

ENERGETICS



- Every chemical rxn which occurs is accompanied by a heat change.
- A heat change can also be called an enthalpy change.
- An enthalpy change is given the symbol ΔH
- A '+' ΔH shows that heat energy is being absorbed into the system. It shows that it is an endothermic process.
- A '-' ΔH shows that heat is being released from the system. It shows that it is an exothermic process.
- For uniformity to be achieved, rxns should be done at standard state conditions.
- Standard state conditions can be represented by the symbol \ominus
- Standard state conditions are as follows:
 - 298 K - temperature
 - 1 Atm - pressure
- Therefore it implies ΔH - heat enthalpy change of rxn
 ΔH^\ominus - standard heat enthalpy change of rxn.

Enthalpy change of rxn / standard enthalpy change of rxn

- ΔH is the heat change during a chemical rxn
- ΔH^\ominus is the heat change during a chemical rxn per mole of products / reactants at 298 K and 1 Atm.

When defining a named standard enthalpy change (e.g. $\Delta H_{\text{at}}^\ominus$ or standard enthalpy change of atomisation), one has to pay attention to:

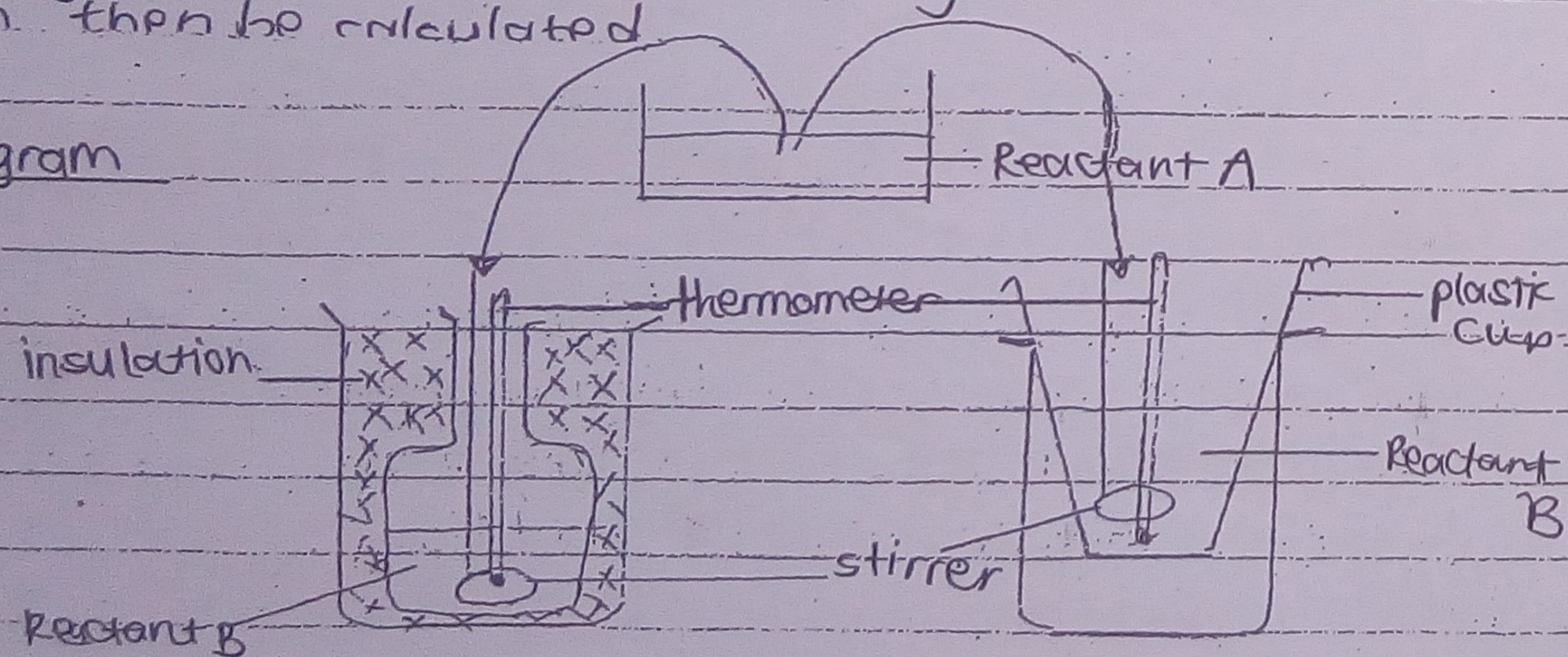
- (i) heat change (heat gained or heat loss). If heat can either be gained or lost during that particular rxn, then we say it's a heat change.

- i) We should also specify whether the rxn is per mole of the reactants or per mole of the products.
- ii) Standard state conditions should be stated.
- iii) One should also know the supporting eqn. and provide it if asked.

Measuring \bar{e} enthalpy change of rxn

- Heat change in a chemical rxn is measured using a calorimeter.
- During the process, the initial temperatures of the reactants are measured and their values recorded.
- Reactants of known concentrations and volumes are then allowed to react.
- The highest or the lowest temperature rise or fall during the rxn is then recorded.
- Therefore, the temp change during the chemical rxn can then be calculated.

Diagram



The enthalpy change of rxn can then be calculated using $\Delta H = mc\Delta T$.

When performing calculations using \bar{e} above formula

assumptions can be made i.e. $1g = 1cm^3$ of the reactant. When $A(l)$
 The density of the resultant solution is $1g/cm^3$
 In the relationship above c reps specific heat capacity (heat energy required to raise the temp of $1g$ of the solution by $1K$)

Task 1. Consider the following equation $A(l) + B(l) \rightarrow C + D$
 $24cm^3$ of $0,18M$ of A was allowed to react with $31cm^3$ of $0,14M$ of B . During the rxn the temp rose from $25^\circ C$ to $44^\circ C$. $25J$ of energy was found to be required to raise the temp of the resulting solution by $1K$. Calculate the standard enthalpy change of rxn

Solution

$$\begin{aligned} \text{Mols of } A &= 0,18 \text{ mol dm}^{-3} \times (24 \times 10^{-3}) \text{ m}^3 \\ &= 0,00432 \text{ mols} \end{aligned}$$

$$\Delta H = mc\Delta T$$

$$m = 31g + 24g = 55g$$

$$c = 25$$

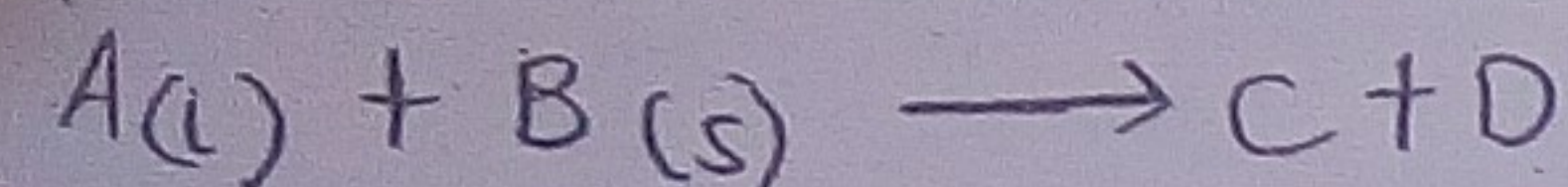
$$\Delta T = 19^\circ C \text{ (heat is released)}$$

$$\begin{aligned} \Delta H &= 55 \times 25 \times 19 \\ &= 26125 \text{ J} \end{aligned}$$

$$\begin{aligned} \text{Mols of } B &= 0,14 \text{ M} \times 31 \text{ cm}^3 \\ &= 0,00434 \text{ mols} \end{aligned}$$

Therefore B is an excess reactant. Thus if $0,00432$ mols equal to $26125J$, $1 \text{ mol} = -6047 \text{ KJ/mol}$

Consider the rxn below



When 400cm^3 of $0,2\text{M}$ A was reacted with 6g of element B with an Ar of 120 . During the rxn, the initial temp of A was 25°C . The lowest temp fall during the reaction was 7°C . It was found that 15J of energy was required to raise the temp of 1kg of the resultant mixture by 1K . Calculate the standard enthalpy change of the rxn.

If a mix solid & liquid, consider mass of liquid

Solution

$$\begin{aligned}\Delta H &= mc\Delta T \\ &= 400\text{g} \times 15\text{J} \times 18 \\ &= 108000\text{J}\end{aligned}$$

$$\begin{aligned}\text{Mols of A} &= 0,4 \times 0,2 \\ &= 0,08\text{ mols}\end{aligned}$$

$$\text{Mols of B} = \frac{6\text{g}}{120} = 0,05\text{ mols}$$

B is the limiting reagent.

$$\begin{array}{l} 0,05\text{ mols} = 108000\text{J} \\ 1 = \text{more} \end{array}$$

$$\Delta H^\ominus = +2160\text{KJmol}^{-1}$$

It should always be that when performing calculations involving standard enthalpy changes of rxn, one has to calculate the enthalpy change first before deducing a

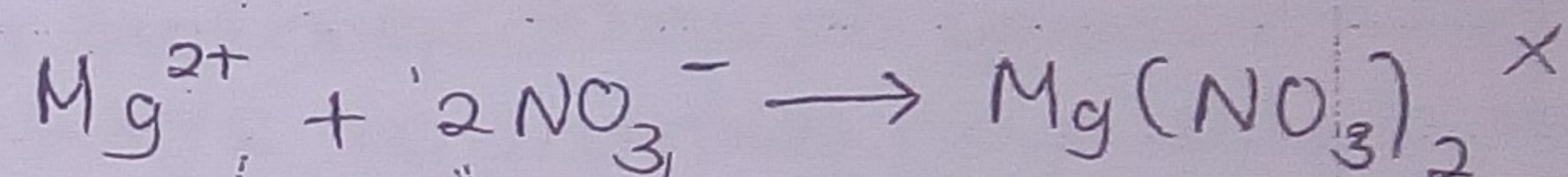
standard enthalpy change of rxn

* Standard enthalpy change of formation (ΔH_f^\ominus)

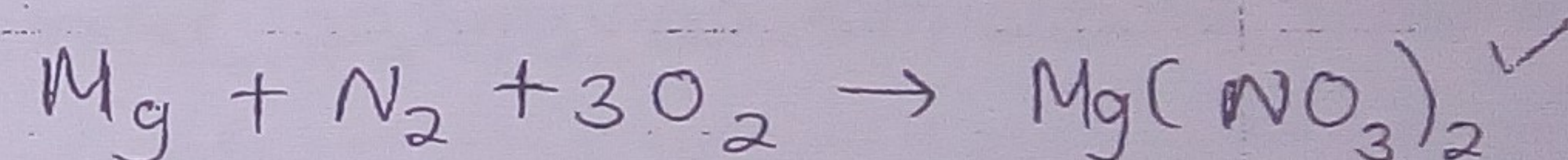
Dfn This is the heat energy change when one mole of a compound is formed from its constituent elements at 298K and 1atm .

For example

Enthalpy change of formation of magnesium nitrate $\text{Mg}(\text{NO}_3)_2$

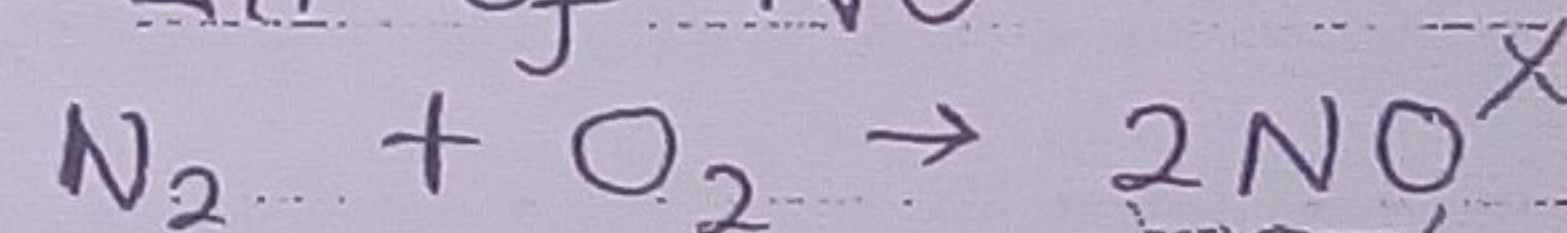


Consider \rightarrow They are not constituents in their natural states

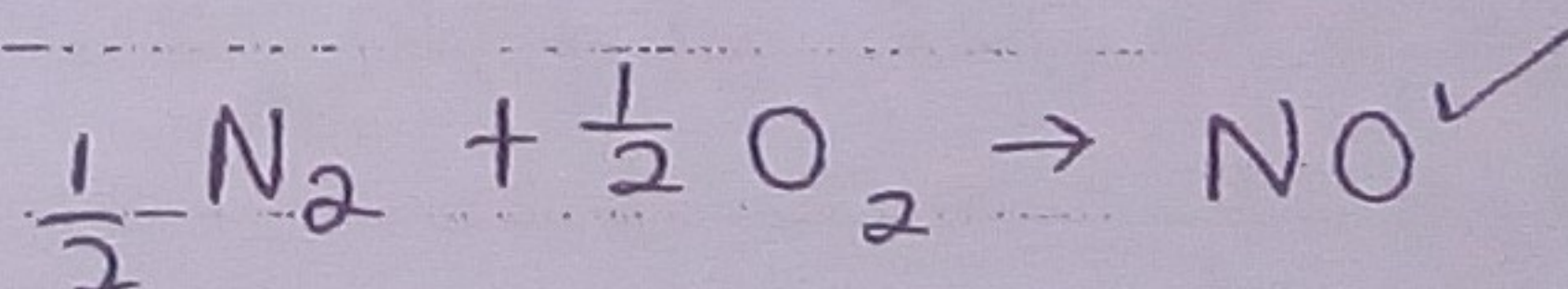


Because constituent elements are in their natural forms

Consider ΔH of NO



Wrong because one mole of the product should be formed, not two moles.



- When the enthalpy change of formation has a positive heat change, it implies that the reactants are energetically more stable than the products.

- It also shows that the amount of energy required to break bonds in reactants will be more than the amount of energy released during bond formation.

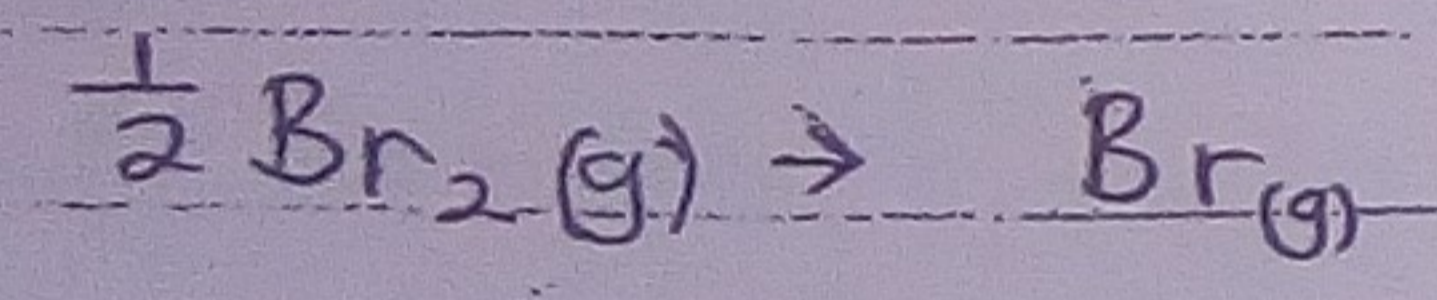
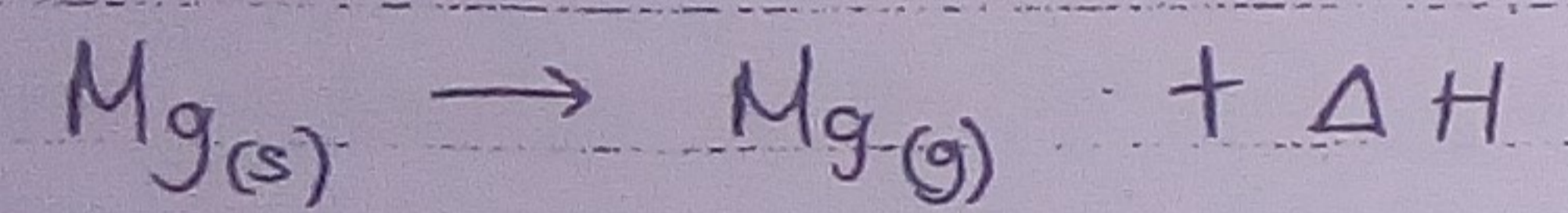
When \bar{e} enthalpy change of formation has a negative heat change it implies that the products are energetically more stable than the reactants

It also shows that \bar{e} amt of energy released during bond formation is more than the amount of energy required to break the bonds of the reactants

Enthalpy change of atomisation (standard) $\Delta H_{\text{atm}}^{\ominus}$

It is the heat energy required to form one mole of separate gaseous atoms of an element at 298 K and 1 atm

Consider atomisation energies ^{equations} of bromine and magnesium



Enthalpy change of atomisation is a positive heat change because heat is required to break the bonds as we move from solid to gas, liquid to gas or from gaseous molecules to gaseous atoms.

Task

Compare the atomisation energies of lithium and potassium

Solution

Lithium and potassium are group 1 elements held together by metallic bonding. Due to the smaller size of lithium atoms

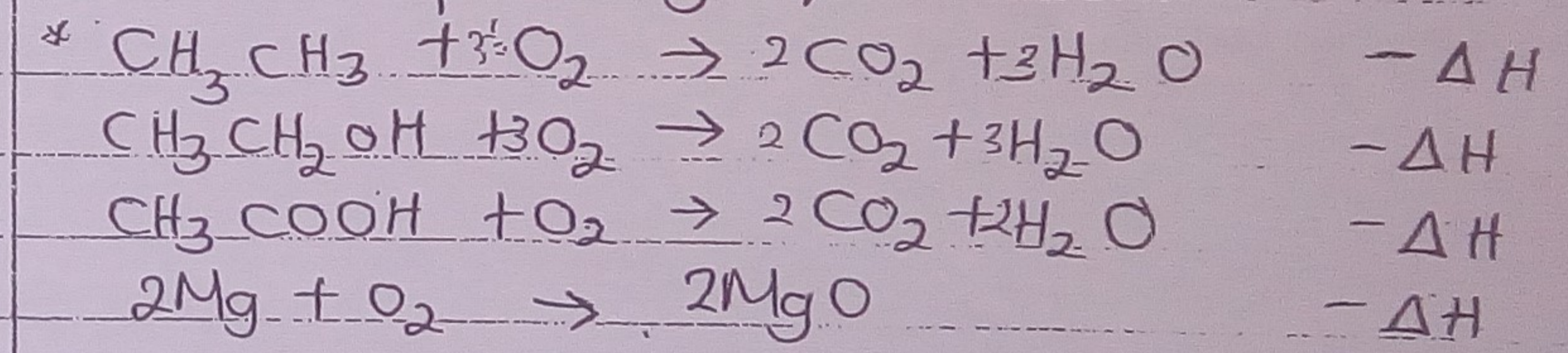
compared to the potassium atoms the metallic bonding in lithium is stronger. Therefore it has got a more positive enthalpy change

NB It should be known that the enthalpy change of atomisation of noble gases is zero.

Enthalpy change of combustion (standard) $\Delta H_{\text{comb}}^{\ominus}$

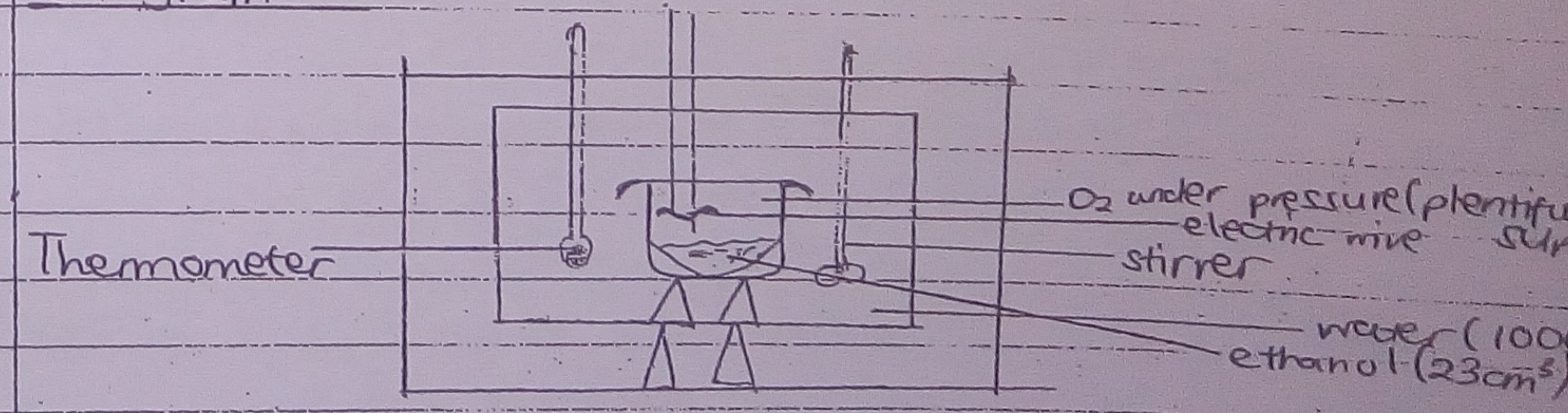
Defn It is the ^{heat} energy evolved when one mole of a compound completely burns in a plentiful supply of oxygen at 298 K and 1 atm

Consider the following equations



When measuring \bar{e} enthalpy change of combustion, we use the bomb calorimeter

Diagram



The above apparatus has features which promote complete combustion and minimization of heat loss by conduction

and radiation.

Consider the situation below:

When 23 cm³ of ethanol was burnt in a bomb calorimeter, the temperature of the water rose from 26 °C to the boiling point of the water. Calculate $\bar{\Delta}_c H^\ominus$ enthalpy change of combustion of ethanol given specific heat capacity of water is 4,18. What assumptions have you made during the calculations.

Solution

$$\Delta H = mc \Delta T$$

m = mass of water 100g

c = specific heat capacity of water 4,18

$$\Delta T = 100 - 26 = 74 \text{ }^\circ\text{C}$$

$$\Delta H = 100 \times 4,18 \times 74 = 30\,932 \text{ J}$$

$$n(\text{C}_2\text{H}_5\text{OH}) = \frac{23\text{g}}{46} = 0,5 \text{ moles}$$

$$0,5 \text{ mols} = 30\,932 \text{ J}$$

1 mols = more

$$\Delta H_{\text{comb}}^\ominus \text{ Ethanol} = -61\,864 \text{ J mol}^{-1} = -61,864 \text{ kJ mol}^{-1}$$

Assumptions

$$1 \text{ cm}^3 = 1 \text{ g} \quad / \quad 100 \text{ cm}^3 = 100 \text{ g}$$

Boiling point of water / water boils at 100 °C

In the above situation the process of measuring the enthalpy change of combustion was found to be 76% efficient. Calculate the standard enthalpy change of combustion when 30 cm³ of propanol was burnt resulting in the temperature of ^{250 cm³ of} water rising from 24 °C to 89 °C

Solution

$$\Delta H = mc \Delta T = 250 \text{ g} \times 4,18 \times 65 \text{ }^\circ\text{C} = 67\,925 \text{ J}$$

$$n(\text{Propanol}) = \frac{30}{60} = 0,5 \text{ mol}$$

$$0,5 \text{ mol} = 67\,925 \text{ J}$$

1 mol = more

$$\Delta H^\ominus = 135,85 \text{ kJ mol}^{-1}$$

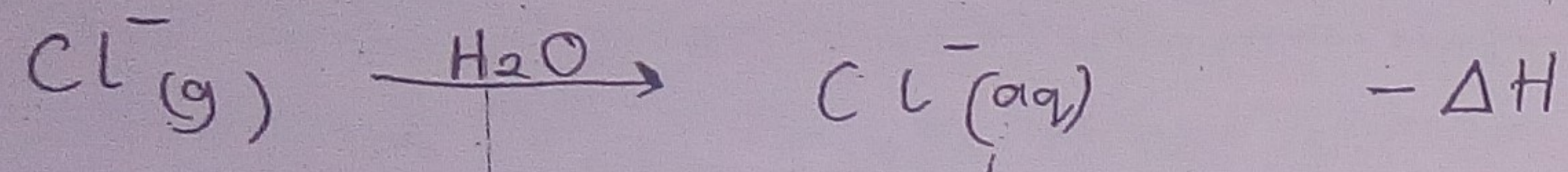
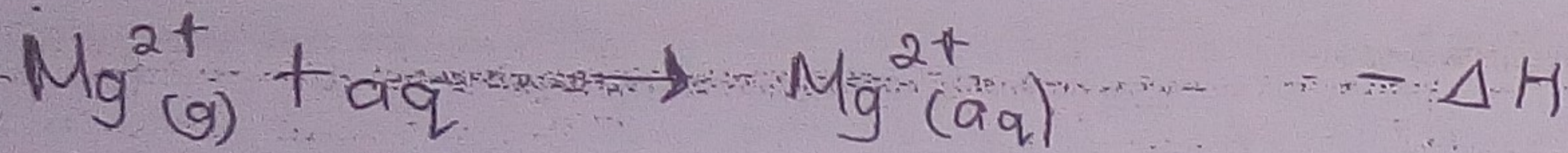
but was 76% efficient

$$0,76 = \frac{135,85 \text{ kJ mol}^{-1}}{1} = 178,750 \text{ kJ mol}^{-1}$$

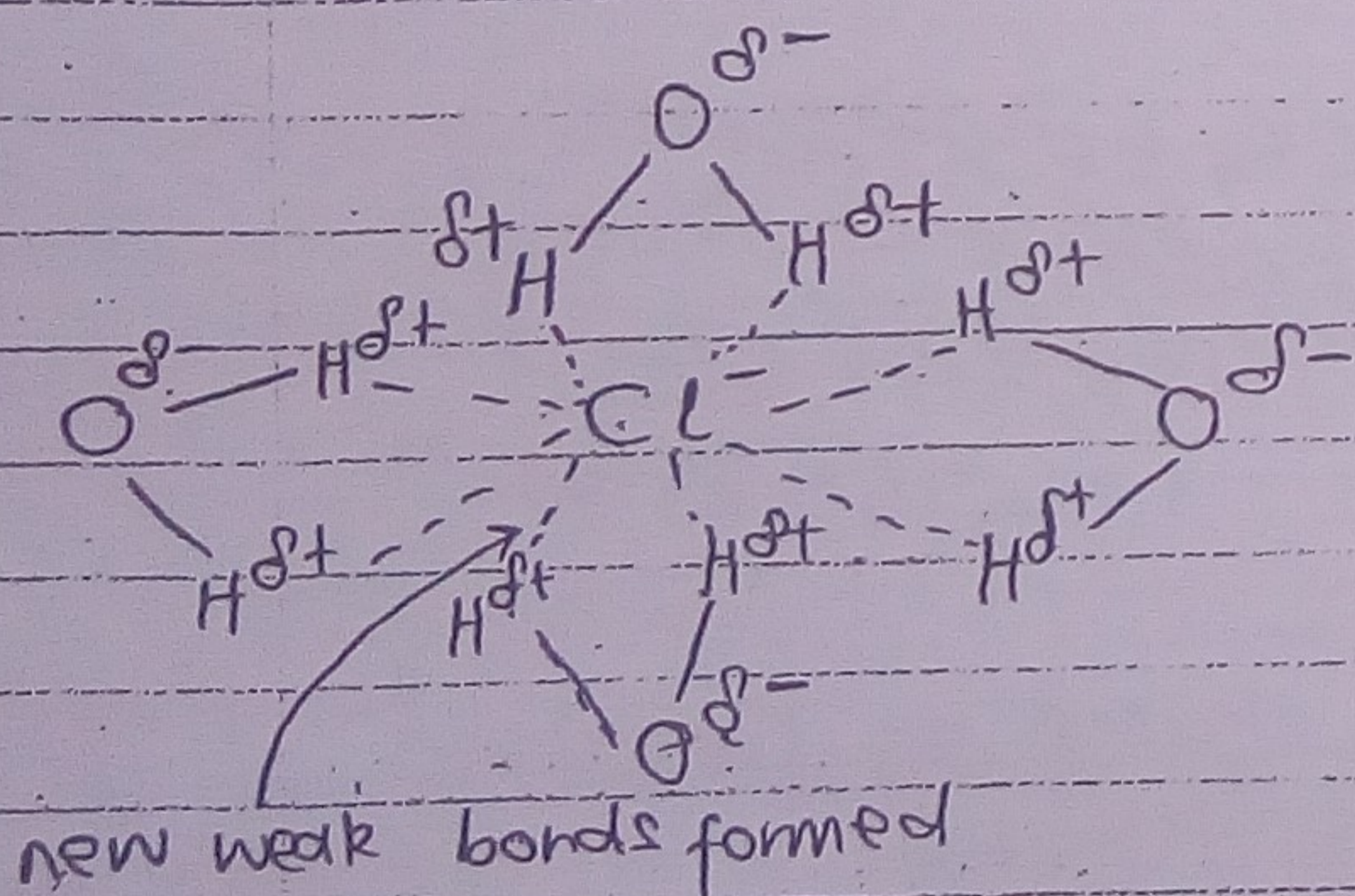
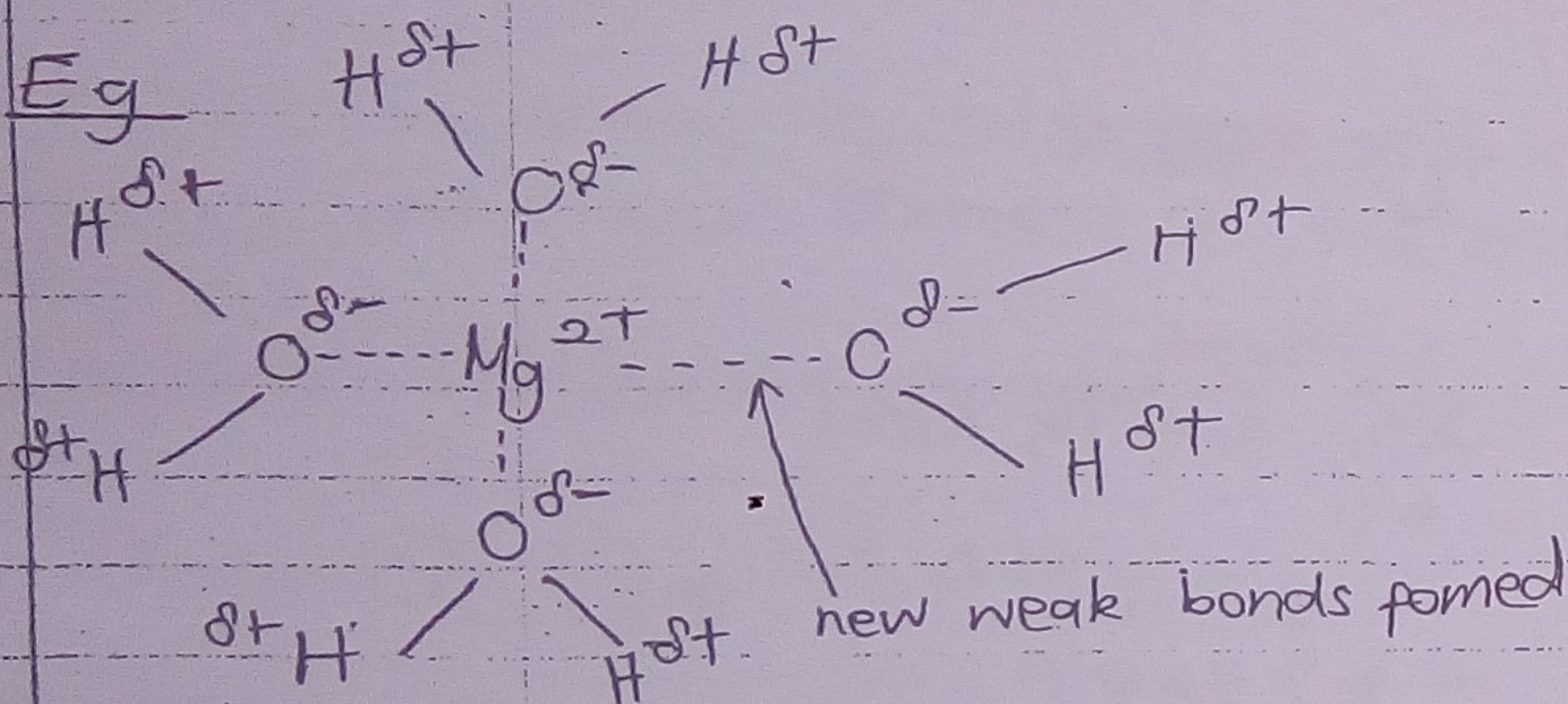
Standard enthalpy change of hydration

Heat energy evolved / released when one mole of separate gaseous ions completely dissolves in water to form aqueous ions at 298K and 1 atm

Equations showing enthalpy change of hydration



Enthalpy change of hydration is a negative enthalpy change because bonds are formed between the ions and the water molecules

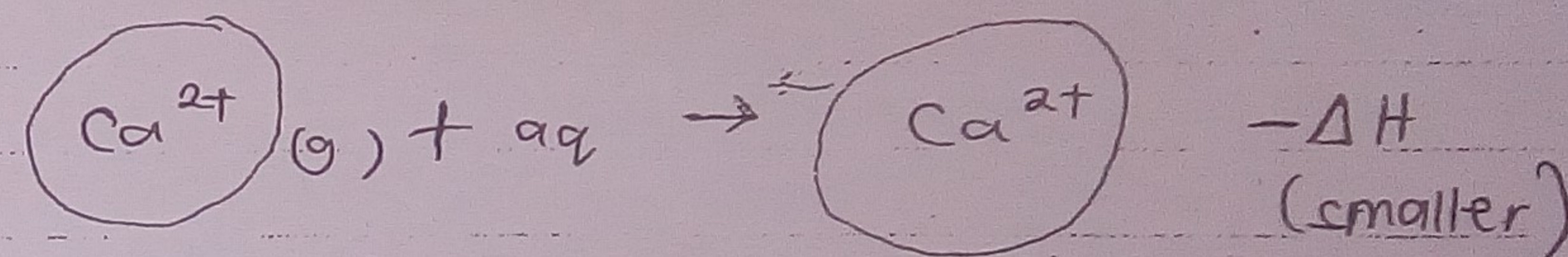
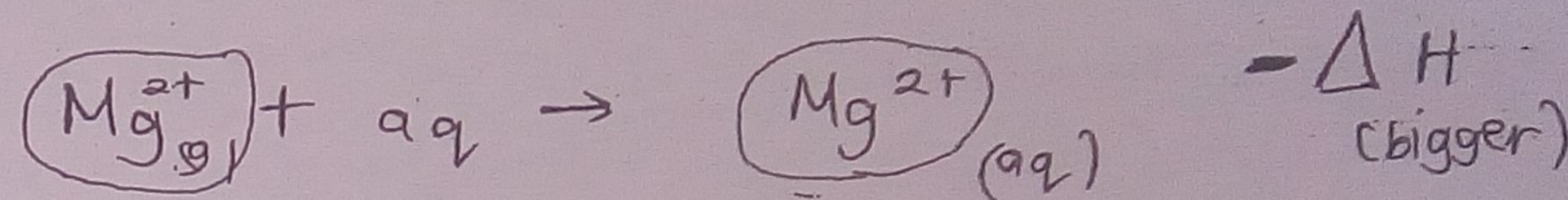


The magnitude of enthalpy change of hydration is affected by the size of the ions. If the charge of the ions would be the same

The small sized ions interact more with water molecules than they form stronger bonds, resulting in the enthalpy change

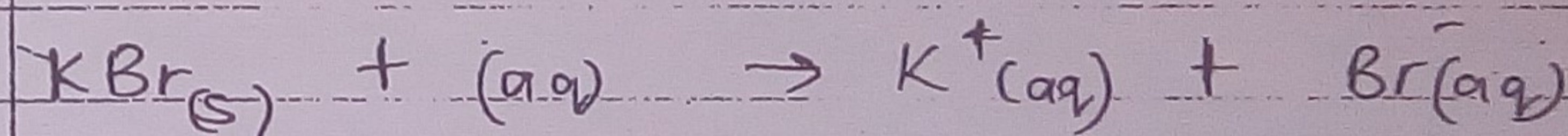
of hydration being more exothermic

E.g



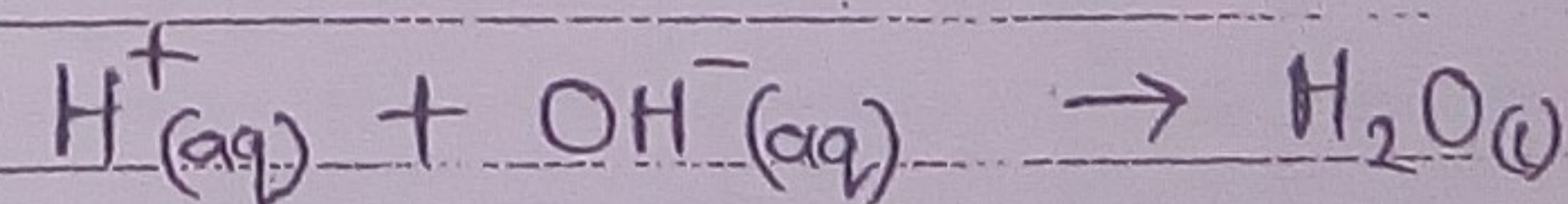
Enthalpy change of solution (standard)

- Heat energy change when one mole of a compound completely dissolves in a plentiful supply of water so that no further heat change is involved at 298 K and 1 atm



Enthalpy change of neutralisation (standard)

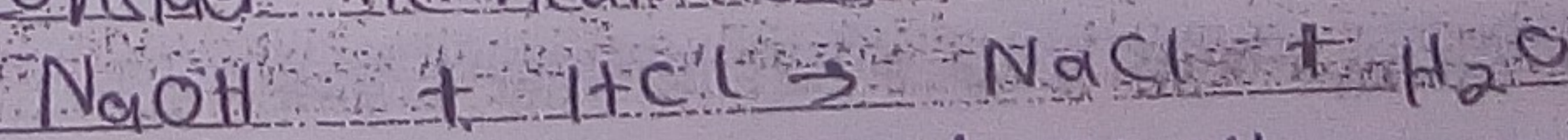
- Heat energy evolved when an acid reacts with a base per mol of acid and base at 298 K and 1 atm



Enthalpy change of neutralisation evolves heat because new bonds are being formed.

Task

Consider the neutralisation rxn below



When 30 cm³ of 0.39 M NaOH was mixed with 40 cm³ of

0,33 M HCl. The temp rose from 23°C to 79°C. Given that it required 10 joules of energy to raise temp of 1g of the resultant solution by 1K. Calculate standard enthalpy change of neutralisation.

Solution

$$\begin{aligned} \Delta H &= mc \Delta T \\ &= 70 \times 10 \times 56 \text{ } ^\circ\text{C} \\ &= 39200 \text{ J} \end{aligned}$$

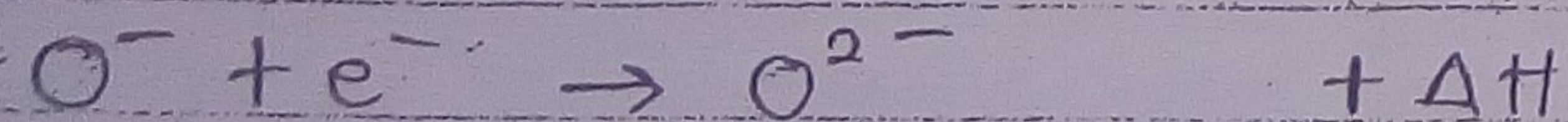
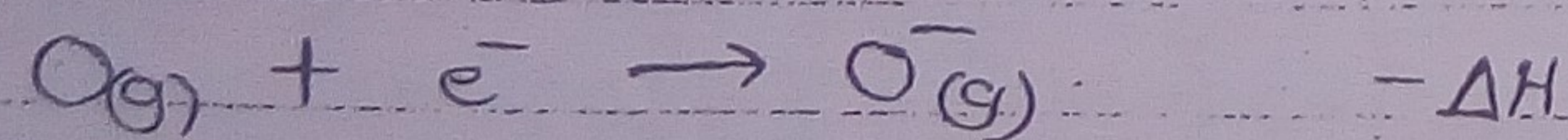
$$\begin{aligned} n(\text{HCl}) &= 0,04 \times 0,33 \\ &= 0,0132 \text{ mols} \end{aligned}$$

$$\begin{aligned} n(\text{NaOH}) &= 0,03 \times 0,39 \\ &= 0,0117 \text{ mols} \end{aligned}$$

$$\begin{aligned} \therefore 0,0117 \text{ mols} &= 39200 \text{ J} \\ &= \text{more} \end{aligned}$$

$$\therefore \Delta H_{\text{neu}}^\ominus = 3350 \text{ kJ mol}^{-1}$$

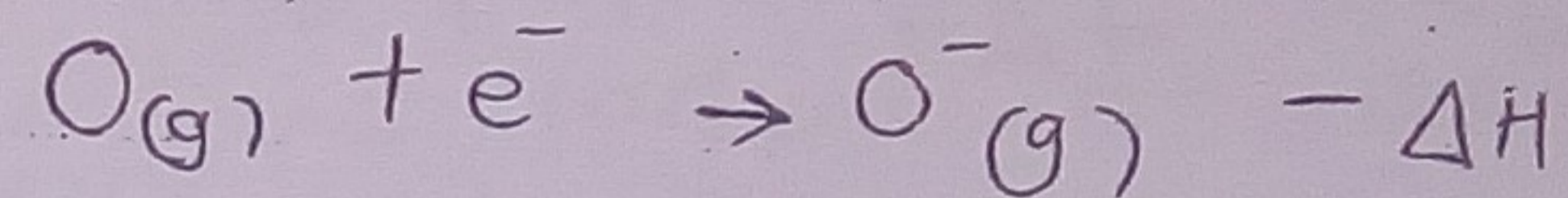
Enthalpy change of electron affinity



Electron affinity

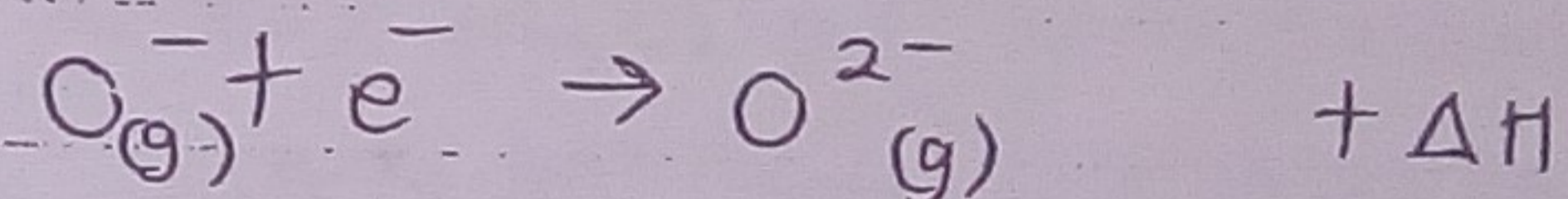
Dfn It is the heat energy change when one mole of a separate gaseous substance (atom or ion) gains one mole of an electron to produce one mole of a separate gaseous ions.

Consider the eqn for the first electron affinity of oxygen



$\text{O}^- \rightarrow \text{O(g)} + e^-$
reverse enthalpy change of electron affinity
negative first electron affinity

2nd electron affinity eqn



- The first electron affinity of an element is negative because heat is evolved when an atom gains an electron
- The 2nd electron affinity is positive. This shows that heat is gained. This is because energy is required to work against the repulsive forces which the incoming electrons will be experiencing

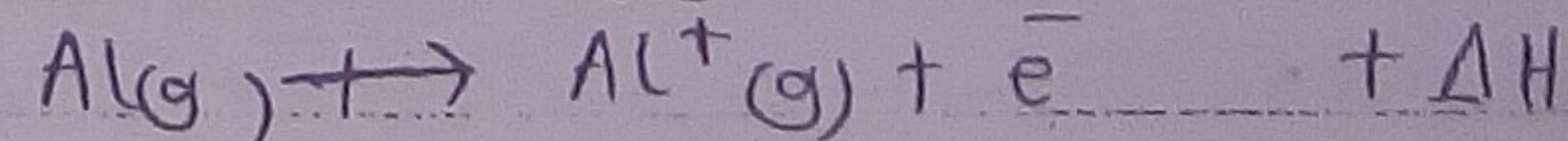
Enthalpy change of ionisation energy

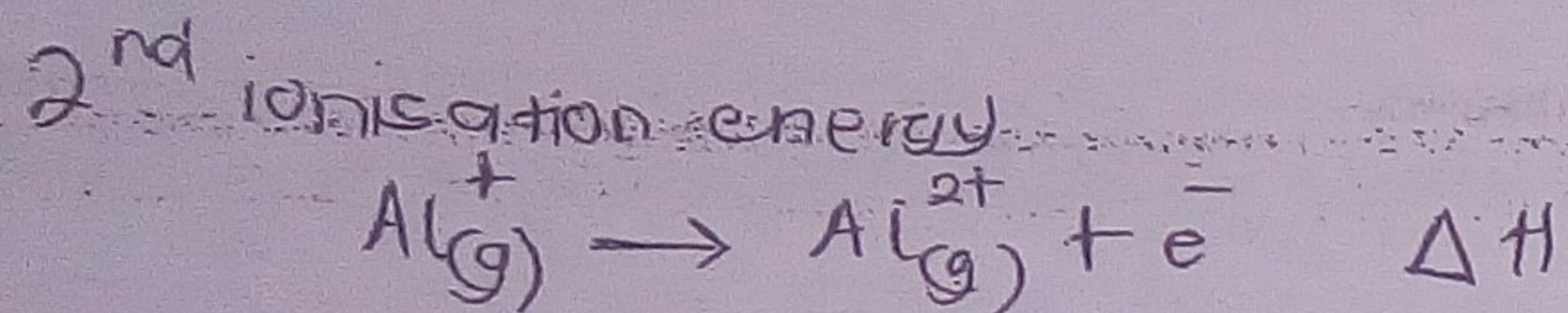
- It can simply be referred to as ionisation energy

Dfn It is the heat energy required/gained to remove one mole of electrons from one mole of a separate gaseous substance (atom or ion) to form one mole of positively charged gaseous ions.

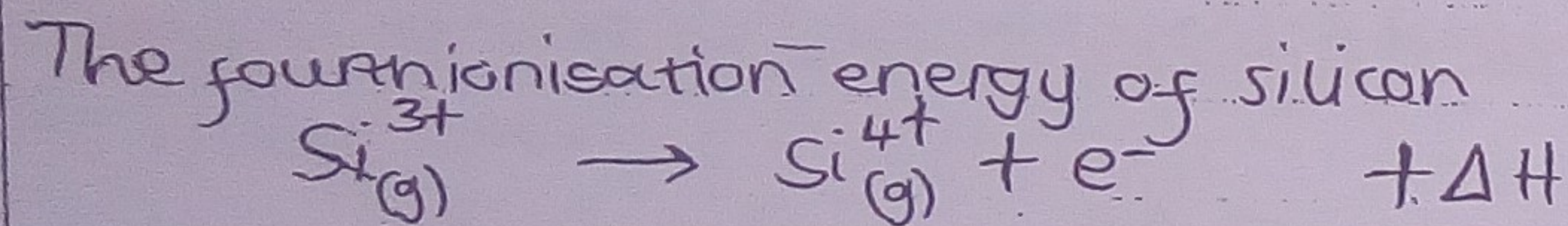
Consider aluminium

First ionisation energy



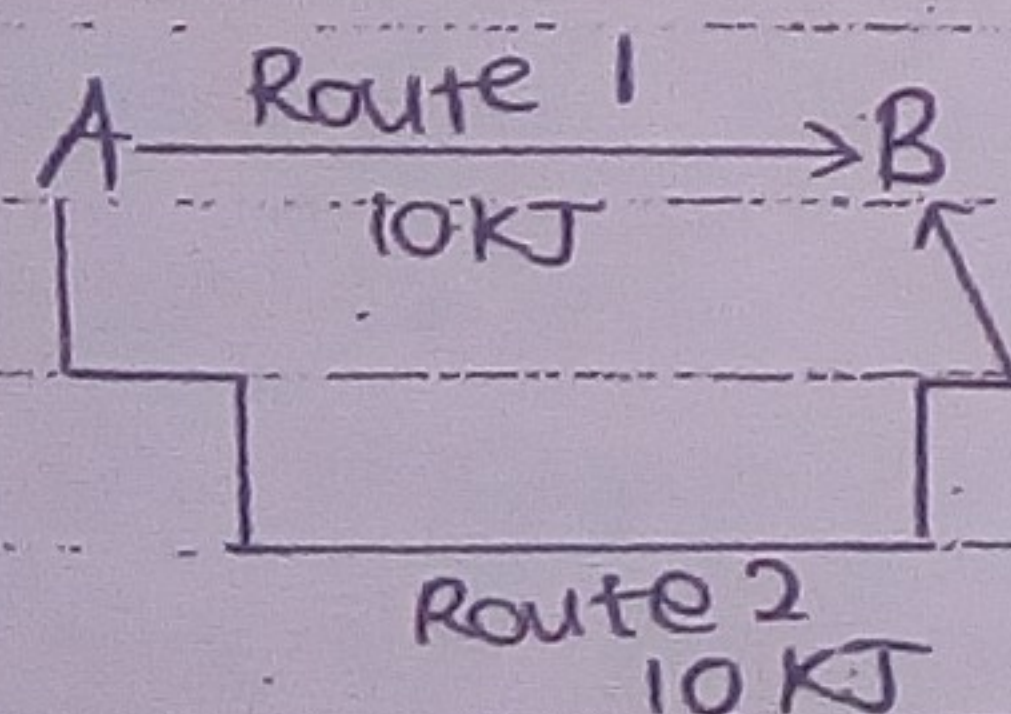


During ionisation energy heat is gained so as to overcome the attractive forces between the electrons and the nucleus.



Hess Law

States that the overall heat change in a chemical reaction is constant and it is not dependent on the route taken, provided that all the other conditions remain the same.



Application of the Hess Law

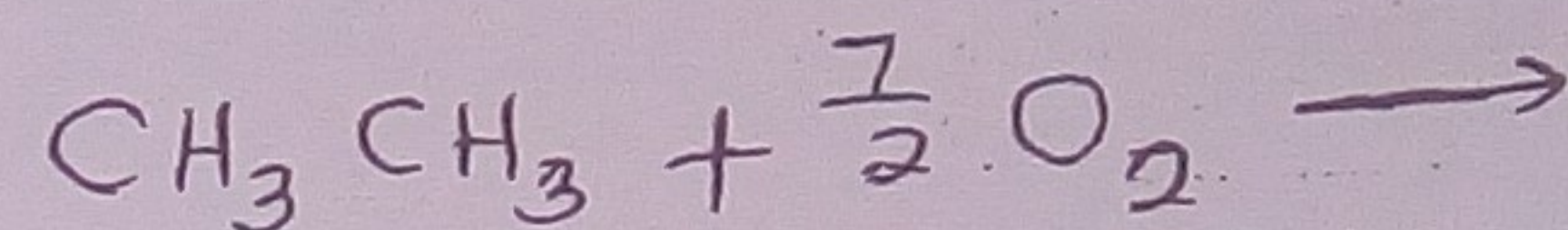
The Hess law can be used to

- Calculate the enthalpy change of reaction from given values of enthalpy change of formation.
- Calculate the enthalpy change of reaction from given values of enthalpy change of combustion.
- Determining lattice energy using Born Haber Cycle.

Determination of enthalpy change of reaction using enthalpy change of formation

Consider the following information

Methane burns in the presence of oxygen according to the following equation



Calculate ΔH_{comb} of ethane given the following info

Solution

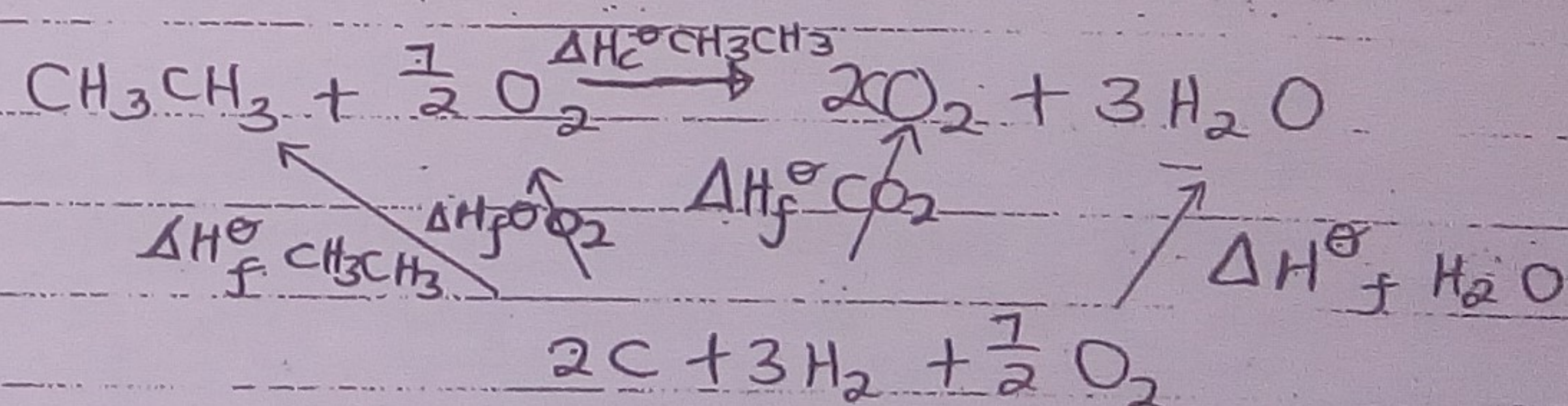
Using enthalpy change of formation values to calculate the enthalpy change of reaction.

Of the enthalpy change of reaction in this eqn is $\Delta H_{\text{comb}}^\ominus$

$$\Delta H_f^\ominus \text{CO}_2 = -230 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{CH}_3\text{CH}_3 = -480 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{H}_2\text{O} = -170 \text{ kJ mol}^{-1}$$



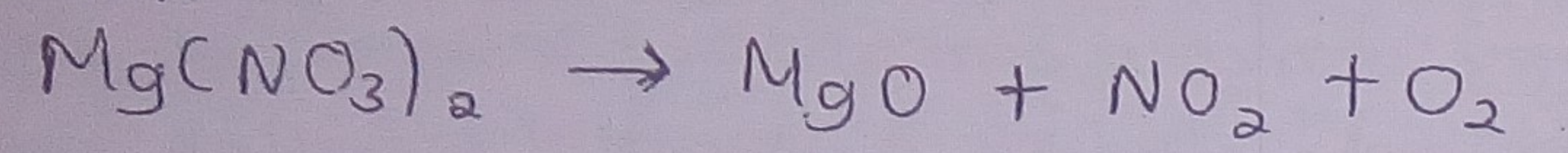
$$\Delta H_c^\ominus \text{CH}_3\text{CH}_3 - 2\Delta H_f^\ominus \text{CO}_2 - 3\Delta H_f^\ominus \text{H}_2\text{O} + \Delta H_f^\ominus \text{CH}_3\text{CH}_3 = 0$$

$$\Delta H_c^\ominus \text{CH}_3\text{CH}_3 - 2(-230) - 3(-170) + (-480) = 0$$

$$\Delta H_c^\ominus \text{CH}_3\text{CH}_3 = -490 \text{ kJ mol}^{-1}$$

In the cycle above the arrow is pointing at the product being formed after combining the reactant elements. It should be known that the enthalpy change of formation from an element to form the same element is zero.

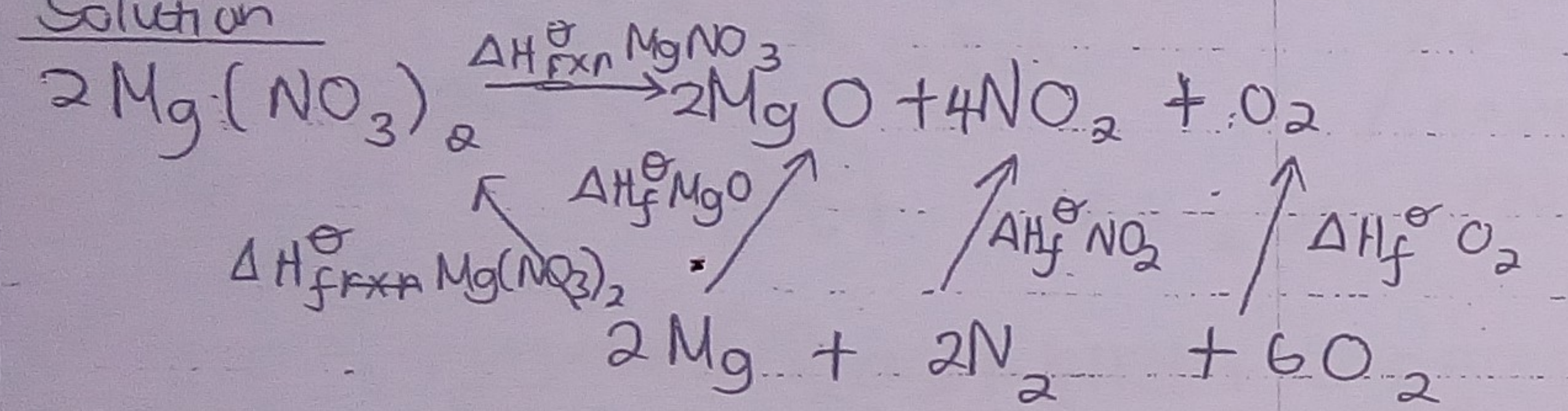
Consider the decomposition of magnesium nitrate below
 Magnesium nitrate decomposes according to the following equation:



Calculate the enthalpy change of the rxn given the following information

- $\Delta H_f^\ominus \text{NO}_2 = +240 \text{ kJ mol}^{-1}$
- $\Delta H_f^\ominus \text{MgO} = -1200 \text{ kJ mol}^{-1}$
- $\Delta H_f^\ominus \text{Mg}(\text{NO}_3)_2 = -690 \text{ kJ mol}^{-1}$

Solution



$$\Delta H_{\text{rxn}}^\ominus - 2\Delta H_f^\ominus \text{MgO} - 4\Delta H_f^\ominus \text{NO}_2 + 2\Delta H_f^\ominus \text{Mg}(\text{NO}_3)_2 = 0$$

$$\frac{\Delta H_{\text{rxn}}^\ominus}{2} - 2(-1200) - 4(240) + 2(-690) = 0$$

$$\frac{\Delta H_{\text{rxn}}^\ominus}{2} = \frac{-60}{2}$$

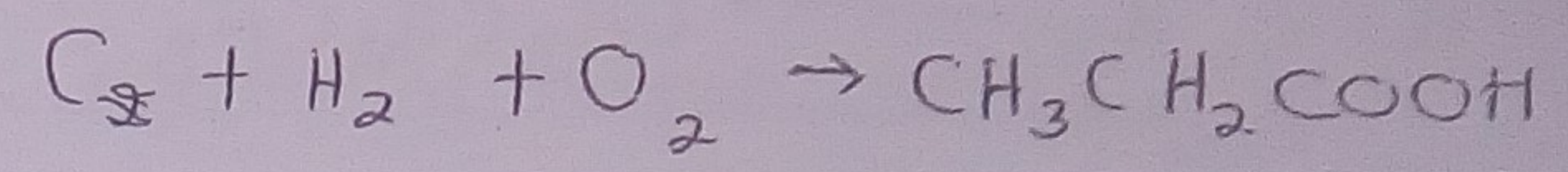
$$\Delta H_{\text{rxn}}^\ominus = -30 \text{ kJ mol}^{-1}$$

The enthalpy change of rxn had to be divided by two since two moles of the reactant were present in the reaction

Determination of enthalpy change of rxn using enthalpy changes of combustion

Consider the situation below

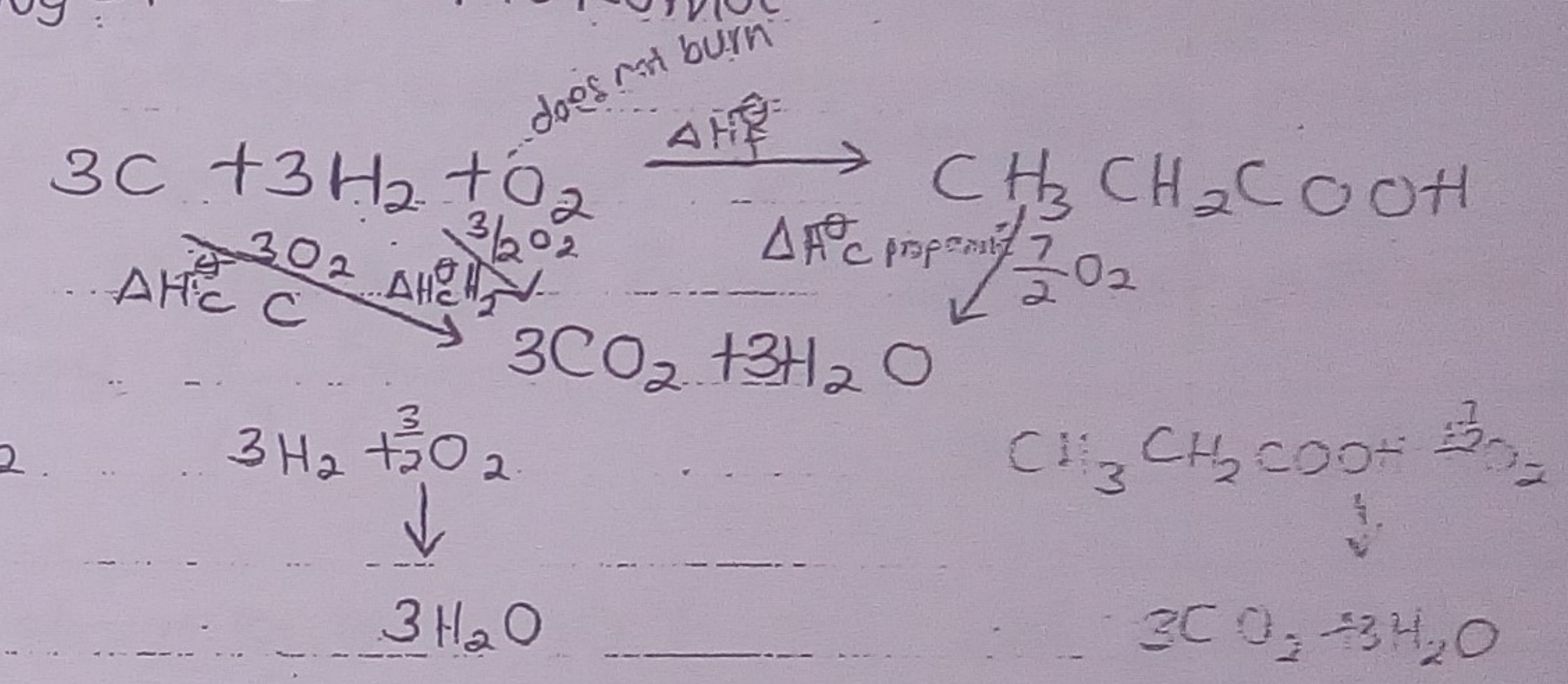
Propanoic acid can be formed according to the eqn below



Calculate the ΔH_f^\ominus of propanoic acid given the following info

- $\Delta H_{\text{comb}}^\ominus \text{ propanoic acid} = -480 \text{ kJ mol}^{-1}$
- $\Delta H_{\text{comb}}^\ominus \text{ carbon} = -340 \text{ kJ mol}^{-1}$
- $\Delta H_c^\ominus \text{ hydrogen} = -190 \text{ kJ mol}^{-1}$

Solution



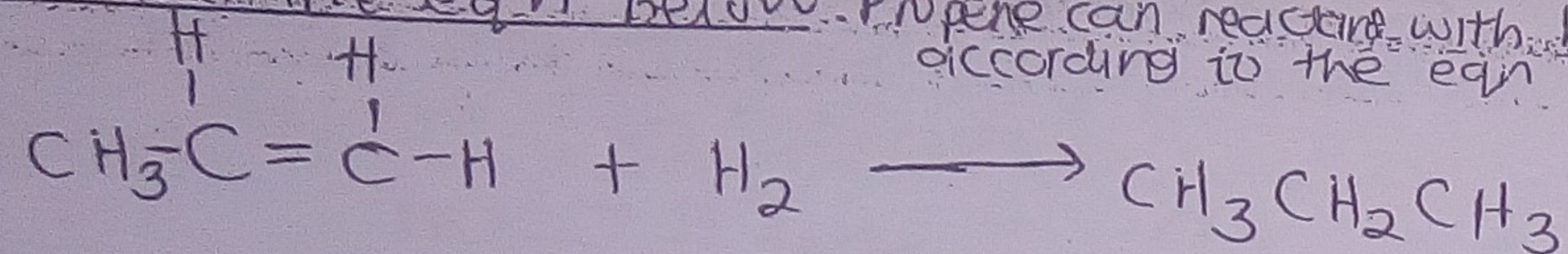
$$\Delta H_f^\ominus + \Delta H_c^\ominus \text{ propanoic acid} - 3\Delta H_c^\ominus \text{H}_2 - 3\Delta H_c^\ominus \text{C} = 0$$

$$\Delta H_f^\ominus + (-480) - (3 \times (-190)) - (3 \times (-340)) = 0$$

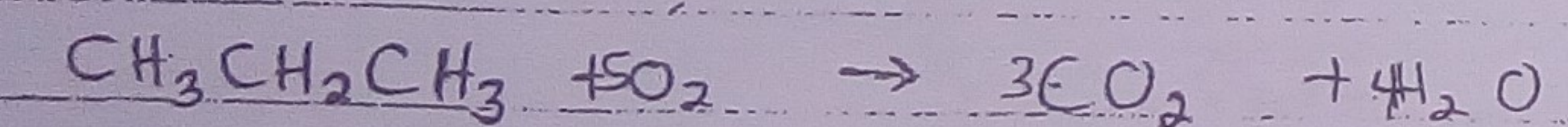
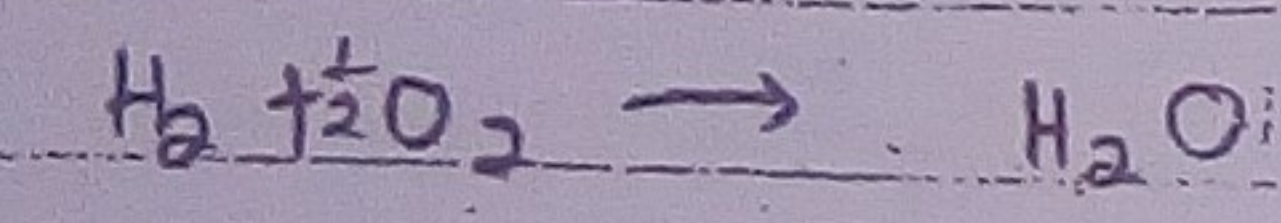
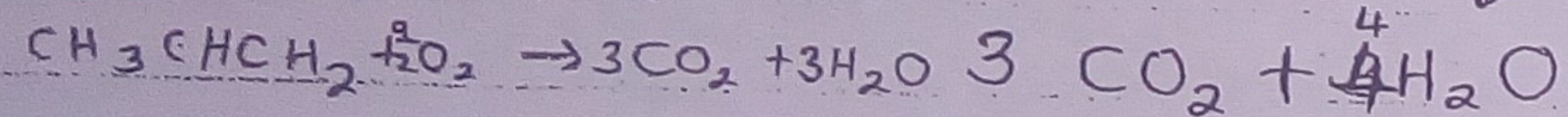
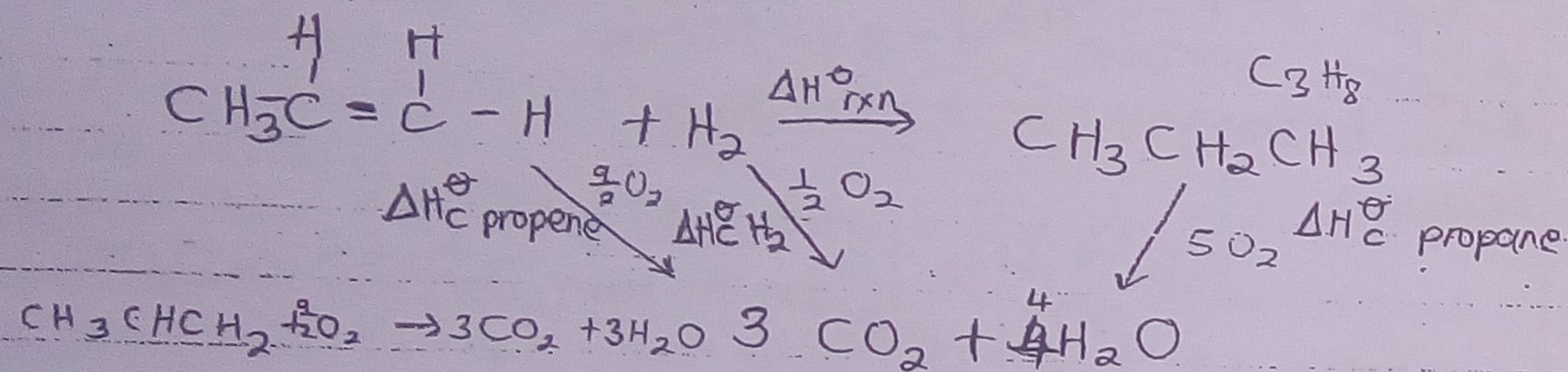
$$\Delta H_f^\ominus + 110 = 0$$

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

Consider the eqn below. Propene can react with hydrogen according to the eqn below



$$\begin{aligned} \Delta H_c^\ominus \text{ propene} &= -300 \text{ kJ mol}^{-1} \\ \Delta H_c^\ominus \text{ hydrogen} &= -190 \text{ kJ mol}^{-1} \\ \Delta H_c^\ominus \text{ propane} &= -550 \text{ kJ mol}^{-1} \end{aligned}$$



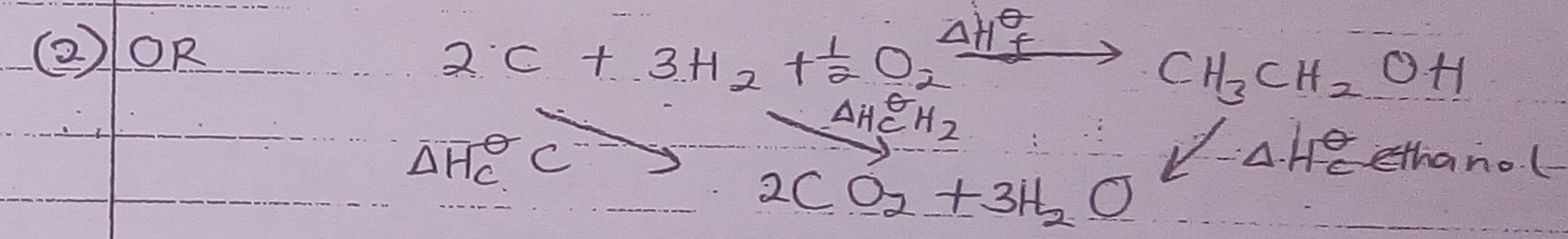
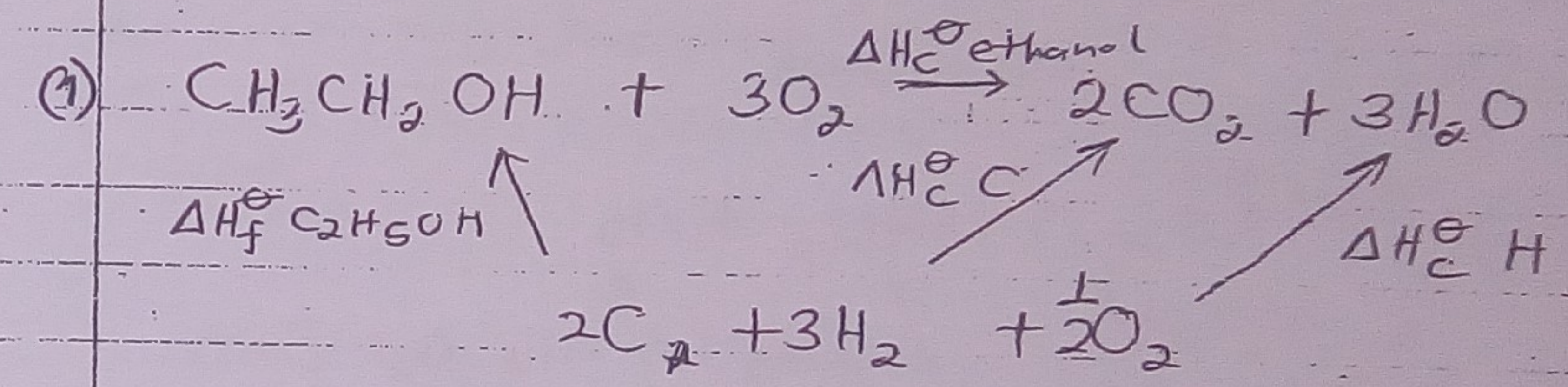
Calculate the enthalpy change of rxn

$$\begin{aligned} \Delta H_{\text{rxn}}^\ominus + \Delta H_c^\ominus \text{ propane} - \Delta H_c^\ominus \text{ H}_2 - \Delta H_c^\ominus \text{ propene} &= 0 \\ \Delta H_{\text{rxn}}^\ominus + (-550 \text{ kJ mol}^{-1}) - (-190 \text{ kJ mol}^{-1}) - (-300 \text{ kJ mol}^{-1}) &= 0 \\ \Delta H_{\text{rxn}}^\ominus - 60 \text{ kJ mol}^{-1} &= 0 \\ \Delta H_{\text{rxn}}^\ominus &= 60 \text{ kJ mol}^{-1} \end{aligned}$$

Consider the following situation

The enthalpy change of formation of ethanol was found to be -200 kJ mol^{-1} . Deduce the standard enthalpy change of combustion of ethanol given the following information

$$\begin{aligned} \Delta H_c^\ominus \text{ carbon} &= -230 \text{ kJ mol}^{-1} \\ \Delta H_c^\ominus \text{ Hydrogen} &= -170 \text{ kJ mol}^{-1} \end{aligned}$$



$$\begin{aligned} 1. \Delta H_c^\ominus \text{ ethanol} - 2\Delta H_c^\ominus \text{ C} - 3\Delta H_c^\ominus \text{ H} + \Delta H_f^\ominus \text{ ethanol} &= 0 \\ 2. \Delta H_f^\ominus + \Delta H_c^\ominus \text{ ethanol} - 3\Delta H_c^\ominus \text{ H}_2 - 2\Delta H_c^\ominus \text{ C} &= 0 \\ -700 + \Delta H_c^\ominus \text{ ethanol} - (3 \times -170) - (2 \times -230) &= 0 \\ \Delta H_c^\ominus \text{ ethanol} &= -270 \text{ kJ mol}^{-1} \end{aligned}$$

When chemical reactions are occurring bonds are either broken or formed. These bonds include covalent bonding and ionic bonding.

