CCXIX.—*The Dynamics of the Decomposition of Persulphuric Acid and its Salts in Aqueous Solution.*

By Leila Green and Orme Masson.

Levi and Migliorini (*Gazzetta*, 1906, **36**, ii, 599) have shown that potassium and sodium persulphates decompose in aqueous solution unimolecularly, and that the action is much accelerated by the addition of acids. Our own experiments confirm both of these results. It is, however, somewhat difficult to reconcile them with one another, for the action itself produces acid sulphate, and can, indeed, be followed throughout its course by the increasing acidity, so that the curve should exhibit the features of an auto-accelerated, rather than those of an unmodified, unimolecular action. The difficulty, however, disappears if the acid sulphate product be assumed to ionise only into metal and HSO_4', and to provide practically no $H^{\bullet}$ ions, or if, in other words, sulphuric acid be regarded as a monobasic acid under the conditions of the experiments. The action may then be formulated by the equation:

$$S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$

which makes it strictly unimolecular in form. On general grounds the assumption may be objected to, but it does not appear possible to explain without it the behaviour of persulphuric acid and its salts, and it will be shown that one can, by its aid, co-ordinate the various results obtained with the acid, its potassium and sodium salts, its barium salt, and mixtures of these with each other, with other salts, and with acids. One or two unexplained difficulties remain, which will be dealt with in the sequel.

The persulphate solutions employed by us were obtained from solutions of the barium salt, prepared from commercial ammonium persulphate by treatment with excess of barium hydroxide in a vacuum and subsequent neutralisation with dilute sulphuric acid.

The initial strength of each persulphate solution was determined by measuring the final acidity produced by boiling a measured volume, the titrations being carried out with standard sodium hydroxide, using methyl-orange as indicator. Comparative tests were made in some cases by the ferrous sulphate and permanganate method, and also by gravimetric determinations of the metal as sulphate. The results in all cases agreed fairly well, but the acidimetric method was found to be the most accurate, besides having the advantage of rapidity. The progress of the decomposition in each experiment was also followed by acidimetry. In all cases the temperature of the thermostat was 80·0°, which was found to give a convenient rate of action, except in the experiments conducted at 70° and 90° for the purpose of fixing a temperature-coefficient. The solution was always divided at the outset into a number of 5 c.c. samples, and these were heated in closed tubes, according to the method described in a previous research on cyanates (Masson and Masson, *Zeitsch. physikal. Chem.*, 1910, **70**, 290).

The persulphates which we have examined may be divided, for the present purpose, into three classes. The first contains those of sodium, potassium, and ammonium, which are neutral salts convertible into soluble acid sulphates. The magnesium salt properly belongs to this class, but differs somewhat in its behaviour from the other members. The second class contains persulphuric acid itself, which doubles its acidity by conversion into sulphuric acid.

The third class contains barium persulphate, which, originally neutral, produces persulphuric acid and insoluble barium sulphate. The course of the action is quite different in each of these classes, and they therefore require separate consideration.

In the sequel we have thought it desirable to economise space by suppressing most of the numerical details of our work, and have therefore given only the essential results, except where fuller treatment appeared necessary.

Class I.—Neutral Persulphates which form Soluble Acid Sulphates.

These cases conform to the equation for simple unimolecular action:

$$\frac{dx}{dt} = k_1(A - x), \text{ or } k_1 = \frac{1}{t_2 - t_1}\log_e\frac{A - x_1}{A - x_2},$$

where A is the initial concentration of persulphate, and $A - x$ is its value at any subsequent time, t. To avoid some slight uncertainty due to the time required to raise the tubes to the bath temperature, the time at which the first sample was taken from the bath was selected, rather than the moment of immersion, as t_1. The values of k_1 given in table I are averages calculated in each case from several points in a curve covering nearly the whole course of the action. Separate values in any one experiment were found to agree well. It is evident that k_1 is but slightly dependent on the initial concentration, or even on the nature of the metallic radicle.

In this and subsequent tables, the concentrations are expressed in gram-molecules of persulphate per litre, and the times are measured in minutes:

TABLE I.

Salt.	A.	k_1.
$Na_2S_2O_8$	0·226	0·00541
$Na_2S_2O_8$	0·125	0·00577
$Na_2S_2O_8$	0·127	0·00533
$K_2S_2O_8$	0·108	0·00545
$(NH_4)_2S_2O_8$	0·229	0·0061

The curve for the ammonium salt showed rather more irregularity than the others, and its mean velocity-coefficient was, as shown, perceptibly higher. This is perhaps explained by the formation of traces of nitric acid by oxidation, with consequent acceleration, but the divergence from the normal course is only slight.

