

THE CATALYTIC ACTIVITY OF SEA-WATER I. METHOD OF DETERMINATION AND SOME PHYSICO-CHEMICAL CHARACTERISTICS

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THE CATALYTIC ACTIVITY OF SEA-WATER

I. METHOD OF DETERMINATION AND SOME PHYSICO-CHEMICAL CHARACTERISTICS

By

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Introduction

It is generally acknowledged as a result of experiments on plankton cultivation, that sea-waters, coastal, off-shore or artificial, have some effect on the multiplication and living power of plankton brought about through the activity of some undetermined physiological elements which they possess (E. J. Allen, 1914, C. Matsudaira, 1939). This phenomenon has hitherto been explained by two different theories which are quite different: one asserts the existence of some substances in sea-water which promote the multiplication of plankton (H. Gran, 1931, H. W. Harvey, 1940), while the other claims the existence of those which control it (E. J. Allen, 1910, H. W. Harvey, 1925). Arguments of these two opinions put their basis on the results of experiments which ascertained the stimulating effect caused by some substances and the antidotal function of sea-water. It is sure, however, that neither the phenomenon itself will be explained nor the mutual relation between these two statements will be found, so long as the physiological functions of the substances can not be determined.

It can be suggested that sea-water possesses some unknown physiological elements which act on the physiological functions of living things, like pH, and that the stimulative substances and antidotal functions of sea-water, which have already been ascertained, act on these hypothetical elements as acid or alkali does on pH, and give some indirect influence on the multiplication and living power of plankton. In order to prove this hypothesis positively, experiments were set up to clarify these hypothetical elements. It occurred in the course of this study, that the catalytic action of sea-water on H_2O_2 could be found to have parallel relation with the phenomenon above, and the author took up this special property of sea-water as a chief subject of study, defining it as "catalytic activity of sea-water".

In this paper, both the method of determination and some physico-chemical characteristics of the activity were dealt with. Though other studies in this field have hitherto paid attention only to the functions of catalytic substances which promote the chemical reaction in sea-water (E. Kreps, 1933), H. W. Harvey (1925) took up the subject from the side of mutual reaction between sea-water and H_2O_2 in his study on oxidation in sea-water, and the author made a comparative study with his results.

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Definition of the Catalytic Activity

As will be shown later, sea-water possesses the ability to decompose hydrogen peroxide. This activity differs in strength and is considered to be characteristic of various sea-water samples. The author wishes to call it the "catalytic activity of sea-water" in this paper.

The catalytic activity of sea-water thus defined can be expressed by the reaction velocity of decomposing hydrogen peroxide. If it is a monomolecular reaction, the rate of hydrogen peroxide decomposition in sea-water should be approximately proportional to the amount of hydrogen peroxide present at any moment, that is

$$\frac{-d(H_2O_2)}{dt} = K (H_2O_2)$$

Dissolving the differential equation,

$$\log_{10}(H_2O_2) = -0.4343 Kt + C$$

$$C = \log_{10} a$$

$$\log_{10}(H_2O_2) = \log_{10}(a - x)$$

$$K = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \dots\dots\dots (1)$$

Where t is the time of reaction in hours, a the initial concentration of H_2O_2 , x the amount of H_2O_2 decomposed in time t and K the velocity constant.

The mode of reaction, actually observed in natural and artificial sea-water revealed the resemblance to that of a monomolecular reaction. Therefore,

it will be admitted to use the velocity constant, K , as a measure of catalytic activity in various sea-water samples.

Determination of the Catalytic Activity

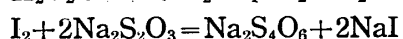
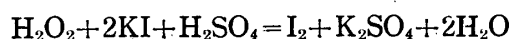
1. Method.

General method used for quantitative determination of hydrogen peroxide is to titrate H_2O_2 directly with $KMnO_4$ in acid solution of H_2SO_4 . The method has been generally used in the determination of catalase and also of the catalytic activity in spring water.

Harvey (1925) also used this method for measurement of oxidation intensity in sea-water. But in our experience, it was found that the reaction of H_2O_2 to $KMnO_4$ was very slow in sea-water and moreover in the titration, the end point was hard to determine. Therefore in the present study, the iodometric method was adopted and ammonium molybdate was used as a catalyst according Koltoff's suggestion (1921). The procedure was as follows.

A 100 c.c. sample of sea-water was placed in a clean Matsuda Telex Ehlenmeyer flask (It was found unnecessary to coat the flask with paraffin when it had been thoroughly washed). The flask was dipped in running well-water of constant temperature before measurements were made. The temperature varied within only $2^\circ C$ during a given day, though it varied from $15^\circ C$ to $25^\circ C$ depending on season. In the later part of study, however a thermostat was used and the determination was carried at a constant temperature of $30^\circ C$.

Guaranteed 30% H_2O_2 was diluted to 1/100 by adding redistilled water which was free from copper. The volumetric flask was stoppered and rotated for ten minutes to obtain a homogeneous solution. Then, 10 c.c. of this solution was added to the flask of sea-water samples and mixed thoroughly. 10 c.c. of the mixture was measured into another 100 c.c. Ehlenmeyer flask in which 10 c.c. of distilled water, 1 c.c. of 10% potassium iodide and 1 c.c. of sulphuric acid (1:3) were previously added and the time was recorded. Then, one drop of 10% solution of ammonium molybdate was added in order to accelerate the reaction. The flask was stoppered, shaken and allowed to stand for a few minutes. The iodine evolved was titrated with N/100 thiosulphate solution with starch indicator. The chemical reaction will be expressed as below.



Thus, the initial concentration of H_2O_2 , a was given by the amount (c.c.) of $Na_2S_2O_3$ used for titration. Similarly, the concentration of H_2O_2 after 24

hours, $a-x$, was determined. The reaction time t was reduced to less than 24 hours when the catalytic activity was found to be strong. Thus, the catalytic activity, K was calculated by putting a and $a-x$ in equation (1).

2. Relation between the Initial Concentration of H_2O_2 and the Catalytic Activity.

If H_2O_2 decomposing reaction in sea-water is a monomolecular reaction the catalytic activity of sea-water, K , must be constant irrespective of the initial concentration of H_2O_2 , and the reaction time, t . Harvey (1925) pointed out that the value of K was different more or less in some kinds of sea-waters depending on the initial concentration and also on reaction time. Therefore, before proceeding further, we had to examine such effects in natural and artificial sea-water. The result is shown in Table I.

