ART. XXIX. — *On the Smee Battery and Galvanic Polarization;* by WM. HALLOCK.*

1. INTRODUCTION.

THE electromotive force of the Smee battery, when determined with the greatest care by different methods, gives values which differ greatly from each other and are larger or smaller than the theoretically calculated value, E = 0·75 D.,† according as the resistance in the circuit used is larger or smaller than about 300 or 400 S. E.† It was with a view to obtaining an explanation of this fact if possible, and to obtain further data which might help to decide between various conflicting explanations already offered, especially those of Exner‡ and Fromme,§ that the first part of this research was undertaken.

The second part has to do with the question whether the electromotive force of galvanic polarization can be computed *a priori* from the thermal equivalents of the chemical reactions which take place thereby, and is intended to check the already determined values of this force and to obtain new ones in order to collect as large a number of values as possible, to see to what extent the experimentally determined values correspond with the theoretically calculated ones.

2. APPARATUS.

Not having at my disposal an electrometer which answered all the requirements of delicacy, damping, etc., it was determined to use a galvanometer with large resistances in the circuit. The instrument used was a Wiedemann reflecting galvanometer with a coil of 17,800 turns and a resistance of 6,700 S. E. The small ring magnet had a short time of vibration (1·1 second) and was so strongly damped that it came to rest

* Being an abbreviated translation by the author, the original having appeared in Wiedemann's Annalen, vol. xvi, p. 56, 1882.

† As this work originally appeared in Germany the Daniell (D.) and Siemens Unit (S. E.) were used.

‡ F. Exner, Wien. Ber., lxxx, 1879, und Wied. Ann., x, p. 265, 1880.

§ C. Fromme, Sep.-Abdr. a. d. 20, Ber. d. Oberh. Ges. f. Natur- u. Heilkunde. Wied. Ann., xii, p. 399, 1881.

in from 4 to 6 sec., even after a large deflection. It was so delicate that a single Daniell cell gave a deflection of 170 scale-divisions with the scale 2^m from the mirror and 330,000 S. E. in the circuit.

Inasmuch as resistance coils of the necessary length of wire would have been very expensive, and moreover, as it was interesting to know to what extent one can substitute liquid resistances for wire ones, where a certain degree of accuracy is needed, it was determined to try them in this research. The idea is not at all new and has often been applied; Hittorf* for example used a solution of iodide of cadmium between cadmium terminals; but as far as I know great importance has never been placed upon their accuracy or constancy. Exner† used a solution of $ZnSO_4$ between amalgamated zinc terminals, but one only need read the method in which his resistances were constructed and calculated to see that they can lay no claim whatever to accuracy.

The resistance used in this research was that offered by a column of a solution of $ZnSO_4$ in alcohol, 1^{mm} in diameter in section and 200^{mm} long; this capillary tube was horizontal and each end expanded into a vertical receiver 20^{mm} in diameter and 100^{mm} high, in which stood the amalgamated zinc terminals. A better form however is to simply invert a capillary U-tube into the two receivers as a siphon, since in the other form the precipitate which forms around the terminals falls into the capillary tube, thus reducing its section and increasing the resistance. An alcoholic solution was used because Kohlrausch‡ found that the specific resistance of such solutions was less influenced by slight impurities than in the case of the same salts dissolved in water. Care was taken to prove that the polarization of the terminals could be neglected, which was the case even when a very strong current was used (5 Bunsen cells through 40 S. E.). When afterward this resistance was compared with a wire coil of 200,000 S. E. there could be no difference detected in the results obtained. It moreover remained during the three months of its use constant to within the limits of an error caused by an error of 0·1° C. in the determination of its temperature. Of course the great objection to liquid resistances is their large heat coefficient (from 1·5 to 3·5 per cent for 1·0° C.). However there seems no reason why such resistances should not be used, where they can stand still in a case or water-bath and where about 0·2 to 0·5 per cent is sufficiently accurate. In all cases it is better to determine the resistance experimentally than to calculate it; the above

* W. Hittorf, Wied. Ann., vii, p. 563, 1879.
† F. Exner, Wien. Ber., lxxxiv, p. 528–529, 1881.
‡ F. Kohlrausch, Pogg. Ann. Ergbd., viii, p. 1, 1877.

resistance column was determined from time to time in the Wheatestone's bridge in the ratio 1,000 to 10,000. The resistance can of course be easily varied by varying the dimensions of the capillary tube or the amount of water and salt dissolved in the alcohol.