Experiments with sodium persulphate solution containing added sodium nitrate (selected as a typical neutral salt of the same metal) have proved that the only effect of such addition is to raise slightly the unimolecular constant. Thus, in a test with 0·1283-sodium persulphate and 0·25-sodium nitrate solution, with twelve experimental points covering a range of 85 per cent. decomposition, k_1 was found to vary irregularly between the extreme values 0·0062 and 0·0068, with a mean value of 0·0065. On the other hand, it will be shown that acids largely accelerate the action, and the special influences of added sulphates will also be dealt with later.

The magnesium salt, in contrast to those of the alkali metals, shows distinctly the effect of auto-acceleration, which, in this case, is probably to be explained by the formation of some non-ionised magnesium sulphate and free hydrogen ions, according to the equation:

$$Mg^{\cdot\cdot} + HSO_4' \rightleftharpoons MgSO_4 + H^{\cdot}.$$

Thus, in an experiment in which the initial concentration of magnesium persulphate was 0·2414, the unimolecular coefficient, calculated in the usual way, was found to increase steadily from about 0·0055 (appreciably equal to that of the sodium or potassium salt) at the start to 0·0066 when the action was half completed, and 0·0092 when less than 10 per cent. remained undecomposed. A similar, but much more pronounced, auto-acceleration will be shown to occur in the case of the barium salt, where the precipitation of the insoluble sulphate necessarily adds hydrogen ions to the solution. But the case of persulphuric acid itself must be discussed first.

Class II.—Persulphuric Acid.

In this case the curves obtained are again of the simple unimolecular form, with no sign of acceleration by increase of hydrogen ions; but it differs in two respects from that of the persulphates of the alkali metals. In the first place, the velocity is considerably greater, and, in the second place, the value of its coefficient is dependent on the initial concentration, so as to vary in different experiments while constant in any one. These facts are in accordance with the hypothesis already put forward, that the action proceeds practically according to the equation:

$$S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$

and that it is accelerated by the hydrogen ions which are initially present and remain unchanged in concentration. Such a hypothesis leads to the differential equation:

$$\frac{dx}{dt} = (k_2 + kA)(A - x),$$

where $k_2 + kA$ is necessarily a constant (K) in any given experiment, and

$$K = k_2 + kA = \frac{1}{t_2 - t_1}\log_e\frac{A - x_1}{A - x_2}.$$

A simple explanation suggests itself for this accelerative action of hydrogen ions. It may be assumed that, at the dilutions employed, the great bulk of the persulphuric acid is completely ionised into $2H^{\cdot}$ and S_2O_8'', while a small proportion is converted into $H^{\cdot}$ and HS_2O_8'. If this proportion be small enough, the total $H^{\cdot}$ concentration may be taken as constant and equal to $2A$, whilst that of the S_2O_8'' is appreciably equal to $A-x$, and that of the HS_2O_8' itself is therefore proportional to $A(A-x)$. If, further, the HS_2O_8' has a sufficiently high rate of reaction as compared with the S_2O_8'', it will make itself felt in spite of its small concentration, and the total velocity of the action will be the sum of two velocities, $k_2(A-x)$ and $kA(A-x)$, in accordance with the equation already given.

By comparison of experiments with different A values, it is easy to evaluate k_2 and k; and it has been found in this way that $k_2 = 0{\cdot}010$ and $k = 0{\cdot}163$. These figures are illustrated by a comparison of the found and calculated velocity coefficients in table II. The fact that k_2 is nearly twice as great as the k_1 of sodium or potassium persulphate is difficult to explain on any hypothesis, for it implies some influence of the hydrogen ions other than that represented by the term $kA(A-x)$ and independent of their concentration. It is a fact, however, that, whilst $dx/dt = 0{\cdot}0055(A-x)$ holds for the sodium and potassium salts, the equation for persulphuric acid is

$$\frac{dx}{dt} = (0{\cdot}010 + 0{\cdot}163A)(A-x) = K(A-x).$$

TABLE II.

Persulphuric Acid.

A.	K (found).	K (calculated).
0·2566	0·0527	0·0518
0·1251	0·0304	0·0304
0·1237	0·0302	0·0302
0·0923	0·0258	0·0250
0·0644	0·0210	0·0205
0·0416	0·0184	0·0168

The solutions used in the first, third, and fourth of these tests were prepared from barium persulphate by adding the calculated quantity of sulphuric acid, and were filtered from the barium sulphate; while those used in the second, fifth, and sixth were obtained by allowing barium persulphate solution to decompose automatically at 80°, and contained the precipitated sulphate in suspension. These cases will be discussed later.

