The catalytic decomposition of hydrogen peroxide by ferric salts. Part I. The experimental data

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Özet : Hidrojen peroksit'in demir (III) tuzları karşısında katalitik parçalanması konusu üzerinde yeniden bir çok deneyler yapılmıştır. Bu alandaki çalışmalardan olmak üzere biz de hidrogen peroksit'in, demir (III) tuzları tesiri altında ve 25°C. da parçalanma hızını, demir (III) klorür ve demir (III) perklorat karşısında, çözeltinin P_H sına tabi olmak üzere inceledik.

Bu deneylerle Andersen'in dar asit sınırı içerisinde ve demir (III) nitrat çözeltileri için bulduğu konkav log C_0/C — t eğrileri teyit edildiği gibi, asit konsantrasyonunun artması neticesi eğrilerin daha az konkavlaştığı ve klorür çözeltilerinde konveks bir hal aldığı görüldü. Buna mukabil perklorat çözeltilerinde 1,13 - 0.96 P_H sınırında log C_0/C - t eğrileri birer doğrudur.

Parçalanma Andersen tarafından bulunan denklemle gösterilebilirse de verilen A ve B hız kat sayıları, Andersen tarafından teklif edilen ve reaksiyon mekanizmasına göre icap eden, çözelti P_H sına olan tabiliği göstermemektedir. Yeni bir reaksiyon mekanizmasının ortaya konması, yeni ve emin tecrübî bir esasa dayanacaktır ki, bu da ancak çözeltideki stasyoner demir (II) iyon konsantrasyonlarının ve parçalanma hızının demir (III) - iyon konsantrasyoniyle gösterdiği tabiliğin tedkikiyle kabildir.

It is known that the decomposition of hydrogen peroxide by ferric salts is not of first order in hydrogen peroxide as assumed by von BERTALAN (1). This was stated for the first time by BOHNSON and ROBERTSON (2), who claim that... the reaction due to disturbing effects is not strictly monomolecular, the values attained for 'velocity constants' varying slightly as the reaction proceeds..... SPITALSKY and PETIN (3) observed a regular change in the velocity constants during

a run. The same applies to the velocity constants as calculated by SIMON, HAUFE, REETZ and PREISSLER (4). ANDERSEN (5) with his experiments showed that in a very limited interval of the acidity of the solution, in the presence of nitrate ions as anions the reaction definitely does not follow the first order course. The differential equation found by ANDERSEN to represent the data is

$$(I) \qquad -\frac{dC}{dt} = \frac{BC^2}{A+C}$$

where C denotes the concentration of hydrogen peroxide at time t. A and B are constants which depend on ferric ion and hydrogen ion concentrations of the solution. Integrating, the equation yields

$$(II) \qquad \log \frac{C_0}{C} + A'\left(\frac{1}{C} - \frac{1}{C_0}\right) = B't$$

with $A' = \frac{A}{2.303}$ and $B' = \frac{B}{2.303}$, C_0 refers to the concentration of hydrogen peroxide at the commencement of the reaction.

PETERSON (6) claimed that the deviation from the first order occurs only in nitrate, and not in perchlorate solutions. ANDERSEN (7) published recently a single series of experiments with perchlorate as anion and found the proposed law (I) confirmed. ABEL (8) asserts - without bringing new experimental data - that the deviation from the first order will be apparent only in the last stages of the reaction.

It is known from the investigation (4) that anions have specific influences on the velocity of the reaction. This is explained by the formation of complexes between ferric ions and the anions. We have investigated the reaction in the presence of chloride and perchlorate ions, in as big a range of hydrogen ion concentrations as possible. In solutions with lower hydrogen ion concentrations the reaction proceeds so fast that due to the exothermicity the constancy of temperature is not preserved and at higher hydrogen ion concentrations it proceeds at such slow rates that times of the order of 20 hours were necessary in chloride solutions to achieve 90% decomposition of the original hydrogen peroxide present. A preliminary report of this work was given by ONAT and PARTS (9).

Although the discussion of the reaction mechanism does not fall within the scope of the present publication but is reserved for the following paper a few general remarks are appropriate. The macroscopically determined kinetic law must follow from the molecular reaction mechanism. The mechanisms proposed for this reaction can be classified into three groups. They are discussed extensively by MEDALIA and KOLTHOFF (10).

Into the first group we classify proposals of BOHNSON and ROBERTSON (2) who assume the intermediate formation of ferrate ions, while later BRAY and GORIN (11) assumed the intermediate formation of tetravalent iron.

Into the second group we put the assumption of HABER and WEISS (12) of the intermediate formation of hydroxyl and perhydroxyl radicals. Hydroxyl radical is postulated to be able to react with ferrous ion and with hydrogen peroxide molecule while perhydroxyl radical reacts with hydrogen peroxide, ferrous and ferric ions. This reaction mechanism is discussed in many papers of which the latest is (13). The reaction scheme of BARB, BAXENDALE, GEORGE and HARGRAVE as exposed in the latest paper (14) is the HABER - WEISS scheme in which the reaction between perhydroxyl radical and hydrogen peroxide is not allowed for. Finally, the mechanism of ABEL (15) belongs also to this group. This mechanism rejects the possibilities of the reaction of hydroxyl radical except with ferrous ion and that of perhydroxyl radical except with ferric ion.

The third group is formed by the reaction scheme of ANDERSEN (5) which in it original form contained the steps.

$$Fe^{+++} + HO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe(HO)^{++} + O$$

$$O + HO_2^- \xrightarrow{k_2} HO^- + O_2$$

Later it was modified by CHRISTIANSEN and ANDERSEN (16) to

$$Fe^{+++} + HO_2^- \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} Fe(HOO)^{++}$$

$$Fe(HOO)^{++} \underset{k_{52}}{\overset{k_{25}}{\rightleftarrows}} Fe^{+++} + HO_2^- \quad \text{(activated)}$$

$$HO_2^- \text{ (activated)} + H_2O_2 \xrightarrow{k_{50}} O_2 + H_2O + HO^-$$

From this reaction mechanism the kinetic expression (I) of ANDERSEN follows unambiguously. The coefficients B and A are expressed by the velocity constants of the reactions as

(III) $$A = \frac{k_{-1}}{k_2} \frac{K_{Fe}}{K_{H_2O_2}} \cdot \frac{C_{H^+}}{K_{Fe} + C_{H^+}} \cdot C_{Ferric}$$

or

$$A = \frac{k_{21}\, k_{52}}{(k_{21} + k_{25})\, k_{50}} \cdot \frac{C_{H^+}}{K_{Fe} + C_{H^+}} \cdot C_{Ferric}$$

and

(IV) $$B = \frac{2k_1\, K_{H_2O_2}}{K_{Fe} + C_{H^+}} \cdot C_{Ferric}$$

or

$$B = \frac{2k_{12}\, k_{25}}{k_{21} + k_{25}} \cdot \frac{K_{H_2O_2}}{K_{Fe} + C_{H^+}} \cdot C_{Ferric}$$

where $K_{H_2O_2}$ and K_{Fe} are the acid dissociation constants of hydrogen peroxide and ferric ion respectively.

Materials

Water : twice distilled, last distillation with permanganate.

Ferric chloride : Merck, A.R. - was dissolved in water to yield a solution of ca 38% by weight.

Hydrochloric acid: Baker, A.R.

Ferric perchlorate : was prepared according to LINDSTRAND (17) from ferric chloride and perchloric acid. During the evaporation of surplus acid the temperature of the substance was not allowed to raise above 130°C. At the and of the evaporation the temperature was lowered to 100-110°C. The product does not show the presence of ferrous ions but it contained a trace of chloride ions. The salt was dissolved, perchloric acid added and again evaporated after which it was chloride free. The salt was snow white and it was kept in a

dessicator. The content of ferric ion was determined by titration and a stock solution of 0.0400 molarity prepared.

Perchloric acid : Baker 60%, A.R.

Hydrogen peroxide : Perhydrol Merck, A.R. Most of the experiments were performed with a product which contained a trace of sulphate ions. Some of the experiments were made with peroxide free from sulphate obtained from Istanbul University. The experiments with this hydrogen peroxide are marked with an asterisk*.

Other chemicals were A.R. grade.

Performance of the experiments

All experiments were performed at 25.00 $\mp$ 0.05° C. In all experiments iron salt concentration was 0.00400 molar. The concentration of hydrogen peroxide at the commencement of the reaction varied from 0.040 to 0.051 molar with the exception of series 26 where the hydrogen peroxide was 0.060 molar.

Two 250 ml volumetric flasks which contained the properly acidified solutions of hydrogen peroxide and iron salt were kept in the thermostat. The iron salt solution was transferred thereafter to the reaction flask of Pyrex brand glass of one liter volume, which was also in the thermostat. After a time hydrogen peroxide solution was added under good stirring the mixture thoroughly shaken, and left in the thermostat. A sample, using a pipette with a wide orifice, was taken from the solution and transferred to a weighed flask with 25 ml of 2-molar sulfuric acid. According to SIMON et al. (4) the hydrogen peroxide decomposition is practically inhibited in this solution. By special experiments we were able to confirm this assertion. ANDERSEN (5) has used the same technique to stop the reaction. The flask was again weighed an so the amount of solution taken from the reaction mixture determined. The solution was titrated with potassium permanganate using the well known technique. The time was counted from the moment of transfer of the half of the first sample to sulphuric acid. In two series, in which decomposition of hydrogen peroxide was relatively slow, the samples were taken by volume. They are indicated in the corresponding tables.

Temperature of the reaction mixture was followed by an inserted thermometer. In the reaction proceeding fastest, the temperature was found to rise not more than corresponding to an increase of 2% in the instanteaneous reaction rate. As the temperature in the flask rises and then falls again to that of the thermostat the inaccuracy in the velocity constant from this source is less than 2%. At low pH-values of the solution no measurable rise of temperature could be detected.

The pH of the solution was determined by a glass electrode and a Beckman potentiometer. Carefully repeated determinations of the pH of all the used solutions were made. The found values were plotted against the molarity of the acid in the reaction mixtures and a smooth curve drawn through the points. From this curve the pH of the solution corresponding to the added amount of acid was found. These values are indicated in the following tables and figures. The reading of the pH-meter could be performed within an accuracy of $\mp$ 0.01, the values in the tables, however, are indicated to the third decimal point.

Evaluation of the experiments

The experimental results are given in Tables 1 to 59(*). Every table contains the number of the series, the molarity of the acid in solution, the concentration of hydrogen peroxide at the commencement of the reaction according to the first titration, pH of the solution and the molarity of the potassium permanganate used for the titration. The first column contains the time in minutes, second - weight of the solution taken for analaysis, third - ml of potassium permanganate used, fourth - $\log \frac{C_0}{C}$, fifth - $\frac{C_0 C}{C_0 - C} \log \frac{C_0}{C}$ and sixth - $\frac{C_0 C}{C_0 - C} \cdot t$ The tabels 1 to 33 refer to chloride solutions and tables 34 to 59 to perchlorate solutions, arranged in the order

(*) Due to the limited space the tables 2, 3, 7, 8, 13, 15, 16, 18, 21, 22, 27, 28, 35, 38, 45, 46, 49 and 50 are omitted in this published text; These unpublished tables may be obtained from the authors upon the request.

of increasing acidity. As mentioned previously, an asterisk after the number of the experiment shows that hydrogen peroxide, free from traces of sulphate ion was used.

