

## INDUCED REACTIONS WITHIN THE PEROXY COMPOUNDS. III

### Copper(II)-Ion Catalysis of the Induced Reaction Occurring in the $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—Ce}(\text{SO}_4)_2$ System

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The effect of copper (II) ion exerted on the induced reaction occurring in the  $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8\text{—KMnO}_4$  (and  $\text{—Ce}(\text{SO}_4)_2$ , resp.) system was investigated in detail and found that cupric ions do not change the properties of induced reaction, only strongly catalyze the induced change.

In Part I of this series the features of the induced reaction occurring in the  $\text{H}_2\text{O}_2\text{—H}_2\text{S}_2\text{O}_8$  system were dealt with [1] and the effect of foreign substances was described in Part II. [2]. In this paper data will be delivered to prove the copper(II) ion catalysis of the induced reaction. This seems to be interesting then as far as we know there are no references in the literature concerning the catalysis of induced reactions.

#### *Experimental*

0,1 N hydrogen peroxide solution was prepared from stabilisator-free Merck Perhydrol and 0,1 N peroxydisulphate solution from Merck c. p. N-free potassium peroxydisulphate reagent. 0,1 N cerium(IV) sulphate and 0,1 N arsenous acid reagent solution were prepared from c. p. substances and standardized in the usual manner.

Measurements: 10 ml of about 0,1 N hydrogen peroxide solution was acidified with 5 ml of 20% sulphuric acid, added to it 10 ml of 0,1 N peroxydisulphate and copper(II)-sulphate solution in the required amount and then filled up to 40 ml. Thereafter by vigorous stirring hydrogen peroxide was titrated in presence of 1 drop. 0,025 m ferroin indicator with cerium(IV) sulphate, at a constant delivery rate. The titration time was  $120 \pm 10$  sec at each measurement.

In another group of experiments (inversed titrations) cerium(IV) sulphate and peroxydisulphate solutions were poured together and titrated with about 0,1 N hydrogen peroxide solution. The acid concentration and the initial volume were as given. Having measured the hydrogen peroxide and cerium(IV) sulphate, respectively, the peroxydisulphate content was determined, too. The method was described in an earlier paper [3].

### Experimental results

#### I. Direct titrations

Data of Table I show that on effect of increasing amount of copper(II)-ions the induced error increases. The change can be represented by a curve of saturation value. As it can be seen, the values of the  $H_2O_2$ - and  $H_2S_2O_8$ -error practically agree.

Table I

Cu mg	Taken		Found		$\Delta H_2O_2$ ml	$\Delta K_2S_2O_8$ ml
	0,1 N $H_2O_2$	ml	0,1 N $K_2S_2O_8$	ml		
—	8,58	7,93	9,29	8,62	0,65	0,67
0,3978	8,58	7,70	9,29	8,43	0,88	0,86
0,7956	8,58	7,20	9,29	7,88	1,38	1,41
1,5912	8,58	6,99	9,29	7,67	1,59	1,62
3,1824	8,58	6,82	9,29	7,51	1,76	1,78
6,366	8,58	6,36	9,29	7,09	2,22	2,20
7,9572	8,58	6,28	9,29	6,92	2,30	2,37
9,9462	8,58	6,23	9,29	6,88	2,35	2,41
12,732	8,58	6,28	9,29	6,88	2,30	2,41
19,098	8,58	6,23	9,29	6,92	2,35	2,37
25,464	8,58	6,28	9,29	6,88	2,30	2,41

At constant peroxydisulphate concentration, changing the amount of hydrogen peroxide and at constant hydrogen peroxide concentration the amount of the peroxydisulphate, respectively, the induced error increases in both instances (Table II).

