STUDIES ON THE MANGANESE DIOXIDE FOR DRY CELLS

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Introduction

Of the various constituent materials for dry cells (frequently referred to as Leclanché cells), the one most important in decisively affecting their character and activity is manganese dioxide. Of natural oxide ores, called manganese dioxide, there are several varieties distinguishable, depending upon the content of MnO_2, that of water, color and luster, as well as hardness, all varying with their place of production. This also applies to artificial oxides, in which the contents of MnO_2 and water vary according to the method of manufacture. See Tables below:

Table 1

Place of production	Appearance	Water content %	MnO_2 in dried samples %	1g : 1cc pH	Iso-acidic point
A (Shizuoka Pref.)	Brown-black	7.79	62.37	3.5	3.52
B (Gumma Pref.)	do.	4.56	71.10	3.9	3.85
C (Gifu Pref. I)	do.	3.41	84.3	3.9	3.42
C' (Gifu Pref. II)	do.	3.46	81.2	—	3.42
D (Nagano Pref.)	Black, with slight luster	3.02	82.5	—	3.85
E (Aomori Pref. I)	Gray-black, rather soft	1.52	90.8	4.5	4.45
E' (Aomori Pref. II)	do.	1.57	88.5	—	3.91
F (Hokkaidō I)	do.	1.62	95.7	4.2	4.92
F' (Hokkaidō II)	do.	1.28	90.5	4.2	4.07
G (South Seas)	Black	0.79	85.5	5.5	6.00

Table 2

Method of preparation or manufacture	Appearance	Water content %	MnO_2 %	Iso-acidic point
H Merck	Violet-black	12.68	70.21	2.98
I I. G.	Brown-black	19.05	69.39	3.20
J Schreyer 1	Bluish-black	13.38	71.47	3.18
K Schreyer 2	Gray-black	3.48	74.36	4.18
L Electrolytic, from $Mn(NO_3)_2$	Brown-black	1.20	93.39	—
M Electrolytic, from $MnSO_4$	Brown-black	1.50	89.00	2.10
N Air Oxidation, T - - - Co.	Brownish black	6.67	71.83	1.88
O Heat decomposed from $Mn(NO_3)_2$	Black, in crystal form	0.12	98.71	4.5

Because there has been much difficulty in establishing definite relations between the chemical composition of these oxides and their electro-chemical properties when used in the depolarization of dry cells, these relations have generally been considered quite complex. There have been attempted to determine the electro-chemical properties of oxides in two ways: (A) *Physical*, including: (1) X-ray[1] and (2) electron diffraction methods,[2] (3) electron micrographs,[3] (4) determination of electrical conductivity;[4] (B) *Chemical*, including (5) the corrosion method by chemical reagents,[5] (6) rate of dissolution in acid reducing agents,[6] (7) state of thermal decomposition,[7] (8) quantities of combined water.[8] However, it must be said that, in spite of these numerous methods, the properties of manganese dioxide have not yet been explained satisfactorily.

The present paper records the results of researches on the electro-chemical properties of manganese dioxide in order to clarify methods of selection and uses of this oxide in dry cells. Methods of manufacture, too, are included in the discussion.

Though the electro-chemical properties of manganese dioxide for dry cells may be divided into (a) those referring to electro-motive force and (b) those referring to the discharging capacity of cells. The capacity is considered to depend exclusively upon the durability of the electro-motive force, and accordingly these properties stand in intimate relations with the electro-motive force itself, that is to say, with the potential, especially at the anode. For this reason a full discussion of the potential will be given first.

I. Relationship between the potential of manganese dioxide and the pH value of solutions

Theoretically it is possible to consider that straight-line relationship, expressed by the epuation

$$E = E_{\text{const}} - 0.059\,\text{pH} \quad (25°\text{C})$$

exists between the potential of manganese dioxide and the pH value of solutions. Many experiments have been performed in the past to demonstrate this. As a result of these experiments, shown in Figs. 1 and 2, straight-line relationships were established in some cases. However, cases in which curves were obtained were quite as numerous. The reasons which at times led to straight lines and at others, to curves, however, were not made clear. In all the experiments, with the exception of those performed by Thompson,[9] the pH value of the original solution was used, without any change, as the pH value of the solution after it had been brought in contact with manganese dioxide. The present writ-

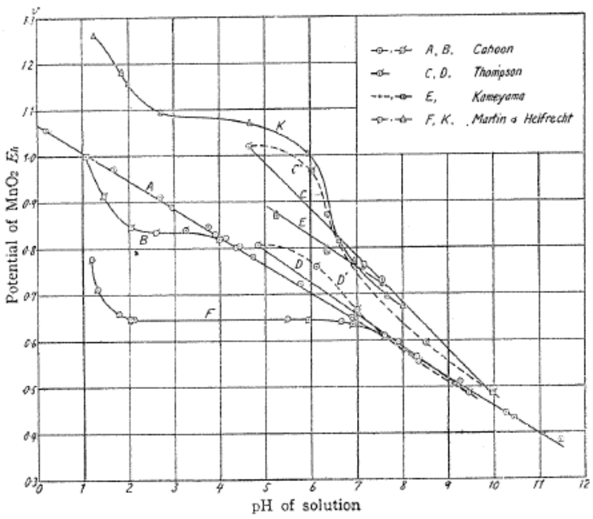

Fig. 1

er noticed in his experiments, that the pH value of a solution is greatly changed by the presence of manganese dioxide in it. He also noticed that if this change is taken into consideration, straight-line relationships would be established; and furthermore, that in order to ascertain the correct relationships between the potential and the pH value, it is essential that this change be so taken into consideration. The writer's experiments in this connection are described below.

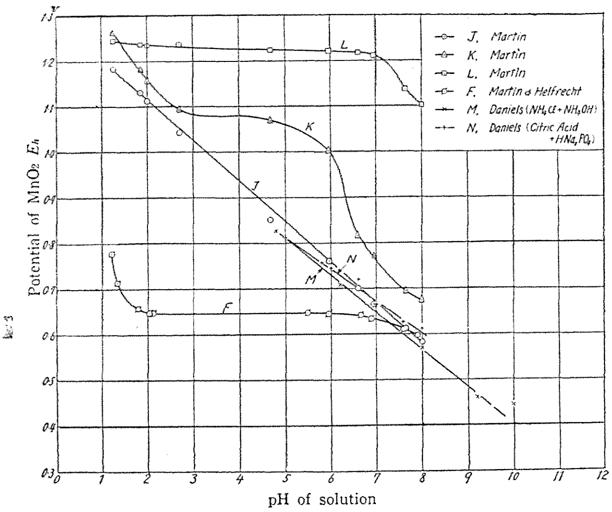

Fig. 2

II. Change of the pH value of solutions due to the presence of manganese dioxide

In his experiments, the writer used natural manganese dioxide in fine powder form, produced in Shizuoka (*A.* (MnO_2)) and that produced in Hokkaidō (*F.* (MnO_2)). For solutions, he used the following two kinds: (1) Ammoniun chloride solution (250 g of NH_4Cl, 1000 g of H_2O) and (2) the solution containing zinc chloride (250 g of NH_4Cl, 50 g of $ZnCl_2$, 1000 g of H_2O). The latter solution shall hereinafter be referred to as the solution for dry cells. To both the solutions, hydrochloric acid or ammonia was added to change the pH value. In the case of the former, solutions with pH values from 0.5 to 7.6, and in the case of the latter, those with pH values from 2.0 to 5.1 were made. For every one gram of manganese dioxdide in fine powder form, 5 cc of solutions of different pH values were mixed and shaken. The shaking was continued until the change in pH value could be considered reasonably perfect. As a result of experimentation, it was discovered that the number of days required varied from ten to more days, depending on the place of production of the oxide used. First the solution was shaken; then the manganese dioxide was separated from the solution by means of a centrifugal separator; the pH value of the solution was then carefully and accurately measured by a hydrogen electrode. The results of the experiment are shown in Fig. 3. The solution used in the experiment described in the figure was a solution of NH_4Cl.

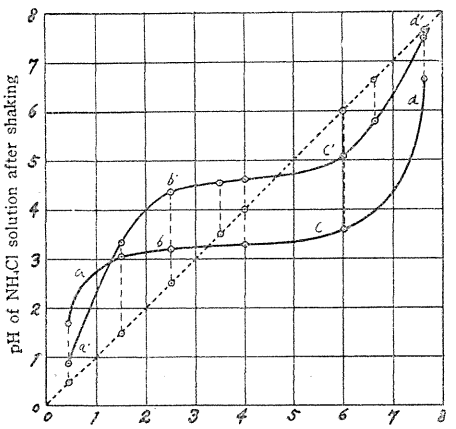

Fig. 3. pH change of the solution (NH_4Cl 250 g H_2O 1000 g) with MnO_2 after shaking.

