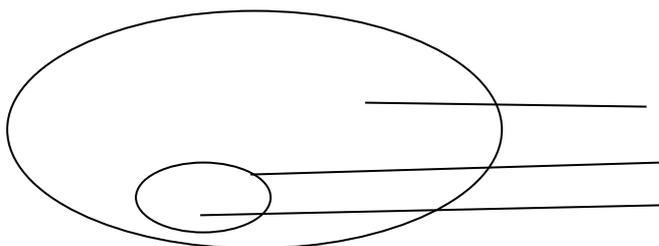


**XI - CHEMISTRY - WORK SHEET****UNIT- 7 THERMODYNAMICS****IMPORTANT TERMS :**

- System, surrounding and boundary
- Types of systems - Properties of the system - Thermodynamic processes
- State functions and path functions - Internal energy
- Heat , Work and Pressure – volume work
- Zeroth law of thermodynamics – First law of thermodynamics
- Enthalpy - Enthalpy changes for different types of reactions
- Thermo chemical Equations
- Standard enthalpy of reaction - standard enthalpy of formation
- Molar heat capacities - Relation between Cp and Cv for an ideal gas.
- Heat of combustion - Bomb calorimeter – Coffee cup calorimeter
- Applications of the heat of combustion
- Heat of solution - Heat of neutralization -Molar heat of fusion - Molar heat of vapourisation
- Molar heat of sublimation -Heat of transition
- Hess's law of constant heat summation
- Lattice energy - Born - Haber cycle
- Various statements of Second law of thermodynamics
- Entropy- Unit of entropy - Spontaneity and Randomness - Standard Entropy Change
- Entropy of fusion - Entropy of vapourisation - Entropy of transition
- Gibbs free energy - Gibbs free energy and the net work done by the system
- Effect of Temperature on Spontaneity of Reactions
- Relationship between standard free energy change and equilibrium constant
- Third law of Thermodynamics

**ANSWER THE FOLLOWING****1. Label the parts of the universe**

( system, surrounding, boundary)

**2. Define the following terms:**

System	Surrounding	Boundary

3. List out the types of thermodynamic systems depending on the nature of the boundary.

- 1.
- 2.
- 3.

3. Match the following;

- i) Isolated system - All living things and chemical reactions  
 ii) Closed system - Hot water contained in a closed beaker  
 iii) Open system - Hot water contained in a thermos flask

i) \_\_\_\_\_ ii) \_\_\_\_\_ iii) \_\_\_\_\_

3. Fill the gaps with appropriate answer

- a) The property that \_\_\_\_\_ on the \_\_\_\_\_ or \_\_\_\_\_ of the system is called an extensive property.  
 b) The property that is \_\_\_\_\_ of the \_\_\_\_\_ or \_\_\_\_\_ of the system is called an intensive property.

4. Arrange the following examples:

volume, mass, molar volume, molarity, amount of substance (mole), specific heat capacity, energy, enthalpy, molality, entropy, free energy, heat capacity, density, molar, mole fraction, molar mass.

Extensive properties	Intensive properties

6. Fill the following missing terms :

Process	Condition
Adiabatic	
	$dT=0$
Cyclic	
	$dV =0$
Isobaric	

7. Pick out the odd one out and give the proper reason:

Pressure (P), Volume (V), Work (w), Temperature(T), Internal energy (U), Enthalpy (H),

Odd one:

Reason:

8. Give the proper sign conventions of the following:

1. Work done by the system =
  2. Heat released by the system =
  3. Work on the system =
  4. Heat absorbed by the system =
- ( +q, -q, +w, -w )

9. Define Zeroth law of thermodynamics.

10. Define First law of thermodynamics.

11. The mathematical statement of the first law of thermodynamics is  $\Delta U = q + W$ , and write the different values of  $\Delta U$  for different processes.