TABLE 1

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.012	17.70	—	—	—	
4	19.319	13.30	0.1088	17.93	0.6290	
9	18.825	9.25	0.2553	14.97	0.5279	
14	19.127	6.94	0.3870	12.63	0.4569	
21	20.125	4.81	0.5683	9.87	0.3648	
28	19.575	3.25	0.7266	7.88	0.3035	
35	19.001	2.28	0.8675	6.39	0.2577	
41	18.611	1.79	0.9636	5.52	0.2347	
48	20.485	1.43	1.1028	4.43	0.1929	
55	19.435	1.16	1.1708	3.97	0.1867	
62	19.505	0.89	1.2876	3.28	0.1582	
68	19.647	0.75	1.3650	2.89	0.1439	
75	18.347	0.64	1.4491	2.51	0.1297	
81	20.050	0.54	1.5164	2.23	0.1193	
91	19.840	0.43	1.6108	1.90	0.1072	

Series No: 1

HCl : 0.001 M H_2O_2 : 0.04691 M

pH : 2.475 $KMnO_4$: 0.02130 M

TABLE 4

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.790	31.72	—	—	—	
2	19.390	25.08	0.0717	15.97	0.4454	
4	18.355	20.28	0.1402	14.71	0.4197	
6	20.540	19.49	0.2063	13.56	0.3945	
8	19.935	16.31	0.2706	12.52	0.3700	
10	20.430	14.48	0.3330	11.55	0.3469	
12	21.780	13.41	0.3941	10.66	0.3247	
15	20.170	10.15	0.4817	9.48	0.2952	
20	20.860	7.71	0.6157	7.87	0.2557	
25	19.535	5.43	0.7395	6.59	0.2226	
30	21.550	4.67	0.8476	5.61	0.1985	
35	21.225	3.64	0.9492	4.81	0.1772	
40	21.065	2.93	1.0402	4.17	0.1604	
50	17.520	1.63	1.2148	3.15	0.1298	
60	17.910	1.19	1.3610	2.48	0.1092	
70	18.040	0.91	1.4807	2.02	0.0957	
80	18.535	0.70	1.6064	1.63	0.0812	

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
90	18.290	0.57	1.6898	1.41	0.0751
100	17.600	0.43	1.7955	1.17	0.0651
110	19.495	0.37	1.9052	0.98	0.0567

Series No:4*

HCl : 0.001 M H_2O_2 : 0.03998 M

pH : 2.475 $KMnO_4$: 0.010524 M

TABLE 5

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	20.300	17.84	—	—	—
5	20.480	13.66	0.1198	17.57	0.7331
11	19.290	9.10	0.2702	14.59	0.5940
18	20.100	6.50	0.4342	11.78	0.4885
24	19.200	4.60	0.5644	9.86	0.4193
31	19.340	3.35	0.7053	8.07	0.3547
38	19.315	2.55	0.8234	6.78	0.3130
46	18.790	1.84	0.9530	5.57	0.2690
54	19.199	1.41	1.0780	4.58	0.2296
63	18.833	1.06	1.1934	3.81	0.2010
73	19.135	0.83	1.3068	3.16	0.1766
82	20.180	0.71	1.3975	2.72	0.1594
89	20.060	0.59	1.4754	2.38	0.1436
98	20.330	0.50	1.5531	2.08	0.1315

Series No: 5

pH : 2.410 H_2O_2 : 0.04661 M

HCl : 0.002 M $KMnO_4$: 0.02130 M

TABLE 6

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	20.982	36.31	—	—	—
9	20.109	20.31	0.2339	14.91	0.5736
15	18.557	13.29	0.3833	12.30	0.4814
22	19.120	9.30	0.5512	9.70	0.3911
29	19.125	6.73	0.6919	7.19	0.3015
41	19.218	4.05	0.9145	5.77	0.2585
49	19.247	3.02	1.0426	4.73	0.2221
58	19.688	2.19	1.1920	3.72	0.1812
67	20.990	1.89	1.2838	3.20	0.1672
76	18.450	1.32	1.3836	2.71	0.1490
85	20.110	1.11	1.4963	2.24	0.1273
94	19.077	0.89	1.5694	2.00	0.1199
107	19.678	0.67	1.7062	1.56	0.0976

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
117	20.997	0.59	1.7895		1.34	0.0878
128	20.160	0.45	1.8895		1.12	0.0761

Series No: 6

pH : 2.410 H_2O_2 : 0.04547 M

HCl : 0.002 M $KMnO_4$: 0.010553 M

TABLE 9

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	17.530	30.24	—		—	—
2	18.460	27.36	0.0659		18.15	0.5510
5	20.220	24.24	0.1580		16.27	0.5149
8	19.720	19.34	0.2452		14.61	0.4768
11	19.915	15.96	0.3329		13.06	0.4315
15	16.955	10.58	0.4419		11.31	0.3839
18	20.740	10.82	0.5194		10.18	0.3527
20	19.580	9.11	0.5691		9.50	0.3339
24	19.305	7.27	0.6609		8.34	0.3030
27	18.895	6.08	0.7292		7.56	0.2799
31	19.465	5.23	0.8076		6.74	0.2585
35	20.780	4.62	0.8898		5.95	0.2341
38	19.170	3.80	0.9396		5.51	0.2230
40	18.655	3.42	0.9736		5.23	0.2149
46	17.435	2.53	1.0751		4.46	0.1910
54	19.835	2.20	1.1918		3.70	0.1678
63	18.820	1.56	1.3183		3.01	0.1438
73	19.285	1.24	1.4286		2.50	0.1278
82	19.685	1.03	1.5181		2.15	0.1160
89	18.025	0.73	1.6294		1.77	0.0967
98	23.645	0.85	1.6811		1.62	0.0943

Series No: 9*

HCl : 0.002 M H_2O_2 : 0.04520 M

pH : 2.410 $KMnO_4$: 0.010524 M

TABLE 10

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	20.605	17.95	—		—	—
9	19.940	11.95	0.1514		16.77	0.9967
18	19.443	8.00	0.3258		13.47	0.7444
27	18.506	5.42	0.4733		11.08	0.6320
33	19.010	4.48	0.5678		9.73	0.5655
43	19.457	3.23	0.7200		7.83	0.4677
52	19.000	2.45	0.8297		6.66	0.4173
59	20.508	2.14	0.9216		5.79	0.3708

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
72	20.573	1.56	1.0602	4.67	0.3172
80	17.695	1.12	1.1388	4.12	0.2895
91	19.095	1.00	1.2211	3.61	0.2688
103	19.955	0.78	1.3481	2.93	0.2235
111	20.470	0.70	1.4061	2.65	0.2096
130	18.318	0.45	1.5498	2.08	0.1743
141	19.390	0.40	1.6256	1.82	0.1580
153	20.270	0.37	1.6787	1.66	0.1513
163	19.370	0.30	1.7501	1.46	0.1364

Series No: 10

HCl : 0.005 M H_2O_2 : 0.04620 M

pH : 2.220 $KMnO_4$: 0.02131 M

TABLE 11

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	18.715	33.24	—	—	—
2	18.980	30.28	0.0466	19.02	0.8163
4	21.115	30.49	0.0899	18.20	0.8097
6	19.290	25.35	0.1308	17.32	0.7948
9	21.095	23.89	0.1954	16.00	0.7371
12	19.920	19.60	0.2565	14.83	0.6936
18	17.710	13.23	0.3761	12.71	0.6083
20	17.685	12.07	0.4154	12.07	0.5809
27	19.700	10.04	0.5422	10.16	0.5057
30	18.815	8.51	0.5940	9.45	0.4772
33	19.065	7.70	0.6432	8.81	0.4521
43	17.420	5.00	0.7968	7.05	0.3802
52	18.615	3.96	0.9216	5.84	0.3293
59	18.855	3.25	1.0130	5.07	0.2951
72	18.935	2.33	1.1594	4.02	0.2495
80	17.300	1.74	1.2470	3.48	0.2235
91	19.440	1.55	1.3478	2.95	0.1991
103	18.250	1.13	1.4577	2.45	0.1732
111	18.430	0.96	1.5327	2.16	0.1561
130	18.590	0.74	1.6495	1.76	0.1387

Series No: 11*

pH : 2.220 H_2O_2 : 0.04654 M

HCl : 0.005 M $KMnO_4$: 0.01524 M

TABLE 12

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	19.690	17.80	0.	—	—	—
7.5	21.086	15.55	0.0885	18.63	1.579	
15.0	20.066	12.02	0.1788	16.71	1.402	
20.0	20.508	10.73	0.2375	15.54	1.309	
25.0	20.318	9.28	0.2944	14.46	1.228	
34.0	21.218	7.70	0.3964	12.66	1.086	
40.5	20.390	6.52	0.4697	11.48	0.989	
46.0	21.337	5.73	0.5272	10.61	0.926	
56.5	19.965	4.11	0.6362	9.11	0.809	
64.0	21.388	3.80	0.7066	8.23	0.746	
76.0	21.367	2.92	0.8206	6.96	0.645	
92.5	19.870	2.00	0.9533	5.69	0.552	

Series No: 12

pH : 1.990 H_2O_2 : 0.04763 M

HCl : 0.01 M $KMnO_4$: 0.02116 M

TABLE 14

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.236	36.39	—	—	—	
8	19.626	28.59	0.0914	18.43	1.613	
15	19.588	23.60	0.1738	16.68	1.440	
24	19.867	18.87	0.2771	13.92	1.206	
31	20.870	16.45	0.3581	13.21	1.143	
42	19.060	11.37	0.4791	11.24	0.985	
50	19.805	9.81	0.5599	10.06	0.898	
61	19.825	7.66	0.6677	8.64	0.789	
73	19.730	5.99	0.7725	7.42	0.701	
85	18.780	4.45	0.8801	6.31	0.610	
93	20.435	4.17	0.9450	5.72	0.563	
106	19.910	3.21	1.0473	4.66	0.472	
117	19.950	2.71	1.1217	4.33	0.452	
132	20.230	2.21	1.2164	3.72	0.404	
142	19.788	1.86	1.2817	3.34	0.370	
151	20.485	1.69	1.3383	3.04	0.343	
163	20.075	1.41	1.4082	2.70	0.313	
170	20.425	1.34	1.4378	2.57	0.304	

