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著者	MATSUDAIRA Chikayoshi
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THE CATALYTIC ACTIVITY OF SEA-WATER

IV. EFFECT OF ADDED COPPER ON THE CATALYTIC ACTIVITY

By

Chikayoshi MATSUDAIRA

*Department of Fisheries, Faculty of Agriculture,
Tohoku University, Sendai, Japan*

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Lacking the necessary information of catalysts to describe the catalytic reaction of sea-water to the decomposition of the hydrogen peroxide accurately, the following results obtained by a few investigators are referred to the present work.

Harvey, H. W. (1925)⁶⁾ reported that an organic compound of iron in solution in sea-water may act as a catalyst in the catalytic reaction of sea-water to the decomposition of the hydrogen peroxide. However, there was no actual proof of catalyst being an iron compound. Also in the catalytic reaction of spring-water to hydrogen peroxide, iron or manganese worked as catalysts (Fresenius, Eichler, Lederer 1927)⁵⁾. In more recent contributions, Skopintsev, B. A. (1949)^{12) 13)} reported on the effect of copper on the decomposition of hydrogen peroxide by chloride solution and Uri N., (1949)¹⁴⁾ the catalytic decomposition of hydrogen peroxide by Na_2WO_4 and Na_2MoO_4 in the presence of simple cations. (Cu^{++} , CO^{++} , Ni^{++} , Mn^{++} , Cd^{++} , and Zn^{++}).

These various observations indicate that heavy metals contained in sea-water may accelerate catalitically the decomposition of hydrogen peroxide. The present paper dealt with the effect of added copper on the catalytic activity of sea-water from a theoretical standpoint.

Micro-Determination of the Catalytic Activity

The standard method used in the previous experiments in which 100 cc. of samples was necessary for the determination was unfavourable to handle many samples such as those in the present experiments. For this reason, the standard method was modified to develop it so that it could be used for small quantity of samples.

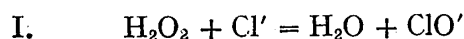
A 10 cc. of the sample was placed in a clean test tube with a capacity of 30 cc.. The test tube was dipped into a cylindrical water-bath coated with enamel on the metal. The temperature of the water-bath was adjusted with hot water to 30°C. When the temperature of the sample became constant at 30°C, 1 cc. of 0.3 per cent hydrogen peroxide was added to the sample in the test tube by using a micro-burette and mixed thoroughly. 0.3 per cent hydrogen peroxide was prepared in the same manner as the standard method. The water-bath with test tubes was placed in a thermostat kept at 30°C. An adequate reaction time was allowed for the samples according to the strength of the activity. Then, the water-bath was taken out from a thermostat and 1 cc. of sulphuric acid (1:3) was added quickly to the samples. The content of test tubes was decanted into Ehrlenmyer flasks washing thoroughly with distilled water in quantity not exceeding 10 cc. And then, one drop of 10 per cent solution of ammonium molybdate was added to the samples and allowed to stand for a few minutes. The iodine evolved was titrated with N/100 thiosulphate solution with starch indicator. The reading of a burette gave a concentration of hydrogen peroxide after reaction. Similarly, the initial concentration of hydrogen peroxide was determined by titrating the solution contained 1 cc. of 0.3 per cent hydrogen peroxide solution in 10 cc. distilled water. The reading of this titration should be 16~17 cc.. The method of the calculation of the catalytic activity was the same as the standard method. The present method gave an error of $K_{30} \pm 0.005$ at the reaction time of five hours.

The Chloride Ion Catalysis of the Decomposition of Hydrogen Peroxide

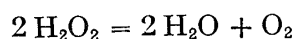
1. The Catalytic Reaction

Now, if the chloride ion in sea-water catalyzes the decomposition of hydrogen peroxide, the following intermediate reactions are to be considered.

In alkaline solution,

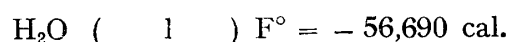
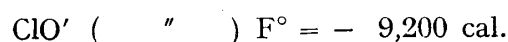
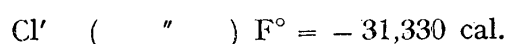
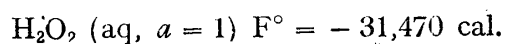


If these two reactions occur simultaneously,



The hydrogen peroxide is to be decomposed to water and oxygen by the intermediate reaction. In these reactions, it is necessary to examine the thermodynamical possibility of the reaction. Dr. F. Ishikawa gave me valuable advice on the thermodynamical treatment. In the reaction I, the values, in calories,

of free energies of formation of the products and reacting substances are given in their water solutions of unit activity and for 25°C as follows.



$$\Delta F^\circ = F^\circ_{\text{H}_2\text{O}} + F^\circ_{\text{ClO}'} - F^\circ_{\text{H}_2\text{O}_2} - F^\circ_{\text{Cl}'} = -3,090 \text{ cal.}$$

The free energy of the reaction I is $\Delta F^\circ = -3,090$ cal., as given above.

Similarly, for the reaction II,

$$\Delta F^\circ = F^\circ_{\text{H}_2\text{O}_2} + F^\circ_{\text{ClO}'} - F^\circ_{\text{H}_2\text{O}} - F^\circ_{\text{O}_2} - F^\circ_{\text{Cl}'} = -47,350 \text{ cal.}$$

Thus, the result of calculations from the free energy of the reaction shows the thermodynamical possibility of the reaction I and II, and therefore, of the decomposition of hydrogen peroxide by chloride ion. However, it is assumed that the reaction I proceeds very slowly because its free energy is only $\Delta F^\circ = -3,090$ cal., showing lower chemical affinity and far smaller value than that of the reaction II. Therefore, the velocity of the decomposition of hydrogen peroxide by chloride ion must be equal approximately to the velocity of the reaction I. If the decomposition of hydrogen peroxide in alkaline chloride solution proceeds in pure chloride ion catalysis given by the reaction I, without being effected by other factors, the velocity of the catalyzed reaction must be:

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{Cl}'][\text{H}_2\text{O}_2]$$

As the concentration of chloride ions is maintained constant by the successive reaction II.

$$[\text{Cl}'] = c = \text{const.},$$

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = kc[\text{H}_2\text{O}_2] = K[\text{H}_2\text{O}_2],$$

$$K = kc,$$

Where k is a constant, c the concentration of chloride ion, and K the velocity constant of the reaction. Therefore, the velocity constant of the decomposition of hydrogen peroxide or the catalytic activity in alkaline chloride solution must be proportional to the concentration of chloride ion.