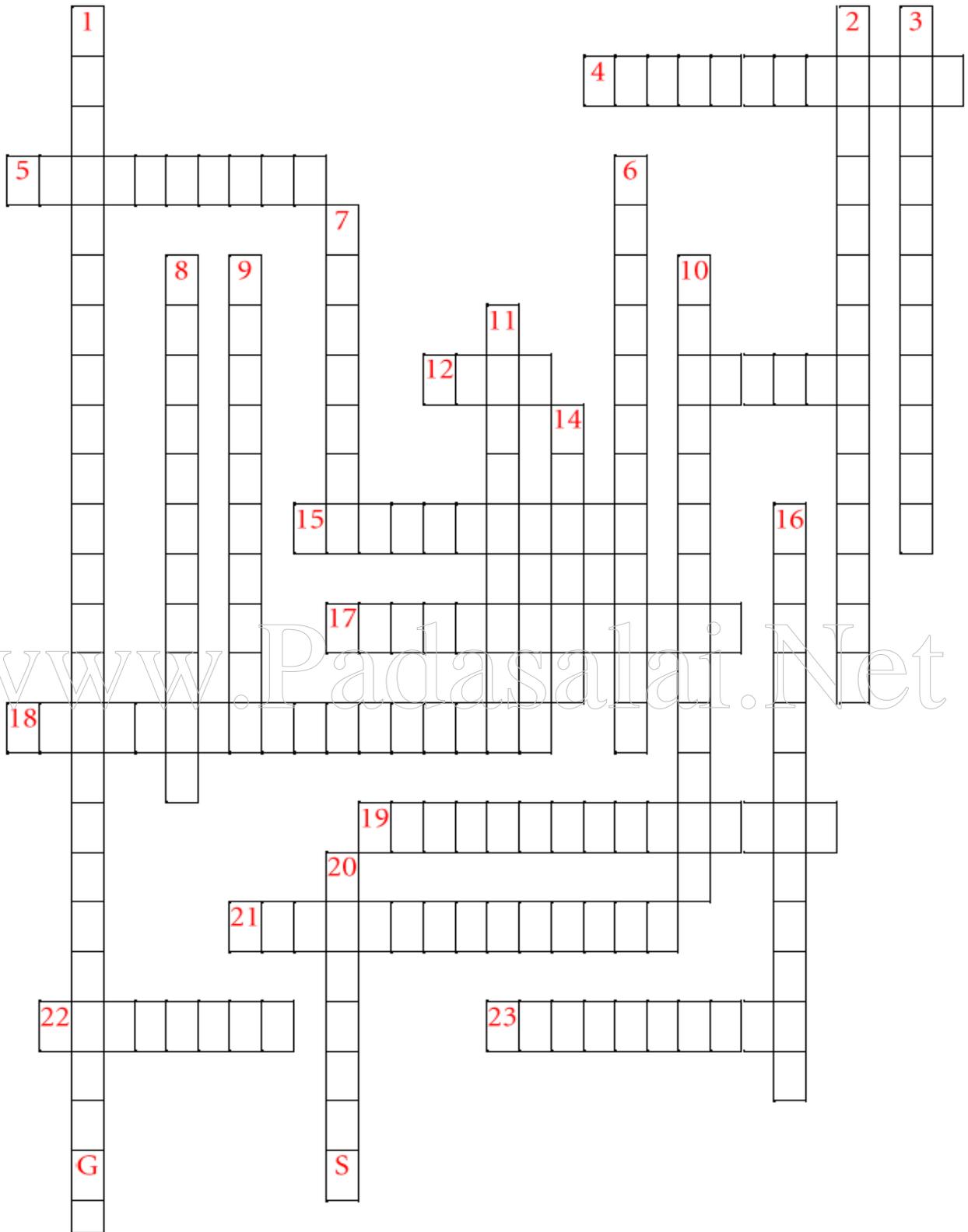
CASE	PROCESS	$\Delta U$
1	Cyclic	
2	Isothermal	
3	Adiabatic	
4	Isobaric	

(  $\Delta U = w$ ,  $\Delta U = 0$ ,  $\Delta U = q_v$ ,  $\Delta U = q - P\Delta V$  )

