

Multiple Choice Questions

Single Correct Answer Type

Q1. Thermodynamics is not concerned about .

- (a) energy changes involved in a chemical reaction.**
- (b) the extent to which a chemical reaction proceeds.**
- (c) the rate at which a reaction proceeds.**
- (d) the feasibility of chemical reaction.**

Sol: (c) Thermodynamics is not concerned with rate at which a reaction proceeds. The rate of reaction is dealt by kinetics.

Q2. Which of the following statements is correct?

- (a) The presence of reacting species in a covered beaker is an example of open system.**
- (b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.**
- (c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.**
- (d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.**

Sol: (c) For a closed vessel made up of copper, no matter can be exchanged between the system and the surroundings but energy exchange can occur through its walls.

Q3. The state of gas can be described by quoting the relationship between

- (a) pressure, volume, temperature**
- (b) temperature, amount, pressure**
- (c) amount, volume, temperature**
- (d) pressure, volume, temperature, amount**

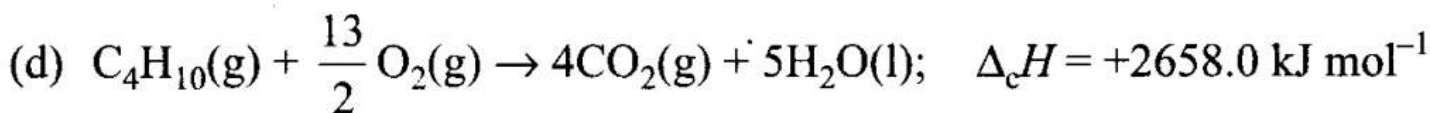
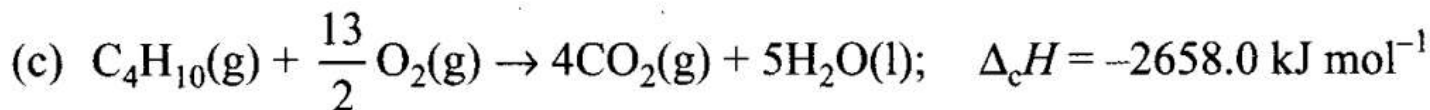
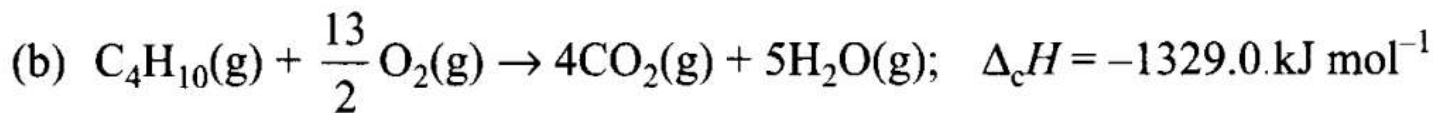
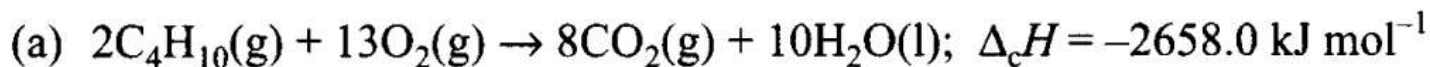
Sol: (d) State of a system can be described by state functions or state variables which are pressure, volume, temperature and amount of the gas ($PV = nRT$).

Q4. The volume of gas is reduced to half from its original volume. The specific heat will .

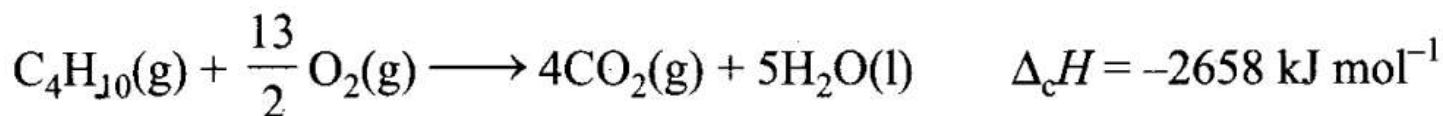
- (a) reduce to half (b) be doubled**
- (c) remain constant (d) increase four times**

Sol: (c) The specific heat of a substance is the heat required to raise the temperature of 1 gram of a substance by one degree (1 K or 1 °C). It is an intensive property and is independent of the volume of the substance.

