Topic: Thermodynamics

Very Short Answer Questions

1. When 430 J of work was done on a system, it lost 120 J of energy as heat. Calculate the value of internal energy change (ΔU) for this process.
2. Predict the sign of ΔS° for the following reaction:
   $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$.
3. Classify the following as extensive and intensive properties: Molar heat capacity, Temperature, Enthalpy and Volume.
4. Give two examples of state functions.
5. Give an example of a spontaneous process which is endothermic.
6. Name the state variables which remain constant in *(i)* isobaric process. *(ii)* isothermal process.
7. What is bond energy? Why is it called enthalpy of atomisation?
8. Define:
   (i) intensive properties (ii) adiabatic process.
9. Predict in which of the following, entropy increases/ decreases. Give reason:
   (i) Temperature of crystalline solid is raised from 0 K to 115 K.
   (ii) $H_2(g) \rightarrow 2H(g)$
10. When is the entropy of a perfectly crystalline solid zero?
11. Which one of the following is not extensive state function? Enthalpy change, Internal energy change and Pressure
12. Write an expression in the form of chemical equation for the standard enthalpy of formation $(\Delta_f H)$ (of *CO(g)*.
13. State a chemical reaction in which ÄH and ÄU are equal.
14. Which of the following is an intensive property? Surface tension, Mass, Volume, Enthalpy, Density
15. Will the change in enthalpy of the system be zero in an adiabatic process?
16. What happens to the internal energy of the system if.
   (i) work is done on the system?
   (ii) work is done by the system?
17. What is the value of internal energy for I mole of a monoatomic gas?
18. For the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ predict whether the work is done on the system or by the system.
19. What is the limitation of first law of thermodynamics?
20. Which of the following is an extensive property?
   (a) Volume (b) Surface tension
   (c) Viscosity (d) Density
21. Which of the following is not a state function?
   (a) $U + PV$ (b) $q + w$
   (c) $\dfrac{q_{rev}}{T}$ (d) q
22. Which one of the following has the same value as $\Delta_f H^\circ(CO)$?
   (a) $1/2\Delta_f H^\circ(CO_2)$
   (b) $1/2\ \Delta_c H^\circ$ (graphite)
   (c) $\Delta_f H^\circ,(CO_2) - \Delta_f H^\circ$ (graphite)
   (d) $\Delta_c H^\circ$(graphite)- $\Delta_c H^\circ,(CO)$
23. Predict $\Delta H > \Delta U$ or $\Delta H < \Delta U$ or $\Delta H = \Delta U$.
   (i) C(graphite) + $O_2(g) \rightarrow CO_2(g)$
   (ii) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
24. What are the ways by which the internal energy of a system can be changed?
25. State why heat changes in physical and chemical processes are indicated by enthalpy changes and not by internal energy changes.
26. Under what conditions ΔH and ΔU are equal?
27. Which of the following is an endothermic process?
   (i) $2H_2 + O_2 \rightarrow 2H_2O;\ \Delta H = -q\ kJ$
   (ii) $N_2 + O_2 \rightarrow 2NO - Y\ kJ$
   (iii) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;\ \Delta H = -X\ kJ\ mol^{-1}$
   (iv) $NaOH + HCl \rightarrow NaCl + H_2O + Z\ kJ$
28. The energy released in the neutralisation of H_2SO_4 and KOH is 57.1 kJ mol^{-1}. Therefore, calculate the value of ΔH for the reaction:
   $H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$
29. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.
   $\Delta H = -890\,kJ\ mol^{-1}$.
   What is the calorific or fuel value of 1 kg of CH_4?

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   $\Delta H = -890\,kJ\ mol^{-1}$.
   What is the calorific or fuel value of 1 kg of CH_4?

30. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 185\,kJ$.
   State whether this reaction is exothermic or endothermic and why.
31. Which of the following are state functions?
   (i) Height of a hill
   (ii) Distance travelled in climbing the hill
   (iii) Energy consumed in climbing the hill
32. In the equation: $N_2(g) + 3H_2(g) \Rightarrow 2NH_3(g)$,what would be the sign of work done?
33. What is the value of ΔG when ice and water are in equilibrium?

34. If $\Delta G°$ for a reversible reaction is found to be zero, what is the value of its equilibrium constant?
35. Why does NH_4NO_3 dissolve in water spontaneously even when this process is endothermic?
36. If ΔH for a reaction has a negative value, how would you know the sign requirement of ΔS for it so that the reaction is spontaneous at low temperatures?
37. Which have more entropy, real crystal or ideal crystal and why?
38. How is change in entropy during melting of solid related to its melting point?
39. Why does entropy increase on mixing of two gases?
40. At what temperature, the entropy of a perfect crystalline substance is taken as zero?
41. What is the effect of temperature on entropy?
42. How is standard free energy change related to equilibrium constant?
43. Which has larger absolute entropy per mole?
    (i) $H_2O(l)$ at 298K or $H_2O(l)$ at 350 K,
    (ii) N_2 or NO both at 298 K
44. Determine the sign of entropy change in
    $$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
45. Will entropy increase or decrease in the following changes?

(i) Sugar dissolved in water,
(ii) Normal egg to hard boiled egg.

46. Does an aqueous solution of Mg^{2+} ions have a larger entropy before or after hydration of the ions?
47. The standard absolute entropy of a substance, (S°) is the entropy of the substance in its standard state at I arm, temperature being:
    (a) 0 K (b) 298 K
    (c) 398 K (d) 273 K
48. For a spontaneous process, which of the following is always true?
    (a) $\Delta G > 0$ (b) $\Delta S_{total} < 0$
    (c) $-T\Delta S > 0$ (d) $\Delta G < 0$
49. For which of the following processes S is negative?

(i) $H_2(g) \rightarrow 2H(g)$
(ii) $N_2(g, 1\ atm) \rightarrow N_2(g,\ 5\ atm)$
(iii) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$
(iv) C (diamond)→C(graphite)

50. Why is entropy of a solution higher than that of pure liquid?
51. Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes
(ii) whose value is independent of path
(iii) used to determine pressure volume work
(iv) whose value depends on temperature only.

52. For the process to occur under adiabatic conditions, the correct condition is:
    (i) Δ T = 0 (ii) Δ P = 0
    (iii) q = 0 (iv) w = 0
53. The enthalpies of all elements in their standard states are:
    (i) unity (ii) zero (iii) < 0
    (iv) different for each element.
54. ΔU° of combustion of methane is -X kJ mol^{-1}. The value of ΔH° is
    (i) = ΔU° (ii) >ΔU°
    (iii) < ΔU° (iv) = 0.
55. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, -890.3 kJ mol^{-1}, -393.5 kJ mol^{-1} and -285.8 kJ mol^{-1} respectively. Enthalpy of formation of CH_4(9) will be
    (i) -74.8 kJ mol^{-1} (ii) -52.27 kJ mol^{-1}
    (iii) +74.8 kJ mol^{-1} (iv) +52.26 kJ mol^{-1}
56. A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be
    (i) possible at high temperature
    (ii) possible only at low temperature
    (iii) not possible at any temperature
    (iv) possible at any temperature.
57. (i) Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres.
    How much heat is absorbed and how much work is done in the expansion?

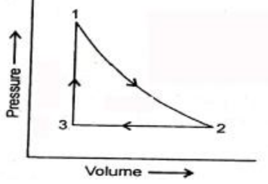
(ii) Consider the same expansion, but this time against a constant external pressure of 1 atm.
(ii) Consider the same expansion, to a final volume of 10 litres conducted reversibly.

58. State second law of thermodynamics.
59. Write the conditions in terms of ΔH andΔS when a reaction would be always spontaneous.
60. When ΔH > 0 and ΔS < 0, a reaction is never spontaneous. Explain.
61. 18.0 g of water completely vaporises 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 vaporising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?
62. One mole of acetone requires less heat to vaporise than 1 mole of water. Which of the two liquids has higher enthalpy of vaporisation?
63. Standard molar enthalpy of formation, $\Delta_f H°$ is just a special case of enthalpy of reaction, $\Delta_r H°$. Is the $\Delta_r H°$ for the following reaction same as $\Delta_f H°$? Give reason for your answer.
    $$CaO(s) + CO_2(g) \rightarrow CaCO_3(s);$$
    $$\Delta_f H° = 178.3\ kJ\ mol^{-1}.$$
64. The value of $\Delta_f H°$ for NH_3 is -45.9 kJ mol^{-1}. Calculate

enthalpy change for the following reaction:

$2NH_3(g) \rightarrow N_2(g)+3H_2(g)$

65. Enthalpy is an extensive property. In general, if enthalpy of an overall reaction: $A \rightarrow B$ 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?
66. The enthalpy of atomisation for the reaction: $CH_4(g) \rightarrow C(g)+4H(g)$ is 1665. What is the bond energy of C-H bond?
67. 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.
68. 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?
66. At 298 K, Kp for reaction: $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ is 0.98. Predict whether the reaction is spon- taneous or not.
70. A sample of 1.0 mole 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?



71. The standard molar entropy of $H_2O(l)$ is 70 J K^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more, or less than 70 J $K^{-1}mol^{-1}$
72. The molar enthalpy of vaporisation of acetone is less than that of water. Why?
73. Which quantity out of $\Delta_r G$ and $\Delta_r G^\circ$ be zero at equilibrium?
74. Predict the change in internal energy for an isolated system at constant volume.

Short Answer Type Questions

1. Give reasons for the following:

(i) The enthalpy of neutralisation is alway constant, i.e. 57.1 kJ/mol when a strong acid neutralises a strong base.

(ii) Neither *q* nor *w* is a state function but *q* + *w* is a state function.

2. Define the following terms:
   (i) Enthalpy of neutralisation
   (ii) Hess's law of constant heat summation
3. Calculate the bond enthalpy of Cl-Cl bon(from the following data:

$CH_4(g) \rightarrow Cl_2(g) \rightarrow CH_3Cl(l)+HCl(l);$

[ΔH = -100.3 KJ mol^{-1}]

Given, bond enthalpies of C—H, C—Cl and H—Cl bonds are 413, 326 and 431 kJ mol^{-1}respectively.

