

Inter (Part-I) 2019

Chemistry	Group-I	PAPER: I
Time: 20 Minutes	(OBJECTIVE TYPE)	Marks: 17

Note: Four possible answers A, B, C and D to each question are given. The choice which you think is correct, fill that circle in front of that question with Marker or Pen ink in the answer-book. Cutting or filling two or more circles will result in zero mark in that question.

- 1-1- The order of effusion of NH_3 , SO_2 , Cl_2 and CO_2 gases is:
- $\text{NH}_3 > \text{SO}_2 > \text{Cl}_2 > \text{CO}_2$
 - $\text{NH}_3 > \text{CO}_2 > \text{SO}_2 > \text{Cl}_2$ ✓
 - $\text{Cl}_2 > \text{SO}_2 > \text{CO}_2 > \text{NH}_3$
 - $\text{NH}_3 > \text{CO}_2 > \text{Cl}_2 > \text{SO}_2$
- 2- The nature of positive rays in discharge tube depends upon the nature of:
- Anode
 - Cathode
 - Residual gas ✓
 - Discharge tube
- 3- 18 g glucose dissolved in 90 g water has relative lowering of vapour pressure equal to:
- $\frac{18}{90}$
 - $\frac{1}{6}$
 - $\frac{10}{51}$
 - $\frac{1}{51}$ ✓
- 4- The unit of rate constant is same as that of rate of the reaction having order:
- Zero ✓
 - One
 - Fractional
 - Two
- 5- The largest number of molecules is present in:
- 5.4 g of N_2O_4
 - 2.8 g of CO
 - 4.8 g of $\text{C}_2\text{H}_6\text{O}$
 - 3.6 g of H_2O ✓
- 6- The amount of heat absorbed when one mole of gaseous atoms are formed from the element is called enthalpy of:
- Formation
 - Reaction
 - Combustion
 - Atomization ✓

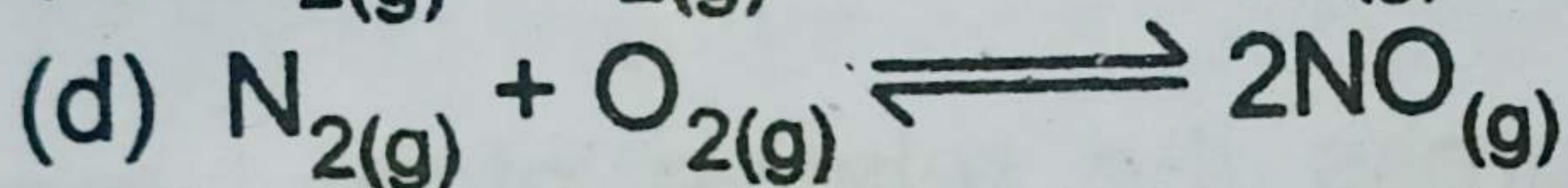
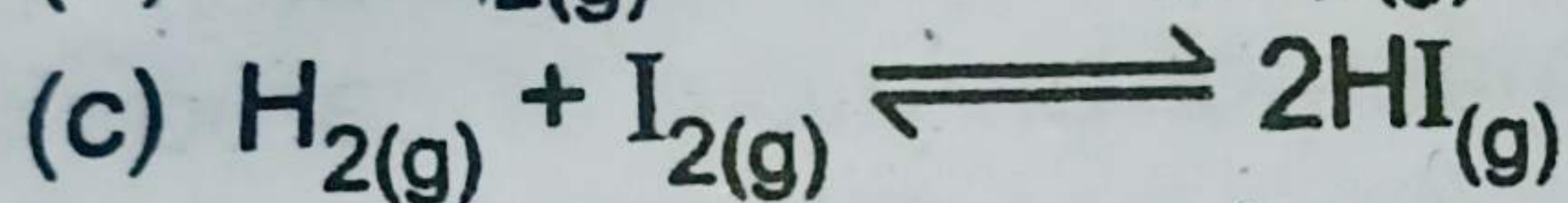
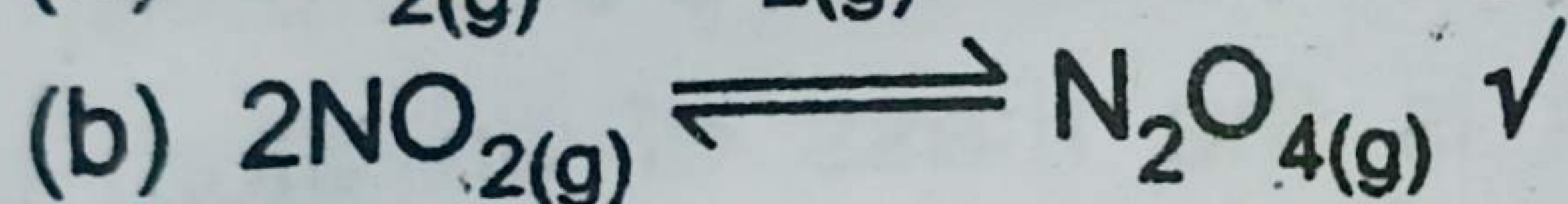
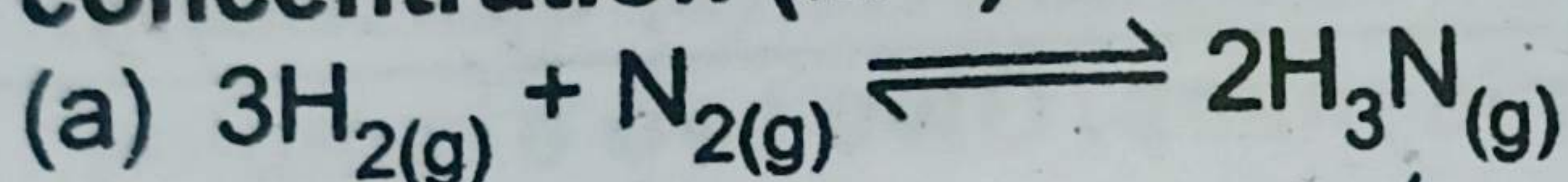
- 7- Solvent extraction is a separation technique used for the product, which is:
(a) Non-volatile; thermally unstable
(b) Volatile; thermally stable
(c) Non-volatile; thermally stable
(d) Volatile; thermally unstable ✓
- 8- For HF molecule μ_{obs} is 1.90 D; μ_{ionic} is 4.4 D. The percentage ionic character of HF molecule is:
(a) 100
(b) 80
(c) 57
(d) 43 ✓
- 9- The oxidation state of oxygen in OF_2 is:
(a) -2
(b) -1
(c) +1
(d) +2 ✓
- 10- The solid which has no definite crystalline shape:
(a) Sugar
(b) Salt
(c) Glass ✓
(d) Dry ice
- 11- 1.00 mole of SO_2 contains:
(a) 6.02×10^{23} atoms of oxygen
(b) 3.01×10^{23} molecules of SO_2
(c) 6.02×10^{23} molecules of SO_2 ✓
(d) 3.01×10^{23} atoms of sulphur
- 12- Quantum numbers, which represent 2p orbitals are:
(a) $n = 2, l = 1$ ✓
(b) $n = 1, l = 2$
(c) $n = 1, l = 0$
(d) $n = 2, l = 0$
- 13- Density of ice is minimum at 4°C due to:
(a) Empty spaces in structure of ice ✓
(b) Tetrahedral shape of crystal of ice
(c) Large bond lengths
(d) Large bond angles
- 14- Nature of bonds in N_2 molecule is:
(a) One sigma; two pi bonds ✓
(b) Two sigma; two pi bonds
(c) Two sigma; one pi bond
(d) Three pi bonds

15- The deviation of a gas from ideal behaviour is maximum at:

