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MEASUREMENT OF TRANSFERENCE NUMBER AT HIGHER TEMPERATURE

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ABSTRACTS:-

As the cations and anions usually have different speed under the same potential gradient the quantity of electricity carried by the cations in one direction will differ from that carried by anions in the other. The knowledge of Transference number is quite important. To measure the transference number at higher temperature Hittrioff's apparatus is failed due to the possibility of inter mixing of the anode and cathode solution through diffusion and convection is large. So W shaped apparatus is fabricated so that the transference number of Na_2SO_4 can be measured even at higher temperature. The accuracy and the working of the W shaped apparatus is tested by calculation of Transference number of Cu^{+2} .The most stuking observation in case of Na_2SO_4 is that as temperature increases the transference number of Na^+ increases what as that of SO_4^{-2} decreases. The observation is in accordance with the known effect of temperature according to which the transference number of both cation and anion tends to closer to 0.5 the ion for which it is less than 0.5 tends to increase and for the ion for which it is more than 0.5 tends to decrease with temperature.

Key Words- Transference number, W shaped apparatus, Cluster of cations, Cluster of anions, Hittroff's apparatus,

INTRODUCTION

The current in the solution of electrolyte is carried by virtue of migration of ions between the electrodes and the amount of electricity carried by a particular ion is proportional to the speed of that ion. As cations and anions usually have different speed under the same potential gradient the quantity of electricity carried by the cations in one direction will differ from that carried by anions in the other. It is because of this reason that the change in the concentration around the electrode is not the same inspite of the fact that the equivalent amount of positive and negative ions are discharge at the electrodes. The knowledge of transference number is quite important. The some of the important application of this knowledge are fundamental information, structural investigation, separation, constitution of electrolytes from transference number. In the Laboratory transference number is determined by three methods i) Hittorf's method ii) The moving boundary method iii) from the measurement of EMF of concentration cell with a liquid junction.

Objective of work

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The temperature affects the transference number in such a way that both t_+ and t_- tend to come closer to 0.5. Therefore this work was increases to measure the transference number at various temperatures. The Hittorf's apparatus is not convenient and in case of moving boundary method a special indicator is required and it is also not possible to mesure at different temperature. In EMF method also we are not able to measure the transference number at different temperature. Threfore a specially arranged apparatus is to be made to measure the transference number at different temperature this will require putting the apparatus in thermostat so that the temperature can be varied. In case of Hittorf's apparatus it is not easy to carry out such experiments.

Further in Hittorf's apparatus at higher temperature the possibility of inter mixing of the anode and the cathode solution through diffusion and convection (thermal and mechanical) is large . Thus the main object of the work was to fabricate a modified version of Hittorf's apparatus which can be suitably used to measure the transference number at different temperature. The apparatus so fabricate will be used to determine transference number of alkali salts i.e.Na_2 SO_4 at different temperature.

Methods and Materials

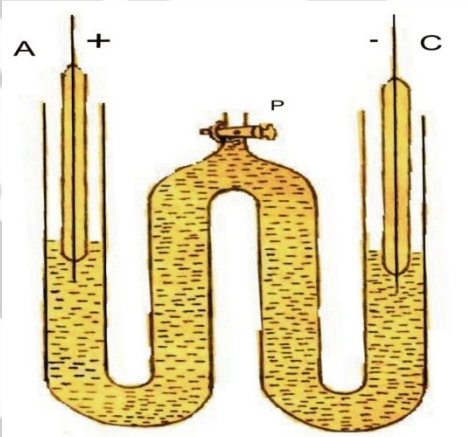
All the chemicals used are of A.R.Grades. The coppercolo meter is prepared by taking 15 gms copper sulphate, 5 gm sulphuric acid, 5 gms ethyl alcohol and 100 gms water in a beaker.

a) Estimation for SO_4^{-2} :- Sulphate in acid solution can not be titrated directly against a solution of barium salt because rhodizonic acid is unstable and soon decomposes. A known excess of barium chloride solution is added excess of barium chloride solution is added to sulphate solution and add 1 to 2 ml of alcohol and excess of barium titrated with 0.025 M sulphuric acid unitll the colour changes from red to colourless. This preocedure is done before and after electrolysis and from this result the concentration of SO_4^{-2} can be calculated. The estimation of sodium is done by flame photometry instrument.

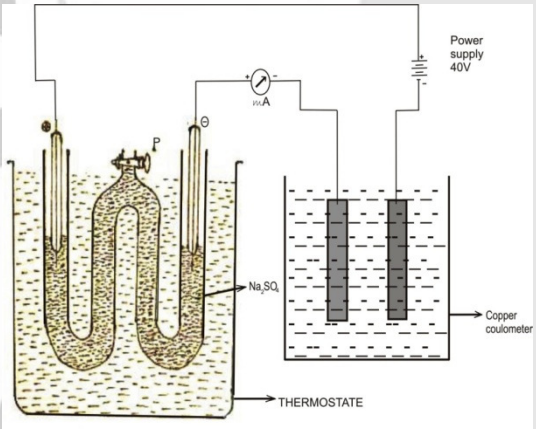
b) Design of apparatus for determination of Transference number:- A double bent tube with a long horizontal portion say as long as two and a half falt is used as the cell.