Q5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is



Sol: (c) Exothermic reaction for combustion of one mole of butane is represented as:

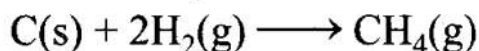


6. $\Delta_f U^\circ$ of combustion of $\text{CH}_4(\text{g})$ at certain temperature is -393 kJ mol^{-1} . The value of $\Delta_f H^\circ$ is

- (a) zero (b) $< \Delta_f U^\circ$ (c) $> \Delta_f U^\circ$ (d) equal to $\Delta_f U^\circ$

Sol. (b) $\Delta_f H^\circ = \Delta_f U^\circ + \Delta n_g RT$

For the reaction,



$$\therefore \Delta n_g = 1 - 2 = -1$$

$$\therefore \Delta_f H^\circ = \Delta_f U^\circ - 1RT$$

$$\text{or } \Delta_f U^\circ = \Delta_f H^\circ + RT$$

$$\text{or } \Delta_f H^\circ < \Delta_f U^\circ$$

Q7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.

(a) $q = 0, \Delta T \neq 0, w = 0$

(b) $q \neq 0, \Delta T = 0, w = 0$

(c) $q = 0, \Delta T = 0, w = 0$

(d) $q = 0, \Delta T < 0, w \neq 0$

Sol: (c) For free expansion $w = 0$ For adiabatic process $q = 0$ From first law of thermodynamics,

$$\Delta U = q + w$$

$$= 0 + 0 = 0$$

Since there is no change of internal energy, hence temperature will also remain constant, i.e., $\Delta T = 0$

Q8. The pressure-volume work for an ideal gas can be calculated by using the expression

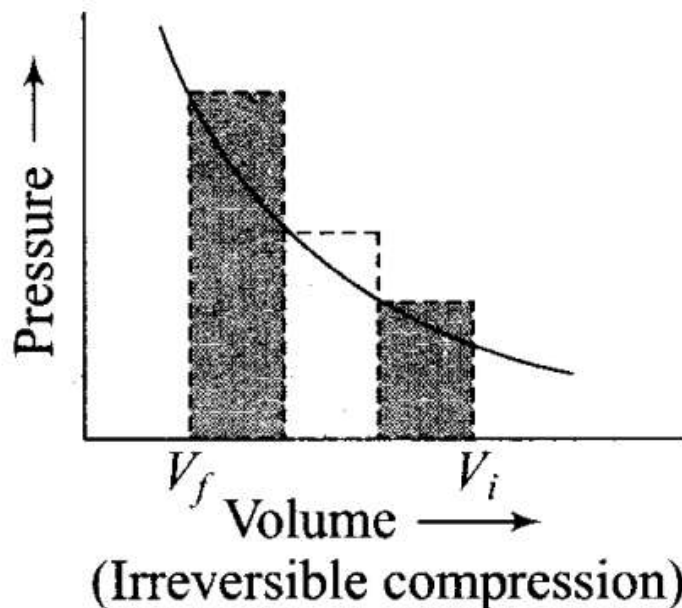
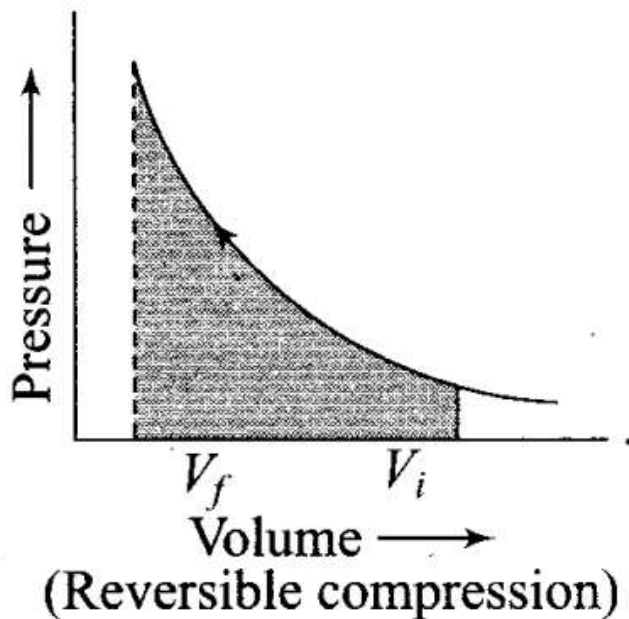
$$w = - \int_{V_i}^{V_f} p_{\text{ex}} dV$$

The work can also be calculated from the pV

plot by using the area under curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from V_i to V_f , choose the correct option.