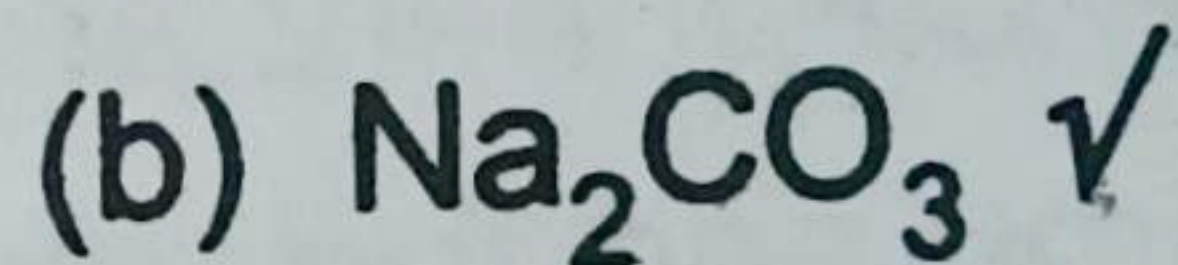
- (a) -10°C and 5 atm ✓ (b) -10°C and 2 atm
(c) 100°C and 2 atm (d) 0°C and 2 atm

16- For which of the following reaction, the unit of equilibrium constant (K_c) is reciprocal of molar

concentration (M^{-1}):



17- The salt dissolved in water forms a solution of pH greater than 7:



Inter (Part-I) 2019

Chemistry	Group-I	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

2. Write short answers to any EIGHT (8) questions: (16)

(i) Define relative atomic mass. Give two examples.

Ans Relative atomic mass is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12.

The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is $1/12^{\text{th}}$ of the mass of one carbon atom. On carbon-12 scale, the relative atomic mass of $^{12}_6\text{C}$ is 12.0000 amu and the relative atomic mass of ^1_1H is 1.008 amu.

(ii) Calculate the percentage of nitrogen in NH_2CONH_2 .
(Atomic masses of C = 12, N = 14, O = 16 and H = 1)

Ans NH_2CONH_2 (Urea)

$$\text{Molar Mass of Urea} = 14 + 2 + 12 + 16 + 14 + 2 \\ = 60 \text{ g mol}^{-1}$$

$$\text{Mass of nitrogen in the molecule} = 28 \text{ g mol}^{-1}$$

$$\% \text{age of Nitrogen} = \frac{28}{60} \times 100 \\ = 46.67 \%$$

(iii) Define gram formula giving one example.

Ans The formula unit mass of an ionic compound expressed in grams is called gram formula of the substance. The gram formula is also referred to as gram mole or simply a mole. *i.e.*,
1 gram formula of NaCl = 58.50 g

(iv) Write two disadvantages of drying crystals in the folds of filter paper.

Ans Pressing it between several folds of filter papers and repeating the process several times dries the crystallized substance. This process has the disadvantage *i.e.*,
1. Crystals are crushed to a fine powder.

2. Sometimes the fibres of filter paper contaminate the product.

(v) **Define distribution law about solvent extraction.**

Ans Solvent extraction is an equilibrium process and follows the distribution law or partition law. This law states that a solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added. The law is based on experimental evidence.

(vi) **Derive Graham's law of diffusion from kinetic equation.**

Ans **Graham's Law of Diffusion:**

Applying the kinetic equation,

$$PV = \frac{1}{3} mN\bar{c}^2 \quad (i)$$

If we take one mole of a gas having Avogadro's number of molecules ($N = N_A$), then the equation (i) can be written as:

$$PV = \frac{1}{3} mN_A\bar{c}^2$$

$$PV = \frac{1}{3} M\bar{c}^2 \quad (M = mN_A)$$

where M is the molecular mass of the gas.

$$\bar{c}^2 = \frac{3PV}{M}$$

Taking square root,

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3PV}{M}}$$

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad \left(\frac{M}{V} = d\right)$$

' V ' is the molar volume of gas at given conditions. Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas.

$$\sqrt{\bar{c}^2} \propto r$$

So, $r \propto \sqrt{\frac{3P}{d}}$

At constant pressure,

$$r \propto \sqrt{\frac{1}{d}}$$

which is Graham's law of diffusion.

- (vii) Give two reasons for deviation of real gases from ideal behaviour.

Ans It was van der Waals (1873), who attributed the deviation of real gases from ideal behaviour to two of the eight postulates of kinetic molecular theory of gases. These postulates are as under:

1. There are no forces of attraction among the molecules of a gas.
2. The actual volume of gas molecules is negligible as compared to the volume of the vessel.

- (viii) Write down two characteristics of plasma.

Ans Following are the two characteristics of plasma state:

1. A plasma must have sufficient number of charged particles. So, as a whole, it exhibits a collective response to electric and magnetic field.
2. Although, plasma includes electrons and ions and conducts electricity, it is macroscopically neutral. In measurable quantities, the number of electrons and ions are equal.

- (ix) Derive the SI units of van der Waals' constant 'a'.

Ans Units of 'a':

Since,
$$P' = \frac{n^2 a}{V^2}$$

So,
$$a = \frac{P' V^2}{n^2}$$

$$a = \frac{\text{atm} \times (\text{dm}^3)^2}{(\text{mol})^2}$$

$$a = \text{atm dm}^6 \text{ mol}^{-2}$$

In S.I, units, pressure is in Nm^{-2} and volume in m^3 .

So,
$$a = \frac{\text{Nm}^{-2} \times (\text{m}^3)^2}{(\text{mol})^2}$$

$$a = \text{Nm}^4 \text{ mol}^{-2}$$

- (x) Sea water has 5.65×10^{-3} g of dissolved oxygen in one kg of water. Calculate the concentration of oxygen in sea water in parts per million (ppm).

Ans Mass of oxygen dissolved = 5.65×10^{-3}

Mass of water = 1 kg = 1000 gm

Concentration of O_2 in sea water (ppm) = ?

$$\text{Part per million} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$\text{Concentration of } O_2 \text{ in sea water} = \frac{5.56 \times 10^{-3}}{1000} \times 10^6 = 5.65 \text{ ppm}$$

(xi) **Define molal boiling point constant. Give one example.**

Ans It is the elevation of boiling point of the solvent, when one mole of the non-volatile non-electrolyte solute is dissolved in one kg of the solvent. The molal boiling point constant is also called ebullioscopic constant. It is denoted by K_b . For example: You may dissolve 6 g of urea in 500 g of H_2O or 18 g of glucose in 500 g of H_2O ; both give 0.2 molal solution and both have same elevation of boiling points, i.e., $0.1^\circ C$, which is $1/5^{\text{th}}$ of $0.52^\circ C$.

(xii) **Define solubility curve. Name its two types.**

Ans A graphical representation between temperature and solubility of solution is called solubility curves. There are two types of solubility curves:

1. Continuous solubility curves
2. Discontinuous solubility curves

3. Write short answers to any EIGHT (8) questions: (16)

(i) **Why ice occupies 9% more volume than liquid water?**

Ans When the temperature of water is decreased and ice is formed, then the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure. That is why, when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water.

(ii) **Why evaporation causes cooling?**

Ans Evaporation causes cooling because when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of liquid falls and heat moves from surrounding to liquid and then temperature of surrounding also falls.

(iii) **Write two applications of liquid crystals.**

Ans Following are the two applications of liquid crystals:

1. In chromatographic separations, liquid crystals are used as solvents.

2. Oscillographic and TV displays also use liquid crystal screens.

(iv) Why heat of sublimation of I_2 is very high than other halogens?

Ans Iodine has greater number of electrons about 53 electrons around its nucleus. So unsymmetrical electronic distribution or polarization of iodine is also very high. Due to this, strong London dispersion forces are present among iodine molecules. That's why, heat of sublimation of iodine is very high.