Table II

Taken		Found		$\Delta H_2O_2$ ml	$\Delta K_2S_2O_8$ ml
0,1 N $H_2O_2$	ml	0,1 N $K_2S_2O_8$	ml		
1,65	0,84	7,86	7,19	0,81	0,67
2,48	1,60	7,86	6,94	0,88	0,92
3,31	2,30	7,86	6,87	1,01	0,99
4,14	3,05	7,86	6,77	1,09	1,09
4,97	3,64	7,86	6,64	1,33	1,22
6,63	5,10	7,86	6,19	1,53	1,67
8,29	6,73	7,86	6,09	1,56	1,77
11,60	9,54	7,86	5,91	2,06	1,95
13,25	11,05	7,86	5,84	2,20	2,02
14,91	12,76	7,86	5,72	2,15	2,14
16,57	14,27	7,86	5,69	2,30	2,17
8,87	8,24	1,61	0,92	0,63	0,69
8,87	7,87	3,21	1,93	1,00	1,28
8,87	7,45	4,82	3,31	1,42	1,51
8,87	7,19	6,43	4,64	1,68	1,79
8,87	6,95	8,03	5,80	1,92	2,23
8,87	6,36	11,24	8,50	2,51	2,74
8,87	6,11	12,85	9,92	2,76	2,93
8,87	6,02	14,46	11,60	2,85	2,86
8,87	5,77	16,07	12,93	3,10	3,14

Each sample contains 2,38 mg Cu(II)-ion.

Increasing the acid concentration the induced error decreases (Table III).

Table III

20% H <sub>2</sub> SO <sub>4</sub> ml	Taken 0,1 N H <sub>2</sub> O <sub>2</sub>	Found ml	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Found ml	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
3	8,33	6,03	7,87	5,65	2,30	2,22
5	8,33	6,57	7,87	6,03	1,76	1,84
10	8,33	6,65	7,87	6,15	1,68	1,72
15	8,33	6,86	7,87	6,44	1,47	1,43
20	8,33	6,99	7,87	6,44	1,34	1,43

Reducing the speed of titration the induced error increases (Table IV).

Table IV

Time sec	Taken 0,1 N H <sub>2</sub> O <sub>2</sub>	Found ml	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Found ml	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
20	8,47	6,61	7,99	6,13	1,86	1,86
35	8,47	6,56	7,99	6,13	1,91	1,86
39	8,47	6,52	7,99	6,04	1,95	1,95
70	8,47	6,47	7,99	6,00	2,00	1,99
120	8,47	6,42	7,99	5,90	2,05	2,09
245	8,47	6,32	7,99	5,82	2,15	2,17
289	8,47	6,27	7,99	5,79	2,20	2,20
363	8,47	6,22	7,99	5,72	2,25	2,27

Each sample contains 2,38 mg Cu(II) ion.

On increasing the dilution of the titrated solution — maintaining the acid and the copper(II)-ion concentration constant — the error increases (Table V).

Table V

Volume ml	Taken 0,1 N H <sub>2</sub> O <sub>2</sub>	Found ml	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Found ml	Cu mg	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
25	6,28	1,53	8,64	7,16	7,95	1,53	1,48
50	6,28	1,73	8,64	7,00	15,90	1,73	1,64
100	6,28	1,96	8,64	6,72	31,80	1,96	1,92
150	6,28	2,12	8,64	6,56	47,70	2,12	2,08
200	6,28	2,18	8,64	6,52	63,60	2,18	2,12

On the effect of cerium(III) nitrate the induced reaction slightly increases (Table VI).

Table VI

Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O g	Taken 0,1 N H <sub>2</sub> O <sub>2</sub> ml	Found	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Found	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
—	9,63	7,50	9,75	7,52	2,13	2,23
0,086	9,63	7,50	9,75	7,50	2,13	2,25
0,086	9,63	7,45	9,75	7,52	2,18	2,23
0,434	9,63	7,42	9,75	7,40	2,21	2,35
0,434	9,63	7,40	9,75	7,42	2,23	2,33
0,860	9,63	7,28	9,75	7,20	2,35	2,55
1,500	10,20	7,30	9,60	—	2,90	—
2,170	9,63	6,50	9,75	—	3,13	—
2,170	9,63	6,50	9,75	6,50	3,13	3,25

Each sample contains 12,732 mg Cu(II) ion.

