Experiment 3: Thermodynamic functions from EMF measurements: Zinc-Copper system

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Part-A:

Determination of single electrode potentials of M/M^{n+} system ($E^{o}M/Mn+$) at two different concentrations.

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)	$E_{M/M+} = E_{cell} + E_{calomel}$	$E^{o}_{M/M+}$
Zn/Zn^{2+}	0.05 M	-1.047	-0.803V	-0.757V
	0.1 M	-1.043	-0.799V	-0.759V
Cu/Cu^{2+}	0.05 M	0.037	0.281V	0.327V
	0.1 M	0.044	0.288V	0.327V

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

According to Nernst Equation:

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

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

Calculation for Part A:

PART A: The potential of saturated calomel electrode (SCE)
$= 0.244 \pm 0.0007$ (25°C)

I) ⇒ for Zn/Zn^{2+},

① 0.05 M

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

$= -1.047 + 0.244$

$E_{M/M^+} = -0.803V$

$\therefore E^\circ_{M/M^+} = -\frac{0.0595}{2} \times \log(0.570 \times 0.05) - 0.803$

$= -0.803 + 0.046$

$\boxed{E^\circ_{M/M^+} = -0.757V}$

② 0.1M

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

$= -1.043 + 0.244$

$E_{M/M^+} = -0.799V$

$\therefore E^\circ_{M/M^+} = -0.799 - \frac{0.0595}{2} \times \log(0.485 \times 0.1)$

$= -0.799 + 0.0391$

$\boxed{E^\circ_{M/M^+} = -0.759V}$

II) ⇒ for Cu/Cu^{2+}

① 0.05 M

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

$$= 0.037 + 0.244$$
$$= 0.281V$$

$$\therefore E^\circ_{M/M^+} = 0.281 - \frac{0.0595}{2} \log(0.570 \times 0.05)$$

$$= 0.281 + 0.046$$

$$\boxed{E^\circ_{M/M^+} = 0.327\,V}$$

② 0.1 M

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

$$= 0.044 + 0.244$$
$$E_{M/M^+} = 0.288V$$

$$\therefore E^\circ_{M/M^+} = 0.288 - \frac{0.0595}{2} \log(0.485 \times 0.1)$$

$$= 0.288 + 0.0391$$

$$\boxed{E^\circ_{M/M^+} = 0.327\,V}$$

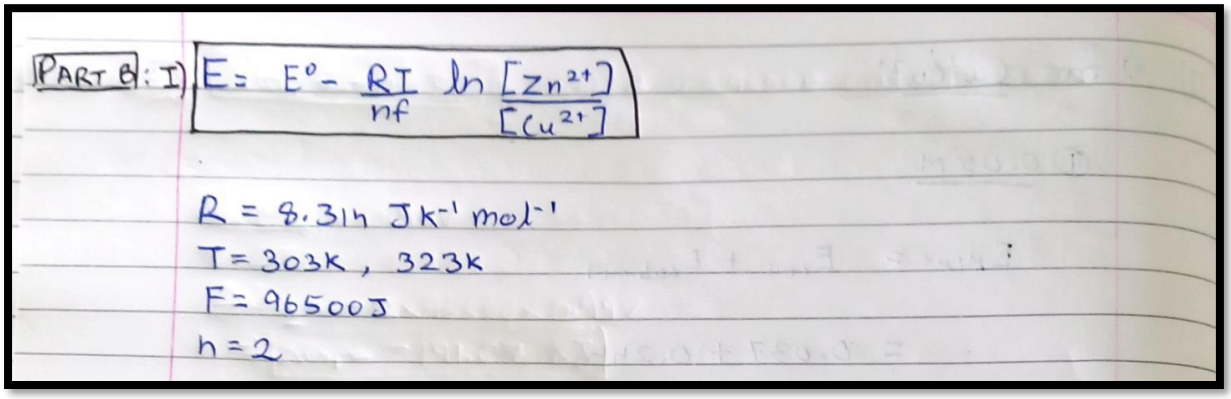
Part-B:

Construction of Daniell cell and measurement of its voltage with three different concentrations of Copper and Zinc Salt Solutions.