The curve *a, b, c, d* represents changes in pH value obtained by using manganese dioxide produced in Shizuoka (*A*. (MnO_2)), and the curve *a′, b′, c′, d′* represents those changes obtained by using manganese dioxide from Hokkaidō (*F*. (MnO_2)).

In both the cases pH values became greater where the solutions were acidic, and where the solutions were of weak acid or base, pH values became smaller. In both cases there was observed a range in which the pH value was constant. The point of intersection of the curves with the 45° dotted line indicates the point where the pH value of the solution showed no change even after being shaken with manganese dioxide. This point the writer has called the iso-acidic point.

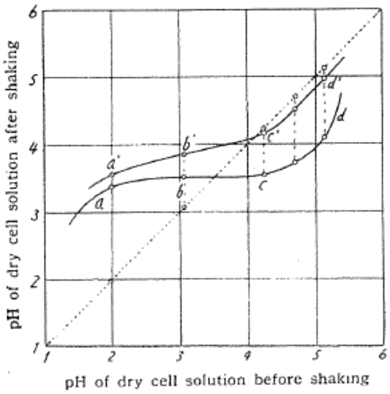

Fig. 4. pH change of dry cell solution (NH_4Cl 250 g, $ZnCl_2$ 50 g, H_2O 1000 g) with MnO_2 after shaking.

Fig. 4 shows the results obtained when the solution used was the solution for dry cells. The curve *a, b, c, d* shows the changes in pH value when manganese dioxide (*A*) was used, and the curve *a′, b′, c′, d′* shows those changes which took place when manganese dioxide (*F*) was used. What has been said in regard to the curves in the preceding figure is likewise applicable to the curves in this figure.

III. Relation between the potential of manganese dioxide and the pH value after shaking

Figs. 5 and 6 show the relationship between the pH value (after it has been changed by shaking the solution with manganese dioxide), and the potential (of the cell (Fig. *a*) made with that manganese dioxide and solution). Fig. 5 shows the results obtained when ammonium chloride solution was used. The relations between the pH value and the potential are obviously straight-line relations. The dotted curve shows the relation between the pH value of the original solution and the potential. Fig. 6 shows the results obtained when manganese dioxide (*A*) and the solution for dry cells were used; the results showed the existence of the same relations.

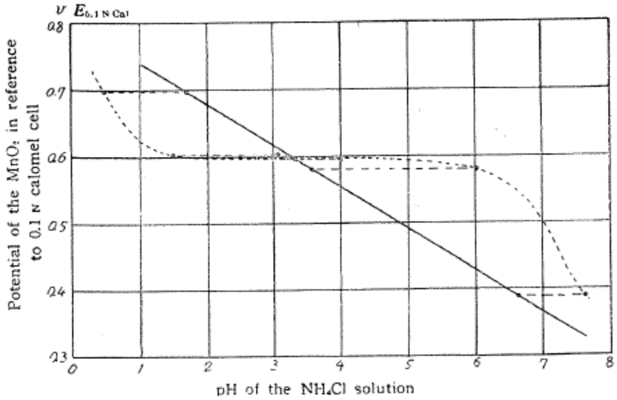

Fig. 5. The relation between pot. of *A* (Sizuoka Pref.) MnO_2 and pH of NH_4Cl (250 g/kg H_2O) solution at 25°C

As will be reported in VII below the present writer studied the relations between the pH value and the potential of the natural manganese dioxides given in Table 1 above, and also of the artificial manganese dioxides given in Table 2, also above. The results of his experiments he has shown in six figures. From these experiments it was made clear to him that correct straight-ling relations invariably exist, no matter what kind of manganese dioxide, from whatever places of production, may be used; or no matter what the elements and composition of the solutions may be. It is possible, as a result of his experiments, to explain clearly the reasons for the curves as well as the causes of the straight-lines obtained in researches carried out in this field in the past (cf. Fig. 1 and Fig. 2). Furthermore, though theoretically the inclination of the straight-lines showing these relaions should indicate a lowering of 0.059 volts (25°C) for changes in each unit pH value, it must be said that the results of past researches fail to show this inclination correctly. Again in trying to establish the relations between the pH value (after shaking) and the potential, the inclination did not correspond to the theoretical value, or it varied with the kind, or with the place of production, of the manganese dioxide, making it difficult to establish fixed relations. The present writer, however, examined the causes that brought about changes in the inclination; and basing himself upon his observations, he was able to discover a method of experimentation whereby he succeeded in obtaining straight-lines showing an inclination that agrees perfectly with theory, as described in VIII below and shown in the figures. In his experiments he used several varieties of manganese dioxide, as well as solutions varying in composition.

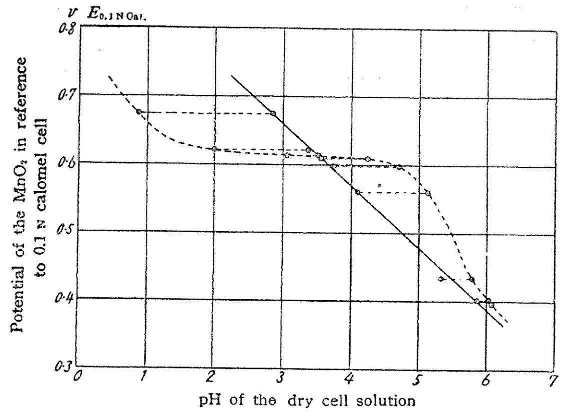

Fig. 6. The relation between potential of A (Sizuoka Pref.) MnO_2 and pH of the dry cell solution (NH_4Cl 250 g, $ZnCl_2$ 50 g, H_2O 1000 g).

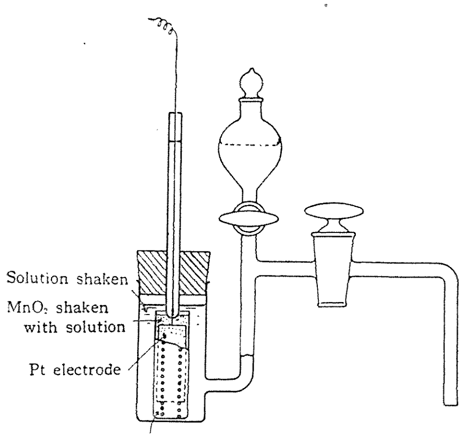

Fig. *a*

IV. Changes in the pH value, when using natural, artificial, or MnO_2 refined with nitric acid, in NH_4Cl solution and in the solution for dry cells

The writer, in order to make further investigation into the change in pH values of solutions, performed experiments using various kinds of solutions of different degrees of concentration, as well as natural and artificial manganese dioxides.

In the NH_4Cl solution, he used natural manganese dioxide from Gifu (*C*), Hokkaidō (*F*) and the South Seas (*G*), and artificial manganese dioxide manufactured by the *T*---Company (*N*) by means of heat oxidation with alkali. In the case of the first three, he obtained results which showed greater or smaller pH values of iso-acidic points; he also observed that the smaller the pH value of iso-acidic points, the greater the range in which the pH value is constant. Manganese dioxide obtained from the South Seas proved an exception in that when it was used, though the pH value of the iso-acidic point was large, the range of constant pH value was also large (Fig. 7).

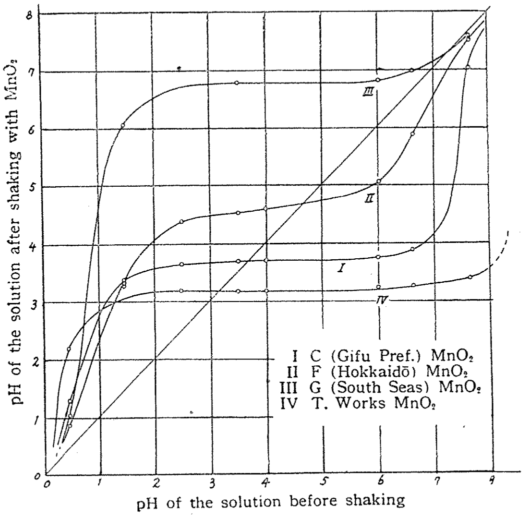

Fig. 7. pH change of the solution (NH_4Cl 250 g, H_2O 1000 g) with miscellaneous MnO_2.

The reason why the manganese dioxide obtained from the South Seas, though having a water content of 0.8% had, by exception, a pH value of the iso-acidic point of 6.0 is that it contains within itself a basic substance soluble in water.

The manganese dioxide manufactured by the *T*---Company showed, as a common characteristic of artificial products, that the pH value of the iso-acidic point was small, while, the range of constant pH value was very large.