- (a) w (reversible) = w (irreversible)
- (b) w (reversible) < w (irreversible)
- (c) w (reversible) > w (irreversible)
- (d) w (reversible) = w (irreversible) + $p_{\text{ex}} \cdot \Delta V$

Sol: (b) w (reversible) < w (irreversible)



Area under the curve is greater in irreversible compression than that of reversible compression.

Q9. The entropy change can be calculated by using the expression $\Delta S = q_{\text{rev}} / T$. When water freezes in a glass beaker, choose the correct statement amongst the following:

When water freezes in a glass beaker, choose the correct statement amongst the following:

- (a) ΔS_{system} decreases but $\Delta S_{\text{surroundings}}$ remains the same.
 (b) ΔS_{system} increases but $\Delta S_{\text{surroundings}}$ decreases.
 (c) ΔS_{system} decreases but $\Delta S_{\text{surroundings}}$ increases.
 (d) ΔS_{system} decreases but $\Delta S_{\text{surroundings}}$ also decreases.

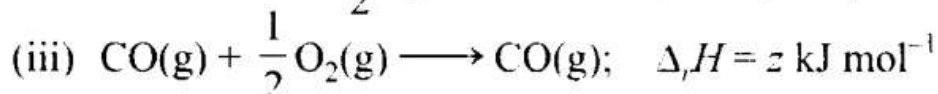
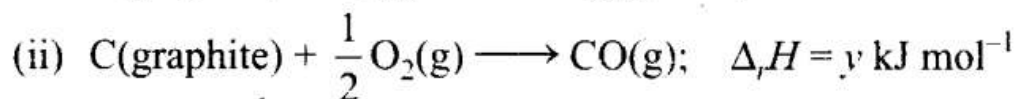
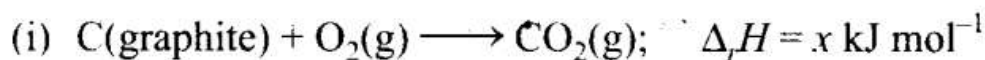
Sol. (c) During the process of freezing energy is released, which is absorbed by the surroundings.

$$\therefore \Delta S_{\text{system}} = -\frac{q_{\text{rev}}}{T};$$

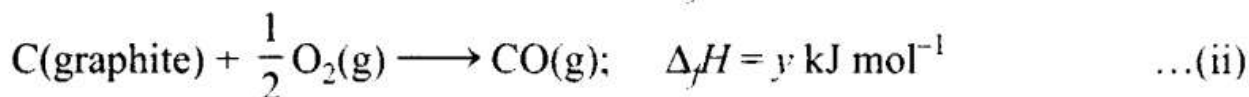
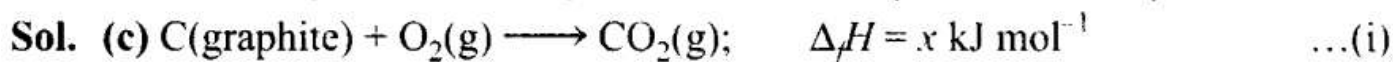
$$\Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}}{T}$$

Therefore, the entropy of the system decreases and that of surroundings increases.

Q10. On the basis of thermochemical equations (i), (ii) and (iii), find out which of the algebraic relationships given in options (a) to (d) is correct.



- (a) $z = x + y$ (b) $x = y - z$ (c) $x = y + z$ (d) $y = 2z - x$



Subtracting equations (i) and (ii) we get



Equation (iii) is obtained by subtracting (ii) from (i)

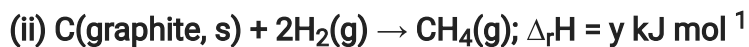
Therefore,

$$z = x - y$$

or $x = y + z$

Q11. Consider the reactions given below. On the basis of these reactions find out which of the algebraic relations given in options (a) to (d) is correct?





