UNIT : 5 - CHEMICAL THERMODYNAMICS

Important Points

$\Delta E = E_p - E_r = q_v$ $\qquad$ $\Delta E = q - P\Delta V$ $\qquad$ $\Delta E = q + w$

$w = -nRT \log_e \frac{V_2}{V_1}$ $\qquad$ $\Delta H = \Delta E + P\Delta V$ $\qquad$ $\Delta H = \Delta E + \Delta n_g RT$

Hess Law $\Delta H_{steps} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$$\text{Heat Capacity} = \frac{\text{Heat absorbed}}{\text{Temperature difference}}$$
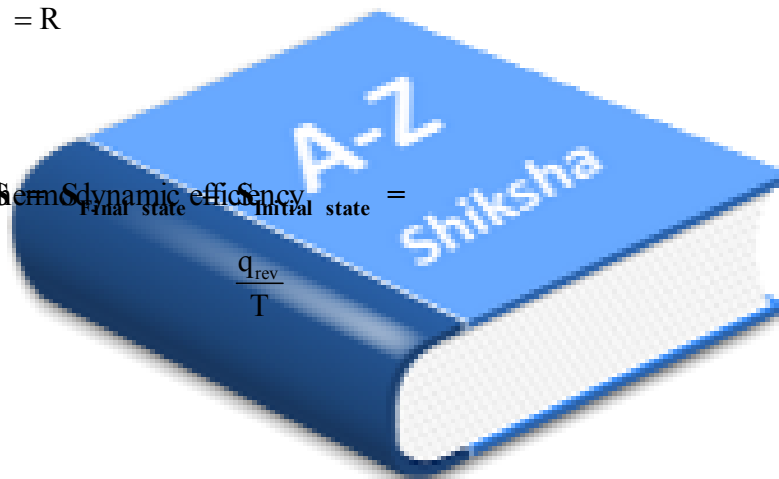
$$\text{Specific heat capacity} = \frac{\text{Heat absorbed}}{(\text{Temperature difference}) \times (\text{Weight of subs ta nce in gram})}$$

$$\text{Molar heat capacity} = \frac{\text{Heat absorbed}}{(\text{Temperature difference}) \times (\text{Molecular weight})}$$

$C_{pv} - C = R$

$\dfrac{C_p}{C_v} = $ **(gamma)**

$\dfrac{w}{q_2} = \dfrac{T_2 - T_1}{T_2} = $ Thermodynamic efficiency $= $ Final state − Initial state $= \dfrac{q_{rev}}{T}$

Δ

$$\Delta S = nC_v \ \ln \ \frac{T_2}{T_1} + nR \ \ln \ \frac{V_2}{V_1}. \text{ Assuming } C_v \text{ is constant}$$

(ii) When T and p are two variables, $\Delta S = nC_P \ \ln \ \dfrac{T_2}{T_1} - nR \ \ln \ \dfrac{p_2}{p_1}$. Assuming C_p, is constant

(a) Thus, for an *isothermal process* (T constant), $\Delta S = nR \ \ln\dfrac{V_2}{V_1} \ \text{or} = -nR \ \ln\dfrac{p_2}{p_1}$

(b) For *isobaric process* (*p* constant), $\Delta S = n \ C_p \ \ln\dfrac{T_2}{T_1}$

(c) For *isochoric process* (*V* constant), $\Delta S = n \ C_v \ \ln\dfrac{T_2}{T_1}$

(d) Entropy change during adiabatic expansion : In such process q = 0 at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called isoentropic process.

S⚛ +S ⚛⚛⚛ >S0 ⚛S ⚛⚛⚛⚛⚛ S0 The⚛Sreaction. w⚛⚛l0Cherrsactionⅿⅽⅸⅼ5Fhⅇⅿⅽⅹⅹⅰⅺⅿⅽⅹⅹⅰⅺⅿⅽⅹⅹⅰⅺⅿ in equilibrium

$$\Delta S = R \ln \frac{V_2}{V_1} \qquad\qquad \Delta G = \Delta H - T\Delta S$$

$$\Delta_f G^o{}_{reaction} = \Sigma \Delta_f G^o{}_{Product} - \Sigma \Delta_f G^o{}_{Reactant}$$

$$\Delta_f G^o{}_{reaction} = \left(\begin{array}{c}\text{total standard free energy of}\\ \text{formation of product}\end{array}\right) - \left(\begin{array}{c}\text{total standard free energy of}\\ \text{formation of reactant}\end{array}\right)$$

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

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

$$\Delta G = -nFE_{Cell}$$

Kirchhoff's equation. $\dfrac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$

Kirchhoff's equation at constant volume, $\dfrac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_v$

Effect of Temperature on Spontaneity of Reactions

Δ			
−	+	−	Reaction spontaneous at all temperature
−	−	− (at low T)	Reaction spontaneous at low temperature
−	−	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	− (at high T)	Reaction spontaneous at high temperature
+	−	+ (at all T)	Reaction nonspontaneous at all temperature

Joule thomson coeffient $\mu = \left(\dfrac{\partial T}{\partial p}\right)_H$

For cooling $\mu = +$ ve

For Heating $\mu = -$ve

Neither cooling nor heating $\mu = 0$

The temperature at which a real gas shows neither cooling nor heating effect on adiabatic expansion (i.e., $\mu = 0$) is called inversion temperature.

Hydrogen has highest calorific value.

13.7 Kcal/mol = 57 KJ/mol (be cause of 1cal = 4.2 Joule)

Enthalpy of fusion of ice per mole is 6KJ.

Order of bond energy in halogen $Cl_2 > Br_2 > F_2 > I_2$.

Heat of vapourisation of water per mole is 10.5 KCal.

The heat of reaction is independent of the time consumed in the process.

Joule thomson coeffient $\mu = \left(\dfrac{\partial T}{\partial p}\right)_H$

$H^0{}_r S^0{}_r G^0$ **Description***

## M.C.Q.

1. The temperature of the system decreases in an
    (A) Adiabatic compression   (B) Isothermal compression
    (C) Isothermal expansion   (D) Adiabatic expansion

2. If a refrigerator's door is opened, then we get
    (A) Room heated   (B) Room cooled
    (C) More amount of heat is passed out   (D)No effect on room

3. The cooling in refrigerator is due to
    (A) Reaction of the refrigerator gas   (B) Expansion of ice
    (C) The expansion of the gas in the refrigerator   (D) The work of the compressor

4. The process, in which no heat enters or leaves the system, is termed as
    (A) Isochoric   (B) Isobaric   (C) Isothermal   (D) Adiabatic

5. Warming ammonium chloride with sodium hydroxide in a test tube is an example of :
    (A) Closed system   (B) Isolated system   (C) Open system   (D) None of these

6. Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are –
    (A) I, II   (B) I, II, III   (C) I, III, IV   (D)All the above

7. A thermodynamic state function is
    (A) one which obeys all the laws of thermodynamics
    (B) a quantity which is used in measuring thermal changes
    (C) one which is used in thermo chemistry
    (D) a quantity whose value depends only on the state of the system.

8. In thermodynamics, a process is called reversible when
    (A) surroundings and system change into each other
    (B) there is no boundary between system and surroundings
    (C) the surroundings are always in equilibrium with the system
    (D) the system changes into the surroundings spontaneously

9. Which one of the following statement is false–
    (A) work is a state function   (B) temperature is a state function
    (C) change in the state is completely defined when the initial and final states are specified
    (D) work appears at the boundary of the system.

10. A mixture of two moles of carbon monoxide and one mole of oxygen, in a closed vessel is ignited to convert the carbon monoxide to carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then
    (A) $\Delta H < \Delta E$ (B) $\Delta H > \Delta E$ (C) $\Delta H = \Delta E$
    (D) The relationship depends on the capacity of the vessel

11. At constant T and P, which one of the following statements is correct for the reaction,
    $$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$
    (A) ΔH is independent of the physical state of the reactants of that compound
    (B) $\Delta H < \Delta E$ (C) $\Delta H > \Delta E$ (D) $\Delta H = \Delta E$

12. If ΔH is the change in enthalpy and the change in internal energy accompanying a gaseous reaction
    (A) ΔH is always greater than ΔE
    (B) ΔH < ΔE only if the number of moles of the products is greater than the number of the reactants
    (C) ΔH is always less than ΔE
    (D) ΔH < ΔE only if the number of moles of the products is less than the number of moles of the reactants

13. Enthalpy is an ————— property.
    (A) Extensive   (B) Exclusive   (C) Intensive   (D) Inclusive

14. Select the correct set of statement/s :
    I.   Work done by the surrounding in case of infinite stage expansion is more than single stage expansion
    II. Irreversible work is always greater than reversible work.
    III. On an ideal gas in case of single stage expansion and compression system as well as surrounding are restored back to their original states
    IV. If gas is in thermodynamic equilibrium is taken from state A to state B, by four successive single stage expansions. Then we can plot 4 points on the P–V indicator diagram.
    (A) II   (B) I, II, III, IV   (C) II, IV   (D) I, II, IV