(v) Write defects of Rutherford atomic model.

Ans Following are the defects in Rutherford's atomic model:

1. The outer electrons could not be stationary.
2. The behaviour of electrons remained unexplained in the atom.
3. Planet-like picture was defective because the moving electron must be accelerated towards the nucleus.

(vi) State Moseley's law and also give its importance.

Ans This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it.

Importance of Moseley's Law:

1. Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev's periodic table.
2. This law has led to the discovery of many new elements like Tc(43), Pr(59), Rh(45).
3. The atomic number of rare earth metals have been determined by this law.

(vii) Why e/m value of cathode rays is equal to that of electron?

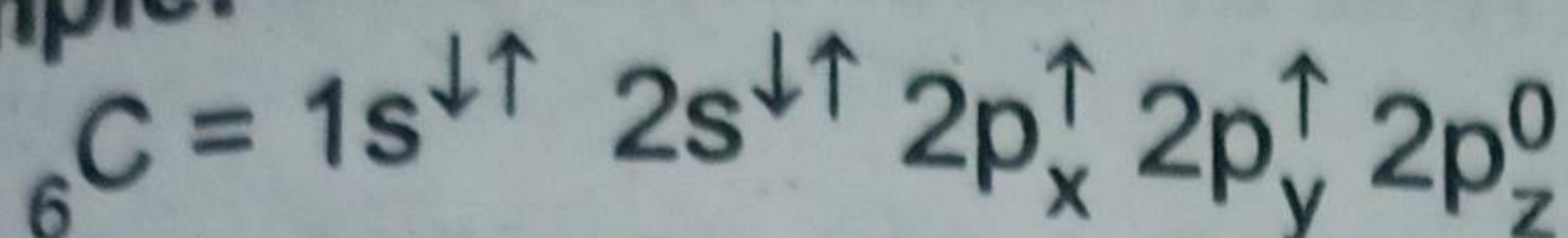
Ans The e/m value of cathode rays shows that they are simply electrons. J.J. Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles. Stoney named these particles as electrons. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same as no matter from which gas was used in the discharge tube.

(viii) State Hund's rule.

Ans Hund's Rule:

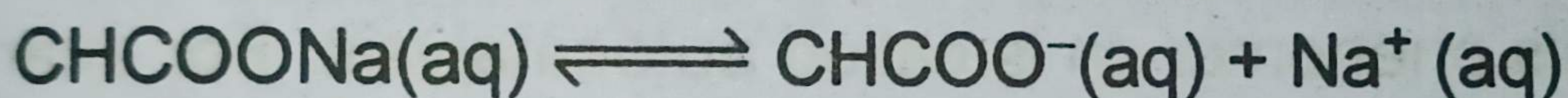
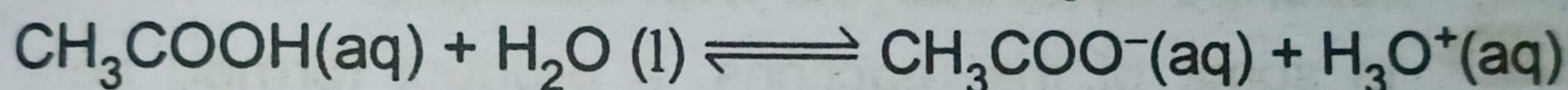
If degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbital with same spin rather than putting them in same orbital with opposite spins.

Example:



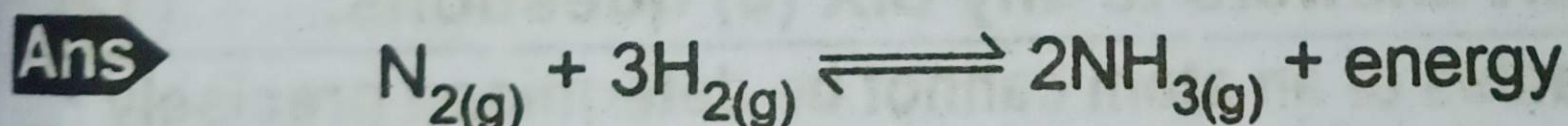
(ix) How does buffer act?

Ans Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa . Common ion effect helps us to understand how the buffer will work. CH_3COOH , being a weak electrolyte undergoes very little dissociation. When CH_3COONa , which is a strong electrolyte, is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^- .



If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COOH and the pH of solution increases. Greater the concentration of acetic acid as compared to CH_3COONa , lesser is the pH of solution.

(x) Give optimum conditions to get maximum yield of NH_3 .



When we look at the balanced chemical equation, it is inferred from Le-Chatelier's principle that one can have three ways to maximize the yield of ammonia:

1. By continual withdrawal of ammonia after intervals, the equilibrium will shift to forward direction in accordance with Le-Chatelier's principle. To understand, it look at the effect of change of concentration in Le-Chatelier's principle.
2. Increase the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of the products. High pressure will shift the equilibrium position to right to give more and more ammonia.
3. Decreasing the temperature will shift it to the forward direction according to Le-Chatelier's principle.

So high pressure, low temperature and continual removal of the ammonia will give the maximum yield of ammonia.

(xi) Justify that radioactive decay is always a first order reaction.

Ans In first order kinetics, the rate of reaction is proportional to the concentration of a reactant.

In radioactive decay, the no. of radioactive atoms decaying per unit time is proportional to the total no. of radioactive atoms present at that time, i.e.,

$$\Delta N = -(\text{decay constant}) N \Delta t$$

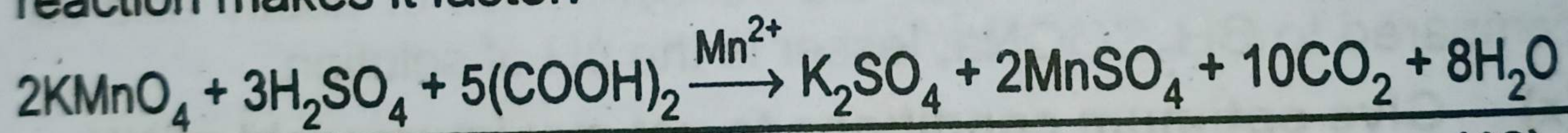
$$\left(\frac{\Delta N}{\Delta t}\right) = -(\text{decay constant}) N$$

Since the decay rate is proportional to first power of radioactive atoms present, therefore, radioactive decay is first order reaction.

(xii) Describe autocatalysis with example.

Ans In some of the reactions, a product formed acts as a catalyst. This phenomenon is called autocatalysis. For example:

The reaction of oxalic acid with acidified KMnO_4 is slow at the beginning, but after sometimes, MnSO_4 produced in the reaction makes it faster.



4. Write short answers to any SIX (6) questions: (12)

(i) Why the radius of an atom cannot be determined precisely?

Ans The radius of an atom cannot be determined precisely due to the following reasons:

1. There is no sharp boundary of an atom. The probability of finding an electron never becomes exactly zero even at large distances from the nucleus.
2. The electronic probability distribution is affected by neighbouring atoms. For this reason, the size of an atom may change from one compound to another.

(ii) Define ionization energy. Give its trend in periods and group of periodic table.

Ans The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion.



In the periodic table, the ionization energies increase from left to right in a period with the increase in the proton number, until a maximum value is reached at the end of the period.

In groups, the ionization energy decreases in spite of the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy. Moreover, the force of attraction also decreases due to increasing shielding effect of the intervening electrons.

(iii) **How electronegativity changes in a group?**

Ans The tendency of an atom to attract a shared pair of electrons towards itself is called electronegativity. It has no units.

Electronegativity decreases from top to bottom in group. This is due to successive increase in the number of electronic shells. The addition of extra shells in larger atoms screens the shared pair from the nucleus and the pair is less attracted by the element in the combined state.

