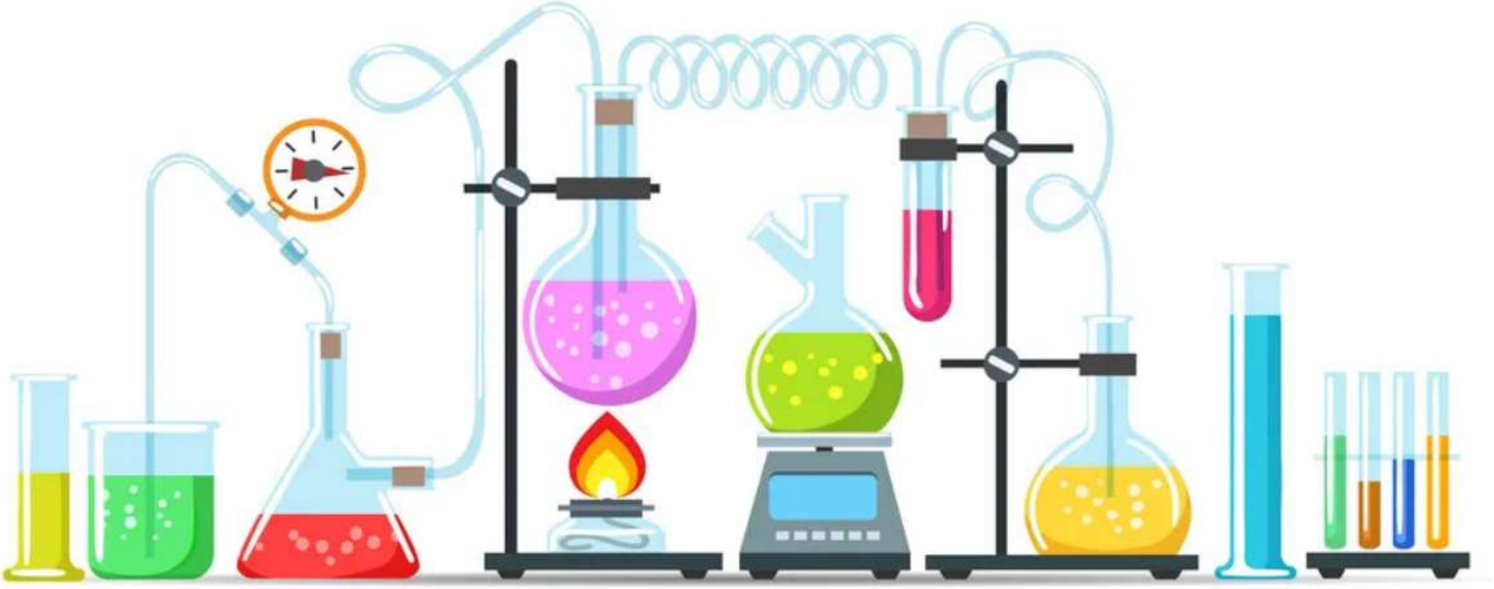
CHEMISTRY



THERMODYNAMICS

Introduction

Chemical thermodynamics deals with the relationship between various form of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System:** A specific portion of universe under study which is seperated from rest of the universe with a boundary is called system.
2. **Surroundings:** Rest of the universe which might be in a position to exchange energy and matter with the system is known as surrounding.

Types of System:

1. **Open system:** System can be open if it can exchange both energy and matter with surroundings.
2. **Closed system:** System can be closed if it can exchange energy but not matter with surroundings.
3. **Isolated system:** System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

A state is the condition of a system as specified by its physical 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.

State Functions

The thermodynamic parameters which depends only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions

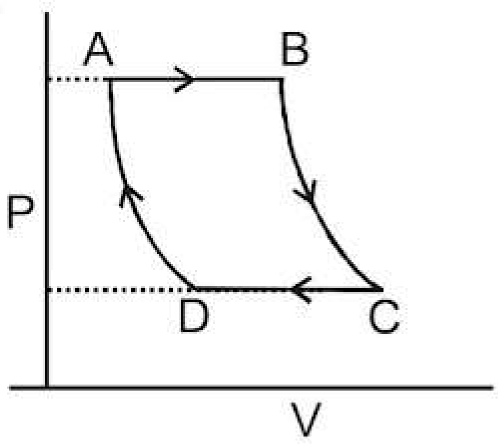
The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process

The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1. **Isothermal process:** It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.
2. **Isobaric process:** It is the process in which pressure is kept constant for entire process.
3. **Isochoric process:** It is the process in which volume is kept constant.
4. **Adiabatic process:** The process in which heat transaction across boundary is not allowed.
5. **Reversible process and Irreversible process:** In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

   Any process which does not take place in the above mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.
6. **Cyclic process:** It is the process which run in close loop means process in which initial and final states are identical.

