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The effect of different concentrations of the hydrogen-ion upon the solubility of manganese sulfate in solutions of six representative nutrient salts

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Thesis for the degree Master of Science,
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Memorandum

Dept. Chemistry Date, May 15, 1930.

To: The Director of the Graduate School.

Subject: Thesis for Master's Degree.

The thesis of Mr. Oliver S. Plantinga entitled "The Effect of Different Concentrations of the Hydrogen Ion upon the Solubility of Manganese Sulfate in Solutions of Six Representative Nutrient Salts" has been examined by the committee appointed by the Director of the Graduate School. ~~A conference has been held with the candidate, and~~ The undersigned committee herewith approves and accepts the thesis as in part fulfilling the requirement for the degree of Master of Science.

C. A. Peters
W. F. Powers.
F. C. Moore

Signed:

THE EFFECT OF DIFFERENT CONCENTRATIONS OF THE HYDROGEN-ION UPON THE SOLUBILITY OF MANGANESE SULFATE IN SOLUTIONS OF SIX REPRESENTATIVE NUTRIENT SALTS

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Thesis submitted for
the degree of
Master of Science

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THESIS OUTLINE

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I. INTRODUCTION

Experiments with soil and nutrient solution cultures have shown that manganese, in very small amounts, is essential to the normal growth of plants.

Since the availability of the different plant nutrients varies widely with the hydrogen-ion concentration, or pH, it has been found necessary to regulate and to control very carefully the pH of the nutrient medium; the range for the different plants being about pH 3.4 - pH 8.2. Since manganese is normally present in soil in very small amounts, its availability at different pH s, and in the presence of the different plant nutrients, is an important problem.

II. PURPOSE

It is the purpose of this investigation to study the solubility of manganese in solutions of six typical nutrient salts, and mixtures of these salts, over the pH range of plant growth. By thus determining how much soluble manganese is present under stated conditions, future workers will have some guide to the amount of manganese available, knowing the pH of the solution and the kinds of salts present.

It is further the object of this work to find if there are any unusual combinations of manganese with nutrient salts, which give sharp variations in the pH, or in the amounts of manganese available. A previous worker, Miss MacMasters (47) has shown that iron in the form of ferric phosphate may possibly combine with nutrient salts to lower the pH.

III. REVIEW OF LITERATURE

A. The Presence of Manganese in the Living World.

Perhaps the earliest reference to the subject of manganese in relation to plant life is that of Scheele (1774) (71). He found that the soil contained small amounts of this element, and that plants growing in the soil assimilated small quantities of it. He made no effort, however, to determine whether or not the manganese was an element essential to the growth of plants.

De Saussure (1804) (21) detected manganese in plant ash. He found a smaller percentage in the seeds than in the stems, and also noted that the leaves of trees contained less in autumn than in spring. At first the oxides of iron and manganese were classed together as "metallic oxides", and little or no attempt was made to separate them and get some idea of their relative abundance. John (1814) (34) in several rough analyses of plants indicated the presence of manganese. Among the plants he analyzed were Solanum tuberosum (the potato), Brassica oleracea viridis L. (wild mustard), Conium maculatum (poison hemlock), Aesculus (horse chestnut) (outer bark), and Arundo sacchar (sugar cane). No further references were found until 1847, as probably manganese was overlooked and classed with iron in any analyses made during that time.

Kane (1847) (37) found traces of manganese in the ashes of some samples of flax, but none in others. Upon examination of the soil on which the flax was grown he found that the flax which contained no manganese grew on a soil deficient in that element, and that the flax containing manganese came from a soil which had the element present in significant amounts. Mayer and Brazier (1849) (51) confirmed Kane's results.

Herapath (1849) (32) from an analysis of vegetables found manganese in cauliflowers, swede turnips, beet root, and in one variety of potato (Fortyfold).

Malagati and Durocher (1858) (49) made a quantitative investigation but did not separate manganese from iron and aluminum. The mean percentage of the three was 0.85 - 5.06%, according to the varieties of plants concerned, Cruciferae possessing the least and Leguminosae the most. Analytical data were also presented by Wolff (1871) (90) including Trapa natans (water chestnut) (0.15% Mn_3O_4), Acorus calamus (sweet flag) (1.52% Mn_3O_4), Alnus incana (the alder) (0.73% Mn_3O_4), and Pyrus communis (the common pear) (2.15% Mn_3O_4). Wolff found that many other plants also contained manganese.

Campani (1876) (17) detected a phosphate of manganese in plant ash, and claimed to be the first to discover the element in wheat. He is, however, preceded by LecLerc (1872) (40) who found wheat to contain 0.0113% Mn_2O_3. He also gave results on

rice (0.0010% Mn_2O_3). The ash of oak yielded 1.488% Mn_2O_3, of the fir tree 4.51% Mn_2O_3, and of the lime tree 3.74% Mn_2O_3. Leclerc used the lead dioxide test for manganese.

Dunnington (1878) (23) detected manganese in the ash of wheat. After separation from iron he estimated that 0.027% of the ash was manganese.

Maumené (1884) (50) found that wheat contained 0.0067 to 0.02% manganese. He also detected the element in rye, barley, potatoes, beets, carrots, lentils, peas, lettuce, parsley and in infinitely small traces in the fruit, apples and grapes.

Riccicardi (1889) (66) and Hattensaur (1890) (31) added to the list of plants proved to contain manganese. Guerin (1897) (30) studied the manganese content of woody tissue and found 0.402% manganese in a brown precipitate which he separated from sawdust. He regarded the precipitate as a "nucleinic" combination, which he supposed to occur generally in the woody tissue of all plants.

