

CXXXVIII.—*The Action of Hydrogen Peroxide on Potassium Cyanide.*

By ORME MASSON, D.Sc., F.R.S.

THE formation of oxamide by the action of hydrogen peroxide on hydrocyanic acid was discovered in 1863 by Attfield (*Journ. Chem. Soc.*, 1863, 16, 94). Radziszewski afterwards (*Ber.*, 1885, 18, 355) showed that oxamide is only one of the products of an apparently complex change and that its formation is very slow, but he found that cyanogen in the presence of a trace of potassium cyanide is rapidly and quantitatively converted into oxamide by hydrogen peroxide.

The rate with which potassium cyanide disappears under the influence of hydrogen peroxide was investigated by C. J. Martin and R. A. O'Brien (*Proc. Soc. Chem. Ind. Victoria*, 1901, 1, 119). The curves obtained, whilst sufficient for the purpose the authors had in view, are irreconcilable with any simple theory of oxidation, and their investigation left the real nature of the reaction and its products unexplained. It seemed likely that results of interest might be obtained by combining analyses of the finished product with titration both of the residual cyanide and of the residual peroxide during the course of the action. An account of the work done on these lines is given in the sequel.

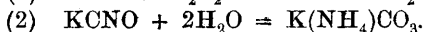
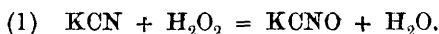
The Nature of the Action.

When aqueous solutions of potassium cyanide and hydrogen peroxide are mixed, the action at first proceeds quietly and without gas evolution, but with rise of temperature, which, if it be not counteracted by cooling precautions, may soon cause the action to be completed with almost explosive violence. If solutions containing 2 or more gram-molecules per litre are to be mixed in any considerable quantity, careful ice-cooling is required to prevent the action from getting beyond control, but in the case of solutions of 1 gram-molecule per litre or less, the heating effect is practically counteracted by immersing the mixing vessel in a bath of water at the ordinary temperature.

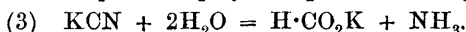
In this action, oxamide crystals are never produced; they are, however, formed in small quantity if the peroxide is mixed beforehand with sulphuric acid equivalent in amount to the potassium cyanide, but they have not been observed when smaller amounts of acid are used, nor when neutral peroxide is added in any proportion to potassium

cyanide. It seems, therefore, that Attfield's action does not occur unless the mixture is actually acid to indicators. Ordinary commercial preparations of peroxide may give rise to white precipitates in the course of the action with cyanide, but these are derived from inorganic impurities in the peroxide itself. They are generally amorphous, but in some cases crystals have been obtained which might be mistaken for oxamide on casual inspection, but which turned out on analysis to be magnesium ammonium phosphate. With pure peroxide (Merck's) there is never any trace of solid matter formed, the solution remaining clear and colourless from first to last. Not only is oxamide entirely absent, but tests for soluble oxalate also give negative results when applied to the mixed solution after action is complete.

The main products of the action are potassium cyanate and potassium and ammonium carbonates. Of these, the former seems to be the primary product, whilst the latter probably results from a secondary hydrolytic action in which hydrogen peroxide acts as a catalyst :



Taken together, the cyanate and carbonate are found to account for approximately four-fifths of the original cyanide and an equimolecular quantity of peroxide. The balance of the cyanide (one-fifth) is never oxidised, even though a large excess of peroxide be employed, but is converted by hydrolysis into potassium formate and ammonia, and in this action also the peroxide plays the part of a catalytic agent :



No free oxygen is produced during the action so long as any appreciable amount of cyanide remains unchanged, but as soon as it has disappeared there sets in a decomposition of the remaining peroxide, which will be present if the original molecular ratio of the peroxide to the cyanide exceeded about 4 : 5. This decomposition, which causes a brisk escape of oxygen, is practically completed in a few hours at the ordinary temperature, and is evidently due to the catalytic influence of one or more of the substances derived from the cyanide.

The solution ultimately obtained contains, therefore, no peroxide and no cyanide, unless the latter was present in too large an excess at the start, but it contains the oxidation and hydrolysis products of the reactions already mentioned.

Materials and Analytical Methods.

The hydrogen peroxide used in all the experiments recorded, except those of Tables II and III, was Merck's pure 30 per cent., diluted

as required. The crystallised potassium cyanide employed was found to be free from impurities except a trace of carbonate. The solutions were made up with distilled water, which was boiled and cooled immediately before use.

Determinations of cyanide were made by titration with standard silver nitrate after adding a little potassium hydroxide and potassium iodide. This precaution is necessary in testing after or during the peroxide action, as ammonia is one of its products. It was proved that the accuracy of the method is not otherwise interfered with.

Determinations of peroxide were made by titration with standard potassium permanganate in presence of excess of sulphuric acid. It was proved by special tests that neither cyanide, as such, nor formate spoils the accuracy of the indications.

In the solutions containing the products of the action, the carbonate was determined by precipitating a measured volume with excess of barium nitrate and weighing the washed and ignited barium carbonate.

The cyanate was determined in the filtrate from the barium carbonate by adding excess of silver nitrate and sufficient very dilute nitric acid to neutralise exactly the free ammonia present. The silver cyanate was ignited and weighed as silver.

The formate was detected by mixing the product with dilute sulphuric acid, boiling off the carbon dioxide, and distilling; for quantitative purposes a modification of Lieben's method was used. Preliminary tests proved the accuracy of this method when applied to formate solutions made from pure formic acid, but the results obtained by it in the present investigation are less satisfactory, although every care was taken to ensure accuracy. The formate so determined generally fell rather short of the amount expected as the result of other methods of inquiry, which will be described later. The cause of the discrepancy has not been ascertained.

Free ammonia could always be detected during the progress of the action. The quantity found by titration at the end was variable and was always less than the equivalent of the formate; this being doubtless due to loss by evaporation.

The Final Products of the Action.

The analyses summarised in Table I were all made with residual solutions at the conclusion of velocity experiments to be described later; and in each case, except where recorded, the complete previous destruction of both peroxide and cyanide was proved. Each result recorded is the mean of two or more determinations, which were always closely concordant in the cases of carbonate and cyanate, although less so

in those of formate. All results are reduced to a uniform basis by referring them to one molecule of original potassium cyanide, but the actual initial strengths of potassium cyanide and hydrogen peroxide in gram-molecules per litre are given in the second and third columns. The values given in the last column, under the heading "hydrolysed," are obtained from the velocity curves, as will be explained later, and agree well with those in the preceding column, which shows the difference between the cyanide destroyed and the amount represented by the carbonate and cyanate found. These values are probably more trustworthy than the direct determinations of formate.

TABLE I.—Action of H_2O_2 on KCN in Aqueous Solution at 20° .

