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Electrolysis of water in a copper sulphate solution

Hermann Otto Schulze

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Thesis

for the

Degree

Backeloz of Science in Moining Engineering

Subject

Electrolysis of Water in a Copper Sulphate Solution

Hermann Otto Schulze.

ELECTROLYSIS OF WATER IN A

COPPER

SULPHATE SOLUTION.

Electrolysis of Water in a Copper Sulphate Solution.

It was originally proposed to find the relations between First. Density of solution and electromotive forced to produce electrolysis of water, when the current is constant.

Second. Density of solution and current density when the electrometive force is constant.

Third. Current density and electromotive force to produce an electrolysis, when the density of solution is constant.

Fourth. Distance between terminals and difference of potential between them when all other quantities are constant.

As the work progressed, it was soon apparent, that the difference of potential or the electromotive force used , had practically no influence on the current required to produce the electrolysis of water, but that the current varied with the density of solution, the temperature of the electrolyte, and the percentage of sulphuric acid in the solution.

Professor Timmerman under whose direction the work was done, has also found that the difference of potential between the copper plate and hydrogen, and between hydrogen and oxygen may be obtained by experimenting with different densities of current, and different distances between the electrodes for each, and plotting the intercept of the lines obtained. Inconsequence of the results first obtained, II was modified to find the relation between density of solution and current required to produce electrolysis when temperature of solution and proportion of sulphuric to copper sulphate acid, were constant.

IV was modified to find the difference of potential between the copper plate and hydrogen, and hydrogen and oxygen.

Other experiments were made to determine the relation between V

Temperature of Solution and current required to produce electrolysis,

when density of molution and percentage of sulphuric acid were constant.

VI percentage of Sulphuric Acid and current required to produce electrolysis, when density of solution and temperature weere constant.

The final determinations in II, IV and V were made with my assistance by Professor Timmerman who has also been engaged in transforming the results of the experiments into formulae.

Aparatus.

The experiments involving difference of potential were made in a wooden trough with the following inside dimensions: Length 3.05 matters width .077 milliometers, depth .08 millimeters.

The other experiments were made in glass jars of circular cross sections and about 800 c.c. capacity.

The cathodes were made of sheet copper .75 mm. thick, and of dimensions given in figure, having on each side a surface area equal to 50 square Cm.

7om 7.2 on

They were hung from brass rods seven mm diameter to which the conducting wires were attached.

The anodes had a similar shape of a little larger dimensions but no pains were taken to make them of an exact size, the sheet copper used for them was 3 mm thick.

For the experiments in the wooden trough which was coated with asphalt the anodes were hung from the same kind of brass rods as the cathode. one on each side at an equal distance.

For those in the glass jars the anodes were soldered to a bent copper wire 3 mm thick at a distance of 5 cm from each other, the cathode being put in between them, taking deposits on both sides.

The copper sulphate was commercial, at was dissolved in distilled water and filtered before use.

The current was for densities below 2 amperes generally taken from

a storage battery, but some times as well as all these stronger currents from a dynamo of 5 Horse Power compound system, which was driven by a 15 Horse Power Otto Gas Engine, this latter current was at first considerably unsteady, owing to the gas Engine being new but improved after some time when the regulations of the engine worked smoother.

The current for the highest density and potential in the trough were taken from the city lighting plant.

Two volt meters were used, one for intermittant reading and 15 volts capacity for the smaller potential, and the other for reading to 150 volts.

Two ammeters were also used, one reading to 1.5 amperes, the other to 50 amperes.

The current was regulated by using several sets of lamps connected in parallel, and also some German silver resistance coils.

The density of the solutions was determined by first determining in air the weight of a small glass ball filled with shot then in distilled water and finally in the solution whose density was then calculated. The weight in air was 8061 mgm., its volume is 1.959 c.c., it was hung by a fine silk thread from a chemical balance.

The first determinations were made with a solution of 1.20 density to see if small currents up to 4 amperes would produce electrolysis of water when the electrodes were up to 150 cm distance from each other. No acid was added, but the solution showed a slightly acid reaction on litmus paper, and no electrolysis was obtained with a difference of potential up to 100 volts.

