STUDIES OF CELLS WITH LIQUID JUNCTIONS

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1. INTRODUCTION

An electrochemical cell usually includes at least one junction between two different electrolytes of different concentrations of the same electrolyte where interdiffusion of ions occurs. This diffusion of ions gives rise to a potential due to their different mobilities. A steady state is reached soon after interdiffusion starts and a steady potential is observed.

In the present work the liquid junction is formed in a capillary tube of cylindrical symmetry in a cell vessel shown in fig. 1. This is a slight modification of a previous one developped by the author[1] and shown in fig. 2.

The experimental values are compared with calculated ones using Harper's[2] program.

2. EXPERIMENTAL

2.1. Electrodes

Silver silver bromide electrodes were prepared by the thermal--electrolytic type[3]. Their bias potential was less than 0.05 mV. The reproducibility of different batches of electrodes was checked measuring the potential of the cell

$$Ag|AgBr|HBr(0.1\ mol\ Kg^{-1})|(0.1\ mol\ Kg^{-1})\ KBr|AgBr|Ag$$

each time a new batch was made. The value obtained was 28.28 ± 0.03. The values were taken for different batches prepared over a period of approximately 2 years.

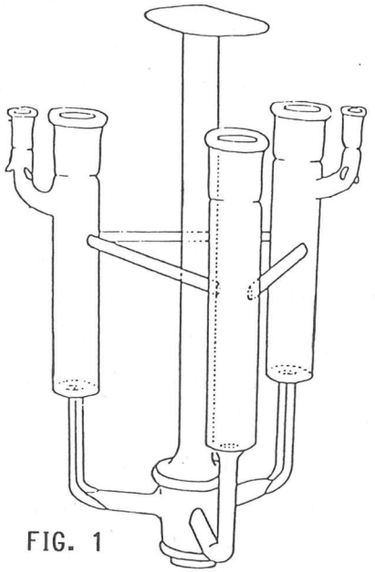

FIG. 1

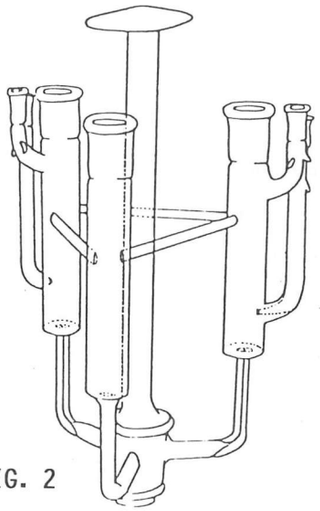

FIG. 2

2.2. Materials

HBr-BDH AnalaR (46-48%) and Merck proAnalysis (47%) were used. BDH AnalaR was distilled and the middle third collected. The whole apparatus was protected from exposure to light. The concentration of the azeotropic mixture thus obtained was determined gravimetrically by weighing silver bromide. Exposure to light was also avoided during the titration procedures.

No distillation was found necessary for the Merck HBr whose concentration was also determined gravimetrically.

KBr, NaBr BDH AnalaR were dried at 110°C and used without further purification.

LiBr - xH_2O - Suprapure - Merck; $MgBr_2$ - $6H_2O$ and $BaBr_2$ - $2H_2O$ purum p.a. Fluka were used without further purification. Each of these last three substances were dissolved in conductivity water to form concentrated stock solutions which were gravimetrically analysed by weighing silver bromide. The solutions were prepared by weight with conductivity water redistilled from distilled water, to which potassium permanganate and sodium hidroxide were added. They were purged of O_2 by bubbling with N_2.

2.3. Results

The potentials of the following cells were measured on a HP 3478 A DVM.

$$\mathrm{Ag|AgBr|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{HBr}}\mathrm{|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{MBr_\nu^-}}\mathrm{|AgBr|Ag} \qquad \text{(I)}$$

$$\mathrm{Ag|AgBr|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{KBr}}\mathrm{|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{MBr_\nu^-}}\mathrm{|AgBr|Ag} \qquad \text{(II)}$$

$$\mathrm{Ag|AgBr|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{HBr}}\mathrm{|}\underset{(3.5\ \mathrm{mol\ Kg^{-1}})}{\mathrm{KBr}}\mathrm{|}\underset{(0.1\ \mathrm{mol\ Kg^{-1}})}{\mathrm{MBr_\nu^-}}\mathrm{|AgBr|Ag} \qquad \text{(III)}$$

with M - Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}.

The results obtained were

TABLE I

M	CELL I	CELL II	CELL III
Li	34,30	6,90	3,90
Na	32,56	4,50	2,19
K	28,27	----	2,35
Mg	12,70	-1,45	-11,12
Ba	10,75	-7,60	-17,15

The values for cells I and II are similar to the corresponding chlorides referred in the literature[4]. They confirm the fact that MacInnes values must be in error whenever KCl is used.

Cell III is similar to cell

$$Hg|Hg_2Cl_2|\underset{(0.1\ mol\ dm^{-3})}{KCl}|\underset{(x\ mol\ dm^{-3})}{KCl}|\underset{(0.1\ mol\ dm^{-3})}{HCl}|Hg_2Cl_2|Hg$$

studied by Guggenheim[5]. He varied the concentration of KCl in the bridge solution and observed a decrease in the potential of these cells when the KCl concentration increased.

2.4. Calculations

The general formula of the liquid junction potential between two electrolyte solutions, I and II, containing ions i is [6]

$$E_j = -\frac{RT}{F}\int_I^{II}\sum_i \frac{t_i}{Z_i}\,d\ln a_i$$

Although there are several ways of integrating this equation the most widely used is the Henderson equation which reduces to the Lewis and Sargent formula when the two electrolytes have one ion in common and the same concentration.

He assumed ideal behaviour and that the junction was formed by continuous series of mixtures of the two end solutions:

Harper[2] retaining the continuous nature of the junction, considered the nonideal behaviour of the ions, assuming that the equivalent conductance and the logarithm of the activity coefficient both decrease in linear proportion to the cube root of the ionic strength.

We applied Harper's program to calculate the liquid junction potential for KBr(0.1 m)/NaBr(0.1 m).

The agreement with the measured value is very good as shown in table II. We could not find conductivity values for the other bromides at this concentration in the literature so we tried the program considering the conductivity at infinite dilution. The agreement is also good (Table III) (except in the case of Mg which must be in error) and would certainly be better if the appropriate values were used. Experiments are in course to measure these missing conductivities.

TABLE II. Calculated potentials of the junction KBr(0.1 m)/NaBr(0.1 m) (mV)

Experimental	Lewis and Sargent (inf. dil.)	Lewis and Sargent (0.1)	Harper (inf.dil.)	Harper (inf. dil.)
4.50	4.31	4.39	4.30	4.53

TABLE III. Measured potentials of cells Ag|AgBr| M_1Br $_{(0.1\ mol\ Kg^{-1})}$ | | M_2Br $_{(0.1\ mol\ Kg^{-1})}$ |AgBr|Ag and calculated potentials of the corresponding liquid junctions

		OBSERVED	CALCULATED	
M_1	M_2	mV	HARPER inf. dil.	HARPER (0.1 m)
H	Li	34,30	33,37	
H	Na	32,56	30,95	
H	K	28,27	26,65	
H	Mg	12,70	28,46	
H	Ba	10,75	26,68	
K	Li	6,90	6,71	
K	Na	4,50	4,30	4,53
K	Mg	- 1,45	12,55	
K	Ba	- 7,60	10,73	

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