In the solution for dry cells, whereas the writer used natural manganese dioxide from Shizuoka (*A*), Gifu (*C*), Nagano (*D*), Aomori (*E*), Hokkaidō (*F*), and from the South Seas (*G*), (Fig. 8) he observed that the pH value of the iso-acidic point was generally smaller, the greater the water content. In the Tables above, the writer has listed manganese dioxides beginning with those with greater water content, followed by those with less. The first three have a water content of from 3.0% to 8.0%, and their pH values of iso-acidic points vary from 3.4 to 3.8, showing that these oxides have strong acid properties. On the other hand, manganese dioxides produced in Aomori and Hokkaidō have a water content of 1.3% to 1.6%, their pH values of iso-acidic points varying from 3.9 to 4.5, showing that these oxides have weak acid properties. Then in

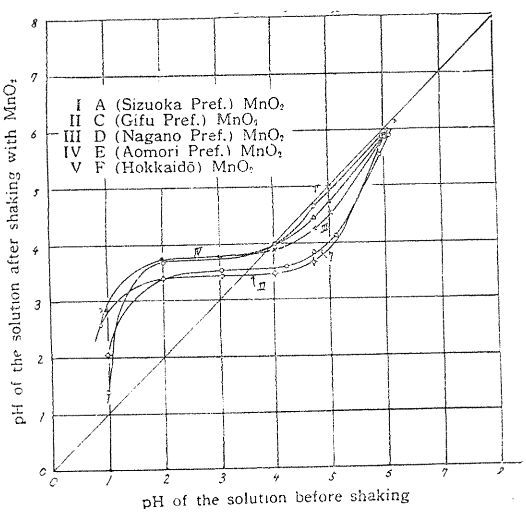

Fig. 8. pH change of the dry cell solution (NH_4Cl 250 g, $ZnCl_2$ 50 g, H_2O 1000 g) with natural MnO_2.

regard to the range in which the pH value is constant, the writer observed that in the first three, it was large, and in the following two, small, showing that this range is larger, the smaller the pH value of the iso-acidic point.

The writer used artificial manganese dioxide manufactured by the Merck Company (*H*) in Germany, the I. G. Company (*I*), and two kinds made by the Schreyer Company (*J*) (*K*) (four all together) (Fig. 9). He found that with three out of these four, the pH value of the iso-acidic point was small and the range of constant pH value was large, thus differing from natural products. However with one of the two products of the Schreyer Company (*K*), it was observed that it resembled the natural manganese dioxide from Aomori (*E*) to such an extent that doubt arose as to whether it was indeed an artificial product.

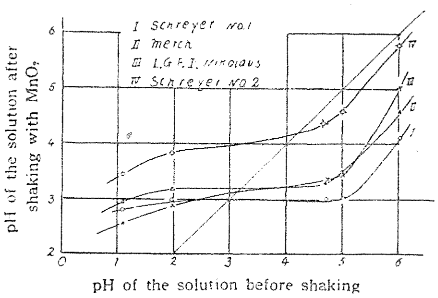

Fig. 9. pH change of the dry cell solution with artificial MnO_2.

The writer also experimented with artificial manganese dioxides prepared by himself by electrolysis of $Mn(NO_3)_2$ and of $MnSO_4$ (Fig. 10). He discovered that their pH values of the iso-acidic points were extremely small, being 2.1 and 1.9 respectively. He then experimented with natural products from Gifu, Hokkaidō, and the South Seas, refined by washing in nitric acid (Fig. 11). The results showed that as compared with unrefined products, the pH values of the iso-acidic points were perceptibly smaller.

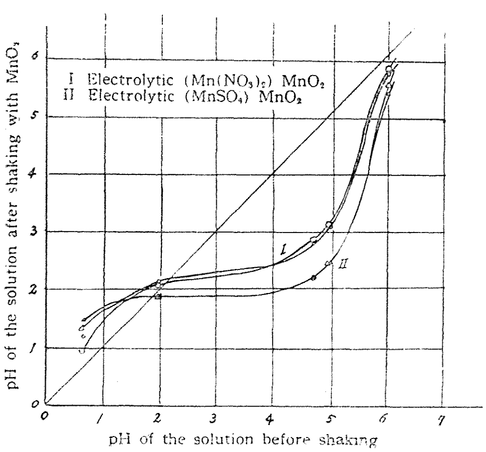

Fig. 10. pH change in the dry cell solution with electrolytic MnO_2.

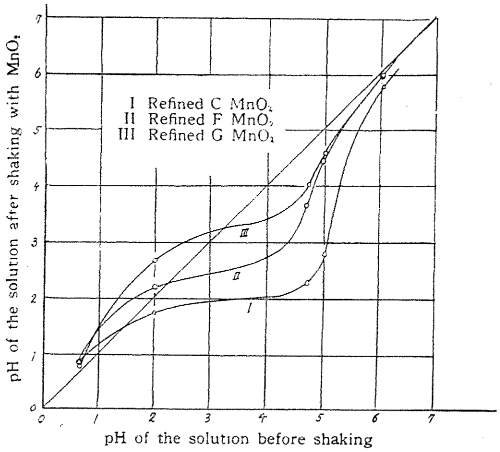

Fig. 11. pH change in the dry cell solution with refined MnO_2.

In view of the results of the foregoing experiments, the writer feels that changes in the pH value can be satisfactorily explained when it is understood that the property of making acidic[10] the neutral ammonium chloride solutions and neutral solutions for dry cells is not more pronounced in those with greater MnO_2 content, but is more so in those in which, though the MnO_2 content is small, the water content is large; and that by means of this property, a part of manganese dioxide acts by virtue of its water content as a variety of acid. In other words, though this acid, about which studies have been made in connection with artificial hydrated manganese dioxide,[11] is really per-manganous acid (H_2MnO_3), and this being indissoluble in water, does not make that water acid, yet it has the property of adding H^+ to the solution by replacing the NH_4^+ in solutions of NH_4Cl, or when it is shaken with solutions for dry cells. And in the latter case, there are grounds for believing that probably the acid replaces the Zn^{++} together with the NH_4^+. It is for this reason that in solutions whose pH value is greater than the iso-acidic point, there is possibility of decrease of the pH value. In solutions whose pH value is smaller than the iso-acidic point and hence having strong hydrochloric acid properties, the pH value is increased as a result of reaction on the basic substance contained in the manganese dioxide. The iso-acidic point is the point at which these two reactions are in mutual antagonism ; again, the range of constant pH value is the result of buffer action due to these two reactions. In general, artificial manganese dioxides have a high water content as well as per-manganous acid content, so that their pH values at the iso-acidic point are small. However, manganese dioxide prepared by heat decomposition of manganese nitrate have a low water content and its pH value at the iso-acidic point is also great. Again, if refined manganese dioxides, though their pH value at the iso-acidic point is small, show no change in the range of constant pH value, it must be because there is no change in the properties of the manganese dioxide even when basic substances are removed by refining with nitric acid.

V. Causes for the changes in pH value of solutions due to manganese dioxide

Using manganese dioxides from Gifu (*C*), Nagano (*D*), Aomori (*E*), and Hokkaidō (*F*), changes in the concentration of Cl^-, NH_4^+, H^+ due to shaking with 0.5 M of NH_4Cl solution (Fig. 12) were measured (Table 3), and it was found that at the iso-acidic point, H^+ does not change, but that the NH_4^+ in the solution is decreased, and instead, the basic substances such as Mn^{++}, Fe^{+++}, etc., in the manganese dioxide are dissolved out into the solution.

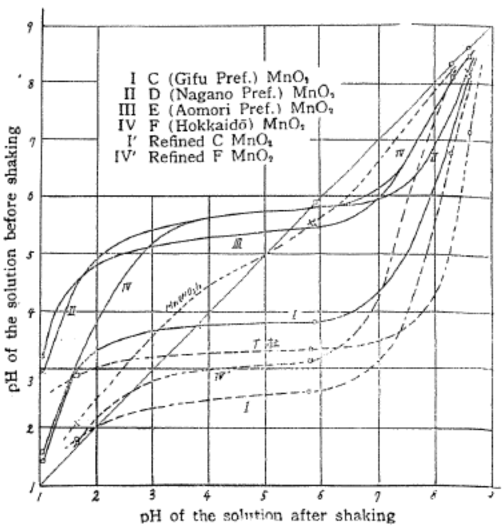

Fig. 12. pH change of 0.5 M NH_4Cl solution with miscellaneous MnO_2

In solutions whose pH value is greater than the iso-acidic point, the NH_4^+ is decreased, and instead, H^+ operates to make the solution acidic, while at the same time, metal ions in the basic substances are dissolved out into the solution.