4. Derive the relationship between C_p and C_v for an ideal gas.
5. Derive the relationship between isothermal anc free expansion of an ideal gas.
6. Given:

   $N_2(g)+3H_2(g) \rightarrow 2NH_3(g);$

   $\Delta_r H^\circ = -92.4\,kJ\ mol^{-1}$

   What is the standard enthalpy of formation of NH_3 gas?
7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?
8. Calculate the heat of combustion of glucose from the following data:

   C (graphite) $+O_2(g) \rightarrow CO_2(g)$;

   $\Delta H = -395.0\ kJ\ mol^{-1}$

   $H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(l);\quad \Delta H = -269.4\,kJ\ mol^{-1}$

   $6C(graphite)\ +\ 6H_2(g)+O_2(g) \rightarrow \underset{glu\cos e}{C_6\,H_{12}O_6(s)}$

   $\Delta H = -1169.8\ kJ\ mol^{-1}$.
9. 1 m3 of C_2H_4 at STP is burnt in oxygen, according to the thermochemical reaction:

   $C_2H_4(g)+3O_2(g) \rightarrow 2CO_2(g)+2H_2O(l)$;

   $\Delta H = -1410\,kJ\ mol^{-1}$.

   Assuming 70% efficiency, determine how much of useful heat is evolved in the reaction.
10. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and I atmospheric pressure according to the equation:

    C(graphite) $+O_2(g) \rightarrow CO_2(g)$
11. During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, then what is the enthalpy change for the above reaction at 298 K and 1 atm?
12. A swimmer coming out from a pool is covered with a film of water weighing about 18 g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of vaporisation at 100 °C.

    $\Delta_{vap}H^\circ$ for water at 373 K = $40.66\,kJ\ mol^{-1}$.
13. For oxidation of iron,

    $4Fe(s)+3O_2(g) \rightarrow 2Fe_2O_3(s)$

Entropy change is -549.4 JK^{-1} mol^{-1} at 298 K. Inspire of negative entropy change of this reaction, why is the reaction spontaneous? ($\Delta_r H^\circ$ for this reaction is $1648 \times 10^3 J\ mol^{-1}$).

14. The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion $CO_2(g)$ and $H_2O(l)$ are produced and 3267.0 kJ. of heat is liberated. Calculate the standard enthalpy of formation of benzene

    $\Delta_f H^\circ CO_2(g) = -393\ kJ\ mol^{-1}$ and

    $\Delta_f H^\circ H_2O(l) = -285.83\ kJ\ mol^{-1}$

15. The reaction of cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

    $$NH_2CN(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l).$$

16. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55 °C. Molar heat capacity of At is 24 J mol^{-1} K^{-1}.

17. Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0 °C to ice at –10.0 °C.

    $\Delta_{fus} H = 6.03$ kJ mol^{-1} at 0°C.

    $C_p\ [H_2O(l)] = 75.3\ J\ mol^{-1} K^{-1}$

    $C_p[H_2O(s)] = 36.8\ J\ mol^{-1} K^{-1}$.

18. Enthalpy of combustion of carbon to CO_2 is 2 is –393.5 kJ mol^{-1}. Calculate the heat released in the formation of 35.2 g of CO_2 from carbon and dioxygen gas.

19. The enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are -110, –393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the the reaction: $N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

20. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

    (i) $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l);$

    $\Delta_r H^\circ = -726\, kJ\ mol^{-1}$.

    (ii) $C(g) + O_2(g) \rightarrow CO_2(g);$

    $\Delta_c H^\circ = -393\, kJ\ mol^{-1}$

    (iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$;

21. Calculate the enthalpy change for the process $CCl_4(g) \rightarrow C(g) + 4Cl(g)$ and calculate bond enthalpy of C-Cl in $CCl_4(g)$.

    $\Delta_{vap} H^\circ(CCl_4) = 30.5$ kJ mol^{-1}

    $\Delta_f H^\circ(CCl_4)$ = -135.5 kJ

    = 715.0 kJ

    = 242 kJ

    Where is enthalpy of atomization.

22. For an isolated system, $\Delta U = 0$, what will be ΔS ?

23. For the reaction $2Cl(g) \rightarrow Cl_2(g)$

    What are the signs of ΔH and ΔS?

24. The equilibrium constant for a reaction is 10. What will be the value of ΔG° ?

    [$R = 8.314\ J\,K^{-1}\ mol^{-1}$, T = 300 K]

25. Comment on the thermodynamic stability of NO(g),. Given

    $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$; $\Delta_r H^\circ = 90$ kJ mol^{-1}

    $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g);$ $\Delta_r H^\circ = -74\, kJ\ mol^{-1}$.

26. Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^\circ$ = -286 $kJ\ mol^{-1}$.

27. Which of the following has the highest heat of combustion out of the following and why?

    (i) C_2H_6 (ii) C_2H_4 (iii) C_2H_2 (iv) CH_4

28. The heat of combustion of C_2H_6 is -368.4 kcal. Calculate heat of combustion of C_2H_4, heat of combustion of h_2 is 68.32 kcal mol^{-1}. ΔH for the following reaction is -37.1 kcal.

    $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.

29. The equilibrium constant at 25ºC for the process $Co^{3+}(aq) + 6NH_3(aq) \Leftrightarrow [Co(NH_3)_6]^{3+}(aq)$ is 2.5×10^6. Calculate the value of ΔG° at 25°C (R = 8.314 JK^{-1} mol^{-1}). In which direction is the reaction spontaneous under standard conditions?

30. What is the value of equilibrium constant for the following reaction at 400 K?

    $2NOCl(g) \Leftrightarrow 2NO(g) + Cl_2(g)$

    ΔH° = 77.5 kJ mol^{-1}, R = 8.314 J mol^{-1} K^{-1}, Δ S = 135 $J\,K^{-1}$ mol^{-1}.

31. Calculate the standard free energy change ΔG° for the reaction

    $2HgO(s) \rightarrow 2Hg(I) + O_2(g)$

    $\Delta H^\circ = 91 kJ\ mol^{-1}$ at 298 K.

$S^\circ_{(HgO)} = 72.0\ J\ K^{-1}\ mol^{-1}$.

$S^\circ_{(Hg)} = 77.4\ J\ K^{-1}\ mol^{-1}$ and $S^\circ_{(O_2)}$ =205 $J\ K^{-1}$ at 298 K.

32. A 5 litre cylinder contained 10 moles of oxygen gas at 27ºC. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure was 1.0 atm, calculate the work done by the gas.

33. Calculate the temperature above which the reduction of lead oxide in the following reaction comes spontaneous:

    $PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$

    Given: [$\Delta H = 108.4\ kJ\ mol^{-1}$; ΔS = 190 $J\ K^{-1}\ mol^{-1}$]

34. Starting with the thermodynamic relationship $G = H - TS$, derive the following relationship; $\Delta G = -T\Delta S_{total}$.

35. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K. (Given lattice energy of NaCl = -777.8 kJ mol^{-1}, Hydration energy = -774.1 kJ mol^{-1} and ΔS = 0.043 kJ K^{-1} mol^{-1} at 298 K)

36. Calculate $\Delta_r G^\circ$ for conversion of oxygen to ozone, $3/2O_2(g) \rightarrow O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}.

37. Find out the value of equilibrium constant fo r the following reaction at 298 K.

    $2NH_3(g) + CO(g) \Leftrightarrow NH_2CONH_2(aq) + H_2O(l)$

    Standard Gibbs energy change, $\Delta_r G^\circ$ at the given temperature is – 13.6 kJ mol^{-1}.

38. Calculate the electron gain enthalpy of fluorine from the data given below.

    $\Delta_f H^\circ$ of KF = -560.8 $kJ\ mol^{-1}$. Dissociation energy of F_2 is 158.9 $kJ\ mol^{-1}$. Lattice energy of K is 414.2 $kJ\ mol^{-1}$.

39. Use the following thermodynamic data to calculate the enthalpy change for the formation of solid lithium fluoride, LiF(s) from Li(s) and $F_2(g)$.

    $Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$

    $Li(s) \rightarrow Li(g);\ \ \Delta_s H^\circ = 155\ kJ\ mol^{-1}$

    $\frac{1}{2}F_2(g) \rightarrow F(g);\ \ \Delta H^\circ = 75$ kJ

    $Li(g) \rightarrow Li^+(g) + e^-;\ \Delta H^\circ = 520\ kJ\ mol^{-1}$

    $F(g) + e^- \rightarrow F^-(g);\ \Delta H^\circ = -333\ kJ\ mol^{-1}$

    $Li^+(g) + F^-(g) \rightarrow LiF(s)$; $\Delta H^\circ = -1012\ kJ\ mol^{-1}$

40. Explain with the help of example, the difference between bond dissociation energy and bond energy.

41. Compound with carbon-carbon double bond, such as ethylene (C_2H_4) and hydrogen in a reaction is called hydrogenation

    $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$;
    $\Delta H = -1401\ kJ/mol$

    $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$;
    $\Delta H = -1550\ kJ/mol$

    $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -286.0\ kJ/mol$

42. Comment on the spontaneity of a reaction at constant temperature and pressure in the following cases
    (i) $\Delta H < 0$ aand $\Delta S > 0$
    (ii) $\Delta H > 0$ and $\Delta S < 0$
    (iii) $\Delta H < 0$ and $\Delta S < 0$
    (iv) $\Delta H > 0$ and $\Delta S > 0$

43. State the third law of thermodynamics

44. Explain the term residual entropy.

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

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

    Ionization enthalpy of sodium = 108.4 $kJ\ mol^{-1}$

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

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

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

46. 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.

47. Identify the state functions and path functions out of the following:
    Enthalpy, Entropy, Heat, Temperature, WoiM, Free energy

48. 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.

49. 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.

50. If the combusion of 1 g of graphite produces 20.7 kJ of

heat, what will be the molar enthalpy change? Give the significance of sign also.