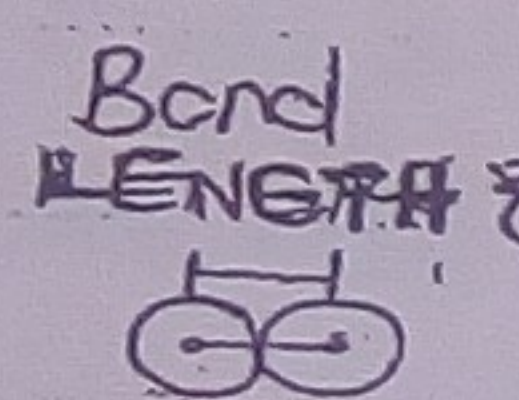
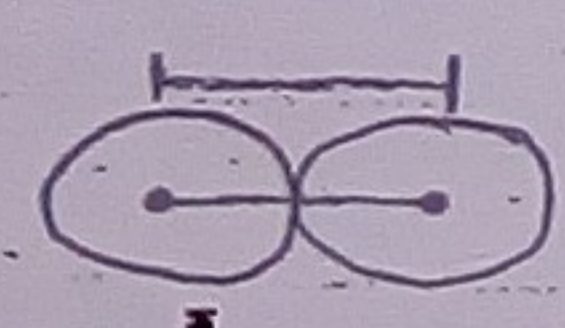
The strength of a covalent bond is measured using bond energy values while the strength of an ionic bond is measured using lattice energy

Bond energy

It is heat energy required to break 1 mole of a covalent bond or heat energy released during the formation of 1 mole of a covalent bond.

The bigger the atoms in a covalent bond, the weaker the covalent bond becomes, therefore there is an inverse relationship between bond energy and bond length.

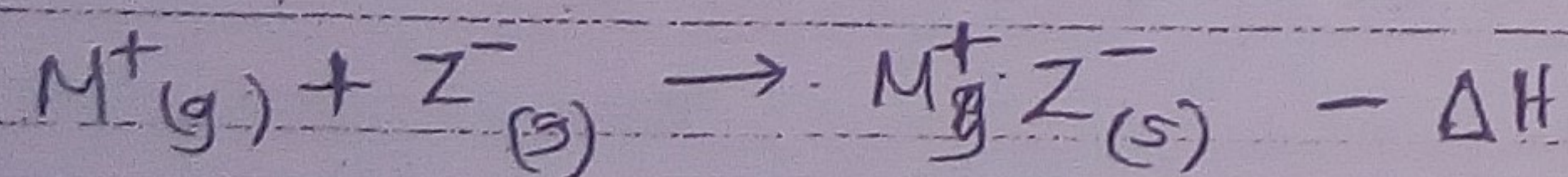
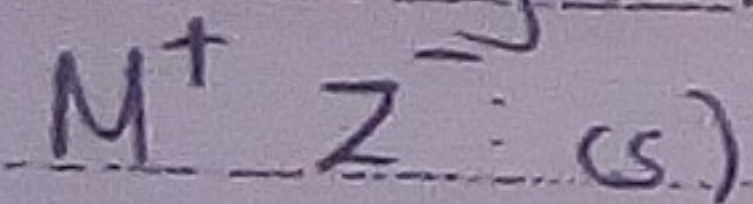
$$\text{Bond Energy} \propto \frac{1}{\text{Bond length}}$$

| | Bond Length | Bond Energy kJ mol^{-1} |
|-------|---|----------------------------------|
| Cl-Cl |  | 244 |
| Br-Br |  | 193 |

When a covalent bond is being broken the energy required can also be referred to as the bond dissociation energy.

Lattice energy

This is the heat energy evolved when one mole of an ionic compound is formed from its separate gaseous ions.



Lattice energy is always a negative lattice enthalpy because heat is given out when new bonds are formed.

$$\text{Lattice Energy} \propto \frac{Q^+ \cdot Q^-}{r^+ + r^-}$$

$$L.E. \propto \frac{Q^+ \cdot Q^-}{r^+ + r^-}$$

Factors affecting lattice energy

The magnitude of lattice energy is affected by

- the charge of e^- ions
- the ionic radius of the ions

A general formula can be given which shows the relationship between the factors stated above and the magnitude of lattice energy.

$$\text{Lattice energy} = \frac{Q^+ \cdot Q^-}{r^+ + r^-}$$

Q - charge of e^- ions

r - ionic radius

Using the relationship above it can easily be deduced that

- larger the ionic charge, the higher the value of the lattice energy hence the stronger the ionic bond and vice versa the opposite would be true.
- larger the ionic charge radius, the lower the value of lattice energy and hence the weaker the ionic bond.

Task

Consider magnesium oxide and SrO. Which one of the two has a higher melting point and explain why.

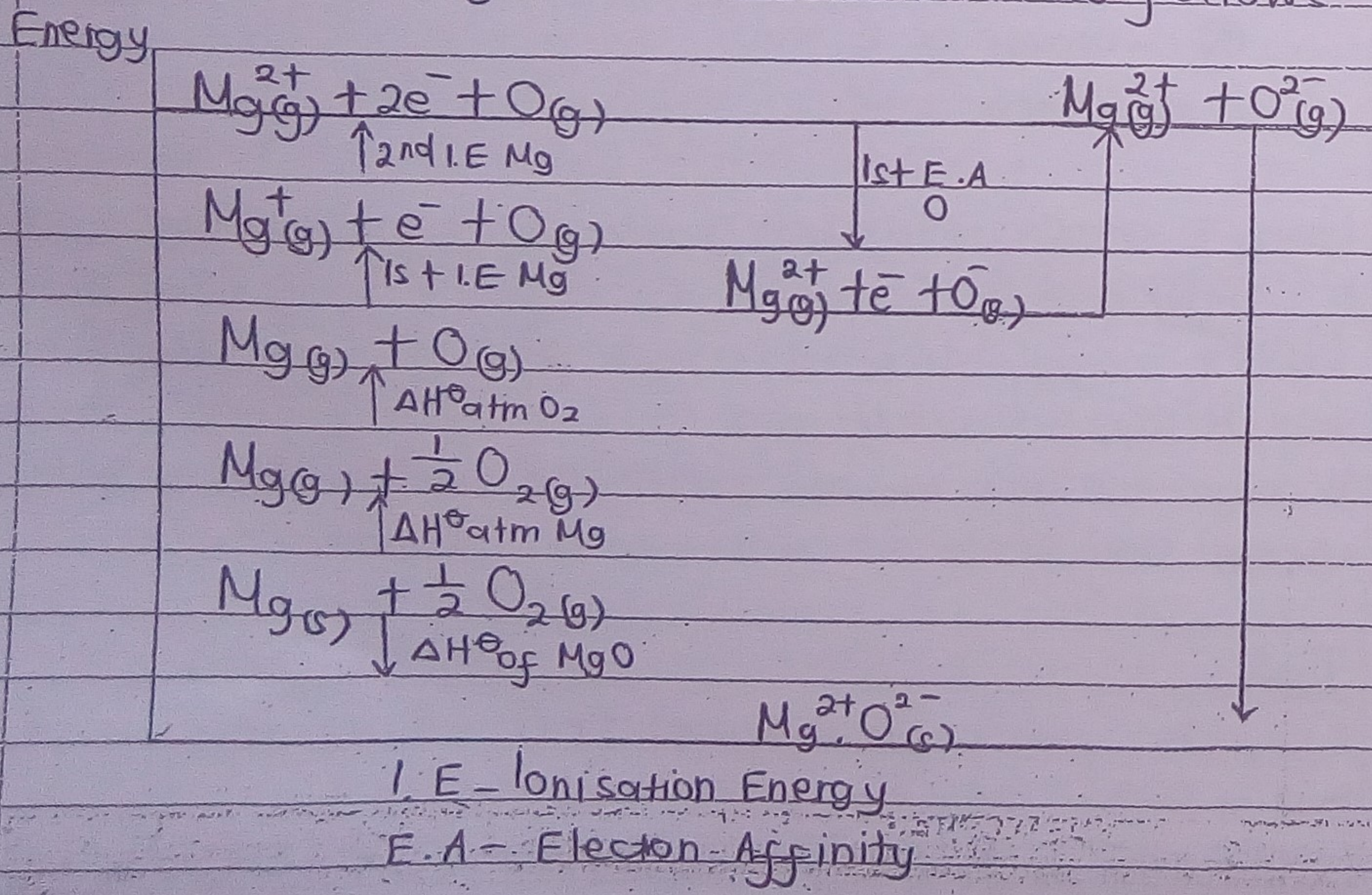
Solution

Both MgO and SrO are ionic compds. Strength of an ionic bond is measured using lattice energy. The magnitude of lattice energy of MgO is higher than that of SrO. This is because the ionic radius of MgO is smaller than that of SrO. Therefore magnesium oxide has a melting point because more energy is required to break the stronger bonds in MgO.

Apart from the use of the general formula stated above, lattice energy can be indirectly obtained using the Born Haber cycle.

The Born Haber Cycle
Consider MgO

The Born Haber cycle can be constructed as follows



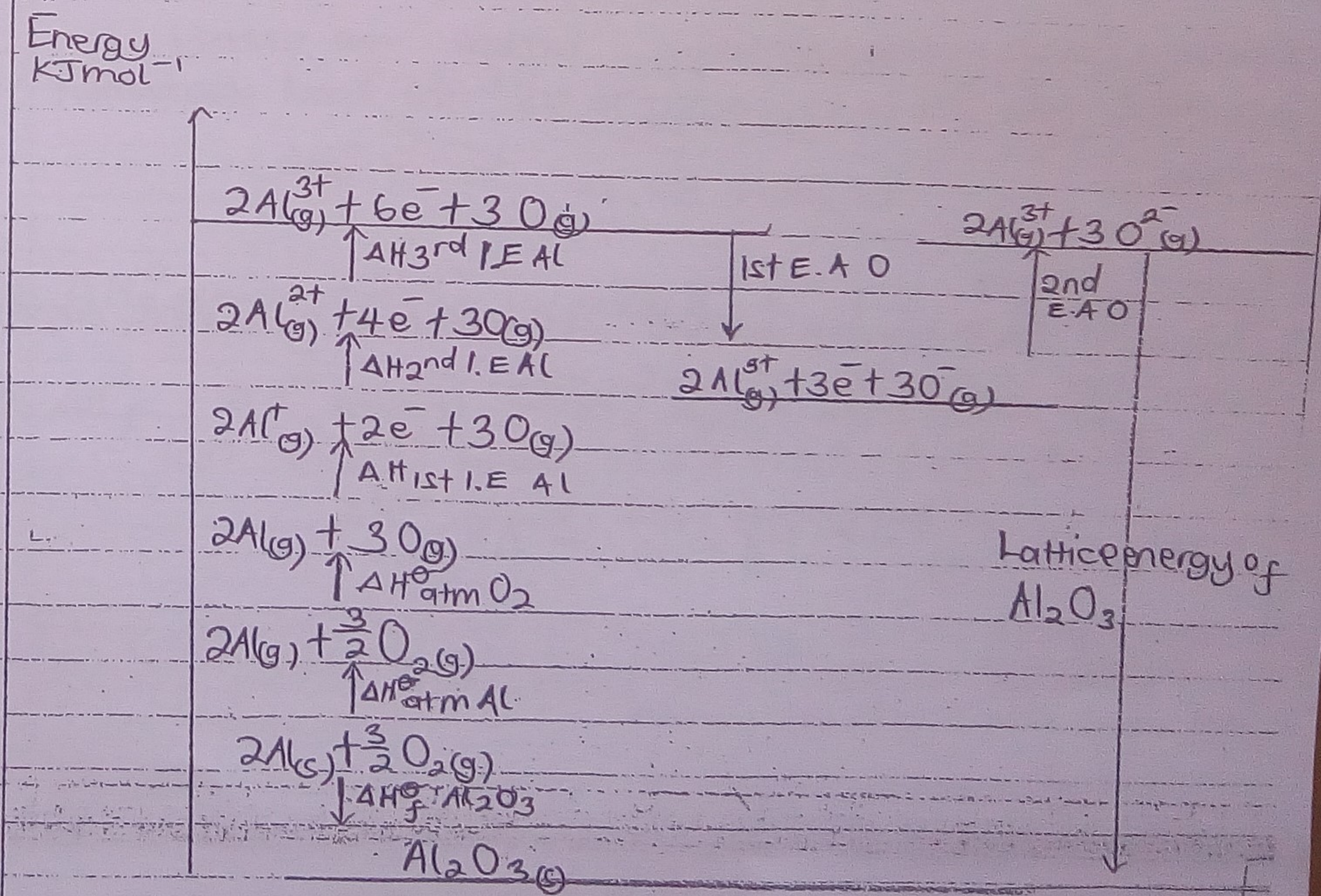
Using Hess Law, lattice energy can be calculated

$$\Delta H^{\circ}_{atm} Mg + \Delta H^{\circ}_{atm} O_2 + \Delta H^{\circ}_{1st I.E.} Mg + \Delta H^{\circ}_{2nd I.E.} Mg + \Delta H^{\circ}_{1st E.A.} O + \Delta H^{\circ}_{2nd E.A.} O + L.E. - \Delta H^{\circ}_{f} MgO = 0$$

When calculating the value of lattice energy, the enthalpies below are obtained from a data booklet

- 1) ΔH°_{1st} ionisation energy Mg ^{nc} given is
- 2) ΔH°_{2nd} ionisation Energy Mg ^{nc} is
- 3) $\Delta H^{\circ}_{atm} O_2$ given by bond energy value
 $\therefore \frac{1}{2} (O=O) = \frac{1}{2} (B.E \text{ value})$

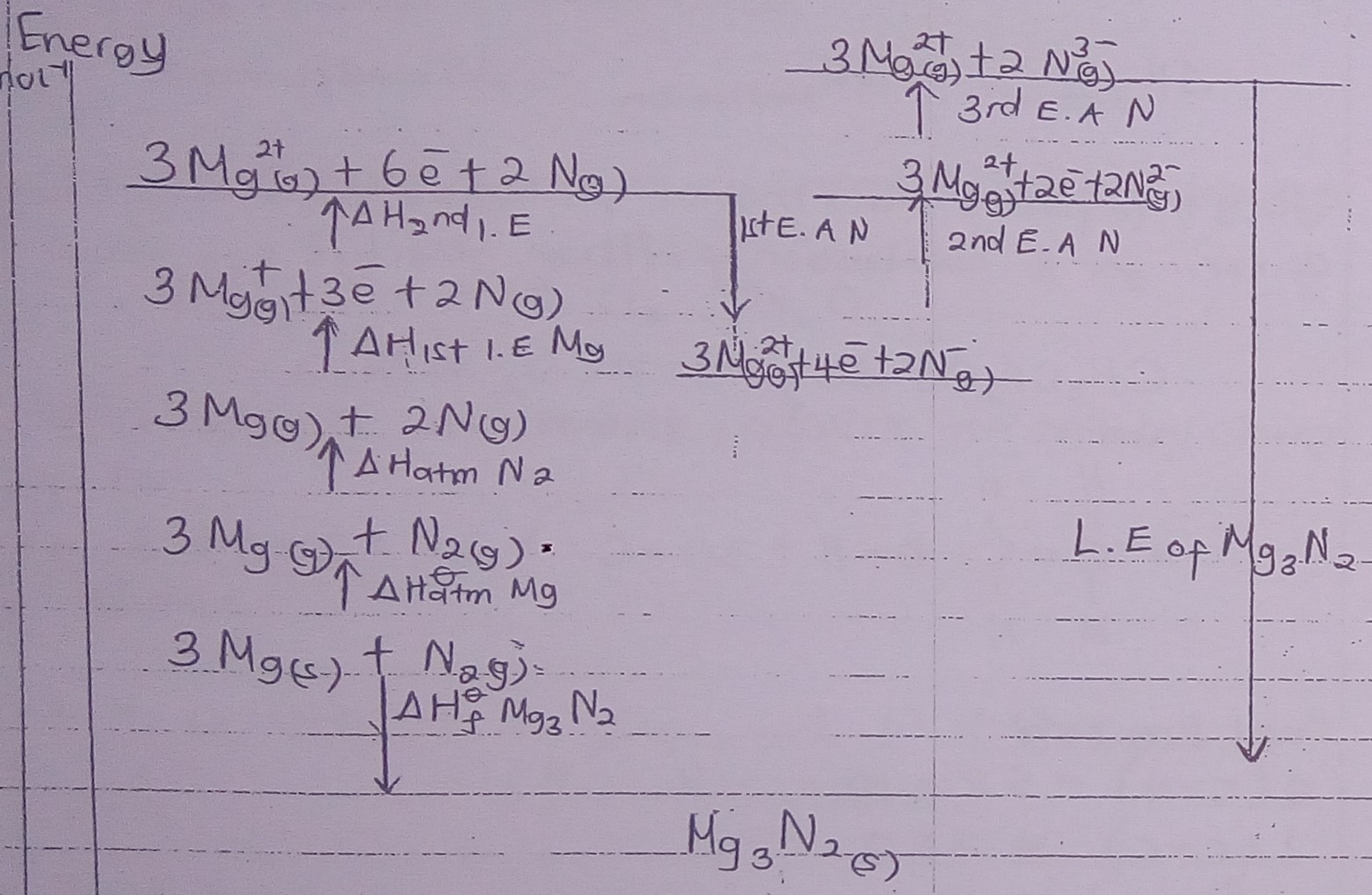
Consider Al₂O₃



Calculating lattice energy using Born-Haber cycle

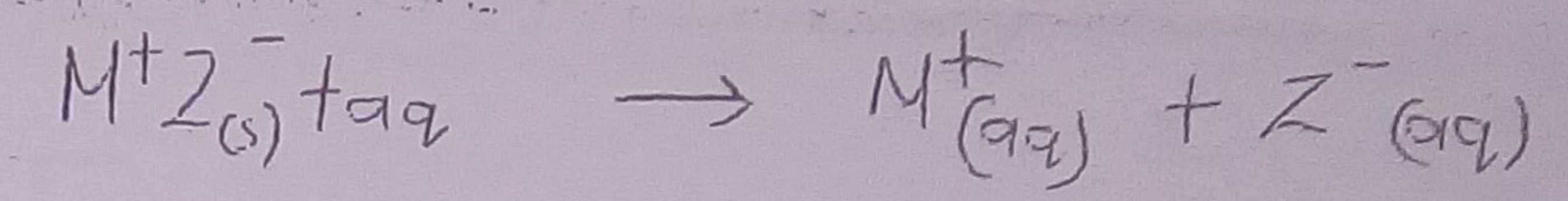
$$\frac{3}{2}(\text{B.E})$$

$$2\Delta H_{\text{atm Al}}^{\ominus} + \Delta H_{\text{atm O}_2}^{\ominus} + 2\Delta H_{\text{1st I.E Al}}^{\ominus} + 2\Delta H_{\text{2nd I.E Al}}^{\ominus} + 2\Delta H_{\text{3rd I.E Al}}^{\ominus} + 3\Delta H_{\text{1st E.A O}}^{\ominus} + 3\Delta H_{\text{2nd E.A O}}^{\ominus} + \text{L.E} - \Delta H_f^{\ominus} \text{Al}_2\text{O}_3 = 0$$



Dissolving of an ionic solid

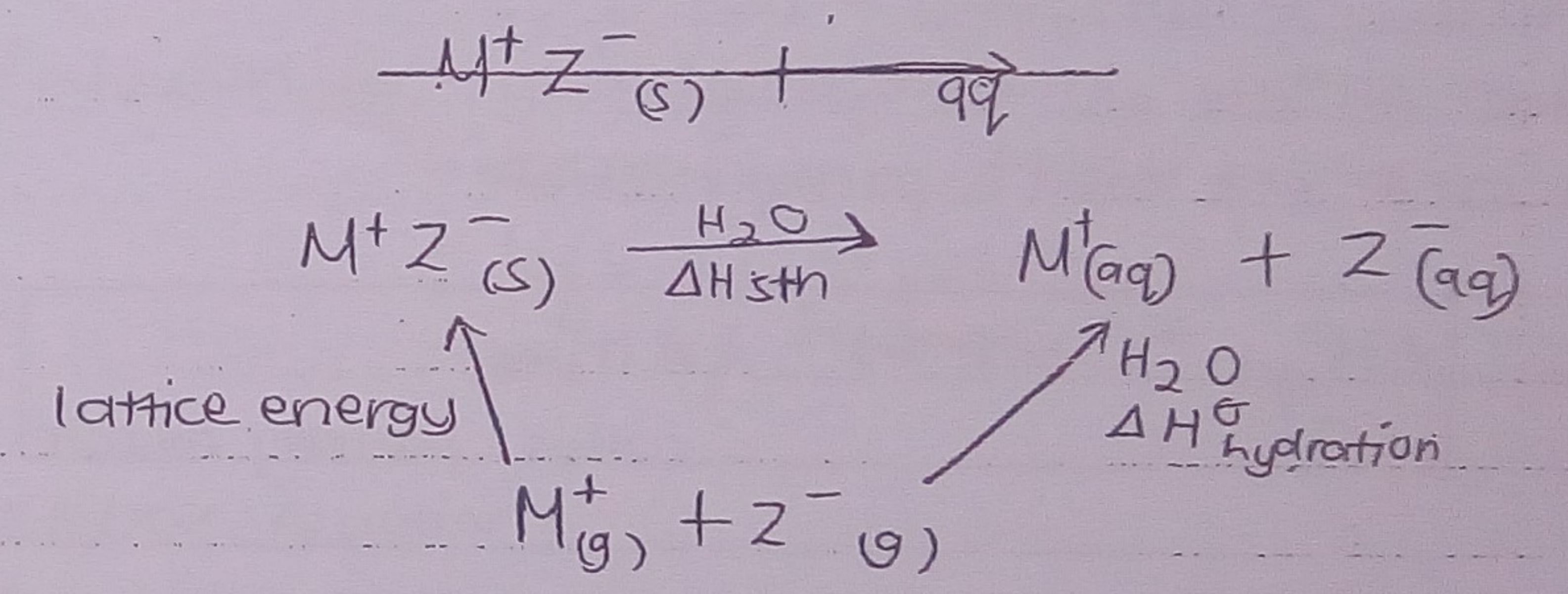
This can also be referred to as the dissolution of an ionic ~~emp~~ solid. The heat change which occurs when an ionic solid dissolves can be described using enthalpy change of solution, therefore the dissolution of a ionic solid can be described using enthalpy change of sltn.



The value of the enthalpy change of solution is affected by other enthalpies and these are:

- (i) enthalpy change of hydration
- (ii) enthalpy change of lattice energy

The relationship between enthalpy change of sltn, $\Delta H_{\text{hydratn}}$ and lattice energy can be shown in an energy cycle given below



Using Hess Law, the above enthalpies can be related as follows:

$$\Delta H_{\text{sltn}}^{\ominus} - \Delta H_{\text{hydratn}}^{\ominus} + \text{L.E} = 0$$

$$\Delta H_{\text{sltn}}^{\ominus} = \Delta H_{\text{hydratn}}^{\ominus} - \text{L.E}$$

The magnitude of lattice energy and $\Delta H_{\text{hydratn}}^{\ominus}$ affects how an ionic salt behaves in water

Scenario 1

When $\Delta H_{\text{hydratn}}^{\ominus} > \text{L.E}$ $-\Delta H_{\text{sltn}}^{\ominus}$
 (e.g. $-20 \text{ kJ mol}^{-1} - 10 \text{ kJ mol}^{-1}$) ... salt is soluble

Using \bar{e} relationship below

$$\Delta H_{\text{sltn}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus} - L.E$$
$$(-10 = -20 - (-10))$$

It implies that $\Delta H_{\text{sltn}}^{\ominus}$ will be negative.

We therefore say the ionic solid is soluble in water

Scenario 2

When $\Delta H_{\text{hydration}}^{\ominus} < L.E$

e.g. -10 kJ mol^{-1} -20 kJ mol^{-1}

Using \bar{e} relationship below

$$\Delta H_{\text{sltn}}^{\ominus} = \Delta H_{\text{hydration}}^{\ominus} - L.E$$

It implies that $\Delta H_{\text{sltn}}^{\ominus}$ will be positive

We therefore say \bar{e} ionic solid is partially soluble

| |
|---|
| $\Delta H_{\text{hyd}}^{\ominus} < L.E \rightarrow +\Delta H_{\text{sltn}}^{\ominus}$ \therefore salt is partially soluble |
|---|

Scenario 3

When $\Delta H_{\text{hyd}}^{\ominus} \ll L.E$ (way way less)

-10 kJ mol^{-1} -100 kJ mol^{-1}

Using \bar{e} relation below

$$\Delta H_{\text{sltn}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus} - L.E$$

It implies that $\Delta H_{\text{sltn}}^{\ominus}$ will have a large positive value

We therefore say \bar{e} ionic solid is insoluble

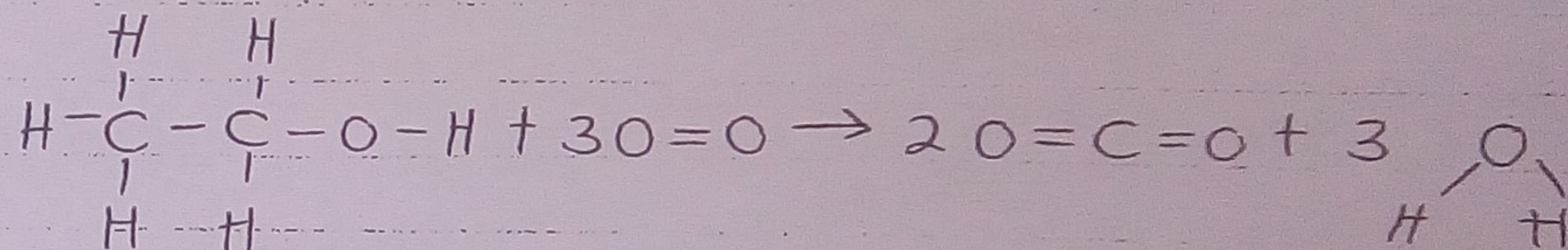
| |
|---|
| $\Delta H_{\text{hyd}}^{\ominus} \ll L.E \rightarrow +\Delta H_{\text{sltn}}^{\ominus}$ \therefore salt is insoluble |
|---|

Calculating enthalpy changes of rxn from bond energy values

When calculating ΔH_{rxn} from bond energy values the following formula is used

$$\Delta H_{\text{reaction}} = \Delta H_{\text{Bond breaking}} - \Delta H_{\text{bond formation}}$$

Using info from \bar{e} data booklet, calculate the enthalpy change of rxn for \bar{e} combustion of ethanol given by \bar{e} eqn below



Bond Breaking

$$5(\text{C}-\text{H}) = 5 \times 410$$

$$1(\text{C}-\text{C}) = 350$$

$$1(\text{C}-\text{O}) = 360$$

$$1(\text{O}-\text{H}) = 460$$

$$3(\text{O}=\text{O}) = 496 \times 3$$

$$\underline{4708 \text{ kJ mol}^{-1}}$$

Bond formation

$$4(\text{C}=\text{O}) = 4 \times 740$$

$$6(\text{O}-\text{H}) = 460 \times 6$$

$$\underline{5720 \text{ kJ mol}^{-1}}$$

Using \bar{e} formula

$$\Delta H_{\text{rxn}} = \Delta H_{\text{Bond breaking}} - \Delta H_{\text{Bond formation}}$$

$$\Delta H_{\text{rxn}} = 4708 \text{ kJ mol}^{-1} - 5720 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{rxn}} = -1012 \text{ kJ mol}^{-1}$$

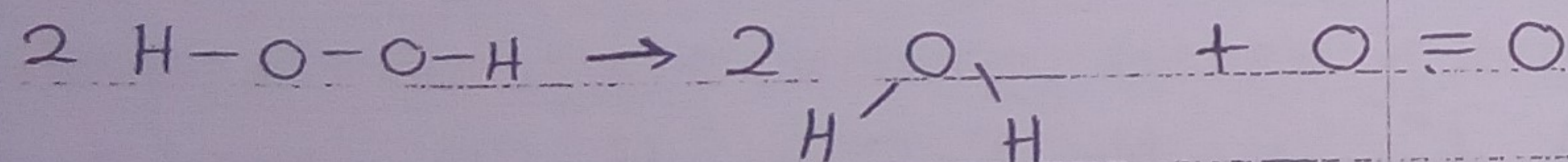
Bond Energy released during bond formation was more than the energy required to break bonds.

Qn
Hydrogen Peroxide decomposes according to the following eqn:



Using info from \bar{e} data booklet, calculate the enthalpy change of rxn

Solution



Bond breaking

$$4(\text{O}-\text{H}) = 4 \times 460$$

$$2(\text{O}-\text{O}) = 150$$

$$\text{Total} = 2140 \text{ kJ mol}^{-1}$$

Bond formation

$$4(\text{O}-\text{H}) = 4 \times 460$$

$$1(\text{O}=\text{O}) = 496$$

$$\text{Total} = 2336 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H_{\text{rxn}} &= \Delta H_{\text{Bond breaking}} - \Delta H_{\text{Bond formation}} \\ &= 2140 \text{ kJ mol}^{-1} - 2336 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta H_{\text{rxn}} = -196 \text{ kJ mol}^{-1}$$

ELECTROCHEMISTRY

Oxidation and Reduction

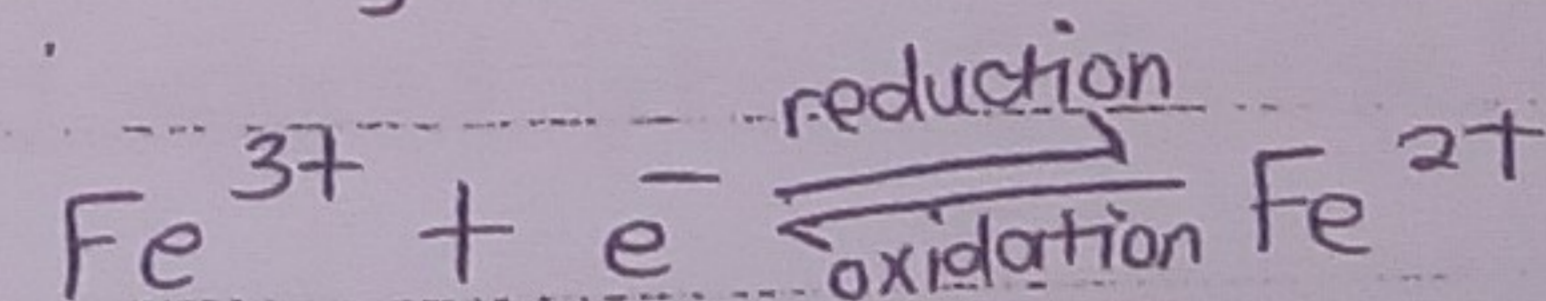
Oxidation is - the loss of electrons
- increase in oxidation number
- gain in oxygen
- loss of hydrogen

Reduction is - gain of electrons
- decrease in oxidation number
- loss of oxygen
- gain of hydrogen

REDOX Reaction

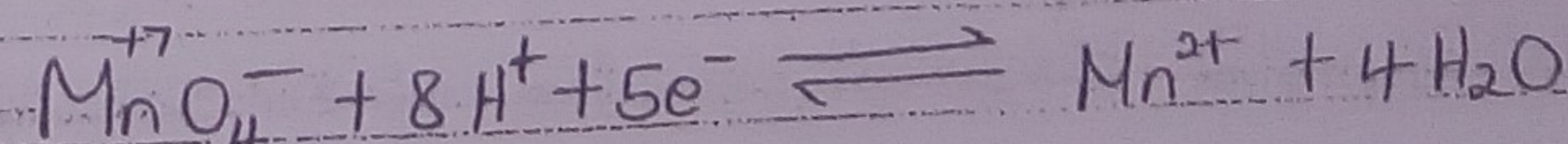
Dfn. A reaction where both oxidation and reduction are occurring.

e.g. Consider the half eqn below.



A half eqn is an eqn w/c shows the actual movement of electrons as they are being transferred from one specie to the next. When two half eqns are combined we get a full eqn.

Another e.g of a half eqn



When the REDOX rxns are occurring, oxidising agents and reducing agents can be identified in the full equation.

A reducing agent

- A species w/c facilitates reduction of another substance whilst it is being oxidised

A oxidising agent

- A species w/c facilitates oxidation of another substance whilst it is being reduced.

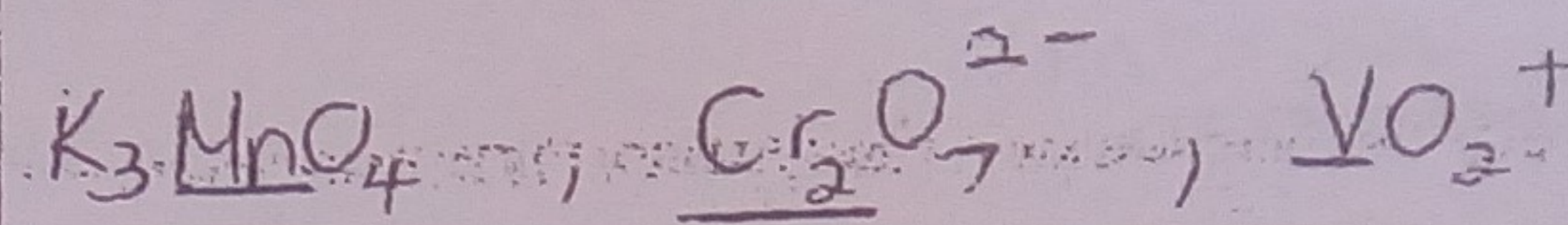
For us to deduce whether oxidation or reduction has occurred, \bar{e} changes in the oxidation number of species should be calculated.

Calculating oxidation numbers of elements in different substances

When calculating oxidation numbers of elements in cmpds or ions, one should be aware of the elements with fixed oxidation numbers

| Element | Fixed oxidation # |
|------------------|----------------------------------|
| Group 1 | +1 |
| Group 2 | +2 |
| Group 3 i.e (Al) | +3 |
| Flourine | -1 |
| Oxygen | (-2) expt in peroxide (-1) |
| Hydrogen | +1 except in metal hydrides (-1) |

Calculate \bar{e} oxid state of the underlined element in \bar{e} given species.



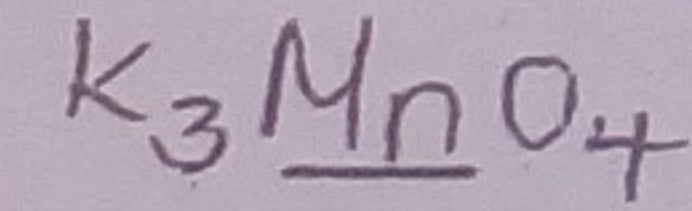
0
x + 1
+ x

Solution

$$(3 \times 1) + x + (4x - 2) = 0$$

$$3 - 8 + x = 0$$

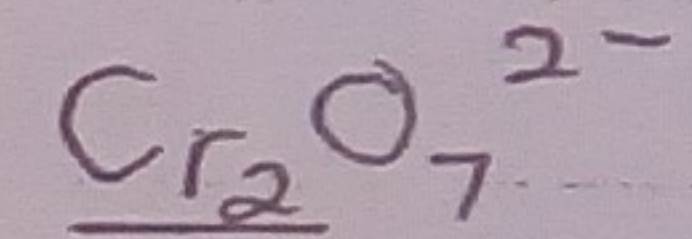
$$x = +5$$



$$2x + (7x - 2) = -2$$

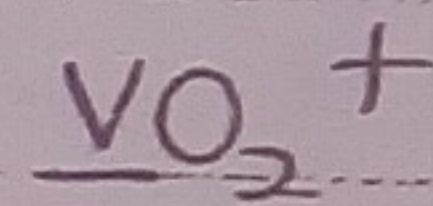
$$2x = 12$$

$$x = +6$$



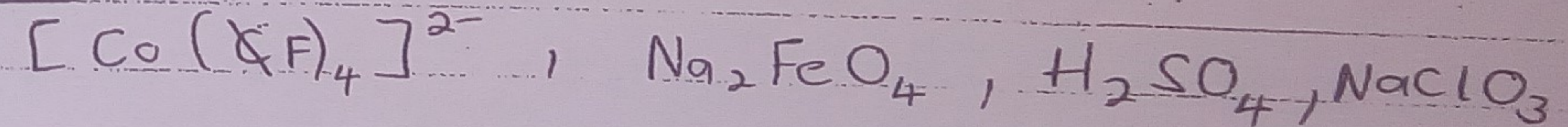
$$x + (2x - 2) = 1$$

$$x = +5$$



Calculate the oxid # of the relevant element in the species below (Element without a fixed oxid #)

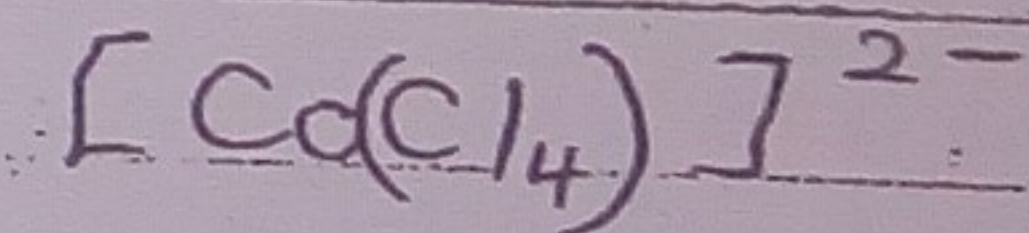
Solution



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

$$x - 4 = -2$$

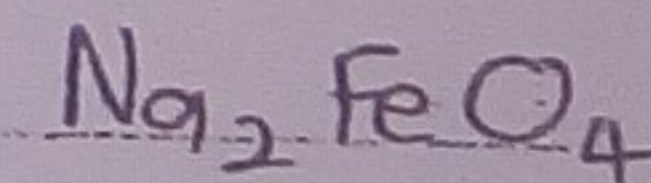
$$x = 2 \therefore x = +2$$



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

$$2 + x - 8 = 0$$

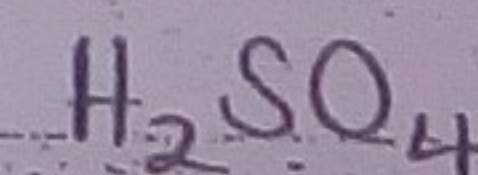
$$x = +6$$



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

$$2 + x - 8 = 0$$

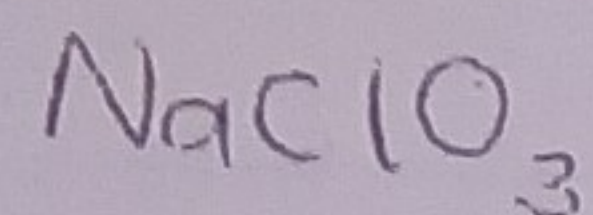
$$x = +6$$



$$1+x+(3x-2) = 0$$

$$1+x-6 = 0$$

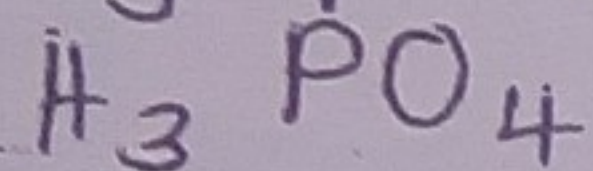
$$x = +5$$



Write \bar{e} electronic configuration for an element isoelectronic to the charge of phosphorus in phosphoric acid

Solution

Oxidation state of phosphorus in phosphoric acid



$$(1 \times 3) + x + (4 \times -2) = 0$$

$$3 + x - 8 = 0$$

$$\therefore x = +5$$

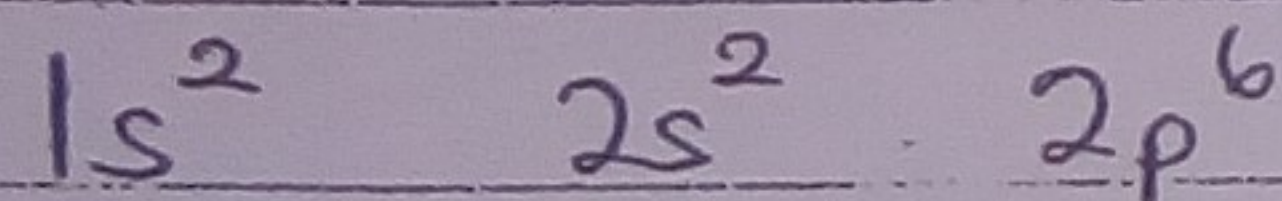
Isoelectronic = same number of electrons

Therefore in \bar{e} case we are writing the electronic configuration of an element with the same number of electrons as the ion of phosphorus

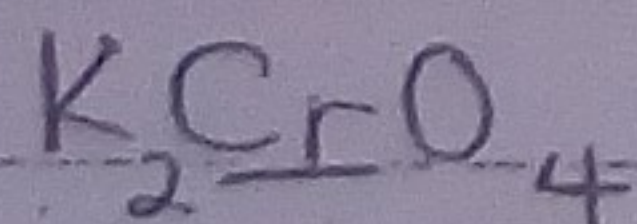
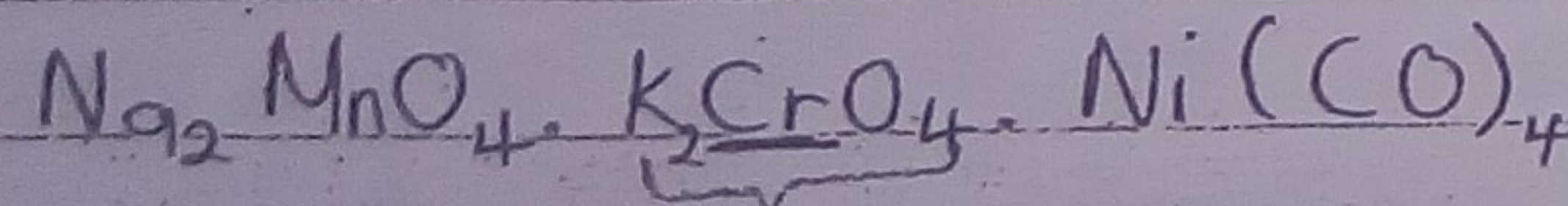
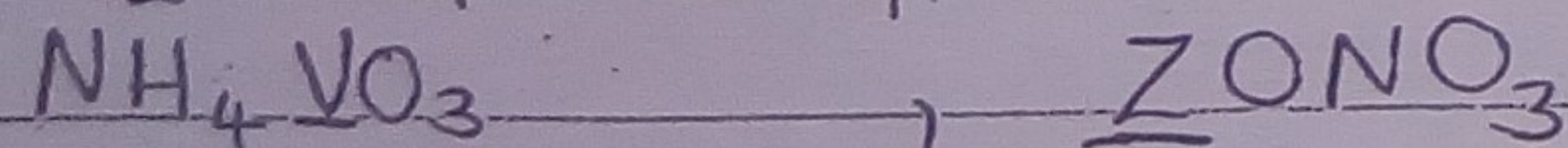
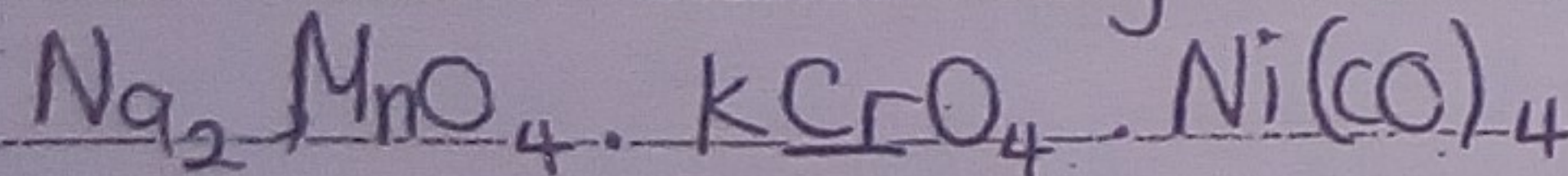
P atom has $15e^-$

\therefore in the +5 oxid state it will be $10e^-$, $5e^-$ lost

Implying \bar{e} element has $10e^-$



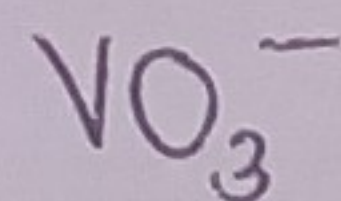
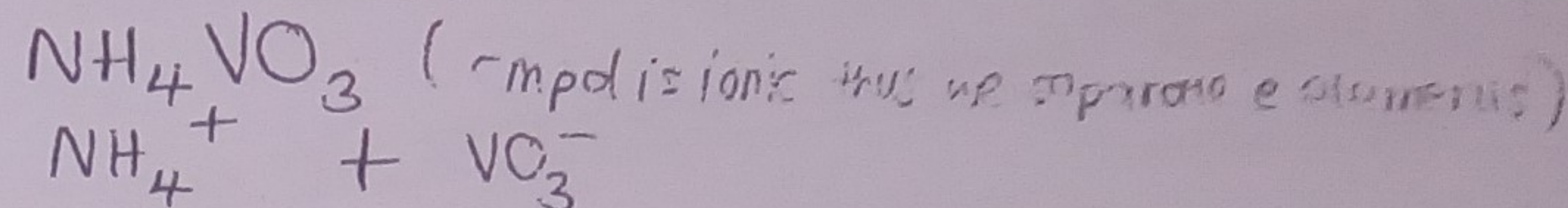
Calculate the oxid # of the underlined elements in \bar{e} species below



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

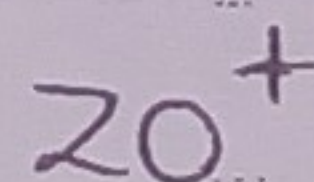
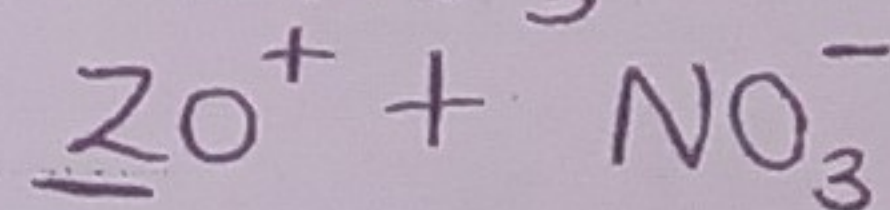
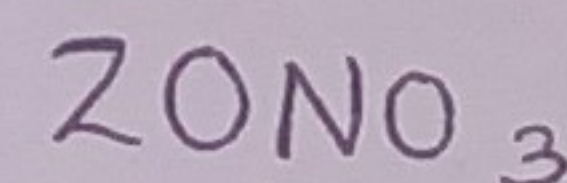
$$2 + x - 8 = 0$$

$$\underline{x = +6}$$



$$x + (3 \times -2) = -1$$

$$\underline{x = +5}$$



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

$$\underline{x = 3}$$

Disproportionation reaction

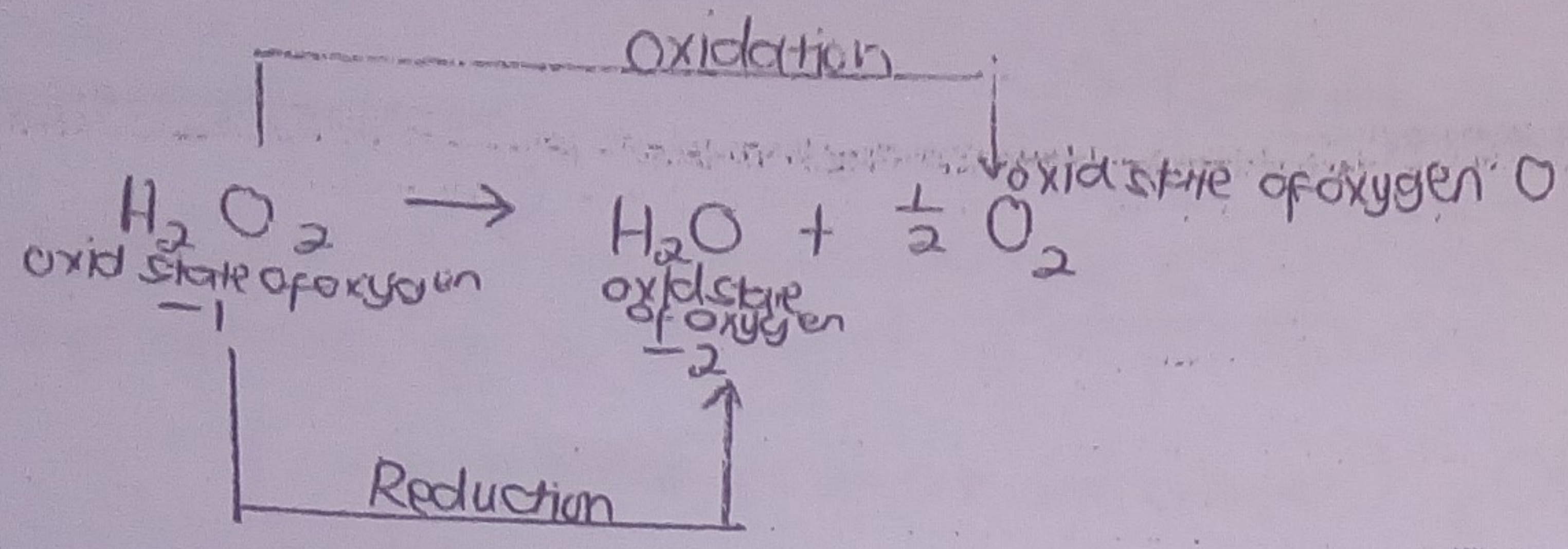
A disproportionation rxn is a rxn whereby an element is simultaneously oxidised and reduced at the same time/in the same rxn.

Example

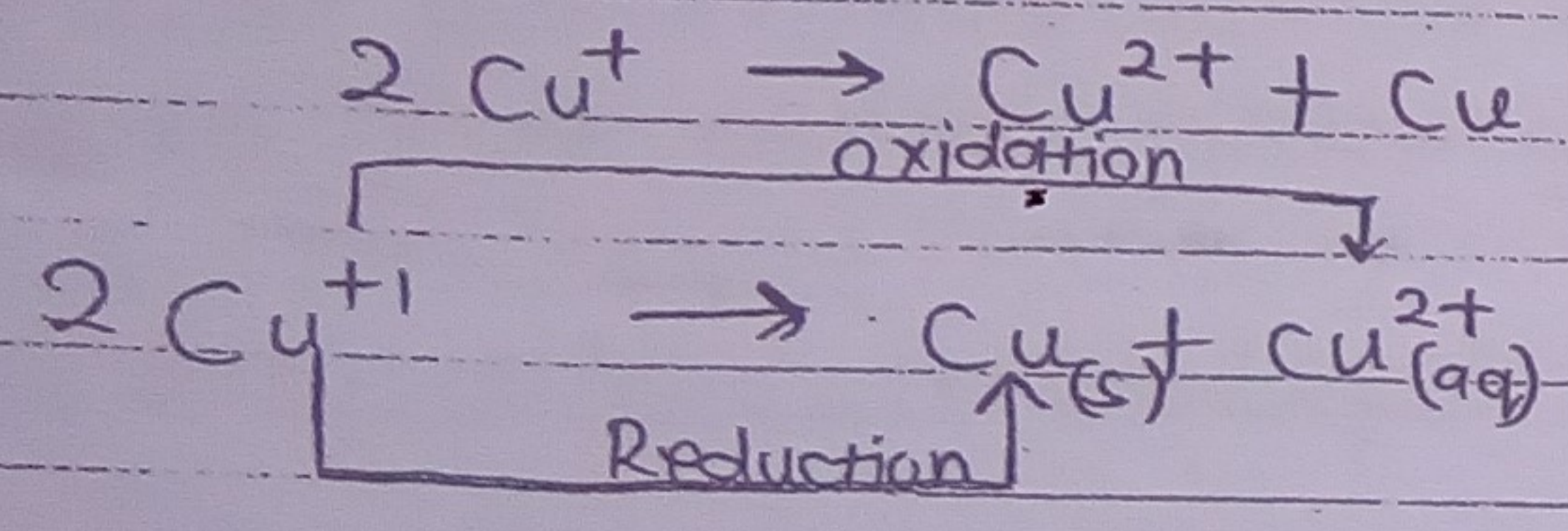
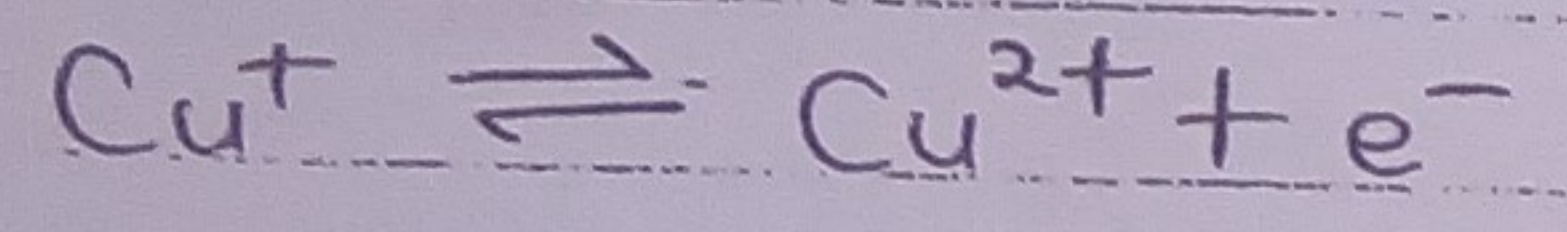
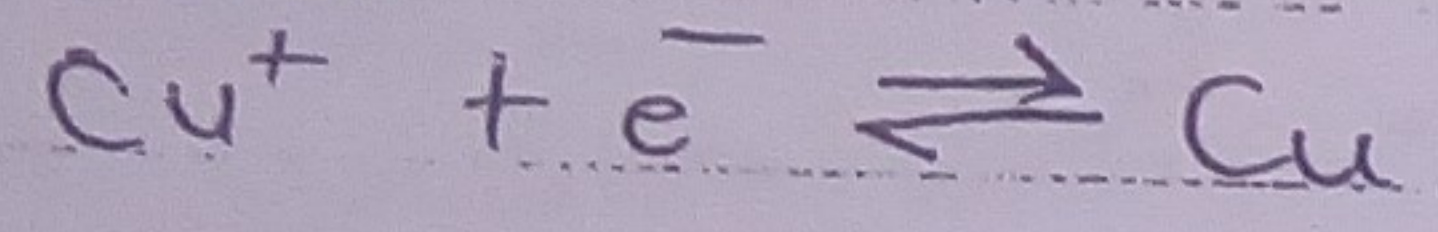
Consider the decomposition of hydrogen peroxide

.. the DIRECTOR ..

0712 105 452



Cu^+ in an aq sln is unstable, as a result it undergoes disproportionation



Electrode potential

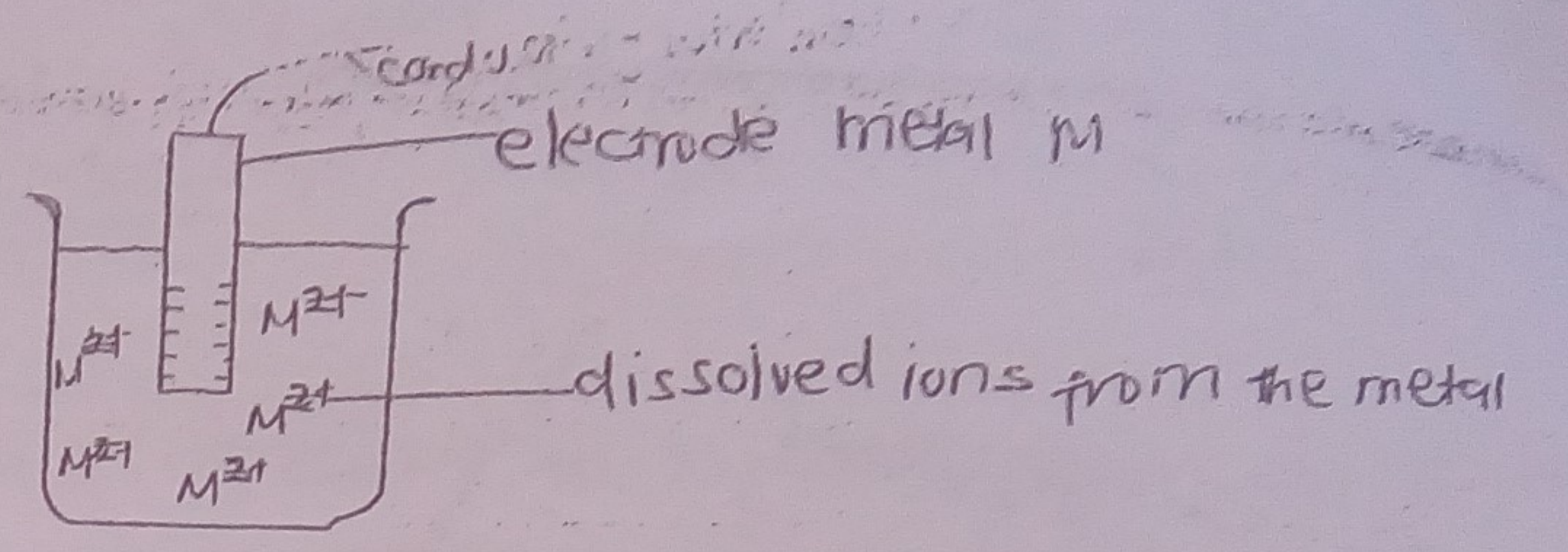
An electrode is a conducting solid (usually a metal or carbon) which conducts electricity to/from the electrolyte.

Potential difference (also called voltage)

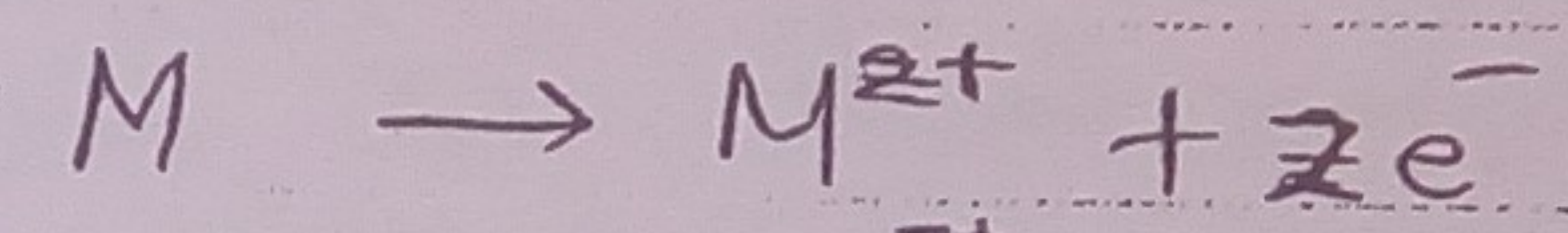
Consider an electrode made from metal M dipped in an aqueous solution or water

... the DIRECTOR ...

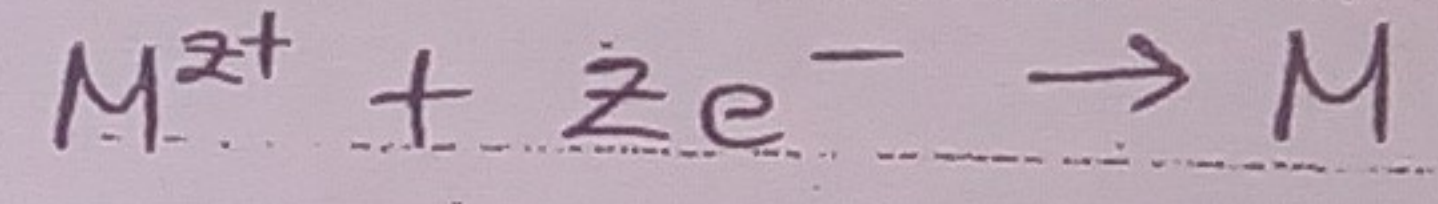
0712 105 452



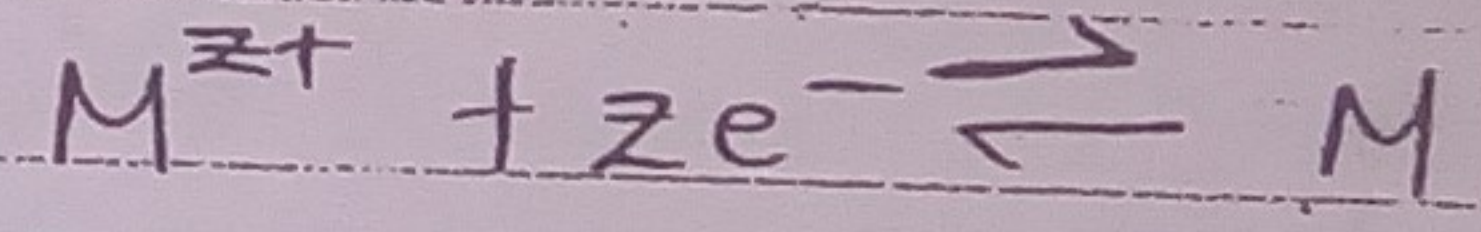
When metal M is placed in an aqueous sltn, it dissolves in the sltn to produce ions and leave electrons behind



The released M^{z+} ions will then be attracted back to the metal with excess electrons



The two processes above continue repeatedly until an equilibrium is established



At equilibrium, \bar{e} electrons in \bar{e} metal (the electrode) will then move along the rod to the conducting wire, the movt of the electrons can be described as current, while the force $n\bar{e}$ is pushing \bar{e} electrons will be the voltage. Thus we say, a potential difference has been created (voltage).

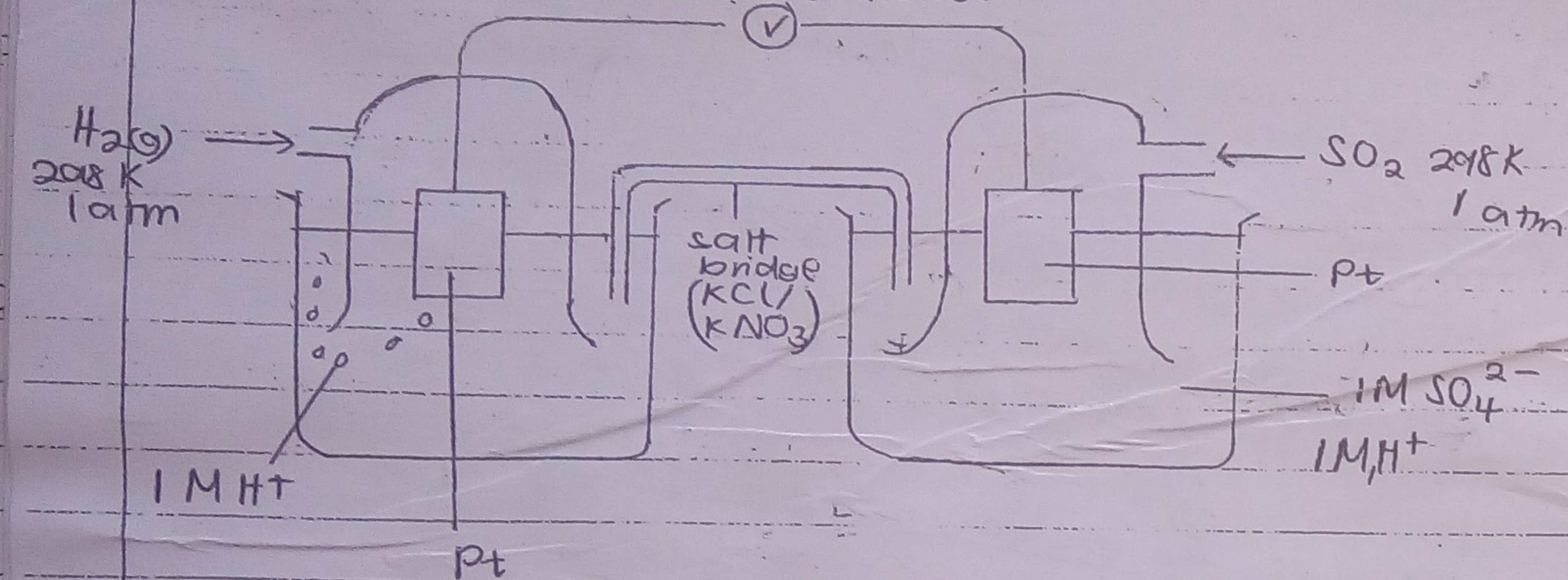
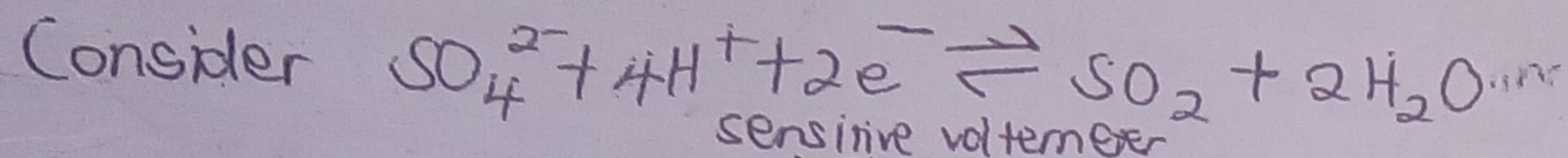
Therefore we can then formally define an electrode potential as:

An electrode potential is \bar{e} potential difference / voltage of an electrode system.

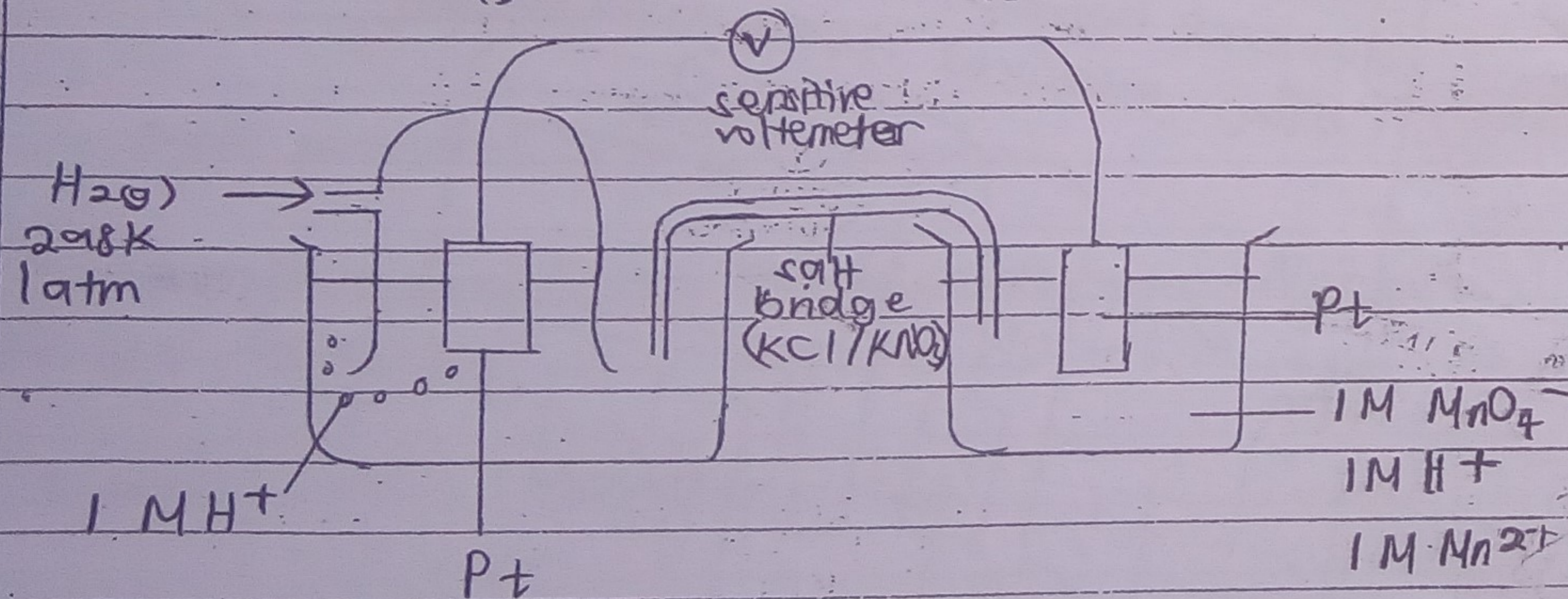
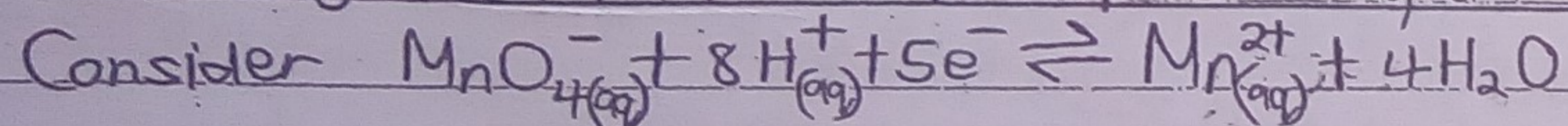
The electrode system stated above created a potential, in the section below we are going to consider another electrode system we does not create a voltage known as the standard hydrogen electrode.

Standard hydrogen electrode (SHE)

Measuring the standard electrode potential of a gas



Measuring the standard electrode potential of a REDOX system



The method being used above to measure the voltage of an electrode system has some limitations when practically performing it

Drawbacks of the E^\ominus Method

- (1) The concentration of the solutions varies as the reactions proceed.
- (2) Some of the metals react very rapidly with the solutions (the rxns are too fast) as a result the voltage then becomes difficult to note.
- (3) Some of the elements react very slowly with the solutions as a result the voltage then becomes difficult to note.

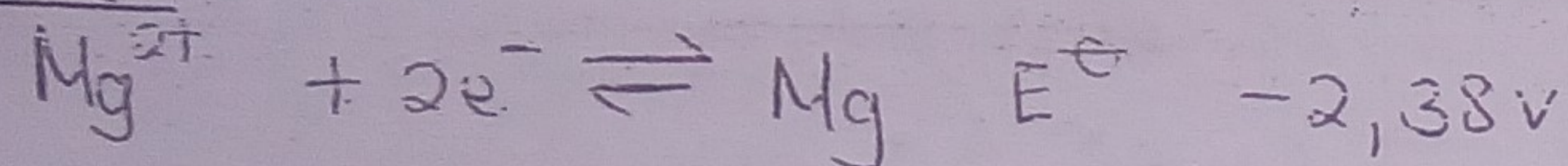
The Electrochemical Series

- Elements can be arranged by the way they react forming an electrochemical series.
- Species MnO_4^- are high up in the electrochemical series have a very large ^{negative} E^\ominus value.
- These species are very reactive.
- Species which are said to be low in the electrochemical series have a large positive E^\ominus value.
- These species are generally unreactive as metal atoms but all the other species with a large positive are very reactive.
- Species with a negative E^\ominus value

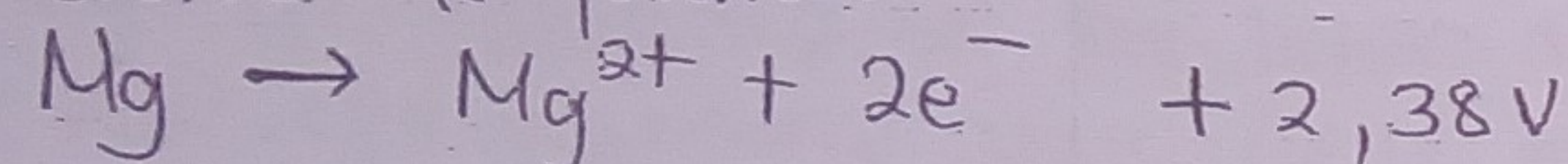
As stated above, species with a large negative E^\ominus value, are said to be high up in the electrochemical series and they are very reactive.

These species have a great tendency of losing electrons. Thus we say species with a -ve E^\ominus value are reducing agents, but,

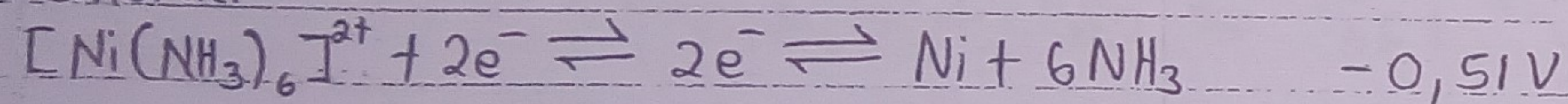
Consider



When interpreting the above half eqn, since it has got a -ve E^\ominus value, it implies that the species on the right hand of the ^{half} eqn have a ^{great} tendency of losing electrons. Therefore the above above half eqn can then be reversed as follows:

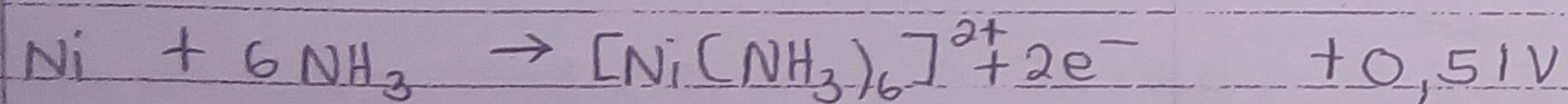


2. Consider



The above half equation can be interpreted as follows:

Since it has a negative E^\ominus value, it implies that the species on the right handside of the eqn has a tendency of losing electrons. Therefore we say nickel in the presence of ammonia has got a tendency of losing electrons ^{forming} the Ni^{2+} complex.

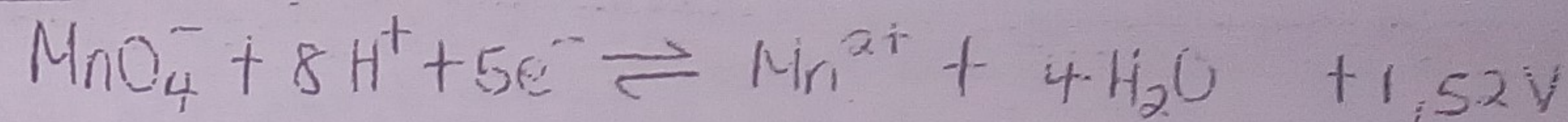


Species with a +ve E^\ominus value

- As stated above, species with a large positive E^\ominus value are said to be low down in the electrochemical series and they are unreactive.

- The species in ionic form have great tendency of accepting electrons. Thus we say species with a +ve E^\ominus value are oxidising agents.

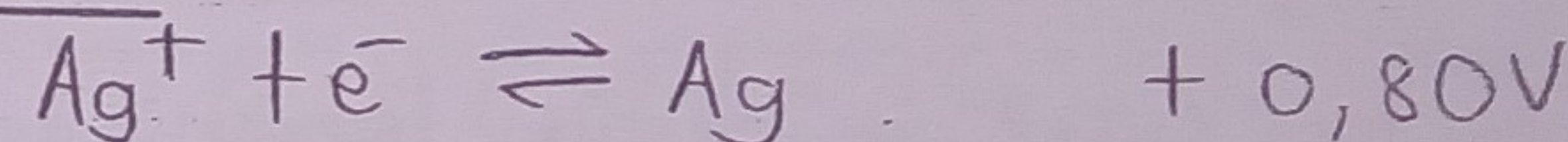
Consider



When interpreting the above half eqn, since it has got a +ve E^\ominus value, it implies that the species on the left handside of the half equation have got a great tendency of accepting electrons, this makes them strong oxidising agents.

