

# Effect of Anodic Mass Transfer in the Electrowinning of Copper in Presence of Organic Compounds

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The effect of anodic oxygen bubbles on the rate of mass transfer was studied by measuring the limiting current of deposition of copper from acidified CuSO<sub>4</sub> solution using parallel plate cell. Different factors studied as types of inhibitors, their concentrations and temperatures. The organic additives used are glucose, fructose, mannose, sucrose, lactose and maltose. The rate of mass transfer was found to decrease over the natural convection value by an amount ranging from 1.8-32.3 % depending on the types of additives and its concentration. Thermodynamic parameters  $E_a$ ,  $\Delta H^*$ ,  $\Delta S^*$ ,  $\Delta G^*$  were evaluated and discussed. The adsorption of organic additives was found to obey Langmuir, Temkin, Flory-Huggin and kinetic adsorption isotherm.

Key Words: Electrodeposition, Limiting current, Thermodynamic parameters, Carbohydrates, Adsorption.

## INTRODUCTION

Copper is the metal of choice, replacing aluminum in integrated circuit interconnections<sup>1</sup>. This switch are emerged and simulated due to copper advantage characteristics such as low resistivity and high immunity to electromigration, which in turn results in greater circuit reliability and markedly higher cock frequency. Copper dual damascene technology includes two main electrochemical steps. First step is copper electrochemical deposition step<sup>2-7</sup> (or copper electroplating) into trenches and vias. Second electrochemical step utilizes chemical mechanical polishing.

In electrowinning of metals usually an insoluble anode is used where oxygen evolution takes place. Anodic oxygen evolution consumes a considerable portion of the electrical energy provided to the cell and could also adversely affect the performance of the cell by increasing the ohmic drop<sup>8-10</sup> and distributing the uniformity of current distribution<sup>11-14</sup>. On the other hand, anodic oxygen bubbles were found to enhance the rate of mass transfer at the cathode<sup>11-13</sup> to the modest degree in vertical parallel electrode cells to a modest degree. An attempt to maximized the electricians effect of counter electrode, glass bubbles, different cell designs were proposed where the working electrodes was placed up steams of the gas involving counter electrode; an enhancement in the rate of mass transfer to 60 % over the natural convection values obtained. The object of the present work is to study the effect of different carbohydrates on the rate of electrodeposition of copper using lead anode.

### EXPERIMENTAL

Fig. 1 shows the cell and the circuit used in the present work. The cell consisted of a rectangular plastic container (5.1 cm  $\times$  5 cm  $\times$  10 cm) with electrodes fitting the whole cross section area. The cathode was rectangular copper sheet (10 cm height  $\times$  5 cm width); the anode was lead sheet with an inter-electrode distance was 5 cm. The cell was placed in 3 L glass container filled with the electrolyte to ensure that the cell is always filled with the electrolyte to minimize the decrease in Cu<sup>2+</sup> concentration in the cell during polarization.



Fig. 1. Electrolytic cell and the electrical circuit showing the position of the two parallel vertical plates and the reference electrode. The ammeter connected in series, while the potentiometer in parallel

The electrical circuit consists of (6 V d.c). Power supply connected in series with the cell along and rheostat and (multi-range digital ammeter). A voltammeter is connected in parallel with the cell to measure the voltage.

Polarization curves from which the limiting current was determined were constructed by increasing the current stepwise and measuring the steady state cathode potential against a copper reference electrode placed in the cup of a luggin tube whose tip was placed at about 1mm from the cathode surface. To make sure that the decrease of Cu<sup>2+</sup> concentration during polarization was negligible in case of lead anode, the limiting current was measured again potentiostatically using a fresh solution, the galvanostatic and the rapid potentiostatic methods gave almost the same limiting current. Before electrolysis the cathode and anode were isolated from their backs and sides with epoxy resin except at the contact with the feed wires. Electrode treatment was simillar to that used by Wilke *et al.*<sup>14</sup>. Concentrations of CuSO<sub>4</sub> were used, namely, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35 M, in all cases 1.5 M  $H_2SO_4$  was used as a supporting electrolyte. All chemicals were of Analar grade. Physical properties of the solution  $(\rho, \mu, D)$  used to correlate the present data were measured<sup>9</sup>. Temperature was  $23 \pm 0.5$  °C.

## **RESULTS AND DISCUSSION**

Fig. 2 shows a typical current-potential curve in presence and in absence of compounds at 25 °C. It is seen that the limiting current decreases with the increase of concentration of organic compounds. Fig. 2 show typical current-potential curves for different carbohydrates at constant concentration. It is seen that, the decrease in limiting current depend on the type of carbohydrate and its structure.



Fig. 2. Electrolytic cell and the electrical circuit using rotating cylinder electrode

These polarization curves are served to determine the limiting current from which the mass transfer coefficient was calculated according to the equation:

$$K = \frac{I_1}{ZFC_b}$$

where K is the mass transfer coefficient,  $I_i$  is the limiting current densities under natural convection, Z is the number of electrons involved in the reaction and C<sub>o</sub> is the initial concentration of copper ions. Table-1 gives the values of  $I_i$  at different temperatures for all additives. Fig. 2 shows that in the absence of carbohydrate, the blank data when we used lead anode fits well into equation which agrees with data derived from the hydrodynamic boundary layer theory<sup>15</sup>.

$$J = 1.096 (Re Fr)^{-0.17}$$

J is mass transfer rate (mole  $L^{-2} s^{-1}$ ), J is factor (st . Sc<sup>0.66</sup>), St (Stanton number (K/V), Sc (Schmidt number ( $\mu/\rho$ D), Fr is Froude number where Fr = v<sup>2</sup>/hg, v is oxygen gas discharge velocity (cm s<sup>-1</sup>), h electrode height, g is the acceleration due to gravity (cm s<sup>-2</sup>), Re is Reynolds number where Re = ud/v, U is electrode peripheric velocity cm s<sup>-1</sup>,

$$U = \omega r$$

 $\boldsymbol{\omega}$  is angular velocity,  $\boldsymbol{r}$  the radial distance.

The gas discharge velocity V used in calculating J, Re and Fr were calculated from eqn. 5

$$V = \frac{(IRT)}{(4PF)}$$

I is the current density, R is the gas constant, T is the absolute temperature, P is the pressure and F is Faraday constant.

In presence of organic substance, the following relation was obtained

#### $k\alpha(V)^{b}$

where "b" is constant depends on organic substances.

Ahmed *et al.*<sup>16</sup> predicted that

 $k\alpha(V)^{0.18}$ 

From Table-2 we noticed that the velocity (V) and mass transfer coefficient (k) for all organic compounds are decreased with increase the concentration of the organic compounds.

Plot log k against log V for different organic compounds gave a good straight line as shown in Fig. 3 and Table-2. The values of the slope (b) were found to be constant for all studied additives and its values approximately equal to unity (Table-2), which indicates that the discharge velocity of oxygen gas is affected by the presence of additives compounds with the same extent as the mass transfer coefficient does.





**Effect of carbohydrate on the limiting current:** If the limiting current in absence of organic compounds (I<sub>b</sub>) and in

LIMITIN	G CURRENT OF DIF	TAE FERENT ORGANIC CO	BLE-1 OMPOUNDS (mA) AT D	IFFERENT TEMPERAT	URES	
		Limiting current (L) at different temperatures				
Organic compounds	$C \times 10^{-4}$	25 °C	<u>30 °C</u>	35 °C	40 °C	
	5	350	370	390	410	
	10	310	330	350	370	
	15	300	310	320	330	
Compound (I)	25	280	300	310	320	
	30	250	260	270	280	
	40	230	220	230	340	
	0	350	370	390	410	
	10	300	320	340	350	
Common d (III)	15	290	300	310	330	
Compound (II)	25	270	280	290	300	
	30	240	250	260	270	
	40	220	230	240	250	
	0	350	370	390	410	
	10	330	350	370	390	
Compound (III)	15	310	330	350	370	
Compound (III)	25	300	320	335	350	
	30	280	290	310	330	
	40	240	260	270	280	
	0	350	370	390	410	
	10	320	340	360	380	
Compound (IV)	15	310	325	340	360	
	25	290	310	330	350	
	30	270	280	290	300	
	40	240	250	260	270	
	0	350	370	390	410	
	10	290	310	330	350	
Compound (V)	15	260	275	290	310	
Compound (V)	25	240	245	260	275	
	30	220	230	240	250	
	40	210	220	230	240	
	0	350	370	390	410	
	10	270	280	300	320	
Compound (VI)	15	250	270	280	290	
	25	240	250	260	270	
	30	200	220	230	240	
	40	200	210	220	230	

TABLE 2 RELATION BETWEEN C (mol L-1) AND PERCENTAGE INHIBITION AT 25 °C Inhibition (%) at 25 °C  $C \times 10^4 (mol L^{-1})$ Organic compounds II V VI I Ш IV 10 11.40 14.20 51.70 8.60 17.40 20.00 15 17.40 11.20 11.40 25.70 28.57 14.20 25 20.20 22.85 14.20 14.20 31.40 31.40 30 25.57 31.40 20.00 22.85 37.10 40.0040 34.20 37.14 31.40 31.40 40.00 42.80

the presence of organic compounds (I), the percentage inhibition can be calculated from the equation:

Inhibition (%) = 
$$\left(\frac{I_b - I}{I_b}\right) \times 100$$

Table-4 and Fig. 4 show the relation between percentage inhibition and concentration of amino acids at 25 °C. Fig. 4 shows that the percentage inhibition caused by carbohydrates ranges from 1.8-33.3 % depending on the type of the carbohydrate and their concentration. The order of decreasing inhibition is as follow:

Fructose > Lactose > Sucrose > Mannose > Maltose > Glucose



Fig. 4. Relation between C (mol  $L^{\text{-}1}$ ) and % inhibition at 25  $^{\circ}\text{C}$ 

The obtained results show that, the presence of organic compounds has an inhibiting effect on the kinetic of the copper discharge process, pointed out by the decrease<sup>17</sup> of the exchange current density. The inhibition enhancing due to