No. of expt.	Gram-mol. per litre in original mixture.		Ratio of H_2O_2 to KCN.	Fraction of original CN found finally as						
	H_2O_2 .	KCN.		Cyan- ide, CN.	Cyan- ate, CNO.	Car- bonate, CO_3 .	Form- ate, CHO_2 .	Total oxi- dised.	Hydrolysed. (Diff.)	(Curve).
I.	0·477	0·483	0·988	0	0·331	0·454	0·201	0·785	0·215	0·22
II.	0·240	0·240	1·000	0	0·290	0·490	0·150	0·780	0·220	0·20
III.	0·127	0·125	1·016	0	0·402	0·416	0·155	0·818	0·182	0·17
IV.	0·299	0·248	1·206	0	0·229	0·568	0·190	0·797	0·203	0·20
V.	0·254	0·248	1·024	0	0·324	0·455	0·182	0·779	0·221	0·20
VI.	0·204	0·249	0·819	0	0·447	0·339	0·189	0·786	0·214	0·21
VII.	0·196	0·251	0·781	trace	0·459	0·332	0·203	0·791	0·209	0·21
VIII.	0·149	0·248	0·601	0·207	0·430	0·193	—	0·623	0·170	0·18

It may be noted that carbamide does not figure among the products of oxidation, although it might be expected to occur in a solution containing both cyanic and ammonium ions. But the formation of carbamide is a very slow process at the ordinary temperature, and these solutions were not raised above 20° , and were analysed without delay. Any undetected traces of carbamide which may have been present would, if allowed for, tend slightly to raise the estimate of total oxidation and correspondingly lower the estimate of hydrolysis by difference. The error arising from the trace of carbonate in the original cyanide, which would tend in the opposite direction, was proved to be very small.

A study of Table I leads to the following conclusions. The amount of carbonate produced per molecule of original cyanide depends mainly on the original ratio of peroxide to cyanide, increasing with it, although not in simple proportionality. The cyanate decreases as the carbonate increases, so that their sum, or the total fraction of the original cyanide which has undergone oxidation, remains nearly constant at about 0·79. It seems likely, as already suggested, that the cyanate is the primary product of the oxidation process, and that its natural tendency to form

carbonate by hydrolysis is catalytically accelerated by hydrogen peroxide. The unaided hydrolysis is very slow, for cyanate solutions may be kept nearly unchanged for a long time.

The ratio of total oxidation (cyanate plus carbonate) to original cyanide is but slightly affected by comparatively large changes in the initial concentration of the latter, and appears to be quite independent of the initial ratio of hydrogen peroxide to potassium cyanide, so long as this is not less than the requisite minimum of about 4 to 5. The same rule applies to the unoxidised or hydrolysed fraction, which is roughly one-fifth of the original. Other evidence for this conclusion will be dealt with later.

All of the peroxide which is not used for oxidation of cyanide, namely, all originally present in excess of the 4 to 5 ratio, is represented ultimately by free oxygen, as already mentioned. Accurate measurements of the gas evolved cannot be made unless the solution be confined over mercury, as errors arise from supersaturation and other causes. The following experiments were therefore made with small quantities of material confined over mercury in a nitrometer at the laboratory temperature. The materials used were not quite so pure as those employed in the rest of the work recorded in this paper, but experience has shown that practically identical results are obtained with cyanide and peroxide from various sources.

The nitrometer having been filled with mercury, small measured volumes of potassium cyanide and hydrogen peroxide solutions of known strengths were admitted and washed in with measured volumes of water, and the whole mixed by shaking. No oxygen was formed at first, the time elapsing before its appearance varying with the composition of the solution. When, after several hours, the evolution appeared to be complete, the dissolved gas was pumped out by lowering the mercury column, and measurements were made of volume, pressure, and temperature. This was repeated at intervals of an hour or so until the result was constant. The volume so obtained was reduced to 0° and 760 mm., with a correction for moisture, and the equivalent of hydrogen peroxide was calculated. As examination of the residual solution proved it to be quite free from hydrogen peroxide, as well as from potassium cyanide, the difference between the original hydrogen peroxide and the equivalent of the free oxygen so calculated may obviously be put down as peroxide reduced by the cyanide, or (since the reaction is an equimolecular one) as potassium cyanide oxidised. It should be stated that the gas evolved during the action was in several cases proved by analysis to be pure oxygen.

In the following table the results of the actual experiments have been reduced to the basis of one molecule of original cyanide. The

strengths and volumes used differed in each case, but it was always arranged that the mixture should contain from one-fifth to one-half of a gram-molecule of each reagent per litre.

TABLE II.—*Nitrometer Tests with H_2O_2 : KCN greater than 1.*

Mols. of H_2O_2 used per KCN.	H_2O_2 equiv. of O_2 gas obtained.	Balance of H_2O_2 = KCN oxidised.	Balance of KCN = KCN hydrolysed.
2.5	1.71	0.79	0.21
2.25	1.46	0.79	0.21
2.0	1.22	0.78	0.22
1.75	0.98	0.77	0.23
1.5	0.72	0.78	0.22
1.33	0.54	0.79	0.21
1.0	0.22	0.78	0.22
1.0	0.22	0.78	0.22

It is evident that approximately 0.78 of the original potassium cyanide is oxidised to cyanate and carbonate and 0.22 hydrolysed to formate, and that the whole of the unused peroxide is converted into water and free oxygen; also that these results are independent of the initial ratio of peroxide to cyanide, at least within the limits cited. This confirms the conclusions already based on other evidence.

The experiments cited in the next table were conducted similarly, but with mixtures containing less than one molecule of peroxide to one of cyanide. In each case the complete destruction of the peroxide was proved by titration with permanganate, and the surviving cyanide was detected and determined by titration with silver nitrate. No appreciable free oxygen was formed, so that the whole of the peroxide was used in oxidising the cyanide to cyanate and carbonate. The cyanide simultaneously destroyed by hydrolysis is necessarily the difference between the original quantity and the sum of that oxidised and that surviving unchanged. The results show that this hydrolysis still bears the same ratio to the original (a little over one-fifth) until the initial H_2O_2 : KCN ratio falls below 0.5, after which it gradually diminishes. In the only previously quoted experiment bearing on this point (VIII of Table I) some diminution was observed when this ratio was 0.6, but there the temperature was somewhat higher and the action quicker.

TABLE III.—*Nitrometer Tests with H_2O_2 : KCN less than 1.*

Mols. of H_2O_2 used per KCN.	H_2O_2 equiv. of free O_2 .	Unchanged KCN found.	KCN oxidised.	KCN hydrolysed.
1.0	0.21	0.00	0.79	0.21
0.67	0.01	0.13	0.66	0.21
0.5	0.02	0.31	0.48	0.21
0.5	0.0	0.30	0.50	0.20
0.4	0.0	0.42	0.40	0.18
0.33	0.0	0.51	0.33	0.16

Study of the Action in Progress.