(iv) **Define coordinate covalent bond. Give one example.**

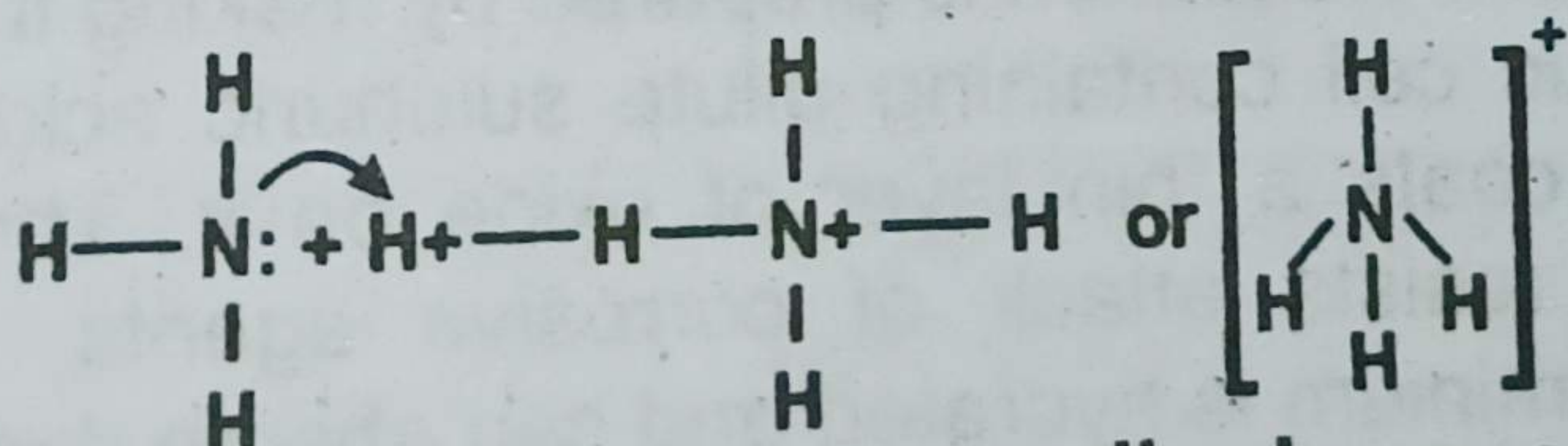
Ans **Definition:**

A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.

Example:

- Formation of ammonium ion:

Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ ion.



(v) **Explain that burning of candle is a spontaneous process. Justify.**

Ans A reaction will be called a spontaneous process, if it needs energy to start with, but once it is started, then it proceeds on its own.

Burning of candle is example of spontaneous reaction. A candle does not burn in air on its own rather the reaction is initiated by a spark and once it starts burning, then the reaction goes spontaneously to completion.

(vi) **Define state and state function.**

Ans **State:**

The condition of a system is called state of a system. When any process is performed on a system, its state is altered in some ways. Let us consider a beaker containing water. It will be a system having certain temperature and volume.

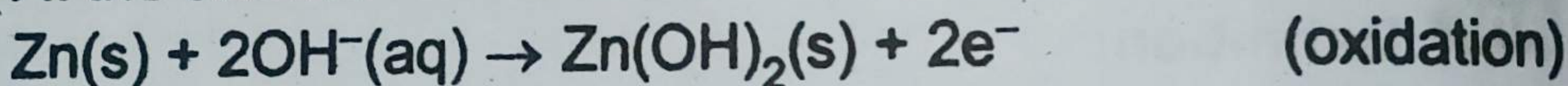
State function:

A state function is a macroscopic property of system which has some definite values for initial and final states and which is independent of path adopted to bring about a change.

(vii) **Write reactions taking place at anode and cathode in silver oxide battery.**

Ans The cathode is of silver oxide, Ag_2O and the anode is of zinc metal. The following reactions occur in a basic electrolyte:

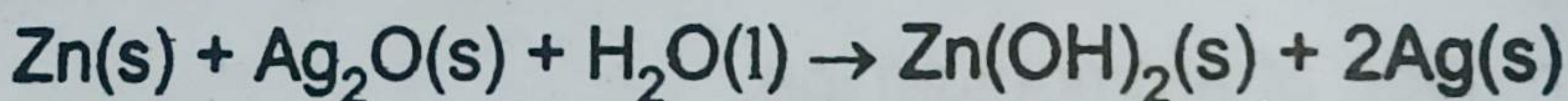
At the anode:



At the cathode:



The overall reaction is:



The voltage of silver oxide battery is about 1.5 V.

(viii) **How is aluminium anodized in an electrolytic cell?**

Ans Anodized aluminium is prepared by making it an anode in an electrolytic cell containing dilute sulphuric acid or chromic acid, which coats a thin layer of oxide on it. The aluminium oxide layer resists attack of corrosive agents. The freshly anodized aluminium is hydrated and can absorb dyes.

(ix) **Calculate oxidation number of Cr in K_2CrO_4 .**

Ans Let the oxidation number of Cr = x

Oxidation number of K = +1

Oxidation number of O = -2

By applying formula,

$$2(\text{O.N. of K}) + (\text{O.N. of Cr}) + 4(\text{O.N. of O}) = 0$$

$$2(+1) + (x) + 4(-2) = 0$$

$$2 + x - 8 = 0$$

$$x - 6 = 0$$

$$x = 6$$

Oxidation number of Cr = 6

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) Describe combustion analysis method for the determination of percentage composition of an organic compound. (4)

Ans **Combustion Analysis:**

A weighed sample of the organic compound is placed in the combustion tube. This combustion tube is fitted in a furnace. Oxygen is supplied to burn the compound. Hydrogen is converted to H_2O and carbon is converted to CO_2 . These gases are absorbed in $\text{Mg}(\text{ClO}_4)_2$ and 50% KOH, respectively. The difference in the masses of these absorbers gives us the amounts of H_2O and CO_2 produced. The amount of oxygen is determined by the method of difference.

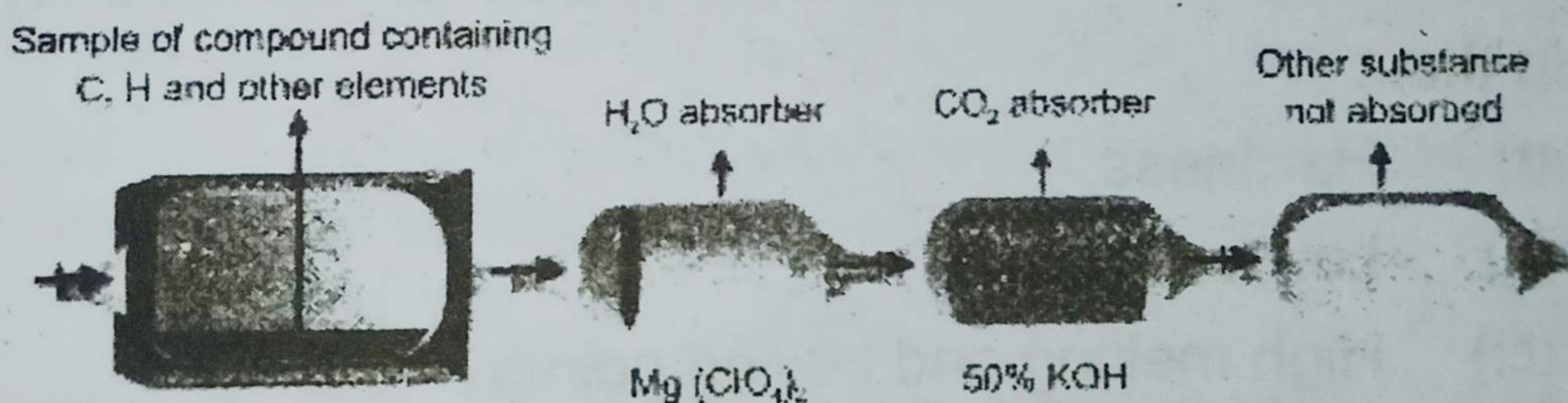


Fig. Combustion analysis.

