XL.—On a Method of Investigating the Dissolution of Metals in Acids.

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Introduction.

IN recent years, various accounts have been published on the dissolution of metals in acids as a result of a chemical change. Thus Kajander in *Bull. Soc. Chim.* [2], 34, 325 (an abstract from a Russian communication), has determined the relation between the weights of magnesium dissolved per unit time, and the concentration of the acids used, as also the variation produced by the addition to the acid of foreign salts and liquids. Thorpe (*Trans.*, 1882, 287) has studied the reduction of ferric salts in acid solutions by various metals. Divers (*Trans.*, 1885, 598) has ascertained the relative effects of sulphuric and nitric acids, taken separately and together on metallic zinc. More recently, Spring and van Aubel (*Ann. Chim. Phys.* [6],

11, 505) conducted some elaborate experiments on the interaction of zinc, containing a small proportion of lead, with sulphuric and the halogen acids. In most of the experiments described in these memoirs, a more or less regular surface of the metal has been placed at rest within the dissolving acid, and either the loss in weight of the metal determined at given intervals or the times noted which were required for the evolution of a definite volume of hydrogen or other gas. From these experiments the observations of those familiar with the preparation of hydrogen from zinc and sulphuric acid have been confirmed, namely, that within certain limits the more concentrated the acid and the higher the temperature, the more rapid the solution* of the zinc. But in the method of experiment adopted the measured result is one of mixed causes, each one of which is variable at any moment of time, and its peculiar effect not susceptible of mathematical analysis. For it is obvious that if the metal is *at rest* within the acid its measured rate of solution is dependent, *inter alia*, not only upon the surface exposed and the local rise of temperature due to the chemical reaction, but also upon the rate of diffusion of the metallic salt formed in the acid liquid, the actual disengagement of the gas-bubbles from the surface of the metal, and the rate of removal by these bubbles of the concentrated salt solution in the immediate vicinity of the metal. Thus if a cylinder of zinc be placed in dilute sulphuric acid, it is a common matter of observation that at first the bubbles of hydrogen gas persistently cling to the metallic surface, but subsequently are more readily removed owing to the formation of points on the surface due to the production of local electric circuits. In another paper (*Phil. Trans.*, 1888, A, 285), I have remarked that the increase in the rate of evolution of hydrogen from zinc and dilute sulphuric acid caused by the reduction of the superincumbent pressure, can partly be explained by the formation of larger bubbles of gas, whereby the solution of the zinc sulphate is more readily removed. Again, though as is well known, zinc under the same conditions dissolves more readily in dilute hydrochloric than in sulphuric acid containing the same quantity of replaceable hydrogen per unit volume, yet it is possible that this result may be due to the greater diffusibility of zinc chloride in hydrochloric acid than of zinc sulphate in sulphuric acid. Spring and van Aubel in their experiments either kept the surface of the metal constant or allowed for its variation, but the results of others, obtained with sheets of metal, are comparatively valueless in that the actual surface owing to inequalities may vary within almost infinite limits. To

* Here and throughout this paper the word "solution" will be used, it being understood to imply solution as a result of chemical change, between the metal and the acid.

avoid some of the above difficulties, attempts were made to devise a method which could be applied to measure the rate of solution of metals in acids under such conditions that not only fresh surfaces of a regular geometric figure of the metal are continually being exposed, but also the products of the change, whether gas or metallic salt, are continually being removed from the vicinity of the dissolving metal. An outline of the research has already been indicated in this Journal (Abstr., 1888, 104).

Apparatus.

The first apparatus used consisted of two watch-glasses (Fig. 1) placed one above the other in opposite positions, so that the upper one presented from above a concave, the lower a convex surface. These

FIG. 1.

glasses were wired to one another, as also to a hollow glass bulb by means of which they were floated under the surface of the acid liquid contained in a beaker. The liquid was kept stirred by a current of carbonic acid produced in a Kipp's apparatus and washed by bubbling through a Wolff's bottle containing water; thence it passed into a piece of quill glass tubing bent twice at right angles, and ending in a small thistle-funnel. The horizontal and lower vertical limb of the tube were of such lengths and the containing beaker of such a dimension that each bubble of the gas as it issued from the thistle-funnel struck the lower of the two watch-glasses on one side, and thus in passing by tilted the whole arrangement of glasses and bulb. The

down-draught of the liquid caused the apparatus to return to its former position in time for another gas-bubble to tilt it again. Thus the whole of the acid liquid was continually stirred, and a spherical bullet of metal on the upper of the two watch-glasses continually rolled about.

