17BIT0028

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Construction and working of an electrochemical cell

Expt No. 10

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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$_2$Cl$_2$ (s), saturated KCl ‖ (N/10) electrolyte of the metal / Metal

From the emf of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1N electrolyte, electrode potential of the metal electrodeis 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 the total emf of the cell. The electrode potential of the metal electrode is given by Nernst equation as;

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

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

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

$$E_{M/M^+} = E^\circ_{M/M^+} - \frac{0.0595}{n} \log [\gamma_c \times c]$$

for Zn, $n = 2$

(i) 0.02 N

$$E^\circ_{M/M^+} = -0.651 - \frac{0.0595}{2} \log [0.02 \times 0.675]$$

$$= -0.651 + 0.055$$

$$= -0.596$$

(ii) 0.05 N

$$E^\circ_{M/M^+} = -0.685 - \frac{0.0592}{2} \log [0.05 \times 0.570]$$

$$= -0.685 + 0.046$$

$$= -0.639$$

(iii) 0.01 N

$$E^\circ_{M/M^+} = -0.641 - \frac{0.0595}{2} \log [0.01 \times 0.785]$$

$$= -0.641 + 0.039 = -0.602$$

For Cu, $n = 2$

(i) 0.02 N

$$E^\circ_{M/M^r} = 0.271 - \frac{0.0595}{2} \log (0.02 \times 0.675)$$

$$= 0.271 + 0.055$$

$$= 0.326$$

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

Electrode/ Electrolyte	Concentration of Electrolyte (N)	E_{cell} (V) (EMF of the cell)	$E_{M/M+} = E_{cell} + E_{calomel}$	$E^{\circ}_{M/M+}$
Zn/Zn^{2+}	0.01 N	-0.895	-0.651	-0.596
	0.05 N	-0.932	-0.685	-0.639
	0.1 N	-0.885	-0.641	-0.602
Cu/Cu^{2+}	0.01 N	0.027	0.271	0.326
	0.05 N	0.030	0.274	0.320
	0.1 N	0.022	0.276	0.315

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 (Y$_c$)	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405

Solution Temperature (T) = °C

The potential of saturated calomel electrode (SCE) = 0.244 + 0.0007 (25°C)

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

where E° is the standard electrode potential of the metal electrode; a_M^{n+} is the activity of metal ions in the solution ($a_M^{n+} = Y_c[C]$); Y_c is the activity coefficient (Table 2) and C is the concentration of the electrolyte solution.

Requirements:

Reagents and solutions: Copper sulphate stock solution (0.1N), zinc sulphate stock solution (0.1N), KCl salt.

Apparatus: Digital potentiometer, copper electrode, zinc electrode, calomel electrode, 100 mL beaker, burette, standard flask.

Procedure:

Calibrate the digital potentiometer with the help of the wires to display 1.018V. 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

(ii) 0.05N

$$E^0_M|M^+ = 0.274 - \frac{0.0595}{2} \log [0.05 \times 0.570]$$

$$= 0.274 + 0.046$$

$$= 0.320$$

(iii) ~~0.0~~ 0.1N

$$E^0_M|M^+ = 0.276 - \frac{0.0595}{2} \log (0.1 \times 0.485)$$

$$= 0.276 + 0.039$$

$$= 0.315$$

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 of and the calomel electrode is connected to the negative terminal of the potentiometer. The emf of the cell (E_{cell}) is measured and noted in Table 1. The standard electrode potential [$E°_{M/M2+}$] is computed using Nernst equation (eqn. no. 1).

Construction of Daniel cell and measurement of its voltage with three different concentrations of Copper and Zinc Solutions:
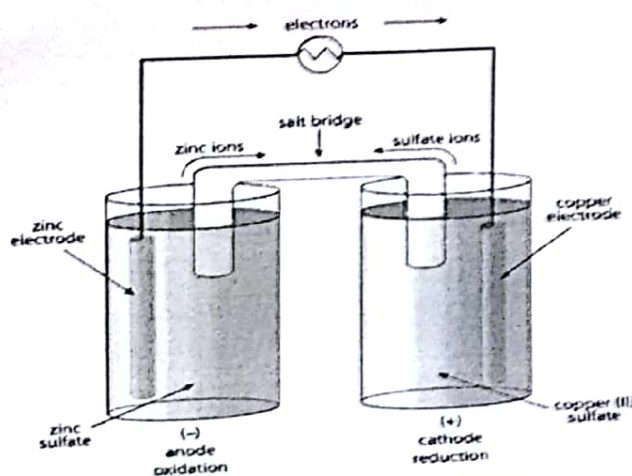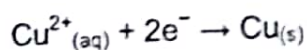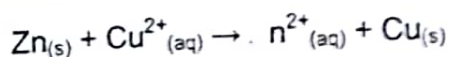

Fig.1.Daniel cell

In the Daniel cell, copper and zinc electrodes are immersed in the equimc lar solution of copper(II)sulfate and zinc(II) ulfate respectively. At the anode, zinc is oxidized as per the following half-reaction:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
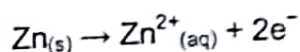
At the cathode, copper is reduc d as per the following reaction:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

The overall reaction is:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow n^{2+}_{(aq)} + Cu_{(s)}$$

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

Table 3: EMF of Daniel Cell observed from three different concentrations of zinc and coppersolutions

Metal	Concentration (N)	Metal	Concentration (N)	EMF observed (E_{cell} / V)
Zn/Zn^{2+}	0.01 N	Cu/Cu^{2+}	0.01 N	~~0.515~~ -1.002
	0.05 N		0.05 N	~~1.0101~~ -1.015
	0.1 N		0.1 N	~~1.115~~ -1.035

Result:

(a) The single electrode potential of zinc and copper systems are ~~-0.7~~ -0.712 V and 0.320 V respectively.

(b) Potentials (V) of Daniel cell: -1.003 , -1.015 , -1.035

Evaluation of result:

Sample No.	Experimental Value	Actual Value	Percentage of error	Marks awarded

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