BEHAVIOUR OF THE SURFACE OF THE SOLUTION OF ELECTROLYTE AGAINST ELECTRONIC IMPACTS.

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Received January 8th, 1934. Published March 28th, 1934.

Introduction.

The glow-discharge between the surface of the solution of an electrolyte and the metallic cathode, which is suspended above the solution, has been investigated by various authors. The earliest literature is that of Gubkin.(1) He used the solutions of zinc sulphate, silver nitrate and potassium chloroplatinate and obtained respectively zinc oxide, metallic silver as striped dark rings at the surface of the solution under the metallic cathode and the metallic platinum in finely divided form. Günther-Schulze(2) studied on various sorts of salt-solutions and obtained oxides and hydroxides in the neutral solutions. According to his view, the electrons accelerated in the electric field between the cathode and the surface of the solution and impinged on the surface do not discharge directly the cations of the solute but the hydrogen ions in the solution, and the residual (OH) react chemically with the cations to form the oxides or the hydroxides. Corbino(3) who obtained the metallic powder using copper sulphate, silver nitrate and potassium chloroplatinate as the electrolytes, informed that the chief difference between the process of the ordinary electrolysis and that of the glow-electrolysis lies upon the character of the deposition, the latter being apt to give colloidal solutions of metals.

Haber and Klemenc,(4) Makowetzky,(5) and Klemenc and Hohn(6) investigated the efficiencies of the oxidation and reduction by the electrolysis using the anode or cathode in the gaseous space above the solu-

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(1) Gubkin, *Pogg. Ann. Phys.*, **32** (1887), 114.

(2) A. Günther-Schulze, *Z. Electrochem.*, **12** (1903), 833; **30** (1924), 289; **31** (1925), 187.

(3) O. M. Corbino, *Atti acad. Lincei, Roma*, **6. 5.** (1927), 377; *Chem. Abstr.*, **21** (1927), 2437.

(4) F. Haber u. A. Klemenc, *Z. Electrochem.*, **20** (1914), 458.

(5) A. Makowetzky, *Z. Electrochem.*, **17** (1911), 217.

(6) A. Klemenc u. H. F. Hohn, *Z. Electrochem.*, **37** (1931), 742; *Z. physik. Chem.*, **130** (1927), 378; *Z. physik. Chem.*, A–**154** (1931), 385; A–**166** (1933), 356.

tion and immersing the other electrode in the solution. They found that the efficiencies of the current were larger than that calculated by Faraday's law. Klemenc and Hohn attributed this characteristic behaviour of the glow-electrode to the photochemical action induced by the light emitted by the hydrogen accompanied by the neutralization of the hydrogen ions which were drawn out from the solution into the gaseous space by the potential difference due to the space-charge above the solution. Recently they informed that it is due to the neutral particles e.g. atomic hydrogen, which are produced by the glow-discharge in the gaseous space.

The present authors carried out the glow-electrolysis with the cathode above the solution or the solution covered with a thin film of oil. In the latter case, as the thickness of the oil layer was very thin, it is conceivable as being considerably transparent even against the ultra-violet light, while it could act as an energy absorber against the electrons and the decomposition products of water vapour, if the characteristic properties of the glow-electrode are due to the impacts of them. From the results of such a glow-electrolysis it was concluded that it is not the effect of photons. Hence, it is necessary to decide whether it was caused by the electrons or by the decomposition products of water vapour. In order to distinguish the characteristic behaviour of the surface of the solution against the electronic impacts in comparison with the metallic surface, the authors undertook the differential measurements employing a hot cathode as the source of electrons.

Experimental.

(1) **Glow-Electrolysis.** The apparatus employed for the glow-electrolysis is shown in Fig. 1. The discharge-cell (D) is a U-tube to the one end of which the cathode, an aluminium or a platinum wire, is held by a binding post and to the other the anode is immersed in the solution. A copper coulometer (C) is connected in series to the cathode of the discharge-cell so that the weight increase of the cathode in the coulometer should show the total electricity passed through the cell. The potential difference (E') between the cathode terminal of the coulometer and the anode of the discharge-cell is measured by the vacuum tube voltmeter (V) and is regulated by the resistances (R′) and (R″) which are connected in series and in parallel to the supply unit respectively. The potential drop due to the internal resistance of the coulometer can be neglected as it is so small compared to (E') that (E') can be considered as the potential difference between the cathode and the surface of the solution in the discharge-cell.

