Expt. No.: **Date:**

Experiment	**Thermodynamic functions from EMF measurements: Zinc-Copper system**
Aim	To construct and to measure electromotive force (EMF) of a Daniell cell at varied concentrations of metal ions and temperatures To determine the thermodynamic functions (**ΔG, ΔH and ΔS)**
Problem definition	Construction of a Daniell Cell, measurement of EMF and determination of **ΔG, ΔH & ΔS**
Solution	The measurement of EMF will be carried out by a **Potentiometer** and followed by the calculation of different thermodynamic functions through the EMF values
Student learning outcomes	Students will be able to understand the construction of a Daniell cell (Zn-Cu system) • To observe the influence of metal-ion concentration and temperature on the EMF on Zn-Cu system • To calculate the thermodynamic functions (**ΔG**, **ΔH** and **ΔS**)

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 cell-electrodes. The potential difference between the two single electrode potentials is a measure of EMF of the cell ($E_{cell;}$ Cathode-Anode/V). 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; $E_{Calomel,}$ $E^o = 0.244$ V) whose potential is known, is used as **a reference electrode** (Anode; +ve terminal, black-colored wire) and it is coupled with the metal electrode (Cathode, -ve terminal; red-colored wire) for which the potential is to be determined. The substance that loses electrons is said to be oxidized, while the one gaining electrons is reduced. Thus if a piece of zinc metal were immersed into a solution containing copper (II) ions, zinc would be oxidized by copper (II) ions. Zinc loses electrons and is oxidized, and the copper (II) ions gain electrons and are reduced. We can conveniently express these processes together as a Daniel cell by the following reactions (Figure 1):

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

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ ($E^o = -0.760$ V)

At the cathode, copper is reduced as per the following reaction:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ ($E^o = +0.340$ V)

The overall reaction:

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ **$E_{cell} = 0.340 - (-0.760) = 1.10$ V**

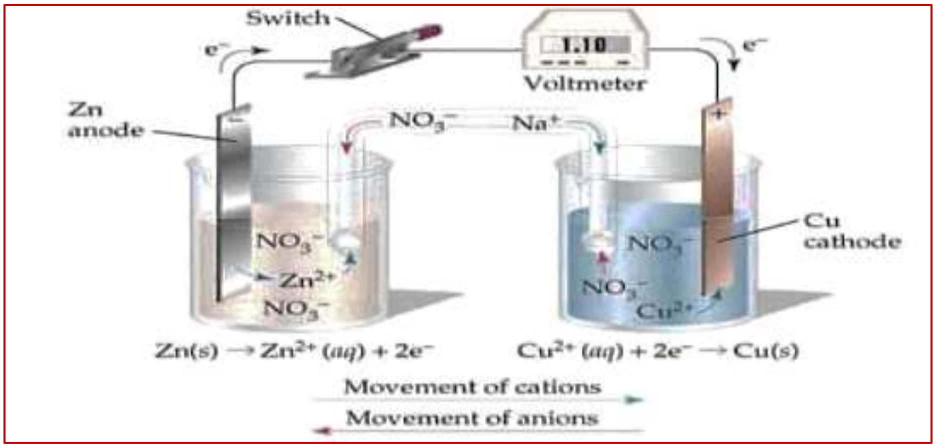


Figure 1: Functioning of a Daniell cell (Zn-Cu) using a salt bridge

Importance of Thermodynamic functions:

ΔG: Gibbs free energy determines whether a given chemical change is thermodynamically possible or not. The change in Gibbs free energy (**ΔG)** is the symbol for spontaneity, and there are two factors which can affect it: enthalpy and entropy. Enthalpy - the heat content of a system at constant pressure. A negative ΔG means that the reactants, or initial state, have more free energy than the products, or final state.

ΔH: Measuring the change in enthalpy allows us to determine whether a reaction was endothermic (absorbed heat, positive change in enthalpy) or exothermic (released heat, a negative change in enthalpy.) It is used to calculate the heat of reaction of a chemical process.

ΔS: Entropy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Entropy has been regarded as a measure of disorder or randomness of a system. Thus when a system goes from a more orderly to less orderly state, there is an increase in its randomness and hence entropy of the system increases.