298 mg., 149 mg. and 28 mg. of H_2O_2 were added respectively to 100 c.c. of a sea-water sample with a chlorinity of 16.45 ‰, taken from Fukuoka Bay and an artificial sea-water with a chlorinity of 18 ‰. The catalytic activity was determined in these samples at various reaction time. However, in the case of artificial sea-water, the activity was found to be different depending on the initial concentration and reaction time. However, in the case of natural sea-water, the activity was found to be different depending on the initial concentration of H_2O_2 . The activity showed no marked difference between the cases of 298 mg. and 158 mg. of H_2O_2 . But it was very high when only 32 mg. of H_2O_2 was added.

According to Harvey (1925), the effect of the initial concentration of H_2O_2 upon the activity depended on the property of sea-water. In some sea-waters, no effect was observed, while in others the activity was increased at high initial concentration. He attributed such effect to the amount of dissolved organic substances which inhibited the catalytic activity in sea-water. He considered that in high concentrations of H_2O_2 the organic substances were destroyed and therefore, their power of inhibiting activity was reduced. It may not be proper to compare his result with the one presented here because the initial concentration of H_2O_2 was much higher in the present experiment. But it should be noted here that the higher the initial concentration, the less was the activity, contrary to Harvey's case. For the explanation of the present result, it may be assumed that at high initial concentration of H_2O_2 , either the quantity of catalyst present is not sufficient for the reaction or the catalyst is destroyed by such higher concentration of H_2O_2 .

As a result, the activity at high initial concentration of H_2O_2 was found to be lower than at low concentration. Considering the possible effect of

Table I Relation between Initial Concentration of H₂O₂ and the Catalytic Activity.

Samples	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c. (a)	Reaction time in hours (t)	Concentration of H ₂ O ₂ after experiment in mgs. per 100 c.c. (a-x)	Catalytic* activity (K ₂₂)
Natural sea-water pH 8.2 Temp. 22°C Cl 16.45%	298	0	298	
		2	289	0.015
		4	279	0.016
		6	268	0.017
		24	190	0.019
	149	0	149	
		2	144	0.017
		4	139	0.018
		6	134	0.017
		24	94	0.019
	28	0	28.0	
		2	27.1	0.017
4		26.0	0.019	
6		25.2	0.018	
24		17.8	0.019	
Artificial sea-water pH 8.2 Temp. 22°C Cl 18.00%	298	0	298	
		2	260	0.067
		4	224	0.070
		6	175	0.088
		12	90	0.099
		18	33	0.122
	158	0	158	
		2	136	0.075
		4	118	0.075
		6	91	0.092
		12	45	0.105
		18	17	0.124
	32	0	32.0	
		2	22.1	0.184
		4	14.2	0.203
		6	8.2	0.228
		12	2.0	0.231
		18	0.5	0.231
	24	0	—	

$$* K = \frac{2.303}{t} \cdot \log_{10} \frac{a}{a-x}$$

high initial concentration of H₂O₂ on the activity as discussed, it was decided in the present study to use the low initial concentration of H₂O₂ as 30 mg. H₂O₂ per 100 c.c. as standard.

Then, the effect of reaction time on the activity will be considered. As shown in Table I, there was a noticeable tendency for the activity of

natural sea-water to increase slightly as reaction time increased, but it could be considered as constant irrespective of reaction time. In the case of artificial sea-water, the activity was not affected by reaction time when the initial concentration was 32 mg/100 c.c., it did however, show a marked difference depending on the period of reaction time in the samples to which 298 mg. and 158 mg. of H_2O_2 were added. In short periods of reaction until the concentration of H_2O_2 fell as low approximately 100 mg/100 c.c., the activity showed only a slight increase, but when the concentration dropped below 100 mg/100 c.c., the activity increased rapidly.

So far as the present experiment is concerned, the difference in the activity as affected by the reaction time, was not considered to be due to the substances in sea-water which inhibited the catalytic activity, as presumed by Harvey, but it was more likely due to the effect of the concentration of H_2O_2 .

3. Thermal Effect in the Catalytic Activity and Temperature Correction.

In the determination of the catalytic activity, the effect of temperature

Table II The Thermal Change in the Catalytic Activity.

Exp. No.	Temp. °C	K^*	$\log_{10} K$	$\frac{1}{T}$	a	b
I	11	0.0069	-2.16115	0.003521	-4256	12.85
	21	0.0249	-1.60380	0.003401		
	30	0.0635	-1.19723	0.003300		
II	11	0.0126	-1.89963	0.003521	-4302	13.24
	21	0.0400	-1.39794	0.003401		
	30	0.1106	-0.95624	0.003300		
III	11	0.0188	-1.72584	0.003521	-4212	13.09
	21	0.0575	-1.24033	0.003401		
	30	0.1567	-0.80493	0.003300		
IV	11	0.0233	-1.63264	0.003521	-4402	13.86
	21	0.0771	-1.11295	0.003401		
	30	0.2168	-0.66394	0.003300		
V	11	0.0274	-1.56067	0.003521	-4352	13.76
	21	0.0911	-1.04048	0.003401		
	30	0.2512	-0.59998	0.003300		
VI	19	0.0070	-2.15490	0.003424	-4942	14.77
	30	0.0287	-1.54212	0.003300		
VII	19	0.0140	-1.85387	0.003424	-4465	13.43
	30	0.0501	-1.30016	0.003300		
VIII	19	0.0216	-1.66555	0.003424	-4093	12.35
	30	0.0695	-1.15802	0.003300		
IX	19	0.0256	-1.59176	0.003424	-4210	12.84
	30	0.0892	-1.04964	0.003300		

* $\log_{10} K = a \frac{1}{T} + b$, T : Absolute temperature.

should be made clear. As Table II shows, the value of the catalytic activity of natural and artificial sea-water varies remarkably with changes in temperature. Therefore, comparison of the activities in natural or artificial sea-water should be made at a constant temperature. The activity K measured at a temperature $t^\circ\text{C}$ was denoted as K_t . An experiment was planned to find the equation converting K_t to K_{20} or K_{30} measured at a standard temperature 20°C or 30°C by finding the relation between K and temperature.

The thermal effect of the catalytic activity in spring-water had been studied by *K. Okabe* (1941). It was expressed by equation of Arrhenius as follows;

$$\log_{10}K = -0.4343 \frac{A}{RT} + C \dots\dots\dots (2)$$

Where A is a energy of activation in the reaction, C a constant and R a gas constant.

