May 9, 1895.

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Bakerian Lecture was delivered as follows:—

BAKERIAN LECTURE.—"On the Laws of Connexion between the Conditions of Chemical Change and its Amount." By A. VERNON HARCOURT, M.A., F.R.S., Student of Christ Church, and Lee's Reader in Chemistry, and WILLIAM ESSON, M.A., F.R.S., Fellow of Merton College, and Deputy Savilian Professor of Geometry in the University of Oxford. "III. Further Researches on the Reaction of Hydrogen Dioxide and Hydrogen Iodide." Received March 15, 1895.

(Abstract.)

In this paper are considered the effect upon the reaction of (1) substances not directly participating in it, (2) temperature.

A short description is given of the manner in which the observations were made.

The equation which expresses the result of a single set of observations was shown in a previous paper to be

$$y_1 = y_0 e^{-\alpha(t_1 - t_0)},$$

where $$y_0(H^2O^2 + 2HI = I^2 + 2H^2O),$$

and $$y_1(H^2O^2 + 2HI = I^2 + 2H^2\mathrm{O}),$$

are the amounts of potential change at the times t_0, t_1 respectively.

Each set of observations gives a mean value of α, which is taken to be the value of the rate of change under the conditions of the set.

The effect of the variation of the conditions upon the value of α is considered to be a measure of their effect upon the course of the reaction.

Variation of Hydrogen Sulphate.

It is shown from the results of three sets of experiments at temperatures of 16°, 20°, and 30°, that the increment in the value of the

rate of change per unit of sulphate per unit of iodide is constant when an unit volume contains quantities of sulphate ranging from 45 to 515 H^2SO^4.* This increment is again constant for the range 515 to 762 H^2SO^4, but has a higher value. For quantities of sulphate greater than 762 H^2SO^4 this increment, which again becomes constant, is further increased in value. The explanation given of this discontinuity in the successive values of the increment, is that the gradual addition of the sulphate to the water gives rise to the gradual formation of one hydrate at the expense of another, and the increment per unit of sulphate is the resultant of the increment per unit of each of the hydrates.

For the range 515 to 762 H^2SO^4 the hydrate which is decreasing, is H^2SO^4, 106 H^2O, and the hydrate which is increasing, is H^2SO^4, 71 H^2O.

At a temperature of 30° the values of α in a solution containing in 1 c.c. 1 HI, sH^2SO^4 are

$$(1) \text{ from } s = 45 \text{ to } s = 515,$$
$$\alpha = (1230 + 18{\cdot}1\, s)10^{-6};$$
$$(2) \text{ from } s = 515 \text{ to } s = 762,$$
$$\alpha = \{1230 + 18{\cdot}1 \times 515 + 22{\cdot}4(s - 515)\}10^{-6};$$
$$(3) \text{ from } s = 762 \text{ to } s = 1140,$$
$$\alpha = \{1230 + 18{\cdot}1 \times 515 + 22{\cdot}4(762 - 515) + 26{\cdot}5(s - 762)\}10^{-6}.$$

Theoretically the rate 1230×10^{-6} is the rate with water and hydrogen iodide only, present in amounts per cubic centimetre 55400 H^2O, 1HI. The increments per unit of hydrogen sulphate are in the three cases 18·1, 22·4, and 26·5 millionths.

When the medium consists of water, hydrogen iodide, and hydrogen sulphate, and the ratio of the numbers of H^2SO^4 and HI falls below 20, the rate with unit of HI has a value different from 1230×10^{-6}; but the value of the increment per unit of sulphate is the same for the range of numbers of H^2SO^4 from 45 to 515.

Variation of Hydrogen Chloride.

It is shown from the results of one set of experiments at a temperature of 30° that the increment in the value of the rate of change per unit of chloride per unit of iodide is constant when a cubic centimetre contains 14 HI, and quantities of chloride ranging from 70 to 280 HCl, the value of the increment being $16{\cdot}8 \times 10^{-6}$. An examination of four sets of observations made in the course of the experiments

* As in our former papers, we use H to represent one-millionth of a gram of hydrogen, and other symbols italicized for the corresponding proportions of other elements. Thus H^2SO^4 is 98 millionths of a gram of hydrogen sulphate.

upon temperature, and of the experiments recorded in a previous paper, made to determine the law of variation of the rate of change with iodide, shows that when the ratio of the numbers of *HCl* and *HI* is higher than it is in the set quoted above, the value of the increment per unit of chloride per unit of iodide falls to $16{\cdot}2 \times 10^{-6}$. This lower value is the same for values of the number of *HCl*, ranging from 190 to 547, and for values of the ratio of the numbers of *HCl* and *HI*, ranging from 20 to 210.