Series No: 14

HCl : 0.01 M H_2O_2 : 0.04725 M

pH : 1.990 $KMnO_4$: 0.010553 M

TABLE 17

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	19.837	18.01	—	—	—	
5	20.192	17.79	0.0130	20.31	7.813	
12	20.776	16.03	0.0707	19.11	3.243	
19	20.140	14.03	0.1150	18.11	2.992	
30.5	21.238	12.67	0.1824	16.72	2.796	
39	19.230	10.01	0.2416	15.53	2.506	
51	21.387	9.40	0.3151	14.14	2.289	
65	20.637	7.48	0.3988	12.68	2.066	
96	20.282	4.89	0.5758	9.96	1.661	
111	20.220	4.01	0.6607	8.83	1.484	
132	20.021	3.10	0.7682	7.55	1.298	
161	20.225	2.25	0.9118	6.09	1.075	
181	20.628	2.00	0.9715	5.55	1.035	

Series No: 17

HCl : 0.02 M H_2O_2 : 0.04784 M

pH : 1.730 $KMnO_4$: 0.02116 M

TABLE 19

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.310	35.41	—	—	—	
14	20.195	28.74	0.0882	17.96	2.851	
40	19.775	19.22	0.2538	14.65	2.308	
53	19.980	16.13	0.3344	13.21	2.094	
88	19.427	9.58	0.5439	9.97	1.613	
113	19.937	7.17	0.6856	8.16	1.345	
144	19.681	4.91	0.8444	6.46	1.102	
175	19.375	3.40	0.9948	5.13	0.903	
205	20.875	2.68	1.1329	4.13	0.747	
231	20.662	2.10	1.2344	3.50	0.655	
256	19.255	1.54	1.3384	2.95	0.564	
279	19.909	1.32	1.4199	2.57	0.505	

Series No: 19

HCl : 0.02 M H_2O_2 : 0.04581 M

pH : 1.730 $KMnO_4$: 0.010553 M

TABLE 20

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20 ml	17.86	—	—	—	
30	» »	14.74	0.0834	18.74	6.742	
60	» »	12.15	0.1673	16.95	6.079	

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
90	» »	10.00	0.2519	15.24		5.445
120	» »	8.11	0.3429	13.56		4.747
150	» »	6.68	0.4271	12.14		4.263
180	» »	5.48	0.5131	10.70		3.789
210	» »	4.50	0.5987	9.59		3.365
240	» »	3.70	0.6837	8.50		2.982
270	» »	3.10	0.7605	7.60		2.697
300	» »	2.55	0.8453	6.69		2.375
330	» »	2.15	0.9194	5.98		2.147
360	» »	1.77	1.0039	5.25		1.883
390	» »	1.49	1.0787	4.67		1.688
420	» »	1.24	1.1584	4.11		1.490
450	» »	1.05	1.2307	3.66		1.337
480	» »	0.87	1.3124	3.20		1.169
510	» »	0.77	1.3654	2.86		1.067
540	» »	0.66	1.4323	2.61		0.985
570	» »	0.59	1.4810	2.41		0.926
600	» »	0.50	1.5529	2.13		0.822

Series No: 20

HCl : 0.04 M H_2O_2 : 0.04755 M

pH : 1.442 $KMnO_4$: 0.02130 M

TABLE 23

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.173	35.66	—	—		—
30	19.980	29.17	0.0831	18.30		6.608
60	20.135	24.09	0.1695	16.49		5.837
120	20.675	16.60	0.3427	13.25		4.640
180	20.335	11.03	0.5131	10.55		3.701
240	20.422	7.56	0.6790	8.35		2.953
300	20.140	5.16	0.8388	6.60		2.362
330	19.600	4.13	0.9237	5.81		2.074
360	18.513	3.26	1.0017	5.15		1.850
390	19.877	2.93	1.0789	4.56		1.648
420	20.413	2.50	1.1594	4.01		1.452
450	20.950	2.18	1.2301	3.57		1.307
480	20.805	1.81	1.3079	3.14		1.154
510	20.085	1.49	1.3771	2.80		1.038
540	20.093	1.28	1.4432	2.51		0.938
570	19.883	1.09	1.5085	2.24		0.847

Series No: 23

pH : 1.442 H_2O_2 : 0.04645 M

HCl : 0.04 M $KMnO_4$; 0.010553 M

TABLE 24

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.250	33.40	—	—	—	—
30	21.255	29.71	0.0509	17.67	10.417	
60	21.145	26.30	0.1016	16.60	9.804	
90	21.035	23.24	0.1531	15.61	9.174	
120	21.070	20.70	0.2041	14.65	8.615	
180	19.605	15.12	0.3092	12.83	7.469	
210	19.055	13.09	0.3595	12.02	7.021	
240	21.270	12.99	0.4105	11.24	6.572	
300	20.355	9.80	0.5138	9.77	5.707	
330	21.100	8.97	0.5679	9.07	5.270	
360	20.400	7.72	0.6184	8.45	4.917	
390	20.160	6.71	0.6742	7.80	4.512	
420	20.710	6.31	0.7251	7.24	4.196	
450	20.575	5.39	0.7781	6.70	3.876	
510	19.500	4.00	0.8843	5.72	3.297	
540	19.915	3.61	0.9381	5.28	3.037	
570	19.420	3.13	0.9891	4.87	2.805	

Series No: 24

pH : 1.274 H_2O_4 : 0.04307 M

HCl : 0.06 M $KMnO_4$: 0.011006 M

TABLE 25

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	18.320	28.53	—	—	—	—
30	18.995	26.35	0.0502	17.49	10.453	
60	21.995	27.18	0.1004	16.46	9.836	
90	21.500	23.66	0.1508	15.50	9.250	
120	18.950	18.47	0.2035	14.53	8.565	
150	22.385	19.39	0.2548	13.63	8.021	
180	15.470	11.91	0.3060	12.77	7.509	
210	18.830	12.97	0.3543	11.99	7.107	
240	20.425	12.40	0.4091	11.16	6.545	
300	25.775	12.31	0.5133	9.69	5.664	
330	22.535	9.53	0.5661	9.00	5.249	
360	22.580	8.50	0.6167	8.39	4.897	
390	19.520	6.55	0.6666	7.81	4.572	
420	18.970	5.61	0.7215	7.22	4.200	
450	21.255	5.54	0.7763	6.66	3.859	
480	18.950	4.40	0.8265	6.18	3.590	
510	16.540	3.41	0.8782	5.72	3.320	
540	21.535	3.97	0.9267	5.31	3.095	

Series No: 25

HCl : 0.06 M H_2O_2 : 0.04268 M

pH : 1.274 $KMnO_4$: 0.011006 M

TABLE 26

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20 ml	22.57	0. —	—	—	—
30	» »	20.86	0.0342		24.96	21.90
60	» »	19.29	0.0682		24.10	21.20
120	» »	16.40	0.1387		22.16	19.17
180	» »	13.80	0.2137		20.20	17.01
240	» »	11.73	0.2842		18.48	15.61
300	» »	9.93	0.3566		16.83	14.16
360	» »	8.38	0.4303		15.27	12.78
420	» »	7.00	0.5084		13.74	11.35
480	» »	5.94	0.5797		12.47	10.33
540	» »	4.92	0.6616		11.08	9.04

Series No: 26

pH : 1.154 H_2O_2 : 0.06009 M

HCl : 0.08 M $KMnO_4$: 0.02130 M

TABLE 29

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	20.540	38.00	—	—	—	—
30	18.725	32.10	0.0331		21.22	19.23
60	23.930	37.77	0.0690		20.29	17.65
180	24.305	27.90	0.2073		17.19	14.93
300	24.675	20.26	0.3528		14.28	12.14
360	23.545	16.40	0.4242		12.99	11.03
420	19.240	11.31	0.4979		11.76	9.92
510	21.840	9.92	0.6099		10.06	8.42
570	20.065	7.66	0.6854		9.04	7.52
630	20.095	6.46	0.7600		8.11	6.72
690	21.600	5.79	0.8389		7.21	5.93
750	20.510	4.58	0.9183		6.39	5.22
810	24.205	4.01	0.9969		5.66	4.60
930	19.870	2.54	1.1605		4.37	3.50
990	20.360	2.22	1.2296		3.90	3.14
1110	20.340	1.56	1.3824		3.03	2.43
1170	18.385	1.12	1.4824		2.56	2.02
1260	17.905	0.81	1.6117		2.05	1.60
1320	23.815	0.87	1.7005		1.75	1.36

Series No: 29

HCl : 0.08 M H_2O_2 : 0.05071 M

pH : 1.154 $KMnO_4$: 0.011006 M

TABLE 30

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	19.280	34.73	0.	—	—	—
30	20.215	34.36	0.0252		20.83	24.79
60	19.690	31.53	0.0511		20.20	23.72
180	19.845	24.99	0.1555		17.83	20.64
240	21.135	23.58	0.2081		16.71	19.28
300	21.560	21.19	0.2631		15.60	17.78
420	20.110	15.47	0.3695		13.59	15.45
480	20.450	13.67	0.4305		12.54	13.98
600	20.010	10.40	0.5398		10.81	12.01
780	19.970	6.89	0.7178		8.39	9.12
840	19.835	5.98	0.7763		7.63	8.29
900	19.205	4.99	0.8409		7.00	7.49
1050	20.905	3.77	0.9995		5.49	5.77
1200	20.060	2.52	1.1565		4.28	4.44
1320	19.210	1.81	1.2814		3.49	3.60
1380	20.390	1.66	1.3449		3.14	3.23
1440	19.800	1.40	1.4061		2.84	2.90

Series No: 30

HCl : 0.10 M H_2O_2 : 0.04937 M

pH : 1.061 $KMnO_4$: 0.011006 M

TABLE 31

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	21.990	38.14	—		—	—
30	18.765	31.83	0.0257		20.08	23.44
60	19.040	30.42	0.0517		18.73	21.74
180	21.600	27.16	0.1558		17.16	19.82
240	19.695	21.83	0.2105		16.04	18.24
300	22.765	22.30	0.2642		15.00	17.04
420	18.565	14.13	0.3738		13.02	14.63
480	22.860	15.30	0.4296		12.09	13.57
600	20.035	10.31	0.5438		10.35	11.42
780	15.894	5.50	0.7161		8.10	8.83
840	17.205	5.17	0.7774		7.40	8.00
900	19.585	5.12	0.8379		6.77	7.27
1050	22.375	4.08	0.9943		5.33	5.63
1200	18.875	2.33	1.1638		4.07	4.20
1320	20.645	1.97	1.2756		3.39	3.51
1380	22.430	1.86	1.3365		3.07	3.17
1440	19.485	1.40	1.3988		2.76	2.85