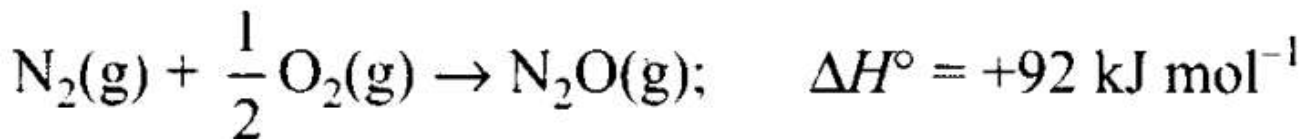
(a) $x = y$ (b) $x = 2y$ (c) $x > y$ (d) $x < y$

Sol: (c) $x > y$ because same bonds are formed in reactions (i) and (ii) but bonds between reactant molecules are broken only in reaction (ii). As energy is absorbed when bonds are broken, energy released in reaction (i) is greater than that in reaction (ii).

Q12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

- (a) is always negative
- (b) is always positive
- (c) may be positive or negative
- (d) is never negative

Sol:(c) Heat of formation of a compound may be positive or negative, e.g.,



Q13. Enthalpy of sublimation of a substance is equal to

- (a) enthalpy of fusion + enthalpy of vapourisation
- (b) enthalpy of fusion
- (c) enthalpy of vapourisation
- (d) twice the enthalpy of vapourisation.

Sol: (a) Enthalpy of sublimation of a substance is equal to enthalpy of fusion + enthalpy of vapourisation.

Sublimation is direct conversion of solid to vapour, i.e., solid \rightarrow vapour

Writing in two steps, we have solid \rightarrow liquid \rightarrow vapour.

Solid \rightarrow liquid requires enthalpy of fusion.

Liquid \rightarrow vapour requires enthalpy of vapourisation

Q14. Which of the following is not correct?

- (a) ΔG is zero for a reversible reaction.
- (b) ΔG is positive for a spontaneous reaction
- (c) ΔG is negative for a spontaneous reaction
- (d) ΔG is positive for a non-spontaneous reaction.

Sol:(b) ΔG gives a criterion for spontaneity at constant pressure and temperature.

- (i) If ΔG is negative (< 0), the process is spontaneous.
- (ii) If ΔG is positive (> 0), the process is non-spontaneous.
- (iii) If ΔG is zero then reaction is at equilibrium.

More than One Correct Answer Type

Q15. Thermodynamics mainly deals with

- (a) interrelation of various forms of energy and their transformation from one to another.**
- (b) energy changes in the processes which depend only on initial and final states of the microscopic system containing a few molecules.**
- (c) how and at what rate these energy transformations are carried out.**
- (d) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.**

Sol: (a, d) Thermodynamics deals with interrelation of various forms of energy and their transformation into each other. It also deals with thermal or mechanical equilibrium. However, it does not tell anything about the rate of reaction.

Q16. In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. For such system

- (a) q_p will be negative**
- (b) $\Delta_r H$ will be negative**
- (c) q_p will be positive**
- (d) $\Delta_r H$ will be positive.**

Sol: (a, b) For an exothermic reaction, $q_p = -ve$, $\Delta_r H = -ve$

Q17. The spontaneity means, having the potential to proceed without the assistance of external agency.

The processes which occur spontaneously are

- (a) flow of heat from colder to warmer body.**
- (b) gas in a container contracting into one corner.**
- (c) gas expanding to fill the available volume.**
- (d) burning carbon in oxygen to give carbon dioxide.**

Sol: (c, d) Gas expands or diffuses in available space spontaneously, e.g., leakage of cooking gas gives smell of ethyl mercaptan spontaneously. Moreover, burning of carbon to CO_2 is also spontaneous.

Q18. For an ideal gas, the work of reversible expansion under isothermal condition 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments.

The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option.

can be calculated by using expression $w = -nRT \ln V_f / V_i$ A sample containing

- (a) Work done at 600 K is 20 times the work done at 300 K.**
- (b) Work done at 300 K is twice the work done at 600 K**

(c) Work done at 600 K is twice the work done at 300 K.

(d) $\Delta U = 0$ in both cases.