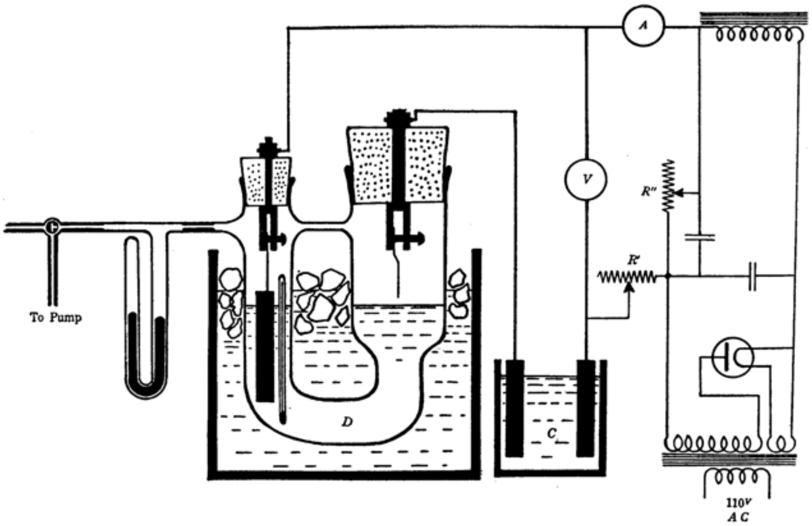

Fig. 1.

Table 1.

Electrolyte	Product	Weight of product mg.	Coulomb. Cu-eq. mg.	Coulomb-Efficiency %	Volt.	Current m.a.
$CuSO_4$	$Cu(OH)_2$ $Cu_2(OH)_2$	13.9	11.9	76	550	14.7
		15.8	12.3	84	510	20
		18.7	13.5	90	480	21
		16.0	9.6	108	550	28
		8.5	7.5	74	550	10
$ZnSO_4$	ZnO, Zn, $Zn(OH)_2$	11.4	12.7	87	540	19
		4.1	7.0	57	500	7.5
		6.7	9.0	72	510	25
		7.4	11.8	61	520	15
		11.0	12.9	84	580	13
		3.0	5.4	54	560	12
		5.6	5.2	104	510	13
		2.5	2.5	104	630	3
$ZnCl_2$	ZnO, Zn, $Zn(OH)_2$	5.2	5.3	96	560	9
$HgCl_2$	HgO & white ppt.	10.7	5.8	—	650	6.5
		4.6	2.4	—	695	2.2
$Pb(NO_3)_2$	PbO	37.5	17.6	61	410	19
$MnSO_4$	Mn_3O_4	7.1	5.1	—	570	10
$NiSO_4$	$Ni(OH)_2$ & black ppt.	15.0	13.9	—	500	25

The electrolytes used for the glow-discharge are shown in the first column of Table 1. As products, hydroxides were obtained, as a rule; however, when the oxides are more stable they were also formed, as shown in the second column of the same table. Most of them appeared in the form of cloud under the cathode in the solutions. In the case of zinc salts, the metallic zinc was observed besides the hydroxide and the oxide which deposited in the form of ribbons of thin films. The mechanism of the formation of the metallic zinc can be considered as the same as that when the surface was covered with liquid paraffin.

In this case, the deposits and the solution in the discharge-cell were taken out and filtered with a paper, the residue was washed down in a beaker, then all the products were dissolved in an excess of diluted sulphuric acid which was previously standardized with a normal solution of caustic soda and the excess of the acid was titrated with the same alkali solution using methyl orange as the indicator.

The chief deposits in the solution of copper sulphate were of two kinds, the greater portion was the greenish blue cupric hydroxide and the smaller was the yellow cuprous hydroxide, their proportion varied largely. The formation of metallic copper was almost imperceptible. In the table the weights were given as cupric hydroxide.

When the surface of the solutions were covered with thin films of liquid paraffin neither hydroxide nor oxide was observed, but the finely divided powders of metals were obtained. When silver nitrate was used as an electrolyte, a brilliant mirror of metallic silver was observed besides the fine powders in the solution. Moreover, the thin layer of liquid paraffin showed an intense bluish green fluorescence during the electrolysis.

