{ L}$$

$$\therefore T = 273 \text{ K}$$

$$\text{Also At constant } V$$

$$\Delta U = P \times \Delta V \quad \Delta U = C_v \times \Delta T$$

$$= 1 \times 22.4 \text{ L atm} = \frac{1 \times 22.4}{0.0821} \times 8.314 \text{ J} =$$

$$0.075 \times 40 \times 4.12 = 2268.37 \text{ J} = 3.44 \text{ kJ}$$

$$= 2.27 \text{ kJ}$$

98. (b) For max rise in temp; max neutralization of H^+ and OH^- required

if we take equal volume, all H^+ (5 m-mole) will react with all OH^- (5m-mole)

99. (B) all are correct

$$100. (C) \Delta S_v = \frac{\Delta H_v}{373} = \frac{540}{373};$$

$$\therefore \Delta H = -809 \text{ kJ mol}^{-1}$$

Let the temperature be T and assume volume of 1 mole of a gas is V litre at this condition.

$\therefore V$ litre of 1 mole of CH_4 gives energy on combustion = 809 kJ

$\therefore X$ litre of CH_4 gives energy on

$$\text{combustion} = \frac{809(X)}{V} \text{ kJ}$$

$\therefore 2878 \text{ kJ}$ energy is obtained by 1 mole of V litre C_4H_{10}

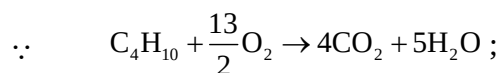
$$\therefore \frac{809(X)}{V} \text{ kJ energy is obtained}$$

$$\therefore \frac{809(X) \times V}{V \times 2878} \text{ litre } \text{C}_4\text{H}_{10} = 0.281 (X)$$

litre C_4H_{10}

Thus, butane supplied for the same calorific

output = 0.281 (X) litre



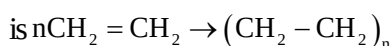
$\Delta H = -2878 \text{ kJ/mol}$

Volume of O_2 required = 3 volume of O_2 for combustion of C_4H_{10}

$$= 3 \times \frac{13}{2} \times \text{volume of } \text{C}_4\text{H}_{10}$$

$$= 3 \times \frac{13}{2} \times 0.281(X) = 5.48(X) \text{ litre } \text{O}_2$$

104. The polymerisation reaction



In this process, one double bond ($\text{C}=\text{C}$) breaks and two $-\text{CO}_2$ groups are linked with single bonds thus forming three single bonds (two single bonds are formed when each CH_2 group of ethylene ($\text{CH}_2 = \text{CH}_2$) links with another CH_2 - group of another ethylene molecule).

Therefore, in polymerisation reaction one $\text{C}=\text{C}$ is replaced by two $\text{C}-\text{C}$ bonds or one mole of $\text{C}=\text{C}$ bonds are replaced by 2 moles of $\text{C}-\text{C}$ bonds

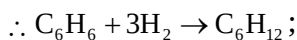
Energy Released = Energy due to formation of 2 single bonds.

$$= (2 \times 331) \text{ kJ} = 662 \text{ kJ}$$

Energy needed to dissociate one mole of $\text{C}=\text{C}$ bonds = 590 kJ

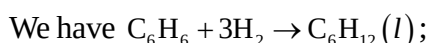
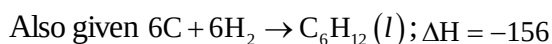
$$\Delta H_{\text{pot}} \text{ or enthalpy of polymerisation} = (590 - 662) \text{ kJ} = -72 \text{ kJ moles}$$

105. $\text{C}_6\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$; $\Delta H = -119 \text{ kJ}$
(involves breaking up of three double bond and additional of three H_2 molecule)

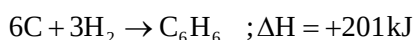


$$\Delta H = 3 \times (-119) = -357 \text{ kJ}$$

(involves breaking up of three double bond and additional of three H_2 molecule)



$$\Delta H = -357$$



Therefore, resonance energy = 49–201

$$= -152 \text{ kJ}$$

106. Energy available for muscular work by 1 mole

$$\text{of glucose} = \frac{2880 \times 25}{100} = 720 \text{ kJ}$$

Thus, 180 g (1 mole) of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) supplies energy = 720 kJ