→ The half eqn is not going to be reversed, the interpretation is in line with what is happening in the half equation.

Consider



Interpretation of the equation

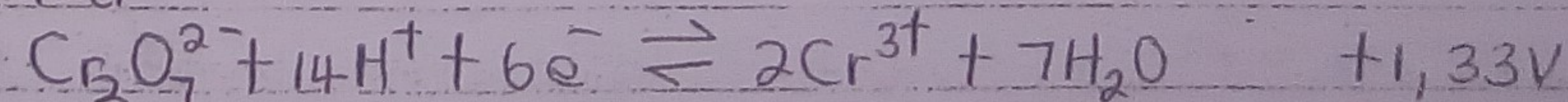
Since it has got a positive E^\ominus value, it implies that the species on the ^{left} handside of the half eqn have a tendency of accepting electrons.

The two half equations above can be summarised as follows:

1. The permanganate ions in an acidic environment has a great tendency of accepting electrons to form Mn^{2+} and H_2O .
2. Silver ions have a tendency of accepting electrons to form solid silver metal.

Effect of concentration on the e.m.f values of different half eqns

Consider



Effect of increasing conc. Cr^{3+}

- An increase in the conc of Cr^{3+} , will result in the voltage being less positive.
- Due to the high conc of the product, Cr^{3+} in solution, less reactants will be combining to form the products. Thus voltage decreases

Effect of decrease in conc of $\text{Cr}_2\text{O}_7^{2-}$

- This results in the decrease of the voltage. Thus it will be less positive.
- This is due to the less $\text{Cr}_2\text{O}_7^{2-}$ in solution hence electron acceptance will also be less

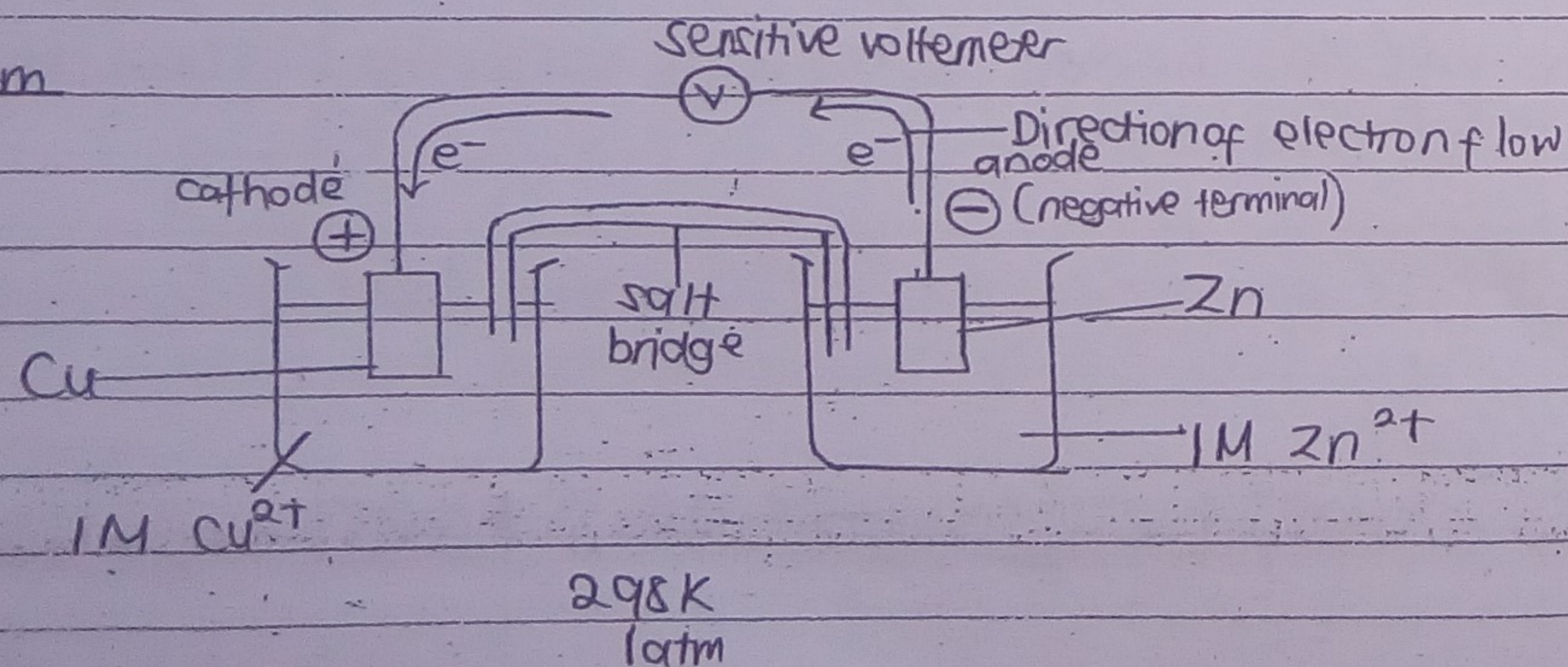
Electric cells

- When two electrode systems are combined (when two half cells are combined) one produces an electric cell

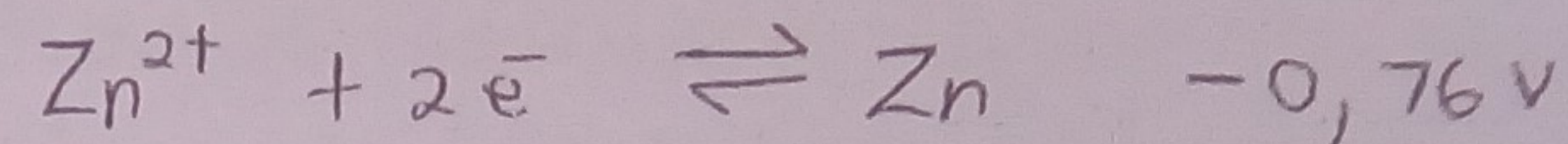
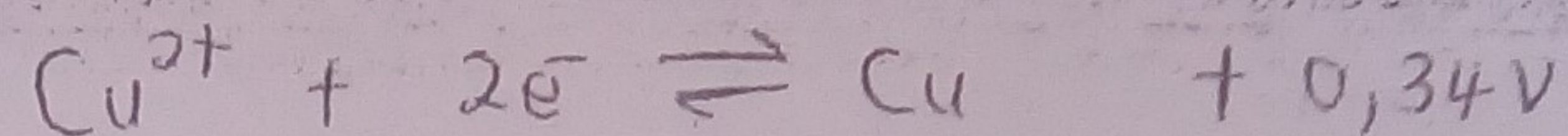
Consider the galvanic cell

- This is made by joining copper half cell and zinc half cell

Diagram

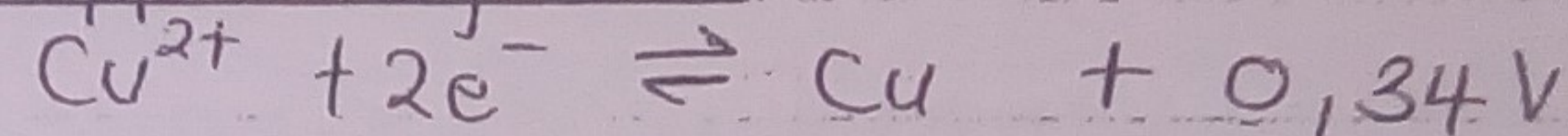


The half equations of interest

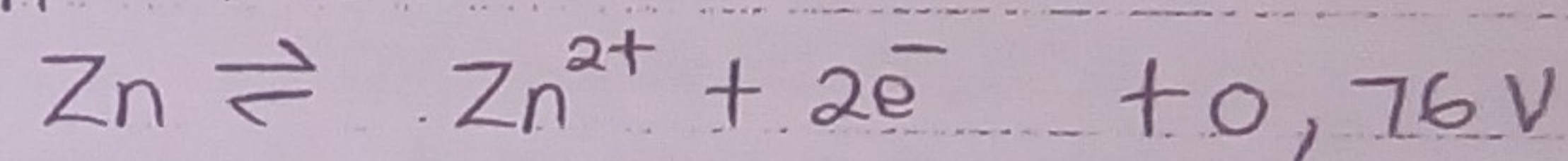
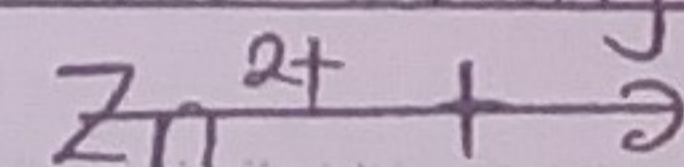


After interpreting the half eqns, Cu^{2+} ions will gain electrons while Zn metal will lose electrons

Copper half cell

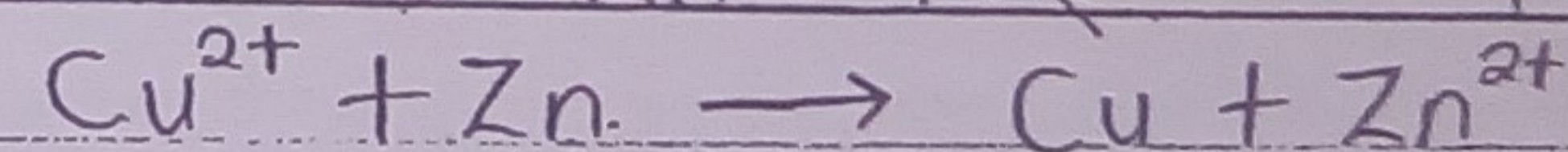
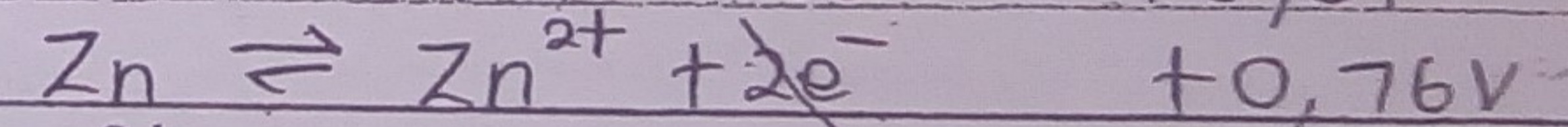
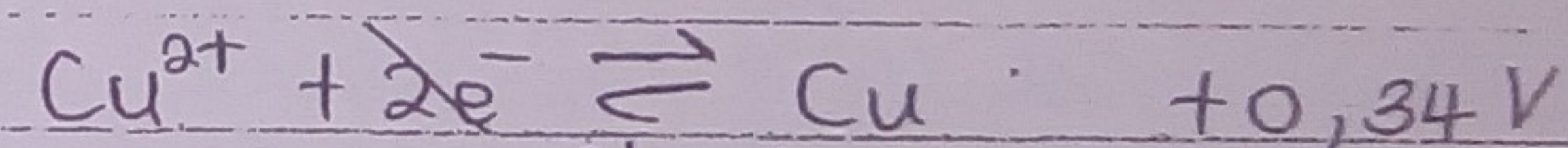


Zinc half cell



Overall equation of the cell

The overall eqn of the cell can be obtained by combining the two half cells equations



The above is the overall equation of the cell

Calculating the e.m.f of the cell

- To obtain the emf of the cell, the voltages in the half cells above are added together

$$E_{\text{cell}}^{\ominus} = E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} + E_{\text{Zn}/\text{Zn}^{2+}}^{\ominus}$$

$$E_{\text{cell}}^{\ominus} = (+0,34\text{V}) + (+0,76\text{V})$$

$$= \underline{\underline{+1,1\text{V}}}$$

The direction of electron flow

After drawing the cell as done above, the direction of electron flow can be stated if required to

Clearly from the half cell equations, zinc metal will be giving away electrons. Therefore electrons will flow from the zinc half cell to the copper half cell.

Terminals on the electric cell

The half cell providing electrons (in this case - the zinc half cell) becomes the negative terminal.

The half cell gaining electrons (in this case - copper half cell) becomes the positive terminal.

The negative terminal is the anode in an electric cell, this is because oxidation is occurring at the negative terminal as shown above in the half equations

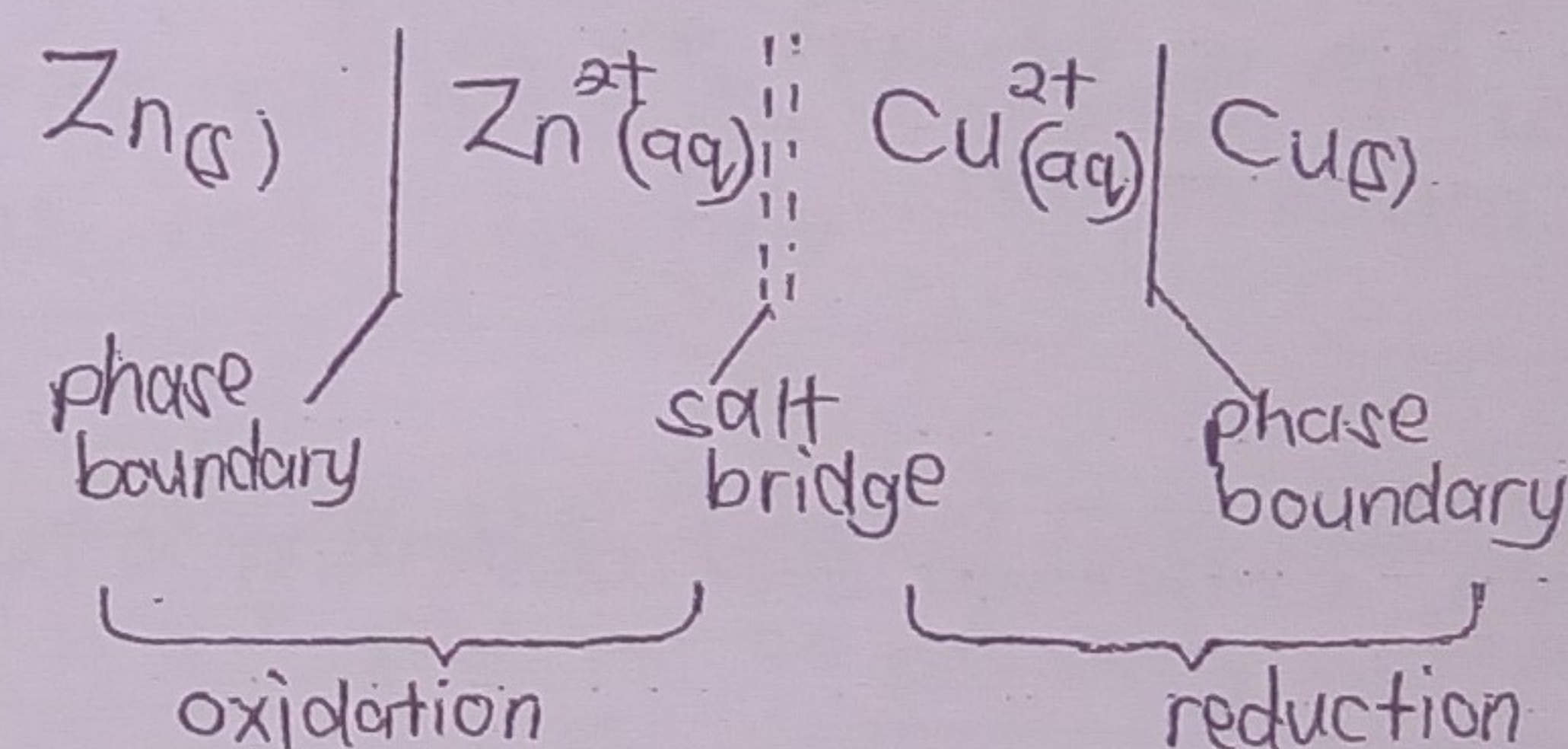
The positive terminal is the cathode in an electric cell, this is because reduction is occurring at the positive terminal

The Shorthand Representation of an electric cell

It can also be referred to as the conventional representation of an electric cell.

- When writing the shorthand representation, we always start with the half cell where oxidation was occurring.
- Solid components are always separated from gaseous, aqueous or liquid components using a bold straight line.
- Two half cells are combined with a salt bridge which is represented as a double dotted line.
- We then finish writing the shorthand representation by writing components in the half cell where reduction was occurring.

Consider the cell above



Effect of concentration on the voltage of the cell

Consider increasing the concentration of $[\text{Cu}^{2+}]$
 increasing (Zn^{2+})
 decreasing the thickness of the Zn electrode

Solution



Using the above eqn from the electric cell, increasing the conc of a reactant will increase the voltage of the cell

Decreasing the concentration of a reactant will decrease the voltage of the cell

Increasing the concentration of a product will decrease the voltage of the cell while decreasing the concentration of a product will increase the voltage of the cell.

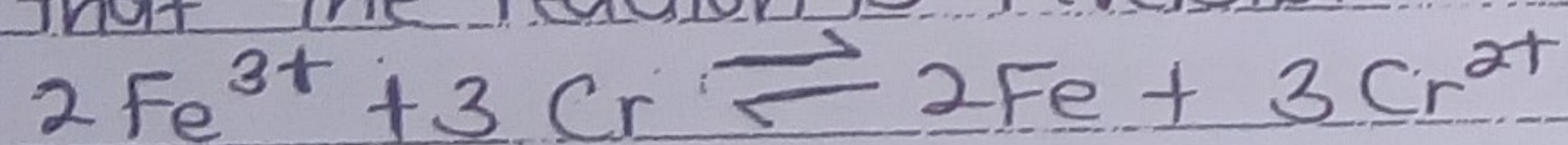
Therefore it implies that increasing conc of copper will increase the voltage, increasing the concentration of Zn^{2+} will decrease the voltage.

Decreasing \bar{e} thickness of the zinc electrode has no effect on the voltage of the cell. This is because, the solid electrode has a constant concentration.

Consider

Fe^{3+} ions can react with chromium solid according to the equation below.

Assuming that the reaction is reversible



What is the effect of adding iron filings to the reaction (E^{\ominus} value).

Solution

Voltage will decrease. This is because more iron will be reacting with Cr^{2+} to form the products ($Fe^{3+} + Cr$).

Q1) Draw a diagram to show an electric cell formed between H_2O/H_2 system and Mn^{2+}/Mn system

(b) On your diagram

(i) Show the direction of electron flow

(i) label the positive and negative terminal

(ii) label the anode and the cathode

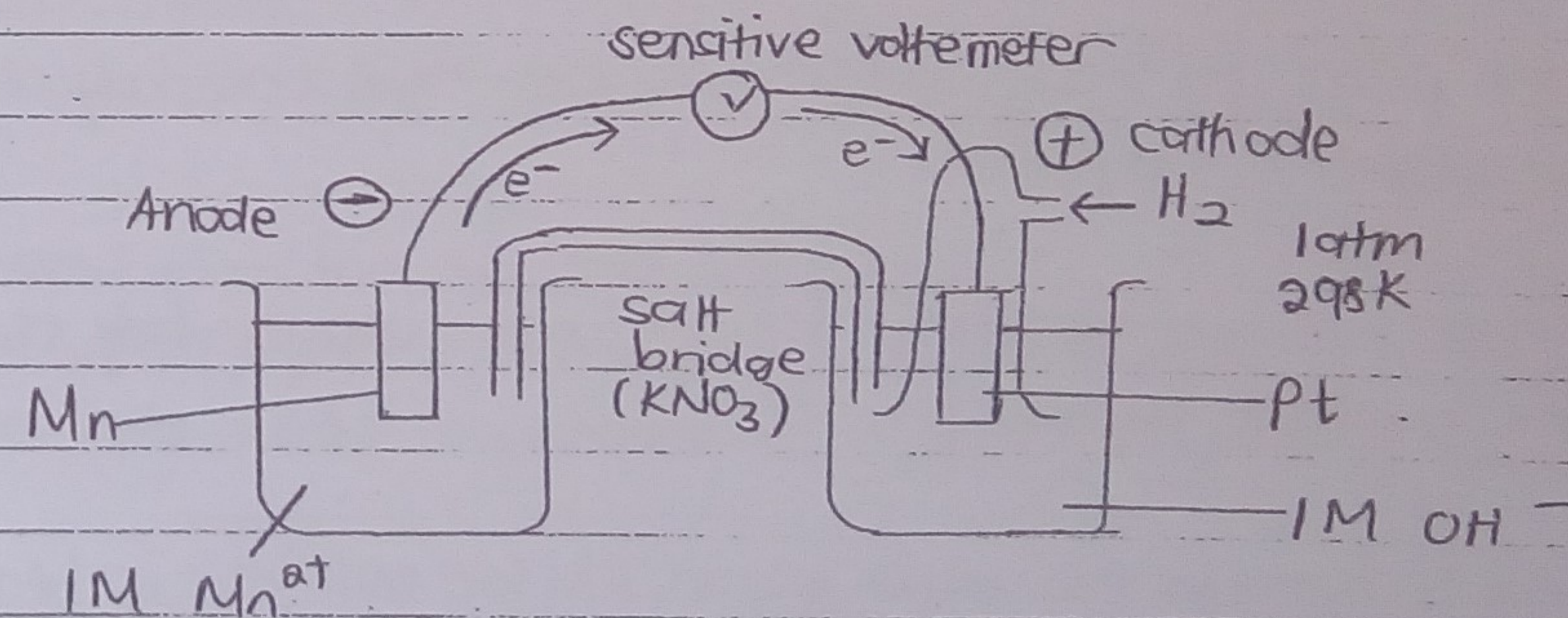
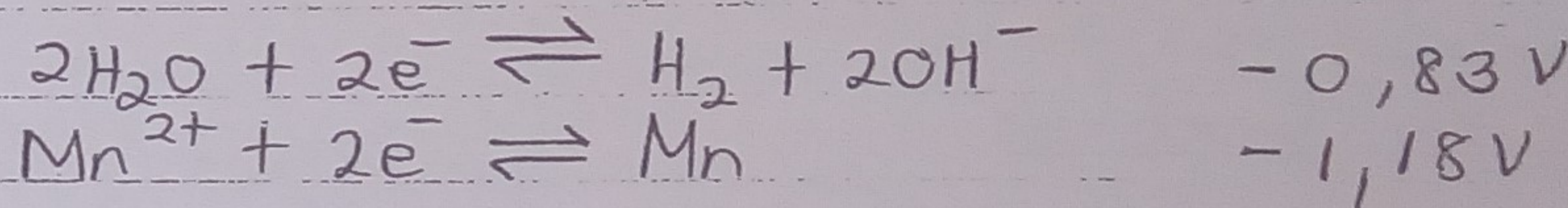
(c) Write the overall eqn of the cell

(ii) Calculate the voltage of the cell

(d) Write a full shorthand representation of the cell.

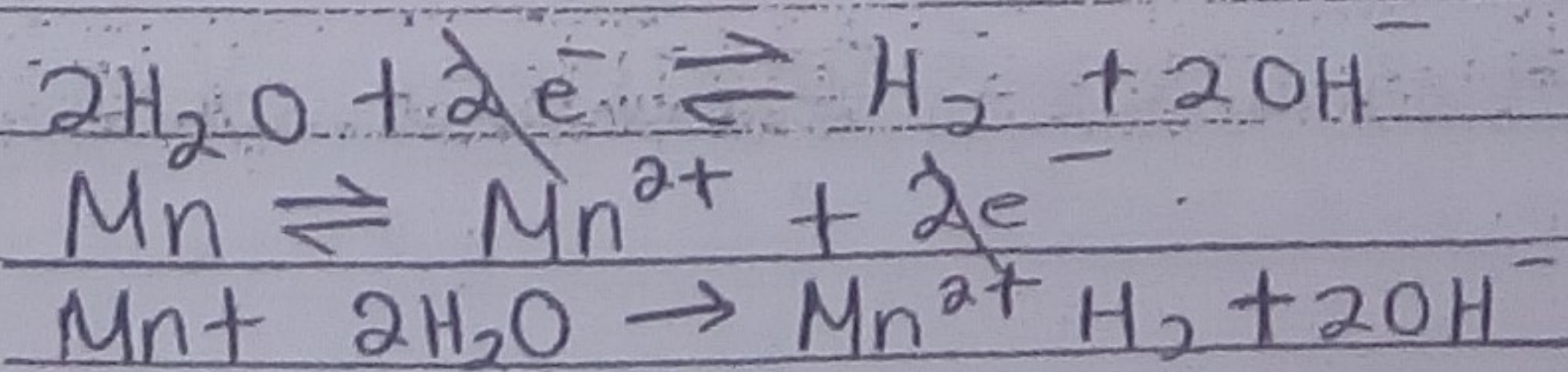
(ii) What is the effect of decreasing the conc of Mn^{2+} and OH^- on the voltage of the cell.

Solution

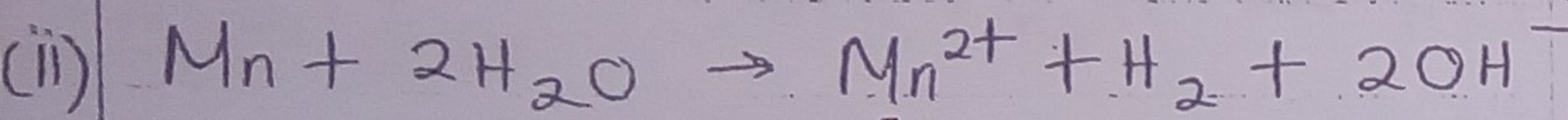
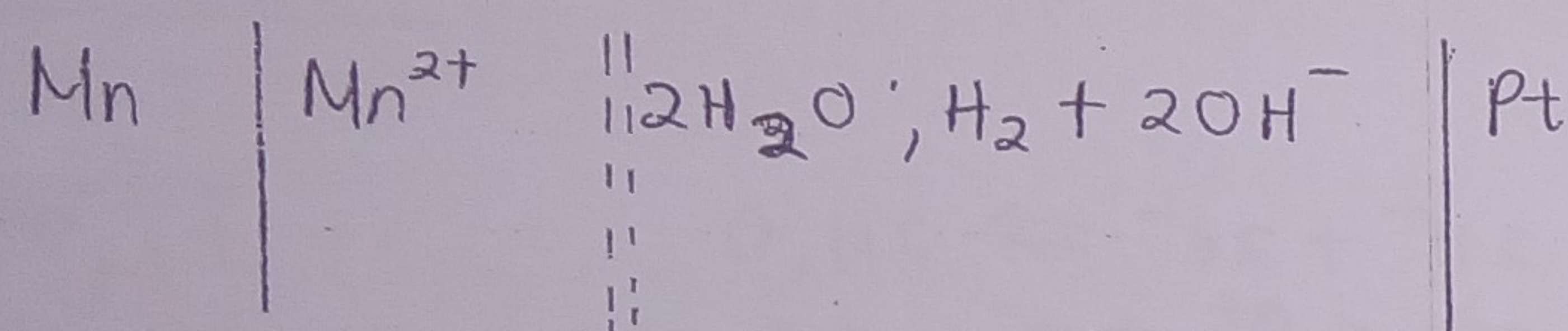
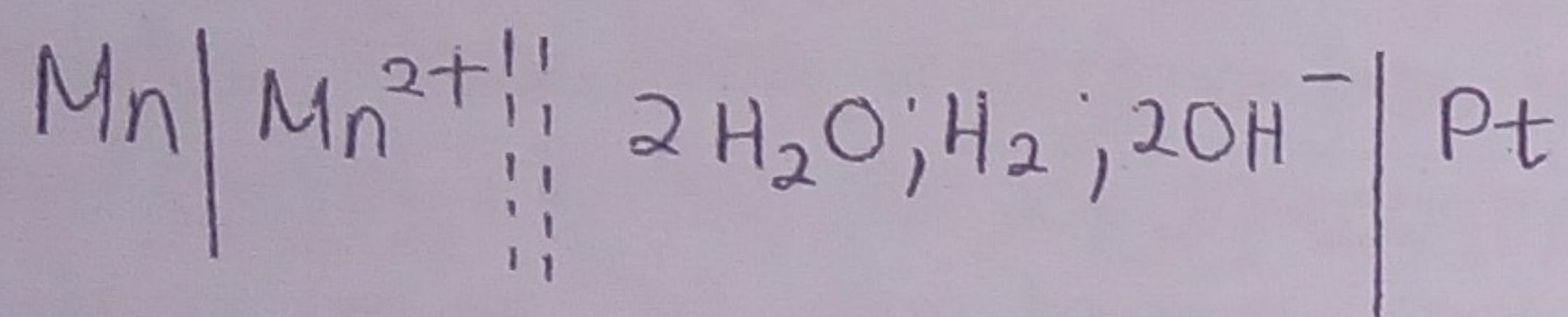


(i) Manganese having a greater tendency of losing electrons is the one which provides electrons, therefore electrons will flow from the manganese half cell.

(ii) From the half eqns, the manganese half eqn will be reversed because it is the one which has the greatest tendency of losing electrons from the E^{\ominus} value



$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{H}_2\text{O}/\text{H}_2}^- + E_{\text{Mn}^{2+}/\text{Mn}}^0 \\
 &= (-0,83\text{V}) + (+1,18\text{V}) \\
 &= +0,35\text{V}
 \end{aligned}$$



The voltage increases if we decrease conc of Mn^{2+} and OH^-

The electric cells drawn above all contained a salt bridge.

Uses of a salt bridge

- Maintains electrical neutrality by providing ions to the solutions
- It completes the electric circuit
- It prevents the two solutions from the two half cells from mixing.

What is a salt bridge?

fn: An absorbent material e.g. filter paper which would have been dipped in an aqueous solution of ionic salts e.g. KNO_3 or KCl and it is placed between two half

cells in an electric cell.

Predicting feasibility of reactions

- After combining two half equations to form one full equation, the overall voltage of the reaction should also be calculated.
- If the calculated voltage is positive, it implies that the given rxn occurs, we therefore say the rxn is feasible
- If the calculated voltage is negative, it implies that the given rxn will not spontaneously occur, therefore we say the rxn is not feasible

Consider the following questions

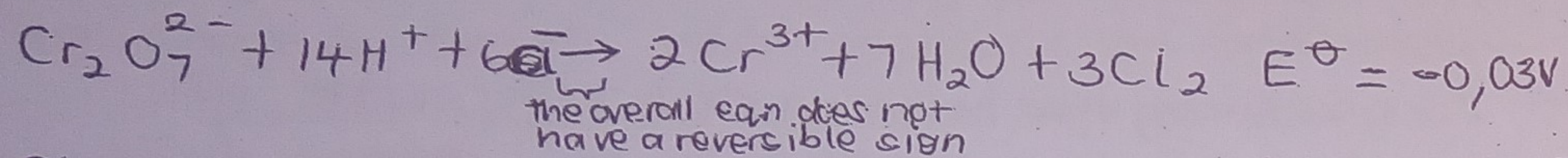
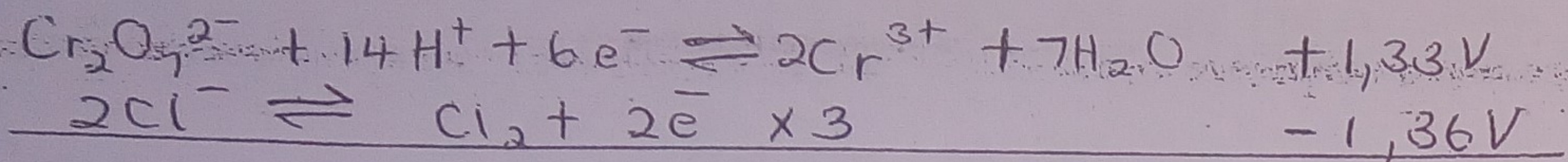
Predict whether the following species react

1. $\text{Cr}_2\text{O}_7^{2-}$ and Cl^-
2. Co^{2+} and MnO_4^-
3. Pb^{2+} and Ni
4. Zn^{2+} and SO_2

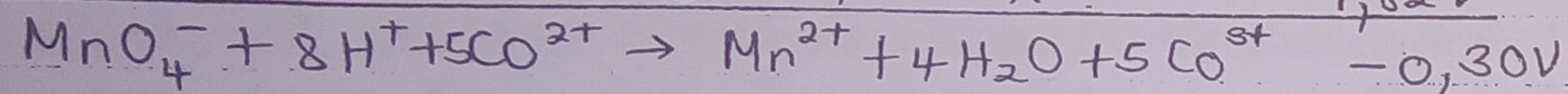
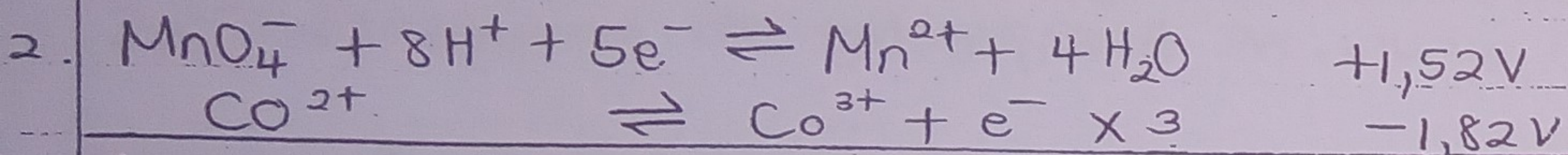
Solution

When constructing the equations for the given species above using the data booklet, always remember that the given species are reactants and should always be on the reactants side of the constructed equation.

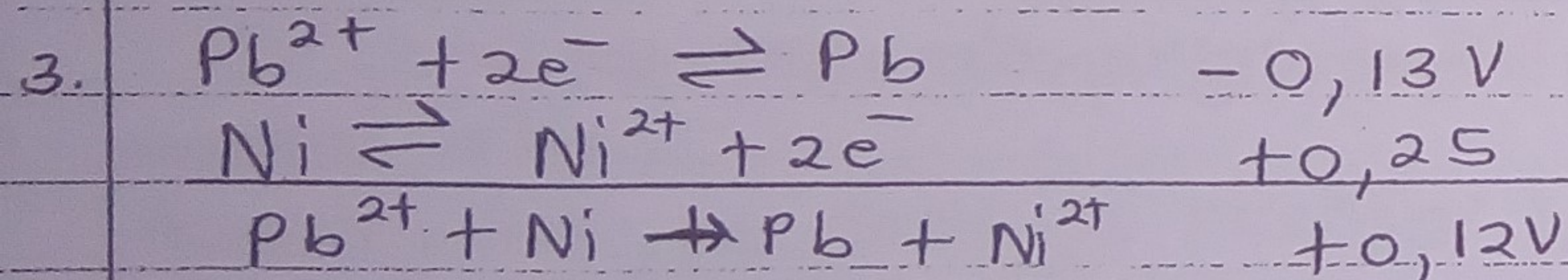
1. $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad +1,33\text{V}$
 $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$ - but Cl^- is supposed to be a reactant therefore we reverse the eqn



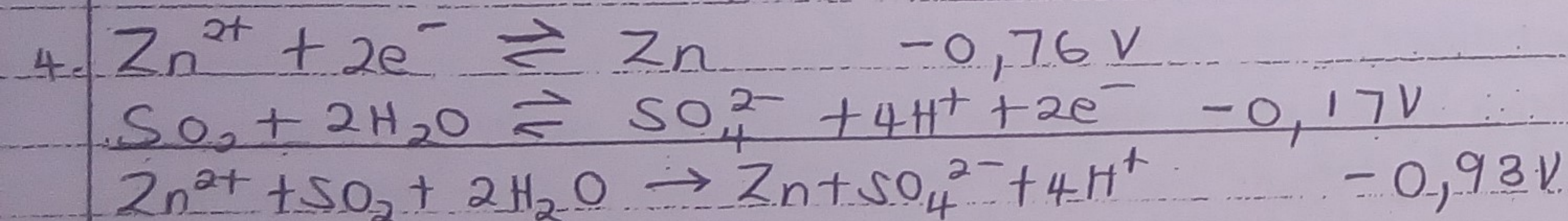
Since the voltage of the eqn is negative, it therefore implies that the rxn is not feasible.



Since the voltage of the overall eqn is negative, it therefore implies that the rxn is not feasible.



Since the voltage of the overall eqn is positive, it therefore implies that the rxn is feasible.

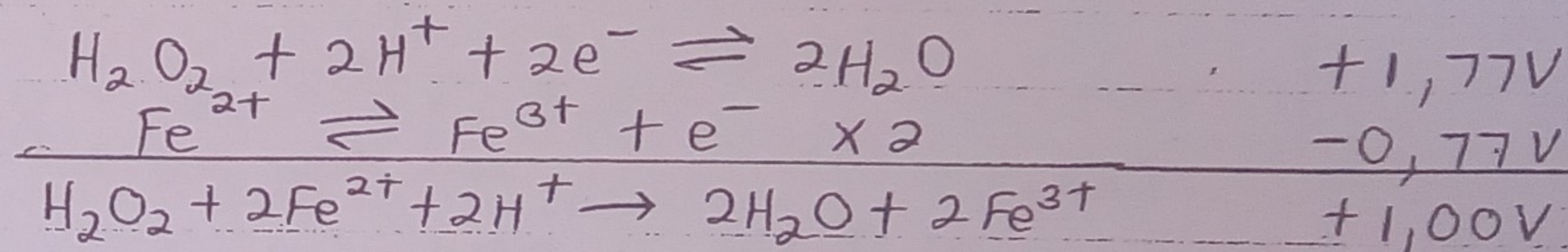


Since the voltage of the overall eqn is negative, it therefore implies that the rxn is not feasible.

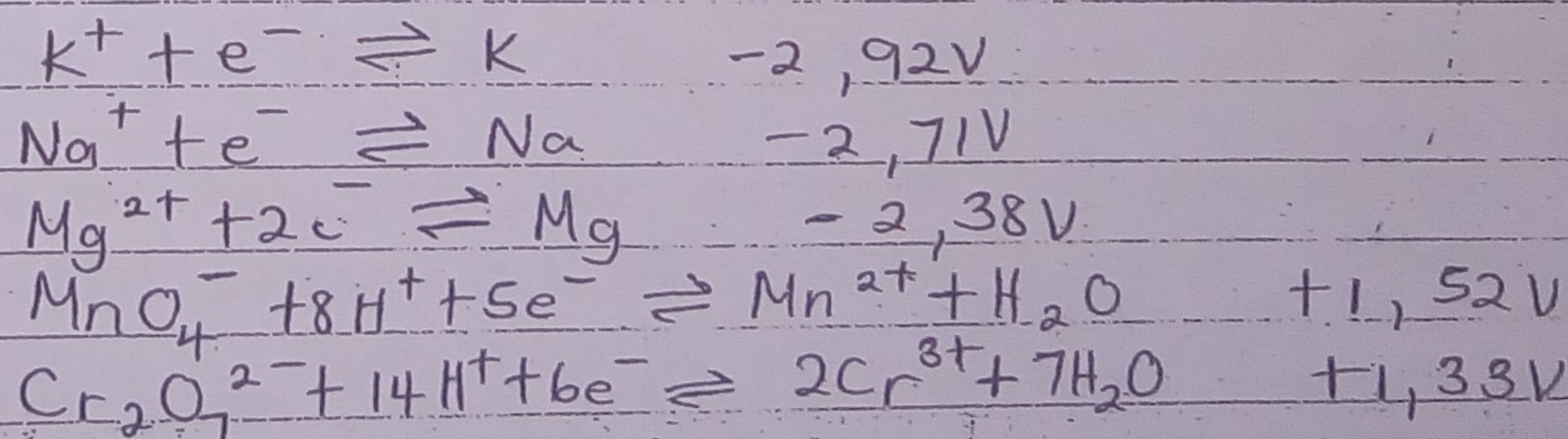
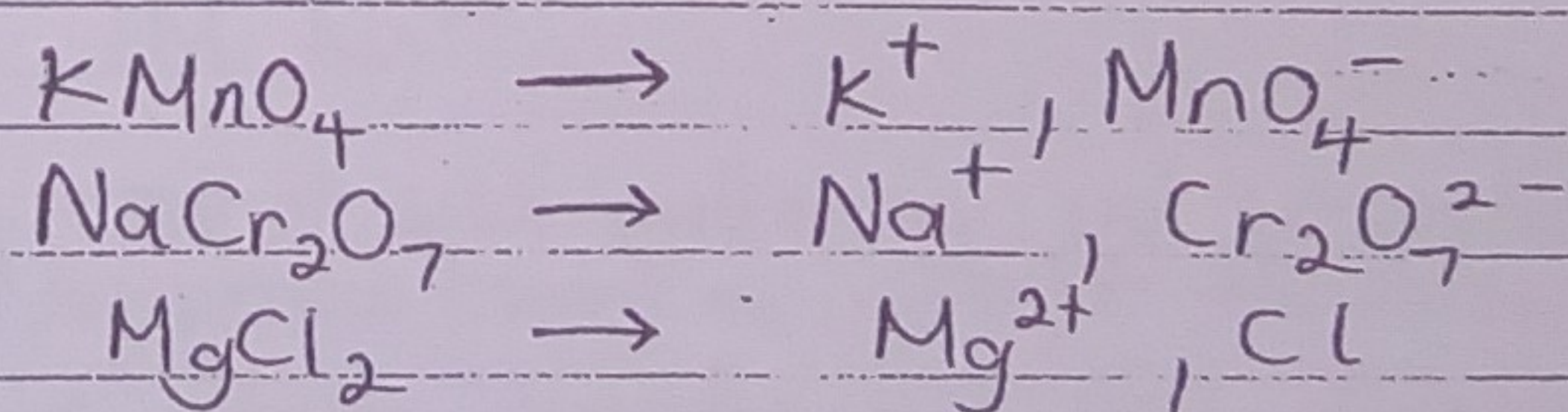
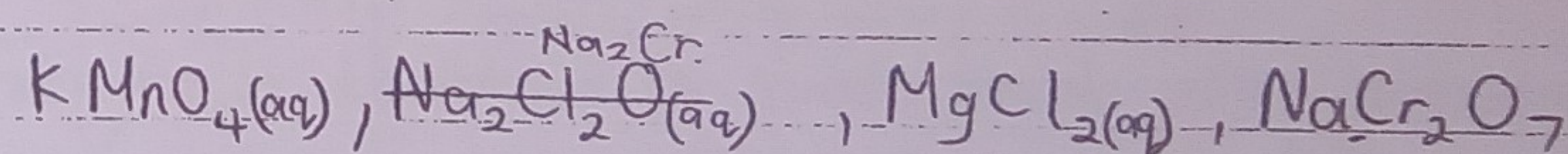
Construct the eqn we occurs when solid iron(II) dissolved in sulphuric acid and then reacted with hydrogen peroxide. sulphuric conc. most r. the MnO₄⁻ ion the ion which is Cl⁻ ions

Solution

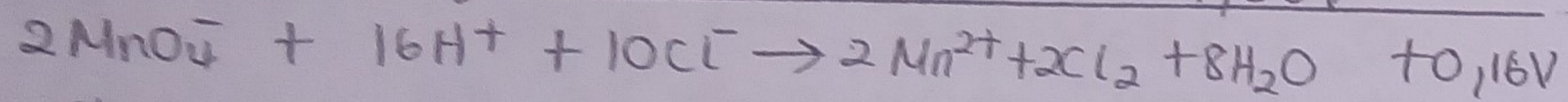
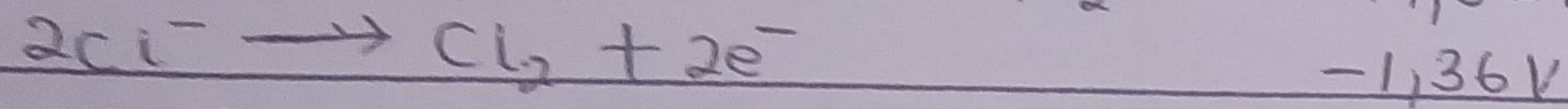
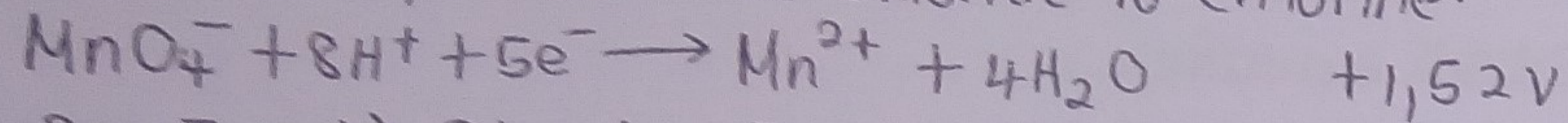
Sulphuric acid which was used to dissolve solid iron(II) sulphate created an acidic environment for the reaction. When hydrogen peroxide was added it then reacted with Fe²⁺ in an acidic environment.



Write the eqn if any which occurs when the aqueous solns of the following ionic salts were mixed



we consider the ions in solution we can clearly see that the most reactive will be the oxidising agent. As a result the MnO_4^- ion being the most oxidising it will oxidise the ion which is most easily oxidised in solution which is Cl^- ions. $\therefore \text{MnO}_4^-$ will oxidise chloride to chlorine.



More cells

Consider

1. Dry cell
2. Lead Acid Accumulator
3. Fuel cells

Dry cell

e.g. small torch cells

Advantages

- They have a reliable voltage.
- They are portable
- They do not leak

Disadvantages

- They have a low voltage.
- They have low current
- Most of them cannot be recharged

Lead Acid Accumulator

- That is the car battery

Advantages

- Large voltage
- large current
- can be recharged

Disadvantages

- It leaks
- not portable

Fuel cell

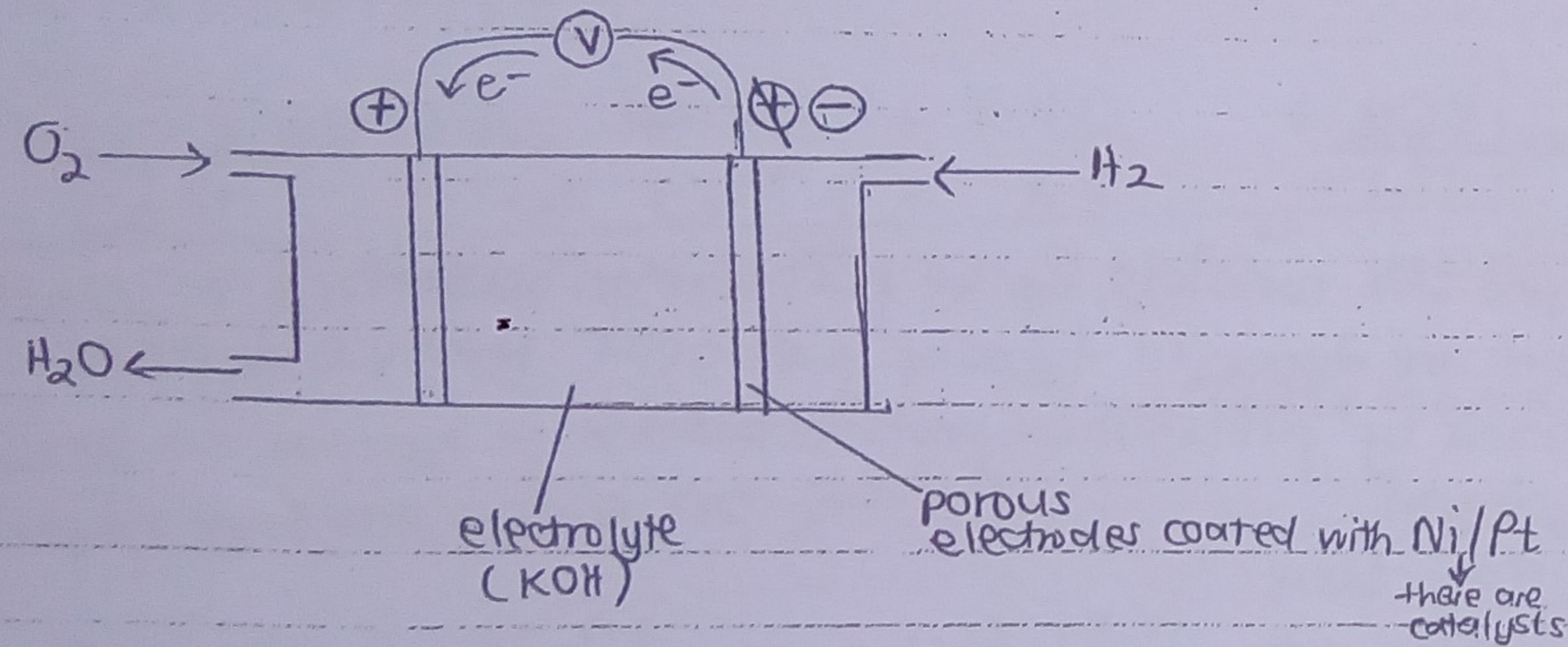
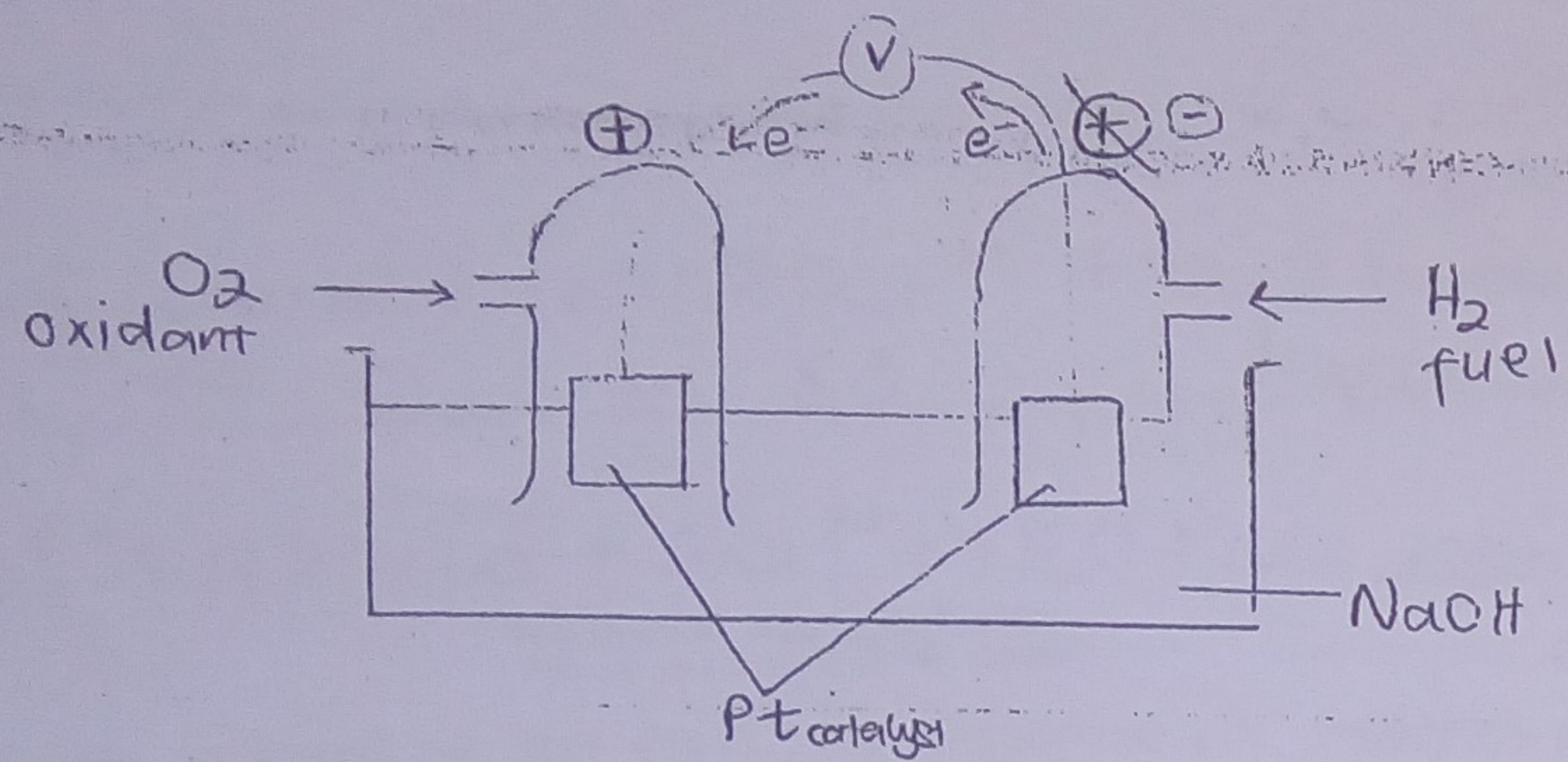
- A fuel cell consists of a fuel and an oxidant
- There are different types of fuel cells which use different forms of fuels. These fuels include:

- (i) hydrogen
- (ii) hydrocarbons
- (iii) alcohols etc.

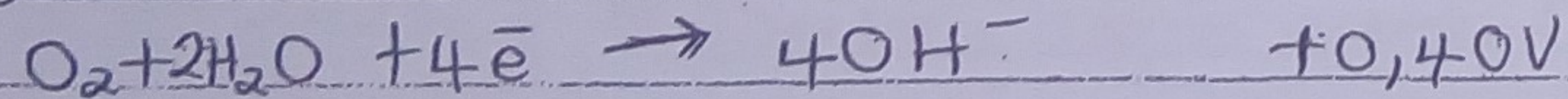
The hydrogen oxygen fuel cell

- This consists of the fuel which is hydrogen gas and the oxidant which would be oxygen gas.
- Fuel cells convert chemical energy to electrical energy
- The energy conversion is about 60-70% which is a high percentage. Therefore we say fuel cells are efficient

Diagram

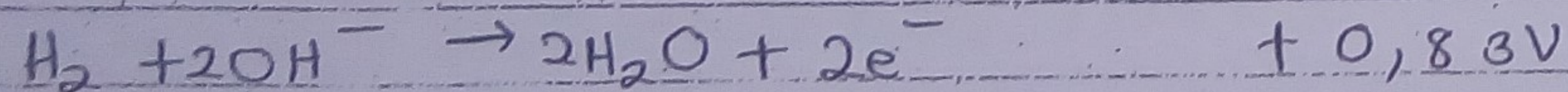


At the oxygen electrode



Oxygen and H₂O is gaining electrons at this electrode as a result the oxygen electrode is the positive electrode

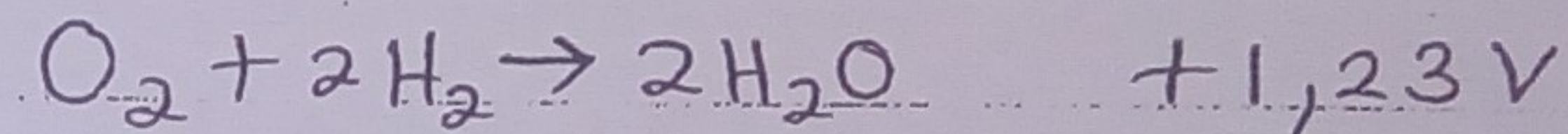
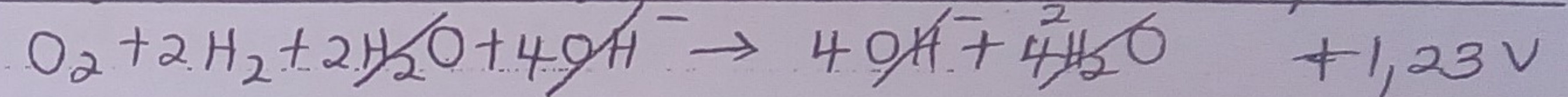
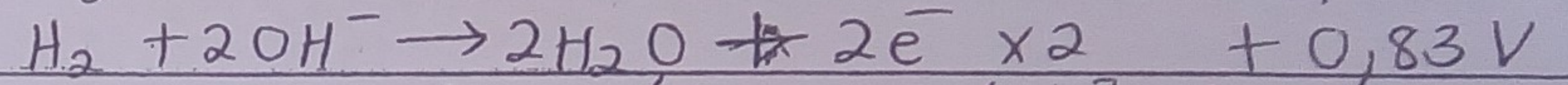
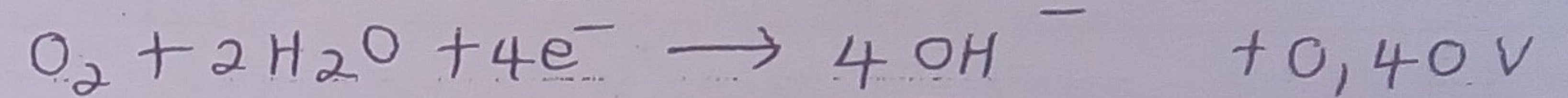
At the hydrogen electrode



When hydrogen and the hydroxide ions react, it produces water and electrons. Due to the electrons produced in the rxn, the hydrogen electrode becomes the negative electrode

We can therefore say in a fuel cell, the fuel provides to an electrode which then transfers e⁻ electrons to oxygen on the another electrode

The overall equation



A fuel cell works indefinitely because reactants are continuously added and products are continuously removed

Uses of a fuel cell

- Empowering electrical cars
- To provide water for Astronauts from urine
- For heating in homes
- Lighting in homes

Advantages of a fuel cell

- Hydrogen oxygen fuel car - it does not produce pollutants
- Its an efficient cell i.e very little energy losses during conversion of chemical energy to electrical energy
- It works indefinitely because reactants are continuously added and products are continuously removed

Advanta
duces a
low current
It is bulky

electrolysis

advantages

- produces a low voltage
- low current
- It is bulky
- It's expensive

Electrolysis

It is the use of an electric current to break down a compound

During electrolysis, positively charged ions are discharged at the cathode while negatively charged ions are discharged at the anode

In a situation where multiple positively charged or multiple negatively charged ions are in solutions, different factors have to be considered before decided on the species to be discharged on an electrode

Factors which affect species to be discharged during Electrolysis

- Position in the electrochemical series
- Nature of the electrolyte
- Type of electrodes

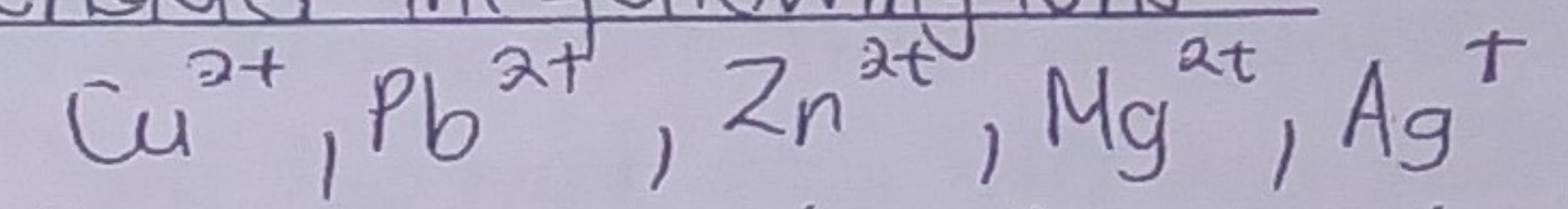
Position in the electrochemical series

Species with a large negative E^\ominus value are considered to be high up in the electrochemical series while species with a large positive E^\ominus value are considered to be low in the electrochemical series

During electrolysis, species which are low in the electrochemical

series are going to be selectively discharged but it should be known that radicals (e.g sulphates, nitrates, carbonates) except for OH^- are not discharged during electrolysis

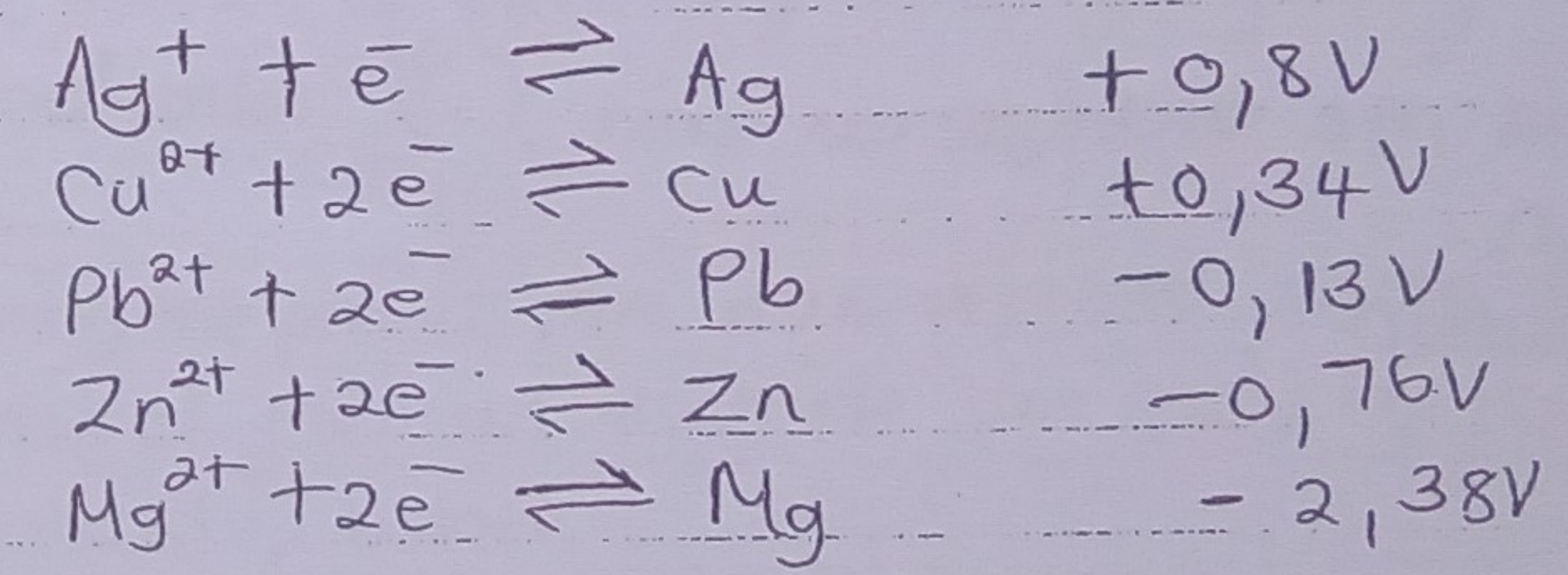
Consider the following ions



Which one of the above ions is going to be selectively discharged first during electrolysis?

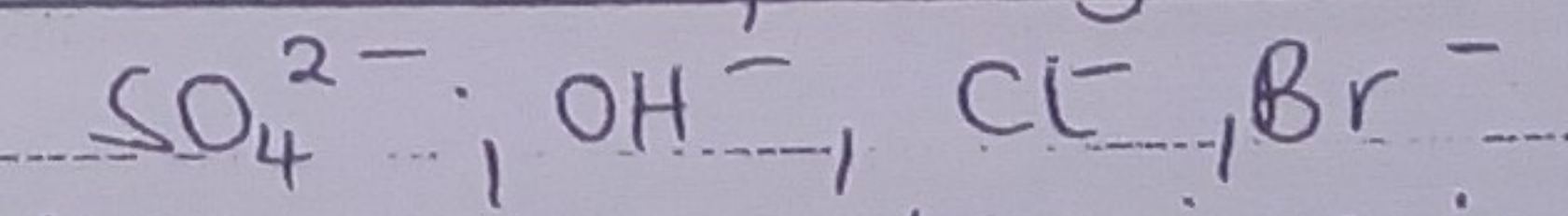
Solution

The discharge process involves gaining of electrons



From the above E^\ominus values, it clearly shows that Ag^+ ions have the largest positive E^\ominus value, therefore it is going to be discharged first

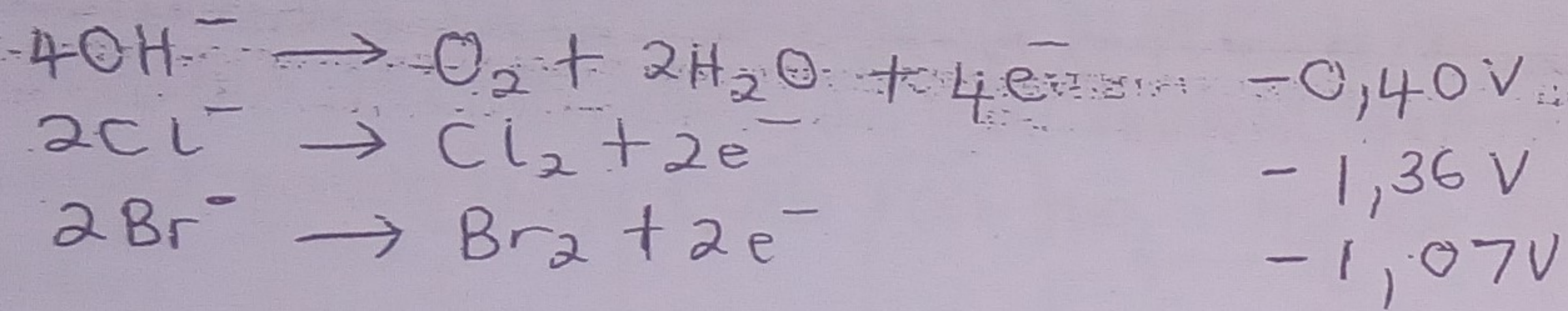
Consider the following ions



Which one the above ions is going to be selectively discharged first during electrolysis?

Solution

The discharge process involves the loss of electrons at the anode. The eqns are as follows:



The SO_4^{2-} ions are not discharged. From the above E^\ominus values, it clearly shows that the OH^- ions have got the smallest negative E^\ominus value which means that it is lowest in the electrochemical series among the given ions. Therefore it is selectively discharged.

Nature of the electrolyte

During electrolysis, the electrolyte can exist:

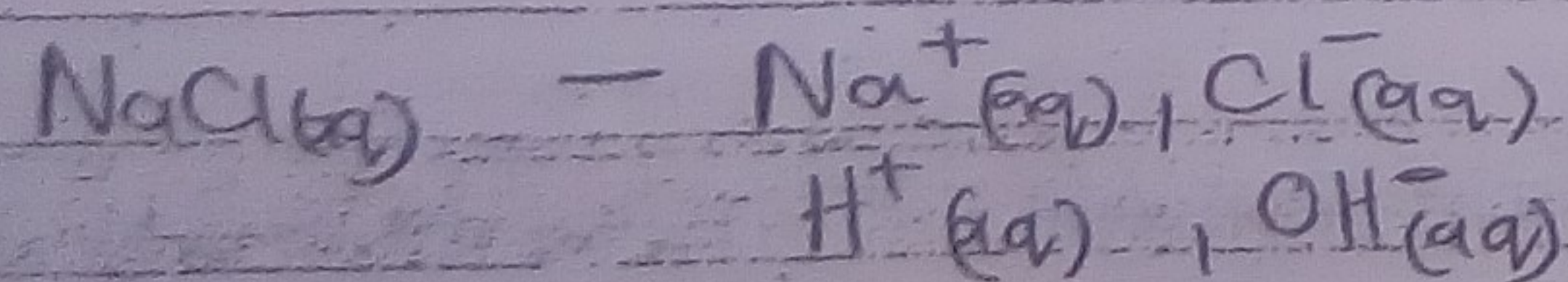
- i) a dilute solution
- ii) concentrated solution
- iii) molten solution

The nature in which an electrolyte exists in will affect the products to be discharged during electrolysis.

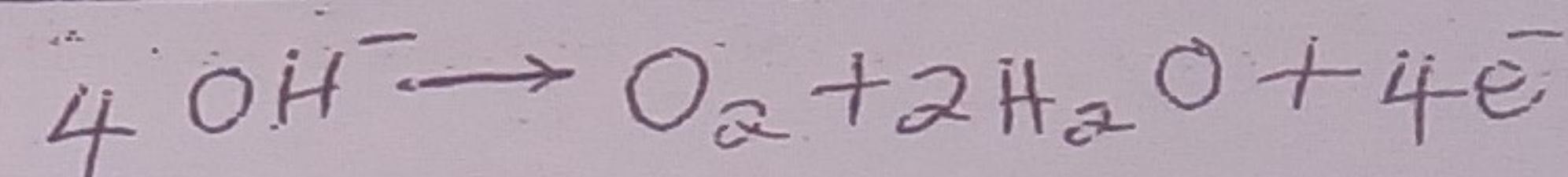
→ To understand the above points let's consider sodium chloride as our electrolyte

i) Using dilute aqueous sodium chloride

→ If we've got a dilute sltn, we always consider the positions of the ions in the electrochemical series when considering or choosing the species to be selectively discharged.

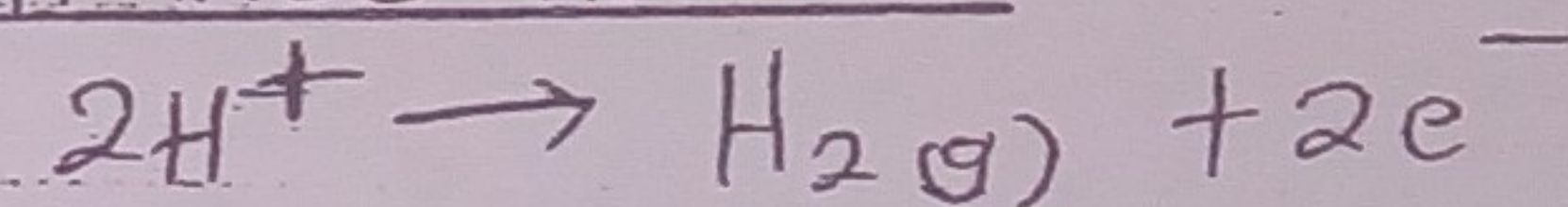


at the anode:



Therefore oxygen gas is being collected at the anode

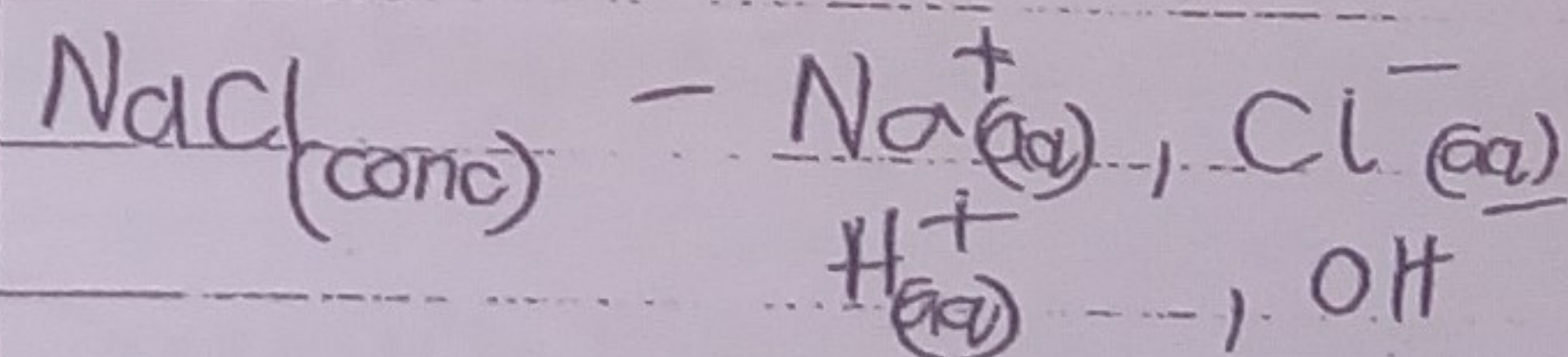
At the cathode



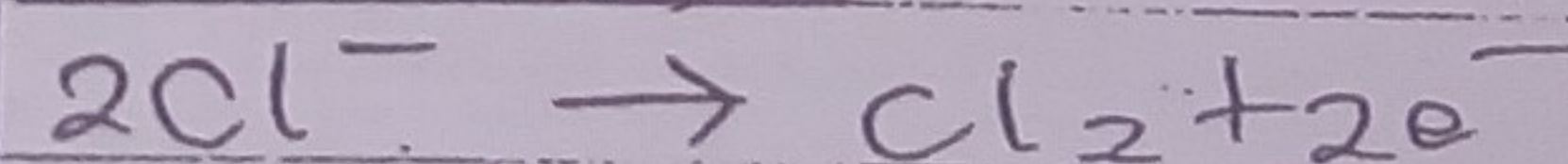
Hydrogen gas is collected at the cathode

Using concentrated sodium chloride solution

→ When electrolyzing a conc sltn, the ions in high conc are going to be selectively discharged regardless of their position in the electrochemical series.

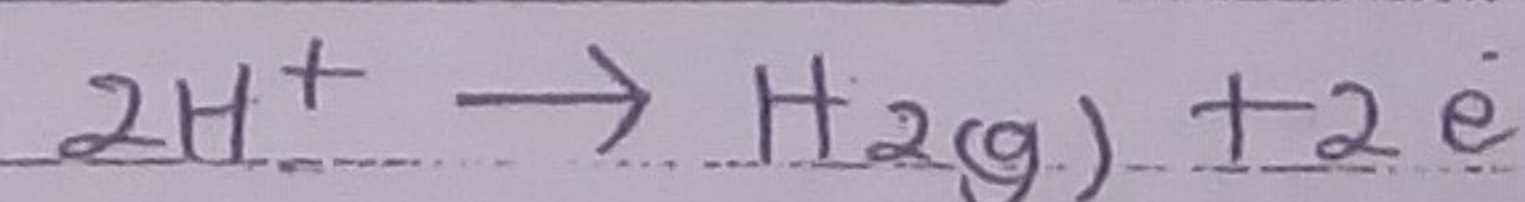


At the anode



Due to ^{its} high concentration in solution

At the cathode

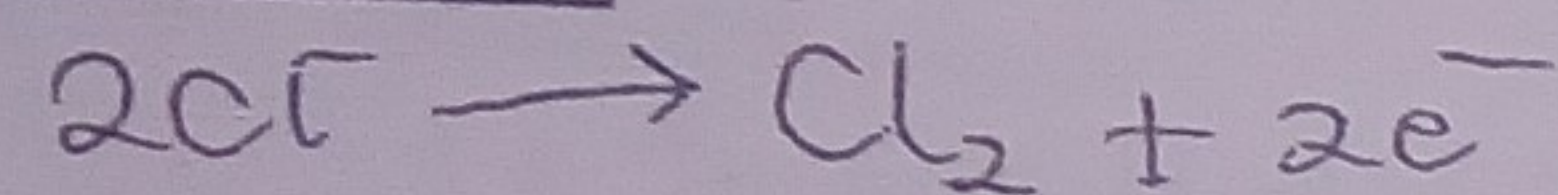


Sodium ions although in high conc are not going to be selectively discharged because they are more stable as ions than as solids in an aqueous environment

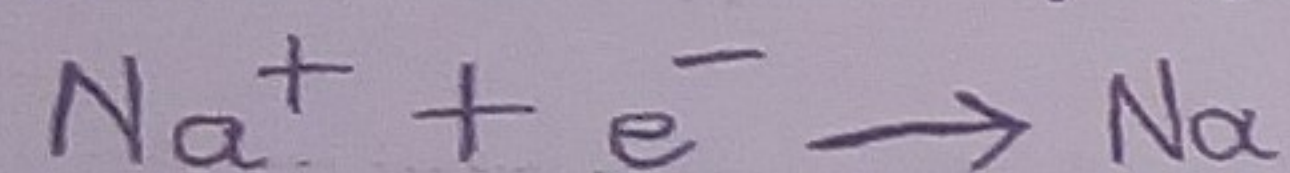
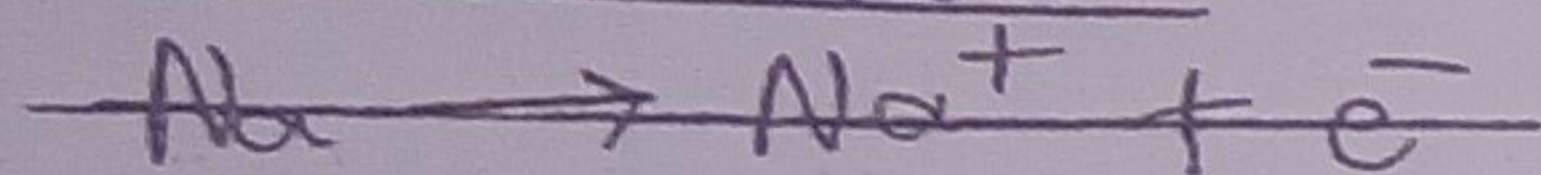
Electrolysis of molten sodium chloride

Molten sodium chloride only has two ions i.e. Na^+ and Cl^- ions. Therefore:

At the anode



At the cathode



#1/W - Effect of type of electrodes

Quantitative Electrolysis

Charge, Q

During electrolysis, the amt of electricity flowing can be referred to as the charge. Therefore, the charge flowing during the process can be given by the following relationship

$$\text{Amount of electricity} = \text{Charge} = \text{Current (Amps)} \times \text{time (secs)}$$

$$\therefore Q = I \times t$$

The amount of electricity or charge flowing is measured in Coulombs (C)

During the process, the mass deposited at the electrode or the mass dissolved from an electrode can easily be calculated using the relationship below

$$\frac{\text{Mass deposited}}{\text{dissolved}} = \frac{\text{current} \times \text{time} \times A_r}{\text{Total Charge} \times \text{Faraday's constant}}$$

$$= \frac{I \times t \times A_r}{Z \times F}$$

I - in amps

t - in seconds

F - 96500

The relationship above can be rearranged to obtain the number of moles of the substance discharged at the electrodes

$$\frac{\text{Mass}}{M_r} = \frac{I \times t}{Z \times F} = \text{number of moles}$$

Usually the number of moles calculated with the above relationship are then usually used to calculate the volume of a gas produced during an electrolytic process.