Natural sea-water with low activity taken from Fukuoka Bay was mixed with artificial sea-water in various proportions and water samples with various grades of activity were prepared. The activities of these samples were determined at 11°C , 21°C and 30°C respectively. The reaction time was 6 hours. The results are shown in Exp. No. I~V, Table II. In Fig. 1, the values of $\log_{10}K$ are plotted against the reciprocal of absolute temperature $1/T$. A straight line relation is observed between them. If we express this relation as,

$$\log_{10}K = a \frac{1}{T} + b \dots\dots\dots (3)$$

coefficient a and b can be calculated respectively from the equation by substituting K and T obtained experimentally as shown in Table II. The slope of line, a , was nearly constant and it was -4305 in average. Therefore, straight lines shown in Fig. 1 are nearly parallel. If K_{obs} denotes K measured at an absolute temperature T_{obs} , it can be converted to K_{cal} measured at a standard absolute temperature T_{cal} by the following equation.

$$\log_{10}K_{\text{cal}} = -4305 \frac{1}{T_{\text{cal}}} + \log_{10}K_{\text{obs}} + 4305 \frac{1}{T_{\text{obs}}} \dots\dots\dots (4)$$

In experiment VI~IX, the thermal effect of K was determined at the low range of K between $0.02 \sim 0.089$ at 30°C . In this series, the determination of K at low temperature was omitted because it was found too small to be determined at such a low temperature as 10°C . Assuming the relation between $1/T$ and $\log_{10}K$ to be linear, the coefficients a and b were calculated in the same manner as preceding experiments from the equations which were obtained by connecting the two points showing respectively the

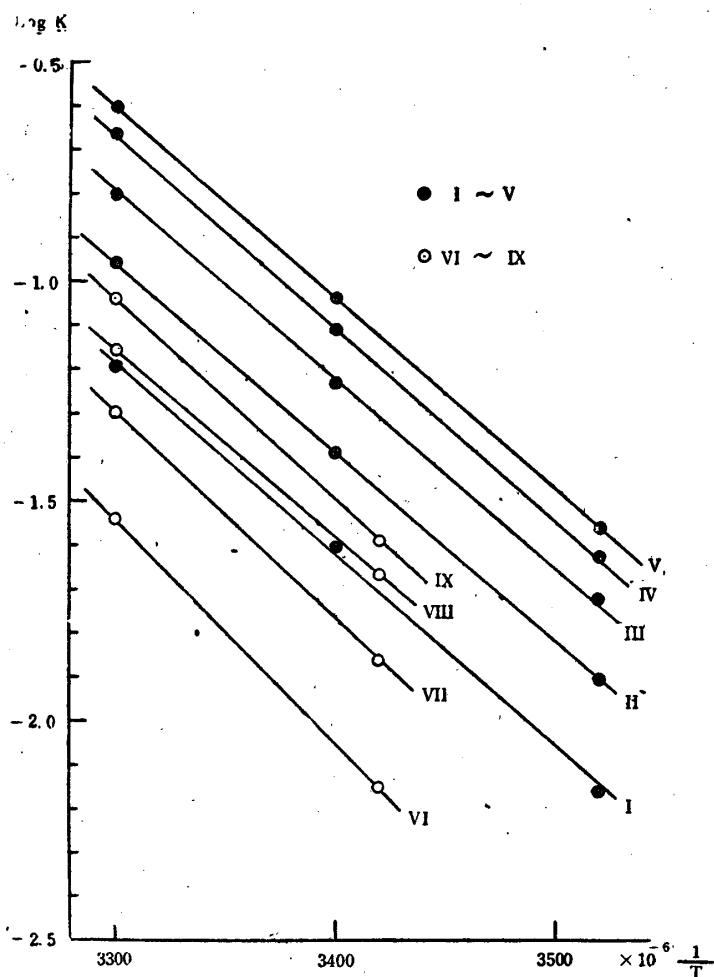


Fig. 1. The thermal effect of the catalytic activity.
For explanation see text.

$\log_{10} K$ value at 19°C and 30°C. They are shown in Exp. No. VI~IX of Table II.

Comparing with preceding experiments, the experimental error was a little large, but the slope of the straight lines was almost same as preceding ones. Though the value of a in Exp. No. VI was larger than the others, it seemed to be due to experimental error. Therefore for the temperature correction of the catalytic activity, the mean value of $a - 4305$ obtained in the experiments I~V was used, rejecting the result of the experiment VI~IX.

As a result, it was confirmed in this experiment that the thermal effect of K was not connected with the values of K . Then, the activities measured at an arbitrary temperature, K_t can be converted into "standard catalytic activity" K_{20} or K_{30} by equation (4).

Some Physico-Chemical Characteristics of the Catalytic Activity

1. *Water Samples.*

The natural sea-water used in this experiments was collected either from the surface layer in Fukuoka Bay or from the layer of ten meter depth in Tsushima Channel. The activity of the former was weak, while that of the latter was strong.

The sea-water collected from Fukuoka Bay was filtered through the absorbent cotton of good quality washed with boiled distilled water, in order to remove the plankton and detritus while the sea-water of Tsushima Channel was used without filtration. They were stored in water-bottles with a capacity of 20 L at dark place and used for experiments within at least two weeks.

Artificial sea-water was prepared, just before the experiments, with chemicals shown in the following list, and was filtered. The chemicals used were all of guaranteed quality made in Japan.

Chemicals	Amount g/l
NaCl	28.13
KCl	0.77
CaCl ₂	1.20
MgCl ₂	2.55
MgSO ₄	3.50
NaHCO ₃	0.20

The salinity of artificial sea-water thus prepared was 35 ‰, with same composition as Dettmar's analysis of sea-water. The sea-water of lower salinity was prepared by adding distilled water.

2. *The Catalytic Activity in Different Chlorinity.*

In order to discuss the catalytic activity of sea-water, either artificial or natural, it is necessary to form some idea concerning the nature of the catalytic substances. Prior to experiments the following hypotheses were made concerning the catalytic substance: (a) It was a special substance, such as an enzyme or metallic ions present in minute quantities in sea-water, or (b) it was one of the chief ingredients of sea-water which was present in large quantities and is considered an integral part of the very nature of sea-water.

Harvey (1925) took the first view and concluded that the catalytic substances in the sea-water might be organic iron compounds dissolved in a minute quantity. However, it was important to investigate why the artificial sea-water possessed strong activity as already shown in Table I.

Therefore, the following experiments were carried out under the second hypothesis.