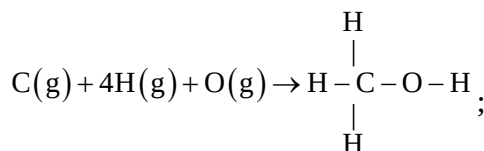
$$\text{Will supply 120 g glucose} = \frac{720}{180} \times 120 = 480 \text{ kJ}$$

Distance covered by 100 kJ energy = 1 km or 100 kJ is need to walk 1 km

$\therefore$ Distance covered by 480 kJ energy

$$= \frac{1}{100} 480 = 4.8 \text{ km}$$

107. The concerned thermochemical reaction is



$\Delta H = ?$

$$\Delta H_f = \left[\Delta H_{\text{C(s)} \rightarrow \text{C(g)}} + 2\Delta H_{\text{H-H}} + \frac{1}{2}\Delta H_{\text{O=O}} \right]$$

$$- \left[3\Delta H_{\text{C-H}} + \Delta H_{\text{C-O}} + \Delta H_{\text{O-H}} + \Delta H_{\text{vap(CH}_3\text{OH)}} \right]$$

$$= [715 + 2 \times 436 + 249] - [3 \times 415 + 365 + 463 + 38] = -275 \text{ kJ mol}^{-1}$$

108. Total hydration energy of Al^{3+} and 3 Cl^- ions of AlCl_3

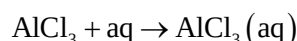
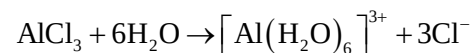
$$(\Delta H_{\text{Hydration}}) = \text{Hydration energy of } \text{Al}^{3+} + 3$$

$\times$ Hydration energy of Cl^-

$$= [-4665 + 3 \times (-381)] \text{ kJ mol}^{-1} = -5808 \text{ kJ mol}^{-1}$$

This amount of energy exceeds the energy needed for the ionisation of Al to Al^{3+} (i.e., 5808 > 5137). Because of this AlCl_3 becomes less ionic in aqueous solution.

In aqueous solution AlCl_3 exists in ionic form as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and 3 Cl^-



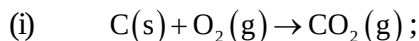
; $\Delta H = ?$

$$\Delta H = (\text{Energy released during})$$

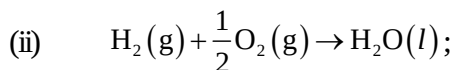
hydration) – (Energy used during hydration)
 $= (-4665) - (3 \times 381) + 5137 =$
 -671 kJ mol^{-1}

Thus, formation of ions will take place.

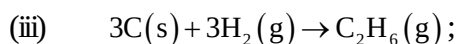
109. Following equation can be obtained from the available data



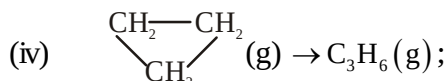
$$\Delta H = 393.5 \text{ kJ}$$



$$\Delta H = 2858 \text{ kJ}$$

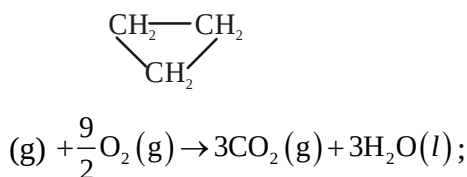


$$\Delta H = +20.42 \text{ kJ}$$



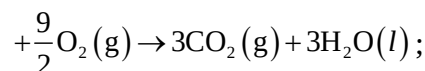
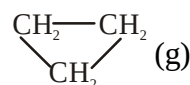
$$\Delta H = -33.0 \text{ kJ}$$

The desired equation is



$$\Delta H = 2091.32 \text{ kJ mol}^{-1}$$

To get the desired equation compute as follows
 $[3 \times (\text{i}) + 3 \times (\text{ii})] + [(\text{vi}) - (\text{iii})]$