In the case of basic solutions, the ammonia was easily decreased, showing that neutralization with the acid of the manganese dioxide had taken place.

In the case of solutions whose pH value was smaller than their iso-acidic point, H^+ was decreased, and instead, Mn^{++}, Fe^{+++}, Cu^{++}, alkali earth metal

Table 3. Increase and decrease of Cl^-, NH_4^+ and H^+ with natural MnO_2

		C (Gifu Pref.)	D (Nagano Pref.)	E′ (Aomori Pref.)	F′ (Hokkaidō)
Cl^- 10^{-5} Mol / 1 g MnO_2 content only	Acidic pH 1.05	− 7.27	− 4.12	− 4.24	− 4.86
	Neutral pH 5.885	− 0.62	− 1.21	− 1.47	− 1.88
	Basic pH 8.585	− 0.00	− 0.18	− 0.57	− 1.11
NH_4^+ 10^{-5} Mol / 1 g MnO_2 content only	Acidic pH 1.045	− 4.25	−10.75	− 4.85	− 1.20
	Neutral pH 5.885	− 7.59	−21.53	− 7.805	− 2.72
	Basic pH 8.585	−35.48	−35.70	−17.38	−11.29
H^+ 10^{-5} Mol / 1 g MnO_2 content only	Acidic pH 1.045	− 28.3	−50.5	− 48.0	−30.37
	Neutral pH 5.885	+ 0.31	− 0.0	0.0	0.0
	Basic pH 8.585	+38.74	−34.55	+ 17.5	+15.47

ions, etc., in the basic substances were dissolved out into the solution. Moreover, a considerable quantity of NH_4^+ was decreased, showing, thereby, that NH_4^+ is an ion which is extremely easy to obtain by selection.

VI. Relation between the iso-electric point and the iso-acidic point of manganese dioxide

In view of the fact that there are certain works of research which consider manganese dioxide as an amphoteric electrolyte,[12] and also since there is a report[13] which states that the iso-acidic point mentioned in the present research is to be identified with the iso-electric point,[14] the writer performed experiments with the apparatus[15] (Fig. 13) in order to make this relation clear, using diluted hydrochloric

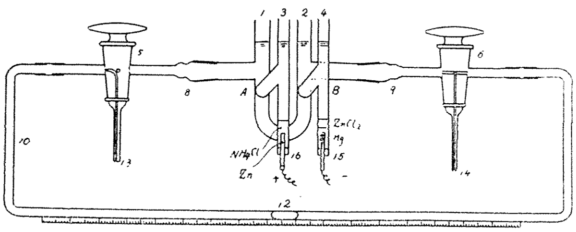

Fig. 13. Measuring apparatus for the elrctro-osmosis of MnO_2 with pH of solution.

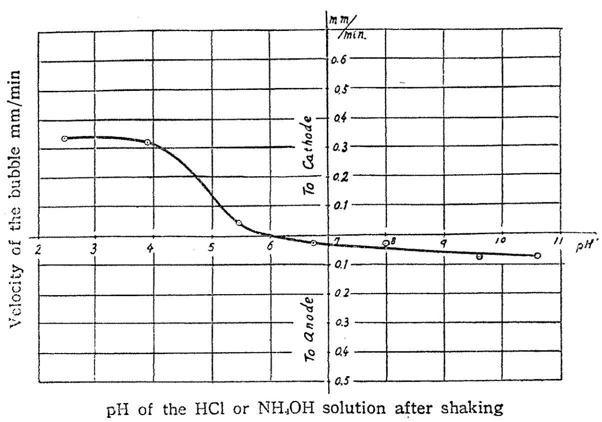

Fig. 14. Electro-osmosis of *B* (Gifu Pref.) MnO_2 in HCl or NH_4OH solution with varying pH value.

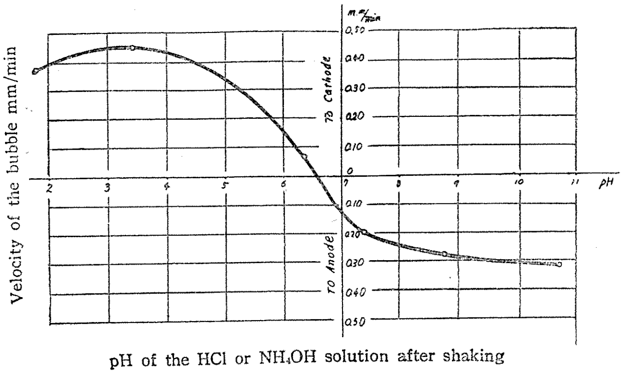

Fig. 15. Electro-osmosis of *F′* (Hokkaidō) MnO_2 in HCl or NH_4OH solution with varying pH values.

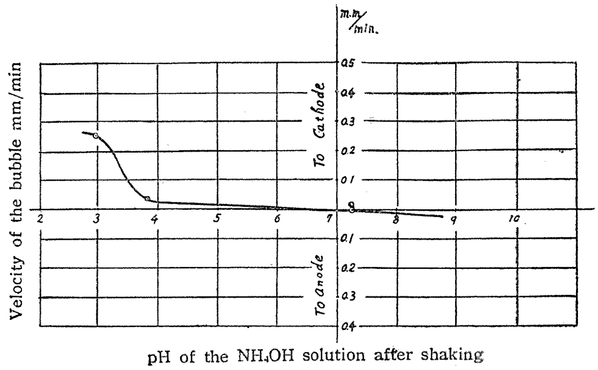

Fig. 16. Electro-osmosis of *B* (Gifu Pref.) MnO_2 in the pH of 0.5 M of NH_4Cl solution.

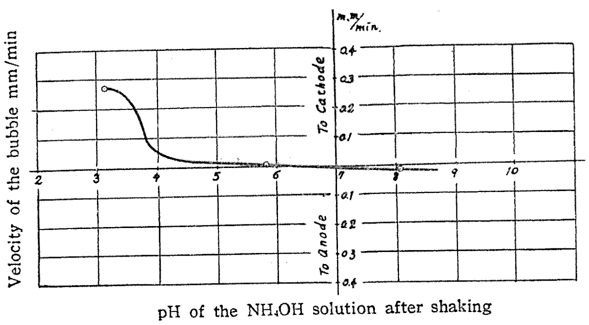

Fig. 17. Electro-osmosis of *F′* (Hokkaidō) MnO_2 in 0.5 M of NH_4Cl solution.

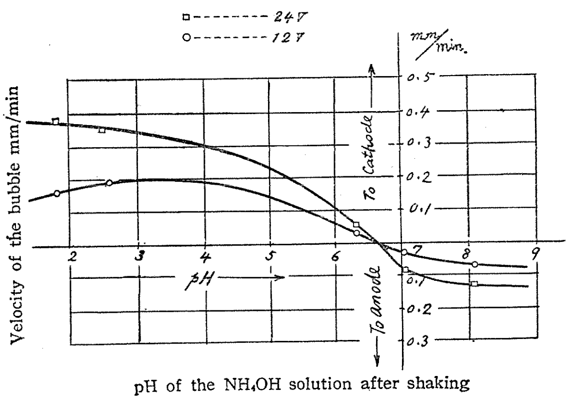

Fig. 18. Electro-osmosis of the refined *B* (Gifu Pref.) MnO_2 in 0.5 M of NH_4Cl solution.

acid or ammonia solutions of different pH values, and also a solution of 0.5 M of NH_4Cl to which either hydrochloric acid or ammonia was added, to vary its pH values. For manganese dioxide, produces from Gifu (Fig. 14) and Hokkaidō (Fig. 15) with the former solution, untreated natural products (Figs. 16 and 17), as well as refined (Figs. 18 and 19) with the latter solution, were used. But in all the cases, the iso-electric point was found approximately to lie around pH value 6.5, and in those cases in which the pH value was greater, the manganese dioxide was found to carry a negative charge, and in those cases in which the pH value was smaller, it was found to carry a positive charge. Hence it was made clear that quite unlike the iso-acidic point, the iso-electric point is essential to manganese dioxide (Fig. 20).