GENERAL C	ORREI ATIO	N OF FREE CONV	TAE	BLE-3 TRANSFER FOR DIFFI	FRENT ACIDS (	SUBSTANCES A	T 25 ℃
			Compo	ound (I)	LICEI II MEIDO	JODD IT II (CLD I	11 25 C
$C \times 10^4 \text{ (mol } L^{-1}\text{)}$	rpm	$I_{c}$ (mA cm <sup>-2</sup> )	$v (cm^2 s^{-1})$	$D \times 10^4 (\text{cm}^2 \text{ s}^{-1})$	Sh	Sc	Re
Blank	1	380	1.338	7.41	124.00	1805.67	20653.87
10		330	1.311	6.17	129.32	2124.80	21079.24
15	100	310	1.296	5.62	133.38	2306.05	21323.21
25	100	290	1.235	5.37	130.58	2299.81	22376.42
30		270	1.222	4.79	136.29	2551.15	22614.47
40		250	1.211	4.37	138.33	2771.17	22819.88
Blank		420	1.338	6.03	168.42	2218.91	41307.85
10		360	1.311	4.79	181.73	2736.95	42158.58
15	200	330	1.296	4.27	186.87	3035.13	42646.53
25		310	1.235	4.07	184.17	3034.40	44752.96
30		290	1.222	3.72	188.50	3284.95	45229.05
40		270	1.211	3.39	192.58	3572.27	45639.88
Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		390	1.311	5.50	1/1.46	2383.64	63237.87
15	300	330	1.290	4.08	180.85	2769.23	67120.42
25 30		310	1.235	4.47	170.51	2702.80	67843 58
30 40		300	1.222	3.98	182.26	3042 71	68459.83
Blank		490	1 338	5.25	225.68	2548 57	82615 38
10		430	1 311	4 37	225.00	3000.00	84316 84
15		400	1.296	3.98	243.01	3256.28	85292.73
25	400	360	1.235	3.55	245.20	3478.87	89505.57
30		340	1.222	3.31	248.37	3691.84	90457.76
40		320	1.211	3.02	256.21	4009.93	91279.42
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		460	1.311	4.37	254.52	3000.00	105396.13
15	500	420	1.296	3.80	267.25	3410.53	106616.00
25	500	390	1.235	3.55	265.64	3478.87	111882.05
30		360	1.222	3.16	275.46	3867.09	113072.28
40		350	1.211	3.09	273.88	3919.09	114099.36
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		520	1.311	4.37	287.72	3000.00	147554.71
15	700	510	1.296	4.27	288.80	3035.13	149262.52
25		450	1.235	3.72	292.50	3319.89	156635.00
30		410	1.222	3.24	305.98	3//1.00	158301.33
40		400	Compo	3.10	300.07	3832.28	139739.23
Blank		380	1 338	7 /1	124.00	1805.67	20653.87
10		340	1.338	6.46	124.00	1992.26	20055.87
15		320	1.272	6.03	127.20	2109.45	21725.53
25	100	300	1.264	5.50	131.89	2298.18	21863.04
30		280	1.217	5.13	131.97	2372.32	22707.38
40		260	1.183	4.68	134.33	2527.78	23360.00
Blank		420	1.338	6.03	168.42	2218.91	41307.85
10		360	1.287	4.90	177.65	2626.53	42944.76
15	200	340	1.272	4.57	179.89	2783.37	43451.18
25	200	320	1.264	4.17	185.55	3031.18	43726.19
30		300	1.217	3.98	182.26	3057.79	45414.87
40		280	1.183	4.68	144.66	2527.78	46720.12
Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		410	1.287	6.03	164.41	2134.33	64417.13
15	300	360	1.272	5.01	173.75	2538.92	65176.77
25		340	1.264	4.57	179.89	2765.86	65589.28
30 40		320	1.21/	4.37	175.54	2784.90	08122.31
40 Dlank		310	1.103	4.27	173.34	2770.49	82615.29
		490	1.338	5.25 A A7	223.08	2348.37	02013.38 85880.19
15		400	1.207	4.47	237.64	3125 31	86902.03
25	400	380	1.264	3.80	241.80	3326.32	87452.04
30		360	1.217	3.63	239.80	3352.62	90829.40
40		340	1.183	3.39	242.51	3489.68	93439.88

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Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		510	1 287	5.13	240.38	2508 77	107361 56
10		510	1.207	J.1J	240.00	2010.77	107501.50
15	500	450	1.272	4.37	248.99	2910.76	108627.62
25	200	420	1.264	3.89	261.07	3249.36	109315.13
30		390	1.217	3.63	259.78	3352.62	113536.84
40		270	1 192	2.47	257.80	3400.22	116700.04
40		570	1.165	5.47	237.62	3409.22	110/99.94
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		540	1.287	4.79	272.59	2686.85	150306.32
15		520	1.272	4.57	275.13	2783.37	152078.80
25	700	480	1.264	2.08	201.61	2175.88	1520/1122
25		400	1.204	5.90	291.01	5175.66	153041.32
30		430	1.217	3.55	292.88	3428.17	158951.71
40		420	1.183	3.55	286.07	3332.39	163520.06
			Compour	nd (III)			
Dlamb		290	1 220	7.41	124.00	1905 67	20652.97
Blank		380	1.558	/.41	124.00	1803.07	20033.87
10		350	1.271	6.92	122.30	1836.71	21742.63
15	100	330	1.252	6.46	123.52	1938.08	22072.59
25	100	310	1.244	5.89	127.26	2112.05	22214.53
20		200	1.210	5.50	127.40	2202.64	2221100
30		290	1.212	5.50	127.49	2205.04	22801.00
40		270	1.185	5.01	130.31	2365.27	23320.57
Blank		420	1.338	6.03	168.42	2218.91	41307.85
10		380	1.271	5.37	171.10	2366.85	43485.37
15		360	1 252	5.12	160.68	2440.55	44145 20
15	200	300	1.232	5.15	109.08	2440.55	44143.29
25		340	1.244	4.68	175.66	2658.12	44429.18
30		320	1.212	4.37	177.06	2773.46	45602.23
40		300	1.185	4.07	178.23	2911.55	46641.27
Blank		460	1 338	5.62	107.01	2380.78	61061 77
Dialik		400	1.550	5.02	157.00	1000.04	(5220.05
10		430	1.271	0.01	157.30	1922.84	65228.05
15	200	400	1.252	6.03	160.40	2076.29	66217.93
25	500	380	1.244	5.50	167.06	2261.82	66643.77
30		360	1 212	5.25	165.80	2308 57	68403 34
30		220	1.212	5.25	172.10	2500.57	(00(1.00
40		520	1.185	4.47	1/5.10	2031.01	09901.90
Blank		490	1.338	5.25	225.68	2548.57	82615.38
10		460	1.271	5.01	222.01	2536.93	86970.40
15		420	1.252	4.47	227.19	2800.89	88290.24
25	400	400	1.244	4.17	231.04	2083 21	88858 02
25		400	1.244	4.17	231.94	2963.21	00030.02
30		380	1.212	3.98	230.86	3045.23	91204.11
40		340	1.185	3.39	242.51	3495.58	93282.18
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		490	1 271	4 90	241.80	2593.88	108713.08
10		470	1.271	4.00	241.00	2575.00	1102(2.00
15	500	470	1.252	4.68	242.83	26/5.21	110362.88
25	200	440	1.244	4.27	249.16	2913.35	111072.61
30		410	1.212	3.98	249.09	3045.23	114005.22
40		390	1 185	372	253 50	3185.48	116602.81
Diaula		(00	1.105	5.72	235.50	2401.(2	144577.15
Blank		600	1.558	5.57	270.16	2491.62	144577.15
10		570	1.271	5.25	262.52	2420.95	152198.45
15	700	550	1.252	5.01	265.44	2499.00	154508.17
25	700	500	1 244	4 37	276.65	2846.68	155501 79
20		460	1.212	2.00	270.05	2045.00	150607.45
30		400	1.212	5.98	279.40	3043.23	139607.43
40		440	1.185	3.80	279.97	3118.42	163244.08
			Compou	nd (IV)			
Blank		380	1.338	7.41	124.00	1805.67	20653.87
10		330	1.257	6.46	123.50	1045.82	21084 70
10		330	1.257	0.40	125.52	1945.82	21904.79
15	100	310	1.244	5.89	127.26	2112.05	22214.53
25	100	300	1.224	5.62	129.07	2177.94	22577.52
30		290	1.196	5.50	127.49	2174.55	23106.09
40		260	1 157	4 70	131.25	2415.45	23884.94
		400	1.137		1/0.42	2415.45	41207.05
Blank		420	1.338	6.03	168.42	2218.91	41307.85
10		350	1.257	4.79	176.68	2624.22	43969.69
15	200	330	1.244	4.47	178.51	2783.00	44429.18
25	200	310	1 224	417	179 75	2935 25	45155.15
20		200	1.106	2.09	192.26	2005.02	46212.20
50		300	1.190	3.98	182.20	5005.03	40212.29
40		280	1.157	3.72	182.00	3110.22	47770.01
Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		370	1.257	5.25	170.41	2394.29	65954.53
15		350	1.244	4.00	170.11	2528 79	66642 77
15	300	330	1.244	4.90	172.71	2556.76	(7722 72
25		330	1.224	4.57	174.60	26/8.34	67732.72
30		310	1.196	4.27	175.54	2800.94	69318.44
40		300	1.157	4.17	173.95	2774.58	71655.01

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Blank		490	1.338	5.25	225.68	2548.57	82615.38
10		390	1 257	3.98	236 94	3158 29	87939.05
10		270	1.2.57	3.70	230.74	2244.00	01757.05
15	400	370	1.244	3.72	240.50	3344.09	88858.02
25	400	350	1.224	3.47	243.89	3527.38	90309.95
20		220	1 100	2.04	246.07	2601.26	00404.00
30		330	1.196	3.24	246.27	3691.36	92424.23
40		310	1.157	3.02	248.20	3831.13	95539.65
	-	500	1.220	5.12	245.10	2600.10	1022(0.20
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		410	1.257	3.80	260.89	3307.89	109923.89
10		200	1.2.37	2.00	200.05	2501.02	111070 (1
15	500	390	1.244	3.55	265.64	3504.23	1110/2.61
25	500	370	1 224	3 31	270.29	3697.89	112887 52
20		270	1 106	2.16	2(7.01	2704.01	115520.20
30		350	1.196	3.16	267.81	3/84.81	115530.38
40		330	1.157	2.95	270.48	3922.03	119424.66
DI I		(00	1 220	5.27	270.16	2401.62	144577.15
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		440	1.257	3.55	299.69	3540.85	153893.58
10		410	1.244	2.2.4	205.00	2020 51	155501 70
15	700	410	1.244	3.24	305.98	3839.51	155501.79
25	700	400	1.224	3.16	306.07	3873.42	158042.67
20		200	1 106	2.02	225.02	40.41.10	161740.67
30		380	1.196	2.82	325.82	4241.13	161/42.67
40		360	1 157	2.82	308.68	4102.84	167194 67
-10		500	1.157	2.02	500.00	4102.04	10/1/4.07
			Compou	nd (V)			
Dloph		200	1 229	7.41	124.00	1905 67	20652.97
DIAIIK		560	1.556	7.41	124.00	1805.07	20055.87
10		300	1.230	5.62	129.07	2188.61	22467.38
15		200	1 104	5.25	129.06	2274 20	22144 70
15	100	280	1.194	3.23	128.90	2274.29	23144.79
25	100	220	1.161	3.72	143.00	3120.97	23802.65
20		200	1 100	2.21	146.10	2407.95	24400.01
30		200	1.128	3.31	146.10	3407.85	24499.01
40		180	1.111	2.88	151.12	3857.64	24873.88
		100	1.220	2.00	160.10	20210.01	41007.05
Blank		420	1.338	6.03	168.42	2218.91	41307.85
10		320	1 230	4 27	181 21	2880 56	44934 88
10		320	1.250	7.27	101.21	2000.50	++>5+.00
15	200	300	1.194	3.98	182.26	3000.00	46289.70
25	200	240	1 161	2.95	196 72	3935 59	47605 43
20		210	1.100	2.55	190.72	1000.07	10000.10
30		220	1.128	2.63	202.26	4288.97	48998.14
40		200	1.111	2.34	206.66	4747.86	49747.88
		160	1.000	2.0	200.00		(10 (1 ==
Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		340	1 230	4 79	171.63	2567.85	67402.32
10		200	1.104	1.17	171.05	2501.05	67 102.52
15	300	320	1.194	4.47	1/3.10	26/1.14	69434.55
25	500	280	1 161	3 72	182.00	3120.97	71408 14
20		200	1.100	2.12	101.15	2250.57	71100.11
30		260	1.128	3.47	181.17	3250.72	73497.21
40		240	1 111	3.09	187.80	3595 47	74621.83
		240	1.111	5.07	107.00	3373.47	74021.05
Blank		490	1.338	5.25	225.68	2548.57	82615.38
10		360	1 230	3 55	245 20	3464 79	89869 41
10		500	1.250	5.55	243.20	5464.77	07007.41
15	400	340	1.194	3.39	242.51	3522.12	92579.05
25	400	300	1 161	2.88	251.87	4031 25	95210.49
25		500	1.101	2.00	231.07	4051.25	)5210.4)
30		280	1.128	2.63	257.43	4288.97	97995.90
40		260	1 1 1 1	2.40	261.95	4629.17	00405 30
40		200	1.111	2.40	201.75	+027.17	)) <del>-</del> )).))
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		380	1 230	3 47	264 79	3544.67	112336.85
10		500	1.250	5.47	204.79	3344.07	112550.05
15	500	360	1.194	3.31	262.98	3607.25	115723.89
25	500	310	1 161	2.60	278.65	4315.00	119013 20
25		200	1.101	2.07	270.05	1010.99	10015.20
30		300	1.128	2.63	275.81	4288.97	122494.97
40		280	1.111	2.40	282.10	4629 17	124369 33
		200	1.111	2.10	202.10	029.17	121007.00
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		400	1 230	3.09	313.00	3980 58	157271 73
10		100	1.230	5.07	515.00	10.50	107211.75
15	700	380	1.194	2.95	311.47	4047.46	162013.59
25	700	330	1 161	2 4 5	325.68	4738 78	166618.63
20		330	1.100	2.13	225.00	1/30.70	171.00.11
30		310	1.128	2.29	327.32	4925.76	1/1493.11
40		300	1 1 1 1	2 24	323.83	4959.82	174117 22
-10		500	1.111	2.2T	525.05	1757.02	1/711/.22
			Compour	nd $(\mathbf{VI})$			
Blank		380	1 3 3 8	7.41	124.00	1805.67	20653.87
Dialik		500	1.330	7.41	124.00	1005.07	20055.07
10		280	1.216	5.13	131.97	2370.37	22726.05
15		260	1 199	1.68	12/ 22	2528 16	22261 69
15	100	200	1.100	4.00	154.55	2330.40	23201.08
25		200	1.161	3.24	149.26	3583.33	23802.65
20		190	1 126	2.75	150 07	4120.01	21226 10
30		180	1.130	2.15	138.27	4130.91	24320.48
40		160	1.098	2.40	161.20	4575.00	25168.38
Dlagle		420	1 2 2 0	6.02	169.40	2219.01	41207.95
Blank		420	1.338	0.03	108.42	2218.91	41307.85
10		300	1.216	3.98	182.26	3055.28	45452.22
10		200	1 100	2.00	106.51	2070.70	4(502.40
15	200	280	1.188	3.03	186.51	3212.13	40523.48
25	200	230	1.161	2.75	202.23	4221.82	47605.43
20		200	1 120	2.24	215.00	5071 42	19652.00
30		200	1.136	2.24	215.89	50/1.43	48653.08
40		180	1.098	2.00	217.62	5490.00	50336.89

