Expt. No.: 3

Date: 14.01.2020

Experiment	**Construction and working of an Zn-Cu electrochemical cell**
Problem definition	Measurement of electrode potential and construction of a battery system
Methodology	Single electrode potentials of Zn/Zn^{2+} and Cu/Cu^{2+} system and Daniel Cell
Solution	Electromotive force measurement (EMF) as voltage
Student learning outcomes	Students will learn to perform a) Electrode potential relevant to battery b) Understanding of a normal battery system

Principle: The electromotive force (emf) of an electrochemical cell is measured by means of a potentiometer. An electrochemical cell (E_{cell}) is considered as a combination of two individual single electrodes. The potential difference between the two single electrode potentials is a measure of emf of the cell (E_{cell}). In order to measure the potential difference between electrodes in contact with electrolyte containing the same cation, it is necessary to have another electrode in contact with electrolyte of same cation, both the half-cells connected through a salt bridge. Saturated calomel electrode (SCE; $E_{calomel}$) whose potential is known, is used as a reference electrode and it is coupled with the metal electrode for which the potential is to be determined.

$$Hg / Hg_2Cl_2 (s), \text{ saturated } KCl \parallel (N/10) \text{ electrolyte of the metal / Metal}$$

From the emf of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1 N electrolyte, electrode potential of the metal electrode is readily calculated using the standard potential of calomel electrode as;

$$E_{cell} = E_{M/M^+} - E_{calomel}$$

$$E_{M/M^+} = E_{cell} + E_{calomel}$$

E_{cell} is total emf of the cell. Electrode potential of the metal electrode is given by Nernst equation as;

$$E_{M/M^+} = E^\circ + \frac{RT}{nF} \ln a_{M^{n+}}$$

$$E^\circ_{M/M^+} = E_{M/M^+} - \frac{RT}{nF} \ln a_{M^{n+}}$$

$$E^\circ_{M/M^+} = E_{M/M^+} - \frac{0.0595}{n} \log a_{M^{n+}}$$

Requirements:

Reagents and solutions: $CuSO_4$ stock solution (0.1N), $ZnSO_4$ stock solution (0.1N), KCl salt.

Apparatus: Digital potentiometer, copper electrode, zinc electrode, calomel electrode, 100 mL beaker, burette, 50 ml standard flasks.

Procedure:

Calibrate the digital potentiometer with the help of the wires to display 1.018 V. The metal electrode is sensitized by dipping in a small quantity of 1:1 nitric acid containing a small quantity of sodium nitrite until effervescence occurs. Then the electrode is washed well with distilled water. 50 mL of the given concentration of the electrolyte solution is taken in a beaker and its corresponding metal electrode is introduced. This is connected with the saturated calomel electrode (half-cell) by means of a salt bridge. The metal electrode is connected to the positive terminal and the calomel electrode is connected to the negative terminal of the potentiometer. EMF of the cell (E_{cell}) is measured and noted in **Table 1.** Standard electrode potential [$E^{\circ}_{M/M^{2+}}$] is computed using Nernst equation (**Eq. 1**).

Table 1: EMF measured for various concentrations of M/M^{n+} system

Electrode/ Electrolyte	Electrolyte conc. (N)	E_{cell} (V)	$E_{M/M+} = E_{cell} + E_{calomel}$	E°_{M/M^+} [From Eq. (1)]	Average E°_{M/M^+}
Zn/Zn^{2+}	0.01 N	−0.781	−0.5363	~~−0.4818~~	−0.5325
	0.02 N	−0.826	−0.5952	−0.5360	
	0.05 N	−0.863	−0.6003	−0.5799	
Cu/Cu^{2+}	0.01 N	+0.013	+0.3191	0.3121	0.3096
	0.02 N	0.018	+0.3078	0.3079	
	0.05 N	0.026	+0.380	0.3090	

Solution Temperature (T) = $^{\circ}$C; Potential of SCE = 0.244 + 0.0007 (25 °C)

$$E^{\circ}_{M/M^+} = E_{M/M^+} - \frac{0.0595}{n} \log [\gamma_c \times C] \quad ------ \quad (1)$$

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where, E° is standard electrode potential of metal electrode; $a_{M^{n+}}$ is activity of metal ions in solution ($a_{M^{n+}} = \gamma_c[C]$); γ_c is activity coefficient (Table 2) and C is concentration of electrolyte solution.

Table 2: Individual activity coefficients of Cu^{2+} and Zn^{2+} in water at 25 °C

Metal ion system (Cu^{2+}/Zn^{2+})	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
Activity coefficient (γ_c)	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405

Use this space for detailed calculation

Zinc

$E_1^o = -0.537 - 0.02975 \log(0.02 \times 0.675) = -0.4818$

$E_2^o = -0.5360 - 0.02975 \log(0.05 \times 0.570) = -0.5360$

$E_3^o = -0.619 - 0.02975 \log(0.1 \times 0.485) - 0.5799$

$$Avg = \frac{E_1 + E_2 + E_3}{3} = -0.5325$$

Copper

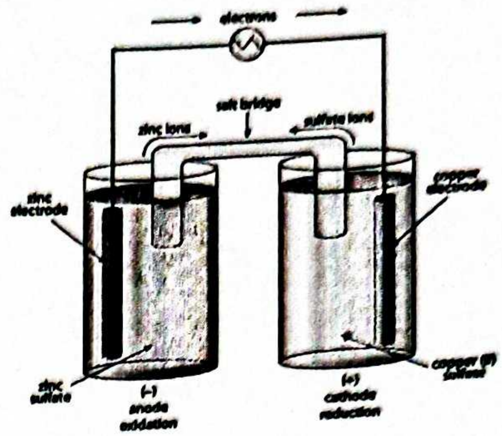
$E_1^o = 0.257 - 0.0295 \log(0.02 \times 0.675) = 0.3121$

$E_2^o = 0.262 - 0.02975 \log(0.05 \times 0.570) = 0.3019$

$E_3^o = 0.270 - 0.02975 \log(0.1 \times 0.405) = 0.3090$

$$Avg = \frac{E_1 + E_2 + E_3}{3} = 0.3016.$$

Construction of Daniel cell and measurement of its voltage with three different concentrations of Cu/Zn solutions:



In the Daniel cell, copper and zinc electrodes are immersed in the equimolar solution of $CuSO_4$ and $ZnSO_4$ respectively.

At the anode, zinc is oxidized as per the following half-reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

At the cathode, copper is reduced as per the following reaction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

The overall reaction is: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Construct Daniel cell using the following concentrations of Copper and Zinc solutions and record the voltage of the cells in Table 3.

Table 3: EMF of Daniel Cell observed from three different conc. of Zn and Cu solutions

Metal	Concentration (N)	Metal	Concentration (N)	EMF observed (E_{cell} / V)
Zn/Zn^{2+}	0.01 N	Cu/Cu^{2+}	0.01 N	0.370
	0.02 N		~~0.02 N~~ 0.05	0.883
	0.05 N		~~0.05 N~~ 0.1	0.923
			Average	0.892

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Results:

(a). Standard electrode potential of Copper (E^o) = 0.3096 *vs.* SCE

(b). Standard electrode potential of Zinc (E^o) = −0.5725 *vs.* SCE

(c). EMF of the constructed Daniel cell = 0.892

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Evaluation of result:

Sample No.	Experimental Value	Actual Value	Percentage of error	Marks awarded
a) $E^o_{Cu/Cu^{2+}}$				
b) $E^o_{Zn/Zn^{2+}}$				9/10
c) EMF of Daniel cell				