Series No: 31

HCl : 0.10 M H_2O_2 : 0.04753 M

pH : 1.061 $KMnO_4$: 0.011006 M

TABLBE 32

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.525	38.30	—	—	—	—
30	21.685	36.96	0.0187		20.78	33.33
60	20.925	34.06	0.0387		20.26	31.41
150	19.940	28.26	0.0988		18.85	28.63
360	20.980	21.10	0.2478		15.71	22.83
420	22.045	20.00	0.2925		14.84	21.31
480	20.755	17.01	0.3368		14.02	19.98
600	20.365	13.71	0.4221		12.53	17.81
720	20.595	11.11	0.5183		11.00	15.28
780	20.135	9.73	0.5661		10.29	14.18
930	20.700	7.65	0.6826		8.73	11.89
1080	21.290	5.91	0.8068		7.28	9.74
1230	19.875	4.13	0.9326		6.01	7.93
1350	20.445	3.33	1.0384		5.10	6.63
1500	20.975	2.53	1.1688		4.14	5.32
1560	21.965	2.32	1.2265		3.77	4.80
1620	20.900	1.95	1.2804		3.45	4.37

Series No: 32

HCl : 0.12 M H_2O_2 : 0.04876 M

pH : 0.985 $KMnO_4$: 0.011006 M

TABLE 33

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	23.805	42.37	—		—	—
30	22.475	38.20	0.0200		20.62	30.93
60	22.870	37.12	0.0401		20.15	30.15
150	24.180	34.04	0.1019		18.80	27.68
360	17.905	17.90	0.2505		15.66	22.50
420	18.425	16.69	0.2933		14.83	21.23
480	19.645	15.99	0.3398		13.97	19.73
600	19.685	13.02	0.4299		12.40	17.31
720	19.140	10.23	0.5224		10.94	15.07
780	19.295	9.21	0.5716		10.22	13.94
930	22.770	8.32	0.6876		8.66	11.72
1080	17.745	4.89	0.8102		7.24	9.65
1230	19.245	3.97	0.9359		5.98	7.86
1350	18.535	3.00	1.0412		5.08	6.59
1500	24.090	2.78	1.1882		4.02	5.07
1560	20.270	2.13	1.2289		3.76	4.77
1620	24.075	2.25	1.2798		3.46	4.38

Series No: 33

HCl : 0.12 M H_2O_2 0.04878 M

pH : 0.985 $KMnO_4$: 0.011006 M

TABLE 34

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	27.605	44.47	—	—	—	—
2	23.885	33.69	0.0672	18.18		0.5405
4	26.405	32.08	0.1321	16.78		0.5083
6	24.835	26.09	0.1952	15.53		0.4774
9	25.645	21.69	0.2894	13.79		0.4289
14	20.620	12.38	0.4382	11.36		0.3626
18	26.250	12.12	0.5422	9.85		0.3270
24	20.425	6.67	0.7026	7.85		0.2680
30	19.800	4.63	0.8477	6.33		0.2242
35	20.960	3.80	0.9582	5.35		0.1955
40	20.305	2.96	1.0529	4.62		0.1754
48	17.955	1.91	1.1898	3.71		0.1496
58	17.575	1.35	1.3312	2.95		0.1284
69	18.875	1.04	1.4755	2.36		0.1078
77	17.010	0.74	1.5781	1.93		0.0943
85	21.580	0.78	1.6586	1.68		0.0861
94	21.625	0.62	1.7592	1.41		0.0751

Series No: 34

pH : 2.460 H_2O_2 : 0.04513 M

$HClO_4$: 0.001 M $KMnO_4$: 0.011006 M

TABLE 36

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.385	37.20	—	—	—	—
2	21.055	30.28	0.0838	18.02		0.4301
4	19.555	23.65	0.1673	16.27		0.3891
6	18.510	18.89	0.2328	15.01		0.3868
9	18.105	14.45	0.3395	13.09		0.3471
12	13.595	8.52	0.4445	11.40		0.3077
14	19.730	10.63	0.5102	10.42		0.2860
18	17.620	7.13	0.6345	8.76		0.2486
20	18.970	6.67	0.6955	8.03		0.2309
24	18.000	5.02	0.7962	6.93		0.2089
30	18.380	3.58	0.9521	5.47		0.1724
35	19.480	2.93	1.0643	4.59		0.1510
40	18.360	2.15	1.1730	3.86		0.1316
48	19.665	1.69	1.3074	3.10		0.1137
58	18.065	1.09	1.4610	2.39		0.0950
69	19.825	0.88	1.5943	1.90		0.0824

Series No: 36*

$HClO_4$:0.001 M H_2O_2 : 0.04571 M

pH : 2.460 $KMnO_4$: 0.010524 M

TABLE 37

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	23.445	39.03	0. —	—	—	—
4	22.095	28.11	0.1158	17.28	0.5970	
9	19.335	17.82	0.2558	14.55	0.5119	
14	17.530	11.73	0.3948	12.16	0.4310	
20	23.485	11.00	0.5397	9.99	0.3702	
25	18.135	6.46	0.6686	8.40	0.3114	
30	21.925	6.06	0.7788	7.14	0.2732	
36	19.825	4.18	0.8964	5.98	0.2387	
48	22.835	2.91	1.1151	4.25	0.1820	
55	23.035	2.24	1.2319	3.52	0.1563	
69	21.645	1.39	1.4127	2.60	0.1266	
85	22.675	0.93	1.6074	1.86	0.0982	
93	20.220	0.72	1.6688	1.67	0.0930	
101	22.375	0.67	1.7441	1.46	0.0843	
110	23.870	0.60	1.8200	1.28	0.0771	
121	20.230	0.41	1.9135	1.08	0.0682	
131	22.270	0.36	2.0118	0.90	0.0587	

Series No: 37

$HClO_4$: 0.002 M H_2O_2 : 0.04562 M

pH : 2.380 $KMnO_4$: 0.011006 M

TABLE 39

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	20.235	36.35	—	—	—	
2	19.750	30.04	0.0723	18.78	0.5195	
4	19.445	25.33	0.1396	17.32	0.4963	
6	18.985	21.20	0.2065	15.97	0.4640	
9	18.830	16.90	0.3014	14.16	0.4229	
12	17.165	12.40	0.3956	12.53	0.3800	
14	18.375	11.50	0.4579	11.53	0.3524	
20	16.575	7.05	0.6257	9.14	0.2921	
25	18.225	5.73	0.7569	7.55	0.2495	
30	17.690	4.25	0.8737	6.35	0.2180	
36	18.550	3.30	1.0042	5.22	0.1872	
42	19.065	2.60	1.1197	4.33	0.1624	
48	20.090	2.14	1.2270	3.64	0.1424	
55	19.275	1.59	1.3380	3.03	0.1246	
63	19.805	1.25	1.4543	2.49	0.1080	
69	20.170	1.07	1.5297	2.19	0.0988	
75	19.760	0.86	1.6157	1.89	0.0877	
80	19.020	0.72	1.6763	1.74	0.0830	

Series No: 39*

$HClO_4$: 0.002 M H_2O_2 : 0.04726 M

pH : 2.380 $KMnO_4$: 0.010524 M

TABLE 40

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.415	40.13	—	—	—	—
9	20.005	23.89	0.1957		17.06	0.7847
18	19.600	15.09	0.3863		13.38	0.6233
27	18.200	9.29	0.5648		10.50	0.5018
33	18.420	7.30	0.6747		8.98	0.4391
43	18.795	5.02	0.8461		6.98	0.3548
52	18.480	3.59	0.9843		5.65	0.2987
59	18.855	2.90	1.0858		4.82	0.2619
72	19.525	2.07	1.2474		3.71	0.2143
80	18.815	1.58	1.3486		3.14	0.1863
91	20.360	1.32	1.4610		2.60	0.1619
103	19.790	0.97	1.5824		2.11	0.1373
111	19.835	0.84	1.6459		1.89	0.1274
130	20.050	0.61	1.7895		1.47	0.1065
141	20.795	0.52	1.8747		1.26	0.0946
153	21.965	0.49	1.9243		1.15	0.0915
165	20.440	0.39	1.9922		1.02	0.0832

Series No: 40

$HClO_4$: 0.005 M H_2O_2 : 0.04964 M

pH : 2.190 $KMnO_4$: 0.010638 M

TABLE 41

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	25.320	47.03	—	—	—	—
9	20.685	24.39	0.1974		16.87	0.7692
18	21.925	16.60	0.3897		13.20	0.6096
27	24.075	12.11	0.5673		10.37	0.4934
33	22.140	8.67	0.6761		8.89	0.4337
43	9.630	2.53	0.8494		6.88	0.3484
52	9.775	1.95	0.9690		5.74	0.3079
59	6.750	1.07	1.0688		4.91	0.2709
72	18.680	1.97	1.2458		3.69	0.2133
80	22.345	1.89	1.3416		3.15	0.1878
91	19.955	1.30	1.4550		2.60	0.1628
103	19.265	0.97	1.5669		2.15	0.1412
121	24.575	0.85	1.7299		1.62	0.1130
130	17.915	0.57	1.7633		1.51	0.1113
141	22.335	0.60	1.8397		1.39	0.1067
153	20.430	0.45	1.9160		1.16	0.0924
165	24.370	0.49	1.9656		1.07	0.0898

Series No: 41

$HClO_4$: 0.005 M H_2O_2 : 0.04920 M

pH : 2.190 $KMnO_4$: 0.010638 M

TABLE 42

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.885	41.10	—	—	—	—
10	20.900	27.92	0.1479	18.13	1.226	
20	20.335	19.41	0.2939	15.11	1.028	
30	19.450	13.37	0.4365	12.54	0.862	
50	18.860	7.10	0.6980	8.73	0.626	
70	20.335	4.45	0.9336	6.13	0.459	
90	20.245	2.73	1.1438	4.40	0.346	
100	19.025	2.08	1.2349	3.80	0.308	
120	18.680	1.37	1.4083	2.85	0.243	
140	18.750	1.04	1.5297	2.32	0.213	
160	19.690	0.76	1.6871	1.76	0.167	
180	21.005	0.60	1.8179	1.40	0.133	
200	20.000	0.48	1.8935	1.22	0.129	
220	19.325	0.39	1.9687	1.06	0.119	
230	19.660	0.32	2.0621	0.90	0.100	

Series No: 42

$HClO_4$: 0.01 M H_2O_2 : 0.04975 M

pH : 1.970 $KMnO_4$: 0.010638 M

TABLE 43

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	19.765	37.40	—	—	—	—
10	18.040	24.46	0.1448	18.33	1.266	
20	20.005	19.40	0.2903	15.30	1.054	
30	17.210	12.04	0.4321	12.71	0.882	
50	17.705	6.83	0.6906	8.86	0.642	
70	19.150	4.29	0.9267	6.24	0.471	
90	22.535	3.12	1.1357	4.49	0.356	
100	17.090	1.98	1.2131	3.97	0.327	
120	20.500	1.58	1.3900	2.96	0.255	
140	22.585	1.17	1.5626	2.20	0.198	
160	18.845	0.73	1.6888	1.77	0.168	
180	19.975	0.58	1.8140	1.42	0.141	
200	18.845	0.41	1.9394	1.13	0.117	
220	20.845	0.39	2.0049	1.00	0.110	
235	18.830	0.31	2.0605	0.91	0.102	