51. The enthalpy of vaporisation of CCl_4 is 30.5 $kJ\ mol^{-1}$. Calculate the heat required for the vaporisation of 284 g of CCl_4 at constant pressure (Molar mass of $CCl_4 = 154 g\ mol^{-1}$)

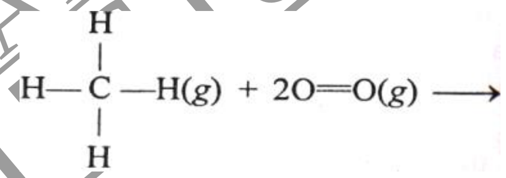
Short Answer Type Questions

1. Find out whether it is possible to reduce MgO using carbon at 298 K. If not, at what temperature it becomes spontaneous? For reaction:
   $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$
   $\Delta_r H^\circ = 91.18 kJ\ mol^{-1}$
   $\Delta_r S^\circ = 197.67\ J\ K^{-1}\ mol^{-1}$.
2. Calculate $\Delta_f H^\circ$ of HCl if bond energy is H-H bond is 437 kJ mol^{-1}, Cl-Cl bond is 244 kJ mol^{-1} and H-Cl is 433 kJ mol^{-1}.
3. Calculate bond energy of C –H bond if $\Delta_c H$ of CH_4 is -891 kJ mol^{-1}, $\Delta_c H$ of $C(s)$ is -394 kJ mol^{-1}, $\Delta_c H$ of $H_2(g)$ is -286 $kJ\ mol^{-1}$, heat of sublimation of C(s) is 717 kJ mol^{-1}, heat of dissociation of H_2 is 436 $kJ\ mol^{-1}$.
4. Calculate the standard Gibbs energy change for the formation of propane at 298 K.
   3C(graphite) $+ 4H_2(g) \rightarrow C_3H_8(g)$
   $\Delta_f H^\circ$ for propane, $C_3H_8(g) = 270.2\ J\ K^{-1}\ mol^{-1}$,
   and $S^\circ_m(graphite) = 5.70\ JK^{-1}\ mol^{-1}$ and
   $S^\circ_m H_2(g) = 130.7\ J\ K^{-1}\ mol^{-1}$.
5. What is meant by entropy? Predict the sign of entropy change in each of the following
   (i) H_2 (at 298 K, 1 atm) $\rightarrow H_2$ (at 298 K, 10 atm)
   (ii) H_2O (at 298 K , 1 atm) $\rightarrow$ H_2O (at 330K, 1 atm)
   (iii) $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g)\ + O_2(g)$
   (iv) Crystallization of copper sulphate from its saturated solution
   (v) $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$.
6. (i) classify the following processes as reversible or irreversible:
   (a) Dissolution of sodium chloride
   (b) Evaporation of water at 373K and 1 atm pressure
   (c) Mixing of two gases by diffusion
   (d) Melting of ice without rise in temperature .
7. State the law of thermodynamics that was first formulated by Nernst in 1906. What is the utility of this law? The equilibrium constant for the reaction $A \Leftrightarrow B$ is 1.8×10^{-7} at 298K. Calculate the value of ΔG° for the reaction [$R = 8.314\ JK^{-1}\ mol^{-1}$]. Predict the feasibility of the reaction under standard states.
8. Why is entropy of a substance taken as zero at 0K? Calculate the standard Gibbs free energy change for the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ at 298 K. The value of equilibrium constant for the above reaction is 6.6×10^5. [R= 8.314 $JK^{-1}mol^{-1}$].
9. How is the third law of thermodynamics useful in calculation of the absolute entropies? Calculate the value of ΔS° for the following reaction at 400K:
   $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$
   If the value of equilibrium constant for the reaction at 400 K is 1.958×10^{-4} and $\Delta H^\circ = -77.2\ kJ\ mol^{-1}$. (R= 8.314 $JK^{-1}\ mol^{-1}$).
10. Explain the term 'standard molar free energy of formation of a compound. Calculate the equilibrium constant for the reaction :
    $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$ at 25ºC .
    Given $\Delta_f G^\circ SO_3(g)$ =-371.1 $kJ\ mol^{-1}$,
    $\Delta_f G^\circ SO_2(g) = -300.2 kJ\ mol^{-1}$,
    R= 8.31 $JK^{-1}\ mol^{-1}$.
11. (i) Using the data given below, calculate the value of equilibrium constant for the reaction at 298K.
    $3CH \equiv CH(g) \Leftrightarrow C_6H_6(g)$
    Assuming ideal gas behaviour.
    $\Delta_f G^\circ\ [HC \equiv CH(g)] = 2.09 \times 10^5\ J\ mol^{-1}$
    $\Delta_f G^\circ [C_6H_6(g)] = 1.24 \times 10^5\ J\ mol^{-1}$,
    $R = 8.314\ J\ K^{-1}\ mol^{-1}$.
    (ii) Based on your calculated value, comment whether this process
12. (i) State Hess's law of constant heat summation. How does it follow from the first law of thermodynamics.
    (ii) Determine $\Delta_r H^\circ$, at 298K for reaction C(graphite) $+ 2H_2(g) \rightarrow CH_4(g)$; $\Delta_r H^\circ = ?$
    You are given:
    (a) $C(graphite) + O_2(g) \rightarrow CO_2(g)$; $\Delta_r H^\circ$ = -393.51 kJ/mol.
    (b) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$;
    $\Delta_r H^\circ = -285.8 kJ/mol$.
    (c) $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;
    $\Delta_r H = +890.3 kJ/mol$

13. (i) Define the following
 (a) First law of thermodynamics
 (b) Standard enthalpy of formation.
 (ii) Standard heat of formation of hydrazine $[N_2H_4(l)]$, hydrogen peroxide $[H_2O_2(l)$ and water $[H_2O(l)]$ are -50.4, -193.2 and -242.7 kJ/mole respectively. Calculate the standard heat of formation for the following reaction.
 $N_2H_4(l) + 2H_2O(l) \rightarrow N_2(g) + 4H_2O(l)$
14. Calculate the lattice enthalpy of $MgBr_2$, given that
 Enthalpy of formation of $MgBr_2$ =-524 kJ mol^{-1}.
 Sublimation energy of Mg = 148 $kJ\,mol^{-1}$
 Ionization energy of Mg = 2187 $kJ\,mol^{-1}$.
 Vaporization energy of $Br_2(l)$ = 31 $kJ\,mol^{-1}$
 Dissociation energy of $Br_2(g) = 193$ $kJ\,mol^{-1}$
 Electron gain enthalpy of $Br(g)$ =331 $kJ\,mol^{-1}$
15. 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.

Long Answer Type Questions

1. (i) State Hess's law.
 (ii) Give a brief note on the following thermodynamic temrs:
 (a) Standard enthalpy of combustion
 (b) Standard enthalpy of formation
 (ii) For the reaction:
 $2A(g) + B(g) \rightarrow 2D(g)$
 ΔU° =-10.5 kJ and
 ΔS° =-44.1 $J\,K^{-1}$ mol^{-1}
 Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously.
2. (i) For the reaction at 298K; $2A + B \rightarrow C; \Delta H = 400$ $kJ\,mol^{-1}$ and ΔS =0.2 kJ $mol^{-1}K^{-1}$.
 At what temperature will the reaction becomes spontaneous considering ΔH and ΔS to be constant over the temperature range.
 (ii) State the first law of thermodynamics.
 (iii) Give one point to differentiate the following thermodynamic terms
 (a) Extensive properties and intensive properties
 (b) Isothermal process and isobaric process.
3. (i) Define standard enthalpy of formation. Explain why the enthalpy changes for the reaction given below are not enthalpies of formation of $CaCO_3$ and HBr.
 (a) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$; $\Delta_r H^\circ =$ -178.3 $kJ\,mol^{-1}$
 (b) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$; $\Delta_r H^\circ = -72.8\,kJ\,mol^{-1}$.
 (ii) Calculate the standard enthalpy change $(\Delta_r H^\circ)$ and standard internal energy change $(\Delta_r U^\circ)$ for the following reaction at 300K:
 $OF_2(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$. Standrd enthalpy of formation $(\Delta_f H^\circ)$ of various species are given below:
 $\Delta_f H^\circ$/kJ mol^{-1}: $OF_2(g)$=23.0.
 H_2O (g) = -241.8, $HF(g) = -268.6$,
 $R = 8.314\,J\,K^{-1}$ mol^{-1}.
4. (i) State the first law of thermodynamics. Heat(q) and work done (w) individually are not state function. Explain why.
 (ii) Used the bond enthalpies listed below to determine the enthalpy of reaction.



$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H(g) + 2O{=}O(g) \longrightarrow$$

 Bond enthalpy $(\Delta H^\circ)/kJ$ mol^{-1} of $C=O=741$; C-H = 414; H-O = 464;
 $O-O=498$.
5. (i) Define enthalpy of neutralization. The enthalpy of neutralization of strong acid and strong base is constant. Why?
 (ii) What is the basis of Hess's law?
 (iii) For a gaeous reaction
 $2A_2(g) + 5B_2(g) \rightarrow$ $2A_2B_5(g) \rightarrow 2A_2B_5(g)$ at 27 °C, the heat change at constant pressure is found to be -50.16 kJ. Calculate the value of internal energy change (ΔU).
 Given: R=8.314 $J\,K^{-1}\,mol^{-1}$.
6. (i) Derive the mathematical expression for first law of thermodynamics.
 (ii) q and w are not state function but their sum is state function. Why?
 (iii) Calculate the $\Delta_r H^\circ$ for the reaction
 $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
 Bond enthalpy are given as,
 H-H = 436 $kJ\,mol^{-1}$ $Br-Br$ = 192 kJ mol^{-1} and
 $H-Br =$ 368 kJ mol^{-1}

Value Based Questions

1. Fuel is a substance which produces energy in the form that can be used for practical purposes. Most of the energy our body needs, comes from carbohydrates and fats. The fuel value of food can be measured by calorimeter. The average energy of fat is 38 kJ/g. Proteins are essential for growth and maintenance of the body. Mrs. Sarin uses pure *ghee* at home and her family members do not walk or do exercise that is why her family members are overweight.

(i) From which of the following, we get more energy; fats or carbohydrates?
(ii) How much fat is present in full cream milk?
(iii) What is the major source of fats?
(iv) Is junk food, good for health? Give reason.
(v) Are fruits and vegetables good for health? Give reason.
(vi) What should Mrs. Sarin do to keep her family healthy?

2. Wood has calorific value 18 kJ/g, coal has 32 kJ/g, natural gas has 49 kJ/g and hydrogen has 142 kJ/g. One promising way to utilize our coal reservoirs is, to use them to produce a mixture of gaseous hydrocarbons called synthesis gas which consist of CH_4, H_2 and CO, all of which have high calorific value. In Kosli village, all people are using LPG whereas in Malasiawas all people use cowdung cakes and wood as fuel.

