

number of observations on the temperature of the sea and air have been collected and published by the Government of the United States of America. From these observations the result has been deduced that the difference of temperature between the two hemispheres is insensible, and probably slightly in favour of the higher mean temperature of the hemisphere which possesses the largest water-covering\*. In this way my theoretical views have been fully confirmed by the crucial test of leading to conclusions which did not seem likely to be true at the time I originally placed them on record.

Some further illustrations of the question under consideration may be obtained from the results of observations on the distribution of a well-known class of plants. The conditions most favourable to the growth of the larger ferns were recognized by Robert Brown and other eminent botanists to be humidity, shade, and uniformity of moderately elevated temperature. These conditions exist in their most perfect form among the smaller islands of the great oceans. In islands like New Zealand and others of inferior size the tribes of plants alluded to are widely spread and highly developed. The relative distribution of these plants in the northern and southern hemispheres is highly instructive. The extratropical regions of the northern hemisphere contain thirteen times as much land as the corresponding portion of the southern hemisphere, and in the latter arborescent ferns are known to grow much further from the equator than in the former.

Professor Lindley remarked long since that at the time of the deposit of the Lias formation, a geological epoch of somewhat higher general temperature than the present, the vegetation was similar to that of the southern hemisphere in the Pines as well as in the Cycads.

LIII. *On Retardation of Chemical Change.* By JOHN J. HOOD, D.Sc. (Lond.), Assoc. Royal School of Mines†.

IN a short paper published in this Journal‡ some time ago, on Retardation of Chemical Action, it was shown that

\* Dr. J. Hann has published in the Proceedings of the Academy of Vienna a good résumé of the facts as to the distribution of temperature in the two hemispheres of the earth, and he concludes that their temperatures are almost equal. See Ferrel, *American Journal of Science*, August 1882, page 89, "The Relative Temperature of the two Hemispheres of the Earth."

† Communicated by the Author.

‡ Phil. Mag. [5] xiii.

the rate at which ferrous-sulphate solution is oxidized by potassic chlorate is retarded in a remarkable manner by the addition of various sulphates. The principal results obtained were these—that the amount of such retardation is proportional to the quantity of the sulphate added, and that certain groups of analogous sulphates produce, for equal weights, the same retardation-effect. For instance, equal weights of the sulphates of sodium, potassium, and ammonium were found to produce the same amount of retardation; so also did the potash- and ammonia-alums; whereas the sulphates of zinc and magnesium, although classed together as analogous salts in the same sense as those of the alkali metals, produced different retardations. The natural inference that was drawn from these experiments was, that the study of retardation might afford a means of classifying chemical substances on a dynamical basis, and of determining for each salt or group of salts a numeric, the coefficient of retardation, of a character somewhat similar to what Mills\* has termed the “bergmannic” of a salt. Owing to the small number of soluble sulphates that can be employed in the above reaction for studying their retardation-effects, it is very limited in its application; consequently search was made for other reactions that could be employed for the same purpose, of such a nature that nitrates or chlorides could be experimented with. Of the several reactions that were tested for this purpose, it was found that the oxidation of ferrous chloride by potassic chlorate was by far the best, being analogous in all respects to that of the oxidation of ferrous sulphate, and capable of being rendered as quick or as slow, by alteration of conditions, as might be necessary for the purpose in view; besides, the list of soluble chlorides whose retardation-effects could be studied is a comparatively large one. The results, however, that have been obtained with these salts are such as have modified somewhat the author’s original notions concerning retardation and the molecular movements that are generally supposed to take place in a system undergoing chemical change.