That cyanide should be partly oxidised to cyanate and carbonate and partly hydrolysed to formate when exposed to the action of hydrogen peroxide, and that the excess of peroxide should undergo decomposition into water and oxygen seem in no way remarkable; but that the ratio of oxidation to hydrolysis, or of either to the total cyanide, should be so nearly independent of the absolute and relative concentrations of the reagents is somewhat surprising. Moreover, the experiments still to be described make two other facts certain. The first is that, when excess of peroxide is employed, the hydrolysing action becomes imperceptible long before the oxidising action is finished, that is, while there is still much cyanide, as well as peroxide, unchanged. The second fact is that the catalytic decomposition of the peroxide does not begin, or at any rate does not cause evolution of oxygen gas, until the cyanide is gone or on the point of vanishing. The whole action may thus be divided into three stages as follows.

First stage: the cyanide undergoes both hydrolysis and oxidation, and therefore disappears faster than the peroxide, no free oxygen appearing.

Second stage: the residual cyanide undergoes oxidation only, and therefore disappears equimolecularly with the peroxide, no free oxygen appearing.

Third stage: the residual peroxide, if any, after disappearance of the cyanide, is catalytically decomposed, and oxygen gas is evolved. This stage does not occur unless the initial ratio of peroxide to cyanide exceeds about 4:5.

The evidence on which these statements are based was obtained in the following manner.

Potassium cyanide and hydrogen peroxide solutions were made up of approximately predetermined strength, each in a stoppered 100 c.c. flask, and placed in a thermostat maintained at 20.0°. The exact strength of each solution was determined by titration immediately before mixing, equal volumes being removed for this purpose, and half of each value so found was set down as the initial strength of the mixture. The cyanide was decanted into a larger thin glass flask (also in the thermostat), and the experiment was afterwards begun by rapidly adding the peroxide and starting a stop-watch. Care was taken to drain both flasks always to the same extent, and to ensure complete immediate mixture by rapid rotation of the large flask.

The temperature of the mixture was in some cases observed by means of an immersed thermometer. Generally it showed a rapid rise of a few tenths of a degree above the thermostat temperature.

followed by a very slow fall to it. In those cases where action was slower the disturbance was proportionately less, but all the results are undoubtedly affected to some extent by this cause, although the errors due to it cannot be large except in the case of the strongest solutions.

The course of the reaction was followed by withdrawing samples at short intervals and titrating alternately for cyanide and peroxide. Each sample intended for cyanide determination was delivered into a beaker containing some alkaline iodide indicator and then rapidly titrated with $N/40$ silver nitrate, and each sample for peroxide was delivered into excess of dilute sulphuric acid and at once titrated with $N/10$ potassium permanganate. Thus, when 5 c.c. samples were used, each c.c. of the reagent corresponded to one centigram-molecule of potassium cyanide or hydrogen peroxide per litre of the solution. It should be mentioned that the delivery of the test samples into excess of alkali or acid tends in either case greatly to retard further action, as will be shown later. No known systematic error affects the results, which are believed to be trustworthy.

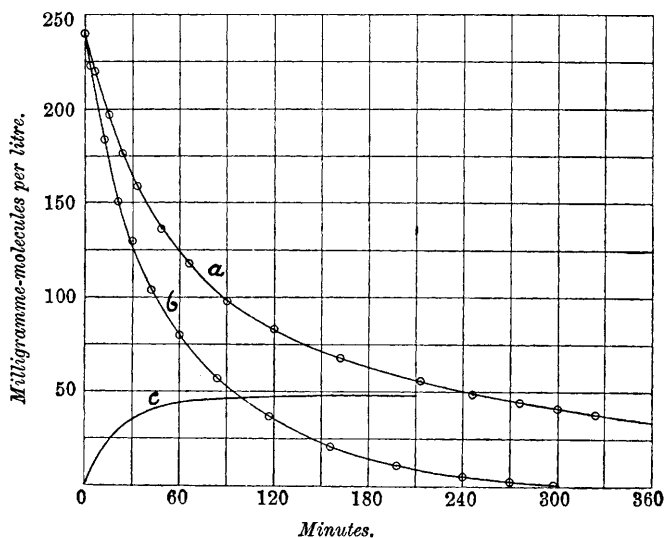
As a rule, a portion of the mixture was removed at the commencement of the experiment to a small flask in the thermostat and put in connexion with a gas burette for the measurement of oxygen evolved. It was found that supersolution occurred, which could be partly counteracted by shaking the flask, but that, even with this precaution, the measurements were not reliable. They served, however, to prove the non-formation of oxygen during the early stages of the action, and to indicate the rapid evolution which sets in practically simultaneously with the disappearance of appreciable cyanide. The same facts are very clearly proved also by observing the liquid sucked up from time to time into the sampling pipette, where the reduced pressure favours the formation of gas bubbles at the earliest opportunity. After the beginning of what has been called the third stage of the action, this bubbling is so brisk that some care is necessary in sampling to take a correct measure of liquid.

After it was no longer possible to detect peroxide, the residual liquid was, as a rule, subjected to quantitative analysis. The results of these determinations have been discussed already and are summarised in Table I. The numbers there used to designate the separate experiments are adhered to in the sequel.

In the following tables, times are given in minutes and all other values in milligram-molecules per litre, and the symbols that head the various columns are defined as follows. A and B stand respectively for the original concentrations of peroxide and cyanide, $A - x$ and $B - y$ representing their residual concentrations at any time (t), as determined by titration. Inasmuch as no oxygen is liberated or

otherwise used up until the third and last stage of the action is entered on (namely, until the cyanide has vanished), it is obvious that, until then, x is the measure of the oxidation products (cyanate and carbonate) and $y - x$, which is represented by the symbol w , is that of the hydrolysis product (formate). The maximum value reached by w is expressed as W .

Curves were drawn to represent the results of each experiment, and



EXPT. II.

a. Peroxide curve. b. Cyanide curve. c. Hydrolysis (by difference).

contemporaneous values were read from them and are given in the tables. The case of Expt. II, which may be taken as typical, is shown in the accompanying figure, in which curves are given for the peroxide and cyanide, and their differences, which are the values of w , since in this case the initial concentrations are equal. Every curve drawn passed through ten or more experimental points, so that the interpolated simultaneous values given in the tables may be taken as trustworthy.

