ART. VIII.—On *Electrosynthesis*; by W. G. MIXTER.

[Contributions from the Sheffield Laboratory of Yale University.]

THE action of the electric current on compounds, as is well known, usually decomposes them whether they are in solution, in the molten or gaseous state. As an example of the last we have the electrolysis of steam* with the separation of hydrogen and oxygen equal to the volume of these gases evolved by the same current through dilute sulphuric acid that passes in sparks through the steam. The heat of the sparks also decomposes the steam, but this has not prevented the determination of the electrolytic results. Some physicists consider that the molecules of simple as well as compound gases are decomposed by the electrical discharge and that free atoms, or ions, carry the electricity. If this is true, then the primary effect of electricity may be solely electrolytic and the synthetic results may be due to combinations of free ions. Without discussing this now, let it be understood that the term *electrosynthesis* is applied in this paper to chemical union effected by means of electricity, not, however, by the heat of the discharge. Ammonia, nitric acid, and a few other compounds have been produced in small quantities by the action of electricity, and recently Losanitsch and Jovitschitsch† have made an important addition to our knowledge of electrosynthesis. Their results may be indicated by the equations $\text{H}_2\text{O} + \text{CO} = \text{HCOOH}$, $\text{CO}_2 + \text{H}_2\text{O} = \text{HCOOH} + \text{O}$, $\text{CO} + \text{H}_2 = \text{CH}_2\text{O}$, $\text{CO}_2 + \text{H}_2 = \text{HCOOH}$, $\text{CO} + \text{CH}_4 = \text{CH}_3\text{CHO}$. They state that the dark discharge (*dunkle Entladung*) effects synthesis only, but my observations are that a feeble glow visible only in a dark room causes decomposition as well as combination.

Early last year I observed that feeble sparks in an ozonizing tube with an inner conducting wire did not cause an explosion of acetylene gas under a pressure at which it exploded promptly when the ordinary spark was passed through it. This led to experiments with various forms of electrical discharge in a mixture of two volumes of hydrogen and one of oxygen. It was found that such a mixture at a pressure of 235^{mm} was not exploded in an ozonizing tube, by sparks visible in daylight and giving a distinct snapping noise. The combination was slow. At the pressure given the mixed gases are exploded by the ordinary electric spark, while, as is known, they do not

* J. J. Thomson: *Recent Researches in Electricity and Magnetism*, pp. 181 and 559.

† Ueber chemische Synthesen mittels der dunkler elektrischen Entladung, *Ber. d. deutsch. chem. Gesellsch.*, xxx, 135.

explode when under a pressure of 70^{mm} or less. Dixon* found that a mixture of cyanogen and oxygen exhibits a similar deportment and that it is exploded by a strong but not by a feeble spark. Hautefeuille and Chappius† state that hydrogen is indifferent when oxygen is ozonized, and Berthellot‡ found that two volumes of hydrogen and one of oxygen did not combine under the influence of the current (l'effleuve) and that ozone was formed. These observations do not

accord with mine and the different results may be due to different conditions of experiment. The glow discharge in the apparatus described later causes the slow combination of hydrogen and oxygen, during which very little ozone is formed.

* Jour. Chem. Society, xlix, 384.

† Comptes Rendus, xci, 522, 762.

‡ Ann. Chim. et Phys., [5], xvii, 142.