Volume of gas produced during electrolysis

When calculating the volume of a gas produced during electrolysis molar gas volumes are used

At 25°C / 298 K and 1 atm thus at room temperature and pressure conditions we say:

$$1 \text{ Mole gas} = 24\,000 \text{ cm}^3 / 24 \text{ dm}^3$$

At 0°C / 273 K and 1 Atm thus at standard temperature and pressure conditions we say:

$$1 \text{ Mole gas} = 22\,400 \text{ cm}^3 / 22,4 \text{ dm}^3$$

It therefore implies that using the no of moles calculated in the section above together with the molar gas volumes, the volume of a gas collected during an electrolysis process can then be calculated

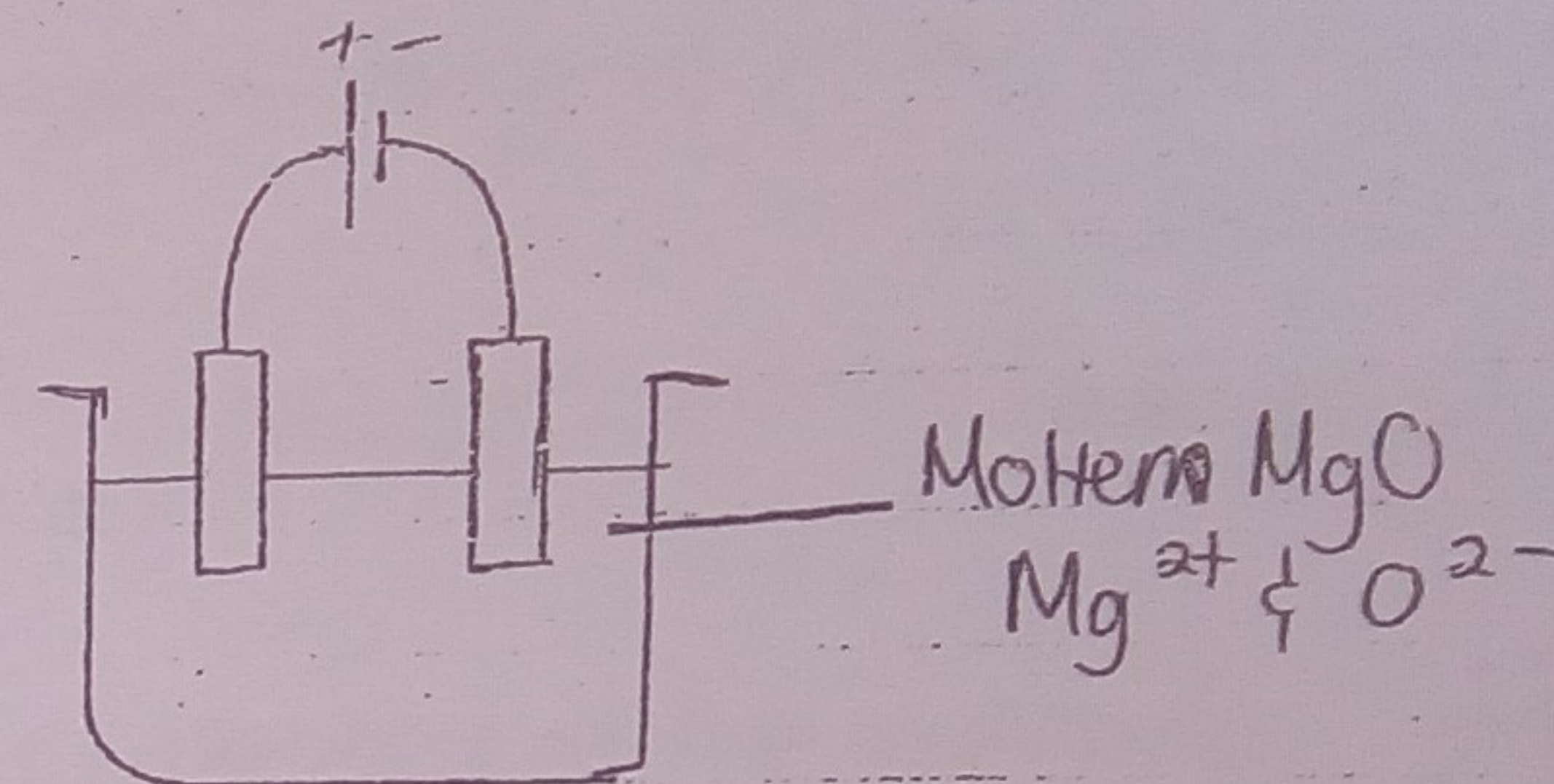
Consider the following situation

During the electrolysis of molten magnesium hydroxide^{oxide} with inert electrodes, a solid and a gas were produced at different electrodes.

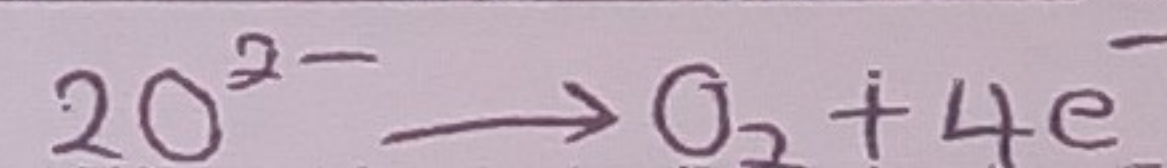
Given that the process occurred for half an hour and a current of 3 Amps was used, calculate the amounts of

products i.e. mass of a solid and volume of a gas produced at the electrodes at 25°C and 1 Atm

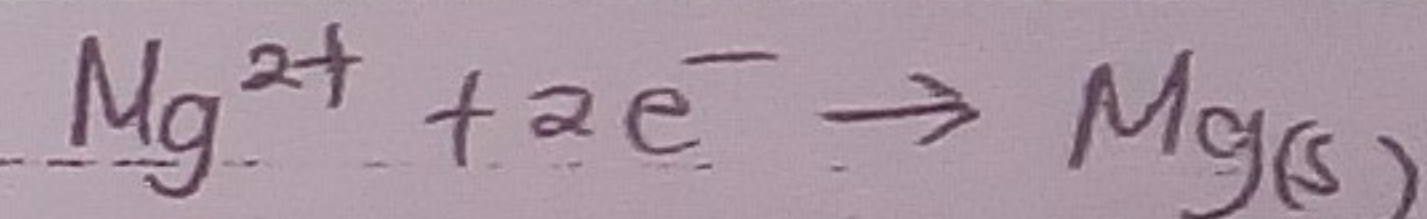
Solution



Rxn at the anode



Rxn at the cathode



$$\text{Mass deposited at the cathode} = \frac{I \times t \times A_r}{Z \times F} = \frac{3 \times 0,5 \times 60 \times 60 \times 24,3}{2 \times 96\,500}$$

$$= 0,6799 \text{ g (4 s.f.)}$$

$$\text{Moles of O}_2 \text{ deposited} = \frac{I \times t}{Z \times F} = \frac{3 \times 0,5 \times 60 \times 60}{4 \times 96\,500}$$

$$= 0,01398 \text{ moles}$$

But 1 Mole = 24 000 cm³

∴ 0,0139896 moles = more

$$0,013989637 \times 24\,000 \text{ cm}^3 = 335,75 \text{ cm}^3$$

Consider the situation below

Calculate volume of gas produced at 0°C and 1 Atm during electrolysis aqueous silver nitrate given that 7g of silver were produced in the process

solution

$$\text{Mass} = \frac{I \times t \times Ar}{2 \times F}$$

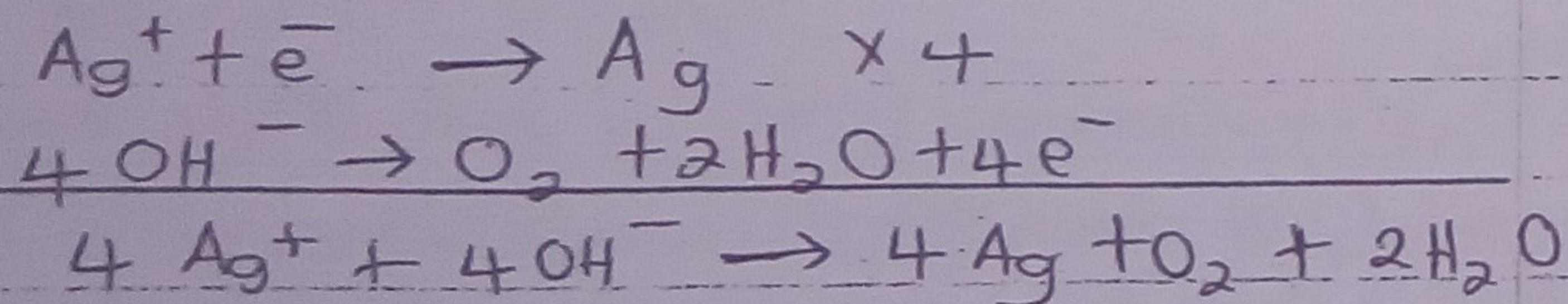
$$7g = \frac{Q \times 108}{1 \times 96500}$$

$$Q = I t = 6254,63$$

$$\begin{aligned} \therefore n(O_2) &= \frac{Q}{2 \times F} \\ &= \frac{6254,63}{4 \times 96500} \\ &= 0,0162 \end{aligned}$$

$$\begin{aligned} 1 \text{ mole} &= 22400 \text{ cm}^3 \\ 0,0162 \text{ mols} &= \text{less} \end{aligned}$$

$$= \underline{362,96 \text{ cm}^3}$$



$$n(Ag) = \frac{7}{108} = 0,0648$$

Ratio Ag : O₂
4 : 1

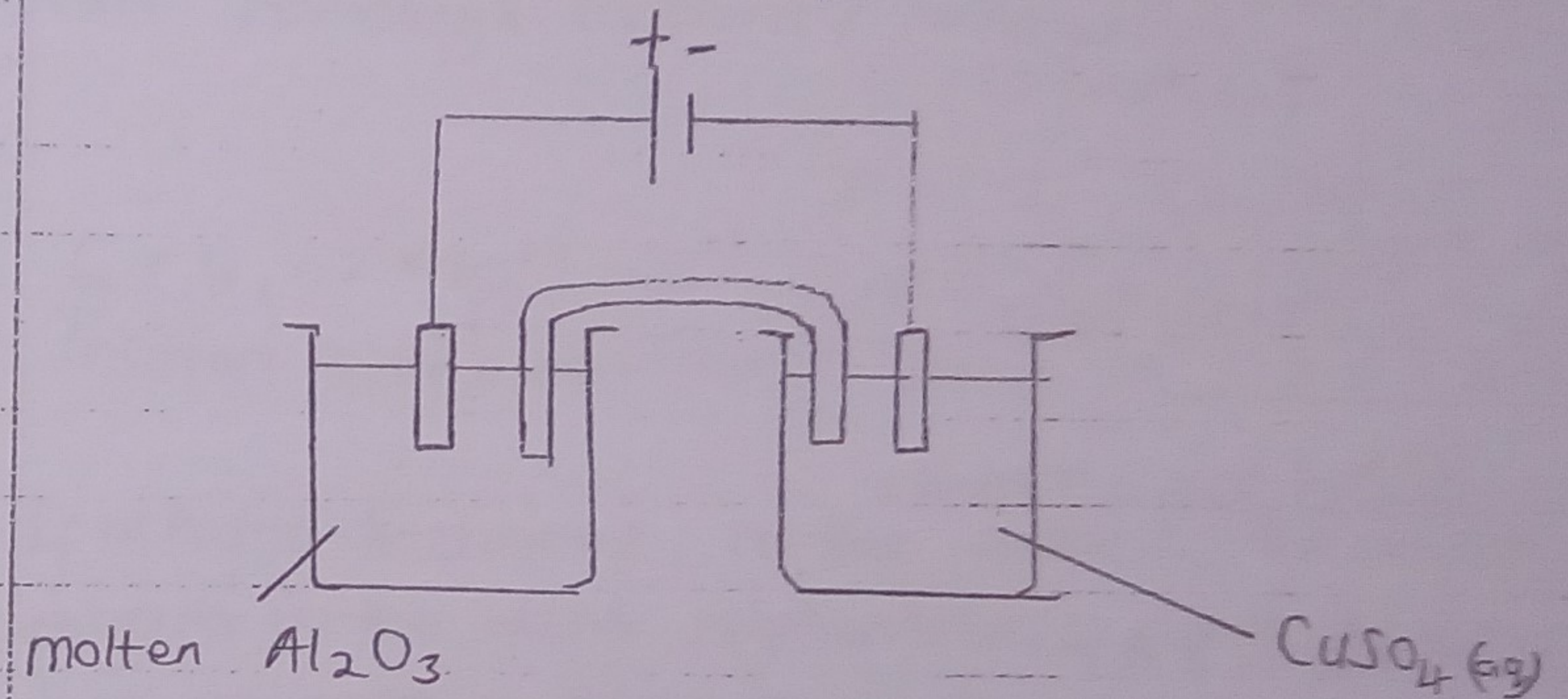
$$\begin{aligned} 4 &= 0,0648 \\ 1 &= \text{less} \end{aligned}$$

$$n(O_2) = 0,0162$$

$$\begin{aligned} 1 \text{ mole} &= 22400 \text{ cm}^3 \\ 0,0162 \text{ moles} &= \text{less} \end{aligned}$$

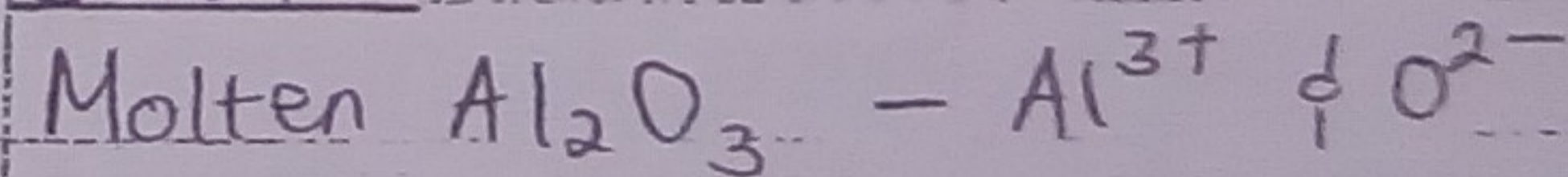
$$= \underline{362,96 \text{ cm}^3}$$

The electrolysis of molten aluminium oxide and copper (II) sulphate was done in a setup below.

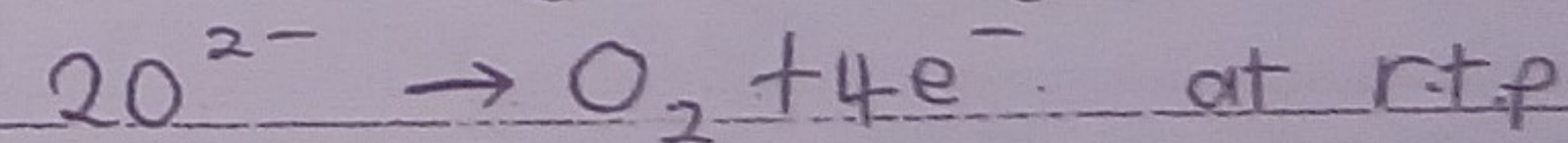


During the process, 750 cm³ of oxygen was produced at r.t.p. Calculate the mass of copper deposited during the process.

Solution



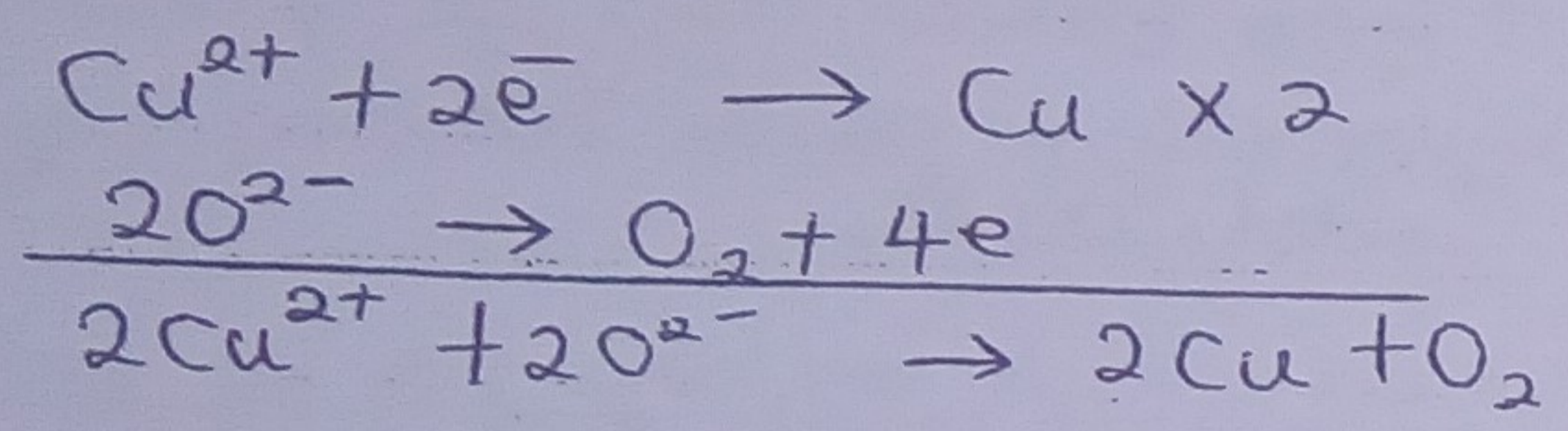
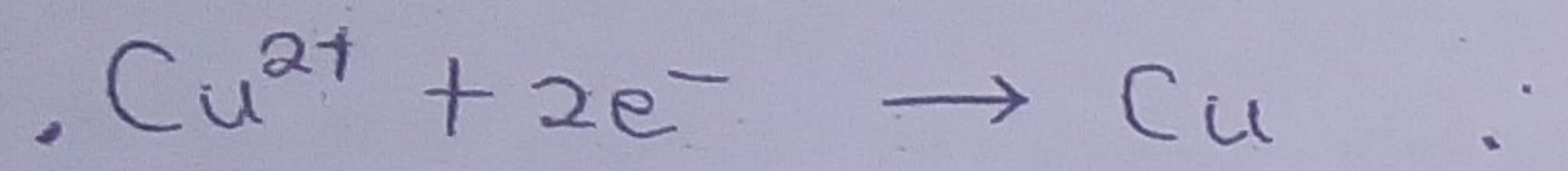
∴ O²⁻ will be discharged



It implies that 1 mole = 24000 cm³
less = 750 cm³

$$n(O_2) = 0,03125 \text{ moles}$$

$\text{CuSO}_4(\text{aq}) \rightarrow \text{Cu}^{2+}, \text{SO}_4^{2-}, \text{H}^+, \text{OH}^-$
 Cu^{2+} will be discharged



Ratio Cu: O₂
2:1

$\therefore 2 = \text{more}$
 $1 = 0,03125 \text{ mols}$

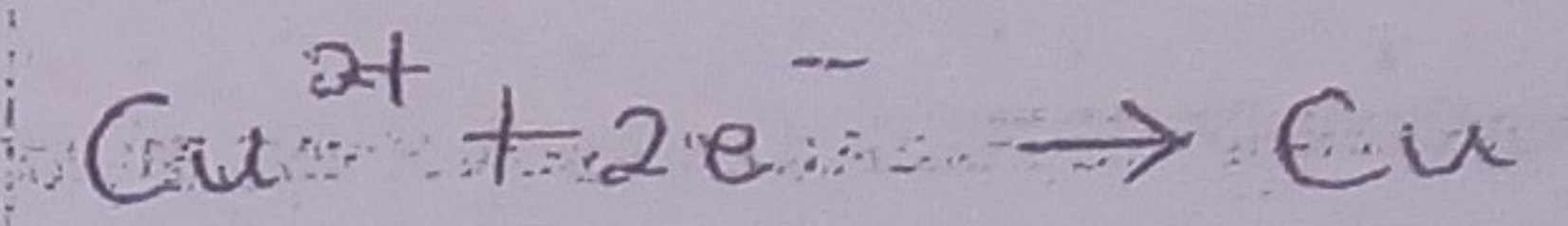
$n(\text{Cu}) = 0,0625 \text{ moles}$

$\therefore \text{Mass} = \text{moles} \times A_r$
 $= 0,0625 \times 63,5$
 $= 3,96875$
 $= 3,97\text{g} (2 \text{ d.p.})$

OR
$$\text{Moles} = \frac{I \times t}{z \times F}$$

$$0,03125 = \frac{Q}{4 \times 96500}$$

$$I \times t = Q = 12062,5$$



$$\begin{aligned} \text{Mass} &= \frac{Q}{z \times F} \times A_r \\ &= \frac{12062,5}{2 \times 96500} \times 63,5 \\ &= 3,97\text{g} (2 \text{ d.p.}) \end{aligned}$$

Applications of electrolysis

- (1) Determination of the avogadro's constant or the electron charge.
- (2) Extraction of aluminium
- (3) Anodising of aluminium
- (4) Manufacture of chlorine, sodium hydroxide and hydrogen from brine
- (5) Purification of copper

The above methods are examples of methods where electrolysis is employed, for us to achieved the desired outcome

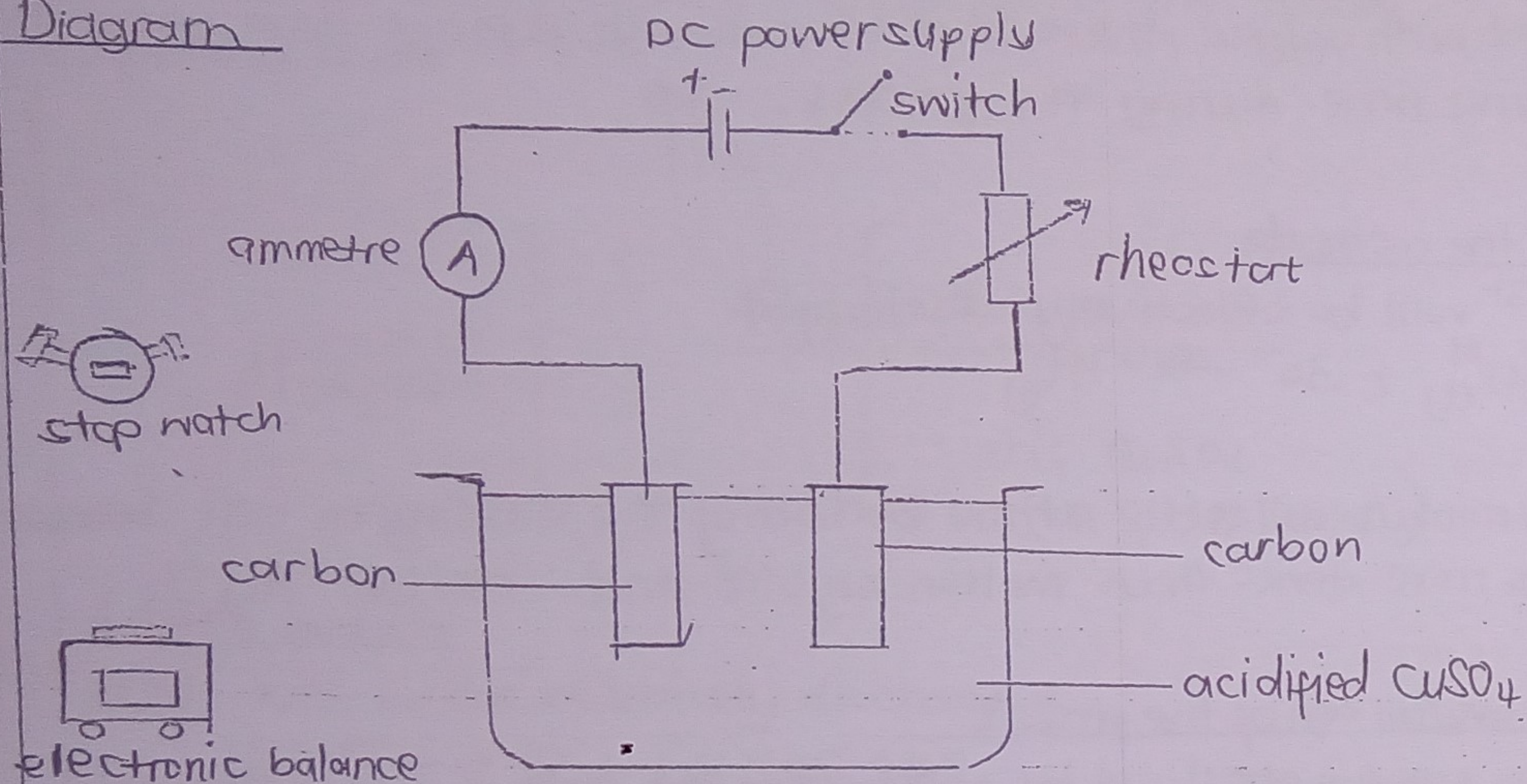
Determination of the avogadro's constant / Electronic charge using electrolysis

- The electrical method, i.e electrolysis can be done with the intention of determining the avogadro's constant / Electronic charge.

This would require:

apparatus - ammeter, DC power supply, stopwatch, switch, electronic balance, rheostat and other electrolysis equipments.

Diagram



Procedure

- 1) Weigh the electrodes (esp the cathode) using an electronic balance and record the mass m_1 (grams)
- 2) Set up the apparatus as shown above in the diagram
- 3) Simultaneously close the switch and start the stopwatch
- 4) Stabilise the current using the rheostat
- 5) Note and record from the ammeter, the current (I) flowing in the circuit in amps
- 6) After some time (30 mins) simultaneously ^{open the switch and} stop the stopwatch, note and record, T in seconds from the stopwatch (30×60)
- 7) Wash the electrodes using distilled water and then dry them
- 8) Using an electronic balance remeasure the mass the electrodes (especially cathode) and record the mass m_2 in grams

Treatment of results

Mass deposited, $m =$ final mass of electrode, m_2 - initial mass of electrode, m_1

$$m = m_2 - m_1$$

Using the recorded values of current, I and time, t in seconds together with formula $\text{mass deposited} = \frac{I \times t \times Ar}{Z \times F}$

the recorded values can then be substituted in the formula. But Faraday's constant (F) = Avogadro's constant (L) \times electronic charge (e)

$$F = L \times e \text{ where}$$

$$L = 6.02 \times 10^{23} \text{ mol}^{-1} \text{ and } e = -1.60 \times 10^{-19} \text{ C}$$

$$\text{Therefore after substitution: } \text{mass} = \frac{I \times t \times Ar}{Z \times L \times e}$$

If asked to determine L , we then make L the subject of the formula in the above relationship, if asked to determine e then we make e the subject of the formula in the above relationship.

Extraction of aluminium

- Aluminium is mined in its oxide ore, bauxite
- Bauxite is then purified using different processes to produce pure aluminium oxide.
- The pure aluminium oxide is then put into the electrolytic cell where it is electrolysed to produce pure aluminium.

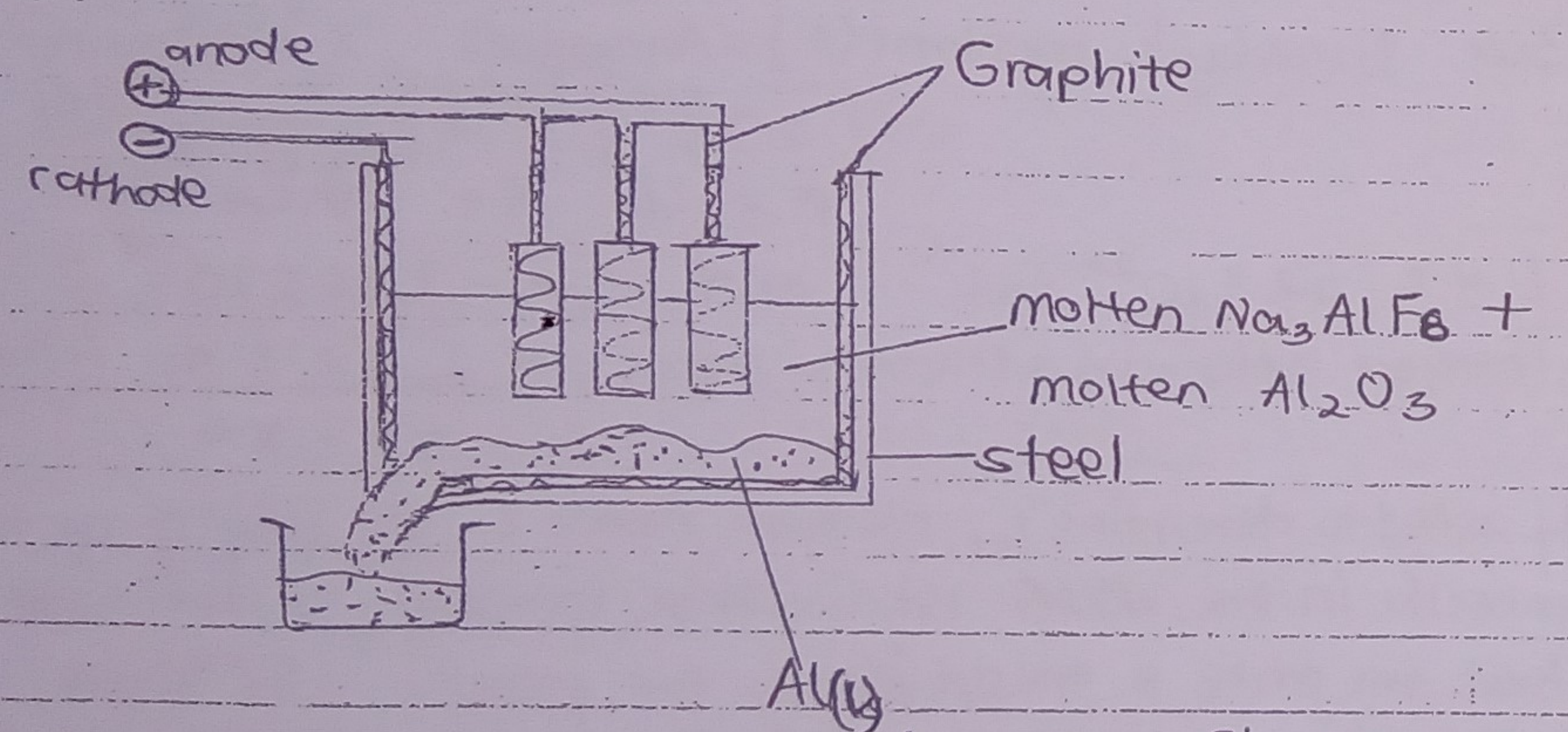
During the electrolytic process the electrolyte, cryolite is used.

Cryolite has got the formula Na_3AlF_6 and it contains the following ions in its molten state: 3Na^+ , AlF_6^{3-}

Cryolite was used as an electrolyte in this process because:

- lowers the melting point of aluminium oxide (from abt 1900°C down to abt 1000°C) to save energy
- it acts as a flux
- It is also a very good conducting electrolyte

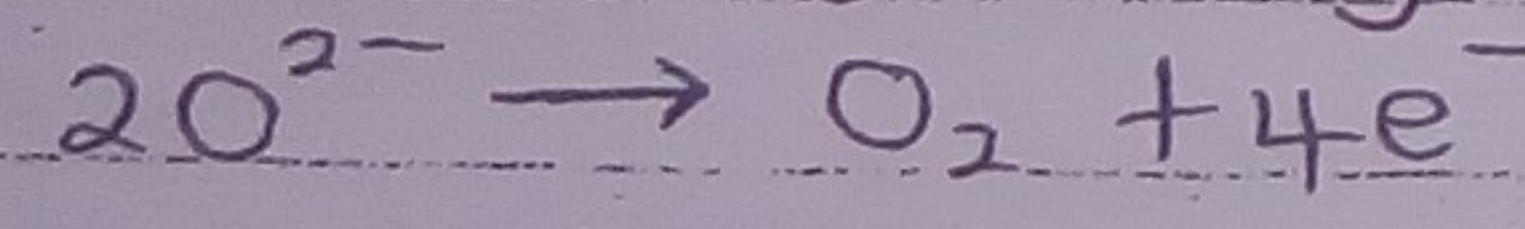
Diagram



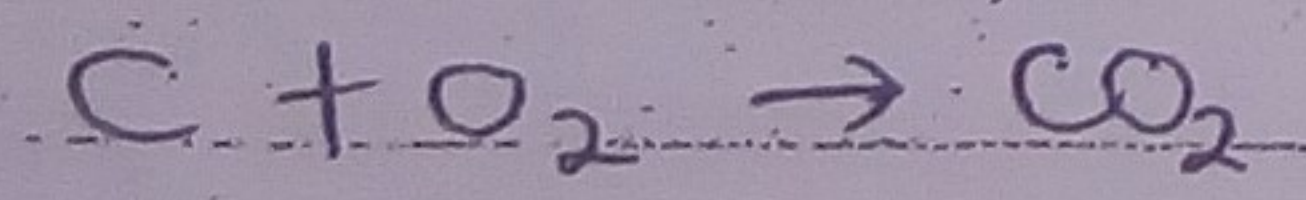
Ions present in the molten sltn are Na^+ , AlF_6^{3-} , Al^{3+} , O^{2-}

At the anode

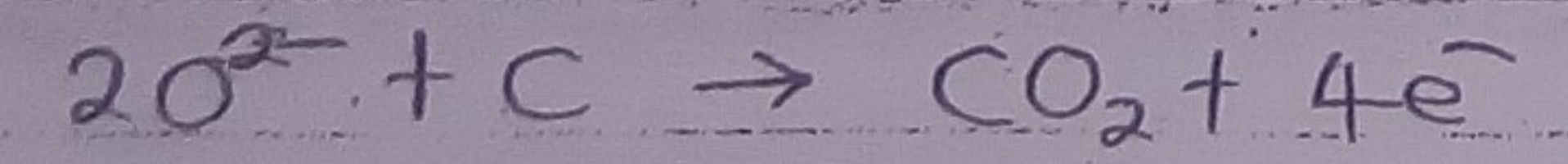
O^{2-} will be selectively discharged



But due to the high temperatures under which the rxn is occurring, the produced oxygen will react with carbon (graphite) electrodes



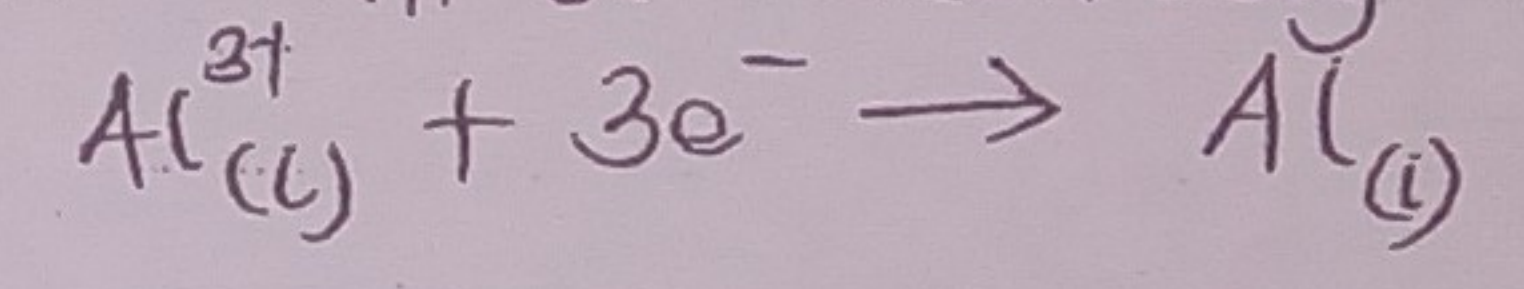
Combining eqn 1 and eqn 2, the overall eqn at the anode becomes



Graphite is used as an electrode in this process because it got a very high melting point and hence it resists the high temperatures in the electrolytic cell. But because the electrodes react with oxygen, there is need to always replace them after some time during the process.

At the cathode

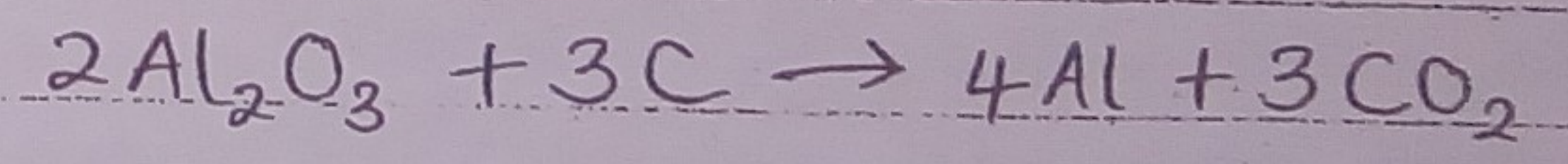
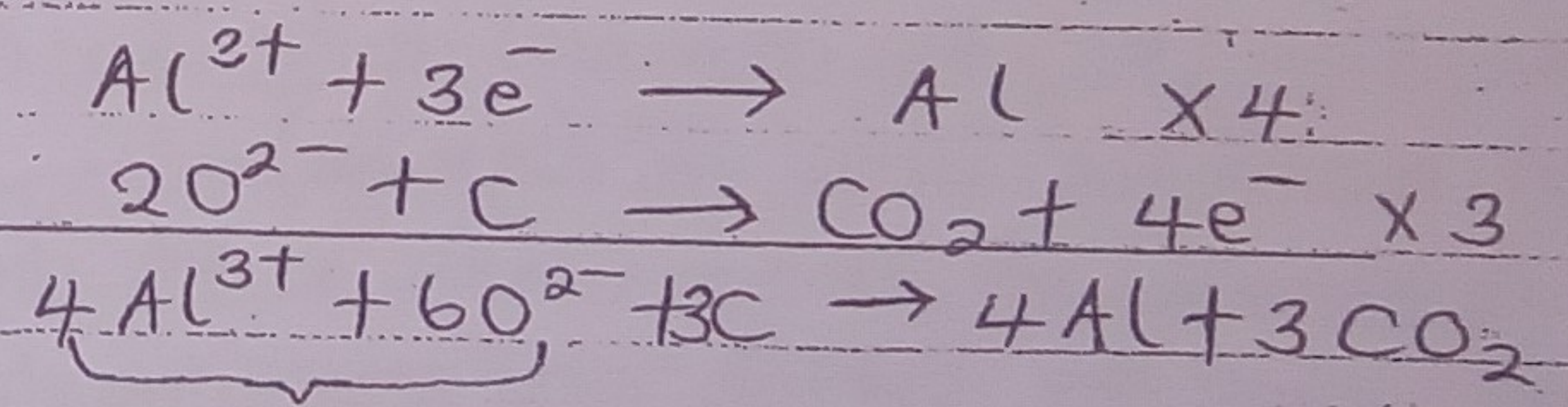
Al^{3+} will be selectively discharged.



Aluminium will settle at the bottom of the electrolytic cell because it is more dense than molten cryolite and molten Al_2O_3

The overall eqn of the process

This can be obtained by combining the half eqns at the anode and at the cathode as follows

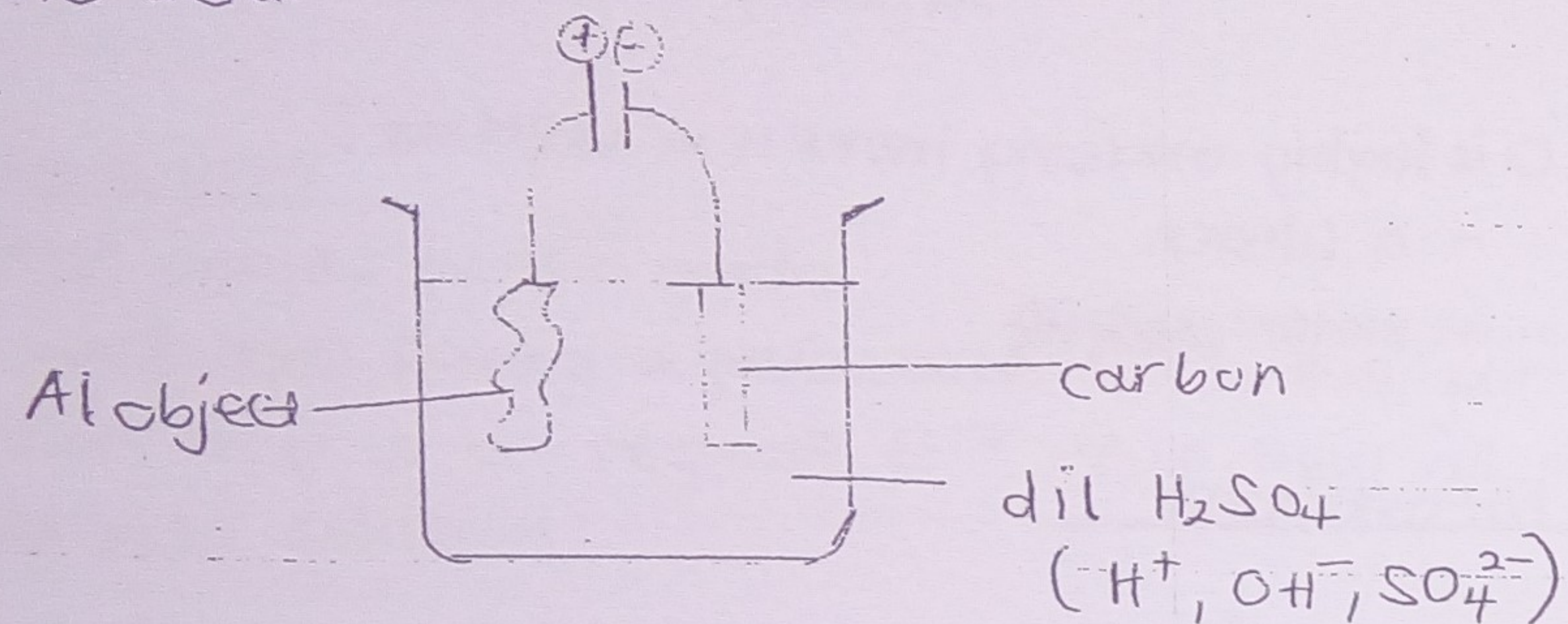


The overall eqn can be referred to as an oversimplification because carbon seems to be directly reducing Al_2O_3 to produce Al and CO_2 during the process (which is not the case)

After pure aluminium has been produced during the above process, it can then be used to make different objects e.g. aeroplane bodies because it is light

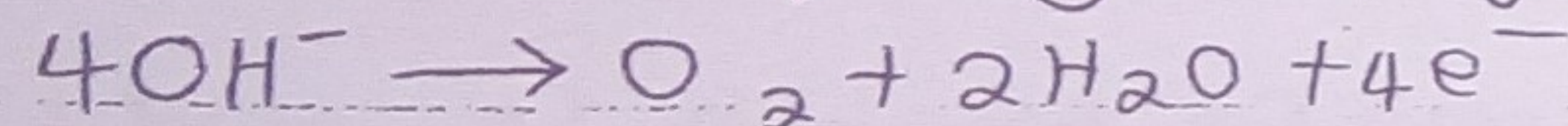
Anodising aluminium

Anodising aluminium is the process whereby aluminium object is made ~~an~~ ^{the} anode during electrolysis with dilute sulphuric acid.

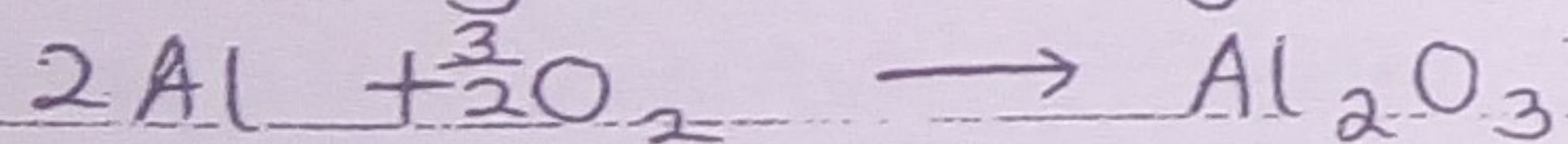


At the anode

OH^- ions will be selectively discharged



Because Al is a reactive element, the produced oxygen will then immediately react with ~~it~~ aluminium as shown below:

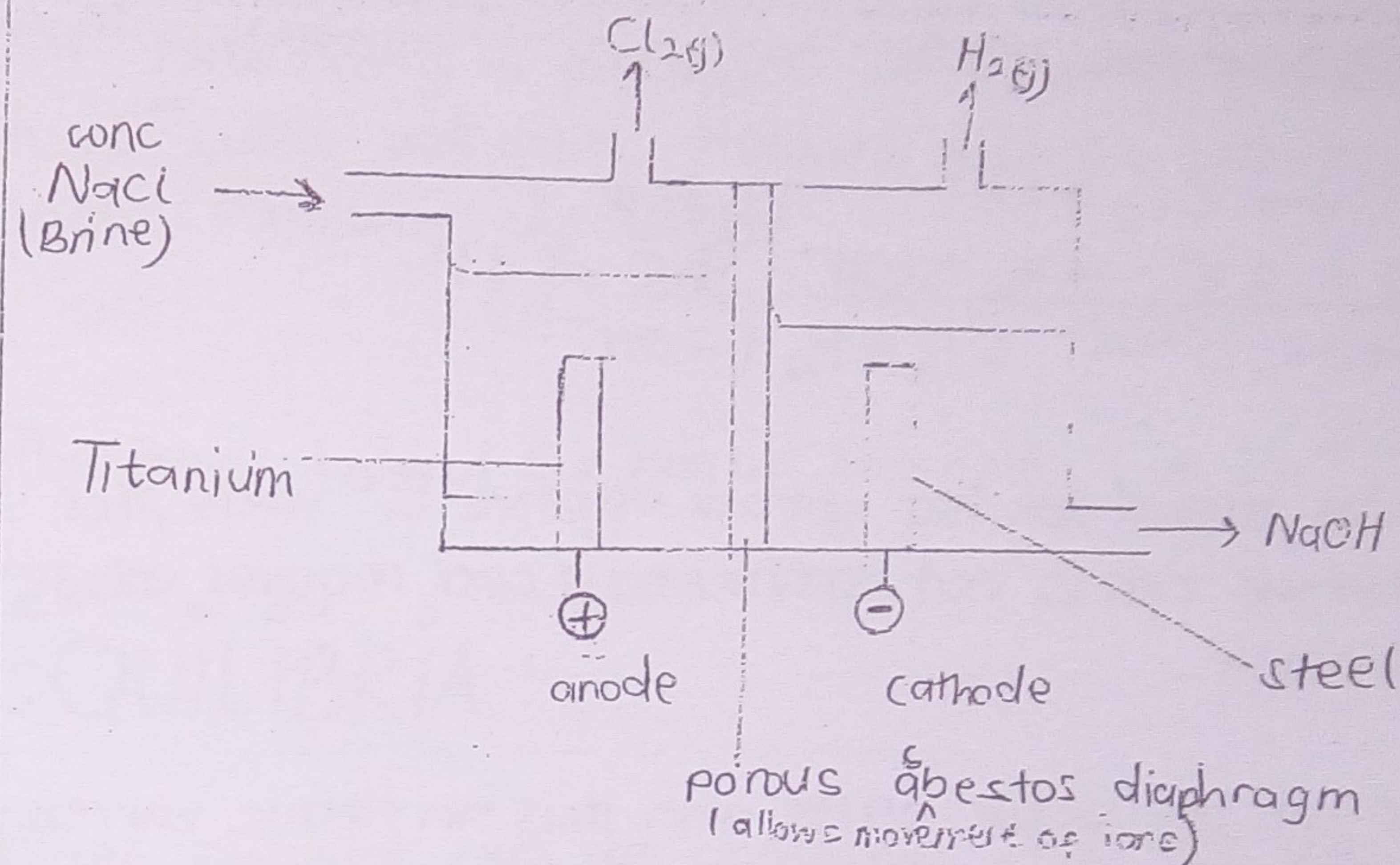
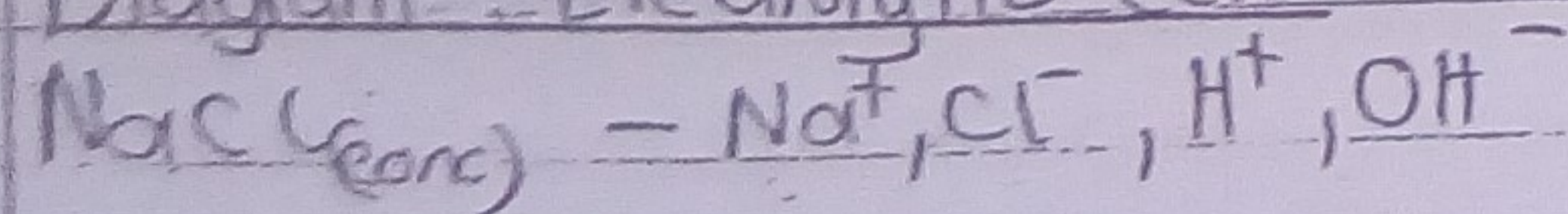


The produced Al_2O_3 will form a layer on the aluminium object. This layer of Al_2O_3 is impervious, non-porous, relatively unreactive, therefore it protects the aluminium metal inside.

Manufacture of chlorine, hydrogen and sodium hydroxide

- Chlorine, H_2 and NaOH can be manufactured using the electrolysis of brine
- Brine is a concentrated solution of sodium chloride

Diagram: Electrolytic cell

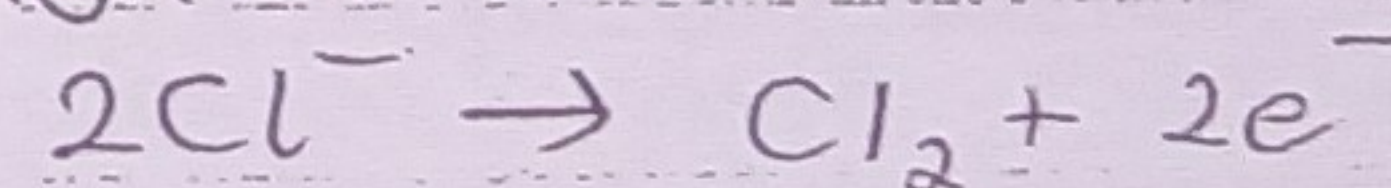


In the above electrolytic cell:

- The level of brine in the compartment with anode is higher than the level of brine in the compartment with the cathode. This is done to prevent the backflow of NaOH which would react with the product at the anode which is chlorine

At the anode

The chloride ion is going to be selectively discharged because it is in high concentration



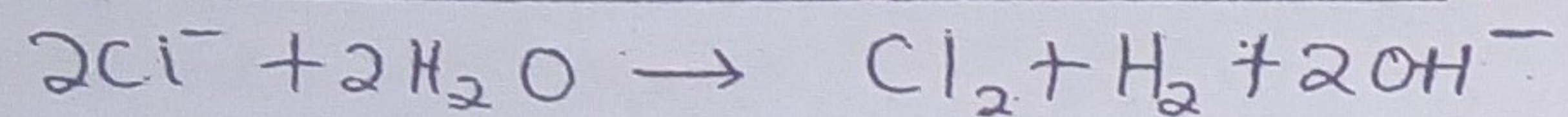
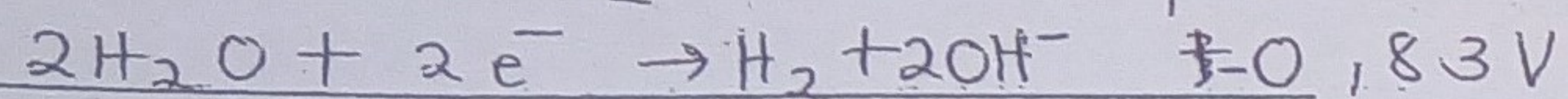
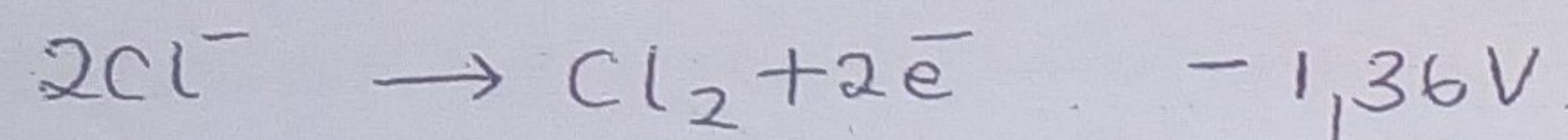
At the cathode

Sodium ions are not selectively discharged because sodium ions cannot easily be oxidised. Thus in an aqueous environment sodium ions are more stable than sodium atoms.

Therefore the following rxn occurs



Overall rxn of the rxn



The above overall rxn has got a negative E^\ominus value, this means that the rxn is not spontaneous and requires energy for it to occur.

The rxn will not occur on its own thus an electric current is used to facilitate this process.

During the electrolytic process, titanium is used as an anode because it is corrosion resistant.

It implies that the highly oxidising Cl_2 produced at the anode will not be able to oxidise it.

At the cathode, steel is used because the products produced at that electrode is not reactive.

The porous asbestos diaphragm allows mvt of ions.

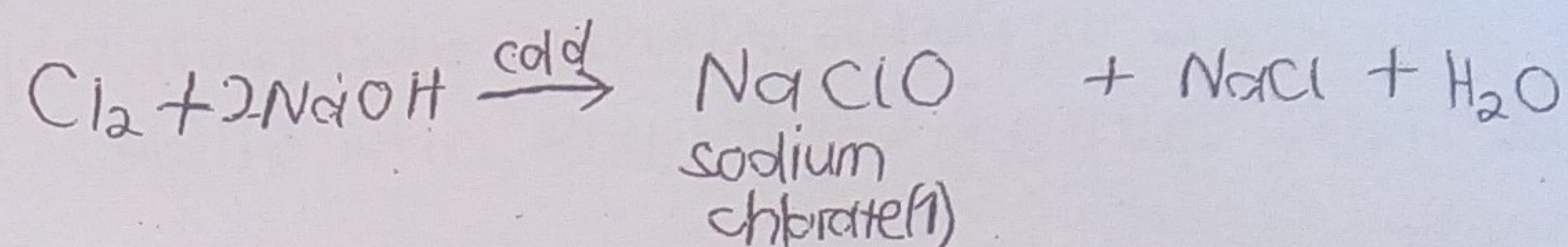
Disproportionation rxn

As stated above, sodium hydroxide is prevented from flowing back which would result in it reacting with chlorine by the different levels of brine in both components.

Sodium hydroxide reacts with Cl_2 under different conditions.

In a disproportionation rxn:

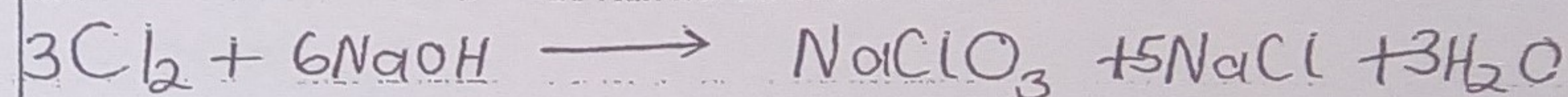
Under cold conditions



NaClO is highly oxidising hence it is used as:

- a bleach
- water purifier

Under hot conditions



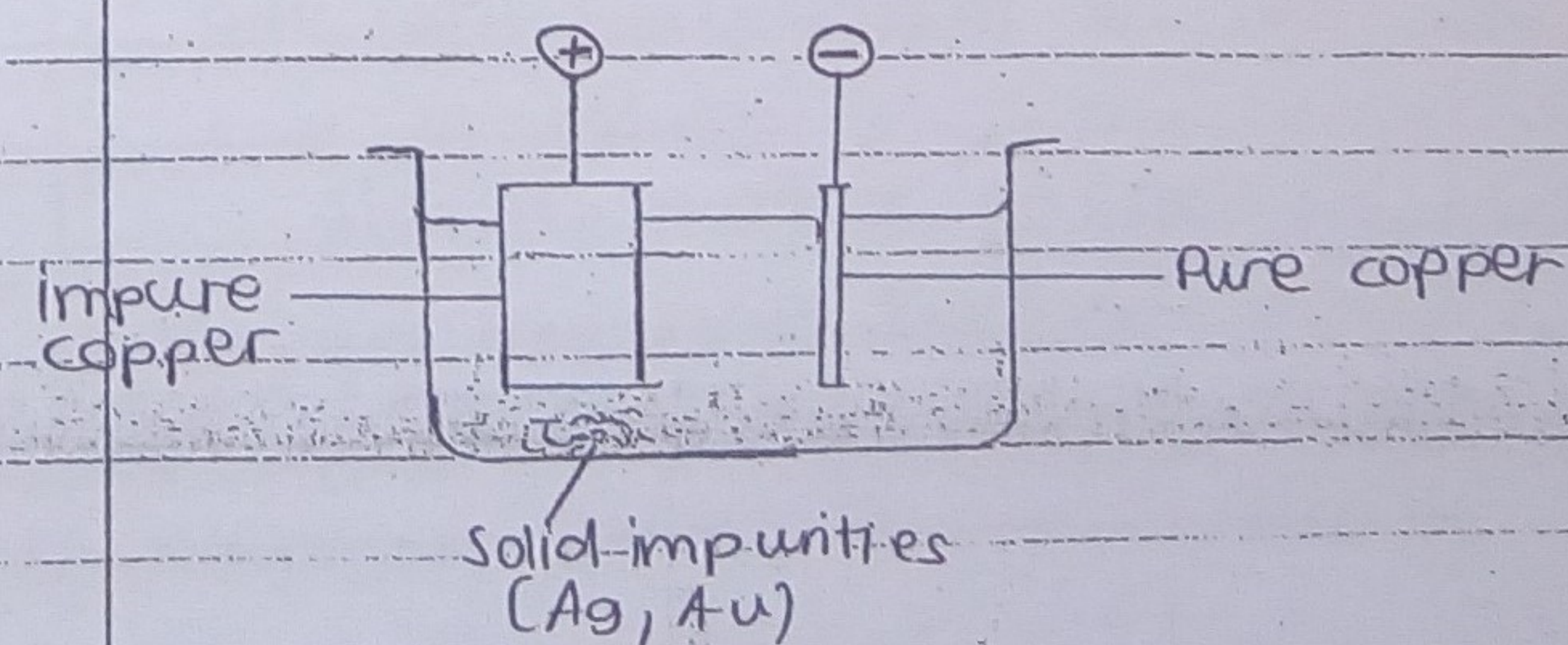
NaClO_3

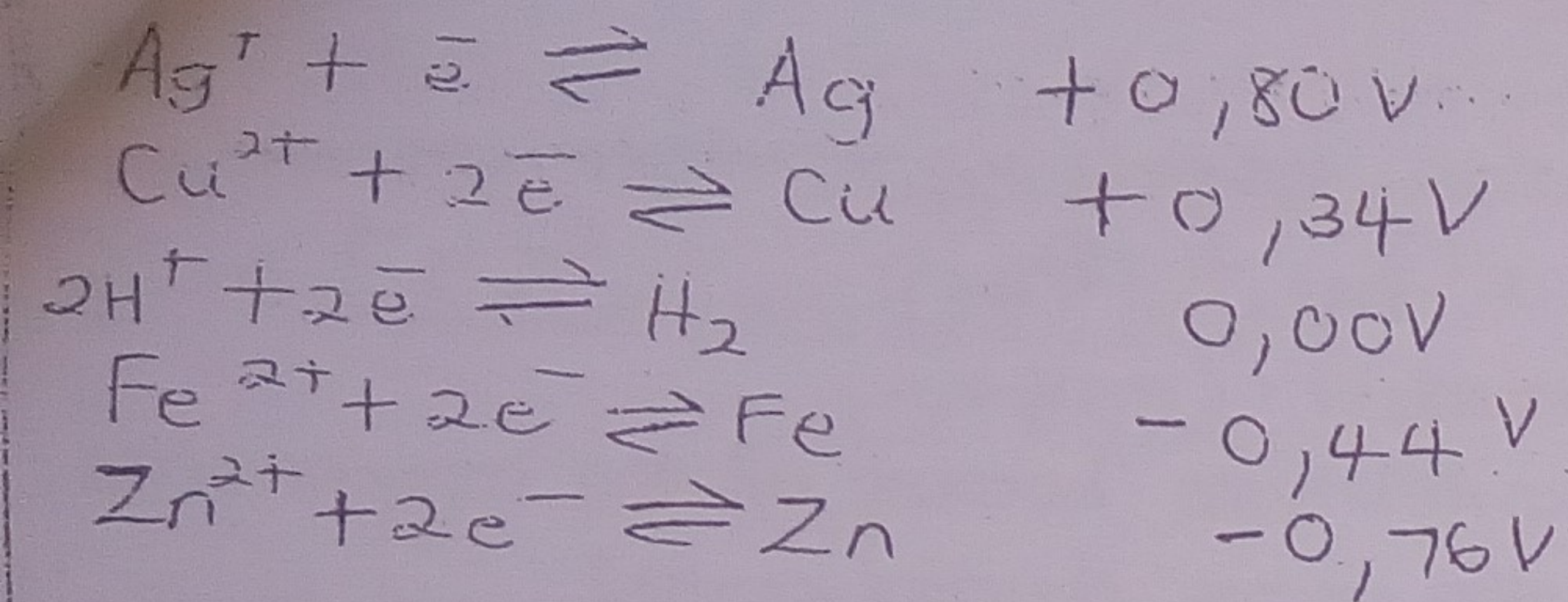
- can be used as a non-selective herbicide i.e. weed killer

Purification of copper

- Impure copper i.e. blister copper contains impurities like Ag (silver), Au (gold), Fe, Zn
- An electrical method i.e. electrolysis can then be used to remove these impurities from copper.
- During the process, acidic CuSO_4 is used as the electrolyte

Diagram

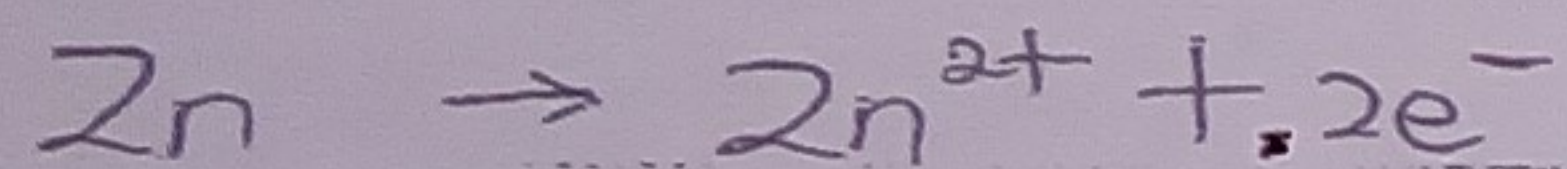
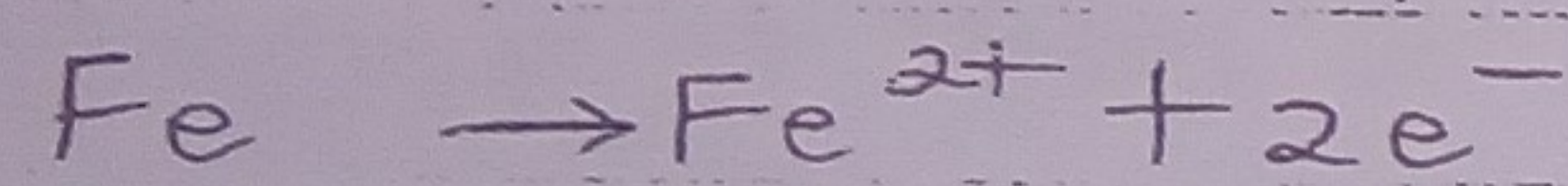




At the anode

Oxidation occurs at the anode

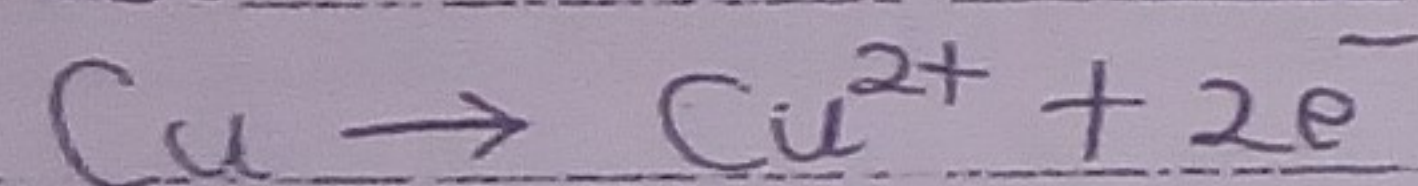
Zinc and iron having a favourable ^(forming loss of electrons) E^\ominus value for oxidation that is a negative E^\ominus value, they will dissolve and get into solution.



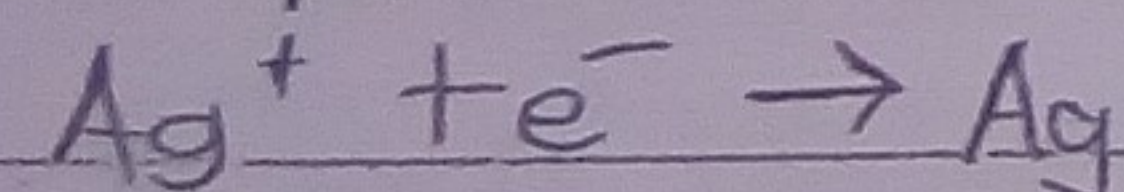
This leaves behind copper and silver

Copper and silver will then make an electric cell and since copper has a less positive E^\ominus value than silver, it donates electrons to silver ions. Thus copper dissolves and gets into solution while silver drops down as a solid

Copper dissolves



Silver drops as solid



It can also be said that since silver is an unreactive element it simply drops down as a solid.

At the cathode - Reduction occurs at the cathode
 Cu^{2+} ions having a favourable E^\ominus value for reduction i.e. a positive E^\ominus value will gain electrons from the cathode and become selectively discharged

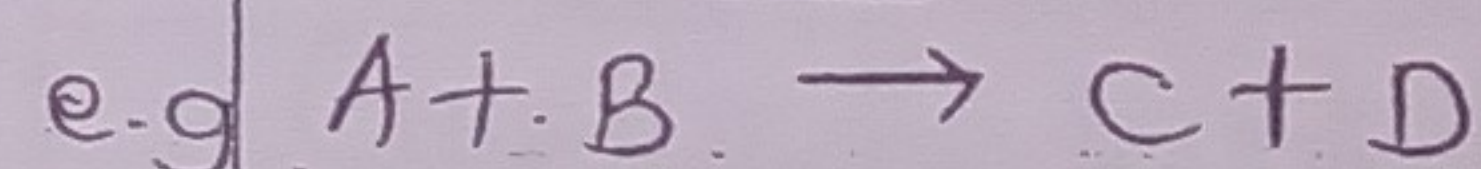
$$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$$

This leaves behind the ions of impurities i.e. Zn^{2+} , Fe^{2+}

EQUILIBRIA

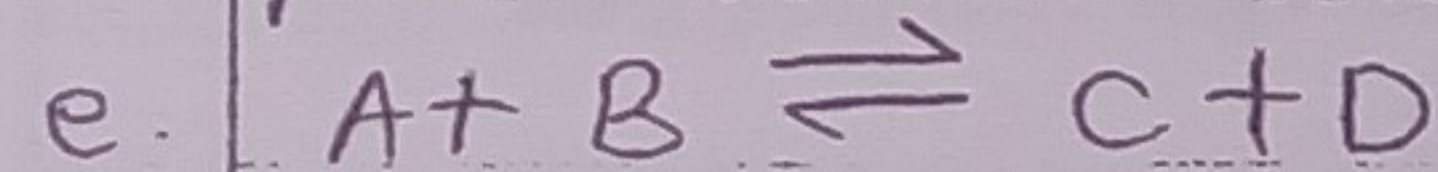
When chemical rxns are occurring, two scenarios can occur

Scenario 1 - all reactants can react to produce products



In such a case we say the reaction has reached completion

Scenario 2 - reactants can react to produce products and in the very same system, the products will react to produce reactants again



In such a case we say the rxn does not reach completion

In short we can say irreversible reactions reach completion while reversible rxns do not reach completion.

During this chapter, we are going to be focusing on rxns we do not reach completion i.e. reversible rxns.

Equilibria is divided into two depending on the components in the system which would be at equilibrium.

(1) Chemical equilibria

(2) Ionic equilibria

o Chemical equilibria

- When a reversible reaction is occurring, it proceeds in both directions until an equilibrium is reached.

- We therefore say the reaction has reached a state of dynamic equilibrium.

- At dynamic equilibrium, the rate of forward rxn will be equal to the rate of backward rxn.

- Also, at dynamic equilibrium the concentration of the reactants and products in the rxn will be constant. This means that the concentrations will not be changing, it does not mean the concentration will be the same.

When a chemical rxn has reached a state of dynamic equilibrium we have different equilibrium constants associated with the ~~sys~~ equilibrium.

Equilibrium constants

When studying chemical equilibria, we are going to be interested in:

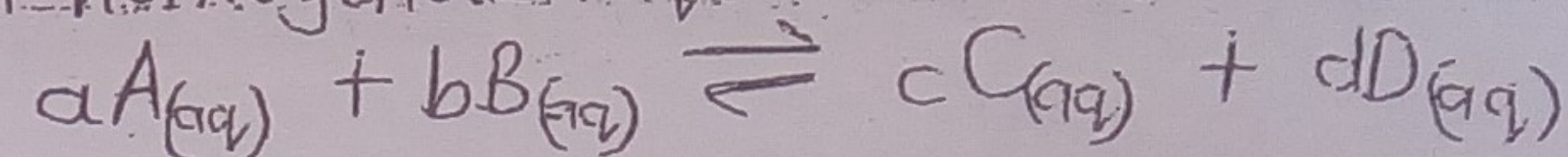
- (i) equilibrium constant in terms of concentrations, K_c
- (ii) equilibrium constant in terms of partial pressures, K_p

Equilibrium constant in terms of concentration, K_c

- When a system has reached a state of dynamic equilibrium, the K_c expression can be deduced.

Consider

A homogeneous equilibrium below



a, b, c and d - number of moles

(It is a homogeneous equilibrium because all the components in the equation are in the same physical state)

$$K_c = \frac{[\text{Products}]_{\text{equilib}}}{[\text{Reactants}]_{\text{equilib}}} = \frac{[C]_{\text{equilib}}^c [D]_{\text{equilib}}^d}{[A]_{\text{equilib}}^a [B]_{\text{equilib}}^b}$$

We can therefore define K_c as an equilibrium constant we relates the ratio of the concentration of the products and the concentration of the reactants all raised to appropriate powers.

Units of equilibrium constants (K_c)

Assuming that in the above expression $a=2$, $b=3$, $c=3$ and $d=1$, it implies that K_c units will be equal to

$$K_c \text{ units} = \frac{[C]^3 [D]^1}{[A]^2 [B]^3} = \frac{(\text{mol dm}^{-3})^3 (\text{mol dm}^{-3})^1}{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})^3} = \frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1} \text{dm}^3$$

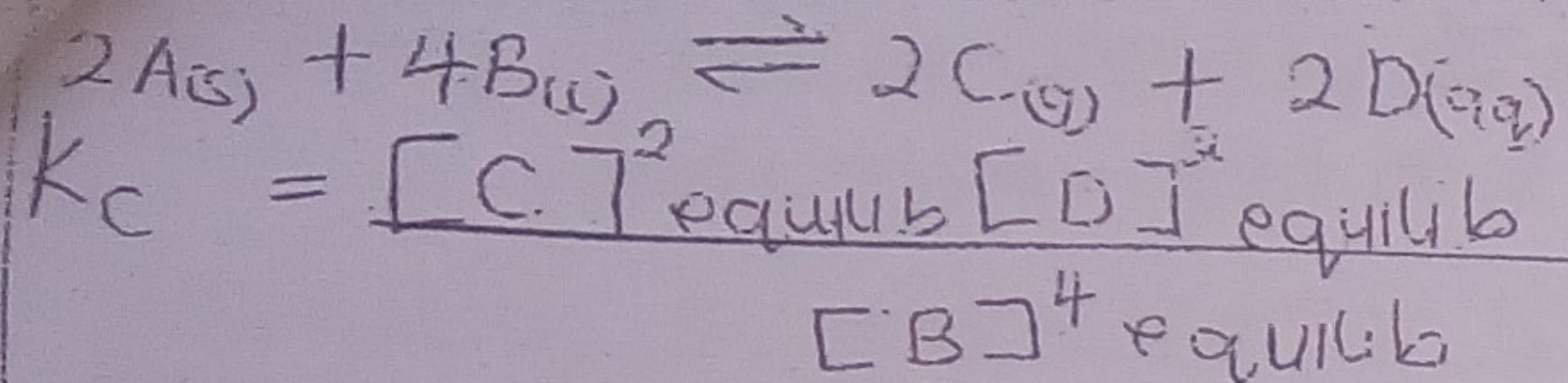
Heterogeneous equilibrium (because components are in different physical states)

- When writing the K_c expression for a heterogeneous equilibrium, one should know that solids are not included in the K_c expression. This is because solids have a constant concentration.