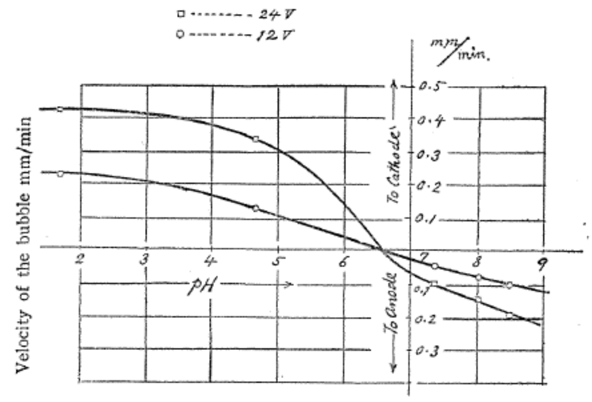

Fig. 19. Electro-osmosis of the refined *F* (Hokkaidō) MnO_2 in 0.5 M of NH_4Cl solution

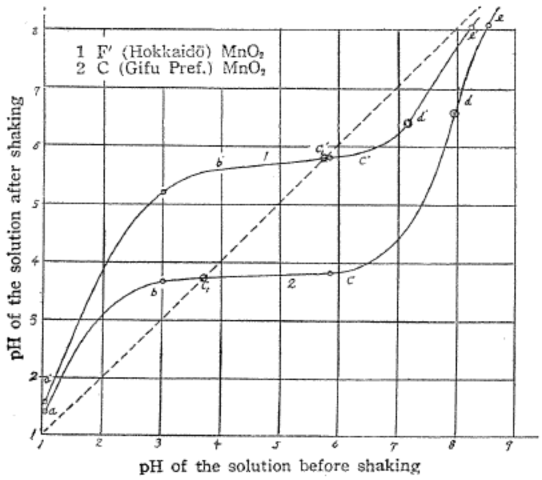

Fig. 20. Iso acidic point and iso-electric point of *B*, and *F′* MnO_2 in 0.5 M of NH_4Cl solution

VII. Relation between the potential and the pH value of various kinds of manganese dioxide in various solutions

For experimentation, the following samples of manganese dioxides were used by the present writer: Natural products, five kinds; German artificial products, four kinds; products obtained by the writer by electrolysis of manganese nitrates; products obtained by electrolysis of manganese sulphates; refined products from Gifu; refined Hokkaidō products; refined South Seas products. For solutions, the followings were used: Solutions for dry cells, (Fig. 21), (Figs. 24∼26), ammonium chloride solution (Fig. 22), and solutions of 0.5 M of ammonium chloride (Fig. 23). In all the cases it was observed that the relation between the pH value and the potential after shaking could be expressed by straight lines. Next, an attempt was made to arrange various kinds of manganese dioxide in the order of their potential (Table 4). Results showed that comparing the value of $E°$, those refined

Table 4. MnO_2 normal potentials ($E°$) and inclinations after shaking with MnO_2

Place of production	$E°$ (Volt)	Inclination
NH_4Cl 250 g solution		
C (Gifu Pref.)	0.841	0.0650
F' (Hokkaidō)	0.867	0.0675
G (South Seas)	0.868	0.0725
T. Company	0.900	0.069
NH_4Cl 0.5 M solution		
C (Gifu)	0.834	0.067
D (Nagano)	0.888	0.0707
E (Aomori)	0.871	0.0677
F' (Hokkaidō)	0.963	0.0770
T. Company	0.910	0.0440
$Mn(NO_3)_2$ Heat decomposed)	0.905	0.0810
C (purified)	0.955	0.0675
F' (purified)	0.955	0.0698

Dry cell solution (NH_4Cl 250 g, $ZnCl_2$ 50 g, H_2O 1000 g)

	MnO_2 production	$E°$(Volt)	Inclination
Natural	*C* (Gifu Pref.)	0.837	0.0645
	D (Nagano Pref.)	0.880	0.0707
	E (Aomori Pref.)	0.881	0.0685
	F' (Hokkaidō)	0.905	0.0758
Artificial	*J* (Schreyer No. 1)	0.960	0.0690
	H (Merck)	0.983	0.0746
	I (I.G.)	0.922	0.0558
	K (Schreyer No. 2)	0.907	0.0770
	L (Electrolytic $Mn(NO_3)_2$)	0.9145	0.0731
	M (Electrolytic $MnSO_4$)	0.9325	0.0646
	C (purified)	0.9578	0.0637
	F' (purified)	0.9651	0.0652
	G (purified)	0.9240	0.0888

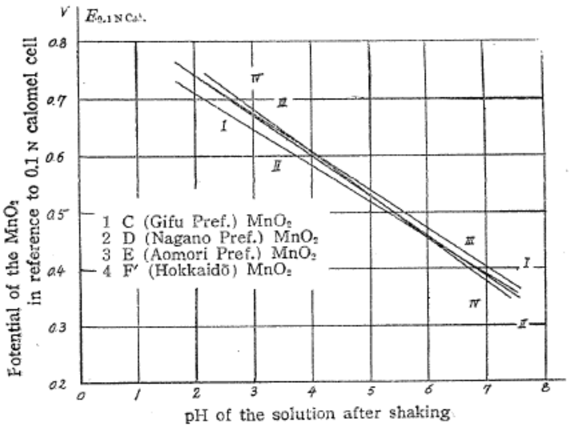

Fig. 21. Relation between potential and pH of natural MnO_2 in solution for dry cell.

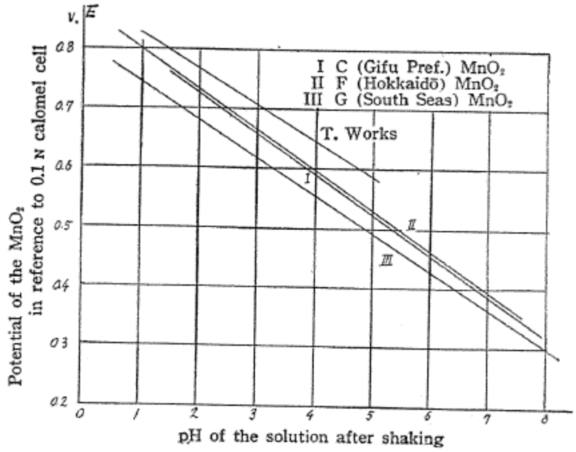

Fig. 22. Relation between the potential and pH of NH_4Cl (250 g H_2O 1000 g) solution after shaking.

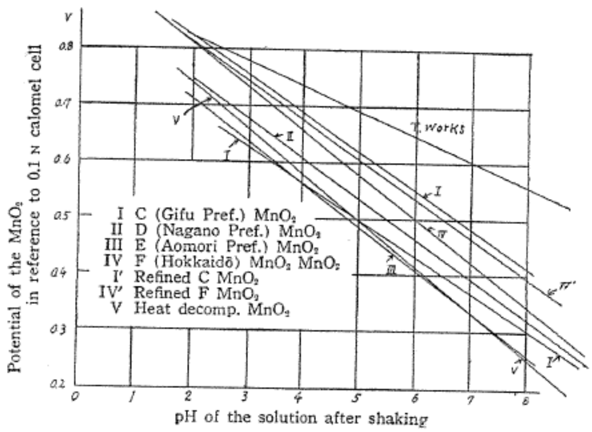

Fig. 23. Relation between the potential and pH of 0.5 M NH_4Cl solution after shaking

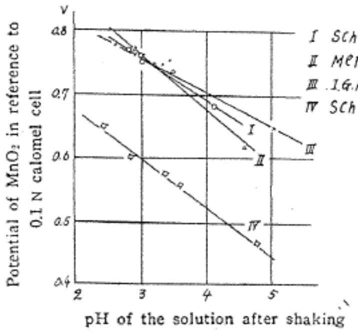

Fig. 24. Relation between potential of artificial MnO_2 and pH of the solution for dry cell.

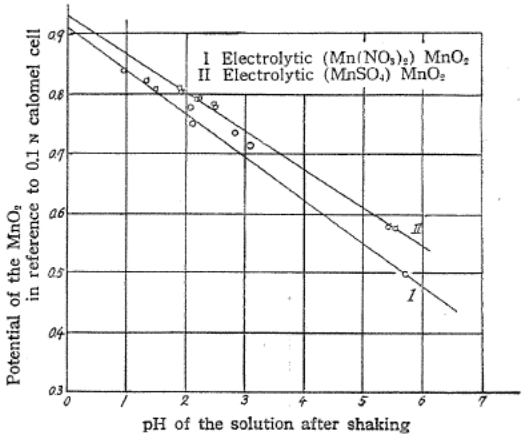

Fig. 25. Relation between potential of electrolytic MnO_2 and pH of the solution for dry cell.