TABLE IV.—*Expt. I.* $A : B = 0.988$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
0	477	483	0	0	0
7.5	384	320	93	163	70
15	312	236	165	247	82
22.5	261	173	216	310	94
30	227	134	250	349	99
37.5	203	104	274	379	105
45	185	84	292	399	107
52.5	167	69	310	414	104
60	155	56	322	427	105
75	134	35	343	448	105
90	119	19	358	464	106
105	105	9	372	474	102
120	95	3	382	480	98
150	76	0	—	—	—
180	63	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 150 minutes.

$$W : B = 105 : 483 = 0.217.$$

TABLE V.—*Expt. II.* $A : B = 1.00$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
0	240	240	0	0	0
7.5	216	202	24	38	14
15	196	171	44	69	25
30	165	130	75	110	35
45	141	100	99	140	41
60	123	80	117	160	43
90	99	53	141	187	46
120	83	36	157	204	47
150	71	23	169	217	48
180	63	14	177	226	49
210	57	9	183	231	48
240	51	5	189	235	46
270	46	2	194	238	44
300	41	0	199	240	41
330	37	—	—	—	—
360	33	—	—	—	—
420	26	—	—	—	—
480	20	—	—	—	—
540	14	—	—	—	—
600	9	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 300 minutes.

$$W : B = 48 : 240 = 0.200.$$

TABLE VI.—*Expt. III.* $A : B = 1.02$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
0	127	125	0	0	0
7.5	121	115	6	10	4
15	114	104	13	21	8
30	104	90	23	35	12
45	96	80	31	45	14
60	88	70	39	55	16
90	76	55	51	70	19
120	66	44	61	81	20
180	52	29	75	96	21
240	43	20	84	105	21
300	37	14	90	111	21

HYDROGEN PEROXIDE ON POTASSIUM CYANIDE. 1459

TABLE VI (continued).—*Expt.* III. $A : B = 1.02$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
360	33	9	94	116	22
420	29	5	98	120	22
480	25	2	102	123	21
540	23	1	104	124	20
600	17	0	—	—	—
660	13	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 600 minutes.

$$W : B = 21 : 125 = 0.168.$$

TABLE VII.—*Expt.* IV. $A : B = 1.20$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
0	299	248	0	0	0
7.5	270	202	29	46	17
15	244	164	55	84	29
22.5	220	136	79	112	33
30	205	114	94	134	40
37.5	190	95	109	153	44
45	177	80	122	168	46
60	157	58	142	190	48
75	143	42	156	206	50
90	132	31	167	217	50
105	122	21	177	227	50
120	115	14	184	234	50
135	107	8	192	240	48
150	101	4	198	244	46
180	89	0	—	—	—
240	70	—	—	—	—
300	55	—	—	—	—
360	43	—	—	—	—
420	32	—	—	—	—
480	22	—	—	—	—

NOTE.—Oxygen evolution perceptible at and after 180 minutes.

$$W : B = 50 : 248 = 0.202.$$

TABLE VIII.—*Expt.* V. $A : B = 1.02$.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x.</i>	<i>y.</i>	<i>w.</i>
0	254	248	0	0	0
7.5	229	208	25	40	15
15	206	176	48	72	24
30	173	127	81	121	40
45	149	99	105	149	44
60	130	78	124	170	46
75	117	61	137	187	50
90	105	49	149	199	50
120	88	32	166	216	50
150	75	20	179	228	49
180	66	11	188	237	49
210	59	6	195	242	47
240	55	2	199	246	47
270	48	0	—	—	—
300	42	—	—	—	—
360	30	—	—	—	—
420	21	—	—	—	—
480	13	—	—	—	—
540	8	—	—	—	—

NOTE.—Oxygen evolution perceptible after 270 minutes.

$$W : B = 50 : 248 = 0.202.$$

TABLE IX.—*Expt.* VI. $A : B = 0.82$.

<i>t</i> .	<i>A - x</i> .	<i>B - y</i> .	<i>x</i> .	<i>y</i> .	<i>w</i> .
0	204	249	0	0	0
7.5	184	220	20	29	9
15	167	190	37	59	22
30	138	151	66	98	32
45	116	123	88	126	38
60	101	101	103	148	45
90	80	79	124	170	46
120	63	61	141	188	47
180	45	38	159	211	52
240	34	25	170	224	54
300	25	17	179	232	53
360	20	12	184	237	53
480	13	5	191	244	53

NOTE.—No oxygen gas formed.

 $W : B = 53 : 249 = 0.213$.TABLE X.—*Expt.* VII. $A : B = 0.78$.

<i>t</i>	<i>A - x</i> .	<i>B - y</i> .	<i>x</i> .	<i>y</i> .	<i>w</i> .
0	196	251	0	0	0
7.5	176	220	20	31	11
15	159	192	37	59	22
30	133	158	63	93	30
45	112	128	84	123	39
60	97	110	99	141	42
90	76	85	120	166	46
120	61	67	135	184	49
180	41	44	155	207	52
240	29	32	167	219	52
300	22	25	174	226	52
360	17	20	179	231	52
420	13	16	183	235	52
480	11	13	185	238	53
540	9	10	187	241	54
720	5	6	191	245	54

NOTE.—No oxygen gas formed.

 $W : B = 53 : 251 = 0.211$.TABLE XI.—*Expt.* VIII. $A : B = 0.60$.

<i>t</i> .	<i>A - x</i> .	<i>B - y</i> .	<i>x</i> .	<i>y</i> .	<i>w</i> .
0	149	248	0	0	0
7.5	135	227	14	21	7
15	120	204	29	44	15
30	102	176	47	72	25
45	86	155	63	93	30
60	73	140	76	108	32
90	54	119	95	129	34
120	41	102	108	146	38
180	26	84	123	164	41
240	16	72	133	176	43
300	11	66	138	182	44
360	8	61	141	187	46
480	4	57	145	191	46
580	2	55	147	193	46

NOTE.—No oxygen gas formed.

 $W : B = 46 : 248 = 0.185$.

The values of $W:B$ appended to the preceding tables have been collected already in the last column of Table I, where they were compared with the corresponding values deduced from the quantitative determinations of carbonate and cyanate and with the direct determinations of formate. Similar values were also deduced from the measurements of oxygen gas evolved, as indicated in Tables II and III; so that there can be but little doubt of the correctness of the conclusion, which has been based on all these methods of inquiry, that the final hydrolysed fraction ($W:B$) is nearly independent of the initial concentrations (A and B), provided that the ratio of these ($A:B$) is not much below 0.8. The following summary includes a measurement of $W:B$ made with a solution containing at the outset 1 gram-molecule of potassium cyanide and an equivalent amount of hydrogen peroxide per litre. This was useless for testing the velocity of the action, as strong cooling had to be resorted to during the first stage, but it served perfectly for the measurement of W in the second stage.