When adding fluoride ions the induced error increases, however, it decreases in presence of chloride, bromide and iodide ions (Table VII).

Table VII

Fluoride mg	Taken 0,1N H <sub>2</sub> O <sub>2</sub> ml	Found	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Found	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
—	9,35	9,12	10,53	10,25	0,23	0,28
—	9,35	6,98	10,53	17,98	2,37	2,55
1,90	9,35	5,65	10,53	7,30	3,70	3,23
3,80	9,35	4,80	10,53	—	4,55	—
3,80	9,35	9,30	—	—	0,05	—
38,0	9,35	9,80	—	—	+0,45	—
38,0	9,35	2,83	10,53	3,90	6,52	6,63
3,80	9,35	3,21	10,53	4,45	6,14	6,08
1,90	9,35	4,03	10,53	5,15	5,32	5,38
0,95	9,35	5,03	10,53	6,20	4,32	4,43
19,00	9,35	3,05	10,53	4,15	6,30	6,38
28,50	9,35	2,88	10,53	4,05	6,47	6,48
Chloride mmole/l						
—	10,03	7,85	11,73	9,53	2,18	2,20
0,570	10,03	8,60	11,73	10,18	1,43	1,55
2,850	10,03	9,50	11,73	11,08	0,53	0,65
5,700	10,03	9,65	11,73	11,20	0,38	0,53
Bromide mmole/l						
0,250	10,03	8,95	11,73	10,63	1,08	1,10
1,250	10,03	9,40	11,73	11,08	0,63	0,65
2,500	10,03	9,75	11,73	11,58	0,28	0,15
Jodide mmole/l						
0,157	10,03	9,05	11,73	10,85	0,98	0,88
0,785	10,03	9,45	11,73	11,28	0,58	0,45
1,570	10,03	10,00	11,73	12,65	0,03	+0,92

Samples contain 12,73mg Cu(II) ion except the first one.

If besides hydrogen peroxide and peroxydisulphate the solution contains arsenous acid, too, the H<sub>2</sub>O<sub>2</sub>-error markedly decreases, the H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-error remains practically unchanged and the amount of arsenite becomes erroneous, too (Table

VIII). The value of  $\text{As}_2\text{O}_3$ -error equals to the sum of the  $\text{H}_2\text{O}_2$ - and  $\text{H}_2\text{S}_2\text{O}_8$ -errors.

Table VIII

No	Taken 0,1 N $\text{H}_2\text{O}_2$ ml	Found	Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml	Found	Taken 0,1 N $\text{As}_2\text{O}_3$ ml	Found	$\Delta \text{H}_2\text{O}_2$ ml	$\Delta \text{K}_2\text{S}_2\text{O}_8$ ml	$\Delta \text{As}_2\text{O}_3$ ml
1	8,62	8,48	10,23	9,25	10,23	9,00	0,14	0,98	1,23
2	8,62	8,20	10,23	8,49	10,23	8,03	0,42	1,74	2,20
3	8,62	8,20	10,23	7,95	10,23	7,45	0,42	2,28	2,78
4	8,62	8,16	10,23	7,63	10,23	7,18	0,46	2,60	3,05
5	8,62	8,03	10,23	6,16	10,23	6,65	0,59	3,07	3,58
6	8,81	8,30	9,83	6,38	10,23	6,28	0,51	3,44	3,95
7	8,81	8,18	9,83	6,17	10,23	5,96	0,63	3,66	4,27
8	8,81	8,03	9,83	5,69	10,23	5,31	0,78	4,14	4,92
9	8,81	7,95	9,83	5,65	10,23	5,31	0,86	4,18	4,92