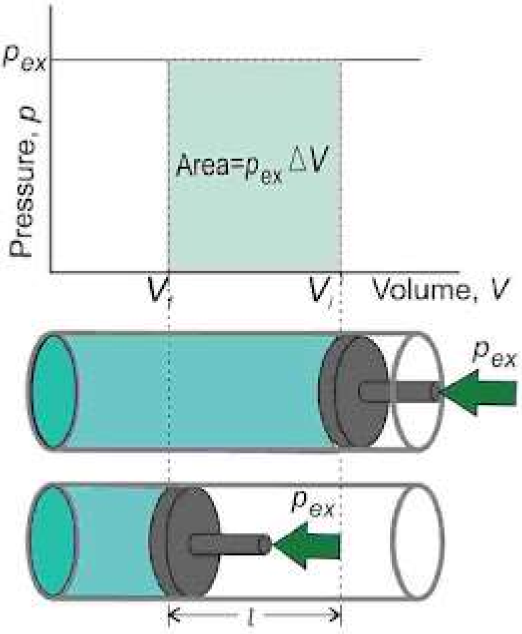


Internal Energy

Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.



Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

$$\omega = -\int_{V_i}^{V_f} P_{ex} dv$$

Heat

The change in internal energy of a system can be brought about by the transfer of heat from the surroundings to the system or vice-versa. This exchange of energy between the system and surroundings is possible as a result of the temperature difference between them. This energy called heat is represented by Q.

First Law of Thermodynamics

First law of thermodynamics states the law of conservation of energy in a different manner. According to this law, whenever a quantity of one kind of energy disappears an equivalent amount of energy appears in some other form.

According to first law of thermodynamics,

$\Delta U = q + W$

Where, Q = Heat change

W = Work done

ΔU = Change in internal energy

Enthalpy (H)

The total heat content of a system at constant pressure is known as its enthalpy. Mathematically it is the sum of internal energy and pressure-volume energy

$\Delta H = \Delta U + P\Delta V$

It is an extensive property and a state function. Increase in enthalpy H is equal to heat absorbed at constant pressure.

Heat Capacity

Heat capacity is amount of heat require to raise the temperature of a system by unity. It is represented as "C". It is an extensive property and temperature dependent.

Types of heat capacity

1. Specific heat: For 1 gram system the heat loose or gained by system to bring one unit change in temperature is called specific heat denoted by 's'. specific heat is the intensive property.

$$S = \frac{C}{m}$$

2. Molar heat capacity: It is heat capacity for a system having 1 mole of material. It is represented as Cm. It is an intensive property.

$$C_m = \frac{C}{m}$$

3. Heat capacity at constant volume: Heat capacity of a system in isochoric condition is called heat capacity at constant volume, it is represented as C_v means molar heat capacity at constant volume.

$$C_v = \frac{dU}{dT}$$

4. Heat capacity at constant pressure: Heat capacity of a system in isobaric condition. It is represented by C_p means molar heat capacity at constant pressure.

$$C_p = \frac{dH}{dT}$$

Relation between Cp and Cv

We know that,

$\Delta H = \Delta U + P\Delta V$ .....(i)

As per ideal gas equation

$P\Delta V = R\Delta T$ .....(ii)

From (i) and (ii)

$\Delta H = \Delta U + R\Delta T$

$$\frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + R$$

$C_p = C_v + R$

$C_p - C_v = R$

Hess’s Law

According to Hess's law, If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

1st method: $C(s) + O_2(g) \rightarrow CO_2(g) = \Delta H$

2nd method: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) = \Delta H_1$

$$CO(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) = \Delta H_2$$

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2$$

Application of Hess's Law

1. Calculation of enthalpy of formation.
2. Determination of standard enthalpies of reactions.

Bond Dissociation Energy

The energy required to break one mole bond of a particular type in gaseous molecule is known as bond dissociation energy. For example, we consider the dissociation of water,

$$H - OH(g) \rightarrow H(g) + OH(g) = \Delta H \ = 498 \text{ kJ/mol}$$

Entropy

Entropy is a measure of degree of randomness or disorder in a system. Entropy is an extensive property and a state function.. Its value depends upon the amount of substance present in the system.