Series No: 43

$HClO_4$: 0.01 M H_2O_2 : 0.5012 M

pH : 1.970 $KMnO_4$: 0.010638 M

TABLE 44

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	20.960	59.51	—	—	—
6	20.390	34.33	0.0491	20.54	2.510
13	20.455	30.10	0.1075	19.13	2.312
21	20.220	25.50	0.1746	17.64	2.122
30	20.430	21.70	0.2491	16.07	1.935
37	18.810	17.50	0.3067	14.94	1.802
54	19.000	12.83	0.4458	12.44	1.507
90	17.970	6.32	0.7291	8.36	1.033
119	19.145	4.19	0.9352	6.14	0.781
144	21.700	3.19	1.1080	4.68	0.609
163	19.305	2.19	1.2205	3.91	0.523
179	19.990	1.82	1.3161	3.34	0.466
198	21.610	1.54	1.4224	2.79	0.389
215	19.505	1.15	1.5048	2.43	0.347
232	19.550	1.95	1.5887	2.10	0.307
254	19.625	0.74	1.6989	1.73	0.259

Series No: 44

$HClO_4$: 0.02 M H_2O_2 : 0.04993 M

pH : 1.692 $KMnO_4$: 0.010638 M

TABLE 47

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	21.960	37.40	—	—	—
6	17.575	26.72	0.0493	18.99	2.299
13	20.410	26.58	0.1165	17.41	1.943
21	20.440	22.45	0.1905	15.93	1.756
30	16.515	15.08	0.2707	14.41	1.597
37	18.955	14.92	0.3352	13.26	1.464
45	20.540	13.73	0.4062	12.08	1.338
54	20.515	11.45	0.4845	10.87	1.212
60	23.505	11.56	0.5394	10.08	1.122
75	19.070	6.95	0.6696	8.39	0.940
90	22.140	6.05	0.7947	6.99	0.792
119	22.170	3.60	1.0207	4.95	0.577
144	19.145	2.04	1.2037	3.70	0.442
163	21.400	1.70	1.3312	3.00	0.367
179	21.775	1.40	1.4231	2.57	0.323
189	27.715	1.56	1.4808	2.33	0.297

Series No: 47*

$HClO_4$: 0.02 M H_2O_2 : 0.04604 M

pH : 1.692 $KMnO_4$: 0.010856 M

TABLE 48

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C}.t$
0	21.205	40.11	—	—	—	
15	20.375	33.39	0.0632		20.23	4.870
30	20.390	28.88	0.1256		18.77	4.484
45	10.630	24.02	0.1892		17.37	4.132
60	19.105	20.20	0.2526		16.05	3.812
90	20.035	15.83	0.3791		13.63	3.236
120	19.395	11.42	0.5068		11.48	2.718
150	20.130	8.96	0.6284		9.69	2.313
180	20.965	7.05	0.7501		8.13	1.950
210	21.630	5.49	0.8723		6.78	1.632
240	21.440	4.13	0.9921		5.65	1.364
270	20.680	3.07	1.1052		4.72	1.152
300	20.840	2.40	1.2155		3.95	0.975
330	20.910	1.89	1.3207		3.32	0.830

Series No: 48

$HClO_4$: 0.04 M H_2O_2 : 0.05010 M

pH : 1.409 $KMnO_4$: 0.010638 M

TABLE 51

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C}.t$
0	19.985	34.28	—	—	—	
8	20.390	32.18	0.0362		19.67	4.348
15	21.985	32.20	0.0686		18.90	4.132
20	20.420	28.37	0.0915		18.37	4.016
40	16.205	18.34	0.1806		16.48	3.650
45	17.250	18.46	0.2049		16.00	3.513
55	16.160	15.59	0.2499		15.12	3.327
60	19.900	18.19	0.2734		14.68	3.221
75	16.140	12.58	0.3426		13.43	2.940
90	11.515	7.71	0.4085		12.31	2.712
110	18.920	10.23	0.5027		10.84	2.372
120	16.725	8.19	0.5444		10.23	2.256
140	19.500	7.74	0.6356		9.00	1.983
150	14.290	5.11	0.6809		8.44	1.859
165	18.645	5.71	0.7483		7.65	1.687
180	15.730	4.20	0.8078		7.01	1.561
200	17.865	3.89	0.8964		6.13	1.368
210	20.060	3.95	0.9401		5.74	1.281
240	18.435	2.75	1.0606		4.75	1.076
270	19.805	2.22	1.1848		3.90	0.888
300	22.380	1.92	1.3010		3.22	0.743
330	26.695	1.11	1.5449		2.13	0.456

Series No: 51*

$HClO_4$: 0.04 M H_2O_2 : 0.04704 M

pH : 1.409 $KMnO_4$: 0.010856 M

TABLE 52

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	22.070	40.91	—	—	—
15	20.575	34.72	0.0408	20.40	7.500
30	21.475	32.95	0.0821	19.41	7.092
60	20.440	25.90	0.1652	17.50	6.356
90	22.175	23.25	0.2475	15.82	5.755
120	22.285	19.36	0.3231	14.37	5.336
150	19.970	14.39	0.4103	12.82	4.686
180	19.735	11.79	0.4917	11.49	4.205
210	20.160	9.96	0.5743	10.55	3.747
240	22.200	9.13	0.6539	9.16	3.360
270	19.955	6.81	0.7349	8.15	2.993
300	19.380	5.53	0.8127	7.26	2.681
330	19.945	4.71	0.8948	6.42	2.367
360	21.160	4.20	0.9703	5.71	2.120
390	20.510	3.37	1.0524	5.03	1.863
420	19.760	2.75	1.1245	4.71	1.760
450	19.980	2.31	1.2050	3.94	1.470
480	21.900	2.12	1.2821	3.47	1.299

Series No: 52

$HClO_4$: 0.06 M H_2O_2 : 0.04910 M

pH : 1.243 $KMnO_4$: 0.010638 M

TABLE 53

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	21.560	38.37	—	—	—
15	21.155	33.96	0.0448	19.91	6.667
30	19.730	28.68	0.0879	18.90	6.452
60	20.700	24.56	0.1761	16.98	5.786
90	19.875	19.18	0.2658	15.19	5.143
120	20.575	16.20	0.3542	13.56	4.592
150	20.625	13.21	0.4438	12.04	4.068
180	19.790	10.36	0.5314	10.68	3.619
210	20.645	8.89	0.6163	9.49	3.233
240	21.135	7.46	0.7026	8.38	2.864
270	16.220	4.69	0.7892	7.38	2.526
300	19.400	4.57	0.8782	6.46	2.208
330	19.120	3.75	0.9578	5.72	1.971
360	19.530	3.16	1.0414	4.79	1.657
390	17.815	2.37	1.1264	4.39	1.520
420	17.730	1.95	1.2090	3.84	1.335
450	21.340	1.90	1.3008	3.30	1.143
480	19.010	1.44	1.3710	2.94	1.029

Series No: 53*

$HClO_4$: 0.06 M H_2O_2 : 0.04824 M

pH : 1.243 $KMnO_4$: 0.010638 M

TABLE 54

Time in minutes	Volume of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	21.750	40.41	—	—	—	
30	20.645	33.54	0.0583	19.97	10.274	
60	21.855	30.93	0.1182	18.61	9.449	
90	21.870	26.99	0.1777	17.30	8.763	
120	21.745	23.36	0.2379	16.05	8.097	
150	20.960	19.67	0.2966	14.90	7.534	
180	21.105	17.26	0.3564	13.79	6.966	
210	21.105	15.10	0.4144	12.77	6.473	
240	22.130	13.77	0.4751	11.77	5.948	
300	22.055	10.38	0.5963	9.96	5.009	
330	19.575	8.10	0.6522	9.20	4.654	
360	20.145	7.27	0.7117	8.44	4.270	
390	20.970	6.57	0.7731	7.72	3.892	
420	21.240	5.83	0.8305	7.09	3.584	
480	21.540	4.51	0.9481	5.93	3.000	
510	21.330	3.90	1.0069	5.41	2.740	
540	22.540	3.57	1.0693	5.16	2.605	
570	18.505	2.59	1.1230	4.50	2.285	
600	17.875	2.19	1.1808	3.97	2.015	
630	18.465	1.98	1.2387	3.73	1.899	

Series No: 54

$HClO_4$: 0.08 M H_2O_2 : 0.04921 M

pH : 1.125 $KMnO_4$: 0.010638 M

TABLE 55

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	20.900	38.35	—	—	—	
30	21.045	33.28	0.0647	19.61	9.091	
60	19.835	27.13	0.1278	18.15	8.523	
90	19.735	23.29	0.1913	16.81	7.909	
120	21.310	21.71	0.2557	15.51	7.277	
150	20.120	17.73	0.3187	14.30	6.732	
180	20.225	15.41	0.3819	13.17	6.209	
210	21.185	13.87	0.4477	12.07	5.662	
240	19.750	11.18	0.5109	11.08	5.203	
300	19.865	8.38	0.6402	9.24	4.332	
330	20.110	7.33	0.7021	8.45	3.975	
360	22.020	6.90	0.7677	7.66	3.603	
390	20.295	5.51	0.8300	6.98	3.291	
420	21.260	5.00	0.8924	6.36	3.002	
480	21.575	3.79	1.0191	5.23	2.473	
510	19.730	3.00	1.0818	4.74	2.241	

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
540	20.090	2.62	1.1484	4.26	2.009
570	16.355	1.92	1.1941	3.96	1.894
600	18.220	1.80	1.2681	3.50	1.660
630	18.920	1.62	1.3312	3.16	1.499

Series No: 55*

$HClO_4$: 0.08 M H_2O_2 : 0.04863 M

pH : 1.125 $KMnO_4$: 0.010638 M

TABLE 56

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	21.040	37.72	—	—	—
30	18.790	30.17	0.0480	19.59	12.25
60	20.615	29.65	0.0958	18.46	11.56
90	18.490	23.73	0.1453	17.40	10.78
120	19.165	21.94	0.1949	16.38	10.08
180	19.660	17.90	0.2944	14.45	8.83
210	17.280	14.09	0.3423	13.58	8.33
270	18.380	11.98	0.4395	11.94	7.34
300	17.770	10.31	0.4901	11.15	6.83
330	18.965	9.81	0.5399	10.40	6.37
360	19.435	9.01	0.5875	9.73	5.97
390	19.350	8.03	0.6356	9.09	5.59
420	18.230	6.75	0.6851	8.37	5.14
450	18.825	6.24	0.7332	7.82	4.80
510	18.255	4.80	0.8338	6.80	4.17
570	19.660	4.12	0.9323	5.86	3.59
630	21.950	3.69	1.0280	5.05	3.10
690	17.610	2.37	1.1246	4.34	2.67
720	19.340	2.33	1.1727	4.01	2.47
750	18.770	2.04	1.2175	3.73	2.30