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 Equation)	E_{cell} (Experimental)	% Error	Free-energy change (ΔG) or W_{max} (KJ/mol)
At Room Temperature, T_1 = 30 °C / 303K					
0.01 M	0.05 M	1.079V	0.990V	8.2 %	-191
0.05 M	0.01 M	1.121V	1.013V	9.6 %	-196
0.1 M	0.1 M	1.100V	1.068V	2.9 %	-206
At T_{1a} = 50°C / 323 K					
0.01 M	0.05 M	1.078V	1.020V	6.4 %	-197
0.05 M	0.01 M	1.122V	1.036V	6.6 %	-200
0.1 M	0.1 M	1.100V	1.082V	1.6 %	-208

Calculation for Part B:



② $[Zn^{2+}] = 0.01M$, $[Cu^{2+}] = 0.05M$, $T = 303K$

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

$$= 1.1 - (-0.021)$$

$$\boxed{E = 1.121V}$$

④ ① $[Zn^{2+}] = 0.05M$, $[Cu^{2+}] = 0.01M$, $T = 303K$

$$E = 1.1 - \frac{8.314 \times 300}{2 \times 96500} \ln\left[\frac{0.05}{0.01}\right]$$

$$= 1.1 - 0.021$$

$$\boxed{E = 1.079V}$$

③ $[Zn^{2+}] = 0.1M$, $[Cu^{2+}] = 0.1M$, $T = 303K$

$$E = 1.1 - \frac{8.314 \times 303}{2 \times 96500} \ln\left[\frac{0.1}{0.1}\right]$$

$$= 1.1 - 0$$

$$\boxed{E = 1.1V}$$

⑤ $[Zn^{2+}] = 0.05M$, $[Cu^{2+}] = 0.01M$, $T = 323K$

$$E = 1.1 - \frac{8.314 \times 323}{2 \times 96500} \ln\left[\frac{0.05}{0.01}\right]$$

$\Rightarrow E = 1.1 - 0.022$

$\Rightarrow \boxed{E = 1.0776V}$

⑤ $[Zn^{2+}] = 0.01M$, $[Cu^{2+}] = 0.05M$, $T = 323K$

$$E = 1.1 - \frac{8.314 \times 323}{2 \times 96500} \ln\left[\frac{0.01}{0.05}\right]$$

$\Rightarrow E = 1.1 - (-0.022)$

$\boxed{E = 1.122V}$

⑥ $[Zn^{2+}] = 0.1M$, $[Cu^{2+}] = 0.1M$, $T = 323K$

$$E = 1.1 - \frac{8.314 \times 323}{2 \times 96500} \log\left[\frac{0.1}{0.1}\right]$$