The solution was then diltued to down to a density of 1.037 and the series of experiments given in Table I was run.

A comparison of the different determinations will show, that each

day in starting in, when the solution was cooled down it required not only less distance between the electrodes to produce the same potential as with the solution heated up to the current, but that also the current, at which hydrogen was given off at the cathodes was lower with a lower temperature, only the closest values are given in the tables.

With these nearly neutral solutions the deposit was very poor consisting with current density enough to give up hydrogen of loosly adhering small browniah grains, the bubbles of which came off very sluggishly and for the potential below 10 volts the electrodes had to be put so near together that it was impossible to observe well amough in the wooden trough, which was near a window at each end only, while the cathode where the observation had to be made was at the middle.

Artifical illumination was reflected from the surface to the greater part, and the determinations are of necessity not very accurate.

To overwome the difficulties one percent by volume was added of Sulphuric acid to give greater conductivity to the electrolyte, also a glass jar was substituted for the torugh and a solution of 1.20 density used.

The difference in the appearance of the deposit was very striking, it being firm and of a beautiful salmon pink color, the upper edges only were browning, with a moderate evolution of hydrogen, while a considerable excess of current was necessary to get a loose brownish deposit all over the plate. As the high qurrent required to electrolyze a nearly saturated solution caused a rapid increase in temperature the trough was again used, with the same solution of 1.03 density to which one percent by volume of sulphuric acid was added.

Table II shows that the addition of one percent of sulphuric acid decreased the current required to produce the electrolysis to nearly 1/4 its value in an approximately neutral solution.

These experiments show the same change (due to temperature) in the current required to produce electrolysis of water as Table I but proves also that this current is independent of the difference in potential between the electrodes.

Table III gives the data of a series of experiments again made in a glass jar to find the effect, of polarization and shows that the difference of potential first rises rapidly owing to polarization and locally, to then sinks, nearly its former value, the current being kept constant.

Table IV gives the variation of the difference of potential with the distance between the electrodes and on plotting the intercepts, the curve showing the difference of potential between the copper plate and hydrogen. On the first part of the curve only point .7 disagrees with it, and it was taken at 7 degrees C. less temperature than the greater part of the rest, while above 4 amplifes the curve is very uncertain, on account of uneaveness of temperature in the trough, which was heated up near the cathode, by those denser currents to several degrees C. above the temperature near the ends, causing a relatively higher difference of potential for longer distances between the electrodes, than for shorter ones, for which the conductivity in the electrolytes of higher temperature was higher. Also the slope obtained in the plotting distance for higher currents, are large as compared to the intercept, and makes a precise determination of the latter difficult.

A second curve has been plotted in blue on the same sheet from calculated intercepts. For the current was between 1.4 and 6 ampères, the potentials at the distance of 10 and and 50 cm. between the terminals were used only, and for currents between 6 and 10 at distances of 10 and 20 cm. because they seem less interferred by unequal temperatures, but the intercepts between 3.5 are still very unreliable.

The same difficulties but magnified by the still higher currents used, appear in working with a saturated solution Cu SO of 1.24 density, from which a considerable amount of copper sulphate crystallized out on addition of 1 percent of sulphuric acid.

No electrolysis of wa ter was obtained in these experiments because when the larger currents were tried, the solution rose so rapid in temperature, that the currents, required for the electrolysis were beyond what the dynamo could furnish with the E.M.F. obtainable under the present arrangement of pullies. The determinations made are given in Table V and have not been plotted.

Table VI gives another series of experiments with a solution of 1.1 density and 1/2 percent of H_{2SO_4} , the cruve obtained on plotting the calculated intercept is given on sheet II. Unfortunately the importanc of keeping a constant temperature throughout the trough during all the experiments involving potential was not fully recognized until after working up the results , while lack of time, and facilities to regulate the temperature, prevented another more accurate determination.