Effect of Anodic Mass Transfer in the Electrowinning of Copper 1193

Blank		460	1.338	5.62	197.91	2380.78	61961.77
10		320	1.216	4.37	177.06	2782.61	68178.33
15	200	300	1.188	4.07	178.23	2918.92	69785.23
25	500	240	1.161	2.95	196.72	3935.59	71408.14
30		220	1.136	2.63	202.26	4319.39	72979.62
40		200	1.098	2.34	206.66	4692.31	75505.33
Blank		490	1.338	5.25	225.68	2548.57	82615.38
10		340	1.216	3.31	248.37	3673.72	90904.10
15	400	320	1.188	3.09	250.40	3844.66	93046.62
25	400	260	1.161	2.29	274.53	5069.87	95210.49
30		240	1.136	2.09	277.66	5435.41	97305.79
40		220	1.098	1.86	286.00	5903.23	100673.39
Blank		520	1.338	5.13	245.10	2608.19	103269.30
10		360	1.216	3.24	268.66	3753.09	113630.21
15	500	340	1.188	3.02	272.22	3933.77	116308.36
25	500	280	1.161	2.29	295.65	5069.87	119013.20
30		260	1.136	2.09	300.80	5435.41	121632.33
40		240	1.098	1.91	303.83	5748.69	125841.83
Blank		600	1.338	5.37	270.16	2491.62	144577.15
10		380	1.216	2.88	319.04	4222.22	159082.43
15	700	360	1.188	2.75	316.53	4320.00	162831.84
25	700	300	1.161	2.14	338.97	5425.23	166618.63
30		280	1.136	1.95	347.19	5825.64	170285.41
40		260	1.098	1.82	345.42	6032.97	176178.72

increasing the organic compounds concentration<sup>18</sup> could be related to strong adsorption of organic compound which is in agreement of current density<sup>19</sup> observed on polarization curves. The presence of organic compounds changes the electro-deposition of copper<sup>20</sup> as it can be seen from decreasing the cathodic transfer coefficient.

The decrease in mass transfer coefficient as well as discharge velocity is attributed to: (1) Adsorption of organic substance on the cathode surface where they screen a part of cathode<sup>17</sup> thus is reducing the active cathode area with consequent reduction in the limiting current. (2) The adsorbed organic substance increases the local solution viscosity at the cathode surface with consequent decrease in the diffusivity of copper ions, resulting in a decrease of the mass transfer coefficient k and the limiting current.

Adsorption isotherm: The electrochemical processes on the metal surface are likely to be closely related to the adsorption of the inhibitor and the adsorption is known to depend on the chemical structure of the inhibitor<sup>21-24</sup>. The adsorption of the inhibitor molecules from aqueous solutions can be regarded as (quasi-substitution) process between the organic compound in the aqueous phase, (org.<sub>(aq)</sub>) and water molecules at the electrode surface  $[H_2O(s)]$ 

$$(\text{org.}_{(\text{aq})}) + \text{H}_2\text{O} = (\text{org.}_{(\text{s})}) + \text{xH}_2\text{O}$$

where x (the size ratio) is the number of water molecules displaced by one molecule of organic inhibitor. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions.

The most frequently used isotherms are those of Langmuir, Frumkin, Parson, Temkin, Flory-Huggins and Bockris-Swinkels<sup>25-28</sup>. All these isotherms are of the general form:

$$f(\theta, x) \exp(-a\theta) = kC$$

where f ( $\theta$ , x) is the configuration factor depends essentially on the physical model and assumptions underlying the derivation of the isotherm<sup>29</sup>. The mechanism of inhibition of reaction is generally believed to be due to the formation ad maintenance of a protective film on the metal surface<sup>30</sup>.

Inhibitor adsorption characteristics can be estimated by using Langmuir isotherm given as<sup>31</sup>:

$$\mathrm{KC} = \frac{\theta}{1 - \theta}$$

where K is the equilibrium constant of adsorption process, C is the concentration and  $\theta$  is the surface coverage.

The degree of surface coverage ( $\theta)$  at constant temperature was determined from  $^{32}$ 

$$\theta = \frac{(I_b - I_{org})}{I_b}$$

A plot of  $(\theta/1 - \theta) vs. \theta$  should yields straight line, Fig. 4 show straight line indicating that all the inhibitors verify Langmuir adsorption isotherm.

Fig. 6 show the Flory-Huggins adsorption isotherm plotted as  $\log \theta/C vs. \log (1-\theta)$  for CuSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> organic compounds at 303 K yield a straight line with slope x and intercept log xK. Table-5 shows the values of X and K. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:





Fig. 5. Overall mass transfer correlation for all organic compounds at different rpm

$$\log \frac{\theta}{C} = \log xK + x \log(1 - \theta)$$

1

here x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of either electrostatic or covalent bonding between the adsorpates and the metal surface atoms<sup>34</sup>.

The free energy of adsorption  $\Delta G_{ads}$ . At different concentrations was calculated from the equation

$$\Delta G_{ads} = -RT \ln (55.5k)$$

The value 55.5 is the concentration of water in the solution.

The values of  $\Delta G_{ads.}$  are given in Table-5. In all cases; the  $(\Delta G_{ads.})$  values are negative and lie in the range of -14.525 to -21.308 kJ/mol. The most efficient inhibitor shows the most negative ( $\Delta G_{ads.}$ ) value. This suggests that they are strongly adsorbed on the metal surface. The negative values of ( $\Delta G_{ads.}$ ) indicate the spontaneous adsorption of the inhibitor. This usually characteristic of strong interaction with metal surface. It is found that the ( $\Delta G_{ads.}$ ) values are more positive than -40 kJ/mol indicating that inhibitors are physically adsorbed on the metal surface. Similar results have also been reported by Talati *et al.*<sup>35</sup>.

**Effect of temperature:** The electrodeposition of copper in presence of different inhibitors was studied by measuring the limiting currents over the temperature ranges between (25-40 °C). Table-1 shows the limiting currents obtained in presence of organic additives at different temperatures. The results indicate that the rate of electrodeposition increases with increase the temperature. The above behaviour is indicative of the occurrence of the electrodeposition through physical adsorption of additive on the metal surface. Desorption is aided by increasing the reaction temperature.

The values of  $(I_i)$  obtained at different temperatures permits the calculation of activation energy,  $E_a$ , according to Arrhenius equation:

$$\log I_t = \frac{-E_a}{2.303RT} + \log A$$

The plot of log I against 1/T gave a straight line, where A is pre-exponential factor, R is the gas constant and T is the absolute temperature. The slope of the straight line is proportional to  $E_a$ . The activation energy of the process is an important parameter for determining the rate controlling step. If the rate controlling step is a diffusion of species of the species in the boundary layer,  $E_a$  is generally  $\leq 28$  kJ/mol, while  $E_a$  values usually > 43 kJ/mol when the reaction is chemically controlled. Table-7 shows that the values of  $E_a$  are lower than 43 kJ/mol; characterizing diffusion process to be the controlling electrodeposition reaction.

**Thermodynamic treatment of the reaction:** The value of the enthalpy of activation  $\Delta H^*$ , entropy of activation  $\Delta S^*$  and free energy of activation  $\Delta G^*$ , can be obtained by using equation:

$$\frac{\Delta \mathbf{H}^* = \mathbf{E}_a - \mathbf{R}\mathbf{I}}{\mathbf{R}} = \ln \mathbf{A} - \ln \left(\frac{\mathbf{B}\mathbf{T}\mathbf{e}}{\mathbf{h}}\right)$$