Objection might be made to the use of the galvanometer for such work, on the ground that the polarization would be diminished by the consumption of the gases by the current through the galvanometer, but a simple calculation will show that it would require a polarization equal to one and a half Daniell's to consume $0{\cdot}1^{cmm}$ of hydrogen per minute working in a circuit whose resistance was 150,000 S. E. That this quantity of gas may be neglected at first when the electrodes are still heavily coated is evident. This theoretical refutation of the above objection was strengthened by the following experiment. Two platinum plates were twice equally strongly polarized, and the first time connected through 150,000 S. E. and left and the curve of the diminution of the polarization plotted; the second time the similar circuit was only closed once a minute and only for from 6 to 8 sec. and then opened again, and the curve plotted in this case. The two curves showed that the consumption of gas by the current when left closed did not make itself apparent until after 17 min., i. e. it may be neglected for the first five minutes at least.

The electromoter possesses the advantage, that with the proper use of a switch or commutator it can be charged to a potential representing that electromotive force of polarization which is active *immediately* after opening the primary or polarizing circuit. It is, however, not as convenient for use, and necessarily has a long time of vibration and is weakly damped; a very convenient form of the switch is that made by Hartman in Würzburg, being a slight improvement upon the Weber quicksilver commutator.

3. On the Rise of the Electromotive Force of the Smee Battery.

Exner* endeavors to explain those values of the electromotive force of the Smee which fall above that calculated, from the thermal equivalents of its chemical reactions, $E=0{\cdot}75\,D$, on the ground that the acid contains oxygen in solution which oxidizes the hydrogen evolved, and thus increases the thermal equivalent of the battery.

This question could be easily answered if it were possible to get and keep a cell entirely free from dissolved gases. Exner used the method of short circuiting the cell for a long time, but

* F. Exner, Wien. Ber., lxxx, 1879 und Wied. Ann., x, p. 265, 1880.

it is evident that this method simply substitutes evolved hydrogen for any other gases which may happen to be dissolved in the acid, and it is just the hydrogen which it is necessary to remove, since to its presence is generally ascribed the diminution of the electromotive force below that obtained with the electrometer or by the compensation method (about 1·5 D).

In this research the following method was used to obtain a cell free from dissolved gases.

A strip of zinc 1×6^{cm} and a platinum wire $0{\cdot}1^{cm}$ in diameter and 5^{cm} long, fastened in the cork of a 100^{cc} flask, constituted the cell used. Its force, when freshly filled with 5 per cent H_2SO_4, through a circuit of 150,000 S. E. was found E=1·07 D. It was then closed in a circuit of only 0·2 S. E. external resistance containing a tangent compass, and its force at the expiration of the first minute determined to E=0·71 D. after 20 min. to E=0·06 D. and after 70 min. to E=0·03 D. These small values, although they agree well with those obtained by Fromme,* can only be considered as approximations owing to the difficulty of accurately determining the internal resistance of inconstant cells. The cell was then left short-circuited for 20 hours in order to let the evolved hydrogen drive out the other gases as completely as possible; at the expiration of this time its force through a circuit of 150,000 S. E. was found quite constant E=0·69 D. In order now to drive out the hydrogen, the flask was placed over a burner and kept at a sharp boil for 20 min., the steam and gas passing off through a long narrow tube in the cork. A layer of petroleum about 1^{cm} deep was poured over the acid while boiling, to assist in keeping gases from redissolving in the acid. The flask was then sealed shut with hard wax and cooled. Its force 5 sec. after being closed in a circuit of 150,000 S. E. was found E=0·86 D. and after 15 sec. to be constant at E=0·70 D. An analysis showed that the liquid in the cell still contained 3 per cent free H_2SO_4. A repetition of the experiment gave the following more marked results.