Table VII gives two determinations on the relations between density of solution, and current required to produce electrolysis of water when proportion of ${\rm H_2SO_4}$ to ${\rm CU_2SO_4}$ is constant.

For the second determination a solution containing three times as much H SO was taken as for the former the former, producing a lower 2 4 saturation point and reducing the current required for the same density as is obvious from the plot on sheet III. which have both the same scale. It is thought that the points would have plotted as a straight line, if the percentage of H2SO in the solution had been kept constant instead of making it proportional to the density, but there was not sufficient time to verify such a conclusion.

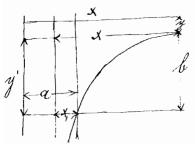
In experimenting with solutions nearly or quite saturated, the hydrogen came from the cathode for a few minutes only, then with a simultaneous dropping of the current by about 2 amperes, great masses of very small bubbles came from the anodes, but did not break through the liquid, sinking down instead of being absorbed by the solution as fast as they were formed. Attempts were made to determine the gas qualitatively but failed. It did not give the smell ozone.

It may be assumed that the current required to produce electrolysis varies directly with the density, of the percent of sulphuric acid by volume, of the solution is constant.

Table VII gives the data for the determination of the relation between temperature and surrent, density of volume and percent of Sulphuri acid being constant. The first experiments were made with using a strong electric current to heat up the solution, but gave no good results and are not recorded. Those given were made by heating the solution in a flask or beaker over a gas burner, letting it cool after the first determinations, in air, then by surrounding the jar by cold water, by ice, and finally a freezing mixture of salt and ice.

The lower lines on Sheet V was obtained from a solution containing one-half percent of Sulphuric Acid but the current required had too much heating effect so more acid was added to the others to reduce the current required to liberate hydrogen. The density for the first determinations was 1.1 for the last 1.6.

The curve was assumed to be a rectangular hyperbola



 $x'y'=c=ab \qquad x'=[a+(x+x)] \qquad y'=b-y$ $[a+(x-x)](b-y)=ab \qquad ab-ay+b(x-x)-y(x-x)=ab$ $(b-y)(x-x)=ay \qquad \frac{b-y}{y}=\frac{a}{x-x}, \qquad b'y-1=\frac{a}{x-x}, \qquad \frac{b}{a}(y')-\frac{1}{a}=\frac{1}{x-x}, i$ where $\frac{b}{a}$ is the slope and $-\frac{1}{a}$ the intercept on the y axis, x the surrent, x, the abscissa of any point on the surve, and ythe temperature

Plotting x = x along the vertical and $\frac{1}{y}$ along the horizontal gives the straight line on sheet V with $-\frac{1}{a} = -1.57$, a = 6.36 $\frac{b}{a} = \frac{2 \times 6.36}{100} = 125$

Transforming the assumed equation $\frac{b-y}{y} \ge \frac{a}{x-x}$ to x-x, $\frac{ay}{b-y}$

 $x = x_1 + \frac{ay}{k - y}$ and putting I and I, for x and x_8 and t for y we have $I = I_0 + \frac{at}{k - t}$ substituting the

values of a,b and I the equation becomes $i = 1.4 + \frac{6.36 t}{125 - t}$

 $\mathbf{i} = 1.4 + \frac{6.36 \times 10}{12.5 - 10} =$ $\mathbf{i} = 1.4 + \frac{6.36 \times 60}{125 - 60} = 7.27/27$ for 40 degrees C $\mathbf{i} = 1.4 + \frac{6.36 \times 40}{125 - 60} = 4.4$ 1.94 and for 60 degrees C.

which agrees with the obtained values in the experiment. The formula may therefore be assumed to be correct.

I a and b are constant for constant percentage of sulphuric acid and constant density of solution only. Table IX gives the data for the variation of the current with the amount of sulphuric acid in the solution. All the determinations whose data are given were made with a solution of 1,06 density, but the first one plotted in red circles had about 10 degrees C less temperature than the other three.

The plotson Sheet VI are in cc of H2SO4 per 800 cc. and the one in black in cc. of H2SO4 per 900 cc of solution, they do therefore not exactly correspond. All the different determinations are plotted in two different scales and the last as seeming the most reliable has been samected to find a formula to it.