It has been usual, in establishing the formulæ that are employed in the study of the rate of chemical change, to ignore the fact that the products of the reaction, however inactive they may be in the chemical sense, may retard the rate of the change considerably. In the experiments with ferrous sulphate referred to, it was shown that the introduction of so small a quantity as one gram of the sulphates of the alkali metals in 260 cubic centims., the volume of the experimental

\* *Phil. Mag.* [5] i.

solution, caused the oxidation to progress at a rate 10 per cent. less than when no such salt was added ; an effect which might be produced even to a much greater extent by the products gradually formed during the course of any chemical change, especially where the quantities of material in unit volume are comparatively large, as, for instance, in the many cases of etherification that have been studied dynamically during the last few years, and might consequently vitiate somewhat the inferences drawn from such experiments.

As it was found in the experiments alluded to that the amount of retardation was proportional to the amount of the sulphate added, it would naturally be supposed that the products formed during a reaction would produce a retarding or accelerating effect (for the latter is possible, as these experiments show) proportional to their quantity ; and it is easy on this hypothesis to introduce this effect into the equations.

Suppose in a chemical system undergoing change there are  $n$  different bodies taking part in the reactions, and the measurements that are made of the progress of the change relate to one of these  $n$  bodies. Let  $A_1, A_2, \dots A_n$  be the initial quantities of the active substances, and at time  $t$  from the commencement of the change  $\alpha_1, \alpha_2, \dots \alpha_n$ , the quantities of these that have become chemically inactive members of the system, and let the measurements that are made relate to the body  $A_k$ . At time  $t$  the quantities of these substances that are still capable of reacting one with the other will be  $A_1 - \alpha_1, A_2 - \alpha_2, \dots A_n - \alpha_n$  ; and the inactive products resulting from the changes that have taken place will be  $\alpha_1 + \alpha_2 + \dots \alpha_n$ . Then, on the usual hypothesis that the amount of change that takes place in unit of time with regard to any one of these bodies,  $A_k$ , is proportional to the product of the active substances, and that the retardation- or acceleration-effect of the products of the reaction is proportional to their amount, the equation representing this would be written

$$\frac{d\alpha_k}{dt} = \mu \frac{(A_1 - \alpha_1)(A_2 - \alpha_2) \dots (A_n - \alpha_n)}{B \pm (\lambda' \alpha_1 + \lambda'' \alpha_2 \dots \lambda^n \alpha_n)}, \quad \dots (1)$$

where  $\lambda', \lambda'',$  &c. are the coefficients of retardation or acceleration of  $\alpha_1, \alpha_2,$  &c., and  $\pm$  is taken according as these effects are all of the first or of the second character. The nature of the effect of each individual product  $\alpha_1, \alpha_2,$  &c., whether  $\pm$ , could be determined experimentally by adding a considerable quantity, and noting the difference in the rate of

such an experiment and of one where no such substance is present excepting what is formed during the reaction.

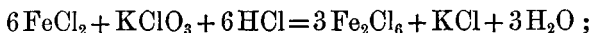
If the initial quantities  $A_1, A_2, \dots A_n$  are in equivalent proportions, they may be expressed in terms of  $A_k$ , thus  $A_1 = \epsilon_1 A_k \dots A_n = \epsilon_n A_k$ . But suppose for the most general case that they are multiples of these quantities, or  $A_1 = \nu_1 \epsilon_1 A_k \dots A_n = \nu_n \epsilon_n A_k$ ;  $\alpha_1, \alpha_2, \dots \alpha_n$ , however, are always in equivalent proportions, or  $\alpha_1 = \epsilon_1 \alpha_k \dots \alpha_n = \epsilon_n \alpha_k$ . Substituting these values, (1) becomes

$$\frac{da_k}{dt} = \frac{\mu(\nu_1 \epsilon_1 A_k - \epsilon_1 \alpha_k) \dots (A_k - \alpha_k) \dots (\nu_n \epsilon_n A_k - \epsilon_n \alpha_k)}{B \pm \alpha_k(\lambda_1 \epsilon_1 + \lambda_2 \epsilon_2 \dots + \lambda_n \epsilon_n)}.$$

