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Time : 6 Hour

STD 11 Science Chemistry

kd 90+ ch -5 Thermodynamics

Total Marks : 170

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* Choose The Right Answer From The Given Options.[1 Marks Each] [34]

1. The energy of a system available to do work is called as:

(A) Gibbs free energy
(B) Heat of formation
(C) Heinsenberg uncertainty principle
(D) Heat of vaporization

Ans. :

a. Gibbs free energy

Explanation:

The energy of a system available to do work is called as Gibbs free energy.

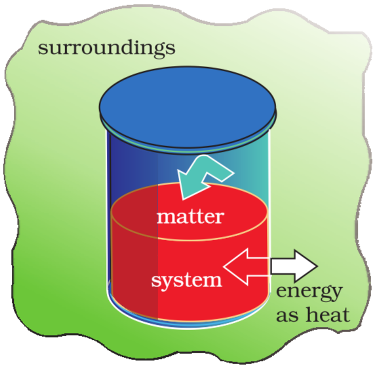
Heat required to rise one unit mass of a substance by 1 degree Celsius is known as Specific heat.

Heat absorbed or released during production of a substance from elements in their standard states is known as Heat of formation.

Heinsenberg uncertainty principle states that, "It is not possible to determine simultaneously the position and momentum of a moving microsopic particle (electron) with absolute accuracy".

Heat required to vaporize unit mass of a substance without changing its temperature at constant pressure is called Heat of vaporization.

2.



Name the type of wall used in the above figure.

(A) Adiabatic walls.
(B) Thermally insulating walls.
(C) Thermally conducting walls.
(D) None of the above.

Ans. :

c. Thermally conducting walls.

3. The heat required to raise the temperature of a body by 1K is called:

(A) Specific heat
(B) Thermal capacity
(C) Water equivalent
(D) None of these

Ans. :

b. Thermal capacity

Explanation:

The heat required to raise the temperature of a body by 1K is called thermal capacity.

In other words, when q is the heat supplied to the body and the temperature raises by 1K, then the thermal capacity of body is q.

4. The bond dissociation energies of H_2, Cl_2, and HCl are 104, 58 and 103kcal mol^{-1} respectively. The enthalpy of formation of HCl would be:

(A) -22kcal mol^{-1}
(B) -44kcal mol^{-1}
(C) +44kcal mol^{-1}
(D) +22kcal mol^{-1}

Ans. :

a. -22kcal mol^{-1}

5. Which of the following is an extensive property?

(A) Temperature.
(B) Density.
(C) Gibbs free energy.
(D) Molar volume.

Ans. :

c. Gibbs free energy.

Explanation:

Gibbs free energy is an extensive propety.

6. "The change of enthalpy of a chemical reaction is the same whether the reaction takes place in one step or in several steps". This law was presented by:

(A) Hess
(B) La Chatelier
(C) Kirchhoff
(D) Lavoisier and Laplace

Ans. :

a. Hess

Explanation:

According to Hess's law of constant heat summation, even if a chemical reaction takes place by several different routes, the change in enthalpy of the reaction will be same for all the routes.

7. Whether a reaction is endothermic or exothermic can be indicated by:

(A) Enthalpy change.
(B) Entropy change.
(C) Activation energy.
(D) Specific heat capacity.

Ans. :

a. Enthalpy change.

Explanation:

Whether a reaction is endothermic or exothermic can be indicated by enthalpy change.

Enthalpy change is the difference in the enthalpy of products and the enthalpy of reactants.

A positive value of enthalpy change indicates endothermic reaction as the enthalpy of products is more than the enthalpy of reactants.

A negative value of enthalpy change indicates exothermic reaction as the enthalpy of products is less than the enthalpy of reactants.

8. Which of the following process is non-spontaneous?

(A) Heat flow from hot end to cool end.

(B) Water flow from higher level to lower level.

(C) Gas flow from lower pressure region to higher pressure region.

(D) Gas flow from higher pressure region to lower pressure region.

Ans. :

c. Gas flow from lower pressure region to higher pressure region.

Explanation:

Gas flowing from higher pressure region to lower pressure region is a natural process. Similarly, option A and B are natural.

Natural processes are spontaneous. Therefore, flow of gas from lower pressure to higher pressure region is non-spontaneous.

9. The enthalpy change when one mole of solute dissolves in a specified amount of solvent is called:

(A) Enthalpy of dilution.
(B) Enthalpy of solution.
(C) Enthalpy of association.
(D) Enthalpy of dissociation.

Ans. :

b. Enthalpy of solution.

Explanation:

Enthalpy of solution is the enthalpy change when one mole of solute dissolved in a specified amount of solvent.

10. Hess’s law deals with:

(A) Heat changes in a chemical reaction.

(B) Rate of reaction

(C) Equilibrium constant

(D) Influence of pressure on volume of a gas

Ans. :

a. Heat changes in a chemical reaction.

Explanation:

Hess law deals with the heat changes in a chemical reaction.

11. Entropy is:

(A) A thermodynamic concept.
(B) A state function.
(C) Independent of path.
(D) All of the above.

Ans. :

d. All of the above.

12. Hess's law is based on:

(A) Law of conservation of mass.
(B) Law of conservation of energy.
(C) Law of active mass.
(D) Both (a) and (b).

Ans. :

b. Law of conservation of energy.

Explanation:

Hess's law is based on law of conservation of energy.

13. All natural processes are:

(A) Spontaneous (B) Non- spontaneous

(C) Exothermic (D) Endothermic

Ans. :

a. Spontaneous

Explanation:

A spontaneous process is one that occurs on its own, without any energy used from the outside. For example, a ball will roll down an incline; water will flow downhill; ice will melt into water; radioisotopes will decay; and iron will rust.

So all natural process are spontaneous.

14. The volume of gas is reduced to half from its original volume. The specific heat will be ______.

(A) Reduce to half. (B) Be doubled.

(C) Remain constant. (D) Increase four times.

Ans. :

c. Remain constant.

Explanation:

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

15. Which of the following properties is the measure of the degree of randomness or disorder in the system?

(A) Entropy. (B) Enthalpy.

(C) Internal energy. (D) None of these.

Ans. :

a. Entropy.

16. What is the free energy change $\triangle G$, when 1.0 mole of water at 100oC and 1 atm pressure is converted steam at 100oC and 1 atm pressure:-

(A) +540 cal (B) -9800 cal (C) +9800 cal (D) 0 cal

Ans. :

d. 0 cal

Explanation:

As we know that ΔG at equilibrium is always 0.

So, here also is equilibrium; so $\Delta G = 0$

17. Actual flame temperature is always lower than the adiabatic flame temperature, because there is ______________:

(A) no possibility of obtaining complete combustion at high temperature.

(B) always loss of heat from the flame.

(C) both (a) and (b).

(D) neither (a) nor (b).

Ans. :

c. both (a) and (b).

