LII. On the measurement of temperatures by thermo-electric currents

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LII. *On the Measurement of Temperatures by Thermo-electric Currents.* By M. REGNAULT*.

[With a Plate.]

IT is known, from the beautiful discovery of Seebeck, that when a closed circuit is formed with two plates of different metals soldered at their extremities, and that the temperature of one of the junctions is raised, an electric current is formed, which is in general the more intense the greater the difference of temperature at the two places of soldering. Philosophers immediately sought to turn this property to account for measuring temperatures.

As we possess extremely delicate apparatus, by means of which, to a certain point, the weakest currents may be detected and measured, while on the other hand the metallic plates forming the circuit may be replaced by wires of very small diameter, exceedingly small thermoscopic apparatus, capable of demonstrating the feeblest variations of temperature, have been constructed. Every one is aware of the advantage which MM. Becquerel and Breschet have derived from these apparatus in measuring the differences of temperature exhibited by the several parts of the human body, and the beautiful results which Melloni obtained with his thermo-electric pile in his researches on radiant heat.

M. Pouillet has used the same principle for the measurement of high temperatures†; and he has described, under the name of magnetic pyrometer, an apparatus which is compared with his air pyrometer, and by means of which he states that he is able to measure the highest temperatures of our furnaces.

* Extracted from his *Recherches sur la Chaleur*. This is the memoir of which we promised to give a full translation in our former notice of M. Regnault's experiments, p. 56 of the present volume.—ED.

† *Elémens de Physique*, 4th edit. vol. ii. p. 684. *Comptes Rendus*, vol. iii. p. 786.

The employment of thermo-electric couples for measuring temperatures would, under many circumstances, present such great advantages over the ordinary processes, especially when it is desired to determine temperatures within limited spaces, that I have frequently devoted attention to this subject; but I must confess, that, notwithstanding the very numerous and varied experiments which I have made, my researches have met with little success, and I have not been able to obtain a comparable instrument whose indications might at all times inspire confidence. There is such instability in the molecular conditions which determine the thermo-electric currents, that we are never certain of obtaining a current of constant intensity when the two solderings are raised at repeated intervals to the same temperatures; the variations are especially considerable when, during the interval, the apparatus has been heated to very different temperatures.

The instrument which is used for determining the intensity of currents is far from presenting the perfection which is necessary in accurate investigations, especially if these intensities vary considerably, as happens when thermo-electric currents are employed for the measurement of temperatures.

The intensity of electric currents is measured, either by the deflexions which they produce upon a freely suspended magnetic needle, or by the chemical decompositions which they effect. The second method, which is of great importance for the measurement of powerful currents, is inapplicable in the case of thermo-electric currents, which are always very feeble, and present too little after resistance to overcome the least obstacles introduced into the circuit.

The only instruments which have hitherto been employed for measuring thermo-electric currents, are based, therefore, on the deviations which these currents impress on the magnetic needle; they are the galvanometer and the sine compass.

The galvanometers with two partially compensated magnetic needles are most suited for measuring very weak currents; they appear, consequently, to be adapted principally for thermo-electric currents. Unfortunately, the deviations of the needles are not proportional to the intensity of the currents except between very restricted limits; and for somewhat considerable deflexions, it is necessary to construct a table in which the intensities corresponding to the observed deviations are found. The direct construction of this table would not be a matter of any moment if the same table were of service for any time; but experience has shown, that in a system of two partially compensated needles, the magnetic intensity

varies somewhat considerably, owing to circumstances which it is impossible to foresee and guard against, so that it is necessary to make this table very frequently. Frequently in the midst of a series of experiments a perceptible alteration may occur, and the experimenter is always uneasy on this point. Moreover, the sensitiveness of the galvanometer decreases rapidly with the amplitude of the deviations; and it must not be used to measure deviations of more than 60° , because beyond that limit the indications of the instrument become very uncertain.

A part of these inconveniences is obviated in the apparatus to which M. Pouillet has given the name of sine compass. In this instrument the needle is simple, and its magnetic axis is always placed so that it shall coincide with the direction of the current; the intensities of the current are then proportional to the sines of the angles which the magnetic meridian forms with the direction of the axis of the needle. To be convinced at any time of the identity of the measuring apparatus, it suffices to pass through the wire a current of constant intensity, and easily producible always of the same strength; if the needle indicates the same deflexion, we are certain that the apparatus has remained comparable.