Pichard (1898) (64) gives a list of thirty-six orders of plants, including both phanerograms and cryptograms, in which he detected manganese. The manganese was concentrated in those parts of the plant where the greatest amount of chemical activity occurs (leaves, flowers). The seeds also contained relatively large amounts of manganese. The significance of these facts will be discussed later.

Guerin's view, that manganese is present in plants as a "nucleinic" or organic combination, was supported by Schlagdenhauffen and Reeb (1904) (72). These investigators detected manganese in a petrol extract of such cereals as barley, oats, and maize. Since inorganic manganese salts are not soluble in such a solvent, they concluded that the manganese must be present in organic combination. Maumene (50) in his work stated that manganese was present in wheat as the salt of an organic acid but gave no evidence to support this view.

The gymnosperms seem to be particularly rich in manganese content. Schroeder (1878) (74) tested for the element in firs and pines and found the following amounts of manganese present.

Mn_3O_4 in Per Cent

Ash		Dry Matter	
Fir	Pine	Fir	Pine
33.18	13.46	.276	0.077

During the past two decades much activity has been manifested in determining the presence of manganese in plants, but only a few of the more outstanding results can be mentioned here. In 1920 Bertrand (9), in a review of French investigations on the subject of plant stimulants, states that arsenic, boron, bromine, iodine, silicon, aluminum, copper, manganese, vanadium and zinc exist normally in plants and animals in small but

constant amounts. Bertrand and Rosenblatt (10, 11, 12) found that in 15 out of 17 species the ash of young leaves contained more manganese than the ash of old leaves. Vegetables averaged 3 to 4 mg. manganese per 100 grams of dry material. The orange, citron and manderin contained 0.21 to 0.71 mg. manganese per 100 grams dry matter. In wild tobacco the bark, branches, and roots contained 2.18 to 4.20 mg. manganese per 100 grams dry matter, calyxes 6.87 mg., leaves 8.32 mg. and seeds 5.65 mg. manganese per 100 grams dry matter. This shows very well how the element is present in larger amounts in the growing and reproductive parts of the plant.

Jadin and Astruc (33) state that all organs of plants show arsenic and manganese, the chlorophylliferous parts containing much more than the subterranean portions. They considered vegetables to form one of the most important sources of the arsenic and manganese found in animal tissues.

The following table representing work done by Lindlow and Peterson (1927) (43) and McHargue (1923) (57), shows the amount of manganese present in various plant and animal tissues. The results are expressed on the moisture free basis.

TABLE I

Substance	Manganese Per Cent	
11 Bush and vine foods	0.00178	Lindlow and Peterson
10 Roots and tubers	0.00184	" "
4 Nuts	0.00186	" "
4 Leguminous seeds	0.00200	" "
5 Cereals	0.00268	" "
12 Leafy vegetables	0.00670	" "
7 Animal tissues	0.00062	" "
Wheat seeds	0.0047	McHargue
Spring Oat seeds	0.0049	"
Pea seeds	0.0012	"
Clover seeds	0.0039	"
Grass seeds	0.0111	"

Hence it is seen that the largest amounts of manganese occur in leafy vegetables and in plant seeds, the former, in most cases, exceeding the latter in the amount of manganese present.

Wester (87) upon examination of forty-eight different kinds of seeds grown in Holland, found that in the majority of cases 0.002 to 0.006% of manganese was present.

Munger and Peterson (61) found that from 20 to 40% of the total manganese present in a food could be extracted with boiling water.

Rieman and Minot (67) presented a review of literature showing that most animals contain 0.02 mg. of manganese per liter of blood. Their own analyses showed that manganese is contained in all body tissues, occurring in the largest amounts in the liver, kidney and spleen. There was some indication that the manganese content of the various tissues is lowered in anemia.

The literature cited above seems to show rather conclusively the general distribution of manganese, in very small amounts, in the plant and animal world. De Saussure (21), Pichard (64), Bertrand and Rosenblatt (10, 11, 12), Jadin and Astrue (33), Rieman and Minot (67) and others, found that the manganese content of the various organs of plants and animals varied quite markedly. In plants the manganese occurred in largest amounts in the parts where chemical activity is greatest, and also in the seeds. In animals more of the element was found present in the liver, kidney, and spleen, than in the other organs.

Bertrand and Rosenblatt also showed that young leaves contain more manganese than old leaves. This seems to show that when the element is no longer necessary for growth it is withdrawn from the leaf.

Guerin (30), Schlagdenhauffen and Reeb (72), Maumene (50), and Munger and Peterson (61), have presented evidence which indicates that at least a portion of the manganese in the plant exists in combination with organic radicals. Petrol dissolved some of the manganese from the tissue, and boiling water only 20 to 40% of the total. It is the author's opinion that manganese could hardly be present in the plant in other than the organic state. It is possible, however, that it may exist in protoplasm as a colloidal oxide.

Since the natural source of manganese for animals is the plant, it is probable that manganese exists in animals in a form similar to that which it takes in plants. This is borne out by the fact that its absence causes similar effects in both. Evidence supporting this will be presented in the following sections.

B. The Effect of Manganese on Plant Growth in Soil Cultures.

1. Toxicity

Manganese may be directly or indirectly responsible for the poor growth of plants. Directly through being present in large quantities, causing toxicity, and indirectly because in insufficient amounts for proper growth.

The toxic action of manganese has, on the whole, attracted comparatively little attention until recent years, possibly because it is less manifest under soil conditions, possibly because the observation of toxic action has been almost completely overshadowed by the interest in the stimulation observed under the same conditions. Then too, the amount of manganese necessary to produce toxicity shows very large variance with different types of soils.