12. Write the definitions of the following terms.

TERMS	DEFINITION	EXAMPLE
Heat of solution		
Heat of neutralisation		
Molar heat of fusion		
Molar heat of vapourisation		

13. Puzzles of Thermodynamics: Find out the answers using the clues given.



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**Across**

4. The quantity of energy needed to raise the temperature of 1 kg of a substance by 1°C at constant pressure
5. Energy flows out of a system
12. A flow of energy due to a temperature difference
13. The ability to do work or produce heat
15. A measure of the random motions of the components of a substance
17. Energy due to the motion of the object
18. Kinetic energy transferred to a surface as heat
19. Energy due to position or composition
21. Sum of the kinetic and potential energies of all "particles" in the system
22. To measure how much energy is produced or absorbed by a given reaction
23. Heat that is transferred by movement of a fluid

**Down**

1. Energy can be converted from one form to another but can be neither created nor destroyed
2. the study of heat energy
3. Used to determine the heat associated with a chemical reaction
6. The lowest possible temperature on the Kelvin scale where all molecules would stop
7. Amount of energy (heat) required to raise the temperature of one gram of water by one degree Celsius
8. Energy flows into a system
9. Heat transferred method between objects in contact as a result of temperature difference
10. 1 atm pressure, water freezes at 0 degrees Celsius
11. A transfer of heat energy through space by means of electromagnetic waves
14. 4.184 \_\_\_\_\_ = 1 calorie
16. 1 atm pressure, liquid water always changes to gaseous water at 100 degrees Celsius
20. a unit of measurement that was once called Centigrade because there are 100 degrees between the freezing and boiling points of water in this scale

**14. What is molar heat of sublimation? Give an example.**

**15. Define heat of transition. Give an example.**

**16. State Hess's law**

The enthalpy change of a reaction either at constant \_\_\_\_\_ or constant \_\_\_\_\_ is the same whether it takes place in a single or \_\_\_\_\_ steps provided the initial and \_\_\_\_\_ states are same

**17. What is Lattice Energy?**

**18. Define Entropy.**

Entropy is a measure of \_\_\_\_\_

Unit of entropy :

Entropy is a \_\_\_\_\_ function.

**19. What is Gibbs free energy?**

$$G = H - TS$$

G is a \_\_\_\_\_ function.

**20. Identify the conditions for spontaneity.**

$$\Delta S > 0, \Delta S = 0, \Delta S < 0, \Delta H = 0, \Delta H > 0, \Delta H < 0, \Delta G < 0, \Delta G = 0, \Delta G > 0$$

**21. Define Third law of thermodynamics.**

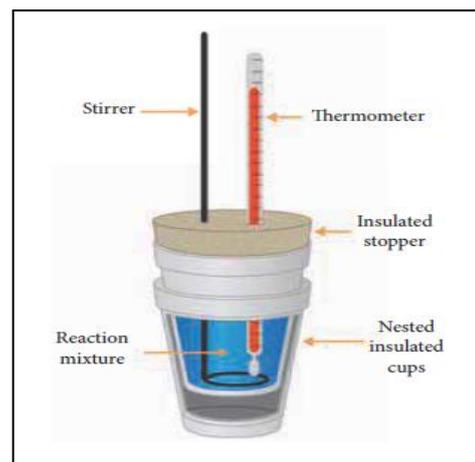
**22. What is Heat of combustion?**

“The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”.

Example:  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$   $\Delta H_C =$  \_\_\_\_\_

### 23. Explain $\Delta H$ measurements by Coffee cup calorimeter.

- Heat change at constant pressure (at atmospheric pressure) can be measured using a **coffee cup calorimeter**.
- Instead of bomb, a **styrofoam cup** is used in this calorimeter.
- It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding.
- This entire heat energy is absorbed by the water inside the cup.
- This method can be used for the reactions where there is no appreciable change in volume.