The edge of the upper glass was slightly corrugated, so that the bullet should not roll off. The friction between the glass and bullet, together with a slight spin given by the gas-bubbles, prevented the bullet from rolling always on the same axis, and thus become spheroidal. This apparatus was devised some years ago by Mr. Vernon-Harcourt for experiments on the same subject.

The beaker was placed on an iron plate, under which was a small gas-flame; the variations of temperature did not exceed a few tenths of a degree on either side of that required. To prevent access of dust the beaker was covered with a glass plate provided with two holes, through one of which passed the thermometer, through the other the carbonic anhydride tube. Experience showed that it was above all things necessary to pass the same number of gas-bubbles per minute.

The apparatus described above, though simple, yet presented some disadvantages. Firstly, it is obvious that, assuming the impact given by each bubble of carbonic anhydride to be equal, a smaller bullet would receive a greater shock than a larger one, and as all experiments showed that the rate of solution, *ceteris paribus*, varied with the motion imparted to the bullet, the amount dissolved per unit area would increase with decrease of its size. This was found to be the case after a certain limit had been passed. Secondly, it was found difficult in practice to ensure the passage of the same number of gas-bubbles per minute. The results, however, obtained with the apparatus were sufficiently accurate to determine the relation between the rate of solution and the temperature, and are recorded below in Tables I to X. To obviate this source of error and inconvenience an integrating machine was devised, by means of which the bullet was caused to revolve round the same path the same number of times, whatever its diameter. The apparatus consisted essentially of a wooden cone C (Fig. 2), rotated by means of a water-motor; a brass disc, D, worked by friction on the cone, and the former could be moved along a brass rod, R, provided with a scale of 200 mm., and set parallel to the cone; the rod rested above and below upon guides, G, G', screwed to a wooden base-board. The lower extremity of the rod ended in a hollow ferrule, into which was inserted a rubber cork; through this passed a sealed piece of glass tubing, bearing at a convenient distance from the end of the rod, a small flat glass dish, D, about 70 mm. in diameter, with upturned edges. The dish was

pierced with several holes to allow the liquid to flow out continually. The tube and dish were set at angle of 45° within the beaker contain-

FIG. 2.

ing the dissolving liquid; the metallic bullet rested on the rim of the dish.

When the cone is rotated at a uniform rate, the rotation of the brass rod, as also of the glass vessel, varies with the position of the disc on the cone; accordingly, for any known diameter of the bullet the disc is placed at a certain mark on the graduated scale of the brass rod. Thus, the rotation of the rod and of the dish can be made proportional to the diameter of the bullet, so that it will be revolved round the same path the same number of times, whatever be its diameter. The glass dish was set slightly eccentrically on the tube to prevent the bullet from always revolving on the same axis. To reduce the velocity of the rotation of the water-motor, the driving wheel of which revolved about 1560 times per minute, a tangent screw (S) was interposed between it and the cone; the rotation of a driving wheel connected with the screw was kept constant at 26 times per minute, whereby the rotation of the cone, worked by an endless band, was also kept constant. This apparatus was devised in outline by my friend Mr. V. P. Sells, of New College, Oxford (to whom I would express my thanks); it was constructed and improved by the

Cambridge Philosophical Instrument Company. The results obtained by its use are recorded in Tables XI to XXI. In these latter experiments, a fairly uniform current of carbonic anhydride was passed as before, and the arrangements for keeping the temperature constant (not represented in cut) were slightly modified.

Determination of the Surfaces of the Bullets.

If it could be insured that a metallic bullet, initially spherical, retained its form perfectly, its surface could be calculated from its mass and specific gravity. As, however, this was not always the case, it was thought to be more exact to calculate the area from a measurement of the axes taken in different directions; this was effected by means of a micrometer caliper, which measured to 0.013 mm.