Persulphuric Acid with Added Nitric Acid.

In this case there is a permanent increase of the hydrogen ions, and, if the initial concentrations of the two acids (both reckoned as dibasic, that is, as $H_2S_2O_8$ and $H_2N_2O_6$) be respectively A and B, the course of the action should be expressed by the equation:

$$\frac{dx}{dt}=\{k_2+k(A+B)\}(A-x),$$

where $k_2+k(A+B)$ appears as a unimolecular constant in any given experiment, and

$$K=k_2+k(A+B)=\frac{1}{t_2-t_1}\log_e\frac{A-x_1}{A-x_2}.$$

This was confirmed by the experiments summarised in table III. The first of these tests was made with an original mixture of persulphuric acid and nitric acid, while the other three were the later parts of experiments, in which barium persulphate, mixed with nitric acid, was allowed to decompose at 80° until there remained only persulphuric acid and nitric acid in solution, and the subsequent decomposition was then studied. These tests will be referred to later. The figures in the last column of the table show the value which K would have if the nitric acid were absent (compare table II), and are given to indicate clearly its effect.

TABLE III.

Persulphuric Acid with Added Nitric Acid.

A.	*B*.	*K* (found).	*K* (calculated).	*K* (original).
0·1248	0·1242	0·0500	0·0506	0·0304
0·0635	0·1845	0·0508	0·0504	0·0204
0·0628	0·1255	0·0414	0·0407	0·0202
0·0630	0·0634	0·0315	0·0306	0·0203

Mixed Persulphuric Acid and Sodium Persulphate.

The theory for such a case may be given on the assumption that the k_1 and k_2 constants are active approximately in proportion to the unchanging relative quantities of $Na^{\cdot}$ and $H^{\cdot}$, and that the latter also contributes its special accelerative effect. Thus, if the initial $H_2S_2O_8$ be A, and the initial $Na_2S_2O_8$ be B, whilst x represents the total S_2O_8 destroyed, A and B will also represent at any time the $(H^{\cdot})_2$ and the $(Na^{\cdot})_2$ respectively, and

$$\frac{dx}{dt}=\{k_2\frac{A}{A+B}+k_1\frac{B}{A+B}+kA\}(A+B-x).$$

In any given experiment therefore a unimolecular constant should be obtained, and

$$K = k_2\frac{A}{A+B} + k_1\frac{B}{A+B} + kA = \frac{1}{t_2 - t_1}\log_e\frac{A+B-x_1}{A+B-x_2}.$$

In one test, in which $A = 0{\cdot}1285$ and $B = 0{\cdot}1234$, a mean value of 0·0276 was found for K in place of the calculated value 0·0288. In another, in which $A = 0{\cdot}0625$ and $B = 0{\cdot}1250$, the found and calculated values were respectively 0·0183 and 0·0172. The agreement is thus fairly satisfactory in both cases.

Persulphuric Acid with Added Sodium Nitrate.

This case is similar to the last, except that, the permanent concentrations of the $(H^{\cdot})_2$ and $(Na^{\cdot})_2$ being respectively A and B, that of the S_2O_8'' at any time is $A - x$ instead of $A + B - x$. The constant is here therefore

$$K = k_2\frac{A}{A+B} + k_1\frac{B}{A+B} + kA = \frac{1}{t_2 - t_1}\log_e\frac{A-x_1}{A-x_2}.$$

In the only test carried out, $A = 0{\cdot}1377$ and $B = 0{\cdot}0625$, giving the calculated value of the constant as 0·0311. The mean experimental value was 0·0325, which is identical with that calculated on the assumption that the sodium nitrate is quite without effect. The difference is in any case too small to be significant, but it may be pointed out that a similar discrepancy was exhibited by the mixture of sodium persulphate and sodium nitrate, indicating that the latter has a small accelerative effect, not included in the theory, which may, in the present case, compensate for the expected small lowering of the K value.

Class III.—Barium Persulphate.