After trying various forms of apparatus, that shown in the figure was adopted. The wires E from the induction coil dip into the tap water in the inner tubes A and the tap water in the jacket tubes C is connected by the insulated wire D. The wires are supported by the insulating cords F, and the standards and clamps are of wood. The eudiometers are placed about three feet apart, it having been found when they were only a few inches apart that an electrical discharge in one sometimes produced a glow in the other from which the conducting wires were removed, and when close together and in series that the results were discordant. Experience also showed that it is necessary to let the apparatus stand some hours before commencing an experiment. A current of 2.2 volts and 1 to 1.6 amperes from one storage cell was used on the primary of the coil, giving a spark in air of 7 to 10 millimeters and of course a much feebler current through the wire D. A current of higher potential discharged perceptibly into the air from the wires E. Two cells were used and the coil was connected at times with only one eudiometer to complete the reaction in order to find the residual gas not entering into combination. The gases were dried by solid potassium hydroxide at B. To absorb carbon dioxide half to one cubic centimeter of a saturated solution of potassium hydroxide was introduced and made to coat the eudiometer four or five centimeters above B. The vapor tension of the solution was too small to interfere with the results. The absorption of water and carbon dioxide was so rapid while the discharge was taking place in the eudiometers that only one or two per cent of the volume of the gases was water or carbon dioxide or both together. This was found by reading the eudiometer when the current from the coil was stopped and again some hours later. With gases at a pressure of 150^{mm} or less a glow about the tube A, visible only in a darkened room, usually appeared on putting the coil in action, while in some cases a stronger current than that described was required to start the glow discharge, but when once started the feeble current gave a fairly constant glow. The discharge between the glass surfaces in the eudiometers was of course alternating and so was the current in the connecting wires and hence not measurable by electrolytic methods. Many experiments were made with the discharge from large metallic electrodes in oxygen and hydrogen at low pressures. Sometimes there was slow combination, but usually the mixture exploded, and hence attempts to use the direct discharge were abandoned. A Wimshurst machine was also tried without success. When connected with the eudiometers described they appeared to act as condensers, the discharge in them being alternating. At some future time I hope to measure the current by electrical methods and to determine the quantity of

electricity causing the combination of gases, and also to determine the conductivity of gases when uniting. Thus far in the work an empirical measure has been used which is the amount of oxygen and hydrogen combining in one endiometer while gases in the other endiometer also combined, the same current passing through both endiometers. The mixture of hydrogen and oxygen used in all of the work was obtained by the electrolysis of dilute sulphuric acid. The following experiments with hydrogen and oxygen in both endiometers were made to test the method. The reduced volume is calculated for 0° C. and 760^{mm} pressure. The time of the action of the current is given in hours in the column on the left.

Eudiometer No. 3.						Eudiometer No. 1.					
Hours.	Temp.	Pres- sure.	Observed volume.	Reduced volume.	c. c. of gas com- bined.	c. c. of gas com- bined.	Reduced volume.	Observed volume.	Pres- sure.	Temp.	
	14.5	1.3	121	0.2			0.02	118	0.1	14.5	
	16.6	190.5	152.7	36.1			34.8	146.8	191.1	16.4	
1	16.6	177.5	150.5	33.1	3	3.7	31.1	144.3	173.5	16.6	
1	16.6	161.5	148.1	29.7	3.4	4.1	27	141.6	153.5	16.6	
1	17	147	145.8	26.6	3.1	4	23	138.7	134	17	
*											
	13.6	132.8	142.4	23.7			22.6	137.3	131.3	13.4	
1	14.6	119.5	140.4	21	2.7	3	19.6	135.1	116	14.6	
1	13.6	103.5	137	17.8	3.2	3.1	16.5	132	99.5	13.6	
1	13.6	85	134	14.3	3.5	3.4	13.1	129.2	81	13.6	
1	11.6	64.5	131	10.7	3.6	3.5	9.6	126.3	60.5	11.6	
1	12	47	127.9	7.6	3.1	3.1	6.5	123.5	42	12	
1	12.6	33.3	126.1	5.3	2.3	2.2	4.3	121.4	27.9	12.6	
1	13.6	20	124	3.1	2.2	2.1	2.2	119.5	15	13.5	
					30.1	32.2					
		Resi dual gas.					Resi dual gas.				
	14	4	121.6	0.61			0.58	117	4	14	