Voelcker (1902) (86) obtained toxic effects on the growth of wheat and barley in pots. Various soluble and insoluble manganese compounds were added to the pots at the rate of 200 pounds per acre. Except for the pots containing manganese nitrate and phosphate, those not receiving manganese produced as good plants as the ones which did. The plants that grew did well eventually but development of the spike was greatly retarded. Manganese iodide retarded germination and growth, but since sodium iodide gave similar results, the toxicity in this case must be attributed to iodine.

Perhaps the most important work on this subject has been done in Hawaii in connection with pineapple cultivation. Kelley (1909) (38) investigated the cause of poor growth of pineapples on black Hawaiian soils. An analysis showed the soils to contain an average of 5.61% Mn_3O_4 or about 23,755 pounds Mn_3O_4 per acre foot of soil. The pines of the plants were yellow and the root system poor. The yellow pines, however, due to their high manganese content, were more active oxidizing agents than the green pines. In contrast to pineapples, sugar cane grew well on the manganese soil. The soil was improved by addition of soluble phosphates. Kelly (1912) (39) also found that in the manganese soil excessive amounts of calcium were absorbed by the pineapple. McGeorge (1923) (53) concluded that the chlorosis of pineapples on manganiferous soils was caused by greater assimilation of calcium, which was indirectly produced by the presence of excessive amounts of manganese in the soil.

Johnson (1917) (35) from a study of the ash of pineapple plants thought the toxic effect of manganese to be due to a depression of iron assimilation, as a low iron content was found. When sprayed with a salt of iron the plants recovered from the toxic effects of manganese.

Gile (28) stated that manganese chlorosis may be due in part to a deficiency of iron in the plant, induced by the action

of manganese in the plant or soil, and in part due to the toxic action of manganese. Lime chlorosis may be due merely to a lack of iron in the plant, the iron being made unavailable in the soil by the action of lime.

McHargue (58) showed that application of manganese sulfate to an acid soil decreased the crop yield. The same soil, on addition of a mixture of manganese sulfate and calcium carbonate, gave increases in yield. The etiolated condition of the young tender leaves and buds of the plants, when manganese was lacking, showed that the element has a function in photosynthesis. Legumes were thought to be more sensitive in this manner than non legumes.

2. Reactions of Manganese in the Soil Which Explain to a Certain Degree its Toxicity.

Some work has been performed recently on the reactions undergone by mangnaese in the soil. The following review seems to the author to explain to some extent how manganese acts as a toxic agent to plants.

Funchess (26) gave data which showed that some soils which are acid contain soluble salts of manganese in rather large amounts. He describes experiments with acid soils which he found to contain soluble manganese. These soils were toxic to plants which were grown on them. After neutralization with calcium carbonate the toxic effect of the soil was destroyed. McHargue (58) obtained similar results.

Skinner and Sullivan (77) of the United States Bureau of Soils carried out a series of experiments with manganese at the Arlington Experiment Farm. The application of manganese sulfate, fifty pounds per acre, to an acid silty-clay loam soil resulted in decreased yields as compared to untreated soils. Upon neutralizing the acid in the soil with calcium carbonate, the plots receiving manganese produced very marked increases in yields. This shows that the soil reaction is an important factor in determining whether or not an application of manganese sulfate will exert a beneficial influence on plant growth.

Schollenberger (73) in a series of experiments with calcite, to find the relation between the amount of surface exposed by the calcite in the soil, and its rate of decomposition, noticed the calcite to become coated with a dark film which contained a large percentage of manganese. In untreated soil only 0.2 mg. equivalent of manganese was present, whereas soil treated with calcite had 1.6 mg. equivalent. It was found that the manganese dioxide precipitated by alkali (not in excess) from the manganous chloride in a soil sample, produced a regular decrease in the hydrogen-ion concentration. Schollenberger considered the manganese as reducing active acidity in the same manner as lime. It is the author's opinion that the alkali added was responsible for the decrease in acidity, rather than the precipitated manganese dioxide. Sen (75) has shown that alkalies are readily adsorbed by manganese dioxide. This being the case

manganese dioxide would have a tendency to increase soil acidity.

Conner (19) stated that lime may act in three ways to remove soil toxicity: it neutralizes the acidity of the soil; it precipitates injurious compounds from solution; it acts in an antagonistic manner toward excesses of soluble salts which are not precipitated. Aluminum, iron, manganese, boron and zinc are rendered less soluble and less harmful by lime. Carr and Brewer (18) showed that precipitation of iron and aluminum by lime is complete at pH 5.5. Manganese, however, does not start to precipitate until pH 7.2, and is not completely precipitated until pH 7.9 is reached. Such a procedure to eliminate manganese toxicity would be impracticable as it raises the pH above the optimum for most crops (pH 5.5 to pH 6.5).

Nottin (63) found the carbonates of the soil but little effective in precipitating manganese, whereas calcium oxide had a strong influence.

Magistad (48) studied the action of manganese in base exchange reactions in the soil, and found that it readily replaced calcium in artificial zeolites.

It is the author's opinion that the following explains in some manner the toxic action of manganese on plants. The soluble manganese salts used as a fertilizer (sulfate or chloride), when added to an acid soil will hydrolyze, and may increase the amount of acid in the soil to the point of plant toxicity. The soil is thus so acid that manganese remains in the soluble unoxidized condition, and then may be absorbed in toxic amounts.

The large amount of acid will act to dissolve ferric iron present. If the iron is present in moderate amounts it becomes available and acts beneficially on plants. If, however, the iron is present in large amounts it acts on the plant as a poison.

If lime is added to such an acid soil containing manganese it neutralizes the acid. When the pH goes above 5.5 ferric iron is precipitated and thus iron chlorosis results (18). If the pH approaches 7.0 some manganese will be oxidized to the insoluble condition. Enough, however, will be available for plant needs. The presence of oxidized manganese also tends to keep the iron in the less soluble ferric condition, so that soluble salts of iron should be applied in order to prevent chlorosis (35). A manganese salt when added to a neutral soil, deficient in manganese, should thus be beneficial.