Explanation:

The constant volume adiabatic flame temperature is the temperature that results from a complete combustion process that occurs without any work, heat transfer or changes in kinetic or potential energy. The constant pressure adiabatic flame temperature is the temperature that results from a complete combustion process that occurs without any heat transfer or changes in kinetic or potential energy. Its temperature is lower than the constant volume process because some of the energy is utilized to change the volume of the system (i.e., generate work).

18. Combustion is:

(A) Exothermic reaction
(B) Endothermic reaction
(C) Addition reaction
(D) None of these

Ans. :

a. Exothermic reaction

Explanation:

Combustion is an oxidation reaction and during this reaction, heat is produced.

In this type of reaction, bonds are broken first and then new bonds may be created results in new material formation.

So, it is always an exothermic reaction.

19. The temperature at the bottom of a high water fall is higher than that at the top because:

(A) by itself heat flows from higher to lower temperature
(B) the difference in height causes a difference in pressure
(C) thermal energy is transformed into mechanical energy
(D) mechanical energy is transformed into thermal energy

Ans. :

d. mechanical energy is transformed into thermal energy

Explanation:

The water at the top of the waterfall, falls and gains velocity.

The potential energy it has converts into kinetic energy.

When the water lands at the bottom, the kinetic energy converts into heat and hence the water is warmer at the bottom.

20. If the bond energies of H-H, Br-Br and H-Br are 433, 192 and 364kJ mol^{-1}, respectively, then ΔH° for the reaction.
$H_2(g) + Br(g) \rightarrow 2HBr(g)$ is:

(A) -261kJ
(B) -103kJ
(C) +261kJ
(D) -1031kJ

Ans. :

b. -103kJ

Explanation:

$$\Delta H = B_{H-H} + B_{Br-Br} - 2B_{H-Br}$$
$$= 433 + 192 - 2 \times 364$$

$$= 625 - 728$$
$$= -103\text{kJ}$$

21. The most abundant element in the universe is thought to be:

(A) Hydrogen (B) Carbon (C) Oxygen (D) Nitrogen

Ans. :

a. Hydrogen

Explanation:

Hydrogen is the most abundant element in the universe followed by Helium.

22. Calculate the difference between C_P and C_V for 10 moles of an ideal gas.

(A) 83.14J (B) 8.314J (C) 831.4J (D) 0.831J

Ans. :

a. 83.14J

23. You are given a lump of an unknown metal. You perform an experiment and figure out the specific heat is close to 0.89 J/g oC. What could be the identity of the metal?

(A) Gold (B) Silver

(C) Aluminum (D) None of the above

Ans. :

e. None of the above

Explanation:

Specific heat of aluminium is close to 0.89J/ g ^{o}C.

24. Hess's law is applicable for the determination of heat of:

(A) Reaction (B) Transition

(C) Formation (D) All of the above

Ans. :

d. All of the above

Explanation:

Hess's law of constant heat summation deals with the enthalpy change for a chemical reaction. The chemical reaction can involve any chemical change. It may include formation or transition.

25. When we take acetone in a test tube it feels cold. Which reaction occurs in the process?

(A) Endothermic reaction (B) Exothermic reaction

(C) Reversible process (D) Adiabatic process

Ans. :

a. Endothermic reaction

Explanation:

Acetone is a very volatile solvent, it evaporates quickly.

The heat is absorbed from the surface.

This process is called a endothermic reaction.

26. Maximum entropy will be in which of the following?

(A) Ice. (B) Liquid water.

(C) Snow. (D) Water vapour.

Ans. :

d. Water vapour.

27. Which of the following endothermic processes are spontaneous?

(A) Melting of ice
(B) Evaporation of water
(C) Heat of combustion
(D) Both (a) and (b)

Ans. :

d. Both (a) and (b)

Explanation:

The reaction of baking soda with other acids, like hydrochloric acid, is also endothermic.

Melting of ice and Evaporation of water is show endothermic process.

28. In a thermodynamic system working subtance is ideal gas, its internal energy is in the from of:

(A) Kinetic energy only
(B) Kinetic and potential energy
(C) Potential energy
(D) None of these

Ans. :

a. Kinetic energy only

Explanation:

Internal energy is associated with the atoms or molecules of the gas.

In an ideal gas the energy is in the form of Kinetic energy only.

29. Which specific process has negative value of specific heat?

(A) Saturated vapours
(B) Ice
(C) Water
(D) Vapours

Ans. :

a. Saturated vapours

Explanation:

In case of saturated vapors, when a certain quantity of heat is removed, the temperature increases. Hence, the specific heat is negative for saturated vapors.

30. For the process to occur under adiabatic conditions, the correct condition is:

(A) $\Delta T = 0$
(B) $\Delta p = 0$
(C) $q = 0$
(D) $w = 0$

Ans. :

c. $q = 0$

31. For an ideal solution containing two liquid components A and B, the Gibbs free energy of mixing is minimum, when the molar ratio of the liquids is:

(A) 1 : 1
(B) 1 : 2
(C) 1 :10
(D) 1 : 1000

Ans. :

a. 1 : 1

32. Which of the following is not a thermodynamic coordinate?

(A) Gas constant (R)
(B) Pressure (P)
(C) Volume (V)
(D) Temperature (T)

Ans. :

a. Gas constant (R)

Explanation:

R is a constant and is not a thermodynamic constant.

33. A liquid boils at such a temperature at which the saturated vapour pressure, as compared to atmospheric pressure, is :

(A) One-third (B) Equal (C) Half (D) Double

Ans. :

b. Equal

Explanation:

The vapor pressure at which a liquid boils is equal to the atmospheric pressure**.**

34. The internal energy of a piece of lead when beaten by a hammer will:

(A) Increase

(B) Decrease

(C) Remain constant

(D) Sometimes increases and sometimes decreases

Ans. :

a. Increase

Explanation:

When beaten by a hammer the material heats up due to the impact.

As the work done by this heat is zero there is a net increase in internal energy.

*** a statement of Assertion (A) is followed by a statement of Reason (R). [2]**
Choose the correct option.

35. **Notes:** In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A) : Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

i. Both A and R are true and R is the correct explanation of A.
ii. Both A and R are true but R is not the correct explanation of A.
iii. A is true but R is false.
iv. A is false but R is true.

Ans. :

ii. Both A and R are true but R is not the correct explanation of A.

Explanation:

For spontaneus process, energy factor should be favourable means $\Delta \mathrm{H} = -\mathrm{ve}$ and randomness should be positive.

36. **Notes:** In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the Choices given below each question.

Assertion (A): Combustion of all organic compounds is an exothermic reaction.

Reason (R) : The enthalpies of all elements in their standard state are zero.

i. Both A and R are true and R is the correct explanation of A.
ii. Both A and R are true but R is not the correct explanation of A.
iii. A is true but R is false.
iv. A is false but R is true.

Ans. :
ii. Both A and R are true but R is not the correct explanation of A.

Explanation:

Combustion of organic compounds is always exothermic. Heat or enthalpy of formation of natural elements in their standard state is considered to be zero.

