

November 22, 1866.

Lieut.-General SABINE, President, in the Chair.

In accordance with the Statutes, notice was given from the Chair of the ensuing Anniversary Meeting, and the list of Council and Officers nominated for election was read as follows :—

President.—Lieut.-General Edward Sabine, R.A., D.C.L., LL.D.

Treasurer.—William Allen Miller, M.D., LL.D.

Secretaries.— { William Sharpey, M.D., LL.D.
 { George Gabriel Stokes, Esq., M.A., D.C.L., LL.D.

Foreign Secretary.—Professor William Hallows Miller, M.A., LL.D.

Other Members of the Council.—Lionel Smith Beale, Esq., M.B. ; William Bowman, Esq. ; Commander F. J. Owen Evans, R.N. ; Edward Frankland, Esq., Ph.D. ; John Hall Gladstone, Esq., Ph.D. ; William Robert Grove, Esq., M.A., Q.C. ; William Huggins, Esq. ; Thomas Henry Huxley, Esq., LL.D. ; William Lassell, Esq. ; Professor Andrew Crombie Ramsay, LL.D. ; Colonel William James Smythe, R.A. ; William Spottiswoode, Esq., M.A. ; Thomas Thomson, M.D. ; William Tite, Esq. ; Vice-Chancellor Sir W. P. Wood, D.C.L. ; The Lord Wrottesley, M.A., D.C.L.

The following communications were read :—

- I. “ On the Laws of Connexion between the conditions of a Chemical Change and its Amount.” No. II. “ On the Reaction of Hydric Peroxide and Hydric Iodide.” By A. VERNON HARCOURT, M.A., and W. ESSON, M.A. Communicated by Sir BENJAMIN COLLINS BRODIE, Bart. Received July 13, 1866.

(Abstract.)

In a former paper, of which an abstract appeared in the Royal Society's Proceedings, vol. xiv. p. 470, the authors gave an account of their first experiments on this subject.

The second chemical change chosen for investigation was that which occurs in a solution containing hydric iodide (hydriodic acid) and hydric peroxide. In this case the amount of change stands in relation to the following conditions,—(1) the nature of the solution, that is to say, its temperature, and the nature and quantity of the different ingredients which it contains in a unit of volume, (2) the quantity of the solution, or the number of such units of volume, (3) the time during which the change proceeds. The relation of the amount of change to the second and third of these conditions is determinate: it varies directly with each; for the solution is homogeneous, and, if all other conditions are fixed, the rate of change is uniform. But the first condition comprises an almost indefinite number of particular conditions; for not only may various iodides and per-

oxides be used without, as far as we know, altering the nature of the reaction, but other substances may be introduced into the solution, and their influence upon the amount of change determined.

The present paper contains an account of the methods employed for observing this reaction, and of the results obtained by varying two particular conditions, namely the amounts of peroxide and of iodide.

If hydric peroxide and hydric iodide, or barytic peroxide, potassic iodide, and hydric chloride, be brought together in dilute solution at the ordinary temperature, a gradual development of iodine takes place. If a drop of a dilute solution of sodic hyposulphite be added to the mixture capable of reducing to iodide all the iodine which has been formed up to the time of its addition, but not all that will be formed in the course of the reaction, the liquid which had become yellow becomes colourless, remains colourless for a while, and then suddenly becomes yellow again. This yellow colour may be exchanged for a more intense blue colour by putting starch into the solution. It was found that in dilute solutions no direct oxidation of hyposulphite by peroxide took place; and that the quantity of hyposulphite required to reduce the iodine liberated by a measure of peroxide was the same, whether the hyposulphite were added little by little during the course of the reaction, or after the primary reaction had completed itself, and when no peroxide remained in the solution.

The method of observation founded upon these facts was briefly as follows:—

Measured quantities of all the standard solutions, except that of hydric peroxide, were introduced into a glass cylinder about 11 inches high by 3 broad, and water was added till the upper surface of the liquid was level with a line drawn round the cylinder. This adjustment of volume was made through a hole in the bung, which closed the cylinder; two other holes admitted a thermometer and an inverted funnel-tube. A current of carbonic acid passing down the funnel-tube to the bottom of the cylinder, and rising in large bubbles from the mouth of the funnel, served at once to stir the liquid constantly, and to protect its upper surface from the air. When the volume and the temperature of the solution had been adjusted, a small measure of hyposulphite was first added, and then the pipetteful (10 cub. centims.) of peroxide. The cylinder was placed on a sheet of white paper in front of a clock beating seconds. By watching the surface of the fluid and counting the seconds when the time of an observation was near, it was possible to note accurately the moment at which the colour changed. A second small measure of hyposulphite was then introduced, and at the proper interval a second observation was made. Each such addition of hyposulphite, with the observation preceding and following it, is spoken of as an experiment, and these experiments were continued until the reducing power of the last measure of hyposulphite being greater than the oxidizing power of the remaining peroxide the blue colour did not return.