- Water is also not included in the K_c expression again because it has a constant concentration. Water can only be included in a K_c expression in a situation whereby its

vertical
 $A_{(s)} + 4H_{(g)} \rightleftharpoons [C]$
 $K_c = [C]$

concentration will have been stated



$$\text{Units of } K_c = \frac{[C]^2 [D]^2}{[B]^4} = \frac{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^4}$$

Therefore K_c has no units

Equilibrium constant in terms of partial pressures

Partial pressure

- It is a pressure which an individual gas exerts in a mixture of gases.

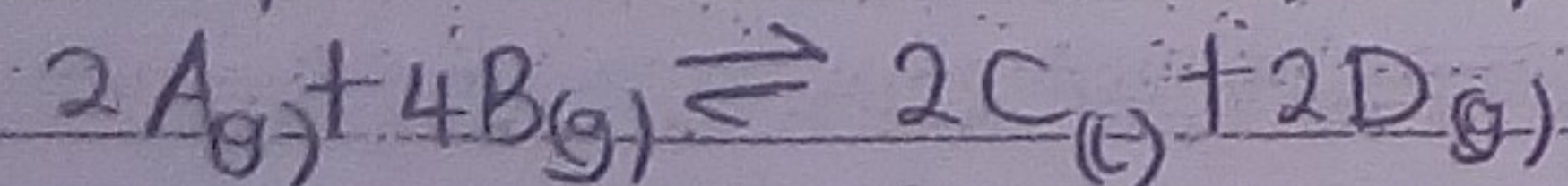
Consider

A mixture of gases A, B and C with moles a, b, c and a total pressure of two atmospheres (2 atm). It implies that partial pressure of gas A (P_A) can be given by the relationship below: (P_A)

$$P_A = \text{mole fraction of gas A} \times \text{Total Pressure}$$
$$= \frac{a}{a+b+c} \times 2 \text{ atm}$$

When representing the partial pressure of a gas, the following representations must not be used: p_A , $[P_A]$, $[p_A]$

Therefore consider the eqn below



The K_p expression:

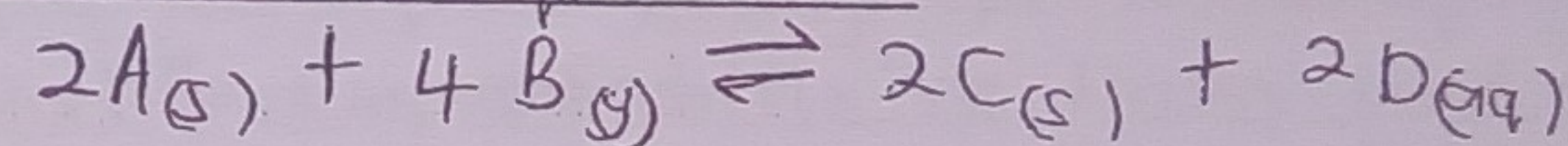
$$K_p = \frac{(P_D)^2}{(P_A)^2 (P_B)^4}$$

When writing the K_p expression, we only consider the gaseous components of the system or reaction, thus C was omitted in the rxn because it is a liquid.

Units of K_p

$$K_p \text{ units} = \frac{(\text{Pa})^2}{(\text{Pa})^2 (\text{Pa})^4} = \text{Pa}^{-4}$$

Consider the eqn below



The K_p expression

$$K_p = (P_B)^4$$

Units of K_p

$$K_p \text{ units} = (\text{Pa})^4 = \text{Pa}^4$$

NB During chemical rxns, the values of K_p or K_c can only be affected by changes in temperature.

- Any other change we can occur in the equilibrium system will only affect the equilibrium ^{position} ~~condition~~ and hence the equilibrium composition.

- The effect of the changes we occur for a system at equilibrium can be best explained using the Le Chateliers Principle

The Le Chatelier's Principle

It states that if a system at equilibrium is disturbed, the equilibrium position will shift so as to minimize the disturbance.

Conditions which can affect a system at equilibrium

- (i) concentration
- (ii) pressure
- (iii) temperature

the DIRECTOR..

0772 666 148

The above conditions can be referred to as disturbances which can affect a system at equilibrium

When a system at equilibrium is disturbed, it can alter:

(i) equilib position - it may result in either the forward rxn of the system or the backward rxn being favoured

(ii) equilibrium composition - the amounts of the components present in the new equilibrium will vary. If the forward reaction is favoured after a disturbance, the equilib ^{sition} composition of products will increase. If the backward rxn is favoured after a disturbance, the equilibrium amounts of the reactants will increase.

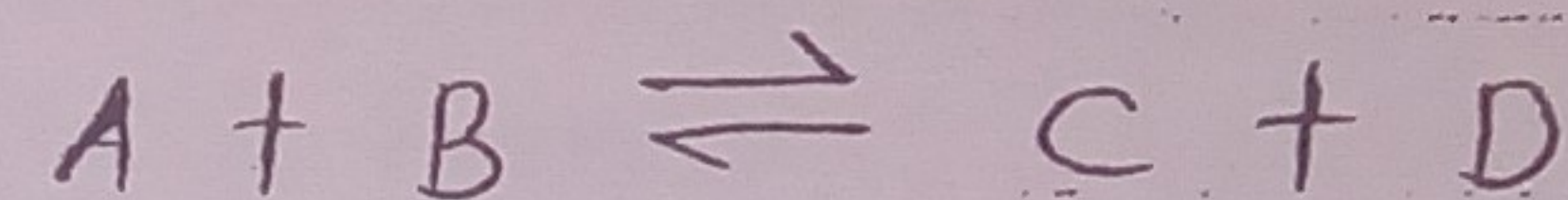
(iii) equilibrium constant - this refers to the values of K_p and K_c but as stated above, these values of K_p and K_c are only affected by temperature

When explaining the effect of a disturbance on a system at equilibrium we usually emphasize on the equilib position

The equilib comp and equilib constant are usually given when a question requires us to talk about them

Effect of concentration

Consider the eqn below



What is the effect of

- (i) increasing conc of B
 - (ii) decreasing conc of D
- on the equilib above

Solution

(i) Increasing the conc of B results in the equilib position shifting to the right / i.e it favours the forward rxn. This is because more of A will be reacting with excess of B resulting in the formation of more C and D. Therefore the new equilib composition will have more of C and D and less of A. The equilib constant remains the same, it is not affected by conc.

(ii) A decrease in the conc of D shifts the equilib position to the right i.e it favours the forward rxn, This is because more of A and B will be reacting to produce and replace the decreased amounts of D. ^{more} C is also produced. It therefore means that the new equilib composition will have less of A and B and ^{more} more of C.

Considering the equilib above, what is the effect of decreasing the conc of A on the system of equilib?

Decreasing the concentration of A on equilibrium

- This will shift the equilib position to the left i.e it favours the backward rxn. This is because more of C and D would be reacting to produce and replace the decreased amount of A. More B is also produced.

Therefore it implies that the new equilibrium composition will have less of C and D and more of B. Changes in conc have got no effect on equilib constant.

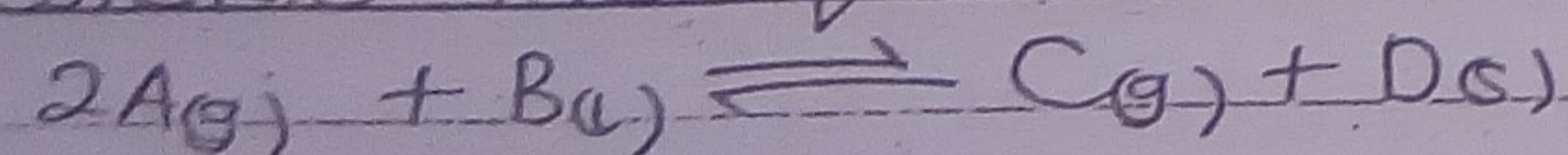
Effect of pressure

- Pressure will only affect reactions which contain gases as either reactants or products or both. That is, we are saying the system at equilib should have at least one gaseous component in it.

- But when equal no. of moles of a gas are present in a system at equilibrium we say pressure has got no effect on that system at equilibrium.

- When dealing with equilib systems no contain gases, changes in volume will affect pressure. Thus increase in volume results in a decrease of pressure. A decrease in volume results in an increase in pressure.

Consider the equilib below



What is the effect of (i) decreasing volume of the equilib system

(i) decreasing pressure of the system

(ii) increasing the partial pressure of A on the equilibrium above

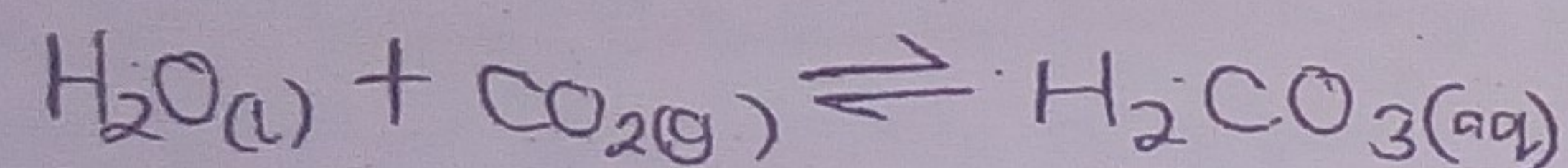
Solution

(i) - When the volume of an equilib system is decreased, the pressure of the system increases. In this equilib system we have two moles of the gas at the left hand side of the eqn and one mole of a gas on the right hand side of the eqn. - It therefore means that an increase in pressure would favour the forward reaction. It also means that the new equilib composition will have more of C and D and less of A & B. Changes of pressure has got no effect on the equilib constant.

(ii) The right hand side of the eqn has got one mole of a gas while the left hand side has got two moles of a gas, therefore decreasing pressure will shift the equilib position to the direction where there is more moles of a gas. i.e it favours the backward reaction. Thus the equilib comp will have more of A & B and less of C & D. The equilib constant remains unchanged.

(iii) When the partial pressure of a gas increase in a system, it implies that the number of moles of a gas will have increased. When the moles of a gas has increased it implies that the amount of that gas (conc of that gas) would have increased. Therefore it shifts the equilib position to the right.

Consider the equilib below



What is the effect of increasing the volume of the above system at equilibrium on the equilib position and composition?

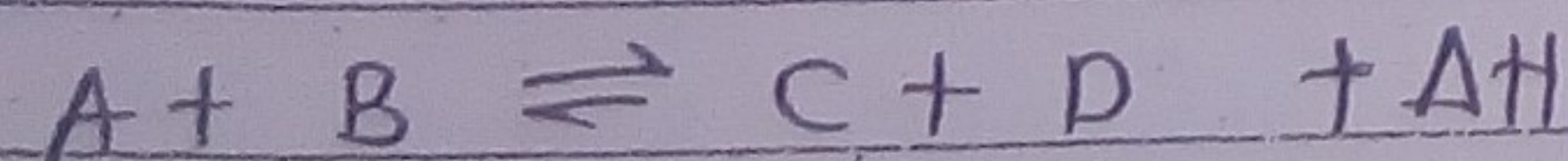
Solution

When volume is increased, the pressure of the system decreases. We have one mole of a gas on the left hand side of the eqn and zero moles of a gas on the right hand side. As a result, a decrease in pressure will favour the direction with more number of moles of a gas, thus an decrease in pressure will favour the backward reaction. The new equilib composition will be having more of water and carbon dioxide gas and less of carbonic acid

Effect of temperature

- Effect of temp on a system at equilibrium depends on the nature of the forward reaction i.e the forward rxn can either be - (i) heat releasing (exothermic)
(ii) heat absorbing (endothermic)

Consider the following equilibrium systems

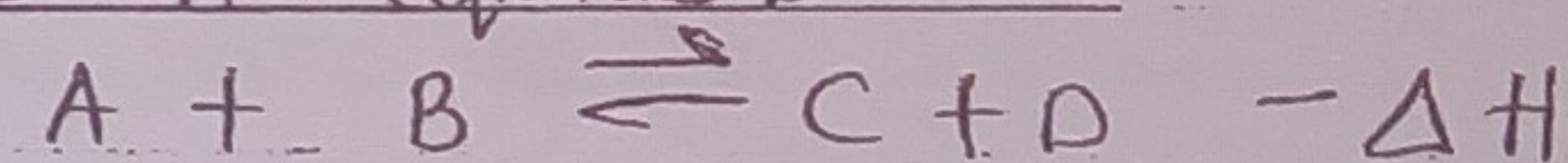


What is the effect, given that the above equilibrium was reached at 25°C, of establishing the same equilibrium at 10°C to the equilib position, composition and constant

Solution

In the above equilib, the forward rxn is endothermic hence is absorbing heat. When the temp is decreased that disturbance is minimized by producing more heat i.e by favouring the backward reaction which is exothermic. The new equilib composition will have more of A and B and less of C & D. The equilib constant e.g K_c will decrease: $K_c = \frac{[C][D]}{[A][B]}$

Consider the equilib below



What is the effect of decreasing temp on the equilib of the above system?

Solution

The forward rxn is exothermic hence it is heat releasing. When the temperature is decreased that disturbance is minimized by producing more heat, i.e by favouring the forward rxn. The new equilib comp will have more C and D and less A and B. Therefore the equilib constant increases.

Effect of a catalyst on a reversible rxn

When a catalyst is introduced on a reversible rxn, it increases the rate at which an equilib is established. This is because a catalyst increases both the forward and the backward rxn. Therefore we say a catalyst has got no effect on the equilib position, composition or even equilib constant.

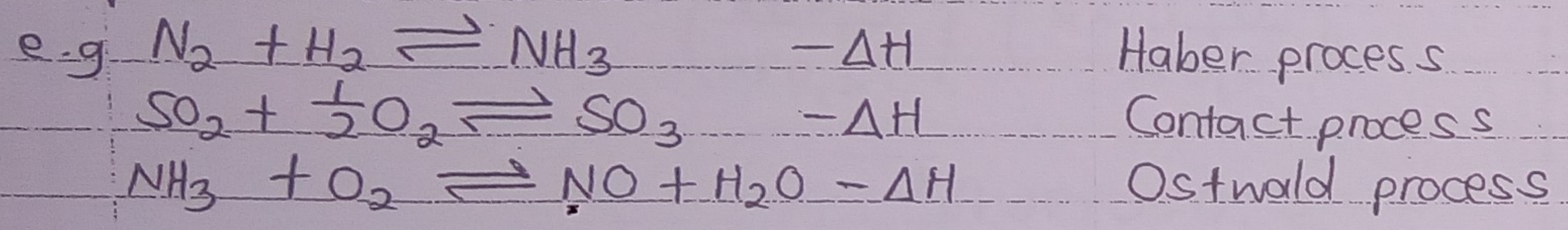
Application of the Le Chatelier's principle in the industry

The Le Chatelier's principle can be used to justify the conditions used in industrial processes.

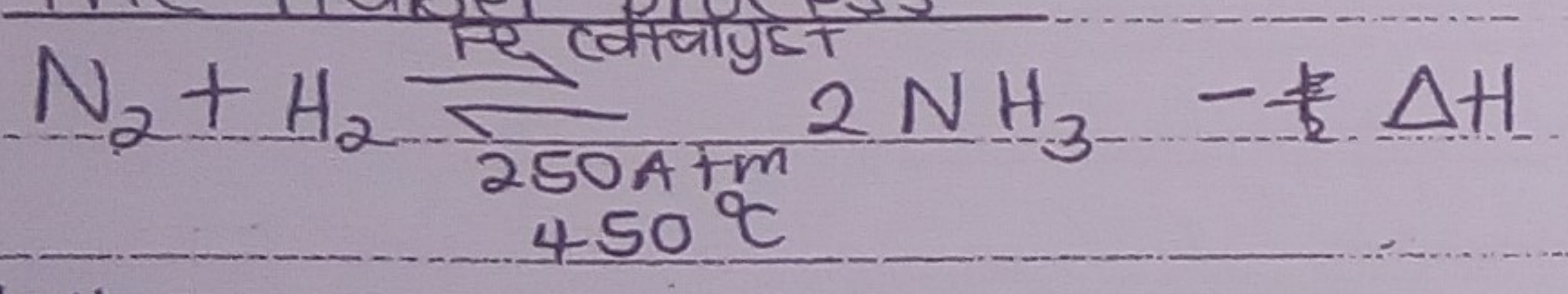
These industrial processes include:

- (i) Haber process
- (ii) Contact process
- (iii) Ostwald process

It should be noted that all the main reactions in the processes above are exothermic.



The Haber process



When manufacturing ammonia using the Haber process certain operating conditions are used. These conditions include:

- (i) Fe catalyst
- (ii) Pressure of 250 Atm
- (iii) Temperature of 450 °C

Pressure

- 250 Atm can be referred to as a high pressure.
- Employing a high pressure on the above equilibrium increases the percentage yield of ammonia.
- This therefore implies that employing a higher pressure e.g. 300 Atm for the process would increase the % yield of ammonia. But gives rise to problems in the plant.

High pressures are difficult and expensive to maintain, the plant will be characterised by explosions, it would also require thicker pipes to be installed at the plant which is expensive

Temperature

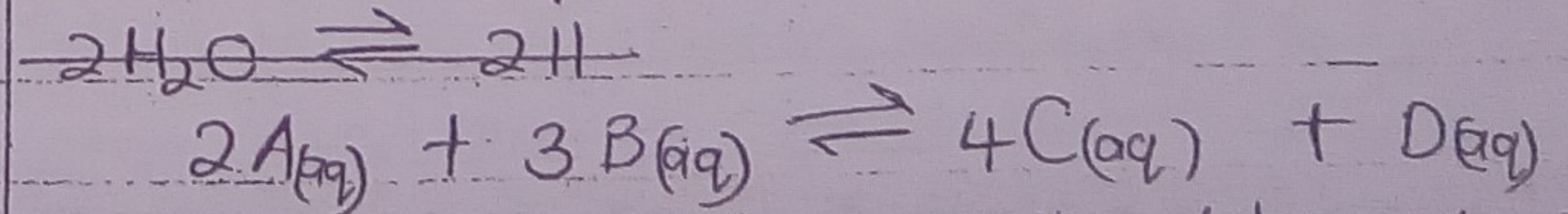
- A temperature of 450 °C is said to be a moderate temperature.
- Since the forward reaction in the industrial process is exothermic, a low temperature would increase the % yield of ammonia, but the reaction will be too slow.
- As a result, a compromise temperature of 450 °C is used.
- We refer to it as a compromise temp because it lowers the % yield of ammonia but at the same time the rxn will be occurring at a faster rate.

Catalyst

- Iron catalyst is used in the reaction because it increases the rate of the forward reaction.
- The ammonia is removed from the reaction vessels before it decomposes back to its reactants this ensures that a high % yield of ammonia is collected.

Chemical equilibria calculations

Qn Consider the equilibrium below



When 0,5 moles of A were allowed to react with 0,6 moles of B, the equilibrium moles of C was found to be 0,05

- (a) Calculate the equilibrium moles of A, B and D
 (b) Calculate the K_c value given that the total volume is 1 dm^3

Solution

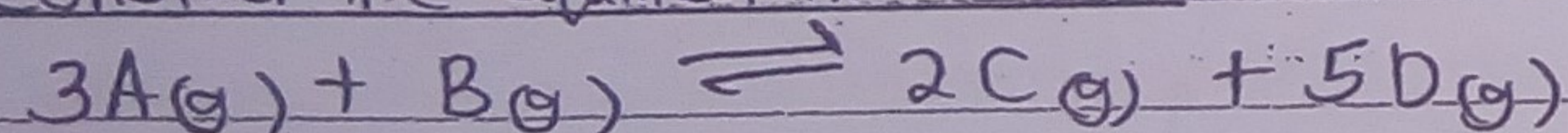
| | | | | |
|-------------|---|------------|------|--------|
| | $2A(g) + 3B(g) \rightleftharpoons 4C(g) + D(g)$ | | | |
| Initial | 0,5 | 0,6 | 0 | 0 |
| Equilibrium | $0,5 - 2x$ | $0,6 - 3x$ | $4x$ | x |
| Equilibrium | 0,475 | 0,5625 | 0,05 | 0,0125 |

$$K_c = \frac{[C]^4 [D]}{[A]^2 [B]^3}$$

$$= \frac{\left(\frac{0,05}{1}\right)^4 \left(\frac{0,0125}{1}\right)}{\left(\frac{0,475}{1}\right)^2 \left(\frac{0,5625}{1}\right)^3}$$

$$= 1,9455 \times 10^{-6}$$

Consider the equilibrium below



When 0,9 moles of A were mixed with 1 mole of B, a rxn occurred and an equilibrium was established. At equilibrium, 0,7 moles of A were found to be present. Calculate the K_p of the equilibrium system given that the equilb total pressure is 2 Atm.

Solution

Initial
Equilib
Equilib

| | | | | |
|---------|---|---------|-------|-------|
| | $3A(g) + B(g) \rightleftharpoons 2C(g) + 5D(g)$ | | | |
| Initial | 0,9 | 1,0 | 0 | 0 |
| Equilib | $0,9 - 3x$ | $1 - x$ | $2x$ | $5x$ |
| Equilib | 0,7 | 0,933 | 0,133 | 0,333 |

$$K_p = \frac{(P_C)^2 (P_D)^5}{(P_A)^3 (P_B)}$$

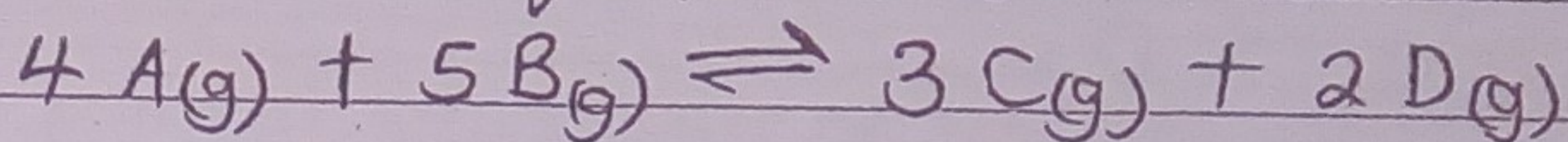
$$K_p = \frac{\left(\frac{0,133 \times 2}{2,099}\right)^2 \left(\frac{0,333 \times 2}{2,099}\right)^5}{\left(\frac{0,7 \times 2}{2,099}\right)^3 \left(\frac{0,933}{2,099}\right)}$$

$$= 0,000196 \text{ Pa}^3$$

COMPILED BY
 .. the DIRECTOR ..
 0772666148

Chemical equilibria calculations

Consider the equilibrium below



0,6 moles of A, 0,8 moles of B, 0,8 moles of C and 0,4 moles of D were mixed and an equilibrium was reached as above. At equilibrium 0,35 moles of D was found to be present.

Calculate the equilibrium moles of C, B and A

Solution

| | $4 A(g)$ | $+ 5 B(g)$ | \rightleftharpoons | $3 C(g)$ | $+ 2 D(g)$ |
|------------------|------------|------------|----------------------|------------|------------|
| Initial | 0,6 | 0,8 | | 0,8 | 0,4 |
| Equilib moles | $0,6 + 4x$ | $0,8 + 5x$ | | $0,8 - 3x$ | $0,4 - 2x$ |
| Equilib moles | 0,7 | 0,925 | | 0,725 | 0,35 |

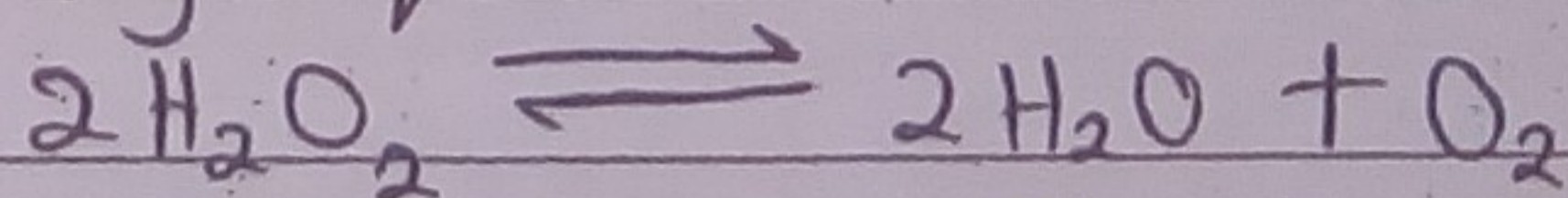
$$0,4 - 2x = 0,35$$

$$0,4 - 0,35 = 2x$$

$$0,025 = x$$

Consider

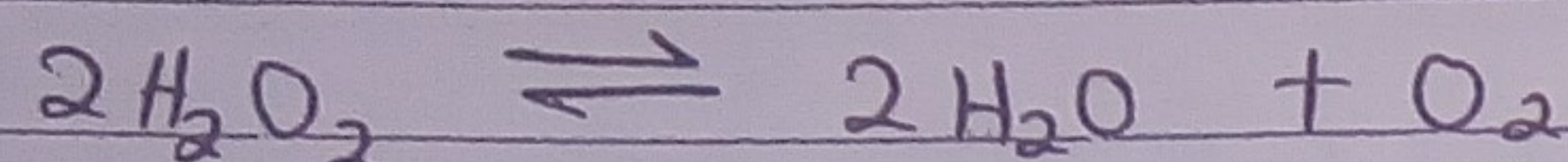
The decomposition of hydrogen peroxide occurs according to the following equation



It was found that when equilibrium was reached 70% of hydrogen peroxide had decomposed.

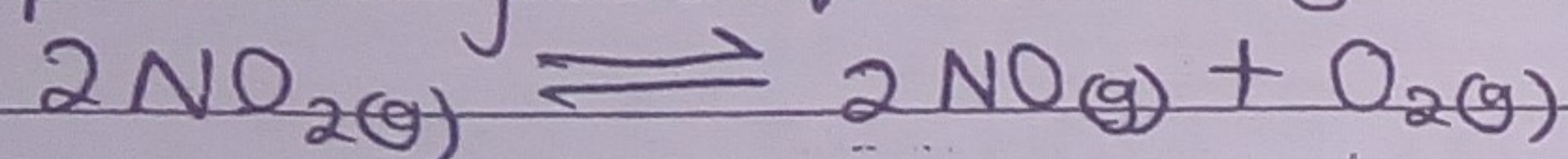
Calculate the equilibrium moles of the components in the system given that 0,5 moles of hydrogen peroxide was initially present.

Solution

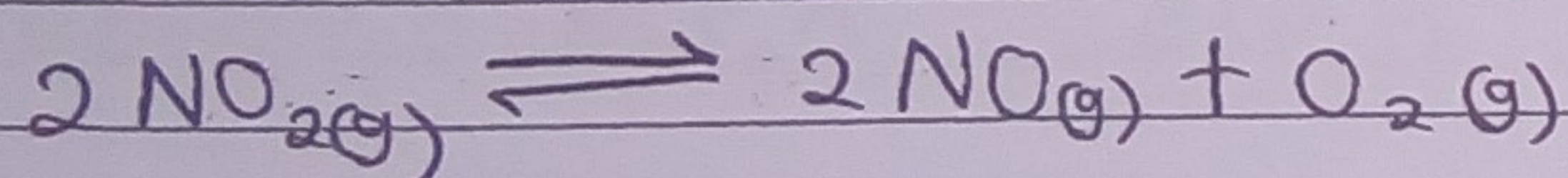


| | | | |
|---------------|------------|------|-------|
| Initial | 0,5 | 0 | 0 |
| Equilib moles | $0,5 - 2x$ | $2x$ | x |
| Equilib moles | 0,15 | 0,35 | 0,175 |

Qn The equation below shows the dynamic equilibrium at room temperature. Calculate the equilibrium constant, K_p given that 40% of nitrogen dioxide had dissociated and the total pressure of the equilibrium system is 2 Atm



Solution



| | | | |
|---------------|----------|------|-----|
| Initial | 1 | 0 | 0 |
| Equilib moles | $1 - 2x$ | $2x$ | x |
| Equilib moles | 0,6 | 0,4 | 0,2 |

$$1 - 2x = 0,6$$

$$1 - 0,6 = 2x$$

$$0,4 = 2x$$

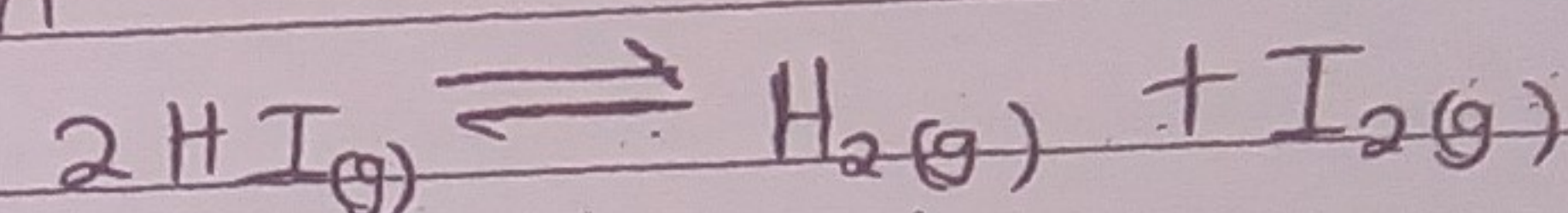
$$0,2 = x$$

$$K_p = \frac{(P_{\text{O}_2}) (P_{\text{NO}})^2}{(P_{\text{NO}_2})^2}$$

$$K_p = \frac{\left(\frac{0,2 \times 2}{1,2}\right) \left(\frac{0,4 \times 2}{1,2}\right)^2}{\left(\frac{0,6 \times 2}{1,2}\right)^2}$$

$$K_p = 0,148$$

Qn The decomposition of HI occurs according to the following rxn



Describe the effect of

- increasing pressure
- lowering the temperature
- introducing a catalyst

Solution

(i) We have got 2 moles of a gas on each side of the equation. therefore changes in pressure has got no effect on such an equilibrium

(ii) The question doesn't really specify / directly specify whether the rxn is exothermic or endothermic. But if we take a closer look at the info given, important conclusions can be made. In the question we were given the word decomposition, decomposition of HI involves bond breaking of H-I bond breaking requires energy. Therefore we can conclude that the forward rxn is endothermic

Since the forward reaction is endothermic, lowering the temp will favour the heat releasing backward reaction. Thus more of hydrogen and iodine would be reacting to

produce H^+

(iii) A catalyst increases the rate of both the forward and backward rxn as a result it has got no effect on both the equilibrium position and equilibrium composition.

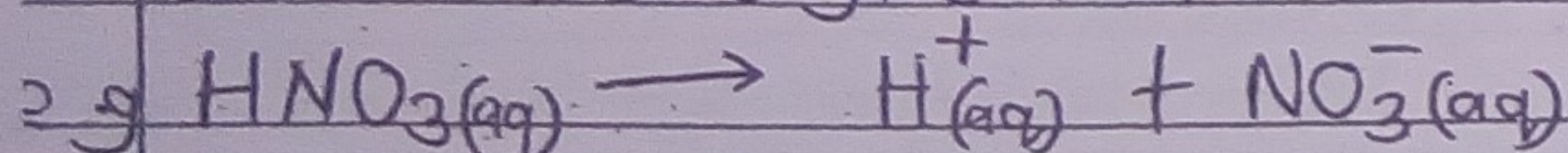
Ionic Equilibria

ACIDS AND BASES

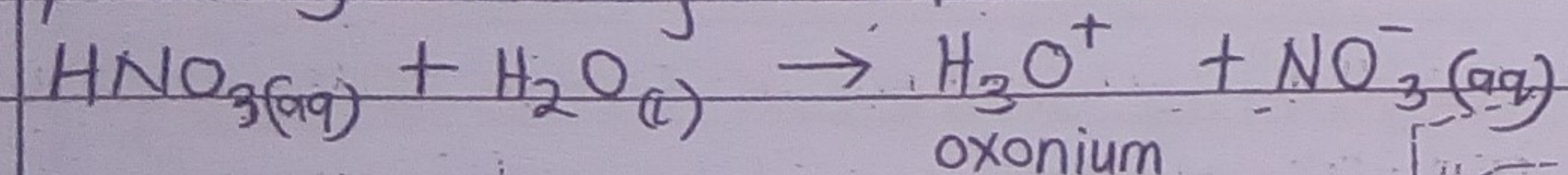
- An acid is a substance w/c when placed in water dissociates to give an H^+ .
- Acids can be classified into two: (i) strong acids (ii) weak acids

Strong acid

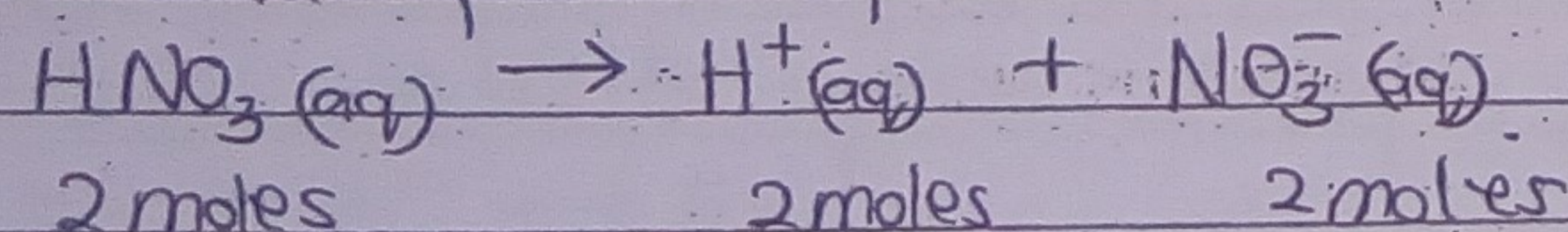
- Is an substance w/c when placed in water completely dissociates to give H^+ ions



Complete dissociation is being shown by an arrow pointing in the forward direction/reaction.



It also implies that if two moles of a strong acid will be present therefore the produced ions will also be 2 moles

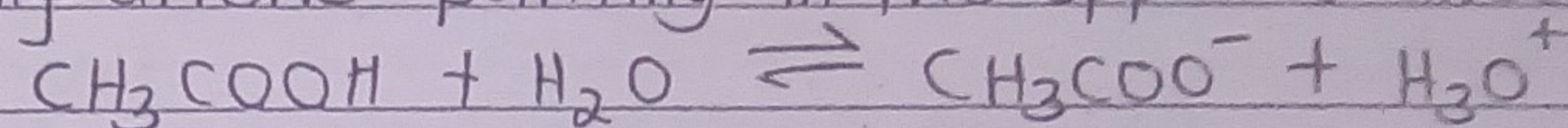


Weak acid

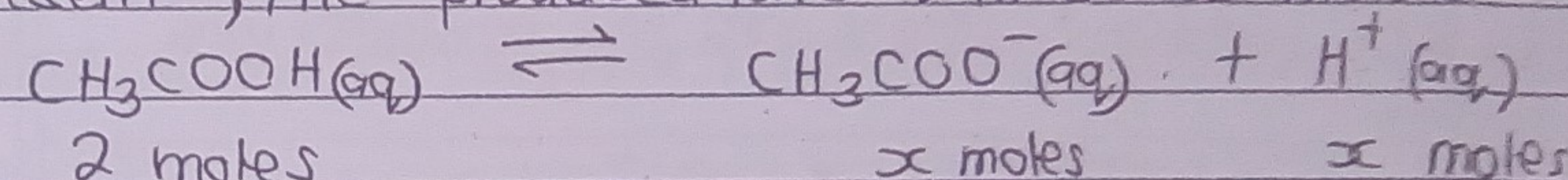
- Is a substance w/c when dissolved in water partially

dissociates or ionises to give an H^+ ion e.g.
 $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

The partial ionisation of the ~~ion~~ acid is being shown by half arrows pointing in two opposite directions



- It also implies that if two moles of a weak acid are present, the produced ions will be x moles



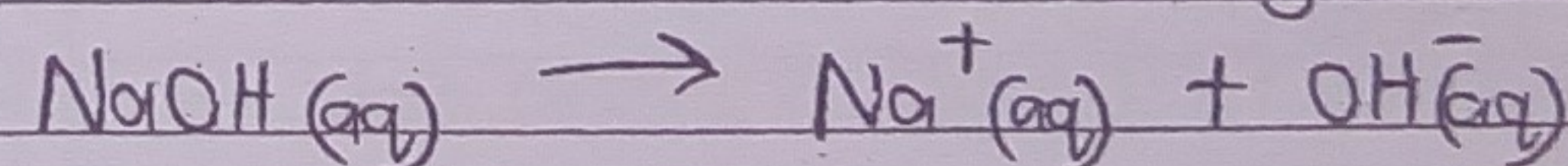
where $2 \text{ moles} \gg x \text{ moles}$

Bases

- It is a substance w/c when dissolved in water dissociates to produce an OH^- ions
- They can be classified into two: (i) strong bases (ii) weak bases

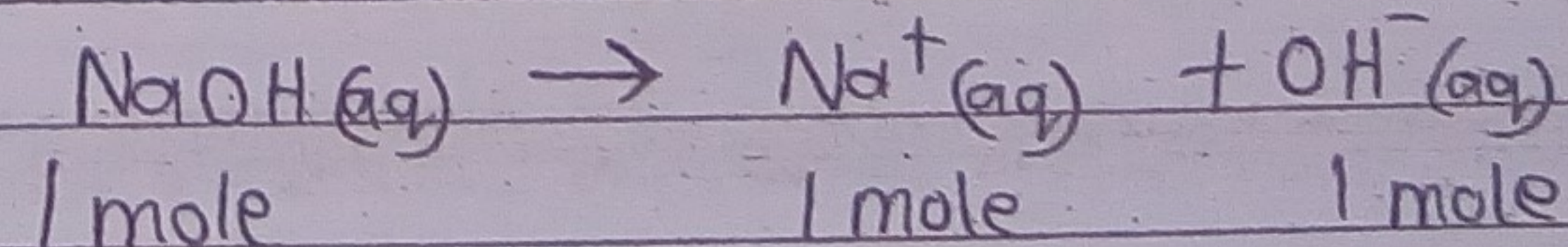
Strong bases

- Is a substance w/c when dissolved in water completely ionises or dissociates to give OH^- ions e.g.



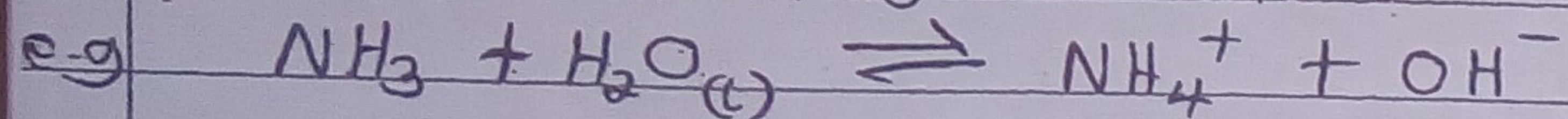
Complete dissociation is being shown by one arrow pointing in the forward direction.

Complete dissociation also implies that if one mole of a strong base will be present therefore the produced ions will also be one mole each



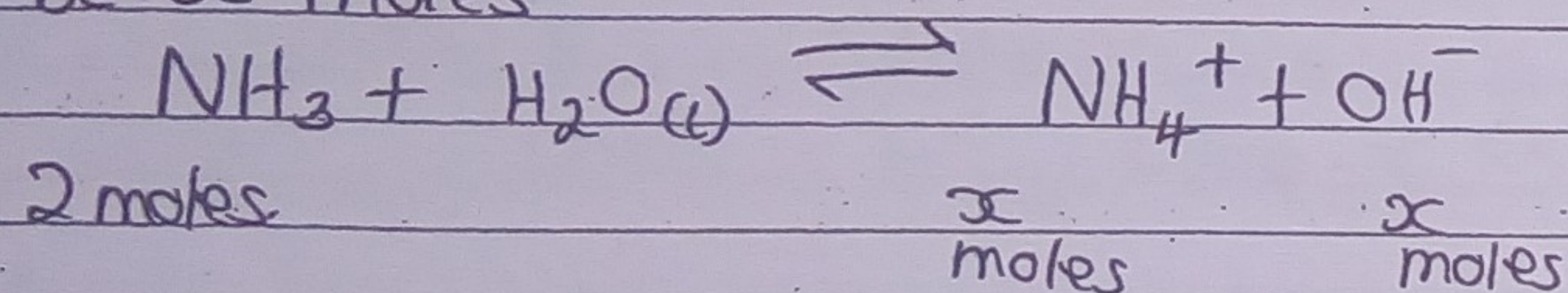
Weak bases

- There are substances w/c when dissolved in water partially ionise to give OH^- ions



- The partial ionisation of the base is being shown by two half arrows pointing in opposite directions.

- Partial ionisation also implies that if two moles of a weak base are present therefore the products ions will be x moles



Where 2 moles \Rightarrow x moles

Many Chemists went on to give different definitions of acids and bases. These chemists include:

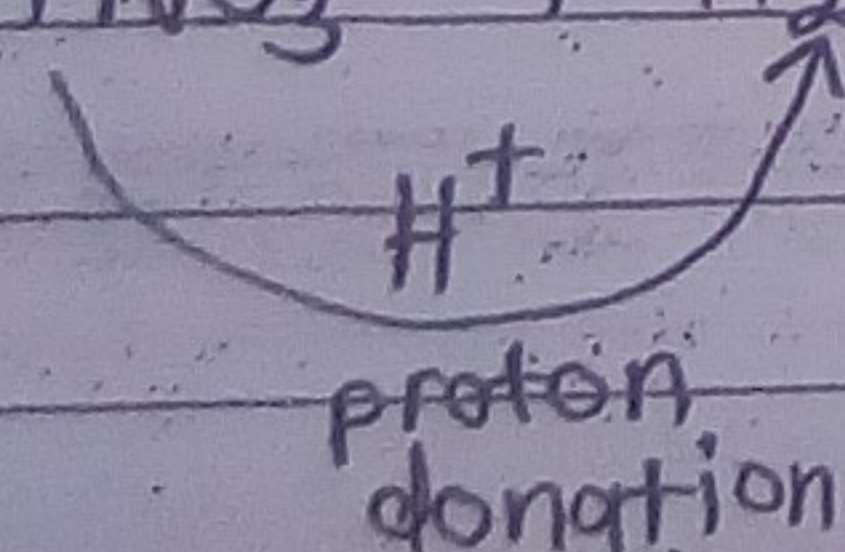
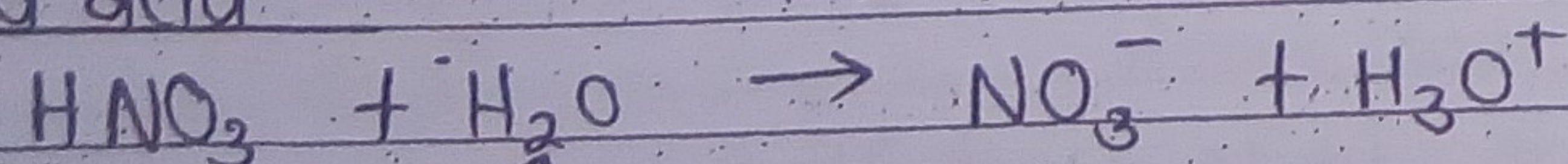
- (i) Bronsted and Lowrey - B & L Theory
- (ii) Lewis - Lewis Theory
- (iii) Arrhenius - Arrhenius Theory

The Bronsted and Lowrey Theory of Acids and Bases

i) The theory states that an acid is a proton donor / H^+ donor

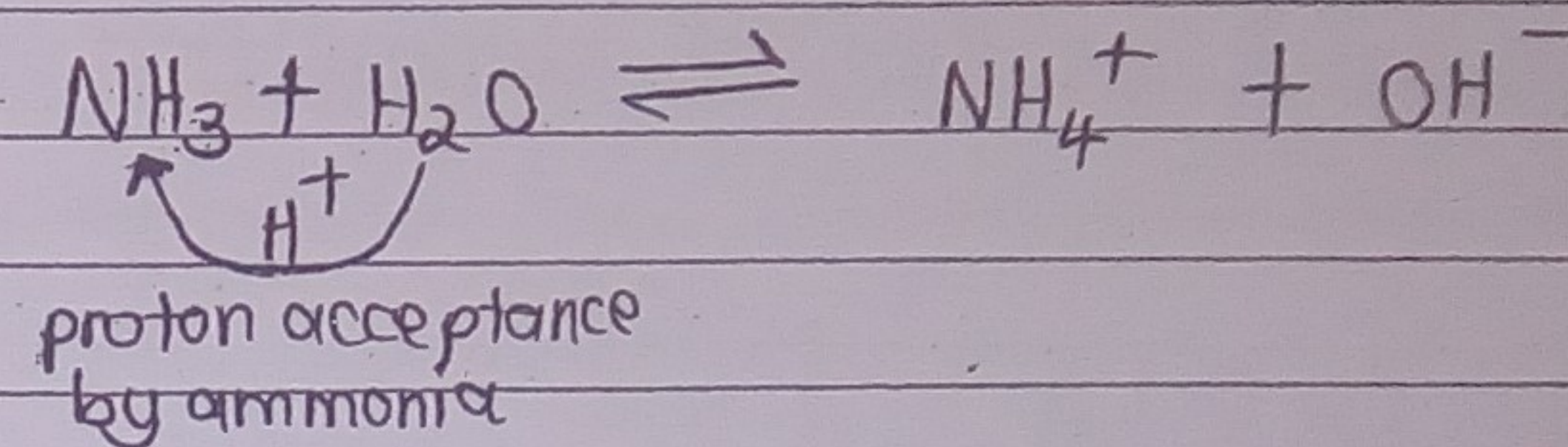
(ii) A base is a proton acceptor

Bronsted acid



In this eqn we say water is acting as a conjugate base

Bronsted base



In this eqn we say water is acting as a conjugate acid

Conjugate acids and bases

A conjugate acid is a substance that ^{has the} behaviour of an acid in a chemical rxn but might not necessarily be ^{an} acid in nature

e.g. consider the rxn of HNO_3 and H_2O above

A conjugate base is a substance w/c behaves like a base in a particular chemical rxn but might not necessarily be a base in nature.

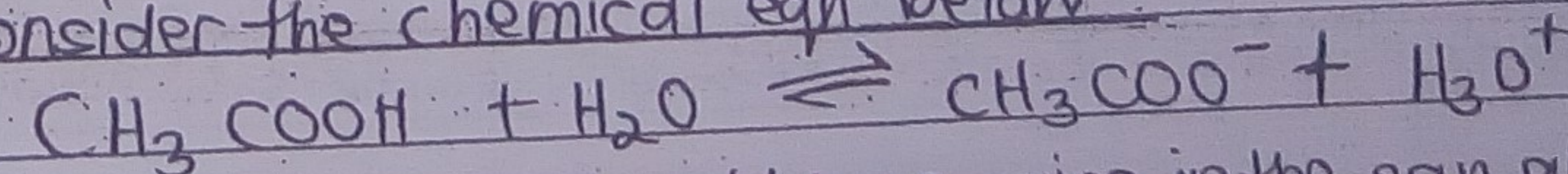
e.g. consider the rxn of NH_3 and H_2O above

Conjugate acid-base pairs

- When chemical rxns containing acids and bases occurring, conjugate acid-base pairs in the eqns can be determined

- A conjugate acid-base pair is a pair of species whose formula differs by a proton

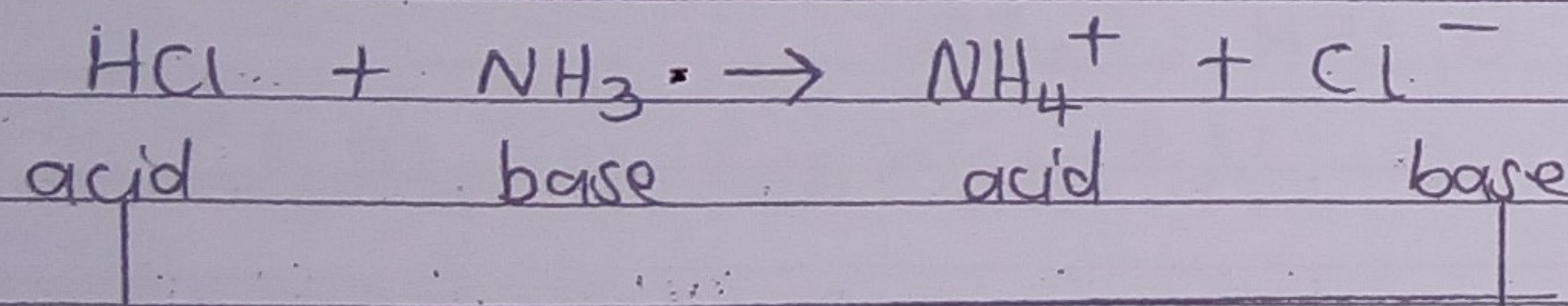
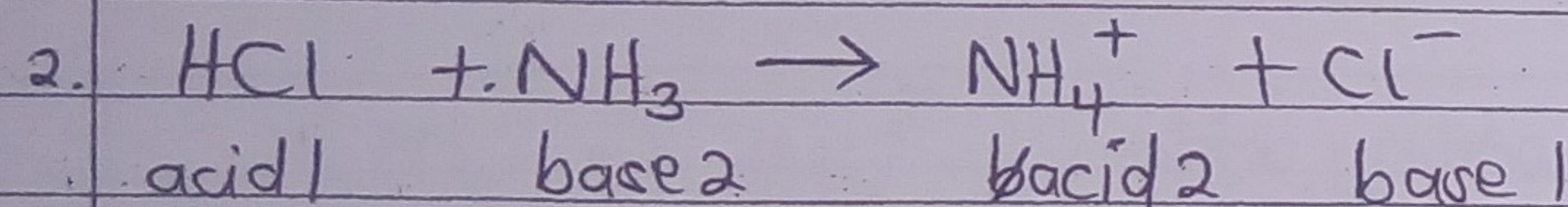
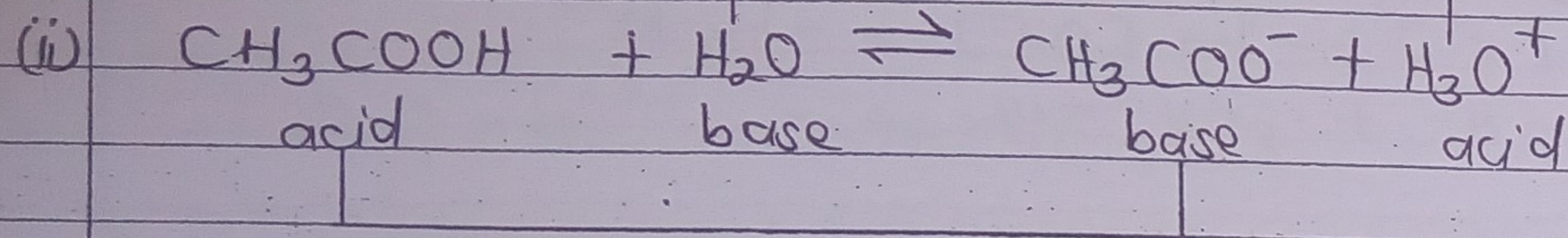
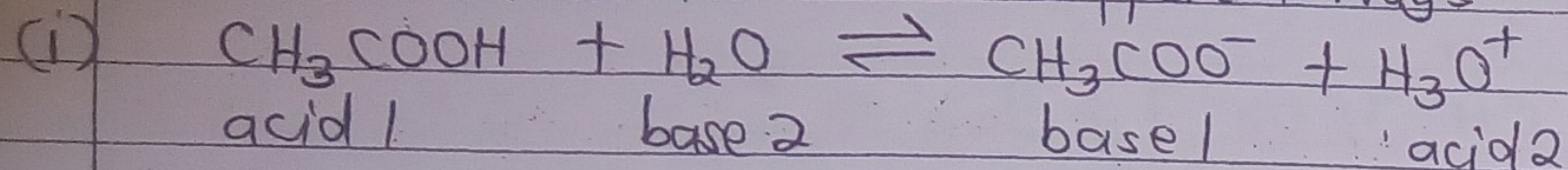
Consider the chemical eqn below



Show the conjugate acid-base pairs in the eqn above

solution

This can be done in two different ways

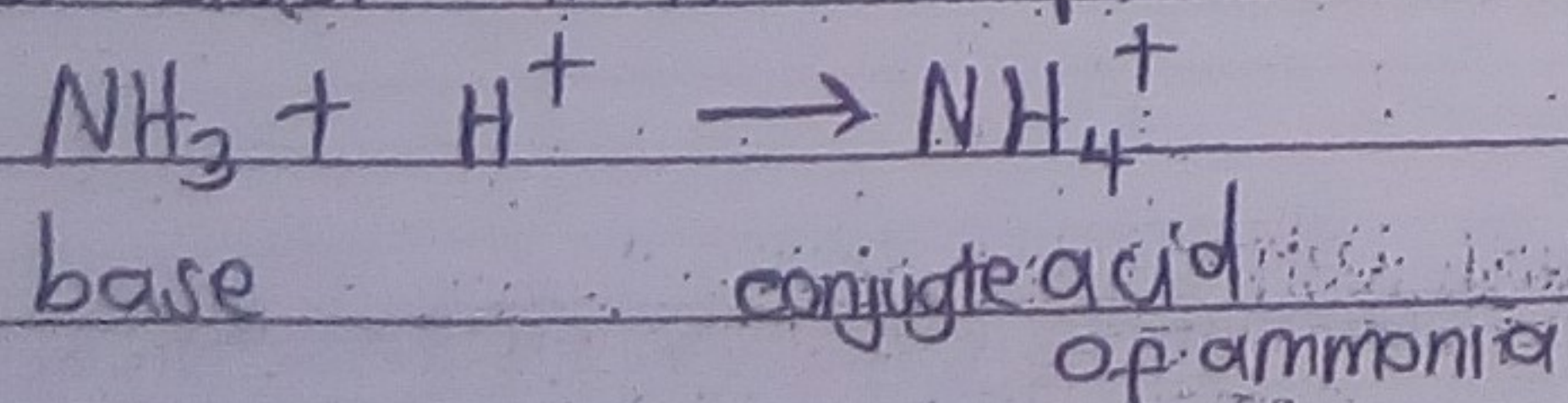


Qustn

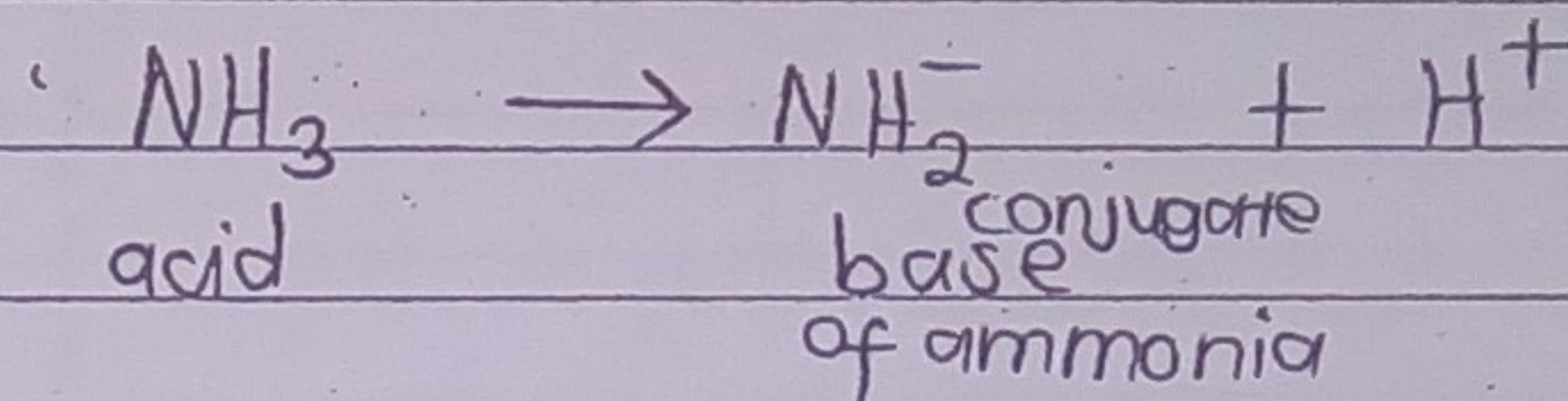
- (a) What is the conjugate acid of ammonia?
- (b) What is the conjugate base of ammonia?

Solution

(a) When asked to give the conjugate acid of ammonia, it only implies that we are taking ammonia as the base hence we just add an H^+ to produce the acid



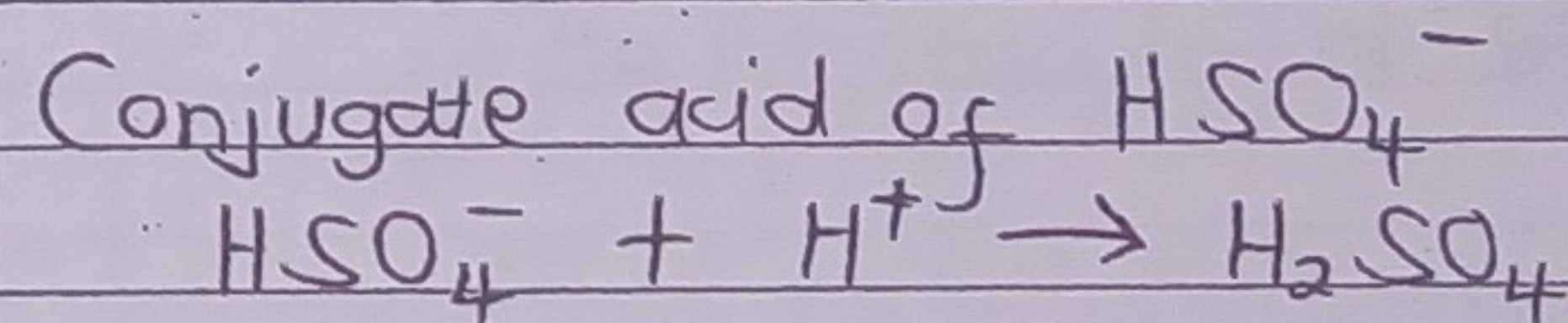
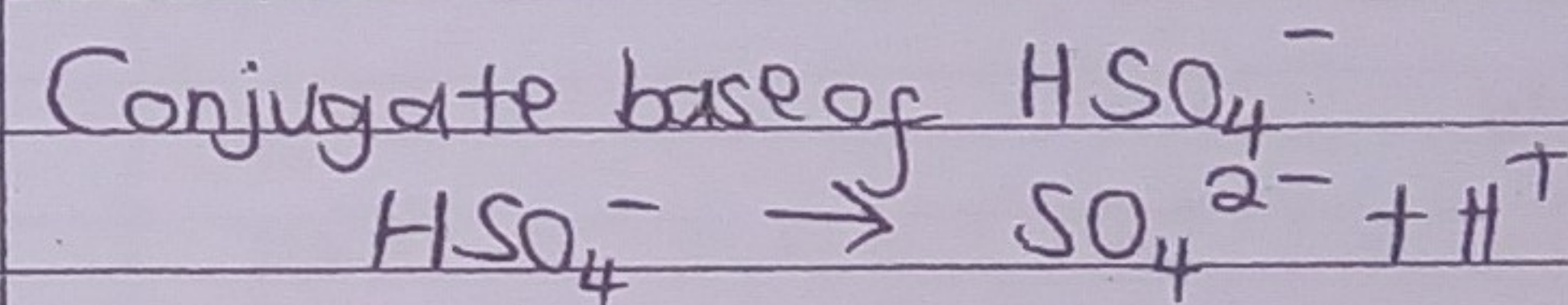
(b) When asked to give the conjugate base of ammonia, it only implies that we are taking ammonia as the acid hence we remove an H^+ to produce the base.



Qn

What is the conjugate base and conjugate acid of HSO_4^- ?

Solution



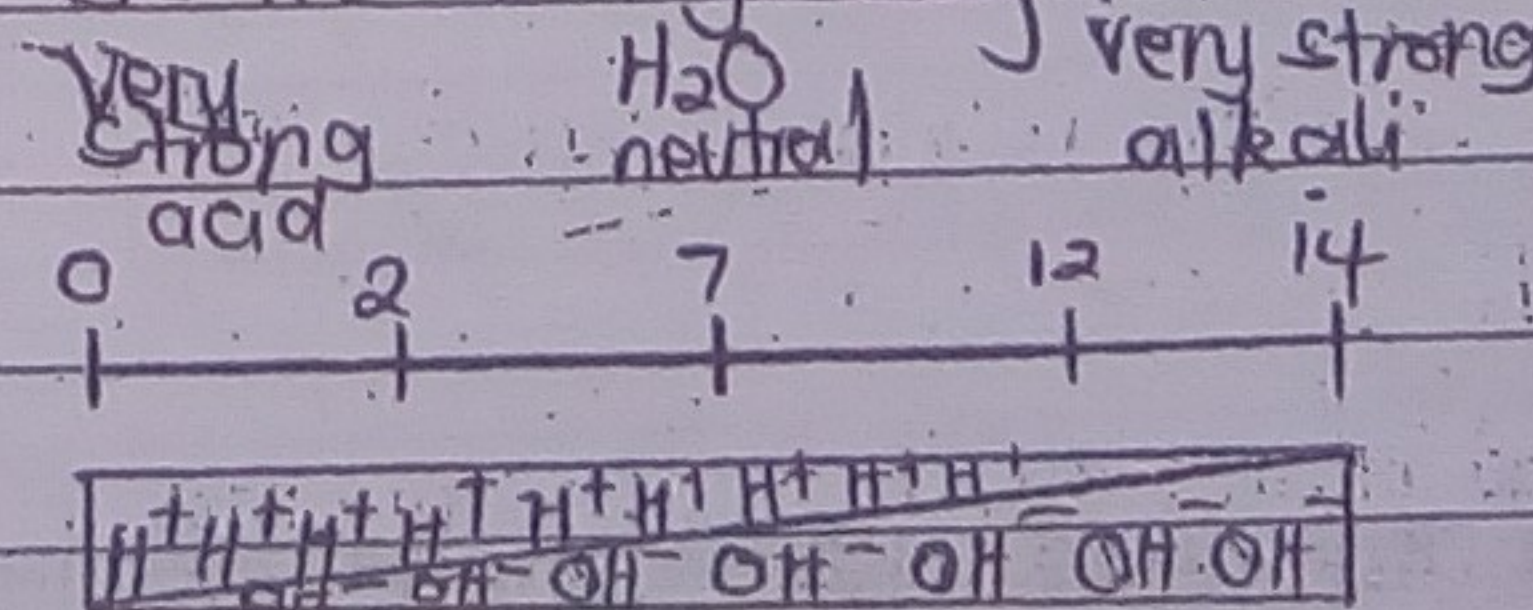
The level of acidity or basicity of a solution can be determined using the pH scale

pH scale

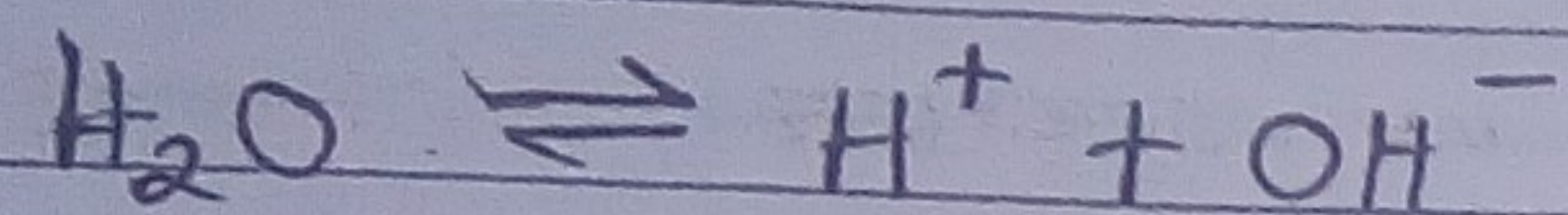
- pH is the negative logarithm to base 10 of the concentration of hydrogen ions

$\text{pH} = -\log_{10} [\text{H}^+]$

- The pH scale ranges from zero to fourteen



Water naturally dissociates according to the eqn



Kc expression

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

But at 25°C/298K

$$K_c [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

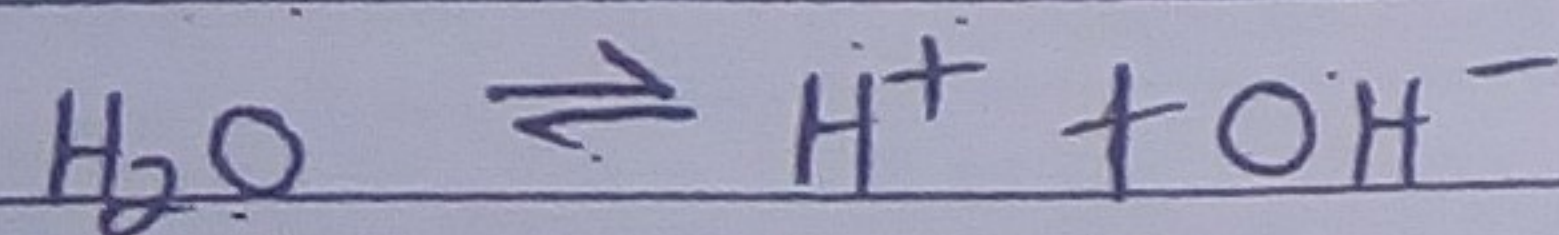
and the product of the ions of water was found to be 1×10^{-14}

- This constant value K_w is valid at 25°C is called the ionic product of water (K_w).

$$\therefore K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

The K_w relationship can be used to calculate the pH of water.

Calculating pH of water at 25°C



$$\text{Using } K_w \Rightarrow [\text{H}^+][\text{OH}^-] = 10^{-14} \dots (1)$$

$$\text{but } [\text{H}^+] \equiv [\text{OH}^-]$$

substituting in eqn 1

$$[\text{H}^+][\text{H}^+] = 10^{-14}$$

$$\therefore [\text{H}^+] = \sqrt{10^{-14}} = 10^{-7}$$

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log 10^{-7} = 7$$

- The K_w relationship is also a very useful relationship when calculating the pH of bases

- The expression can be used to calculate another important relationship during the calculation of pH values of bases.

Consider K_w

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

Introducing log

$$\log [\text{H}^+][\text{OH}^-] = \log 10^{-14}$$

Introducing negative

$$-\log [\text{H}^+] + -\log [\text{OH}^-] = -\log 10^{-14}$$

$$\text{pH} + \text{pOH} = 14$$

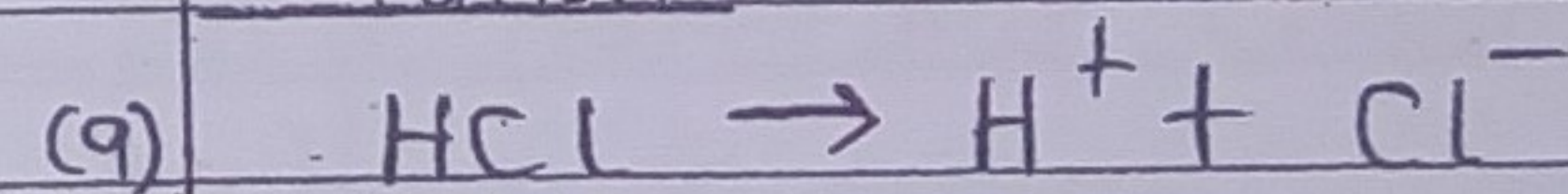
Using the above relationship, the pH values of acids and bases can now be easily calculated.