Second Law of Thermodynamics

This states that the entropy of the universe always increases in every spontaneous (natural) change.

Free Energy (G)

Gibb's free energy is defined as,

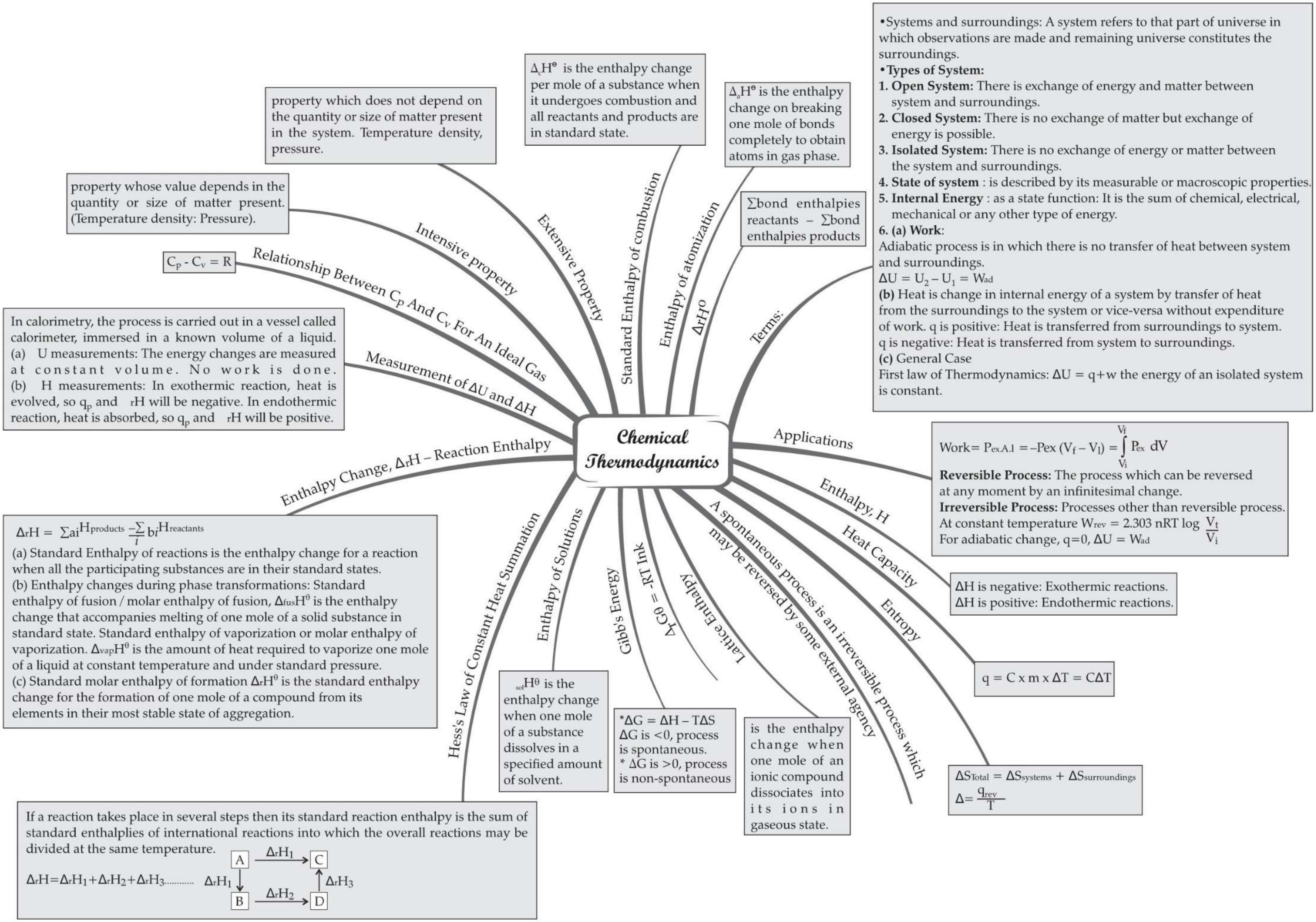
$$\Delta G = \Delta H - T\Delta S$$

H is enthalpy, S is entropy and T is the temperature on Kelvin scale.