Among ions in sea-water, Cl^- , is contained in the largest quantity. So it was considered to be necessary to examine the effect of it upon the activity.

In the experiment of natural sea-water, a surface water of Fukuoka Bay with weak activity and the water of 10 m layer in Tsushima Channel with strong activity were used. They were mixed at various proportions and thus a series of mixed samples with different grades of activity was prepared. The chlorinities of these sea-water samples were lowered respectively by adding distilled water. After adjusting pH values of sea-water samples to 8.2 by 3N/20 NaHCO_3 , their chlorinities and activities were measured. The relations between chlorinity and activity in each sea-water samples of a series were shown in Exp. No. I~VI of Table III A and Fig. 2 A.

In the sea-water of Fukuoka Bay with a low activity, the rate of activity gradually slowed down as the chlorinity increased, as shown in Exp. No. I of Fig. 2 A. Whereas, in the sea-water of Tsushima Channel, the rate of increase was fairly constant, strictly speaking, it probably shows a logarithmic progression as shown in Exp. No. VI of Fig. 2 A. In mixed samples of both sea-waters, the relations of chlorinity to activity were similar to the case of either Fukuoka Bay or Tsushima Channel sea-water according to the proportions used, as shown in Exp. No. II~V of Fig. 2 A. However, the activity of mixed samples of the same chlorinity were not proportional to the proportions of the two samples used. In order to clear this relation, activities at the same chlorinity in Fig. 2 A were plotted into another figure according to the proportions used in the mixed samples. Thus, Fig. 3 was prepared. In this figure, the curves 1, 2, 3, and 4 show the relationship between the activity and mixing proportion respectively at Cl 17‰, 14‰, 10‰ and 7‰. If the activity were proportional to mixing proportions, the activity when plotted would coincide with the dotted lines shown in Fig. 3, however when the actual results obtained from the experiments were plotted, the curves below the dotted lines when the activity K_{20} was <0.08 and above it when K_{20} was >0.08 . Harvey (1925) had already obtained the relation of activity to mixing proportion of two kinds of sea-water. His curve coincided with the curve 4 in Fig. 3, taking the shape of arc which was drawn under dotted line. Therefore, his result appeared to be a result obtained in the mixture of two sea-waters with low activity. He stated that it might be the effect of inhibitory substances on catalysis so that the activity in the mixture of two sea-waters was reduced considerably below the proportional value of mixing. This explanation fitted in my case too.

Table III The Relation between the Catalytic Activity and the Chlorinity.

A. Natural Sea-Water

Samples	Exp. No.	Chlorinity %	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c.	Concentration of H ₂ O ₂ after 24 hours in mgs. per 100 c.c.	Catalytic activity	
					K _t	K ₂₀
100% Fukuoka Bay sea-water + 0% Tsushima Channel sea-water	I	0	28.0	26.3	K _{17.9} 0.003	K ₂₀ 0.004
		1.75	28.0	23.6	0.007	0.009
		3.55	28.0	23.0	0.008	0.010
		7.00	28.0	21.3	0.011	0.015
		10.50	28.0	20.4	0.013	0.017
		14.00	28.0	19.5	0.015	0.019
17.50	28.0	18.8	0.017	0.021		
80% Fukuoka Bay sea-water + 20% Tsushima Channel sea-water	II	0	28.5	27.0	K _{18.7} 0.002	K ₂₀ 0.003
		1.76	28.5	24.5	0.006	0.007
		3.52	28.4	23.2	0.008	0.010
		7.04	28.4	19.1	0.016	0.019
		10.56	28.4	17.0	0.021	0.025
		14.08	28.4	15.2	0.026	0.030
17.60	28.4	13.6	0.031	0.035		
60% Fukuoka Bay sea-water + 40% Tsushima Channel sea-water	III	0	27.9	25.9	K ₁₈ 0.002	K ₂₀ 0.003
		1.77	27.9	24.6	0.005	0.007
		3.54	27.9	22.0	0.010	0.012
		7.08	27.9	17.5	0.019	0.024
		10.62	27.9	14.3	0.028	0.035
		14.16	27.9	11.2	0.038	0.048
17.70	27.9	9.0	0.047	0.059		
40% Fukuoka Bay sea-water + 60% Tsushima Channel sea-water	IV	0	27.4	26.8	K _{17.3} 0.001	K ₂₀ 0.001
		1.78	27.4	24.5	0.005	0.006
		3.56	27.4	20.6	0.012	0.016
		7.13	27.4	14.6	0.021	0.029
		10.69	27.4	9.4	0.045	0.060
		14.26	27.4	5.3	0.068	0.091
47.82	27.4	3.1	0.091	0.122		
20% Fukuoka Bay sea-water + 80% Tsushima Channel sea-water	V	0	27.2	25.7	K _{17.3} 0.002	K ₂₀ 0.003
		1.79	27.2	23.5	0.006	0.008
		3.58	27.3	21.6	0.009	0.014
		7.16	27.2	14.2	0.027	0.036
		10.74	27.2	8.0	0.051	0.069
		14.32	27.2	4.3	0.075	0.102
17.90	27.2	2.4	0.101	0.138		
0% Fukuoka Bay sea-water + 100% Tsushima Channel sea-water	VI	0	29.3	28.8	K _{19.7} 0.001	K ₂₀ 0.001
		1.80	29.2	22.3	0.011	0.012
		3.60	29.2	16.9	0.023	0.024
		7.19	29.2	8.5	0.052	0.053
		10.78	29.2	3.6	0.088	0.091
		14.38	29.2	2.0	0.113	0.117
17.98	29.2	0.9	0.147	0.153		