This case differs from the others in the precipitation of the product barium sulphate, and it differs also in the form of the curve in which x is plotted against t; for this, being at first concave towards the x axis, at once points to strong auto-acceleration. The total change affecting the barium salt is represented by the equation:

$$2BaS_2O_8 + H_2O = H_2S_2O_8 + 2BaSO_4 + \tfrac{1}{2}O_2,$$

and it must occur in two steps, namely:

$$(1)\ S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$
$$(2)\ 2Ba^{\cdot\cdot} + 2HSO_4' = 2BaSO_4 + 2H^{\cdot}.$$

The first of these is a relatively slow action, and the second keeps pace with it. Thus $2Ba^{\cdot\cdot}$ disappear from the solution for one S_2O_8'' destroyed; and if the latter be x, as in previous cases, it is evident that x also represents the persulphuric acid (or acidity) produced, and $A - 2x$ represents the barium persulphate remaining.

This holds until $A-x=x=\frac{1}{2}A$, when the precipitation of the barium is complete, and subsequent action is concerned only with persulphuric acid. The whole action may thus be divided into two consecutive stages, the characters of which are shown in the following summary:

	Total S_2O_8.	BaS_2O_8.	$H_2S_2O_8$.	Form of curve.
First stage	$A-x$	$A-2x$	x	Autocatalytic
Half-way point	$x=\frac{1}{2}A=A-x$	0	$\frac{1}{2}A$	—
Second stage	$A-x$	0	$A-x$	Simple unimolecular

Three of the six experiments with persulphuric acid solutions summarised in table II were, in fact, the second stages of experiments with barium persulphate, which will now be dealt with in greater detail. Comparison of these with the others shows that the presence of precipitated barium sulphate (since there was no other real difference) does not appreciably affect the velocity of persulphate decomposition by any kind of contact catalysis. A similar conclusion may be drawn from the sodium persulphate solutions of table I, one of which (the third) was mixed with the precipitate beforehand in order to test this question. It may therefore be concluded safely that the formation of this product has no such direct effect on the decomposition of barium persulphate itself in the first stage of the action.

In table II, which referred only to persulphuric acid, A and x were given the corresponding significance, and were equal respectively to $\frac{1}{2}A$ and $x-\frac{1}{2}A$, where the symbols are used in reference to the original barium persulphate contents, as in the above summary. But they must now be used in this latter sense, and the equation for the curve, after the complete precipitation of the barium, must be written $dx/dt=(k_2+kA/2)(A-x)$.

Now, since the whole curve is continuous, it is evident that the equation for the first, or autocatalytic, stage must be such as to become identical with that just given at the half-way point, where $x=\frac{1}{2}A$. But it has been shown already that the k_2 of persulphuric acid and the k_1 of sodium or potassium persulphates have very different values, so that it might fairly be expected that the constant (k_3) for barium persulphate should differ from k_2, and perhaps also from k_1. Such proves to be the case, for it can be shown by a graphic method that the initial velocity of the decomposition of the pure barium salt solution, when it is as yet unmixed with persulphuric acid (when $x=0$), approximates to $dx/dt=0{\cdot}0040A$. We thus have $k_3=0{\cdot}0040$, whilst $k_1=0{\cdot}0055$ and $k_2=0{\cdot}010$, and the catalytic constant $k=0{\cdot}163$. It must therefore be assumed that, in any mixture of two of these salts, the appropriate constants will be operative in proportion to the amounts present, and that, consequently, the equation for the first stage of the barium persulphate action is:

$$\frac{dx}{dt}=(k_3\frac{A-2x}{A-x}+k_2\frac{x}{A-x}+kx)(A-x).$$

This conforms to the requirements, for the contents of the first bracket are equal to k_3 at the starting point, where $x=0$, and to $k_2+kA/2$ at the half-way point, where $x=A/2$. It will be shown, also, that it expresses the whole of the experimental results with considerable accuracy. It is, perhaps, not superfluous to point out that, if hydrogen and barium persulphates had the same velocity constant (if $k_3=k_2$), the equation would be the ordinary one expressing an autocatalysed unimolecular action, for it would then become $dx/dt=(k_2+kx)(A-x)$.

By integration of the above differential equation, we obtain an equation which may be written:

$$k(M+N)=\frac{1}{t}\log_e\frac{M(N+x)}{N(M-x)},$$

where M and N are constants in any given experiment, but vary with the initial concentration, and have the values:

$$M=\sqrt{\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}A}+\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)$$

$$N=\sqrt{\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}A}-\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right).$$

Such an equation is of but little use for theoretical purposes unless M and N can be evaluated by independent measurements of the fundamental constants from which they are derived; but we are able to do this in the present case, having found already k_2 and k from the study of persulphuric acid, and k_3 from the initial velocity of pure barium persulphate solutions. We are thus enabled to compare the results calculated from the integrated equation with those obtained by experiment.