Following formulas are used to get the percentages of carbon, hydrogen and oxygen, respectively.

$$\% \text{ of carbon} = \frac{\text{Mass of } \text{CO}_2}{\text{Mass of organic compound}} \times \frac{12.00}{44.00} \times 100$$

$$\% \text{ of hydrogen} = \frac{\text{Mass of } \text{H}_2\text{O}}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$$

The percentage of oxygen is obtained by the method of difference.

% of oxygen = $100 - (\% \text{ of carbon} + \% \text{ of hydrogen})$.

(b) Define ionic solids. Give their three properties. (4)

Ans Ionic Solids:

Definition:

"Crystalline solids which consist of positively and negatively charged ions that are held together through strong electrostatic forces of attraction (ionic bonds) are called ionic solids."

Examples:

NaCl, KBr, NaNO_3 , etc.

Properties:

1. **Physical state:**

They are solids at room temperature under ordinary conditions of temperature and pressure. They never exist in the form of liquids or gases.

2. **Stability:**

Ionic crystals are very stable compounds. This greater stability is due to the fact that cations and anions are held together through very strong forces of attraction. Therefore, very high energy is required for the separation of cations and anions from each other. This high stability of the ionic crystals explain their:

- (i) Hardness,
- (ii) Low volatility,
- (iii) High melting and boiling points.

3. **Molecular existence:**

Ionic solids do not exist as individual neutral independent molecules. Therefore, we always represent ionic solids in terms of formula units.

Q.6.(a) One mole of methane gas is maintained at 300 K, its volume is 250 cm^3 . Calculate the pressure exerted by the gas, when the gas is ideal. (4)

Ans When the gas is ideal, general gas equation is applied i.e.,

$$PV = nRT$$

$$V = 250 \text{ cm}^3 = 0.25 \text{ dm}^3$$

$$n = 1 \text{ mole}$$

$$T = 300 \text{ K}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ dm}^3 = 1000 \text{ cm}^3$$

$$P = \frac{nRT}{V}$$

Putting the values along with units,

$$P = \frac{1 \text{ mol} \times 0.0821 \text{ dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3}$$

$$P = \boxed{98.5 \text{ atm}}$$

If CH_4 gas had ideal under the given conditions, 98.5 atm pressure would have been exerted.

(b) Write four defects of Bohr's atomic model. (4)

Ans The defects are as follows:

- It can successfully explain origin of spectrum of H – atom and ions like He^{+1} , Li^{+2} , etc. These are all one electron systems. But this theory is not able to explain origin of spectrum of multi-electrons or poly electron systems like He, Li, etc.
- When spectrum of H_2 is observed by means of high resolving power spectrometer, individual spectral lines are replaced by several very fine lines *i.e.*, original lines are seen divided into other lines. The H_α – line in Balmer series is found to consist of five component lines. This is called fine structure or multiple structure. Actually, the appearance of several lines in a single line suggests that only one quantum no. is not sufficient to explain origin of spectral lines.
- Bohr suggested circular orbits of electrons around nucleus of hydrogen atom, but researches have shown that motion of electron is not in a single plane but takes place in three dimensional space. It is not flat.
- When excited atoms of hydrogen are placed in magnetic field, its spectral lines further split up into closely spaced lines. This type of splitting is called as Zeeman effect. So, if source which is producing Na-spectrum is placed in

weak magnetic field, it causes splitting of two lines of Na into components lines. Similarly, when excited hydrogen atoms are placed in electric field, similar splitting of spectral lines takes place which is called "Stark effect". Bohr's theory does not explain either Zeeman or Stark effect.

Q.7.(a) Draw the molecular orbital picture of O_2 molecule. (4)

Ans

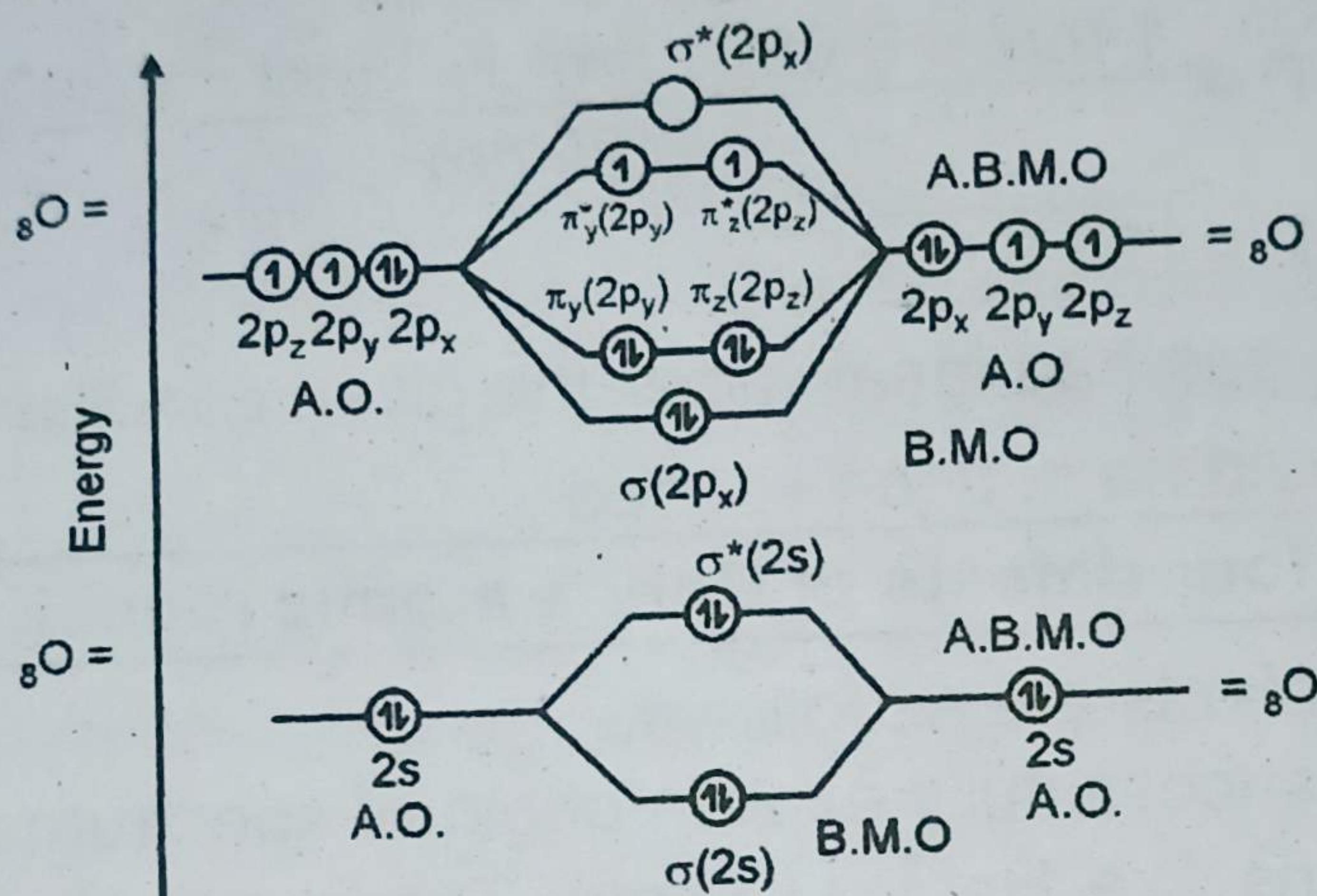


Fig. Molecular orbitals in O_2 molecule.