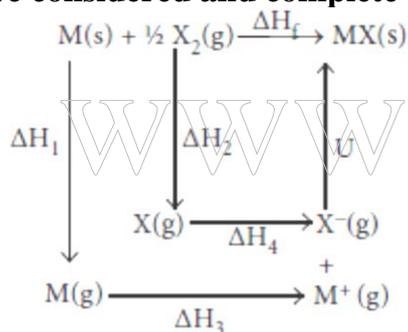
The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where,  $m_w$  is the molar mass of water and

$C_w$  is the molar heat capacity of water ( $4184 \text{ kJ K}^{-1} \text{ mol}^{-1}$ )

### 24. The formation of a simple ionic solid such as an alkali metal halide MX, the following steps are considered and complete the given data.



$$\Delta H_1 =$$

$$\Delta H_2 =$$

$$\Delta H_3 =$$

$$\Delta H_4 =$$

$$\Delta H_f =$$

### 25. Write the mathematical expressions for the following terms.

First law of thermodynamics	$\Delta U = \underline{\hspace{2cm}}$
Enthalpy change	$\Delta H = \Delta U + \underline{\hspace{2cm}}$ $\Delta H = \Delta U + \Delta n(g) \underline{\hspace{2cm}}$
Molar heat capacities	$C = q / \underline{\hspace{2cm}}$
Relation between $C_p$ and $C_v$	$C_p - C_v = \underline{\hspace{2cm}}$
% Efficiency	$\eta = \underline{\hspace{2cm}}$
Gibbs free energy	$G = \underline{\hspace{2cm}}$
Gibbs free energy change	$\Delta G = \underline{\hspace{2cm}}$
Third law of thermodynamics	$\lim_{T \rightarrow 0} S = \underline{\hspace{2cm}}$
Internal energy	$U = \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}$

### 26. The First Law of Thermodynamics helps you to understand the

- a. conservation of entropy.    b. conservation of energy.  
c. perpetual motion.    d. enthalpy.

Ans: \_\_\_\_\_

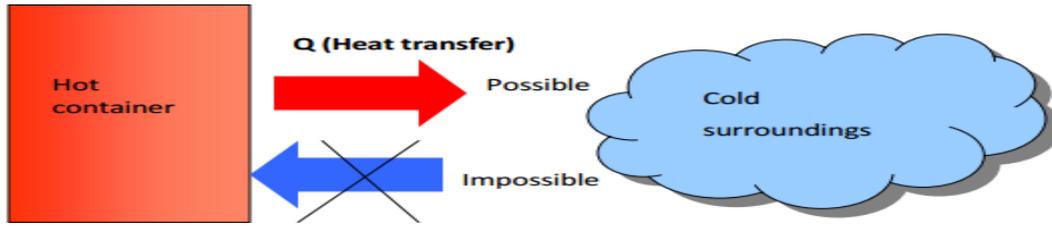
27. Which of the following expressions correctly describes Gibb's free energy change for a chemical reaction that is carried out at constant temperature?

- i)  $\Delta G = \Delta H - T\Delta S$       ii)  $\Delta G = \Delta H + T\Delta S$       iii)  $\Delta G = \Delta H \div T\Delta S$       iv)  $\Delta G = \Delta H \times T\Delta S$

Ans: \_\_\_\_\_

- $\Delta G$  = Gibb's free energy change
- $\Delta H$  = Change in \_\_\_\_\_
- $\Delta S$  = Change in entropy of the system

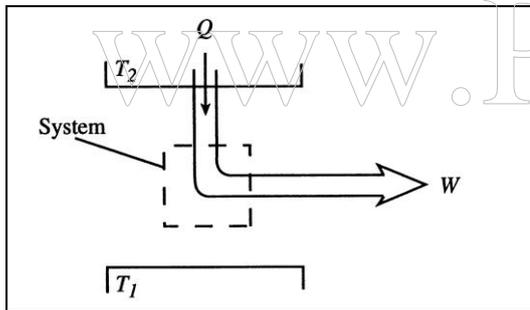
28. The following picture refers to which statement of Second law of thermodynamics?



Heat transfer from a hot container to the cold surroundings is possible; however, the reverses process (although satisfying the first law) is impossible.