(i) What is the advantage of synthesis gas over coal?
(ii) Why does synthesis gas produce less pollution?
(iii) How can synthesis gas be supplied?
(iv) Which is better fuel out of CH_4, H_2 and CO?
(v) Why is H_2 the best fuel?
(vi) Why should villagers prefer LPG than wood?

3. Fossil fuels also contain compounds of sulphur and nitrogen. During combustion, these compounds are oxidised to form oxides of sulphur and nitrogen which are corrosive and poisonous. During rain, these oxides dissolve in water and are known to cause acid rain which damages marble of buildings and crops. A method for control of SO_2 from power plants, waste gases, currently being used in Japan is to pass the fuel gases over MgO at about 425 K.

$$MgO(s) + SO_2(g) \xrightarrow{\Delta} MgSO_3(s)$$

(i) What happens when SO_2 is passed through MgO at 425 K?
(ii) How can we get SO_2 from $MgSO_3$?
(iii) How can we use SO_2?
(iv) How can we convert oxides of nitrogen to nitric acid?
(v) What is the most important use of sulphuric acid?
(vi) What value is possessed by scientists of Japan?

4. Vehicles on roads are increasing day-by-day. Emission levels of gases are very high which are leading to respiratory diseases. CNG and LPG are being used instead of diesel.

(i) What are technological options for reduction of harmful emissions?
(ii) Has CNG in place of diesel reduced pollution in Delhi? Should it be adopted in other states also?
(iii) Which is better -CNG or LPG? Why?
(iv) Diesel vehicles should be taxed to more extent. Do you agree? Give reason.
(v) Are electric cars better than CNG? Why?

5. Biogas technology being promoted to harness the fuel value of cattle dung, human waste and other non-woody organic wastes without destroying their manurial value. When organic materials decompose in absence of air, biogas is produced. Okhla village in Delhi is using biogas plant for disposal of waste and use biogas as fuel.

(i) Why is biogas clean and efficient fuel?
(ii) What is the major gas present in biogas?
(iii) What is the use of biogas?
(iv) What is the use of residue left in biogas plant?
(v) Should government help in installing biogas plants in villages?
(vi) What are the values associated with people using biogas?

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Solutions

1. $\Delta U = -q + w$

   $\Delta U = -120 + 430$

   $\Delta U = 310\ J$

2. $\Delta S°$ *i.e.* entropy decreases during the reaction. Hence, the sign of $\Delta S°$ will be negative in the given reaction.

3. **Extensive property:** Volume, Enthalpy.

   Intensive property: Temperature, Molar heat capacity.

4. ΔH (Enthalpy change) and ΔU (Internal energy change) are state functions as they depend upon initial and final state and not on the path.

5. $N_2(g) + O_2(g) \rightarrow 2NO(g)$

   It is endothermic as well as spontaneous.

6. (i) **Isobaric process:** In this process, pressure remains constant *i.e* $\Delta p = 0$

(ii**) Isothermal process:** In this process, tempera-ture remains constant *i.e.* $\Delta T = 0$

7. Bond energy is the amount of energy released when bonds are formed between isolated atoms in gaseous state to form one mole of gaseous molecule. It is called enthalpy of atomisation because it may also be defined as the amount of energy required to dissociate bonds present between the atoms of I mole of a gaseous molecule into constituting atoms.

8. (i) **Intensive properties:**

   The properties which depend only on the nature of the substance and not on the amount of the substance are called intensive properties, *e.g.* density.

(ii) **Adiabatic process:**

   A process during which no heat flows between the system and the surroundings is called an adiabatic process, *i.e.* $q = 0$.

9. (i) Entropy will increase on increasing the temperature since the particles of solid move with greater speed at higher temperature. At 0 K, there is perfect order of the constituent particles, entropy is minimum, tends to zero.

(ii) $H_2(g) - \rightarrow 2H(g)$

   Entropy will increase because the number of particles of product are double than that of reactant.

10. The entropy of a perfectly crystalline solid is zero at absolute zero temperature i.e., 0 K or -273.15°C.

11. Pressure is not a state function.

12. $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

13. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

    Since $\Delta n = 0, \quad \therefore \Delta H = \Delta U$

14. Surface tension and density are intensive properties

15. Yes. In adiabatic process, $\Delta H = 0$

16. (i) If work is done on the system, internal energy will increase.

(ii) If work is done by the system, internal energy will decrease.

17. $U = \frac{3}{2}RT$ for monoatomic gas.

18. Volume is decreasing, therefore, work is done the system.

19. It cannot tell us the direction of the process.

20. (a) Volume is an extensive property

21. *(d)* q is not a state function.

22. *(d)* C(graphite) $+\frac{1}{2}O_2(g) \rightarrow CO(g); \Delta_f H°CO(g) = x$

(i) C(graphite) $+O_2(g) \rightarrow CO_2(g); \Delta_c H°C(graphite) = y$

(ii) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta_c H°CO(g) = y - x$

   Subtracting(ii) from (i), we get

   C(graphite) $+\frac{1}{2}O_2(g) \rightarrow CO(g)\ \ \Delta H = y - (y - x)$

Therefore $\Delta_f H°CO(g) = \Delta_c H°(graphite) - \Delta_c H°CO(g)$

23. (i) $\Delta H = \Delta U$ becasue Δn =0

    (ii) $\Delta H > \Delta U$ becasue Δn =1 $[[\Delta H = \Delta U + \Delta nRT]$

24. (i) Exchanging heat with the surroundings.

(ii) Work done on the system or by the system

25. Most of the processes are carried out in open container, *i.e*, at constant pressure. Therefore enthalpy changes are indicated and not internal energy changes.

26. When $\Delta n = 0$, $\Delta H = \Delta U$

27. (ii) $N_2 + O_2 \rightarrow 2NO(g) - Y\ kJ$ is an endothermic process as heat is being absorbed.

28. $\Delta H = -2 \times 57.1 = -114.2\,kJ$

29. Calorific value/kg $= \frac{890}{16} \times 1000 = 55625\ kJ/kg$

30. It is an exothermic reaction because heat is being evolved.

31. (i) Height of a hill.

32. The sign of work done will be +ve, i.e. work will be done on the system due to decrease in volume.

33. $\Delta G = 0$ at equilibrium.

34. $\Delta G° = 0$ (Given)

    $\Delta G° = 0\ \ \Delta G° = -2.303RT$ log K = 0 $\Rightarrow \log K = 0$

    $\Rightarrow \log K = \log 1 \Rightarrow K = 1$

35. NH_4NO_3 dissolves in water spontaneously even when this process is endothermic because entropy increasing due to free movement of ions on dissolving. $\Delta S = +ve$ favours the process and makes it spontaneous.

36. ΔS must be positive.

37. Real crystal has more entropy because it has more disorderness.

38. $\Delta S_{fusion} = \dfrac{\Delta H_{fusion}}{\text{melting point in kelvin}}$

39. The disorder increases when two gases are mixed together, that is why entropy increases.

40. 0 kelvin

41. Entropy increases with increase in temperature.

42. $\Delta G^\circ = -2.303RT \log K$

43. $H_2O(l)$ at 350 K has larger absolute entropy per mole.

(ii) NO at 298 K has greater entropy.

44. $\Delta S = +ve$ because it is endothermic process and spontaneous.

45. (i) When sugar dissolves in water, entropy increases.

(ii) Hard boiled egg has more entropy because denatured protein has random coil structure.

46. Mg^{2+} has more entropy before hydration of ions.

47. (b) 298 K

48. (d) $\Delta G < 0$ is always true for spontaneous process.

49. (ii) At higher pressure N_2(g) will have less entropy, i.e. ΔS will be –ve.

50. In solution, there is more disorderness than in pure liquid.

51. (ii) Whose value is independent of path

52. (iii) $\Delta P = 0$ 53. (ii) zero

54. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(iii) $< \Delta U^\circ \because \Delta n = -2$

55. (i) -74.8 kJ mol^{-1}

56. (iv) Possible at all temperatures.

57. (i) $q = -w = p_{ext}(10-2) = 0 \times 8 = 0$

(ii) $q = -w = p_{ext}(10-2) = 1 \times 8 = 8\ litre\ atm$

(iii) $q = -w = 2.303 \times 10 \times \log\frac{10}{2}$

$= 2.303 \times 10 \times 0.6990 = 16.1\ \ litre\ atm.$

58. It states "The entropy of universe is continuously increasing due to spontaneous processes taking place in it $\Delta S_{sys} + \Delta S_{surr} > 0 \Rightarrow \Delta S_{total} > 0$

59. When ΔH is -ve and ΔS is +ve, then ΔG will be -ve and process will always be spontaneous as $\Delta G = \Delta H - T\Delta S$.

60. When $\Delta H > 0$ *and* $\Delta S < 0$, then ΔG will be +ve at all temperatures, therefore, processs will never be spontaneous.

62. $\Delta H = 2 \times 40.79 = 81.58kJ$

$\Delta_{vap}H^\circ = 40.79 kJ\ mol^{-1}$

63. No, because $CaCO_3$(s) is being formed from compounds and not constituting elements.

64. $\Delta H = +45.90 \times 2 = 91.8kJ$

65. $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + ...$

66. Bond energy of C-H bond $= \frac{1665}{4} = = 416.25 kJ\ \ mol^{-1}$

67. $\Delta S = \frac{\Delta H_{rev}}{T} = \frac{q_{rev}}{T}$

68. Yes, the temperature of system and surrounding will be same when they are in thermal equilibrium.

69. $\Delta_r G^\circ = -2.303RT\ \log\ K_p$

Since K_p is +ve, ΔG° will be –ve, therefore, reaction will be spontaneous.

70. $\Delta H = 0$ for cyclic process.

71. It will be less because ice is less ordered than liquid water.

72. It is because acetone has weak van der Waals' forces of attraction whereas water molecules have strong H-bonding, therefore, $\Delta_{vap}H^\circ$ of water is more.

73. $\Delta_r G$ will always be zero at equilibrium.

$\Delta_r G^\circ$ will be zero only if K = 1.

$\Delta_r G^\circ$ =- 2.303 RT log K

It will be non-zero for other values of K.