The areas corresponding to each of the several diameters were calculated, and their mean value A_1 taken. After the bullet had been rolled about in the acid liquid for one hour, it was removed, washed with distilled water, and dried at 80–90°; its axes were again measured, their corresponding areas calculated, and their mean value A_2 taken. The average of the former and latter mean values, namely, $\frac{A_1 + A_2}{2} = A$, was taken as the mean area of the bullet during the course of the experiment. The difference between the greatest and least axis seldom exceeded 0.05 mm. (the difference being generally 0.026 mm.); when, however, this was the case, the area was calculated by means of the following approximate formula:—Let $2a, 2b, 2c$ be the greatest, mean, and least axis respectively, and let e be the eccentricity of the ab section ellipse given by (i) $b^2 = a^2 (1 - e_1^2)$, and e^2 that of the bc section ellipse given by (ii) $c^2 = b^2 (1 - e_2^2)$. Then total surface of the ellipsoid, e_1 and e_2 , being very small;

$$(iii) A = 4\pi C^2 \left(1 - \frac{e_1^2 - e_2^2}{3} \right),$$

wherein e_1 and e_2 are given by (i) and (ii).

Method of Experiments.

The bullet was weighed before and after each experiment, and the loss in weight M , divided by the mean area A , was taken as the factor for the comparison of the results. For convenience this is expressed in terms of decimilligrams dissolved per one square millimetre surface. To make clear the whole course of the experiments, all the measurements and weighings are given below in Table I(a) and (b).

Throughout the various manipulations, the metallic bullet was never touched by the fingers, but only with a pair of brass pincettes,

as it is well known that the presence of a trace of grease materially affects the rate of solution of metals in acids.

In the first series of experiments, such metals and acid solutions were used that no gas was evolved as such, as for example, zinc and copper in chromic acid (potassium bichromate and sulphuric acid). As the results with pure redistilled zinc were rather irregular, pure electrotype copper was used. Messrs. Johnson and Matthey made from my instructions a set of copper bullets from one rod cast from the purest electrotype copper, each bullet weighing about 5 grams and turned to 0.013 mm. Before any measurements and weighings were made the bullets were rolled about in a solution of chromic acid of similar strength to that used in the actual experiments. By this means any polishing material used by the workmen, as also any superficial coating of oxide were removed, so that the bullet at the commencement of the first experiment presented a surface similar to that in all the subsequent experiments. It was invariably found that this exterior coating was much less readily dissolved off than the remainder; this was doubtless due to a denser structure of the metal produced by the external pressure to which the bullets were subjected in the processes of turning and polishing. The same result was produced in a more exaggerated degree by heating the bullets for some time at a temperature just short of that at which they softened, and subsequently allowing them to cool slowly. In this preliminary operation about 0.25 gram was removed. After the copper bullets had been in the chromic acid solution for several hours, their surfaces were, with few exceptions, as smooth and regular as at the start; the absence of any irregularities was at least one criterion of the homogeneity of the copper.

For each separate experiment, a solution of potassium bichromate was made by dissolving a known weight of the crystals in water; to it was added a volume of diluted sulphuric acid containing a known weight of the acid; the whole was then made up to one litre. The strength of the sulphuric acid, a considerable quantity of which was made up at one time, was determined either by precipitation with barium chloride, or by titration with sodium carbonate. In the first series of experiments, such quantities of potassium bichromate were used that taking the average quantity 0.33 gram of copper dissolved off in each experiment, the quantities of bichromate and acid should each be diminished by about 2 per cent. with formation of 0.2 per cent. of water, if the action is supposed to be expressed by the following equation:—

Thus if 59 grams of the bichromate and 64.4 grams of sulphuric

acid are taken, 2.0 per cent. of the former acid and 2.1 per cent. of the latter are used up per hour, with increase of dilution of 0.022 per cent. Thus at the end of the experiment the composition of the dissolving liquid did not differ materially from that at the commencement. It is probable that the above change takes place in two successive stages; first the copper reduces the chromic acid to the sesquioxide, it being itself converted to the oxide; and secondly, these metallic oxides dissolve in the sulphuric acid present. If the movement either of the bullet or of the liquid were insufficient, the temporary formation of a dark green coating on the metal was always observed.

As a preliminary basis it was obviously necessary to prove firstly, that the mass dissolved varied directly with the area, namely, that the values for M/A under constant conditions of acidity and temperature were constant, and secondly, that under the same conditions two different bullets dissolved at the same rate. In Table I (a) are given (I) the weight in grams of the copper bullet at the commencement of each experiment, (II) its weight at the conclusion, and (III) the difference between (I) and (II) or the quantity dissolved off, (IV) the mean area calculated as explained above, and (V) the value of M/A expressed as decimilligrams dissolved off per 1 square millimetre per hour. In Table I (b) are given the measurements of the axes in millimetres as a sample of the variations from true sphericity; in other series these measurements will be omitted.