Calculations involving strong acids

(a) Calculate pH of 0,048 M HCl

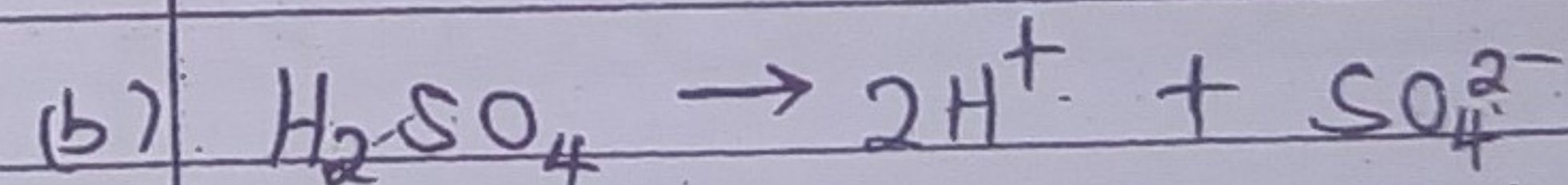
(b) pH of 0,15 M H_2SO_4

Solution



$$\text{p } 0,048\text{M} \quad 0,048\text{M} \quad 0,048\text{M}$$

$$\text{but } \text{pH} = -\log [\text{H}^+] = -\log [0,048] = 1,32$$



$$0,15\text{M} \quad 0,3\text{M} \quad 0,15\text{M}$$

$$\text{but } \text{pH} = -\log [\text{H}^+] = -\log [0,3] = 0,52$$

Qn

Calculate the concentration of

(i) HNO_3 with pH = 3,1

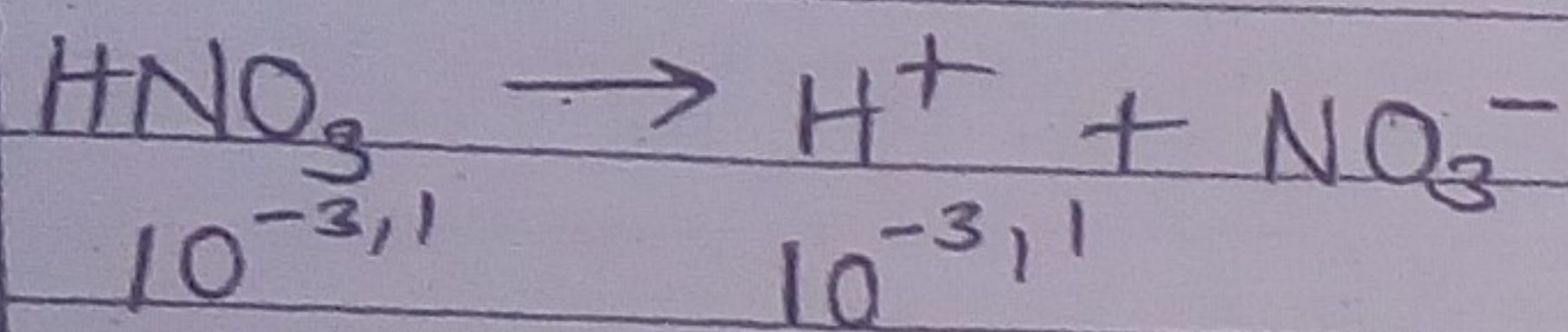
(ii) H_3PO_4 with pH = 1,7

Solution

$$\text{pH} = -\log [\text{H}^+] = 3,1$$

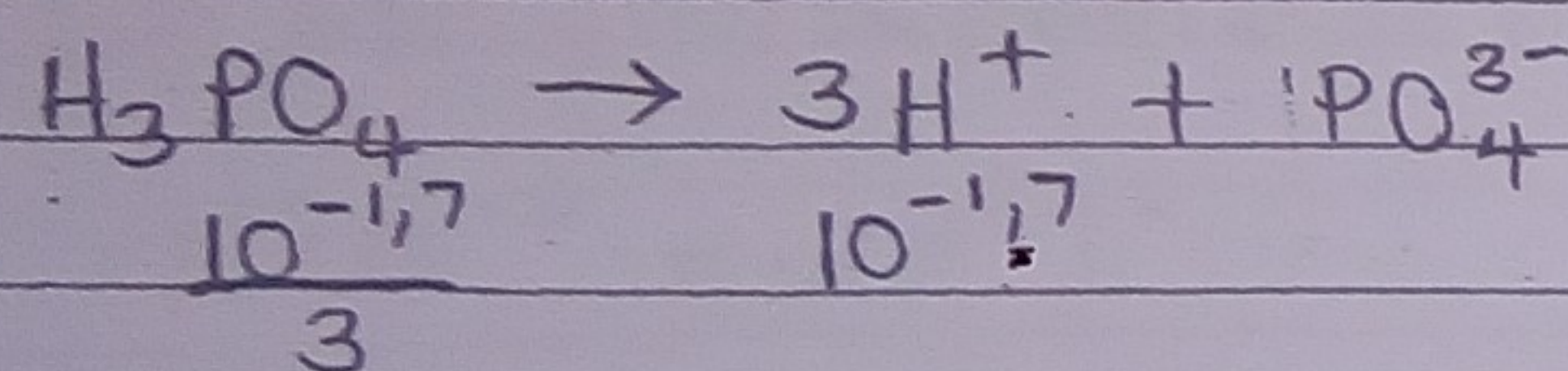
$$\log [\text{H}^+] = -3,1$$

$$[\text{H}^+] = 10^{-3,1}$$



$$[\text{HNO}_3] = 10^{-3,1} = 7,943 \times 10^{-4} \text{ M}$$

1) $\text{pH} = 1,7$
 $\therefore [\text{H}^+] = 10^{-1,7}$



$$\therefore [\text{H}_3\text{PO}_4] = 6,65 \times 10^{-3} \text{ M}$$

Calculations involving strong bases

When bases dissociate they release an OH^- ion

\therefore when calculating pH of a base, they is need for us to relate the conc of OH^- ions and concentration of H^+ ions. This can easily be done using

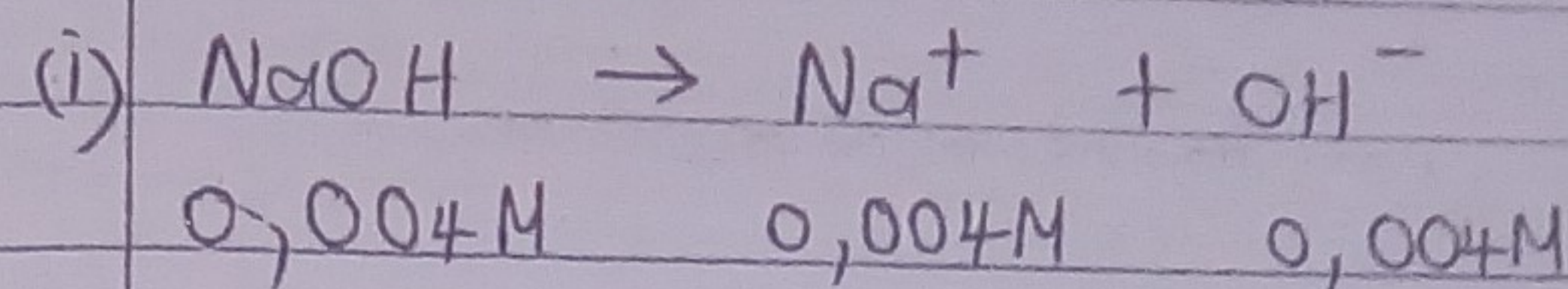
(i) $[\text{H}^+][\text{OH}^-] = 10^{-14}$

(ii) $\text{pH} + \text{pOH} = 14$

Qn

- (a) Calculate the pH of 0,004M NaOH
 (b) 0,02M $\text{Mg}(\text{OH})_2$

Solution

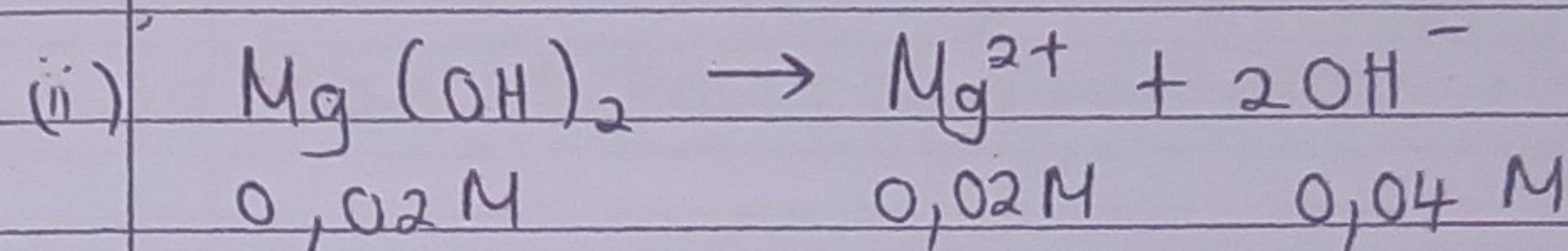


$$\therefore \text{pOH} = -\log [\text{OH}^-] = -\log 0,004 = 2,4$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + 2,4 = 14$$

$$\text{pH} = 11,6$$



$$\therefore \text{pOH} = -\log [\text{OH}^-] = -\log 0,04 = 1,40$$

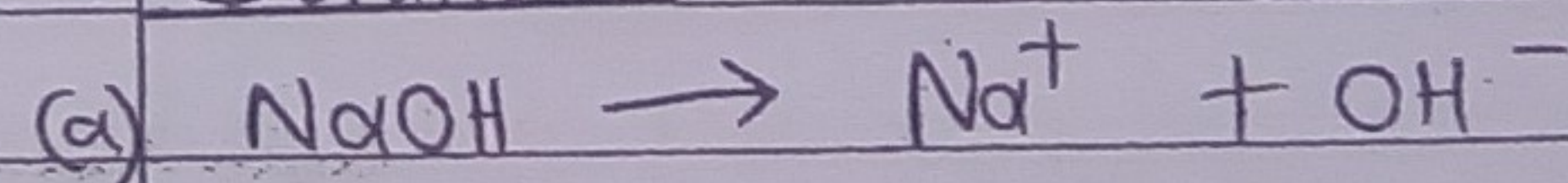
$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + 1,40 = 14$$

$$\text{pH} = 12,60 \text{ (2d.p)}$$

- Qn(a) Calculate the conc of NaOH with pH 11,8
 (b) $\text{Mg}(\text{OH})_2$ with pH 12,5

Solution



$$\text{pH} + \text{pOH} = 14$$

$$11,8 + \text{pOH} = 14$$

$$\text{pOH} = 2,2$$

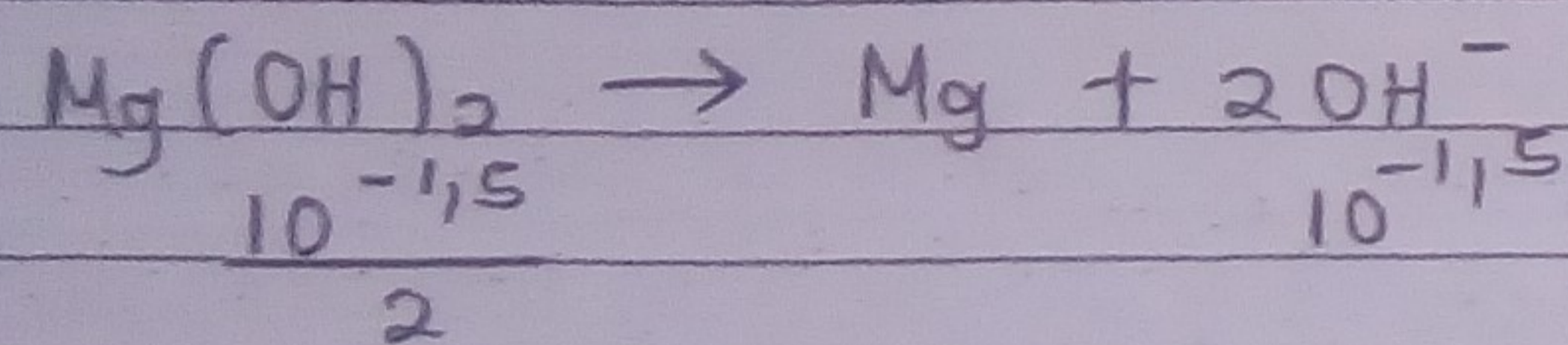
$$\text{pOH} = -\log [\text{OH}^-]$$

$$\therefore [\text{OH}^-] = 10^{-2,2}$$

$$[\text{OH}^-] = 6,3 \times 10^{-3}$$

(b) $pH + pOH = 14$
 $12,5 + pOH = 14$
 $pOH = 1,5$

$\therefore [OH^-] = 10^{-1,5}$
 $[OH^-] = 3,16 \times 10^{-2}$



$[Mg(OH)_2] = 1,58 \times 10^{-2}$

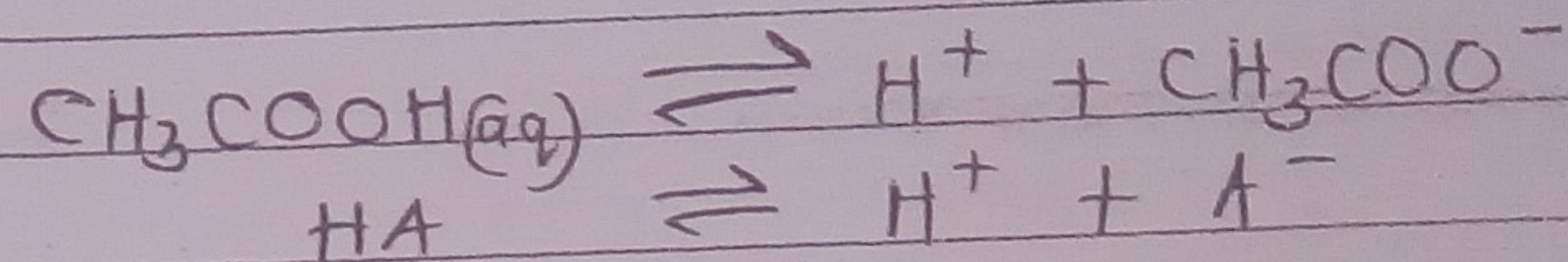
Acid dissociation constant

- When a weak acid is dissolved in water, it partially dissociates to give an H^+ ion
- The extent to which a weak acid dissociates can be given by the acid dissociation constant (K_a). Thus since K_a measures the way the acid dissociates, it implies that K_a measures the strength of an acid

The K_a expression

Consider

A weak monobasic or monoprotic acid, ethanoic acid CH_3COOH (N.B. A monobasic or monoprotic acid is an acid which dissociates to give one proton and it can be given a general formula, HA)



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- From the expression it implies the higher the K_a expression, the stronger the acid and the lower the K_a expression, the weaker the acid.
- The K_a expression can be used to calculate pH of a weak acid.
- When performing such calculations important assumptions have to be made

Assumptions when calculating pH using the K_a expression

- The conc of the weak acid does not change even after it has partially dissociated to give two ions
- The conc of H^+ and conc of A^- will be constant

Therefore using the above assumptions, the K_a expression above can then be represented as

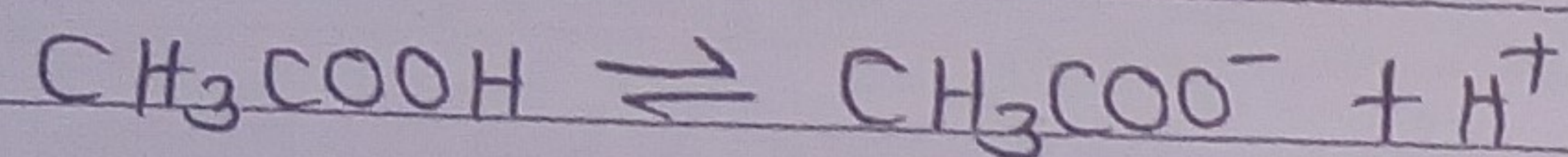
$$K_a = \frac{[H^+]^2}{[HA]}$$

Thus using the above expression H^+ can easily be made subject of the formula and pH can be calculated

Consider the following question

Calculate the pH of 0,05M CH_3COOH given that the acid dissociation constant (K_a) of CH_3COOH is $3,5 \times 10^{-4}$

Solution



$$\therefore K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

$$3,5 \times 10^{-4} = \frac{[\text{H}^+]^2}{0,05}$$

$$1,75 \times 10^{-5} = [\text{H}^+]^2$$

$$\text{pH} = -\log [\text{H}^+] = -\log \sqrt{1,75 \times 10^{-5}} = 4,76 \text{ R } 38$$

Calculate the pH of boric acid whose conc is 0,0073 M given that the acid dissociation constant of boric acid is $4,66 \times 10^{-4}$. Boric acid is a weak monobasic acid

Solution

Let Boric acid be HA

$$\therefore K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{but } [\text{H}^+] = [\text{A}^-]$$

$$\therefore K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

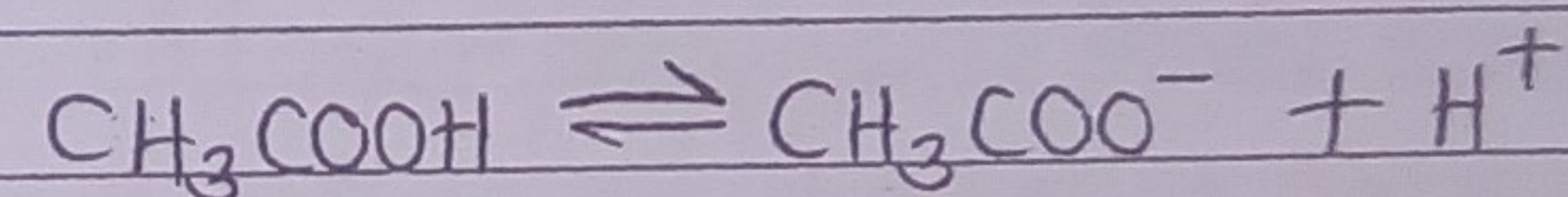
$$4,66 \times 10^{-4} = \frac{[\text{H}^+]^2}{0,0073 \text{ M}}$$

$$\therefore [\text{H}^+] = 1,84 \times 10^{-3}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 1,84 \times 10^{-3} = 2,73$$

Qn Calculate the conc of CH_3COOH whose pH is 3,45 given that the acid dissociation constant is $7,2 \times 10^{-4}$

Solution



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \sqrt{K_a [\text{CH}_3\text{COOH}]} \quad [\text{CH}_3\text{COOH}] = \frac{[\text{H}^+]^2}{K_a}$$

$$\text{but pH} = -\log [\text{H}^+] = 3,45$$

$$\therefore [\text{H}^+] = 10^{-3,45}$$

$$[\text{H}^+] = 3,55 \times 10^{-4}$$

$$\therefore \rightarrow [\text{CH}_3\text{COOH}] = \frac{(10^{-3,45})^2}{7,2 \times 10^{-4}}$$

$$= 1,75 \times 10^{-4}$$

pK_a

$$pK_a = -\log_{10} K_a$$

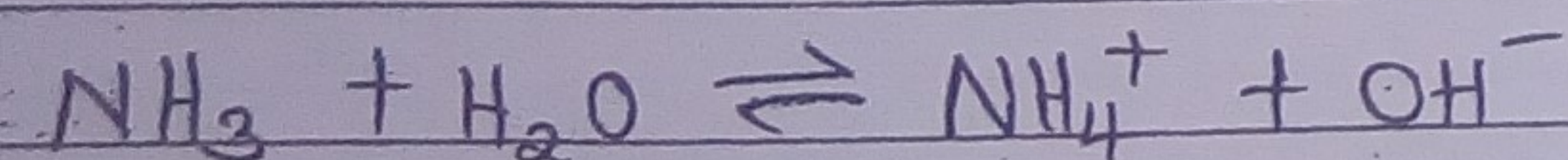
- pK_a is used to measure the strength of an acid
- The higher the pK_a value, the weaker the acid and the lower the pK_a value, the stronger the acid

The base dissociation constant, K_b

- When a weak base dissolves in water, it partially dissociates to give an OH^- ion
- The extent to which a weak base dissociates can be given by the base dissociation constant K_b
- Since K_b measures the way a base dissociates it implies that K_b measures the strength of a weak base

The K_b expression

Consider a weak base ammonia, the weak base dissociates to give one OH^- ion according to the following equation



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Clearly from the expression above the higher the pK_b value, the stronger the base, the lower the pK_b value, the weaker the base

- The K_b expression can be used to calculate the pH of a weak base
- When performing such calculations, important assumptions have to be made

Assumptions when calculating pH using pK_b

- (i) The conc of the weak base does not change even after the weak base has dissociated to give two ions
- (ii) We also assume that the conc of OH^- ions and the conc of, e.g. NH_4^+ will be constant

Using the above assumptions the pK_b expression can then be rearranged to

$$K_b = \frac{[OH^-]^2}{[NH_3]}$$

Thus using the above expression, OH^- can easily be made subject of the formula.

With the obtained value of conc of OH^- ions, the pOH can easily be calculated

$$pOH = -\log [OH^-]$$

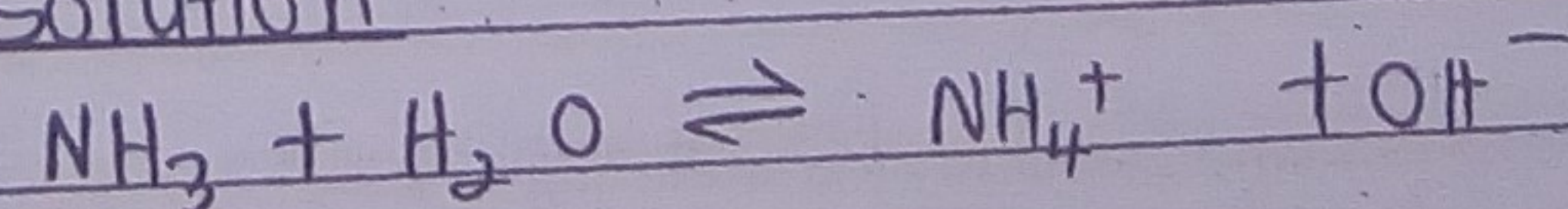
And using the relationship below pH can then be calculated

$$pH + pOH = 14$$

Qn

Calculate the pH of 0.03M ammonia given that the $K_b = 4.3 \times 10^{-5}$ at $25^\circ C$

Solution



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3]}$$

$$[\text{OH}^-] = \sqrt{K_b[\text{NH}_3]} =$$

$$[\text{OH}^-] = \sqrt{4,3 \times 10^{-5} \times 0,03}$$
$$= 1,14 \times 10^{-3}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1,14 \times 10^{-3}) = 2,94$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - 2,94$$

$$= 11,06$$

pK_b

- $\text{pK}_b = -\log K_b$

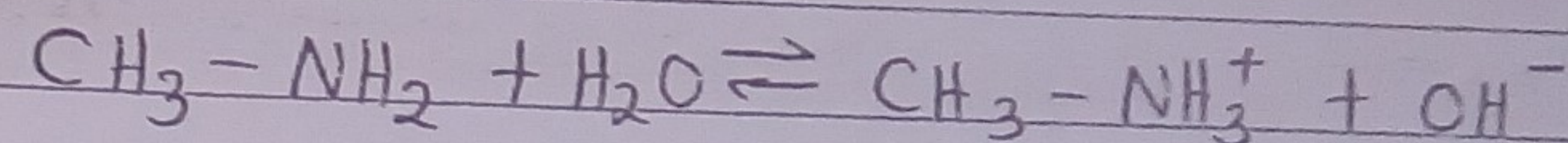
- pK_b measures the strength of a base.

- The higher the pK_b value, the weaker the base and the lower the pK_b value, the stronger the base.

Qn

Calculate the conc of a weak base methyl amine ($\text{CH}_3\text{-NH}_2$) whose pH is 8,42. Given that the pK_b value of ^{methyl amine} ~~ammonia~~ is 4,9. Calculate the conc of the weak base at 25°C

Solution



$$K_b = \frac{[\text{CH}_3\text{-NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{-NH}_2]}$$

$$K_b = \frac{[\text{OH}^-]^2}{[\text{CH}_3\text{-NH}_2]}$$

$$[\text{CH}_3\text{-NH}_2] = \frac{[\text{OH}^-]^2}{K_b}$$

but $\text{pK}_b = -\log K_b = 4,9$

$$K_b = 10^{-4,9}$$

$$K_b = 1,26 \times 10^{-5}$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - 8,42$$

$$\text{pOH} = 5,58$$

$$\text{pOH} = -\log [\text{OH}^-] = 5,58$$

$$-\log [\text{OH}^-] = 5,58$$

$$[\text{OH}^-] = 10^{-5,58}$$

$$[\text{OH}^-] = 2,63 \times 10^{-6}$$

$$[\text{NH}_3] = \frac{[\text{OH}^-]^2}{K_b} = \frac{(2,63 \times 10^{-6})^2}{1,26 \times 10^{-5}}$$

$$= 5,50 \times 10^{-7}$$

More Important Relationships During pH calculations

When calculating pH of weak solutions of weak acids and weak bases, the relationships below must be known

$$K_a \times K_b = K_w$$

It also implies that

$$pK_a + pK_b = pK_w$$

Lets consider an aqueous solution of ammonia which dissociates as follows:

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

Remember ammonium ion is acid and NH_3 is basic.

$$\text{Therefore } K_b(\text{NH}_3) = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$K_a(\text{NH}_4^+) = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

If we multiply K_a by K_b above

$$\frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}^+][\text{OH}^-] = K_w$$

Qustn

Calculate pH of ammonia whose conc is 0,005M given that the K_a of the ammonium ion is $4,8 \times 10^{-4}$.

Solution

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{OH}^-]^2}{[\text{NH}_3]}$$

$$\text{But } K_a \times K_b = K_w$$

$$\therefore K_b = 2,08 \times 10^{-11}$$

$$[\text{NH}_3] = \frac{[\text{OH}^-]^2}{K_b}$$

$$\sqrt{K_b[\text{NH}_3]} = [\text{OH}^-]$$

$$3,22 \times 10^{-7} = [\text{OH}^-]$$

$$-\log [\text{OH}^-] = -\log 3,22 \times 10^{-7} = \text{pOH}$$

$$\text{pOH} = 6,49$$

$$\text{pH} = 14 - 6,49$$

$$= 7,51$$

BUFFERS

Dfn A buffer is a solution which resists pH change when a little acid or base is added to it.

Where we have two different types of buffers which are:

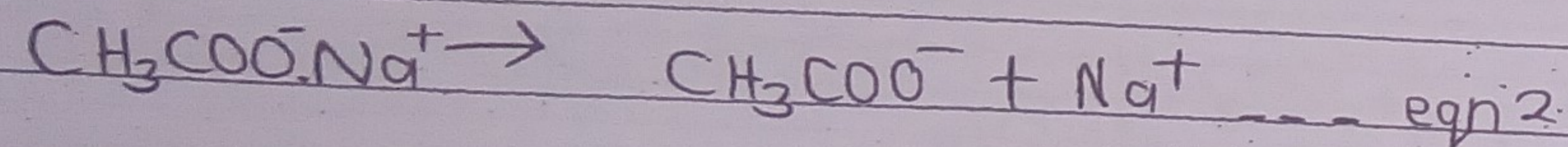
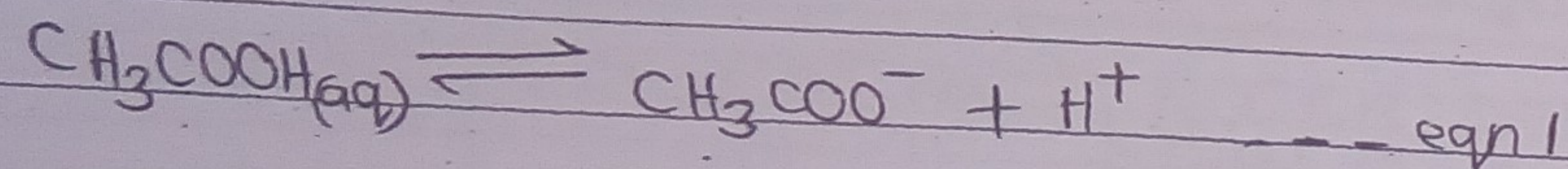
- (i) The acidic buffer
- (ii) The basic or alkaline buffer

Acidic buffer

An acidic buffer is a solution which is made up of a weak acid and a salt of the weak acid and it resists pH change when a little acid or little base is added to it.

solution containing ethanoic acid (weak acid) and sodium ethanoate (the salt)

Therefore in the solution the following occurs



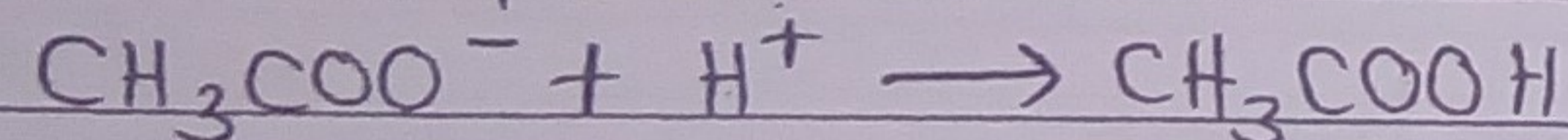
How the buffer works

o When explaining how a buffer works, equations are used

Upon the addition of a little acid

The added H^+ reacts with the COO^- from the salt

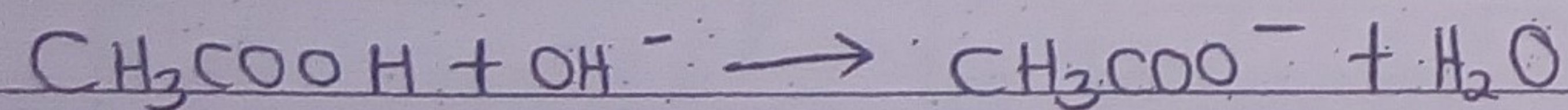
Eqn 1 shifts to the left due to the increase in the H^+ ions



NB, When writing eqns of the rxns $\bar{w}c$ will be occurring as the buffer works we do not use the reversibility sign

Upon the addition of a little base

When a little base is added it reacts with ethanoic acid which is in high concentration.

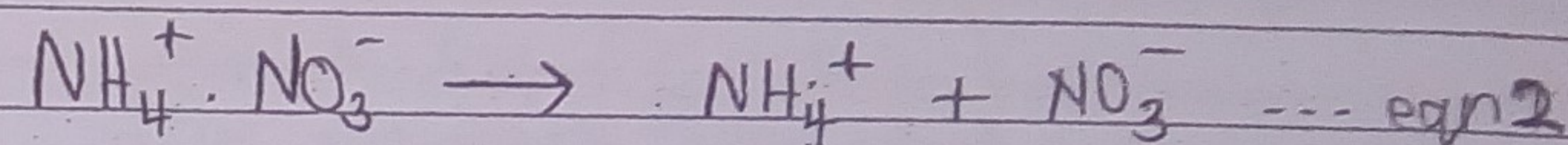
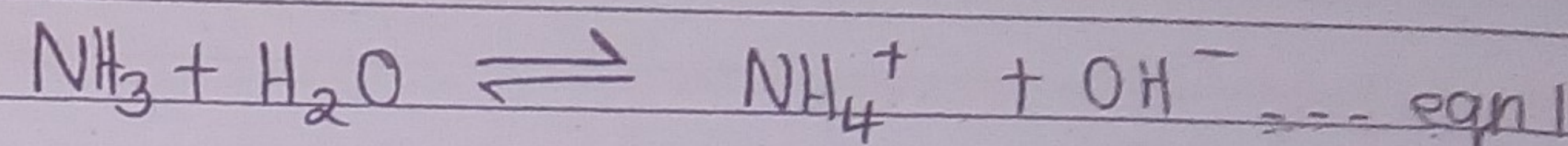


Basic buffer

n: It is a sltn $\bar{w}c$ is made up of a weak base and a salt of a weak base and it resists pH change when a little acid or little base is added to it.

e.g. a solution containing ammonia (weak base) and ammonium nitrate (salt of the weak base).

Therefore in the solution the following occurs

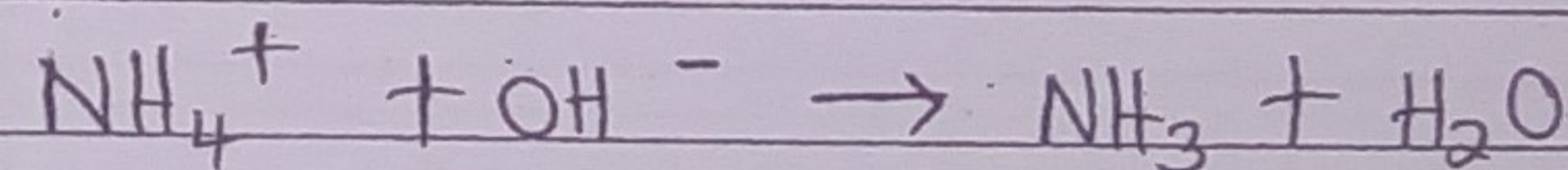


How the buffer works

Upon the addition of a little base

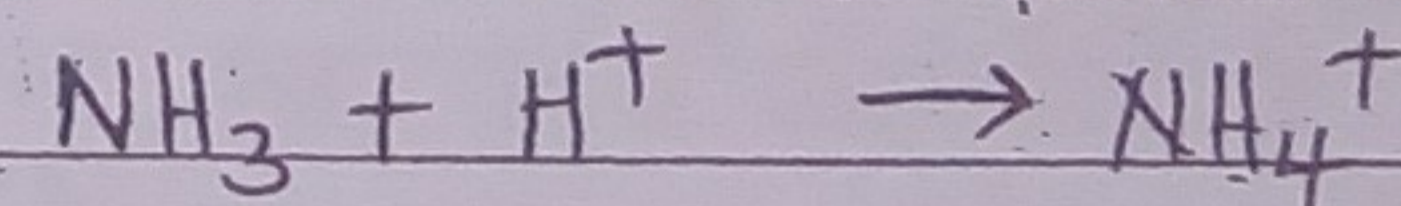
Eqn 1 shifts to the left

The added OH^- reacts with the NH_4^+ mainly from the salt



Upon the addition of a little acid

The added acid will react with the base NH_3 $\bar{w}c$ is in high conc



Applications of buffers

- Buffers play an important role in many industrial rxns and also in animals.

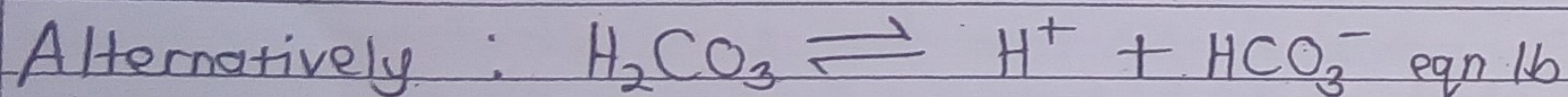
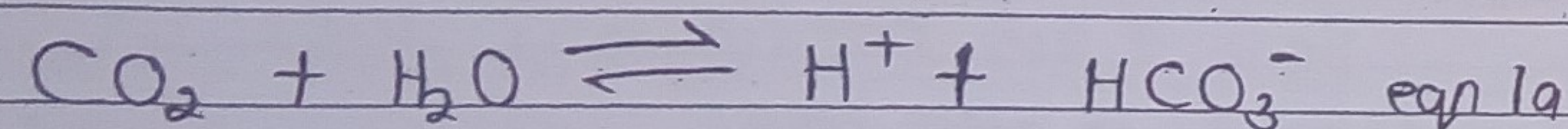
- In both situations stated, the buffer will be maintaining the pH at a certain level, for example in humans, different buffers maintain the pH at a pH range of about 7.35 to 7.45

Examples of buffers present in the blood include

- i) hydrogen carbonate ions (HCO_3^-)
- ii) dihydrogen phosphate ions (H_2PO_4^-) and ^{hydrogen} phosphate ions (HPO_4^{2-})

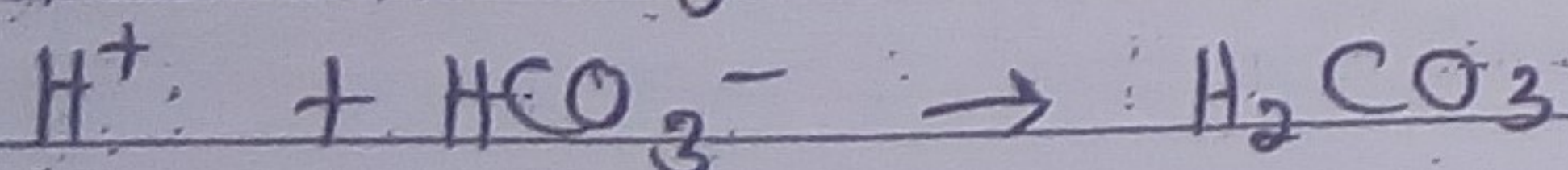
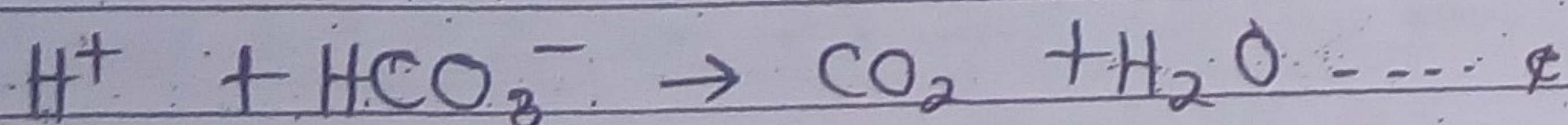
Consider the HCO_3^- ions

CO_2 produced in the human body cells combines with water to produce a buffer as shown by the equation below



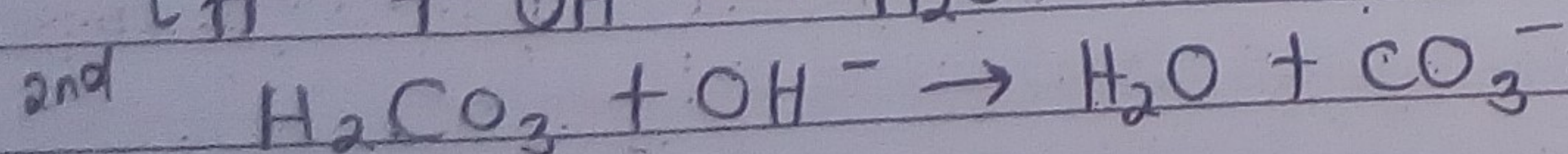
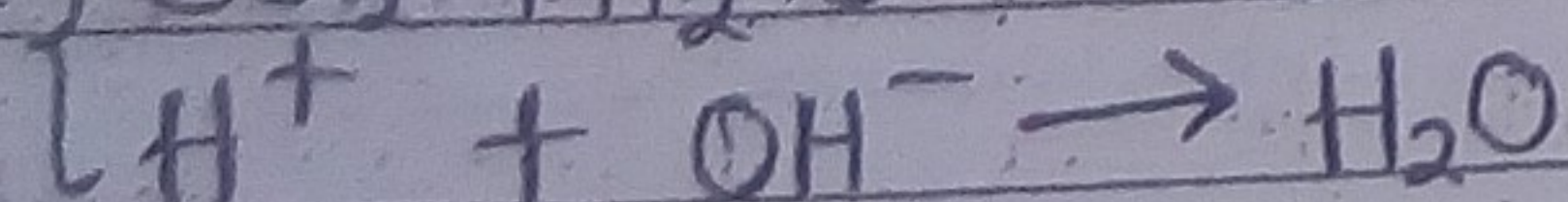
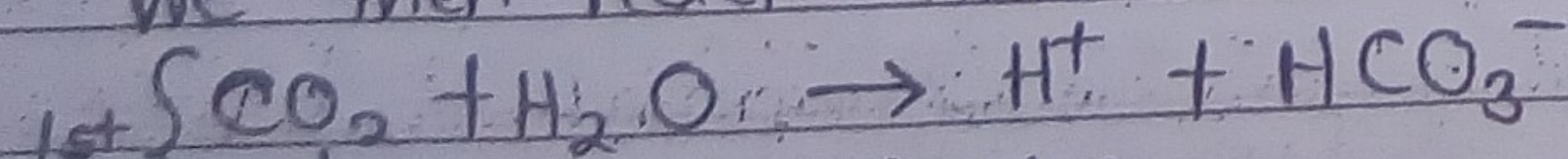
When the conc of H^+ increases in the blood i.e when a little acid added

Equilib shifts to the left. Effect of the increased H^+ is minimized



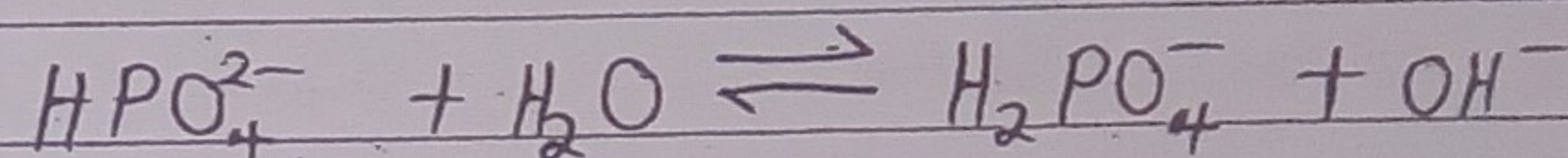
When the conc of OH^- increases in the blood i.e when a little base is added

Equilib shifts to the right in Eqn 1a & b to produce more H^+ we then react with excess OH^- in the solution

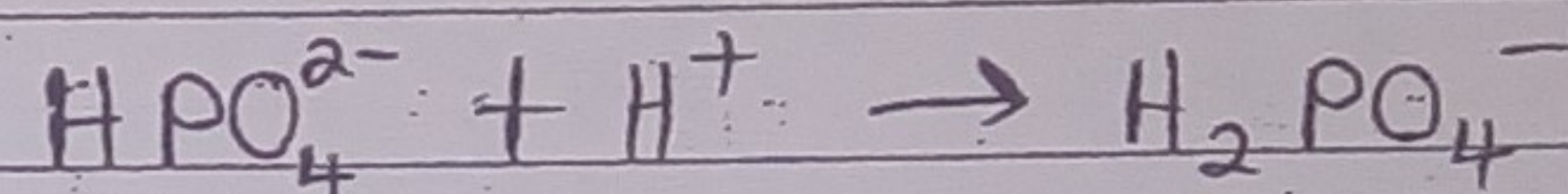


The Phosphate buffer system ($\text{HPO}_4^{2-} / \text{H}_2\text{PO}_4^-$)

- it plays a role in maintaining pH of blood

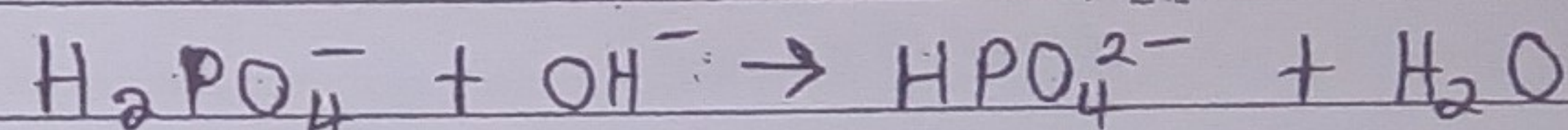


When a little H^+ is added



When a little OH^- is added

Eqn 1 shifts to the left



Calculations involving buffers

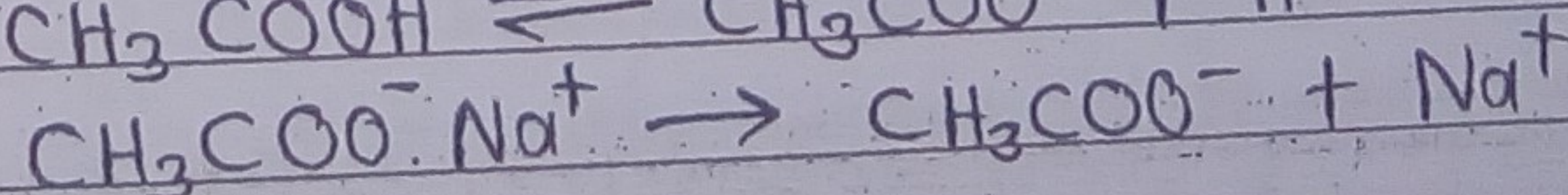
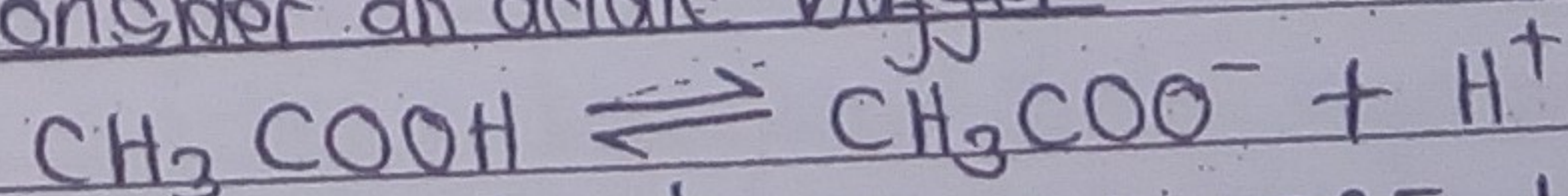
Acidic buffer

Since an acidic buffer is made from a weak acid and a salt of a weak acid, the K_a expression can be used to calculate the pH of the solution.

But when performing the calculations, some assumptions have to be made.

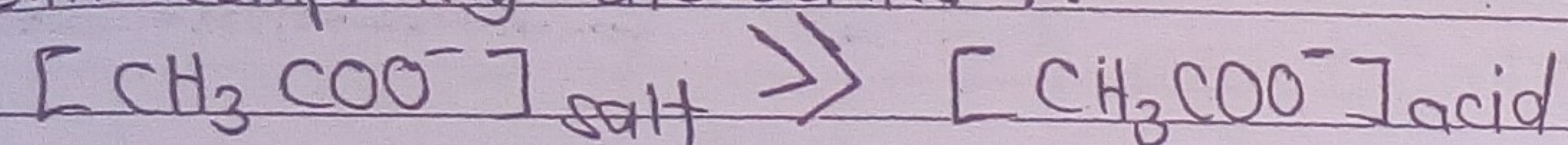
Assumptions when calculating pH of a buffer

Consider an acidic buffer



$$[\text{CH}_3\text{COO}^-]_{\text{Total}} = [\text{CH}_3\text{COO}^-]_{\text{acid}} + [\text{CH}_3\text{COO}^-]_{\text{salt}}$$

the salt completely dissociates:



$$[\text{CH}_3\text{COO}^-]_{\text{total}} \approx [\text{CH}_3\text{COO}^-]_{\text{salt}} = \frac{[\text{salt}]}{[\text{CH}_3\text{COOH}]}$$

| | |
|------------|---|
| Assumption | $[\text{CH}_3\text{COO}^- \cdot \text{Na}^+]_{\text{salt}} = [\text{CH}_3\text{COO}^-]$ |
|------------|---|

it implies that $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

making $[\text{H}^+]$ subject of formula:

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Introducing logs

$$\log [\text{H}^+] = \log K_a + \log \left(\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right)$$

Introducing negatives

$$-\log [\text{H}^+] = -\log K_a + -\log \left(\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right)$$

$$\therefore \text{pH} = \text{p}K_a + \log \left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

Assumption 2

Concentration of the acid remains constant

Question

Calculate the pH of a solution made by mixing 0,05M ethanoic acid and 0,35M CH_3COONa , sodium ethanoate given that the acid dissociation constant of CH_3COOH is $3,8 \times 10^{-5}$.

Solution

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

$$\begin{aligned} \text{p}K_a &= -\log K_a \\ &= -\log 3,8 \times 10^{-5} \\ &= 4,42 \end{aligned}$$

$$\text{pH} = 4,42 + \log \left(\frac{0,35}{0,05} \right)$$

$$\text{pH} = 5,27$$

Qn. Calculate the pH of a solution made when 6g of sodium ethanoate is dissolved in 50cm^3 of 0,001M ethanoic acid given that the acid dissociation constant of CH_3COOH is $3,8 \times 10^{-5}$.

Solution

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

$$\begin{aligned} \text{p}K_a &= -\log K_a \\ &= -\log 3,8 \times 10^{-5} \\ &= 4,42 \end{aligned}$$

$$n(\text{salt}) = \frac{6g}{82} = 0,0732$$

$$\therefore [\text{salt}] = \frac{0,0732}{0,050\text{dm}^3} = 1,46\text{M}$$

$$\text{pH} = 4,42 + \log\left(\frac{1,46}{0,001}\right)$$

$$\text{pH} = 7,59$$

NB When a little acid or little base is added to a buffer solution, the buffer resists a significant change in pH. But practically the pH value of the solution changes slightly. This is going to be demonstrated by the question below:

Calculate the pH change which occurs when 1cm^3 of 1M sodium hydroxide is added to a solution which was made by mixing $0,09\text{M}$ sodium ethanoate and $0,007\text{M}$ ethanoic acid given that the acid dissociation constant of CH_3COOH is $3,8 \times 10^{-5}$

Solution

Steps

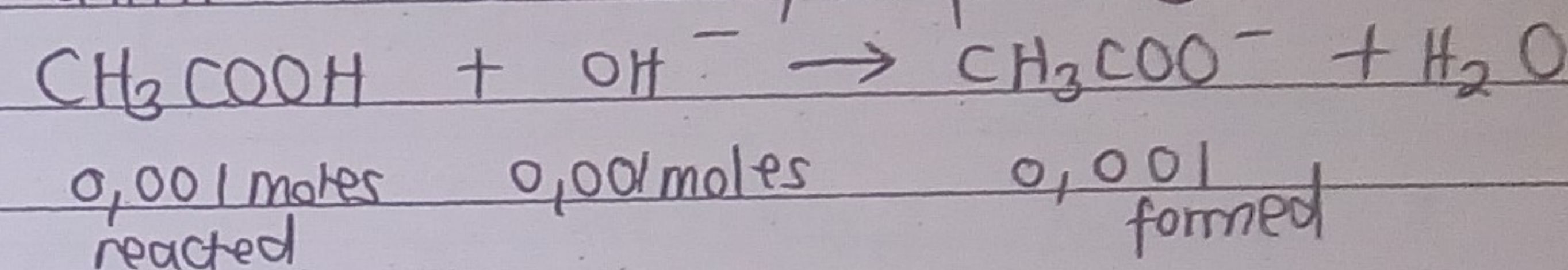
1. Calculate pH of the buffer
2. Then calculate the new pH after the addition of 1cm^3 of base
3. To obtain the pH change subtract the pH in step 1 from pH in 2

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{salt}]}{[\text{Acid}]}\right)$$

$$\text{pH} = -\log 3,8 \times 10^{-5} + \log\left(\frac{0,09}{0,007}\right)$$

$$\text{pH} = 5,53$$

Step 2 When a little base is added, the following rxn occurs



$$\begin{aligned} n(\text{CH}_3\text{COOH})_{\text{remain}} &= 0,007 - 0,001 \\ &= 0,006 \text{ moles} \end{aligned}$$

$$[\text{CH}_3\text{COOH}] = 0,006 \text{ mol dm}^{-3}$$

$$\begin{aligned} n(\text{CH}_3\text{COO}^-) &= 0,09 + 0,001 \\ &= 0,091 \text{ moles} \end{aligned}$$

$$[\text{CH}_3\text{COO}^-] = 0,091 \text{ mol dm}^{-3}$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{salt}]}{[\text{Acid}]}\right)$$

$$\text{pH} = -\log 3,8 \times 10^{-5} + \log\left(\frac{0,091}{0,006}\right)$$

$$\text{pH} = 5,60$$

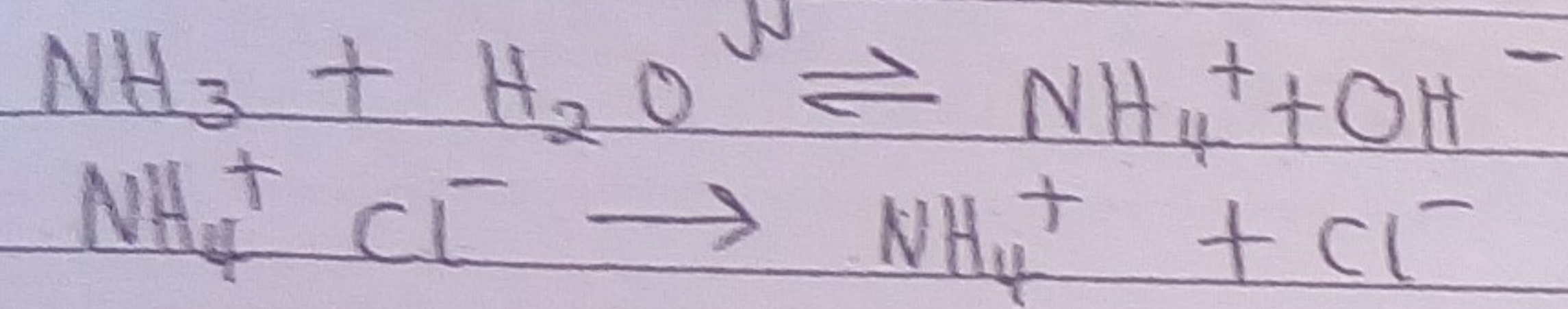
$$\text{Step 3} \quad 5,60 - 5,53 = 0,07$$

Basic buffers

Since a basic buffer is made from a weak base and a salt of a weak base, it therefore means the K_b expression can be used to calculate pH of the solution, but when performing the calculations some assumptions can be made

assumptions when calculating pH of a basic buffer

Consider basic buffer



$$[\text{NH}_4^+]_{\text{total}} = [\text{NH}_4^+]_{\text{base}} + [\text{NH}_4^+]_{\text{salt}}$$

Since the salt completely ionises it implies

$$[\text{NH}_4^+]_{\text{salt}} \gg [\text{NH}_4^+]_{\text{base}}$$

$$\therefore [\text{NH}_4^+]_{\text{total}} \approx [\text{NH}_4^+]_{\text{salt}} = [\text{salt}]$$

Thus assume 1 $[\text{NH}_4^+ \text{Cl}^-] = [\text{NH}_4^+]$

It \therefore implies that $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

making $[\text{OH}^-]$ subject of formula

$$[\text{OH}^-] = \frac{K_b [\text{NH}_3]}{[\text{NH}_4^+]}$$

Introducing logs

$$\log [\text{OH}^-] = \log K_b + \log \left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

Introducing negatives

$$-\log [\text{OH}^-] = -\log K_b + -\log \left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

$$\text{pOH} = \text{p}K_b + \log \left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \right)$$

but $\text{pOH} = 14 - \text{pH}$

$$\therefore 14 - \text{pH} = \text{p}K_b + \log \left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \right)$$

$$\text{pH} = 14 - \text{p}K_b - \log \left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \right)$$

Assumption 2: Concentration of the base remains constant

Qn Calculate the pH of a solution made by mixing 0,04 M ammonia and 0,8 M ammonium chloride given that the K_b of ammonia is $7,8 \times 10^{-4}$

Solution

$$\text{pH} = 14 - \text{p}K_b - \log \left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \right)$$

$$\text{pH} = 14 - (-\log 7,8 \times 10^{-4}) - \log \left(\frac{0,8}{0,04} \right) = 9,59$$

$$\text{pH} = 9,59$$

Question

Calculate the pH of the solution made by dissolving 40g of ammonium chloride in 150 cm³ of 0,025 M ammonia given that the K_b of ammonia is $7,8 \times 10^{-4}$

Solution

$$\text{pH} = 14 - \text{p}K_b - \log \left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]} \right)$$

$$n(\text{salt}) = \frac{40\text{g}}{53,5} = 0,75$$

$$[\text{salt}] = \frac{0,75}{0,1} = 4,98\text{M}$$

$$pH = 14 - (-\log 7,8 \times 10^{-4}) - \log \left(\frac{4,98}{0,025} \right)$$

$$pH = 8,59$$

Question

30cm³ of 0,5M ammonia was mixed with 20cm³ of 1,5M ammonium chloride, to form a buffer. Calculate the pH of the solution given that K_b is 7,8 × 10⁻⁴

Solution

$$pH = 14 - pK_b - \log \left(\frac{[salt]}{[Base]} \right)$$

$$n(salt) = 1,5 \times 0,020 = 0,03 \text{ mole}$$

$$[salt] = \frac{0,03}{0,05 \text{ (total vol)}} = 0,6M$$

$$n(Base) = 0,5 \times 0,030 = 0,015$$

$$[Base] = \frac{0,015}{0,05} = 0,3$$

$$pH = 14 - (-\log 7,8 \times 10^{-4}) - \log \left(\frac{0,6}{0,3} \right)$$

$$pH = 10,59$$

Calculate the pH change when 5cm³ of 1M HCl is placed in a solution made by mixing 50cm³ of 0,03M ammonia and 30cm³ of 0,7M ammonium chloride given that the base dissociation constant of ammonia is 7,8 × 10⁻⁴.

Solution

$$pH = 14 - pK_b - \log \left(\frac{[salt]}{[Base]} \right)$$

$$n(salt) = 0,7M \times 0,03 = 0,021 \text{ moles}$$

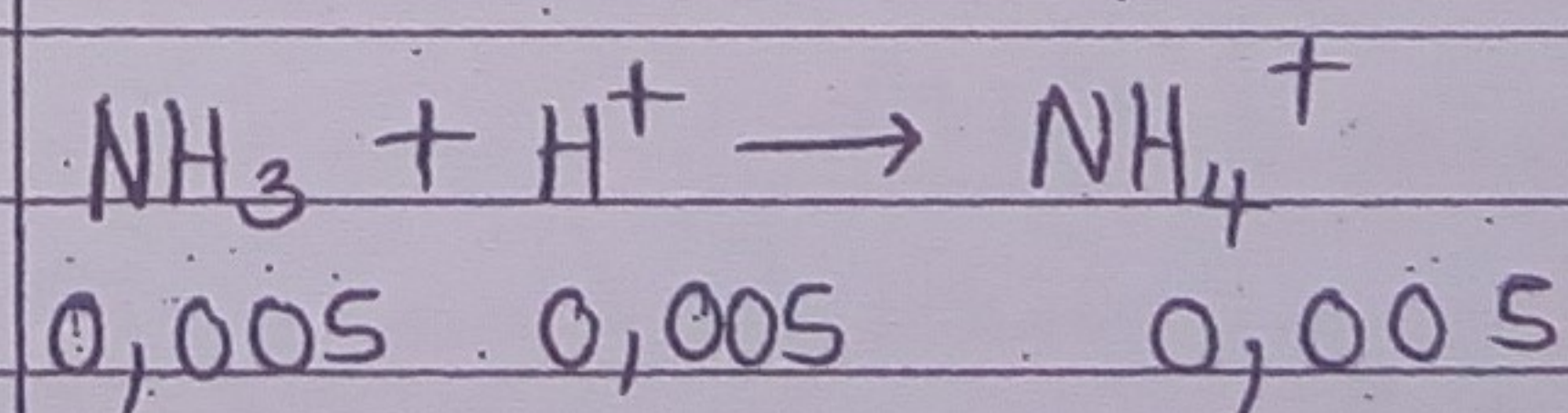
$$[salt] = \frac{0,021}{0,08} = 0,2625M$$

$$n(base) = 0,03 \times 0,050 = 0,0015$$

$$[base] = \frac{0,0015}{0,08} = 0,01875M$$

$$pH = 14 - (-\log 7,8 \times 10^{-4}) - \log \left(\frac{0,2625}{0,01875} \right)$$

$$pH = 9,75$$



$$n(NH_3) \text{ remain} = 0,01875 - 0,005 = 0,01375$$

$$[NH_3] = 0,01375 \text{ mol dm}^{-3}$$

$$n(\text{NH}_4^+) = 0,2625 + 0,005$$

$$= 0,2675$$

$$[\text{NH}_4^+] = 0,2675 \text{ mol dm}^{-3}$$

$$\text{pH} = 14 - (-\log 7,8 \times 10^{-4}) - \log \left(\frac{0,2675}{0,01375} \right)$$

$$\text{pH} = -9,60 + 9,75$$

$$= 0,142893052$$

$$= 0,14$$

COMPILED BY

.. the DIRECTOR.. 0772666148
0712105452

Indicators and Titrations

During titrations, indicators are used to determine the end point of a given titration.

A titration is the dropwise release of a reactant into the reacting solution so as to find the exact point when the two solutions have completely reacted together.

Where we have different types of titrations which use different types of indicators, some of them include:

- (i) Acid/Base Titrations
- (ii) Redox Titrations
- (iii) Iodine Titrations

Acid/Base Titrations

> These use acid/base indicators

• An acid/base indicator is a mixture which changes colour at a specific pH range. Thus it can also be defined as a substance which changes colour at different hydrogen ion concentration.

Examples of acid/base titration indicators include:

- (i) phenolphthalein
- (ii) bromothymol blue
- (iii) methyl orange

| Indicator | pH range | Colour in | | Approx end point pH |
|------------------|----------|------------|-------------|---------------------|
| | | Acid | Base | |
| phenolphthalein | 8,2-10 | colourless | Pink/violet | 9,3 |
| methyl orange | 3,2-4,4 | red | yellow | 3,7 |
| bromothymol blue | 6,0-7,6 | yellow | blue | 7 |

REDOX TITRATIONS

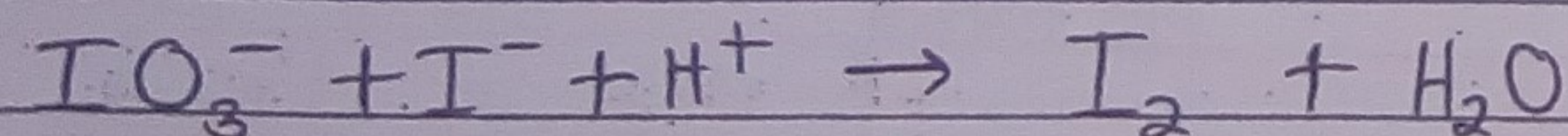
- Usually done in the presence of potassium permanganate and potassium dichromate.
- Reactions which involve potassium permanganate and potassium dichromate usually have no indicators.
- We say potassium permanganate and potassium dichromate are self indicators

| Self indicator | Initial colour | End point colour |
|--------------------------------------|----------------|----------------------|
| Potassium permanganate $KMnO_4$ | purple | permanent pale pink |
| Potassium dichromate $K_2Cr_2O_7$ | orange | permanent pale green |

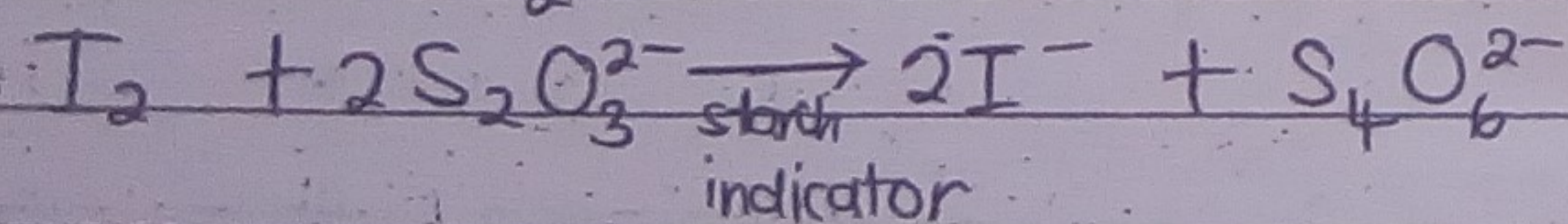
IODINE TITRATIONS

- These occur when iodine is liberated from any stated or given reaction.
- The liberated iodine is then titrated with the $S_2O_3^{2-}$ ions (this sulphate ions) in the presence of an indicator i.e. freshly prepared starch indicator

Consider



the liberated I_2 above then rxns as follows



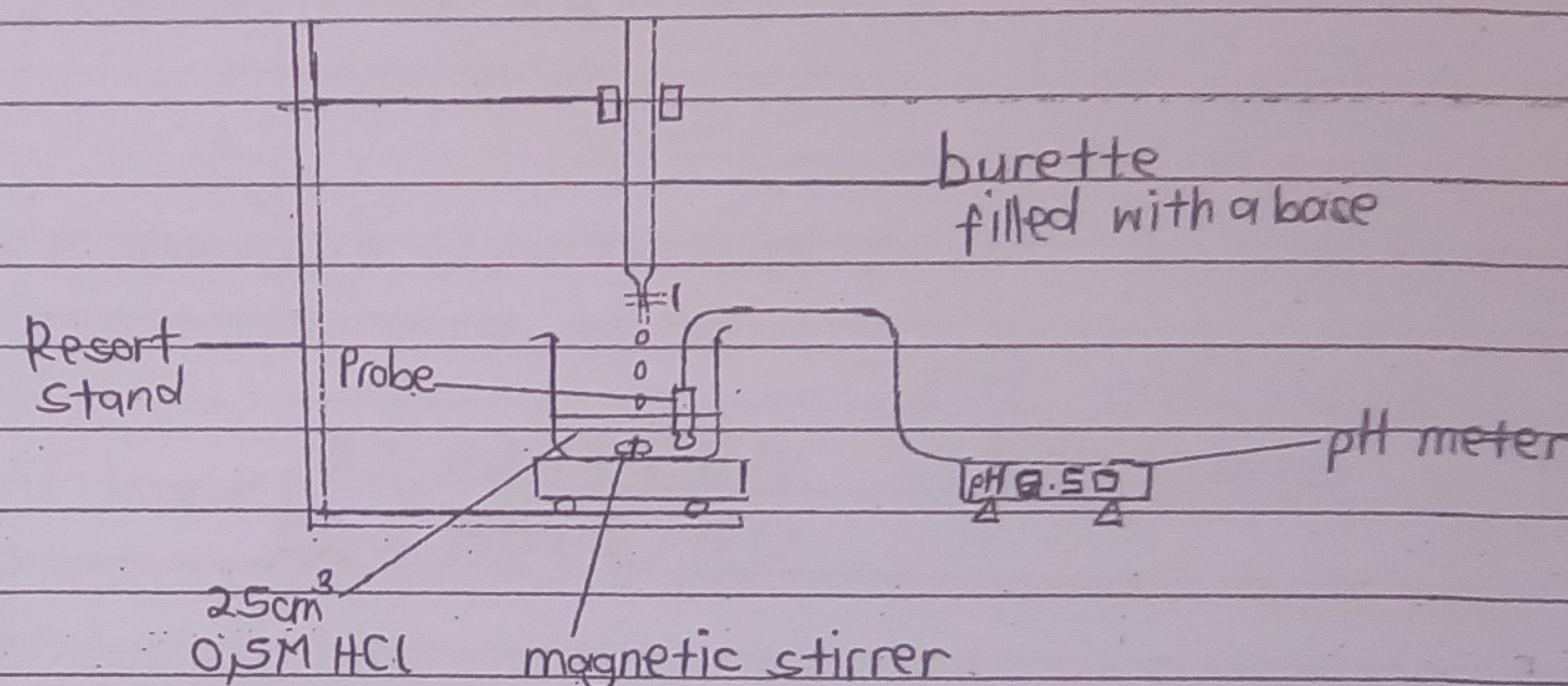
In the titration flask, upon the addition of a few drops of starch indicator, a blue-black or dark blue colour is

observed, signifying the presence of iodine in the solution.

At the end of the titration, all the iodine would have reacted and the colour in the titration will be off white

Titration curves for Acid/Base Titrations

- For us to be able to plot a titration curve, the pH changes during the titrations have to be monitored
- The process of monitoring pH change can be done using the apparatus below.



Method

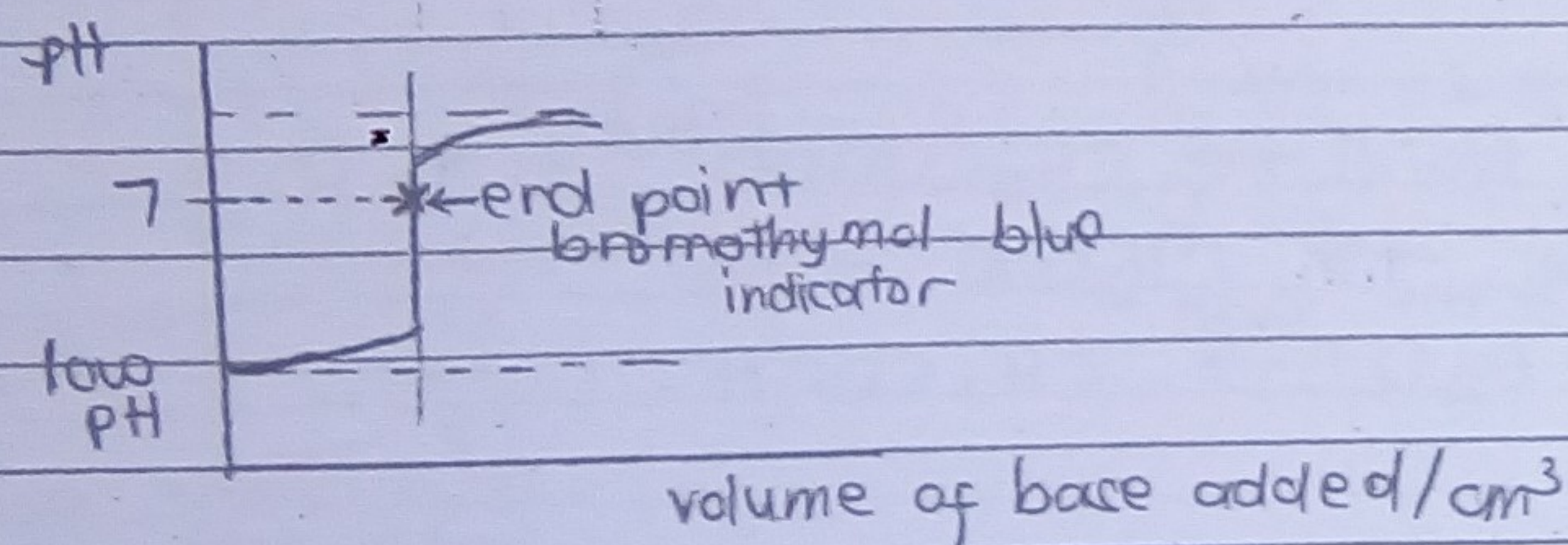
- Set up the apparatus as shown above
- Switch on the magnetic stirrer
- Deliver the base at a constant slow rate from the burette into the acid in the beaker
- Record the different pH values at different volumes i.e. at 0.1 cm^3 intervals.
- Stop when the pH has reached a nearly constant high value
- A graph of pH against volume of a base added can then be plotted, and different titration curves can be obtained

The titration curves obtained can be from:

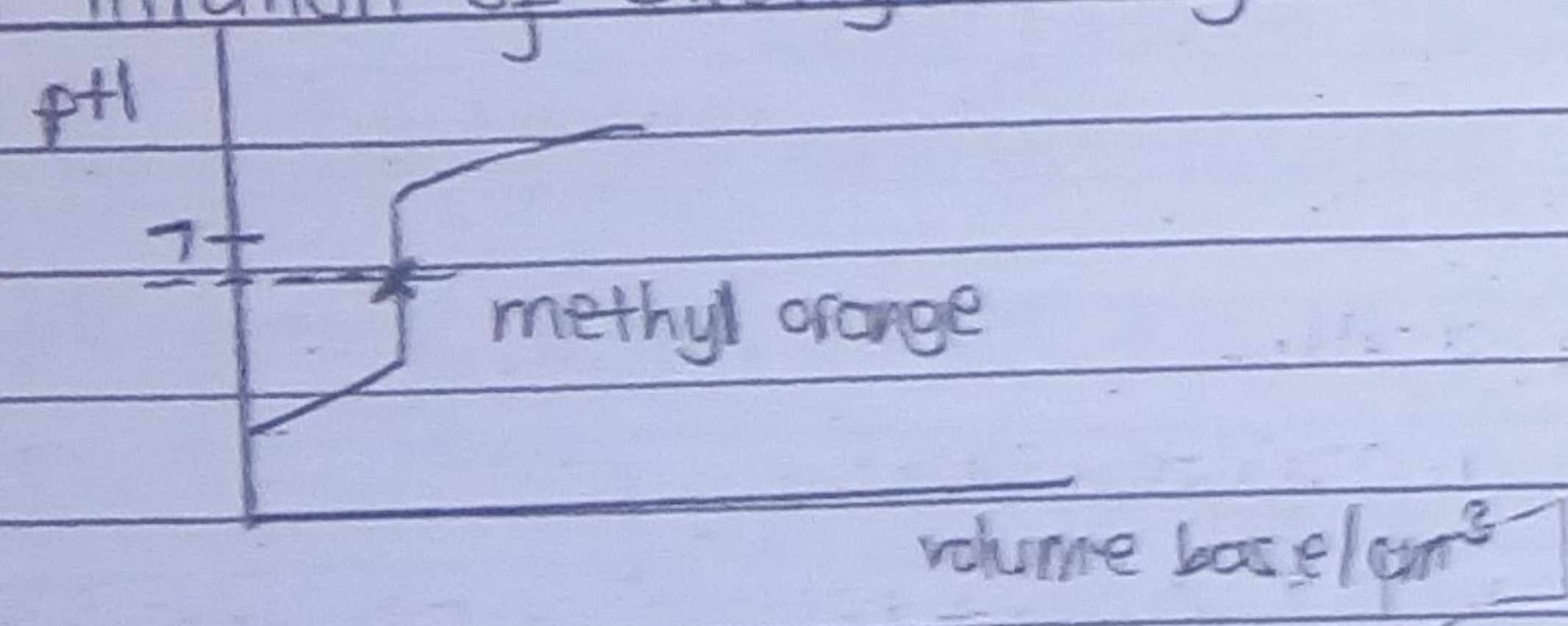
- * strong acid and strong base
- * strong acid and weak base
- * weak acid and strong base
- * weak acid and weak base

- In the four given titrations above, usually the ^(substance) one which is mentioned first is the one which will be in the beaker.
- Therefore in all the four scenarios given above, the starting pH on the p titration curve will be acidic

Consider titration of strong acid against strong base

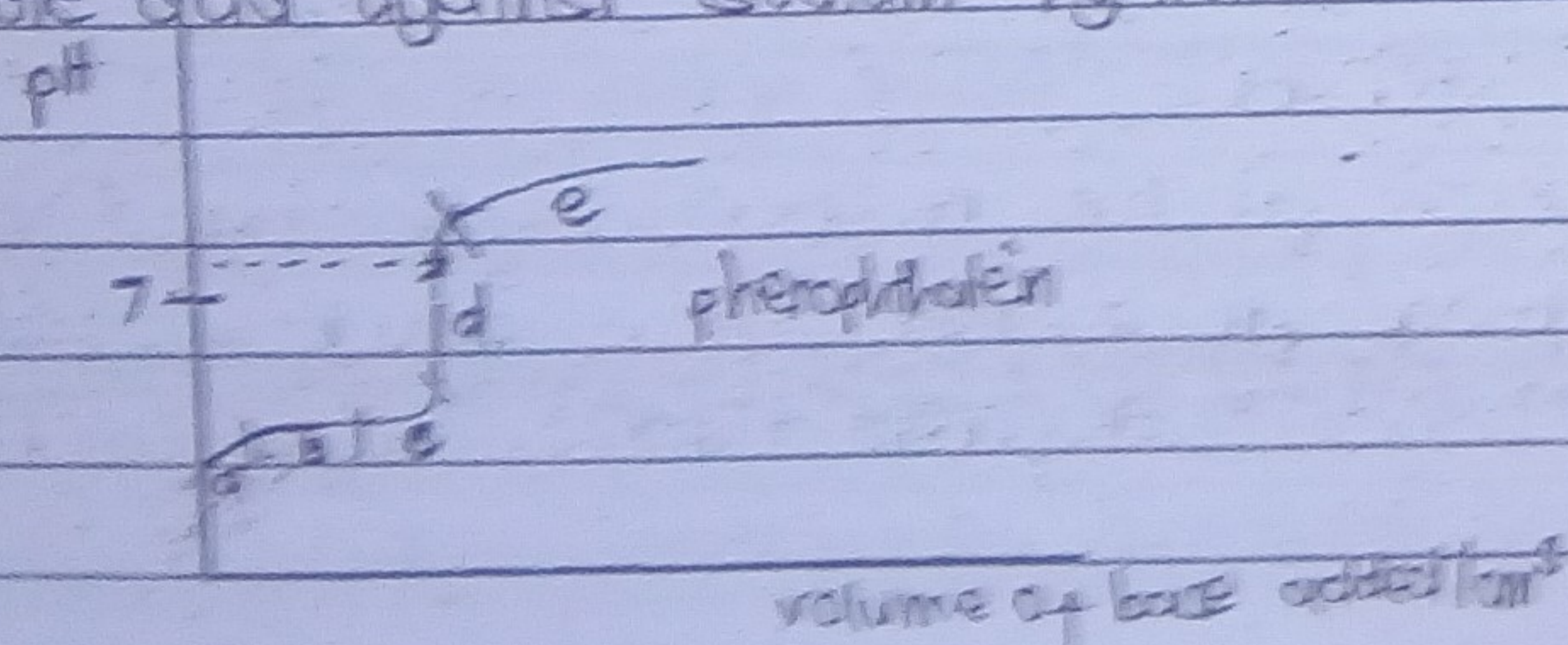


Consider titration of strong acid against weak base



Weak acid and strong base

e.g. ethanoic acid against sodium hydroxide



Explaining the graph

Region a

- Upon the addition of a few drops of a base, the pH gradually increases as the base is being neutralized to form a salt



Region b

- Upon the addition of drops of a base, the pH remains almost constant. This is because the solution will be acting as a buffer
- The formed salt from the neutralization rxn, i.e. sodium ethanoate together with the weak acid already present in the beaker i.e. CH_3COOH , a buffer is formed.

- Eventually the buffer will reach its maximum buffer capacity (maximum amt of acid or base can be added before the buffer pH starts to change).

Region c

- The maximum buffer capacity of the solution would have been exceeded hence, upon the addition of drops of a base, pH gradually increases.