The formulæ for α in these two cases in a solution containing in 1 c.c. 1 *HI* and *c HCl* are at a temperature of 30°,

$$(1.)\ \alpha = (1345 + 16{\cdot}8c)10^{-6},$$

$$(2.)\ \alpha = (1230 + 16{\cdot}2c)10^{-6}.$$

Variation of Iodide.

It was shown in a previous paper that when quantities of iodide are introduced into the medium sufficiently small in amount, in comparison with other substances not participating directly in the reaction, the rate of chemical change varied directly with the amount of iodide. It was conjectured that when the amount of iodide is large enough to modify considerably the character of the medium, it would have the same kind of effect upon the reaction as hydrogen sulphate and hydrogen chloride. It is now shown that the increment of the rate per unit of hydrogen iodide per unit of iodide is $19{\cdot}4 \times 10^{-6}$ at a temperature of 30°, the rate with 1 *HI* at the same temperature being 1210×10^{-6}. The formula for the rate with *iHI* is

$$\alpha = i\{1210 + 19{\cdot}4(i-1)\}10^{-6}.$$

It will be observed that the actual rate with unit of hydrogen iodide in a medium consisting of water and hydrogen iodide is approximately the same as the theoretical rate with unit of iodide in a medium consisting of water, hydrogen iodide, and either hydrogen sulphate or hydrogen chloride when the ratio of the numbers of H^2SO^4 and *HI* and of the numbers of *HCl* and *HI* exceeds 20. It has been shown above that this rate is 1230×10^{-6}.

Variation of Sodium Hydrogen Carbonate.

In a medium consisting mainly of water and sodium hydrogen carbonate the increment of the rate per unit of $NaHCO^3$ per unit of iodide is 40×10^{-6} at a temperature of 15°, the formula for the rate with 8·59 *NaI* and quantities of the carbonate ranging from 25 $NaHCO^3$ to 227 $NaHCO^3$, being at this temperature

$$\alpha = 8{\cdot}59\{192 + 40b\}10^{-6}.$$

The rate with 1 *NaI* and $bNaHCO^3$ is

$$\alpha = (155 + 40b)10^{-6},$$

so that the theoretical rate with 1 *NaI* only, in this medium, is 155×10^{-6} at a temperature of 15°. At the same temperature the actual rate with 1 *HI* in a medium consisting of water and hydrogen iodide is 356×10^{-6}, a rate more than twice as great as the corresponding rate with the neutral iodide. The increment of the rate per unit of carbonate per unit of iodide is more that four times the highest increment per unit of sulphate per unit of iodide at the temperature of 15°.

Variation of Potassium Iodide, Sodium Iodide, and Sodium Chloride, in a medium consisting mainly of Water and Sodium Hydrogen Carbonate.

In this medium at a temperature of 15°, the increments of the rate per unit of these substances per unit of iodide are (1) for the range 10 *KI* to 30 *KI*, $4{\cdot}15 \times 10^{-6}$; (2) for the range 10 *NaI* to 30 *NaI*, $4{\cdot}84 \times 10^{-6}$; (3) for the range 1 *NaCl* to 14 *NaCl*, $27{\cdot}7 \times 10^{-6}$. In this medium sodium chloride has a considerable effect on the rate, but in a medium consisting of water and hydrogen chloride its effect is almost nil.

General Conclusion as to the effect of the Medium upon the reaction.

Each constituent of the medium produces an effect on the rate of change of unit peroxide and unit iodide, proportional to the mass, and varying with the nature of the constituent. The increment of this rate per unit mass of each constituent is constant so long as the quantity of the predominant constituent present in the medium is sufficiently large, in comparison with the other constituents of the medium, to render the media in successive experiments practically homogeneous. For example, when the ratio of the numbers of H^2SO^4 and *HI* in the medium exceeds 20 the formula for the rate at a given temperature is

$$\alpha = i\{a + b(i-1) + ds\},$$

a being the theoretical rate with unit of *HI*, *b* the increment per unit of hydrogen iodide per unit of iodide, and *d* the increment per unit of hydrogen sulphate per unit of iodide. If the ratio falls below 20 the formula is

$$\alpha = i\{a + b'(i-1) + d's\},$$

in which b' and d' depend upon the relative masses of sulphate and iodide present in the medium.

