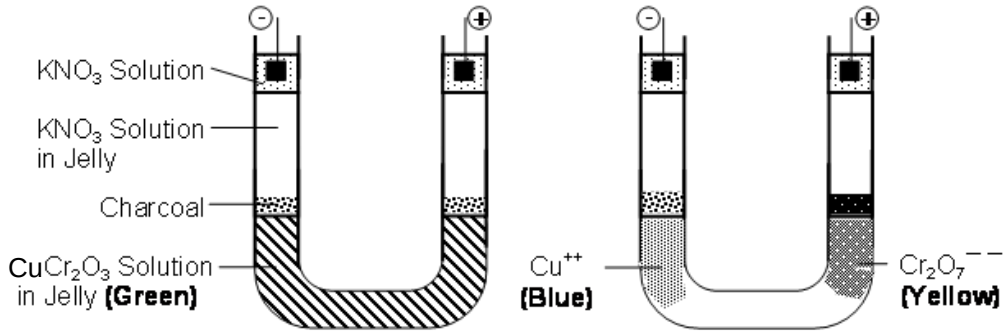
Shri R. L. T. College of Science,

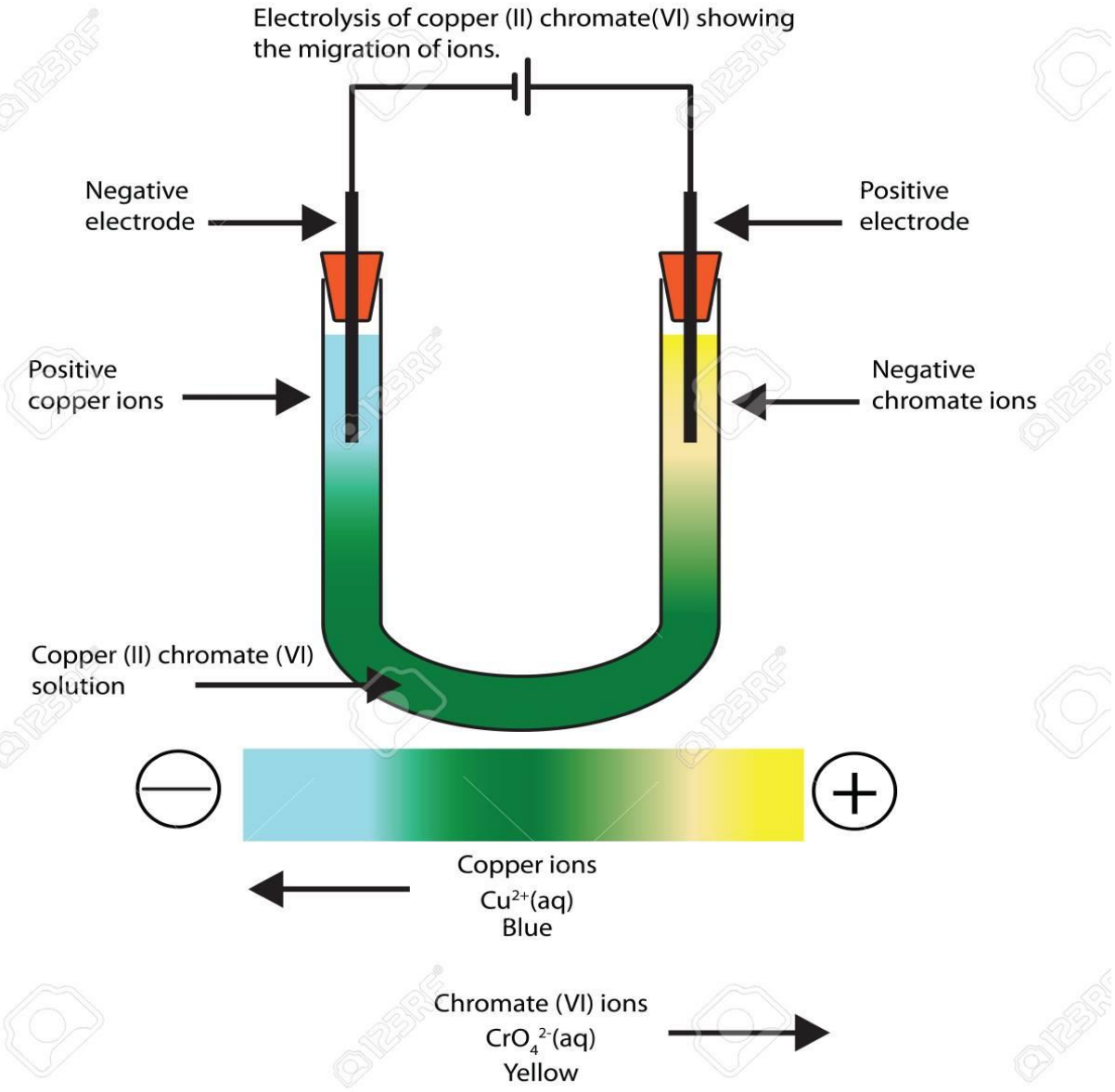
Chapter 6 (Physical chemistry)

B. Electrochemistry

Migration of ions under influence of electric field:



- On passing electric current through electrolyte solution, ions migrate and discharged oppositely charged electrodes. The migration of ions can be demonstrated by simple experiment.
- The lower portion of U-tube is filled with 5% agar-agar solution in water with small quantity of $CuCr_2O_7$.
- It is allowed to set by cooling as dark green jelly. Some charcoal powder is sprinkled in both limbs.
- Then solution of KNO_3 and agar-agar is placed in each limb and allowed to set as jelly.
- Finally solution of KNO_3 in water is filled in each limb and platinum electrodes are placed as shown in figure.
- When electric current is passed, Cu^{2+} ions migrate towards cathode (-ve electrode). Due to this blue colour appears in cathode side and yellow colour in anode side by $Cr_2O_7^{2-}$ ions. From the movement of these colour bands, speed of ions can be compared.