TABLE XII.—*Hydrolysis Fractions Found by Different Methods.*

Initial KCN in gram-molecules per litre.....	1	0.5	0.25	0.125
Hydrolysis fraction from velocity tests	0.22	0.22	0.20	0.17
„ „ „ oxidation products ...	—	0.22	0.21	0.18
„ „ „ formate found	—	0.20	0.18	0.16
„ „ „ free oxygen found ...	—	0.22 to 0.20		—

The Rate of the Oxidising Action.

Facts already proved make it evident that this rate is given by the slope of the peroxide curve at any moment, so long as there is residual cyanide present. Inspection of the peroxide curve of Expt. II (see figure) shows that it has, until the last stage of the action is setting in, the form characteristic of actions of the second order, or that $\frac{dx}{dt} = k(A-x)^2$. This is also found to hold good in other experiments in which the peroxide and cyanide are originally equimolecular, or when $B=A$, but examination of other cases, where the initial strengths are unequal, shows that the equation must be written $\frac{dx}{dt} = k(A-x)(B-x)$. Expressed in words, this means that the rate of formation of oxidation products (cyanate and carbonate) is proportional at any moment to the concentration of the peroxide and to the sum of the concentrations of the cyanide and its hydrolysis product; for $B-x$ is the same thing as $B-y$ (cyanide) + w (formate). Although the theoretical interpretation of this presents difficulties which have not been overcome by further investigation, it is easy to show that the

equation is in agreement with the experimental facts. It may be tested in the first place by calculating the values of k by means of the well-known expression obtained by integrating the above equation for actions of the second order, namely, $kt = \frac{1}{(B-A)} \log_e \frac{A(B-x)}{B(A-x)}$, or, for

the special case where $B = A$, as in Expt. II, $kt = \frac{x}{A(A-x)}$. The

results of such calculation are shown in Table XIII, where the k values are given for gram-molecules per litre per minute multiplied by 1000. Their approximation to constancy is certainly noteworthy, especially as the figures cover practically the whole range of each oxidation. The divergencies, such as they are, are undoubtedly due in the main to internal heating, as already explained.

TABLE XIII.—*Values of the Velocity Constant ($k \times 10^3$) of the Oxidising Action at 20°.*

t.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
7.5	72	62	61	59	61	57	60	55
15	72	62	62	62	66	58	60	55
22.5	77	—	—	67	—	—	—	—
30	77	63	58	65	64	61	60	55
37.5	74	—	—	66	—	—	—	—
45	72	65	60	67	65	63	61	58
60	71	66	59	67	65	63	61	58
75	69	—	—	66	64	—	—	—
90	68	66	60	66	65	61	60	60
105	68	—	—	66	—	—	—	—
120	68	66	62	65	65	63	60	60
150	—	—	—	67	66	—	—	—
180	—	65	65	—	66	61	61	60
210	—	64	—	—	66	—	—	—
240	—	64	66	—	64	60	60	61
300	—	—	66	—	—	61	61	—
360	—	—	65	—	—	60	60	58
420	—	—	66	—	—	—	—	—
480	—	—	70	—	—	60	58	56
540	—	—	70	—	—	—	58	—
720	—	—	—	—	—	—	56	—

NOTE.—For corresponding concentration values, see Tables IV to XI.

In most of the experiments the peroxide curve was traced for a few hours through the final stage, that is, after the disappearance of cyanide and during the escape of oxygen gas. $B - y$ being now nil, the preceding equation becomes $\frac{dx}{dt} = kW(A - x)$, where both k and W are constant, and therefore the curve should appear of the first order. So far as the evidence goes, the action does seem to be unimolecular, but it proceeds somewhat faster than is compatible with the previously determined values of k and W . Similar results were obtained when the finished product was made to act on a fresh supply of peroxide, in

which case oxygen evolution proceeded briskly from the first and the course of the last stage of an ordinary experiment was practically repeated.

The Rate of the Hydrolysing Action.

As the destruction of cyanide is due partly to oxidation by the peroxide and partly to hydrolysis under its influence as a catalyst, and as the former action consumes cyanide and peroxide in equimolecular proportion and no oxygen is used in any other way, we have $dy = dx + dw = k(A-x)(B-x)dt + dw$. Now one would naturally expect the hydrolytic action at any moment to be proportional to the concentration of the cyanide and to that of the catalyst, as expressed by the equation $\frac{dw}{dt} = k_1(A-x)(B-y)$, but, if this were the law, w would not cease to increase perceptibly long before the disappearance of either cyanide or peroxide. Further, since this maximum value which it does reach is retained apparently undiminished, as shown both by analysis of the final products and by the curves themselves until incipient oxygen evolution and total destruction of cyanide alter their significance, it follows that no simple theory of consecutive action is tenable, such as that the hydrolysis product is subject to oxidation by the peroxide, nor yet any theory of reversible action. Therefore, in attempting to formulate the facts, we seem driven to represent the cyanide as consisting originally of a larger oxidisable portion and a smaller hydrolysable one, each subject to its own peculiar action and neither convertible into the other. Thus W (the ultimate quantity of hydrolysed product) is the measure of the original hydrolysable portion and $W-w$ is its measure at any later moment, and the rate of hydrolysis under the catalytic influence of the peroxide at any instant is $\frac{dw}{dt} = k_1(A-x)(W-w)$, or, to put it in words, it is proportional to the concentration of the residual peroxide and to the amount of hydrolysis still to be performed. It is easy to show that this leads to a satisfactory calculation of the observed values, although no claim can be made for it as a guide to the true theory of the action.

Starting with the two differential equations already given for oxidation and hydrolysis, namely, $\frac{dx}{dt} = k(A-x)(B-x)$ and $\frac{dw}{dt} = k_1(A-x)(W-w)$, and that obtained by dividing one by the other, namely, $\frac{dw}{dx} = \frac{k_1}{k} \frac{W-w}{B-x}$, and remembering that $x = 0$ and $w = 0$ when $t = 0$, we get the following by integration :

$$\frac{A-x}{A} = \frac{A-B}{A-Be^{(B-A)kt}}, \quad \frac{B-x}{B} = \frac{(A-B)e^{(B-A)kt}}{A-Be^{(B-A)kt}}, \quad \text{and} \quad \frac{W-w}{W} = \left(\frac{B-x}{B}\right)^{\frac{k_1}{k}} = \left(\frac{(A-B)e^{(B-A)kt}}{A-Be^{(B-A)kt}}\right)^{\frac{k_1}{k}}; \text{ or, in the special case where } A=B,$$

$\frac{A-x}{A} = \frac{B-x}{B} = \frac{1}{1+kAt}$ and $\frac{W-w}{W} = \left(\frac{1}{1+kAt}\right)^{\frac{k_1}{k}}$. The evaluation of k from the experimental numbers has been already dealt with. That of k_1 follows; for evidently it is given by

$$\frac{k_1}{k} = \log \frac{W-w}{W} / \log \frac{B-x}{B}.$$

As w is in all cases small, and as it is affected by such titration errors as occur in the determination of either $A-x$ or $B-y$ (and these are as likely to be cumulative as they are to compensate one another), no very precise agreement can be expected between the values of k_1/k so obtained at different points in a curve. But in all the experiments they are never far from the mean value 3.5, and this is found to yield calculated concentrations which agree with those actually recorded within a small limit of error.