The same cell was refilled and short-circuited for 18 hours, when its force in a circuit of 150,000 S. E. was found E=0·51 D. during the first minutes, it rose gradually, however, and became constant after six minutes at E=0·70 D. On being boiled and covered with petroleum and sealed as before, its force through 150,000 S. E. was found E=1·01 D., it sank, however, in 4 min. to E=0·88 D. in 25 min. to E=0·83 D., and in $2\frac{1}{2}$ hours to E=0·73 D.

Thus it would seem that the value E=0·70 D. represents that force which is active when the liquid immediately around

* C. Fromme, l. c.

the platinum plate is saturated with hydrogen, and the evolution is just equal to the diffusion of the gas into the liquid.

This experiment would seem to show conclusively that the values above E=0·70 D. are not caused by any oxygen which may be dissolved in the acid.

A similar conclusion was reached in a series of experiments where the other gases were removed by leading CO_2 over the acid for a long time. It however appeared that it would cause a difference of as much as 10 per cent in the force of the cell according as the acid was saturated with air or CO_2, it being larger in the former case. Another series of experiments proved that the force of the Smee could be diminished by saturating the platinum plate with hydrogen without depriving the acid of its dissolved oxygen.*

All the above results are opposed to Exner's theory, that these larger values are due to the oxidation of the evolved hydrogen, and rather support the older theory that they are due to the small force of the hydrogen polarization which acts against the true force of the cell.

4. Experiments on the Fall of the Electromotive Force of the Smee Battery.

When the electromotive force of the Smee is measured in a circuit where the resistance is small in proportion to the size of the cell, i. e. when the density of the current on the platinum plate is large, values are obtained which fall decidedly below that of E=0·75 D.

Exner† says, this is due to the formation of $ZnSO_4$ in the cell which has a larger specific resistance than H_2SO_4, and that zinc is precipitated upon the platinum, thus increasing the internal resistance and diminishing the thermal equivalent of the cell.

To test this question a cell was constructed such that the zinc and platinum were in separate vessels connected by an inverted U-tube filled with 5 per cent H_2SO_4, the ends being tied up with parchment paper. The vessel containing the platinum was furnished with a lid so that CO_2 could be conducted through the vessel or it could be shut up air-tight. Owing to the large internal resistance of such a cell, it was not possible to get a very great density of current on the platinum, still its electromotive force fell as low as E=0·31 D. on being short-circuited, and rose again in a long circuit, even when the vessel containing the platinum was filled with CO_2, as high as E=0·92 D., and finally to E=1·07 D. An analysis proved that the liquid

* Compare also here C. Fromme, l. c.

† F. Exner, Wien. Ber., lxxx, 1879 und Wied. Ann., x, p. 265, 1880.

around the platinum did not contain a trace of $ZnSO_4$. It may be here remarked that had all the H_2SO_4 around the zinc become $ZnSO_4$, the consequent increase in the resistance of the cell, either in this case or that of the flask cell of § 3, it would have made a scarcely perceptible difference in the intensity of the current measured.

These results seem to throw us back upon the old explanation, which ascribes the variations in the electromotive force of the Smee battery, to the variations in the counteracting force of the hydrogen polarization of the platinum plate.

5. Determination of the Electromotive Force of Polarization.

The maximum value of this force can be arrived at in two ways, either by measuring it while the primary current is closed, or by plotting the curve of the fall of the force after opening the primary current, and from it deducing by exterpolation, the value for the instant of opening.

Exner* and Beetz† assume that the value obtained immediately after opening the primary current is practically this maximum value. Fromme,‡ on the contrary, says, "if one wishes to obtain the true maximum value, it is absolutely necessary to measure the polarization while the primary current is still closed." I must admit, from my experience, that values could only then be considered as approximating the maximum when they were determined *immediately* after opening the primary current, which it is scarcely possible to accomplish, unless perhaps with an electrometer and switch as before mentioned.

An example will show how rapidly the polarization vanishes. The following is the falling off of the polarization of 5 per cent H_2SO_4 between electrodes of gas-retort carbon.