Part-A: Determination of single electrode potentials of M/M^{n+} system ($E^o_{M/Mn+}$) at three different concentrations

Hg/Hg_2Cl_2 (s), saturated KCl (Anode)║(N/10) electrolyte of the Metal/Metal (Cathode)

From the EMF of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1 M electrolyte, electrode potential of the metal electrode is readily calculated using the standard potential of calomel electrode as E_{cell} (measured from potentiometer) = E_{M/M^+} (Cathode, V) – $E_{calomel}$ (0.244V, Anode) or $E_{M/M^+} = E_{cell} + E_{calomel}$. E_{cell} is the total EMF, i.e., net voltage of the cell measured using a potentiometer. Then, the electrode potential of the metal electrode (E^o_{M/M^+}/ V) can be calculated after incorporating the observed E_{M/M^+} and a_M^{n+} parameters in **Nernst equation** as given below:

$E_{M/M^+} = E^o_{M/M^+} + \frac{RT}{nF} a_M^{n+}$

or, $E^o_{M/M^+} = E_{M/M^+} - \frac{RT}{nF} \ln a_M^{n+}$

$E^{o}{}_{M/M^{+}} = E_{M/M^{+}} - \frac{0.059}{n} \log a_{M}{}^{n+}$

Requirements:

Reagents and solutions: Copper sulphate stock solution (0.1 M), Zinc sulphate stock solution (0.1 M), KCl salt.

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

Procedure:

Calibrate the digital potentiometer with the help of an inbuilt battery support 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 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 [$E°_{M/M^{2+}}$] is computed using Nernst equation (Eq. 1).

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} + $E_{calomel}$	$E^{o}{}_{M/M+}$/V (from Nernst Eq.1)
Zn/Zn^{2+}	0.05 M			
	0.1 M			
Cu/Cu^{2+}	0.05 M			
	0.1 M			

Table 2: Individual activity coefficients of Cu^{2+} and Zn^{2+} in water at room temperature

Metal ion (Cu^{2+}/Zn^{2+}) system (in M)	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

where, E° is the standard electrode potential of the metal electrode; $a_{M}{}^{n+}$ is the activity of metal ions in the solution ($a_{M}{}^{n+} = \gamma_c[C]$); γ_c is the activity coefficient (Table 2) and C is the concentration of the electrolyte solution. Solution Temperature (T) = **30 ˚C**

The potential of saturated calomel electrode (SCE) = 0.244 ± 0.0007 (30 °C)

$E^\circ_{M/M^+} = E_{M/M^+} - \frac{0.059}{n} \log [\gamma_c \times C]$ Eq.1

The EMFs can be calculated by the Nernst equation (Eq.1).

Part-B: Construction of Daniell cell and measurement of its voltage with three different concentrations of Copper and Zinc Salt Solutions:

The construction of the Daniell cell using the following concentrations of Copper and Zinc salt solutions will be performed and the voltage of the cells will be entered into the Table 3.

Calculation of E_{cell} by Nernst Equation

For example, if $[Zn^{2+}]$ and $[Cu^{2+}]$ are given as 0.05 M and 0.01 M, respectively, then

$$\boxed{E_{Cell} = E_{Cell}^{o} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

$R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$;
$T = 303\ K$;
$n = 2$;
$F = 96500$ (constant)

$$= 1.1 - \frac{8.314 \times 303}{2 \times 96500} \ln \frac{[0.05]}{[0.01]}$$

$$= 1.1 - 0.01305 \ln \frac{[0.05]}{[0.01]}$$

$$= 1.1 - (0.01305 \times 1.6094)$$

$$= 1.1 - 0.021$$

$$\boxed{E_{Cell} = 1.079\ V \text{ at } T = 303\ K}$$

In a similar way, **E_{cell} values** for other concentrations are to be calculated at specific temperatures**.**

Calculation of ΔG_1 (at $T_1 = 30$ °C) and ΔG_{1a} (at $T_{1a} = 50$ °C) based on the E_{Cell} measurements

$\Delta G_1 = -\ n F E_{Cell}$ $\quad n = 2;\ E = 0.99\ V;\ F = 96500$

$$= -\ 2 \times 96500 \times 0.99$$

$$\boxed{= -\ 191\ KJ/mol} \quad \text{at } T_1 = 30\ ^oC$$

$\Delta G_{1a} = -\ n F E_{Cell}$ $\quad n = 2;\ E = 1.020\ V;\ F = 96500$

$$= -\ 2 \times 96500 \times 1.020$$

$$\boxed{= -\ 197\ KJ/mol} \quad \text{at } T_{1a} = 50\ ^oC$$

In a similar way, **ΔG_2, ΔG_{2a}, ΔG_3, and ΔG_{3a} are to be calculated from EMFs for other metal ion concentrations.**

Table 3: **EMF of Daniell Cell observed (by calculation and experiment) from two different concentrations of zinc and copper solutions**