(b) State Hess's law of constant heat summation. Explain it giving two examples. (4)

Ans Hess's law of constant heat summation:

This law states that:

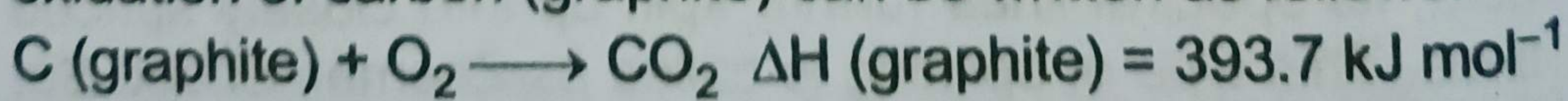
"If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."

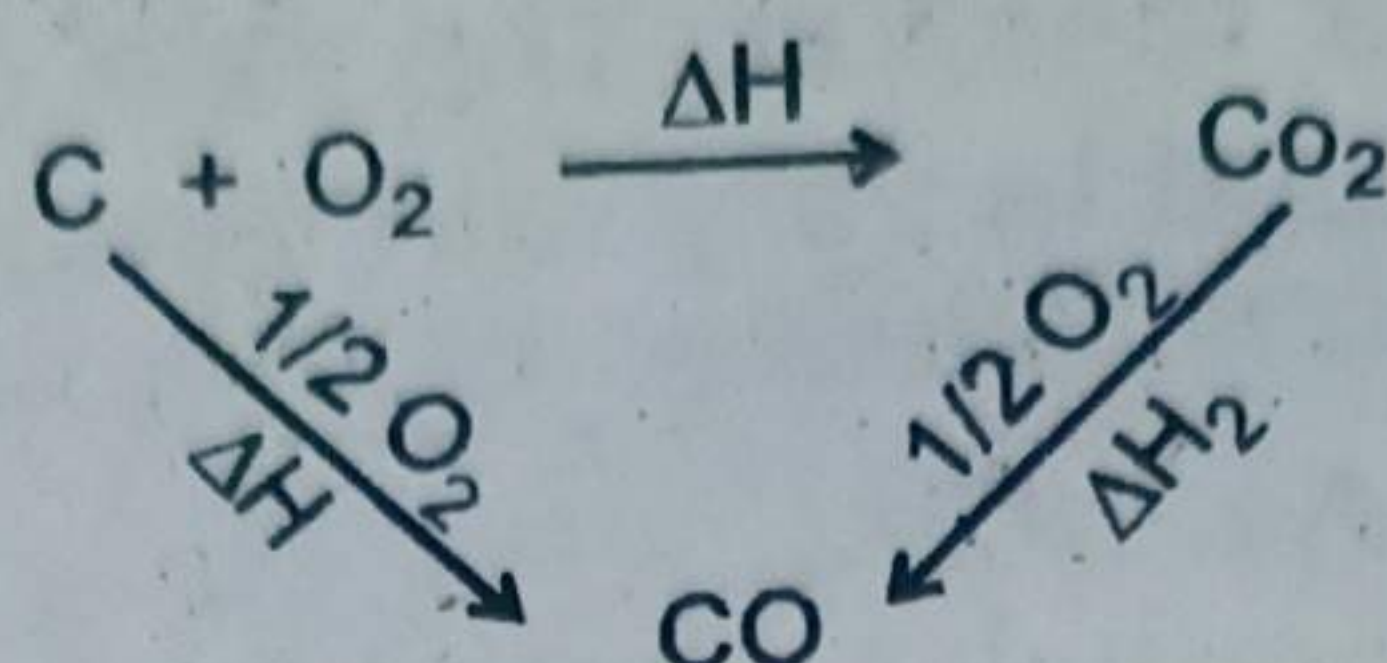
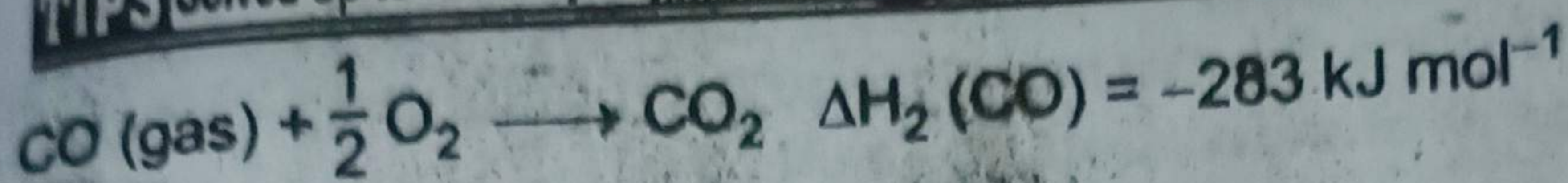
Let A can be converted to D directly in a single step and heat evolved is ΔH . If the reaction can have a route from $A \rightarrow B \rightarrow C$ as shown below:

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Mathematically, $\Sigma \Delta H (\text{cycle}) = 0$

Example: If the enthalpy of combustion for graphite to form CO_2 and the enthalpy of combustion of CO to form CO_2 are known, we can determine the enthalpy of formation for CO. The oxidation of carbon (graphite) can be written as follows:





Applying equation of heat summation:

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

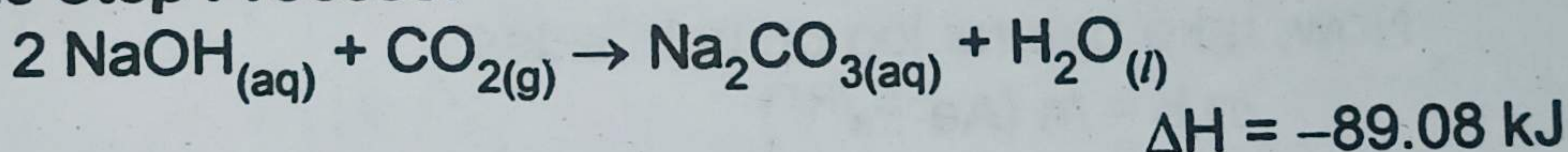
$$\Delta H_1 = \Delta H - \Delta H_2$$

$$= -393 - (-283)$$

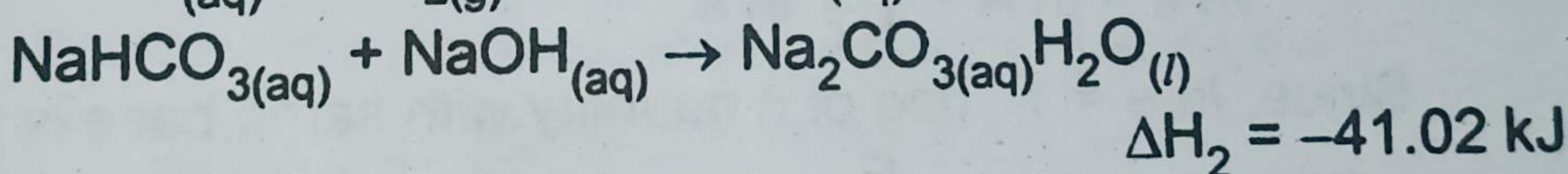
$$= -110 \text{ kJ mol}^{-1}$$

The formation of sodium carbonate is another example for the verification of Hess's law. The formation of sodium carbonate may be studied as a single step process, or in two steps as via sodium hydrogen carbonate.

Single Step Process:



Two Step Process:



According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 \quad (\text{i})$$

Putting the values of ΔH , ΔH_1 , ΔH_2 , in equation (i).

$$-89.08 = -48.06 - 41.02$$

$$-89.08 = -89.08$$

This illustrates, how heats of reactions may be added algebraically and this proves Hess's law.