(2) **Discharge with Hot Cathode.** In order to distinguish the characteristic behaviour of the surface of the solution against the electronic impacts from that of the metallic surface, it is necessary to remove the effects of the gaseous space; for this purpose, the authors undertook the differential measurements with the arrangement as shown in Fig. 2.

In the discharge-cell a filament used as the hot cathode was placed in the gaseous space parallel to the surface of the solution which serves as an anode and a nickel plate which serves as an auxilliary anode. The distances from the hot cathode and the two anodes must be equal as far as possible.

The two internal resistances i.e. the resistance between the hot cathode and the surface of the solution, and that between the hot cathode

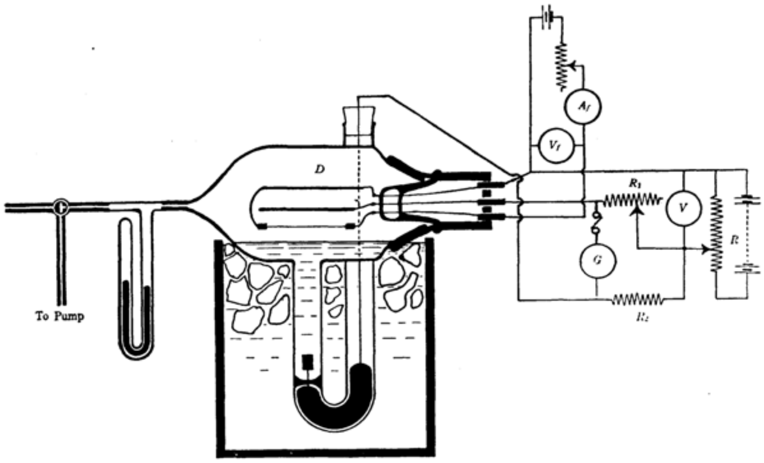

Fig. 2.

and the metallic anode form the arms of the Wheatstone's bridge with two external resistances (R_1) and (R_2) which are much smaller than internal ones. The potential difference applied between the hot cathode and the two anodes, which is regulated by the potentiometer (R), can be regarded as indicated by the voltmeter (V). The value of (R_1) in the equilibrium of the bridge which is determined by the galvanometer (G) gives the current ratio in an arbitrary unit, provided (R_2) is kept constant, throughout these measurements (R_2) was fixed at 5734 ohms.

As the hot cathode, a platinum coated with barium oxide or a blanck platinum wire was used, this was heated by the electric current whose intensity and terminal voltage were measured respectively by the ammeter (A_f) and the voltmeter (V_f).

The inside of the discharge-cell should be absolutely free from oils and greases, if there is a slight trace of them, the anode process is very much affected, showing the similar behaviour as when covered with liquid paraffin. The solutions must be brought into reduced pressure before introducing in the discharge-cell to avoid the risk of bubbling in the cell due to the dissolved gas. The hot cathode and the auxilliary anode were then fitted and the gas above the solution was exhausted at ca. 100 mm. of mercury, cooled to the temperature slightly above the freezing point of the solution and exhausted the gas once more to 5–15 mm. of mercury.

On account of too high pressure for such experiments, if the currents were not so small, it was liable to form the space charge. In this experiments, the thermo-electronic currents were about the order of 10^{-6} ampére. Therefore, the imperfection of the compensation of the effect of the space charge due to the inexactitude of the location of the hot cathode was able to lessen.

The current ratio was measured with respect to E, the accelerating potential difference for electrons impinging on the surface of the solution and the nickel plate as described above. As represented in Fig. 3 a-c each of the diagrams showing the relation between the current ratio and E shows a maximum at E'_m. The values in these diagrams, as well as in the table were corrected with a half value of the terminal voltage of the hot cathode. In the case the blanck platinum wires used as the hot cathodes, the maxima were given in the vicinity of 17 volts, whereas in the case of the platinum wire coated with barium oxide, the maxima were found in the neighbourhood of 22 volts. This discrepancy is due to the difference in the initial velocities of the electrons emitted from the hot cathodes. The initial velocity of the electrons ejected by the platinum is 6.27 volts,(7) hence the E'_m obtained on the diagrams using blanck platinum wires was corrected with this value. The value of correction applied for the E'_m, using platinum wire coated with barium oxide was 1.69 volt.(8) These values are tabulated in Table 2, the corrected values of E'_m of both cases denoted by E_m, coincide with each other. With the most kinds of solutions employed in this experiment, every E_m is found about 23 volts, except in the case of ammonium sulphate the value is somewhat higher. When the surface of the solution was covered with a very thin film of liquid paraffin the curve takes a steadily increasing form as shown in Fig. 3-d.