THERMODYNAMIC PARAMETRIS FOR I PECHOPPION OF COPPER IN PRESENCE OF ORGANIC SUBSTACK AT 25 °C           Compound (h)           State of the second of the seco			TABLE-4
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	THERMODYNA	MIC PARAMETERS FOR ELECTR	ODEPOSITION OF COPPER IN PRESENCE OF ORGANIC SUBSTANCE AT 25 °C
Compound (1)           5         AF (1cl and <sup>1</sup> )         \$194.031757123 + OK - 51.99991989135742           5         AF (1cl and <sup>1</sup> )         \$715.23243157 + OK - 51.99991989135742           6         AG (1cl and <sup>1</sup> )         \$715.23243157 + OK - 51.99991989135742           10         AG (1cl and <sup>1</sup> )         \$916.4051178157 + OK - 51.99991989135742           10         Af (1cl and <sup>1</sup> )         \$665.6778125 + OK - 70.298770146016           10         Af (1cl and <sup>1</sup> )         \$665.6778125 + OK - 70.298770146016           11         Af (1cl and <sup>1</sup> )         \$665.6778125 + OK - 70.298770146016           15         Af (1cl and <sup>1</sup> )         \$67.6178125 + OK - 70.29877014753           15         Af (1cl and <sup>1</sup> )         \$688.6990875 + OK - 1.21722791671753           16         Af (1cl and <sup>1</sup> )         \$688.6990875 + OK - 2.12722791671753           25         Aff (1cl and <sup>1</sup> )         \$688.69908714 - OK - 323.498862304688           26         Aff (1cl and <sup>1</sup> )         \$688.69908714 - OK - 323.498862304688           27         Aff (1cl and <sup>1</sup> )         \$989233333125 + OK - 923.449862304688           28         Aff (1cl and <sup>1</sup> )         \$9802333333125 + OK - 923.498862304688           29         Aff (1cl and <sup>1</sup> )         \$98023304623475 - OK - 924.99149840159501           30         Aff (1cl and <sup>1</sup> )         \$	$C \times 10^{-4}$		Thermodynamic parameters
E, (d, mol <sup>+</sup> )         8194.051758125 408: 51.9999198135742           S         Aff (d, mol <sup>+</sup> k <sup>-</sup> )         -177.03530837806 408: -17021439063394           Aff (d, mol <sup>+</sup> )         9164.491171875 408: 70.20987701416016           Aff (d, mol <sup>+</sup> )         9164.491171875 408: 70.20987701416016           Aff (d, mol <sup>+</sup> )         9164.495117875 408: 70.20987701416016           Aff (d, mol <sup>+</sup> )         147.873671386719 408: -20987701416016           Aff (d, mol <sup>+</sup> )         147.873671386719 408: -2048622760971388           Aff (d, mol <sup>+</sup> )         2493423954 508: -10.573570161753           Aff (d, mol <sup>+</sup> )         1499.254440076172 408: -508.71060152986644:003           Aff (d, mol <sup>+</sup> )         1499.254440076172 408: -908.70991951416           Aff (d, mol <sup>+</sup> )         499.2544902145 -008: 20187280210615           Aff (d, mol <sup>+</sup> )         490.255458161660867 5042: 3102739915146           Aff (d, mol <sup>+</sup> )         1433.67119787402: 408: 20802           Aff (d, mol <sup>+</sup> )         5988.6969073125 408: 20802           Aff (d, mol <sup>+</sup> )         1580.5969871475 408: 3089091015           Aff (d, mol <sup>+</sup> )         1438.0719787175 408: 3089919501615           Aff (d, mol <sup>+</sup> )         1580.596973125 408: 20802           Aff (d, mol <sup>+</sup> )         1580.596973125 408: 202330625           Aff (d, mol <sup>+</sup> )         1620.3837121875 408: 30.3999195015742           Aff (d, m			Compound (I)
s         Aff (d) mol <sup>+</sup> (x)         5715.332421873 +008-51.99901989135742           AG <sup>+</sup> (d) mol <sup>+</sup> (x)		$E_a (kJ mol^{-1})$	8194.0517578125 +OR- 51.99991989135742
-         AG' (J mal' k')         -17703308378006 0.08. 170214399632034           -         -         54893.508573 0.08. 1.02.94348522003           -         -         6489.508573 0.08. 1.02.94348522003           -         -         648.57379357 0.08. 1.02.94348522003           -         -         7.47375671386719 0.08. 2.023722791617733           -         -         7.47375671386719 0.08. 2.123722791617733           -         -         6.417 (J mal' k')         -           -         -         7.453545516046675 0.08. 2.123722791617733           -         -         6.417 (J mal' k)         -           -         -         7.45454551604675 0.08. 2.123722791617733           -         -         7.45454551604675 0.08. 2.123722791617733           -         -         7.45458586234068           -         -         7.4545852347408           -         -         7.45585854431314708           -         -         7.85886234068           -         -         7.85886234068           -         -         7.85886234468           -         -         7.8588623479463           -         -         7.8588623479463           -         -         7.858862347	5	$\Delta H^* (kJ mol^{-1})$	5715.232421875 +OR- 51.99991989135742
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	5	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-177.0353088378906 +OR1702143996953964
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta G^* (kJ mol^{-1})$	58498.30859375 +OR- 102.7493438720703
10         Aff (Q mol <sup>+</sup> )         6665:67578125 +008. 78:02957701416016           AG <sup>+</sup> (Q mol <sup>+</sup> )         5879855984375 +008. 150.5570513910016           E, (d mol <sup>+</sup> )         4934.274902375 +008. 21227291671733           Aff (Q mol <sup>+</sup> )         2455.455810546675 +008. 212227291671733           Aff (Q mol <sup>+</sup> )         2455.455810546675 +008. 21222791671733           Aff (Q mol <sup>+</sup> )         2455.455810546675 +008. 21227291671733           Aff (Q mol <sup>+</sup> )         58881.6679675 +008. 2125722791671733           Aff (Q mol <sup>+</sup> )         6444.5520125 +008. 228.3458862304688           25         Aff (Q mol <sup>+</sup> )         6444.5520125 +008. 228.3458862304688           26         Aff (Q mol <sup>+</sup> )         59023.30212 +008. 328.8458621280402           Aff (Q mol <sup>+</sup> )         59023.30212 +008. 32033754619. 590801           Aff (Q mol <sup>+</sup> )         59023.30212 +008. 3203325906605115           Aff (Q mol <sup>+</sup> )         18079205978125 +008. 320332590660511402           Aff (Q mol <sup>+</sup> )         18079205978125 +008. 320332590660525           Aff (Q mol <sup>+</sup> )         18079205978125 +008. 320332590660525           Aff (Q mol <sup>+</sup> )         18079205978125 +008. 1204202590625           Aff (Q mol <sup>+</sup> )         18040115778125 +008. 130999198915742           Aff (Q mol <sup>+</sup> )         5977777851525 +008. 130999198915742           Aff (Q mol <sup>+</sup> )         5115325 +008. 13099198915742		$E_a$ (kJ mol <sup>-1</sup> )	9164.4951171875 +OR- 76.20987701416016
AS' (J mol' k')         -147.873501386119-00839482276091391601           AG' (Al mol')         5978.5598.457 +0.0812.872279161735           AH' (kl mol')         4934.2740023475 +0.0812.8722791617735           AG' (M mol')         2455.45581054675 +0.0812.12722791617735           AG' (M mol')         5888.66796875 +0.0812.05722791617735           AG' (M mol')         6354.4400076172 +0.0805817000112598641+0.03           AG' (M mol')         6444.45200125 +0.08928.3458862340868           AG' (M mol')         6444.45200125 +0.08928.3458862340862           AG' (M mol')         6407.4570.821.25102 +0.08.3458062340862           AG' (M mol')         13309.44900243405 +0.08304379463195801           AG' (M mol')         5407.63325264464.1+0.08.303809061050415           AG' (M mol')         14879.20070125 +0.08.1242.025906055           AG' (M mol')         14879.20070125 +0.08.1242.025906055           AG' (M mol')         1461.59371001012 +0.08.1242.025906055           AG' (M mol')         1461.59371001012 +0.08.1242.025906055           AG' (M mol')         1461.59371001012 +0.08.1242.025906055           AG' (M mol')         1461.5937100112 +0.08.1242.02590625           AG' (M mol')         1461.5937101012 +0.08.1242.02590625           AG' (M mol')         1461.593710121 +0.08.1242.025906055           AG' (M mol')        <	10	$\Delta H^*$ (kJ mol <sup>-1</sup> )	6685.67578125 +OR- 76.20987701416016
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-174.7875671386719 +OR2494622766971588
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta G^* (kJ mol^{-1})$	58798.58984375 +OR- 150.5870513916016
15         Aff (U and' k)         243534581034687 > 408 - 21257227016015298864E-003           AG' (U and')         5881.66796875 + 208 - 4395730126 108         25345580204688           Aff (U and')         6744.552015 + 008 - 292.3455862204668           25         Aff (U and')         4265.7620933125 + 008 - 293.3455862204668           26         Aff (U and')         193024300125 + 008 - 293.3455862204668           27         Aff (U and')         19302320125 + 008 - 193.34558621204668           28         Aff (U and')         19308 - 49305234357 + 008 - 19345349519501           30         Aff (U and')         19308 - 49305234357 + 008 - 193798202514648           29         Aff (U and')         19679.205078125 + 008 - 1927925200514648           40         Aff (U and')         19679.205078125 + 008 - 1927925200514648           20         Aff (U and')         19679.205078125 + 008 - 1927925200514648           21         Aff (U and')         19679.205078125 + 008 - 1927925200514648           22         Aff (U and')         19679.205078125 + 008 - 1927925200514648           23         Aff (U and')         19679.205078125 + 008 - 1927925200514648           24         Aff (U and')         19679.20507812 + 008 - 1927925200514648           25         Aff (U and')         515.235211777373           26 (U and')		$E_a$ (kJ mol <sup>-1</sup> )	4934.27490234375 +OR- 2.123722791671753
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	15	$\Delta H^*$ (kJ mol <sup>-1</sup> )	2455.455810546875 +OR- 2.123722791671753
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-189.2544403076172 +OR- 6.951706018298864E-003
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta G^{*} (kJ mol^{-1})$	58881.66796875 +OR- 4.19637393951416
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_a$ (kJ mol <sup>-1</sup> )	6744.58203125 +OR- 928.3458862304688
$ \begin{array}{c} \Delta S \ (l \ mol^+ k^-) & -1.83.6/115/8.59141+0.04.30.380001050415 \\ \Delta G \ (l \ mol^+) & 5903.730125 +0.04.834.566821280062 \\ E, (kl \ mol^+) & 3398.4965234375 +0.04.99.49379463195801 \\ \Delta S^* (l \ mol^+ k^+) & -1.87.6355285644531 +0.08.3209325298666954E.002 \\ \Delta G^* (l \ mol^+) & 19333.382125 +0.04.93.279463195801 \\ \Delta S^* (l \ mol^+) & 19333.382125 +0.04.93.279463195801 \\ \Delta S^* (l \ mol^+) & 19333.382125 +0.04.93.279463195801 \\ \Delta S^* (l \ mol^+) & 10200.3857421375 +0.08.1124.2025390625 \\ \Delta G^* (l \ mol^+) & 10200.3857421375 +0.08.1124.2025390625 \\ \Delta G^* (l \ mol^+) & 10200.3857431375 +0.08.12920.20390625 \\ \Delta G^* (l \ mol^+) & 59777.78515625 +0.08.2213.701171875 \\ \hline & Compound (II) \\ F, (kl \ mol^+) & 5175.232421875 +0.0830.9991989135742 \\ \Delta G^* (l \ mol^+) & 5715.232421875 +0.087102143906953964 \\ \Delta G^* (l \ mol^+) & 5715.232421875 +0.087102143906953964 \\ \Delta G^* (l \ mol^+) & 5610.385393635 +0.081702143906953964 \\ \Delta G^* (l \ mol^+) & 5610.385393635 +0.081702143966935964 \\ \Delta G^* (l \ mol^+) & 5613.53393435 +0.081702143966935964 \\ \Delta G^* (l \ mol^+) & 5613.53393437 +0.08.45.6814375195312 \\ 10 \ \Delta H^* (l \ mol^+) & 5613.53393437 +0.08.45.6814375195312 \\ \Delta G^* (l \ mol^+) & 5613.637597656 +0.082.762187592046 \\ \Delta G^* (l \ mol^+) & 5898.6589375 +0.084091486401367188 \\ \Delta G^* (l \ mol^+) & 5493.639375 +0.084091486401367188 \\ \Delta G^* (l \ mol^+) & 5493.63914502 +0.08409143886566162 \\ \Delta G^* (l \ mol^+) & 5493.63091375 +0.08409143886566162 \\ \Delta G^* (l \ mol^+) & 5493.6309375 +0.08409143886566162 \\ \Delta G^* (l \ mol^+) & 5493.6309375 +0.08409143886566162 \\ \Delta G^* (l \ mol^+) & 5493.6309375 +0.08409138342079 +0.02 \\ \Delta G^* (l \ mol^+) & 5493.6409375 +0.08409138342666162 \\ \Delta G^* (l \ mol^+) & 5493.6409375 +0.0840913834266162 \\ \Delta G^* (l \ mol^+) & 5493.6409375 +0.0840913834266162 \\ \Delta G^* (l \ mol^+) & 5493.6409375 +0.0840913834266162 \\ \Delta G^* (l \ mol^+) & 5493.6409375 +0.0840913834266162 \\ \Delta G^* (l \ mol^+) & 5493.64937575082 \\ AG^* (l \ mol^+) & 5493.64937575082 \\ AG^* (l \ mol^+) & 5493.64937$	25	$\Delta H^{*}$ (kJ mol <sup>-1</sup> )	4265.7626953125 +OR- 928.3458862304688
$\frac{1}{10} + \frac{1}{10} $		$\Delta S^{*}$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-183.6/115/8369141 +OR- 3.038809061050415
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta G^{-}$ (kJ mol <sup>-1</sup> )	59027.3203125 +OR- 1834.366821289062
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_a$ (kJ mol <sup>-1</sup> )	5868.66845703125 +OR- 9.804379463195801
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	30	$\Delta H^{*} (kJ mol^{-1})$	3389.849365234375 +OR- 9.804379463195801
$\frac{1}{40} + \frac{1}{100} + \frac{1}{100} + \frac{1}{100} + \frac{1}{1000} + \frac{1}{100$		$\Delta S^* (J \text{ mol}^{-1} k^{-1})$	-187.6355285644531 +OR- 3.209325298666954E-002
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta G (kJ mol^{-1})$	59333.3828125 +OR- 19.37298202514648
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_a$ (kJ mol <sup>-</sup> )	186/9.2050/8125 +OR- 11242.025390625
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	40	$\Delta H$ (kJ mol <sup>-1</sup> )	10200.3857421875 +OR- 11242.025390025
$\frac{10}{10} + \frac{10}{10} + 10$		$\Delta S (J \text{ mol}^* K^*)$	-140.13931/0100010 +OK- 30./991/90//14844
$\frac{\text{Compound (II)}}{\text{F}_{4}(k  \text{mol}^{1})} = \frac{\text{F}_{6}(k  \text{mol}^{1})}{8194.0517578125 + OR-51.99991989135742} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1}  k^{1})}{3715.232421875 + OR-51.99991989135742} \\ = \frac{\text{AS}'(I  \text{mol}^{1}  k^{1})}{38498.30859375 + OR-845.6814575195312} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{38498.30859375 + OR-845.6814575195312} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{3849} = \frac{1788466559375 + OR-845.6814575195312}{385'(I  \text{mol}^{1}  k^{1})} \\ = \frac{\text{Compound}(III)}{38460559375 + OR-845.6814575195312} \\ = \frac{\text{Ad}''(k  \text{mol}^{1})}{38460559375 + OR-8405.8614575195312} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{3646559375 + OR-840.9186401367188} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{39306505859375 + OR-840.9186401367188} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{393068505859375 + OR-840.9186401367188} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{39306850589375 + OR-840.9186401367188} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{39306850589909375 + OR-6449143886566162} \\ = \frac{\text{Ad}'(k  \text{mol}^{1})}{3930685069609375 + OR-6449143886566162} \\ = \frac{\text{Ad}'(k  \text{mol}^{1})}{39306625 + OR-10.10268780670166} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{39306625 + OR-10.10278479839670166} \\ = \frac{\text{F}_{6}(k  \text{mol}^{1})}{3930} \\ = \frac{\text{F}_{6}$		2G (KJ MOI)	39/11.76313023 +OK- 22213.7011/1873
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			Compound (II)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$E_a$ (kJ mol <sup>-1</sup> )	8194.0517578125 +OR- 51.99991989135742
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5	$\Delta H^{-}$ (kJ mol <sup>-1</sup> )	5/15.232421875 +OR- 51.99991989135742
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta S^{+}$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-177.0353088378906 +OR1702143996953964
$ \begin{array}{c} \begin{array}{c} & {\rm L}_{\rm e}  ({\rm kl \ mol}^{-1}) & {\rm S140}  6^{-1}  3^{-3}  5^{-0}  {\rm Ch}^{-8}  85.  8815  5^{-5}  195. 12 \\ {\rm AH}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm S160}  1833  984375  {\rm Ch}^{-8}  85.  8815  575122046 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm C516}  87597656  {\rm +OR}  - 2.768218755722046 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm S8865. 59375  +OR  160. 102587890625 \\ {\rm L}_{\rm e}  ({\rm kl \ mol}^{-1}) & {\rm C516}  78759765625  {\rm +OR}  - 840. 9186401367188 \\ {\rm AH}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm C516}  78759765625  {\rm +OR}  - 840. 9186401367188 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm C516}  7875975525  +OR  - 840. 9186401367188 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm C516}  7875975525  +OR  - 840. 9186401367188 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm C184}  27978515625  +OR  - 84. 9143886566162 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm S4890. 9882125  +OR  - 1661.  61474009375 \\ {\rm L}_{\rm e}  ({\rm kl \ mol}^{-1}) & {\rm 2980.  0464599009375  +OR  - 64. 49143886566162 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 2980.  0464599009375  +OR  - 64. 9143886566162 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 29142.  8164025  +OR  - 10.77808780670166 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 59142.  8164025  +OR  - 10.77808780670166 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 50434.  600375  +OR  - 27. 81762504577637 \\ {\rm L}_{\rm e}  ({\rm kl \ mol}^{-1}) & {\rm 59434.  600375  +OR  - 27. 81762504577637 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 59434.  600375  +OR  - 27. 81762504577637 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 59434.  60375125  +OR  - 41.07808780670166 \\ {\rm AS}^{-1}  ({\rm mol}^{-1}) & {\rm 59434.  90375125  +OR  - 41.0585780029297 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 59434.  90375125  +OR  - 41.05455780029297 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 59434.  903755125  +OR  - 41.05455780029297 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 51715232421875  +OR  - 51.99991989135742 \\ {\rm AG}^{-1}  ({\rm kl \ mol}^{-1}) & {\rm 51749243375  50R $		$\Delta G^{-} (kJ mol^{-1})$	58498.30859375 +OR- 102.7493438720703
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_a$ (kJ mol <sup>-1</sup> )	8140.677734375 +OR- 845.6814575195312