B. Artificial Sea-Water and Some Chlorides.

Samples	Exp. No.	Chlorinity %	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c.	Concentration of H ₂ O ₂ after 24 hours in mgs. per 100 c.c.	Catalytic activity K ₂₀
Guaranteed NaCl solution	VII	0	27.8	25.3	0.004
		1.80	27.8	18.1	0.018
		3.60	27.8	11.4	0.037
		7.20	27.8	3.7	0.084
		10.80	27.8	1.3	0.128
		14.40	27.8	0.4	0.179
		18.00	27.8	0.1	0.235
Extra pure NaCl solution	VIII	0	27.8	25.6	0.003
		1.92	27.9	23.3	0.007
		3.84	27.8	20.7	0.012
		7.68	27.8	16.4	0.022
		11.52	27.8	13.2	0.031
		15.36	27.8	10.4	0.041
		19.20	27.8	9.0	0.047
Extra pure KCl solution	IX	0	27.9	27.0	0.001
		1.32	27.8	24.2	0.006
		2.64	27.8	20.4	0.013
		5.28	27.8	14.7	0.029
		7.92	27.8	8.4	0.050
		10.56	27.9	5.5	0.068
		13.20	27.8	3.4	0.088
Extra pure MgCl ₂ solution	X	0	27.8	25.6	0.003
		1.78	27.8	23.1	0.007
		3.57	27.8	20.9	0.012
		7.13	27.8	15.5	0.025
		10.70	27.9	11.7	0.036
		14.27	27.8	7.7	0.054
		17.84	27.9	5.6	0.067
Artificial sea-water contained VII	XI	0	27.2	26.0	0.005
		3.59	27.8	19.7	0.033
		7.18	27.7	13.1	0.076
		10.77	27.7	12.4	0.081
		14.36	27.6	11.7	0.088
		17.95	27.4	11.4	0.098
Artificial sea-water contained VIII	X	0	27.8	27.2	0.001
		1.82	27.9	24.5	0.005
		3.63	27.8	21.6	0.011
		7.27	27.8	17.0	0.021
		10.90	27.8	13.0	0.032
		14.54	27.8	11.1	0.039
		18.17	27.8	12.6	0.033

K₁: Catalytic activity measured at t°C and pH 8.2.

K₂₀: Standard catalytic activity at 20°C and pH 8.2.

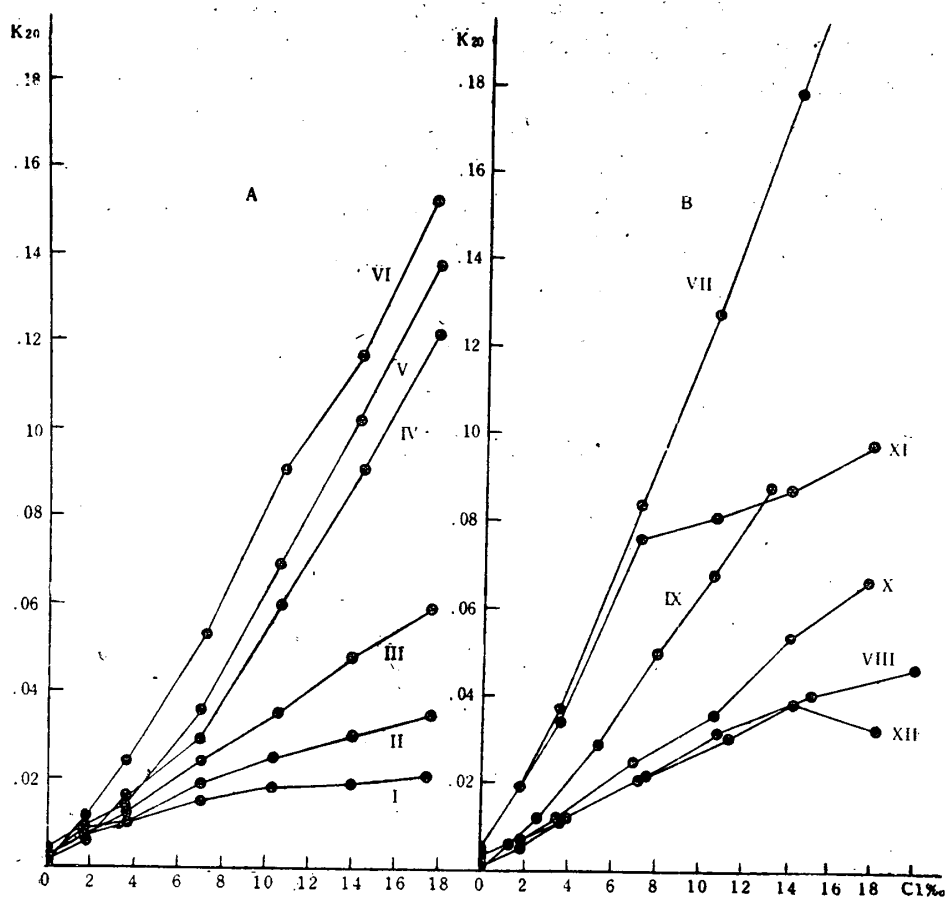


Fig. 2. The Relation between the Catalytic Activity and Chlorinity.

Exp. No.	A. Natural sea-water		B. Artificial sea-water and some chlorides	
	Surface sea-water from Fukuoka Bay	Sea-water from 10m depth at Tsushima Channel		
I	100%	+ 0%	VII	Guaranteed NaCl solution
II	80%	+ 20%	VIII	Extra pure NaCl solution
III	60%	+ 40%	IX	Extra pure KCl solution
IV	40%	+ 60%	X	Extra pure MgCl ₂ solution
V	20%	+ 80%	XI	Artificial sea-water contained VII
VI	0%	+ 100%	XII	Artificial sea-water contained VIII

Next, the effect of chlorinity upon the activity was examined in an artificial sea-water and some chloride solutions as shown in Table III B and Fig. 2B. Exp. No. VII and VIII in Table III B and Fig. 2B were results in sodium chloride solution, respectively prepared from guaranteed and extra pure chemicals made in Japan. The activity of guaranteed NaCl solution shown in Exp. No. VII was slightly stronger than that of Tsushima Channel sea-water (Exp. No. VI) and the relation of the activity to chlorinity was similar, both samples showing nearly straight line. This solution was considered

to contain no impurities which act as catalytic substances. Therefore, it was supposed that the activity of the solution was due to Cl' . Furthermore, if the relationship between the activity and the chlorinity in guaranteed NaCl solution and natural sea-water were similar, the activity of natural sea-water might also be due to Cl' . The activity of extra pure NaCl solution shown in Exp. No. VIII was remarkably low, differing from Exp. No. VII, while the relationship between activity and chlorinity was similar to that of Fukuoka Bay sea-water (Exp. No. I).