Writing  $A_k - \alpha_k = y$ , the amount of  $A_k$  that remains active at time  $t$ , and  $\frac{d\alpha_k}{dt} = -\frac{dy}{dt}$ . This equation may be written in the form

$$\frac{dy}{dt} = -\frac{ay\{(v_1-1)A+y\}\{(v_2-1)A+y\}\dots\{(v_n-1)A+y\}}{b \mp y}. \quad (2)$$

The reaction under consideration (the oxidation of ferrous chloride by potassic chlorate) is represented by the equation



and consists of a system of three active members, in which the iron, or  $y$ , was made the subject of measurement. In the preliminary experiments that were made, the ratios of the chlorate and acid to the iron were varied, in order to find the quantities, and consequently the rate, of the oxidation most suitable for bringing out the retardation-effects of the chlorides. Some experiments were made with all three materials in equivalent quantities which would be represented by the equation

$$\frac{dy}{dt} = -\frac{ay^3}{b \mp y}.$$

But such conditions were unsuitable; for the experiments showed, as is evident from this equation, that, as the rate varies as the third power of  $y$ , at the start the reaction proceeds very rapidly, and quickly becomes very slow, a state of matters most inconvenient for the purpose in view. It was ultimately found best to employ different multiples of equivalents of acid and chlorate for the different purposes of studying retardation of sulphates, of chlorides, and influence of temperature, as given below.

The preliminary experiments with the chlorides showed

that these substances, even in large quantity, influenced the rate of the change comparatively little; and that consequently the term in (2) relating to the retarding or accelerating effects of the products of the reaction could be neglected; as indeed the calculations from the experimental numbers showed to be true, as is illustrated in the experiments with  $\text{MgSO}_4$  given in detail below.

For part of the work relating to the retardation of sulphates and influence of heat, the following equation was employed:—

$$\frac{dy}{dt} = -ay \{ (\nu_1 - 1)A + y \} \{ (\nu_2 - 1)A + y \},$$

which, on integrating, gives

$$f \left\{ (\nu_2 - 1) \log_{10} \frac{y + (\nu_1 - 1)A}{y} - (\nu_1 - 1) \log_{10} \frac{y + (\nu_2 - 1)A}{y} \right\} = g + t; \quad (3)$$

whilst in the experiments with chlorides the iron and chlorate were in equivalent quantities, and the acid several multiples, represented by the equation

$$\frac{dy}{dt} = -ay^2 \{ (\nu_2 - 1)A + y \},$$

which, on integrating, becomes

$$f' \left\{ (\nu_1 - 1)A - \frac{y}{.4343} \log_{10} \frac{y + (\nu_2 - 1)A}{y} \right\} = y(g' + t). \quad (4)$$

Taking either of these equations (3) and (4), it is easy to see that  $\frac{dy}{dt} \propto f^{-1}$ , or that the time required to oxidize the iron from  $y'$  to  $y''$  is proportional to  $f$ ; consequently in a series of experiments in which everything is the same excepting the presence of inactive salts, by a comparison of the values obtained for  $f$  with its value for an experiment in which no such extraneous salt is added, or a blank experiment, a measure is obtained of the effect of such a salt on the rate of the oxidation; so also in the case of variations of temperature a measure is obtained of the accelerating effect of heat on the rate.

#### *Sulphates.*

The original design of this investigation was to determine the retardation-effects of the various soluble chlorides. The

results, however, obtained for these salts, to be found further on, being of a rather anomalous character, the influence of sulphates was made the subject of a long series of experiments, the results obtained being contained in Table I.

Each experimental solution had a volume of 110 cubic centims., and contained  $\cdot 3736$  gram  $\text{Fe}''$  as chloride, and  $1\cdot 321$  gram free  $\text{HCl}$ . To this was added 25 cubic centims.  $\text{KClO}_2$  solution, equal to  $\cdot 3406$  gram, making the total volume = 135 cubic centims., care being taken to have the solutions at the same temperature before mixing. From such a solution 10 cubic centims. were withdrawn, run into a small flask containing a few cubic centimetres of a nearly saturated solution of  $\text{MgSO}_4^*$ , and titrated with permanganate.