* Answer The Following Questions In One Sentence.[1 Marks Each] [22]

37. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890 kJ\ mol^{-1}$
What is the calorific or fuel value of 1kg of CH_4?

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

38. When 430J of work was done on a system, it lost 120J of energy as heat. Calculate the value of internal energy change (ΔU) for this process.

Ans. : $\Delta U = q + w\ q = -120J$
$\Delta U = -120 + 430\ w = +430J$
$\Delta U = 310J$

39. What is the value of ΔG when ice and water are in equilibrium?

Ans. : $\Delta G = 0$ at equilibrium.

40. Name the state variables which remain constant in:
i. Isobaric process.
ii. Isothermal process.

Ans. :
i. **Isobaric process:** In this process, pressure remains constant i.e. $\Delta p = 0$.
ii. **Isothermal process:** In this process, temperature remains constant i.e. $\Delta T = 0$.

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

Ans. : The standard molar entropy of $H_2O(l)$ is $70JK^{-1}mol^{-1}$. The solid form of H_2O is ice. In ice, molecules of H_2O are less random than in liquid water. Thus, molar entropy of $H_2O(s)$ < molar entropy of $H_2O(l)$. The standard molar entropy of $H_2O(s)$ is less than $70JK^{-1}mol^{-1}$.

42. Name the thermodynamic system to which following belong:
i. Human body.
ii. Milk in thermos flask.

Ans. :
i. Human body is an open system because it can exchange matter as well as energy with the surroundings.
ii. Milk in thermos flask is an isolated system which can neither exchange matter nor energy with the surroundings.

43.

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

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

44. Why is entropy of a solution higher than that of pure liquid?

Ans. : In solution, there is more disorderness than in pure liquid, so entropy is more.

45. Which one of the following is not extensive state function?
Enthalpy change, Internal energy change and Pressure.

Ans. : Pressure is not a state function because it depends upon path.

46. Choose the correct answer.
The enthalpies of all elements in their standard states are:
   i. Unity
   ii. Zero
   iii. < 0
   iv. Different for each element.

Ans. :
   ii. Zero

Explanation:

The enthalpy of all elements in their standard state is zero.

47. Give an example of a spontaneous process which is endothermic.

Ans. : $N_2(g) + O_2(g) \rightarrow 2NO(g)$
It is endothermic as well as spontaneous because entropy is increasing and $\Delta G = -ve.$

48. Why does entropy increase on mixing of two gases?

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

49. What is the limitation of first law of thermodynamics?

Ans. : It cannot tell us the direction of the process i.e. feasibility of Process.

50. When is the entropy of a perfectly crystalline solid zero?

Ans. : The entropy of a perfectly crystalline solid is zero at absolute zero temperature, i.e. 0K or -273.15°C because there is perfect order and no disorder at this temperature.

51. Define standard enthalpy of formation.

Ans. : It is defined as enthalpy change when I mole of substance is fanned from constituenting elements in their standard states.

52. Predict the sign of ΔS for the reaction:
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

Ans. : $\Delta S = +ve.$ because more number of products are being formed and solid reactant is changing to solid and gas.

53. Predict the sign of entropy change for the change.
$H_2O(g) \rightarrow H_2O(l)$

Ans. : $\Delta S = -ve$ because disorder or randomness is less in liquid water than steam.

54. What happens to the internal energy of the system if:

i. Work is done on the system?
ii. Work is done by the system?

Ans. :

i. If work is done on the system, internal energy will increase.
$\because \Delta U = q + w$
ii. If work is done by the system, internal energy will decrease.
$\because \Delta U = q - w$
[work is -ve when done by the system.]

55. At 1atm will the $\Delta_f H^\circ$ be zero for Cl_2(g) and Br_2(g)? Explain.

Ans. : $\Delta_f H^\circ$ for Cl_2(g) will be zero but $\Delta_f H^\circ$ for Br_2(g) will not be zero because liquid bromine is its elementary state and not gaseous bromine.

56. How can you say that universe is going towards chaos?

Ans. : Most of the naturally occurring processes are accompanied by increase of randomness. Hence, randomness of the universe is continuously increasing. Thus, we are going towards chaos.

57. If ΔG° for reversible reaction is found to be zero, what is the value of its equilibrium constant?

Ans. : $\Delta G^\circ = 0 \text{ (given)}$
$\Delta G^\circ = -2.303 \text{ RT} \log K = 0$
$\Rightarrow \log K = 0$
$\Rightarrow \log K = \log 1$
$\Rightarrow K = 1. [\because \log 1 = 0]$

58. Why is standard enthalpy of formation of diamond not zero although it is an element?

Ans. : It is because diamond is not standard state of element. Standard state of carbon is graphite whose $\Delta_f H^\circ = 0$.

*** Given Section consists of questions of 2 marks each. [24]**

59. Calculate the total entropy change, ΔS_{total} and state if the process is spontaneous, when one mole of liquid mercury Hg(l) changes to mercury vapour, Hg(g) at 298K. The molar entropy of vapourisation of Hg is 99$JK^{-1}mol^{-1}$ and molar enthalpy of vapourisation is 59.1k J mol^{-1}.

Ans. : $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-59100\text{J mol}^{-1}}{298\text{K}}$
$= -198\text{JK}^{-1}\text{mol}^{-1}$
$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
$= 99\text{J} - 198\text{J} = -99\text{JK}^{-1}\text{mol}^{-1}$
Since $\Delta S_{\text{total}} = -\text{ve}$, therefore, process is non-spontaneous at 298K.

60. Derive the relationship between isothermal and free expansion of an ideal gas.

Ans. : Work done in isothermal reversible expansion of an ideal gas

$$w = -2.303n\,RT\log\frac{V_2}{V_1}$$

$$= -2.303n\,RT\log\frac{P_1}{P_2}$$

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

$$w = -P_{ext}\Delta V$$

$$P_{ext} = 0$$

$$w = 0$$

61. ΔH and ΔS for a reaction are found to be -10000J mol^{-1} and -33.3JK^{-1}. Under what conditions reaction will proceed in reverse direction.

Ans. : $\Delta G = \Delta H - T\Delta S$

$$0 = -10000 - T \times (-33.3)J$$

$$\Rightarrow T = \frac{10000}{33.3} = 300.3K$$

The reaction will proceed in backward direction above 300.3K because ΔG will +ve for forward reaction above 300.3K, hence ΔG will -ve for backward reaction.

62. What is bond energy? Why is it called enthalpy of atomisation?

Ans. : 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 1 mole of a gaseous molecule into constituting atoms.

63. A 1.25g sample of octane (C_8H_{18}) is burnt in excess of oxygen in a bomb calorimeter. The temperature of calorimeter rises from 294.05 to 300.78K. If heat capacity of the calorimeter is 8.93kJ K^{-1}. Find heat transferred to calorimeter.