This relationship is confirmed by the result obtained in the previous experiments⁷⁾ in which the catalytic activity of sea-water or sodium chloride solution has been proportional to the chlorinity so long as it was not inhibited by negative catalyts. It can be assumed, therefore that the catalytic activity is due to the chloride ion catalysis as given above. However, in a subsequent experiment it has been found that sodium chloride solutions prepared from different chemicals with a proportionality between the activity and chlorinity did not show a constant activity in the same chlorinity. Neither the fact is explained by the chloride ion catalysis alone nor by the presence of negative catalyts (when negative catalyts exist, the activity is not proportional to the chlorinity)⁷⁾. This appears to be due to the effect of some heavy metals known as catalyts by many investigators upon the chloride ion catalysis. The experimental evidence will be given in the following pages.

2. *The Activation Energy of the Catalytic Reaction*

In order to inquire the quality of catalysis in the catalytic activity of sea-water, it is important to determine the activation energy of the catalytic reaction. The activation energy can be calculated from the thermal change of the catalytic activity by Arrhenius equation.

$$\log_{10} K = -0.4343 \times \frac{A}{RT} + C$$

Where K is the velocity constant of the catalytic reaction, A the activation energy, R the gas constant, T the absolute temperature and C a constant. If the experimental equation of thermal change obtained in preceding experiments is referred,

$$\log_{10} K = -4305 \times \frac{1}{T} + 13.36$$

Therefore,
$$0.4343 \times \frac{A}{R} = 4305$$

$$R = 1.9858 \text{ cal/T}$$

$$A = 19.68 \text{ kcal.}$$

Hence the activation energy of the catalytic reaction is 19.68 kcal.. This value is close to 19.72 kcal. for a spring-water obtained by K. Okabe¹⁰⁾. These calculation indicates that the agent of catalysis in sea-water is very similar to that of spring-water. On the other hand, it was observed by a few investigators that the catalytic activity of spring-water was effected by some heavy metals contained in it. Therefore, a similarity of the activation energy observed

between spring-water and sea-water gives a ground to suppose that heavy metals may effect the activity of sea-water.

Effect of added Copper on the Hydrogen Peroxide ~Chloride Reaction

From the results of previous experiments^{7) 8) 9)} and their theoretical considerations, the effect of heavy metals upon the chloride ion catalysis was expected. A preliminary experiment showed that cupric ion had a remarkable effect on the acceleration of the hydrogen peroxide-chloride reaction. (Table 1). As a first step, the present experiments dealt with the effect of copper.

Table 1. Effect of some metallic ions upon the catalytic activity of sea-water.

Ion	Addition γ/L	Catalytic activity of sea-water* $K_{30} \times 10^3$
Control	0	69
Hg ⁺⁺	50	83
Fe ⁺⁺	"	66
Fe ⁺⁺⁺	"	68
Co ⁺⁺	"	145
Cu ⁺⁺	"	421
Mn ⁺⁺	"	72
Zn ⁺⁺	"	71
MoO ₄ ⁻⁻	"	72

Remarks : * Collected from off Kinkazan.

1. Experiments on Sodium Chloride Solutions

As noted previously, the catalytic activity of sodium chloride solutions prepared from different chemicals did not take a constant value in a definite concentration, ranging from K_{30} 0.030 to K_{30} 0.700. According to chemical analysis, it was found that 3 per cent solution of guaranteed sodium chloride would contain the copper at the concentration ranging between 10 γ/L and 60 γ/L . The procedure adopted in this experiment was as follows. A 3 per cent sodium chloride solution with the activity of K_{30} 0.064 was prepared from a guaranteed chemical and the distilled water free from copper. It was diluted to various concentrations with distilled water. The diluted samples thus obtained were buffered at pH 3.2 by adding 1 cc. of 3 N/20 sodium bicarbonate solution per 100 cc. of samples. And then, they were enriched with copper by adding 10, 20, 30, 40, and 50 γ Cu/L. The catalytic activity of those samples were determined and shown in Table II.

Table 2. Effect of added copper upon the chloride ion catalysis of the decomposition of hydrogen peroxide.

Addition Cu γ /L	Catalytic activity of NaCl solution* ($K_{30} \times 10^3$) against					
	0 M	0.1 M	0.2 M	0.3 M	0.4 M	0.5 M
0	6	13	19	33	48	65
10	11	51	83	92	127	150
20	33	88	140	186	240	249
30	47	133	216	262	338	382
40	61	161	276	390	440	522
50	75	200	318	474	558	619

Remarks: * buffered at pH 8.2 with NaHCO_3 .