$\frac{\Delta S (I mol+ k-) = -17.8.46197397.9536-054-0K- 2.7.98218757.22046}{\Delta G2 (kJ mol+) = -5865.59375+OR-1671.02587890625 = E_{k} (kJ mol+) = -58865.59375+OR-1641.02587890625 = -25268326416016 = -2526832641788 = -25268326416016 = -25268326416016 = -25268326416016 = -25268326416016 = -25268326416016 = -25268326416016 = -25268326416016 = -25268326416016 = -252683264178805656162 = -252683264178805566162 = -252683264178805566162 = -252683264178805566162 = -25268326417880575106 = -25268277539 = -25268257687 = -267871862594577539 = -267871862594577637 = -267871862594577637 = -267871862594577637 = -2678716253447880745E-002 = -256625+0R-20.7771053314209 = -2678434788074529457637 = -2678716578126294577637 = -26879101362 + OR-20.7771053314209 = -2678427826525 + OR-20.7771053314209 = -26784278265625 + OR-20.7771053314209 = -267842782265625 + OR-20.7771053314209 = -26784278241875 + OR-51.99991989135742 = -2678427826562 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683306121826172 = -2683305121826172 = -2683305121826172 = -2683305121826172 = -2683305121826172 = -2683305121826172 = -2683305121826172 = -256751549243927 = -256751549243927 = -256751549243927 = -256751549243927 = -256751549243927 = -256751549243927 $	10	$\Delta H$ (kJ mol <sup>-1</sup> )	5661.8583984375 +OR- 845.6814575195312
$\frac{\text{L}}{10} + \frac{\text{L}}{\text{L}} (\text{L} \text{Imol}^{-1}) = \frac{38885,39375 + 0\text{K}^{-1} 107.253785002.5}{6516,7875975625 + 0\text{R} - 84.0.9186401367188} \\ = \frac{\text{L}}{\text{L}} (\text{L} \text{Imol}^{-1}) = \frac{6516,78759756525 + 0\text{R} - 84.0.9186401367188}{401367188} \\ = \frac{\text{L}}{\text{A}} (\text{L} \text{Imol}^{-1}) = \frac{184.27978515625 + 0\text{R} - 24.0.9186401367188}{401367188} \\ = \frac{\text{L}}{\text{A}} (\text{L} \text{Imol}^{-1}) = \frac{184.27978515625 + 0\text{R} - 24.9143886566162}{401367189} \\ = \frac{\text{L}}{\text{L}} (\text{L} \text{Imol}^{-1}) = \frac{5459,28369140625 + 0\text{R} - 1641.61474609375}{5898.098828125 + 0\text{R} - 164.161474609375} \\ = \frac{\text{L}}{\text{L}} (\text{L} \text{Imol}^{-1}) = \frac{5459,28369140625 + 0\text{R} - 64.49143886566162}{4052 + 0\text{R} - 64.49143886566162} \\ = \frac{\text{A}}{\text{A}} (\text{L} \text{Imol}^{-1}) = \frac{59142.81640625 + 0\text{R} - 21.714319839477539}{506466666666666666666666666666666666666$		$\Delta S (J mol^{+} K^{+})$	-1/8.44019/509/050 +OK- 2./08218/55/22040
$ \begin{array}{c} 15 & \begin{array}{c} 4 \text{H}^{2}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 4037.963593575+0\text{R} - 84.9198401367188 \\ 4037.968505859375+0\text{R} - 84.0.9186401367188 \\ 45 (1 \text{mol}^{-1} \text{k}^{-1}) & \begin{array}{c} 4037.968505859375+0\text{R} - 84.0.9186401367188 \\ 45 (1 \text{mol}^{-1} \text{k}^{-1}) & \begin{array}{c} 184.27978515625+0\text{R} - 2.752628326416016 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 58980.98828125+0\text{R} - 1661.61474609375 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 58980.98828125+0\text{R} - 6.449143886566162 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 2980.464590609375+0\text{R} - 6.449143886566162 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 2980.46458007812+0\text{R} - 2.111036144196987\text{E}-002 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 59142.81640625+0\text{R} - 12.74319839477539 \\ \hline & \begin{array}{c} \text{E}_{a}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5025.219970703125+0\text{R} - 14.07808780670166 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5025.219970703125+0\text{R} - 14.07808780670166 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5025.2219970703125+0\text{R} - 14.07808780670166 \\ \hline & \begin{array}{c} 405^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 59434.609375+0\text{R} - 20.7771053314209 \\ \hline & \begin{array}{c} 400 & \begin{array}{c} \text{AH}^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 59649.9453125+0\text{R} - 20.7771053314209 \\ \hline & \begin{array}{c} 400 & \begin{array}{c} \text{AH}^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 818.40517578125+0\text{R} - 51.99991989135742 \\ \hline & \begin{array}{c} 40^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5715.232421875+0\text{R} - 51.99991989135742 \\ \hline & \begin{array}{c} \text{AS}^{\circ}(\text{l} \text{mol}^{-1}) & \begin{array}{c} 5715.232421875+0\text{R} - 51.99991989135742 \\ \hline & \begin{array}{c} 40^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 58498.30859375+0\text{R} - 102.7493438720703 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5715.232421875+0\text{R} - 51.99991989135742 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 5715.232421875+0\text{R} - 51.99991989135742 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mol}^{-1}) & \begin{array}{c} 58498.30859375+0\text{R} - 02.83306121826172 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mo}^{-1}) & \begin{array}{c} 58498.30859375+0\text{R} - 02.83306121826172 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mo}^{-1}) & \begin{array}{c} 58498.30859375+0\text{R} - 62.83306121826172 \\ \hline & \begin{array}{c} \text{AG}^{\circ}(\text{k} 1 \text{mo}^{-$		$\frac{\Delta G (KJ mol^{-1})}{E (kI mol^{-1})}$	516 79750765625 LOB 940 0196401267199
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$E_a (KJ IIIOI)$	0310.76739703023 +OK- 640.9160401307168
$\frac{\Delta G^{*}(kI mol^{-1})}{\Delta G^{*}(kI mol^{-1})} = \frac{5898.098828125 + OR - 1661.61474609375}{5898.098828125 + OR - 1641.61474609375} = \frac{AG^{*}(kI mol^{-1})}{2980.464599609375 + OR - 6.449143886566162} = \frac{\Delta H^{*}(kI mol^{-1})}{\Delta S^{*}(I mol^{-1} k^{-1})} = \frac{2980.464599609375 + OR - 6.449143886566162}{\Delta S^{*}(I mol^{-1} k^{-1})} = \frac{188.3694458007812 + OR - 2.111036144196987E + 002}{\Delta G^{*}(kI mol^{-1})} = \frac{59142.81640625 + OR - 12.74319839477539}{5142.81640625 + OR - 12.74319839477539} = \frac{A(kI mol^{-1})}{59142.81640625 + OR - 12.74319839477539} = \frac{A(kI mol^{-1})}{266070101562 + OR - 14.07808780670166} = \frac{AG^{*}(kI mol^{-1})}{266070101562 + OR - 14.07808780670166} = \frac{AG^{*}(kI mol^{-1})}{266070101562 + OR - 4.608263447880745E + 002} = \frac{AG^{*}(kI mol^{-1})}{266070101562 + OR - 20.7771053314209} = \frac{AG^{*}(kI mol^{-1})}{26607010162} = 16000000000000000000000000000000000000$	15	$\Delta \mathbf{H}  (\mathbf{KJ} \text{ Intol})$	4057.908505859575 +OR- 840.9180401507188
$\frac{1}{25} + \frac{1}{2} + 1$		$\Delta S (J \text{ Inol} \mathbf{K})$	52020 0222125 LOD 1661 61/77/600275
$\frac{1}{25} \frac{\Delta H^2 (kJ mol^{-1})}{\Delta S^2 (J mol^{-1} k^{-1})} = \frac{3}{2980.464599609375 + OR - 6.449143885656162}{25}$ $\frac{25}{\Delta S^2 (J mol^{-1} k^{-1})} = \frac{188.3694458007812 + OR - 2.111036144196987E-002}{\Delta G^2 (kJ mol^{-1})} = \frac{59142.81640625 + OR - 12.74319839477539}{5} = \frac{E_a (kJ mol^{-1})}{6104.0390625 + OR - 14.07808780670166}$ $\frac{30}{\Delta S^2 (J mol^{-1} k^{-1})} = \frac{6104.0390625 + OR - 14.07808780670166}{26} = \frac{20}{2000} = \frac{20}{20000} = \frac{20}{2000} = $		$\frac{\Delta G (kJ mol-1)}{E (kI mol-1)}$	5450 28260140625 +OR - 1001.014/4009575
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$\Delta H^*$ (kI mol <sup>-1</sup> )	2980 464599609375 +OR- 6 449143886566162
$\frac{\Delta G^{\circ} (kJ mol^{-1})}{\Delta G^{\circ} (kJ mol^{-1})} = \frac{106.307430007101000271000271000271000027}{59142.81640625 + OR - 12.74319839477539} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{6104.0390625 + OR - 14.07808780670166} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{3625.219970703125 + OR - 14.07808780670166} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{\Delta S^{\circ} (J mol^{-1} k^{-1})} = \frac{-187.1856079101562 + OR - 4.608263447880745E-002}{26625 + OR - 27.81762504577637} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{6618.1416015625 + OR - 27.81762504577637} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{6618.1416015625 + OR - 20.7771053314209} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{\Delta S^{\circ} (J mol^{-1} k^{-1})} = \frac{-186.1835479736328 + OR - 6.801091134548187E-002}{26625 + OR - 20.7771053314209} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{26949.9453125 + OR - 6.801091134548187E-002} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{26949.9453125 + OR - 41.05455780029297} = \frac{Compound (III)}{26949.9453125 + OR - 51.99991989135742} = \frac{\Delta H^{\circ} (kJ mol^{-1})}{265^{\circ} (J mol^{-1} k^{-1})} = \frac{-177.0353088378906 + OR1702143996953964}{265^{\circ} (kJ mol^{-1})} = \frac{8498.30859375 + OR - 10.27493438720703}{265(kJ mol^{-1})} = \frac{E_a (kJ mol^{-1})}{2649.8720703125 + OR - 62.83306121826172} = \frac{\Delta H^{\circ} (kJ mol^{-1})}{265^{\circ} (kJ mol^{-1})} = \frac{-175.9946594238281 + OR2056751549243927}{265751549243927} = \frac{\Delta G^{\circ} (kJ mol^{-1})}{265^{\circ} (kJ mol^{-1})} = \frac{-175.9946594238281 + OR2056751549243927}{265^{\circ} (kJ mol^{-1})} = -175.994$	25	$\Delta \mathbf{S}^* (\mathbf{I} \operatorname{mol}^{-1} \mathbf{k}^{-1})$	$-188,3694458007812 \pm \Omega R_{-}2,111036144196987E_002$
$\frac{1}{30} = \frac{1}{30} \begin{bmatrix} E_a (kJ mol^{-1}) & 6104.0390625 + OR - 14.07808780670166 \\ \Delta S^* (J mol^{-1} k^{-1}) & 3625.219970703125 + OR - 14.07808780670166 \\ \Delta S^* (J mol^{-1} k^{-1}) & -187.1856079101562 + OR - 4.608263447880745E-002 \\ \Delta G^* (kJ mol^{-1}) & 59434.609375 + OR - 27.81762504577637 \\ E_a (kJ mol^{-1}) & 6618.1416015625 + OR - 20.7771053314209 \\ \Delta H^* (kJ mol^{-1}) & 4139.322265625 + OR - 20.7771053314209 \\ \Delta H^* (kJ mol^{-1}) & -186.1835479736328 + OR - 6.801091134548187E-002 \\ \Delta G^* (kJ mol^{-1}) & -186.1835479736328 + OR - 6.801091134548187E-002 \\ \Delta G^* (kJ mol^{-1}) & -186.1835479736328 + OR - 6.801091134548187E-002 \\ \Delta G^* (kJ mol^{-1}) & -186.1835479736328 + OR - 51.99991989135742 \\ \Delta G^* (kJ mol^{-1}) & 59649.9453125 + OR - 51.99991989135742 \\ \Delta G^* (kJ mol^{-1}) & 5715.232421875 + OR - 51.99991989135742 \\ \Delta G^* (kJ mol^{-1}) & -177.0353088378906 + OR1702143996953964 \\ \Delta G^* (kJ mol^{-1}) & 58498.30859375 + OR - 102.7493438720703 \\ E_a (kJ mol^{-1}) & 6171.052734375 + OR - 62.83306121826172 \\ \Delta S^* (J mol^{-1}k^{-1}) & -175.9946594238281 + OR2056751549243927 \\ \Delta G^* (kJ mol^{-1}) & 58643.859375 + OR - 124.1551055908203 \\ \end{bmatrix}$		$\Delta G^*$ (kI mol <sup>-1</sup> )	59142 81640625 +OR- 12 74319839477539
$\frac{\Delta H^{2} (kl mol^{-1})}{\Delta S^{2} (lmol^{-1}k^{-1})} = 181940825 (1000000000000000000000000000000000000$		$\frac{1}{E (kI mol^{-1})}$	6104 0390625 +OR 12, 1819659 (1765)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		$\Delta H^*$ (kI mol <sup>-1</sup> )	3625.219970703125 +OR- 14.07808780670166
$\frac{\Delta G^{*}(kJ mol^{-1})}{E_{a}(kJ mol^{-1})} = \frac{59434.609375 + OR- 27.81762504577637}{6618.1416015625 + OR- 20.7771053314209}$ $\frac{\Delta H^{*}(kJ mol^{-1})}{\Delta S^{*}(J mol^{-1} k^{-1})} = \frac{6618.1416015625 + OR- 20.7771053314209}{\Delta S^{*}(J mol^{-1} k^{-1})} = \frac{-186.1835479736328 + OR- 6.801091134548187E-002}{\Delta G^{*}(kJ mol^{-1})} = \frac{59649.9453125 + OR- 6.801091134548187E-002}{59649.9453125 + OR- 41.05455780029297} = \frac{Compound (III)}{Compound (III)}$ $\frac{5}{2} = \frac{E_{a}(kJ mol^{-1})}{\Delta S^{*}(J mol^{-1})} = \frac{8194.0517578125 + OR- 51.99991989135742}{\Delta S^{*}(J mol^{-1})} = \frac{-177.0353088378906 + OR1702143996953964}{\Delta G^{*}(kJ mol^{-1})} = \frac{58498.30859375 + OR- 102.7493438720703}{S8498.30859375 + OR- 102.7493438720703} = \frac{E_{a}(kJ mol^{-1})}{\Delta S^{*}(J mol^{-1})} = \frac{6171.052734375 + OR- 62.83306121826172}{\Delta S^{*}(J mol^{-1}k^{-1})} = \frac{-175.9946594238281 + OR2056751549243927}{\Delta G^{*}(kJ mol^{-1})} = \frac{58643.859375 + OR- 124.1551055908203}{S8643.859375 + OR- 124.1551055908203} = \frac{10}{2} + \frac{10}{$	30	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-187.1856079101562 +OR- 4.608263447880745E-002
$\begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ \\ & \end{array}{} \\ \\ & \end{array}{} \\ \\ & \begin{array}{c} & \end{array}{} \\ \\ & \end{array}{} \\ \\ \\ \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \end{array}{} \\ \\ \end{array}{} \begin{array}{c} & \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \begin{array}{c} & \end{array}{} \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \begin{array}{c} & \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \begin{array}{c} & \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \begin{array}{c} & \end{array}{} \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \end{array}{} \\ \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \\ \end{array}{} \\ \\ \\ \\ \\ \\ \\ \\ \end{array}{} \\ \\ \\ \\ \\ \\ \\ \end{array}{} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}{} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$		$\Delta G^*$ (kJ mol <sup>-1</sup> )	59434.609375 +OR- 27.81762504577637
$\begin{array}{c} 40 & \Delta H^{*}\left(k J  mol^{-1}\right) & 4139.322265625 + OR - 20.7771053314209 \\ \Delta S^{*}\left(J  mol^{-1}  k^{-1}\right) & -186.1835479736328 + OR - 6.801091134548187E-002 \\ \Delta G^{*}\left(k J  mol^{-1}\right) & 59649.9453125 + OR - 41.05455780029297 \\ \hline \\ \hline \\ \hline \\ Compound (III) \\ 5 & \frac{E_{a}\left(k J  mol^{-1}\right) & 8194.0517578125 + OR - 51.99991989135742 \\ \Delta H^{*}\left(k J  mol^{-1}\right) & 5715.232421875 + OR - 51.99991989135742 \\ \Delta S^{*}\left(J  mol^{-1}  k^{-1}\right) & -177.0353088378906 + OR1702143996953964 \\ \Delta G^{*}\left(k J  mol^{-1}\right) & 58498.30859375 + OR - 102.7493438720703 \\ \hline \\ \hline \\ 10 & \frac{\Delta H^{*}\left(k J  mol^{-1}\right) & 8649.8720703125 + OR - 62.83306121826172 \\ \Delta S^{*}\left(J  mol^{-1}\right) & 6171.052734375 + OR - 62.83306121826172 \\ \Delta S^{*}\left(J  mol^{-1}\right) & -175.9946594238281 + OR2056751549243927 \\ \Delta G^{*}\left(k J  mol^{-1}\right) & 58643.859375 + OR - 124.1551055908203 \\ \hline \end{array}$		$E_{2}$ (kJ mol <sup>-1</sup> )	6618.1416015625 +OR- 20.7771053314209
$ \begin{array}{c} 40 & \Delta S^{*} (J mol^{-1} k^{-1}) & -186.1835479736328 + OR- 6.801091134548187E-002 \\ \Delta G^{*} (kJ mol^{-1}) & 59649.9453125 + OR- 41.05455780029297 \\ \hline \\ \hline \\ \hline \\ \hline \\ Compound (III) & \\ \hline \\ 5 & \Delta H^{*} (kJ mol^{-1}) & 8194.0517578125 + OR- 51.99991989135742 \\ \Delta H^{*} (kJ mol^{-1}) & 5715.232421875 + OR- 51.99991989135742 \\ \Delta S^{*} (J mol^{-1} k^{-1}) & -177.0353088378906 + OR1702143996953964 \\ \Delta G^{*} (kJ mol^{-1}) & 58498.30859375 + OR- 102.7493438720703 \\ \hline \\ \hline \\ \hline \\ 10 & \Delta H^{*} (kJ mol^{-1}) & 8649.8720703125 + OR- 62.83306121826172 \\ \Delta S^{*} (J mol^{-1} k^{-1}) & -175.9946594238281 + OR2056751549243927 \\ \Delta G^{*} (kJ mol^{-1}) & 58643.859375 + OR- 124.1551055908203 \\ \hline \end{array} $	10	$\Delta H^*$ (kJ mol <sup>-1</sup> )	4139.322265625 +OR- 20.7771053314209
$\frac{\Delta G^{*}(kJ \text{ mol}^{-1})}{Compound (III)} \\ 5 \\ \frac{E_{a}(kJ \text{ mol}^{-1})}{\Delta S^{*}(J \text{ mol}^{-1})} \\ \frac{E_{a}(kJ \text{ mol}^{-1})}{\delta S^{*}$	40	$\Delta S^*$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-186.1835479736328 +OR- 6.801091134548187E-002
$\frac{Compound (III)}{5}$ $\frac{E_a (kJ mol^{-1})}{\Delta H^* (kJ mol^{-1})}$ $\frac{E_a (kJ mol^{-1})}{\Delta S^* (J mol^{-1}k^{-1})}$ $\frac{E_a (kJ mol^{-1})}{\Delta S^* (J mol^{-1}k^{-1})}$ $\frac{E_a (kJ mol^{-1})}{\delta S^* (kJ mol^{-1})}$ $\frac{E_a (kJ mol^{-1})}{\delta S^* (J mol^{-1}k^{-1})}$ $\frac{E_a (kJ mol^{-1}k^{-1})}{\delta S^* (J mol^{-1}k^{-1})}$ $E_a $		$\Delta G^*$ (kJ mol <sup>-1</sup> )	59649.9453125 +OR- 41.05455780029297
$\frac{E_{a} (kJ \text{ mol}^{-1})}{\Delta H^{*} (kJ \text{ mol}^{-1})} = \frac{8194.0517578125 + OR- 51.99991989135742}{5199991989135742}$ $\frac{\Delta H^{*} (kJ \text{ mol}^{-1})}{\Delta S^{*} (J \text{ mol}^{-1} k^{-1})} = \frac{-177.0353088378906 + OR1702143996953964}{58498.30859375 + OR1702143996953964}$ $\frac{\Delta G^{*} (kJ \text{ mol}^{-1})}{58498.30859375 + OR102.7493438720703} = \frac{E_{a} (kJ \text{ mol}^{-1})}{8649.8720703125 + OR- 62.83306121826172}$ $\frac{\Delta H^{*} (kJ \text{ mol}^{-1})}{\Delta S^{*} (J \text{ mol}^{-1})} = \frac{6171.052734375 + OR- 62.83306121826172}{58643.859375 + OR2056751549243927}$ $\frac{\Delta G^{*} (kJ \text{ mol}^{-1})}{\Delta G^{*} (kJ \text{ mol}^{-1})} = \frac{58643.859375 + OR- 124.1551055908203}{58643.859375 + OR- 124.1551055908203}$			Compound (III)
$\frac{\Delta H^{*} (kJ mol^{-1})}{\Delta S^{*} (J mol^{-1} k^{-1})} = \frac{5715.232421875 + OR - 51.99991989135742}{5715.232421875 + OR - 51.99991989135742}$ $\frac{\Delta G^{*} (kJ mol^{-1} k^{-1})}{58498.30859375 + OR - 102.7493438720703} = \frac{C}{2} C$		$E_r$ (kJ mol <sup>-1</sup> )	8194.0517578125 +OR- 51 99991989135742
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$\Delta H^*$ (kI mol <sup>-1</sup> )	5715.232421875 +OR- 51.99991989135742
$\frac{\Delta G^{*} (kJ mol^{-1})}{10} \frac{\Delta G^{*} (kJ mol^{-1})}{\Delta S^{*} (J mol^{-1})} \frac{58498.30859375 + OR- 102.7493438720703}{8649.8720703125 + OR- 62.83306121826172} \\ \frac{\Delta H^{*} (kJ mol^{-1})}{\Delta S^{*} (J mol^{-1} k^{-1})} \frac{6171.052734375 + OR- 62.83306121826172}{-175.9946594238281 + OR2056751549243927} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{\Delta G^{*} (kJ mol^{-1})} \frac{58643.859375 + OR- 124.1551055908203}{-175.9946594238281 + OR2056751549243927} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.9946594238281 + OR2056751549243927} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.994659423828} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.9946594238} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.9946594238} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.994659423} \\ \frac{\Delta G^{*} (kJ mol^{-1})}{-175.9946$	5	$\Delta S^*$ (I mol <sup>-1</sup> k <sup>-1</sup> )	-177.0353088378906 +OR- 1702143996953964
$\frac{E_{a} (kJ mol^{-1})}{\Delta S^{*} (J mol^{-1})} = 1000000000000000000000000000000000000$		$\Delta \mathbf{G}^*$ (kI mol <sup>-1</sup> )	58498.30859375 +OR- 102.7493438720703
$10 \qquad \begin{array}{c} \Delta H^{*} (kJ \text{ mol}^{-1}) & 6171.052734375 + OR - 62.83306121826172 \\ \Delta S^{*} (J \text{ mol}^{-1} k^{-1}) & -175.9946594238281 + OR2056751549243927 \\ \Delta G^{*} (kJ \text{ mol}^{-1}) & 58643.859375 + OR - 124.1551055908203 \end{array}$		$E_{\rm c}$ (kJ mol <sup>-1</sup> )	8649.8720703125 +OR- 62.83306121826172
$\frac{10}{\Delta S^{*} (J \text{ mol}^{-1} \text{ k}^{-1})} = \frac{-175.9946594238281 + \text{OR}2056751549243927}{58643.859375 + \text{OR} - 124.1551055908203}$		$\Delta H^*$ (kJ mol <sup>-1</sup> )	6171.052734375 +OR- 62.83306121826172
$\Delta G^*$ (kJ mol <sup>-1</sup> ) 58643.859375 +OR- 124.1551055908203	10	$\Delta S^*$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-175.9946594238281 +OR2056751549243927
		$\Delta G^*$ (kJ mol <sup>-1</sup> )	58643.859375 +OR- 124.1551055908203