The details of one complete experiment with initially neutral barium persulphate solution are shown in table IV. The values of M and N, given at the head of the table, were calculated from those of A, k, k_2, and k_3; and the theory of the first stage of the action may be tested by the constancy of $\frac{1}{t}\log_{10}\frac{M(N+x)}{N(M-x)}$ at different values of t, and also by its agreement with the calculated value of $0{\cdot}4343k(M+N)$. Also the time is noted (as read from the curve) at which $x=\frac{1}{2}A$, that is, the time of the complete precipitation of the barium sulphate. The simple unimolecular character of the decomposition of the persulphuric acid in the second stage is shown by the practical constancy of the normal logarithmic function, calculated from the observed values of x and t, and the theory of its dependence on A by a comparison of its mean value with that of $k_2+kA/2$ (compare table II).

TABLE IV.

Barium Persulphate. $A=0{\cdot}2502$.

First Stage. $M=0{\cdot}2840$, $N=0{\cdot}0216$.

t.	x.	$1/t\log_{10}\dfrac{M(N+x)}{N(M-x)}$.
10°	0·0131	0·0226
25	0·0398	0·0208
35	0·0663	0·0207
45	0·0974	0·0205
50	0·1160	0·0206

Mean constant found .... = 0·0210.
Calculated value of $0{\cdot}4343\,k(M+N)$ = 0·0216.

Second Stage, after complete precipitation of Ba at $t=52{\cdot}5°$.

t.	x.	$1/t-60\log_{10}\dfrac{A-0{\cdot}1558}{A-x}$.
60°	0·1558	—
70	0·1796	0·0126
85	0·2068	0·0135
100	0·2221	0·0132
115	0·2336	0·0137
135	0·2411	0·0135
155	0·2441	0·0125

Mean constant found .... = 0·0132.
Calculated value of $0{\cdot}4343(k_2+kA/2)$ = 0·0132.

The details of two tests with smaller concentrations of barium persulphate may be given more briefly. In one of these the value of A was 0·1288, whence $0{\cdot}4343k(M+N)=0{\cdot}0128$ by calculation, and during the first stage of the action (sixty-five minutes) the values found for $\dfrac{1}{t}\log_{10}\dfrac{M(N+x)}{N(M-x)}$ ranged from 0·0130 to 0·0134 (mean $=0{\cdot}0132$). During the second stage of the same experiment, the mean unimolecular constant found was 0·0091 in place of the calculated value 0·0089. In the other case, A was 0·0832, whence $0{\cdot}4343k(M+N)=0{\cdot}0093$, and the constant found during the first stage (seventy minutes) ranged from 0·0103 to 0·0112 (mean, 0·0109), while the calculated and found unimolecular constants of the second stage were 0·0073 and 0·0080. In this case therefore the numerical agreement was not quite so good as in those of the stronger solutions.

It seems worth while to call attention here to a striking contrast between the persulphate case and that of the decomposition of cyanates in aqueous solution, which in some respects is very similar (Masson and Masson, *loc. cit.*). Barium cyanate, which precipitates barium carbonate, gives a simple unimolecular curve, whilst the cyanates of sodium and potassium, which yield soluble ammonium carbonate, give strongly auto-accelerated unimolecular curves. Barium persulphate, which precipitates barium sulphate, gives strongly auto-accelerated unimolecular curves, whilst the persulphates of sodium and potassium, which yield soluble acid sulphates, give simple unimolecular curves. In the former case, it was proved that ammonium carbonate accelerates the action, whilst in the latter case soluble acid sulphates have no such influence, but their hydrogen ions have, when liberated by the precipitation of insoluble sulphate.

Mixed Barium Persulphate and Barium Nitrate.

If the latter be added in quantity equivalent to the former (or more), the barium ions cannot become exhausted by precipitation as barium sulphate so long as persulphate ions remain, and the whole action can be written:

$$BaS_2O_8 + BaN_2O_6 + H_2O = 2BaSO_4 + 2HNO_3 + \tfrac{1}{2}O_2.$$

The action therefore does not divide into two distinct stages as in the case of initially pure barium persulphate, but is marked throughout its course by continuous precipitation and increase of hydrogen ion concentration. Hence the auto-catalytic character must be also continuous, and this is found to be the case.

If A represent the initial concentration of the barium persulphate and B that of the barium nitrate, the composition of the solution at any subsequent time is such that it contains barium and hydrogen persulphates and nitrates with the following concentrations: $S_2O_8'' = A - x$, $(NO_3')_2 = B$, $Ba^{\cdot\cdot} = A + B - 2x$, and $(H^{\cdot})_2 = x$. The total cations or anions (considered as bivalent) are thus always equal to $A + B - x$.