15. If w1 , w2, w3 and w3 are work done in isothermal, adiabatic, isobaric and isochoric reversible process, the correct order (for expansion) will be
    (A) w1 > w2 > w3 > w4   (B) w3 > w2 > w1 > w4
    (C) w3 > w2 > w4 > w1   (D) w3 > w1 > w2 > w4

16. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at is
    (A) $2.303 \times 298 \times 0.082 \log 2$ (B) $298 \times 10^7 \times 8.31 \times 2.303 \log 2$
    (C) $2.303 \times 298 \times 0.082 \log 0.5$ (D) $8.31 \times 10^7 \times 298 - 2.303 \log 0.5$

17. When Fe (s) is dissolved in aqueous HCl in a closed vessel the work done is _____.
    (A) positive   (B) negative   (C) Zero   (D) cannot be defined

18. Hess law of heat summation includes
    (A) Initial reactants only   (B) Initial reactants and final products
    (C) Final products only   (D) Intermediates only

19. Ice – Water mass ratio is mantained as 1 : 1 in a given system containing water in equilibrium with ice at constant pressure. If CP (ice) = CP (water) = 4.18 J mol^{-1} K^{-1} molar heat capacity of such a system is
    (A) Zero   (B) Infinity   (C) 4.182 JK^{-1} mol^{-1} (D) 75.48 JK^{-1} mol^{-1}

20. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is **correct**, for the above process?

(A) The randomness of the universe decreases

(B) The randomness of the surroundings decreases

(C) Increase is randomness of surroiundings equals the decrease in randomness of system

(D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.

21. The enthalpy change for a given reaction at 298 K is – x J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature

(A) can be negative but numerically larger than x/298

(B) can be negative but numerically smaller than x/298

(C) cannot be negative

(D) cannot be positive

22. Spontaneous adsorption of a gas on a solid surface is exothermic process because

(A) enthalpy of the system increases.

(B) entropy increases.

(C) entropy decreases.

(D) free energy change increases.

23. Identify the correct statement regarding entropy :

(A) At absolute zero, the entropy of a perfectly crystalline substance is +ve.

(B) At absolute zero, the entropy of a perfectly crystalline substance is zero.

(C) At 0°C the entropy of a perfectly crystalline substance is taken to be zero.

(D) At absolute zero of temperature the entropy of all crystalline substances is taken to be zero.

24. Identify the correct statement regarding a spontaneous process :

(A) Exothermic processes are always spontaneous.

(B) Lowering of energy in the reaction process is the only criterion for spontaneity.

(C) For a spontaneous process in an isolated system, the change in entropy is positive.

(D) Endothermic processes are never spotaneous.

25. ΔS will be highest for the reaction

(A) $Ca_{(s)} + 1/2\ O_{2(g)} \rightarrow CaO_{(s)}$

(B) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

(C) $C_{(s)} + 0_{2(g)} \rightarrow CO_{2(g)}$

(D) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

26. The spontaneous flow of heat is always

(A) unidirectional from higher temperature to lower temperature

(B) from high to low pressure

(C) unidirectional from lower temperature to higher temperature

(D) from low to high pressure.

27. Which of the following is zero during adiabatic expansion of the gas

(A) ΔT (B) ΔS (C) ΔE (D) All the above

28. The occurrence of a reaction is impossible if

(A) ΔH is +ve; ΔS is also + ve but $\Delta H < T\Delta S$

(B) ΔH is −ve; ΔS is also −ve but $\Delta H > T\Delta S$

(C) ΔH is − ve; ΔS is + ve

(D) ΔH is + ve; ΔS is − ve

29. Identify the correct statement regarding entropy
    (A) At 0^0C, the entropy of a perfectly crystalline substance is taken to be zero
    (B) At absolute zero of temperature, the entropy of a perfectly crystalline substance is +ve
    (C) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero
    (D) At absolute zero of temperature, the entropy of a perfectly crystalline substance is taken to be zero

30. A container has hydrogen and oxygen mixture in ratio of 4 : 1 by weight, then
    (A) Internal energy of the mixture decreases   (B) Internal energy of the mixture increases
    (C) Entropy of the mixture increases   (D) Entropy of the mixture decreases

31. The second law of thermodynamics says that in cyclic process.
    (A) Work cannot be converted into heat   (B) Heat cannot be converted into work
    (C) work cannot be completely converted into heat
    (D) Heat cannot be completely converted into work

32. A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2. Work done by the engine is $(Q_1 + Q_2)$. This data
    (A) Violates Ist law of thermodynamics
    (B) Violates Ist law of thermodynamics if Q_1 is –ve
    (C) Violates Ist law of thermodynamics if Q_2 is –ve
    (D) Does not violate Ist law of thermodynamics

33. The molar neutralization heat for and as compared to molar neutralization heat of NaOH and HCl
    (A) Less   (B) More   (C) Equal   (D) Depends on pressure

34. If the enthalpy of B is greater than of A, the reaction A→B is
    (A) Endothermic   (B) Exothermic   (C) Instantaneous   (D) Spontaneous

35. Which of the following fuels will have the highest calorific value (kJ/kg)
    (A) Charcoal   (B) Kerosene   (C) Wood   (D) Dung

36. Which is the best definition of "heat of neutralization"
    (A) The heat set free when one gram molecule of a base is neutralized by one gram molecule of an acid in dilute solution at a stated temperature
    (B) The heat absorbed when one gram molecule of an acid is neutralized by one gram molecule of a base in dilute solution at a stated temperature
    (C) The heat set free or absorbed when one gram atom of an acid is neutralized by one gram atom of a base at a stated temperature
    (D) The heat set free when one gram equivalent of an acid is neutralized by one gram equivalent of a base in dilute solution at a stated temperature

37. Compounds with high heat of formation are less stable because
    (A) High temperature is required to synthesise them
    (B) Molecules of such compounds are distorted
    (C) It is difficult to synthesis them   (D) Energy rich state leads to instability

38. When a gas undergoes adiabatic expansion, it gets cooled due to
   (A) Loose of kinetic energy
   (B) Fall in temperature
   (C) Decrease in velocity
   (D) Energy used in doing work
39. For a reaction to occur spontaneously
   (A) $(\Delta H - T\Delta S)$ must be negative
   (B) $(\Delta S + T\Delta S)$ must be negative
   (C) ΔH must be negative
   (D) ΔS must be negative
40. If for a given substance melting point is T_B and freezing point is T_A, then correct variation shown by graph between entropy change and temperature is

   (A)   (B)   (C)   (D)
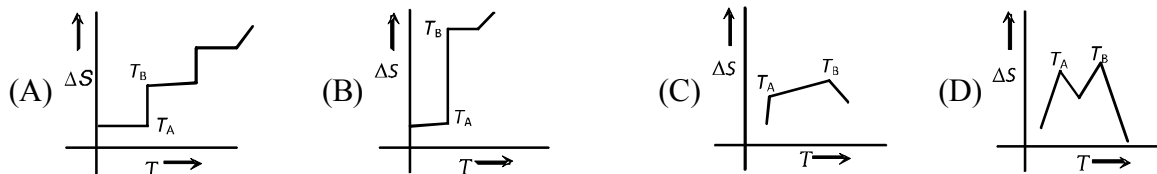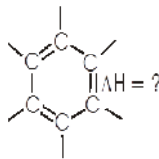
41. A Beckmann thermometer is used to measure
   (A) High temperature   (B) Low temperature   (C) Normal temperature   (D) All temperature
42. The calorific value of fat is ……….
   (A) less than carbohydrates and protein
   (B) less than that of protein but more than carbohydrates
   (C) less than that of carbohydrates and more than that of protein
   (D) more than thant of carbohydrates and protein
43. Which of the following processes is accompanied by an increase in entropy ?
   (A) Normal rubber band to stretched rubber band   (B) Normal egg to hard boiled egg
   (C) Decomposition of N_2O_5 to N_2O to O_2 (D) Formation of NH_3 for N_2H_2.
44. Which of the following does not exhibit zero entropy at absolute zero
   (A) Benzene   (B) Glass   (C) Pyridine   (D) CCl_4
45. The favourable conditions for a spontaneous reaction are
   (A) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$
   (B) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = -ve$
   (C) $T\Delta S = \Delta H$, $\Delta H = -ve$, $\Delta S = -ve$
   (D) $T\Delta S = \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$.
46. A block of ice at $-10\,°C$ is slowly heated and converted into steam at $100°C$ .Which of the following curves represents the phenomenon qualitatively ?