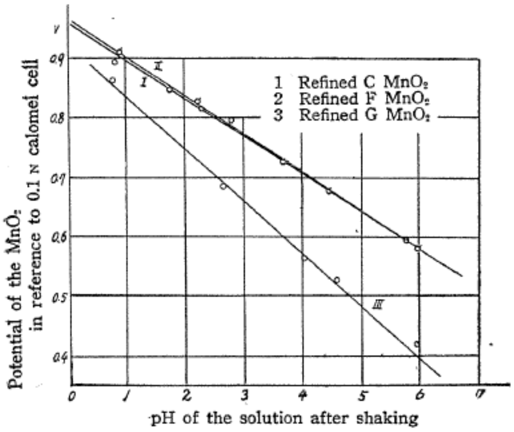

Fig. 26. Relation between potential of refined MnO_2 and pH of the solution for dry cell.

by washing in nitric acid were highest, products obtained by electrolysis next, and natural products generally lower. Among natural products, those from Hokkaidō were highest, those from Aomori and Nagano next, and those from Gifu lowest. But as one of the reasons for this difference, the degree of purity of manganese dioxide must be given. In other words, with the exception of the product obtained from Aomori, the order in the natural products coincides with the order of the MnO_2 content; and even in the case of refined products, those with the highest $E°$ were those from which impurities had been removed, and the purity of the surface of the particles was highest. However, in the case of products obtained by electrolysis, the fact that their potential was high though their MnO_2 content was small, leads one to think that it is necessary to take into consideration the influence exerted by their physical or chemical condition.

VIII. The inclination of the straight line showing the relation between the potential and the pH value

In the foregoing experiments, though straight-line relations were obtained, their inclination was in all the cases greater than the theoretical value of 0.059.

A number of researches on the relation between the potential and pH value of solution have been attempted to determine the theoretical relation, but so far as the writer is aware, there has been neither experimental evidence nor research on the theoretical inclination.

Hence study was made by the present writer of the conditions whereby the theoretical inclination might be obtained, as the theory above proposed had yet to be demonstrated by experiment. For the inclination of the straight line showing the relation between potential and pH value, Cahoon obtained 0.061 (cf. Fig. 1), a figure close to the theoretical value; but the solution used by him was a specially concentrated one (cf. Table 5), in which the buffer action was particularly pronounced. Consequently the present writer observed that changes in pH value

Table 5. Composition of buffer solution and its pH value

Composition of solution	$ZnCl_2$ (%)	62.5	50.1	49.0	38.20	11.14	10.75
	NH_4Cl (%)	—	—	18.0	26.80	27.16	26.20
	NH_4OH (%)	—	—	—	—	—	3.50
	H_2O (%)	37.5	49.9	33.0	35.00	61.70	59.55
pH of the solution	Glass electrode (Cahoon)	1.66	2.94	2.69	3.75	4.73	5.76
	Hydrogen electrode (Sasaki)	1.44	2.14	1.79	2.14	4.33	5.74

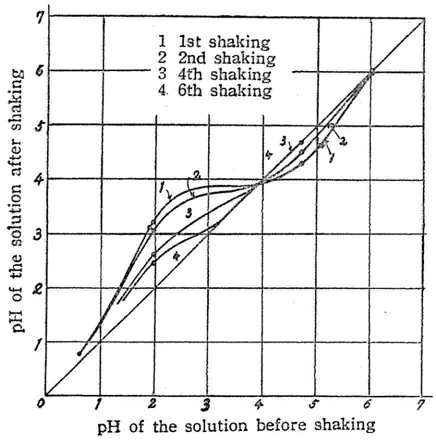

Fig. 27. Relation between pH changes and number of shakings of *A* (Sizuoka Pref.) MnO_2.

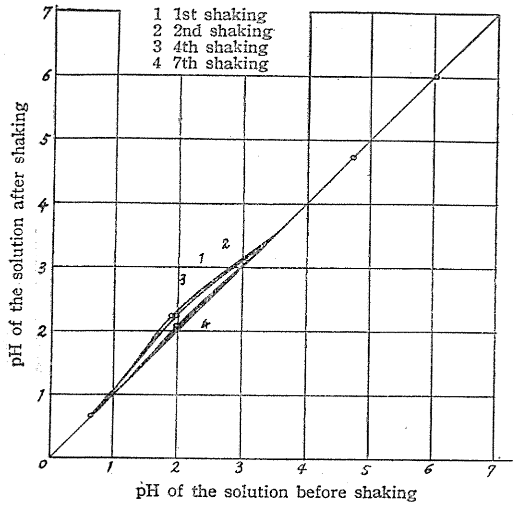

Fig. 29. Relation between pH changes and number of shakings of *F′* (Hokkaidō) MnO_2.

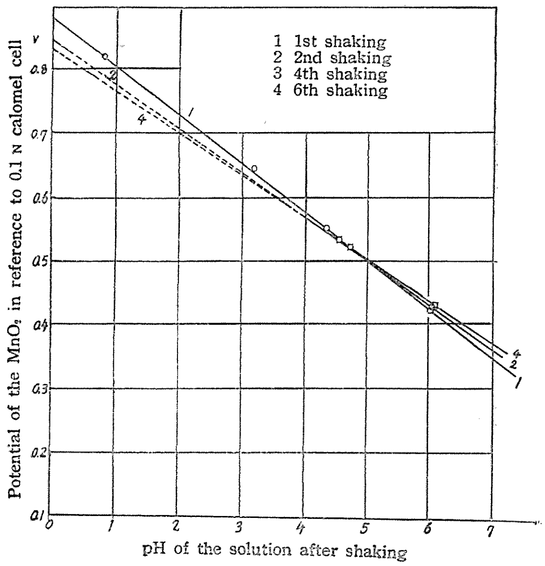

Fig. 28. Relation between inclination changes and number of shakings of *A* (Sizuoka Pref.) MnO_2.

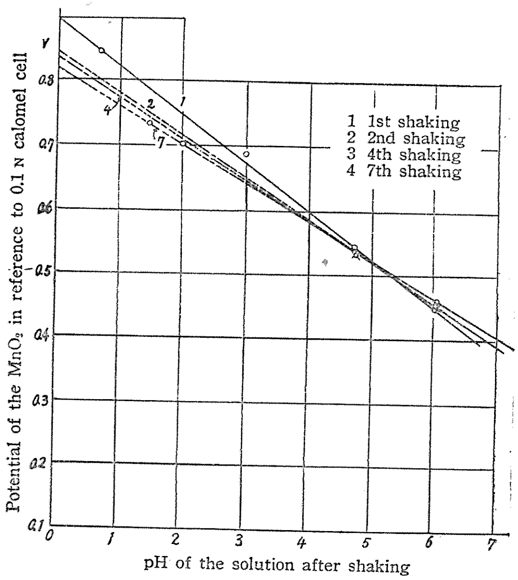

Fig. 30. Relation between inclination changes and number of shakings of *F* (Hokkaidō) MnO_2.

were small; whereupon assuming that better results would be obtained if measurements of the potential were made under conditions such that the solution would retain the original pH value, he proceeded to experiment, and with success. It is clear that if for a definite quantity of manganese dioxide, an indefinite quantity of solution were used, there should be no changes in pH value; therefore only the solution was changed and repeatedly shaken (Figs. 27~40). For the experi-

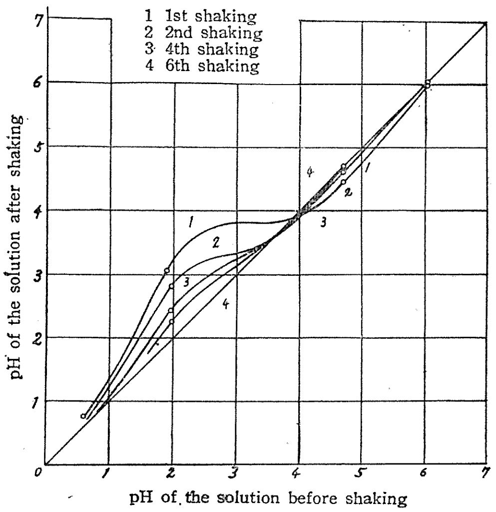

Fig. 31. Relation between pH changes and number of shaking of *C* (Gifu Pref.) MnO_2.

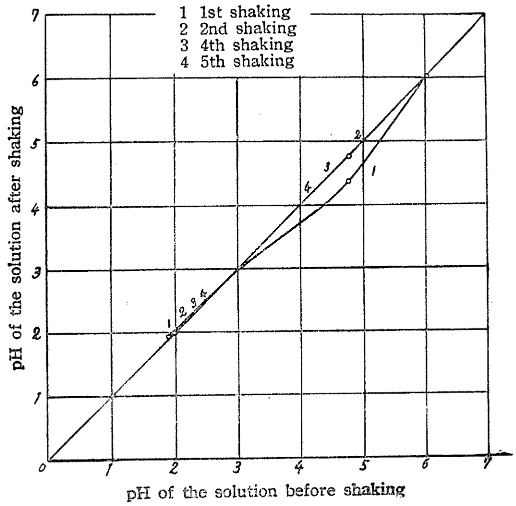

Fig. 33. Relation between pH changes and number of shaking of heat decomposed MnO_2.