Sol. (c, d) $w = -nRT \ln \frac{V_f}{V_i}$. Here, n , R and $\ln \frac{V_f}{V_i}$ are same in both the cases, therefore,

$$\frac{w_2}{w_1} = \frac{T_2}{T_1} \text{ or } \frac{w(600 \text{ K})}{w(300 \text{ K})} = \frac{600 \text{ K}}{300 \text{ K}} = 2$$

i.e., work done at 600 K is twice the work done at 300 K. Since each case involves isothermal expansion of an ideal gas, there is no change in internal energy, i.e., $\Delta U = 0$.

Q19. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given below:



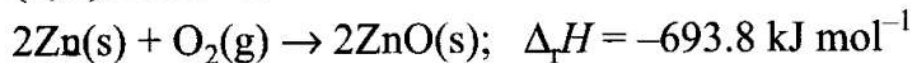
(i) The enthalpy of two moles ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(ii) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(iii) 8 kJ mol⁻¹ energy is evolved in the reaction.

(iv) 693.8 kJ mol⁻¹ energy is absorbed in the reaction.

Sol. (a, c) In the reaction:



$$\Delta_r H = \Sigma \text{ Enthalpy of formation of products}$$

$$- \Sigma \text{ Enthalpy of formation of reactants}$$

$$= [2\Delta_f H_{\text{ZnO}}] - [2\Delta_f H_{\text{Zn}} + \Delta_f H_{\text{O}_2}]$$

For exothermic reactions, $\Delta_r H$ is negative, i.e., 693.8 kJ heat is evolved.

\therefore Enthalpy of 2 moles of ZnO will be less than the enthalpy of two moles of zinc and one mole of O₂.

Short Answer Type Questions

Q20. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is

40.79 kJ mol⁻¹. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

Sol: Enthalpy of a reaction is the energy change per mole for the process.

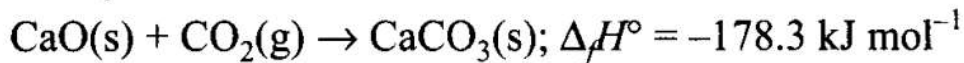
18 g of H₂O = 1 mole ($\Delta H_{\text{vap}} = 40.79 \text{ kJ mol}^{-1}$)

Enthalpy change for vapourising 2 moles of H₂O = $2 \times 40.79 = 81.58 \text{ kJ}$ $\Delta H_{\text{vap}}^{\circ} = 40.79 \text{ kJ mol}^{-1}$

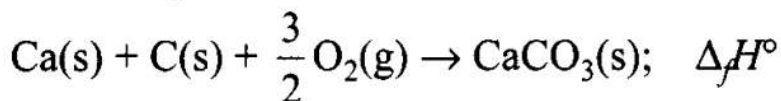
Q21. One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?

Sol: Water has higher enthalpy of vapourisation. $(\Delta H_r)_{\text{water}} > (\Delta H_r)_{\text{acetone}}$

22. Standard molar enthalpy of formation, $\Delta_f H^{\circ}$ is just a special case of enthalpy of reaction, $\Delta_r H^{\circ}$. Is the $\Delta_r H^{\circ}$ for the following reaction same as $\Delta_f H^{\circ}$? Give reason for your answer.



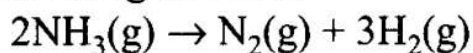
Sol. No, standard molar enthalpy of formation is the enthalpy of the reaction when 1 mole of compound is formed from its constituent elements.



As the close reaction is different from the given reaction,

$$\therefore \Delta_r H^{\circ} \neq \Delta_f H^{\circ}$$

23. The value of $\Delta_f H^{\circ}$ for NH₃ is $-91.8 \text{ kJ mol}^{-1}$. Calculate enthalpy change for the following reaction:



Sol. $\frac{1}{2} \text{N}_{2(\text{g})} + \frac{3}{2} \text{H}_{2(\text{g})} \rightarrow \text{NH}_{3(\text{g})}$, $\Delta_f H^{\circ} = -91.8 \text{ kJ mol}^{-1}$

or $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$,

$$\Delta_r H^{\circ} = -2 \times 91.8 = -183.6 \text{ kJ mol}^{-1}$$

So, for the reverse reaction,

$$\Delta_r H^{\circ} = 183.6 \text{ kJ mol}^{-1}$$

\therefore The value of $\Delta_r H^{\circ}$ for NH₃ is $+183.6 \text{ kJ mol}^{-1}$

Q24. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction and $\Delta_r H_1$, $\Delta_r H_2$ etc. for intermediate reactions.