In the following tables are given the values of $A-x$ and of w calculated by means of the above equations and those of $B-y$ obtained from the calculated x and w by the rule that $y=x+w$. For each experiment a mean k value has been taken from those given in the appropriate column of Table XIII, and k_1/k has been taken as 3.5. The value of W used is in each case the experimental value already given, which is always near to $1/5$ of B . For comparison, the experimental values of $A-x$, w , and $B-y$ are reproduced. In the four experiments selected for tabulation the initial cyanide strength (B) is approximately 0.25 of a gram-molecule per litre, whilst the initial ratio of peroxide to cyanide (A/B) is approximately 1.2, 1.0, 0.8, and 0.6.

TABLE XIV.—*Expt. IV. Comparison of Calculated and Found Values.*

$t.$	$A-x.$		$w.$		$B-y.$	
	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	299	299	0	0	248	248
7.5	268	270	19	17	198	202
15	242	244	30	29	161	164
22.5	221	220	37	33	133	136
30	204	205	40	40	113	114
37.5	191	190	43	44	97	95
45	178	177	45	46	82	80
60	159	157	47	48	61	58
75	144	143	48	50	45	42
90	132	132	49	50	32	31
120	115	115	49	50	15	14
150	103	101	49	46	3	4

HYDROGEN PEROXIDE ON POTASSIUM CYANIDE. 1465

TABLE XV.—*Expt. V. Comparison of Calculated and Found Values.*

<i>t.</i>	<i>A - x.</i>		<i>w.</i>		<i>B - y.</i>	
	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	254	254	0	0	248	248
7·5	227	229	16	15	205	208
15	206	206	24	24	176	176
30	171	173	37	40	128	127
45	148	149	43	44	99	99
60	130	130	45	46	79	78
75	116	117	46	50	64	61
90	105	105	48	50	51	49
120	88	88	48	50	34	32
150	76	75	49	49	21	20
180	67	66	49	49	12	11
210	60	59	49	47	5	6
240	54	55	49	47	0	2

TABLE XVI.—*Expt. VII. Comparison of Calculated and Found Values.*

<i>t.</i>	<i>A - x.</i>		<i>w.</i>		<i>B - y.</i>	
	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	196	196	0	0	251	251
7·5	177	176	13	11	219	220
15	159	159	23	22	191	192
30	133	133	33	30	155	158
45	113	112	39	39	129	128
60	97	97	43	42	109	110
90	76	76	47	46	84	85
120	60	61	49	49	66	67
180	41	41	50	52	46	44
240	30	29	51	52	34	32
360	17	17	51	52	21	20
480	10	10	52	52	13	13

TABLE XVII.—*Expt. VIII. Comparison of Calculated and Found Values.*

<i>t.</i>	<i>A - x.</i>		<i>w.</i>		<i>B - y.</i>	
	Calc.	Found.	Calc.	Found.	Calc.	Found.
0	149	149	0	0	248	248
7·5	134	135	9	7	224	227
15	121	120	16	15	204	204
30	101	102	24	25	176	176
45	86	86	30	30	155	155
60	73	73	34	32	138	140
90	55	54	37	34	117	119
120	43	41	40	38	102	102
180	27	26	42	41	84	84
240	17	16	43	43	74	72
300	12	11	43	44	68	66
360	8	8	44	46	63	61
480	4	4	44	46	59	57

In spite of the close agreement between the found and calculated values, shown in the preceding tables as well as in other cases not cited, the equations on which the calculations are based must, as already stated, be regarded as devoid of direct theoretical significance. If they truly represented the action, we should be forced to conclude, not only that the cyanide consists originally of an oxidisable form and a hydrolysable form in fixed proportion, each behaving independently and inconvertible into the other form, but also that the oxidisable form is subject to simultaneous attack by the peroxide itself and by nascent oxygen liberated through the catalytic agency both of the hydrolysable form and of its hydrolysed product, and that all these three reactions of the peroxide proceed with the same specific velocity. But, apart from its inherent chemical improbability, such a theory is directly contradicted by experiments designed to test the effects of adding at the outset one or more of the products of a previous action. Such initial increase of the hydrolysis product should, according to the equation, have a definite effect on the velocity of oxidation, but the tests show that this is not the case. The only claim, therefore, that is made for the equations given is that they do enable the course of any normal experiment to be foretold with satisfactory accuracy. It seems probable that the agreement is not purely accidental, at all events in the case of the oxidising action, and that it might be explained if methods were available for the detection of intermediate processes while the actions are in progress.

The Influence of the Products on the Oxidation Velocity.

The following experiments were made with the view of testing the apparent truth of the rule that the oxidation proceeds at a rate proportional to the concentration of the peroxide and to the sum of the concentrations of the cyanide and its hydrolysis product.

In the first place, cyanide which had already been treated with peroxide in quantity insufficient to complete the oxidation, although enough almost to finish the hydrolysis, was mixed with a further supply of peroxide so as to continue the oxidation. In this case the differential equation should take the form $\frac{dx}{dt} = k(A - x)(B + C - x)$, where C stands for the constant quantity of original hydrolysed product, and if, for simplicity, A and B be made equal, the integrated equation is $k = \frac{1}{Ct} \log_e \frac{A(A + C - x)}{(A + C)(A - x)}$. The details of the test were as follows. Strong solutions of cyanide and peroxide were mixed in such proportions that the mixture was estimated to contain at the first moment 2541 milligram-molecules per litre of the former and 1521 of

HYDROGEN PEROXIDE ON POTASSIUM CYANIDE. 1467

the latter. The action was controlled by jacketing with ice and no free oxygen was evolved. Next day, when titration showed no residual peroxide, the strength of the residual cyanide was 405, so that the liquid now contained also 1521 of oxidised and 615 of hydrolysed product. The ratio of the last to the original cyanide was thus rather higher than in the cases previously quoted (0.24 instead of from 0.18 to 0.22), which confirms previous indications that the $W:B$ ratio increases, although not much, as B increases. The solution was now mixed at 20° with an equal volume of peroxide of strength 407, and the course of the action was followed in the usual manner. The initial concentrations were estimated as 202.5 of cyanide, 203.5 of peroxide, and 307.5 of hydrolysed product, so that practically $A = B = 203$. Table XVIII shows the concentrations read from curves drawn through the experimental points and also the values of k calculated by means of the above equation. It is evident that the same law holds here as in normal tests, although k has an unusually small value. The fresh hydrolytic action, although small, is by no means negligible. When the test was repeated, allowing the partially acted-on solution to stand a week before using it, exactly similar results were obtained.