Variation of Temperature.

The discussion of the numerous experiments made at temperatures ranging from 0° to 50°, in media in which the quantities of iodide range from 3·64 *HI*, to 23 *HI*, the quantities of hydrogen sulphate from 45 H^2SO^4 to 468 H^2SO^4, and the quantities of hydrogen chloride from 70 *HCl* to 547 *HCl*, leads to the following law of connexion between chemical change and temperature.

If α_1 is the rate of chemical change at a temperature $t_1°$ in a homogeneous medium consisting of given constituents per unit volume, and α_2 is the rate at a temperature $t_2°$ in the same medium, the ratio of α_1 to α_2 is $\{(273+t_1)/(273+t_2)\}^m$. m being a constant depending upon the character of the constituents of the medium. When the temperatures are measured from the absolute zero −273°, and are denoted by T_1, T_2, the formula assumes the simpler form,

$$\alpha_1/\alpha_2 = (T_1/T_2)^m.$$

The constancy of the value of m for a particular medium is secured when the quantity of the predominant constituent of the medium is sufficiently large in comparison with the quantities of the other constituents to make the medium practically homogeneous. When this is not the case m has some value intermediate to the values which it has when one or other of the constituents is sufficiently predominant to secure a constant value.

In media in which hydrogen sulphate is sufficiently predominant, the value of m is 20·38; similarly for hydrogen chloride the value of m is 21·17. When the medium consists of water and hydrogen iodide, the value of m is 24·1. The introduction of sodium sulphate in large quantity into a medium otherwise consisting mainly of hydrogen sulphate reduces the value of m from 20·38 to 18·1. In a medium in which the main ingredient is sodium hydrogen carbonate, the value of m is approximately 10.

A further confirmation of the law of connexion between chemical change and temperature is obtained from the discussion of experiments on the rate of change of hydrogen chlorate and potassium iodide made by W. H. Pendlebury and M. Seward. The value of m is in the case of this chemical change 40·5.

It follows from the law enunciated above that at the temperature of absolute zero no chemical change can take place.

If the smallest value of m, viz., 10, is taken, a chemical change which is completed in one minute at a temperature zero, would require for its completion at a temperature of −200° a little more than a year. If 20 is taken as the value of m, the minute would be increased to more than half a million of years by the same reduction of temperature.

The law enunciated above may also be stated in the following form.

The increment of each unit of chemical change due to a rise of temperature varies as the increment of each unit of absolute temperature.

This law is expressed by the formula

$$D\alpha/\alpha = mDT/T.$$

Chemical Equilibrium.

A case of equilibrium between the reactions

$$H^2O^2+2HI = 2H^2O+I^2,$$
$$2H^2O+I^2 = H^2O^2+2HI,$$

leads to a discussion of the general equations of chemical equilibrium which is given in an appendix to the paper. These equations are employed to interpret the results of experiments published by Dr. Gladstone in the Transactions of the Royal Society ('Phil. Trans.,' vol. 145). They had been previously applied to the case of chemical equilibrium investigated by Professor Dixon in a paper published in vol. 175 of the Transactions of the Royal Society, the reactions in that case being

$$H^2O+CO = H^2+CO^2,$$
$$H^2+CO^2 = H^2O+CO.$$

The following Papers were also read:—

I. "On the new Gas obtained from Uraninite. Second Note." By J. Norman Lockyer, C.B., F.R.S. Received May 8, 1895.

Since my communication on the gas obtained from uraninite (bröggerite) was sent into the Society, on the 25th ultimo, I have been employing the method I there referred to in several directions, among them to determine whether the spectrum of the gas indicates a simple or a complex origin.

I was led to make this special inquiry on account of the difference in the frequency of the appearance of D_3 and the other lines to which I referred in the previous communication in the solar chromosphere. For instance, if we take the lines D_3, 4471, and 4302, the frequencies are as follows, according to Young*:—

* See 'Solar Physics,' Lockyer, p. 612.