$[Cu^{2+}]$	$[Zn^{2+}]$	E_{cell} (calculated by Nernst Eqn)	E_{cell} (experimental)	% Error	Free-energy change (ΔG) or W_{max} (KJ/ mol)
At Room Temperature, T_1 = 30 ºC/ 303 K					
0.1 M	0.05 M				
0.05 M	0.1 M				
0.1 M	0.1 M				
At T_{1a} = 50 ºC/ 323 K					
0.1 M	0.05 M		This value will be provided by the lab faculty.		
0.05 M	0.1 M		This value will be provided by the lab faculty		
0.1 M	0.1 M		This value will be provided by the lab faculty		

Part-C: Calculation of ΔH and ΔS at 40 ºC / 313 K based on the T_1 and T_{1a} parameters

ΔG_1 at 30 ºC = -191 KJ/ mol and ΔG_{1a} at 50 ºC = -197 KJ/ mol, Then

$$\triangle G^{1*} \text{ at } 40\ ^{o}\text{C } (T = 313\text{ K}) = \frac{-191-197}{2} \boxed{= -194 \text{ KJ/ mol}}$$

ΔG_2 at 30 ºC = -195 KJ/ mol and ΔG_{2a} at 50 ºC = -199 KJ/ mol, Then

$$\triangle G^{2*} \text{ at } 40\ ^{o}\text{C } (T = 313\text{ K}) = \frac{-195-199}{2} \boxed{= -197 \text{ KJ/ mol}}$$

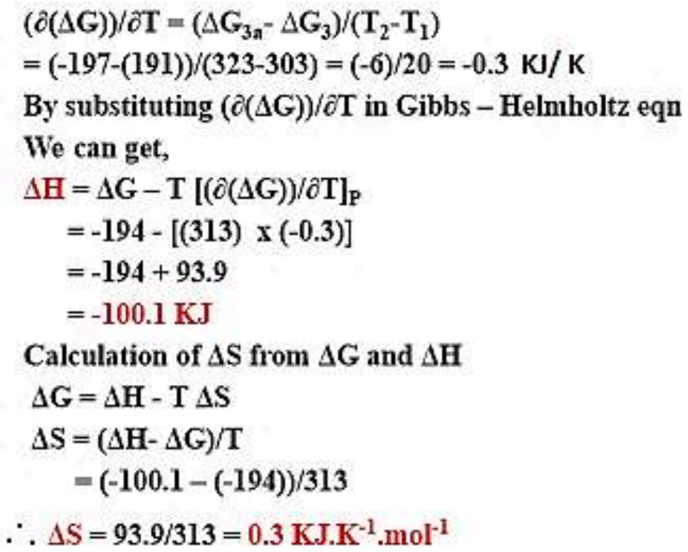
ΔG_3 at 30 ºC = -206 KJ/ mol and ΔG_{3a} at 50 ºC = -208 KJ/ mol, Then

$$\triangle G^{3*} \text{ at } 40\ ^{o}\text{C } (T = 313\text{ K}) = \frac{-206-208}{2} \boxed{= -207 \text{ KJ/ mol}}$$

According to the Gibbs-Helmholtz equation, the ΔH can be calculated for Daniell Cell having [Zn^{2+}]/[Cu^{2+}] = [0.05 M]/ [0.01 M],

$\Delta G = \Delta H + T\,[(\partial(\Delta G))/\partial T]_P$,

then



$(\partial(\Delta G))/\partial T = (\Delta G_{3a} - \Delta G_3)/(T_2 - T_1)$

$= (-197-(191))/(323-303) = (-6)/20 = -0.3$ KJ/ K

By substituting $(\partial(\Delta G))/\partial T$ in Gibbs – Helmholtz eqn

We can get,

$\Delta H = \Delta G - T\,[(\partial(\Delta G))/\partial T]_P$

$= -194 - [(313) \times (-0.3)]$

$= -194 + 93.9$

$= -100.1$ KJ

Calculation of ΔS from ΔG and ΔH

$\Delta G = \Delta H - T\,\Delta S$

$\Delta S = (\Delta H - \Delta G)/T$

$= (-100.1 - (-194))/313$

$\therefore\ \Delta S = 93.9/313 = 0.3\ KJ.K^{-1}.mol^{-1}$

In a similar way, the **ΔH and ΔS for other concentrations of [Zn^{2+}] and [Cu^{2+}] as given in Table-4 are to be calculated.**

Table-4: Final Results: At 313 K (40 ºC)

[Cu^{2+}]	[Zn^{2+}]	ΔG, KJ/ mol	ΔH, KJ/ mol	ΔS, KJ·K^{-1}·mol^{-1}	Marks Awarded
0.1 M	0.05 M				
0.05 M	0.1 M				
0.1 M	0.1 M				