Eudiometer No. 3.						Eudiometer No. 1.					
Hours.	Temp.	Pres- sure.	Observed volume.	Reduced volume.	c. c. of gas com- bined.	c. c. of gas com- bined.	Reduced volume.	Observed volume.	Pres- sure.	Temp.	
	14	224.5	156.5	44			43	151.2	226.8	14	
1	14	204.8	153.6	39.4	4.6	4.7	38.3	148.4	206.3	13.8	
1	15.7	188	151.2	35.4	4	4.1	34.2	145.9	188.5	15.7	
1	17	172	144.8	31.7	3.7	3.5	30.7	143.7	172.5	17	
1	17	158.4	146.4	28.7	3	3	27.7	141.3	158.2	17	
1	17	141.1	143.1	25	3.7	3.6	24.1	138.0	141.1	17	
1	17.4	118.2	139	20.4	4.6	4.5	19.6	134.9	117.2	17.4	
1	17.9	97.4	136.1	16.4	4	3.9	15.7	131.6	96.8	17.9	
1	18	74.5	132.8	12.2	4.2	3.8	11.9	128.6	74.8	17.8	
1	18	55.5	129.6	8.9	3.3	3.3	8.6	125.6	55.3	18	
1	18	37.5	126.8	5.9	3	2.9	5.7	122.9	37.5	18	
1	16.6	20.5	124.8	3.2	2.7	2.4	3.3	121	22.2	16.6	
					40.8	39.7					
		Resi dual gas					Resi dual gas.				
	15	4.8	120.6	0.72			0.70	116.4	4.8	15	

* Passed the current through 3 only for a time to equalize the pressure, then through both for a few minutes and observed the volume later.

The eudiometers were filled with gas for the second experiment without removing the residual gas of the first, namely 0.61 and 0.58^{cc} and the increase of 0.1^{cc} of residual gas in the second experiment shows that almost no ozone was formed. Moreover, the mercury was only slightly tarnished. During half of the time of the first experiment the current was reversed in the primary of the coil with no marked difference in the relative rate of combination in the two tubes. The direction of the current was not changed in the second experiment. The lack of uniformity in the results from hour to hour is only in small part due to errors of observation and is probably owing to leakage of electricity from the wires or its passage over the surface of the glass above the jacket tubes. The marked discrepancies during the first three hours of the first experiment show the liability to error in the method. Leaving out these hours, the results accord fairly and the total amount of combination is 20.6^{cc} and 20.4^{cc} respectively.

It will be observed that the gases in the two tubes were under nearly equal pressures. This is essential, for the higher the pressure the more rapid the combination as shown by the following: the results in each horizontal line were by the same current acting on a hydrogen-oxygen mixture in two eudiometers.

c. c. combined.	Mean pressure.	c. c. combined.	Mean pressure.
6.22	133 ^{mm}	3.87	73 ^{mm}
5.42	160	4.39	110
21.95	186	13.3	91
14.43	81	11.25	76

The reason for these results is not apparent and the rate of combination bears no simple relation to the pressure.

Vapor of water, as already mentioned, is electrolyzed by the spark discharge, and it is also dissociated by the feeble glow discharge. Three experiments made with the vapor at low pressures in apparatus like that figured gave small volumes of permanent gas. Hence it may be that some of the water from the oxidation of hydrogen is decomposed, but it is probable that little if any is decomposed in a mixture of gases in which water is constantly forming and which contains on account of rapid drying a very small proportion of water.

In order to determine the ozonizing effect on pure oxygen of the glow discharge, one eudiometer was filled with 36^{cc} (reduced to 0° and 760^{mm}) of oxygen at 193^{mm} pressure and the other eudiometer with 30.6^{cc} of hydrogen and oxygen. A saturated solution of potassium hydroxide and iodide was put into each eudiometer to dry the gases and absorb ozone. A current from two storage cells on the primary of the coil was used for an hour and a half. The oxygen contracted 0.3^{cc}, and

the hydrogen-oxygen mixture 11.2°C (reduced to 0° and 760^{mm}). The light in the oxygen was much feebler than in oxygen and hydrogen. The current was next passed through the oxygen only for two hours and the contraction was 2.2°C .

Carbonic Oxide and Oxygen.

The carbonic oxide used was made by heating a mixture of formic acid and oil of vitriol. Two measures of the gas were mixed over water with one measure of oxygen from pure potassium chlorate. The mixed gases left after exploding and treating with potassium hydroxide less than 1 per cent of gas. The following table contains the observations and results of four experiments.