Summary

1. **System:** A part of universe which is under investigation.
2. **Surroundings:** The rest of the universe which is not a part of the system.
3. **State of the system:** The conditions of existence of a system when its macroscopic properties have definite values.
4. **State functions:** The thermodynamic quantities which depend only on the initial and final state of the system.
5. **Energy:** Energy is exchanged between the system and the surroundings as heat if they are at different temperatures.
6. The properties of the system whose value is independent of the amount of substance are called intensive properties. e.g., temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity.
7. The properties of the system whose value depends upon the amount of substance present in the system are called extensive properties. e.g., mass, volume, surface area, energy, enthalpy, entropy, free energy, heat capacity.
8. Work is also a mode of transference of energy between system and the surroundings. Work done by the system on the surroundings is given by $p\Delta V$.
9. **Internal energy (U):** The energy associated with the system at a particular conditions of temperature and pressure.
10. **Enthalpy (H):** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content ($H = E + pV$).
11. **Hess's law:** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.
12. **Bond enthalpy:** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.
13. **Entropy (S):** It is a measure of randomness or disorder of the system. Thus, the order is Gas > Liquid > Solid.

MIND MAP : LEARNING MADE SIMPLE CHAPTER - 6



Chemical Thermodynamics

Terms:

- Systems and surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
- **Types of System:**

1. **Open System:** There is exchange of energy and matter between system and surroundings.
2. **Closed System:** There is no exchange of matter but exchange of energy is possible.
3. **Isolated System:** There is no exchange of energy or matter between the system and surroundings.
4. **State of system** : is described by its measurable or macroscopic properties.
5. **Internal Energy** : as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.
6. **(a) Work**:

Adiabatic process is in which there is no transfer of heat between system and surroundings.

$\Delta U = U_2 - U_1 = W_{ad}$

(b) Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system. q is negative: Heat is transferred from system to surroundings.

(c) General Case

First law of Thermodynamics: $\Delta U = q+w$ the energy of an isolated system is constant.

Applications

$\text{Work} = P_{ex.A.1} = -P_{ex}(V_f - V_l) = \int_{V_i}^{V_f} P_{ex}\, dV$

Reversible Process: The process which can be reversed at any moment by an infinitesimal change.

Irreversible Process: Processes other than reversible process.

At constant temperature $W_{rev} = 2.303\ nRT \log \frac{V_t}{V_i}$

For adiabatic change, $q=0$, $\Delta U = W_{ad}$

Enthalpy, H

ΔH is negative: Exothermic reactions.

ΔH is positive: Endothermic reactions.

Heat Capacity

$q = C \times m \times \Delta T = C\Delta T$

Entropy

$\Delta S_{Total} = \Delta S_{systems} + \Delta S_{surroundings}$

$\Delta = \frac{q_{rev}}{T}$

A spontaneous process is an irreversible process which may be reversed by some external agency

Lattice Enthalpy

is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state.

$\Delta_r G\theta = -RT \ln k$

Gibb's Energy

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

ΔG is <0, process is spontaneous.

* ΔG is >0, process is non-spontaneous

Enthalpy of Solutions

$_{sol}H^\theta$ is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

Hess's Law of Constant Heat Summation

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalpies of international reactions into which the overall reactions may be divided at the same temperature.

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots\ldots$

$$\begin{tikzcd}
\boxed{A} \arrow[r, "\Delta_r H_1"] \arrow[d, "\Delta_r H_1"'] & \boxed{C} \\
\boxed{B} \arrow[r, "\Delta_r H_2"] & \boxed{D} \arrow[u, "\Delta_r H_3"']
\end{tikzcd}$$

Enthalpy Change, $\Delta_r H$ – Reaction Enthalpy

$\Delta_r H = \sum a_i H_{products} - \sum_i b_i H_{reactants}$

(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.

(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus}H^\theta$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap}H^\theta$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.