Ans. : $m = n \times c \times (T_2 - T_1)$

$$= \frac{\text{mass}}{\text{molar mass}} \times C \times (T_2 - T_1)$$

$$= \frac{1.25}{114} \times 8.93\text{kJ K}^{-1} \times (300.78K - 294.05K)$$

$$= \frac{1.25 \times 8.93 \times 6.73}{114} = \frac{75.124}{124}$$

$$= 0.66\text{kJ mol}^{-1}$$

64. Consider the following reaction:

$H_2(g) + F_2(g) \rightarrow 2HF(g)$

$$\Delta H^\circ = -542kJ,\ \Delta S^\circ = 14JK^{-1}$$

Calculate the ΔG° value for the reaction and state if the reaction is spontaneous at 298K.

Ans. : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = -542kJ - \frac{298 \times 14}{1000}kJ$$

$$= -542 - 4 = -546kJ$$

Since ΔG° is negative, therefore, reaction is spontaneous at 298K.

65. Establish a relationship between ΔH and ΔU in Haber's process of synthesis of ammonia assuming that gaseous reactants and products are ideal.

Ans. : Haber's process of synthesis for ammonia is,

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

$$\Delta n_g = 2 - (1+3) = -2$$

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

$$\therefore \Delta H = \Delta U - 2RT$$

66. 18.0g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

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

$$18\text{g of } H_2O = 1\text{mole}\left(\Delta H_{vap} = 40.79\text{kJ mol}^{-1}\right)$$

Enthalpy change for vapourising 2 moles of H_2O = 2 × 40.79 = 81.58kJ ΔH°_{vap} = 40.79kJ mol^{-1}

67. Give one point to differentiate the following thermodynamic terms:

a. Extensive properties and intensive properties.

b. Isothermal process and isobaric process.

Ans. :

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 properties 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.

68. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298K. (Given, lattice energy of NaCl = -777.8kJ mol^{-1}, hydration energy = -774.1kJ mol^{-1} and $\Delta S = 0.043\text{kJ K}^{-1}\text{mol}^{-1}$ at 298K).

Ans. : $\Delta H =$ hydration energy - lattice energy

$$\Delta H = -774.1\text{kJ mol}^{-1} - (-777.8\text{kJ mol}^{-1})$$

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

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

$$= +3.7 - 298 \times 0.043 = +3.7 - 12.81$$

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

69. The standard heat of formation of CH_4(g), CO_2(g) and H_2O(g) are -76.2, -394.8 and -241.6kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1m^3 of

methane measured at NTP.

Ans. : The burning of methane may be expressed as,

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

$\Delta_f H^\circ = [\Delta_f H^\circ(CO_2) + 2\Delta_f H^\circ(H_2O)]$

$- [\Delta_f H^\circ(CH_4) + 2\Delta_f H^\circ(O_2)]$

$= [-394.8 + 2 \times (-241.6)] - [-76.2 + 2 \times 0]$

$= -801.8kJ$

1 mole or 22.4L of CH_4 evolve heat = 801.8kJ

$1m^3$ or 1000L of CH_4 evolve heat $= \frac{801.8 \times 1000}{22.4}$

= 35794.6kJ

70. The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^\ominus$? R = $8.314JK^{-1}\ mol^{-1}$, T = 300K.

Ans. : $\Delta G^\ominus = -RT \ln k = -2.303RT \log K.$

$R = 8.314Jk^{-1}\ mol^{-1}; T = 300K; K = 10$

$\Delta G^\ominus = -2.303 \times 8.314Jk^{-1}\ mol^{-1} \times (300k) \times \log 10$

$= -5527J\ mol^{-1} = -5.527kJ\ mol^{-1}.$

*** Given Section consists of questions of 3 marks each. [60]**

71. The heat of combustion of C_2H_6 is -368.4kcal. Calculate heat of combustion of C_2H_4, heat of combustion of H_2 is 68.32kcal mol^{-1}. ΔH for the following reaction is -37.1kcal.

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

Ans. : $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g);$

$\Delta H = -37.1kcal$

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

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

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

$\Delta H = \Delta_c H^\ominus C_2H_4 + \Delta_c H^\ominus H_2(g)$

$- \Delta_c H^\ominus C_2H_6(g)$

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

$\Delta_c H^\ominus C_2H_4 = -337.18kcal$

72. Two moles of an ideal gas initially at 27°C and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10atm. Calculate q, W and ΔU for the process.

Ans. : Here, n = 2 moles, T = 27°C = 300K, P_1 = 1atm, P_2 = 10atm

$W = 2.303nRT \log \frac{p_2}{p_1}$

$= 2.303 \times 2 \times 8.314JK^{-1}mol^{-1} \times 300K$

$\times \log \frac{10}{1} = 11488.28J$

For isothermal compression of ideal gas, $\Delta U = 0$

Further, $\Delta U = q + W$

$\therefore \mathrm{q} = -\mathrm{W} = -11488\mathrm{J}$

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

Ans. : Mass of Al = 60g

Rise in temperature, $\Delta \mathrm{T} = 55 – 35 = 20^{\circ}\mathrm{C}$

Molar heat capacity of Al $= 24\mathrm{J\ mol}^{-1}\mathrm{K}^{-1}$

Specific heat capacity of Al $= \frac{24}{27}\mathrm{Jg}^{-1}\ \mathrm{K}^{-1}$

$\therefore$ Energy required $\mathrm{m} \times \mathrm{c} \times \Delta\mathrm{T}$

= $60 \times \frac{24}{27} \times 20 = \frac{28800}{27} = 1066.67\mathrm{J}$

$= 1.068\mathrm{kJ}$ or $1.07\mathrm{kJ}$

74. In a process, 701J of heat is absorbed by a system and 394J of work is done by the system. What is the change in internal energy for the process?

Ans. : According to the first law of thermodynamics,

$\Delta\mathrm{U} = \mathrm{q} + \mathrm{W}(\mathrm{i})$

Where,

$\Delta\mathrm{U} =$ change in internal energy for a process

q = heat

W = work

Given,

q = +701J (Since heat is absorbed)

W = –394J (Since work is done by the system)

Substituting the values in expression (i), we get

$\Delta\mathrm{U} = 701\mathrm{J} + (-394\mathrm{J})$

$\Delta\mathrm{U} = 307\mathrm{J}$

Hence, the change in internal energy for the given process is 307J.

75. It has been found that 221.4J is needed to heat 30g of ethanol from 15° to 18°. Calculate:

a. specific heat capacity.

b. molar heat capacity of ethanol.