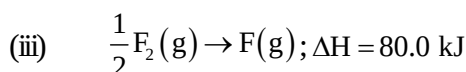
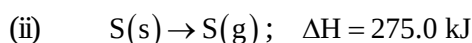
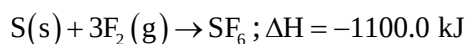
$$\Delta H = 2091.32 \text{ kJ mol}^{-1}$$

110. Given: $\text{SF}_6(\text{g}) \rightarrow \text{S(g)} + 6\text{F(g)};$

$$\Delta H = ?$$

From the available data, we can write the following equation

(i)



To get the required equation carry out the

following computation $[6 \times (\text{iii}) + (\text{ii})] - (\text{i})$
 i.e.

$$\Delta H = (6 \times 80 + 2745) - (-1100.0) = 1855 \text{ kJ}$$

Now, in SF_6 we find S–F bonds, therefore the bond energy

Thus average bond energy for S – F bond

$$= \frac{1855}{6} = 309.16 \text{ kJ mol}^{-1}$$

111. For adiabatic expansion of a gas, we have

$$\ln \frac{T_1}{T_2} = \frac{R}{C_V} \ln \frac{V_2}{V_1}$$

$$\text{or } \ln \frac{300}{T_2} = \frac{8.31}{12.48} \ln \frac{2.50}{1.25}$$

Solving the above equation, we get $T_2 = 188.5 \text{ K}$

Number of moles of argon gas,

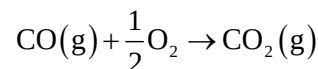
$$n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.082 \times 300} = 0.05$$

Now, we know that $\Delta H = n.C_p.\Delta T$

$$\therefore \Delta H = 0.05 \times 20.8(188.5 - 300) \quad [C_p = C_V + R = (12.48 + 8.314) \approx 20.8]$$

$$= -115.96 \text{ J}$$

112. Following reaction takes place



We know, $\Delta G^\circ = \Delta G^\circ_{(\text{Product})} - \Delta G^\circ_{(\text{Reactant})}$

$$= -394.4 - [-137.2 + 0] = -257.2 \text{ kJ mol}^{-1}$$

Since ΔG° is negative so the reaction is feasible
 i.e., spontaneous,

$$\text{Again, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

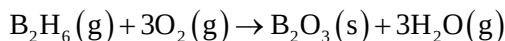
$$-257.2 = \Delta H^\circ - 300(-0.094) \Rightarrow \Delta H^\circ = -285.4 \text{ kJ mol}^{-1}$$

Since the value of ΔH is negative so the reaction is exothermic.

$$-iv + (i) + 3(iii) + 3(ii)$$

113. $-36 + (-1273) + 3(44) + 3(-286)$

Subtracting given equation (iv) from (vi), we get



$$\Delta H = -2035.0 \text{ kJ}$$

114. Calculation of ΔG

$$\Delta G^\circ = -2.303RT \log \frac{(\text{Product})}{(\text{Reactant})}$$

For the equilibrium reaction $\text{B} \rightleftharpoons \text{A}$, we get

and for the reaction $\text{B} \rightleftharpoons \text{C}$, we get

$$\Delta G_1^\circ = \left(-2.303 \times 8.314 \times 448 \log \frac{1.3}{95.2} \right) \\ = 15.992 \text{ kJ mol}^{-1}$$

$$\Delta G_2^\circ = \left(-2.303 \times 8.314 \times 448 \log \frac{3.5}{95.2} \right) \\ = 12.312 \text{ kJ mol}^{-1}$$

Again, for the reaction $\text{A} \rightleftharpoons \text{C}$

$$\Delta G_3^\circ = \left(-2.303 \times 8.314 \times 448 \log \frac{3.5}{1.3} \right) \\ = -3.688 \text{ kJ mol}^{-1}$$

From the above calculations, we have

$$\text{B} \rightleftharpoons \text{A}, \Delta G_1^\circ = +15.992 \text{ kJ mol}^{-1}$$

$$\text{B} \rightleftharpoons \text{C}, \Delta G_2^\circ = +12.312 \text{ kJ mol}^{-1}$$

$$\text{A} \rightleftharpoons \text{C}, \Delta G_3^\circ = -3.688 \text{ kJ mol}^{-1}$$