74. For isolated system, $q = 0,\ w = 0$

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

$\therefore\ \Delta U = 0$

75. (i) It is because strong acid and strong base are completely ionised in aqueous solution.

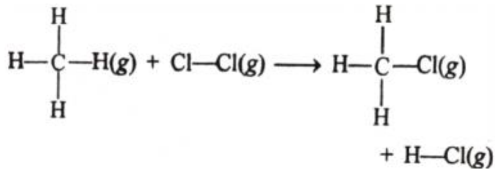
(ii) $\Delta U = q + w$

Since, ΔU is a state function and it is equal to q + w which is state function, because ΔU depends upon initial and final states and not on path.

76. (i) **Enthalpy of Neutralisation:** It is defined as enthalpy change (heat evolved) when 1 mole of H^+ from acid combines with 1 mole of OH^- from base to form water.

(ii) **Hess's law of constant heat summation:** It states that total enthalpy of reaction remains the same whether the reaction takes place in one step or several steps.

77.



$$CH_4(g) + Cl{-}Cl(g) \longrightarrow CH_3Cl(g) + H{-}Cl(g)$$

ΔH = -100.3 kJ mol^{-1}

Enthalpy of reaction = Bond energy of reactants - Bond energy of products

$\Delta H = [4 \times B.E.(C-H) + B.E.(Cl-Cl) -$

$[3 \times B.E.(C-H) + B.E.(C-Cl) + B.E.(H-Cl)]$

$\Delta H = B.E.(C-H) + B.E.(Cl-Cl) - B.E.(C-Cl)$

$- B.E.(H-Cl)$

$-100.3 = 413 + B.E.(Cl-Cl) - 326 - 431$

or B.E. (Cl-Cl) =-100.3+ 326 +431

or B.E. (Cl-Cl) = 243.7 kJ mol^{-1}

78. At constant volume

$C_V = \left(\frac{dE}{dT}\right)_V$ for an ideal gas

$C_P = \left(\frac{dH}{dT}\right)_P$ for an ideal gas

$H = E + PV = E + RT$

$\frac{dH}{dT} = \frac{dE}{dT} + R$

$\Rightarrow C_P = C_V + R \qquad \Rightarrow C_P = C_V = R$

79. Work done is isothermal reversible expansion of an ideal gas.

$w = -2.303nRT \ \log \frac{V_2}{V_1} = -2.303 \ nRT \log \frac{P_1}{P_2}$

In free expansion of an ideal gas $w = 0$ because ideal gas have negligible force of attraction, therefore, work done is zero in free expansion becasue no external force is acting.

$w = -P_{ext}\Delta V \qquad P_{ext} = 0 \quad w = 0$

80. $\Delta_f H = -46.2 kJ \ mol^{-1}$

81. $\Delta U = q - w = 701 - 394 = 307 \ J$

82. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

$\Delta H = ?$

$C(graphite) + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -395.0 \ kJ \ mol^{-1}$ ... (i)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);$

$\Delta H = -249.4 \ kJ \ mol^{-1}$ ....(ii)

6C(graphite) $+ 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$

$\Delta H = -1169.8 \ kJ \ mol^{-1}$ .....(iii)

Multiplying equaitons (i) and (ii) each by 6 and reversing (iii), we get

6C(graphite) $+ 6CO_2(g) \rightarrow 6CO_2(g);$

$\Delta H = -2370 kJ$ ....(iv)

$6H_2(g) + 3O_2(g) \rightarrow 6H_2O(l);$

$\Delta H = -1616.4 kJ$ ....(v)

$C_6H_{12}O_6(s) \rightarrow 6C(graphite) + 6H_2(g) + 3O_2(g)$

$\Rightarrow \Delta_c H(C_6H_{12}O_6) = -2370.0 - 1616.4 + 1169.8$

$= -2816.6 \ kJ \ mol^{-1}$

83. $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

$\Delta H = \sum \Delta_f H_{\text{(products)}} - \sum \Delta_f H_{\text{(reactants)}}$

$= \Delta_f H^\circ CO(g) + \Delta_f H^\circ H_2O(g) - \Delta_f H^\circ CO_2(g)$

$- \Delta_f H^\circ H_2(g)$

= - 110.5 - 241.8 - (-393.8) -0
= - 352.3 393.8 = 41.5 kJ

84. $1m^3 = 1000L$

Since 22.4 L of C_2H_4 at STP produces 1410 kJ of energy.

1000 L of C_2H_4 at STP produces $\frac{1410}{22.4} \times 1000$

(if efficiency is 100%)

$= \frac{1410}{22.4} \times 1000 \times \frac{70}{100}$ (if efficiency is 70%)

$= 44.02 \times 10^3 \ kJ$

85. $q = -C_v \times \Delta T = -20.7 KJ / K (299 - 298 K)$

$q = -20.7 kJ$

ΔH for combustion of the 1g of carbon = -20.7 kJ

ΔH for combustion of 1 mole= 12g carbon

$= -\frac{20.7}{1} \times 12 = -2.48 \times 10^2 \ kJ \ mol^{-1}$

86. 18g of H_2O (liquid) $\xrightarrow{vaporisation} 18g \ H_2O$ (vapour)

$\Delta_{vap} H^\circ$ for $H_2O = 40.66 kJ \ mol^{-1}$

No. of moles in 18g of water $= \frac{18g}{18g \ mol^{-1}}$ =1 mole

1 mole of H_2O needs 50.66 kJ of energy for vaporisation

$\Delta_{vap} H^\circ = \Delta_{vap} U^\circ + \Delta nRT$

$\Delta_{vap} U^\circ = \Delta_{vap} H^\circ - \Delta nRT$

$= 40.66 - 1 \times 8.314 \times 10^{-3} \times 373$
= 37.56 kJ mol^{-1}

87. $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

$\Delta S_{\ surr} = -\frac{\Delta_r H^\circ}{T} = \frac{-(-1648 \times 10^3 \ J \ mol^{-1})}{298K}$

$\Delta S_{\ surr} = 5530 \ J \ K^{-1} mol^{-1}$

$\Delta S_{\ sys} = -549.4 \ J \ K^{-1} mol^{-1}$

$\Delta_r S_{total} = 5530 - 549.4 = 4980.6 \ J \ K^{-1} \ mol^{-1}$

Since $\Delta_r S_{total}$ is +ve, therefore, reaction is spontaneous.

88. Combustion of 1 mole of benzene takes place as follows:

$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta_c H^\circ = -3267.0 kJ \ mol^{-1}$

$\Delta_r H^\circ = \Delta_c H^\circ$

$= \sum \left[\Delta_f H^\circ \text{(products)} \right] - \sum \left[\Delta_f H^\circ \text{(reactants)} \right]$

or - 3267.0 kJ mol^{-1}

$$= 6[\Delta_r H^\circ CO_2(g)] + 3[\Delta_f H^\circ H_2O(l)] - 1[\Delta_f H^\circ C_6H_6(l)]$$

$$-\frac{15}{2}[\Delta_f H^\circ O_2(g)] - 3267\ kJ\ mol^{-1}$$

$$= (6)(-393.5\ kJ\ mol^{-1}) + (3)(-285.83 kJ\ mol^{-1})$$

$$-(1)[\Delta_f H^\circ C_6H_6(l)] - 0$$

or $\Delta_f H^\circ C_6H_6(l)$

$$= [6(-393.5) + 3(-285.83) + 3267]\ kJ\ mol^{-1}$$

$$= [-2361.0 - 857.49 + 3267.0]\ kJ\ mol^{-1}$$

$$= 48.51 kJ\ mol^{-1}$$

89. $NH_2CN(s) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$

$$\Delta n = 1 + 1 - \frac{3}{2} = \frac{1}{2}$$

$$\Delta U = -742.7\ kJ\ mol^{-1}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$= -742.7 kJ\ mol^{-1} + \frac{1}{2} \times \frac{8.314 \times 298}{100} kJ\ mol^{-1}$$

$$= -742.7 kJ\ mol^{-1} + \frac{1}{2} \times 2.477 kJ\ mol^{-1}$$

$$= -741.4615\ kJ\ mol^{-1}$$

90. $q = c \times m \times \Delta T$

$$= c \times m \times (T_2 - T_1)$$

$$= 60 \times \frac{24}{27} \times (55 - 35) = 60 \times \frac{24}{27} \times 20\ J$$

$$= \frac{28800}{27 \times 1000} = \frac{28.8}{27} = 1.066\ kJ$$

91. Total ΔH

= (1 mole of H_2O at $10°C$ $\rightarrow$ 1 mole of H_2O at $0°C$

+(1 mole of at $0°C$ $\rightarrow$ 1 mole of ice at $0°C$

+ (1 mole of ice at $0°C$ $\rightarrow$ 1 mole of ice at $-10°C$

$$= C_p[H_2O(l)] \times \Delta T + \Delta H_{freezing} + C_p[H_2O(s)] \times \Delta T$$

$$= 75.3\ J\ K^{-1}\ mol^{-1} \times 10K + (-6.03\ kJ\ mol^{-1})$$

$$+ (36.8\ J\ K^{-1}\ mol^{-1}) \times (-10K)$$

$$= 753\ J\ mol^{-1} - 6.03 kJ\ mol^{-1} - 368\ J\ mol^{-1}$$

$$= -5.645\ kJ\ mol^{-1}$$

92. 44g of CO_2 liberates 393.5 kJ of heat.