Hydrogen, 2 volumes. Oxygen, 1 "						Carbonic oxide, 2 volumes. Oxygen, 1 "				
Hours.	Temp.	Pres- sure.	Observed volume.	Reduced volume.	c. c. of gas com- bined.	c. c. of gas com- bined	Reduced volume.	Observed volume.	Pres- sure.	Temp.
2	16	180.5	144.9	32.5			33.2	148.1	180.5	16
	14.5	147.5	140.7	25.9	6.6	7.9	25.3	144.4	140	14.5
5	15.8	179.8	140	31.3			33.3	145	184.7	15.8
	16.6	69.5	124.3	10.7	20.6	21.1	12.2	128	77.5	16.2
5	15.9	186	148.7	34.4			32	144.5	178.1	16.2
	18	94	135.9	15.8	18.6	22.3	9.7	121.3	65	18.3
2	17	1.5	121.3	0.2			0.5	118	3.5	17
	16.4	188	150	35			39.2	149.6	211	16.4
2	16	153	147.3	28	7	8.4	30.8	146	170	16.5
2	14.7	117.8	140.8	20.7	7.3	9.2	21.6	138.4	124.8	14.7
2	15.8	82.6	135	13.9	6.8	7.2	14.4	132	87.6	15.6
2	16	28.2	125	4.4	9.5	10.2	4.2	122.7	27.2	16
					30.6	35				
	20	3.2	122.4	0.5			0.6	119	4.2	18

In the last experiment the air in the eudiometers, 0.2 and 0.5°C , was noted before filling with the gases, and also the residual gas, 0.5 and 0.6°C , when the electric discharge gave no further rise of the mercury in the tubes. The hydrogen-oxygen mixture was in one eudiometer in the first and third experiments and in the other eudiometer in the second and fourth; that is, the arrangement and filling of the apparatus was reversed each time after the first experiment. In all 76.4°C of hydrogen and oxygen and 86.3°C of carbonic oxide and oxygen combined, a ratio of 1 to 1.13.

Glow Discharge in dry Carbonic Oxide and Oxygen.

The eudiometers were filled with a mixture of two volumes of carbonic oxide and one volume of oxygen, the same mixture

as used in the preceding experiments, and phosphorus pentoxide was put into the eudiometers to dry the gases. The apparatus was allowed to stand for two days and then the glow discharge was passed for two hours. The contraction in volume caused by the discharge was in each case 2.5°C , reduced to 0° and 760^{mm} pressure. The initial volumes were 13.1°C and 18.5°C respectively. The results show that dry carbonic oxide and oxygen slowly combine when acted upon by the glow discharge.

Methane and Oxygen.

The methane was made from methyl iodide by the action of zinc and alcohol. For the following experiments one volume of methane and two volumes of oxygen were mixed over water.

Hydrogen, 2 volumes. Oxygen, 1 "						Methane, 1 volume. Oxygen, 2 "				
Hours.	Temp.	Pressure.	Observed volume.	Reduced volume.	c.c. of gas combined.	c.c. of gas combined.	Reduced volume.	Observed volume.	Pressure.	Temp.
2	15	13	117	1.9			0.8	120	5	15
	14.3	164.5	119	24.5			28.2	143	157.5	14.3
	15.5	129.5	118.5	19.1	5.4	7.1	21.1	139	121.5	15.2
	16.4	90.5	117	13.1	6	9	12.1	131	74.5	16
	18	51	116.5	7.3	5.8	9.5	2.6	123	17	18
2	24	21	116	2.9			1.5	122	10	19
					17.2	25.6				
	17	4.5	119.5	0.7			1	117	7	17
	13.3	192.5	148.7	35.9			30.2	120	200.5	13.3
	14	159.5	144.3	28.8	7.1	9.9	20.3	119	136.5	14.4
2	15.6	122.5	138.4	21.1	7.7	11.1	9.2	118	63.5	16
	17	4.8	120	0.7			2.7	117	19	18.8
					14.8	21				
	14	1.5	120	0.2			0.4	116	3	14
	16	203	129	32.6			34.7	144.5	193	16
2	17.1	161.5	126	25.2	7.4	10.3	24.4	137.3	143.5	17.3
	16.4	111	122.5	16.9	8.3	11	13.4	127	85	16.6
	19	2	117	0.3			3.9	118.5	26.5	17
					15.7	21.3				