The sine compass should not be employed to measure currents which produce deflexions of more than 50° to 60° ; because beyond these limits the sines increase but very slowly for considerable variations of the arc, and the compass becomes useless. Thus all the measures on the sine compass should be comprised between 0° and 60° , and correspond to the intensities of the thermo-electric current between the limits of temperature which it is desired to measure. It thence results, that if we wish to determine elevated temperatures, it is requisite to be content with somewhat weak deviations for a difference of 100° , and the apparatus becomes not very sensitive. Thus, in the magnetic pyrometer of M. Pouillet, the compass indicated a deviation of 4° to 5° for a difference of temperature of 100° of the two solderings of the thermo-electric element. It is true, that, by giving a sufficiently large diameter to the divided circle, and observing the deviation with the assistance of a vernier, the subdivision of the degree may be carried as far as wished; and it is easy, if the divided circle has a diameter of 10 to 15 centimetres, to appreciate angles of $1'$. The deviation produced by a difference of temperature of 100° would consequently be measured to within $\frac{1}{300}$; that is to say, with more than sufficient accuracy. Unhappily, the magnetic needle is far from exhibiting any such sensitiveness. In the ordinary compasses the needle is supported on a pivot; and

with whatever care the bearing and the pivot have been worked, it is impossible to give to the needle a sufficiently great mobility to cause it to obey the feeble variations in the intensity of the current. It is necessary to give the instrument a few shakings to overcome the inertia of the needle; and the direction in which it stops, after having removed it from its position of equilibrium, varies very perceptibly, although the current always preserves the same intensity. Thus, in a perfectly constructed compass with an agate bearing, on which I have experimented, the uncertainty amounted to $\frac{1}{2}^{\circ}$, which consequently gives an uncertainty of 10° per cent.

Much greater mobility is given to the needle by suspending it to a cocoon thread; but then other inconveniences arise, which occasion similar uncertainty. The accurate centring of the needle becomes difficult; it may perceptibly vary during the course of the experiments; the extreme mobility of the needle causes it to oscillate constantly around its position of equilibrium; it is difficult to alter the direction of the current, so that it coincide with that of the magnetic axis of the needle; and if the temperature which it is desired to measure is not absolutely stationary for a pretty long time, it becomes almost impossible to make an observation at the suitable moment. In all cases the measurement of the deviations presents great uncertainty, unless we have much time at our disposal to adjust the apparatus.

If the instrument is not to be employed to measure very high temperatures, but is merely to be used between 0° and 400° Cent., it may be arranged so as to obtain for a difference of temperature of 100° of the two solderings a deflexion greater than 5°. However, this is not always easy when it is desired to use but a single couple, and not to have recourse to a pile composed of several elements; when, moreover, this couple cannot be formed of those metals which produce the most powerful currents, as bismuth and antimony, on account of their great fusibility. Greater deflexions, it is true, are obtained by increasing the number of the convolutions of the wire which act upon the needle; but this increase has a limit, because the wires should possess great conductivity for thermo-electric currents, and consequently present a considerable diameter.

Any degree of sensibility may be obtained by substituting for the simple needle a system of two partially compensated needles; but then we meet with the same inconveniences as the galvanometer presents, especially those dependent on the magnetic alteration of the system. I have made numerous experiments with compasses arranged in this manner, but the

extreme mobility of the needles renders the manipulation very difficult.

The difficulties which are met with in the accurate measurement of the intensities of thermo-electric currents by the galvanometer and sine compass, induced me to seek for a process of measurement which was wholly independent of those instruments; and I think I have succeeded by the following method, which appears to me susceptible of successful application to the study of the laws of thermo-electric currents.

I constructed an element of bismuth and antimony composed of two bars, ABCD, Plate I. figs. 1 and 2, cast in the same mould. These two perfectly similar bars are juxtaposed throughout their extent and kept separate by a blade of ivory; they only touch at the two extremities, A and D, where the two solderings are. The length BC is 20 centimetres, the vertical pieces ABCD are 12 centimetres. This element of bismuth and antimony is the *normal element*, with which I compare all the other thermo-electric elements, but it should not be used for temperatures exceeding 30° .