The chemical conditions represented by these quantities of materials are



The value for  $A$  was determined by diluting 10 cubic centims. of the stock solution of ferrous chloride ( $=\cdot 3736$  gram  $\text{Fe}''$ ) to 135 cubic centims., and titrating 10 cubic centims. of this with the permanganate, the number of cubic centimetres required being taken as equal to  $10\cdot 5$ , the value for  $A$ ; but although only approximately of this strength, the usual proportional corrections were made on the values for  $y$  for each experiment; in which way all the experiments are rendered comparable with each other, as if performed with the same standard solution of permanganate.

Inserting these values of  $v_1=2\cdot 5$ ,  $v_2=5\cdot 425$ , and  $A=10\cdot 5$  in equation (3), it becomes

$$f\left(4\cdot 425 \log_{10} \frac{y+15\cdot 75}{y} - 1\cdot 5 \log_{10} \frac{y+46\cdot 46}{y}\right) = g + t. \quad (5)$$

The following three experiments will illustrate this formula, and how the retardation-effects are determined with magnesian sulphate as the retarding agent. Employing the first and third observations, the values obtained for  $f$  and  $g$  in equation (5) are  $115\cdot 1$  and  $77\cdot 2$  respectively; and side by side with the observed values for  $t$  are the calculated quantities.

\* Besides tending to stop the reaction, the addition of  $\text{MgSO}_4$ , the author has shown (*Chemical News*, vol. 1.), renders the estimation of iron by permanganate in presence of free hydric chloride perfectly reliable. Mr. W. H. Deering has drawn attention to the fact that Zimmermann had previously proposed  $\text{MnSO}_4$  for the same purpose.

Blank.  $10^{\circ}$  C.

Permanganate, g.	Time, minutes.	Time, calculated.
10.31	0	...
7.88	21.3	20.9
6.45	38.4	...
4.72	69.3	68.6
3.08	115.6	115.0
2.11	162.1	160.1
1.58	198.4	196.5
1.10	247.0	244.0

In a similar manner the values for  $f$  and  $g$  when 1 gram  $\text{MgSO}_4$  was added, the total volume being the same as before, are found to be respectively 131.9 and 88.3.

1 gram  $\text{MgSO}_4$ . Temp.  $10^{\circ}$  C.

Permanganate, g.	Time, minutes.	Time, calculated.
10.33	0	...
8.16	21.0	21.1
6.60	41.8	...
5.30	65.2	65.5
3.54	114.3	114.0
2.55	156.0	157.3
1.98	191.0	192.6
1.40	241.0	243.3

With 5 grams  $\text{MgSO}_4$  the values found are  $f=201.3$  and  $g=134.6$ .

5 grms  $\text{MgSO}_4$ . Temp.  $10^{\circ}$  C.

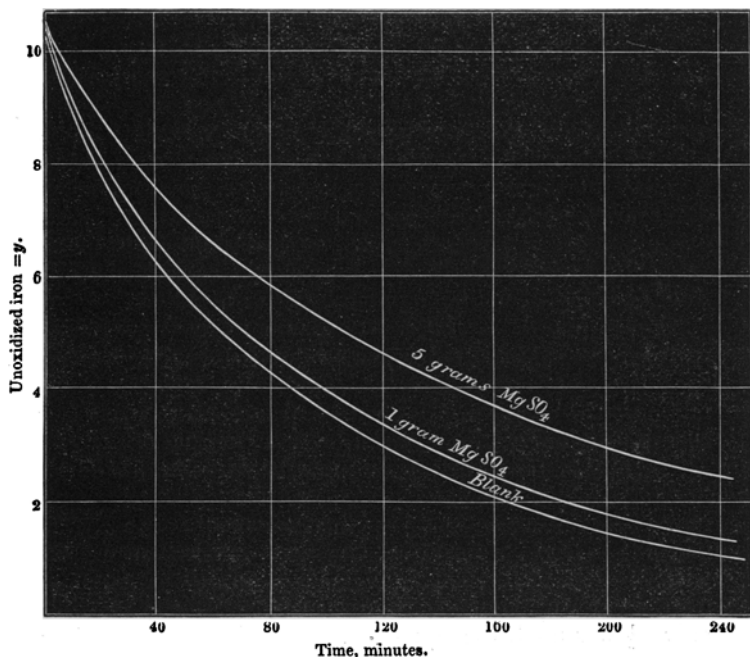
Permanganate, g.	Time, minutes.	Time, calculated.
10.34	0	...
8.19	31.1	31.4
7.60	42.3	...
6.51	65.7	66.1
4.91	113.0	113.4
3.81	158.1	159.9
3.16	194.4	196.4
2.50	245.2	244.3