$= 1.1 - 0$

$\Rightarrow \boxed{E = 1.1V}$

II) $\boxed{\Delta G_n = -nFE_{cell}}$; $n = 2$, $F = 96500$ at $T = 303K$

① $E_{cell} = 0.99V$

$\Delta G_1 = -2 \times 96500 \times 0.99V$

$\Rightarrow \boxed{\Delta G_1 = -191.07\ kJ}$

② $E_{cell} = 1.013$

$\Rightarrow \Delta G_2 = -2 \times 96500 \times 1.013V$

$\Rightarrow \boxed{\Delta G_2 = -195.509\ kJ}$

③ $E_{cell} = 1.068V$

$\Delta G_3 = -2 \times 96500 \times 1.068V$

$\Rightarrow \boxed{\Delta G_3 = -206.124\ kJ}$

III) $\boxed{\Delta G_{n_a} = -nFE_{cell}}$; $n=2, F=96500$ at $T=323K$

① $E_{cell} = 1.020V$

$\Delta G_{1_a} = -2 \times 96500 \times 1.020$

$\Rightarrow \boxed{\Delta G_{1_a} = -196.86\ kJ}$

② $E_{cell} = 1.036V$

$\Delta G_{2_a} = -2 \times 96500 \times 1.036V$

$\Rightarrow \boxed{\Delta G_{2_a} = -199.948\ kJ}$

③ $E_{cell} = 1.082V$

$\Delta G_{3_a} = -2 \times 96500 \times 1.082V$

$\Rightarrow \boxed{\Delta G_{3_a} = -208.826\ kJ}$

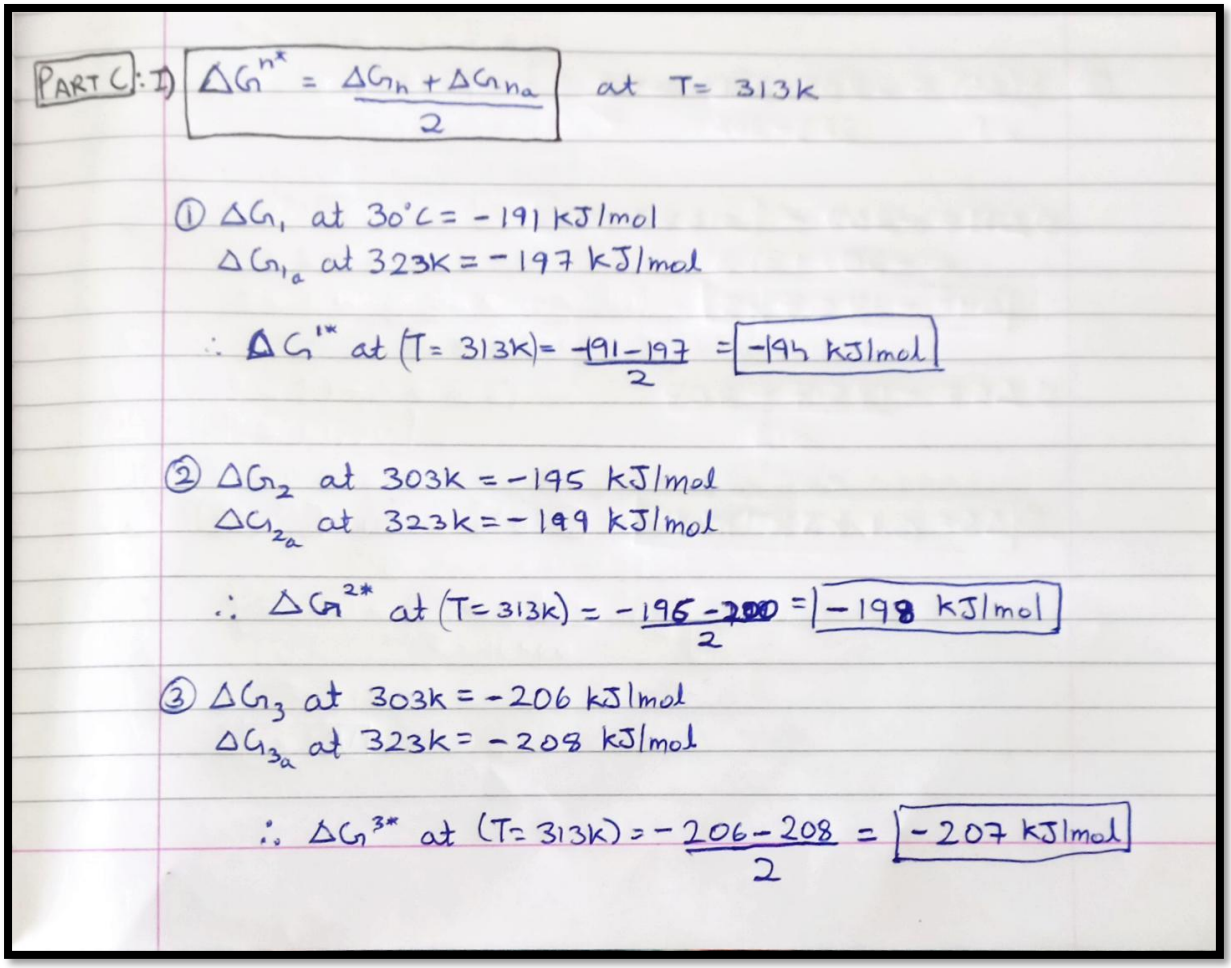
Part-C:

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

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

$[Cu^{2+}]$	$[Zn^{2+}]$	ΔG (KJ/mol)	ΔH (KJ/ mol)	ΔS ($KJ \cdot K^{-1} \cdot mol^{-1}$)
0.01 M	0.05 M	-194	-100.1	0.3
0.05 M	0.01 M	-198	-135.4	0.2
0.1 M	0.1 M	-207	-175.7	0.1

Calculation for Part C:



II) $\boxed{\Delta H = \Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P}$ → Gibbs-Helmholtz equation

where, $\boxed{\frac{\partial(\Delta G)}{\partial T} = \frac{\Delta G_{30} - \Delta G_3}{T_2 - T_1}}$

and $\boxed{\Delta S = \frac{\Delta H - \Delta G}{T}}$

① $\frac{\partial(\Delta G)}{\partial T} = -\frac{197+191}{323-303} = -\frac{63}{210} = -0.3\ kJ/k$

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

$= -194 + 93.9$

$\boxed{\Delta H = -100.1\ kJ}$

$\Rightarrow \Delta S = \frac{-100.1 + 194}{313}$

$\Rightarrow \boxed{\Delta S = 0.3\ kJ\ K^{-1}\ mol^{-1}}$

② $\frac{\partial(\Delta G)}{\partial T} = -\frac{200+196}{323+303} = -\frac{42}{210} = -0.2\ kJ/K$

$\Delta H = -198 - [313 \times (-0.2)]$

$= -198 + 62.6$

$\boxed{\Delta H = -135.4\ kJ}$

$\Delta S = \frac{-135.4 + 198}{313}$

$\Rightarrow \boxed{\Delta S = 0.2\ kJ\ K^{-1}\ mol^{-1}}$

③ $\frac{\delta(\Delta G)}{\delta T} = \frac{-208+206}{323-303} = \frac{-2}{20} = -0.1\ kJ/K$

$\Rightarrow \Delta H = -207 - [313 \times (-0.1)]$

$= -207 + 31.3$

$\boxed{\Delta H = -175.7\ kJ}$

$\Rightarrow \Delta S = \frac{-175.7 + 207}{313}$

$\Rightarrow \boxed{\Delta S = 0.1\ kJ\,K^{-1}\,mol^{-1}}$