The element destined for high temperatures is formed of an iron wire and a platinum wire of 1 millimetre in diameter; the extremities of these wires are soldered with silver. The iron wire, EfF, fig. 4, is about 80 centimetres in length; the two platinum wires, Ec, Fd, are fixed near to the iron wire, from which they are isolated by a non-conducting envelope. In their lower portion these wires are separated by a plate of thin glass. They are terminated by two brass appendages, c and d, which allow of the introduction of a galvanometric apparatus into the circuit.

The two junctions, E and F, are kept in glass tubes filled with a fixed oil containing no oxygen. One of these tubes is placed in the oil-bath mentioned in a former part of this work (p. 57), by the side of a mercurial thermometer extending from 0° to 350° . In some experiments an air-thermometer placed in the bath was employed. The tube which contained the second junction is kept at a constant temperature by means of melting ice, or placed in a great water-bath alongside the mercurial thermometer.

The normal element of bismuth and antimony, ABCD, figs. 5 and 6, is arranged in such a manner that the two solderings, A and D, dip into two vessels, MN, M'N', filled with water at different temperatures, and separated from each other by a partition, SR. The same agitator, FGF'G', serves to agitate at the same time the water in both vessels, and two very accurate and strictly comparable thermometers, T and T', are placed near the two solderings. These thermometers

Fig. 1.

Fig. 2.

Fig. 5.

Fig. 3.

Fig. 4.

Fig. 6.

are the same as those used in my calorimetric experiments: each centigrade degree is divided into eighteen divisions, so that the differences of temperature of the two solderings can be measured with extreme accuracy.

Lastly, a very sensitive differential galvanometer completes the apparatus. This galvanometer has a system of two little compensated needles, to which is fixed a long hollow glass rod drawn out very fine. The extremity of this rod, which is blackened, moves on a divided quadrant 15 centimetres in diameter; it is observed by means of a telescope. The quadrant is divided into quarters of a degree; and it is very easy to appreciate deviations of $\frac{1}{8}$ th, and even of $\frac{1}{10}$ th of a degree. The sensitiveness of the galvanometer is such, that a difference of temperature of 1° in the two solderings of bismuth and antimony produces a deflexion of the needle of 17° .

The galvanometer is connected with the iron and platinum circuit by one of its wires, and with the bismuth and antimony circuit by its second wire.

With this arrangement, the junction of the iron and platinum, E, being maintained at a constant temperature t , if the junction F be raised to a temperature T' measured on the thermometer of the oil-bath, a current will result which will deflect the needle of the galvanometer; but by suitably raising the temperature of one of the solderings of the bismuth and antimony element, a second current, the inverse of the first, will be obtained, by means of which that may be neutralized and the needle of the galvanometer restored to 0. The temperatures θ and θ' , which the two thermometers T and T' indicate at the moment of neutralization, are noted down.

Thus a difference of temperature, $T' - t$, between the two solderings of the iron and platinum, produces a current which is neutralized on the galvanometer by the current developed in the bismuth and antimony element by a difference of temperature $\theta' - \theta$. This difference of temperature, $\theta' - \theta$, is moreover much smaller than $T' - t$, because the electromotive force of the bismuth and antimony element is incomparably greater than that of the iron and platinum element, for with $T' - t = 100$ we have $\theta' - \theta = 6^\circ.5$.

If the oil-bath be raised to the temperature T'' , θ' must be raised to θ'' in order to maintain the needle of the galvanometer at 0° . By continuing in the same manner, we obtain a series of temperatures $T' - t$, $T'' - t$, $T''' - t$, &c., which will produce on the iron and platinum element currents which will hold *in equilibrio* on the galvanometer the currents produced on the bismuth and antimony element by the differences of temperature $\theta' - \theta$, $\theta'' - \theta$, $\theta''' - \theta$, &c. If, consequently,

the two thermo-electric elements remain comparable, it will suffice once for all to form a table, in which are inscribed on one side the differences of temperature, $T'-t$, $T''-t$, $T'''-t$, of the iron and platinum element measured upon an air-thermometer, and on the other side the differences of temperature, $\theta'-\theta$, $\theta''-\theta$, $\theta'''-\theta$, of the bismuth and antimony element.