Mixture Taken.

59.0 grams potassium bichromate }
 64.4 „ sulphuric acid } made up to 1 litre.
 Temperature 21°.

TABLE I (a).

Weight in grams at commencement.	Weight in grams at conclusion.	Loss.	Mean area in sq. mm.	Value for $\frac{M}{A}$.
I. 4.7307	4.3585	0.3722	308.75	12.05
II. 4.3585	4.0133	0.3452	293.04	11.89
III. 4.0133	3.6848	0.3285	275.94	11.91
IV. 3.6848	3.3685	0.3163	265.33	11.92
V. 3.3685	3.0658	0.3027	245.61	12.21
VI. 3.0658	2.7838	0.2933	227.63	12.25
Mean value for M/A				12.05

TABLE I (b).

No.	At commence- ment.	At conclusion.	No.	At commence- ment.	At conclusion.
I.. {	10·046 } 10·033 } 10·020 }	9·804 } 9·791 } 9·779 }	IV.. {	9·246 } 9·220 } 9·195 }	9·017 } 8·979 } 8·941 }
II.. {	9·804 } 9·791 } 9·779 }	9·550 } 9·525 } 9·500 }	V.. {	9·017 } 8·979 } 8·941 }	8·738 } 8·708 } 8·674 }
III.. {	9·550 } 9·525 } 9·500 }	9·246 } 9·220 } 9·105 }	VI.. {	8·738 } 8·708 } 8·674 }	8·376 } 8·319 } 8·280 }

The results given in Table I (a) show that under the same conditions the values for the mass dissolved per unit area are constant within an error of +1·5 per cent., and the measurements in Table I (b) show that the differences between the greatest and least axes is seldom more than 1 per cent.

In Table II the results are given for another bullet under precisely the same conditions of experiment.

TABLE II.

Weight at com- mencement.	Weight at conclusion.	Loss.	Mean area in mm.	Value for $\frac{M}{A}$.
4·7649	4·3801	0·3848	309·65	12·43
4·3801	4·0223	0·3578	292·13	12·25
4·0223	3·6795	0·3438	275·71	12·48
3·6795	3·3528	0·3267	258·9	12·60
3·3528	3·0498	0·3030	242·97	12·53
3·0498	2·7773	0·2725	227·09	12·05
Mean value for M/A				12·38

The mean value for M/A obtained with the second bullet is 2·7 per cent. higher than the first bullet under the same conditions, an approximation sufficiently near. The experiments recorded in Tables I and II. are intended only to prove the efficiency of the apparatus and the method of working.

EFFECTS PRODUCED BY VARIATION OF CONDITIONS.

I. *Temperature.*

To determine the effect produced by variation of temperature a series of experiments were conducted with the following mixture:—

{ 44.2 grams potassium bichromate }
 { 32.0 „ sulphuric acid } in 1 litre of water.

TABLE III.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4.6318	4.3858	0.246	306.12	8.04
4.3858	4.1493	0.2365	294.64	8.03
4.1493	3.9208	0.2285	283.8	8.06
3.9208	3.6973	0.2235	272.27	8.23
3.6972	3.4808	0.2165	261.04	8.30
3.4808	3.2006	0.2082	251.38	8.28
Mean value for M/A.....				8.15

TABLE IV.—*Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4.7160	4.3998	0.3162	309.0	10.23
4.3998	4.0976	0.3022	294.64	10.26
4.0976	3.8041	0.2928	284.94	10.25
3.8041	3.5276	0.2745	266.57	10.30
3.5276	3.2581	0.2695	253.39	10.64
3.2581	3.0156	0.2465	240.45	10.27
3.0156	2.7736	0.2430	228.99	10.61
2.7736	2.5476	0.2270	216.89	10.47
Mean value for M/A.....				10.38

TABLE V.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4.6647	4.2973	0.3674	304.92	12.05
4.2973	3.9499	0.3474	288.96	12.02
3.9499	3.6199	0.33	273.29	12.07
3.6199	3.3138	0.3061	257.55	11.89
3.3138	3.0253	0.2885	242.29	11.94
2.8200	2.5553	0.2652	216.42	12.25
Mean value for M/A.....				12.04