The eudiometers in the first experiment contained 1.9°C and 0.8°C of air and the residual gases at the end of the test were 2.9°C and 1.5°C respectively when the battery gave out. The result shows that the methane and oxygen combined according to the equation

In the second experiment the residual gas, after the discharge ceased to cause a diminution of volume in the methane-oxygen mixture, was 2.7°C , while in the last experiment the residual gas

was 3.9^{cc} and was found to be chiefly oxygen. This excess of oxygen may be due to leakage of the mixed gases from the gas-holder during the time intervening between the first and last experiment. In the three experiments 47.7^{cc} of hydrogen and oxygen and 67.9^{cc} of methane and oxygen combined, or in the ratio of 1 to 1.42. The ratio in the successive experiments is 1 to 1.49, 1 to 1.43, and 1 to 1.36. The smaller ratios for methane and oxygen in the last two are explained by the presence of an excess of oxygen.

Ethylene and Oxygen.

The ethylene used was made from ethylene bromide by means of a zinc-copper couple and was nearly pure.

Hydrogen, 2 volumes. Oxygen, 1 "						Ethylene, 5.2 c. c. Oxygen, 19.1 c. c.				
Hours.	Temp.	Pres- sure.	Observed volume.	Reduced volume.	c. c. of gas com- bined.	c. c. of gas com- bined.	Reduced volume.	Observed volume.	Pres- sure.	Temp.
2	12.8	126.5	138	22	5.6	12.4	24.3	138	140	13.3
	13.7	97.5	134	16.4			11.9	128	74	14
							*6	124	39	18
2					10	18.5	Ethylene, 1 volume. Oxygen, 3 volumes.			
	16	131	137	22.3			25.3	140	145	16
	13	76	129	12.3			6.8	126	43	13
							*5.2	125	33	14
1					4.1	12.5	Ethylene, 1 volume. Oxygen, 2.5 volumes.			
	16.6	101.8	137.5	17.4			21.1	140	121.3	16
	17	80	134	13.3			8.6	130.5	53	16.6
1					3.5	10.7	*0.7	124	4.7	20
	16.8	82	131	13.3			19.1	136	113	16.2
	17.8	62	128	9.8			8.4	128	53	17.8

Three volumes of oxygen are required for the complete oxidation of one volume of ethylene, but in none of the experiments was the gas all oxidized to carbon dioxide and water. In the first experiment with an excess of oxygen 2.5 volumes disappeared to one of ethylene. The residual gas, 5.2^{cc}, of the second experiment was found to be oxygen. The combination of ethylene and oxygen in the third was very nearly in the proportion of 1 to 2.5 volumes. Doubtless some acetic acid was formed, as no oxalic or formic acid was found in an experiment made especially to determine whether these acids were formed. The results of the second experiment except as above

* Residual gas.

stated are worthless, because the action of the discharge was not stopped until the ethylene was nearly all consumed and there was a large excess of oxygen present. The first experiment shows a ratio of the hydrogen and oxygen consumed in two hours to ethylene and oxygen of 5.6 to 12.4^{cc} or as 1 to 2.2, while in the last two the ratio is 1 to 3. The slower rate of combination of ethylene and oxygen in the first case is to be ascribed to the excess of oxygen present.

Acetylene and Oxygen.

The acetylene used in the following experiments was made from calcium carbide and kept over water. It proved to be nearly pure.

Hydrogen, 2 volumes. Oxygen, 1 “						Acetylene, 4.8 c. c. Oxygen, 15.7 c. c.					
Hours.	Temp.	Pres- sure.	Observed volume.	Reduced volume.	c. c. of gas com- bined.	c. c. of gas com- bined.	Reduced volume.	Observed volume.	Pres- sure.	Temp.	
1	17.4	121	139	20.8	3.8	11	20.5	137	121	17.4	
	15.2	101	135	17			9.5	129	59	15.2	
							3.3	123	22	19	
1	10.5	100	136	17.2	4.8	13.1	Acetylene, 6.3 Oxygen, 17.7		c. c. c. c.		
	14	74.5	133	12.4			24	140.5	135	10.5	
							10.9	130.5	66.5	14	
1	16.2	124.4	140	21.6	4.3	13.9	Acetylene, 8.2 Oxygen, 18.4		c. c. c. c.		
	16.2	101.7	137	17.3			26.6	142	151	16	
							12.7	132	77.7	17	
1	16.5	133	139	22.9	4.6	14.6	Acetylene, 1 volume. Oxygen, 2.5 volumes.				
	15.4	108.7	135.4	18.3			26.7	142	152	17	
							12.1	131	74	15.4	
							0.7	123	4.7	18	