Sol: By Hess's law $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$

Q25. The enthalpy of atomisation for the reaction $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ is 1665 kJ mol^{-1} . What is the bond energy of C – H bond?

Sol: $\text{CH}_4 \rightarrow \text{C} + 4\text{H}$, $\Delta H = +1665 \text{ kJ mol}^{-1}$

Bond energy of (C – H) bond = $1665/4 = 416.2 \text{ kJ mol}^{-1}$

26. Use the following data to calculate $\Delta_{\text{lattice}}H^\circ$ for NaBr.

$\Delta_{\text{sub}}H^\circ$ for sodium metal = $108.4 \text{ kJ mol}^{-1}$

Ionisation enthalpy of sodium = 496 kJ mol^{-1}

Electron gain enthalpy of bromine = -325 kJ mol^{-1}

Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

$\Delta_f H^\circ$ for NaBr(s) = $-360.1 \text{ kJ mol}^{-1}$

Sol. (i) $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$, $\Delta_{\text{sub}}H^\circ = 108.4 \text{ kJ mol}^{-1}$

(ii) $\text{Na} \rightarrow \text{Na}^+ + e^-$, $\Delta_i H^\circ = 496 \text{ kJ mol}^{-1}$

(iii) $\frac{1}{2}\text{Br}_2 \rightarrow \text{Br}$, $\frac{1}{2}\Delta_{\text{diss}}H^\circ = \frac{192}{2} = 96 \text{ kJ mol}^{-1}$

(iv) $\text{Br} + e^- \rightarrow \text{Br}^-$, $\Delta_{\text{eg}}H^\circ = -325 \text{ kJ mol}^{-1}$

$\Delta_f H^\circ$ for NaBr = $-360.1 \text{ kJ mol}^{-1}$

Enthalpies in different steps involved in the formation of NaBr(s) are,

$$\Delta_f H^\circ = \Delta_{\text{sub}}H^\circ + \frac{1}{2}\Delta_{\text{diss}}H^\circ + \Delta_i H^\circ + \Delta_{\text{eg}}H^\circ + \Delta_{\text{lattice}}H^\circ$$

$$\begin{aligned}\therefore \Delta_{\text{lattice}}H^\circ &= -360.1 - 108.4 - 96 - 496 + 325 \\ &= -735.5 \text{ kJ mol}^{-1}\end{aligned}$$

Q27. Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?

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

Q28. Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.

Sol: Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. The mathematical relation which relates these three parameters is $\Delta S = q$

q_{rev}/T

Here, ΔS = change in entropy

q_{rev} = heat of reversible reaction

T = temperature

Q29. Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?

Sol: Yes, when the system and the surroundings are in thermal equilibrium, their temperatures are same.

Q30. At 298 K, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not.

Sol: $\Delta_r G^\circ = -RT \ln K_p$

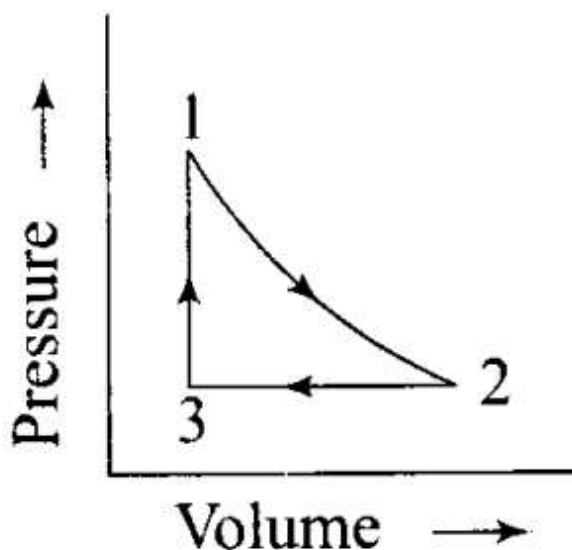
$= -RT \ln (0.98)$

Since $\ln (0.98)$ is negative

$\therefore \Delta_r G^\circ$ is positive

\Rightarrow the reaction is non spontaneous

Q31. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in the figure. What will be the value of ΔH for the cycle as a whole?