TABLE VI.—*Temperature 41°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4·7253	4·3253	0·4002	306·72	13·05
4·3253	3·9523	0·373	290·52	12·84
3·9523	3·5928	0·3595	273·78	13·13
3·2623	2·9558	0·3065	238·82	12·83
2·9558	2·6603	0·2955	222·14	13·31
Mean value of M/A				13·03

It will be seen that the difference of the value of M/A is directly proportional to the differences of the temperatures. This relation will be manifest by the figures given below :—

Temperature.	Value for M/A .	Log M/A .
21°	8·15	0·9114
31	10·38	1·016
36	12·04	1·0805
41	13·03	1·115

Subtracting the first logarithmic value from each of the succeeding, one has—

- (i) $1·016 - 0·9114 = 0·1047 = 2 \times 0·0535$
- (ii) $1·0804 - 0·9114 = 0·1692 = 3 \times 0·0564$
- (iii) $1·115 - 0·9114 = 0·2036 = 4 \times 0·0519$

Thus the differences of the logarithms are practically in the ratio 2 : 3 : 4, which is the same as that of the differences of temperature 10 : 15 : 20. Taking then the mean of the logarithmic differences as 0·0539, and comparing the values given in Tables IV, V, and VI with that of Table III, the observed and calculated results will be as follows :—

Observed values.	Calculated values.
8·15	—
10·38	10·4
12·04	11·84
13·03	13·4

The greatest difference between the observed and calculated values does not exceed 3 per cent., or a variation which might be due to the differences of the rates of solution of individual bullets under identical conditions.

A number of other experiments were made with different mixtures

of potassium bichromate and sulphuric acid to confirm the above relation between temperature and rate of solution.

Mixture Taken.

{ 29·0 grams potassium bichromate } in 1 litre water.
 { 64·4 „ sulphuric acid }

TABLE VII.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4·505	4·2398	0·2652	300·05	8·82
4·2398	3·9863	0·2535	289·53	8·76
3·9863	3·7401	0·2462	276·42	8·87
3·7401	3·5079	0·2322	265·9	8·74
3·2703	3·056	0·2142	242·84	8·82
Mean value of M/A				8·80

TABLE VIII.—*Mixture as in Preceding Series. Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·7153	4·3755	0·3398	308·5	11·01
4·3755	4·0518	0·3237	292·9	11·05
3·7683	3·4707	0·2976	260·15	11·04
3·4707	3·1848	0·2859	248·85	11·49
3·1848	2·9078	0·277	234·85	11·82
2·9078	2·6488	0·259	220·56	11·75
Mean value for M/A				11·36

From the figures given below, it is evident that the difference of the logarithms of the values for M/A is equal to that observed for the difference of 10° in the preceding observations:—

Temperature.	Value for M/A.	Log M/A.	Difference.
21°	8·8	0·9445	0·1108 = 2 × 0·0554
31	11·36	1·0553	

Adopting the above mean value, 0·0539 for 5°, the observed and calculated results will be as follows:—

Observed.	Calculated.
8·8	—
11·36	11·28

Mixture Taken.

59·0 grams potassium bichromate }
 32·2 „ sulphuric acid. } made up with water to 1 litre.

TABLE IX.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·7419	4·4945	0·2474	312·33	7·92
4·4945	4·2560	0·2385	301·56	7·92
4·256	4·0225	0·2335	290·54	8·04
4·0225	3·8009	0·2216	279·4	7·92
3·8009	3·581	0·2158	266·48	8·10
Value for M/A				7·98

TABLE X.—*Mixture as in Preceding Series. Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·7278	4·4111	0·3167	308·26	10·27
4·4111	4·1093	0·3018	293·39	10·28
4·1093	3·8185	0·2908	279·64	10·40
3·8185	3·5418	0·2767	266·64	10·39
3·5418	3·2731	0·2687	253·21	10·61
3·2731	3·0228	0·2503	239·86	10·44
Mean value.....				10·4

The difference of the logarithms of the above mean values is given below :—

Temperature.	Value for M/A.	Log M/A.	Difference.
21°	7·98	0·902	0·1159 = 2 × 0·0574.
31	10·4	1·0169	

Observed values.	Calculated.
7·98	—
10·4	10·26

It will be necessary to quote only one more pair of results to illustrate the above relation between temperature and amount dissolved off ; these were conducted with the cone apparatus :—

Mixture Taken.