(c) Standard molar enthalpy of formation $\Delta_f H^\theta$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

Measurement of ΔU and ΔH

In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.

(a) U measurements: The energy changes are measured at constant volume. No work is done.

(b) H measurements: In exothermic reaction, heat is evolved, so q_p and rH will be negative. In endothermic reaction, heat is absorbed, so q_p and rH will be positive.

Relationship Between C_p And C_v For An Ideal Gas

$C_p - C_v = R$

Intensive property

property whose value depends in the quantity or size of matter present. (Temperature density: Pressure).

Extensive Property

property which does not depend on the quantity or size of matter present in the system. Temperature density, pressure.

Standard Enthalpy of combustion

$\Delta_c H^\theta$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.

Enthalpy of atomization

$\Delta_a H^\theta$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase.

ΔrH^o

Σbond enthalpies reactants – Σbond enthalpies products

Important Questions

Multiple Choice questions-

Question 1. Hesss law is an application of

(a) 1st law of Thermodynamics

(b) 2nd law of Thermodynamics

(c) Entropy change

(d) $\Delta H = \Delta U + P\Delta V$.

Question 2. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. Wirr at 300 K is:

(a) -15.921 kJ

(b) -11.224 kJ

(c) -110.83 kJ

(d) None of these

Question 3. At absolute zero the entropy of a perfect crystal is zero. This statement corresponds to which law of thermodynamics?

(a) Zeroth Law

(b) First Law

(c) Second Law

(d) Third Law

Question 4. Which of the following has the highest entropy?

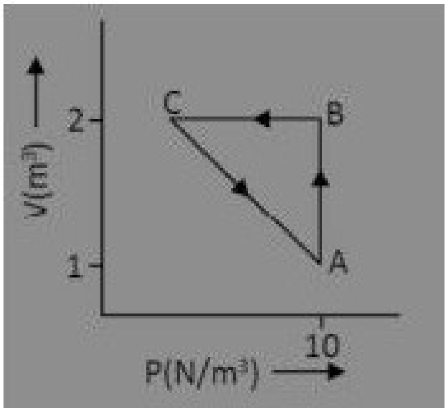
(a) Mercury

(b) Hydrogen

(c) Water

(d) Graphite

Question 5. An ideal gas is taken through the cycle A → B → C → A as shown in figure. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process C → A.



(a) -5 J

(b) -15 J

(c) -10 J

(d) -20 J

Question 6. One mole of which of the following has the highest entropy?

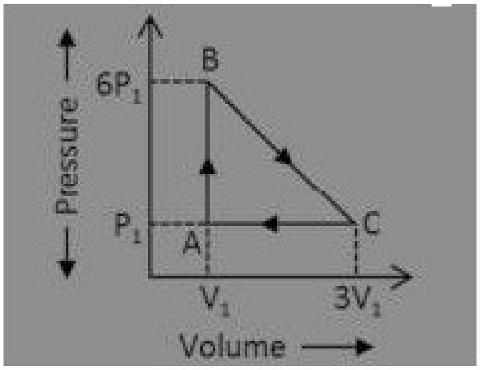
(a) Liquid Nitrogen

(b) Hydrogen Gas

(c) Mercury

(d) Diamond

Question 7. An ideal gas is taken around the cycle ABCA as shown in P-V diagram The next work done by the gas during the cycle is equal to:



(a) $12P_1V_1$

(b) $6P_1V_1$

(c) $5P_1V_1$

(d) P_1V_1

Question 8. Third law of thermodynamics provides a method to evaluate which property?

(a) Absolute Energy

(b) Absolute Enthalpy

(c) Absolute Entropy

(d) Absolute Free Energy

Question 9. Which of the following is/are a reason that water is a desirable heat sink for use in calorimeters?

I) Waters heat specific capacity is very precisely known.

II) Water is readily available.

III) Water has an unusually large specific heat capacity.

(a) I only

(b) I and II

(c) I, II and III

(d) II only

Question 10. In a chemical reaction the bond energy of reactants is more than the bond energy of the products. Therefore, the reaction is

(a) Exothermic

(b) Athermic

(c) Endothermic

(d) Endergonic

Question 11. In a reversible process the system absorbs 600 kJ heat and performs 250 kJ work on the surroundings. What is the increase in the internal energy of the system?