Time in sec.,	0	2	10	20	30	45	60	120	180	480
Force in Daniell,	1·92	1·77	1·63	1·54	1·49	1·43	1·39	1·28	1·20	1·00

The value for "0" sec. is that calculated by closed primary current.§

Inasmuch as a galvanometer was used for the following determinations the method by closed primary current seemed decidedly preferable and was employed. Two difficulties however, arise when this method is applied. In the first place a

* F. Exner, Wien. Ber., lxxviii, 1878 und Wied. Ann., v, p. 388, 1878.

† W. Beetz, Wied. Ann., x, p. 348, 1880, u. Münch. Ber, p. 429, May, 1880.

‡ C. Fromme, Sep. Abdr. a. d. 20, Ber. der Oberh. Gesellsch. f. Natur. u. Heilk., u. Wied. Ann., xii, p. 399, 1881.

§ The vanishing of polarization has also been studied by Beetz and Witkowski, among others, whose results agree with mine; compare here W. Beetz (Pogg. Ann., lxxix, p. 106, 1850) and A. Witkowski (Wied. Ann., xi, p. 759, 1880.)

branch of the primary current goes to strengthen the current from the polarized voltameter through the galvanometer; in the second place a branch of the secondary current (from the polarized voltameter) goes backward through the primary circuit. That these two currents are weak enough to be neglected only under peculiar and rarely fulfilled conditions is evident as soon as we calculate their strength from the given forces and resistances. Call E the electromotive force of the polarizing (primary) battery and γ the resistance in the primary circuit exclusive of that in the voltameter which we will call w, let W be the resistance in the circuit of the galvanometer (150,000 S. E. or 330,000 S. E.); let further i be the intensity of current in the galvanometer, i' that in γ and i'' that in w and I, that when E is closed through $(\gamma+\mathrm{W})$ alone, i. e. $\mathrm{I}=\frac{\mathrm{E}}{(\gamma+\mathrm{W})}$. If now we call the force of polarization P, we have according to Ohm's laws

$$i=i'-i''; \quad \mathrm{E}=i'\gamma+i\mathrm{W}; \quad \mathrm{P}=-i''w+i\mathrm{W},$$

whence we obtain by substitution and transformation,

$$\mathrm{P}=\frac{\mathrm{W}+\gamma}{\gamma}\,.\,w\,.\,i-\mathrm{E}\frac{w}{\gamma}+i\mathrm{W} \text{ or } \mathrm{P}=(i-\mathrm{I})\frac{\mathrm{W}+\gamma}{\gamma}w+i\mathrm{W}.$$

If in this last equation we neglect $\gamma=100$ at the most, as added to $\mathrm{W}=330{,}000$, we have

$$\mathrm{P}=\mathrm{W}\left[i-\frac{w}{\gamma}(i-\mathrm{I})\right]. \qquad (1)$$

From (1) we see that only when $\frac{w}{\gamma}=0$ can we put $\mathrm{P}=\mathrm{W}.i$, which is very seldom the case, for γ rarely exceeds 5 or 6 S. E. and w varies between 0·3 and 5·0 S. E. I increased the resistance γ to 100 S. E. in order to make $\frac{w}{\gamma}$ smaller and more accurately determinable. All the values of polarization given below were calculated with formula (1).

Inasmuch as these experiments on polarization were undertaken with a view to testing whether we can *a priori* calculate the electromotive force of polarization from the thermal equivalent of the chemical reactions which take place thereby, some side experiments, more or less directly allied to this question, were made. For example, Exner* wishes to approximate the thermal equivalent of the compound $PtCl_4$ out of the difference in the polarization of HCl between platinum and between graphite electrodes, 1·26 D. and 1·60 D.; upon the supposition that all the evolved chlorine in the one case dissolved off platinum to $PtCl_4$. To prove the incorrectness of this supposition

* F. Exner, Wien. Ber., lxxviii, 1878, und Wied. Ann., vi, p. 353, 1879.

chlorine was evolved by a weak current upon a platinum plate until it should have dissolved off 0·176 grm. of platinum, the actual loss in weight of the plate was 0·00007 grm., i. e. there was none dissolved off at all. F. Kohlrausch had already obtained the same result in a similar experiment. In fact it is very difficult to explain the differences which almost always exist between the polarization of the same solution between platinum and between carbon electrodes, if we consider the electrodes as mere conductors, as Exner does, and do not admit that they become electrically excited.