Region d

- Upon the addition of a single drop of a base, there is going to be a sharp change in pH. This is because all the acid would have been neutralized by the base and the base will already be in excess.
- Halfway this region signifies the end point

Region e

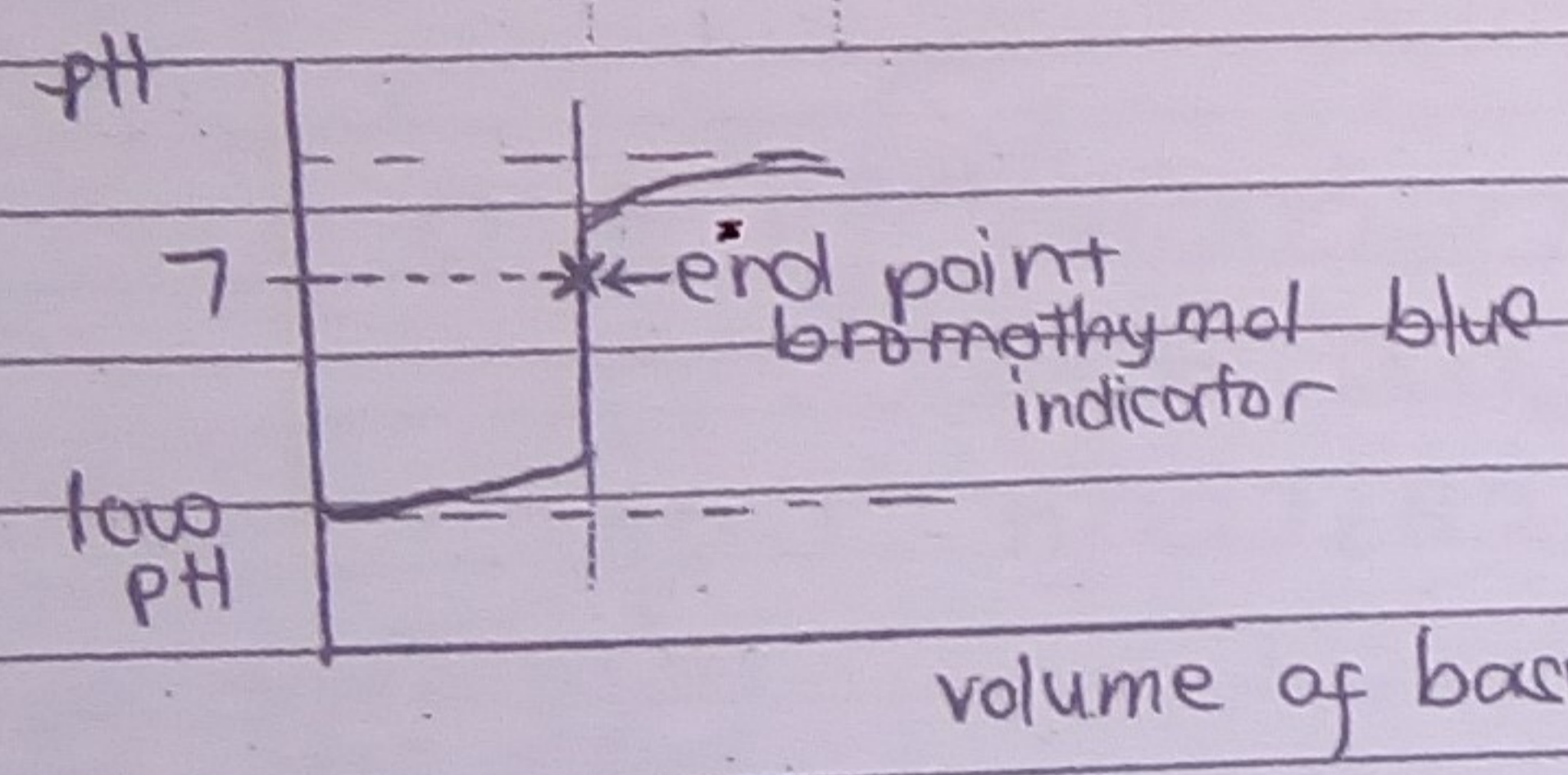
- Upon the addition of more drops of a base, the pH continues to rise until it reaches a constant

The titration curves obtained can be from:

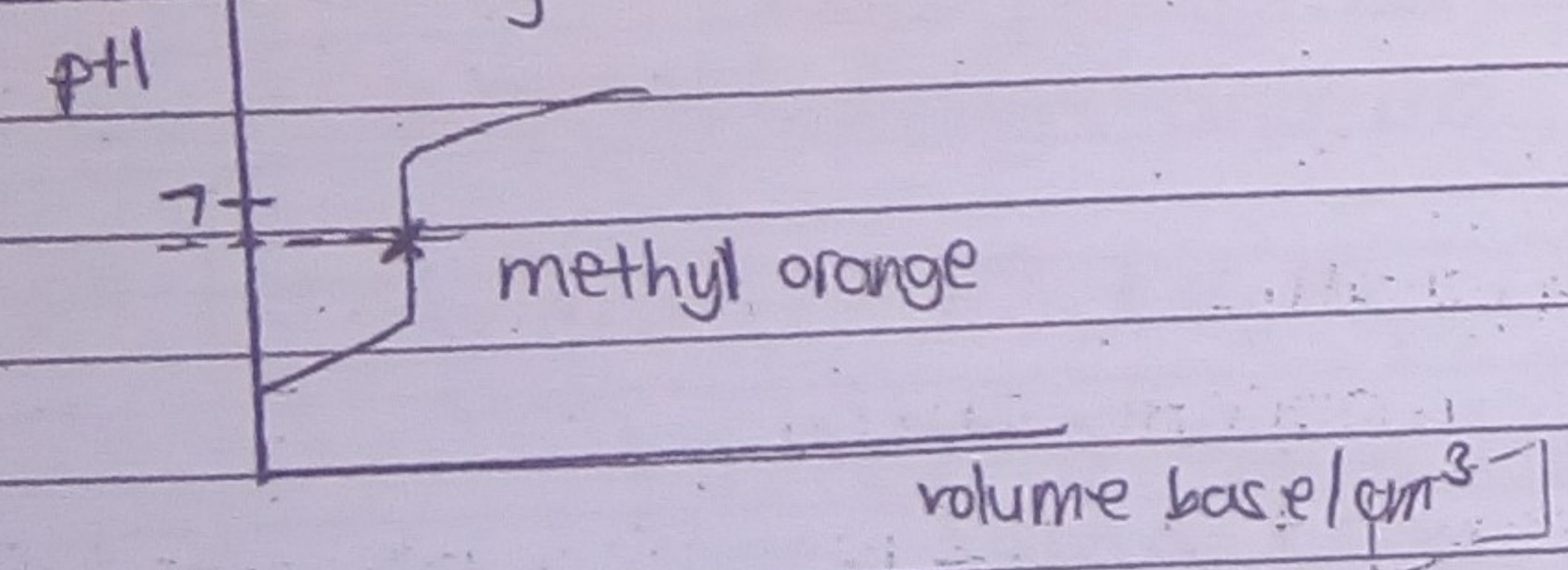
- * strong acid and strong base
- * strong acid and weak base
- * weak acid and strong base
- * weak acid and weak base

- In the four given titrations above, usually the ^(substance) one which is mentioned first is the one which will be in the beaker.
- Therefore in all the four scenarios given above, the starting pH on the p titration curve will be acidic

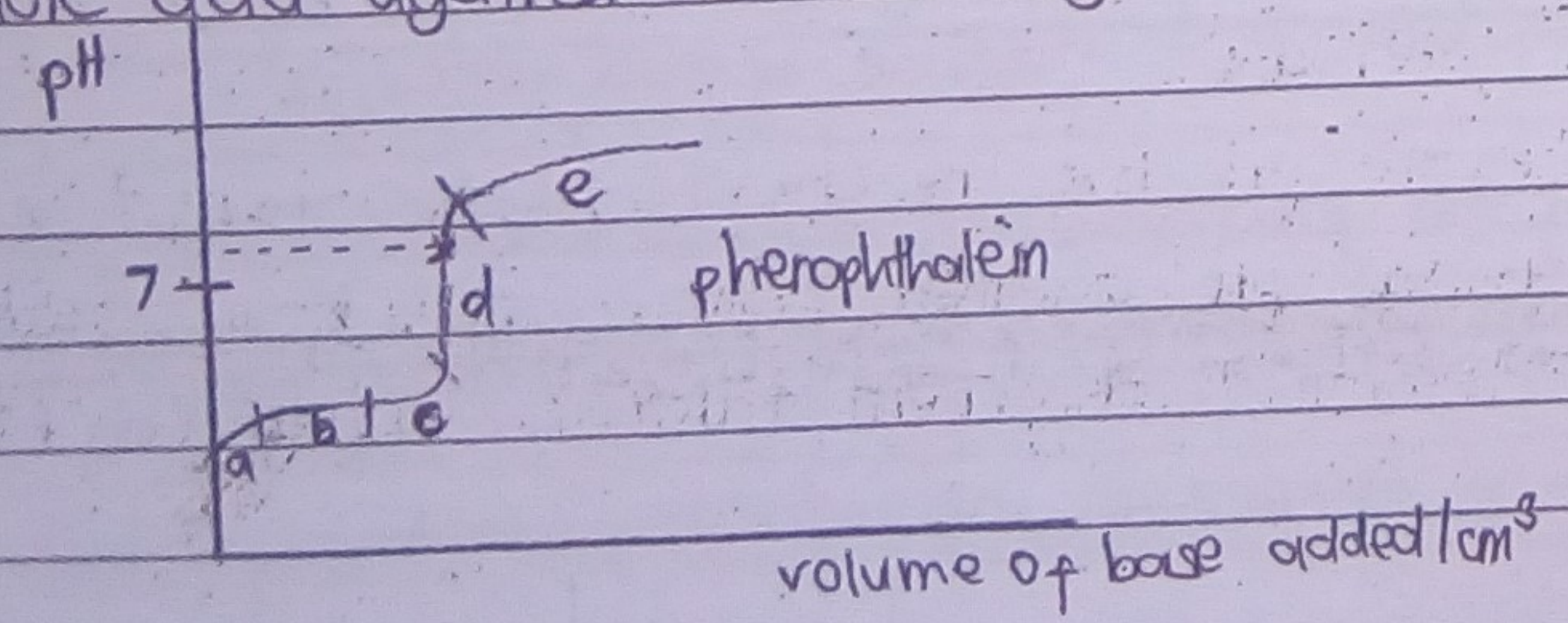
Consider titration of strong acid against strong base



Consider titration of strong acid against weak base



Weak acid and strong base
e.g. ethanoic acid against sodium hydroxide



Explaining the graph

Region a

- Upon the addition of a few drops of a base, the pH gradually increases as the base is being neutralized to form a salt
- $$\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}$$

Region b

- Upon the addition of drops of a base, the pH remains almost constant. This is because the solution will be acting as a buffer
- The formed salt from the neutralization rxn, i.e. sodium ethanoate together with the weak acid already present in the beaker i.e. CH_3COOH , a buffer is formed.

- Eventually the buffer will reach its maximum buffer capacity (maximum amt of acid or base can be added before the buffer pH starts to change).

Region c

- The maximum buffer capacity of the solution would have been exceeded hence, upon the addition of drops of a base, pH gradually increases.

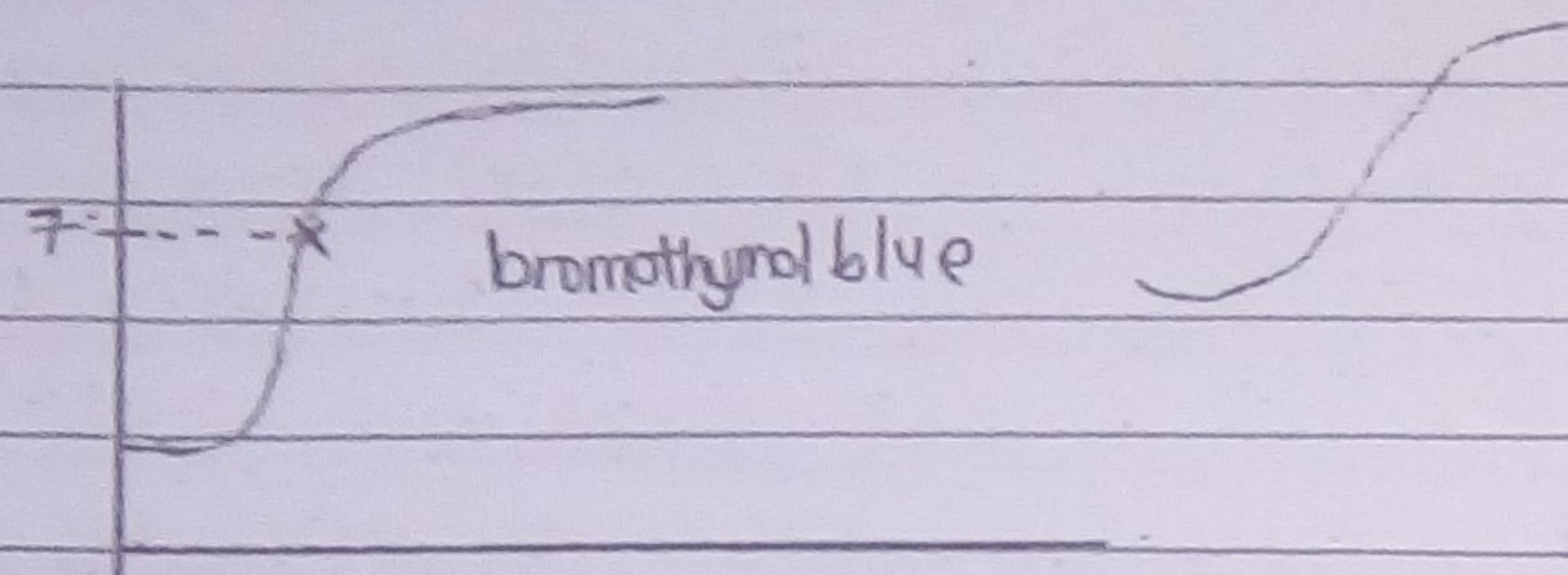
Region d

- Upon the addition of a single drop of a base, there is going to be a sharp change in pH. This is because all the acid would have been neutralized by the base and the base will already be in excess.
- Halfway this region signifies the end point

Region e

- Upon the addition of more drops of a base, the pH continues to rise until it reaches a constant

Weak acid and weak base



The titration between a weak acid and a weak base has no definite end point. Therefore it implies that it has no proper indicator to be used.

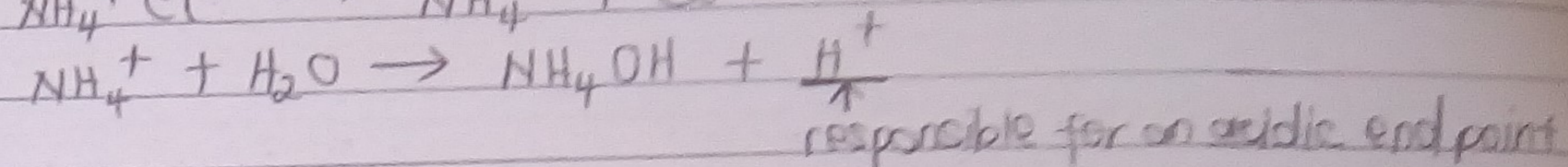
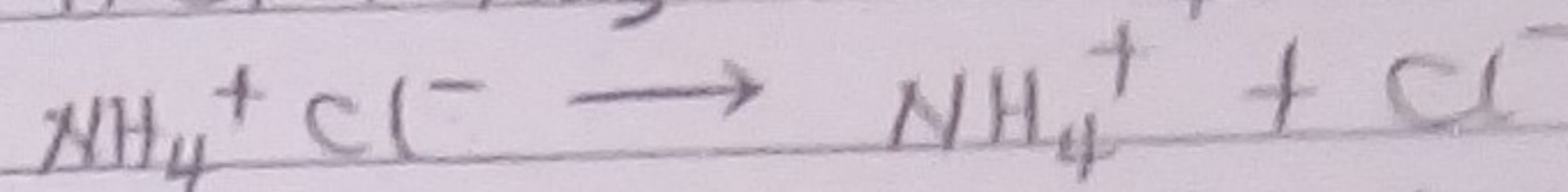
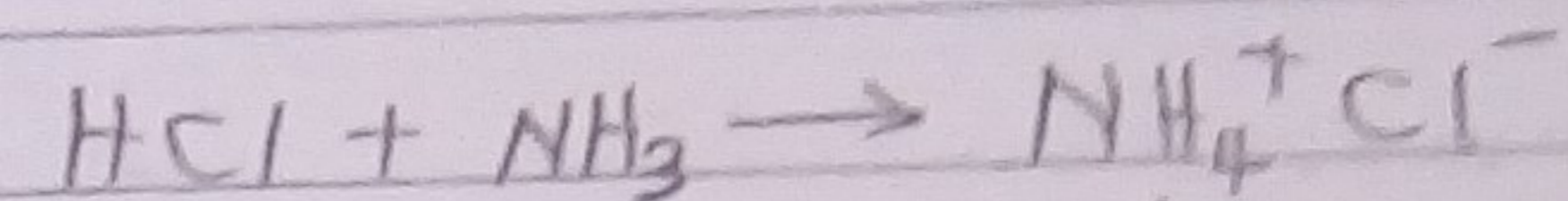
Justification of end points

Although neutralization will have occurred, implying that all the acid and the base would have reacted, we still see the titration between a strong acid and a weak base having an acidic end point implying that H^+ will be in excess. We also see the titration between a weak acid and a strong base having a basic end point. These pH values can be justified if we consider the hydrolysis of the produced salts in the reaction.

Hydrolysis of salts

Let's consider the titration of a strong acid and a weak base with an approximate end point of pH around 3,7

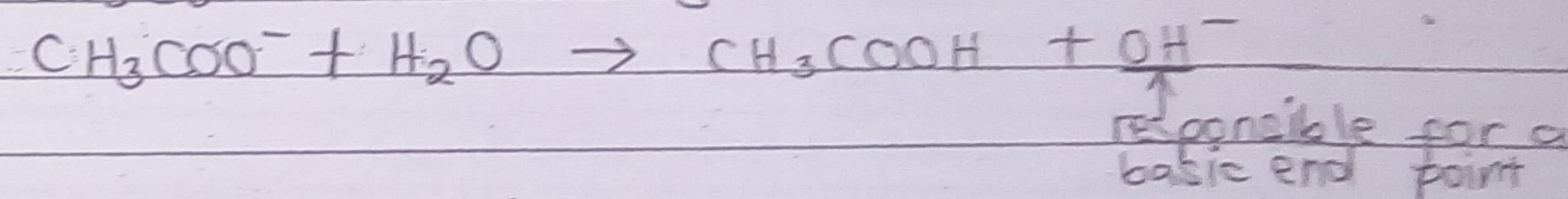
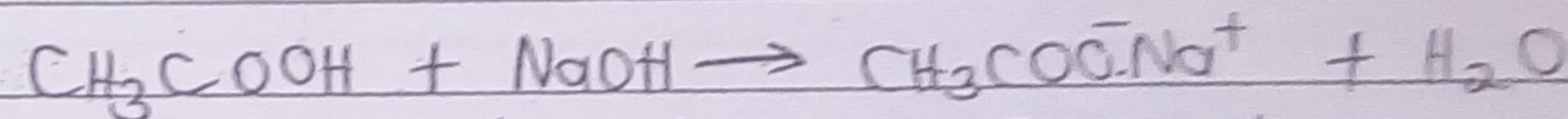
When a strong acid e.g. HCl reacts with a weak base e.g. NH_3 , $NH_4^+ Cl^-$ is formed. Since the formed ammonium chloride is a salt, it then ionises in an aqueous environment to produce different ions



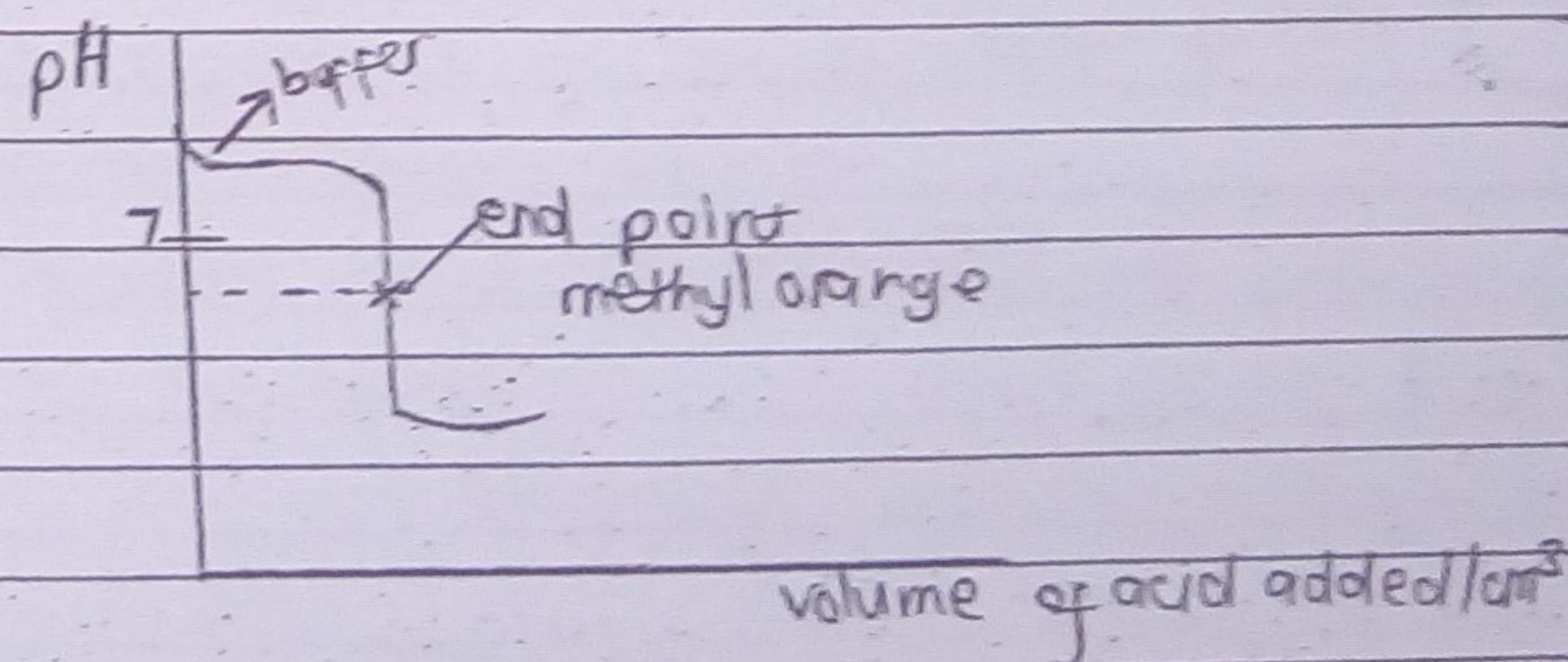
Consider titration between a weak acid and a strong base with an approximate end point of around 9,2

Solution

When a weak acid e.g. CH_3COOH reacts with a strong base e.g. NaOH, $CH_3COO^- Na^+$ is formed. Since the $CH_3COO^- Na^+$ is being produced in an aqueous environment it ionises



Titration curves of bases against acids
Consider titration of ammonia against HCl



The hydrolysis of the produced salt can be used to justify the produced acidic pH end point

In the titrations above, monoprotic acids were being used \therefore one

point was observed.

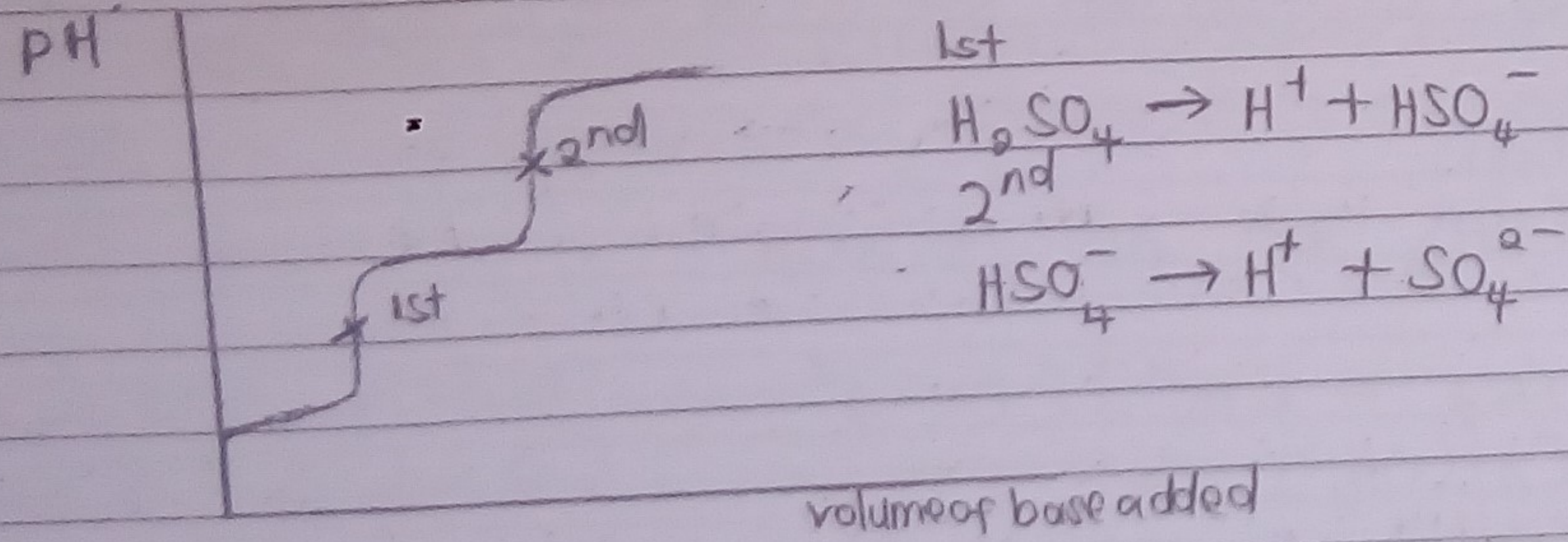
monoprotic acid \equiv monobasic acid \bar{n} releases one H^+ ion.

When diprotic acids or triprotic acids are used in titrations, multiple end points will be observed.

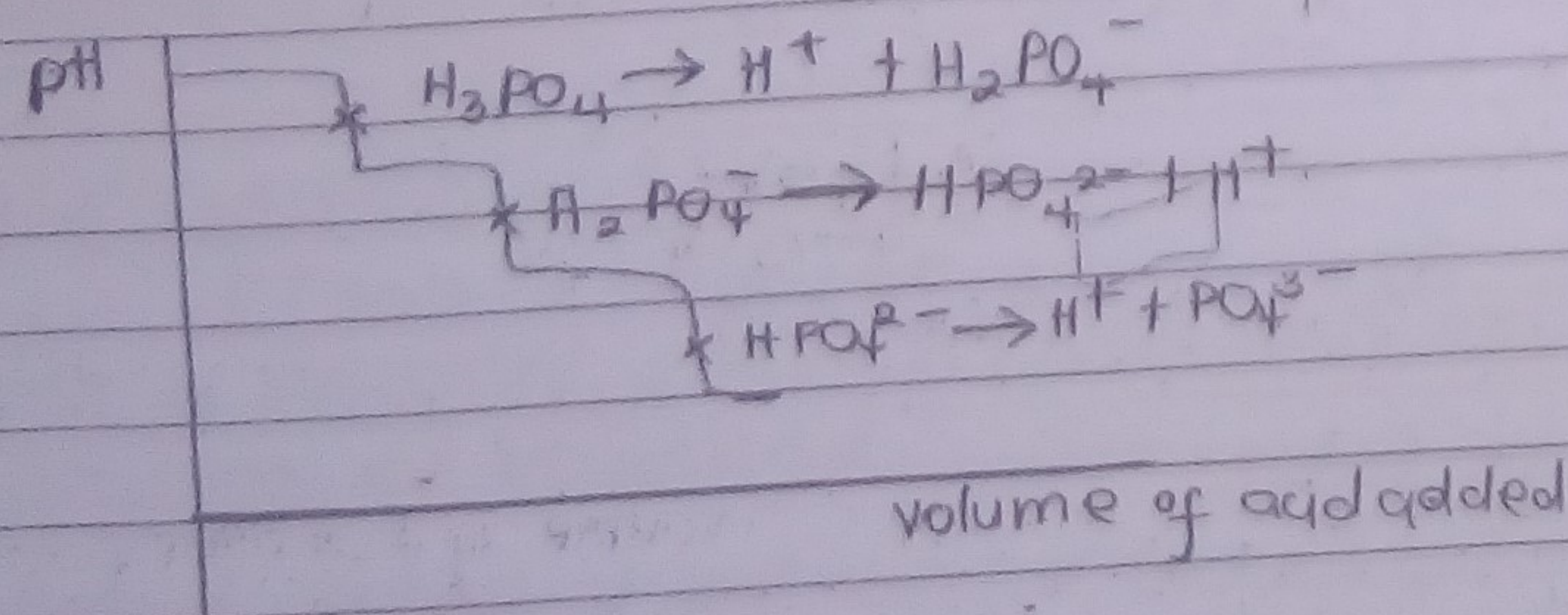
Consider the following two titrations below

- (i) Titration of H_2SO_4 against $NaOH$
- (ii) Titration of KOH against phosphoric acid (H_3PO_4)

Titration of H_2SO_4 against $NaOH$



Titration of KOH against H_3PO_4



Solubility product K_{sp}

What is solubility?

It refers to the amt of substance dissolved in a given

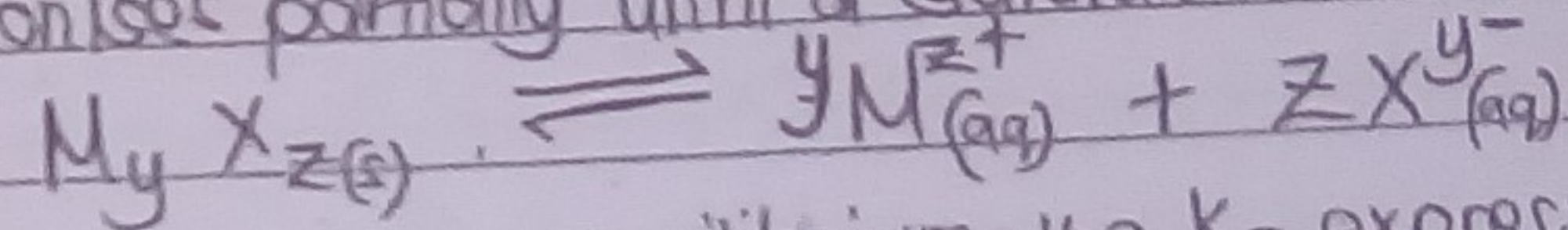
volume of a liquid at a given temperature

The amount of substance dissolved in a given volume of a liquid gives us the concentration of that substance in a liquid.

Therefore solubility also means concentration.

In this section we are going to be concerned with ionic solids which are partially soluble in water

When a partially soluble salt dissolves in water at a given temp, it ionises partially until a saturated solution is formed e.g



Using the above equilibrium, the K_c expression can be given

$$K_c = \frac{[M^{z+}]^y [X^{y-}]^z}{[M_y X_z]}$$

Since a solid has got a constant concentration, the K_c expression can be rearranged to obtain a new constant.

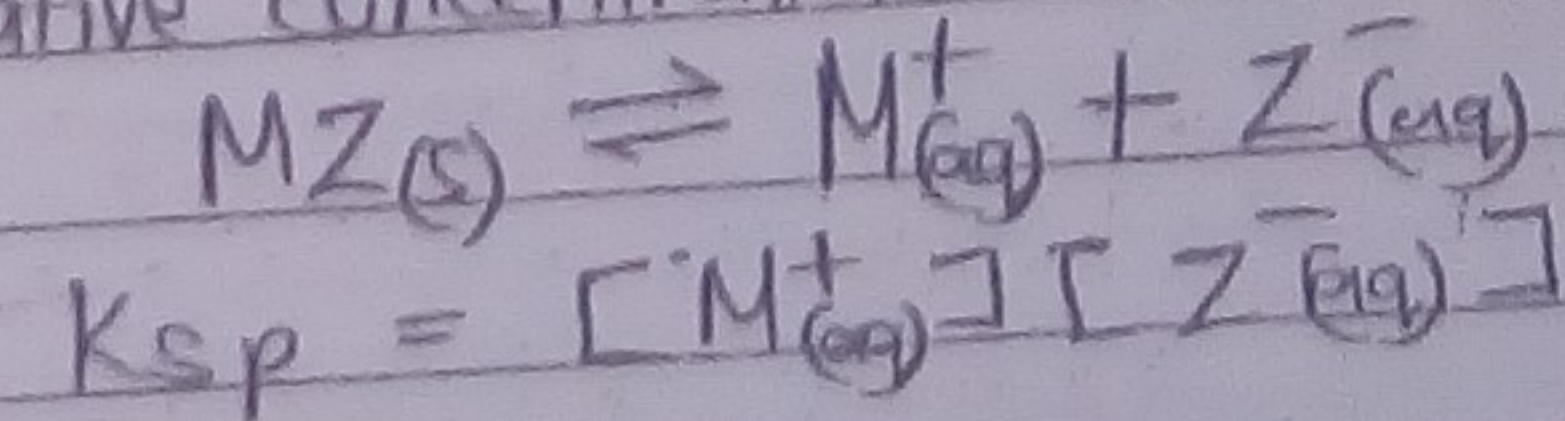
$$K_c [M_y X_z] = [M^{z+}]^y [X^{y-}]^z = \text{constant}$$

constant value constant value

The constant obtained above is referred to as the solubility product constant (K_{sp})

$$K_{sp} = [M^{z+}]^y [X^{y-}]^z$$

K_{sp} can then be formally defined as the product of the conc of each ion in a saturated solution of a partially soluble salt raised to the power of their relative concentrations or simply:



It should be known that K_{sp} is a constant value at a given temperature. It therefore means that changes in temp will change

the K_{sp} value.

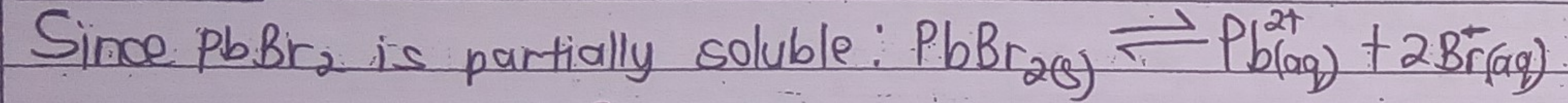
When temp increases, the solubility of an ionic solid increases and hence K_{sp} also increases and the opposite is true.

K_{sp} calculations

Question:

Lead bromide is a partially soluble salt, calculate the solubility product of $PbBr_2$ given that the solubility of $PbBr_2$ is $0,0048 \text{ mol dm}^{-3}$.

Solution:



The K_{sp} expression = $[Pb^{2+}][Br^{-}]^2$
let $[PbBr_2] = s$ and using the mole ratio in the equation it implies $[Pb^{2+}] = s$ and $[Br^{-}] = 2s$

Substituting the above in the K_{sp} expression:
 $\therefore K_{sp} = (s)(2s)^2 = 4s^3$
 $= 4(0,0048)^3$
 $= 4,42 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$

What is the effect of adding

- i) water
 - ii) temperature increase
- to the calculated value above?

Solution:

Adding water will not affect the K_{sp} value. But due to the added water, the ionic product decreases because the conc of the ions will have decreased.

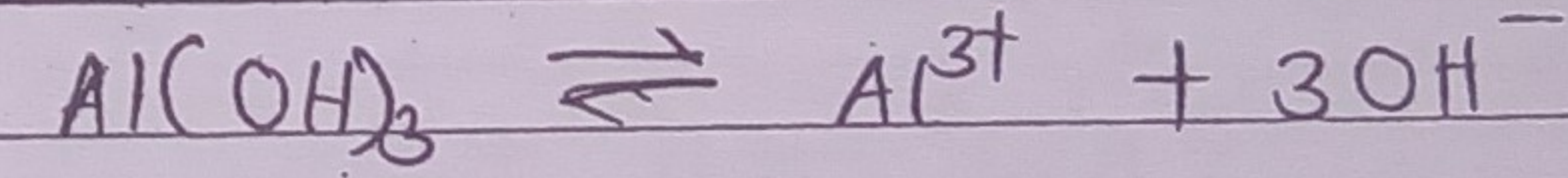
(ii) Since K_{sp} is affected by temp, an increase in temp will result in the increase in the K_{sp} value.

Limitations of K_{sp} concept

- K_{sp} only applies to partially soluble salts, that is the saturated solutions of the partially soluble salts.
- It can also be said to apply to saturated solutions in w/c the total ion conc is less than $0,01 \text{ M}$. Therefore if the total ion conc in the sltn is more than $0,01 \text{ M}$, K_{sp} value will no longer be constant.

Q Calculate the solubility of $Al(OH)_3$ and hence the solubility of OH^{-} ions given that K_{sp} of $Al(OH)_3$ is $6,9 \times 10^{-10}$.

Solution:



$K_{sp} = [Al^{3+}][OH^{-}]^3$

let $[Al(OH)_3] = s$

$\therefore [Al^{3+}] = s$ and $[OH^{-}] = 3s$, using mole ratios in eqn

In K_{sp} expression, substitute the above

$K_{sp} = s(3s)^3 = 27s^4$

$6,9 \times 10^{-10} = 27s^4$

$s = 2,25 \times 10^{-3} = [Al(OH)_3]$

$3s = 6,75 \times 10^{-3} = [OH^{-}]$

Common Ion Effect

- Although the K_{sp} value at any given temp is constant, the concentration of ions in the aqueous sltn may vary.
- As the conc of ions in solution vary, the ionic product value of the ions in solution also vary.
- The variations in the conc of ions in sltn is usually due to the

addition of common ions in a solution, thus we refer to this as the common ion effect

The common ion effect is the reduction in the solubility of a dissolved salt achieved by adding a solution of a compound which has a common ion with the compound/dissolved salt.

Predicting precipitation

- When a common

Consider

- A partially soluble salt AB e.g. AgCl. At any given temp the salt has a constant K_{sp} value
- When the aqueous ions (of different concentrations) of the partially soluble salt are mixed together, the following three scenarios can occur:

1. $K_{sp} >$ ionic product
 $K_{sp} > [A^+][B^-]$

In this case, the added aqueous ions dissolve in each other and no precipitation is observed.

2. $K_{sp} =$ ionic product

We obtain a saturated soln of the ionic salt and traces of a precipitate will be observed.

3. $K_{sp} <$ ionic product

and the solid continues to be formed.
- Precipitation occurs until the ionic product is equal to K_{sp} .
decreases to be equal to the K_{sp} value.

- It also therefore implies that when a common ion is added to a

solution, the three above solutions can occur.

Calculations involving the common ion

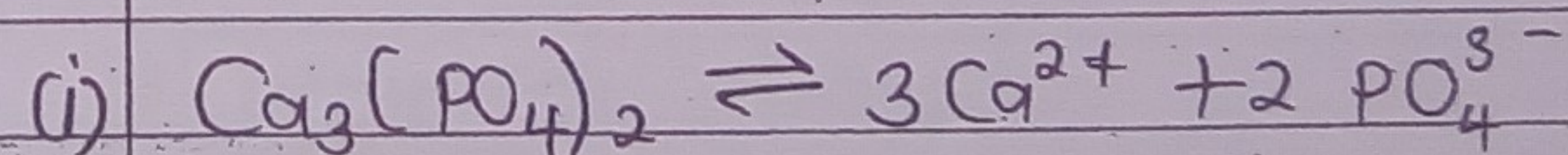
When performing calculations involving the addition of a common ion, certain assumptions have to be made.

eg Consider a partially soluble salt $PbBr_2$ with a concentration, s and another salt $NaBr$ with a conc of $0,1M$. When the two solutions are mixed, the Br^- ion will be the common ion therefore the total conc of the Br^- ion should be equal to $s + 0,1M$ but $s \ll 0,1M$ therefore the Br^- ion concentration in solution will be approximately equal to $0,1M$.

Qn Given that the solubility of calcium phosphate ($Ca_3(PO_4)_2$) is $1,4 \times 10^{-2} \text{ mol dm}^{-3}$. Calculate

- solubility product of $Ca_3(PO_4)_2$
- solubility of $Ca_3(PO_4)_2$ in $0,3M Na_3PO_4$
- solubility of $Ca_3(PO_4)_2$ in $0,1M CaCl_2$

Solution



$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

$$\text{let } [Ca_3(PO_4)_2] = s$$

$$\therefore [Ca^{2+}] = 3s \text{ and } [PO_4^{3-}] = 2s$$

$$\therefore K_{sp} = (3s)^3 (2s)^2 = 108s^5$$

$$K_{sp} = 5,81 \times 10^{-8} \text{ mol}^5 \text{ dm}^{-15}$$

(ii) Common ion is phosphate ion $[PO_4^{3-}] = 0,3M$
 $\therefore K_{sp} = [Ca^{2+}]^3 [0,3]^2$

$$\frac{5,81 \times 10^{-8}}{0,09} = [Ca^{2+}]^3$$

$$6,45 \times 10^{-7} = [Ca^{2+}]^3$$

$$8,64 \times 10^{-3} = [Ca^{2+}]$$

Since $[Ca^{2+}] = 3s$

$$[Ca_3(PO_4)_2] = s$$

$$3s = 8,64 \times 10^{-3}$$

$$s = \text{less}$$

$$\therefore [Ca_3(PO_4)_2] = 2,88 \times 10^{-3}$$

(iii) Common ion $[Ca^{2+}] = 0,1M$

$$\therefore K_{sp} = [PO_4^{3-}]^2 [0,1]^3$$

$$\sqrt{\frac{5,81 \times 10^{-8}}{0,001}} = [PO_4^{3-}]$$

$$7,62 \times 10^{-3} = [PO_4^{3-}]$$

Since $[PO_4^{3-}] = 2s$

$$s = \frac{7,62 \times 10^{-3}}{2}$$

$$s = 3,81 \times 10^{-3}$$

$$[Ca_3(PO_4)_2] = 3,81 \times 10^{-3}$$

Qn A saturated sltn of copper(I) sulphide (Cu_2S) contains $1,91 \times 10^{-12}g$ of copper(I) sulphide dissolved in $1dm^3$ of water.
 Calculate

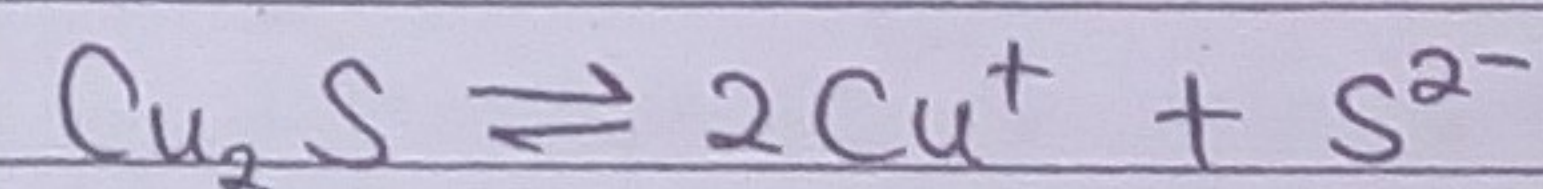
a(i) the solubility product of Cu_2S stating the units

(b) copper(II) chromate has a solubility of $1,9 \times 10^{-3} \text{ mol dm}^{-3}$

copper(II) sulphate has a solubility of $1,4 \times 10^{-1} \text{ mol dm}^{-3}$ in H_2O

What will you observe when $10cm^3$ of aqueous sltn of $0,01 \text{ mol dm}^{-3}$ copper(II) sulphate is added to an equal volume of a saturated solution of copper(II) chromate.
 Explain your answer

Solution



$$K_{sp} = [Cu^+]^2 [S^{2-}]$$

$$\text{let } [Cu_2S] = s$$

$$\therefore [Cu^{2+}] = 2s \quad \text{and} \quad [S^{2-}] = s$$

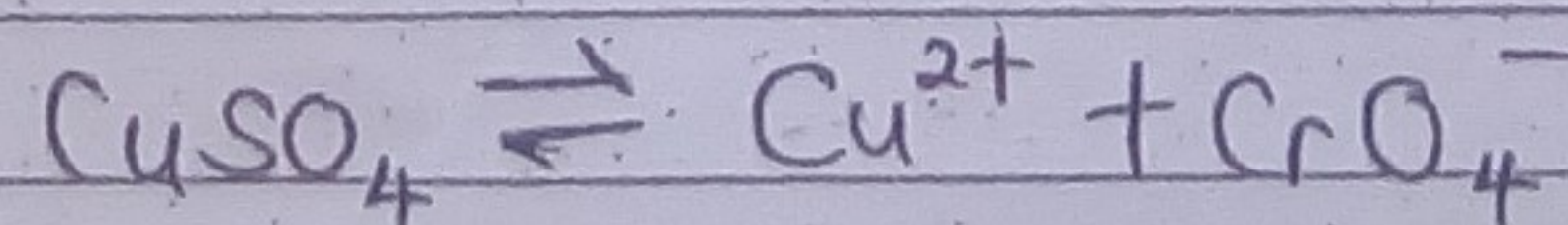
$$\therefore K_{sp} = (2s)^2 (s) = 4s^3$$

$$[Cu_2S] = \frac{1,91 \times 10^{-12}}{(63,5 \times 2 + 32,1)} = 1,2 \times 10^{-14} \text{ converting } g/dm^3 \text{ to } mol/dm^3$$

$$K_{sp} = 4(1,2 \times 10^{-14})^3 = 6,9 \times 10^{-42}$$

$CuCrO_4 = 1,9 \times 10^{-3} M$ (since it is a saturated solution, K_{sp} can be calculated)

$$CuSO_4 = 1,4 \times 10^{-1} M$$



$$K_{sp} = [Cu^{2+}] [CrO_4^{2-}]$$

$$\text{let } [CuCrO_4] = s$$

$$[\text{Cu}^{2+}] = s$$

$$[\text{CrO}_4^{2-}] = s$$

$$K_{sp} = s^2 = (1,9 \times 10^{-3})^2 = 3,61 \times 10^{-6}$$

When equal volumes are added, the concentrations of the solutions are halved \therefore after mixing the two solutions

$$\text{new } [\text{CuCrO}_4] = \frac{1,9 \times 10^{-3}}{2} = 0,00095 \text{ M}$$

$$\text{new } [\text{CuSO}_4] = \frac{1,4 \times 10^{-1}}{2} = 0,07 \text{ M}$$

We then calculate the ionic product (I.p)

$$\begin{aligned} \text{I.p} &= [\text{Cu}^{2+}] [\text{CrO}_4^{2-}] \\ &= [0,07] [0,00095] = 6,65 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

↑
common ion
from the added

To predict precipitation we compare K_{sp} and I.p
Therefore, ^{since} K_{sp} is less than ionic product value

$$3,61 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} < 6,65 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

and using scenario 3 studied it implies that precipitation will occur

The above question tests if you really understand the common ion effect & the assumptions made when performing common ion effect calculations. It continues to test if you are able to predict precipitation using K_{sp} and ionic product values.

REACTION KINETICS

In this chapter we are going to be studying the different rates / speed of chemical reactions

What is the rate of a reaction?

It is the change in concentration of the products or reactants with time.

$$\text{Rate} = \frac{\text{change in concentration}}{\text{change in time}} = \frac{d[\text{Products/Reactants}]}{dt}$$

Units of rate

$$\frac{[\text{mol dm}^{-3}]}{\text{time s}} = \text{mol dm}^{-3} \text{ s}^{-1}$$

Studying, following or simply measuring the rate of rxn can be done using chemical and physical methods to be studied below

Measuring the rate of a reaction: Chemical reaction

The rate of a chemical rxn can be studied or followed using the following methods:

- (i) Titrimetric Analysis
- (ii) Colourimetric Analysis
- (iii) Pressure changes
- (iv) Conductmetric Analysis

..the DIRECTOR..

0712 105 452

0772 666 148

Titrimetric Analysis

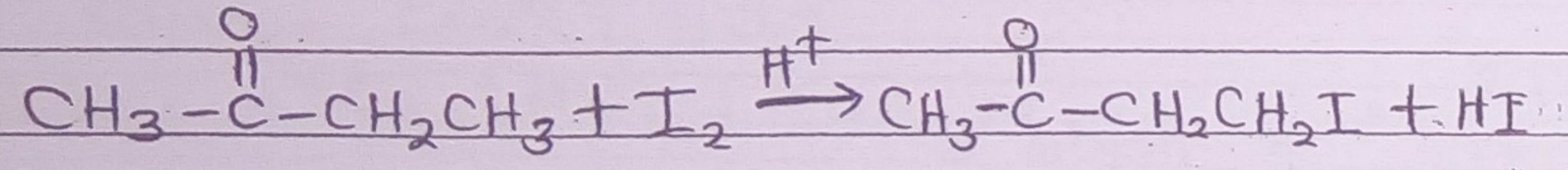
This involves the use of titrations to study the rate of a chemical rxn.

In this method, the rxn can be followed by removing and analysing small portions of the reaction mixture at intervals.

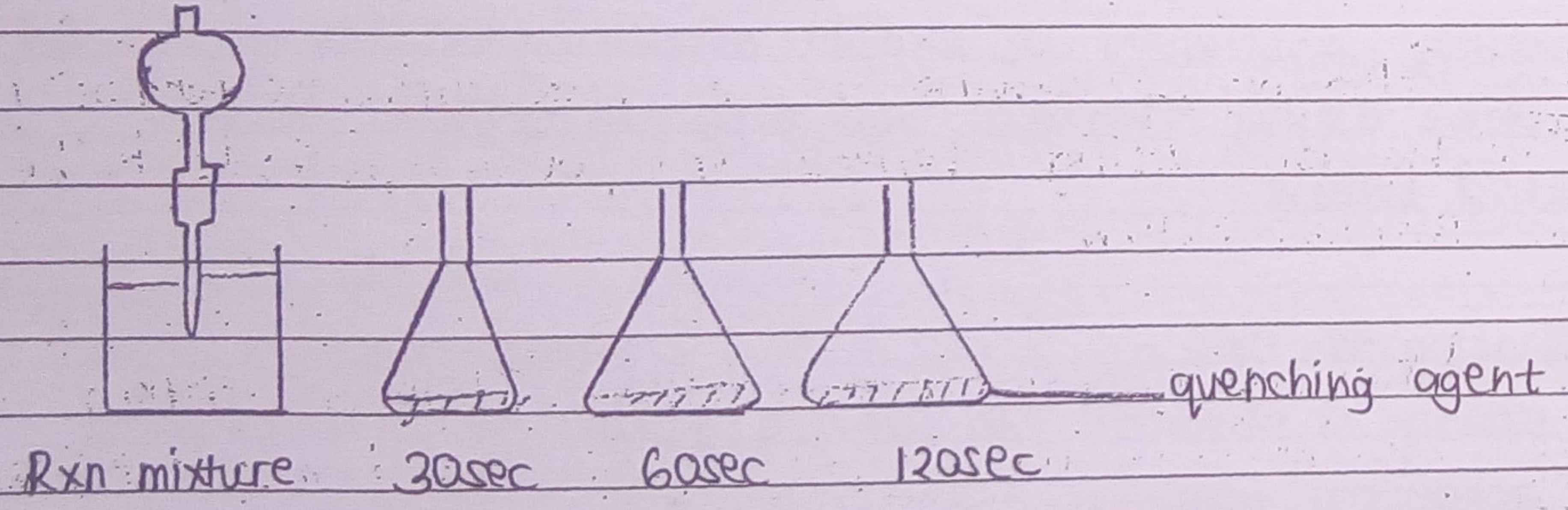
The removed portion is added to a container which already has a quenching agent in it.

A quenching agent stops the rxn to prevent further changes in conc before analysing is done

The quenching agent must not react with the reagent to be analysed using titrations e.g consider the rxn below



A carbonate can be used as the quenching agent



- Titrations are then done using small portions which had their rxns stopped at different times.

- During the titrations different concentrations of the reagent being analysed are obtained for the different times.

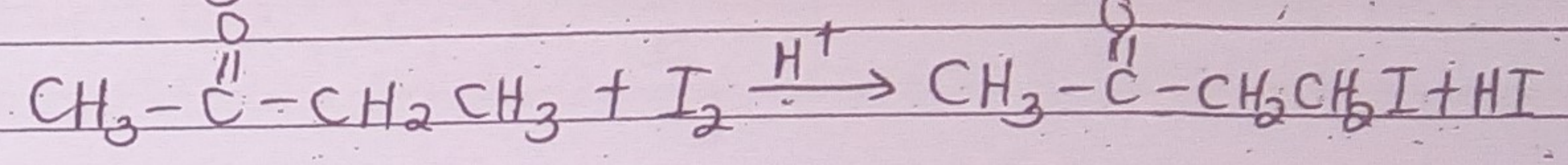
- A graph of conc against time can then be plotted.

The gradient of the tangent at any point of the graph will then give us the rate at that particular point.

Colourimetric Analysis

- This is an example of a physical method of following rate of a chemical rxn.

- It involves the use of a colourimeter to measure different light intensities / absorbences for reactions which involve changes in colour. for example,



- Therefore during this method, using the colourimeter different intensities at a stated time interval as the rxn progresses can be obtained

- A graph of intensity against time can then be plotted. The gradient of a tangent at any point on the plotted graph can then give us the rate of the rxn.

Pressure Changes

- The use of pressure changes to measure the rate of a rxn is an example of a physical method of measuring the rate of a rxn

- In this method pressure changes during a chemical rxn are measured using a pressure gauge

- This method can be employed for any chemical rxn which involves gases provided the # of moles is different on both sides of the equation.

- With the obtained pressure values at different times, a graph of pressure against time can then be plotted

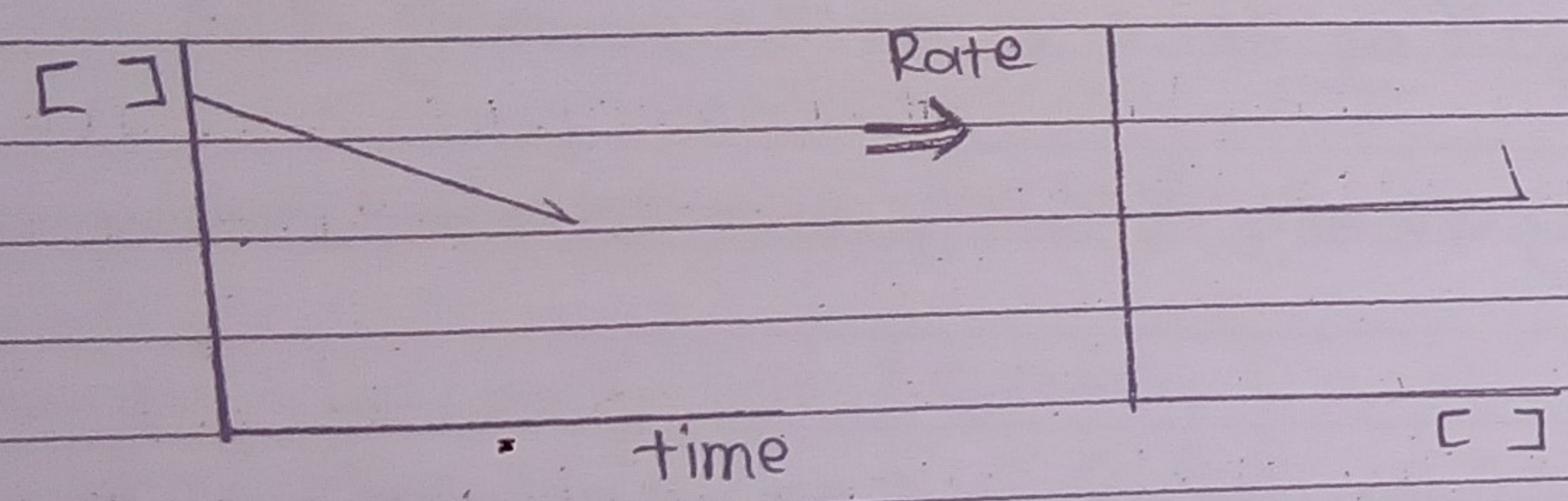
- The gradient of the tangent at any point on the plotted graph will then give us the rate of rxn

Conductometric Analysis

an e.g of a physical method of following the rate of a chemical rxn

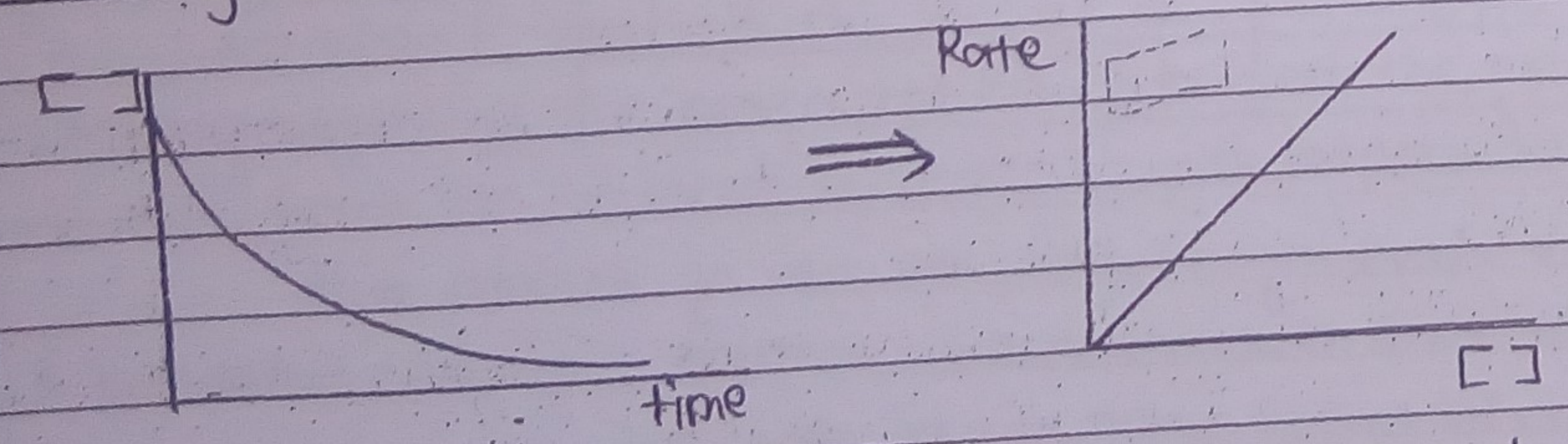
- Involves the use of a conductivity meter to measure the conductivity of a rxn mixture.
- After following the rate of a chemical rxn, different graphs can be obtained (for conc against time)

For a zero order rxn



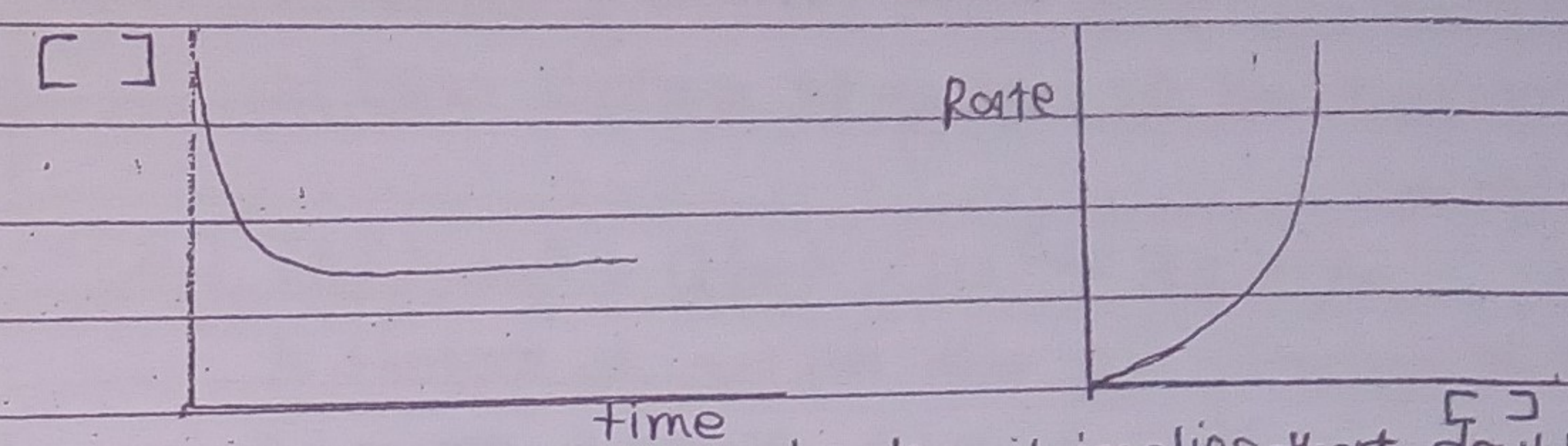
- When we say a rxn is zero order, it implies that the changes in conc of a particular reactant in question has got no effect on the rate of a rxn.
- Thus for a zero order rxn, the rate remains constant while changes in conc occur.

For a first order rxn



When we say the rxn is first order, it implies that doubling the conc of a reactant will double the rate of reaction.

For a second order rxn



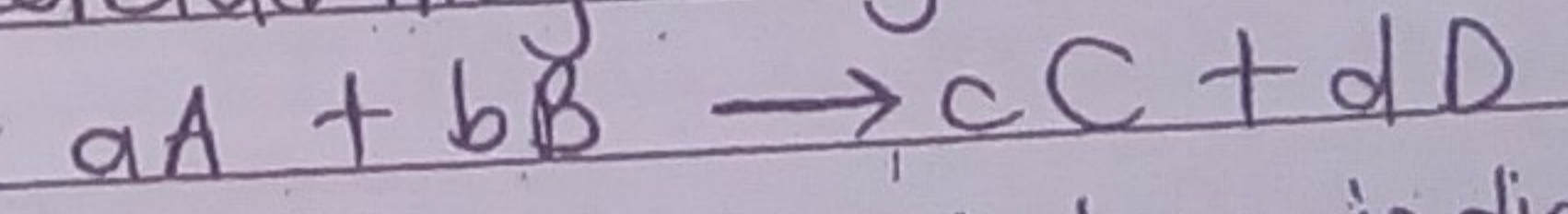
When we say the rxn is second order, it implies that doubling the conc of the reactants will increase by four fold (quadruples) the rate of a chemical rxn.

Relationship between the conc against time graph and the rate against conc

The gradient at any point on the conc against time graph gives us the rate of a rxn at that point therefore it implies that if different gradients at different points on the conc against time graph are calculated, different rates ^{at different points} can be obtained. The obtained different rates can then be used to calculate the rate against conc graph.

Rate equation

Consider the following rxn



The rate of a chemical rxn is directly proportional to the conc of the reactants.

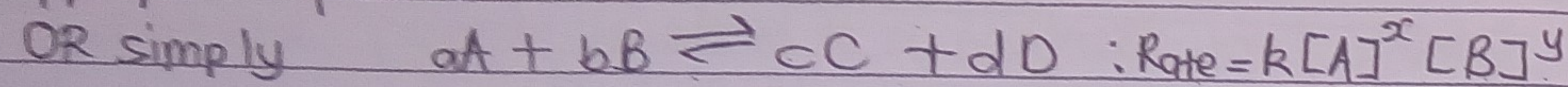
$$\text{Rate} \propto [A]^x [B]^y$$

$$\text{Rate} = k [A]^x [B]^y$$

$$\frac{d[A]^x [B]^y}{dt} = k [A]^x [B]^y$$

The above can be referred to as the rate equation

A rate eqn is an eqn which relates the rate of an ^{chemical} reaction, the rate constant and the conc of the reactants raised to appropriate powers.



Where x is order of rxn with respect to reactant A

y is order of rxn with respect to reactant B

$x + y$ = overall order of rxn

x and y are not number of moles of A and B.

x and y are experimentally determined e.g using the initial rate interval.

From the rate equation, 5 definitions can be obtained

(1) Rate (defined already above)

(2) Rate constant (k)

fn: It is a constant of proportionality which relates the rate of a rxn and the conc of the reactants raised to appropriate powers

(3) Order with respect to a particular reactant

fn: The power to which the conc of a reactant is raised to in an experimentally determined rate eqn

(4) Overall order of rxn

fn: The sum of the powers of the reactants in an experimentally determined rate equation.

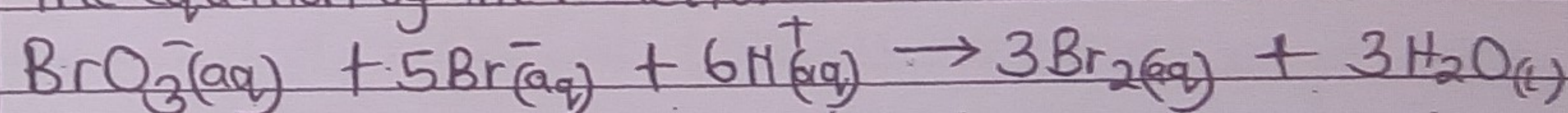
(5) Rate equation (defined above)

The Initial rate method

- This is a method used to deduce rate equations
- It is also often when the reactions are slow
- We perform the technique so that we can be able to calculate the order of reaction with respect to a particular reactant.
- During this technique, several experiments with different known concentrations of each reactant are done
- The initial rates of each experiment is measured by drawing a tangent of the curve at the start of the experiment.
- The gradient of the tangent will give us the initial rate of each reaction

e.g Consider the following results from the initial rate method

The equation of the reaction



The results are summarised below

| Exp | $[\text{BrO}_3^-]/\text{mol dm}^{-3}$ | $[\text{Br}^-]/\text{mol dm}^{-3}$ | $[\text{H}^+]/\text{mol dm}^{-3}$ | Initial Rate of reaction $\text{mol dm}^{-3} \text{s}^{-1}$ |
|-----|---------------------------------------|------------------------------------|-----------------------------------|---|
| 1 | 0,10 | 0,05 | 0,01 | 0,025 |
| 2 | 0,20 | 0,05 | 0,01 | 0,050 |
| 3 | 0,10 | 0,10 | 0,01 | 0,050 |
| 4 | 0,10 | 0,10 | 0,02 | 0,200 |

Using the above information, the order of reaction with respect to each reactant in the reaction can be calculated and hence the overall order can be deduced.

Deducing order of reaction from the experiment

Order with respect to $[\text{BrO}_3^-]$

Considering Exp 1 and 2, doubling the conc of the bromate ions will double the rate of reaction implying its order one

Why did we choose Exp 1 and 2 for our deductions?

It is because all the other reactants' concentrations are not changing while the BrO_3^- ion is changing, therefore any changes in the rate of reaction can be attributed to the BrO_3^- ions

Alternatively a calculation can be done

$$\begin{array}{l} \text{Exp 2} \\ \text{Exp 1} \end{array} \left(\frac{0,20}{0,10} \right)^n = \left(\frac{0,050}{0,025} \right)$$

$$\begin{aligned} 2^n &= 2 \\ n &= 1 \end{aligned}$$

\therefore the rxn is order 1 with respect to $[\text{BrO}_3^-]$

Order with respect to $[\text{Br}^-]$

Consider Exp 1 and 3

Clearly doubling the conc of Br^- doubled the rate of reaction hence the reaction is order 1 with respect to Br^-

Alternatively

$$\begin{array}{l} \text{Exp 3} \\ \text{Exp 1} \end{array} \left(\frac{0,10}{0,05} \right)^n = \left(\frac{0,050}{0,025} \right)$$

$$2^n = 2$$

$$\therefore n = 1$$

the rxn is order 1 w.r.t $[\text{Br}^-]$

Order with respect to $[\text{H}^+]$

Consider Exp 3 and 4

Clearly doubling the conc of H^+ ions increased the initial rate by four fold (quadrupled) the rate of reaction

Therefore the rxn is order 2 with respect to H^+ ions

Alternatively

$$\begin{array}{l} \text{Exp 4} \\ \text{Exp 3} \end{array} \left(\frac{0,02}{0,01} \right)^n = \left(\frac{0,200}{0,05} \right)$$

$$2^n = 4 = 2^2$$

$$\therefore n = 2$$

the rxn is order 2 w.r.t $[\text{H}^+]$

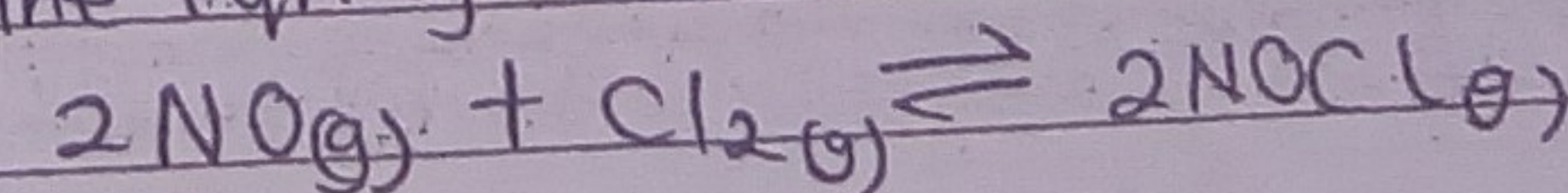
Using the above information, the rate equation can be given

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

$$\begin{aligned} \text{Overall order} &= 1 + 1 + 2 \\ &= 4 \end{aligned}$$

Consider the following rxn

The eqn of the reaction



The progress of the rxn was followed at 25°C and the data below was obtained

| Exp | concentration / mol dm ⁻³ | | Initial rate of increase of NOCl |
|-----|--------------------------------------|------|----------------------------------|
| | [Cl ₂] | [NO] | |
| 1 | 0,1 | 0,1 | 0,00011 |
| 2 | 0,1 | 0,2 | 0,00043 |
| 3 | 0,1 | 0,3 | 0,00093 |
| 4 | 0,2 | 0,1 | 0,00024 |
| 5 | 0,3 | 0,1 | 0,00033 |

Order w.r.t [Cl₂]

Considering Exp 4 and Exp 5

$$\frac{\text{Exp 5}}{\text{Exp 4}} \left(\frac{0,3}{0,2} \right)^n = \left(\frac{0,00033}{0,00024} \right)$$

$$n \log \left(\frac{0,3}{0,2} \right) = \log \left(\frac{0,00033}{0,00024} \right)$$

$$n = 0,985 \approx 1$$

Order w.r.t [NO]

Consider Exp 1 and 2

$$\frac{\text{Exp 2}}{\text{Exp 1}} \left(\frac{0,2}{0,1} \right)^n = \left(\frac{0,00043}{0,00011} \right)$$

$$n \log \left(\frac{0,2}{0,1} \right) = \log \left(\frac{0,00043}{0,00011} \right)$$

$$n = 1,988 \approx 2$$

Calculating the units of the Rate Constant

-the units differ depending on the overall order of reaction

Consider the zero order rxn

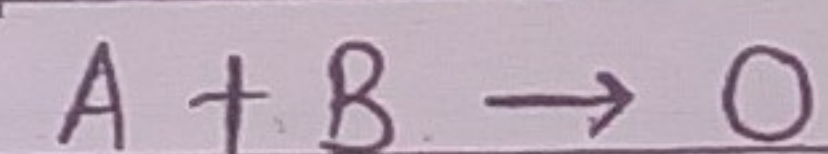


$$\text{Rate} = k[A]^0$$

$$\text{Rate} = k$$

$$\text{mol dm}^{-3} \text{s}^{-1} = k$$

Consider 1st order rxn

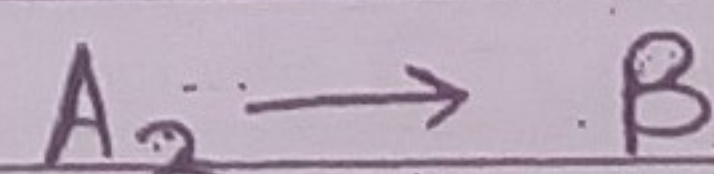


$$\text{Rate} = k[A]^1[B]^0$$

$$\text{mol dm}^{-3} \text{s}^{-1} = k (\text{mol dm}^{-3})$$

$$\therefore \text{units of } k = \text{s}^{-1}$$

Consider 2nd Order rxn



$$\text{Rate} = k[A]^2$$

$$\text{mol dm}^{-3} \text{s}^{-1} = k (\text{mol dm}^{-3})^2$$

$$k = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$$

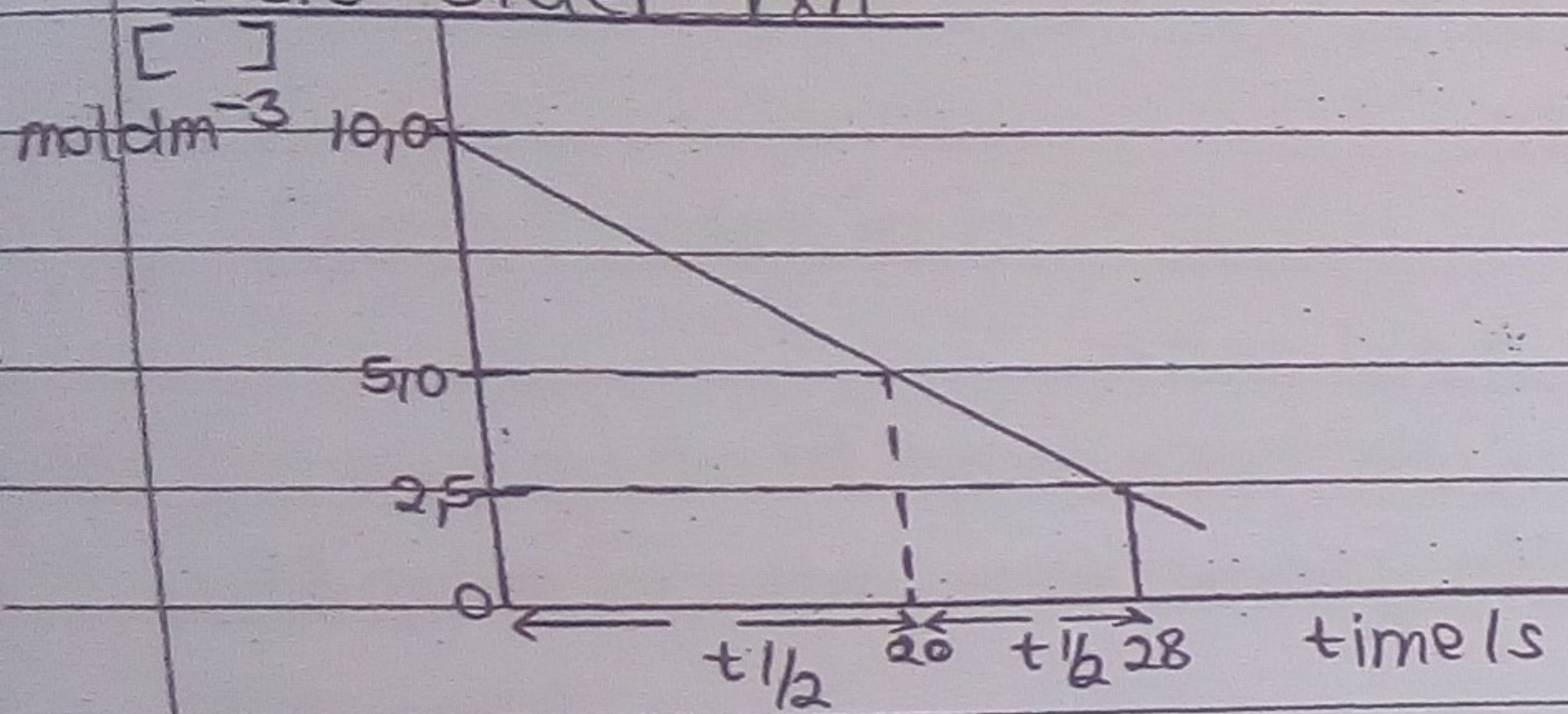
Testing for order of rxn

After plotting the conc against time graph of a particular rxn, half lives can be used to deduce the order of rxn / thus testing the order of reaction

Half life, $T_{1/2}$

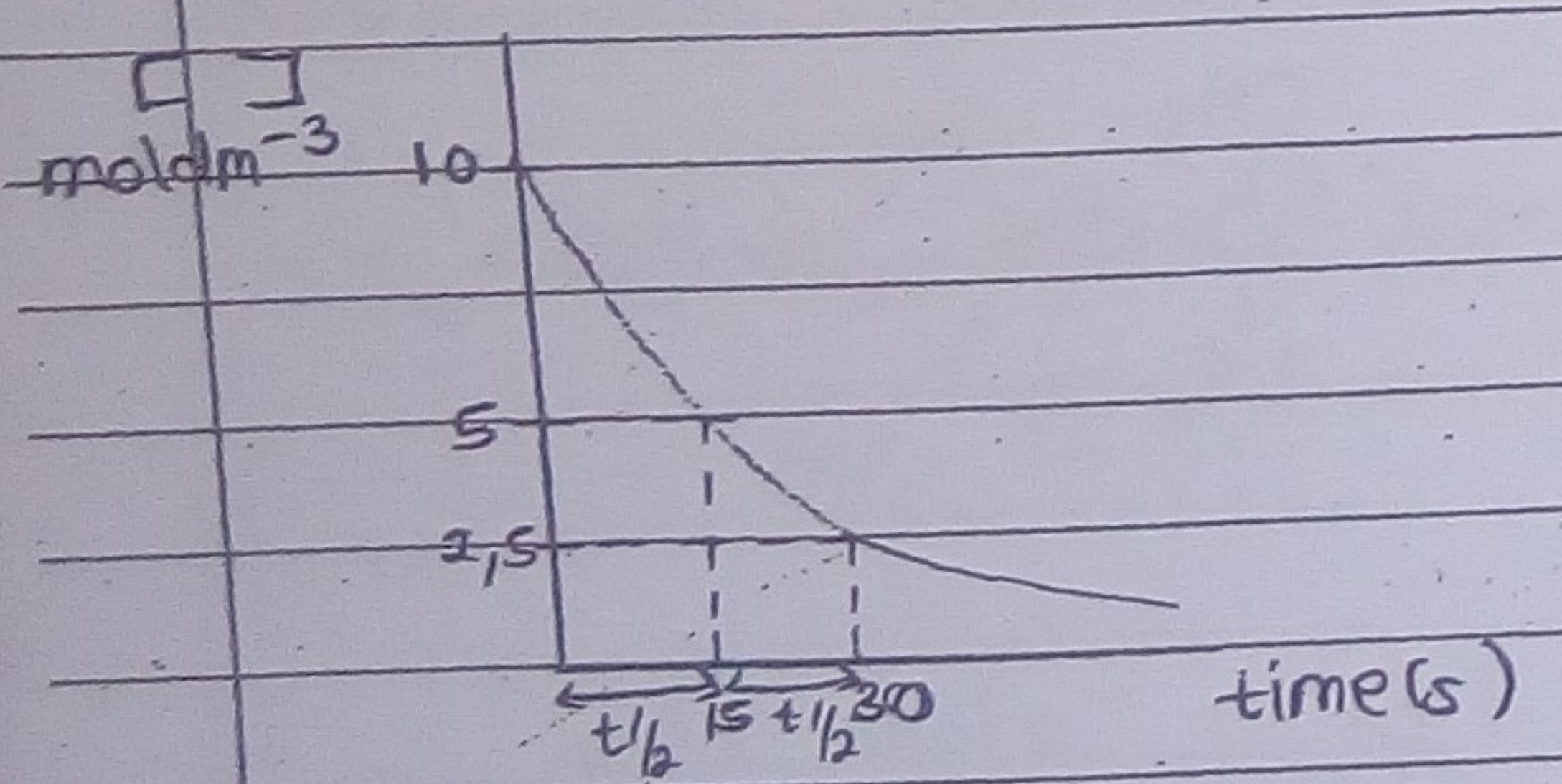
$t_{1/2}$ is the time taken for the initial amount (concentration of a reactant) to decrease by $\frac{1}{2}$

Zero order rxn



- A rxn will be known to be zero order if it has a constant gradient of the conc against time curve.
- Also, zero order rxns have decreasing half lives.