35.2g of CO_2 will liberate $\frac{393.5}{44} \times 35.2$

= 314.8 kJ = 315 kJ of heat

93. $N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

$$\Delta_r H = \Delta_f H^\circ_{products} - \Delta_f H^\circ_{reactants}$$

$$= \Delta_f H^\circ(N_2O) + 3\Delta_f H^\circ(CO_2) - \Delta_f H^\circ(N_2O_4)$$

$$-3\Delta_f H^\circ(CO)$$

$$= 81 + 3 \times -393 - 9.7 - 3\ (-110)$$

$$= 81 - 1179 - 9.7 + 330 = -777.7 kJ = -778\ kJ$$

94. $C(g) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$

Adding eq. (ii) and 2(iii) and substracting (i), we get above equation.

$$\Delta_f H^\circ(CH_3OH) = -393 + 2 \times -286 - (-726)$$

$$\Delta_f H^\circ(CH_3OH) = -393 - 572 + 726$$

$$\Delta_f H^\circ(CH_3OH) = -965 + 726 = -239 mol^{-1}$$

95. $CCl_4(l) \rightarrow CCl_4(g) \Delta_{vap} H^\circ = 30.5\ kJ\ mol^{-1}$

$$\Delta_{vap} H^\circ = \Delta_f H^\circ[CCl_4(g)] - \Delta_f H^\circ = 30.5\ kJ\ mol^{-1}$$

$$30.5 = \Delta_f H^\circ[CCl_4(g)] - (-135.5)$$

$$\Delta_f H^\circ[CCl_4(g)] = 30.5 - 135.5 = -105 kJ\ mol^{-1}$$

$$= 715 + 2 \times 242 - (-105)$$

$$= 715 + 484 + 105 = 1304 kJ$$

$$B_{C-Cl} = \frac{1304}{4} = 326\ kJ\ mol^{-1}$$

96. ΔS will be greatr than zero because in isolated system if two gases are allowed to mix. $\Delta U = 0$ but entropy will increase i.e., ΔS will be greater than zero.

97. $2Cl(g) \rightarrow Cl_2(g)$

$\Delta H = -ve, \Delta S = -ve$

Because the reaction involves formation of bond therefore, it is exothermic, 2 moles of atoms have more randomness than 1 mole of molecule.

$\therefore \Delta S = -ve$

98. $\Delta_r G^\circ = -2.303 RT\ \log K$

$$\Delta_r G^\circ = -2.303 \times 8.314 \times 300 \log 10$$

$$= -19.147 \times 300 \times 1 = -5744.1 J$$

$$\Delta_r G^\circ = -5.7441 kJ\ mol^{-1}$$

99. NO is not thermodynamically stable because its formation is an endothermic process whereas its oxidation to NO_2 is an exothermic process, therefore, NO_2 is thermodynamically stable.

100. $\Delta_f S^\circ = \frac{\Delta_f H^\circ}{T} = \frac{-286 kJ\ mol^{-1}}{298 K}$

$$= \frac{-286000\ J\ mol^{-1}}{298\,K} = -959.7\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^\circ_{surr} = +959.7\ J\ K^{-1}\ mol^{-1}$$

101. (ii) $C_2H_6(g)$ will have highest heat of combustion because it has highest molecular weight and second highest calorific value

ΔH_c =calorific value in kJ/g × Mol. wt.

$= 52 \times 30 = 1560\ kJ/mol$

102. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)\Delta H = -37.1kcal$

$\Delta_c H\ C_2H_6 = -368.4\ kcal,\ \Delta_c H\ \ C_2H_4 = ?$

$\Delta_c H\ \ H_2(g) = -68.32\,kcal$

$\Delta H = \sum \Delta_c H(\text{reactants}) - \sum \Delta_c H(\text{products})$

$\Delta H = \Delta_c H\,C_2H_4 + \Delta_c H\,H_2(g) - \Delta_c H\,C_2H_6(g)$

-37.1 kcal $= \Delta_c H\,C_2H_4 - 68.32 - (-368.4)$

$\Delta_c H\,C_2H_4 = 337.18\,kcal$

103. ΔG° =- 2.303 RTlog K

$= -2.303 \times 8.314 \times 298\ \log\ 2.5 \times 10^6$

$= -5705.8[0.3980 + 6.0000]$

$= -5705.8 \times 6.3980 = -36.505\ kJ\ mol^{-1}$

The reaction is spontaneous in forward reiction under standard conditions.

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

$\Delta G = 77.5 \times 1000J - 400K \times 135\,J\ K^{-1}$

$= 77500J - 54000J = 23500J$

$\Delta G = -2.303\,RT\log K$

$23500J = -2.303 \times 8.314 \times 400K\log K$

$$\log K = \frac{-23500}{19.147 \times 400K} = \frac{-235}{76.588}$$

$= -3.068 + 1 - 1 = \bar{4}.932$

$K = \bar{4}.932$, Antilog $= 8.551 \times 10^{-4}$

105. $\Delta S = 2S^\circ_{(Hg)} + S^\circ_{(O_2)} - 2S^\circ_{(HgO)}$

$= (2 \times 77.4 + 205 - 2 \times 72.0)\ J\ K^{-1}\ mol^{-1}$

$= (154.8 + 205 - 144.0)\,J\ \ K^{-1}\ \ mol^{-1}$

$= (359.8 - 144.0) = 215.8\,J\ K^{-1}\,mol^{-1}$

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

$$= 91\ kJ\ \ mol^{-1} - \frac{298 \times 215.8}{1000}kJ\ \ mol^{-1}$$

$= (91 - 64.3)kJ\ \ mol^{-1} = 26.69\ kJ\ \ mol^{-1}$

106. $W = P\Delta V = 1.0 \times 5 = 5\ litre\ atm$

$= 5 \times 101.3\,J\ \ mol^{-1}$

$W = 10 \times 5 \times 101.3\ J = 50 \times 101.3\,J$

= 5065.3 J W = 5.0653 kJ

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

At equilibrium $\Delta G = 0 \Rightarrow \Delta H = T\Delta S$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{108.4 \times 1000\,J\ \ mol^{-1}}{190\ \ J\ K^{-1}\,mol^{-1}}$$

T = 570.526 K

The reaction will become spontaneous above 570.52K because ΔG is equal to zero at this temperature and above this temperature, ΔG will become -ve.

108. $G = H - TS, G_1 = H_1 - TS_1, G_2 = H_2 - TS_2$

$G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$

$\Delta G = H_2 - H_1 - T(S_2 - S_1)$

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

$$\Delta S_{sys} = \Delta S_{sys} + \Delta S_{surr} \Rightarrow \Delta S_{total} = \Delta S_{sys} = -\frac{q}{T}$$

$\Rightarrow T\Delta S_{total} = T\Delta S_{sys} - q = T\Delta S_{sys} - \Delta H$

$T\Delta S_{total} = \Delta G \Rightarrow \Delta G = -T\Delta S_{total}$

109. ΔH = Hydration energy - Lattice energy

ΔH = -774.1 kJ mol^{-1} - (-777.8 kJ mol^{-1})

$= 3.7\,kJ\ mol^{-1}$

$\Delta G = \Delta H - T\Delta S = +3.7 - 298 \times 0.043$

= +3.7-12.81

$\Delta G = -9.11kJ\ mol^{-1}$

110. $\Delta_r G^\circ = -2.303RT\ \log K_p$

$= -2.303 \times 8.314\ \ J\ K^{-1}\,mol^{-1} \times 298K$

$\times \log 2.47 \times 10^{-29}$

$= 163228\,J\ \ mol^{-1} = 163\ kJ\ \ mol^{-1}$

111. $$\log K = \frac{\Delta_r G^\circ}{2.303RT}$$

$$= \frac{-13.6 \times 1000J\ mol^{-1}}{2.303 \times 8.314 \times 298} = \frac{13.6 \times 1000}{5705.8}$$

$\log K = +2.38$

K= antilog 2.38 = 2.4×10^2

112. $E.G.E = \Delta_f H - S - 1/2D - I.E. - U$

$E.G.E = -560.8 - 87.8 - 1/2 \times 158.9$

dfs $-414.2 - (-807.5)$

E.G.E. = -1142.25 +807.5 = - 334.75 $kJ\ \ mol^{-1}$

113. $\Delta_f H = \Delta_s H^\circ + \Delta_D H^\circ + \Delta_I H^\circ + \Delta_{EA} H^\circ + \Delta_{lattice} H^\circ$

= 155 +75 +520 -333 -1012

=750 -1345 = - 595 $kJ\ mol^{-1}$

114. Bond dissociation energy is energy required to break 1 mole of bonds.

$e.g.,\ H-H(g)\rightarrow 2H(g);\Delta H = 436\ kJ\ mol^{-1}$

Bond energy is energy released when 1 mole of bonds are formed.

$e.g., 2H \rightarrow H_2(g);\ \Delta H = -436\ kJ\ mol^{-1}$

In diatomic molecule, both bond dissociation energy and bond energy are equal in magnitude but opposite in sign.

115. $\Delta H = \Delta H_c$(reactants) - ΔH_c(products)

$= \Delta H_c(C_2H_4) + \Delta H_c(H_2) - \Delta H_c(C_2H_6)$

= - 1401 -286 - (-1550)

= - 1401- 286 + 1550 = - 1687 +1550

= - 137 $kJ\ mol^{-1}$

116.(i) $\Delta H < 0$ and $\Delta S > 0; \Delta G$ will be -ve and process will always be spontaneous.

(ii) $\Delta H > 0\ and\ \Delta S < 0; \Delta G$ will be +ve and process will never be spontaneous.

(iii) $\Delta H < 0\ and\ \Delta S < 0; \Delta G$ will be -ve, if $\Delta H > T\Delta S$ and process will be spontaneous at low temperature.

(iv) $q_p = \Delta HU + p\Delta V$ $= - \Delta = G^\circ$ will be +ve , if $T\Delta S > \Delta H$ and the process will be spontaneous at high temperature.

117.It states ‘The entropy of perfectly crystalline susbtance is zero at absolute zero temperature. We can determine absolute entropy of various substances at any other temperature except at zero kelvin.

118.Residual entropy: Mostly entropy of perfectly crystalline substance is zero at 0K. There are certain substances which possess some entropy even at absolute zero i.e., at zero kelvin. This entropy is known as residual entropy, e.g., in case of CO, the measured residual entropy is $5J\ K^{-1}mol^{-1}$. It is due to some disorder which is also called frozen disorder.

119. $\Delta_f H(NaBr) = \Delta H^\circ_{sub}[Na(s)] + \Delta H^\circ_{ion}[Na(g)]$

$+\Delta_{electron}H^\circ + \frac{1}{2}(BBr - Br) + \Delta_{lattice} + H^\circ$

-360.1= 108.4+ 496 - 325 $+\frac{1}{2}\times 192 + \Delta_{lattice}H^\circ(NaBr)$

$\Delta_{lattice}H^\circ(-360.1 - 108.4 - 496 + 325 - 96)\,kJ\ mol^{-1}$

$= -1060.5 + 325 = -735.5\ kJ\ mol^{-1}$

120. It is spontaneously process because entropy or disorder is increasing

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

$\Delta H = 0, \Delta S = +ve$ therefore, process is spontaneous.