Another experiment was made in which a current was found and measured between one platinum plate saturated with hydrogen and another free from all gases except CO_2, where the force was E=0·68 D. at first, but gradually fell off. There is no apparent thermo-chemical equivalent for this current and the only visible cause for it is the transfer of the hydrogen from the more to the less saturated plate. Beetz* has also shown the electromotive force of polarization between two platinum plates, when one is surrounded with hydrogen, even when the acid had been pumped and boiled out in the most careful manner possible.†

6. Values of the Electromotive Force of Polarization.

The results here obtained are arranged in the tables on the following pages.

In table I, the first column, "electrolyte," gives the solution employed; and the second, "per cent," the percentage of the salt in the solution. Under carbon and platinum are given the values of the polarization; "P," between "gas retort carbon," and bright platinum electrodes (simple surface 8^{sqcm}), where Δ gives the density‡ of the current upon the electrode, 1^{sqmm} taken as a unit, Δ is calculated from the formula $\Delta = \frac{E-P}{(w+\gamma)\,.\,S'}$, where the letters have the same meaning as in formula (1) and S is the surface of the electrode, 800^{sqmm}. The values of "P," the polarization, are, in the cases where the primary current was closed, calculated by formula (1); these values are given under "3 Buns. closed" and "2 Buns. closed," the primary current being furnished by two or three Bunsen cells respectively. Under "open" are given the values determined after opening the primary current, the length of time elapsing until the read-

* W. Beetz, Wied. Ann., x, p. 348, 1880, u. Münch. Ber., p. 429, May, 1880.

† Compare here H. Helmholtz, Ber. Berl., p. 288, 1880; F. A. Flemming, Phil. Mag. V, i, p. 142, 1876; and Helmholtz and Root's. Pogg. Ann., clix, p. 416, 1876.

‡ I unfortunately followed previous examples and kept the electromotive force of the primary circuit constant; whereas it is evident that the only way to obtain results comparable with each other is to keep the density of current on the electrodes constant.

TABLE I.

Electrolyte.	%	Gas Retort Carbon.						Platinum.				Exner.		Newly Calc.
		3 Buns. closed.		2 Buns. closed.		Open.		2 Buns. closed.		Open.				
		Δ	P	Δ	P	Sec.	P	Δ	P	Sec.	P	Obs.	Calc.	
		0·000		0·000				0·000						
H_2SO_4	5	43	2·02	20	1·92	2	1·76	29	1·95	5	1·67	1·42	1·43	1·36
HCl	6	--	----	26	1·54	2	1·45	44	1·33	5	1·16	1·60	1·61	1·57
NaCl	6	38	2·37	16	2·17	2	2·05	28	1·97	6	1·78	2·08	2·06	2·12
NaOH	5	43	1·93	22	1·79	4	1·63	--	----	--	----	----	----	1·36
$NaNO_3$	5	39	2·24	16	2·12	3	1·99	23	2·18	5	1·30	----	----	1·91‡
NaI	5	50	1·48	27	1·43	3	1·36	44	1·24	5	0·97	1·25	1·24	1·07
$Cu(NO_3)_2$	5	54	1·20	31	1·16	1	1·04	40	1·45	6	1·29	1·11	1·09	1·04‡
$CuSO_4$	5	53	1·20	30	1·18	4	1·06	41	1·34	5	0·88	1·13	1·15	1·12
$ZnCl_2$	10	44	1·92	20	1·89	2	1·84	31	1·86	8	1·82	----	----	2·25
$ZnSO_4$	9·8	41	2·07	18	1·99	2	1·90	21	2·26	4	1·88	2·14	2·14	2·12
$MnCl_2$	5	42	2·02*	20	1·91	--	----	30	1·91†	5	1·60	----	----	2·55‡
$MgSO_4$	5	37	2·32	19	1·91	3	1·68	18	2·39	3	1·62	----	----	2·00‡
$AgNO_3$	25	62	0·78	38	0·75	2	0·69	57	0·75	6	0·68	0·42	0·34	0·34‡
$Pb(NO_3)_2$	5	49	1.49	26	1·47	3	1·38	39	1·45	3	1·26†	----	----	1·36‡

* Sank in 20 min. to P=1·88.