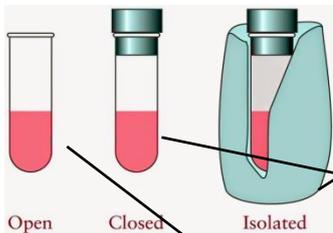
Name of the Statement and its definition:

29. The following picture describes the Kelvin- Planck statement of second law of thermodynamics,



Kelvin- Planck statement:

30. Explain the following pictures of system :

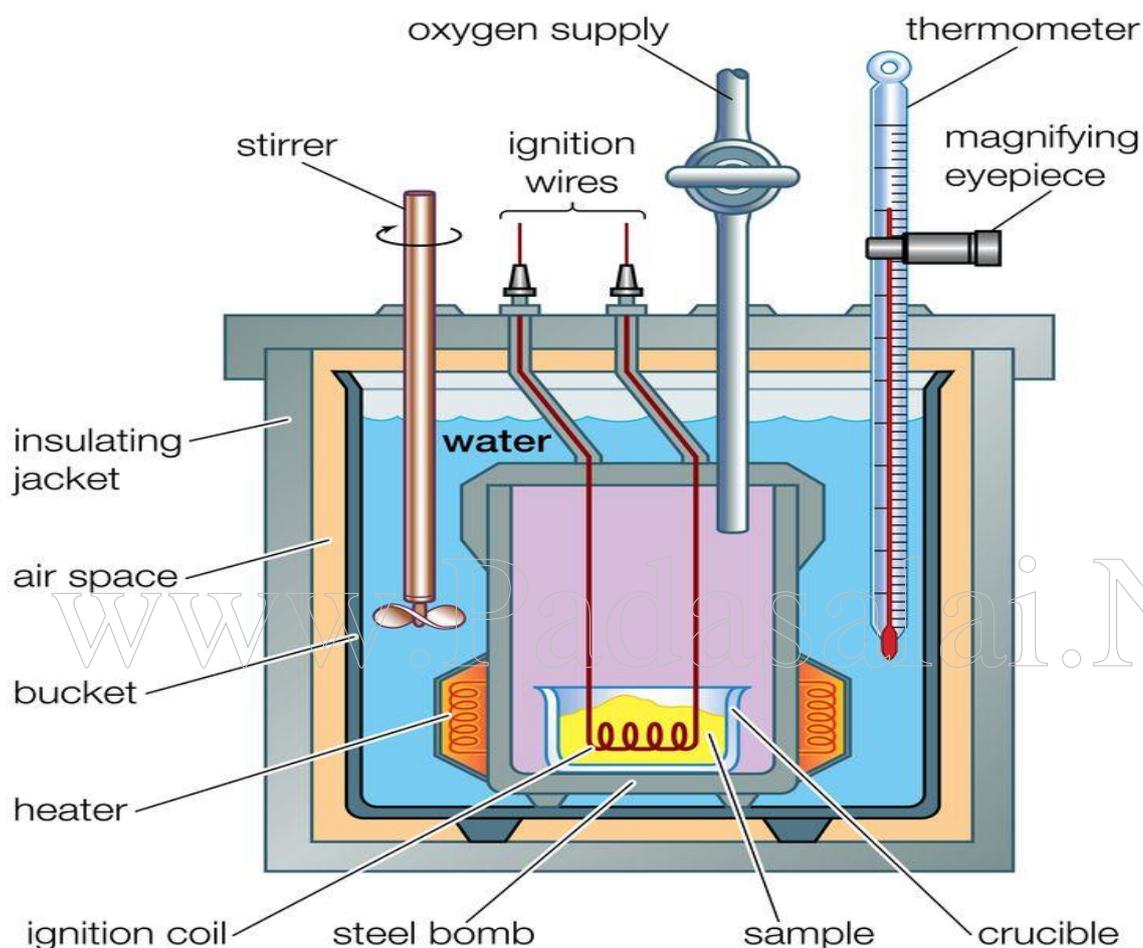


**31. What is reversible process?**

The process in which the system and surrounding can be \_\_\_\_\_ to the \_\_\_\_\_ state from the \_\_\_\_\_ state without producing any changes in the thermodynamic properties of the universe is called a reversible process.

