The Glow Electrolysis and its Mechanism. (II).(1) On the Study of the Formation of Basic Salts.

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Introduction. The study of the mechanism of glow electrolysis, in which one of the electrodes of the ordinary electrolysis is drawn up in the atmosphere and the electric current is flowed by the glow discharge between this electrode and the surface of the solution, has been investigated by the following authors.

Since 1887, Gubkin(2) studied the glow discharge of the solutions of zinc sulphate, silver nitrate and platinic chloride and obtained zinc oxide, metallic silver and metallic platinum, respectively; Günther-Schulze(3), Makowezki(4), Haber(5), Klemenc(6), Corbino(7), Cousin, Jolivois(10), Fichter and Keslenholz(9) studied on various sorts of salt solutions and obtained oxides and hydroxides. Many of them often observed that the current efficiency was about 120% or more, especially for the solutions of copper, zinc, and lead salts. And they attributed the anomalous current efficiency to the photochemical action or adsorption without quantitative analyses of the products.

Yamaguchi and Shiba(1) previously studied on the glow electrolyses for various salt solutions and discussed the experimental results with the theory dissociation of water molecules by the impacts of electrons. Yasuda(11) reported that colloidal solutions were obtained by the similar process.

In the present experiment, the products of the glow electrolyses for cupric sulphate and zinc sulphate solutions at various concentrations were carefully examined by the quantitative analysis, etc. It was found that many products were composed of such basic salts as $2\ CuSO_4 \cdot 5Cu(OH)_2$ H_2O; $CuSO_4 \cdot 3Cu(OH)_2$; $ZnSO_4 \cdot 3Zn(OH)_2$, and the glow electrolysis gave one of the new methods of formation of basic salts. The abnormal discrepancy of the actual current efficiency from that calculated by Faraday's law is attributed to the formation of basic salts.

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(2) J. Gubkin, *Pogg. Ann.*, **32**(1887), 114.

(3) A. Günther-Schulze, *Z. Elektrochem.*, **31**(1925), 187.

(4) A. Makowezki, *Z. Elektrochem.*, **17**(1911), 217.

(5) F. Haber and A. Klemenc, *Z. Elektrochem.*, **20**(1914), 485.

(6) A. Klemenc, *Z. Phys. Chem.*, **130**(1927), 378; A **154**(1931), 385; A **166** (1933), 313; B **27**(1935), 339; A **179**(1938), 1; A **182**(1938), 91; B **40**(1938, 252; *Z. Elektrochem.*, **37**(1931), 742.

(7) O. M. Corbino, *Atti. Acad. Lincei. Roma*, **6.5**.(1927), 377.

(8) M. P. Jolivois, *Ber.*, **71**(1938), 73; *Bull. soc. chim.*, [5] **5**(1938), 1429.

(9) F. Fichter and K. Kestonholz, *Helv. Chim. Acta*, **23**(1940), 209.

(10) M. P. Jolivois, *Helv. Chim. Acta*, **23**(1940), 405.

(11) S. Yasuda, *Japan. Assoc. Advancement*, **15**(1940), 327.

Apparatus. The apparatus is shown in Fig. 1. The discharge cell is a U-tube of 5.5 cm. in diameter, the cathode of platinum wire is held in gas phase and the anode is immersed in the solution. The diameter of the platinum wire is 1.4 mm. and the distance between the tip of the platinum wire of the cathode and the surface of the solution is about 5 mm. The pressure of gas phase is always kept at 5 to 10 mm. Hg., and the voltage of the glow electrolysis is held at 300 to 600 V. The apparatus is put in a mixture of ice and salt. The diagram of circuit is shown in Fig. 2.

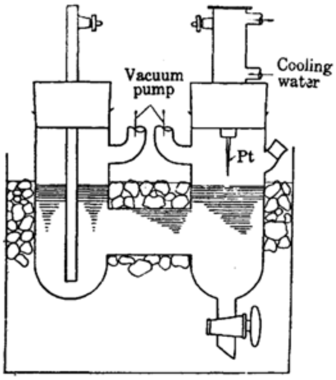

Fig. 1.