Series No: 56*

$HClO_4$: 0.10 M H_2O_2 : 0.04750 M

pH : 1.034 $KMnO_4$: 0.010638 M

TABLE 57

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}\cdot t$
0	20.480	36.53	—	—	—
30	22.045	35.39	0.0458	19.83	12.99
60	21.150	30.60	0.0909	18.89	12.47
90	19.740	25.71	0.1366	17.81	11.73
120	20.345	23.77	0.1837	16.82	10.99
180	21.440	20.24	0.2763	14.98	9.76

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
210	21.570	18.35	0.3215		14.14	9.24
270	23.460	16.17	0.4129		12.54	8.20
300	18.050	11.26	0.4563		11.83	7.78
330	19.020	10.26	0.5044		11.08	7.25
360	21.850	11.00	0.5484		10.43	6.85
390	20.300	9.19	0.5955		9.76	6.40
420	21.295	8.70	0.6401		9.15	6.02
450	23.940	8.76	0.6879		8.53	5.60
510	20.070	5.97	0.7789		7.47	4.90
570	18.870	4.55	0.8691		6.53	4.30
630	22.705	4.22	0.9626		6.02	3.95
690	22.295	3.53	1.0517		4.93	3.24
720	21.750	3.09	1.0988		4.57	3.01

Series No: 57

$HClO_4$ 0.10 M H_2O_2 : 0.04822 M

pH : 1.034 $KMnO_4$: 0.010856 M

TABLE 58

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log \frac{C_0}{C}$	$\frac{C_0C}{C_0-C}$	$\log \frac{C_0}{C} \times 10^3$	$\frac{C_0C}{C_0-C} \cdot t$
0	21.990	39.19	—		—	—
30	20.395	33.17	0.0398		19.61	14.78
60	22.935	34.15	0.0781		18.73	14.39
90	21.830	29.69	0.1174		17.87	13.70
120	23.620	29.40	0.1559		17.04	13.12
180	21.330	22.11	0.2354		15.45	11.81
210	21.600	20.43	0.2752		14.69	11.21
270	20.245	15.90	0.3559		13.24	10.05
300	20.260	14.59	0.3935		12.60	9.61
330	19.035	12.50	0.4336		11.94	9.09
360	20.960	12.60	0.4720		11.34	8.65
390	18.295	10.01	0.5128		10.73	8.16
420	21.490	10.72	0.5530		10.15	7.71
510	21.425	8.10	0.6734		8.56	6.48
570	19.715	6.29	0.7471		7.69	5.87
630	17.240	4.55	0.8295		6.80	5.17
690	19.295	4.21	0.9122		6.17	4.67
720	19.325	3.86	0.9505		5.65	4.28
750	20.640	3.78	0.9882		5.34	4.06

Series No: 58*

$HClO_4$: 0.12 M H_2O_2 : 0.04722 M

pH : 0.960 $KMnO_4$: 0.010638 M

TABLE 59

Time in minutes	Weight of the solution	ml $KMnO_4$ used	$\log\frac{C_0}{C}$	$\frac{C_0C}{C_0-C}\log\frac{C_0}{C}\times10^3$	$\frac{C_0C}{C_0-C}.t$
0	20.880	37.50	—	—	—
30	22.120	36.33	0.0388	20.21	15.63
60	20.710	31.35	0.0742	19.37	15.67
90	19.210	26.72	0.1110	18.50	15.00
120	18.470	23.59	0.1482	17.71	14.34
180	16.150	17.37	0.2227	16.14	13.04
210	18.390	18.18	0.2593	15.42	12.49
270	19.270	16.03	0.3342	14.01	11.32
300	19.710	14.97	0.3738	13.30	10.67
330	20.490	14.32	0.4099	12.68	10.21
360	19.695	12.60	0.4483	12.04	9.67
390	17.280	10.19	0.4837	11.49	9.26
420	19.655	10.62	0.5217	10.90	8.79
450	20.040	9.94	0.5588	10.35	8.34
510	18.270	7.62	0.6341	9.31	7.49
570	19.090	6.74	0.7046	8.39	6.77
630	20.135	5.96	0.7830	7.50	6.03
690	18.615	4.62	0.8595	6.69	5.37
720	20.720	4.75	0.8940	6.35	5.11

Series No: 59

$HClO_4$: 0.12 M H_2O_2 : 0.04855 M

pH : 0.960 $KMnO_4$: 0.010856 M

In the figures 1 to 4 $\log\frac{C_0}{C}$ is plotted against time for experiments Nos. 2, 14, 24, and 32 (chloride solutions) and in figures 5 to 8 the same is plotted for experiments 34,43,52 and 59 (perchlorate solutions). The acidities in experiments 2, 14, 24, 32 correspond to those in 34, 43, 52, 59. The scale for $\log\frac{C_0}{C}$ is the same in all graphs, but the time scale varies. Through the experimental points smooth curves are drawn. If the reactions were of the first order in hydrogen peroxide, the curves shoud be straight lines. Instead of this it is beyond doubt that the $\log\frac{C_0}{C}$ — time curves in most experiments deviate from straight lines and definitely not only in the final stages of the reaction, but during the whole course of the reaction. Of the 8 graphs presented, only series 59 (Figure 8)

shows strictly first order behaviour. All the figures, except No. 8, have a straight line drawn tangentially to the curve at the origin of the coordinates. This tangent has been obtained from the plotting of the data according to ANDERSEN, as explained later. It represents the connection between $\log \frac{C}{C}$ and time in the case of a strictly first order reaction with the velocity constant corresponding to that at the time $t = 0$.

To test the equation proposed by ANDERSEN, $\frac{C_0 C}{C_0 - C} \cdot t$ (ordinate) was plotted against $\frac{C_0 C}{C_0 - C} \log \frac{C_0}{C}$ (absciss) These graphs are represented in the figures 9 to 66. (**). Every figure corresponds to one series of experiments, with the exception of figure 23 which contains series 15 and 16. All experimental points given in tables 1 to 59 are drawn. On these graphs the scale on absciss axis is always the same while the scale on the ordinate axis varies according to the series.

(**) Due to the limited space these figures are omitted, in order to give an idea, only Fig. 9 is shown.