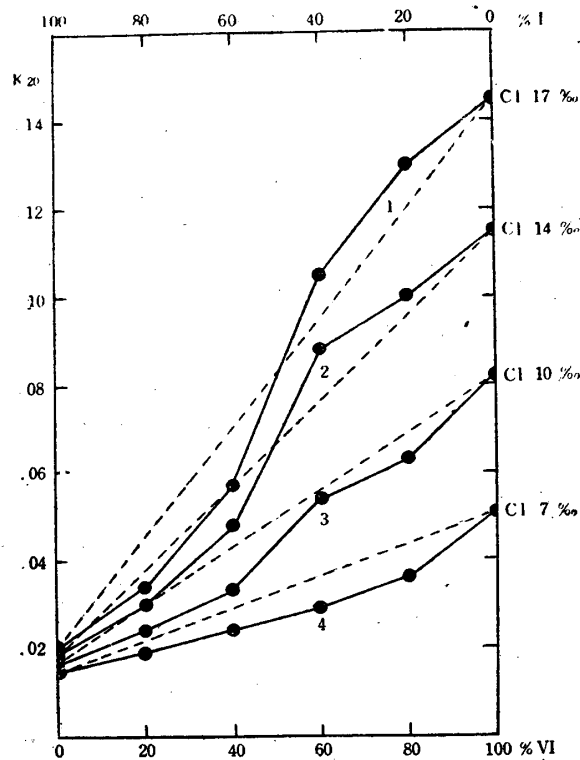


Fig. 3. The change of the catalytic activity in the mixtures of two sea-waters. I. ----- Fukuoka Bay surface sea-water. VI. ----- Tsushima Channel sea-water. For explanation see text.

The activity of solution was found also in chloride solutions other than NaCl solution. The results of the experiments with KCl, and MgCl_2 are shown in Exp. No. IX and X of Table III B and Fig. 2B. The relation of the activity to chlorinity in those solutions was very similar to that of NaCl solution.

The activity of artificial sea-water varied as the purity of the chemicals used in its preparation, especially in the case of NaCl. The artificial sea-water in Exp. No. XI of Table III B and Fig. 2B was prepared from guaranteed NaCl (Exp. No. VII) and other salts. On the other hand, in

Exp. No. XII, an extra pure NaCl (Exp. No. VIII) was used. The activity of the former was stronger than that of the latter. The relation of the activity in the range of low chlorinity increased according to the increase of chlorinity, as in the case of NaCl solution, but upon reaching to a limit of chlorinity, the increase rate of increase of the activity slowed suddenly and sometimes ceased or even decreased. In general, the activity of artificial sea-water, even if pure chemicals were used, was lower than that of the NaCl solution used for its preparation when both were of the same chlorinity. From those facts, it will be suggested that the activity of artificial sea-water changed because of the formation of some substances inhibitory to the activity. This inhibitory substances will be discussed in detail an other paper.

3. The Catalytic Activity in Different pH.

The object of this experiment was to find the physico-chemical properties of catalytic substances and to obtain fundamental data on the catalytic activity of sea-water.

The natural sea-water newly collected from Fukuoka Bay (Cl 16.7‰) and Tsushima Channel (Cl 18‰) and the artificial sea-water (Cl 17‰) were

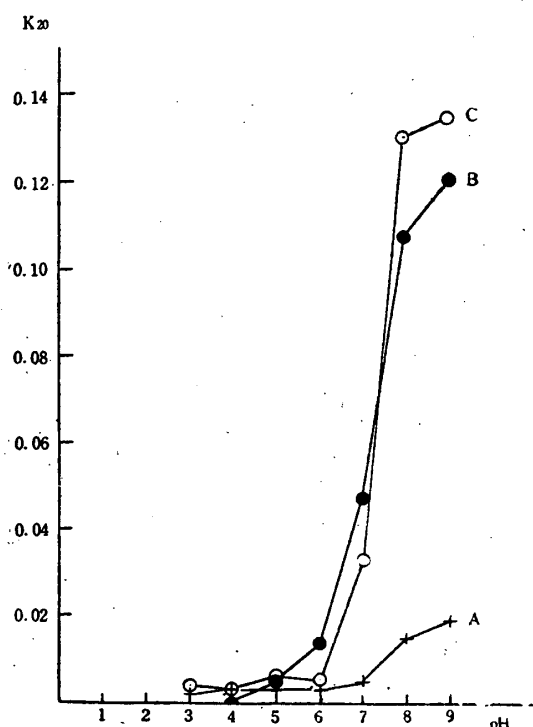


Fig. 4. The relation between the catalytic activity and the pH.
A. Surface sea-water from Fukuoka Bay. B. Sea-water from 10m depth at Tsushima Channel. C. Artificial sea-water.

Table IV The Relation between the Catalytic Activity and the pH.

Exp. No.	Samples	pH	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c.	Reaction time in hours.	Concentration of H ₂ O ₂ after reaction in mgs. per 100 c.c.	Catalytic activity in K ₂₀ *
A	Surface sea-water from Fukuoka Bay. Cl 16.7‰	3.0	29.4	24	27.9	0.002
		4.0	29.6	"	27.7	0.003
		5.0	29.7	"	27.7	0.003
		6.0	29.6	"	27.9	0.003
		7.0	29.4	"	25.8	0.005
		8.0	29.4	"	20.4	0.015
		9.0	29.4	"	18.4	0.019
B	Sea-water from 10m depth at Tsushima Channel. Cl 18‰	1.0	27.0	24	26.9	0.000
		2.0	27.0	"	26.7	0.000
		3.0	27.0	"	25.7	0.000
		4.0	27.0	"	25.6	0.000
		5.0	27.0	"	23.8	0.005
		6.0	27.0	"	19.0	0.014
		7.0	26.2	"	8.5	0.047
		8.0	26.2	"	2.0	0.107
		9.0	27.0	"	1.5	0.120
C	Artificial sea-water. Cl 17‰	3.0	30.9	24	30.3	0.004
		4.0	31.1	"	30.6	0.003
		5.0	30.8	"	29.8	0.006
		6.0	30.6	"	29.8	0.005
		7.0	30.5	"	25.0	0.033
		8.0	30.4	"	1.4	0.130
		9.0	30.0	"	1.2	0.134
D	Distilled water	3.0	30.9	23	30.9	0.0000
		"	"	46	30.9	0.0000
		4.0	30.0	23	27.5	0.0035
		"	"	46	26.9	0.0023
		5.0	29.6	23	27.5	0.0030
		"	"	46	26.0	0.0027
		6.0	30.9	23	28.1	0.0040
		"	"	46	26.0	0.0036
		7.0	31.3	23	27.5	0.0057
		"	"	46	24.5	0.0053
		8.0	31.3	23	27.6	0.0053
		"	"	46	23.1	0.0063
		9.0	31.3	23	26.2	0.0073
		"	"	46	20.9	0.0084

* Measurements carried out at 20°C.

adjusted to various pH values from 3.0 to 9.0 by adding HCl and NaOH and the values of K were determined by the method already described. A, B and C in Table IV and Fig. 4 are respectively the results of both natural and artificial sea-water. Both natural and artificial sea-water, showed nearly zero activity at pH below 7.0. However, when pH was increased from 7.0 to 8.0, the activity increased sharply. At the range of pH 8.0~9.0, the activity tends to increase gradually with the increase of pH, unless precipitation takes place in sea-water. At above pH 9.0, the activity decreased

suddenly, forming a precipitation of hydroxides and other compounds, but this is not shown in the table.