Sol: For a cyclic process, $\Delta H = 0$

Q32. The standard molar entropy of $H_2O(l)$ is $70 \text{ J K}^{-1} \text{ mol}^{-1}$. Will the standard molar entropy $H_2O(s)$ be more, or less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$?

Sol: The standard molar entropy of $H_2O(l)$ is $70 \text{ J K}^{-1} \text{ mol}^{-1}$. The solid form of H_2O is ice. In ice, molecules

of H_2O are less random than in liquid water. Thus, molar entropy of $H_2O(s) < \text{molar entropy of } H_2O(l)$. The standard molar entropy of $H_2O(s)$ is less than $70 \text{ J K}^{-1} \text{ mol}^{-1}$.

Q33. Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy.

Sol: State functions: Enthalpy, entropy, temperature, free energy Path functions: Heat, work

Q34. The molar enthalpy of vapourisation of acetone is less than that of water. Why?

Sol: Molar enthalpy of vapourisation is more for water due to hydrogen bonding between water molecules.

Q35. Which quantity out of $\Delta_r G$ and $\Delta_r G^\circ$ will be zero at equilibrium?

Sol: Gibbs energy for a reaction in which all reactants and products are in standard state. $\Delta_r G^\circ$ is related to the equilibrium constant of the reaction as follows

$$\Delta_r G = \Delta_r G^\circ + RT \ln K$$

At equilibrium, $0 = \Delta_r G^\circ + RT \ln K$ ($\Delta_r G = 0$) or $\Delta_r G^\circ = -RT \ln K$

$$\Delta_r G^\circ = 0 \text{ when } K = 1$$

For all other values of K , $\Delta_r G^\circ$ will be non-zero.

Q36. Predict the change in internal energy for an isolated system at constant volume.

Sol: For an isolated system $w = 0$, $q = 0$

$$\text{Since } \Delta U = q + w = 0 + 0 = 0, \Delta U = 0$$

Q37. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Sol: At constant volume

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

$$-w = p \Delta V = \Delta U + p \Delta V$$

$$\Delta V = 0 \text{ (at constant volume)}$$

Hence, $q_v = \Delta U + 0 = \Delta U = \text{change in internal energy}$ At constant pressure, $q_p = \Delta U + p \Delta V$

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

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

Hence, at constant volume and at constant pressure, heat change is a state function because it is equal to ΔU and ΔH respectively which are state functions.

Q38. Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vacuum until its total volume is 5 litre.

Sol: During free expansion, external pressure is zero, so Work done, $w = -p_{\text{ext}} \Delta V$

$$= -0(5 - 1) = 0$$

Since the gas is expanding isothermally, therefore, $q = 0$

$$\Delta U = q + w = 0 + 0 = 0$$

Q39. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

Sol: For water, molar heat capacity = 18 x Specific heat or

$$C_p = 18 \times c$$

But, specific heat,

$$C = 4.18 \text{ J g}^{-1} \text{ K}^{-1} \text{ Heat capacity,}$$

$$C_p = 18 \times 4.18 \text{ JK}^{-1} = 75.24 \text{ JK}^{-1}$$

Q40. The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for 10 moles of an ideal gas.

Sol: Given that, C_v = heat capacity at constant volume,

C_p = heat capacity at constant pressure Difference between C_p and C_v is equal to gas constant (R).

$$\therefore C_p - C_v = nR \quad (\text{where, } n = \text{no. of moles})$$

$$= 10 \times 8.314 = 83.14 \text{ J}$$

Q41. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

Sol: Molar enthalpy change for graphite (ΔH)

$$= \text{enthalpy change for 1 g} \times \text{molar mass of C} = -20.7 \times 12 = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Since the sign of $\Delta H = -ve$, it is an exothermic reaction.

Q42. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules.

What will be the enthalpy change for the following reaction?



Given that bond energy of H_2 , Br_2 and HBr is 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

$$\begin{aligned} \text{Sol. } \Delta_r H^\circ &= \sum \text{B.E.}_{(\text{reactants})} - \sum \text{B.E.}_{(\text{products})} \\ &= \text{B.E.}_{\text{H}_2} + \text{B.E.}_{\text{Br}_2} - 2 \times \text{B.E.}_{\text{HBr}} \\ &= 435 + 192 - (2 \times 368) \\ &= -109 \text{ kJ mol}^{-1} \end{aligned}$$