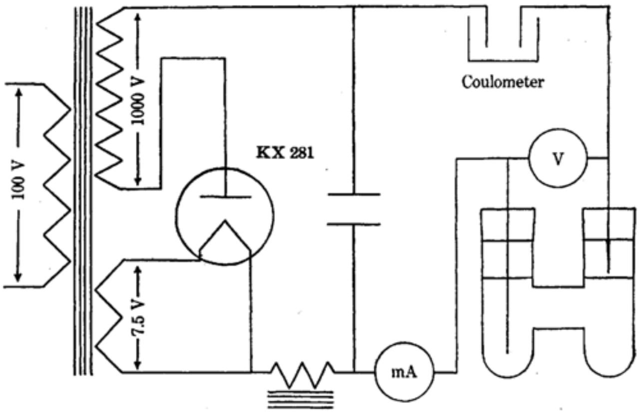

Fig. 2.

Experimental. (1) In the case of the glow electrolysis of zinc sulphate solution, white thin membrane of precipitate is generally formed from the concentrated solution, and white colloid is generally from comparatively dilute one, while white colloid is always formed from the solution which is stirred by bubbles of air.

After the precipitate was filtered, and washed until there was no reaction of SO_4, it is dried between 100°–110°C. and weighed. It is then dissolved in NaOH solution and electro-analysed at 50°C., 4.4V and 0.8A for 2 hours. The total weight of zinc is weighed, and compared with the weight of copper from copper coulometer. Thus the current efficiency of zinc is determined, and the weight per cent of zinc in the precipitate is also obtained.

Table 1.

No.	Conc. (mol./l.)	V	MA	mm. Hg	Current Efficiency (%)	Zn (%)
1	2.00	560	38	51	110	55.5
2	1.79	500	58	26	110	54.9
3	1.02	520	44	28	117	55.7
4	0.77	540	44	26	115	55.5
5	0.46	556	41	56	106	55.4
6	0.062	540	60	31	118	55.5
7	0.046	520	42	30	109	55.5
8	0.032	621	30	68	89	56.3
9	0.031	600	30	27	104	55.7
10	0.013	624	26	55	97	54.5

From Table 1 we can see that the products are in the same composition in these regions of concentration.

Quantitative Analysis. As stated above, the total weight of the precipitate and Zn are weighed, and the weight of SO_4^{--} is also determined by $BaCl_2$. From these results the proportion of $ZnSO_4$ to $Zn(OH)_2$ also is known as 1 to 3 as shown in Table 2. Water of crystallization is also examined by heating. There is found only 29.2% of loss in weight, which will be obtained by the reaction $ZnSO_4 \cdot 3Zn(OH)_2 \rightarrow 4ZnO$. Therefore, the precipitates have no water of crystallization.

Table 2.

No.	Concentration mol/l.	Total Weight (g.)	Zn (g.)	SO_4^{--} (g.)	$ZnSO_4 : Zn(OH)_2$
11	2.77	0.0810	0.0460	0.0172	1:3.06
12	0.02	0.1321	0.0725	0.0326	1:3.02

(2) *Very Dilute Zinc Sulphate Solution.* When a very dilute solution of 8.04×10^{-6} mol./l. is electrolysed at 1000V, 4mA, and 9 mm. Hg. white colloidal solution is obtained. The product is found to be of the composition $Zn(OH)_2$ by quantitative analysis and crystalline by the Debye-Sherrer photograph.

(3) *Cupric Sulphate Solution.* (a) *Current efficiency.* The green precipitates are formed by the glow electrolysis. The total weight of the precipitate is determined by the same treatment as in the case of zinc sulphate. It is then dissolved in nitric acid and electrolysed with 2.2V and 0.6A for 3 hours at 75°C. The weight of the deposited Cu is determined and the current efficiency is calculated.

Table 3.

No.	Concentration (mol./l.)	V	MA	mm. Hg	Current Efficiency (%)	Cu (%)
1	0.775	610	41	28	111	51.0
2	0.412	660	32	23	103	49.6
3	0.016	680	38	28	—	51.2
4	0.015	680	36	26	—	50.4
5	0.011	620	37	26	118	50.9
6	0.009	580	39	19	113	51.0
7	0.005	600	27	19	109	51.0
8	0.004	660	29	23	125	55.0
9	0.002	630	24	19	120	55.2
10	0.002	755	24	—	—	54.1

It is shown in Table 3 that there are two kinds of precipitates which are separately deposited by the different condition of the concentration. The condition will be varied by temperature.