Hittorf's theoretical device:

- We know that ions move to the oppositely charged electrodes under the influence of electric current.
- But the speed of cation migrating towards cathode & those of anions migrating towards the anode are not necessarily same.

- The speed of cations moving away from anode will be proportional to the fall of concentration of these ions at anode. Similarly The speed of anions moving away from cathode will be proportional to the fall of concentration of anions around the cathode.
- Hittorf studied such changes experimentally & gave a general rule known as "Hittorf Rule"
- *It states that the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.*
- Although most of ions differ in their mobilities, the total number of ion discharged at electrodes on electrolysis is same.
- This can be explained by Hittorf's theoretical device as shown in figure. It consists of an electrolytic cell containing same number of positive and negative ions with same valency.
- The electrolytic cell is divided into three compartments by porous partitions B & C. Metal electrodes A and D represent cathode and anode respectively.

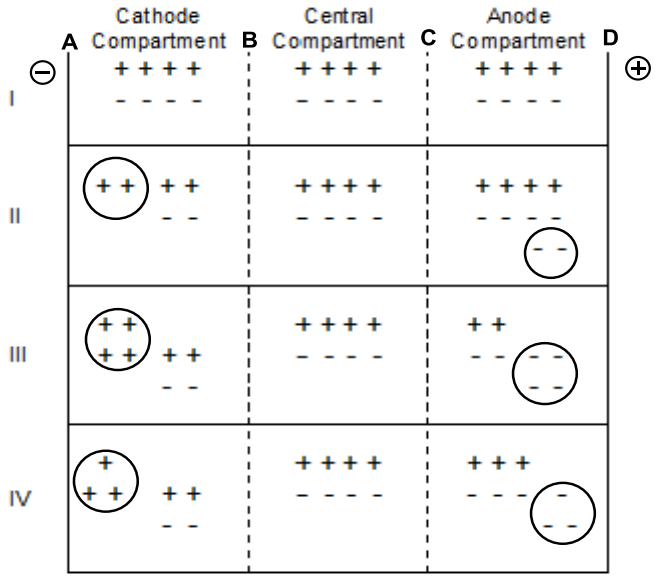


Fig. Hittorf's theoretical device

I. Represents initial state of electrolyte solution before electrolysis in which equal number of positive and negative ions are present.

On passing electric current, three cases may arise:-

II. Suppose, *only anions are migrating and cations remains stationary*.

If speed of anion (v = 2) and speed on cation (u = 0). Then, two anions migrate from cathode to anode compartment and are discharged at anode. The unpaired cations in cathode compartment are discharged at cathode. Therefore, the number of ions discharged in both compartments is two.

III. Suppose, *both ions are moving with same speed*.

Let $u = v = 2$, then the number of ions discharged at respective electrode is four.

IV. Suppose, *both ions are migrating with different speeds* (u = 1, v = 2). In this case, total number of ions discharged is three.

Following conclusions can be drawn about the process of electrolysis:

1) During electrolysis, ions are discharged in equivalent amounts, irrespective of their speeds of migration.
2) Concentration of electrolyte around electrode changes as a result of migration of ions.
3) Fall in concentration around the electrode is directly proportional to the speed of that ion which moves away from that electrode.

$$\therefore \quad \frac{Fall\ in\ concentration\ around\ anode}{Fall\ in\ concentration\ around\ cathode} = \frac{Speed\ of\ Cation}{Speed\ of\ Anion}$$

$$\frac{u}{v} = r\ (Speed\ ratio)$$

4) Total current carried by solution is measure of (u + v). This holds good when the electrodes or ions are not attacked by solutions.

In above illustration concentration of central compartment remains constant. Whatever be the speed of ions, the number of ions discharged on electrode is always equal.

Transference number or transport number or Hittorf's number of ions:

During electrolysis current is carried by cations and anions. *"The fraction of the total current carried by an ionic species is called its transference number or transport number"*. The transport number of ions is proportional to their absolute velocities.

The transport number of cation (t_+) and anion (t_-) is given as

$$t_+ = \frac{u}{u+v} \qquad t_- = \frac{v}{u+v}$$

u = Speed of cation $\qquad$ v = Speed of anion

"Sum of two transport numbers will be one".

$$t_+ + t_- = 1 \qquad \text{OR} \qquad t_- = 1 - t_+$$

If the speed ratio is $r = \frac{u}{v} = \frac{t_+}{t_-}$

$$\therefore \quad r = \frac{t_+}{t_-} = \frac{t_+}{1-t_+} = \frac{1-t_-}{t_-}$$

$$\therefore \quad r\,t_- = 1 - t_- \quad \text{OR} \quad t_- + r\,t_- = 1 \quad \text{OR} \quad t_-(1+r) = 1$$

$$\& \quad t_- = \frac{1}{1+\mathrm{r}}$$