   (A)   (B)   (C)   (D)
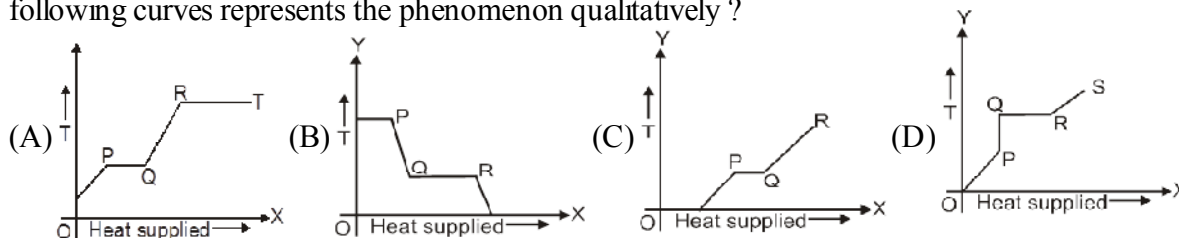
47. On passing CO_2 gas in water, its entropy
   (A) Remains constant   (B) Decreases   (C) Increases   (D) May increase or decrease.
48. When does the reaction occur spontaneously on the basis of the relation $\Delta G° = -RT/nK$?
   (A) $K = 0$ (B) $K = 1$ (C) $K > 1$ (D) $K < 1$

49. In thermodynamics, a process is called reversible when,

(A) Surroundings and system change into each other

(B) The surroundings are always in equilibrium with the system

(C) The system changes into the surroundings spontaneously.

(D) There is no boundary between system and surroundings.

50. Under certain conditions, the value of ΔG for a hypothetical reaction, $X + Y \longrightarrow Z$ is greater than zero, then –

(A) The reaction has tendency to proceed towards Z

(B) The reaction has attained equilibrium

(C) increase in temperature increases the yield of product Z

(D) X and Y predominate in the final mixture

51. For which of the following processes will energy be absorbed –

(A) Separating an electron from an electron   (B) Separating proton from a proton

(C) Separating a neutron from neutron   (D) Separating an electron from neutral atom

52. For the combustion of 1 mole of liquid benzene at 25ºC, the heat of reaction at constant pressure is given by, $C_6H_6(l) + 7 O_2 (g) \rightarrow 6CO_2 (g) + 3H_2O (l)$; $\Delta H = -780980$ cal.

What would be the heat of reaction at constant volume?

(A) –780090 cal   (B) –780890 cal   (C) –780000cal   (D) –780900 cal

53. Calculate heat of the following reaction at constant pressure,

$F_2O(g) + H_2O(g) \rightarrow O_2 (g) + 2HF(g)$

The heats of formation of F_2O (g), $H_2O(g)$ and HF (g) are 5.5 kcal, –57.8kcal and 64.2 kcal respectively.

(A) 76.1 Kcal   (B) 11.9 Kcal   (C) 71.6 Kcal   (D) 91.1 Kcal

54. Calculate the heat of formation of benzene from the following data, assuming no resonance.

Bond energies :

C – C = 83 kcal = 140 kcal C – H = 99 kcal

Heat of atomisation of C = 170 .9 kcal

Heat of atomisation of H = 52.1 kcal

(A) 70 Kcal   (B) 75 Kcal   (C) –75 Kcal   (D) –70 Kcal

55. Calculate ΔH at 358 K for the reaction

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe (s) + 3H_2O(l)$

Given that, $\Delta H_{298} = -33.29$ kJ mole–1 and Cp for Fe_2O_3 (s), Fe (s), H_2O (l) and H_2 (g) are 103.8, 25.1, 75.3 and 28.8 J/K mole.

(A) –22.22 KJ/mole   (B) –25. 123 KJ/mole   (C) –28.136 KJ/mole (D) – 30.135 KJ/mole

56. Ka for CH_3COOH at 25ºC is 1.754×10^{-5}. At 50ºC, Ka is 1.633×10^{-5} What will be value of ΔS° for the ionisation of CH_3COOH?

(A) –94.44 J/mole K   (B) –96.66 J/mole K   (C) –96.44 J/mole K (D) –90.44 J/mole K

57. C_2H_6 (g) + 3.5 O_2 (g) → 2CO_2 (g) + 3H_2O (g)

ΔS_{vap} (H_2O, l) = x_1 cal K^{-1} (boiling point + T_1)

ΔHf (H_2O, l) = x_2

ΔHf (CO_2) = x_3

ΔHf (C_2H_6) = x_4

Hence ΔH for the reaction is –

(A) $2x_3 + 3x_2 - x_4$ (B) $2x_3 + 3x_2 - x_4 + 3x_1T_1$

(C) $2x_3 + 3x_2 - x_4 - 3x_1T_1$ (D) $x_1T_1 + X_2 + X_3 - x_4$

58. C (s) + O_2 (g) → CO_2, (g); ΔH = –94.3 kcal/mol

CO (g) + O_2(g) → CO_2 (g); ΔH = – 67.4 kcal/mol

O_2(g) → 2O (g); ΔH = 117.4 kcal/mol

CO (g) → C (g) + O(g) ; ΔH = 230.6 kcal/mol

Calculate ΔH for C (s) → C (g) in kcal/mol.

(A) 171   (B)154   (C)117   (D)145

59. The difference between ΔH and ΔE on a molar basis for the combustion of n–octane at 25°C would be : 25°C

(A) – 13.6 kJ   (B) – 1.14 kJ   (C) – 11.15 kJ   (D) + 11.15 kJ

60. What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

(A) 1294.0 cals, 11247 cals   (B) 921.4 cals, 11074 cals

(C) 1029.4 cals, 12470.6 cals   (D) 1129.3 cals, 10207 cals

61. In the reaction CS_2 (ℓ) + 3O_2 (g) ⟶ CO_2 (g) + 2SO_2 (g) ΔH = –265 kcal

The enthalpies of formation of CO_2 and SO_2 are both negative and are in the ratio 4 : 3. The enthalpy of formation of CS_2 is + 26 kcal/mol. Calculate the enthalpy of formation of SO_2.

(A) – 90 kcal/mol   (B) – 52 kcal/mol   (C) – 78 kcal/mol   (D) – 71.7 kcal/mol

62. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be

(A) – 44.0 kcal   (B) – 22.0 kcal   (C) 22.0 kcal   (D) 44.0 kcal

63. AB, A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2, AB & B_2 are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from A_2 and B_2 is – 100 kJ/mol–1. What is the bond enthalpy of A_2.

(A) 400 kJ/mol   (B) 200 kJ/mol   (C) 100 kJ/mol   (D) 300 kJ/mol

64. Given the following data :

Substance	$\Delta H°$ (kJ/mol)	$S°$(J/mol K)	$\Delta G°$ (kJ/mol)
FeO(s)	– 266.3	57.49	– 245.12
C (Graphite)	0	5.74	0
Fe(s)0	27.28	0	
CO(g)	– 110.5	197.6	– 137.15

Determine at what temperature the following reaction is spontaneous ?

FeO(s) + C (Graphite)→ Fe(s) + CO(g)

(A) 298 K

(B) 668 K

(C) 966 K

(D) $\Delta G°$ is +ve, hence the reaction will never be spontaneous

65. One mole of a gas occupying 3 dm^3 expands against constant external pressure of 1 atm to a volume of 13 dm^3. The work done is –

(A) – 10 atm dm^3 (B) – 20 atm dm^3 (C) – 39 atm dm^3 (D) – 48 atm dm^3

66. The enthalpy change in the oxidation of glucose is – 2880 kJ mol^{-1}. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometre, then the maximum distance that a person will be able to walk after eating 120 g of glucose will be

(A) 4.8 km   (B) 2.4 km   (C) 8.4 km   (D) 9.8 km

67. The heat of formation of liquid methyl alcohol is kilojoule per mole using the following data will be [Heat of vaporisation of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

Average bond energies : C – H, 415 kJ/mol; C – O, 356 kJ/mol O – H, 463 kJ/mol.]

(A) 46.0 kJ/mole   (B) 50.0 kJ/mole   (C) 73.3 kJ/mole   (D) – 266 kJ/mole

68. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. q, W, ΔE and ΔH for this process are [R = 2.0 cal K^{-1} mol^{-1}, $\log_{10}2 = 0.30$. [Atomic wt. of Ar = 40.]

(A) W = 106.635 cal, q = 103.635 cal, $\Delta E \neq 0$ & $\Delta H = 0$

(B) W = 53.635 cal, q = – 53.635 cal, $\Delta E \neq 0$ & $\Delta H = 0$

(C) W = – 53.635 cal, q = 63.635 cal, ΔE & $\Delta H \neq 0$

(D) W = 103.635 cal, q = – 103.635 cal, ΔE & $\Delta H = 0$
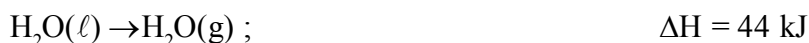
69. Molar heat capacity of water in equilibrium with ice at constant pressure is –

(A) zero   (B) infinity (∞)   (C) 40.45 kJ^{-1} mol^{-1} (D) 75.48 J K^{-1} mol^{-1}

70. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

B_2H_6 (g) + $3O_2$ (g) →B_2O_3 (s) + $3H_2O$(g)
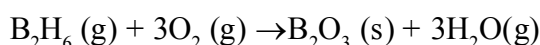
from the following data, the enthalpy change for the combustion of diborane will be

2B(s) + O_2 (g) →B_2O_3(s);	ΔH = – 1273 kJ
H_2(g) + O_2 (g) →$H_2O(\ell)$;	ΔH = – 286 kJ
$H_2O(\ell)$ →H_2O(g) ;	ΔH = 44 kJ
2B(s) + $2H_2$ (g) →B_2H_6 (g);	ΔH = 46 kJ

(A) – 2079 kJ mol–1   (B) – 1091 kJ mol–1   (C) – 2035 kJ mol–1 (D) – 762 kJ mol–1

71. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. The enthalpy change in this process will be……….