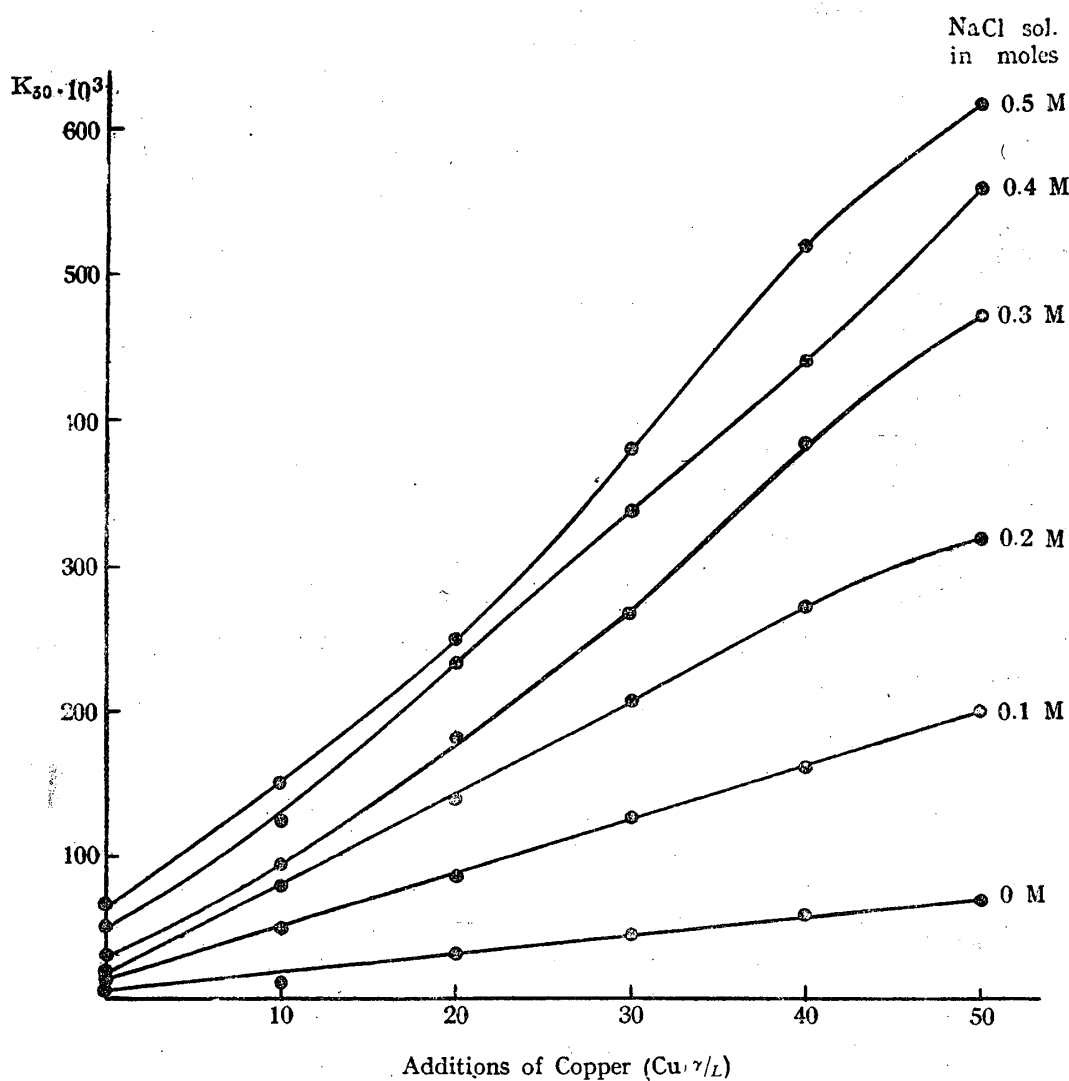


Fig. 1. Curve shows the catalytic activity of sodium chloride solution plotted against added copper.

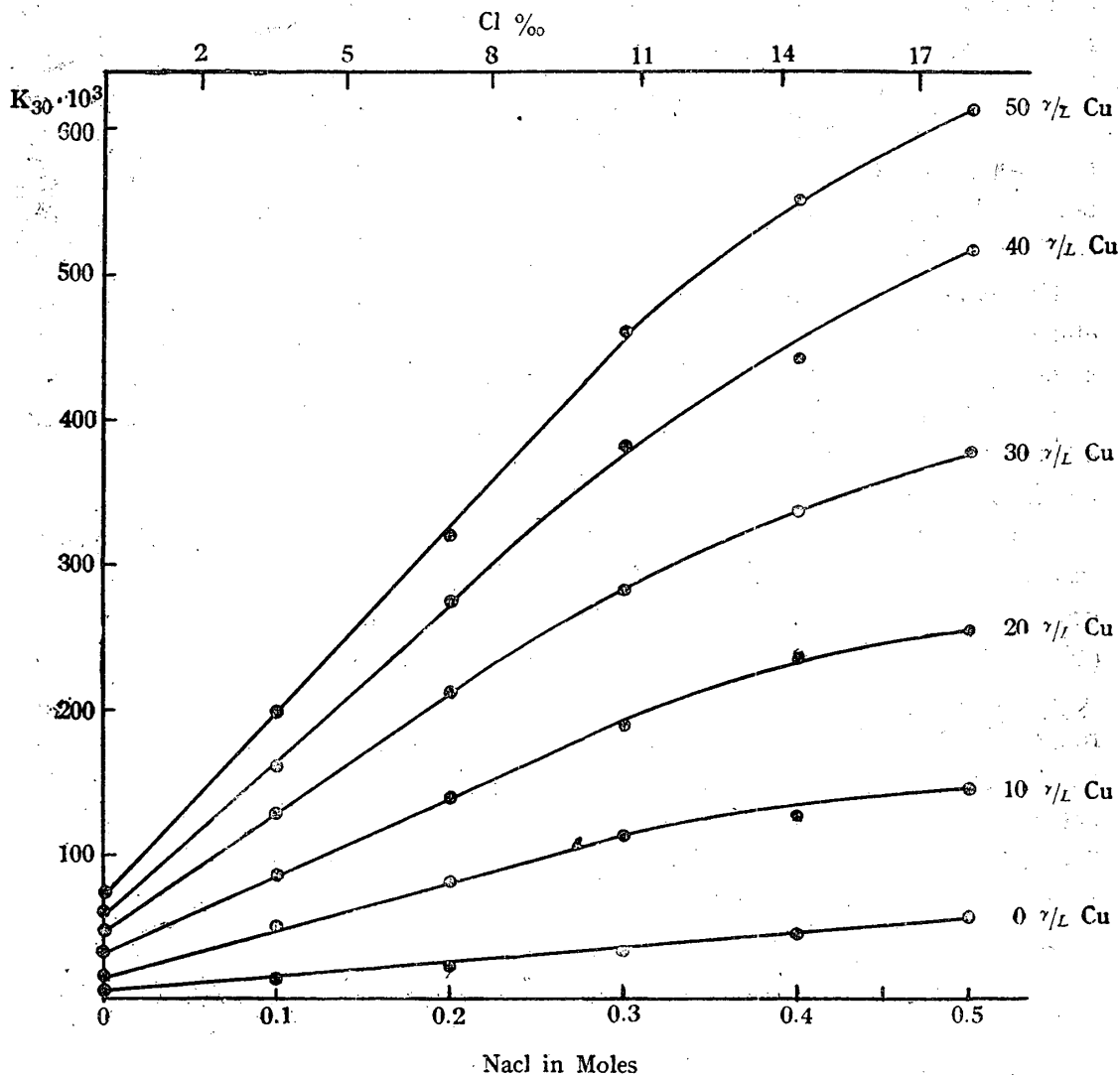


Fig. 2. Curve shows the catalytic activity of samples in different additions of copper plotted against the concentration of sodium chloride.