No.	1	2	3	4	5	6	7	8	9
Cu mg/ sample	0,3978	0,7956	1,591	3,182	6,366	12,73	25,46	50,92	63,65

## II. Inverse titrations

As it appears from Table IX, inverse titrations furnish practically correct hydrogen peroxide values, however, some error appears in the amount of peroxy-

Table IX

Taken 0,1 N $\text{Ce}(\text{SO}_4)_2$ ml	Consumed 0,1 N $\text{H}_2\text{O}_2$ ml	Taken 0,1 N $\text{K}_2\text{S}_2\text{O}_8$ ml	Found	Taken 0,1 N $\text{As}_2\text{O}_3$ ml	Found	$\Delta \text{H}_2\text{O}_2$ ml	$\Delta \text{K}_2\text{S}_2\text{O}_8$ ml	$\Delta \text{As}_2\text{O}_3$ ml	Ferrioin drop
10,10	10,15	10,80	10,70	—	—	+0,05	-0,10	—	1
10,10	10,12	10,80	10,75	—	—	+0,02	-0,05	—	1
10,10	10,15	10,80	10,75	—	—	+0,05	-0,05	—	1
10,10	10,10	10,80	10,70	—	—	0,00	-0,10	—	1
10,10	10,15	10,80	10,75	—	—	+0,05	-0,05	—	—
10,10	10,20	10,80	10,75	—	—	+0,10	-0,05	—	—
10,10	10,15	10,80	10,70	—	—	+0,05	-0,10	—	—
10,10	10,12	10,80	10,78	—	—	+0,02	-0,02	—	—
10,10	9,92	10,80	10,60	10,20	9,75	-0,18	-0,20	-0,45	1
10,10	9,93	10,80	10,55	10,20	9,70	-0,17	-0,25	-0,50	1
10,10	9,90	10,80	10,40	10,20	9,80	-0,20	-0,40	-0,40	1
10,10	9,92	10,80	10,50	10,20	9,75	-0,18	-0,30	-0,45	1
10,10	9,90	10,80	10,65	10,20	9,80	-0,20	-0,15	-0,40	—
10,10	9,92	10,80	10,60	10,20	9,75	-0,18	-0,20	-0,45	—
10,10	9,95	10,80	10,70	10,20	9,85	-0,20	-0,10	-0,35	—
10,10	12,20	10,80	8,50	—	—	+2,10	-2,30	—	—
10,10	12,15	10,80	8,60	—	—	+2,05	-2,20	—	—
10,10	12,18	10,80	8,55	—	—	+2,08	-2,25	—	—
10,10	12,30	10,80	8,50	—	—	+2,20	-2,30	—	—
10,10	10,15	10,80	8,80	10,20	7,95	+0,05	-2,00	-2,25	—
10,10	10,13	10,80	8,90	10,20	7,95	+0,03	-1,90	-2,25	—
10,10	10,20	10,80	8,65	10,20	7,90	+0,10	-2,15	-2,30	—
10,10	10,15	10,80	8,70	10,20	8,00	+0,05	-2,10	-2,20	—

Each sample contains 12,73 mg Cu(II) ion.

disulphate. In presence of arsenite the  $H_2O_2$ -error slightly increases, the  $H_2S_2O_8$ -error remains unaltered and the value of the  $As_2O_3$ -error, similarly to the direct titrations, equals to the sum of  $H_2O_2$ - and  $H_2S_2O_8$ -errors. In presence of copper(II)-ions the amount of hydrogen peroxide consumed for cerium(IV) considerably increases, and we get the peroxydisulphate-values with a greater negative error. When adding arsenous acid the positive  $H_2O_2$ -error is greatly decreased and a negative  $As_2O_3$ -error appears instead, the  $H_2S_2O_8$ -error remains unaltered.

The increasing of the acid concentration, reduces the induced error in case of inverse titrations, too (Table X).