In the first experiment the oxygen consumed was 15.7—3.3 = 12.4 or 2.58 times the acetylene taken. In the last experiment the acetylene and oxygen were in the proportion required for complete oxidation of the former, and of the 26.7^{cc} of gases taken only 0.7^{cc} remained. The results show that acetylene in presence of sufficient oxygen is all converted into carbon dioxide and water by the glow discharge. 2.9, 2.7, 3.2, and 3.2 cubic centimeters respectively of acetylene and oxygen combined to 1 of hydrogen and oxygen. The lower results in the first two are evidently due to the excess of oxygen present in the mixtures.

Ethane and Oxygen.

The ethane used in the following experiment was made from ethyl iodide by the action of the zinc-copper couple in alcohol. The ethane and oxygen were measured in the eudiometers.

Hydrogen, 2 volumes. Oxygen, 1 "						Oxygen, 18.8 c. c. Ethane, 5 c. c.					
Hours.	Temp.	Pressure.	Observed volume.	Reduced volume.	c. c. of gas combined.	c. c. of gas combined.	Reduced volume.	Observed volume.	Pressure.	Temp.	
1	17	115	136	19.4			23.8	139	138	17	
	16	93	133	15.4	4	8.9	14.9	132	91	16	
	18	68	129	10.8	4.6	6.4	8.5	127	54	18	
							7.5	126	48	18	
					8.6	15.3	Oxygen, 16.6 c. c. Ethane, 8 c. c.				
1	17	113.5	136	19.1			24.6	139	143	17	
	17	103.5	135	17.3	1.8	2.6	22	137	129.5	17	
	15.6	79.5	132	13.1	4.2	7	15	132	91	15.6	
1	16.6	55	130	8.9	4.2	6	9	127	57	16.6	
							1.2	120	8	18	
					10.2	15.6	Oxygen, 13.5 c. c. Ethane, 8.5 c. c.				
1	17.6	128	137	21.7			22	138	129	17.6	
	16.8	106	134	17.6	4.1	5.9	16.1	134	97	17	
	14.6	82	133	13.6	4	6.4	9.7	131	59	14.8	
							4.7	123	31	17	
					8.1	12.3					

One volume of ethane, C_2H_6 , requires for complete combustion $3\frac{1}{2}$ volumes of oxygen. In the experiments, however, less than $2\frac{1}{2}$ were consumed. In the first, 5^{cc} of ethane and 11.3^{cc} of oxygen (18.8^{cc} less 7.5^{cc} residual oxygen) combined, and in the second 8^{cc} and 15.4^{cc} ($16.6 - 1.2$). The oxidation was stopped in the third experiment when 9.7^{cc} remained, and the oxygen in the mixed gases was found to be 5^{cc} , leaving 4.7^{cc} per cent ethane. Deducting these numbers from the volumes of gases originally taken, we find that 3.8^{cc} of ethane and 8.5^{cc} of oxygen combined; 1.8 , 1.5 and 1.5 cubic centimeters respectively of ethane and oxygen combined to 1 of hydrogen and oxygen. The rate of combination was most rapid in the first with an excess of oxygen present, and during the first hour was 2.2 times that of the hydrogen-oxygen mixture, while in the second hour it was much less owing to the large excess of oxygen present.

Molecular Changes.