The fact that manganese replaces calcium in soil compounds forming manganese zeolites and calcium manganates ($CaO \cdot 7\ MnO_2 \cdot n\ H_2O$) (48, 63), shows how manganese may act beneficially by making calcium more available. When present in too large amounts manganese would cause toxicity due to too much absorption of calcium.

3. Stimulation of Plant Growth by Manganese

The field of stimulation of plant growth by manganese has attracted many workers, and the literature on this subject is correspondingly plentiful. Some of the work has been carried

out from the economic point of view in order to determine the value of manganese as a fertilizer. Another group of workers has been concerned with determining the necessity, and if possible the function of manganese to the plant.

In Japan where agriculture, of necessity, is carried on intensively we find much of the earlier work on this problem. Loew (1903) (44) found that small amounts of manganese sulfate stimulated the growth of rice, peas, and cabbage. They considered manganese to be a constituent of fertile soils, and, despite its high price, to have a distinct value in agricultural practice.

Nagoaka (1903) (62) obtained increased yields of rice with amounts of manganese up to 22 pounds per acre. Aso (1904) (3) found that the use of manganous chloride as a fertilizer increased theyield of husked full grains by one third.

In 1904 Fukutome (25) found that a joint application of manganese chloride and ferrous sulfate, at the rate of 0.4 gram each per 8 kg. soil, produced a marked increase in the growth of flax over that in check pots. Each element along gave but a small increase in yield.

Uchiyama (1907) (84) obtained similar results with manganese and iron sulfates. In some cases joint application of the manganese and iron salts gave better results than either salt alone. As a rule the manganese sulfate gave better results than the iron sulfate, but its action varied greatly with the character

of the soil, the method of application, and the nature of the fertilizing materials. The best results were obtained when the manganese sulfate was applied as a top dressing, and in fertilizer mixtures which had a nearly neutral reaction. Applications from 18 to 45 pounds per acre of manganese sulfate are considered sufficient.

Gregoire, Hendrick and Carpiaux(1907) (29) found that 99 pounds of manganese sulfate per acre gave a 5 - 9% increase in potatoes. Since the action was the same in soils rich and poor in nitrogen, they concluded that manganese does not make nitrogen more available. Although the manganese sulfate lowered the yield of sugar beets slightly it increased their sugar content. Sijfert (1915) (76) found that the use of manganese resulted in an increase in the potato crop and in the nitrogen content, but decreased the amount of starch present.

Ehrenberg and Schultze (1917) (24), in fertilizer experiments with manganese showed that under suitable conditions the manganese applications acted favorably on the nitrogen content of plants through an exchange of bases. The value of manganese as a fertilizer has recently led many investigators into this field, and as a result of careful work much conclusive evidence has been obtained.

Loew (1924) (45) added monthly, over a two-year period, a 0.1% solution of manganese sulfate to eight Japan Cedar trees 20 inches in height. Each tree received a total of 1.4 grams of

the salt. The trees treated developed markedly and had twice the weight of untreated specimens.

Workers at the Rhode Island Experiment Station (1927) (70) on injecting a manganese salt into the leaf tissue of spinach, where it could have no effect on the soil, found it to be as beneficial as when applied to the soil direct. With beets manganese was more effective when applied as a spray than as a fertilizer. Soil applications were also good for oats and spinach. In neutral soil, when alfalfa, red clover, alsike clover and oats did show poor growth they were benefited by an application of 30 pounds of manganese sulfate per acre. Gilbert and McLean (1928) (27) of the same station, found that manganese cured chlorosis induced by lime when applied as a spray or when applied to the soil.

Lee and McHargue (1928) (41) have found that an application of manganese will cure the Pahala blight of sugar cane. Heretofore Pahala blight was regarded as an attack on the plant by some organism. Any soil treatment which will increase the availability of manganese will cure the blight. The authors concluded that the disease should be called manganese deficiency chlorosis and not Pahala blight.

Willis (1928) (89) noticed that certain unproductive spots in North Carolina produced corn and soy bean plants which were chlorotic. The reaction of the soil was neutral, in contrast to a normal soil which is slightly acid. He stated that an application of manganese sulfate benefited the soy beans but had

no effect on the growth of the corn. He found that the harmful effects to a soil caused by application of lime or tricalcium phosphate may be remedied by manganese sulfate applications in moderate amounts.

C. Effect of Manganese on Plant Growth in Nutrient Solutions.

1. Relation of Manganese to Iron.

The use of nutrient solution is the most general method for determining the effect and function of the various elements on the growth of plants, for here the growth medium is under the control of the experimenter. Since the nutrients used are usually all soluble they must be carefully purified to remove all substances which would in any way affect the results.

Spampani (1891) (79) made water culture experiments with oats, white lupins, and maize. The following materials were ground together to serve as the nutrient: 5 grams potassium acid phosphate (KH_2PO_4), 8 grams calcium nitrate ($Ca(NO_3)_2 \cdot 4\ H_2O$), one gram magnesium sulfate ($MgSO_4 \cdot 7H_2O$) and 0.5 grams potassium chloride (KCl). Solution A contained this mixture in a liter of water. Solution B was the same as A except that 7 or 8 drops 0.05% manganese sulfate were added. Solution C contained iron in place of manganese. It was found that although manganese was absorbed by the plant, it could not replace iron in the formation of chlorophyll. Loew and Sawa (1902) (46) found that 1/400 - $MnSO_4/H_2O$

killed sea plants within five days. Barley and soy beans grow in nutrient solutions with either manganese or iron sulfate or both, showed increased growth at first, but eventually the shoots turned yellow and growth was depressed. This toxic action was thought due to the toxic action of manganese.