Table X

20 % $H_2SO_4$ ml	Taken $Ce(SO_4)_2$ 0,1 N ml	Consumed $H_2O_2$ 0,1 N ml	Taken 0,1 N $K_2S_2O_8$ ml	Found ml	$\Delta H_2O_2$ ml	$\Delta K_2S_2O_8$ ml
3	9,40	11,50	11,67	9,34	+2,10	-2,33
3	9,48	11,70	11,75	—	+2,22	—
5	9,48	11,50	11,75	—	+2,02	—
10	9,40	11,20	11,67	9,77	+1,80	-1,90
15	9,40	10,83	11,67	10,07	+1,43	-1,60
20	9,40	10,70	11,67	10,27	+1,30	-1,40
20	9,48	10,95	11,75	—	+1,47	—

The induced reaction is directly proportional to the titration speed. This is opposite to the behaviour found at direct titrations (Table XI).

Table XI

Time sec	Taken $Ce(SO_4)_2$ 0,1 N ml	Consumed $H_2O_2$ 0,1 N ml	Taken 0,1 N $K_2S_2O_8$ ml	Found ml	$\Delta H_2O_2$ ml	$\Delta K_2S_2O_8$ ml
35	10,20	12,35	10,75	8,50	+2,15	-2,25
30	10,20	12,40	10,75	8,45	+2,20	-2,30
35	10,23	12,45	10,55	8,20	+2,22	-2,35
28	10,23	12,40	10,55	—	+2,17	—
125	10,20	12,00	10,75	8,70	+1,80	-2,05
112	10,20	12,20	10,75	—	+2,00	—
121	10,23	12,25	10,55	7,95	+2,02	-2,60
250	10,20	12,15	10,75	8,70	+1,95	-2,05
278	10,23	11,95	10,55	8,72	+1,72	-1,83
585	10,20	11,87	10,75	9,05	+1,67	-1,70
550	10,23	11,88	10,55	8,85	+1,65	-1,70

On diluting the solution the error increases (Table XII).

Table XII

Volume ml	Taken $Ce(SO_4)_2$ 0,1 N ml	Consumed $H_2O_2$ 0,1 N ml	Taken 0,1 N $K_2S_2O_8$ ml	Found ml	$\Delta H_2O_2$ ml	$\Delta K_2S_2O_8$ ml
50	9,48	11,45	10,75	—	+1,97	—
50	9,48	11,50	10,75	—	+2,02	—
50	9,48	11,52	10,75	—	+2,04	—
100	9,48	11,68	10,75	—	+2,20	—

Volume ml

100	9,48	11,73	10,75	—	+2,25	—
200	9,48	12,05	10,75	—	+2,57	—
200	9,48	12,00	10,75	—	+2,52	—
300	9,48	12,38	10,75	—	+2,90	—
300	9,48	12,40	10,75	—	+2,92	—

Tables X and XI: in presence of 12,73 mg Cu/sample

Table XII in presence of 12,73 mg/50 ml.

Raising the hydrogen peroxide and peroxydisulphate concentrations the error equally increases (Table XIII).

Table XIII

Taken Ce(SO <sub>4</sub> ) <sub>2</sub> 0,1 N ml	Consumed H <sub>2</sub> O <sub>2</sub> 0,1 N ml	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Found ml	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
2,47	3,45	12,77	11,65	+0,98	-1,12
4,95	6,35	12,77	11,20	+1,43	-1,57
9,90	12,00	12,77	10,55	+2,10	-2,22
19,80	22,35	12,77	10,25	+2,55	-2,52
49,50	52,40	12,77	—	+2,90	—
9,90	10,60	3,19	2,50	+0,70	-0,69
9,90	11,10	6,38	5,25	+1,20	-1,13
9,90	11,95	12,77	10,50	+2,05	-2,27
9,90	13,30	25,54	—	+3,40	—
9,90	16,50	63,85	—	+6,60	—

In presence of 25,46 mg Cu/80 ml

On effect of chloride, bromide and iodide ions, just as at direct titrations, the induced error decreases. Fluoride ions increase the error here, too (Table XIV).