[Cv.m. for argon is 12.48 jK^{-1} mol^{-1}].

(A) 114.52 J   (B) – 114.52 J   (C) – 57.26 J   (D) 57.26 J

72. Find $\Delta G°$ and $\Delta H°$ for that the reaction $CO(g) + O_2(g) \rightarrow CO_2(g)$ at 300 K respectively are, when the standard entropy change is $- 0.094$ kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are $- 394.4$ and $- 137.2$ kJ mol^{-1}, respectively.

(A) $\Delta G° = 257.2$ kJ/mol, $\Delta H° = 285.4$ kJ/mol

(B) $\Delta G° = 514.4$ kJ/mol, $\Delta H° = - 570.8$ kJ/mol

(C) $\Delta G° = +514.4$ kJ/mol, $\Delta H° = 570.8$ kJ/mol

(D) $\Delta G° = - 257.2$ kJ/mol, $\Delta H° = - 285.4$ kJ/mol

73. $\Delta H = 30$ kJ mol^{-1}, $\Delta S = 75$ J / k / mol. Find boiling temperature at 1 atm.

(A) 400 K　　　(B) 300 K　　　(C) 150 K　　　(D) 425 K

74. Spontaneous adsorption of a gas on a solid surface is exothermic process because

(A) enthalpy of the system increases.　　(B) entropy increases.

(C) entropy decreases.　　(D) free energy change increases.

75. There is 1 mol liquid (molar volume 100 ml) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by 1 ml under constant pressure of 100 bar. Calculate ΔH and ΔE. [Given 1 bar = 105 N/m^2]

(A) $\Delta E = 0$ J, $\Delta H \neq 0$ J　　(B) $\Delta H = 0$ J, $\Delta E = 10$ J

(C) $\Delta E = 20$ J, $\Delta H = 890$ J　　(D) $\Delta E = 0$ J, $\Delta H = 10$ J

76. The ratio of P to V at any instant is constant and is equal to 1, for a monoatomic ideal gas under going a process. What is the molar heat capacity of the gas

(A) $\frac{3R}{2}$　　　(B) $\frac{4R}{2}$　　　(C) $\frac{5R}{2}$　　　(D) 0

77. The entropy values (in J K^{-1} mol^{-1}) of $H_2(g) = 130.6$ $Cl_2(g) = 223$ and HCl(g) = 186.7 at 298 K and 1 atm pressure are given. Then entropy change for the reaction.

(A) + 540.3　　　(B) +727.3　　　(C) – 166.9　　　(D) +19.8

78. A mixture of 2 mole of CO(g) and one mole of O_2 in a closed vessel, is ignited to convert the carbon monoxide to carbon dioxide. If ΔH and ΔU are enthalpy and internal energy change. Then

(A) $\Delta H > \Delta U$　　　(B) $\Delta H < \Delta U$

(C) $\Delta H = \Delta U$　　　(D) the relationship depends on the capacity of the vessel.

79. For the reaction of one mole zinc dust with one sulphuric acid in a bomb calorimeter, ΔU and w correspond to :

(A) $\Delta U < 0$, w = 0　　(B) $\Delta U < 0$, w < 0　　(C) $\Delta U > 0$, w = 0　　(D) $\Delta U > 0$, w > 0

80. If the enthalpies of formation of Al_2O_3 and Cr_2O_3 are $- 1596$ kJ and $- 1134$ kJ respectively, then the value of ΔH for the reaction ; $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is :

(A) – 462 kJ　　　(B) – 1365 kJ　　　(C) – 2530 kJ　　　(D) +2530 kJ

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

(A) < 40 kJ　　　(B) Zero　　　(C) 40 kJ　　　(D) > 40 kJ

82. $\Delta G°$ for the reaction $x + y \rightarrow z$ is $- 4.606$ kcal. The value of equilibrium constant of the reaction at 227°C is : (R = 2.0 cal K^{-1} mol^{-1})

(A) 100　　　(B) 10　　　(C) 2　　　(D) 0.01

83. The latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10 kcal/mol. What will be the change in internal energy (ΔE) of 3 moles of liquid at the same temperature?

(A) 13.0 kcal (B) – 13.0 kcal (C) 27.0 kcal (D) – 27.0 kcal

84. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litres at 25°C is :

(A) 3.43 KJ (B) 3.43 Kcal (C) 3.43 J (D) 3.43 cal

85. Reaction, $H_2(g) + I_2(g) \rightarrow 2HI$; $\Delta H = 12.40$ kcal.

According to this, heat of formation of HI will be

(A) 12.40 kcal (B) – 12.4 kcal (C) – 6.20 kcal (D) 6.20 kcal

86. The heat of combustions of yellow phosphorus and red phosphorus are – 9.91 kJ and – 8.78 kJ respectively. The heat of transition of yellow phosphorus to red phosphorus is :

(A) – 18.69 kJ (B) +1.13 kJ (B) +18.69 kJ (D) – 1.13 kJ

87. The heat of formation of $CO(g)$ and CO_2 (g) are – 26.4 kcal and – 94.0 kcal respectively. The heat of combustion of carbon monoxide will be :

(A) + 26.4 kcal (B) – 67.6 kcal (C) – 120.6 kcal (D) +52.8 kcal

88. The heats of combustion of rhombic and monoclinic sulphur are – 70960 and – 71030 calorie respectively. What will be the heat of conversion of rhombic sulphur to monoclinic sulphur?

(A) – 70960 cal (B) – 71030 cal (C) 70 cal (D) – 70 cal

89. An ideal gas expands in volume from 1×10^{-3} m³ to 1×10^{-2} m³ at 300 K against a constant pressure of 1×10^5 Nm⁻² . The work is :

(A) – 900 J (B) – 900 kJ (C) 270 kJ (D) + 900 kJ

90. The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol⁻¹ respectively. The enthalpy of formation of carbon monoxide per mole is

(A) 110.5 kJ (B) 676.5 kJ (C) – 676.5 kJ (D) – 110.5 kJ

91. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is – 200 KJ mol⁻¹. The bond dissociation energy of X_2 will be

(A) 100 KJ mol⁻¹ (B) 200 KJ mol⁻¹ (C) 300 KJ mol⁻¹ (D) 800 KJ mol⁻¹

92. Consider the reaction, $N_2(g) + 3H_2(g)$ $2NH_3(g)$; carried out at constant temperature and pressure.

If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true ?

(A) $\Delta H = 0$ (B) $\Delta H = \Delta U$ (C) $\Delta H < \Delta U$ (D) $\Delta H > \Delta U$

93. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If Ti is the initial temperature and Tf is the final temperature, which of the following statements is correct ?

(A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(B) $(T_f)_{rev} = (T_f)_{irrev}$ (C) $T_f = T_i$ for both reversible and irreversible processes

(D) $(T_f)_{irrev} > (T_f)_{rev}$

94. Identify the correct statement regarding a spontaneous process :

(A) Exothermic processes are always spontaneous.

(B) Lowering of energy in the reaction process is the only criterion for spontaneity.

(C) For a spontaneous process in an isolated system, the change in entropy is positive.

(D) Endothermic processes are never spontaneous.

95. In conversion of lime–stone to lime, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of ΔH^0 and ΔS^0 are +179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :

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

96. For a reversible process at T = 300 K, the volume is increased from V_i = 1 L to V_f = 10 L. Calculate ΔH if the process is isothermal

(A) 11.47 kJ   (B) 4.98 kJ   (C) 0   (D) – 11.47 kJ

97. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol–1, the value of enthalpy change for the reaction ;

$H_2C = CH_2(g) + H_2(g) \rightarrow H_3C-CH_3(g)$ at 298 K will be –

(A) +125 kJ   (B) —125 kJ   (C) +250 kJ   (D) — 250 kJ

98. Considering entropy(s) as thermodynamic parameter, the criterion for the spontaneity of any process is :

(A) $\Delta S_{system} + \Delta S_{surroundings} > 0$ (B) $\Delta S_{system} - \Delta S_{surroundings} > 0$

(C) $\Delta S_{system} > 0$ only   (D) $\Delta S_{surroundings} > 0$ only

99. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourization of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be :

(A) 37.904 kJ mol^{-1} (B) 41.00 kJ mol^{-1} (C) 4.100 kJ mol^{-1} (D) 3.7904 mol^{-1}

100. The standard enthalpy of formation (ΔHf°) at 398 K for methane, $CH_4(g)$ is 74.8 kJ mol^{-1}. The additional information required to determine the average energy for C – H bond formation would be.