The cell is a W tube of total capacity of about 120 ml and the electrodes are bright platinum wires. This cell designs (W) as shown in fig. It has the advantages of preventing the intermiking of anode and cathode solutions through diffusion and convection during electrolysis and easy separation of the anolyte the Catholyte .

The outer diameter of tube of a W shaped apparatus is 22 mm. and the height of apparatus is 30 cm.



DESIGN OF APPARATUS



EXPERIMENTAL SET UP

Experimental procedure:-

The W tube is filled up the electrolyte Na_2SO_4 (0.1M) solution as shown in fig.(3) so that the solution levels at the two limbs are always some what below that of P. This can be achieved

by filling the W Tube tube with electrolyte upto a level P, then pipetting out the solution from the side limbs after closing the stop cock P.Before starting the current, calculated amount (on the basis of 1 mA –hour = 0.0373m. equivalent of acid / alkali) of N H_2SO_4 and N NaOH which is enough to neutralize the alkali and acid produced at cathode and anode is added carefully at the respective electrodes. Electrolysis is then immediately carried out.

Result and Discussion. :-

a) Transference number of Cu $^{+2}$:-

In the present work a modified (W-tube) apparatus is used to determine the transference number of anion and cation. In order to test the accuracncy and the working of the apparatus, transference number of Cu ++ was determined by the usual Hittorf's method except that now instead of using the conventional Hittorf's apparatus W. tube apparatus was used. The results are summarized in table I

Concentration of $CuSO_4$	=	0.05M
Current	=	15 mA
Time	=	3 hour
Voltage	=	25 Volts
Temerature	=	25 ^{O}c

Table I

Sr.No.	Apparatus used	Concentration Before Electrolysis	Concentration After Electrolysis	Cu deposited	t_+
1	Hittorf's	0.0573	0.0337	0.0532	0.365
2	W tube	0.0562	0.0186	0.0599	0.372

From table 1 it is observed that the transference number of cation (Cu $^{+2}$) is in good agreement with the one determined from Hittorf's Appartus.

b) Transference number of Na $^{+}$ and SO_4^{-2} : -

The W tube apparatus was fitted in a thermostat and filled with Na_2SO_4 solution (0.1M) . Before starting the current calculated amount of N H_2SO_4 and N NaOH were added at cathode and anode, which were anode during electrolytes. The results are summarized in table II.

Concentration of Na_2SO_4 = 0.1M

Current = 25 mA

Time = 2 Hours

Voltage = 40 Volts

Table II

Sr.No	Temperature	Cathode Solution Na^+ determination			Anode solution SO_4^{-2} determination			Copper deposited
		Before	After	Change in Conc.	Before	After	Change in Conc	
1	25 ^oc	0.0873	0.066	0.0213	0.628	0.378	0.25	0.0726
2	30 ^oc	0.1721	0.1528	0.0193	1.075	0.86	0.215	0.0626
3	35 ^oc	0.1793	0.1613	0.0180	0.855	0.620	0.235	0.0653
4	40 ^oc	0.2385	0.2213	0.0172	0.7465	0.51	0.2365	0.0662

From the data given in table II the transference number calculation on the basis of the analysis of cathodic and anodic solution are summarized in the table III and IV.

Table III

Transference number of Na^+ and SO_4^{-2} by the analysis of cathode compartment solution(Na^+ estimation)

Sr.No	Temperature	t_+	$t_- = 1 - t_+$
1	25 ^oc	0.3964	0.6066
2	30 ^oc	0.396	0.6040
3	35 ^oc	0.4015	0.5985
4	40 ^oc	0.4193	0.5807

Table IV

Transference number of Na^{+} and SO_4^{-2} by the analysis of anodic compartment solution (SO_4^{-2} determination)

Sr.No	Temperature	t -	$t_+ = 1 - t_-$
1	25 ^{O}c	0.6444	0.3556
2	30 ^{O}c	0.6399	0.3601
3	35 ^{O}c	0.6112	0.3888
4	40 ^{O}c	0.5999	0.4001

The most stuking observation is that as the temperature increases the transference of number Na^{+} increases where as that of SO_4^{-2} decreases. The observation is in accordance with the known affect of temperature according to which the transport number of both cation and anion tends to be closer to 0.5 for the ion for which it is less than 0.5 tend to increase and for the ion for which it is more than 0.5 tend to decreases with temperatures.

. These results can be explained if we imagine that only movement of Na^{+} and SO_4^{-2} ions across the partition would lead to liberation of acid and alkali at the electrodes. The liberation of acid and cathode forms and these species take more and more put in the alkali are observed. This means that change clusters of cations and water molecule at the anode and anions and water molecules at the current conductions with increases in temperature. These species break down after moving for some distance.

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