Fig. 1 shows the activity of sodium chloride solution in different grades of concentration plotted against added copper. In higher concentrations of sodium chloride the activity was more remarkably increased by additions of copper. In 0.5 M solution of the chloride, as little as 10 γ Cu/L had a significant effect on the activity, and the activity increased due to the addition of 50 γ Cu/L was about 8 times the control. The relation between the activity and added copper showed logarithmic progression in high concentrations of the chloride, while with its lesser concentrations, the activity bore a linear relationship to the addition of copper. Fig. 2 shows the activity of the samples in different

addition of copper plotted against the concentration of the chloride. The increase in the activity due to the increased concentration of the chloride was remarkably accelerated by the addition of copper. The activity at 0.1 M and 0.5 M NaCl showed respectively K_{30} 0.200 and 0.619 for 50 γ Cu/L, while it was only 0.013 and 0.065 without addition of copper. The relation of the activity to the concentration of chloride bore a linear relationship at the concentration below 0.3 M, irrespective of added copper. However, the rate of increase in activity gradually slowed down as the concentration of chloride increased.

The experiment has provided an evidence that a minute quantity of copper effects the hydrogen peroxide-chloride reaction. Although this mechanism is not yet clear it was confirmed by another experiment on 0.5 M sodium nitrate solution with added copper that in the present experiment no neutral-salt effects can be considered.

2. Experiments on Natural Sea-Waters

Two sea-water samples taken from 50 m and 300 m layers off Kinkazan, respectively with the activity of K_{30} 0.086 and K_{30} 0.245 were diluted to different grades of the concentration with 1.5 milli-equi./L sodium bicarbonate solution (PH 8.2). To the two series of mixed samples thus prepared, cupric sulphate were added respectively, so as to contain different amount of cupric ion in the range of 0~50 γ Cu/L. And then, their catalytic activities were determined at 30°C. The result of determinations is shown in Table III. Fig. 3 shows the activity in different concentrations of sea-water plotted against added copper. The activity of sea-water samples was activated strongly by the addition of copper. In the sea-water collected from 300 m layer with high activity of K_{30} 0.245, the increase of the activity by the addition of 50 γ Cu/L was K_{30} 0.176 and in the sea-water of 50 m layer with low activity of K_{30} 0.086, it was K_{30}

Table 3. Effect of added copper upon the catalytic activity of sea-water.

Sea-water samples	Addition Cu γ /L	Catalytic activity of sea-water ($K_{30} \times 10^3$) against					
		0%	20%	40%	60%	80%	100%
Water collected from 50 m layer off Kinkazan	0	13	45	75	77	82	86*
	10	16	102	124	133	143	156
	20	27	133	159	180	194	198
	30	37	166	194	218	227	248
	40	43	197	230	245	260	276
	50	46	206	276	294	315	325
Water collected from 300 m layer off Kinkazan	0	13	39	80	124	170	245**
	10	16	50	95	169	255	278
	20	27	116	186	240	290	304
	30	37	125	205	282	307	339
	40	43	135	250	307	348	378
	50	46	190	336	378	398	421

Remarks: * Cl 18.70%. ** Cl 18.77%.