(A)   the dissociation energy of H_2 and enthalpy of sublimation of carbon

(B)   latent heat of vapourisation of methane

(C)   the first four ionization energies of carbon and electron gain enthalpy of hydrogen

(D)   the dissociation energy of hydrogen molecule, H2

101. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively.

For the reaction, $1/2\ X_2 + 3/2\ Y_2 \rightarrow XY_3$ $\Delta H = - 30$ kJ. To be at equilibrium the temperature will be :

(A) 500 K   (B) 750 K   (C) 1000 K   (D) 1250 K

102. On the basis of the following thermochemical data : $(\Delta_f G^\circ H^+_{(aq)} = 0)$

$H_2O(\ell) \longrightarrow H^+ (aq) + OH^- (aq.)$; $\Delta H = 57.32$ kJ

$H_2(g) + O_2(g) \longrightarrow H_2O(\ell)$; $\Delta H = -286.20$ kJ

The value of enthalpy of formation of OH$^-$ ion at 25°C is :

(A) –228.88 kJ   (B) +228.88 kJ   (C) –343.52 kJ   (D) –22.88 kJ

103. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$CH_3OH(\ell) + 3/2O_2 (g) \longrightarrow CO_2(g) + 2H_2O(\ell)$

At 298 K, standard Gibb's energies of formation for $CH_3OH(\ell)$, $H_2O(\ell)$ and $CO_2 (g)$ are -166.2, -237.2 and -394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is -726kJ mol^{-1}, efficiency of the fuel cell will be :

(A) 87%   (B) 90%   (C) 97%   (D) 80%

104. The standard enthalpy of formation of NH_3 is -46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1}, the average bond enthalpy of $N-H$ bond in NH_3 is

(A) -964 kJ mol^{-1} (B) $+352$ kJ mol^{-1} (C) $+1056$ kJ mol^{-1} (D) -1102 kJ mol^{-1}

105. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If Te is the temperature at equilibrium, the reaction would be spontaneous when.

(A) Te > T   (B) T > Te   (C) Te is 5 times T   (D) T = Te

106. Choose the correct option about the following sentnences [T= True , F =False]

(i)   Ice in contact with water constitutes a homogeneous system.

(ii)   The process is known as isochoric in which the pressure remains constant throughout the change, i.e., dP = 0.

(iii) A spontaneous process is reversible in nature.

(iv)   In an isolated system, one form of energy cannot be converted into another, i.e., internal energy remains constant.

[A] FFFF   [B] TTTT   [C] FTFT   [D] FFFT

107. Choose the correct option about the following sentnences [T= True , F =False]

(i)   Molar heat capacity at constant pressure = Molar heat capacity at constant volume + PΔV.

(ii)   A spontaneous process is accompanied by a decrease in entropy.

(iii) $\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$.

(iv)   The standard heat of formation represents the formation of the compound from its elements at 25°C and one atmospheric pressure.

(v)   Whenever an acid is neutralised by a base, the net reaction is

$H^+ (aq) + OH^- (aq) \rightarrow H_2O(\ell)$; $\Delta H = -13.7$ kcal

[A] TFTTF   [B] TFTTF   [C]TFTFTF   [D] TFFFF

108. Match the following :

Column I	Column II
(i) A process carried out infinitesimally slowly	(A) Adiabatic
(ii) A process in which no heat enters or leaves the system	(B) $\Delta G = 0$
(iii) A process carried out at constant temperature	(C) Sublimation
(iv) A process in equilibrium	(D) $\Delta E = 0$, $\Delta H = 0$
(v) A(s) $\rightarrow$ A(g)	(e) Reversible
(vi) Cyclic process	(f) Isothermal

(A) (i – e, ii – a, iii – f, iv – b, v – c, vi – e)   (B) (i – e, ii – a, iii – f, iv – e v – c, vi – d)

(C) (i – e, ii – a, iii – f, iv – b, v – c, vi – d)   (D) (i – e, ii – a, iii – c, iv – b, v – f, vi – d)

109. Match the following

Column–I	Column–II
A. Isothermal process	**P.** $q = \Delta U$
B. Adiabatic process	**Q.** $w = -P\Delta V$
C. Isobaric process	**R.** $w = \Delta U$
D. Isochoric process	**S.** $w = -nRT \ln (V_2/V_1)$

(A) A= S B= R C= Q D= P (B) A= P B= Q C= R D= S

(C) A= R B= S C= Q D= P (D) A= S B= R C= P D= Q

Question 110 to 115 are reasoning question choose the correct statement.

(A) Statement –1 is true, Statement –2 is true.Statement –2 is the correct explanation for statement –1

(B) Statement –1 is true,Statement –2 is true.Statement –2 is not the correct explanation for statement –1

(C) Statement –1 is true, Statement –2 is False

(D) Statement –1 is false Statement –2 is True

110. **Statement–1 :** The enthalpy of formation of $H_2O(\ell)$ is greater than of H_2O (g).

   Statement–2: Enthalpy change is negative for the condensation reaction H_2O (g)$\rightarrow$ $H_2O(\ell)$

   (A) A   (B) B   (C) C   (D) D

111. **Statement–1 :** Heat of neutralisation of perchloric acid, $HClO_3$, with NaOH is same as that of HCl with NaOH.

   Statement–2: Both HCl and $HClO_4$ are strong acids.

   (A) A   (B) B   (C) C   (D) D

112. **Statement–1 :** When a gas at high pressure expands against vacuum, the work done is maximum.

   Statement–2: Work done in expansion depends upon the pressure inside the gas and increase in volume.

   (A) A   (B) B   (C) C   (D) D

113. **Statement–1 :** In the following reaction :$C(s) + O_2$ (g) $\rightarrow CO_2$ (g); $\quad \Delta H = \Delta U - RT$

   Statement–2: ΔH is related to U by the equation, $\Delta H = \Delta U - \Delta ng$ RT

   (A) A   (B) B   (C) C   (D) D

114. **Statement I :** The chemical reaction, $3H_2(g) + N_2(g) \longrightarrow 2NH_3$ shows decrease in entropy.

   Statement II: The process passes into equilibrium state when $\Delta GT,P$ becomes zero.

   (A) A   (B) B   (C) C   (D) D

115. **Statement I :** Both H and U are state functions.

   Statement II: Absolute values of H or U can be determined.

   (A) A   (B) B   (C) C   (D) D

116. 1 mole of NH_3 gas at 27° C is expanded adiabatic condition to make volume 8 times (γ = 1.33). Final temperature and work done respectively are –

   (A) 150 K, 900 cal   (B) 150 K, 400 cal   (C) 250 K, 1000 cal (D) 200 K, 800 cal

117. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C form 15 to 50 litres.

(A) −1438 Cal   (B) −1436 cal   (C) −1348 cal   (D) −1346 cal

118. The $\Delta H_f 0$ for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are −393.5, −110.5 and −241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is −

(A) 524.1   (B) 41.2   (C) − 262.5   (D) − 41.2

119. For reaction carried out in automobiles, what is the value of ΔH, ΔS and ΔG ?
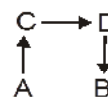
$2C_8H_{18}(g) + 25O_2(g)\ 16CO_2(g) + 18H_2O(g)$
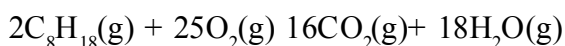
(A) +, −, +   (B) −, + , −   (C) −, +, +   (D) +, +, −

120. At 25° temperature equilibrium constant Kp for given reaction is $= 1.8\ 10^{-7}$ Then what is the value of $\Delta G°$? $PCl_5 \leftrightharpoons PCl_3 + Cl_2$

(A) +9197.5   (B) −9197.5   (C) +771   (D) −771.6

121. The conversion A to B is carried out by the following path :

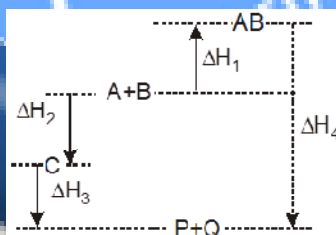Given : $\Delta S(A \rightarrow C) = 50$ e.u. , $\Delta S(C \rightarrow D) = 30$ e.u. , $DS(B \rightarrow D) = 20$ e.u.

Where e.u. is entropy unit then $\Delta S(A \rightarrow B)$ is

(A) +100 e.u.   (B) + 60 e.u.   (C) −100 e.u.   (D) − 60 e.u.

122. For the chemical reaction $A + B \longrightarrow P + Q$ two paths are given in the diagram. Which of the following relationship is correct −
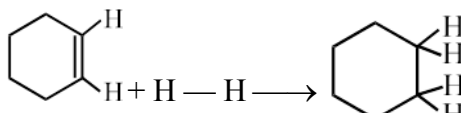

(A) $\Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4$ (B) $\Delta H_1 + \Delta H_2 = \Delta H_3 - \Delta H_4$
(C) $\Delta H_3 - \Delta H_1 = \Delta H_4 - \Delta H_2$ (D) $\Delta H_1 - \Delta H_2 = \Delta H_3 + \Delta H_4$

123. For the reaction, bond energies are given as under −

(i)   C—C, 346 kJ/mol   (ii) C—H, 413 kJ/mol
(iii)   H—H, 437 kJ/mol and   (iv) C = C, 611 kJ/mol

What will be the value of ΔH 25°C for the above reaction ?