† The anode became covered with a brown film.

‡ Values uncertain because one does not know the secondary reactions.

TABLE II.

Substance of the Electrode.	Simple Surface. sq. cm.	H_2SO_4 5%.				HCl 6%.				NaCl 6%.			
		2 Buns. closed.		Open.		2 Buns. closed.		Open.		2 Buns. closed.		Open.	
		Δ	P	Sec.	P	Δ	P	Sec.	P	Δ	P	Sec.	P
		0·000				0·000				0·000			
Platinised platinum	28·6	--	--	6	1·57	09	1·13	5	1·12	06	1·80	2	1·77
Bright platinum	5·3	29	1·95	5	1·67	44	1·33	5	1·16	28	1·97	6	1·78
Gas retort carbon, used	28·0	--	--	5	1·53	--	--	10	1·38	--	--	5	2·05
Electric lamp points, used	2·0	--	--	5	1·48	--	--	7	1·45	--	--	10	2·02
		0·00	--	--	--	0·00	--	--	--	0·00	--	--	
Lead-pencil graphite	1·1	117	2·14	2	1·85	158	1·78	4	1·52	109	2·17	2	1·98
		0·000	--	--	--	0·000	--	--	--	0·000	--	--	--
Retort carbon, old	2·3	67	1·93	4	1·62	84	1·63	4	1·43	--	--	4	1·70
Retort carbon, new, as furnished	8·0	20	1·94	4	1·59	--	--	--	--	--	--	--	--
Retort carbon, new, boiled in HCl	8·0	22	1·81	3	1·52	--	--	--	--	--	--	--	--
Retort carbon, new, boiled in H_2SO_4	8·0	20	1·92	2	1·76	26	1·54	2	1·45	16	2·17	2	2·05

TABLE III.

Electromotive force of the polarizing battery	=1·00 D.	1·72 D.	3·44 D.	5·16 D.	6·88 D.
Density of current in the voltameter (mm, mg, sq. mm.)	=	0·00006	0·00037	0·00073	0·00112
For 5 per cent H_2SO_4 between platinum electrodes	P=	1·46 D.	1·95 D.	2·01 D.	2·07 D.
Density of current in the voltameter (mm, mg, sq. mm.)	=0·000002	0·00006	0·00019	0·00043	0·00067
For 6 per cent NaCl between carbon electrodes	P=0·99 D	1·34 D.	2·17 D.	2·37 D.	2·49 D.

ing from which P was calculated being given under "sec." in seconds. I would here remark, that owing to the difference of rapidity with which the polarization vanishes for different combinations, the quickest time at which it was possible to read off the position of the needle, after opening the primary current, varied from 1 to 5 seconds. In columns 13 and 14 are the values observed and calculated by Exner, and the last column contains the values newly calculated from the thermo-chemical equivalents of J. Thomsen,* which are given in convenient form in a table in the last edition of Richter's Anorganische Chemie. The calculations were made according to the scheme given in Table IV.

TABLE IV.