	$E_a$ (kJ mol <sup>-1</sup> )	9164.4951171875 +OR- 76.20987701416016
	$\Delta H^*$ (kJ mol <sup>-1</sup> )	6685.67578125 +OR- 76.20987701416016
15	$AS^*$ (I mol <sup>-1</sup> k <sup>-1</sup> )	-174.7875671386719 +OR2494622766971588
	$\Delta G^*$ (kI mol <sup>-1</sup> )	5879858984375 + OR - 1505870513916016
	$\frac{1}{E} (kI mol^{-1})$	7905 19287109375 +OR- 464 7861633300781
	$\Delta H^* (k \text{I mol}^{-1})$	5426 37353515625 ±OR- 464 7861633300781
25	$\Delta \mathbf{I}^* (\mathbf{I} \mod \mathbf{I})$	170 2476806640625 + OR = 1.521411776542664
	$\Delta S$ (J IIIOI K)	-1/9.24/0800040025 +OK- 1.321411/70342004
		38809.0703125 +OR- 918.3930803004002
	$E_a (KJ mol^{-1})$	8680.0400390625 +OR- 858.7814331054688
30	$\Delta H$ (kJ mol <sup>-1</sup> )	6201.220/03125 +OR- 858./814331054688
	$\Delta S^{-}(J \text{ mol}^{-1} \text{ k}^{-1})$	-177.3432769775391 +OR- 2.811099529266357
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59076.1171875 +OR- 1696.910766601562
	$E_a (kJ mol^{-1})$	7793.81201171875 +OR- 1088.45654296875
40	$\Delta H^* (kJ mol^{-1})$	5314.99267578125 +OR- 1088.45654296875
40	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-181.4197540283203 +OR- 3.562908887863159
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59405.29296875 +OR- 2150.73779296875
		Compound (IV)
	$E_{\rm c}$ (kI mol <sup>-1</sup> )	8194 0517578125 +OR- 51 99991989135742
	$\Delta H^*$ (k I mol <sup>-1</sup> )	5715 232421875 +OR- 51 99991989135742
5	$\Delta S^* (I \text{ mol}^{-1} k^{-1})$	-177 0353088378906 ±OR- 1702143996953964
	$\Delta \mathbf{C}^* (\mathbf{k} \mathbf{L} \mathbf{m} \mathbf{a} \mathbf{l}^{-1})$	58408 20850275 LOP 102 7402428720702
	E (kLmalt)	2002 400224275 + OR - 102.7493436720703
	$E_a (KJ mol-1)$	8898.490234375 +OR- 69.14267730712891
10	$\Delta H$ (kJ mol <sup>-1</sup> )	6419.6708984375 +OR- 69.14267750172891
	$\Delta S^{+} (J \text{ mol}^{-1} \text{ k}^{-1})$	-175.4161224365234 +OR2263287901878357
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	58719.98828125 +OR- 136.6226043701172
	$E_a$ (kJ mol <sup>-1</sup> )	7661.0380859375 +OR- 357.6551818847656
15	$\Delta H^*$ (kJ mol <sup>-1</sup> )	5182.21875 +OR- 357.6551818847656
15	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-179.8570404052734 +OR- 1.170733690261841
	$\Delta G^* (kJ mol^{-1})$	58806.59375 +OR- 706.7094116210938
	E <sub>a</sub> (kJ mol <sup>-1</sup> )	9737.3330078125 +OR- 92.24694061279297
25	$\Delta H^*$ (kJ mol <sup>-1</sup> )	7258.513671875 +OR- 92.24694061279297
25	$\Delta S^*$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-173.4191436767578 +OR3019573390483856
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	58963.4296875 +OR- 182.2755279541016
	$E_{\rm c}$ (kI mol <sup>-1</sup> )	5459 28369140625 +OR- 6 449143886566162
	$\Delta H^*$ (kI mol <sup>-1</sup> )	2980 464599609375 +OR- 6 449143886566162
30	$AS^*$ (I mol <sup>-1</sup> k <sup>-1</sup> )	-188,3694458007812 + 0R - 2,111036144196987E-002
	$\Delta \mathbf{C}^* (\mathbf{k} \mathbf{I} \operatorname{mol}^{-1})$	501/2 816/0625 +OP 12 7/310830/77530
	$\frac{\Delta O(KJ mol^{-1})}{E(kI mol^{-1})}$	6104 0200625 + OP 14 07808780670166
	$\mathbf{L}_{a}$ (KJ IIIOI )	2625 210070702125 + OR 14.07808780670166
40	$\Delta H$ (KJ mol)	3023.219970703123 +OK- 14.07808780070100
	$\Delta S (J mol^{-1} K^{-1})$	-187.1856079101562 +OR- 4.608263447880745E-002
	$\Delta G (kJ mol^{-1})$	59434.609375 +OR- 27.81762504577637
		Compound (V)
	E <sub>a</sub> (kJ mol <sup>-1</sup> )	8194.0517578125 +OR- 51.99991989135742
5	$\Delta H^*$ (kJ mol <sup>-1</sup> )	5715.232421875 +OR- 51.99991989135742
5	$\Delta S^*$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-177.0353088378906 +OR1702143996953964
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	58498.30859375 +OR- 102.7493438720703
	$E_a$ (kJ mol <sup>-1</sup> )	9737.3330078125 +OR- 92.24694061279297
	$\Delta H^*$ (kJ mol <sup>-1</sup> )	7258.513671875 +OR- 92.24694061279297
10	$\Delta S^*$ (J mol <sup>-1</sup> k <sup>-1</sup> )	-173.4191436767578 +OR3019573390483856
	$\Delta G^*$ (kI mol <sup>-1</sup> )	58963.4296875 +OR- 182.2755279541016
	$\frac{1}{E} (kI mol^{-1})$	7509 20068359375 +OR- 500 3245849609375
	$\Delta H^* (k I mol^{-1})$	5030 38134765625 +OR- 500 3245849609375
15	$\Delta S^*$ (I mol <sup>-1</sup> k <sup>-1</sup> )	-181 7763519287109 ±OR- 1 637741804122925
	$\Delta \mathbf{C}^* (\mathbf{k} \mathbf{I} \operatorname{mol}^{-1})$	50227 ±OP 088 6173005703125
	$E \left( \left  L m n^{1-1} \right  \right)$	7051 70110140625 LOD 1052 001015605
	$\mathbf{E}_{a}$ (KJ IIIOI )	1251.12119140025 +UK- 1055.291015025 4773.00185548975 +OD 1052.301015635
25	$\Delta H (KJ mol^{-1})$	4772.90160046870 +OK-1000.291010620
	$\Delta S (J \text{ mol}^{-1} \text{ k}^{-1})$	-183.433319091/969 +OK- 3.44//99444198608
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59463.546875 +OR- 2081.25244140625
	$E_a (kJ mol^{-1})$	6618.1416015625 +OR- 20.7771053314209
30	$\Delta H^* (kJ mol^{-1})$	4139.322265625 +OR- 20.7771053314209
50	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-186.1835479736328 +OR- 6.801091134548187E-002
	$\Delta G^* (kJ mol^{-1})$	59649.9453125 +OR- 41.05455780029297