The small measures of hyposulphite consisted of single drops collected under circumstances favourable to their perfect uniformity. The peroxide employed was either an acidified solution of sodic peroxide, or dilute hydric peroxide obtained by the distillation of such a solution. In each set of experiments the value of the measures of hyposulphite and of the pipetteful of peroxide could be compared by determining what fraction of a measure of hyposulphite remained in the solution when the set of experiments had been brought to an end. These values could also be compared by determining each with a standard solution of potassic permanganate. In presence of an excess of potassic iodide, sodic hyposulphite may be estimated by this reagent exactly as it may by standard iodine solution.

During each set of experiments, then, all the conditions of the reaction are constant except two, which are progressively modified. One of these is immaterial, the accumulation of a small quantity of sodic tetrathionate; the other is material, the gradual disappearance of the small quantity of peroxide upon whose presence the reaction depends.

The first point, therefore, requiring to be investigated was the law of connexion between the amount of change and the amount of peroxide.

Since the amount of peroxide originally taken is known, and also the amount which corresponds to a measure of hyposulphite, the amount remaining in the solution at the moment of each observation is also known. Thus the data supplied by each experiment are (1) the amount of peroxide present in the solution at a particular moment of time, (2) the time at which this amount is present, (3) the amount present at a subsequent moment of time, (4) the time at which this amount is present. Representing these two amounts of peroxide by y and y' respectively, and the corresponding moments of time by t and t' , the result of each experiment is that an amount of chemical change $y - y'$ has been accomplished in an interval $t' - t$. According to the hypothesis proposed in our former paper, namely that the amount of chemical change varies directly with that of each of the substances partaking in it, these quantities should exhibit throughout a set of experiments the constant relation

$$\frac{y}{y'} = e^{\alpha (t' - t)}.$$

The numerical results obtained in various sets of experiments performed under different circumstances are compared with those calculated from equations of this form, and the two are shown to agree within narrow limits of experimental error. It is inferred that in this case the amount of chemical change taking place at any moment is proportional to the amount of peroxide present at that moment in the solution.

The constant α in the preceding equation represents the effect upon the amount of change of those conditions which do not vary in a set of experiments; and it is possible by varying one of these conditions in different sets of experiments, and determining the value of α in each, to inquire into

the law of connexion between the condition thus varied and the amount of change.

Accordingly a series of sets of experiments was made, in which, all else being kept constant, different quantities of potassic iodide were used in different sets. It is shown that the values of α derived from the different sets of experiments are proportional to the quantities of iodide used in each case. In this series hydric sulphate was an ingredient of the solutions; a second series was made, in which an equivalent quantity of hydric chloride was substituted. The result, as regards the effect of varying the amount of iodide, was the same as in the previous series. The rate of chemical change, that is to say the amount in a given time with a constant quantity of peroxide, was found to be directly proportional to the amount of iodide in the solution. Thus the law of connexion is the same in this case as in that already investigated of the variation of peroxide.

The total amount of chemical change is a function of all the conditions of the system in which it occurs. If we call this amount Σ , the volume of the solution v , its temperature h , the time during which the change proceeds t , and the amounts of the various ingredients, peroxide, iodide, &c. in a unit of volume, $p, i, a, b, c \dots$, then

$$\Sigma = f(a, b, c, \dots h, i, \dots p, \dots t, \dots v \dots).$$

The form of this function is determinate in the case of two of these conditions, viz. v, t , and has now been determined experimentally in the case of p and i , so that the equation may be written in the form

$$\Sigma = i p t v . f(a, b, c \dots h \dots).$$

The number of ingredients, represented by a, b, c , &c., which may be introduced into the system and affect the amount only, and not the nature of the chemical change, and which may therefore be regarded as so many conditions of the reaction, is doubtless very large. The authors believe that the investigation of the influence of some of these may prove of interest, it being possible thus to compare various substances which may be substituted one for another in the system by a new standard. They find, for example, that comparing equivalent quantities (in the ordinary chemical sense) of hydric sulphate and hydric chloride, the effect of the latter is nearly double that of the former. But the most important condition of the change whose influence is still undetermined is that of temperature, for this condition intervenes under all circumstances of the reaction, and indeed in all chemical changes whatever. The authors have already made many experiments on both these points. The results of this investigation, which will complete the study of the reaction, may, they hope, form the subject of a subsequent communication.