Table XIV

Chloride mmole/	Taken Ce(SO <sub>4</sub> ) <sub>2</sub> 0,1 N ml	Consumed H <sub>2</sub> O <sub>2</sub> 0,1 N ml	Taken 0,1 N K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Found ml	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
—	10,00	12,10	11,80	9,55	+2,10	-2,25
0,570	10,00	11,15	11,80	10,65	+1,15	-1,15
2,850	10,00	10,60	11,80	11,20	+0,60	-0,60
5,700	10,00	10,48	11,80	11,20	+0,48	-0,60
<b>Bromide</b> mmole/l						
0,250	10,00	10,90	11,80	10,75	+0,90	-1,05
1,250	10,00	10,55	11,80	11,15	+0,55	-0,65
2,500	10,00	10,35	11,80	11,60	+0,35	-0,20
<b>Iodide</b> mmole/l						
0,157	10,00	10,60	11,80	—	+0,60	—
0,785	10,00	10,27	11,80	—	+0,27	—
1,570	10,00	10,05	11,80	—	+0,05	—

In presence of 12,73 mg Cu/40 ml.

On adding cerium(III)-ions the error remains unchanged. On effect of ferroin indicator the extent of induced reaction decreases (Table XV).

Table XV

Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O g	Taken Ce(SO <sub>4</sub> ) <sub>2</sub> 0,1 N ml	Consumed H <sub>2</sub> O <sub>2</sub> 0,1 N ml	Taken 0,1 N	Found H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Δ H <sub>2</sub> O <sub>2</sub> ml	Δ K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml
—	10,30	12,40	11,80	—	+2,10	—
—	10,30	12,45	11,80	—	+2,16	—
0,086	9,40	11,50	11,76	—	+2,10	—
0,086	9,48	11,50	11,67	—	+2,02	—
0,434	10,30	12,50	11,80	9,50	+2,20	-2,30
0,520	9,40	11,60	11,67	9,34	+2,20	-2,33
0,868	9,40	11,55	11,67	—	+2,15	—
2,170	10,30	12,52	11,80	9,75	+2,22	-2,05

Table XV

0,025 M Ferroin drop	Taken 0,1 N	Found H <sub>2</sub> O <sub>2</sub> ml	Taken K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0,1 N ml	Δ H <sub>2</sub> O <sub>2</sub> ml
—	10,08	6,40	10,10	3,68
—	10,08	6,45	10,10	3,63
1	10,08	7,70	10,10	2,38
4	10,08	8,15	10,10	1,93
9	10,08	8,75	10,10	1,33

In presence of 12,73 mg Cu/40 ml

### III. Complications in the indication of the end point of titrations

During the direct titrations it was observed that even in case of the most carefully performed end-point determination several drops of hydrogen peroxide were required to reduce ferroin, *i. e.* in spite of the utmost care apparently the solution was overtitrated. The phenomenon is even more striking as by potentiometric control it could be established that in this case, too, ferroin indicates the equivalence point correctly. Considering the experience, too, that the induced reaction is markedly decreased on the addition of ferroin, it seems to be probable that the indicator undergoes a complex redox change, *i. e.* a reversible and partly an irreversible change, too. This can be especially clearly observed if hydrogen peroxide is titrated with permanganate using ferroin indicator instead of cerium(IV)-sulphate. In that case the colour of ferroin disappears already considerably before the permanganate end-point. Table XVI shows that the difference between the complete discoloration of the ferroin indicator and the appearance of the permanganate colour expressed in ml (values A) is the greater, the more copper(II)-ions are present in the solution. This is interesting because copper(II)-ions, in absence of peroxydisulphate do not interfere the indication of the end point at most owing to their own colour. It must be further emphasized, that after the titration the ferroin



pink colour could not be recovered even with strong reducing agents added in large quantity (such as tin(II)-chloride or iron(II)-sulphate, *etc.*) neither when the reduction is allowed to proceed for a longer time (24 hours). This clearly shows that during the induced reaction ferroin loses its indicator ability. This is supported by the experience, too, that after the destruction of indicator colour the inhibiting effect of ferroin ceases.