Q.8.(a) Ca(OH)_2 is a sparingly soluble compound. Its solubility product is 6.5×10^{-6} . Calculate the solubility of Ca(OH)_2 . (4)

Ans For Answer see Paper 2015 (Group-II), Q.8.(b).

- (b) How does the Arrhenius equation help us to calculate energy of activation of a reaction? (4)

Ans Arrhenius equation explains the effect of temperature on the rate constant of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature. According to Arrhenius,

$$k = Ae^{-E_a/RT} \quad (1)$$

So, 'k' is exponentially related to activation energy (E_a) and temperature (T). R is general constant and e is the base of natural logarithm. The equation shows that the increase in temperature, increases the rate constant and the reactions of high activation energy have low 'k' values. The factor 'A' is called Arrhenius constant and it depends upon the collision frequency of the reacting substances. This equation helps us to determine the energy of activation of the reaction as well. For this purpose, we take natural log of Arrhenius equation, which is expressed as \ln . The base of natural log is 'e' and its value is 2.718281.

Now, take natural log on both sides,

$$\ln k = \ln (Ae^{-E_a/RT})$$

$$\text{or } \ln k = \ln A + \ln e^{-E_a/RT}$$

$$\ln k = \ln A + \frac{-E_a}{RT} \ln e$$

Since, $\ln e = 1$ (log of a quantity with same base is unity)

$$\text{Therefore, } \ln k = \frac{-E_a}{RT} + \ln A \quad (2)$$

The equation (1) is the equation of straight line, and from the slope of straight line ' E_a ' can be calculated. In order to convert this natural log into common log of base 10, we multiply the \ln term with 2.303.

$$2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A \quad (\text{The base of common log is 10})$$

Dividing the whole equation by 2.303,

$$\log k = \frac{-E_a}{2.303 RT} + \log A \quad (3)$$

This equation (3) is again the equation of straight line resembling.

$$y = -mx + c$$

where 'm' is slope of straight line and 'c' is the intercept of straight line. Temperature is independent variable in this equation, while rate constant k is dependent variable. The other factors like E_a , R and A are constants for a given reaction.

When a graph is plotted between $\frac{1}{T}$ on x-axis and $\log k$ on y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign, so the straight line has two ends in second and fourth quadrants. The slope of the straight line is measured by taking the tangent of that angle θ which this straight line makes with the X-axis. To measure the slope, draw a line parallel to X-axis and measure angle θ . Take $\tan \theta$ which is slope. This slope is equal to $\frac{-E_a}{2.303 R}$.

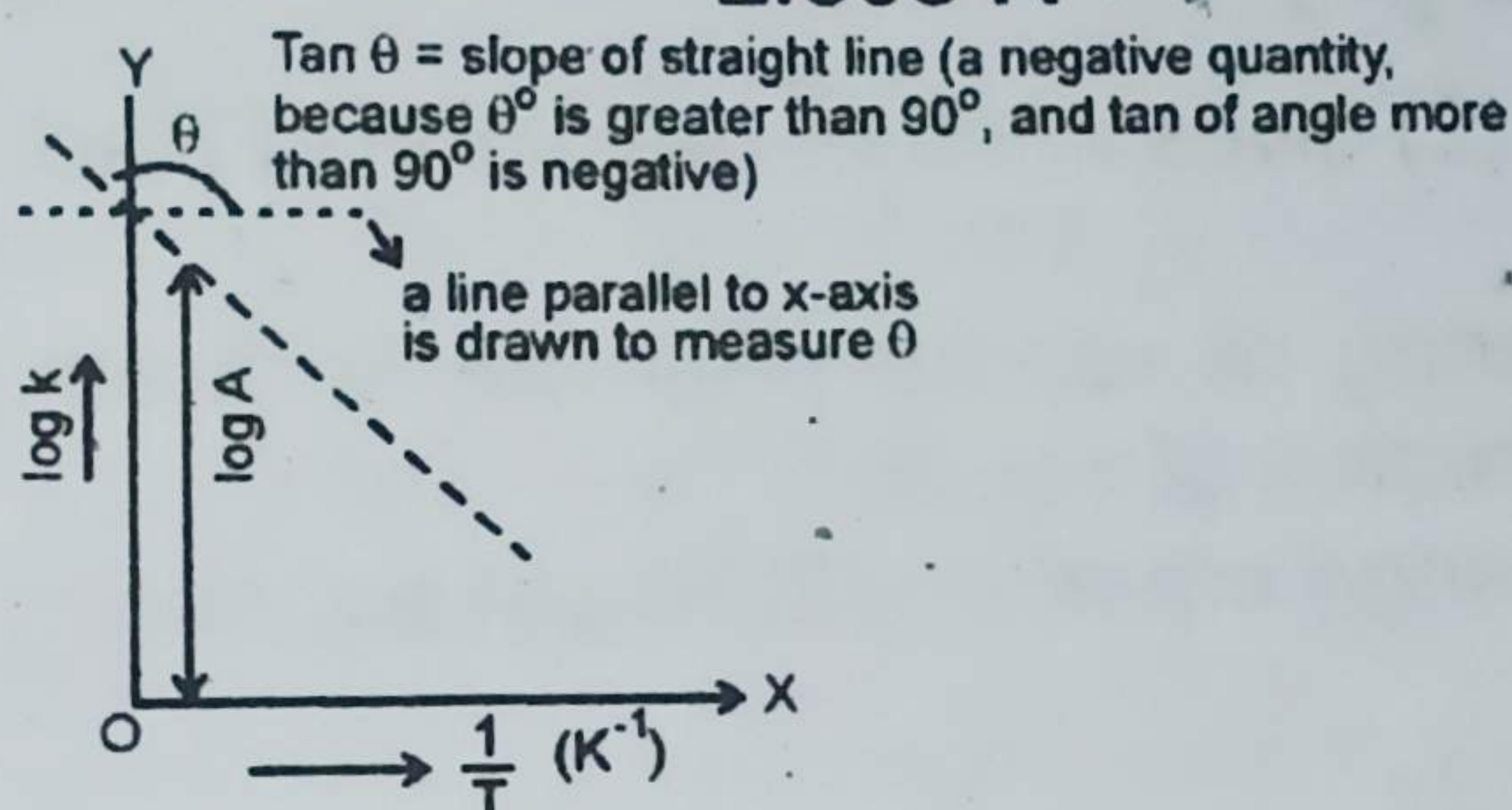


Fig. Arrhenius plot to calculate the energy of activation.

$$\text{Slope} = \frac{-E_a}{2.303 R}$$

$$\text{Therefore, } E_a = -\text{Slope} \times 2.303 R \quad (4)$$

The straight lines of different reactions will have different slopes and different ' E_a ' values. The units of slopes are in kelvins (k).

$$\text{Since, } \text{Slope} = \frac{\text{J mole}^{-1}}{2.303 \text{ JK}^{-1} \text{ mol}^{-1}} = K$$

Q.9.(a) Give the three statements of Raoult's law. (4)

Ans Raoult's Law:

"The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in a solution."

Mathematically, it can be written in equation form as follows:

$$p = p^{\circ} x_1 \quad (1)$$

where p is the vapour pressure of solvent in the solution, p° is the vapour pressure of pure solvent and x_1 is the mole fraction of the solvent.

We also know that:

$$x_1 + x_2 = 1 \quad (x_2 \text{ is the mole fraction of solute})$$

$$\text{or } x_1 = 1 - x_2$$

Putting the value of x_1 in the equation (1),

$$p = p^{\circ} (1 - x_2)$$

$$p = p^{\circ} - p^{\circ} x_2$$

$$\text{or } p^{\circ} - p = p^{\circ} x_2$$

$$\text{or } \Delta p = p^{\circ} x_2 \quad (2)$$

Equation (2) gives another definition of Raoult's law.