{ 44·2 grams potassium bichromate } made up with water to 1 litre.
 { 48·0 „ sulphuric acid }

TABLE XI.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·5269	4·2562	0·2704	302·59	8·95
4·2562	3·9942	0·262	289·23	9·06
3·9942	3·7427	0·2515	277·09	9·08
3·7427	3·5087	0·234	265·64	8·81
3·5087	3·2777	0·231	254·02	9·09
3·2777	3·0532	0·2225	242·33	9·19
Mean value				9·03

TABLE XII.—*Mixture as in Preceding Series. Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·8232	4·4217	0·4015	311·23	12·9
4·2992	3·9229	0·3763	287·53	13·09
3·9219	3·5767	0·3462	271·05	12·77
3·5767	3·2507	0·326	254·51	12·81
3·2507	2·9406	0·31	238·1	13·02
2·9406	2·6542	0·2865	224·79	12·75
2·6542	2·3867	0·2765	207·29	12·9
2·3867	2·1332	0·2525	192·69	13·1
2·1332	1·8969	0·2363	178·65	13·17
1·8969	1·6772	0·2197	166·86	13·17
Mean value				13·07

The difference of logarithms will be as follows:—

Temperature.	Value for M/A .	Log M/A .	Difference.
21°	9·03	0·9556	0·1606 = 3 × 0·0536.
36	13·07	1·1162	

Observed values.	Calculated.
9·03	—
13·07	13·11

All the above experiments show that the increment of the rate of solution produced by increase of temperature is independent of the proportions of potassium bichromate and sulphuric acid present, as

also of the degree and kind of motion imparted to the metallic bullet.

The results show that the velocity of chemical action between copper and chromic acid is an exponential function of the temperature, the former increasing in geometrical as the latter increases in arithmetical proportion. This relation may be expressed by the equation—

$$\begin{aligned} \text{(i)} \quad v_t &= v_{t'} e^{k(t-t')}, \\ \text{or} \quad \text{(ii)} \quad v_t &= v_{t'} k^{(t-t')}, \end{aligned}$$

in which v_t is the velocity at a higher temperature t , $v_{t'}$ the velocity at a lower temperature t' , and k is a constant. (In equation (i) e = base of Napierian logarithms.) The value for k in equation (i) = 0.0108; hence it follows that the velocity is doubled for every increase of 30°.

It is, perhaps, worth calling attention to the very simple relations between temperature and velocity of chemical change, first pointed out by Messrs. Harcourt and Esson in the case of hydrogen peroxide and hydriodic acid (this Journal, 1867, 492). A list of cases investigated which follow the same law is of interest.

Thus the velocity of reaction between potassium chlorate and hydrochloric acid* is doubled for every 5°, that between hydrogen peroxide and hydriodic acid is doubled for every 10°,† that between ferrous sulphate and potassium chlorate is doubled for every 8° (approximately), that between acetic acid and ethyl alcohol is doubled for every 12°,‡ that between marble and hydrochloric acid is doubled for every 20°,§ and that between copper and chromic acid is doubled for every 30°.

As pointed out by Boguski,|| increase of temperature produces not only an increase of the kinetic energy of the molecules within the liquid but also a decrease of viscosity. Upon these factors, concerning which too little is known at present, depends the numbers of heterogeneous molecules, which have a chance of colliding with one other in any unit interval of time.

VARIATION OF CONDITIONS.

II. Sulphuric Acid.

A series of experiments were made in which the only variable in

* W. H. Pendlebury and Miss M. Seward, *Proc. Roy. Soc.*, **45**, 125.

† J. J. Hood, *Phil. Mag.* [5], **20**, 327.

‡ Berthelot and Pean-St. Gilles, *Ann. Chim. Phys.* [3], **66**, 116. This result is calculated from the data given by the authors; these, though few, are sufficient to show that the chemical change follows the same law. This question has also been discussed by Lemoine, *Études sur les Équilibres chimiques*, p. 178.

§ Spring, *Zeit. physikal. Chem.*, **1**, 219.

|| *Zeit. physikal. Chem.*, **1**, 563.

the conditions was the proportion of sulphuric acid, in order to determine the effect produced by this variation.

Mixture Taken.

{ 41·3 grams sulphuric acid. } made up to 1 litre.
 { 44·2 „ potassium bichromate. . . } made up to 1 litre.