Ans. :

a. $\mathrm{q} = \mathrm{m} \times \text{specific heat} \times (\mathrm{T}_2 - \mathrm{T}_1)$

$\mathrm{T}_1 = 15^{\circ}\mathrm{C} + 273 = 288\mathrm{K}$

$\mathrm{T}_2 = 18^{\circ}\mathrm{C} + 273 = 291\mathrm{K}$

$221.4\mathrm{J} = 30\mathrm{g} \times \text{specific heat} \times (291\mathrm{K} - 288\mathrm{K})$

$\text{Specific heat} = \frac{221.4}{30 \times 3} = 2.46\mathrm{J\ g}^{-1}\mathrm{K}^{-1}$

b. Molar heat capacity = specific heat × Molar mass of C_2H_5OH

$= 2.46\mathrm{J\ g}^{-1}\mathrm{K}^{-1} \times 46\mathrm{g\ mol}^{-1}$

$= 113.16\mathrm{J\ K}^{-1}\mathrm{mol}^{-1}$

76. Calculate the work done when 11.2g of iron dissolves in hydrochloric acid in:

i. A closed vessel.

ii. An open beaker at 25°C (Atomic mass of Fe = 56u).

Ans. : Iron reacts with hydrochloric acid to produce H, gas as

$Fe(s) + 2HCl\ (aq) \rightarrow FeCl_2(aq) + H_2(g)$

Thus, 1 mole of Fe, i.e. 56g Fe produces H_2 gas = 1mol.

$\therefore$ 11.2g Fe will produce H_2 gas $= \frac{1}{56} \times 11.2 = 0.2\text{mol}$

i. If the reaction is carried out in closed vessel, $\Delta V = 0$

$\therefore W = -p_{ext}\Delta V = 0$

ii. If the reaction is carried out in open beaker (external pressure being 1atm)

Initial volume = 0 (because no gas is present)

Final volume occupied by 0.2 mole of H_2 at 25°C and 1atm pressure can be calculated as follows pV = nRT

$\therefore V = \frac{nRT}{p}$

$= \frac{0.2\text{mol} \times 0.0821\text{L atm K}^{-1}\text{mol}^{-1} \times 298\text{K}}{1\text{atm}}$

$= 4.89\text{L}$

$\therefore \Delta V = V_{final} - V_{initial} = 4.89\text{L}$

$W = -p_{ext}\Delta V = -1\text{atm} \times 4.89\text{L}$

$= -4.89\text{L atm} = -4.89 \times 101.3\text{J}$

$= -495.4\text{J}$

77. What is meant by entropy? Predict the sign of entropy change in each of the following:

i. H_2 (at 298K, 1atm) → H_2 (at 298K, 10atm)
ii. H_2O (at 298K, 1atm) → H_2O (at 330K, 1atm)
iii. $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(8)$
iv. Crystallization of copper sulphate from its saturated solution.
v. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.

Ans. : 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. $\Delta S = -ve$

78. 10g of argon is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate q, W, ΔU and ΔH for this process. R = 2.0cal K^{-1} mol^{-1}, log2 = 0.30, atomic weight, of Ar = 40.

Ans. : $q = 2.303nRT\log\frac{V_2}{V_1}$

$= 2.303 \times \frac{10}{40} \times 300 \times \log\frac{5}{10}$

$= -103.635\text{cal}$

For isothermal expansion, $\Delta U = 0$

$W = \Delta U - q = 0 - (-103.635)$

$= +103.635\text{cal}$

Also, when temperature is constant,

$p_1V_1 = p_2V_2$ or pV = constant

$$\Delta H = \Delta E + \Delta(pV) = 0 + 0 = 0$$

79. $X(g) + 3Y(g) \rightleftharpoons 2Z(g); \Delta H = -40kJ$ and s° of X, Y and Z are 60, 40 and 50kJ^{-1} mol^{-1} respectively. Calculate the temperature above or below which reaction become feasible?

Ans. : $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$

$$= 2 \times 50 - 60 - 3 \times 40$$

$$= 100 - 60 - 120$$

$$= -80Jk^{-1}mol^{-1}$$

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

$$0 = -40000J - T \times (-80)$$

$$80T = 40000$$

$$T = 500K$$

Below 500K, reaction will be spontaneous.

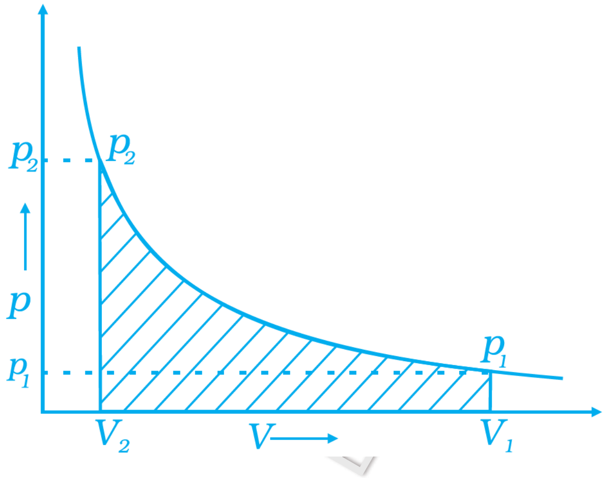
$\therefore \Delta G$ will be -ve because both ΔH and ΔS are - ve.

$$\therefore \Delta H > T\Delta S$$

80. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

Ans. :

The work done can be calculated with the help of p–V plot. A p–V plot of the work of compression which is carried out by change in pressure in infinite steps, is given in Fig. Shaded area represents the work done on the gas.



81. 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 400K is 1.958×10^{-4} and $\Delta H^\circ = 77.2kJ\ mol^{-1}$ (R = 8.314J K^{-1}mol^{-1}).

Ans. : $\Delta S = S_T - S_0$

Where S_T is entropy at temperature TK

But from third law, $S_0 = 0$

Where S_0 is entropy at 0K

$$\therefore S_T = \Delta S$$

If we measure the energy required to raise the temperature of a crystalline substance from 0K to 298K, we can determine entropy change. The entropy S_T at 298K is called absolute entropy.

$$\Delta G^\circ = -2.303RT\log K$$
$$= -2.303 \times 8.314JK^{-1}mol^{-1}$$
$$\times 400K\log 1.958 \times 10^{-4}$$
$$= (-19.147 \times 400\log 1.958 \times 10^{-4})J\ mol^{-1}$$
$$= [-7658.8 \times (\log 1.958 + \log 10^{-4})]J\ mol^{-1}$$
$$= [-7658.8 \times (0.2917 - 4.0000)]J\ mol^{-1}$$
$$\Delta G^\circ = -7658.8 \times -3.7183 = +28477.72J\ mol^{-1}$$
$$= 28.48kJ\ mol^{-1}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$28.48kJ\ mol^{-1} = 77.20kJ\ mol^{-1} - 400\Delta S^\circ$$
$$-400\Delta S^\circ = -48.73kJ\ mol^{-1}$$
$$\Delta S^\circ = \frac{48.73 \times 1000J\ mol^{-1}}{400K} = \frac{487.3}{4}$$
$$= 121.82JK^{-1}mol^{-1}$$

82.
  i. State first law of thermodynamics.
  ii. Heat (q) and work function (w) individually are not state functions but their sum is always a state function. Why?
  iii. Define extensive property with example.