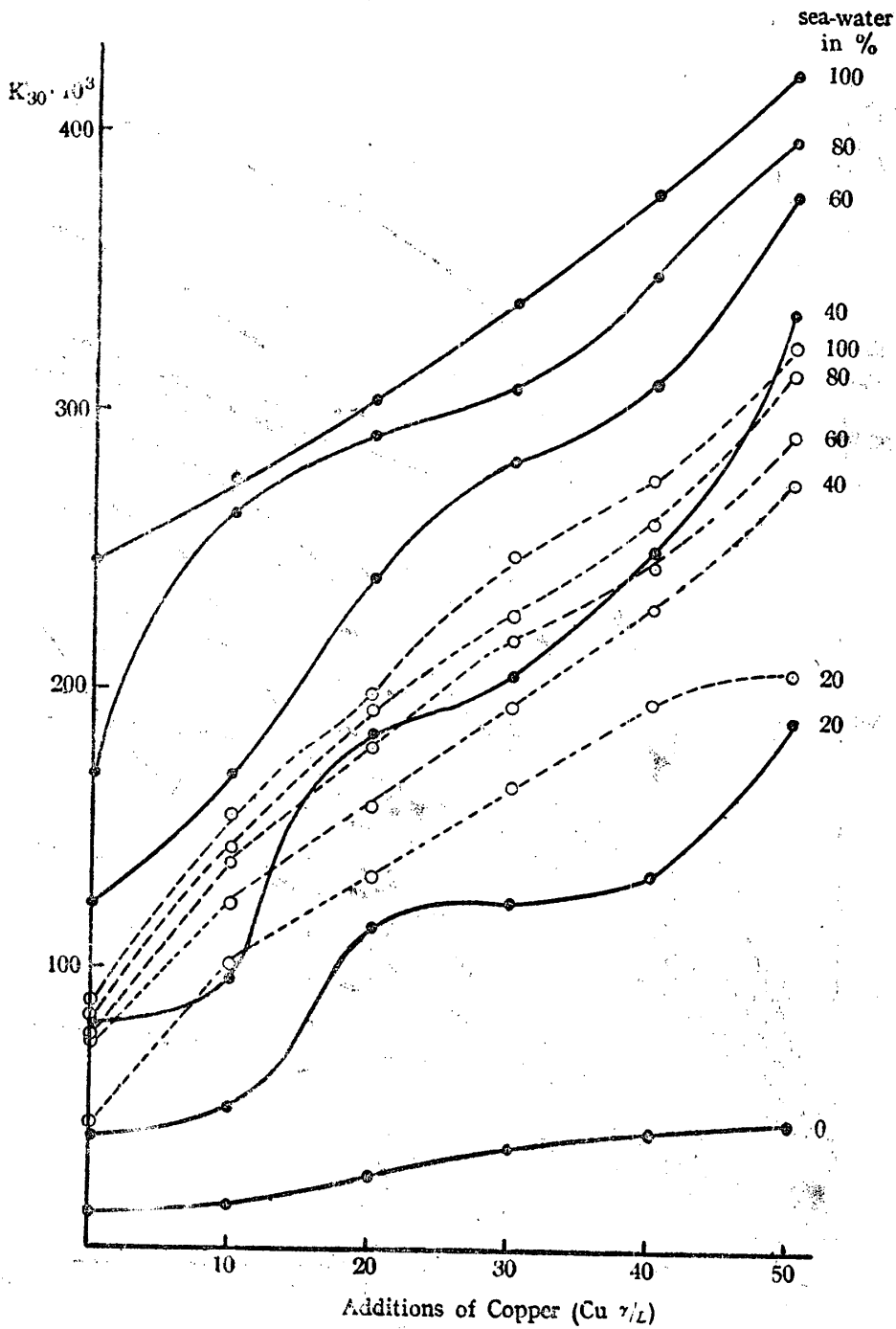


Fig. 3. Curve shows the activity in different concentrations of sea-water plotted against added copper. Solid line is the measurement in sea-water collected from 30 m layer off Kinkazan. Dotted line shows the measurement in sea-water collected from 50 m layer off Kinkazan.

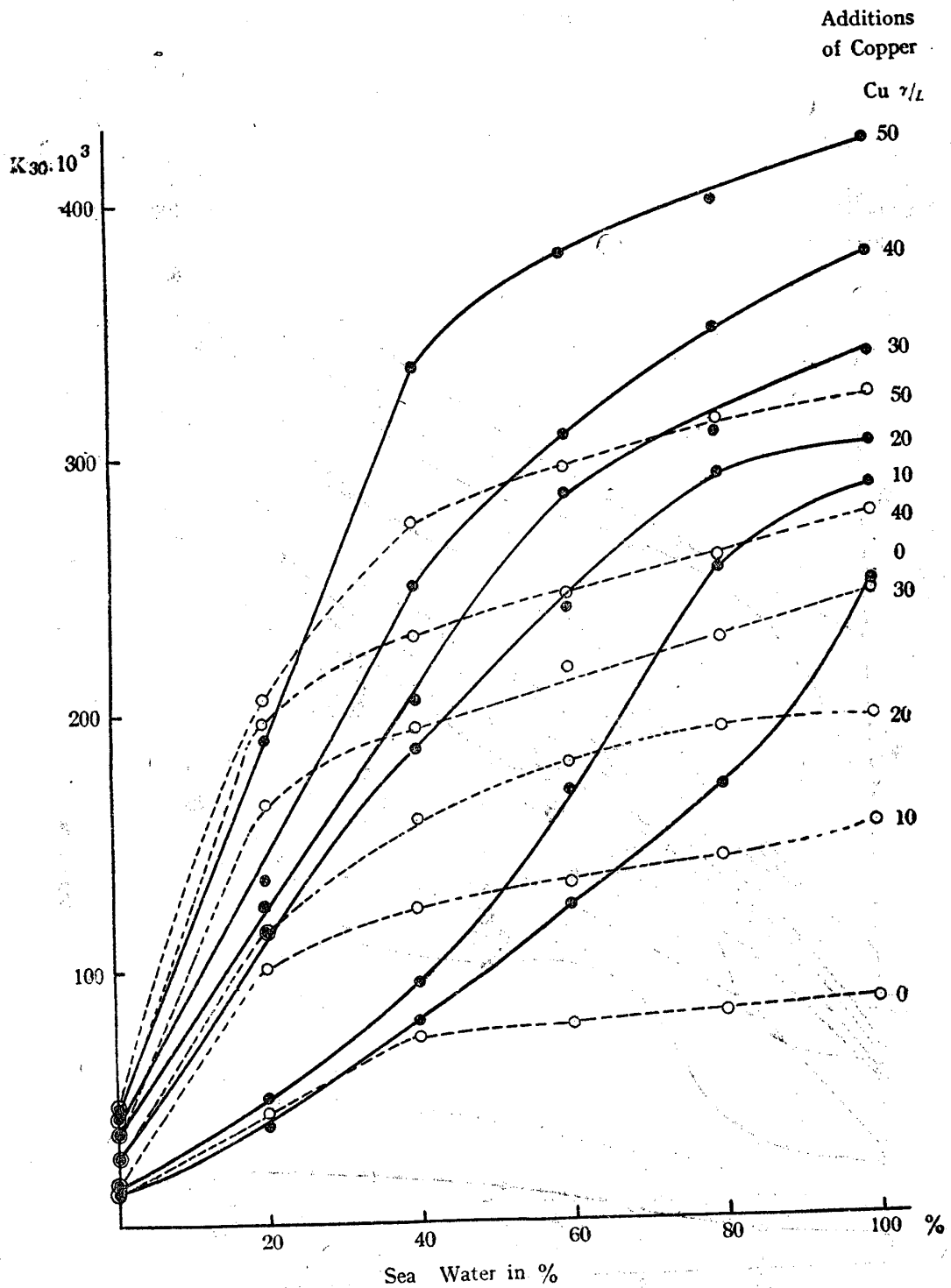


Fig. 4. Curve shows the activity of sea-water in different additions of copper plotted against the concentration of sea-waters. Solid line is the measurement in sea-water collected from 300 m layer off Kinkazan. Dotted line shows the measurement in sea-water collected from 50 m layer off Kinkazan.

0.239. The relation of the activity to added copper showed the logarithmic progression in the sea-water of 300 m layer, while it was parabolic in that of 50 m layer. However, when the addition of copper was above $20 \gamma \text{ Cu/L}$ the both sea-water held the linear relation between the addition of copper and the activity, as can be observed by inspection of Fig. 3. These observations show that the effect of added copper is different by the property of sea-water. On the other hand, in the distilled water with adjusted pH of 8.2 by adding sodium bicarbonate, no significant effect was noticed on the activity by added copper, showing only the increase of K_{30} 0.033 by the addition of $50 \gamma \text{ Cu/L}$. In the diluted sea-water samples, the relationship of added copper to the activity was irregular, especially in sea-water taken from 300 m layer. However, it is sure that the increase of activity by the addition of copper is remarkable in higher concentration of sea-water, probably depending on the increase of chlorinity.

Fig. 4 shows the activity of sea-water in different addition of copper plotted against the concentration of the sea-water. The fact noted in previous paper⁷⁾ that the rate of the activity to the chlorinity differed in the presence of negative catalysts in sea-water was found also among sea-water samples used in the present experiment. This rate in the sample collected from 50 m layer was remarkably reduced in its higher chlorinity but this phenomenon could not be observed in the sample of 300 m layer. When the copper was added to the

Table 4. Decline of catalytic activities during the storage after adding copper.