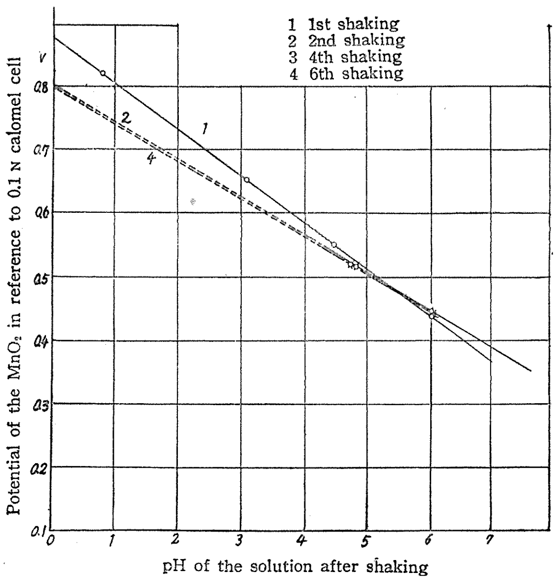

Fig. 32. Relation between inclination changes and number of shakings of *C* (Gifu Pref.) MnO_2.

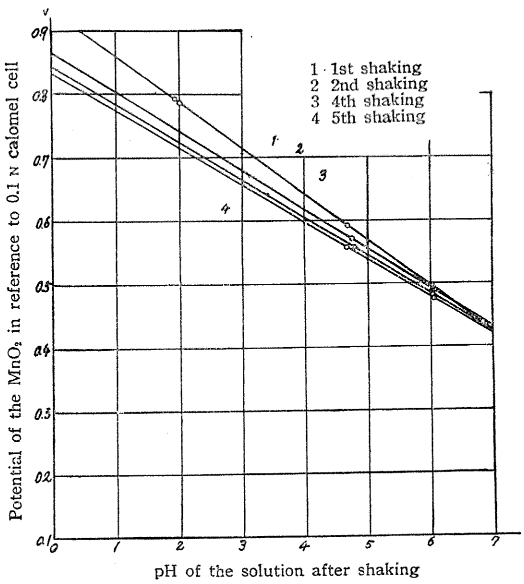

Fig. 34. Relation between inclination changes and number of shaking of heat decomposed MnO_2.

ment the writer used the followings: Products from Shizuoka (Figs. 27 and 28), Hokkaidō (Figs. 29 and 30), and Gifu (Figs. 31 and 32), products (Figs. 33 and 34) obtained by heat decomposition from manganese nitrates, as well as those obtained by electrolysis and by refining (Figs. 35 and 36). For each gram of manganese

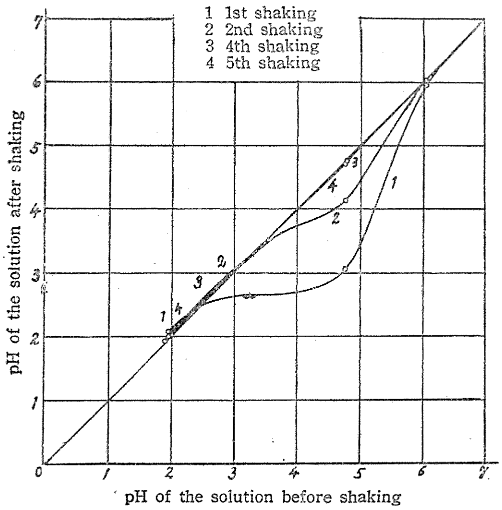

Fig. 35. Relation between pH changes and number of shaking of electrolytic MnO_2.

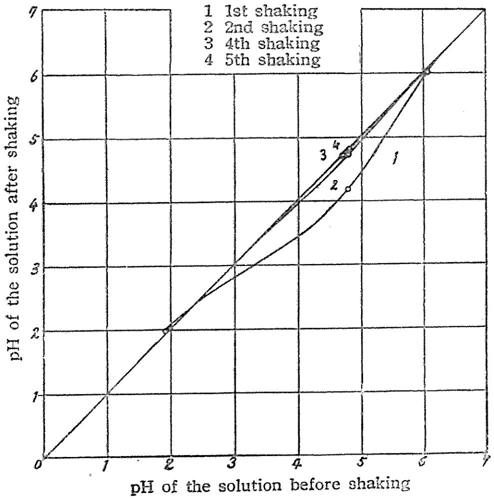

Fig. 37. Relation between pH changes and number of shaking of refined *C* (Gifu Pref.) MnO_2.

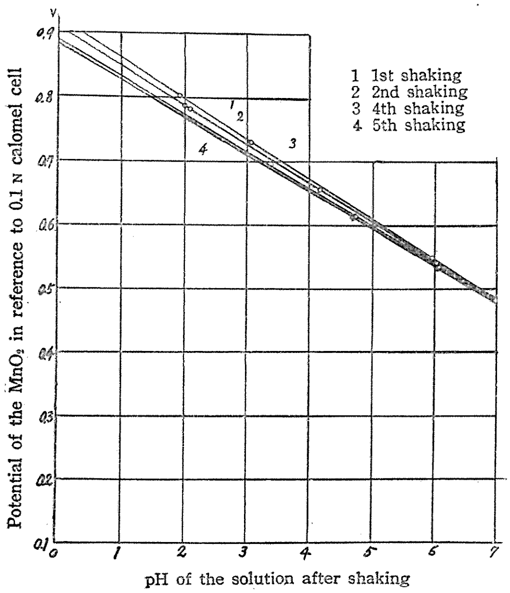

Fig. 36. Relation between inclination changes and number of shaking of electrolytic MnO_2.

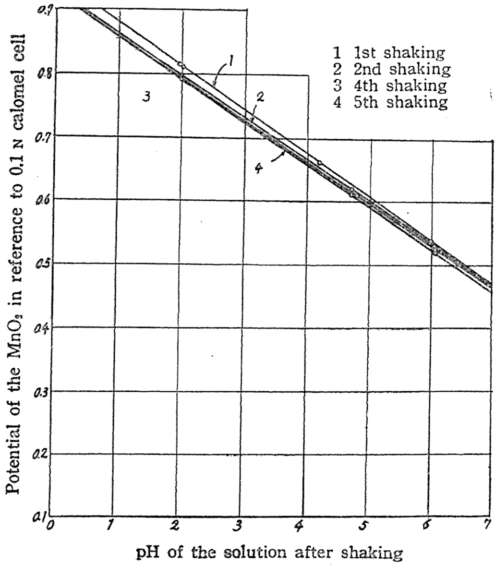

Fig. 38. Relation between inclination changes and number of shaking of refined *C* (Gifu Pref.) MnO_2.

dioxide, acidic, neutral, and basic solutions for dry cells (25 cc) were mixed, shaken at 25°C, and the solution changed, whereupon it was found that the change in pH value became gradually smaller, until with the renewal of the solution for the 4th to the 7th time, the pH value ceased to change altogether, and the inclination of the straight line joining the neutral point with the basic point, excepting cases in which products obtained by electrolysis were used, was strictly in accordance with

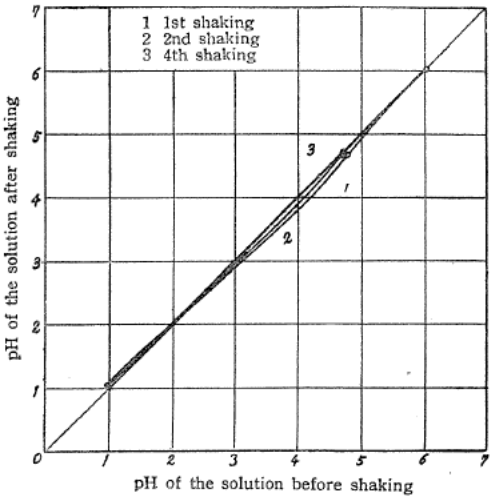

Fig. 39. Relation petween pH changes and number of shaking of refined F (Hokkaiō) MnO_2.