Now since  $f$  varies inversely as the rate of change, by comparing the above three values the ratios are found to be

$$115.1 : 131.9 : 201.3 = 100 : 100 + 14.6 : 100 + 5 \times 14.9 ;$$

showing that the amount of oxidation that takes 100 minutes to be performed in the blank requires 114.6 minutes in the presence of 1 gram  $\text{MgSO}_4$ , and 174.9 minutes with 5 grams of the salt ; or that the retardation is proportional to the quantity of the salt added, and equal to about 14.7 per cent. per gram. These three experiments are shown graphically in the figure.

Curves showing Retardation produced by 1 and 5 grams  $\text{MgSO}_4$ .  
Temp.  $10^\circ \text{C}$ .



The following table contains the values of  $f$  and  $g$  for equation (5), the mean in each case of several experiments, when 2 grams of the various sulphates were employed, the temperature being in every case  $10^\circ \text{C}$ .



TABLE I.

Salt, 2 grams.	<i>f</i> .	<i>g</i> .	Time to oxidize iron from <i>y</i> to <i>y'</i> .
Blank.....	115.8	77.2	100.0
Am <sub>2</sub> SO <sub>4</sub> .....	156.2	105.0	134.8
K <sub>2</sub> SO <sub>4</sub> .....	155.9	104.4	134.6
Na <sub>2</sub> SO <sub>4</sub> .....	155.4	104.2	134.2
Li <sub>2</sub> SO <sub>4</sub> .....	155.3	103.4	134.1
MgSO <sub>4</sub> .....	148.7	99.2	128.4
ZnSO <sub>4</sub> .....	141.3	94.1	122.0
CdSO <sub>4</sub> .....	132.1	88.2	114.0

The noteworthy points exhibited by these numbers are that equal weights of the sulphates of ammonium, sodium, potassium, and lithium produce equal retardation-effects of approximately 17.2 per cent per gram; whereas the sulphates of zinc, cadmium, and magnesium, metals usually grouped together in the same sense as the alkali ones, all produce different effects. If the percentage retardation produced by one gram of a salt be defined as its retardation-coefficient, the values for the above salts are, for the alkali group, 17.2; for ZnSO<sub>4</sub>, 11; CdSO<sub>4</sub>, 7; and for MgSO<sub>4</sub>, 14.2.

The study of the influence of heat on the values of these retardation-coefficients it was considered would be of interest, in view of the general hypothesis regarding the intermolecular motions that take place in a chemical system, as well as the accelerating effect of heat upon these movements.

The numbers that are given in Table II. relate to MgSO<sub>4</sub>, and are selected from a considerable number of experiments in which various sulphates were employed; but the facts brought to light were all of the same general character as with MgSO<sub>4</sub>.

In these experiments, instead of  $2\frac{1}{2}$  molecules of chlorate only  $1\frac{1}{2}$  was used, the equation representing the experiments being consequently

$$f\left(4.425 \log_{10} \frac{y+5.25}{y} - .5 \log_{10} \frac{y+46.46}{y}\right) = g + t.$$

TABLE II.