(A) −289 kJ mol^{-1} (B) − 124 kJ mol^{-1} (C) + 124 kJ mol^{-1} (D) +289 kJ mol^{-1}

124. The value of $\Delta H_f°$ of U_3O_8 is −853.5 KJ mol^{-1}. Also $\Delta H°$ for the reaction

$3UO_2 + O_2 \longrightarrow U_3O_8$, is −76.00 KJ. The value of $\Delta H_f°$ of UO_2 is approx −

(A) −259.17 KJ   (B) −310.17 KJ   (C) + 259.17 KJ   (D) 930.51 KJ

125. The heat procued by complete neutralisation of 100 ml of HNO_3 with 300 ml of decimolar KOH solution is 1.713 kJ. The molarity of HNO_3 solution will be −

(A) 0.1   (B) 1   (C) 0.3   (D) 0.5

126. The heats of neutralisation of four acids a, b,c and d when neutralised against a common strong base are 13.7, 9.4, 11.2 and 12.4 kcal respectively. The weakest among these acids is

    (A) a   (B) b   (C) c   (D) d

127. A gas is allowed to expand at constant pressure from a volume of 1.0 litre to 10.0 litre against an external pressure of 0.50 atm. If the gas absorbs 250 J of heat from the surroundings, what are the values of q, w and ΔE ? (Given 1 L atm = 101 J)

q	w	ΔE
(A) 250 J	$-$ 455 J	$-$ 205 J
(B) $-$250 J	$-$ 455 J	$-$ 710 J
(C) 250 J	455 J	710 J
(D) $-$250 J	455 J	205 J

128. The enthalpy of the reaction

$H_2O_2(l) \rightarrow H_2O(l) + 1/2\ O_2(g)$ is $-$ 23.5 kcal mol^{-1} and the enthalpy of formation of $H_2O(l)$ is $-$ 68.3 kcal mol^{-1}. The enthalpy of formation of $H_2O_2(l)$ is $-$

    (A) $-$44.8 kcal mol^{-1} (B) 44.8 kcal mol^{-1} (C) $-$ 91.8 kcal mol^{-1} (D) 91.8 kcal mol^{-1}

129. The work done by the system in a cyclic process involving one mole of an ideal monoatomic gas is $-$50 kJ/cycle. The heat absorbed by the system per cycle is $-$

    (A) Zero   (B) 50 kJ   (C) $-$ 50 kJ   (D) 250 kJ

130. 9.0 *gm* of H_2O is vaporised at 100^{0}C and 1 atm pressure. If the latent heat of vaporisation of water is *xJ / gm*, then ΔS is given by

    (A) $\frac{x}{373}$ (B) $\frac{18x}{100}$ (C) $\frac{18x}{373}$ (D) $\frac{1}{2} \times \frac{18x}{373}$

131. Equal volumes of monoatomic and diatomic gases at same initial temperature and pressure are mixed. The ratio of specific heats of the mixture (C_p / C_v) will be

    (A) 1   (B) 2   (C) 1.67   (D) 1.5

132. The heat evolved in the combustion of benzene is given by

$C_6H_6 + 7\frac{1}{2}O_2 \rightarrow 6CO_2(g) + 3H_2O(l); \Delta H = -3264.6\,kJ$

Which of the following quantities of heat energy will be evolved when 39 $_g C_6H_6$ are burnt

    (A) 816.15 *kJ*   (B) 1632.3 *kJ*   (C) 6528.2 *kJ*   (D) 2448.45 *kJ*

133. A cylinder of gas is assumed to contain 11.2 *kg* of butane (C_4H_{10}) . If a normal family needs 20000 *kJ* of energy per day. The cylinder will last: (Given that for combustion of butane is $-$2658 *kJ*)

    (A) 20 days   (B) 25 days   (C) 26 days   (D) 24 days

134 Which expression is correct for the work done in adiabatic reversible expansion of an ideal gas

    (A) $W = nRT \ln\frac{V_2}{V_1}$ (B) $W = n_e \ln\frac{T_2}{T_1}$ (C) $W = P\Delta V$ (D) $W = -\int_1^2 PdV$

135. Calculate ΔG^o for a reaction having standard free energy change of NO_2 , NO and O_3 as 12.39, 20.72 and 39.06 Kcal/mole

    (A) 47.39   (B) 47.39   (C) 4.739   (D) $-$4.739

136. The standard Gibbs free energy change ΔG^0 is related to equilibrium constant K_p as

(A) $K_p = -RT \ln \Delta G^\circ$ (B) $K_p = \left(\dfrac{e}{RT}\right)^{\Delta G^\circ}$ (C) $K_p = -\dfrac{\Delta G^\circ}{RT}$ (D) $K_p = e^{-\frac{\Delta G^\circ}{RT}}$

137. The equilibrium concentration of the species in the reaction $A + B \equiv C + D$ are 3, 5, 10 and 15 mole L^{-1} respectively at the for the reaction is

(A) 13.81 (B) -1381.8 (C) -138.18 (D) 1391.6

138. In the reaction for the transition of carbon in the diamond form to carbon in the graphite form, ΔH is -453.5 *cal*. This points out that

(A) Graphite is chemically different from diamond

(B) Graphite is as stable as diamond

(C) Graphite is more stable than diamond

(D) Diamond is more stable than graphite

139. Which one of the following is correct ?

(A) 1 cal. > 1 erg > 1 joule   (B) 1 erg > 1 cal. > 1 joule

(C) 1 cal. > 1 joule > 1 erg   (D) 1 joule > 1 cal. > 1 erg

140. When 2 moles of water is boiled at 100° C temperature which gets converted to vapour at same temperature. Then what will be change in entropy of system ?

(A) 25.12 (B) 52.12 (C) 21.76 (D) 217.6

141. Heat of vapourisation of benzene is 7350 calorie K^{-1} mol^{-1}. Calculate the change in entropy to convert 1 mole gaseous benzene to liquid benzene at 77°C ....

(A) 21 Calorie K^{-1} mol^{-1} (B) -21 Calorie K^{-1} mol^{-1}

(C) -21 Calorie K^{-1} (D) 21 Calorie K^{-1}

142. What is the value of G° at 25°C for the reaction having equilibrium constant 4.0 ?

$C_2H_5OH + CH_3COOHCH_3COOC_2H_5 + H_2O$

(A) -82.11 (B) $+82.11$ (C) $+821.1$ (d) -821.1

143. Standard cell potential of electrochemical cell is 1.20 volt for given reaction. Calculate change in free energy in KJ associated with it. $2Ag^+ + Cd \leftrightarrows 2Ag + Cd^{+2}$

(A) 115.8 (B) -115.8 (C) -231.6 (D) 231.6

144. In reaction $x \rightarrow y$ $\Delta H = 4$ kcal/mol and $\Delta S = 10$ cal/mol k^{-1} then at what temperature reaction will be spontaneously ?

(A) 500 k (B) 350 k (C) 200 k (D) 250 k

145. For the reaction $A + B = C$, the values of standard free energy change for A, B and C are -10, -15 and -25 K.cal.mol^{-1} respectively, then what is the value of equilibrium constant ?

(A) Zero (B) One (C) More than one (D) Less than one

146. If is the change in enthalpy and the change in internal energy accompanying a gaseous Reaction

(A) ΔH is always greater than

(B) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of the reactants

(C) ΔH is always less than ΔE

(D) $\Delta H < \Delta E$ only if the number of moles of the products is less than the number of moles of the reactants

147. A schematic plot of versus inverse of temperature for a reaction is shown below

    The reaction must be

    (A) Exothermic

    (B) Endothermic

    (C) One with negligible enthalpy change

    (D) Highly spontaneous at ordinary temperature
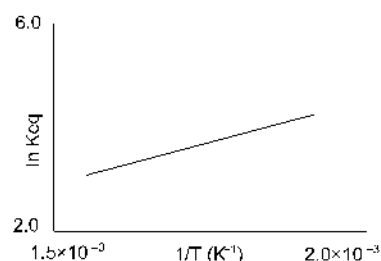
148. The heat of reaction at constant pressure is given by

    (A) $E_P - E_R$ (B) $E_R - E_P$ (C) $H_P - H_R$ (D) $H_R - H_P$

149. 2.2016 gm of acetaldehyde produced 13.95 $kcal$ of heat on combustion in O_2. Calculate the heat of combustion of CH_3CHO

    (a) 279 $kcal$ (B) 972 $kcal$ (C) 27.9 $kcal$ (D) 2.79 $kcal$

150. Calculate equilibrium constant for a reaction $2Br^{-1} + I_2 \leftrightarrows 2I^{-1} + Br_2$ $E°_{cell} = -0.544$ V