Aso (1902) (2) noticed that 1/50,000 $MnSO_4$ gradually caused a browning of the roots and lower leaves of barley. The brown color was caused by the manganese depositing in the tissue. The greatest concentration of manganese sulfate endured by barley without injury was about 1/100,000. The presence of iron in the nutrient seemed to offset the effect of manganese to some extent, because the yellowing of the leaves was delayed. Wheat behaved similar to barley, although more iron was necessary for healthy growth. It is therefore permissible to say that the toxic action of manganese is closely connected with the availability and amount of iron present.

Evidence for the antagonism between manganese and iron, suggested by Aso, has been accumulating from several sources. According to Tottingham and Beck (1916) (83) it was shown that in very low concentrations such as 1/1,500,000 ferric chloride failed to antagonize manganese chloride, but a concentration of 1/15,000 ferric chloride had a strong effect on the color and growth of wheat. It thus seems possible that manganese, in some manner yet unknown, tends to render ineffectual the action of iron in the plant, unless the latter is present in rather large amounts.

The above conclusion was supported by Rippel (1923) (69). Oat plants supplied with iron as ferric phosphate became chlorotic when 0.01 to 0.05 grams $MnSO_4 \cdot 4\ H_2O$ were added to the nutrient solution. This manganese induced chlorosis was cured by the administration of ferrous chloride. Plants supplied with iron, with and without manganese, had the same iron content, so that, as Rippel points out, the manganese does not prevent the intake of iron by the plant, but rather its action in the tissues.

The relationship between manganese and iron was also brought out by Johnson (1924) (36). Experiments with rice in nutrient solutions showed that the effect of manganese was dependent on the amount of iron present. Chlorosis induced by manganese was overcome if the leaves were dipped in ferrous sulfate, or if an excess of soluble iron was supplied to the nutrient medium. Johnson concluded that chlorosis caused by manganese is due either to a deficiency in iron assimilation, or to a deficiency of iron in the plant. Based on the work of Rippel (69) the author believes that this statement must be ruled out, as plants showing manganese chlorosis were found by him to have equal amounts of iron with plants not supplied with any manganese. Both series of plants had been supplied with equal amounts of iron in the nutrient. Perhaps the most regrettable fact of this discussion is that the investigators did not give the pH values of the nutrient solutions, and in some cases the amounts of iron and manganese used.

It is indeed remarkable how well the results of investigators working with nutrient solutions, have corroborated those of workers experimenting with soil cultures. From the results obtained with growth of plants in nutrient solutions we have a deeper insight into the relation of manganese to iron, and, from all appearances, there must be a nicely controlled balance between the amounts of each which are present in the plant, and which are available for nutrient. Johnson (35) and Gile (28) thought that manganese toxicity in soil cultures was caused by a depression in iron assimilation. It is the authors opinion that this is only the first step of the process. The iron of the soil is made less assimilable due to oxidation, by manganese, to the less soluble ferric condition.

The second step probably takes place in the plant itself, and is doubtless of the same nature as the first. Now, chlorophyll, under the influence of light, converts carbon dioxide into starch. Chlorophyll, although containing no iron, cannot be produced in the plant unless iron is present; it is known that iron occurs in the colorless part of the chloroplasts. Iron, since it is present in very small amounts and due to its character of being a redox (reduction-oxidation) agent, is thought to play the part of a catalyst in the formation of chlorophyll. If manganese is present in sufficient amount, it is easily conceivable how the iron could be kept in the ferric condition, due to oxidation by the manganese. The catalytic activity of the iron

being nulified, chlorosis would result. An increase of iron would then be necessary to overcome the action of manganese, (see Aso (2), Tottingham and Beck (83), Rippel (69) and Johnson (36)). Although such a theory explains the findings of Rippel and others it cannot for a moment, however, be considered the whole story, as only circumstantial evidence has been adduced.

2. Toxicity and Stimulation in Nutrient Solutions.

Brenchley (1910) (15) studied the effect of manganese on the growth of barley, and found that amounts of manganese less than 1/ 100,000 had a decided stimulating effect. Higher concentrations of manganese had a retarding influence upon the growth, as the leaves and roots were turned to a brown color. Such leaves when fused with a mixture of sodium carbonate and potassium nitrate gave a green color to the melt which was indicative of high amounts of manganese. Peas gave results similar to barley. Another investigator Stoklasa (1911) (80) considered the optimum amount of manganese to be 3/100,000, as with this amount plants gave the highest yields. He stressed the importance of manganese in chlorophyll formation. In a later work, however, (1918) (81), Stoklasa found amounts of manganese above 1/100,000 were toxic to plants.

Deatrick (1919) (20), experimenting with wheat found low concentrations of manganese to have a stimulating effect on the root oxidizing power, and also that the growth of the plants was increased over that of the controls.

McHargue (1919) (55) gave further evidence that manganese is necessary for adequate growth of wheat. These plants in water cultures showed a chlorosis in the absence of manganese, but became normal upon the addition of the element. Manganese, in suitable dilution, stimulated growth, increased the size and gave a very noticeable enhancement of the nitrogen content of the grain. Further work (1922) (56), with wheat, peas, radish, lettuce, tomato, spinach, carrot, onion, beans, cabbage, oats, and clover showed that these plants would grow normally for six to eight weeks without manganese in the nutrient, because of the small amount of manganese present in the seed. After this was used up the plants became chlorotic. Treatment of such plants with manganese cured the chlorosis and enabled them to grow to maturity. These plants had an average of 135% increase in dry matter over check plants. The plants receiving no addition of manganese to the nutrient died without fruiting. McHargue considers that manganese plays a part equal in importance to iron in chlorophyll synthesis. Since legumes are much more easily stimulated by manganese than non legumes, McHargue thinks that manganese is concerned with nitrogen assimilation and protein formation.