Exp. No.	Water samples	Catalytic activities ($K_{30} \times 10^3$)					
		Without addition	With addition of $50 \gamma \text{ Cu}$				
			0 day	1 days	2 days	3 days	9 days*
1.	collected from 0~200 m layers	67	539	411	395	362	344
2.	300~1000 m layers	72	586	510	492	435	418
3.	200~1000 m layers	129	769	600	594	529	536
4.	300~1000 m layers	219	850	738	631	539	536
5.	3% guaranteed NaCl solution	35	528	406	309	207	189
6.	3% extra pure NaCl solution	51	434	390	330	247	234
7.	Distilled water	15	75	71	71	45	56

Remarks: Exp. No. 1~4 Mixed samples of sea-waters with nearly same activity collected from different layers off Kinkazan.

Exp. No. 5~7 buffered at pH 8.2 with NaHCO_3 .

* Days allowed for the samples after adding copper.

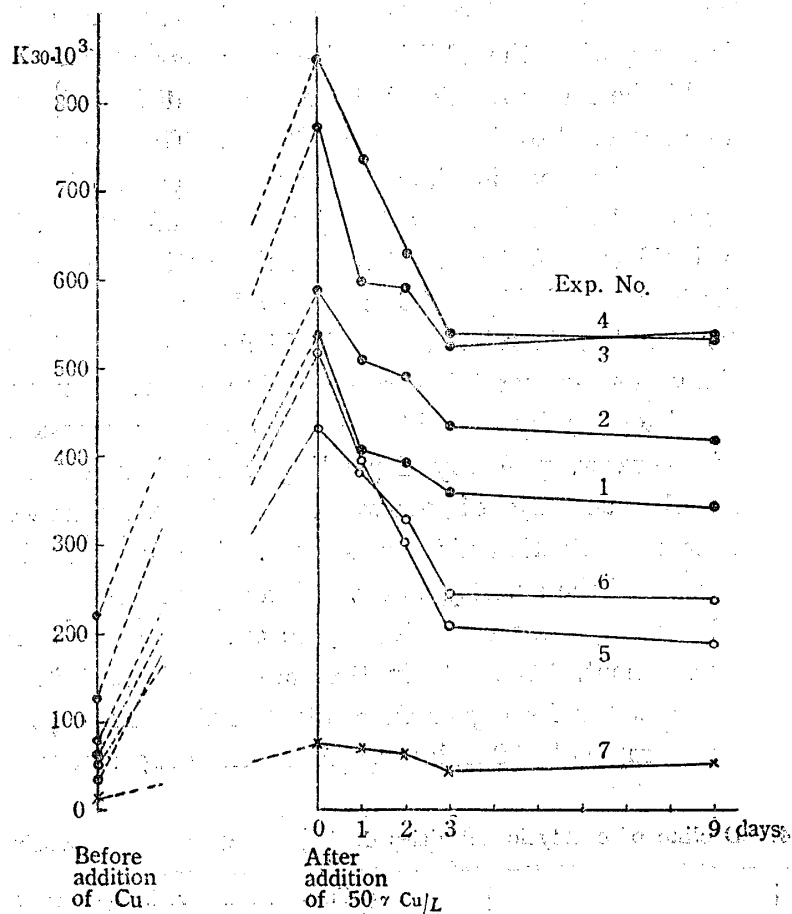


Fig. 5. Decline of catalytic activities of sea-waters and sodium chloride solutions during the storage after adding copper. Exp. No. 1. is mixed sea-water collected from 0~200 m layers, Exp. No. 2. Collected from 300~1000 m layers, Exp. No. 3. collected from 200~1000, layers Exp. No. 4. collected from 300~1000 m layers, Exp. No. 5. 3% guaranteed NaCl solution, Exp. No. 6. 3% extra pure NaCl solution and Exp. No. 7. distilled water.

both sea-water, their activities were increased remarkably in lower chlorinity but this tendency was reduced as the chlorinity increased. These phenomenon may be explained by the incomplete dissociation of copper salt due to the complex formation with negative catalysts. In general, the results obtained in sea-water fairly coincided with the one of sodium chloride solution. Hence the experiment seems to provide the grounds for assuming that the catalytic activity of sea-water was due to the chloride ion catalysis effected by the copper contained in the sea-water. However, actual proof must be obtained by direct determinations of copper contents of sea-water. The relation between the

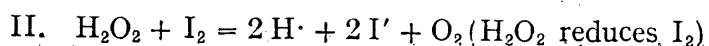
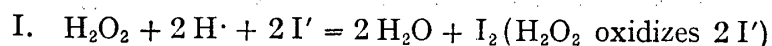
catalytic activity and copper contents in sea-water will be reported in another paper.

3. The Decline of the Catalytic Activity after the Addition of Copper.

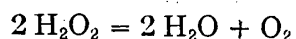
Copper sulphate was added to a few sea-water samples and also 3 per cent sodium chloride solutions to give the concentration of 50γ Cu/L. A time was allowed for samples at room temperature after adding copper. The variation of the activity during the period of storage for 9 days was observed (Table 4). The decline of catalytic activities of samples after adding copper is shown in Fig. 5. As can be seen from Fig. 5, in all samples activated by added copper, the activity declined rapidly during first 3 days of storage. However in the successive storage for 6 days, the activities remained almost constant and this stabilized values of activity differed among samples. Though this mechanism has not yet been discovered, the decline of the activity during storage appeared to be due to the complex formation of copper in the solution.

The Iodide Ion Catalysis of the Decomposition of Hydrogen Peroxide

The process of the decomposition of hydrogen peroxide catalyzed by iodide ion was first investigated thoroughly in neutral reaction by Bredig and Walton (1904)²⁾. They explained their results by a transference of the oxidizing effect from one molecule of hydrogen peroxide to a second by the iodide ion through IO⁻. In acid solution, Abel (1908)¹⁾ succeeded in connecting the catalytic reaction with known processes by another mechanism. According to him, in acid solution, the following processes occur simultaneously :

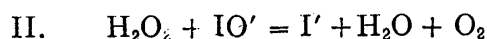
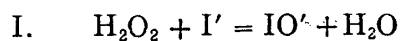


By summing, we obtain :

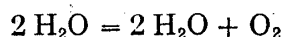


representing simple decomposition.