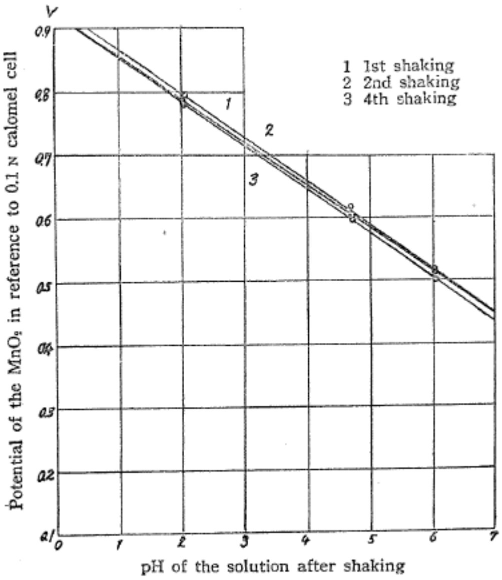

Fig. 40. Relation between inclination changes and number of shaking of refined F (Hokkaidō) MnO_2.

the theoretical inclination, and in all cases acidic points were found to be in a higher position than the straight line which has the theoretical inclination. The reason for this seems to be the fact that these products of acidic point were refined in acid solution. Experimenting with refined products from Gifu (Figs. 37 and 38) and Hokkaidō (Figs. 39 and 40), it was found that upon the 4th or the 5th renewal of the solution, the pH value reached a stage where changes were no longer observable, and the inclination of the straight-line showing the relation between the potential and the pH value was 0.0676 and 0.0698 respectively. But in neither case the theoretical value was reached. It is of interest that the theoretical straight line with 0.059 inclination obtained with the repeated renewal of solution coincides strictly with the result of special buffer solutions (Table 5), where the solution was not renewed but shaken with MnO_2.

IX. Method of determination of the properties, as well as the uses, of the various kinds of manganese dioxides as a depolarizer

Though the discharging capacity of dry cells is chiefly determined by the manganese dioxide used, its oxidation property was generally considered to be the sole determining factor. The writer demonstrated that the property of manganese dioxide to change the pH value of solutions is as important a property as the oxidation property. The former property has direct relation with the anode potential, durability, and consequently, the discharging capacity. In other words, the H^+ produced by the mutual loss of ions in NH_4^+ and Zn^{++} neutralizes the ammonia produced by discharge and keeps the potential high. Again, since towards the end of an electric discharge, there is a property to act as a deterrent to the increase of internal resistance by decreasing the formation of such products as basic zinc compounds and $Zn(NH_3)_2Cl_2$ as results of the discharge, those with smaller pH values of the iso-acidic point or those with greater range of constant pH value, have greater discharging capacity. And in order to prove this, the writer used the following samples: Natural products, three kinds; refined products, two; artificial products, seven; and made dry cells for lamps, and measured the discharging capacity (Table 6, Figs. 42 and 43). He found, thereupon, that with the

Table 6

	Production		MnO_2 g used in mix	Graphite	Service (mean) minutes (4 Ω continuous)	MnO_2 % in product	Iso-acidic point
Natural	*B* (Gifu Pref.)		21.8	practically used	510	81.2	3.42
	E (Aomori Pref.)		21.8	do.	390	88.5	3.91
	F (Hokkaidō)		21.8	do.	360	90.5	4.07
Natural refined	HNO_3 washing	*B*	21.8	market	610	86.37	1.48
		F	21.8	do.	432	92.85	2.27
	Electrodialysis	*B*	21.8	do.	630	87.21	—
		F	21.8	do.	462	93.03	—
Artificial	Germany	Shreryer No.1	10.0	do.	415	70.21	2.98
		I. G	12.0	do.	500	71.47	3.18
		Merch	14.4	do.	510	69.39	3.20
		Scheryer No. 2	21.0	do.	430	74.36	4.18
	Electrolytic	$Mn(NO_3)_2$	13.0	do.	548	93.37	2.0
		$MnSO_4$	21.8	do.	450 (not wash) / 715 (wash treated)	82.12 / 89.00	2.10
	Heat oxidation	with alkali	12	do.	492	71.83	1.88

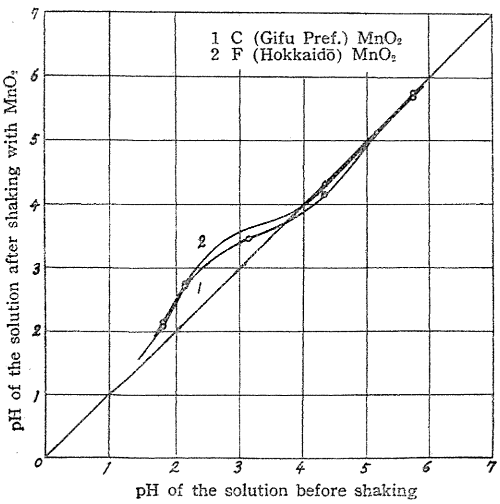

Fig. 41. pH change of the Cahoons solution caused by shaking witn MnO_2.

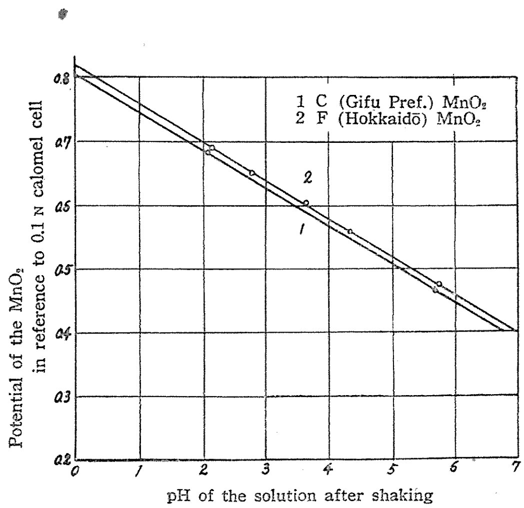

Fig. 42. MnO_2 potential and pH of the buffer solution.

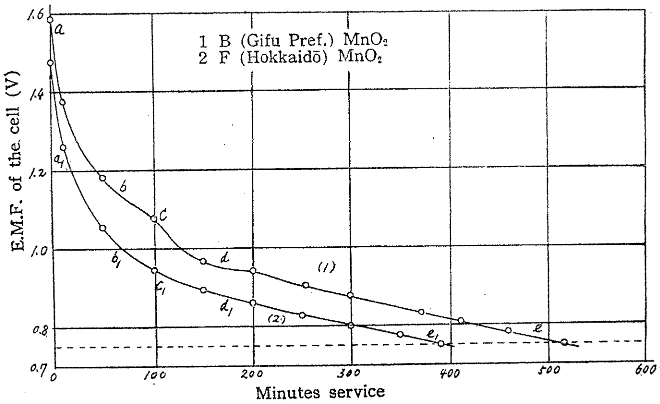

Fig. 43. Characteristic curve in 4 ohm continuous discharge of dry cells with *B* (Gifu Pref.) MnO_2 and *F* (Hokkaidō) MnO_2 as depolarizer.

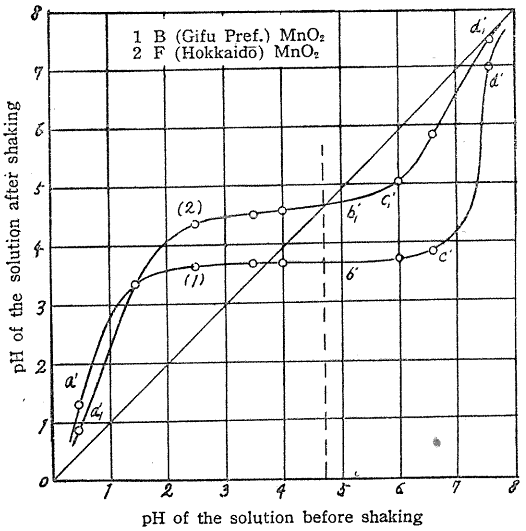

Fig. 44. pH change of solution caused by shaking with MnO_2.

natural products obtained from Gifu, Aomori and Hokkaidō, refined products, and products obtained by electrolysis, the above theory is applicable. But with German artificial products, four kinds, and with products obtained by heat oxidation with alkali and manufactured by the *T*---Company, though the iso-acidic point was smaller, the discharging capacity was not larger, due to the fact that in these products, the apparent specific gravity was small, and consequently, only a small amount of manganese dioxide could be contained in the same mix volume. The result therefore is not necessarily contradictory with the theory. The experiments do show, however, that the discharging capacity depends upon as much the smaller iso-acidic point and the larger content of water of the manganese dioxide as on the content of analytic MnO_2 which acts as oxidizer.

In regard to methods of selecting manganese dioxide for use in dry cells: For the current-type dry cells whose discharge rate is comparatively large and the term during which they can be used is short, manganese dioxide whose pH value of the iso-acidic point is small, the potential high, and capacity large, should be used. On the other hand, for the storage-type dry cells, which, like the B dry cells for Radio, have small discharge rate and the term during which they can be used is long, the kind of manganese dioxide to be used is that with small self-discharge rather than with large capacity. And for this reason, manganese dioxide whose pH value of the iso-acidic point is large and which has few impurities, that is, that with little zinc corrosion, should be used.

The present writer hopes to publish more detailed reports on MnO_2 for dry cells in the near future.

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