(b) *Quantitative Analysis.* The quantity of SO_4^{--} is determined by $BaCl_2$ and that of crystalline water is measured by red heating. The analytical data of the precipitates of 51 and 55% of Cu are shown in Tables 4 and 5 respectively.

Table 4.

No.	Concentration (mol./l.)	Total Weight (g.)	Cu (g.)	SO_4^{--} (g.)	$CuSO_4 : Cu(OH)_2$
1	0.775	0.1061	0.0541	0.0233	1:2.52
2	0.015	0.1275	0.0641	0.0300	1:2.51
3	0.009	0.1354	0.0745	0.0261	1:2.47

Table 5.

No.	Concentration (mol./l.)	Total Weight (g.)	Cu (g.)	SO_4^{--} (g.)	$CuSO_4 : Cu(OH)_2$
8	0.002	0.2192	0.1207	0.0451	1:3.04

46.5% of water is driven off by red heat, and 45.6% is expelled by the reaction: $CuSO_4 \cdot 3Cu(OH)_2 \rightarrow 4CuO$.

(4) *Very Dilute Cupric Sulphate Solution.* Greenish blue colloidal soltuion is obtained from 5.4×10^{-6} mol./l. solution of $CuSO_4$ by the glow electrolysis with 820V and 18mA at 23 mm. Hg. The greenish blue product is known as $CuO \cdot 2H_2O$ by red heat. By heating the green colloidal solution soon changes into black colloid, which is 6 $CuO \cdot H_2O$.

Discussion. As these experiments, basic salts are formed by the glow-electrolysis of zinc and cupric sulphate solutions. The basic salt is formed by the secondary reaction, while the hydroxide is formed by the primary reaction as seen on very dilute solutions.

Basic salts of cupric and zinc sulphate have been usually formed by the following two methods, the one is that an insufficient quantity of alkali is added to a concentrated salt solution, the other is that metal or oxide powders are suspended in a concentrated salt solution. The reaction velocity in the former is much faster than in the latter. By the glow-electrolysis the formation of basic salt is soon observed after the electrolysis, as then it is in the former case. Thus, quantity of zinc combined as zinc hydroxide is in proportion to the amount of coulomb. And the hydroxide is in proportion to the amount of coulomb. And the hydroxide combines secondarily with sulphate in the solution to form basic salts. Hence the current efficiency of total zinc becomes larger than that calculated from the coulometer by Faraday's law, and often over 100%.

If a known amount of zinc oxide is suspended one month in a saturated solution of zinc sulphate and the basic salt formed is weighed, the weight of the basic salt is the sum of the weights of the zinc oxide, and of the zinc sulphate and water combined, as shown in Table 6.

Table 6.

ZnO (g.)	$ZnSO_4 \cdot 3Zn(OH)_2 \cdot H_2O$ (cal.)	$ZnSO_4 \cdot 3Zn(OH)_2 \cdot H_2O$ (obs.)
0.3665	0.5730	0.5725

This fact will verify the above explanation of the current efficiency which is often over 100%.

The basic salt is formed immediately, when an insufficient quantity of alkali is added to cupric sulphate solution,(12) then the activation energy of the following reaction is small, and the heat of reaction is as shown by the following equation,

$CuSO_4(sol.) + 3Cu(OH)_2 = CuSO_4 \cdot 3Cu(OH)_2H_2O + 5.9$ kcal.(13)

Hence it is very reasonable that there is the formation of basic salt which is more stable than simple hydroxide.

Current efficiency. From these facts, it is clear that the true current efficiency of product corresponds to the weight of metal of hydroxide in basic salt.

The calculated true current efficiencies are shown in Table 7.

Table 7.

	Precipitate	Current Efficiency Calculated As Basic Salt (apparent) (%)	Current Efficiency Calculated Hydroxide only (true) (%)
No. 5	$ZnSO_4 \cdot 3Zn(OH)_2$	118	88.5
No. 5	$2CuSO_4 \cdot 5Cu(OH)_2 \cdot H_2O$	118	84.5
No. 8	$CuSO_4 \cdot 3Cu(OH)_2$	125	94.0

When we make allowance for the dissolution of anode metal, its current efficiency is to be comparable to the current efficiency (85%) of the product $CuO \cdot 2H_2O$ formed in a very dilute solution of cupric sulphate

Weights of Cu anodically dissolved per coulomb are shown in Table 8. It is known that the current efficiency are almost 100%.