If, as in the case of initially pure barium persulphate, it be assumed that the barium and hydrogen ions are operative in proportion to their relative concentrations, while the latter also produce their special catalytic effect, we have the following differential equation to express the course of the action:

$$\frac{dx}{dt} = \left\{k_3\frac{A + B - 2x}{A + B - x} + k_2\frac{x}{A + B - x} + kx\right\}(A - x),$$

which, by integration, gives:

$$k(M + N) = \frac{1}{t}\left\{\frac{N + A + B}{N + A}\log_e\frac{A(N + x)}{N(A - x)} - \frac{M - A - B}{M - A}\log_e\frac{A(M - x)}{M(A - x)}\right\},$$

where M and N are constants in any given experiment, and have the values:

$$M=\sqrt{\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}(A+B)}+\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right),$$

$$N=\sqrt{\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}(A+B)}-\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right).$$

An obvious simplification of the formula results where, as in the actual experiment (table V), the barium persulphate and nitrate are given the same initial concentration, or $B=A$. The values of M and N given at the head of the table were calculated from that of A and those of k_3, k_2, and k, as already determined. In the third column are given the found values of the constant:

$$K=\frac{1}{t}\left\{\frac{N+2A}{N+A}\log_{10}\frac{A(N+x)}{N(A-x)}-\frac{M-2A}{M-A}\log_{10}\frac{A(M-x)}{M(A-x)}\right\},$$

which may be compared with each other as to constancy and also with the calculated value of $0{\cdot}4343k(M+N)$, given at the end of the table. The agreement is fairly satisfactory.

TABLE V.

Barium Persulphate and Barium Nitrate in Equimolecular Mixture.

$B=A=0{\cdot}1253.\quad M=0{\cdot}2845.\quad N=0{\cdot}0217.$

t.	*x.*	*K.*
10°	0·0062	0·0240
20	0·0147	0·0255
30	0·0223	0·0239
45	0·0355	0·0228
60	0·0457	0·0208
70	0·0577	0·0229
75	0·0643	0·0219
90	0·0791	0·0220
105	0·0926	0·0223
120	0·1019	0·0220
135	0·1105	0·0223
160	0·1200	0·0238
195	0·1236	0·0238

Mean value of K found .... = 0·0229.
Calculated value of $0{\cdot}4343k(M+N)$ = 0·0217.

Barium Persulphate with Added Nitric Acid.

Here, as in the case of pure barium persulphate, the action may be expected to divide itself into two stages, since the barium must be totally precipitated when $x=A-x=\frac{1}{2}A$. If B stand for the added nitric acid (reckoned as dibasic) or for the initial $(\mathrm{H}^{\cdot})_2$, the quantity of the latter must steadily increase by production of persulphuric acid during the first stage, where its value is $B+x$; but from the middle point onwards through the second stage it must retain the value $B+\frac{1}{2}A$. As in the simple case, the $Ba^{\cdot\cdot}$ must have the value $A-2x$ until this becomes nil at the middle point, whilst the $S_2O_8{}''$ must have the value $A-x$ from first to last. The first stage should therefore show an autocatalytic curve merging into the simple unimolecular one of the second stage, and the respective differential equations should be:

$$\text{(I.)}\quad \frac{dx}{dt}=\left\{k_3\frac{A-2x}{A+B-x}+k_2\frac{B+x}{A+B-x}+k(B+x)\right\}(A-x),$$

$$\text{(II.)}\quad \frac{dx}{dt}=\{k_2+k(B+\tfrac{1}{2}A)\}(A-x),$$

which are identical when $x=\frac{1}{2}A$.

These equations, indeed, follow logically from those already confirmed for the case of a mixture of barium persulphate and barium nitrate, for it is obvious that such a mixture, if it initially contains excess of the former ingredient, must, at a certain point in its history, become converted into a solution of barium persulphate and nitric acid, and subsequently into one of persulphuric acid and nitric acid. There are thus three distinct stages in such an action, and it seems an unavoidable conclusion that the theory which is quantitatively applicable to the mixtures of the first stage (table V) and also to those of the third (table III) must apply equally well to those of the second. Nevertheless, it has been found in a series of experiments with barium persulphate and nitric acid in different proportions that the nitric acid produces initially only about half the acceleration indicated in equation I, although it gradually increases its effect as the action proceeds, and attains full value as an accelerator when the barium is completely precipitated, after which equation II holds well. Without further investigation, it does not seem possible to reconcile these observations.