1st order rxn



- A first order rxn has got a constant half life
- $T_{1/2}$ for a first order rxn can also be represented by the following relationship

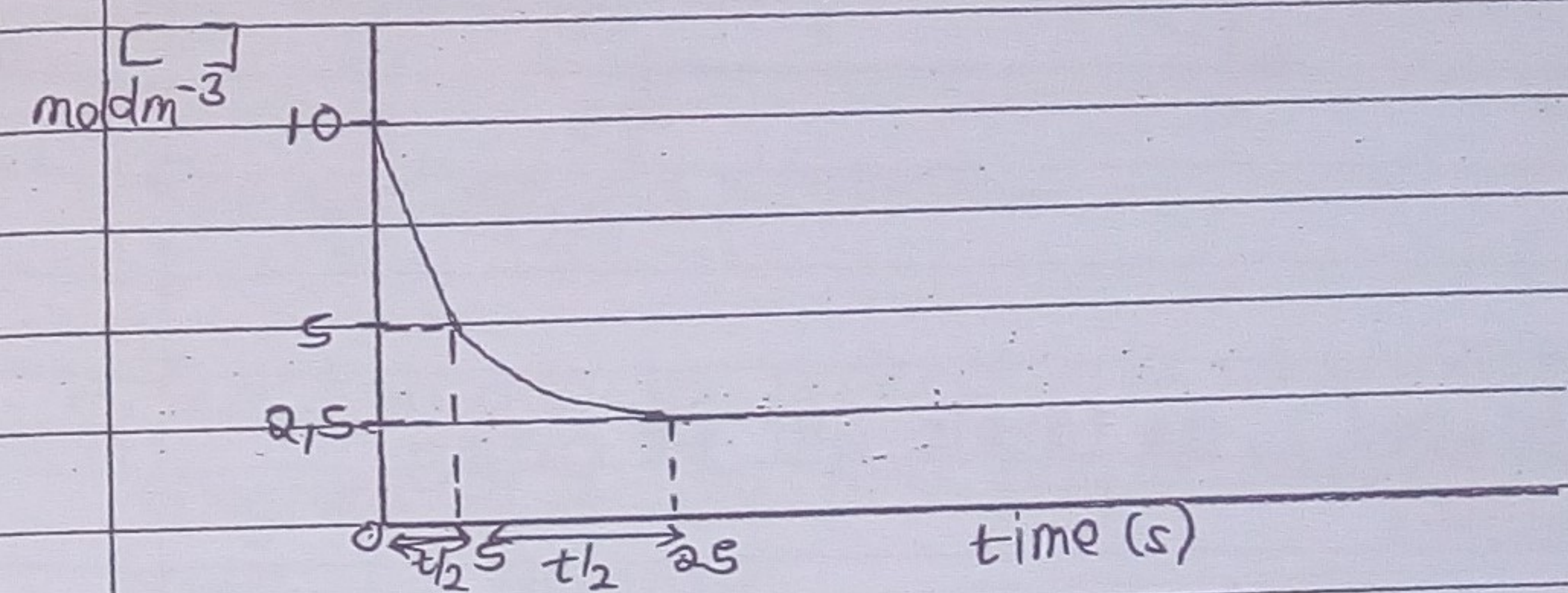
$$T_{1/2} = \frac{\ln 2}{k}$$

The relationship only works for 1st order

where k is the rate constant

- Therefore using the obtained $t_{1/2}$ value, the rate constant can be calculated

Order 2 rxn



- When the rxn is second order, the $t_{1/2}$ increases.
- The above $t_{1/2}$ values can be obtained after graphs have been plotted

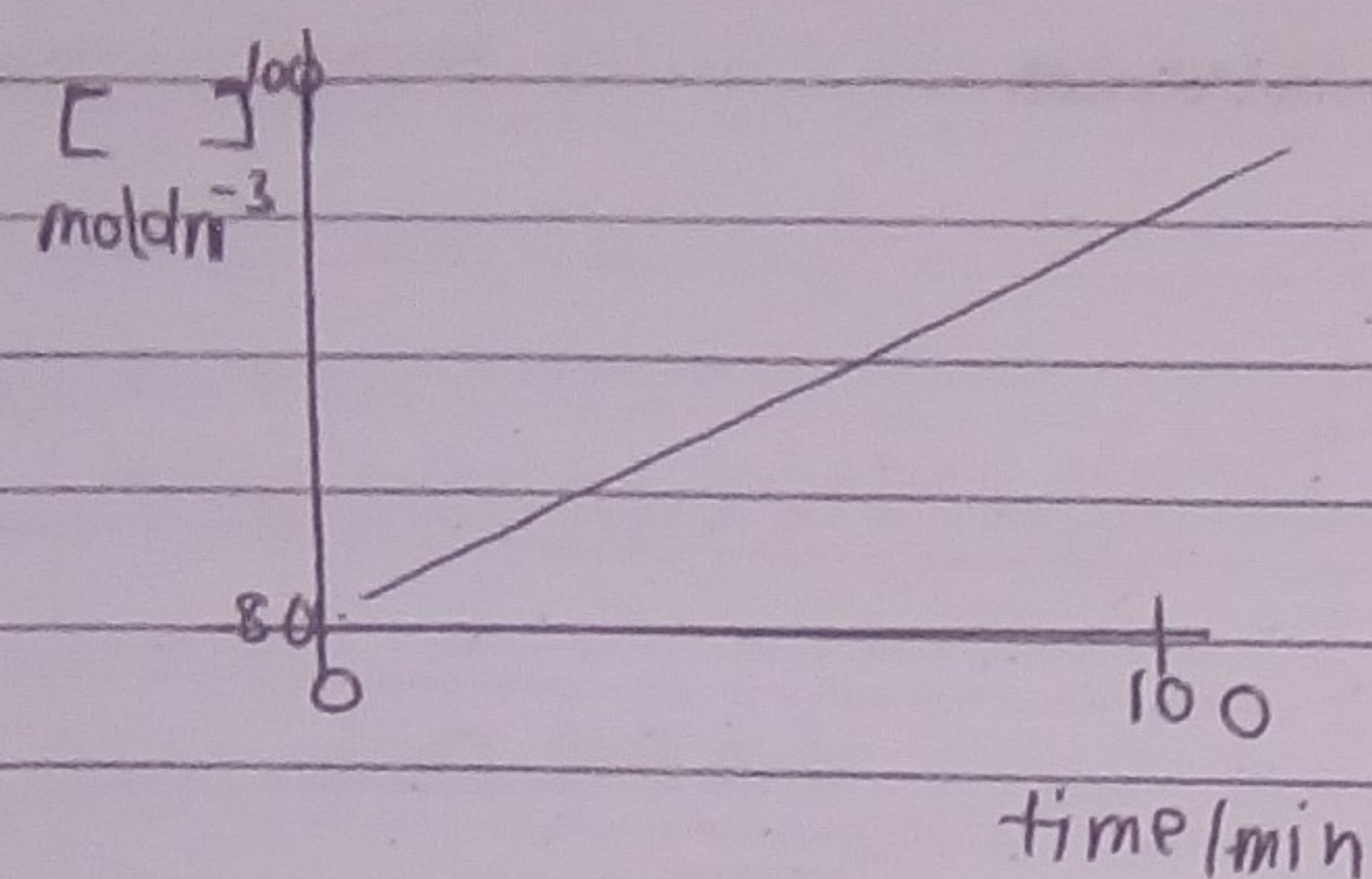
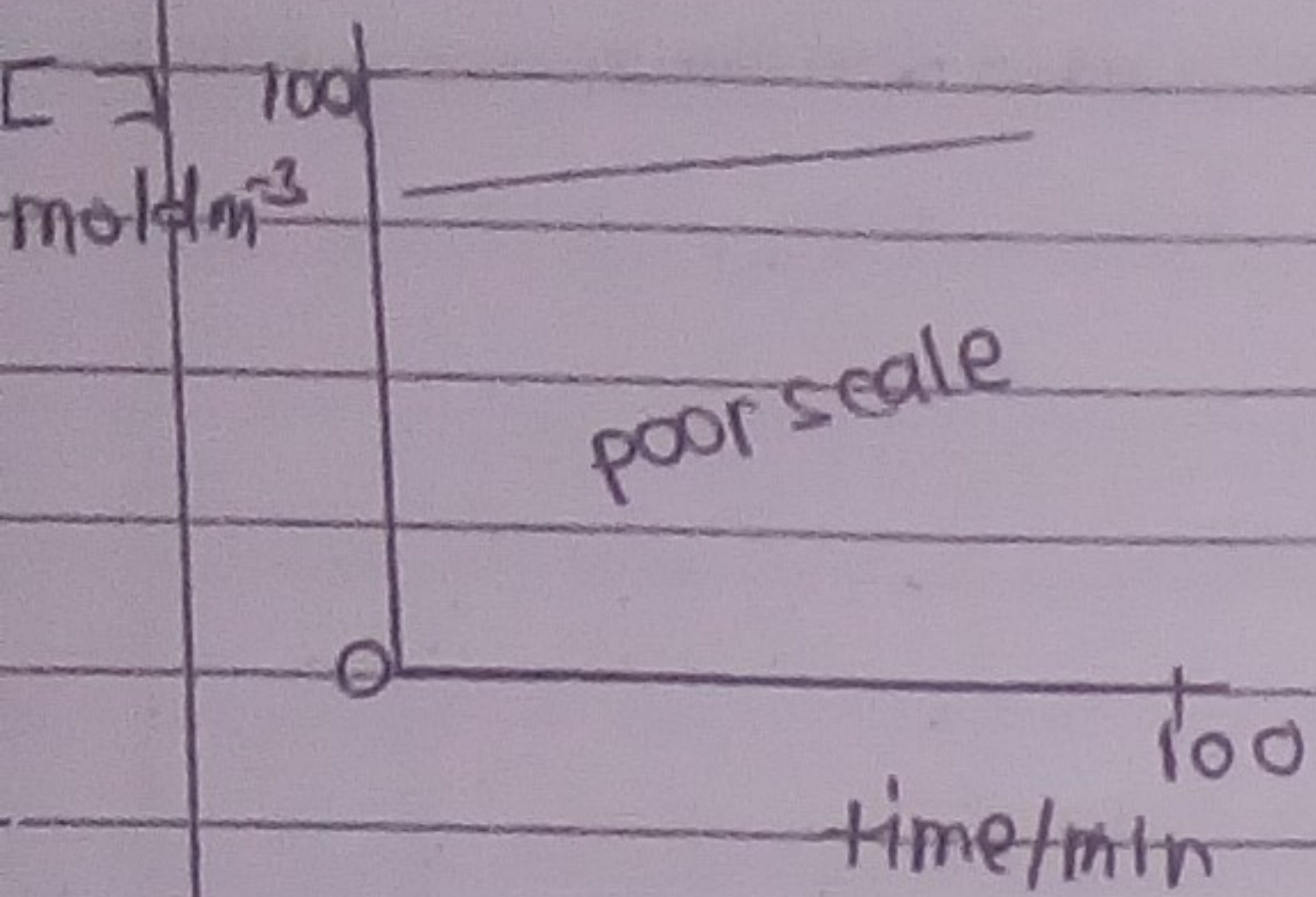
How to plot a graph

When plotting a graph, the following points have to be considered if one is to get all the marks available.

- (i) Scale
 - When choosing a scale, use the one that accommodates all the points to be plotted
 - It should occupy more than half of the graph paper.

Consider

| | | | | | | |
|--------|----|----|----|----|----|-----|
| [A] | 81 | 83 | 89 | 93 | 96 | 100 |
| time/s | 0 | 20 | 40 | 60 | 80 | 100 |



(2) Axis

They should be well labelled, the labels will be coming from the table of results

(3) Plotting the points

- When plotting the points, the following representations can be done: \odot , \times , $+$ just putting a dot on the graph is not plotting
- Plot all the expected points because the examiner will count the plotted points.

(4) Smooth curve

- Find a way of drawing a smooth curve

Evidence of half life

Whenever half life is being considered in the question, dotted lines (evidence) should always be seen on the graph to show how the half life is being obtained.

Reaction Mechanisms

- These are stages which reactants undergo before reaching the products.

- It can also be defined as an ordered set of individual rxns whose overall effect is given by a chemical equation.

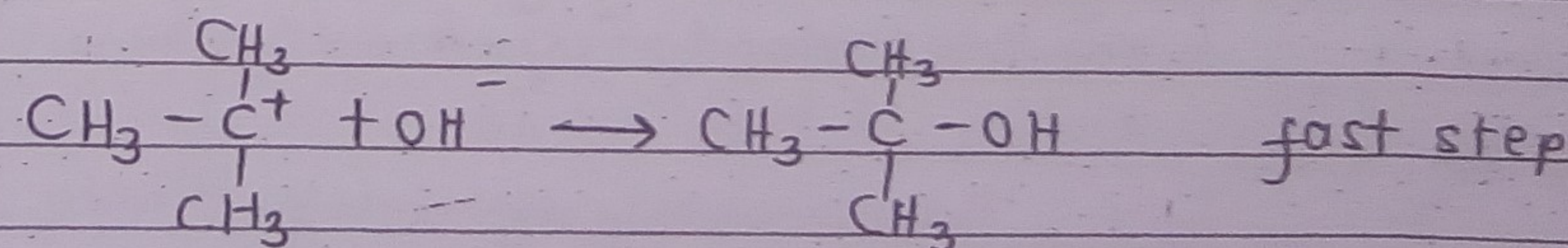
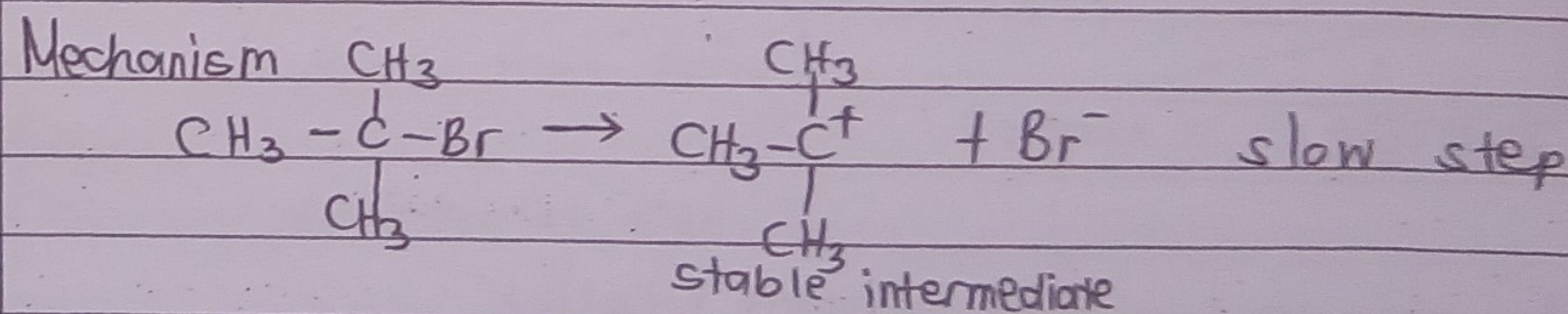
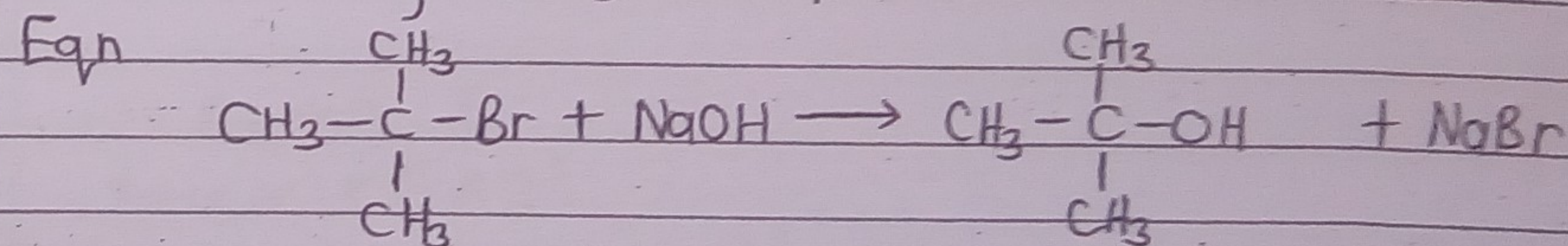
- When looking at rxn mechanisms they occur in different forms i.e.

- the single step rxn mechanism
- a multiple step rxn mechanism

Consider a multiple step rxn mechanism

- In a multiple step rxn mechanism, the rxns in different stages occur at different speeds, some are fast and some are slow
- The slowest step in a multiple step rxn mechanism is an important step because the rate equation is derived from that step
- ← Therefore it is referred to as the rate determining step
- The rate determining step is the slowest step in a multiple step rxn

Consider the following 2 step rxn mechanism



implies: from the rate determining step, the rate equation can be obtained

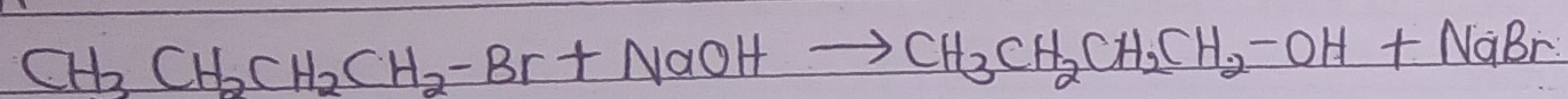
$$\text{Rate} = k [(\text{CH}_3)_3\text{C-Br}]$$

Overall order is 1

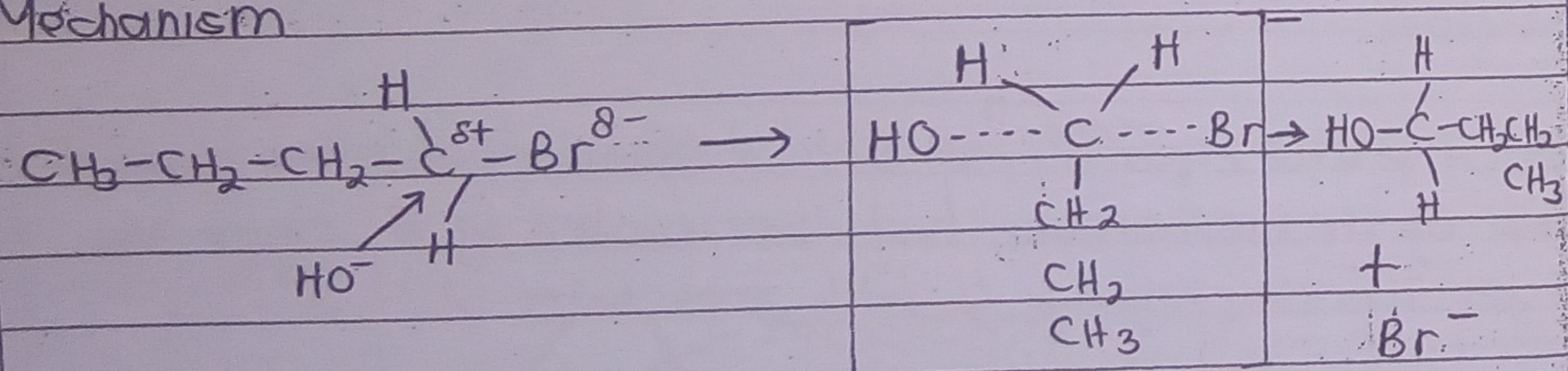
The no. of moles of a reactant in the rate determining step will give us the order of rxn with respect to that particular reactant

Consider a single step rxn mechanism

Eqn



Mechanism



Unstable pentavalent intermediate

Since its a single step rxn we just consider the reactants when constructing the equation

$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{OH}^-]$$

Overall order of rxn is 2

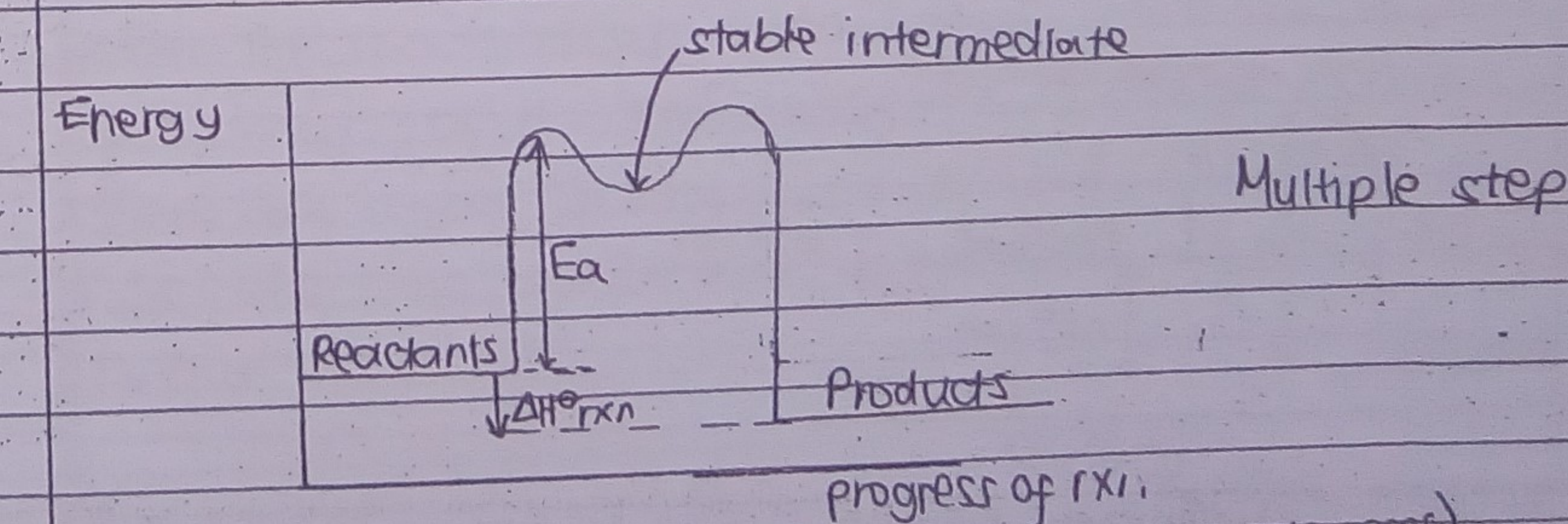
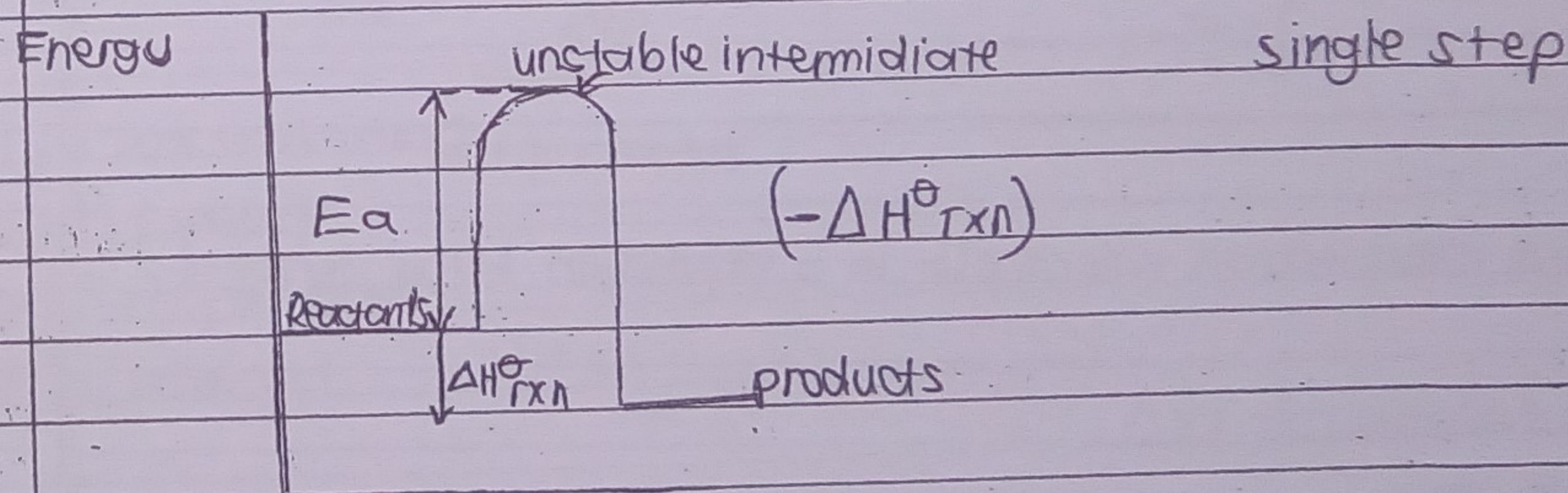
- Intermediate products in a single step rxn are unstable
- Intermediate products in a multiple step rxn are stable

Both multiple step rxns and single step rxns can be represented on an energy profile diagrams.

Energy profile diagram

- This can also be referred to as an energy pathway diagram or a reaction profile diagram or a reaction pathway diagram
- These energy profile diagrams differ depending on the energy changes occurring in that particular rxn

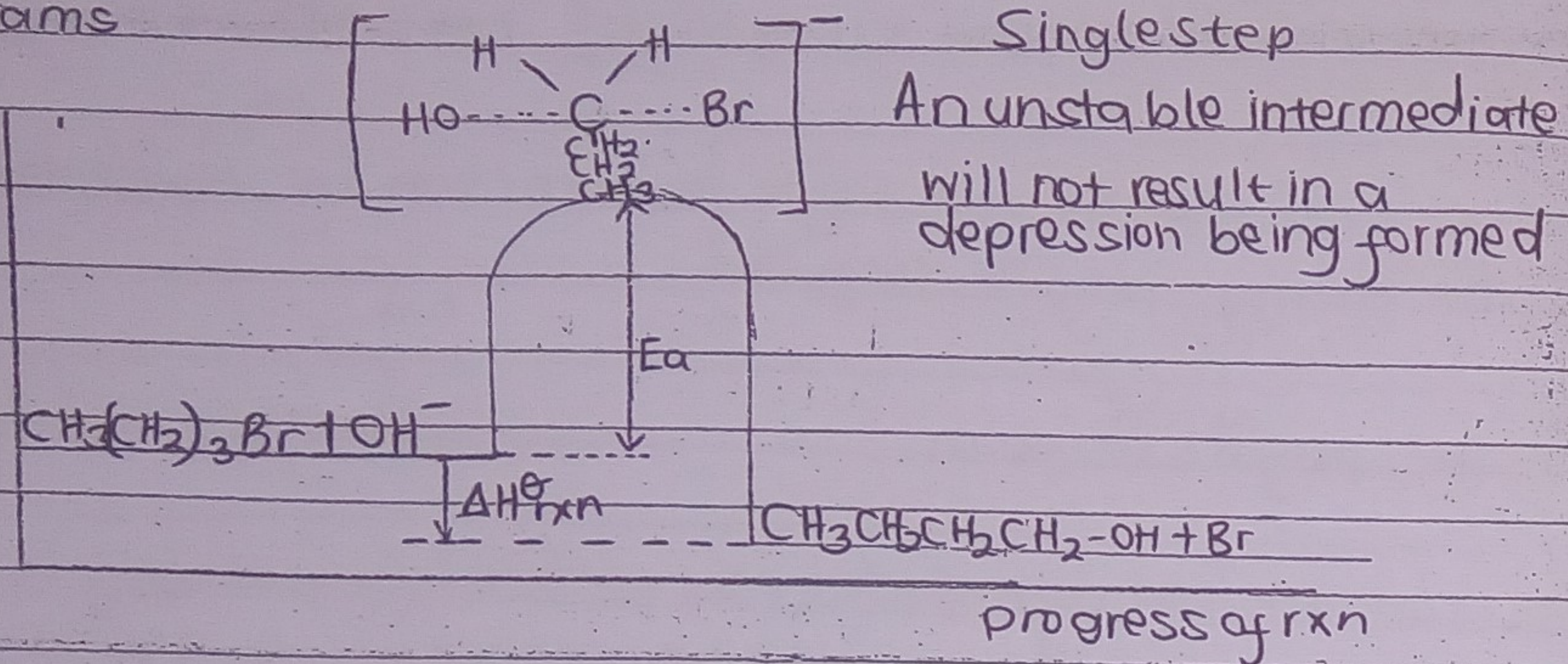
For an exothermic reaction



Therefore considering the two mechanisms above, their energy profile (single and multiple step rxns)

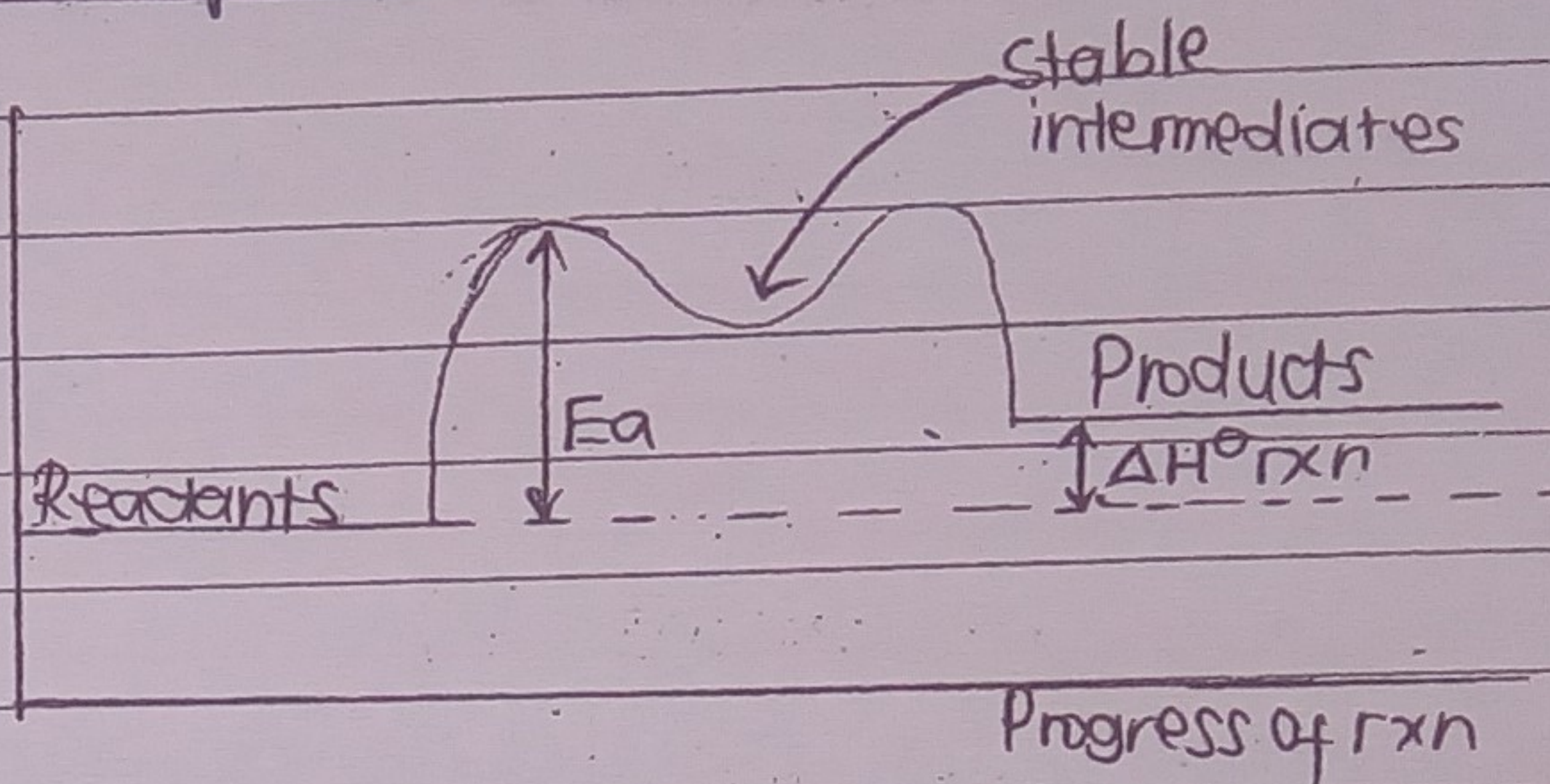
diagrams

Energy
kJ mol⁻¹



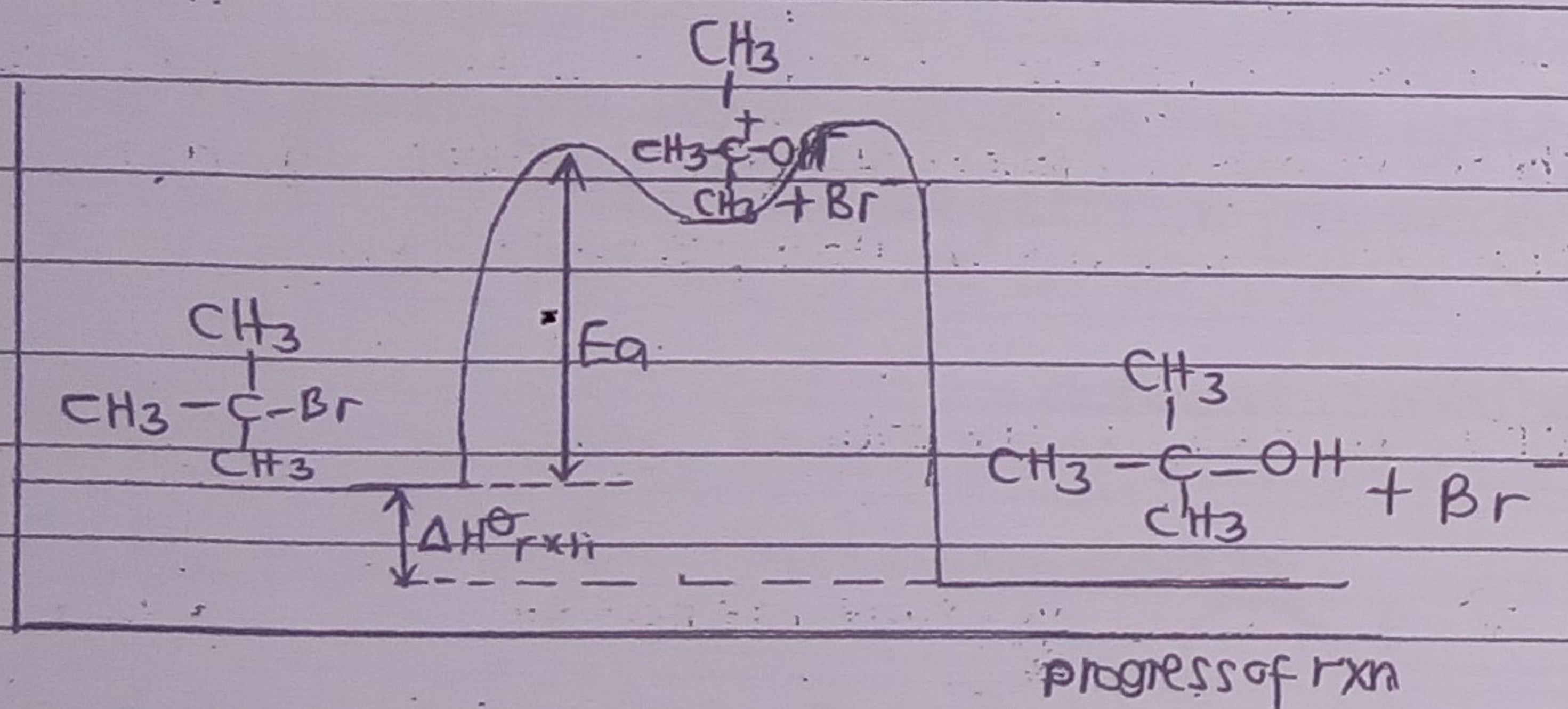
Multiple step rxn

Energy



Multiple step

Energy

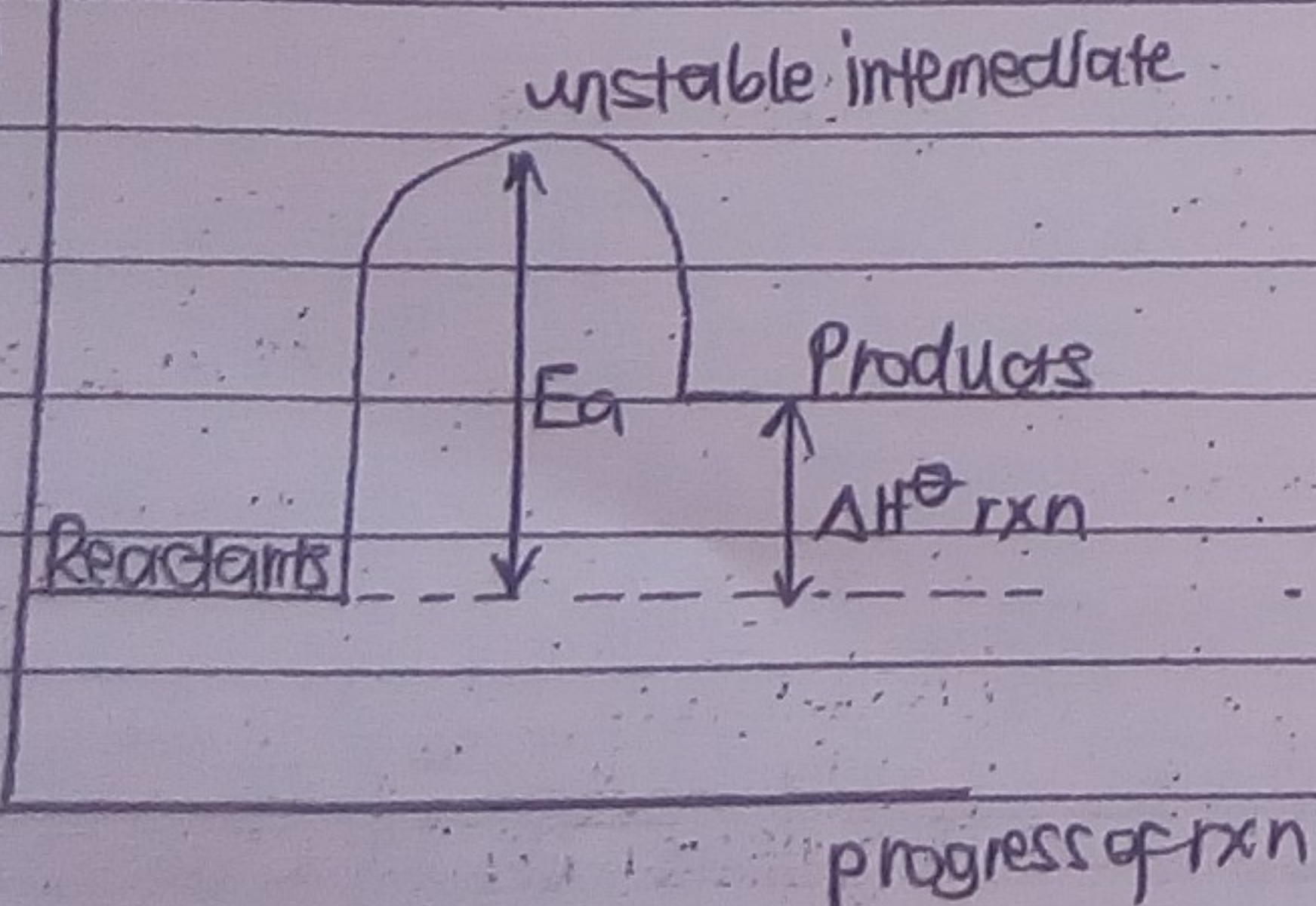


A stable intermediate will result in a depression being formed.

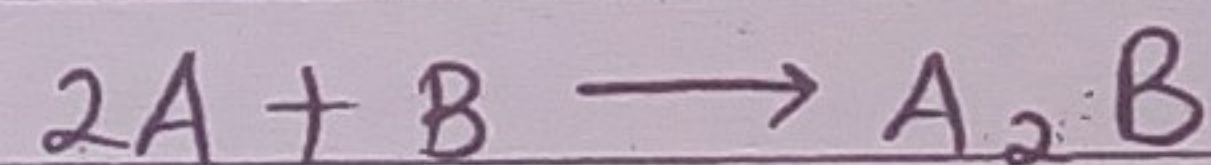
For an endothermic rxn

Single step

Energy
kJ mol⁻¹



Consider the eqn below



Given that Rate Law (Rate eqn) is as follows

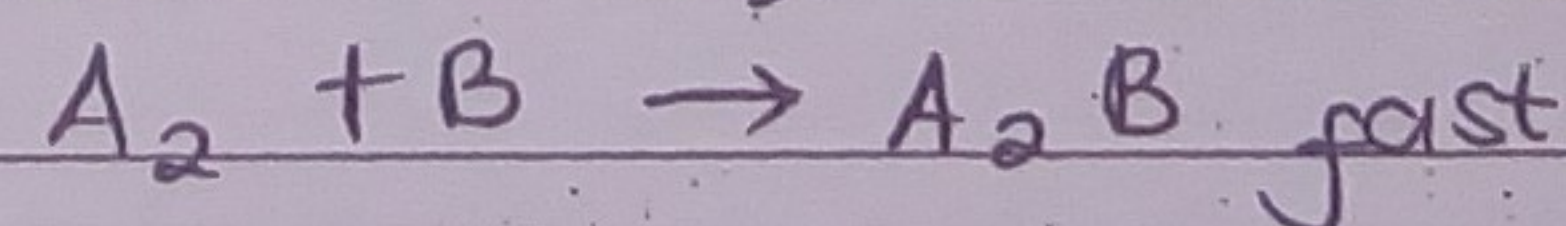
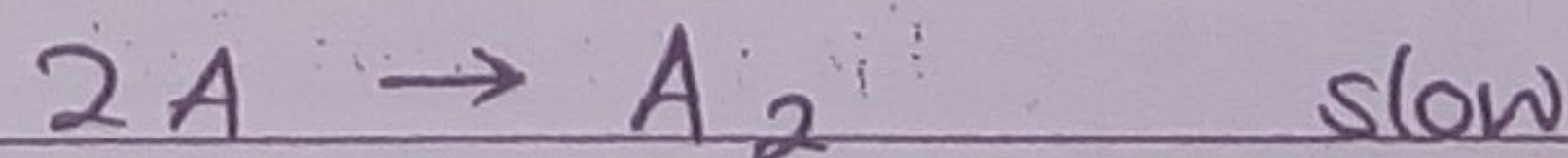
$$\text{Rate} = k[A]^2$$

Suggest a rxn mechanism and hence draw the energy profile diagram

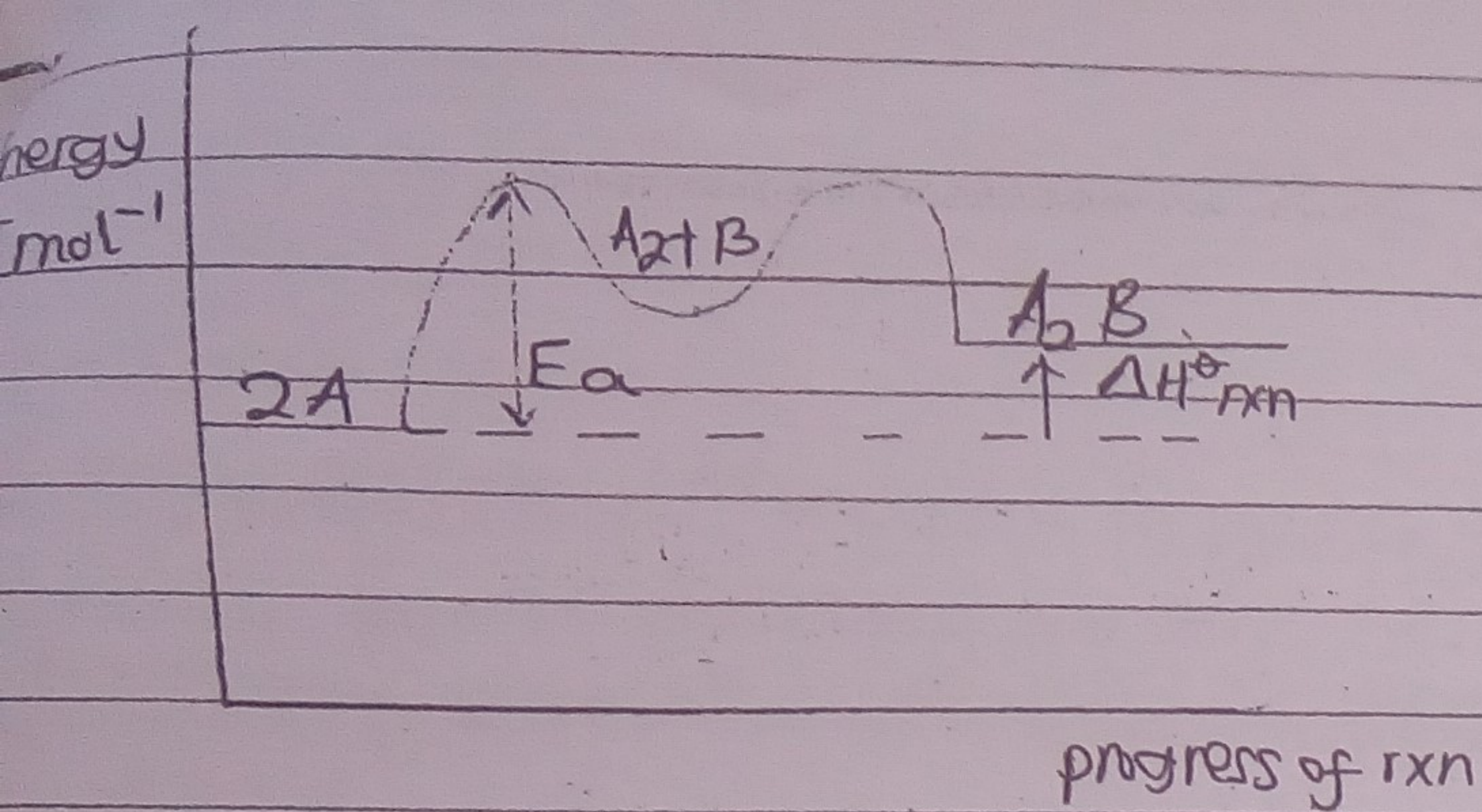
Solution

From the rate equation, it can be deduced that the slow step of the mechanism had two moles of A since the order of reaction is 2 with respect to A.

The mechanism



Multiple step rxns result in stable intermediates thus A₂ is a stable intermediate which is going to be placed in a depression in an energy pathway diagram



Where E_a is activation energy

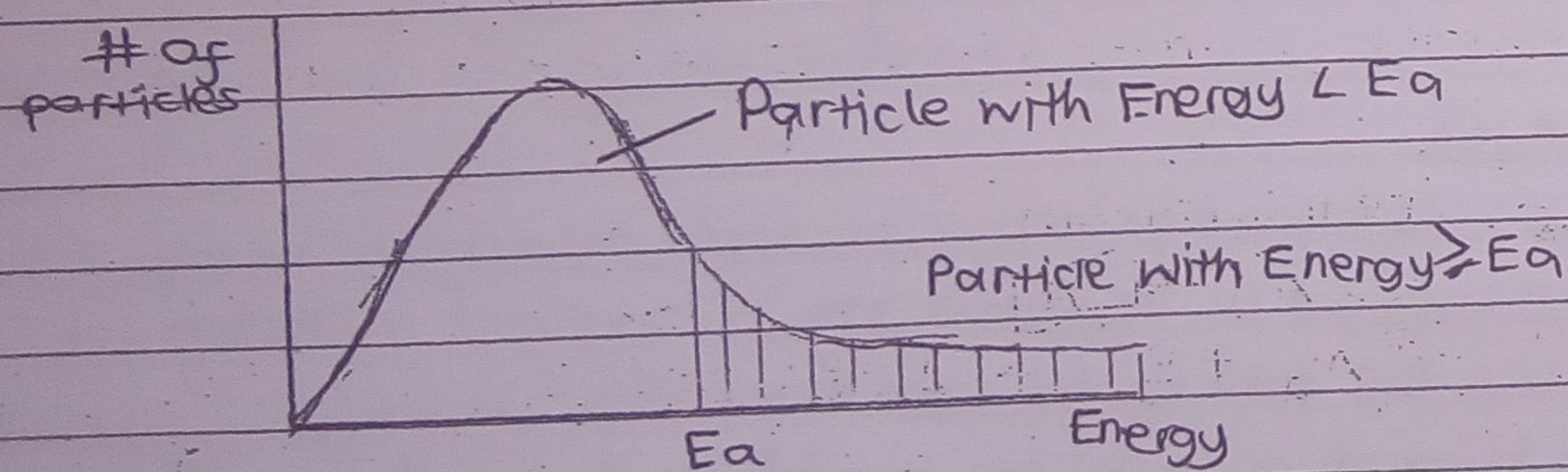
Activation energy, E_a

It is the minimum amount of energy required by colliding particles to react

- Activation energy is symbolised by E_a .
- Activation energy can be represented

- Boltzman's distribution diagram
- Energy profile diagram

Maxwell Boltzman Distribution diagram

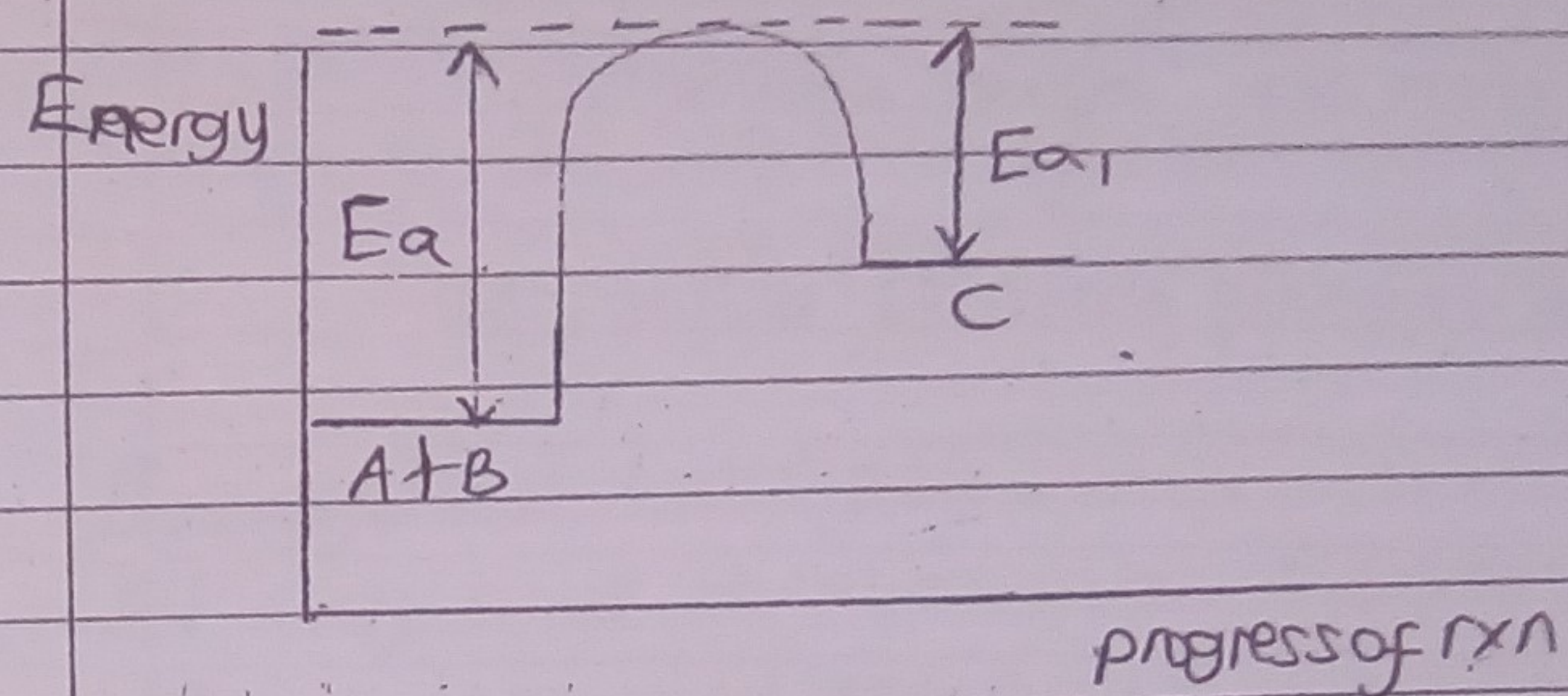
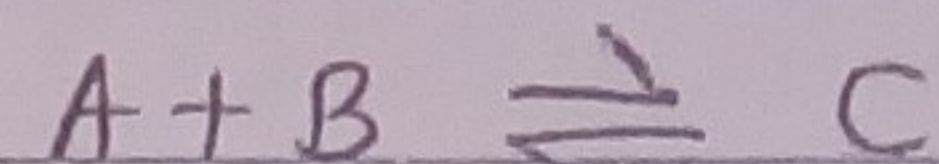


Area under the graph - total # of particles present

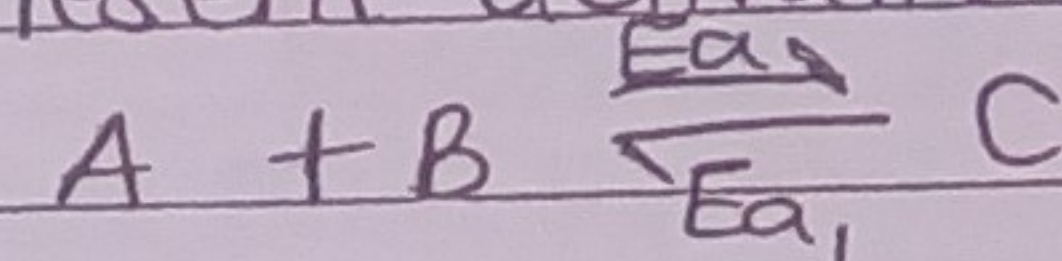
In the above diagram the area under the graph represents the total # of particles present.

Energy profile diagram

Consider a reversible rxn



E_a represents activation energy for the forward rxn and E_{a_1} represent activation energy for backward rxn



Factors affecting the rate of a reaction

- Concentration
- Pressure
- Temperature
- Catalyst

Concentration

- When the concentration of the ~~rate~~ ^{reacting} particles is high, the frequency of the collision of the reactants increase and hence there are higher chances of successful collisions
- When the conc of the ~~rate~~ ^{reacting} particles is low, the opposite is true.

Pressure

When the pressure of the reacting gaseous particles for the

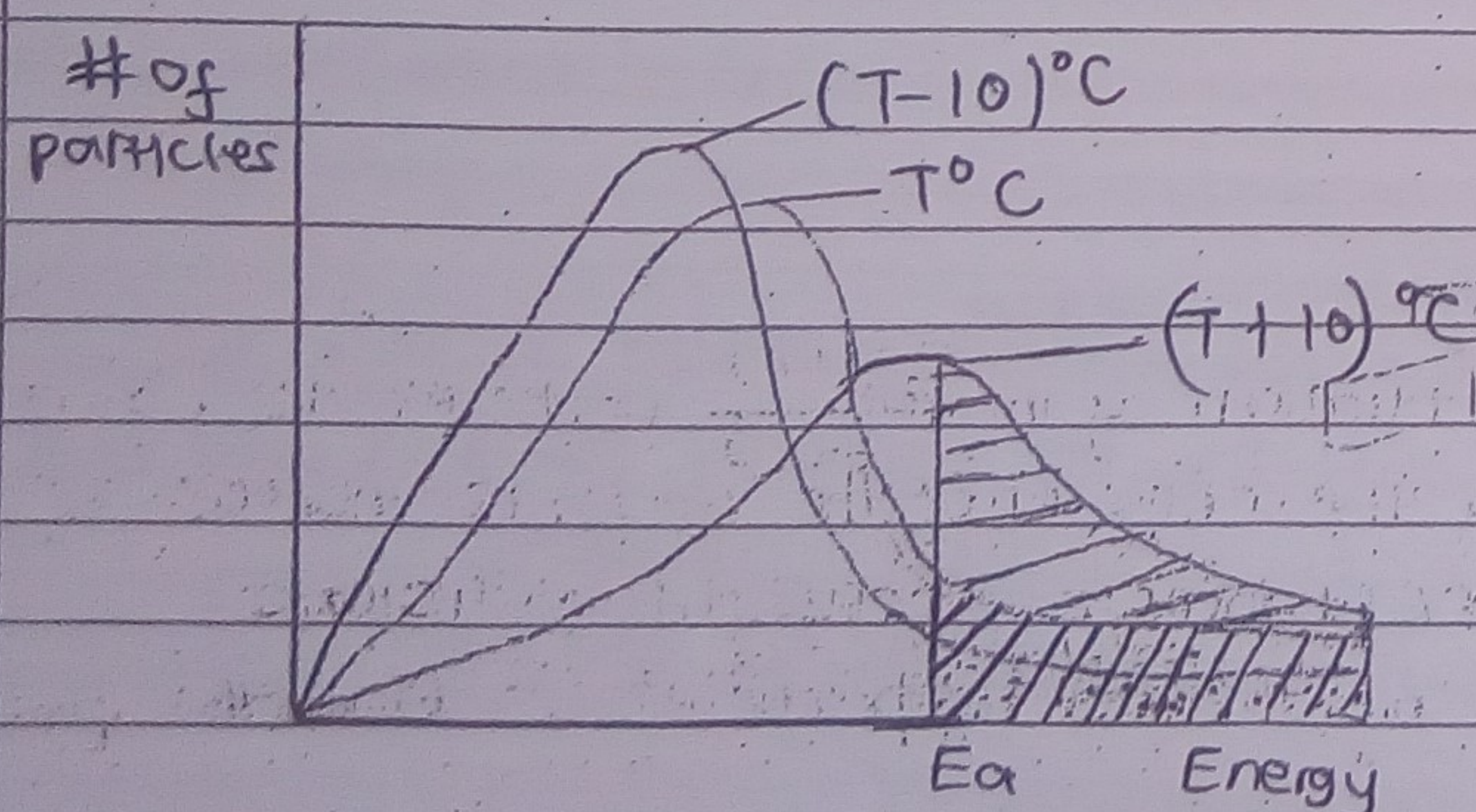
gaseous phase rxn, the rate of the rxn increases.

- Pressure like concentration increases the # of molecules, atoms per cubic centimetre hence increasing \bar{c} collisions.
- With increased collisions, there are higher chances of successful collisions
- When the pressure of the reacting particles is true, the opposite will be true.

Temperature

- When the temp of the reacting particles is increased the rate of rxn increases.
- When the temp of the reacting particles is decreased the rate of rxn decreases.
- To explain the above observations, the Boltzman distribution diagram is employed

The Boltzman distribution diagram showing the effect of temp on the rate of rxn



From the graph

At high temperature

High temp increases the energy of the particles therefore as a result more particles will be possessing energy greater or equal to activation energy. Thus the rate of reaction increases.

- Also at high temp particles gain kinetic energy therefore the frequency of collisions increases.

- This increases the chances of successful collisions occurring

At low temp

- Low temp decreases the energy of the particles therefore less particles will be possessing energy equal or greater than activation energy. Thus the rate of reaction decreases.

- Also at low temp particles will be having less kinetic energy resulting in the frequency of collisions decreasing.

- This decreases the chances of successful collisions occurring

(iii) Catalyst

- When a catalyst is introduced into a chemical reaction, it increases the rate of the reaction.

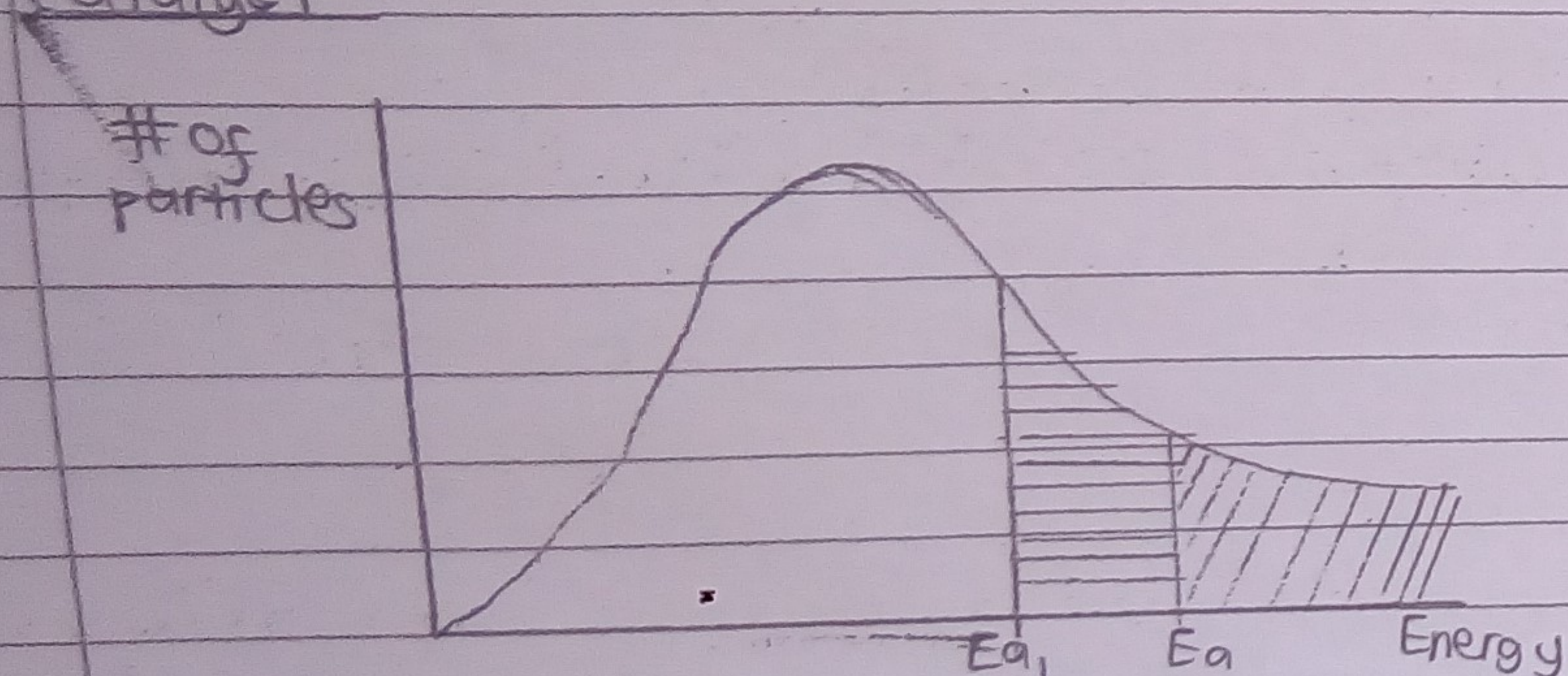
- This is because a catalyst would have found a way (alternative way) or alternative path w/c uses a lower activation energy.

NB, A catalyst does not lower the activation energy

The effect of a catalyst on the rate of a chemical rxn can clearly be illustrated on a

- (i) Boltzman distribution diagram
- (ii) Energy pathway diagram

Boltzman distribution diagram to show the effect of a catalyst

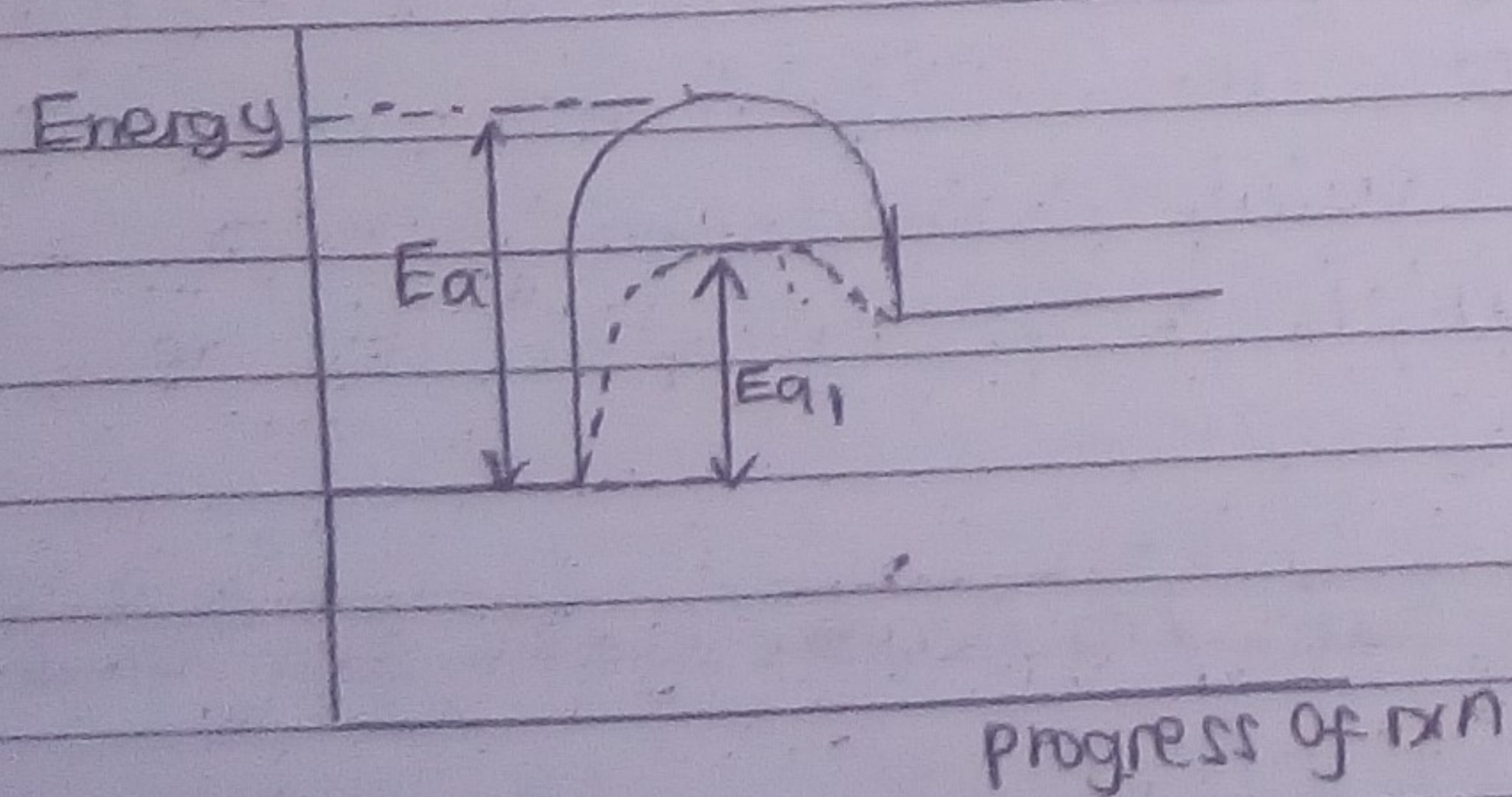


E_a - activation Energy for an uncatalysed rxn

E_{a_1} - activation Energy for a catalysed rxn

Since the E_a for a catalysed rxn is lower, more particles will be having energy equal or greater than activation energy hence the rate of rxn increases

Energy profile diagram to show the effect of a catalyst



Catalysis

- A catalyst is a substance which speeds up the rate of a rxn (chemical rxn)

There are two types of catalysts which can catalyse a chemical rxn and these are: (i) homogenous catalysts
(ii) heterogenous catalysts

Homogenous catalysts

- A homogenous catalyst is a substance which increases the rate of a chemical rxn and it will be in the same physical state as the reactants in the reaction

Since most of these catalysts in chemical rxns are transition elements, properties of transition elements will therefore be used to explain how catalysts work

How a homogenous catalyst works

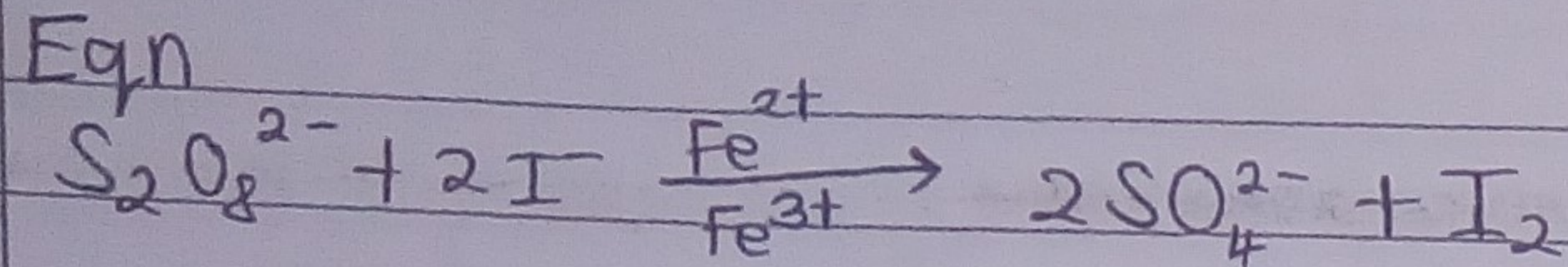
A homogenous catalyst works by transferring electrons from one reactant to the other

Why is it homogenous catalysts are able to transfer electrons?

This is because transition elements have an ability to vary their oxidation states.

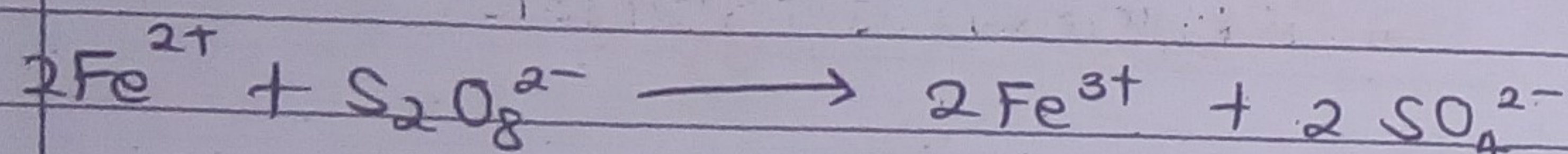
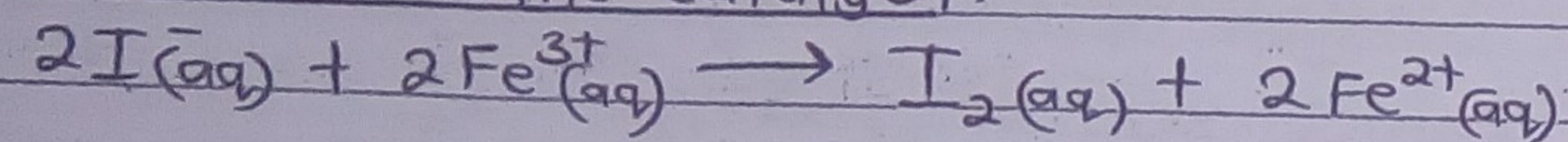
Example of homogenous catalysts

Reaction of the peroxodisulphate ions and the iodide ions being catalysed either by Fe^{2+} ions or Fe^{3+} ions



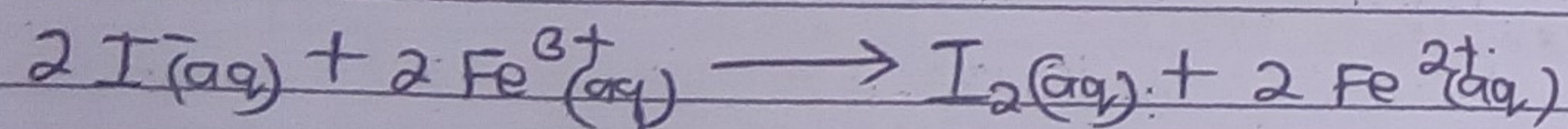
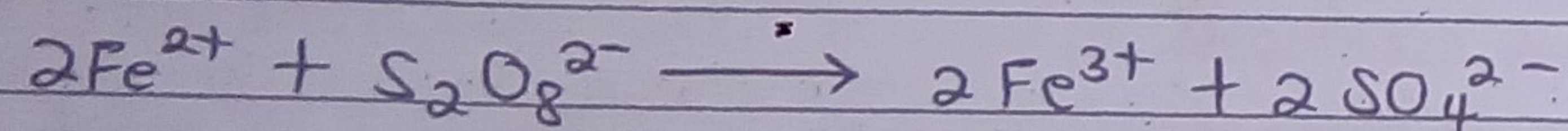
How the catalyst works

When Fe^{3+} is the catalyst.



Fe^{3+} catalyst is generated

When Fe^{2+} is a catalyst



Fe^{2+} catalyst is generated

In the above reaction, the $S_2O_8^{2-}$ ions and iodide ions could not react on their own because they are all negatively charged hence forth they rebel each other

Heterogenous Catalysis

A heterogenous catalyst is a substance which speeds up the rate of a chemical rxn and it will be in different physical states as the reactants in the reaction

How a heterogenous catalyst works

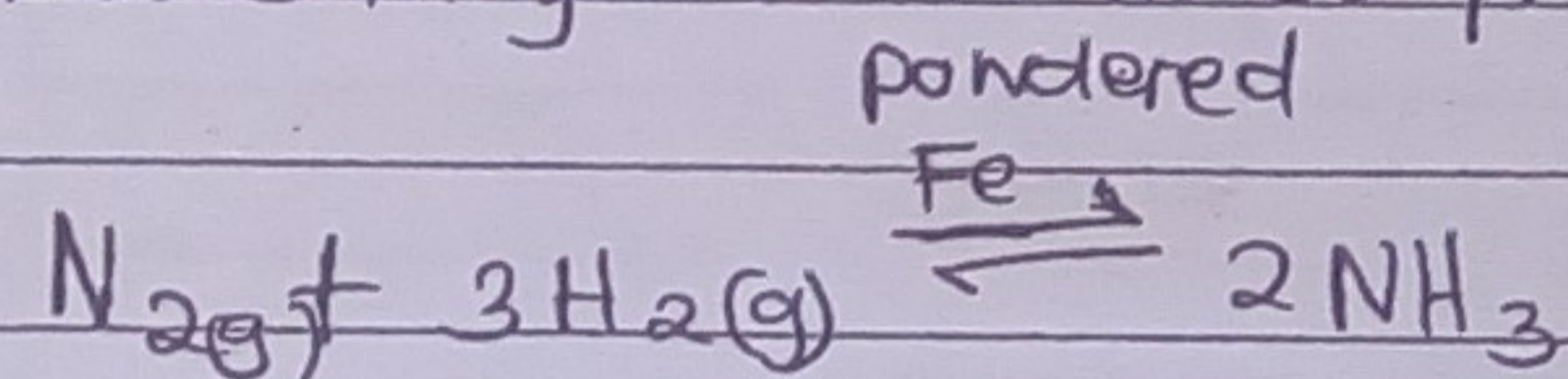
- Heterogenous catalysts work by allowing reactants to adsorb on its surface which results in the formation of temporary dative bonds

- This then weakens the other internal bonds of the reactants resulting in reactions easily occurring

Why do heterogenous catalysts allow formation of dative bonds on their surface

- This is because transition elements contain a partially filled d orbital which allows, accommodate electrons to form dative bonds

e.g Iron catalyst in the Haber process



COMPILED BY

..the DIRECTOR..

0712105452