(a) 850 kJ

(b) 600 kJ

(c) 350 kJ

(d) 250 kJ

Question 12. Which of the following neutralization reactions is most exothermic?

(a) HCl and NaOH

(b) HCN and NaOH

(c) HCl and NH4OH

(d) CH3COOH and NH4OH

Question 13. A student runs a reaction in a closed system. In the course of the reaction, 64.7 kJ of heat is released to the surroundings and 14.3 kJ of work is done on the system. What is the change in internal energy (ΔU) of the reaction?

(a) -79.0 kJ

(b) 50.4 kJ

(c) 79.0 kJ

(d) -50.4 kJ

Question 14. Identify the correct statement from the following in a chemical reaction.

(a) The entropy always increases

(b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction

(c) The enthalpy always decreases

(d) Both the enthalpy and the entropy remain constant

Question 15. 2 mole of an ideal gas at 27° C expands isothermally and reversibly from a volume of 4 litters to 40 litre. The work done (in kJ) is:

(a) w = -28.72 kJ

(b) w = -11.488 kJ

(c) w = -5.736 kJ

(d) w = -4.988 kJ

Very Short:

1. Under what conditions the heat evolved or absorbed is equal to the internal energy change?
2. What is the sign of AH for endothermic reactions and why?
3. What is the relationship between the standard enthalpy of formation and the enthalpy of a compound?
4. Why enthalpy of neutralization of HF is greater than 57.1 kJ mol^{-1}?
5. What are the specific heat capacity and molar heat capacity for water?
6. Why enthalpy of neutralization is less if either the acid or the base or both are weak?
7. What do you mean by a system?

Short Questions:

1. Ice is lighter than water, but the entropy of ice is less than that of water. Explain.
2. Define spontaneity or-feasibility of a process.
3. Enthalpy of neutralization of CH_3COOH and NaOH is 55.9 kJ. What is the value of ΔH for ionization of CH_3COOH?

4. When 1 gm of liquid naphthalene (C10H8) solidifies, 150 J of heat is evolved. What is the enthalpy of fusion of $C_{10}H_8$?
5. Why most of the exothermic processes (reactions) are spontaneous?
6. What is meant by the term state function? Give examples.

Long Questions:

1. Define
   (i) Standard enthalpy of formation.
   (ii) Standard enthalpy of combustion
   (iii) Enthalpy of atomization
   (iv) Enthalpy of solution
   (v) Lattice enthalpy
   (vi) Thermochemical equation.
2. For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K_c = 1.8 \times 10^{-7}$. What is ΔG° for the reaction? ($R = 8.314\ JK^{-1}\ mol^{-1}$).
3. Calculate the equilibrium constant, K, for the following reaction at 400 K?

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

   Given that $\Delta_rH^\circ = 80.0\ kJ\ mol^{-1}$ and $\Delta_rS^\circ = 120\ JK^{-1}\ mol^{-1}$.
4. Calculate the standard entropy change for the reaction $X \rightleftharpoons Y$ if the value of $\Delta H^\circ = 28.40$ kJ and equilibrium constant is 1.8×10^{-7} at 298 K and $\Delta_rG^\circ = 38.484$ kJ.

Assertion Reason Questions:

1. 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

2. 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.

Case Study Based Question:

1. This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

   Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.

$$\begin{tikzcd}
A \arrow[r, "\Delta H_1"] & B \arrow[d, "\Delta H_2"] \\
D \arrow[u, "\Delta H_{\text{direct}}"] & C \arrow[l, "\Delta H_3"]
\end{tikzcd}$$

Total enthalpy change from A to D,

$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_{\text{total}} + \Delta H_{\text{direct}} = 0$

i.e., $\Delta H_{\text{total}} = -\Delta H_{\text{direct}}$

For example, formation of CO_2 from C in two different manners involves a total heat change of -393.5 kJ/ mol

Single step process :

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ kJ/mol

Two step process :

(i) $C(s) + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta H = -110.5$ kJ/mol

(ii) $CO(g) + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -283.0$ kJ/mol

$\Delta H_{\text{Total}} = -110.5 + (-283.0) = -393.5$ kJ/mol

(1) In which of the enlisted cases, Hess's law is not applicable?