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	•	34	18.5	71	4.5	
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		34	13	•	4.25	
5-th		31	5,5	10	4.5	+
	_	30	6.	٦.	4.25	
\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	,	25	1.5	3-	4.75	+
	_	24	2.25	5	4.45	
6 th	1.03	45	44	89	3,5	+
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~		29.5	5-5-	70	3	—
—	,	32	50	~	3.25	+
y th	•	22	35	60	3	+
	~	26	39	4	2.75	
		2,5	30	57	3	+
	~	47	25	4	2.75	
	_	45	26	41	3	+
	_	26	28	••	4.75	
	~	26	19	30	3	+
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	~	44.5	83	8	1	+
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	_	32,5	70	7	1	+
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6	-	2/2	47	6	1.05	+
14th		18.5	55	5	.75	
. ~		19	57	•	.8	+
~	-	19	40	4	.9	+
`		19.5	42	.	.8	
		19.5	20	3	, 8	+
_	_	19.5	19	•	.8	
	•	19.5	19	3	. 8	
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	2 54	_		~	,4	.72	+		3	10			_	1.3	.7	
	2 57	Ĺ	•	~	.75	.72	+		3	40	1		~	1.25	.7	
	4 59	_			.7	.72	+		3	30	,	~	~	1.2	.7	
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23	100	8.5	. 68		18°	100	19.3	1.4	+	32	77	64	7	7
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·	10	1.17	.68			20	4.4	1.4	+		10	10	7	+
		9.8				10	3.65	1.4	+	31	67	65.5	8	+
	57	5,3	.7	+	41	100	29.3	4.45	+		30	20.5	8	+
	40	4.3	.7	+		50	14.8	2.45	+		10	11	8	7
į	30	3.4	.7	+		10	3,8	3.35	+	30	57	64	9	7
	30	2.5	7	+		2	1.5	4.45	+				9	
	10	1.6	.7	+	22.5	100	38,5	3	+		10	/3	9	+
23.3	100	9.25	.75	-		50	19.4	3	+	280	50	63.5	10	+
į	50	4.75	175			10	4.95	3	+		20	26.5	10	+
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	50	.97	. 2		57	7	1.4
	10	, 38	. 2		10	1.6	1.4
	150	5,4	,4	48	150	39,5	3
-	100	3.8	,4		100	26.5	3
	37	2	,4		50	13.5	3
	10	, 5	.4		10	2.8	3
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	100	11.5	1.2				
	57	6	1.2				
	10	1.4	1.2				

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	50	3.27	,4		57	19.4	3		10	14	9
	10	.8	14		10	4.5	3		100	12/.5	10
18	150	13.5	.6		117	63	4		57	60	10
	100	9.3	16		100	53.5	4			13	
	50	4.78	.6		50	46.7	4		. 4	.18	
	10	1.18	16		10	6,3	4	-	.6	.26	
	100	12.3	.8	25	100	62	4.5		.8	,33	
	57	6.35	.8		50	32.5	4.5		1	.41	
	10	1.53	.8		10	7.5	4.5		1.2	,33	
3 3	150	21	1	24	96	62.5	3		1.4	.33	
	100	13	1		50	38.8	5		2	. 26	
	50	6.5	1		10	8.2	5		3	,55	
	10	1.82	1	35	150	124	6		4	1.2	
	150	25	1.2		100	76	6		4.5	1.45	
	100	16.3	1.2		50	36	6		6	1.54	
	37	8.2	1.2		10	8	6		7	1	
	10	1.9	1.2		150	135,5	7		8	1.5	
	100	19.1	1.4		100	85,5	7		9	1.2	
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	10	4.8	2		16	10.5	8				