Temp. C.	Blank.		2 grams $\text{MgSO}_4$ .	
	$f$ .	$g$ .	$f'$ .	$g'$ .
6.13	366.7	152.7	478.6	199.3
10	256.4	106.4	335.8	139.7
13	193.7	80.7	256.6	106.9
17	134.3	56.3	178.7	74.7

The relations among these numbers are shown in the following table :— $\frac{f'}{f}$  gives the retardation produced by 2 grams  $\text{MgSO}_4$  at the different temperatures, or the time required to oxidize the iron from  $y$  to  $y'$ , being for the blank experiment equal to 100. In column  $a$  the values for  $\alpha$  for the blank experiments are given, calculated on the assumption that the relation between rate of change and temperature is  $\rho = \mu \alpha^\theta$ , and in column  $b$  the values for  $\alpha$  when the experiments are retarded by magnesian sulphate.

TABLE III.

Temp. C.	$\frac{f'}{f}$ .	$a$ .	$b$ .
6.13	130.5		
10	130.9	1.097	1.096
13	132.4	1.098	1.094
17	133.0	1.096	1.095
Means .....	.....	1.097	1.095

From the above table it is seen that the retardation-coefficient of  $\text{MgSO}_4$  increases slightly with the temperature, from 15.2 at 6° 13 C. to 16.5 at 17° C., the rate of oxidation between these limits of temperature increasing about three-fold ; also that the rate increases in geometrical progression with temperature both in the blank and in the retardation experiments, the relation being in the former  $\rho = \mu(1.097)^\theta$ , and in the latter  $\rho = \mu'(1.095)^\theta$ . It has been shown\* that

\* Phil. Mag. October 1885.

*Phil. Mag.* S. 5. Vol. 20. No. 126. Nov. 1885. 2 K

when ferrous sulphate is oxidized by chlorate, the same relation  $\rho = \mu(1.093)^t$  holds good.

### Chlorides.

When the present experiments were undertaken, the principal object in view was to determine the retardation-coefficients of the different chlorides; and it was conjectured that, with the evidence obtained from former experiments, these salts would be found to group themselves together as regards retardation-effects. Such a grouping, however, has not been found to exist. Indeed the anomalies that the experiments exhibit are of a very striking character. For instance, instead of a retardation, the presence of certain chlorides has been found to produce a considerable acceleration on the rate of oxidation; whilst in another case, that of sodic chloride, neither retardation nor acceleration occurs.

Instead of employing quantities of iron, chlorate, and acid in accordance with equation (5), it was found that, by using only one molecule of chlorate and so rendering the rate much slower, the effects of the chlorides, being comparatively small, were better brought out. The acid being the same in amount as in the experiments with sulphates, or  $v_2 = 5.425$  and  $A = 10.5$ , inserting these values in (4), the equation becomes

$$f\left(46.46 - \frac{y}{.4343} \log_{10} \frac{y + 46.46}{y}\right) = y(g + t).$$

In the following table are given the values for  $f$  and  $g$ , the means of several experiments, the temperature being  $10^\circ \text{C}$ .

TABLE IV.

Salt, 5 grams.	$f$ .	$g$ .	Time to oxidize iron from $y$ to $y'$ .
Blank.....	49.36	136.3	100
NaCl .....	49.72	136.9	100.8
KCl .....	60.30	166.3	122.2
AmCl.....	51.70	142.2	104.7
ZnCl <sub>2</sub> .....	44.44	121.9	90.0
MgCl <sub>2</sub> .....	40.65	111.9	82.3
CdCl <sub>2</sub> .....	46.34	127.5	93.9

From these numbers it will be seen that no two chlorides give the same retardation-effects. Sodic chloride practically produces no effect whatever, whilst the chlorides of magnesium, cadmium, and zinc produce an *acceleration* of the rate

of oxidation. In the case of the sulphates, the retardation-effects of the three latter stand in order of magnitude thus :  $\text{MgSO}_4 > \text{ZnSO}_4 > \text{CdSO}_4$ ; and the accelerations of the chlorides are seen to be in the same order— $\text{MgCl}_2 > \text{ZnCl}_2 > \text{CdCl}_2$ .