**32. What is irreversible process?**

The process in which the system and surrounding \_\_\_\_\_ restored to the \_\_\_\_\_ state from the \_\_\_\_\_ state without producing any changes in the thermodynamic properties of the universe is called a reversible process.

**33. Explain  $\Delta U$  Measurements for chemical reactions, by *bomb calorimeter*.**

- The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws
- weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion.
- The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter.
- A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly.
- The reaction is started by striking the substance through electrical heating. A known amount of combustible substance is burnt in oxygen in the bomb.

- Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed.
- The change in temperature is measured using a Beckman thermometer.
- The bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume ( $\Delta U$ )<sub>c</sub>.
- The amount of heat produced in the reaction ( $\Delta U$ )<sub>c</sub> is equal to the sum of the heat absorbed by the calorimeter and water.
- Heat absorbed by the calorimeter  $q_1 = k \cdot \Delta T$   
where k is a calorimeter constant equal to  $m_c C_c$  ( $m_c$  is mass of the calorimeter and  $C_c$  is heat capacity of calorimeter)
- Heat absorbed by the water  $q_2 = m_w C_w \Delta T$   
where  $m_w$  is molar mass of water  $C_w$  is molar heat capacity of water (4,184 kJ K<sup>-1</sup> mol<sup>-1</sup>)

Therefore  $\Delta U_c = q_1 + q_2$

$$= \underline{\hspace{2cm}}$$

$$= \underline{\hspace{2cm}}$$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known (-3227 kJmol<sup>-1</sup>)

- The enthalpy of combustion at constant pressure of the substance is calculated from the equation  $\Delta H^0_{c(\text{pressure})} = \Delta U^0_{c(\text{volume})} + \Delta n_g RT$

### 34. calculate the lattice energy of sodium chloride using Born-Haber cycle.

$\Delta H_f$  = heat of formation of sodium chloride = - 411.3 kJ mol<sup>-1</sup>

$\Delta H_1$  = heat of sublimation of Na(s) = 108.7 kJ mol<sup>-1</sup>

$\Delta H_2$  = ionisation energy of Na(s) = 495.0 kJ mol<sup>-1</sup>

$\Delta H_3$  = dissociation energy of Cl<sub>2</sub>(s) = 244 kJ mol<sup>-1</sup>

$\Delta H_4$  = Electron affinity of Cl(s) = - 349.0 kJ mol<sup>-1</sup>

U = lattice energy of NaCl

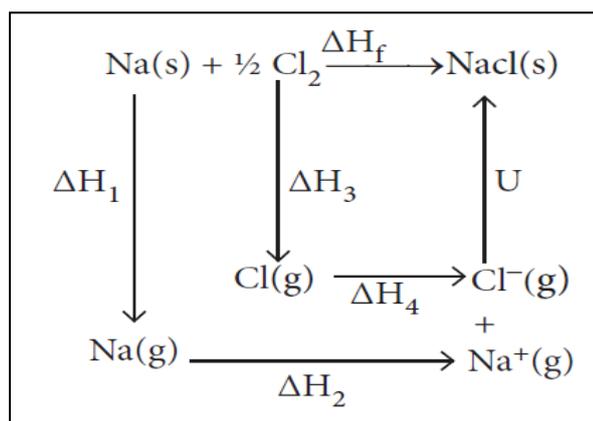
$$\Delta H_f = \Delta H_1 + \Delta H_2 + 1/2\Delta H_3 + \Delta H_4 + U$$