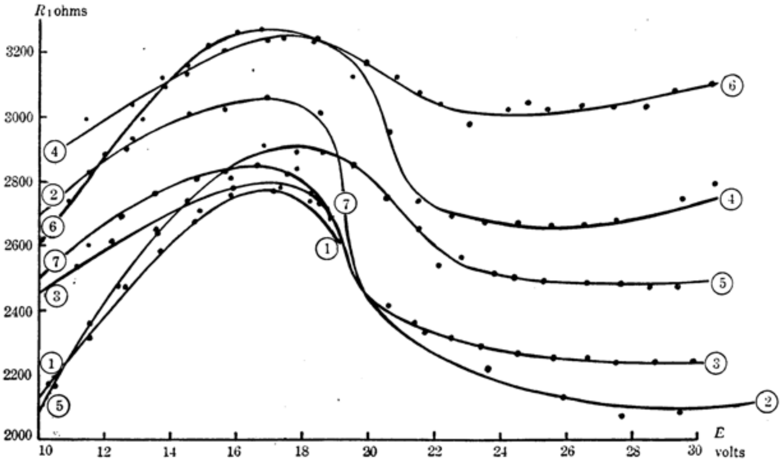

Fig. 3a.

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(7) Du Bridge, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg. II. 5-Aufl.

(8) Michel u. Spanner, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg. I. 5-Aufl.

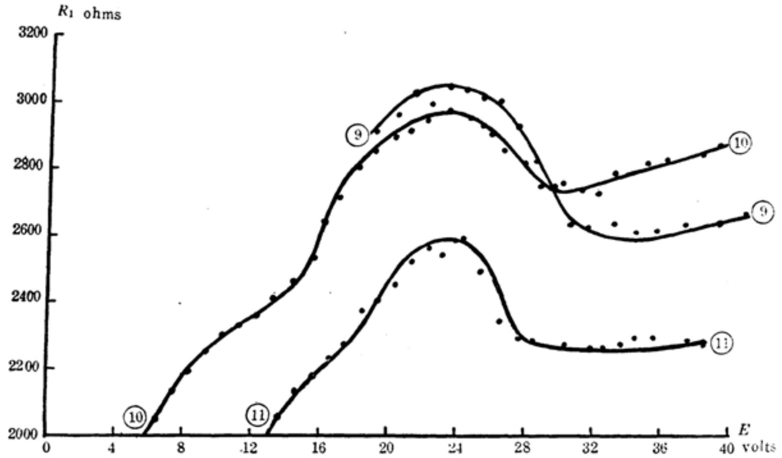

Fig. 3b.

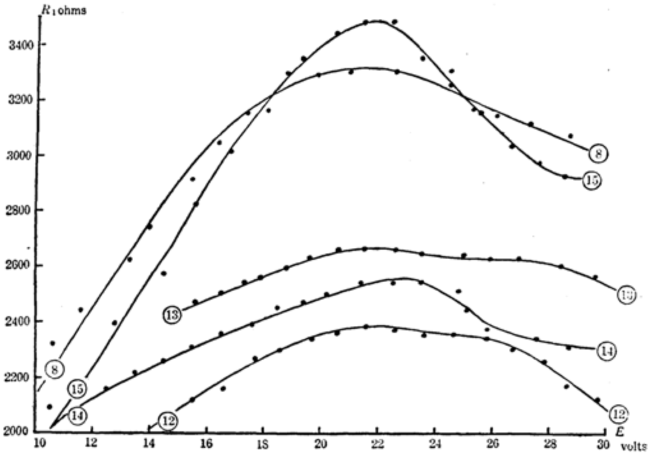

Fig. 3c.

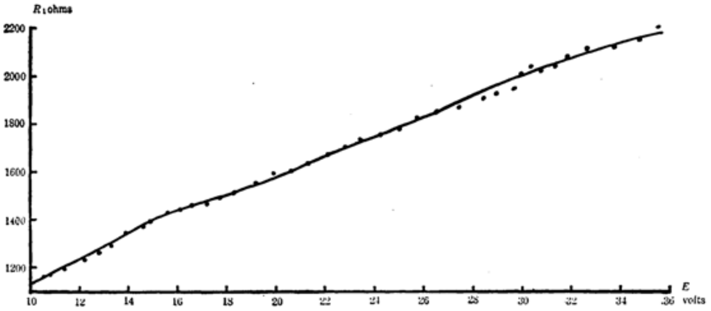

Fig. 3d.