Daniell.	$ZnSO_4 - CuSO_4$		
	248·4 − 198·3 =	50·1	1·00 D.
H_2SO_4	$H_2SO_4 + H_2O - H_2SO_4$		
	210·7 + 68·3 − 210·7 =	68·3	1·36 D.
HCl	HCl		
	39·3 =	39·3	1·57 D.
NaCl	$NaCl + H_2O - NaOH$		
	96·5 + 68·3 − 111·8 =	53·0	2·12 D.
NaOH	$2NaOH + H_2O - 2NaOH$		
	223·6 + 68·3 − 223·6 =	68·3	1·36 D.
$NaNO_3$‡	$2NaNO_3 + 3H_2O - 2HNO_3 - 2NaOH$		
	212 + 204·9 − 98·2 − 223·6 =	95·5	1·91 D.
NaI	$NaI + H_2O - NaOH$		
	70·3 + 68·3 − 111·8 =	26·8	1·07 D.
$Cu(NO_3)_2$‡	$Cu(NO_3)_2 + H_2O - 2HNO_3$		
	82·2 + 68·3 − 98·2 =	52·3	1·04 D.
$CuSO_4$	$CuSO_4 + H_2O - H_2SO_4$		
	198·3 + 68·3 − 210·7 =	55·9	1·12 D.
$ZnCl_2$	$ZnCl_2$		
	112·8 =	112·8	2·25 D.
$ZnSO_4$	$ZnSO_4 + H_2O - H_2SO_4$		
	248·4 + 68·4 − 270·7 =	106·0	2·12 D.
$MnCl_2$‡	$MnCl_2$		
	128·0 =	128·0	2·55 D.
$MgSO_4$‡	$MgSO_4 + 3H_2O - H_2SO_4 - Mg(OH)_2$ (dry)		
	323·0 + 204·9 − 210·7 − 217·2	100·0	2·00 D.
$AgNO_3$‡	$2AgNO_3 + H_2O - 2HNO_3$		
	46·6 + 68·3 − 98·2 =	8·4	0·34 D.
$Pb(NO_3)_2$	$Pb(NO_3)_2 + H_2O - 2HNO_3$		
	97 9 + 68·3 − 98·2 =	68·0	1·36 D.

Values marked with a (‡) in tables I and IV are uncertain because we do not know what secondary reactions take place, nor do we know, if and to what extent the secondary reactions† affect the polarization. Table II contains the polarization of 5 per cent H_2SO_4, 6 per cent HCl and 6 per cent NaCl, between the electrodes named in the first column; other-

* J. Thomsen, Kolbe's Journ., xi, p. 18 and xii, 1875.

† Compare here, Wiedemann Galvanismus, ii (2), p. 498, § 1130–1146, 1874, on the effect of primary and secondary reactions in voltameters.

wise the abbreviations are to be understood as in Table I. Table III gives the polarization as it increases with the increase of the force of the primary battery from E=1·00 D. to E=4 Bunsen=6·88 D. and will be understood without further explanation. In all cases the force of the Daniell battery was taken as the unit of electromotive force.

7. Conclusions.

Although, as is well-known, the force of polarization in general varies according to the chemical affinities of the elements or radicals separated, still we cannot, yet at least, calculate the electromotive force of polarization from the thermal equivalents of the reactions, because we do not know which of the reactions, primary or secondary, should be taken account of, nor do we know their thermal equivalents. Table I seems to establish what has just been said; in most cases the calculated value is much smaller than the observed one, and the latter is not a true maximum value, but only the largest attainable with two or three Bunsens respectively, in the polarizing circuit. Especially in the case of H_2SO_4 is the difference great, and in fact, if its polarization were only P=1·36 D., as calculated one ought to get a good evolution of gas with two Daniell cells, which, on the contrary were only able to evolve 5^{ccm} in 17 hours instead of the 300^{ccm} which they could have produced had the polarization been only P=1·36 D.

Tables I and II confirm the earlier experiments, showing that the polarization is not independent of the substance of the electrode, even when the latter remains chemically unaffected.

Exner* published a series of experiments to prove that the electromotive force of polarization keeps equal to that of the primary battery, when the latter is increased from zero upward, until it reaches the point where the evolution of gas becomes visible, and that from this point it (the polarization) remains constant, no matter how much we increase the force of the primary battery. This result is contradicted by those given in Tables I and III, inasmuch as with two Bunsens =3·4 D., the evolution of gas was very easily visible.† Exner's results are in so far in harmony with the theory of the conservation of energy as that no one will contend that a weaker electromotive force can overcome a stronger; but Helmholtz‡ has shown for

* F. Exner, Wied. Ann., v. p. 388, 1878.

† The results given in Tables I and III only confirm the previous ideas regarding the dependence of the polarization upon the density of the current upon the surface of the electrode.

‡ Helmholtz, Pogg. Ann., cl. p. 483, 1873: compare also F. A. Flemming, Phil. Mag. V, i. p. 142, 1876; A. Bartoli, Nuovo Cim. III, iv, p. 92, 1878, III, v, p. 203, 1879.

platinum, and from results here obtained it would seem to be true for at least carbon also, that an electromotive force which is theoretically too weak to decompose the solution between the platinum electrodes still does generate a current through a voltameter, which was originally free from all dissolved gases, and polarizes the electrodes, assisted by the occlusion of the evolved gases by the platinum.