	$E_a$ (kJ mol <sup>-1</sup> )	6913.685546875 +OR- 25.87574005126953
40	$\Delta H^* (kJ mol^{-1})$	4434.8662109375 +OR- 25.87574005126953
40	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-185.5786743164062 +OR- 8.47005769610405E-002
	$\Delta G^* (kJ mol^{-1})$	59765.1484375 +OR- 51.12921524047852
		Compound (VI)
	$E_a$ (kJ mol <sup>-1</sup> )	8194.0517578125 +OR- 51.99991989135742
5	$\Delta H^*$ (kJ mol <sup>-1</sup> )	5715.232421875 +OR- 51.99991989135742
5	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-177.0353088378906 +OR1702143996953964
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	58498.30859375 +OR- 102.7493438720703
	E <sub>a</sub> (kJ mol <sup>-1</sup> )	8970.958984375 +OR- 884.2886962890625
10	$\Delta H^*$ (kJ mol <sup>-1</sup> )	6492.1396484375 +OR- 884.2886962890625
10	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-176.6717834472656 +OR- 2.894593954086304
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59166.83203125 +OR- 1747.311889648438
	$E_a$ (kJ mol <sup>-1</sup> )	7497.58349609375 +OR- 1043.4931640625
15	$\Delta H^*$ (kJ mol <sup>-1</sup> )	5018.76416015625 +OR- 1043.4931640625
15	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-182.0774230957031 +OR- 3.415727615356445
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59305.1484375 +OR- 2061.892333984375
	$E_a$ (kJ mol <sup>-1</sup> )	6618.1416015625 +OR- 20.7771053314209
25	$\Delta H^*$ (kJ mol <sup>-1</sup> )	4139.322265625 +OR- 20.7771053314209
23	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-186.1835479736328 +OR- 6.801091134548187E-002
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59649.9453125 +OR- 41.05455780029297
	$E_a$ (kJ mol <sup>-1</sup> )	9208.2802734375 +OR- 1314.371948242188
20	$\Delta H^*$ (kJ mol <sup>-1</sup> )	6729.4609375 +OR- 1314.371948242188
30	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-178.1703186035156 +OR- 4.30241060256958
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59850.94140625 +OR- 2597.1357421875
	$E_a$ (kJ mol <sup>-1</sup> )	9908.6357421875 +OR- 997.0340576171875
40	$\Delta H^* (kJ mol^{-1})$	7429.81640625 +OR- 997.0340576171875
40	$\Delta S^* (J \text{ mol}^{-1} \text{ k}^{-1})$	-175.9748840332031 +OR- 3.263649940490723
	$\Delta G^*$ (kJ mol <sup>-1</sup> )	59896.7265625 +OR- 1970.09130859375