Therefore  $U = (\Delta H_f) - (\Delta H_1 + \Delta H_2 + 1/2\Delta H_3 + \Delta H_4)$

$$U = (-411.3) - (108.7 + 495.0 + \underline{\hspace{1cm}} - 349.0)$$

$$U = \underline{\hspace{1cm}} - \underline{\hspace{1cm}}$$

$$U = \underline{\hspace{1cm}} \text{ KJmol}^{-1}$$



35. Calculate the standard entropy change for the following reaction(  $\Delta S^0_f$  ), given the standard entropies of  $\text{CO}_2(\text{g})$ ,  $\text{C}(\text{s})$ ,  $\text{O}_2(\text{g})$  as 213.6 , 5.740 and 205  $\text{JK}^{-1}$  respectively.



$$\Delta S^0_r = \Sigma S^0_{\text{products}} - \Sigma S^0_{\text{reactants}}$$

$$\Delta S^0_r = \{S^0_{\text{CO}_2}\} - \{S^0_{\text{C}} + S^0_{\text{O}_2}\}$$

$$= \underline{\hspace{2cm}} - \underline{\hspace{2cm}} + \underline{\hspace{2cm}}$$

$$= \underline{\hspace{2cm}} - \underline{\hspace{2cm}}$$

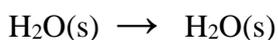
$$= \underline{\hspace{2cm}} \text{JK}^{-1}$$

36. Calculate the entropy change during the melting of one mole of ice into water at  $0^\circ \text{C}$  and 1 atm pressure. Enthalpy of fusion of ice is  $6008 \text{ J mol}^{-1}$ .

Given,

$$\Delta H_{\text{fusion}} = 6008 \text{ J mol}^{-1}$$

$$T_f = 0^\circ \text{C} = 273 \text{K}$$



$$\Delta S_{\text{fusion}} = \Delta H_{\text{fusion}} / \underline{\hspace{2cm}}$$

$$\Delta S_{\text{fusion}} = \underline{\hspace{2cm}} / 273$$

$$\Delta S_{\text{fusion}} = \underline{\hspace{2cm}}$$

37. An engine operating between  $127^\circ \text{C}$  and  $47^\circ \text{C}$  takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

Given,

$$T_h = 127 + 273 = 400 \text{K}$$

$$T_c = 47 + 273 = 320 \text{K}$$

Solution

$$\% \text{ Efficiency} = [T_h - T_c / T_h] \times 100$$

$$= \underline{\hspace{2cm}}$$

$$= \underline{\hspace{2cm}} \%$$

38. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at  $25^\circ \text{C}$  and normal pressure.

Given,

$$n = 2 \text{ moles}$$

$$V_i = 500 \text{ ml} = 0.5 \text{ lit}$$

$$V_f = 2 \text{ lit}$$

$$T = 25^\circ \text{C} = 298 \text{K}$$

$$w = \underline{\hspace{2cm}}$$

$$w = \underline{\hspace{2cm}}$$

$$w = \underline{\hspace{2cm}} \text{ KJ}$$

$$w = -2.303 n RT \log (V_f / V_i)$$

39. For the reaction at 298 K :  $2A + B \rightarrow C$   $\Delta H = 400 \text{ J mol}^{-1}$  ;  $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$  Determine the temperature at which the reaction would be spontaneous.

Given :

$$T = 298 \text{ K}$$

$$\Delta H = 400 \text{ J mol}^{-1} = 400 \text{ J mol}^{-1}$$

$$\Delta S = 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

Solution:

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

$$\Delta G =$$

40. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points ( $^{\circ}\text{C}$ )	$\Delta H$ ( kJ mol $^{-1}$ )
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

For ethanol :

Given :

$$T_b = 78.4^{\circ}\text{C} = (78.4 + 273) = 351.4 \text{ K}$$

$$\Delta H_v(\text{ethanol}) = + 42.4 \text{ kJ mol}^{-1}$$

Solution:

$$\Delta S_v = \Delta H_v / T_b$$

For Toluene:

$$T_b = 110.6^{\circ}\text{C} = 110.6 + 273 = 383.6 \text{ K}$$

$$\Delta H_v(\text{Toluene}) = +35.2 \text{ kJ mol}^{-1}$$

Solution

$$\Delta S_v = \Delta H_v / T_b$$

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