TABLE XIII.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·8033	4·435	0·3683	311·07	11·84
4·435	4·0773	0·3577	294·83	12·14
4·0773	3·7401	0·3372	277·51	12·15
3·7401	3·4282	0·3118	261·92	11·93
3·4282	3·2327	0·2955	247·34	11·95
3·2327	2·9557	0·277	232·41	11·92
2·9557	2·6902	0·2655	217·12	11·94
2·6902	2·4457	0·2445	203·07	12·04
2·4457	2·2157	0·23	190·26	12·07
Mean value				12·00

Mixture Taken.

{ 35·4 grams sulphuric acid. } made up to 1 litre.
 { 44·2 „ potassium bichromate. . } made up to 1 litre.

TABLE XIV.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·7678	4·4438	0·324	308·67	10·50
4·4438	4·1365	0·3073	294·08	10·45
4·1365	3·8403	0·2962	280·15	10·57
3·8403	3·406	0·275	266·53	10·34
3·406	3·154	0·252	240·89	10·46
Mean value				10·44

Mixture Taken.

{ 29·5 grams sulphuric acid. } made up to 1 litre.
 { 44·2 „ potassium bichromate } made up to 1 litre.

TABLE XV.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·6438	4·3715	0·2723	303·96	8·96
4·3715	4·1113	0·2601	292·65	9·06
4·1113	3·8601	0·2512	280·82	8·94
3·8601	3·6228	0·2372	268·96	8·82
3·6228	3·3943	0·2205	256·54	8·91
3·3943	3·1681	0·2255	245·5	9·19
Mean value.....				8·98

Mixture Taken.

{ 23·5 grams sulphuric acid..... } made up to 1 litre.
 { 44·2 „ potassium bichromate. }

TABLE XVI.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$.
4·6632	4·4317	0·2315	310·43	7·46
4·213	3·9927	0·2203	288·65	7·63
3·9927	3·7837	0·209	278·67	7·50
3·7837	3·5877	0·205	268·62	7·63
3·5877	3·3902	0·1965	258·31	7·62
3·3902	3·202	0·1882	247·91	7·58
Mean value				7·60

In the above experiments (Tables XII—XVI), the quantities of sulphuric acid, the only variable in the conditions, have been taken in the arithmetical proportion 2:1·75:1·5:1·25:1; the values for M/A are also in an arithmetical proportion (a result *à priori* probable). Thus assuming a common difference of 1·4 between each successive number in the series of the values for M/A , the values calculated will be—

$$13·2 : 11·8 : 10·4 : 9·0 : 7·6,$$

while those found were

$$13·07 : 12·0 : 10·44 : 8·98 : 7·6,$$

showing a maximum error of 1·5 per cent. between the calculated and the observed numbers.

The increase in the rate of solution is proportional to the quantity of sulphuric acid, or the curve representing the rate of solution as a function of the concentration of the acid is a straight line. The equation for this line is

$$y - 2 = \frac{14}{59} x,$$

in which x is the number of grams of sulphuric acid per litre, and y the value for M/A ; this equation shows that under the same conditions copper would dissolve to a slight extent in an aqueous solution of potassium bichromate of the concentration used in the above experiments, without the presence of the sulphuric acid.

III. *Potassium Bichromate.*

A series of experiments were further made to determine the effect produced by variation of the proportion of the potassium bichromate, other conditions being kept constant.

Mixture Taken.

{ 21.1 grams potassium bichromate }
 { 47.2 „ sulphuric acid } made up to 1 litre.

TABLE XVII.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4.6843	4.3149	0.2694	314.98	8.53
4.3149	4.057	0.2574	296.81	8.67
4.0575	3.8148	0.2427	285.12	8.51
3.8148	3.5818	0.233	274.17	8.50
3.5818	3.3613	0.2205	263.96	8.34
3.1588	2.9503	0.2055	241.95	8.49
2.9503	2.7533	0.197	232.26	8.48
2.7533	2.5629	0.1904	222.45	8.56
Mean value				8.51

Mixture Taken.