    (A) 5.01×10^{-20} (B) 5.01×10^{-19} (C) $5.01 \times 10^{+18}$ (D) 1.9×10^{18}

ANSWER KEY

1	D	2	A	3	C	4	D	5	C
6	C	7	D	8	C	9	A	10	B
11	C	12	D	13	A	14	A	15	D
16	B	17	C	18	B	19	B	20	D
21	B	22	C	23	B	24	C	25	B
26	A	27	B	28	D	29	D	30	C
31	D	32	D	33	C	34	A	35	B
36	D	37	D	38	B	39	B	40	A
41	B	42	D	43	C	44	B	45	A
46	A	47	B	48	C	49	B	50	D
51	D	52	B	53	A	54	B	55	C
56	C	57	B	58	D	59	C	60	C
61	D	62	B	63	A	64	C	65	A
66	A	67	A	68	D	69	B	70	C
71	C	72	D	73	A	74	C	75	B
76	D	77	D	78	B	79	A	80	A
81	B	82	A	83	C	84	A	85	D
86	D	87	B	88	C	89	A	90	D
91	D	92	C	93	D	94	C	95	B
96	C	97	B	98	A	99	A	100	A
101	B	102	A	103	C	104	B	105	B
106	A	107	B	108	C	109	A	110	A
111	A	112	D	113	D	114	B	115	C
116	A	117	B	118	B	119	B	120	A
121	B	122	C	123	B	124	B	125	A
126	C	127	A	128	A	129	B	130	D
131	D	132	B	133	C	134	C	135	A
136	D	137	B	138	C	139	C	140	C
141	C	142	D	143	C	144	A	145	B
146	D	147	A	148	C	149	A	150	B

Hints

(16) $$W = 2.303 \ nRT \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times 10^7 \times 298 \ \log \frac{20}{10}$$

$$= 298 \times 10^7 \times 8.314 \times 2.303 \ \log \ 2$$

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

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

(24) In an isolated system, there is no exchange of energy or matter between the system and surrounding. For a spontaneous process in an isolated system, the change in entropy is positive, i.e. $\Delta S > 0$

(52) $\Delta H = \Delta E + \Delta n_g \ RT$

Here, $\Delta n_g = 6 - 7.5 = - 1.5.$

Thus, $\Delta E = \Delta H + \Delta n_g \ RT = - 780980 - (-1.5) \times 2 \times 298 = - 780090$ calories.

(53) $F_2O (g) + H_2O (g) \rightarrow O_2 (g) + 2HF(g); \quad \Delta H = 76.1$ kcal.
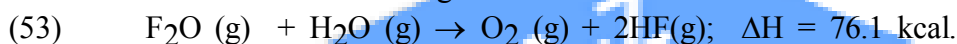
(55) $\Delta C_p = 2 \times 25.1 + 3 \times 75.3 - [103.8 + 3 \times 28.8] = 85.9$ J/K mole.

We have, $\dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$

$$\frac{\Delta H_{358} - (-33290)}{358 - 298} = 85.9$$

$\Delta H_{358} = -28136$ J/mole = −28.136 kJ/mole.

(56) $(G°)_{298} = - 2.303RT \log K = - 2.303 \times 8.314 \times 298 \times \log (1.754 \times 10^{-5}) = 27194$ J.

$(G°)_{323} = 2.303 \times 8.314 \times 323 \times \log (1.633 \times 10^{-5})$ GPT89603 J.

27H94 −298 ΔS°

29ΔS°−323 96.44J/mol.K

(59) $\Delta H - \Delta E = - 4.5 \times 8.315 \times 298$ J = − 11.15 kJ

(61) $Cs_2 (\ell) + 3O_2 (g) \rightarrow Co_2 (g) + 2SO_2 + 2SO_2 \quad \Delta H = -2$

Let $\Delta H_f (CO_2, g) = 4x$ and $\Delta H_f (SO_2 , g) = 3x$

$\Delta H_{reaction} = \Delta H_f (CO_2 ,g) = 2 \Delta H_f (SO_2 .g) - \Delta H_f (CS_2$

$- 265 = 4x + 6x - 26$

$x = -23.9$

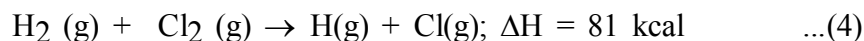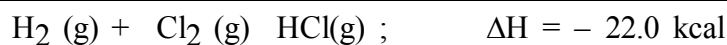$\therefore \Delta H_f (SO_2,g) = 3x = -71.7$ Kcal / mol.

(62)   Given

H_2 (g)→ HCl (g);   ΔH = 104 kcal   ...(1)
Cl_2 (g) → 2Cl(g);   ΔH = 58 kcal   ...(2)
HCl (g)→ H(g) + Cl(g);   ΔH = 103 kcal   ...(3)

Heat of formation for HCl

    H_2 (g) + Cl_2 (g) →HCl (g);   ΔH = ?

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

    H_2 (g) + Cl_2 (g) → H(g) + Cl(g); ΔH = 81 kcal   ...(4)

Subtracting equation (3) from equation (4)

    HCl (g) →H(g) + Cl(g) ;   ΔH = 103 kcal   ...(3)

    –   –   –   –
    _____

    H_2 (g) + Cl_2 (g) HCl(g) ;   ΔH = – 22.0 kcal

∴   Enthalpy of formation of HCl gas = – 22.0 kcal

(76)   From first law of Thermodynamics, $\Delta E = q + w \Rightarrow nC_VdT = nCdT - PdV$ .....(1)

Now according to process, P = V and according to ideal gas equation, PV = nRT

We have, $V^2 = nRT$

On differentiating, $2VdV = nRdT$ and $PdV = VdV = \dfrac{nRdT}{2}$

So from first equation we have, $nC_VdT = nCdT - \dfrac{nRdT}{2}$

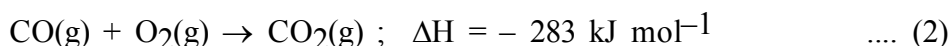So, $C_V = C - \dfrac{R}{2}$ Hence $C = \dfrac{4R}{2}$

(89)   W = – PΔV

= $- 1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3}) = - 1 \times 10^5 \times 9 \times 10^{-3} = - 900$ J.
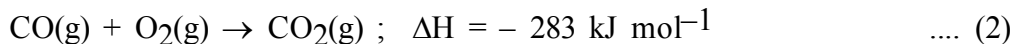
(90)   ΔH = – 393.5 kJ mol^{-1} .... (1)

$CO(g) + O_2(g) \rightarrow CO_2(g)$; ΔH = – 283 kJ mol^{-1} .... (2)

On subraction equation (2) from equation (1), we get $C(s) + O_2(g) \rightarrow CO(g)$; ΔH = – 110.5 kJ mol^{-1}.

The enthalpy of formation of carbon monoxide per mole = – 110.5 kJ mol^{-1}.

            ΔH = – 393.5 kJ mol^{-1} .... (1)

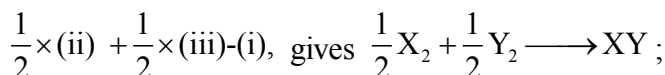$CO(g) + O_2(g) \rightarrow CO_2(g)$; ΔH = – 283 kJ mol^{-1} .... (2)

(91)   Let the bond dissociation energy of XY, X_2 and Y_2 be x,x and x, KJ/mol respectively,

$\dfrac{1}{2} X_2 + \dfrac{1}{2} Y_2 \rightarrow XY$; $\Delta H f$ = – 200 KJ mol^{-1}.
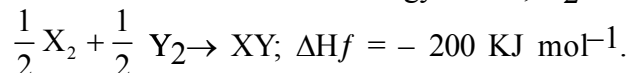
ΔHreaction = [(sum of bond dissociation energy of all reactants) – (sum of bond dissociation energy ofproduct)]

$= \left[\dfrac{1}{2}\Delta H_{x2} + \dfrac{1}{2}\Delta H_{y2} - \Delta H_{xy}\right] = \dfrac{x}{2} + \dfrac{0.5x}{2} - x = - 200$ ∴ x = = 800 KJ mol^{-1}.