TABLE XVIII.—*Expt.* IX. $C = 308$.

t .	$A - x$.	$B - y$.	w .	k .
0	203	203	0	—
7.5	175	163	12	40
15	151	133	18	41
22.5	129	111	18	42
30	111	92	19	44
37.5	97	77	20	44
45	86	65	21	43
60	66	45	21	44
75	52	31	21	44
90	41	21	20	44
105	34	14	20	43
120	27	9	18	43
150	17	2	15	44
180	9	0	—	—

At the conclusion of *Expt.* IX, the total formate in the solution was determined by analysis and found to be 315, as compared with the calculated $C + W = 328$, the method yielding, as usual, rather low results.

In the next experiment the initial conditions were different. Whereas in *Expt.* IX a previously incomplete action, which had never reached the third stage, was finished by adding more peroxide and no fresh cyanide was used, in *Expt.* X new peroxide and cyanide were mixed with the final products (free from either) of an already completed action. This initial difference proved important, for the oxidation now occurred at a rate proportional to the sum of the concentra-

tions of the cyanide and the *new* hydrolysis product, instead of the *total* hydrolysis exerting its influence, as was to be expected from all earlier results. Indeed, apart from a slight increase in the W value, it would be difficult to distinguish this experiment from a normal one. The k values given in Table XIX were calculated by the simple bimolecular formula without reference to the added products of the former action.

In order further to test the influence of the addition of the products of hydrolysis, experiments were made in which peroxide was added to cyanide previously mixed with potassium formate, with ammonia, and with formamide. The first showed no recognisable effect, the second produced only a small, general retardation, whilst the third hastened the hydrolytic action (increasing W) without influencing the course of the oxidation. In each of these cases, as in the last, the simple bimolecular formula was found to suffice, and the k values recorded in the tables were calculated by it.

A comparison of all the evidence, and especially of Expt. IX with the later ones, suggests that that portion of the cyanide which disappears as such, but without oxidation, exists in some intermediate form so long as any unaltered cyanide remains, that in this form it influences the reduction of the peroxide by cyanide in the manner represented in the equation, and that in the last stage, after the total destruction of cyanide, it is converted into formate and ammonia (or possibly formamide) and loses this power. Such a hypothesis, however, presents difficulties of its own, and there is no direct evidence by which it may be tested.

TABLE XIX.—*Expt. X. Added Products of Former Action = 250.*

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>w.</i>	<i>k.</i>
0	249	249	0	—
7·5	221	202	19	68
15	198	170	28	69
22·5	180	144	36	68
30	166	124	42	67
45	142	95	47	67
60	125	71	54	66
75	111	52	59	67
90	100	38	62	66
105	90	28	62	68
120	82	20	62	68
150	71	10	61	67
180	62	4	58	67
210	53	0	—	—

NOTE.—Oxygen evolution perceptible at and after 220 minutes.

$$W : B = 62 : 249 = 0\cdot25.$$

TABLE XX.—*Expt. XI. Added $H \cdot CO_2K = 250$.*

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>w.</i>	<i>k.</i>
0	251	249	0	—
15	210	174	34	52
30	174	134	38	59
45	150	103	45	60
60	131	81	48	61
75	117	64	51	61
90	106	52	52	60
120	89	35	52	60
150	77	22	53	60
180	68	13	53	60
210	60	7	51	60
240	54	3	49	61
270	48	1	45	62
300	41	0	—	—

NOTE.—Oxygen evolution perceptible at and after 290 minutes.

$$W : B = 53 : 249 = 0 \cdot 21.$$

TABLE XXI.—*Expt. XII. Added $NH_3 = 250$.*

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>w.</i>	<i>k.</i>
0	248	250	0	—
15	208	180	30	52
30	182	143	41	49
45	160	114	48	49
60	143	95	50	49
75	129	81	50	50
90	118	68	52	49
120	99	49	52	51
150	85	36	51	52
180	76	27	51	51
210	69	19	52	50
240	62	13	51	50
270	57	8	51	50
300	52	4	50	51
360	44	0	—	—

NOTE.—Oxygen evolution perceptible at and after 380 minutes.

$$W : B = 51 : 250 = 0 \cdot 20.$$

TABLE XXII.—*Expt. XIII. Added $HCO \cdot NH_2 = 250$ (approx).*

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>w.</i>	<i>k.</i>
0	254	254	0	—
15	208	172	36	58
30	172	119	53	63
45	148	89	59	63
60	130	66	64	63
90	106	37	69	61
120	88	19	69	62
150	77	9	68	60
180	69	3	66	59
210	62	1	61	58
240	54	0	—	—

NOTE.—Oxygen evolution perceptible at and after 220 minutes.

$$W : B = 68 : 254 = 0 \cdot 27.$$

The Effects of Previously Added Alkali and Acid.

As hydrogen peroxide is a weak acid and is known to form salts when added to alkaline solutions, it is reasonable to suppose that the mixture of potassium cyanide and hydrogen peroxide contains hydrogen cyanide (beyond the amount due to normal hydrolysis) and peroxide ions as well as hydrogen peroxide and cyanogen ions and non-ionised salts. It might be suggested that some of these interact to produce cyanate, while others give rise to the hydrolysis product, formate. Although this idea does not point the way to any clear explanation of the observed facts, it seemed desirable to try the effect of previous addition of potassium hydroxide, which should promote ionisation, and of sulphuric acid, which should restrain it. Two experiments were carried out in which the cyanide was mixed beforehand with potassium hydroxide, and two in which the peroxide was mixed beforehand with acid; and Expt. II (see Table V) was done without adding either alkali or acid, but otherwise under identical conditions. The five form a series, as is shown in Table XXIII. The concentrations there are given, as usual, in milligram-molecules per litre, except those of the sulphuric acid, which are in half-molecules. The figures given in the last two columns show the times (in minutes) required for the destruction of half the peroxide and of half the cyanide. In the case of Expt. XVII, which was interrupted, one of these values (given in parentheses) was obtained by extrapolation, but as the curve is practically a straight line there can be no great error. These figures serve to indicate the most striking result of the series of tests, which is that the maximum velocity is attained in the case of pure peroxide and cyanide, the addition of either alkali or acid causing a marked retardation.

TABLE XXIII.