The distilled water showed little activity of acid side, but on alkaline side it increased very slightly with the increase of pH as shown in D of Table IV.

As above mentioned, the relations of activity to pH in both natural and artificial sea-water showed similar characteristics, inactive on acid side, but active on alkaline side. From this fact, it could be suggested that the catalytic substances contained in natural sea-water were the same as those in artificial sea-water so far as the pH was concerned. Furthermore, it was found that any comparison of catalytic activity must be made for a definite pH condition, since the effect of pH upon the activity was conspicuous.

4. The Catalytic Activity of Constituents of the Artificial Sea-Water.

As already mentioned, the activity of artificial sea-water was remarkably strong. Judging from this, the active substance in artificial sea-water might be contained in a large quantity. In this experiment, which the constituents of artificial sea-water were catalytically active were examined.

1 molar solutions of the chief salts of the artificial sea-water, that is, NaCl, KCl, CaCl₂, MgCl₂ and MgSO₄ were prepared. The activity of these were determined and the values of K_{20} at the reaction time of 6 hours are shown in Table V. The order of activity was as follows:



Table V The Catalytic Activity of Chief Constituents of the Artificial Sea-Water.

Constituents 1 mol/l	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c.	Concentration of H ₂ O ₂ after 4 hours in mgs. per 100 c.c.	Catalytic activity*	
			K_{22}	K_{20}
NaCl	29.9	4.6	0.467	0.371
KCl	28.9	5.7	0.405	0.322
CaCl ₂	28.4	8.3	0.307	0.244
MgCl ₂	27.5	1.2	0.781	0.621
MgSO ₄	29.1	29.0	0.001	0.001
Na ₂ SO ₄ **	29.9	26.9	0.018	0.014

* K_{22} : Catalytic activity measured at 22°C and pH 8.2.

K_{20} : Standard catalytic activity at 20°C and pH 8.2.

** not constituent of the artificial sea-water.

Chemicals used are all of guaranteed quality made in Japan.

MgCl₂ solution was most effective upon the decomposition of H₂O₂, the value of K_{20} being 0.621. The activity of solutions of NaCl and KCl were nearly of the same order, showing respectively 0.371 and 0.322. The value of CaCl₂ solution was 0.244 and was slightly lower than NaCl or KCl. On the other

hand, MgSO_4 solution showed no catalytic activity and its value of K_{20} was 0.001. Thus, the activity of artificial sea-water was attributed to chloride more than any of the other constituents of artificial sea-water.

From the fact that MgSO_4 was inactive while MgCl_2 showed strong activity, it could be supposed that the activity of artificial sea-water was not related to metallic ions but to the anions. The fact that the activities of NaCl and KCl were nearly of the same order, might also explain such a hypothesis. However, it can not be said that metallic ions had no activity at all. When the activity of the constituents in artificial sea-water were compared using molar solutions, the amount of Cl' in MgCl_2 solution was twice as that of NaCl and KCl solutions. Therefore, it was considered, as a matter of fact, that the activity of MgCl_2 solution was stronger than NaCl and KCl solutions. The activity of CaCl_2 solution should be the same as that of MgCl_2 solution since the chlorinity was the same. However, though it was proven conclusively that effect of metallic ions in these solutions were different in their activities, the activity of metallic ions appeared not to be a main part of the catalytic reaction. This was confirmed in the following experiment.

The activity of Na_2SO_4 was compared with the activity of NaCl (** in Table V). The solution of Na_2SO_4 was almost inactive showing K_{20} 0.014 which was far smaller than the activity of NaCl . As a result, it was found that the activity of Na' hardly effected the activity of sea-water. The effect of metallic ions upon the activity will be discussed again in detail in another paper. From this experiment, it might be said that the catalyst in artificial sea-water is Cl' . Assuming that the catalyst is Cl' , the question arose whether or not the chloride ion in these solutions assumed special characteristics which promoted a special activity, in addition to the known characteristics of this ion. This paper does not deal with this phase of the problem.

As a result of these experiments, the activity of artificial sea-water might be attributed more to NaCl than to any other constituents, because NaCl showed stronger activity and was present in larger quantities than the other constituents. For this reason, studies of properties of catalysts which are present in artificial sea-water can be made in the same manner by using 3% NaCl solution as shown in the following experiment. Furthermore, it is better to use NaCl in these experiments since it is easier to prepare solutions free from impurities with it than with other chlorides.

5. The Resistance of the Catalytic Substances to Heating, Evaporation and Ignition.

In this experiment, the resistance of catalytic substance to heating, evaporation and ignition was examined in natural and artificial sea-water and 3% NaCl solution.

First, 100 c.c. samples of natural or artificial sea-water in beakers were heated to the various temperatures shown in Table VI, the temperature was maintained for ten minutes while the solution was continuously agitated, it was then cooled to room temperature, and the loss by evaporation replenished with distilled water. The activity was determined by ordinary methods, adjusting the pH to 8.2 by adding sodium bicarbonate. The change of the activity due to heating is shown in Table VI.

Table VI The Resistance of the Catalytic Activity to Heating.

Samples	Temperature of heating in °C	Initial concentration of H ₂ O ₂ in mgs. per 100 c.c.	Reaction time in hours.	Concentration of H ₂ O ₂ after reaction in mgs. per 100c.c.	Catalytic activity K ₂₀
Surface sea-water from Fukuoka Bay. Cl 17.0‰	20	31.1	24	22.0	0.015
	40	31.0	"	22.0	0.015
	60	31.0	"	22.3	0.014
	80	31.2	"	22.3	0.014
	100	30.9	"	20.2	0.016
Artificial sea-water Cl 17.0‰	16.8	29.4	6	13.6	0.133
	20	29.8	"	15.3	0.111
	40	29.8	"	15.4	0.110
	60	29.9	"	15.6	0.108
	80	29.9	"	15.2	0.112
	100	29.9	"	15.2	0.113

Measurement carried out at 20°C and pH 8.2.