Ans. :

i. **First law of thermodynamics:** It states energy can neither be created, nor be destroyed. It can change from one from to another. The total energy of universe remains constant.

$$\Delta U = q + w$$

ii. 'q' and 'w' depend upon path, therefore, these are path function.

$$q + w = \Delta U$$

ΔU is internal energy change which is state function because it depends upon initial and final state of the system and not on path, therefore, 'q + w' is state function.

iii. **Extensive property:** The property which depends upon amount of substance is called extensive property, e.g., mass, volume are extensive properties.

83. 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume of V_1 to a final volume of $10V_1$ and does 10kJ of work. The initial pressure was 1×10^7Pa.
  i. Calculate V_1.
  ii. If there were 2 moles of gas, what must its temperature have been?

Ans. :

i. We know that $W = -2.303nRT\log\frac{V_2}{V_1}$

$$10 \times 10^3 \mathrm{J} = 2.303 \times 1 \times 8.314$$
$$\times \mathrm{T} \times \log \frac{10\mathrm{V}_1}{\mathrm{V}_1}$$

T = 522.3K

For initial conditions, $p_1V_1 = n_1RT$,

i.e., $(10^7 \text{Pa})V_1 = 1 \times 8.314 \times 522.3$

$V_1 = 4.342 \times 10^{-4} m^3$

$= 4.342 \times 10^2 cm^3$

$= 434.2 cm^3$

We cannot apply the formula $-\mathrm{W} = \mathrm{p}\Delta\mathrm{V}$ because expansion is not against constant pressure.

ii. If there were 2 moles of the gas, applying $p_1V_1 = n_1RT$, we get $(10^7 \text{Pa})(4.342 \times 10^{-4} m^3) = 2 \times 8.314T$ or T = 261.1K, i.e. half of the first value.

84. i. Classify the following processes as reversible or irreversible:
   - a. Dissolution of sodium chloride.
   - b. Evaporation of water at 373K and 1atm pressure.
   - c. Mixing of two gases by diffusion.
   - d. Melting of ice without rise in temperature.

ii. When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?

Ans. :

i.
   - a. Reversible.
   - b. Irreversible.
   - c. Irreversible.
   - d. Reversible.

ii. It is because no work is done.

i.e., w = 0

$$\because \mathrm{w} = -\mathrm{P}_{\text{ext}} \times \Delta\mathrm{V} = 0 \times \Delta\mathrm{V} = 0$$

$$\Delta\mathrm{U} = \mathrm{q} + \mathrm{w}$$

q = 0 because gas chamber is insulated

$$\therefore \Delta\mathrm{U} = 0 + 0 = 0$$

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

Ans. : Heat capacity of the calorimeter, Cv =20.7KJ/ mol

The temperature change is not mentioned in the question,

so we assume it to be, $\Delta\mathrm{T} = 1\mathrm{K}$

Thus

heat absorbed by the calorimeter

$= \mathrm{Cv} \times \Delta\mathrm{T}$

$= 20.7 \times 1 = 20.7\mathrm{KJ}$

This is the heat evolved in combustion of 1g graphite

So, heat evolved in combustion of 1mole of graphite i.e 12g of graphite = 20.7 × 12 = 284.4KJ

Since heat is evolved and vessel is closed enthalpy change of reaction = -284.4KJ/ mol

−ve sign signifies heat evolved.

86. Give the appropriate reason.

i. It is preferable to determine the change in enthalpy rather than the change in internal energy.
ii. It is necessary to define the 'standard state'.
iii. It is necessary to specify the phases of the reactants and products in a thermochemical equation.

Ans. :

i. Because it is easier to make measurement under constant pressure than under constant volume conditions.
ii. Enthalpy change depends upon the conditions in which a reaction is carried out. For making the comparison of results obtained by different people meaningful, the reaction conditions must be well-defined.
iii. Because enthalpy depends upon the phase of reactants and products.

87. Given

$$\mathrm{N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \Delta_r H^{\ominus} =- 92.4kJ\ mol^{-1}}$$

What is the standard enthalpy of formation of NH_3 gas?

Ans. : Standard enthalpy of formation of a compound is the change in enthalpy that takes place during the formation of 1 mole of a substance in its standard form from its constituent elements in their standard state.

Re-writing the given equation for 1 mole of $NH_{3(g)}$,

$$\frac{1}{2}\mathrm{N_{2(g)}} + \frac{3}{2}\mathrm{H_{2(g)}} \longrightarrow \mathrm{NH_{3(g)}}$$

∴ Standard enthalpy of formation of $NH_{3(g)}$

$$= \frac{1}{2}\Delta_r H^{\ominus}$$

$$= \frac{1}{2}(-92.4\mathrm{kJ})\ \mathrm{mol}^{-1}$$

$$= -46.2\mathrm{kJ\ mol}^{-1}$$

88. A man takes a diet equivalent to 10000kJ per day and does work, in expending his energy in all forms equivalent to 12500kJ per day. What is change in internal energy per day? If the energy lost was stored as sucrose (1632kJ per 100g), how many days should it take to lose 2kg of his weight? (Ignore water loss)

Ans. : Energy taken by a man = 10000kJ

Change in internal energy per day = 12500 - 10000 = 2500kJ The energy is lost by the man as he expends more energy than he takes. Now 100g of sugar corresponds to energy = 1632kJ loss in energy.

2000g of sugar corresponds to energy $= \frac{1632\times2000}{100}$

= 32640kJ

∴ Number of days required to lose 2000g of weight or 32640kJ of energy

$$= \frac{32640}{2500} = 13\mathrm{days}$$

89. 100mL of a liquid is contained in awn insulated container at a pressure of 1bar. The pressure is steeply increased to 100bar. The volume of the liquid is decreased by 1mL at this constant pressure. Find $\Delta\mathrm{H}$ and $\Delta\mathrm{U}$.

Ans. : p_1 = 1bar, p_2 = 100bar, V_1 = 100mL, V_2 = 99mL

For adiabatic process, q = 0, $\Delta U = q + W$

$$\Delta U = W$$

$$W = -p\Delta V$$

$$= -100(99 - 100) = 100\text{bar mL}$$

$$\Delta H = \Delta U + \Delta pV$$

$$= 100 + p_2V_2 - p_1V_1$$

$$= 100 + (100 \times 99) - (1 \times 100)$$

$$= 100 + 9900 - 100 = 9900\text{bar mL}$$

90. Differentiate between the following (with examples)

    i. Open and closed system.
    ii. Adiabatic and isothermal process.
    iii. State function and path function.

Ans. :

i. **Open system:** Open system is a system which can exchange both matter as well as energy e.g. a cup of tea.

Closed system: Closed system is a system which can exchange energy but not matter e.g. tea placed in closed kettle.

ii. **Adiabatic process:** Adiabatic process is a process in which no exchange of heat takes place with the surrounding e.g. carrying out reaction in a isolated system. The conductor should have non-conducting walls.