Bishop (1928) (14) as a result of several experiments drew the following conclusions:

(a) The concentration of the manganese in the nutrient medium must be controlled carefully to obtain the best results.

(b) Manganese is essential for plant development.

(c) The effect of manganese is not due to reduced iron intake by the plant.

(d) There is some relation between manganese and chlorophyll formation, and hence carbon assimilation.

(e) Calcium definitely counteracts the toxicity of high concentrations of manganese.

Thus it seems to be established that manganese is indispensable to the growth of plants. However to prove this fact the plants must be grown for a period of longer than six weeks, as this amount of time is necessary for the plant to use the reserve of manganese which is present in the seed. After this period if manganese is added in amounts less than 1/100,000, and preferably 3 or 4 parts per million, the plants will develop normally and grow to maturity. If larger amounts of manganese than 1/100,000 are present, chlorosis will result due probably to a prevention of iron activity in photosynthesis. The experiments of Tottingham and Beck (83) showed that manganese must always be present in lesser amounts than iron. Total lack of manganese in the nutrient medium will cause the plants to become stunted and chlorotic. The chlorotic effect in this case may be due conceivably, also to the failure of the plant to use iron.

Although much work has been done upon the effect of manganese on the growth of the plant, the experimenters have as yet learned very little of the anabolism and catabolism of manganese

in the plant. In view of its close relation to photosynthesis the author considers the problem of manganese to be an important one in plant physiology.

D. Theoretical Discussion

1. The Element Manganese

In connection with the function of manganese in plants and animals, which will be discussed a little farther on, perhaps, it will not be out of the way to give a brief space to the characteristics and properties of the element itself.

Manganese, although in group seven of the periodic system and having thus a positive valence of seven, bears no close relation to the halogens except in the permanganates which are much like the perchlorates, periodates, etc. In these compounds both manganese and the halogens show a positive valence of seven. Unlike the halogens manganese does not exhibit the common negative valence of one. With positive valences of 2, 3 and 4 manganese is closely related to iron, forming isomorphous salts and frequently replacing iron in the crystal lattice. Iron has positive valences of 2 and 3. Manganese, however, with positive valences of 2, 3, 4, 6 and 7 is much more active as a redox agent than iron.

The ease with which manganese changes in valence probably explains its catalytic activity. Thus manganese salts will greatly increase the speed of oxidation of the drying oils and accelerate oxidations caused by nitric acid. The oxidation of organic compounds by hydrogen peroxide is much hastened by the presence of manganese

salts, for example the oxidation of pyrogallol and hydroquinone. The oxides of manganese can also function as catalysts, and these may be compared favorably with metallic platinum. Manganese dioxide rapidly decomposes hydrogen peroxide without itself being affected. Manganous oxide will dehydrogenate alcohols and dehydrate organic acids. Hydrous manganese dioxide also functions indirectly as a catalyst by adsorption of iron, cobalt and nickel. The dioxide of manganese shows a strong tendency to adsorb hydroxyl ions.

2. The Function of Manganese in Plants

The physiological cause of the stimulation exerted by manganese compounds on plants has aroused much controversy. Loew and Sawa (46) suggested that the action of the sun's rays upon a normal plant puts a certain check on growth, arising out of the action of certain noxious compounds which they believed to be produced in the plant cell under the influence of light. The stimulation by manganese compounds may be due to an increase in the oxidizing powers of the oxidases, so that destruction of the noxious compounds can be accomplished as quickly as they are formed.

The connection of manganese with oxidases had also received the consideration of Aso in (1902) (2). He stated that colorimetric tests for oxidizing enzymes were of a higher intensity in the yellowed leaves from plants poisoned with manganese, than in the green leaves of control plants, the difference being specially marked in barley and less so in the radish.

Bertrand has devoted much time and consideration to the problem of the function of manganese. In 1897 (5,6,7) he proceeded to investigate the essential nature of manganese in the economy of the plant. His experiments showed its constant presence in a ferment, laccase, which he extracted from plants. He obtained from lucerne an enzyme, somewhat inactive, which increased in activity on the addition of manganese. Bertrand stated that manganese apparently was not to be replaced by any other metal, not even iron. He also stated that the small quantity of it occurring in plants was no reason for regarding it as a secondary element in the physiology of plants. The view was also advanced that in the presence of certain organic substances, such as hydroquinone, pyrogallol or similar bodies, manganese is capable of fixing free oxygen from the air, the volume of oxygen absorbed varying according to the compound of manganese used.

Bertrand thought of the oxydases as special combinations of manganese with an organic anion probably of protein nature and variable according to the ferment considered. These oxydases would have just the necessary affinity to keep the manganese dissolved. The following shows how the manganese complex would act as an oxidizing catalyst:

$$R\,Mn + H_2O \rightarrow R\,H_2 + MnO$$

$$MnO + O_2 \rightarrow MnO_2 + O'$$

$$R\,H_2 + MnO_2 \rightarrow R\,Mn + H_2O + O'$$

The catalyst R Mn being regenerated, only a small amount of it would be necessary to keep the oxidation going, the oxidation, of course, being carried on by nascent oxygen (O'). The manganese, according to Bertrand's view would be the active element of the oxydase; the albuminous matter would give to the ferment the special characters which show themselves in their behavior toward reagents and physical agents. From this viewpoint manganese could no longer be considered as a non-essential element, but as an element of vital necessity to the functionf of plant life. The name of "catalytic" elements was suggested for those elements such as manganese, boron, iodine, and zinc, which occur only in traces in the plant, and are usually specialized in their functions. In 1911 (8) Bertrand gave further substantiation to his theory, from results which showed that manganese is essential to photosynthesis. It was concluded that manganese intervenes as a catalytic agent in the material changes of plant growth, and that it participates, therefore, in an indirect manner in the formation of tissues and production of organic matter.