$\Delta G = -ve,$

121.State function: Enthalpy, Entropy, Temperature, Free Energy.

Path functions: Heat, work

122. $-w = p_{ext}(V_2 - V_1)$

$w = 0\times(5-1)$ (in vacuum $p_{ext} = 0$)

$w = 0$

For isothermal expansion , $q = 0$

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

$\Rightarrow 0 = \Delta U + 0 \Rightarrow \Delta U = 0$

123. $C_P - C_V = nR = 10\times 8.314\,J = 83.14\,J$

124. Molar enthalpy change = Enthalpy change for 1 g × Molar mass.

$= -20.7\ kJ\times 12$

$= -248.4 = -2.484\times 10^2\ kJ\ mol^{-1}$

125. $CCl_4(l)\rightarrow CCl_4(g)\quad \Delta H = 30.5\,kJ\ mol^{-1}$

Molar mass of $CCl_4 = 12 + 4\times 35.5$

$= 12 + 142 = 154\,g\ mol^{-1}$

Heat required for vaporisation of 284g of CCl_4

= No. of $\text{moles}\times\Delta_{\text{vap}}H^\circ$

$= \frac{284}{154}\times 30.5 = 2\times 30.5 = 61\,kJ\ mol^{-1}$

126. $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

=91.18 kJ mol^{-1} $-\frac{298K\times 197.67}{1000}kJ\ K^{-1}mol^{-1}$

=91.18 kJ mol^{-1} - 58.91 kJ mol^{-1} = 32.27 mol^{-1}

Since ΔG is +ve, therefore, carbon cannot reduce MgO.

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

0 = 91.18 kJ mol^{-1} $-T\times\frac{197.67}{1000}kJ\ K^{-1}\ mol^{-1}$

$T = \frac{91.18\times 1000}{197.67} = \frac{91180}{197.67} = 461.27K$

127. $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)\rightarrow HCl(g)$

$\Delta_f H^\circ = \frac{1}{2}B_{H-H} + \frac{1}{2}B_{Cl-Cl} - B_{H-Cl}$

$= \frac{1}{2}\times 437 + \frac{1}{2}\times 244 - 433$

= 218.5+122- 433

$= -925kJ\ mol^{-1}$

128. $CH_4(g) + 2O_2(g)\rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -891\ kJ\ mol^{-1}$ ....(i)

$C(s)+O_2(g)\to CO_2(g)$

$\Delta H = -286\ kJ\ mol^{-1}$ ....(iii)

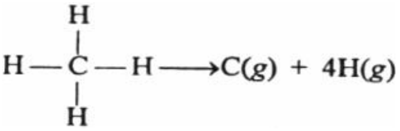
$C(s)\to C(g)$

$\Delta H = +717\ kJ\ mol^{-1}$ .....(iv)

$H_2(g)\to 2H(g)$

$\Delta H = +436\ kJ\ mol^{-1}$ ....(v)

Target equation is



Reversing (ii), multiplying (iii) by 2 and reversing and multiplying (v) by 2 and then adding all together we get:

$CH_4 \to C(g)+4H(g)$

$\Delta H = -891+394+572+717+872$

$\Rightarrow \Delta H = 1664\ kJ$

Now, energy required to break 4 C-H bond = 1664 kJ Therefore, energy required to break 1C-H bond

$$=\frac{1664}{4} = 416 kJ\ mol^{-1}$$

129. $3C_{(graphite)} + 4H_2(g)\to C_3H_8(g)$

$$\Delta_r S° = \sum S_m^{\circ}(\text{products}) \text{ - } S_m^{\circ}(\text{reactants})$$

$$\Delta_r S° = S°_m[C_3H_8(g)] - 3S°_m[C\ (graphite)] - 4S°_m[H_2]$$

$= (270.2 - 3\times 5.70 - 4\times 130.7) J\ K^{-1} mol^{-1}$

$= (270.2 - 17.10 - 522.80)\ J\ K^{-1} mol^{-1}$

$= (270.2 - 539.90) = -269.7\ J\ K^{-1} mol^{-1}$

$\Delta_r H° = \Delta_f H°_{products} - \Delta_f H°_{\text{reactants}}$

$\Delta_r H° = \Delta_f H°(C_3H_8) - 4\Delta_f H°[H_2(g)]$

$- 3\Delta_f H°$ [C(graphite)]

$\Delta_r H° = -103.8\ kJ\ mol^{-1}$

$\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$$=\left(-103.8 - \frac{298\times(-269.7)}{1000}\right) kJ\ mol^{-1}$$

= (-103.80 +80.370)

$kJ\ mol^{-1} = -23.43\ kJ\ mol^{-1}$

130. Entropy is defined as the degree of randomness or disorder

(i) $\Delta S = -ve$ (ii) $\Delta S = +ve$

(iii) $\Delta S = +ve$ (iv) $\Delta S = -ve$

(v) $\Delta S = -ve$

131. (i) (a) Reversible (b) Irreversible

(c) Irreversible (d) Reversible

(ii) It is becasue no work is done.

i.e., $w = 0$

$\because w = -p_{ext}\times \Delta V = 0\times\Delta V = 0$

$\Delta U = q + w$

$q = 0$ because gas chamber is insulated.

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

132. According to Nernst, at absolute zero, the entropy of a perfectly crystalline substance is taken as zero at zero kelvin. This is also known as third law of thermodynamics.

It helps us to calculate the absolute entropies of pure substances at different temperatures.

$K = 1.8\times 10^{-7}, T = 298K, \Delta G° = ?,$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$\Delta G° = -2.303RT\ \log K$

$\Delta G° = -2.303\times 8.314\times 298\ \log 1.8\times 10^{-7}$

$= -19.147\times 298 \log 1.8\times 10^{-7}$

$= -5705.8[\log 1.8 + \log 10^{-7}]$

$= -5705.8\times[0.2552 - 7.0000]$

$= -5705.8\times -6.7448 = +38484.47\ J$

$= 38.484\ kJ\ mol^{-1}$

Since $\Delta G°$ is +ve, therefore, reaction is not feasible at this temeprature, i.e., reaction is non-spontaneous.

133. The entropy of all substances at absolute zero (0K) is taken as zero because of complete order in the system, i.e., the atoms or molecule do not move at all in the perfectly crystalline state.

$\Delta G° = -2.303RT\ \log K$

$= -2.303\times 8.314\, J\, K^{-1}\, mol^{-1}\times 298K\ \log 6.6\times 10^5$

$= -19.147\, J\times 298 \log 6.6\times 10^5$

$= -5705.8[\log 6.6 + \log 10^5]$

$= -5705.8[0.8195 + 5.0000]$

$= -5705.8\times 5.8195\, J = -33204.903\ J$

$\Delta G° = -33.205 kJ\ mol^{-1}$

134. $\Delta S = S_T - S_0$

where S_T is entropy at temperature T K. But from third law, $S_0 = 0$ where S_0 is entropy at 0 K

$\therefore S_T = \Delta S$

If we measure the energy required to raise the temperature of a crystalline substance from K to 298 K, we can determine entropy change. The entropy S_T at 298K is called absolute entropy.

$\Delta G° = -2.303RT\ \log K$

$$= -2.303\times 8.314\ J\,K^{-1}mol^{-1}\times 400K\ \log 1.958\times 10^{-4}$$

$$= (-19.147\times 400\log 1.958\times 10^{-4})J\ mol^{-1}$$

$$= [-7658.8\times(\log 1.958+\log 10^{-4})J\ mol^{-1}$$

$$= [-7658.8\times(0.2917-4.0000)]J\ mol^{-1}$$

$$\Delta G^\circ = -7658.8\times -3.7183 = +28477.72\ J\ mol^{-1}$$

$$= 28.48\ kJ\ mol^{-1}$$

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

$$28.48\ kJ\ mol^{-1} = 77.20\,kJ\ mol^{-1} - 400\ \Delta S^\circ$$

$$-400\ \Delta S^\circ = -48.73\ kJ\ mol^{-1}$$

$$\Delta S^\circ = \frac{48.73\times 1000\ J\,mol^{-1}}{400K} = \frac{487.3}{4}$$

$$= 121.82\ J\,K^{-1}\ mol^{-1}$$

135. Standard free energy of formation of compound is defined as free energy change when a compound is formed from its constituting elements at 298K and 1 atm pressure.

$$2SO_2(g)+O_2(g) \Leftrightarrow 2SO_3(g)$$

$$\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$= 2\Delta_f G^\circ(SO_3) - 2\Delta_f G^\circ(SO_2) - \Delta_f G^\circ(O_2)$$

$$= 2\times(-371.1) - 2\times(-300.2) - 0$$

$$= -742.2 + 600.4 = -141.8$$

$$\Delta G^\circ = -2.303RT\ \log K$$

$$-141.8\times 1000J = -2.303\times 8.314\times 298\log K$$

$$\log K = \frac{1{,}41{,}800}{5705.8} = 24.8519 \Rightarrow K = 7.114\times 10^{24}$$

136.(i) $\Delta G^\circ = \Delta_f G^\circ[C_6H_6(g)] - 3\Delta_f G^\circ[CH\equiv CH(g)]$

$$= 1.24\times 10^5\ J\,mol^{-1} - 3\times 2.09\times 10^5\ J\ mol^{-1}$$

$$= 1.24\times 10^5\ J\,mol^{-1} - 6.27\times 10^5\ J\ mol^{-1}$$

$$= -5.03\times 10^5\ J\ mol^{-1}$$

$$\Delta G^\circ = -2.303\ RT\ \log K$$

$$-5.03\times 10^5 = -2.303\times 8.314\times 298\log K$$

$$\Rightarrow \log K = \frac{5.03\times 10^5\ J}{5705.8J} = +88.1559$$

$$\Rightarrow K = 1.432\times 10^{88}$$

(ii) Yes, this process can be recommended as a practical method for making benzene as value of K is very high.

137.(i) Hess's law states enthalpy change remains the same whether the reaction takes place in one step or in several steps.

It follows from 1st law of thermodynamics that energy can neither be created nor be destroyed. It can change from one form to another. The total energy of universe remains constant.