Table 2.

Electrolyte	E'_m	Initial vel. correction	E_m	Curve No.
H_2SO_4	16.6	6.27	22.9	1
	16.8		23.1	2
$(NH_4)_2SO_4$	16.9	6.27	23.2	3
	17.5		23.8	4
	17.8		24.1	5
$CuSO_4$	16.8	6.27	23.1	6
	17.0		23.3	7
H_2SO_4	21.5	1.69	23.2	8
$(NH_4)_2SO_4$	23.2	1.69	24.9	9
	23.7		25.4	10
	23.5		25.2	11
K_2SO_4	22.0	1.69	23.7	12
	21.8		23.5	13
$NiSO_4$	22.9	1.69	24.6	14
	21.8		23.5	15

Discussion of Results.

(1) **Glow-Electrolysis.** The formation of hydroxides and oxides at the surface of the solution as the products of glow-electrolyses suggests the decomposition of the water molecules; however, it is still in question whether the water molecules to be decomposed belong to the gaseous space or to the solutions, and it is also to be determined in what form the energy is required for the decomposition of the water molecules. Experiment shows the coulomb-efficiencies of the formation of hydroxides or oxides are not so small that it can not be considered as by the mere migration of neutral particles from the gaseous space into the solution, except in the case when the particles have enough energy to dissociate the water molecules in the solution. At any rate the decomposition of the water molecules should also occur at the surface of the solution. Since the cupric hydroxide can be reduced by the nascent hydrogen generated by the decomposition of the water molecules in the solution, the formation of the cuprous hydroxide seems to support this consideration.

The form of the energy is now to be discussed. It may be (1) as photons of ultraviolet region, or (2) the energy possessed by the electrons or (3) by the decomposition products of water vapour. From the facts that the products by the glow-electrolyses of the solutions covered with thin films of oil are entirely different, it must be regarded as it is not by the photons, because the thin films are not entirely impenetrable to the ultraviolet light. If it is the second case, the electrons should acquire enough energy for the dissolution of the water molecules at the surface of the solution before they collide with the surface. However, when the surface is covered with a thin film of oil the kinetic energy of electrons should be absorbed by the oil molecules, and the debilitated electrons set on the film attracting the cations in the solution to form an electric double layer, the strength of which increases until it discharges to deposit the cations in the metallic form similar to the ordinary electrode process.

It may be also explained by introducing the particles produced by the decomposition of water vapour. However, in order to play this rôle, the particles should have rather a long period of average life in their highly excited state which lies sufficiently high above their normal level for the multiple decomposition of water molecules without further acceleration against the particles produced by the decomposition. If it were the case, it may be interpreted as follows. By the collisions of excited particles the dissociation of water molecules take place, which results the deposition of the cations as hydroxides or oxides; however, when the surface of the solution is covered with a thin film of oil, the particles are isolated from the solution, hence the characteristic behaviour of the glow-electrode disappears.

As mentioned above, the most probable of the three cases is the second, and the third is also possible.

(2) **Discharge with Hot Cathode.** The ionization and dissociation in the gaseous space above the solution by the glow-electrolysis are obvious,(9) where the dissociation of the water molecules situated at the surface of the solution is necessary, the latter is presumed to have direct contribution to the characteristic behaviour of the glow-electrode. The cause of this dissociation at the surface is now to be discussed. If it were caused by the electrons, there should be an abrupt increase of the electric conductance at the boundary of the gas and the solution by the dissociation of the water molecules, which gives rise to the deposition of the cations when the kinetic energy of electrons attain a certain value

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(9) W. R. Cousins, *Z. physik. Chem.*, B-**4** (1929), 440; G. I. Lavin & F. B. Stewart, *Nature*, **123** (1929), 607; K. F. Bonhoeffer & T. G. Pearson, *Z. physik. Chem.*, B-**14** (1931), 1. They found OH-band in the emission of gas by the glow-discharge.