If it is now desired to measure a high temperature with the iron and platinum couple, it will suffice to look out the temperature, $\theta'-\theta$, which equilibrates it on the couple of bismuth and antimony; and we shall find in the table, the construction of which I have described, the temperature $T-t$ corresponding to it on the element of iron and platinum.

This method is entirely independent of the measuring apparatus. The magnetic state of the needle may vary without any inconvenience resulting, as it will be modified in the same manner for the two thermo-electric elements. The sole indispensable condition is, that the two elements should always remain perfectly comparable, and experiment will readily decide whether this condition is satisfied.

I shall not transcribe here the numerous experiments which I have made by this method, but shall content myself with relating in detail one of the series, and shall merely give the results of some others in order that the progress of the observations may be judged of.

First Series.

Iron and platinum element.		Bismuth and antimony element.		Differences of temperature.	
Soldering cold. t .	Soldering hot. T' .	Soldering cold. θ .	Soldering hot. θ' .	Iron and platinum. ($T'-t$.)	Bismuth and antimony. ($\theta'-\theta$.)
21.13	100.10	18.12	23.06	78.97	4.94
21.14	100.10	18.11	23.05	78.96	4.94
21.05	100.10	18.13	23.06	79.04	4.93
21.04	116.15	18.08	24.14	95.11	6.06
21.05	116.25	18.12	24.19	95.20	6.07
21.15	152.70	18.04	26.24	131.55	8.20
21.18	153.25	18.11	26.40	132.07	8.29
21.18	161.45	18.08	26.47	140.27	8.39
21.01	161.50	18.12	26.64	140.49	8.52
21.23	174.36	18.07	27.54	153.13	9.47
21.27	174.31	18.12	27.65	153.04	9.53
21.12	205.43	18.08	29.00	184.30	10.92
21.27	205.38	18.13	29.02	184.11	10.89
21.12	246.32	18.08	30.59	225.15	12.51
21.21	246.32	18.11	30.65	225.11	12.54
21.23	279.89	18.10	31.52	258.66	13.42
21.39	279.59	18.13	31.61	258.21	13.48
20.98	304.40	18.11	32.32	283.42	14.21
21.04	304.05	18.12	32.28	283.01	14.16
21.20	303.45	18.14	32.22	282.25	14.08

Second Series.

Third Series.

Fourth Series.

Differences of temperature.		Differences of temperature.		Differences of temperature.	
Iron and platinum solderings. ($\theta' - t.$)	Bismuth and antimony solderings. ($\theta' - \theta.$)	Iron and platinum solderings. ($\theta' - t.$)	Bismuth and antimony solderings. ($\theta' - \theta.$)	Iron and platinum solderings. ($\theta' - t.$)	Bismuth and antimony solderings. ($\theta' - \theta.$)
22.56	1.60	46.29	3.18	84.33	5.46
39.59	2.91	46.22	3.21	84.18	5.45
39.55	2.96	19.62	1.08	124.91	7.85
84.17	5.69	19.47	1.06	124.93	7.83
83.90	5.64	82.05	5.18	183.36	10.64
83.82	5.65	81.87	5.19	183.26	10.64
81.11	5.36	101.37	6.37	239.14	12.65
81.06	5.45	101.97	6.49	239.39	12.67
90.04	6.24	131.07	8.07	280.15	13.88
103.66	6.88	132.35	8.16	280.80	14.02
102.29	6.85	178.23	10.38		
127.30	8.99	177.89	10.42		
126.90	9.03	147.30	9.04		
153.79	10.56	147.47	9.04		
153.59	10.58	163.53	9.82		
174.48	11.70	163.78	9.87		
204.28	12.94	199.65	11.53		
204.07	12.87	199.98	11.65		
235.30	13.94	226.36	12.68		
234.97	13.86	225.89	12.71		
259.22	14.61	249.45	13.50		
259.37	14.55	250.05	13.61		
283.74	15.28	278.31	14.61		
282.40	15.13	278.36	14.61		

I have represented graphically the results of these experiments. To do this easily I took for ordinates the differences of temperature of the iron and platinum junctions divided by 3, and I took for abscissæ the differences of temperature of the bismuth and antimony junctions multiplied by 5.