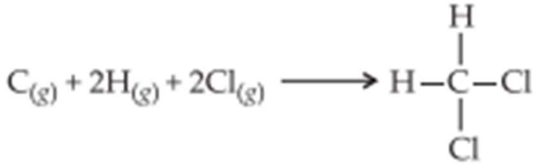
(a) Determination of lattice energy

(b) Determination of resonance energy

(c) Determination of enthalpy of transformation of one allotropic form to another

(d) Determination of entropy

(2) Use the bond energy data and calculate the enthalpy change for



$$C_{(g)} + 2H_{(g)} + 2Cl_{(g)} \longrightarrow H-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-Cl$$

The Bond energies of C – H and C – Cl are 413 and 328 kJ mol^{-1} respectively.

(a) – 1465 kJ/mol

(b) 1465 kJ/mol

(c) – 1482 kJ/mol

(d) 1482 kJ/mol

(3) A hypothetical reaction, A 2B, proceeds through the following sequence of steps:

$$A \longrightarrow C;\ \Delta H = q_1$$
$$C \longrightarrow D;\ \Delta H = q_2$$
$$\frac{1}{2}D \longrightarrow B;\ \Delta H = q_3$$

The heat of reaction is

(a) $q_1 - q_2 + 2q_3$

(b) $q_1 + q_2 - 2q_3$

(c) $q_1 + q_2 + 2q_3$

(d) $q_1 - 2q_2 + 2q_3$

2. The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

$H = U + PV$

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

$\Delta H = q_p,\ \Delta H = \Delta U + P\Delta V$

(1) Which of the following is not correct about enthalpy?

(a) It is an extensive property

(b) It is not a state function

(c) Its absolute value cannot be determined

(d) Enthalpy of a compound is equal to the enthalpy of formation of that compound.

(2) Lattice enthalpies are determined by:

(a) Born-Haber cycle

(b) Hess's law

(c) lattice cycle

(d) None of these

(3) In which of the following thermochemical changes ΔH is always negative?

(a) Enthalpy of solution

(b) Enthalpy of hydrogenation

(c) Enthalpy of reaction

(d) Enthalpy of transition

Answer Key:

MCQ

1. (d) 1st law of Thermodynamics
2. (b) -11.224 kJ
3. (d) Third Law
4. (b) Hydrogen
5. (a) -5 J
6. (b) Hydrogen Gas
7. (c) $5P_1V_1$
8. (c) Absolute Entropy
9. (c) I, II and III
10. (c) Endothermic

11.(c) 350 kJ

12.(a) HCl and NaOH

13.(d) -50.4 kJ

14.(b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction

15.(b) w = -11.488 k

Very Short Answer:

1. At constant volume.

2. AH is positive as $\Delta H = H_p - H_r$ and $H_r < Hp$.

3. They are equal.

4. This is due to the high hydration energy of fluoride ions.

5. Specific heat capacity for H_2O = 4.18 JK^{-1} g^{-1}

Molar heat capacity for H_2O = 4.18 × 18 = 75.24 JK^{-1} mol^{-1}.

6. A part of the heat is used up for dissociation of the weak acid or weak base or both

7. A specified part of the universe that is under thermodynamic observation is called a system.

Short Answer:

Ans: 1. Water is the liquid form while ice is its solid form. Molecular motion in ice is restricted than in water, i.e., a disorder in ice is restricted than water, i.e., a disorder in ice is less than in water.

Ans: 2. Spontaneity or feasibility of a process means its inherent tendency to occur on its own in a particular direction under a given set of conditions.

Ans: 3. The heat of neutralization of strong acid and strong base + ΔH of ionization of CH_3COOH
= Enthalpy of neutralization of CH_3COOH and NaOH
∴ – 57.1 kJ + ΔH of ionization of CH3COOH = – 55.9 kJ
∴ ΔH of ionization of CH_3COOH = (- 55.9 + 57.1) kJ
= 1.2 kJ.

Ans: 4. ΔHsolidifcation = – 150 × 128 = – 19200 J = – 19.2 kJ

[∵ M.wt.of $C_{10}H_8$ = 128]

Ans: 5. ΔG = ΔH – TΔS; For exothermic reactions,

ΔH is -ve For a spontaneous process ΔG is to be -ve.