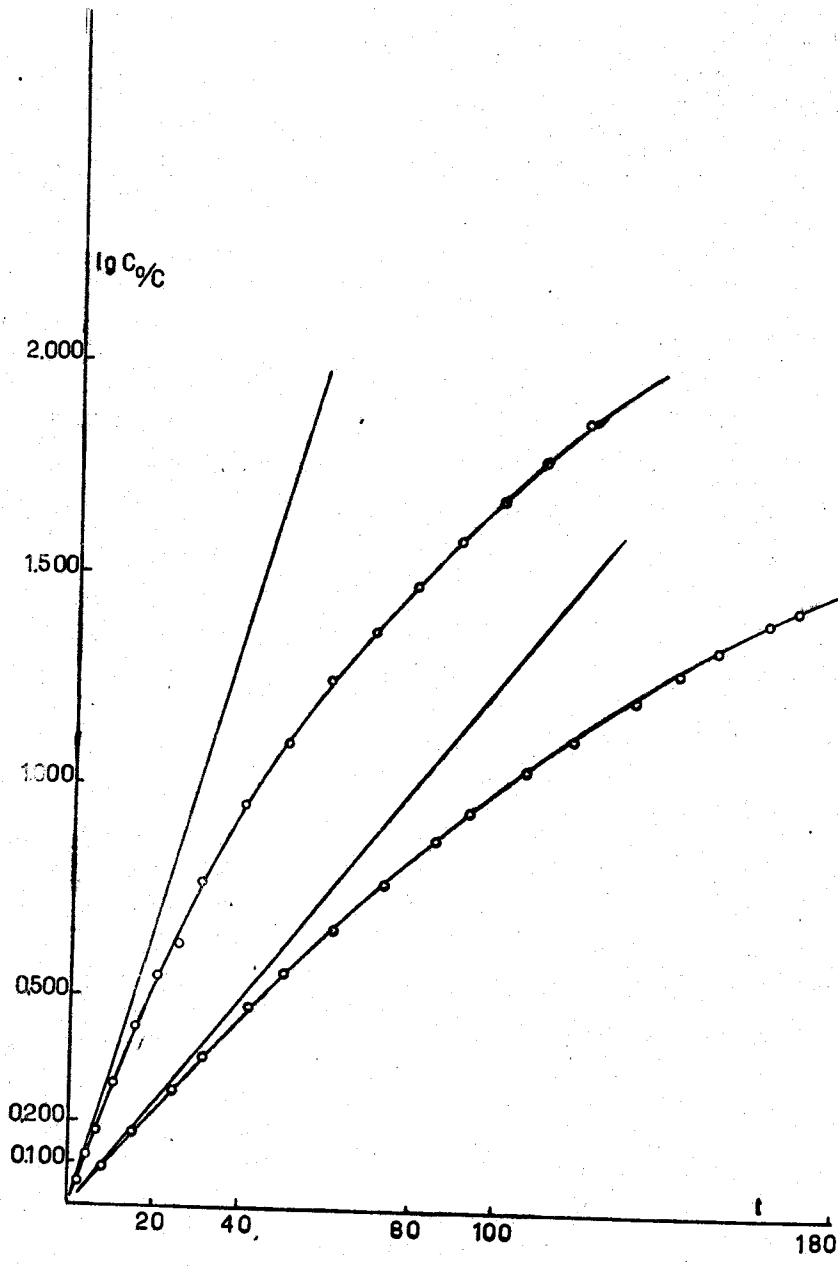

Fig. 1, Fig. 2

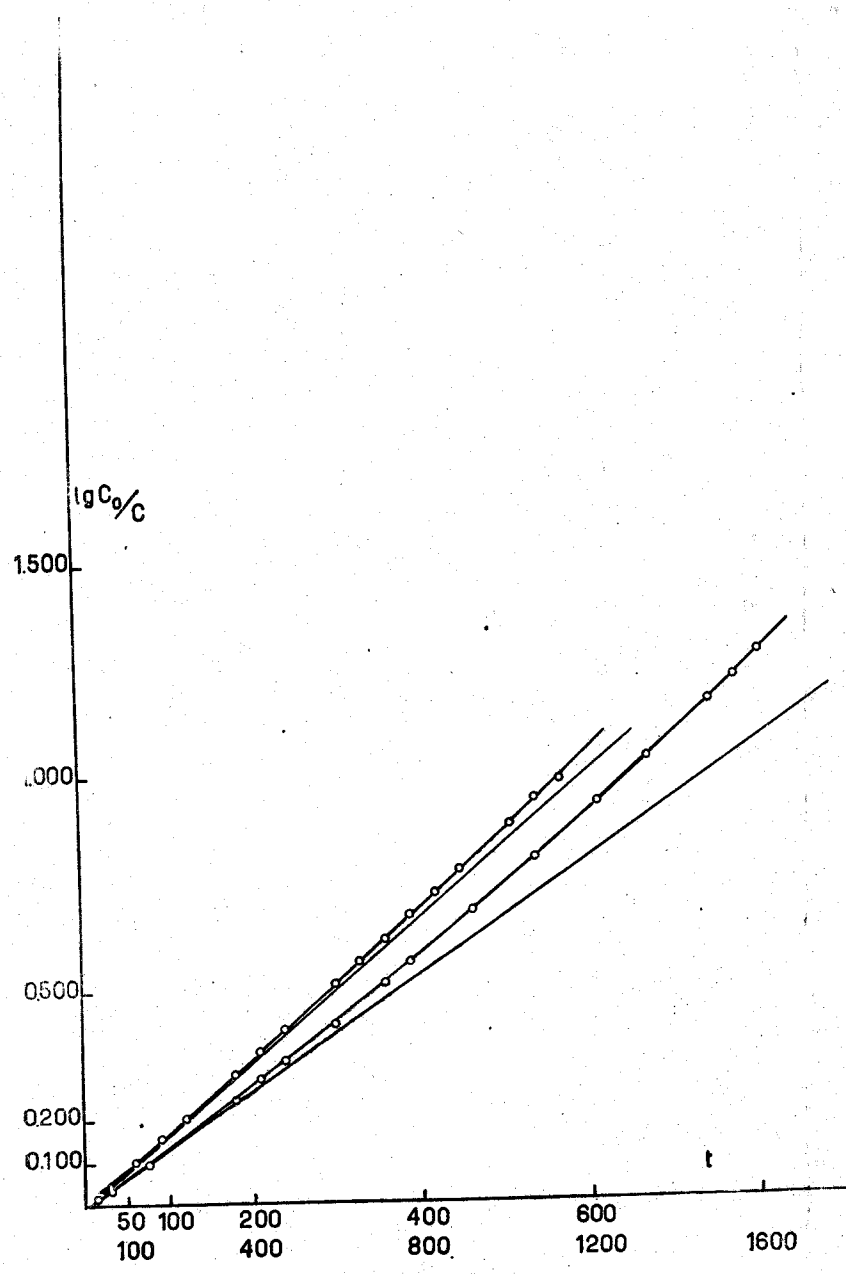
lg C0/C
1.500
.000
0.500
0.200
0.100
t
50 100
100
200
400
400
800
600
1200
1600

Fig. 3, Fig. 4

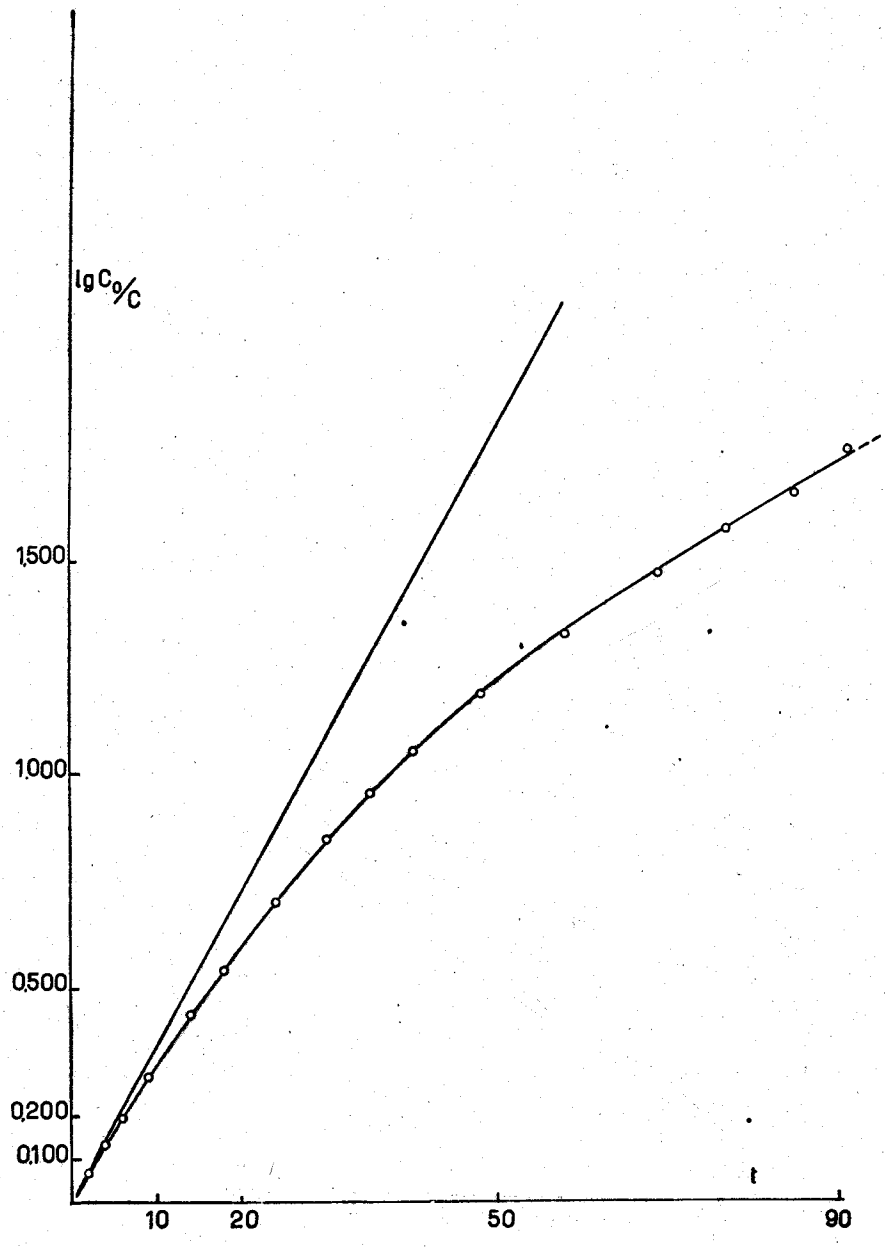

Fig. 5

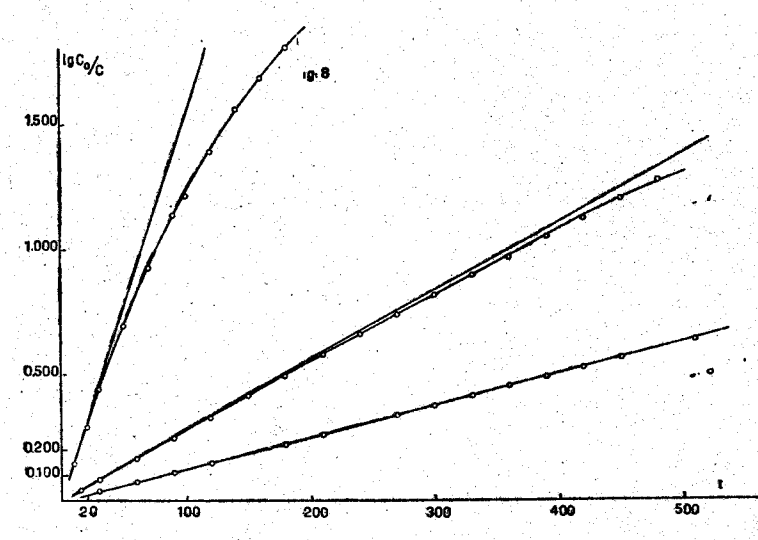

Fig. 6, Fig. 7, Fig. 8

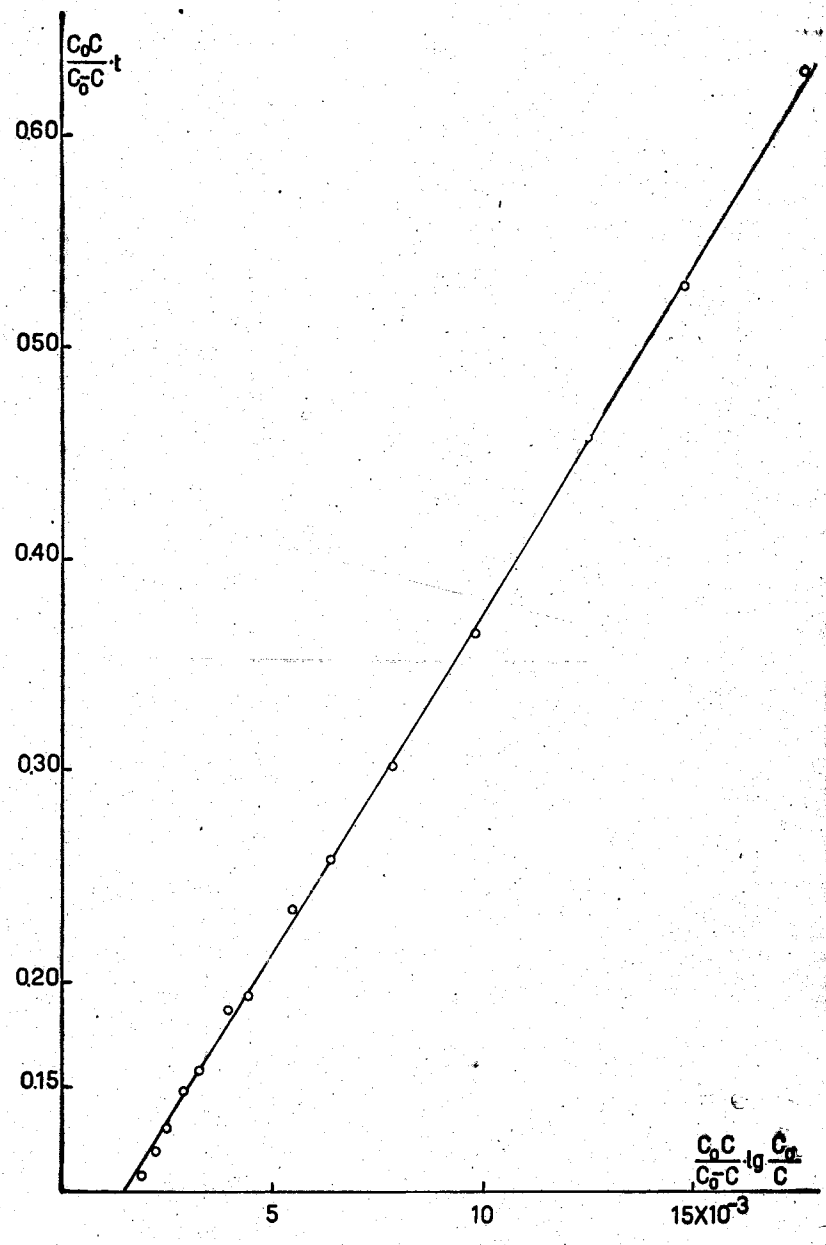
$\frac{C_0C}{C_0-C}\cdot t$
0.60
0.50
0.40
0.30
0.20
0.15
5
10
15X10^{-3}
$\frac{C_0C}{C_0-C}\cdot\lg\frac{C_0}{C}$