The conditions being apparently identical in these several series of experiments, the corresponding curves ought to be susceptible of being superposed : but such is not the case ; in some instances the curve exhibits a very satisfactory regularity throughout its extent ; in other cases, on the contrary, and without its being possible to ascertain the cause, there is a sudden leap at a point, and the second portion of the curve no longer agrees with the first : very rarely the curves furnished by two series of experiments approach sufficiently for the differences to be attributed to errors of observation, and the two curves to be considered as the expression of the same phenomenon.

These variations are probably owing to changes which take place in the molecular condition of the metals at the place of the solderings, and which suffice to modify perceptibly the electromotive forces. Sometimes these changes come on sud-

denly in the midst of a series of experiments, they then produce the leaps which are observed in the curves; in other cases, on the contrary, the alterations are but slowly effected, and they are only detected by causing the elements to pass through the same temperatures.

I thought it might perhaps be possible to cause these irregularities to disappear by avoiding the small quantity of solder which joins the two metals*, and by giving a great section to the worst conducting element. For this purpose I constructed the element represented in fig. 3. A hollow iron tube was curved while red-hot in the direction ABCD; the upper portion of this tube was filed away so as to convert the portion BC into an open channel. The extremities A and D were hammered while red-hot in order to cause the interior aperture to disappear almost entirely, and in it was incorporated, at a white welding heat, two platinum wires of one millimetre in diameter. These wires are placed in the interior of the hollow tubes AB and CD; and to isolate them from the iron sides, they were covered with glass tubes; they terminate in two brass binding-screws, *a*, *b*, situated the one alongside the other, and by means of which the element is brought into connexion with the galvanometer.

This new thermo-electric element was arranged in the apparatus in the same manner as in the preceding experiments; the portion which dipped into the bath was kept in a tube full of oil. I will here give the results of some experiments.

Fifth Series.

Sixth Series.

Differences of temperature.		Differences of temperature.	
Iron and platinum solderings. ($T' - t$.)	Bismuth and antimony solderings. ($\theta' - \theta$.)	Iron and platinum solderings. ($T' - t$.)	Bismuth and antimony solderings. ($\theta' - \theta$.)
96·76	6·24	120·88	9·21
96·32	6·25	120·86	9·20
163·52	9·75	114·31	8·70
163·69	9·71	113·21	8·65
179·94	10·38	158·87	11·69
179·41	10·43	158·94	11·69
217·99	12·01	150·77	11·37
217·16	11·88	151·13	11·36
268·64	13·71	186·71	13·40
270·02	13·65	186·81	13·52
269·89	13·50	216·93	15·15
274·76	13·61	217·07	15·31
273·46	13·55	268·77	17·87
		268·66	17·77
		285·75	18·08
		285·72	18·03

* In the elements employed for the preceding experiments, the two wires of iron and platinum were soldered with silver, but the quantity of silver was inappreciable.

Seventh Series.

Differences of temperature.		Differences of temperature.	
Iron and platinum solderings. ($T' - t.$)	Bismuth and antimony solderings. ($\theta' - \theta.$)	Iron and platinum solderings. ($T' - t.$)	Bismuth and antimony solderings. ($\theta' - \theta.$)
103.80	8.27	221.60	15.75
103.40	8.23	282.18	18.41
117.92	9.08	281.46	18.51
117.96	9.30	149.77	12.36
117.96	9.29	148.97	12.30
152.19	11.64	195.67	15.01
152.29	11.69	195.31	14.97
189.69	13.99	268.76	18.76
188.91	14.00	268.56	18.60
221.95	15.72	268.06	18.55

I represented by the graphic method the results of these new experiments as I had done for those of the first. I ascertained thus that the three curves could not be superposed, but that nevertheless they exhibited less considerable deviations than those of the first four series.

In the second series the oil-bath was allowed to cool after the observation made at 281° , without disturbing any portion of the apparatus, and the experiments recommenced when the temperature of the bath had descended to 140° . It should be observed, that the portion of the curve corresponding to this second period does not agree with that which is given of the first, and nevertheless the apparatus had undergone no change.

I have made numerous experiments on the bismuth and antimony couple in order to ascertain whether these irregularities were not principally due to that couple; but by varying the temperature of the junctions between the limits which had been attained in the preceding experiments, viz. from 15° to 33° , I found that the bismuth and antimony element remained pretty constant. I observed that a difference of temperature of 1° between the two solderings produced sensibly the same deflexion of 17° on my galvanometer, whatever was their absolute temperature, provided it always remained comprised between the limits above indicated. But it is difficult to decide whether this proposition is exact, or merely approximate, because the intensity of the current varies perceptibly with the time, even when the two junctions constantly present the same difference of temperature; and there always remains a little uncertainty as to the value of the deflexion which should be inscribed.