The Influence of Sulphates, Produced or Added.

As already pointed out, sulphuric acid or acid sulphate is a necessary product of the decomposition of persulphuric acid or persulphates of the sodium class of metals, and yet there is in these cases an entire absence of that autocatalysis which is so marked a feature in the case of barium persulphate, where the growing acidity is due to persulphuric acid formed by the precipitation of barium sulphate. The explanation already suggested is that the negative ions produced are in reality $HSO_4{}'$ (not $SO_4{}''$), so that there is no appreciable increase in the concentration of $H^{\cdot}$ ions (the true accelerator) unless the conditions are disturbed by precipitation or, to a smaller extent, by the process mentioned in the case of the magnesium salt. Briefly, the hypothesis is that sulphuric acid acts practically as a monobasic acid in these solutions, while persulphuric acid itself acts as a dibasic one.

The most direct test of this view, apart from the evidence already given in support of it, is obtained by studying the velocity of the decomposition of persulphuric acid and sodium persulphate solutions, to which have been added beforehand known quantities of sulphuric acid, sodium hydrogen sulphate (that is, sodium sulphate and sulphuric acid), or sodium sulphate. According to the hypothesis, the velocity coefficient should not be affected by adding either sodium sulphate or sodium hydrogen sulphate to sodium persulphate; sodium hydrogen sulphate should produce but a slight lowering of the coefficient of persulphuric acid by adding $Na^{\cdot}$ ions to the solution without altering the $H^{\cdot}$ concentration; sodium sulphate should largely reduce this coefficient by converting free $H^{\cdot}$ into $HSO_4{}'$; and added sulphuric acid should accelerate in both cases, but only to the extent due to it as a monobasic acid, or half as much as the equivalent quantity of nitric acid or of persulphuric acid itself. In all cases the numerical results predicted by the hypothesis can be calculated from a knowledge of the fundamental constants already given, namely, $k_1 = 0{\cdot}0055$ for $(Na^{\cdot})_2$, $k_2 = 0{\cdot}010$ for $(H^{\cdot})_2$, and $k = 0{\cdot}163$ for $(H^{\cdot})_2$ acceleration.

The results of the experiments performed confirm these expectations, with one rather notable exception in the case of the addition of sodium sulphate to sodium persulphate. Here the unimolecular constant, although it has at first the normal and expected value of about 0·0055, quickly diminishes until it reaches a steady value, considerably smaller and dependent on the amount of added neutral sulphate. Four tests were made with approximately $\frac{1}{8}$-molar-sodium persulphate, containing respectively 0·060, 0·125, 0·128, and 0·255 molecule of sodium sulphate. In each case the curve showed a similar retardation until about one-fifth of the persulphate was decomposed, and thereafter, and reckoned from this point, a good unimolecular constant was obtained, the respective values being 0·0035, 0·0025, 0·0025, and 0·0020. These results point to some complication, which, as will be shown, is never met with except in the presence of mixed neutral and acid sulphate, and which is perhaps due to a reverse action in which the dissolved oxygen plays a part; for this product is the only substance present whose quantity is initially nil, and tends, on account of its limited solubility, to increase quickly to a maximum.

In all the other cases the curves showed steady unimolecular actions, and the found velocity coefficients agreed fairly well with those calculated in accordance with the hypothesis. Although the agreement is not quantitatively exact, it is noteworthy that the results fully establish the following facts:

(1) Addition of sodium hydrogen sulphate produces no marked acceleration, showing that it does not add $H^\cdot$ ions; (2) addition of sodium sulphate to persulphuric acid produces a large retardation, which points to a suppression of $H^\cdot$ ions; (3) addition of sulphuric acid produces such acceleration as points to the ionisation of about half its hydrogen.

The results are summarised in table VI. In the first column are given the nature and concentration of the persulphate used. In the second, the added sulphate is similarly specified. In the third, under K (found), is given the experimental unimolecular constant, this being, as in previous cases, the mean of several concordant values found over a large range of action. In the fourth column, under K (calculated), is given the value of $k_1\frac{\mathrm{Na}^\cdot}{\mathrm{Na}^\cdot + \mathrm{H}^\cdot} + k_2\frac{\mathrm{H}^\cdot}{\mathrm{Na}^\cdot + \mathrm{H}^\cdot} + k(\mathrm{H}^\cdot)_2$, where the ionic symbols refer to the corresponding concentrations after allowance for the conversion of all SO_4 into HSO_4' ions. In the fifth column, under K (original), is given, for comparison, the value the constant would have if the added sulphate produced no effect whatever.