Second method

$$XY \longrightarrow X_{(g)} + Y_{(g)} \qquad \Delta H = +a \; kJ/mole \; ; \qquad \ldots\ldots(i)$$

$$X_2 \longrightarrow 2X \qquad \Delta H = +a \; kJ/mole \; ; \qquad \ldots\ldots (ii)$$

$$Y_2 \longrightarrow 2Y \qquad \Delta H = 0.5 \; a \; kJ/mole \; ; \qquad \ldots\ldots (iii)$$

$\dfrac{1}{2} \times (ii) + \dfrac{1}{2} \times (iii)-(i)$, gives $\dfrac{1}{2} X_2 + \dfrac{1}{2} Y_2 \longrightarrow XY$;
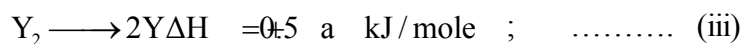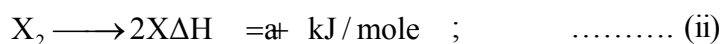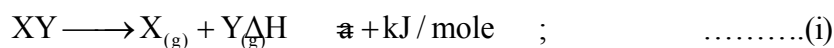
(92) $N_2 + 3H_2 \rightarrow 2NH_3$ $\qquad\qquad \Delta n = 2 - 4 = -2$

$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT.$ $\qquad \therefore \; \Delta H < \Delta U.$

(93) In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e. q = 0 and secondary w_{rev} is always greater than w_{irr}- therefore for reversible process there must be comparatively higher decreases in internal energy i.e. ΔU for reversible process will be more negative. Hence, final temperature in reversible process will be smaller than irreversible process.

$\therefore \; (T_f)_{irrev} > (T_f)_{rev}$

(94) In an isolated system, there is no exchange of energy or matter between the system and surrounding. For a spontaneous process in an isolated system, the change in entropy is positive, i.e. $\Delta S > 0$.

Most of the spontaneous chemical reactions are exothermic. A number of endothermic reaction are spontaneous e.g melting of ice (an endothermic process) is a spontaneous reaction.

The two factors which are responsible for the spontaneity of process are

(i) tendency to acquire minimum energy.

(ii) tendency to acquire maximum randomness.

(95) $\Delta G^o = \Delta H^o - T\Delta S^o$
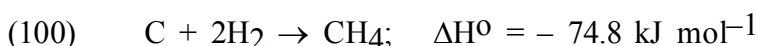
for a spontaneous process $\Delta G^o < 0$

$\qquad\qquad \Delta H^o - T\Delta S^o < 0$

$\qquad\qquad T\Delta S^o > \Delta H^o$

$\qquad\qquad T > \dfrac{\Delta H^o}{\Delta S^o} \quad T > \dfrac{179.1 \times 1000}{160.2}$

$\qquad\qquad T > 1117.9 \; K \approx 1118 \; K.$

(99) $\Delta U = \Delta H - \Delta nRT$

$\qquad = 41000 - 1 \times 8.314 \times 373 = 41000 - 3101.122$

$\qquad = 37898.878 \; J \; mol^{-1} = 37.9 \; kJ \; mol^{-1}.$

(100) $C + 2H_2 \rightarrow CH_4; \quad \Delta H^o = -74.8 \; kJ \; mol^{-1}$

In order to calculate average energy for C – H bond formation we should know the followng data.

$C(graphite) \rightarrow C(g); \Delta H_f^o$ = enthalpy of sublimation of carbon

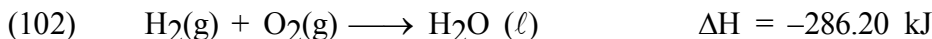$H_2 (g) \rightarrow 2H(g) \; ; \; \Delta H^o$ bond dissociation energy of H_2.
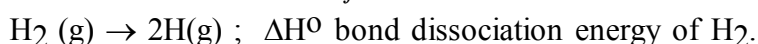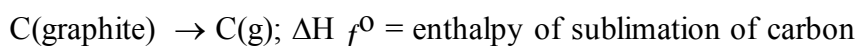
(101) $\Delta S°$ reaction $= 50 - 1/2\ (60) - 3/2\ (40) = -40\ JK^{-1}$
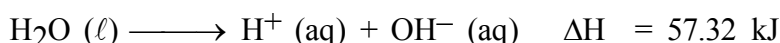
For reaction to be at equilibrium

$$\Delta G = 0$$

$$\Delta H - T\Delta S = 0 \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30000}{40} = 750\ K$$

(102) $H_2(g) + O_2(g) \longrightarrow H_2O\ (\ell) \qquad \Delta H = -286.20\ kJ$

$\Delta H_r = \Delta H_f\ (H_2O, \ell) - \Delta H_f\ (H_2, g)\ \Delta H_f\ (O_2, g)$

$-286.20 = \Delta H_f\ (H_2O\ (\ell))$

So $\Delta H_f\ (H_2O, \ell) = -286.20\ KJ/mole$

$H_2O\ (\ell) \longrightarrow H^+\ (aq) + OH^-\ (aq) \qquad \Delta H = 57.32\ kJ$

$\Delta H_r = \Delta H°_f\ (H^+, aq) + \Delta H°_f(OH^-, aq) - \Delta H°_f\ (H_2O, \ell)$

$57.32 = 0 + \Delta H°_f\ (OH^-, aq) - (-286.20)$

$\Delta H°_f\ (OH^-, aq) = 57.32 - 286.20 = -228.88\ kJ.$

(103) $CH_3OH(\ell) + 3/2\ O_2\ (g) \longrightarrow CO_2(g) + 2H_2O(\ell)$
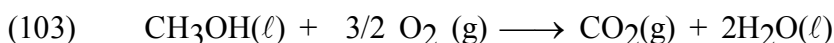
$\Delta G_r = \Delta G_f\ (CO_2, g) + 2\Delta G_f\ (H_2O, (\ell)) - \Delta G_f\ (CH_3OH, (\ell)) - \Delta G_f\ (O_2, g)$

$\qquad = -394.4 + 2\ (-237.2) - (-166.2) - 0 = -394.4 - 474.4 + 166.2 = -868.8 \times 166.2$

$\Delta G_r = -702.6\ kJ$

% efficiency $= \dfrac{702.6}{726} \times 100 = 97\%.$

(105) $\Delta G = \Delta H - T\Delta S$

For spontaneous reaction ΔG must be negative

At equilibrium temperature $\Delta G = 0$

to maintain the negative value of ΔG

T should be greater than T_e.

(117) $W = -2.303\ n\ RT \log \dfrac{V_2}{V_1} = -2.303 \times 2 \times 2 \times 298 \times \log \dfrac{50}{15} = -1436$ calories.

(120) $\Delta G° = -RT \ln Kp$

$= -2.303RT \log Kp$

$= -2.303\ \ 1.987\ \ 298\ \log 1.8\ \ 10^{-7}$

$= -2.303\ \ 1.987\ \ 298\ (-6.7447) = 9197.5\ Cal$

(131) $C_v = \dfrac{3}{2}RT;\ \ C_p = \dfrac{5}{2}RT$ for monoatomic gas

$C_v = \dfrac{5}{2}RT;\ \ C_p = \dfrac{7}{2}RT$ for diatomic gas

Thus for mixture of 1 mole each, $C_v = \dfrac{\dfrac{3}{2}RT + \dfrac{5}{2}RT}{2}$ and $C_p = \dfrac{\dfrac{5}{2}RT + \dfrac{7}{2}RT}{2}$

Therefore, $C_p / C_v = \dfrac{3RT}{2RT} = 1.5.$

(132)   78g of benzene on combustion produces heat $= -3264.6$ kJ

$\therefore$ 39g will produce $= \dfrac{-3264.6}{2} = -1632.3$ kJ.

(137) $\Delta G = -2.303\ RT\ \log\ K'$, Here $R = 2$ cal, $T = 300K$

$K' = \dfrac{10 \times 15}{3 \times 5} = 10;\quad \Delta G = -2.303 \times 2 \times 300 \times \log_{10} 10$

$= \ = -2.303 \times 2 \times 300 \times 1 = -1381.8\ $ cal

(140)   For 2 moles of water vapour, Absorbed energy by system is

$\Delta H_{vap} = 2 \times 9720 = 19440$ Cal.

$\Delta S_{vap} = \dfrac{\Delta H_{Vap}}{T_b}$

$= \dfrac{19440}{(100 + 273)}$

$= 52.12\ $ Cal. K^{-1}. $mole^{-1}$

$= 52.12\quad 4.184$

$= 217.6$ joule.K^{-1}. $mole^{-1}$

(142) $\Delta G° = -2.303\ RT\ \log k$

$= -2.303 \times 1.987 \times 298\ \log 4$

$= -1363.7\ \log 4$

$= -1363.7 \times 0.6021$

$= -821.1$ Cal.

(143) $\Delta G° = -nFE°_{cell} = -2 \times 96500 \times 1.20 J = -231.6$ KJ

(144) $\Delta G = \Delta H - T\Delta S$

$O = 4000 - T \times 10$ \qquad\qquad because $(\Delta G = 0)$

$T = 400\ k$

i.e. At 400 k, temperature reaction will be in equilibrium. But at temperature higher than 400 k the value of ΔG will be negative.

Thus at 500 k temperature reaction will be spontaneous.

(145) $\Delta G° = \Delta G°_P - \Delta G°_R$

$= \Delta G°_C - [\Delta G°_A + \Delta G°_B]$

$= -25 - [-10 - 15]$

$= -25 + 25 = 0$

$\Delta G° = 0$ \qquad so \qquad $K = 1$

(149) $\Delta H = \dfrac{13.95 \times 44}{2.2016} = 278.7$ kcal