Expt. No.	Initial.		Added.		Available alkali.	Time of half action.	
	H ₂ O ₂ .	KCN.	KOH.	$\frac{1}{2}$ H ₂ SO ₄ .		H ₂ O ₂ .	KCN.
XIV	239	239	242	0	481	720	2280
XV	240	239	120	0	359	136	128
II	240	240	0	0	240	63	31
XVI	240	240	0	120	120	117	45
XVII	239	240	0	242	0	(840)	480

Apart from the general retardation, the effects of the addition of alkali are (1) an evolution of oxygen gas from the start, but quickly diminishing; (2) a decrease of the hydrolytic decomposition of the cyanide as compared with its oxidation. In Expt. XV, with the smaller quantity of alkali, the liberation of oxygen and the hydrolysis roughly balanced one another, and the peroxide and

HYDROGEN PEROXIDE ON POTASSIUM CYANIDE. 1471

cyanide curves ran close together throughout their course. In Expt. XIV, with the larger quantity, the peroxide curve was at first much steeper than the cyanide curve, the oxygen escape more than balancing the small hydrolysis, but after some hours they became parallel and remained so for a week, no more oxygen escaping and no more hydrolysis occurring. No simple formulæ express the curves in either of these alkaline tests.

The addition of acid appears to increase the hydrolysis in proportion to the oxidation. Apart from this and the general retardation, the whole course of the action with the smaller quantity of added acid (Expt. XVI) is similar to that of the normal test (Expt. II), no oxygen escaping till after the destruction of the cyanide, and the peroxide curve being represented by the usual equation with a diminished k value. But in Expt. XVII, with excess of acid, which was in fact a test of the action of peroxide on hydrogen cyanide, the form of the peroxide curve was quite new, being curiously rectilinear from the start; gas was evolved, and a considerable fraction of the cyanide was oxidised to oxamide (Attfield's action).

These results are shown in the following tables. In the last case the actual readings are given instead of interpolated simultaneous values, so as to show the evidence for the constant velocity of the peroxide decomposition.

TABLE XXIV.—*Expt. XIV.* Added KOH = 242.

t .	$A - x$.	$B - y$.	$x - y$.
0	239	239	0
60	207	221	14
150	179	205	26
300	154	191	37
600	127	170	43
1200	101	146	45
2400	71	118	47
3600	52	101	49
5400	34	84	50
7200	24	74	50
9000	17	68	51

NOTE.—Oxygen gas evolved from the start, but with diminishing velocity. Formate found by analysis = $16 = 0.067 B$.

TABLE XXV.—*Expt.* XV. *Added* KOH = 120.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>x - y.</i>
0	240	239	0
15	215	203	-11
30	195	183	-11
60	165	154	-10
90	143	135	-7
120	126	123	-2
180	107	107	+1
240	94	96	+3
360	81	84	+4
560	63	66	+4
1260	33	36	+4
2800	7	10	+4
4140	1	4	+4

NOTE.—Oxygen gas evolved during the first four hours with diminishing velocity. Formate found by analysis = 27 = 0·11 *B*.

TABLE XXVI.—*Expt.* XVI. *Added* $\frac{1}{2}$ H₂SO₄ = 120.

<i>t.</i>	<i>A - x.</i>	<i>B - y.</i>	<i>w.</i>	<i>k.</i>
0	240	240	0	—
7·5	227	211	16	32
15	213	186	27	35
30	191	150	41	36
45	174	120	54	35
60	159	99	60	35
90	136	67	69	35
120	118	45	73	36
150	105	28	77	36
180	95	17	78	35
210	86	9	77	36
240	78	4	74	36
270	71	1	70	37
300	65	0	—	—
360	53	—	—	—
420	43	—	—	—
480	34	—	—	—
540	28	—	—	—
660	16	—	—	—
840	5	—	—	—

NOTE.—Oxygen gas first perceptible between 270 and 300 minutes.

$$W : B = 77 : 240 = 0\cdot32.$$

TABLE XXVII.—*Expt.* XVII. *Added* $\frac{1}{2}$ H₂SO₄ = 242.

<i>t.</i>	<i>A - x.</i>	<i>x/t.</i>	<i>t.</i>	<i>B - y.</i>
0	239	—	0	240
9	237·5	0·167	4·5	228
24	235	0·167	15	217
51	230·5	0·167	30	212·5
72	228	0·153	60	204·5
102	224	0·147	90	197·5
132	219	0·152	121	191
180	212·5	0·147	174	179
297	196	0·145	291	158
453	174	0·143	447	127
564	157	0·145	558	107·5
672	142	0·144	669	90

NOTE.—Some gas evolved and oxamide crystals formed.

Summary and Conclusions.

1. Hydrogen peroxide and potassium cyanide react exothermically in aqueous solution at the ordinary temperature.

2. The peroxide is reduced without escape of oxygen so long as residual cyanide is present, but any excess of peroxide is afterwards decomposed fairly rapidly into water and oxygen.

3. The products of the oxidation of the cyanide, which do not include oxamide or oxalate, are potassium cyanate and potassium and ammonium carbonates. The ratio of these depends on the amount of peroxide used. Cyanate is the primary product, and tends to be converted by hydrolysis into carbonate through the catalytic agency of the peroxide.

4. A part of the cyanide is converted by hydrolysis, without oxidation, into potassium formate and ammonia. Here also the peroxide acts as catalyst.

5. The total oxidation product (cyanate and carbonate) accounts for about four-fifths of the original cyanide, and the hydrolysis product (formate) for about one-fifth.

6. The peroxide curve, so long as unchanged cyanide remains, is of the second order and accords well with the equation

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

where A is the initial concentration of the peroxide, B is that of the cyanide, and x is the measure of the peroxide reduced, or cyanide oxidised, at time t . $B - x$ is the sum of the residual cyanide ($B - y$) and its hydrolysed product (w).

7. The hydrolysed product (w) reaches its maximum and final value ($W = 0.2 B$, nearly) before the completion of the oxidising action, and thereafter the slopes of the peroxide and cyanide curves are equal. The rate of hydrolysis is expressed by the empirical rule that

$$\frac{dw}{dt} = k_1(A - x)(W - w).$$

8. If the solutions are made to contain at the outset the ultimate products of the action itself, as well as fresh cyanide and peroxide, these products do not exert the influence indicated by the above equations. Hence, some unknown intermediate condition probably occurs while the action is in progress.

9. The addition of free alkali (KOH) at the outset greatly retards the whole action, diminishes the hydrolysis relatively to the oxidation, and causes the escape of oxygen gas in the early stages. The addition of ammonia has very little effect.

1474 MELDOLA AND HAY: THE DIAZOTISATION OF

10. The addition of free acid (H_2SO_4) at the outset also greatly retards the whole action, and appears to increase the hydrolysis. If enough acid be added to convert all the potassium cyanide into hydrogen cyanide, oxamide crystals are slowly formed (Attfield's action) and the peroxide curve becomes rectilinear.

UNIVERSITY OF MELBOURNE.