E_m. The number of electrons accepted by the metallic anode increases proportionally to the three halves power of E, while the number of the electrons accepted by the surface of the solution is small compared to the former until the potential difference E is raised to E'_m, and in the vicinity of E the number suddenly increases to some extent, but after E exceeded E'_m the number does not increase so abruptly as before.

However, if it were caused by the excited particles produced in the gaseous space by the collisions of the electrons with water molecules, the probability of the formation of such particles should increase as E is raised, because the formation is possible in the zone between the position, where the electrons will gain enough energy to dissociate and excite the water molecules and the surface of the solution. Hence the current should increase gradually as E is raised.

The current in the discharge-cell involves three factors with respect to the potential difference E, the first of them is the effect of the external field on the emission of the hot cathode, the second is the effect of the gaseous medium e.g. formation of space charge etc., and the third is the effect caused by the transportation of negative electricity through the boundary of the gas and the solution. By means of the differential measurements, informed above, the first and the second effects can be removed and the third effect is only admitted in its relative appearance against the metallic surface.

Therefore, if the abrupt increase of the electric conductance at the boundary were caused by the electrons, there must be a maximum on the curve representing the relations between the current ratio and the potential difference E at E'_m; however, if it were by the excited particles, there should not be any maximum on the curve. This maximum was verified with each of the solutions of the electrolytes used in the experiment, as described above. The existence of the maxima offers a proof that the decomposition of the water molecules situated at the surfaces of the solutions should be caused by the impacts of electrons and not by the secondarily produced particles produced by the collisions of the electrons emitted by the hot cathode with the water vapour. As the mean, the value $E = 23.8$ volts was given within the error of 1.6 volt by this experiment, and this value can be interpreted in the following manner.

Ascribing the abrupt increase of the electric conductance of the boundary determined by the maxima on the curves representing the relation between the current ratio and the potential difference applied between the hot cathode and the both anodes to the dissociation of the water molecules situated at the surface of the solution, the dissociation is assumed as:

$$H_2O = H^+ + OH + e$$

where the OH molecule may be excited to $^2\Sigma$ state. The energy required for this dissociation can be obtained as follows.

(1) $H_2O(l) = H_2O(g) - 0.47$ e.v. ......Heat of vapourization of water/molecule at 0°C.(10)
(2) $H_2O(g) = H + OH(^2\Pi) - 5.1$ e.v. :..Heat of dissociation of water/molecule(11)
(3) $OH(^2\Pi) = OH(^2\Sigma) - 4.03$ e.v. .....Energy of excitation of OH/molecule(12)
(4) $H = H^+ + e - 13.53$ e.v. ....Ionization potential of hydrogen atom.

Accordingly, the sum of these equations (1), (2), (3) and (4) gives

$$H_2O = H^+ + OH(^2\Sigma) + e - 23.1 \text{ e.v.}$$

The experimental result showed a good agreement with this value.

The excited OH molecules at $^2\Sigma$ state will immediately drop to the normal level and combine with the electrons by their strong affinities; then the negative electricities are transformed into the ionic forms which are readily soluble in the solution and the OH^- ions react chemically with the cations to form the hydroxides or oxides of metals.

Summary.

(1) The glow-discharge between the metallic cathode and the surface of the solution was examined, and it was found that the products were mostly hydroxides or oxides of the cations in the solution. From the coulomb-efficiencies of their formations and the products obtained by the glow-electrolyses with the solutions covered with oil, it was concluded that the decomposition of water molecules should occur at the surface of the solution and it should be caused by the impacts of the electrons

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(10) W. Schüle, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg. I. 5–Au. 594.8 cal/gr. is given.

(11) Senftleben u. Reichmeier, *Phys. Z.*, **34** (1933), 228.

(12) Calculated from the water-band at 3064 A.U. M. Kimura, *Sci. Pap. Inst. Phys. Chem. Res. Japan*, **18** (1932), 109 offered 71410 cm.$^{-1}$ for the dissociation $H_2O \rightarrow OH(^2\Sigma) + H$.

or other particles having enough energies to dissociate the water molecules.

(2) A characteristic phenomenon by the transportation of the negative electricity through the boundary of the gas and the solution was studied and it was deduced that the dissociation should be caused by the accelerated electrons having the kinetic energy of 23.8 e.v..

Further, the process of the dissociation was proposed, and the energy required for this dissociation was calculated as 23.1 e.v..

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