{ 27·62 grams potassium bichromate } made up to 1 litre.
 { 47·12 „ sulphuric acid }

TABLE XVIII.—*Temperature 36°*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$
4·6873	4·3475	0·3398	305·6	11·12
4·3475	4·0218	0·3257	290·7	11·21
4·0218	3·7075	0·3133	276·85	11·32
3·7075	3·4173	0·2903	260·34	11·15
3·4173	3·1453	0·272	246·57	11·03
3·1453	2·8668	0·2585	233·15	11·11
2·8668	2·6231	0·2437	218·61	11·15
2·6231	2·3908	0·2323	206·47	11·25
2·3908	2·1226	0·2182	194·03	11·25
Mean value				11·17

Mixture Taken.

{ 33·15 grams potassium bichromate } made up to 1 litre.
 { 47·12 „ sulphuric acid }

TABLE XIX.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$
4·6108	4·2408	0·37	301·53	12·27
4·2408	3·8904	0·3504	286·05	12·23
3·8904	3·3133	0·3396	269·54	12·60
3·3133	3·0248	0·2885	236·56	12·20
3·0248	2·7473	0·2775	220·98	12·56
2·7473	2·4897	0·2576	206·17	12·49
Mean value				12·39

Mixture Taken.

{ 55·25 grams potassium bichromate } made up to 1 litre.
 { 47·2 „ sulphuric acid }

TABLE XX.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4·3905	3·9876	0·4009	290·64	13·73
3·9896	3·6118	0·3778	272·28	13·88
3·6118	3·2651	0·3567	254·61	14·00
3·2651	2·9331	0·332	237·1	14·01
2·9331	2·6418	0·2913	220·8	13·81
2·6418	2·3573	0·2845	206·08	13·81
2·3573	2·0893	0·2680	189·75	14·12
Mean value				13·91

Mixture Taken.

{ 66·3 grams potassium bichromate } made up to 1 litre.
 { 47·12 „ sulphuric acid }

TABLE XXI.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4·656	4·2263	0·4297	306·27	14·03
4·2263	3·8258	0·4005	281·62	14·22
3·8258	3·4238	0·372	262·48	14·17
3·4238	3·0888	0·335	241·08	13·92
3·0888	2·7671	0·3217	226·84	14·21
2·7671	2·4666	0·3002	211·63	14·19
2·4666	2·1875	0·2791	195·13	14·31
Mean value				14·15

The results set forth in Tables XVII to XXI and XII are summed up below; the general proportions of potassium bichromate, which were taken in the ratio 1:1·25:1·5:2:2·5:3; in the second column are given the values for M/A , and in the third are given the difference, either calculated or determined, which correspond to each successive addition of 11·1 grams potassium bichromate.

	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
Proportion of potassium bichromate	22·1	27·62	33·15	44·2	55·2	66·3
Values of $\frac{M}{A}$	8·51	11·17	12·39	13·07	13·91	14·15
Differences	5·32		4·36	0·68	0·84	0·24

It is evident from the above figures that the effect produced by each successive addition of potassium bichromate is at first considerable, then is nearly proportional to the amount of potassium bichromate added, and finally is reduced almost to *nil*. (The numbers 0·67 and 0·84 would become equal if there were an error of less than 1 per cent. in any of the three values 12·39, 13·07, and 13·91.) It is probable that potassium bichromate, when added beyond a certain amount, would merely be so much inert matter, or even so much matter in the way of the colliding molecules of copper and sulphuric acid.

Conclusion.

The main results embodied in the present paper may be summed up as follows:—

(1.) When a metallic sphere, placed within an acid liquid, receives an equal number of impacts per unit time, or is regularly rotated, it will dissolve uniformly, the amount dissolved off being, as was to be expected, proportional to the surface exposed.

(2.) In the particular case of metallic copper within a solution of potassium bichromate acidulated with sulphuric acid, the amount of metal dissolved off is dependent upon the conditions of (a) temperature, (b) proportion of sulphuric acid, and (c) proportion of potassium bichromate.

(a.) If the temperature in degrees be varied in an arithmetical proportion, the amount dissolved off varies in a geometrical proportion. This amount is doubled for every 30°, whatever be the concentration or acidity of the solution. This change is thus perfectly analogous to several others quite different from it and from one another in their nature.

(b.) If the quantities of sulphuric acid, other conditions remaining the same, be varied in arithmetical proportion, the amount of metal dissolved off also varies in an arithmetical proportion.

(c.) If the quantities of potassium bichromate, other conditions remaining the same, be varied in arithmetical proportion, the amount

dissolved off is at first increased considerably by each successive addition of potassium bichromate, then varies in arithmetical proportion, and finally is but little affected by the amount of potassium bichromate present.