Iodine is present in sea-water at approximately 0.05 mg/L. The distribution and determination of iodine in sea-water and marine organisms have been discussed by Closs (1931)³⁾ and Reith (1930)¹¹⁾. The form in which iodine occurs in sea-water is not yet clearly understood, but at least part of it is present as iodide and iodate. Therefore, it is necessary in the present work to examine the effect of iodide on the catalytic activity of sea-water. As the sea-water is alkaline solution, if the iodide-hydrogen peroxide reaction occurs in sea-water, the following Bredig-Walton mechanism is to be considered:



By summing, we obtain



representing the simple decomposition.

Assuming that above mechanism is correct, free energies of reaction I and reaction II are calculated as follows.

For reaction I, $\Delta F^\circ = -21,187$ cal.

For reaction II, $\Delta F^\circ = -29,253$ cal.

The free energy of reaction of reaction I is favorable for the oxidation of iodide ion to hypiodite ion by hydrogen peroxide through the reaction and indicates that the reaction proceeds more easily and more rapidly than in the case of chloride ion as given in the chloride ion catalysis though we have no experimental evidence to show that the speed of the reaction is more rapid.

Also, in the iodide ion catalysis, the concentration of iodide ion is maintained constant through the reaction. Hence the velocity constant of the decomposition must be proportional to the concentration of iodide ion. The experimental evidence is shown in Table V and Fig. 6. The iodide ion catalyzed very strongly the decomposition of hydrogen peroxide in its small amount and 1000 mg/L (0.006 M) of potassium iodide increased the activity to K_{30} 0.600. However,

Table 5. The iodide ion catalysis of the decomposition of hydrogen peroxide.

Concentration of potassium iodide		Catalytic activity*	Reaction time
KI, mg/L	KI-I, mg/L	$K_{30} \times 10^3$	hrs.
0	0	2	20
20	15	23	
40	30	45	
60	46	64	
80	61	82	
100	76	108	
200	152	143	1
400	304	271	
600	456	374	
800	603	481	
1000	760	600	

Remarks : * buffered at pH 8.2.

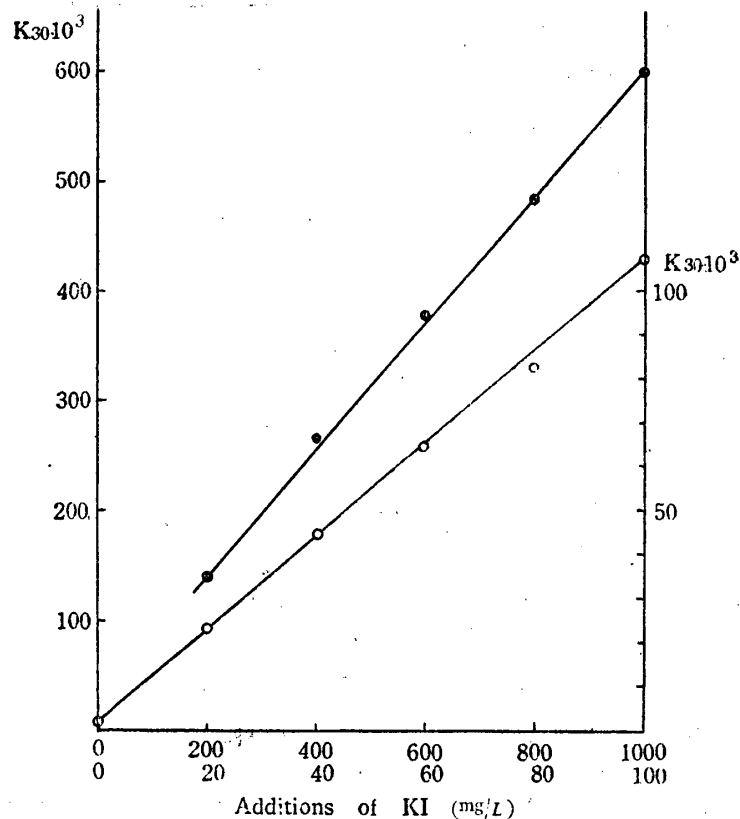


Fig. 6. Relation between the catalytic activity and the concentration of potassium iodide. Dots show the measurement ranging from 200 to 1000 KI mg/L. Circles show the measurement ranging from 0 to 100 KI mg/L.

in spite of the strong catalytic activity of iodide ion, the catalytic activity at the concentration of 15 mg I/L was only K_{30} 0.023. Hence in the sea-water which would contain iodine at 0.05 mg/L, the iodide ion catalysis has only negligible effect upon the catalytic activity.

Finally, it was worth noting that there was no effect of added copper on the iodide ion catalysis though the experimental data are not given in this paper.

The Bromide Ion Catalysis of the Decomposition of Hydrogen Peroxide

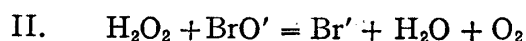
In sea-water, bromine shows very constant ratio to the chlorinity⁴⁾ and is apparently all present as bromide ion. The amount of bromine in the sea-water with the chlorinity of Cl 19 ‰ is 65 mg/kg.

The catalytic reaction of bromine in acid solution to the decomposition of

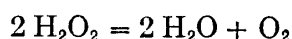
hydrogen peroxide and the effect of metallic ions upon the catalysis are well known but we have no accurate information as to the reaction of the bromide ion catalysis in alkaline solution.

Assuming that the mechanism of the chloride ion catalysis can be extended to the case of bromide ion catalysis, the following intermediate reactions are given.

In alkaline solution,



By summing, we obtain



Free energies for reaction I and II are respectively $\Delta F^\circ = -8,650$ cal. and $\Delta F^\circ = -41,790$ cal. Free energies in both reactions are favorable to proceed the reactions. However the free energy of the reaction I with low chemical affinity has a value close to that of reaction I in the chloride ion catalysis. This reaction, therefore, may account for the slow decomposition of hydrogen peroxide. The experimental evidence obtained in alkaline solution of potassium bromide is shown in Table VI and Fig. 7.