1	23	1.24	12	3	32	1.21	8,5
	43	1.30	12.5		24.3	1.20	8.
	43	1.18	11.2		24.1	1.18	8.05
	23	1.16	10.4		23.4	1.16	8.1
	23	1.14	9.5		27.6	1.15	7.75
	23	1.13	8.7		25.2	1.14	7.8
	23	1.10	7.2		24.4	1.12	6,8
	23.5	1.08	6.3		24.4	1.10	5,3
	73	1.06	4		24,5	1.08	4.27
	. 23	1.04	3		24	1.06	3,5
	23	1.03	1.8		34	1.04	2.2
	3/3	1.02	1.28		34.8	1.03	1.53
	22.6	1.01	.76		43.5	1.03	.97
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olume	of the	solutie	m, on	dolites	n of co	ater to	reduse
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Jany of		Eugrent any	6	Toug . C) 	Current and	6
y	¥	¥	4-X ,	y	y	Y	
82.5	.0121	7.7	. 149		.0128	9.9	. 118
72	.0139	6.17	.193	62,5	.0160	7.6	.161
64	.0156	5,38	.228	5-y	.0175	6.5	.196
59,5	.0168	4.6	1278	42.7	.0234	4.5	.323
55,5	.0180	4.07	,326	34,3	.0292	3.88	.403
50.8	.0197	3,95	, 339	29.4	.034	3.4	سی ر
36.9	.0271	4.93	.518	12.7	.0441	2.8	,714
28,5	,0351	4,36	.735	14.2	.0704	2,3	1.111
22.5	,0444	2.05	.95%	9	.111	1.88	2.08
16.8	, 1595	1.85	1.176	4	.450	1.4	∞
12.3	.08/3	1.5	2,000	3.5	.186	1.4	.∞
11.2	.0893	1.45	2.322		100	1.5	10
8.4	.0119	1.4	2.5	The is	sterce	t ou	the
7	1429	1.35	2.857	Yaxi	coas Ta	ken as	1.4
1	1.000	1.15	10.000	Densi	ty of a	olution	1.1
0	∞	1	•••	Percen	tage of	temp °C	3 ly onl
I, the is	stercepi	on H	e d'exis	7. Hz 804	densely	temp °C	Current
was tes	ken as	h		1/2	1.1	47.5	6.6
Density	of sol	ution.	1.06			33	3.9
		_	3 by ad			43.2	3.3
		! !				20	3.1
		· · · · · · · · · · · · · · · · · · ·			r 1	8.5	2.4
,						6	2.1
						4	3.1

Fine of	kent Helo	Evrest	5	ee LHAO	Current	James Co	% H.S.I.	lureut	- N-4
£my €	neric	such.	31.6	11	4.5	32,5	-X .00011	4.95	-, 4.57
	.03	3.9	31.8	.2	4.28	33.3	, 30055	4,43	-12.17
	.14								1
1	1	, l			l l				-12,12
	I				1 1				-12,86
	.16		j						-12.82
2/1.7	.32	3.78	34.1	20	-				- 9.09
· ·	.48				3.7	33	1	2.88	-9.23
l	I								-9,45
23.4	15	3.5	4	100	2.98	32,4	,187	2/5	- 9,72
1					l i				indeterm
27.8	103	16	31.9	300	2,03	32,4	,35	1.48	- 9.7
32.75	104	7.5	32.3	300	1.30	33,1	,28	1.4	-6.35
32.5	,08	6	31.9	400	1.15	34	,318	1.1	- 9.67
32.8	.16		The aus	ount o	l Cu, 804	37,5	,357	19	-6.43
33	.32	4.9	solution the	n to co	fish !	32.7	. +	.7	-6.1
34.5	167	4.5	the obor	He dit	pas of	32.5	1494	,57	- 4,4
32.5	1.2	4.43	been a	dded o	vas in	1	_		- 4.91
32	2,4	4.55	ersh of Densir	freur Te of so	800 cc	The or	linates	of the	point
32	3	4.55	4		7100.	marken	(indete	minal	t ivere
32.5	6	4.6				1 -			making
32	12	4.53					l .	_	y-y, = 0
31,5	24	4.1							
	34	3.75							* * * * * * * * * * * * * * * * * * *
32.3	89	3.3							
30.7	300	1.7							