In attempting to form a mental image of the state of matters in a chemical system undergoing change, it is customary to think of the moving parts or molecules, their velocities of translation, and the influence of various agencies, such as heat &c., increasing the velocities of the molecules and multiplying the chances of collision in a given time. Employing such language, it is easy to account for the retardation occasioned by the presence of chemically inactive substances in the system by saying that, by the motions of the molecules of such bodies, they interfere with the movements of the chemically active molecules by coming into collision with them ; in fact, continually getting in the way of the molecules of the several bodies undergoing chemical change, and so diminishing the number of impacts in a given time between the latter.

To such an explanation, however, the experiments in the first part of this paper are open to a grave objection. It might be argued, that the introduction of a sulphate into a solution of ferrous chloride in presence of much free HCl would give rise to such double decompositions as would account for the retardation observed in the rate of oxidation. If this were so, however, it is difficult to see how the retardation is the same in amount for equal weights of different sulphates, as well as proportional to the amount of the salt present, being the same result as was obtained with sulphates in a ferrous sulphate solution. In the experiments with chlorides no such double decompositions could occur, but here the results are anomalous. 5 grams of sodic chloride produce no effect whatever, whilst the same weight of the sulphate in ferrous chloride would give a retardation of 85 per cent., and in ferrous sulphate a retardation of 50 per cent. If retardation-effects are to be interpreted on the hypothesis of intermolecular movements and interference, and consequent diminution in the number of impacts, how comes it that so much sodic chloride produces no effect, whereas the same weight of potassic chloride causes a retardation of 22 per cent.? And, considering the subject in the same light, more remarkable still are the effects of magnesian, zincic, and cadmic chlorides, which produce an *acceleration* of the rate of oxidation, or increasing the number of collisions of the active bodies in a given time by an amount varying from 6 to 20 per cent. It seems difficult to account for such results on the hypothesis of interdiffusion and simple contact between the active molecules. Instances

of the difficulties that lie in the way of such a theory are exhibited by the great differences observed in the rates of somewhat analogous chemical changes. To take one example : how could such a theory explain the fact that, under suitable conditions of temperature and dilution, ferrous sulphate is oxidized by potassic chlorate at such a rate that only a fraction of the total work capable of being done is accomplished in ten thousand minutes, whereas permanganate performs the same work practically instantaneously? Interdiffusion and simple contact among the active molecules alone would seem incapable of offering any explanation of this and similar facts ; at the same time it would be dangerous to speculate on the tendencies that chemical compounds undoubtedly possess to resist or undergo change under various conditions, in the face of the small amount of work that has been done bearing on chemical change.

In conclusion, I have to thank W. Crookes, Esq., F.R.S., for affording me facilities for performing the above experiments.

LIV. *Atmospheric Electricity.* By C. MICHIE SMITH, B.Sc., F.R.S.E., F.R.A.S., Prof. Phys. Sc. Madras Christian College\*.

**I**N 1882 I presented to the British Association a short report on observations made on atmospheric electricity in Madras, which, though few in number, were of some interest, as they seemed to show that negative electrification of the air was not necessarily associated with broken or stormy weather. At the same time it may be noted that the observations were by no means conclusive, as they were in each case followed by local showers which fell some hours afterwards. Since my return to India, however, I have obtained a large number of observations, many of which fully bear out the conclusion that, even in fine weather, the air may at times be highly charged with negative electricity.

Neglecting a few single observations, the first series obtained was in September 1883, when, on twelve days between the 3rd and 25th, negative readings were recorded. At the time that these readings were taken I thought they were in some way connected with the green sun and the wonderful sun-glow which appeared that month ; and an account of them will be found in my paper on these phenomena in the Transactions of the Royal Society of Edinburgh, vol. xxxii. p. 389. More recent observations have, however, shown that, under

\* Communicated by the Author.