The catalytic activity of potassium bromide solution was proportional to the concentration of bromide ion but it was only K_{30} 0.032 at 0.5 M. From this experiment, it was confirmed that the bromide in sea-water has no effect upon the catalytic activity of sea-water.

The addition of copper to the bromide solution gave a significant effect upon the bromide ion catalysis (Table VII) and the relationship between the activity and addition of copper was linear (Fig. 8). However, the rate of increase in activity to the addition of copper in the bromide ion catalysis was far smaller than that of the chloride ion catalysis.

Table 6. The bromide ion catalysis of the decomposition of hydrogen peroxide.

Concentrations of potassium bromide KBr, mol/L	Catalytic activity $K \times 10^3$
0	1.5
0.1	8.1
0.2	15.0
0.3	19.5
0.4	27.7
0.5	32.3

Remarks: * buffered at pH 8.2 with NaHCO_3 , reaction time 20 hrs.

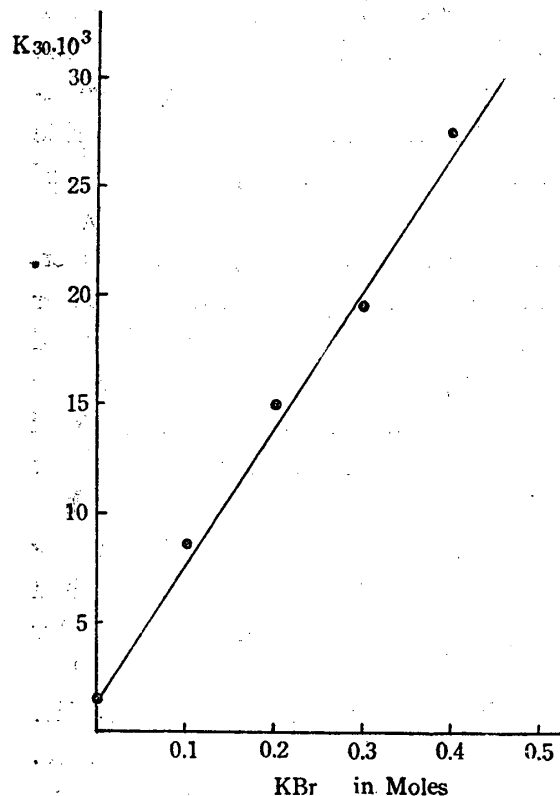


Fig. 7. Relation between the catalytic activity and the concentration of potassium bromide.

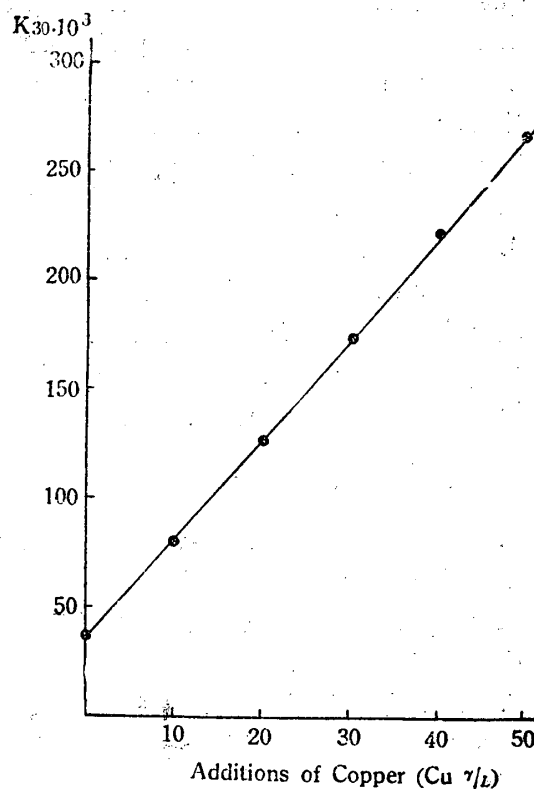


Fig. 8. A line shows the catalytic activity of 0.5 M KBr solution plotted against added copper.

Table 7. Effect of added copper upon the bromide ion catalysis.

Addition Cu %/L	Catalytic activity of 0.5 M KBr solution $K_{30} \times 10^3$
0	36
10	80
20	125
30	173
40	223
50	269

Remarks: buffered at pH 8.2, reaction time 4 hrs.

Summary

1. The mechanism of the chloride ion catalysis of the decomposition of the hydrogen peroxide was evaluated from a thermodynamical standpoint.
2. The activation energy in the decomposition of hydrogen peroxide catalyzed by sea-water was calculated as 19.68 kcal. from the thermal change of the catalytic activity in sea-water.

3. The activity of sodium chloride solution was strongly activated by a minute quantity of added copper. The addition of 50 γ Cu/L to 0.5 M NaCl solution increased the activity from K_{30} 0.065 to K_{30} 0.619. The relationship of the activity to added copper was logarithmic or linear depending on the concentrations of chloride. The relation of the activity to the concentration of chloride bore a linear relationship at the concentration below 0.3 M, irrespective of added copper.
4. The catalytic activity of sea-water was remarkably effected by added copper. The values of the activity activated by added copper differed among sea-water samples at a definite addition. The relation between the activity and added copper was more irregular comparing with that of chloride solution especially in diluted water samples. However, the rate of the activity activated by added copper to the concentration of sea-water gave the same tendency as that of chloride solution.
5. The activities of sea-waters and also sodium chloride solutions activated by added copper gradually declined during the storage for 3 days after the addition of copper but in the successive storage stayed constant at different levels by different samples.
6. The iodide ion showed strong catalytic activity in small quantities. 0.006 M (1000 mg KI/L) potassium iodide solution gave the activity of K_{30} 0.600. However, as the activity at the concentration of 15 mg I/L was only K_{30} 0.023, in the sea-water which would contain iodine at 0.05 mg/L, the iodide ion catalysis had only negligible effect upon the catalytic activity.
7. The catalytic activity of potassium bromide solution was proportional to the concentration of bromide ion but it was only K_{30} 0.032 at 0.5 M. From this result, it was confirmed that the bromide in sea-water has no effect upon the catalytic activity of sea-water. The addition of copper to the bromide solution gave a significant effect upon the bromide ion catalysis, and the relationship between the activity and addition of copper was linear. However the rate of increase in activity to the addition of copper in the bromide ion catalysis was far smaller than that of the chloride ion catalysis.

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