Second way:

"The lowering of vapour pressure is directly proportional to the mole of fraction of solute."

Now rearrange equation (2) to get equation (3),

$$\frac{\Delta p}{p^{\circ}} = x_2 \quad (3)$$

$\frac{\Delta p}{p^{\circ}}$ is called relative lowering of vapour pressure and it is

more important than actual lowering of vapour pressure (Δp). The equation (3) gives us another definition of Raoult's law.

Third way:

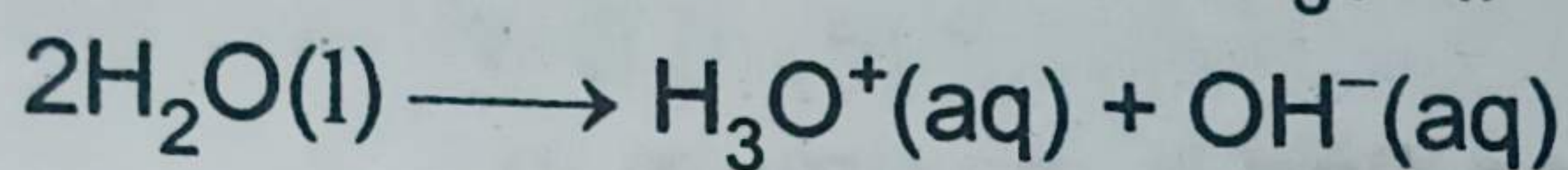
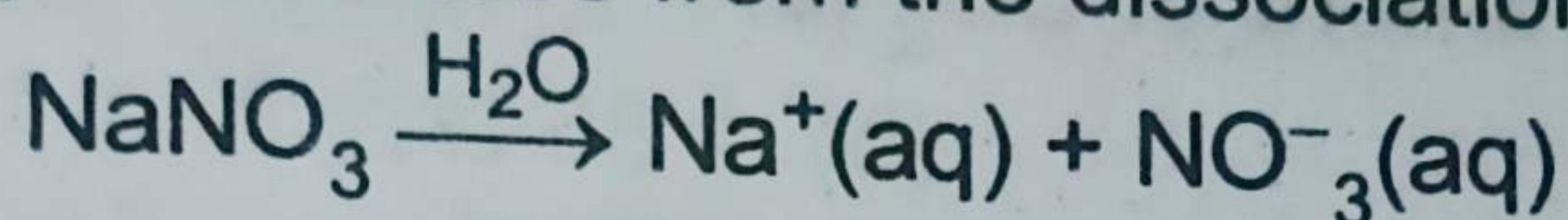
"The relative lowering of vapour pressure is equal to the mole fraction of solute."

The relative lowering of vapour pressure:

- (i) is independent of the temperature.
- (ii) depends upon the concentration of solute.
- (iii) is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

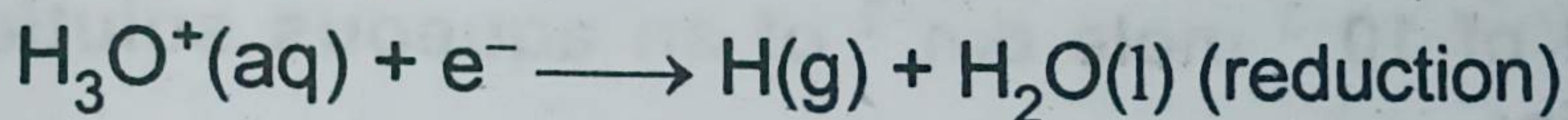
- (b) Describe the electrolysis of concentrated solution of NaNO_3 in aqueous solution. (4)

Ans The electrolysis of aqueous solutions is somewhat more complex. Its reason is the ability of water to be oxidized as well as reduced. Hence, the products of electrolysis are not precisely predictable. Some metal cations are not discharged from their aqueous solutions. e.g., While electrolyzing aqueous sodium nitrate (NaNO_3) solution, sodium ions are not discharged at the cathode. A small concentration of hydronium and hydroxyl ions arises from the dissociation of water:

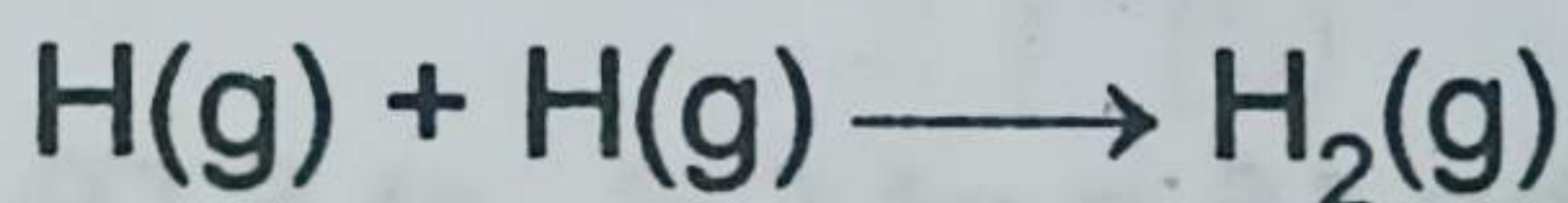


Hydronium ions accept electrons from the cathode to form hydrogen atoms.

At cathode:



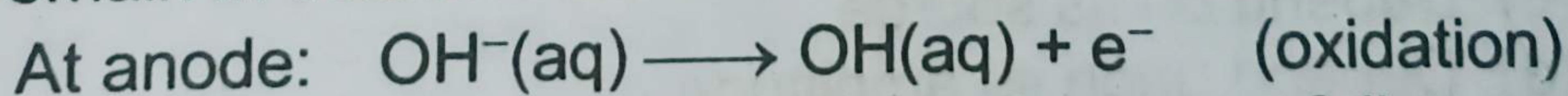
Subsequently, hydrogen atoms combine rapidly to form hydrogen molecules at the cathode.



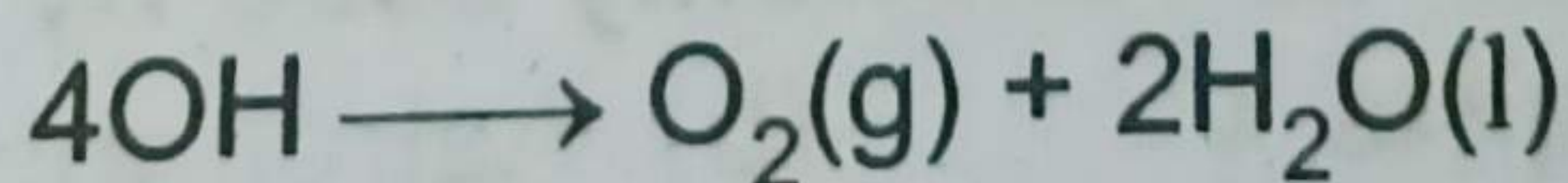
So, H_2 gas evolves at cathode.

The concentration of hydronium ions is only $10^{-7} \text{ mol dm}^{-3}$ in pure water. When these are discharged, then more are formed by further dissociation of water molecules. This gives a continuous supply of such ions to be discharged. Sodium ions remain in solution, while hydrogen is evolved at the cathode. Thus, the reduction of the two cations depends on the relative ease of the two competing reactions.

At the anode, both nitrate and hydroxide ions are present. Hydroxide ions are easier to discharge than nitrate ions. Nitrate ions remain in solution while the electrode reaction is:



The OH groups combine to give O_2 gas as follows:



So, O_2 gas evolves at the anode.

But, remember that the expected order of the discharge of ions may also depend upon their concentrations.