Thus decrease in enthalpy (- AH) contributes significantly to the driving force (To make ΔG negative).

Ans: 6. A state function is a thermodynamic property that depends upon the state of the system and is independent of the path followed to bring about the change. Internal energy change (ΔU), enthalpy change (ΔH) entropy change (ΔS), and free energy change (ΔG) are examples.

Long Answer:

Ans: 1. Standard enthalpy of formation: The heat change accompanying the formation of 1 mole df a substance from its elements in their most stable state of aggregation is called its standard enthalpy of formation.

$H_2(g) + \frac{1}{2} O_2(g)\ H_2O(l)$; Δf He = 285.8 kJ mol^{-1}

(ii) Standard enthalpy of combustion: It is the heat change accompanying the complete combustion or burning of one mole of a substance in its standard state in excess of air or oxygen.

$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(1)$; ΔHθ = – 2658.0 kJ mol^{-1}.

(iii) Enthalpy of atomization: It is defined as the enthalpy change accompanying the breaking of one mole of a substance completely into its atoms in the gas phase.

$H_2(g) \rightarrow 2H(g)$ Δ_cHe = 435.0 kJ mol^{-1}

(iv) Enthalpy of solution: It is defined as the heat change when one mole of a substance dissolves in a specified amount of the solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving 2 moles of the substance in an infinite amount of the solvent.

(v) Lattice Enthalpy: The lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of an ionic compound dissociates into its ions in a gaseous state.

$$\underset{\text{1 mole}}{Na^+Cl^-(s)} \longrightarrow Na^+(g) + Cl^-(g);\ \Delta_{lattice} H^0 = +788\ kJ\ mol^{-1}$$

(vi) Thermochemical Equation: A balanced chemical equation together with the value of its A^H is called a thermochemical equation.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\ \Delta_rH^0 = -1367\ kJ\ mol^{-1}$$

The above equation describes the combustion of liquid ethanol. The negative sign indicates that tills are an exothermic reaction. We specify the physical state along with the allotropic state of the substance in a thermochemical equation.

Ans: 2.

$$\begin{aligned} K_P &= K_C(RT)^{\Delta n} \\ \Delta n &= n_p - n_r = 2 - 1 = 1. \end{aligned}$$

$T = 298\ K,\ R = 8.314\ JK^{-1}\ mol^{-1}$ [*Given*]

$$\begin{aligned} \therefore \quad K_p &= 1.8 \times 10^{-7} \times 8.314 \times 298 = 4.46 \times 10^{-4} \\ \text{Now} \quad \Delta_rG^0 &= -2.303\ RT \log K_p \\ &= -2.303 \times 8.314 \times 298 \times \log (4.46 \times 10^{-4}) \\ &= 19111.86\ J\ mol^{-1} = 19.12\ kJ\ mol^{-1}. \end{aligned}$$

Ans: 3.

$$\begin{aligned} \Delta_rG^0 &= \Delta_rH^0 - T\Delta_rS^0 \\ &= 80.0 - 400 \times 0.12 = 32.0\ kJ \\ \Delta_rG^0 &= -2.303\ RT \log K \\ 32.0 &= -2.303 \times 0.0831 \times 400 \log K \\ \text{or} \quad \log K &= -4.1782 = \bar{5}.8218 \\ \text{or} \quad K &= \text{Antilog}\ \bar{5}.8218 = 6.634 \times 10^{-5}. \end{aligned}$$

Ans: 4.

$$\Delta_rG^0 = -2{:}303\ RT \log K = 38484\ J\ (\text{given})$$

$$\begin{aligned} \Delta_rG^0 &= \Delta_rH^0 - T\Delta_rS^0 \\ \Delta_rS^0 &= \frac{\Delta_rH^0 - \Delta_rG^0}{T} = \frac{28400 - 38484}{298} \end{aligned}$$

$= -33.8\ JK^{-1}\ mol^{-1}$

Assertion Reason Answer:

1. (ii) Both A and R are true but R is not the correct explanation of A.
2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. Answer:

(1) (d) Determination of entropy

(2) (c) – 1482 kJ/mol

(3) (c) $q_1 + q_2 + 2q_3$

2. Answer:

(1) (b) It is not a state function

(2) (a) Born-Haber cycle

(3) (b) Enthalpy of hydrogenation