It is difficult to explain according to the "chemical theory" why, on closing the primary circuit, the polarization does not immediately reach its maximum value instead of doing so gradually, as is the case. According to the "contact theory" the polarization of H_2SO_4 between platinum electrodes, on closing the primary current, increases gradually until we have a platinum kathode saturated with hydrogen opposed to the anode saturated with oxygen, just as in the polarization of $ZnSO_4$ it increases until we have the kathode covered with zinc, opposed to the Pt | O anode, in other words, until our voltameter has become a Smee cell.

That solutions of HCl and NaCl between the same electrodes give different values of the electromotive force of polarization, Exner considers as an argument against the contact theory, because we have the same gases acting upon the same electrodes. The reason, however, is evident. In the one case the series acting is

$$\text{Pt} \mid \text{H}+\text{H} \mid \text{HCl}+\text{HCl} \mid \text{Cl}+\text{Cl} \mid \text{Pt}. \qquad (1)$$

and in the other case

$$\text{Pt} \mid \text{H}+\text{H} \mid \text{NaOH}+\text{NaOH} \mid \text{NaCl}+\text{NaCl} \mid \text{Cl}+\text{Cl} \mid \text{Pt}. \qquad (2)$$

That these two series should not give the same electromotive force is what one would expect.* A test experiment, however, gave the following equation,

$$\text{Pt} \mid \text{NaOH}+\text{NaOH} \mid \text{NaCl}+\text{NaCl} \mid \text{Pt} = 0{\cdot}39 \text{ D}.$$

and furthermore it gave no difference in the polarization when the kathode as well as the anode was surrounded with NaCl solution, and when the vessel containing the kathode was filled with NaOH solution, thus showing that series (2) really represents the forces acting in the polarization of NaCl solution between platinum electrodes.

The secondary reactions in some cases must be very peculiar; for example in the electrolysis of a solution of $MnCl_2$ there was no chlorine gas evolved, and the anode became covered with a brownish-red film insoluble in H_2O, H_2SO_4 or dilute HCl, but concentrated HCl dissolved it off to a reddish-brown solution which gave off quantities of free chlorine. The chlorine had

* Aryton and Perry, Trans. Roy. Soc., i. p. 34, 1880; Helmholtz, Wied. Ann., iii, p. 201. 1878; F. Moser, ibid., p. 216; and E. Kittler, Wied. Ann., xii, p. 577, 1881.

apparently simply added itself to the $MnCl_2$, thus forming a higher chloride of manganese.

Adolfo Bartoli* in an interesting research on polarization proceeds as follows. A very strong battery (400 zinc-carbon cells) is closed a very short time (0·004 sec.) through the voltameter, and the polarization calculated from the first elongation of the galvanometer needle, as a function of the amount of transmitted electricity. All the connections were made and broken automatically. He finds for the following combinations the following maximum values.

Platinum electrodes and

H_2O	HCl	HBr	HI
2·00 D.	1·30 D.	0·94 D.	0·58 D.

The values calculated from the thermal equivalents are

1·36 D.	1·57 D.	1·13 D.	0·52 D.

These values of Bartoli's agree with those given in Table I, but not at all with the calculated ones, so that we cannot calculate the polarization from the thermo-chemical equivalents, even under these circumstances.

Conclusion.

The result of this research may be summarized in the four following propositions. 1. The generally accepted explanation of the variations of the force of the Smee battery, which ascribes them to the variations of the hydrogen polarization of the platinum plate, must still be looked upon as correct. 2. The electromotive force of polarization is by no means independent of the substance of the electrodes. 3. We can not calculate the polarization from the thermo-chemical equivalents. 4. The electromotive force of polarization can be raised considerably above that necessary to produce a visible evolution of gas and the former results upon this question are confirmed.†

* Adolfo Bartoli. Il Nuovo Cim. III, vii. p. 234. 1880.

† Compare Wied. Galv., i. p. 681, 1874.