(ii) $CO_2(g)+2H_2O(l) \rightarrow CH_4(g)+2O_2(g)$

$$\Delta_r H = \Delta_f H(CH_4) + 2\Delta_f H(O_2) - \Delta_f H(CO_2)$$

$$-2\Delta_f H[H_2O(l)]$$

$$+890.3kJ\ mol^{-1} = \Delta_f H\,CH_4 + 2\times 0 -$$

$$-(-393.51\,kJ\,mol^{-1}) - 2\times(-285.8\ kJ\ mol^{-1})$$

$$\Delta_f H(CH_4) = (+890.3 - 393.51kJ - 571.6)kJ\ mol^{-1}$$

$$\Delta_f H(CH_4) = -74.8\ kJ\ mol^{-1}$$

138.(i) (a) **First law of thermodynamics**. It states that energy can neither be created nor be destroyed. It can change from one form to another. The total energy of universe remains constant.

(b) **Standard Enthalpy of Formation.** It is defined as enthalpy change when 1 mole of compound is formed from its constituting elements.

(ii) $N_2H_4(l)+2H_2O_2(l) \rightarrow N_2(g)+4H_2O(l)$

$$\Delta_r H = \Delta_f H(N_2) + 4\Delta_f H(H_2O)$$

$$-\Delta_f H(N_2H_4) - 2\Delta_f H(H_2O_2)$$

$$= 0 + 4\times -242.7 - (-50.4) - 2(-193.2)$$

$$= (-970.8 + 50.4 + 386.4)kJ\ mol^{-1}$$

$$\Delta_r H = -534\ kJ\ mol^{-1}$$

139. $\Delta_f H = \Delta H_{sub} + \Delta H_{ion} + \Delta H_{EA} + \Delta H_D + \Delta H_{lattice}$

$$+\Delta H_{vap}$$

$$-524 = 148 + 2187 - 331 + 193 + 31 + \Delta H_{lattice}$$

$$\Delta H_{lattice} = -524 - 2228 = -2752\ kJ\ mol^{-1}$$

140. At constant volume, according to first law of thermodynamics.

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

$$-w = p\Delta V$$

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

$$\Delta V = 0$$

$$\therefore\ q_V = \Delta U$$

where ΔU is internal energy change. At constant pressure.

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

$q_p = \Delta H$, where ΔH is enthalpy change. At constant volume and pressure, heat change is a state function because it is equal to ΔU and ΔH which are state functions and depend upon initial and final states of the system and not on path.

141.

(i) **Hess's Law:** The total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place ir. one step or in number of steps. in other words, the total amount of heat change in a reaction depends only upon the reactants and the products and is independent of the path taken.

(ii) (a) **Standard enthalpy of combustion** is the amount of heat evolved when one mole of a substance under standard condition is completely burnt to form product also under standard conditions.

(b) **Standard enthalpy of formation** is the enthalpy change accompanying the formation of one mole of a substance from its constituent element in their standard state, e.g. standard enthalpy of formation of CO_2 may be represented as

$C(s) + O_2(g) \rightarrow CO_2(g)$

(iii) (a)

Extensive Property	**Intensive Property**
The property that depends on the quantity of a matter contained in the system e.g., mass, volume and heat capacity	These are the property that depends on the nature of the substance and not on the amount of substance, e.g., refractive index and viscosity.

(b)

Isothermal Process	**Isobaric Process**
When a process is carried out in such a manner that the temperature remains constant, it is called isothermal process	Isobaric process is the one during which the pressure of the system remains constant.

142. (i) Standard enthalpy of formation is defined as enthalpy change when 1 mole of compound is formed from the constituting elements in their standard states.

(a) is not enthalpy of formation of $CaCO_3$ because it is not being formed from constituting elements.

(b) is not enthalpy of formation of HBr because 2 moles of HBr are being formed.

(ii) $OF_2(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$

$\Delta n = 1 + 2 - 2 = 1$

$$\Delta_r H°(O_2) = \sum \Delta_f H°(\text{products}) - \sum \Delta_f H°(\text{reactants})$$

$$= \Delta_f H°(O_2) + 2\Delta_f H°(HF) - \Delta_f H°(OF_2) - \Delta_f H°(H_2O)$$

$$= 0 + 2 \times (-268.6) - 23.0 - (-241.8)$$

= 537.2-23.0 +241.8

= -318.4 kJ

$\Delta_f H° = \Delta_r U° + \Delta nRT$

$$-318.4kJ \ \Delta_r U° + \frac{1 \times 8.314 \times 300}{1000} kJ$$

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

$\Delta H° = (-10500 - 2477.57) J \ mol^{-1}$

= - 12977.575 $J \, mol^{-1}$

$\Delta G° = \Delta H° - T\Delta S°$

$= -12977.58 - 298K \times (-44.1) JK^{-1} \ mol^{-1}$

$= -12977.58 + 13141.80$

$\Delta G° = 0.164 \ kJ \ mol^{-1}$

$\Rightarrow$ Since $\Delta G°$ is positive, the process is non spontaneous.

143.(i) $\Delta G = \Delta H - T\Delta S$; for non-spontaneous reaction

$\Delta G = -ve$

$T\Delta S > \Delta H$

$$\Rightarrow T > \frac{\Delta H}{\Delta S} \ or \ T > \frac{400}{0.2} = 2000K$$

$\Rightarrow$ Above 2000K, the process will be spontaneous.

(ii) First law of thermodynamics states that the total energy of the universe remains constant, although it may undergo transformation from one form to another.

$-318.4kJ = \Delta_r U° + 2.4942 \ kJ$

$\Delta_r U° = -320.8942 kJ$

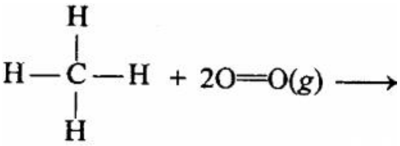
144. (i)f First law of Thermodynamics states that energy can neither be created nor be destroyed. It can change from one form to another. The total energy of universe remains consant.

'q' is not a state function because it depends upon path.

'w' is not a state function because it depends upon path.

$q + w = \Delta U$ which is a state function because it is independent of path.

(ii)



$O = C = O(g) + 2H - O - H(g)$

$\Delta H =$ bond energy of reactants - Bond energy of products.

$= 2B_{O-O} + 4B_{C-H} - 2B_{C=O} - 4B_{O-H}$

$= 2 \times 498 + 4 \times 414 - 2 \times 741 - 4 \times 464$

$= (996 + 1656 - 1482 - 1856) = -686 \ kJ \ mol^{-1}$

145. (i) Enthalpy of Neutralisation is defined as heat evolved when 1 mole of H^+ from acid combines with 1 mole of base to form water.

It is becasue strong acids and bases are completely ionised in aqueous solution.

(ii) Law of conservation of energy is the basis of Hess's law.

(iii) $2A_2g + 5B_2(g) \rightarrow 2A_2B_5(g)$

$$\Delta n = 2-2-5 = 5-5$$

$$\Delta H = -50.16\ kJ \qquad \Delta U = ?$$

$$T = 273+27 = 300K$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Rightarrow \Delta U = \Delta U - \Delta nRT$$

$$\Rightarrow \Delta U = -50.16 kJ - \frac{(-5)\times 8.314 \times 300}{1000}\ kJ$$

$$\Rightarrow \Delta U = -50.16\ kJ + \frac{12471}{1000} kJ$$

$$\Rightarrow \Delta U = -50.16\ kJ + 12.471\ kJ$$

$$\Rightarrow \Delta U = -37.689\ kJ$$

146. (i) U_1 is initially internal energy, 'q' is heat supplied, w is work done on the system, then final internal energy.

$$U_2 = U_1 + q + w \qquad U_2 - U_1 = q + w$$

$$\Delta U = q + w$$

(ii) It is because $\Delta U = q + w$

ΔU is state function $\therefore q + w$ is state function.

(iii) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$$\Delta_r H^\circ = B_{H-H} + B_{Br-Br} - 2B_{H-Br}$$

$$= 436 + 192 - 2\times 368$$

$$\Delta_r H^\circ = 628 - 736 = -108\, kJ\ mol^{-1}$$

147.(i) Carbohydrates (ii) 6%

(iii) Oil is the major source of fats.

No, they are not good for health as they contain lot of sodium, fats and harmful substances.

Yes, they are good for health because they are sources of iron, vitamins, minerals and proteins.

She must use less saturated fats, use PUFA and MUFA and should involve her family members in exercise.

148.(i) Synthesis gas has higher calorific value than coal.

(ii) It is because lot of sulphur in coal is removed during gasification process, i.e. in production of synthesis gas. Combustion of synthesis gas produces less pollution than burning of coal.

(iii) Synthesis gas can be supplied through pipes because it is a gas.

(iv) H_2 is better fuel.

(v) Because it does not create pollution.

(vi) It is because LPG creates very less air pollution as compared to wood and dung cakes.

149. (i) It changes to $MgSO_3$ solid.

(ii) We can get SO_2 from $MgSO_3$ by heating at 1025 K.

$$MgSO_3 \xrightarrow[1025K]{\Delta} MgO + SO_3$$

(iii) It can be used to manufacture sulphuric acid.

$$2SO_2 + O_2 \xrightarrow[770K]{V_2O_5} 2SO_3$$

$$SO_3 + H_2SO_4 \xrightarrow{high\ pressure} \underset{Oleum}{H_2S_2O_7}$$

$$\underset{Oleum}{H_2S_2O_7} + H_2O \rightarrow \underset{sulphuric\ acid}{2H_2SO_4}\ (conc.)$$

(v) It is used for the manufacture of fertilizers.

(vi) They are controlling emission of SO_2 which is harmful for people.

150.(i) (a) Changing the fuel by switching to low sulphur coals, oils and gases.

(b) Cleaning the coal before combustion.

(c) Controlling emission by using catalytic converters.

(d) Using unleaded gasoline.

(ii) Yes, it has reduced pollution in Delhi. It should be adopted in other states also.

(iii) CNG is better because it has high calorific value.

(iv) Yes, because diesel vehicles create more pollution.

(v) Yes, because they do not create pollution.

151.(i) It does not create pollution and has high calorific value.

(ii) It contains 55-70% of methane which is highly combustible.

(iii) It is used as a fuel for cooking and purposes, also as a feedstock for running dual fuel engines.

(iv) It is used as manure.

(v) Yes, it will help the villagers to use clean fuel.

(vi) They are helping to reduce air pollution.

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