Isothermal process: Isothermal process is a process in which no change in temperature takes place e.g. thermostat maintains constant temperature by exchanging heat with the surroundings.

iii. **State function:** It depends upon initial and final state of the system and not on path e.g. ΔU (internal energy change)

Path function: It depends upon path e.g. work.

* Case study based questions [8]

91. Read the passage given below and answer the following questions from (i) to (v).

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g); \triangle_r H^\ominus = -46.1 kJmol^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g); \triangle_r H^\ominus = -92.32 kJmol^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \triangle_r H^\ominus = -285.8 kJmol^{-1}$$

A spontaneous process is an irreversible process and may only be reversed by some external agency.

If we examine the phenomenon like flow of Water down hill or fall of a stone on to the Ground, we find that there is a net decrease in Potential energy in the direction of change. By Analogy, we may be tempted to state that a Chemical reaction is spontaneous in a given Direction, because decrease in energy has Taken place, as in the case of exothermic Reactions. For example:

The decrease in enthalpy in passing from Reactants to products may be shown for any Exothermic reaction on an enthalpy diagram. Thus, the postulate that driving force for a Chemical reaction may be due to decrease in Energy sounds 'reasonable' as the basis of Evidence so far ! Now let us examine the following reactions:

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \triangle_r H^{\ominus} = +33.2 kJmol^{-1}$

$C(graphite,s) + 2s(l) \rightarrow CS_2(l); \triangle_r H^{\ominus} = +128.5 kJmol^{-1}$

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases .

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has randomising influence on the system. Temperature is the measure of average chaotic motion of particles in the system. The entropy change is inversely proportional to the temperature. $\triangle S$ is related with q and T for a reversible reaction as:

$\triangle S = \frac{q_{rev}}{T}$

The total entropy change $(\triangle S_{total})$ for the system and surrounding of a spontaneous process is given by $\triangle S_{total} = \triangle S_{system} + \triangle S_{surr}.0$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\triangle S = 0$. We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$\triangle S_{sys} = \frac{q_{rev,rew}}{T}$

G = H – TS

Gibbs function, G is an extensive property and a state function. The change in Gibbs energy for the system, $\triangle G_{sys}$ can be written as

$\therefore \triangle G_{sys} = \triangle H_{sys} - T\triangle S_{sys} - S_{sys}\triangle T$

At constant temperature, $\triangle T = 0$

$\triangle G_{sys} = \triangle H_{sys} - T\triangle S_{sys}$

Usually the subscript ‘system’ is dropped and we simply write this equation as

$\triangle G = \triangle H – T\triangle S$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of $\triangle H$) and entropy ($\triangle s$, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that $\triangle G$ has units of energy because, both $\triangle H$ and the $T\triangle S$ are energy terms, since $T\triangle S = (K)(J/K) = J$. Now let us consider how $\triangle G$ is related to reaction spontaneity. We know, $\triangle S_{systeam} + \triangle S_{surrounding}$ If the system is in thermal equilibrium with The surrounding, then the temperature of the Surrounding is same as that of the system. Also, increase in enthalpy of the surrounding Is equal to decrease in the enthalpy of the System. Therefore, entropy change of Surroundings,

$\triangle S_{surr} = \frac{\triangle H_{surr}}{T} - \frac{\triangle H_{sys}}{T}$

$\triangle S_{total} = S_{sys} + \left(- \frac{\triangle H_{sys}}{T}\right)$

Rearrangine the above equation:

$T\triangle S_{total} = T\triangle S_{sys} - \triangle H_{sys}$

For spontaneous process,

$\triangle S_{total} > 0$, so

$T\triangle S_{sys} - \triangle H_{sys} > O$

$\Rightarrow -(\triangle H_{sys} - T\triangle S_{sys})$

Using equation, the above equation can Be written as:

$$-\triangle \mathrm{G} > \mathrm{O}$$

$$\triangle \mathrm{G} = \triangle \mathrm{H} - \mathrm{T}\triangle \mathrm{S}, 0$$

$$\triangle \mathrm{H}_{\mathrm{sys}}$$

Is the enthalpy change of a reaction, $\mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}}$ Is the energy which is not available to Do useful work. So $\triangle \mathrm{G}$ is the net energy Available to do useful work and is thus a Measure of the ‘free energy. For this reason, it Is also known as the free energy of the reaction. $\triangle \mathrm{G}$ gives a criteria for spontaneity at Constant pressure and temperature.

If $\triangle \mathrm{G}$ is negative (< 0), the process is

b) If $\triangle \mathrm{G}$ is positive (> 0), the process is non

Entropy and Second Law of Thermodynamics – For an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Absolute Entropy and Third Law of Thermodynamics Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing q T rev increments from 0K to 298K. Standard entropies can be used to calculate standard entropy changes by a Hess’s law type of calculation.

$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D};$ is $\triangle_{\mathrm{r}} \mathrm{G} = 0$

A knowledge of the sign and Magnitude of the free energy change of a Chemical reaction allows: Prediction of the spontaneity of the Chemical reaction. Prediction of the useful work that could Be extracted from it. So far we have considered free energy Changes in irreversible reactions. Let us now Examine the free energy changes in reversible Reactions.‘Reversible’ under strict thermodynamic Sense is a special way of carrying out a Process such that system is at all times in Perfect equilibrium with its surroundings. When applied to a chemical reaction, the Term ‘reversible’ indicates that a given Reaction can proceed in either direction Simultaneously, so that a dynamic Equilibrium is set up. This means that the Reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy. So, the criterion for equilibrium

Gibbs energy for a reaction in which all reactants and products are in standard state, $\triangle_{\mathrm{r}} \mathrm{G} = 0$ is related to the equilibrium constant of the reaction as follows:

$$0 = \triangle_{\mathrm{r}} \mathrm{G}^{\ominus} + \mathrm{RTlnK}$$

or $\triangle_r G^\ominus = -RT\ln K$

or $\triangle_r G^\ominus = -2.303RT\log K$

We also know that

$$\triangle_r G^\ominus = \triangle_r H^\ominus - T\triangle_r S^\ominus - RT\ln K$$

For strongly endothermic reactions, the value of $\triangle_r H^\phi$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\triangle_r H^\phi$ is large and negative, and $\triangle_r G^\phi$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\triangle_r G^\phi$ also depends upon $\triangle_r S^\phi$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\triangle_r S^\phi$ Is positive or Negative, It is possible to obtain an estimate of $\triangle G^0$ From the measurement of $\triangle H^0$ And $\triangle S^0$, And then calculate K at any temperature For economic yields of the products. If K is measured directly in the Laboratory, value of $\triangle G^0$ At any other Temperature can be calculated.

i. A spontaneous process is an ... process.
   a. Irreversible
   b. Reversible
   c. Partially irreversible
   d. Partially reversible
ii. $\triangle S_{\text{systeam}} + \triangle S_{\text{surrounding}}$
   a. < 0
   b. > 0
   c. = 0
   d. None of above
iii. When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\triangle S.\,.\,.\,.\,.0.$
   a. <
   b. >
   c. =
   d. None of above
iv. ... does not discriminate between reversible and irreversible process:
   a. $\triangle H$
   b. $\triangle S$
   c. $\triangle G$
   d. $\triangle U$
v. $T\triangle S = \ \ldots$
   a. Kg
   b. J
   c. M
   d. lit

Ans. :

i. (a) Irreversible
ii. (b) > 0
iii. (c) =
iv. (d) $\triangle U$
v. (b) J

92. Read the passage given below and answer the following questions from (i) to (v).

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The universe = The system + The surroundings However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

The wall that separates the system from the surroundings is called boundary.