But I found, contrary to the opinion generally admitted, that an increase of 1° in the difference of temperature of the

two junctions of the bismuth and antimony element develops an electromotive force, weaker in proportion as the difference of temperature is greater, even between the limits 15° and 35° .

This result is easily verified in the following manner. The bismuth and antimony element being arranged in the two vessels full of water, as in fig. 6, and in communication with the galvanometer, the needle is brought to zero by raising the water of the two vessels to exactly the same temperature; a certain quantity of hot water is then poured into one of the vessels, so as to produce precisely a difference of temperature of 1° between the two solderings. The deflexion n of the needle is noted down.

After this a very feeble and perfectly constant hydro-electric current is passed through the second wire of the differential galvanometer: the needle is deflected a certain quantity by this current, but it is brought back to zero by suitably raising the temperature of one of the bismuth and antimony junctions. The two currents then hold each other *in equilibrio*. The temperature of the same junction is raised 1° , whence results a deflexion of the needle, which is precisely equal to the deviation n previously observed, if the electromotive force developed by an increase of 1° in the difference of temperature is the same whatever that difference may be.

By passing in this manner successively stronger and stronger constant hydro-electric currents through the second wire of the galvanometer, and neutralizing them each time by a suitable difference of temperature between the two solderings of the thermo-electric current, I found that the electromotive force developed by an increase of 1° of difference of temperature was the more feeble as that difference was greater. The thermo-electric element formed of wires of iron and platinum is not the only one which I have experimented with at high temperatures; I likewise made some trials with elements composed of other metallic wires. But the element of iron and platinum has proved to be most suitable; it is that the electromotive force of which decreases least with the elevation of the temperature.

The sensitiveness of a couple of iron and copper decreases very rapidly with the temperature. At about 240° an elevation of 20° to 30° no longer exerts any influence upon the needle, which remains perfectly stationary: the needle retrogrades when the temperature is raised higher; and the intensity of the current, far from increasing with the temperature, now decreases. This observation agrees with what M. Becquerel long ago observed on a couple of iron and copper. According to that able philosopher, the current is even esta-

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blished in a direction contrary to its primitive one when the element of copper and iron is heated in the flame of a spirit lamp*.

I have likewise on several occasions made experiments on thermo-electric currents by interposing variable resistances in the circuit, so as to maintain the needle of the galvanometer at a constant deflexion for the different temperatures communicated to the solderings. For that purpose, I employed sometimes Prof. Wheatstone's rheostat, sometimes a simple metallic wire strung by a weight, and of which I inserted different lengths in the circuit; but I thus obtained much more variable and uncertain results than by the method above described. I added in this manner to anomalies produced by the thermo-electric elements themselves those due to the irregularities of the conductivity of the resisting wires, which will always render this method very uncertain for the study of feeble electric currents.

To conclude, if the numerous experiments which I have made on the thermo-electric currents do not demonstrate that these currents cannot in future be employed for the measurement of temperatures, they at least show that we are still far from being acquainted with all the circumstances which exert influence on the phenomenon, and of being able to establish the conditions in which the thermo-electric elements ought to be placed so that the intensities of the currents may depend solely on the temperature.

LIII. *On the Hail Storm of May 5, 1850, as observed at the Kew Observatory.* By Mr. W. R. BIRT†.

To Richard Taylor, Esq.

MY DEAR SIR,

Kew Observatory, Old Deer Park,
Richmond, Surrey, May 14, 1850.

BY permission of the Committee of the Kew Observatory of the British Association for the Advancement of Science, I annex a record of observations made at Kew on the Hail Storm of May 5, 1850, and beg to add my views of the phenomena.

"At half-past 5 in the afternoon, on May 5, 1850, my attention was arrested by a very heavy and dark collection of clouds (*cumuli*) in the N.E., from which rain was falling in the distance. The appearance of the clouds was very black and threatening. Below this black collection, which occupied a

* *Ann. de Chim. et de Phys.*, vol. xxxi. p. 385.

† Communicated by the Author.