The activities in natural and artificial sea-water did not decrease remarkably even though the samples were heated to 100°C. This shows that the catalytic substances were not affected by temperatures as high as 100°C which were maintained for at least ten minutes. This result coincided exactly with Harvey's experiments. As there were several known cases of oxidising enzymes which withstood a temperature of 100°C or higher for several hours, it was considered that the catalytic substance might be an enzyme. Then, in order to decide whether or not it was an enzyme, its resistance to ignition was examined as follows.

Natural sea-water was gradually evaporated to dryness in a beaker on a water bath. 3.5 g of dry matter was weighed and dissolved into 100c.c. of distilled water. The solution filtered through a filter paper. The chlorinity of the filtrate was adjusted to 15‰ by adding distilled water.

A second portion of the dry matter was ignited in the crucible over a gas burner for about ten minutes and cooled at room temperature. And then, 3.5 g of ignited matter was treated in the same manner as above mentioned. The same treatment was given 3% solutions of NaCl which were prepared respectively from guaranteed NaCl and by mixing of HCl and NaOH. The activities of these six solutions were compared with the control at constant temperature, after being adjusted to be same pH by NaHCO_3 . The result is shown in Table VII.

Table VII The Resistance of the Catalytic Activity for Ignition.

Samples	Treatment	Initial concentration of H_2O_2 in mgs. per 100 c.c.	Concentration of H_2O_2 after 24 hours in mgs. per 100 c.c.	Catalytic activity*	
				$K_{12.3}$	K_{20}
Surface sea-water from Fukuoka Bay.	Control	29.0	21.8	0.012	0.030
	Evaporation	29.0	14.3	0.030	0.075
	Ignition	29.1	7.1	0.059	0.147
3% NaCl sol. made from guaranteed NaCl	Control	29.0	4.6	0.078	0.194
	Evaporation	29.1	1.7	0.119	0.297
	Ignition	29.2	1.1	0.142	0.354
3% NaCl sol. made from HCl and NaOH	Control	29.2	1.7	0.118	0.294
	Evaporation	29.1	1.8	0.115	0.287
	Ignition	29.0	3.2	0.092	0.229

* $K_{12.3}$: Catalytic activity measured at 12.3°C and pH 8.2.

K_{20} : Standard catalytic activity at 20°C and pH 8.2.

The activity of natural sea-water which possessed weak activity was raised from 0.003 to 0.075 and 0.147 for values of K_{20} respectively by evaporation and ignition. This showed the catalytic substance to be a very stable substance and since it was not destroyed by ignition. The reason the activity was enhanced by ignition can be explained as follows: Harvey (1925) already reported that the activity of sea-water was inhibited by some inhibitory substances (negative catalysts) which were probably organic matter contained in the sea-water. If this inhibitory substance was organic matter, it should be destroyed by evaporation and ignition with the resultant loss of inhibitory power. Therefore, the increase of the activity noted after ignition might be attributed to the destruction of such inhibitory substances. On the other hand, the exclusion of hydroxides by the filtration process after evaporation and ignition might also be cited as a cause of increased activity, because it was proved in a later experiment that the hydroxides inhibit the activity.

The increase in activity after evaporation and ignition in 3% NaCl solution prepared from guaranteed chemicals was far smaller than that of natural

sea-water, while the activity of 3% NaCl solution prepared by mixing HCl and NaOH was slightly reduced by the same treatment. The explanation of this fact is not yet clear.

It is clear from the above experiments that catalytic substances in natural sea-water and 3% NaCl solution are not destroyed by evaporation and ignition. The increase of the activity observed after this treatment can be considered to be due to the destruction or the exclusion of the inhibitory substances (negative catalysts) such as organic matter or hydroxides.

Summary

1. Sea-water has the catalytic activity of decomposing hydrogen peroxide. The activities of various kinds of sea-water in decomposing H_2O_2 can be expressed in terms of the velocity constant K , where the value K is defined as a "Catalytic Activity of Sea-water".
2. The value of K differed with the temperature at which the measurements were made. The value of K at $t^\circ C$ was denoted by K_t . The catalytic activities of various kinds of sea-water at $20^\circ C$ and $30^\circ C$ were compared with each other. K_{20} or K_{30} were taken as "Standard Catalytic Activity".
3. The determination of H_2O_2 by the iodometry method gave better results than by using the ordinary method.
4. An H_2O_2 concentration of 30 mg/100 c.c. was found most satisfactory for the determination of catalytic activity.
5. The logarithm of the catalytic activity was found to be linear to the reciprocal of the absolute temperature. From this relationship, K_t was converted to K_{20} or K_{30} .
6. The catalytic activity was found in natural sea-water and also in artificial sea-water and NaCl solutions. The strength of this activity was measured by the velocity constant K_{20} at $20^\circ C$ in the reaction with H_2O_2 . As a result, it was found that the K_{20} value of the sample taken from the 10 m layer of Tsushima Channel and guaranteed NaCl solution was high, while in surface sea-water of Fukuoka Bay and impure NaCl solution it was low.
7. In natural and artificial sea-water of NaCl solutions, the catalytic activity was increased with the increase of chlorinity. In Tsushima Channel sea-water and guaranteed NaCl solution which possessed strong activity, the relation of activity to chlorinity showed nearly a straight line, common to both, while in surface sea-water of Fukuoka Bay and impure NaCl solutions which possessed low activity, it showed parabolic curve. Comparing these results with the results of Harvey's experiment, it was suggested that the sea-water with weak activity or impure NaCl solutions

might contain substances inhibitory to the activity (negative catalyts).

8. The relation of the catalytic activity to the pH in natural and artificial sea-water was similar, being characteristically inactive on acid side but active on alkaline side. From this fact, so far as the pH was concerned it was suggested that the catalytic substances contained in natural sea-water were the same substances as those in artificial sea-water or NaCl solutions. The comparison of catalytic activities had to be made in a definite pH condition, since the effect of the pH upon the activity was conspicuous.

9. Among chief ingredients of the artificial sea-water, only chlorides showed the catalytic activity and none of the others showed the activity.

10. The experiments proved that the catalytic activity of natural sea-water and NaCl solutions was not decreased by heating, evaporation, and ignition. From this result, it was concluded that catalytic substance was neither an enzyme nor organic iron compounds as Harvey had supposed.

11. From the experiments described in this paper, it was suggested that the catalytic substance of sea-water was chloride ion. However, the question arose whether or not the chloride ion in natural and artificial sea-water assumed special characteristics which promoted a special activity, in addition to the known characteristics of this ion. This paper did not deal with this phase of the problem.

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