Types of the System We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system. Here the boundary is an imaginary surface enclosing the beaker and reactants.
2. Closed System In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.
3. Isolated System In an isolated system, there is no exchange of energy or matter between the system and the surroundings. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

The State of the System The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by state functions or state variables. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values. The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\triangle \mathrm{U} = \mathrm{q} + \mathrm{w}$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $\mathrm{q}+\mathrm{w}=\triangle\mathrm{U}$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and q = 0, then $\triangle\mathrm{U}=0.$ The equation i.e., $\triangle\mathrm{U}=\mathrm{q}+\mathrm{w}$ is mathematical statement of the first law of thermodynamics, which states that The energy of an isolated system is constant. It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

i. $\triangle\mathrm{U}=\ ....$
  a. q + w
  b. q + v
  c. q + m
  d. q + z

ii. Which of the following is not an example of state variable?
  a. Pressure
  b. Ionic radius
  c. Volume
  d. Amount

iii. $\triangle\mathrm{U}=\mathrm{q}+\mathrm{w}$ is termed as ...
  a. Third law of thermodynamics
  b. Second law of thermodynamics
  c. First law of thermodynamics
  d. None of above

iv. A ... in thermodynamics refers to that part of universe in which observations are made.
  a. Universe
  b. System
  c. Surrounding
  d. Boundary

v. Which of the following is a type if system ?
  a. Open system
  b. Closed system
  c. Lsolated system
  d. All the above

Ans. :

i. (a) q + w
ii. (b) Ionic radius
iii. (c) First law of thermodynamics.
iv. (b) System
v. (d) All the above

*** Given Section consists of questions of 5 marks each. [20]**

93. i. A cylinder of gas supplied by a company is assumed to contain 14kg of butane. If a normal family requires 20000kJ of energy per day for cooking, how long will the cylinder last?

ii. If the air supplied to the burner is insufficient, a portion of gas escapes without combustion. Assuming that 25% of the gas is wasted due to this inefficiency, how long will the cylinder last (Heat of combustion of butane = 2658kJ/ mol.)?

Ans. :

i. Molecular formula of butane = C_4H_{10}

Molecular mass of butane = 4 × 12 + 10 × 1 = 58

Heat of combustion of butane = 2658kJ mol^{-1}

1 mole or 58g of butane on complete combustion gives heat = 2658kJ

$\therefore$ 14 × 10^3g of butane on complete combustion will gives heat

$= \frac{2658\times14\times10^3}{58} = 641586$

The family needs 20000kJ of heat per day.

$\because$ 20000kJ of heat is used for cooking by a family in 1 day.

$\therefore$ 641586 kJ of heat will be used for cooking by a family in $= \frac{641586}{20000} = 32\text{days}$

The cylinder will last for 32 days.

ii. 25 percent of the gas is wasted due to inefficiency. This means that only 75% of butane gets combusted. Therefore, the energy produced by 75% combustion of butane $= \frac{641586\times75}{100} = 481189.5\text{kJ}$

$\therefore$ The number of days the cylinder will last.

94. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Ans. : Solids and liquids do not show significant change in the volume when heated. Thus ifchange in volume, ΔV is insignificant,

$$\Delta\text{H} = \Delta\text{U} + \text{P}\Delta\text{V}$$
$$\Delta\text{H} = \Delta\text{U} + \text{P}(0)$$
$$\Delta\text{H} = \Delta\text{U}$$

The difference between the change in internal energy and enthalpy becomes significant when gases are involved in the reaction.

Consider a chemical reaction occurring at constant temperature, T and constant pressure, P. Now, let’s say that the volume of the reactants is V_A and the number of moles in the reactants is n_A. Similarly, the volume of the products is V_B and the number of moles in the product is n_B.

We know that according to the ideal gas equation,

$$\text{Pv} = \text{nRT}$$
$$\text{pv}_\text{A} = \text{n}_\text{A}\text{RT}$$
$$\text{pv}_\text{B} = \text{n}_\text{B}\text{RT}$$

Thus $\text{pv}_\text{B} - \text{pv}_\text{B} = \text{n}_\text{B}\text{RT} - \text{n}_\text{A}\text{RT}$

$$\text{p}(\text{v}_\text{B} - \text{v}_\text{A}) = \text{RT}(\text{n}_\text{B} - \text{n}_\text{A})$$
$$\text{p}\Delta\text{v} = \Delta\text{n}_\text{g}\text{RT}$$
$$\Delta\text{H} = \Delta\text{U} + \text{p}\Delta\text{v}$$
$$\Delta\text{H} = \Delta\text{U} + \Delta\text{n}_\text{g}\text{RT}$$

95.

a. Predict the sign of the entropy change for each of the following changes:
   - i. Hg(l) → Hg(g)
   - ii. Steam → Water

b.
   - i. Define Gibb's Energy. Give its mathematical expression. What is Gibb's energy criteria for spontaneity.
   - ii. Give a brief note on the following thermodynamic terms:
     - Standard enthalpy of combustion.

- Standard enthalpy of formation.

Ans. :

a.
  i. $\Delta S = +ve$
  ii. $\Delta S = -ve$

b.
  i. **Gibb's energy:** It is defined as energy which can be converted into useful work.

$G = H - TS$

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

$\Delta G = -ve$ for spontaneous process

  ii.
    - **Standard enthalpy of combustion:** 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.
    - **Standard enthalpy of formation:** 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) → CO_2(g)

96. For the reaction,

2A(g) + B(g) → 2D(g)

$\Delta U^{\ominus} = -10.5 kJ \text{ and } \Delta S^{\ominus} = -44.1 kJ^{-1}$.

Calculate $\Delta G^{\ominus}$ for the reaction, and predict whether the reaction may occur spontaneously.

Ans. : For the given reaction,

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

$\Delta n_g = 2 - (3)$

= –1 mole

Substituting the value of $\Delta U^{\ominus}$ in the expression of ΔH :

$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$

= (–10.5kJ) – (–1) (8.314 × 10^{-3}kJ K^{-1} mol^{-1}) (298K)

= –10.5kJ – 2.48kJ

$\Delta G^{\ominus} = +0.16 kJ$

Since $\Delta G^{\ominus}$ for the reaction is positive, the reaction will not occur spontaneously.

----- He who asks a question is a fool for five minutes; he who does not ask a question remains a fool forever.” — -----