TABLE VI.

The Effects of Added Sulphates.

Persulphate.	Sulphate.	K found.	K calculated.	K original.
$0·1285Na_2S_2O_8$	$0·1338NaHSO_4$	0·0060	0·0055	0·0055
$0·1304Na_2S_2O_8$	$0·1332H_2SO_4$	0·0161	0·0179	0·0055
$0·1273Na_2S_2O_8$	$0·3767H_2SO_4$	0·0372	0·0389	0·0055
$0·1185H_2S_2O_8$	$0·1250Na_2SO_4$	0·0151	0·0160	0·0293
$0·1248H_2S_2O_8$	$0·1366NaHSO_4$	0·0304	0·0288	0·0303
$0·1235H_2S_2O_8$	$0·0508H_2SO_4$	0·0370	0·0343	0·0301
$0·1276H_2S_2O_8$	$0·1194H_2SO_4$	0·0421	0·0405	0·0308
$0·1285H_2S_2O_8$	$0·1544H_2SO_4$	0·0425	0·0435	0·0309

The Effects of Added Alkali.

Levi and Migliorini found that alkalis accelerate the persulphate decomposition, but to a smaller extent than acids. Our experiments, however, with persulphates of the first class do not confirm this. When sodium or potassium persulphate is mixed with the corresponding alkali in equivalent, or greater, amount, a regular unimolecular curve is obtained with a constant which is almost identical with that characteristic of the pure salt solution. It is, indeed, very slightly smaller, which is probably accounted for by the physical effect of the extra dissolved substance, but there is no evidence of positive or negative acceleration by hydroxyl ions. These, of course, become destroyed as the action proceeds, for they necessarily neutralise the acid sulphate product, and any such catalytic effect would thus continuously diminish, and the curve would not be that of a simple unimolecular action. It is noteworthy that the normal sulphate which results from this neutralisation does not produce any such marked retardation as was observed when the same salt was added beforehand to sodium persulphate, so that it may be concluded that the reaction responsible for that complication can occur only in the presence of both normal and acid sulphate, as already mentioned.

The results of four experiments are summarised in table VII. The k_1 values here may be compared with those cited for the pure salts in table I.

TABLE VII.

Effects of Added Alkali.

Persulphate.	Alkali.	k_1 found.
$0{\cdot}1192Na_2S_2O_8$	0·2192NaOH	0·0051
$0{\cdot}1185Na_2S_2O_8$	0·2236NaOH	0·0051
$0{\cdot}1214Na_2S_2O_8$	0·3434NaOH	0·0049
$0{\cdot}0797K_2S_2O_8$	0·2040KOH	0·0050

The behaviour of barium persulphate when mixed with barium hydroxide is quite different, and is difficult to reconcile with any general theory. The autocatalytic curve of the pure salt solution has been fully explained by the production of persulphuric acid, but here it is evident that neutralisation must occur continuously, and that the precipitation of barium sulphate is accompanied by a progressive diminution of alkali instead of an increase of acidity. Indeed, the course of the action is followed in practice by alkalimetry instead of the usual acidimetry. Now, as it has been proved that hydroxyl ions exert no appreciable catalytic effect in the case of the salts of the alkali metals, it seems inevitable that barium persulphate, when mixed with sufficient barium hydroxide, should give a continuous simple unimolecular curve with its own velocity constant (k_3). Nevertheless, the curves obtained show a much higher initial velocity than corresponds with k_3, that is, an initial acceleration by the added alkali, and they also give evidence of a further acceleration as the alkali subsequently diminishes. We are unable to explain these facts.

The Temperature Effect.

Experiments were made with sodium persulphate and with persulphuric acid at 70° and 90° for comparison with those at 80° already described. The mean values of the unimolecular coefficients are given in the following table. In the case of persulphuric acid, it must be remembered that this coefficient is largely dependent on the initial concentration (A), for it has been shown to be the sum of two terms, $k_2 + kA$, whereas in the case of the salt it is a simple constant, k_1. It appears, however, that the constants at 90° are all about tenfold those at 70°.

TABLE VIII.

The Temperature Effect.

Salt.	*A*.	Unimolecular coefficients.	Temperature.
$Na_2S_2O_8$	0·125	0·0016	70°
$Na_2S_2O_8$	0·126	0·0055	80
$Na_2S_2O_8$	0·130	0·0161	90
$H_2S_2O_8$	0·124	0·0111	70
$H_2S_2O_8$	0·124	0·0302	80
$H_2S_2O_8$	0·116	0·1035	90

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