Bertrand's theory has received support from several sources. Jadin and Astruc (1917) (33) considered manganese to have a direct influence on the oxidation reactions of the plant. Popoff (1923) (65) showed that all compounds which are capable of stimulating cell functions, should possess the property of accelerating and increasing the oxidation processes of the living cell. To possess this property the compounds should show a marked affinity for oxygen. Among other compounds, salts of manganese were found to have a marked stimulative action.

Aloy and Valdiguie (1924) (1) found that manganese catalyzed the reaction;

Hydroquinone → quinhydrone.

McHargue (1914, 1927) (54, 60) upon the examination of several species of seeds found that more manganese was present in the seed coats than in the meats. The seed coats gave a much stronger test for oxidases with guiacum than did the meats. McHargue then assumed that manganese bears a very important relation to the oxidizing enzymes, which have much to do with the selecting, synthesis, and storing of reserve materials in the seed kernels. Since fatty seeds absorb large volumes of oxygen on germination, it is probably that manganese in the seed coat, by acting as a redox agent stimulates the enzymes which split up fats, sugars, starches, etc., and render them more available for the young seedling in the early stages of growth.

Kentucky blue grass, which is particularly rich in chlorophyll contains a relatively large amount of manganese. Vitamin A has been found present in young leaves, and may be removed by alcohol extraction. Such extractions contain considerable copper, so that McHargue considers copper to be present in Vitamin A. Since plants grown without copper and manganese are weak and stunted it was postulated that these elements are vitamin factors in plants. The following vitamin cycle was thought to occur: plants obtain their vitamin factors from the elements of the

soil (Mn, Cu, Zn, Co, Ni and B) and with the aid of these elements complex organic compounds are synthesized in the plant. These are passed on to animals, which are incapable of using the raw materials, but can resynthesize the complex organic combinations containing them. In all the foods which contain vitamins, small traces of the previously mentioned elements are also found.

We see thus that McHargue has taken Bertrand's original theory and enlarged upon it. Neither Bertrand's nor McHargue's theory has been proved as the experimental technique in this field has not yet advanced to the point where all interfering factors can be eliminated.

Some workers, however, have not been able to substantiate Bertrand's or McHargue's theory. Van der Haar (1921) (85) after purifying his oxidases and finding only very minute amounts of manganese, thought that manganese may accelerate oxidase action but that it is not a part of the oxidase molecule. Normal ivy plants grown without manganese were found to contain normal oxidases. The same plants contained 0.005 mg. Mn, so that Van der Haar's work is not conclusive.

Dowell (1920) (22) working with grain sorghums found no definite relation existing between the amount of oxidase and the amount of manganese present.

Bleyer (1925) (13) found that manganese had no effect on the speed of reactions caused by catalase.

Smirnow (1925) (78) found that manganese had an in-

jurious influence on the activity of wheat peroxidase. In regard to Bleyer's and Smirnow's work it can be said that manganese may already have been present in the enzymes used, and the addition of more would thus cause a decrease in activity.

The main facts upon which any theory must be based will be briefly summarized. Manganese is present in plants and is necessary for plant growth; the amount in which it occurs is too small to be of nutritional value. Manganese performs an important function in chlorophyll formation and perhaps in photosynthesis, as without manganese plants become chlorotic. Manganese occurs in those parts of the plant (leaves and stems) in which growth is most active. These parts of the plant also contain the large amounts of oxidizing enzymes or oxidases. Due to photosynthesis there is a continual intake of carbon dioxide into the plant tissue and a giving up of oxygen. Another important point is the fact that chlorophyll formation and photosynthesis do not take place in the absence of light, so we see that the reactions caused by light must be an important factor. Light furnishes the energy for many of the chemical reactions in the plant, but the mechanism by which it works is as yet little understood. Without doubt light rays of suitable wave length upon absorption raise the electrons of atoms in the plant to higher quantum levels and thus instigate chain reactions. The relation of iron

to manganese and the reasons why more iron than manganese must be present are points that remain to be determined.

Furthermore it does not seem wise to consider manganese as being wholly an oxidation catalyst. With both manganese and light present photosynthesis takes place, but in the absence of either it does not. Manganese may then function as a reducing agent in picking up oxygen, since the conversion of carbon dioxide to carbohydrate is a reduction not an oxidation process.

3. The Function of Manganese in Animals.

Much less is known of the function of manganese in animals than of its function in plants. What has been discovered seems to indicate that the role of manganese in animal life is very similar to its role in plant life.

Previous data have been given to show that manganese exists normally in small amounts in animals. It occurs in the largest amounts in the liver, kidney and spleen. The amount of manganese in blood seems to be constant at about 0.02 mg. per liter. The presence of manganese in these organs and in the blood does not postulate that it has a specific body function as after absorption most of the food passes through the liver and many of the excretion products of metabolism are carried off through the kidneys. Thus these two organs could be expected to carry the higher percentages of manganese.

Iron as in plants seems to exist in animals in much larger amounts than manganese; there being about 40 mg. of iron per liter of blood.

Riemanand Minot (1921) (68) showed that when manganese is eaten, the manganese content of the blood increases a small amount in the first few hours and then returns quickly to normal. Even when manganous chloride was injected directly into the blood there was a rapid return to normal within a few hours. Manganese was found to be excreted chiefly through the intestines, a fact which does not explain why so much of it occurs in the kidneys. Six dogs fed manganese daily for over a year did not show symptoms of poisoning and the manganese content of the blood was not higher than that of normal dogs. Thus we see that there is some mechanism controlling the amount of manganese present in blood.