TABLE-5

Γ OF DIFFERENT CC	NCENTRATION OF	COMPOUND (I) ON	ILIMITING CURRE	NT AT 25 °C IN CAS	SE Cu-Cu
		]	1		
$5 \times 10^{-4}$	$10 \times 10^{-4}$	$15 \times 10^{-4}$	$25 \times 10^{-4}$	$30 \times 10^{-4}$	$40 \times 10^{-4}$
100	100	100	100	100	100
130	130	130	130	130	130
180	180	180	180	180	180
200	200	200	200	200	200
250	250	250	250	220	200
300	280	280	260	230	210
350	320	300	280	250	240
380	340	320	300	280	250
400	350	330	310	300	260
410	350	340	320	310	280
		$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

## $\Delta G^* = \Delta H^* - T \Delta S^*$

Table-8 shows that the entropy  $\Delta S^*$  posses negative values, indicating a highly ordered organic species in the solution under investigation. It is also noticed that the weak dependence of  $\Delta G^*$  on the compensation of the organic additives can be attributed largely to the general linear composition between  $\Delta H^*$  and  $\Delta S^*$  for the given temperature.

**Isokinetic temperature:** Variation in the rate within a reaction series may be caused by changes in either or both, the enthalpy or the entropy of activation. The correlation of  $\Delta$ H\* with  $\Delta$ S\* is a linear relationship may be stated algebraically;

$$\Delta H^* = \beta \Delta S^* + \text{Constant}$$
$$\delta \Delta H^* = \beta \delta \Delta S^*$$

The operator,  $\delta$ , concerns difference between any two reactions in the series.

Substituting from  $\delta \Delta H^* = \beta \delta \Delta S^*$  into the familiar relationship:

$$\delta \Delta H^* = \delta \Delta G^* + T \delta \Delta S^*$$

We obtain

$$\beta\delta\Delta S^* = \delta\Delta G^* + T\delta\Delta S^*$$

It follows that when  $\delta\Delta G^*$  equal zero,  $\beta$  equals T. In other words, the slope in a linear plot of  $\Delta H^*$  versus  $\Delta S^*$  is the temperature at which all the reactions that conform to the line occur at the same rate.  $\beta$  is therefore known as the isokinetic temperature.

The plots of  $\Delta$ H\* *versus*  $\Delta$ S\* in presence of organic additives, the isokinetic temperatures  $\beta$  were 266.7, 280.3, 295.4, 282, 282.9, 285.7 and 277.4 K for mannose, sucrose, lactose and maltose, respectively, these values which are much lower than that of the experimental temperature 298 K indicating that the rate of the reactions is entropy controlled<sup>13</sup>, but the value of  $\beta$  which are much higher than 298 K such as 324.6 K for glucose in case of Cu-Pb indicating that the rate of the reaction is enthalpy controlled<sup>36</sup>.

## Conclusion

The electrode process on copper in acidified  $CuSO_4$  was finding to depend on the carbohydrate acids as well as their concentrations. They also depend on the type of the carbohydrate as well as their concentrations. They also depend on the type of the cathode and temperature. The activation energy proves that the reaction is diffusion controlled. The overall mass transfer correlation proves that the electroplating reaction is natural convection which is in accordance with our previous studies.

## List of symbols

Ν	:	Total mass transfer rate, mol cm <sup>-2</sup> s <sup>-1</sup>
D	:	Diffusion coefficient of metal ions, cm <sup>2</sup> s <sup>-1</sup>
[dC/dY]	:	Concentration gradient at the interface
i	:	Current density, A cm <sup>-2</sup>
n <sub>c</sub>	:	Transference number of the deposited cation
z or n	:	Number of the transferred electrons = $2$ in case
		of Cu <sup>2+</sup> ions
F	:	Faraday's constant = 96485 A s mol <sup>-1</sup>
$\delta_{\rm N}$	:	is often named as the effective diffusion layer
		thickness, cm
j	:	Mass transfer rate, mol cm <sup>-2</sup> s <sup>-1</sup>
$C_o$ or $C_b$	:	Bulk concentration, mol cm <sup>-3</sup>
Ce	:	Interfacial concentration, mol cm <sup>-3</sup>
Κ	:	Mass transfer coefficient, cm s <sup>-1</sup>
Sh	:	Sherwood number, $Sh = kd/D$
d	:	Cylinder diameter, cm
Gr	:	Grashoff number, $Gr = g\alpha(C_o - C_b)I^3/v^2$
1	:	Cathode height, cm
ν	:	Kinematic viscosity, cm <sup>2</sup> sec <sup>-1</sup>
Sc	:	Schmidt number, $Sc = v/D$
Re	:	Reynolds number, $Re = Ud/v$
U	:	Electrode peripheric velocity or characteristic
		flow velocity, cm s <sup>-1</sup> , U = $\omega$ r, cm rad s <sup>-1</sup>
ω	:	Angular velocity, rad s <sup>-1</sup>
r	:	Radial distance, cm
Fr	:	Froude number, $Fr = V^2/hg$
V	:	Oxygen gas discharge velocity, cm s <sup>-1</sup>
h	:	Electrode height, cm
g	:	Acceleration gravity, cm s <sup>-2</sup>
Θ	:	Surface coverage
iL	:	Limiting current density, A cm <sup>-2</sup>
η	:	Absolute viscosity of solution, centipoises
ρ	:	Density of solution, g cm <sup>-3</sup>
$\Delta H^*$	:	Enthalpy of activation, kJ mol <sup>-1</sup>
$\Delta S^*$	:	Entropy of activation, J mol <sup>-1</sup> K <sup>-1</sup>
$\Delta G^*$	:	Net free-energy change, kJ mol <sup>-1</sup>
R	:	Universal gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Т	:	Absolute temperature, K
Ea	:	Activation energy, kJ mol <sup>-1</sup>

A	: Arrhenius constant
RCE	: Rotating cylinder electrode
RDE	: Rotating disk electrode
δ	: Difference between any two reactions in the series
β	: Isokinetic temperature K
В	: Boltzmann constant

h : Plank's constant

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