Table 8.

	Precipitate	Current Efficiency (%)
No. 1	$2CuSO_4 \cdot 5Cu(OH)_2 \cdot H_2O$	98.9
No. 2	"	101.0
No. 7	$CuSO_4 \cdot 3Cu(OH)_2$	100.0
	$CuO \cdot 2H_2O$	91.0

From these results, it is unable to consider that there is the reaction which deposits metal at cathode and lets free SO_4^{--}, over the number of coulomb passed.

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(12) M. P. Sabatier, *Compt. rend.*, **125** (1897), 301. M. O. Binder, *ibid.*, **193** (1934), 653.

(13) M. P. Sabatier, *Compt. rend.*, **125** (1897), 101.

The weight of copper anodically dissolved is somewhat greater than that of metal in hydroxide, cathodically formed. This discrepancy is attributed to the existence of the reaction $Cu \rightarrow Cu^{+}$ in some extent, together with the main reaction $Cu \rightarrow Cu^{++}$, when copper is anodically dissolved, as the ordinary electrolysis.(14)

The Effect of the Temperature. For the reason that the glow electrolysis gives metallic compounds, it can be suspected that there is an effect of heat, caused by the impacts between electrons and metallic ions or water molecules. From the above experiment, it is known that the product in a very dilute solution of cupric sulphate by the glow electrolysis is $CuO \cdot 2H_2O$ and not $6CuO \cdot H_2O$ and the reaction $CuO \cdot 2H_2O \rightarrow 6CuO.H_2O$ takes place in an aqueous suspension at 77°C.(15) From these facts there is no need to suppose the effect of heat for the formation of the metallic compounds.

From the result of the studies on the state of the deposits, it was found that in zinc sulphate solution by the glow-electrolysis, the deposit becomes the more colloidal the more dilute the solution is. The size of the particle is known as 10^{-5} to 10^{-6} cm. by the Debye-Sherrer Method.

Summary.

(1) It has been said that oxides are formed by the glow-electrolysis of zinc sulphate solution. From the above studies, however, it is known that $ZnSO_4 \cdot 3Zn(OH)_2$ is formed, and the colloidal solution of zinc hydroxide is obtained with very dilute solution, as 8.04×10^{-6} Mol.

(2) It has been said that oxide or hydroxide is formed in the cupric sulphate solution. From the above researches, however, the basic salt, $2CuSO_4 \cdot 5Cu(OH)_2 \cdot H_2O$, is obtained from its concentrated solution of over 0.002 mol., and $CuSO_4 \cdot 3Cu(OH)_2$ is obtained from under 0.002 mol. and colloidal solution of simple hydroxide, $CuO \cdot 2H_2O$, is formed with the very dilute solution of 5×10^{-6} mol./l.

(3) The reason for the abnormally large current efficiency such as about 120% has not been cleared. From the following facts, it is cleared that this is the result of the secondary formation of the basic salt.

(a) The comparison of the ordinary method of formation of the basic salt with its formation by the glow electrolysis.

(b) The agreement between the current efficiency of hydroxide contained in basic salt as a constituent and that of hydroxide produced in a very dilute solution.

(c) The weight of copper anodically dissolved shows the current efficiency of about 100%.

(d) The weight of the basic salt, $ZnSO_4 \cdot 3Zn(OH)_2 \cdot H_2O$ which is formed from ZnO, is the sum of the weight of ZnO taken and the weights of $ZnSO_4$ and water combined.

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(14) F. Fischer, *Z. Elektrochem.*, **10**(1904), 427.

(15) W. Spring and L. Lucion, *Z. anorg. Chem.*, **2**(1892), 195; D. Tommasi, *Bull. soc. chim.*, **37**(1882), 197.

(4) For the mechanism of the glow-electrolysis, there is no need to consider the effect of heat caused by impacts between electrons and ions, etc., because the green $2CuO \cdot H_2O$ which is obtainable at ordinary temperature is formed in a very dilute solution and it changes to black $6CuO \cdot H_2O$ by heating over 77°C.

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