The table below is based on the composition of the gases used and the ratio of the volumes combined to one volume of hydrogen and oxygen also combined under the influence of the glow discharge as before described. The ratio taken for carbonic oxide and oxygen is 1.13, the mean of all the results; for methane and oxygen 1.49, which appears to be the best result; for ethylene and oxygen 3, the result of the last two experiments with these gases; for acetylene and oxygen 3.2; and for ethane and oxygen 1.5. The volume ratios also represent the relative number of molecules combining, and for convenience these ratios are given in the table in whole numbers, and one volume of hydrogen and oxygen is assumed to contain 100 molecules.

Mixture of gases.	Molecules combined.	Molecules oxidized.	Molecules of oxygen consumed.
Hydrogen and oxygen,	100	H ₂ 67	33
Carbonic oxide and oxygen,	113	CO 75	38
Methane " "	149	CH ₄ 49	100
Ethylene " "	300	C ₂ H ₄ 86	214
Acetylene " "	320	C ₂ H ₂ 91	229
Ethane " "	150	C ₂ H ₆ 50	100

The accuracy of the experimental work is by no means what is desirable, nevertheless it is evident that the same electric current caused the oxidation of a different number of molecules of the gases, the variation being as 1 to 2, while the oxygen consumed varied as 1 to 7 molecules. Moreover, the numbers representing the relative proportions of the molecules oxidized fall into two classes, viz: 67, 49, 50, and 75, 86, 91. The former are the numbers of saturated and the latter of unsaturated molecules oxidized. Ethylene and acetylene differ but little in deportment, although the latter is the more endothermic in character. Both combine more rapidly than carbonic oxide; methane and ethane combine at about the same rate but slower than hydrogen. If we calculate the amount of change in a mixture of hydrogen and oxygen on the basis that 3.6^{cc} combine in one hour, we find that 1 cubic millimeter of the mixture unites in a second. The space occupied by the glow discharge in the apparatus was about 30^{cc}, and the volume of gas at $\frac{1}{10}$ th of an atmosphere equals 3000 cubic millimeters at standard pressure, that is, the molecules combining during one second were mixed with 3000 times as many molecules. This slow combustion did not raise the mean temperature of the gases, as the heat evolved was constantly lost by radiation. Whether the energy of oxidation induced by the electric glow

also causes chemical union, it is impossible to say. It seems, however, safe to assume that the heat energy plays little part in effecting chemical change for the reason that the heat of combustion increases in the series tabulated much faster than the number of molecules combining. We shall be sufficiently accurate in assuming the heats of combustion to be proportional to the oxygen consumed. For example, the oxidation of three molecules of acetylene gives seven times as much heat as one molecule of hydrogen. Further, if the energy resulting from the union caused by electricity of two molecules of hydrogen and one molecule of oxygen causes other molecules to combine, we should expect the energy of this phase of combination to cause further combination and rapid combustion or an explosion. If then the chemical changes in the mixed gases tested were not caused in part by heat, it remains to consider the nature of the change caused by electricity. Oxidation was not effected by ozone nor preceded by its formation, as the discharge was too feeble to produce sufficient ozone to account for the amount of oxidation. Moreover, hydrogen, carbonic oxide and methane resist ozone. The hydrocarbons also were but slightly decomposed by the glow discharge, as the following experiments show. 8.85^{cc} of methane, subjected to the discharge for an hour and a half, increased in volume 0.28^{cc} with formation of acetylene. The change may be expressed by the equation

That is, four volumes of methane yield eight volumes of gas. A similar test of 23.8^{cc} of ethane for an hour gave 0.4^{cc} increase in volume; only a small quantity of acetylene was formed. The reaction is

That is, two volumes of ethane yield six volumes of gas. The decomposition of the hydrocarbons by the discharge is, therefore, too slight to account for the amount of change in the mixtures of oxygen. This fact and the non-formation of ozone indicate that the formation of water and carbon dioxide was not due to the union of ions, a view supported by the syntheses by Losanitsch and Jovitschitsch* of organic compounds. If chemical union in the cases discussed is not to be explained by the ion theory, we may infer that the glow discharge of electricity renders molecules chemically active and capable of interacting. We may thus consider the molecular changes involved in electrosynthesis to be analogous to those occurring in synthesis effected by heat or light where combination takes place at a temperature far below that at which the gaseous molecules dissociate.

* Loc. cit.