Fig. 9

TABLE 60

Number of series	A'x10³in moles/litre	B'x10² in min⁻¹	1/B'	Number of determ. in a series	$a_{H^+} = 10^{-pH}$
1	1.76	3.158	31.67	14	3.35×10^{-3}
2	2.08	3.401	29.40	17	
3	1.87	3.288	30.41	16	
4*	1.81	3.858	25.92	19	
5	1.86	2.783	35.93	13	3.89×10^{-3}
6	1.39	2.821	35.46	14	
7	1.62	2.826	35.39	17	
8	1.79	2.932	34.11	17	
9*	2.35	3.559	28.10	20	
10	1.53	1.986	50.35	16	6.03×10^{-3}
11*	1.81	2.411	41.48	19	
12	1.44	1.298	77.04	11	10.2×10^{-3}
13	1.70	1.310	76.34	14	
14	1.27	1.252	81.73	17	
15,16	1.42	1.296	77.16	17	
17	0.60	0.630	158.7	12	18.6×10^{-3}
18	0.65	0.639	156.5	11	
19	0.92	0.672	148.8	11	
20 (volume)	0.21	0.287	348.4	20	36.1×10^{-3}
21	0.22	0.294	340.1	20	
22	0.17	0.289	346.0	16	
23	0.20	0.288	347.2	15	
24	—0.10	0.169	591.7	16	53.2×10^{-3}
25	—0.07	0.168	595.2	17	
26 (volume)	—0.87	0.112	892.9	10	70.2×10^{-3}
27	—0.35	0.119	840.3	14	
28	—0.26	0.117	854.7	18	
29	—0.24	0.116	862.1	18	
30	—0.58	0.0839	1192	16	86.9×10^{-3}
31	—0.56	0.0845	1183	16	
32	—0.57	0.0670	1493	16	103.5×10^{-3}
33	—0.63	0.0665	1504	16	

TABLE 61

Number of series	A'x10³in moles/litre	B'x10² in min⁻¹	1/B'	Number of determ. in a series	$a_{H^+} = 10^{-pH}$
34	1.69	3.654	27.37	16	3.47×10^{-3}
35	1.64	3.605	27.74	17	
36*	1.89	4.301	23.25	15	
37	1.40	3.116	32.09	16	4.17×10^{-3}

38	1.47	3.181	31.44	17	
39*	1.62	3.767	26.55	17	
40	1.24	2.347	42.61	16	6.46×10^{-3}
41	1.25	2.365	42.28	16	
42	0.97	1.563	63.98	14	10.7×10^{-3}
43	0.85	1.531	65.32	14	
44	0.47	0.851	117.5	15	20.3×10^{-3}
45	0.47	0.838	119.3	15	
46*	0.39	0.930	107.5	15	
47*	0.37	0.923	108.3	15	
48	0.14	0.422	237.0	13	39.0×10^{-3}
49	0.17	0.426	234.7	13	
50*	0.18	0.465	215.1	21	
51*	0.19	0.461	216.9	21	
52	0.09	0.275	363,6	17	57.2×10^{-3}
53*	0.14	0.297	336.7	17	
54	0.00	0.197	507.6	19	75.0×10^{-3}
55*	0.00	0.212	471.7	19	
56*	0.00	0.162	617.3	19	92.5×10^{-3}
57	0.00	0.152	657.9	18	
58*	0.00	0.130	769.2	18	$109\ 6 \times 10^{-3}$
59	0.00	0.124	806.5	18	

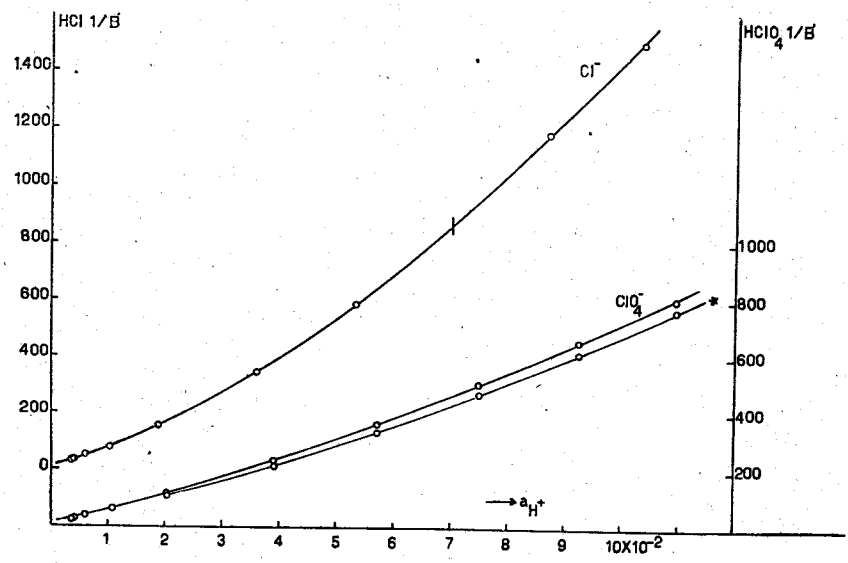

Fig. 67

From these straight lines, the constants A' and B' of the ANDERSEN equation were calculated and their values are also included in the figures. These values together with the values for $\frac{1}{B'}$ the number of determinations in one series and the hydrogen ion activity are given in table 60 for chloride and in the table 61 for perchlorate solutions.

Careful examination of all these figures shows that the straight line could be drawn practically unambiguously through the experimental points. The higher the acidity of the solution — the lower the reaction velocity — the nearer are all the points to a straight line. In the early stages of the reaction (the points in the upper right of the figures 9 to 66) the largest deviations from the straight line occurs, which is explained by the small errors in timing of the sampling so that full minutes resulted. And here too the high reaction velocity — high pH — brings the most marked deviations. But there is, however, no indication of a systematic deviation.

The experiments in the chloride solutions in the high conversion ranges (more than 96% conversion) which were achieved only at the highest pH values investigated, show systematic deviations for $\frac{C_0C}{C_0 - C} \log \frac{C_0}{C}$ values smaller than 2.0 to 2.5. (When Co = 0.0450 moles/litre then for 96% conversion $\frac{C_0C}{C_0 - C} \log \frac{C_0}{C} = 2.62 \times 10^{-3}$ and for 98 % conversion $\frac{C_0C}{C_0 - C} \log \frac{C_0}{C} = 1.56 \times 10^{-3}$). This is clearly indicated in the figures 9 to 17 representing series 1 to 9. The deviation is in the sense that the found decomposition was bigger than expected from the straight line through the experimental points at lower degress of decompositions. Series 10 and 11 as well as 15 and 16 tend to show the same behaviour. Series 12 to 14, 17 to 19 and 24 to 26 were not followed to such a high degree of conversion and no conclusion can be drawn about their behaviour at high degrees of hydrogen peroxide decomposition. Series 20 to 23 do not show any deviation from straight lines for any degree of decomposition. From some series between 27 and 33 we might conclude that a slight deviation in the opposite sense occured, i.e. the

decomposition at high degrees of conversion was lower than that calculated from the straight line relationship.

Values for B' as obtained from the figures are decreasing systematically with increasing acidity of the solutions. The values for A' decrease from 1.90×10^{-3} (mole/litre) at pH = 2.47[5], pass between pH = 1.442 and pH = 1.274 through zero and reach the value of $A' = -0.60 \times 10^{-3}$ (mole/litre) at the highest pH (= 0.985). Zero value for A' means that the reaction of hydrogen peroxide decomposition is strictly of first order in H_2O_2.

With perchlorate solutions we meet mainly with the same behaviour. Series 34, 35 and 37 to 43 show similar deviations from the straight line relationship at high degrees of decomposition as in the series with the corresponding pH having chloride ions as anions. All experiments from series 54 onwards are strictly of first order in hydrogen peroxide — the constant A' being zero. It does not acquire negative values in the investigated acidity range in contrast to the chloride solutions.

In every instance the rate of the decomposition in solutions where hydrogen peroxide with no trace of sulphate was used is higher than in the solutions of the same pH but using hydrogen peroxide which contained traces of sulphate.

From the comparison of tables 60 and 61 the conclusion must be reached that the rate of the decomposition in perchlorate solutions is higher than in the chloride solutions. The difference in B' is $\frac{3.630 - 3.282}{3.282} = \frac{0.348}{3.282}$ or a little over 10 % at the highest pH o fthe solutions, but this difference increases with increasing acidity and the difference between experiments 32, 33 and 59 is $\frac{0.124 - 0.0668}{0.0668} = \frac{0.0572}{0.0668} = 85\ \%$. This shows the specific effect of anions present, upon the reaction.

The fact that the kinetic aquation of ANDERSEN is fulfilled to a high degree of accuracy cannot be interpreted, however, in the sense that the reaction mechanism proposed by ANDERSEN — or as modified by CHRISTIANSEN and ANDERSEN — represents the true state of affairs. This conclusion must be reached by the following reasoning. The dependence of A' on hydrogen ion concentration (identifying

for simplicity activity with concentration) at constant ferric ion concentration is given by (III) as $A' = \text{const.} \frac{C_{H^+}}{K_{Fe} + C_{H^+}}$. In perchlorate solutions the lowest C_{H^+} is 3.5×10^{-3} (moles/litre) and the highest 110×10^{-3} (moles/litre). With $K_{Fe} = 6.5 \times 10^{-3}$ (18) A' should increase - were the CHRISTIANSEN and ANDERSEN reaction scheme right — from 0.35xconst. to 0.94xconst. in this acidity interval. Instead of the required increase A' shows the opposite behaviour — it decreases to zero. ANDERSEN himself uses for K_{Fe} the value of 2.0×10^{-3}, but this changes only the numerical value of the constants. The discrepancy between expectation and reality remains.

The ANDERSEN - CHRISTIANSEN reaction scheme imposes on B' the requirement that its reciprocal value should change linearly with C_{H^+}. It should be $\frac{1}{B'} = m + nc_{H^+}$ — where m and n are constants that are positive. The graph of $\frac{1}{B'}$ against a_{H^+} in Fig. 67 shows that only at high activity of hydrogen ions the linear relationship is valid, but in this case the constant m is negative.

SUMMARY

We may conclude that the reaction of the catalytic decomposition of hydrogen peroxide in the investigated pH-interval, with chloride and perchlorate ions as anions, at constant concentration of ferric salts:

(1) Is not of first order in hydrogen peroxide at most of the hydrogen ion concentrations of the solutions. In the case of perchlorate the decompositions is of first order in acid solutions with pH $\leq$ 1.13. In chloride solutions the reaction is of first order only in a very narrow pH-interval.

(2) Shows a specific influence of anions not only in the way mentioned in the foregoing paragraph, but with increasing acidity the reaction in chloride solutions is retarded considerably more than in corresponding perchlorate solutions.

(3) Shows deviations from first order during the whole course of decomposition and not only in the early stages of it.

(4) Can be represented formally by the kinetic equation proposed

by ANDERSEN. The constant A' decreases with an increase in the acidity of the solution.

(5) Shows that $\frac{1'}{B}$ does not depend linearly upon the concentration of hydrogen ion.

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