Table XVI

Cu mg	Ferroin drop	Taken 0,1 N H <sub>2</sub> O <sub>2</sub>	Found ml	Taken K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ml	Δ H <sub>2</sub> O <sub>2</sub> ml	A ml
12,73	—	10,01	5,95	10,25	—4,06	—
12,73	1	10,01	8,35	10,25	—1,66	0,60
6,36	1	10,01	8,45	10,25	—1,56	0,50
3,18	1	10,01	8,52	10,25	—1,49	0,47
2,55	1	9,50	8,20	10,25	—1,30	0,35
0,25	1	10,01	8,97	10,25	—1,04	0,12
12,73	1	10,01	9,98	—	—0,03	—

To a further clearing up of the question it was studied whether the inhibiting effect of the indicator is connected with the complex itself or with the ligand molecule. These investigations showed that not only the complex but also the phenantroline molecule itself exerts inhibiting effect, however, the complex is more effective. This phenomenon can be observed during inverse titrations, too.

On summarizing the results of our investigations it can be stated that the features of the induced reaction are not altered in presence of copper(II) ions, only the

Table XVII

Added substance drop	Taken 0,1 N H <sub>2</sub> O <sub>2</sub>	Found ml	Taken K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0,1 N ml	Δ H <sub>2</sub> O <sub>2</sub> ml
Cerimetric titration				
—	10,05	6,80	10,15	3,25
1 HCl (0,02 N)	10,05	6,98	10,15	3,07
1 Ferroin	10,05	7,95	10,15	2,10
1 HCl+1 drop Ferroin	10,05	8,10	10,15	1,95
1 Phenantroline·HCl	10,05	7,05	10,15	3,00
1 Phenantroline·NO <sub>3</sub>	10,05	7,20	10,15	2,85
1 Phenantroline·NO <sub>3</sub>	10,05	7,15	10,15	2,90
1 Phenantroline·NO <sub>3</sub>	10,05	7,18	10,15	2,87
Permanganometric titration				
1 Phenantroline·HCl	10,05	6,00	10,15	4,05
1 "	10,05	6,03	10,15	4,02
1 Phenantroline·NO <sub>3</sub>	10,05	6,25	10,15	3,80
2 HCl (0,02 N)	10,05	6,20	10,15	3,85
2 "	10,05	5,95	10,15	4,10
2 "	10,05	5,90	10,15	4,15
	10,05	5,88	10,15	4,17

In presence of 12,73 mg Cu/40 ml

induced error increases considerably, *i. e.* the induced reaction is catalyzed by copper(II) ions. This is not very striking — considering the kinetical nature of the induced reactions — although till now such example cannot be found in the literature. The irreversible oxidation of the ferroin indicator points to that during induced reaction intermediates of very strong oxidizing properties are formed which may destruct partly or wholly the fairly resistant indicator dye.

\* \* \*

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### ИНДУКЦИОННЫЕ РЕАКЦИИ СРЕДИ ПЕРОКСИ-СОЕДИНЕНИЙ. III

*Индукционная реакция в системе  $\text{H}_2\text{O}_2$ — $\text{H}_2\text{S}_2\text{O}_8$ — $\text{Ce}(\text{SO}_4)_2$   
катализована ионами меди (III).*

*Л. Й. Чаньи, Й. Батьяи, Ф. Шольмоши*

Действие ионов меди (II) на индукционные реакции в системе



было изучено и показано что свойства индуцированной реакции не были изменены ионами меди (II), они только сильно катализируют индуцированное изменение.

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