Thus, the correct order of stability $\text{B} > \text{C} > \text{A}$

115. $\Delta H = \Delta U + V\Delta P$

$$(\because \Delta V = 0)$$

$$\Delta U = \Delta H - V\Delta P$$

$$= -560 - [0.1 (40-70) \times 0.1] = -557 \text{ kJ}$$

So, the magnitude is 557 kJ mol^{-1}

116. In case of helium (monoatomic gas) we have only three degrees of freedom which correspond to three translational motion so the total heat capacity will increase. The contributors by vibrational motion is not appreciable at low temperature but increases from 0 to R when temperature increases.

$$C_v = -f \frac{R}{2}, \text{ where } f \text{ is the degree of freedom.}$$

At low temperature only translational motion is

$$\text{considered and } f = 3. \therefore C_v = \frac{3R}{2}$$

At moderate temperature both translational and rotational motions are considered.

$$f = 3+2 \text{ (3-translational and 2 rotational)}$$

$$\therefore C_v = \frac{5R}{2}$$

At still high temperature translational, rotational and vibrational motions are considered.

$$f = 3+2+2 \text{ (3-translational, 2-rotational, 2-vibrational)}$$

$$\therefore C_v = \frac{7R}{2}$$

117. Here, $P_1 = 1 \text{ bar}$ $P_2 = 100 \text{ bar}$;
 $V_1 = 100 \text{ ml}$, $V_2 = 99 \text{ ml}$

For adiabatic process, $q = 0$,

$$\Delta U = W$$

Since, $\Delta U = q + W$ (first law of thermodynamics)

$$= q - P(V_2 - V_1) \quad [W = P(V_2 - V_1)]$$

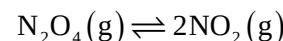
$$= 0 - 100(99 - 100) = 100 \text{ bar mL}$$

$$\text{Also, } \Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + P_2 V_2 - P_1 V_1 ;$$

$$= 100 + (99 \times 100 - 100 \times 1) = 9900 \text{ bar mL}$$

118. (i) Standard Gibbs free energy change for the reaction,



$$\Delta G^\circ = -2.303RT \log K_p = 0 ; K_p = 1$$

$$\text{Initially, } P_{\text{N}_2\text{O}_4} = P_{\text{NO}_2} = 10 \text{ bar}$$

$$\text{Reaction quotient} = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{100}{10} = 10$$

$$\Delta G^\circ = 2\Delta G_{f(\text{NO}_2)}^\circ - \Delta G_{f(\text{N}_2\text{O}_4)}^\circ = 100 - 100 = 0$$

Initial Gibbs free energy of the above reaction,

$$\Delta G = \Delta G^\circ + 2.303RT \log Q_p$$

$$\Delta G = 0 + 2.303 \times 8.314 \times 298 \log 10 \\ = 5.0705 \times 10^3 \text{ kJ mol}^{-1}$$

(ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.

$$141. \left(\frac{\Delta E}{\Delta T} \right)_V = C_V$$

$$\therefore \Delta E = C_V \Delta T$$

$$C_V = \frac{3}{2}R \text{ for monatomic gas}$$

$$\Delta T = 1K$$

$$\therefore \Delta E = \frac{3}{2}R = \frac{3}{2} \times 2 = 3 \text{ cal}$$

$$142. W_{AB} = P\Delta V, W_{BC} = 0$$

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

$$\therefore \Delta U = 0$$

$$\therefore q = -W_T = -[W_{AB} + W_{BC} + W_{CA}]$$

$$\Rightarrow 5 = -[10 + 0 + W_{CA}]$$

$$\text{or } W_{CA} = -5 \text{ J}$$

$$143. = \Delta E - W$$

$$144. \Delta E = n \int C_V \Delta T$$

$$145. \Delta S = \frac{\Delta H}{T}$$

$$146. \Delta G = \Delta H - T\Delta S$$