Controlled nutrition tests with rats by Levine and Sohm (1924) (42) showed that the animals receiving manganese were more active than those which did not. Their fur was sleeker, longer, and thicker, and the offspring grew more rapidly than the average for young rats.

McCarrison (1927) (52) fed two groups of rats on diets containing different amounts of manganese. One group received 0.889 mg. manganese, the other 0.0327 mg. manganese daily. The larger amount had a retarding influence on growth, whereas the smaller had a stimulating effect.

McHargue (1926) (59) added to the diet of rats the metals copper, manganese, and zinc, both singly and in combination. Those rats receiving none of these metals (controls) died first, next those fed zinc, and then those fed copper. The rats receiving manganese, both alone and in combination with copper and zinc, survived the longest. The average gains in weight were: control rats 59.75 grams, Mn 89.75 grams, Cu 76.5 grams, Zn 76.25 grams, and Mn, Cu and Zn 92.0 grams. The diet used was wholly synthetic and was carefully purified.

It has been shown in recent years that the addition of iron alone to the diet of anemic animals does not suffice to cure anemia. Titus, Cane and Hughes (1928) (82) showed, in the case of rats, that either manganese or copper, when given in the right proportion along with iron would cure anemia. Manganese and copper together gave better results than either element alone. It was concluded, therefore, that both manganese and copper are necessary in order that iron may be used in hemoglobin formation.

The foregoing discussion has of necessity been brief, but it shows that manganese is essential to both plant and animal life. Its function in both seems to be similar in that it is concerned with chlorophyll formation in plants, and with hemoglobin formation in animals.

IV. EXPERIMENTAL PART

A. The Problem

Previous investigators have shown that both the pH and substances present in the soil, or added as fertilizer, are determining factors in the availability of manganese as a plant food. The availability of manganese in the presence of the various nutrient salts has not been determined, to the author's knowledge by any other investigator. Since availability in the nutrient solution is determined primarily by solubility, solubility studies of manganese sulfate in various solutions of nutrient salts have been made, and are presented here as the major part of this thesis. In order to make this research as complete as possible the solubility of the manganese sulfate was determined for each type of solution used over the entire pH range of plant growth.

The solubility was first studied in single salt solutions, then in double salt solutions, and finally some of the triple salt combinations were investigated.

It is also the purpose of this investigation to observe whether manganese either in the dissolved or precipitated condition has any influence on the pH of solutions containing it, and to find if manganese forms any unusual combinations with nutrient salts which affect either its solubility of the pH.

The solutions were all studied at much higher concentration than the ordinary nutrient solutions in order that the effects, if any, would be more marked.

B. The Plant Nutrient Solution

The complete plant nutrient solution may be defined as one which contains, in the proper amounts, all the elements necessary in soil solutions to the full growth of the plant. The following elements have been found necessary for a complete nutrient: hydrogen, oxygen, phosphorous, potassium, nitrogen, sulfur, calcium, magnesium, iron, manganese, boron, and perhaps zinc and copper. The four latter elements are usually present in very small amounts as compared with the others. These substances are introduced as the salts; for example, calcium nitrate, potassium dihydrogen phosphate, magnesium sulfate, ferric sulfate. A representative plant nutrient solution is given here in order to convey an idea of the concentrations of the substances necessary for plant growth; 18 cc. M/1 KH_2PO_4, 5.2 cc. M/1 $Ca(NO_3)_2$, 15 cc. M/1 $MgSO_4$ and 3 mg. $FePO_4$, are all added to enough distilled water to make the total volume one liter. Of course there are innumerable combinations of these three salts and their reciprocals in varying concentrations.

1. The pH of the Plant Nutrient Solution.--- Although the range of plant growth extends from pH 3.4 to pH 8.2, there are very few, if any, plants which will grow at every point in this range. Each plant species has an optimum pH which generally lies in the range pH 5.0 - pH 6.5; ranges outside of this usually being toxic.

Due to unequal absorption by the plant of the acidic and basic constituents of the component salts, nutrient solutions, unless buffered, tend to change in pH during growth of plants. The buffered nutrient solution has to a large extent the property of being able to

withstand pH changes which might be caused by unequal absorption of nutrient ions. The acid phosphates of the plant nutrient solution start to act as buffers as soon as any unequal absorption of nutrient ions begins. Thus when in a nutrient solution containing potassium dihydrogen phosphate the negative ions are absorbed, the positive ions left behind react with some of the phosphate to give the monohydrogen salt. Although the monohydrogen salt tends to raise the pH, it is present in such small amounts that its action is greatly neutralized by the ionization of more of the dihydrogen salt.

C. Method of Attack

1. Chemicals Used.---The following nutrient salts were used, each was of the C. P. analyzed grade, manufactured by The Baker & Adamson Chemical Company of Easton, Pa., or The J. T. Baker Chemical Company of Phillipsburg, N. J.

(a) Calcium dihydrogen phosphate ($Ca(H_2PO_4)_2.H_2O$) (B. & A.), stock solution 0.1 molar.

(b) Calcium nitrate ($Ca(NO_3)_2.4H_2O$) (J. T. B.). Stock solution 1.0 molar. (See note at end of this section.)

(c) Potassium dihydrogen phosphate (KH_2PO_4) (B. & A.), stock solution 1.0 molar.

(d) Potassium nitrate (KNO_3) (B. & A.), Stock solution 1.0 molar.

(e) Magnesium sulfate ($MgSO_4.7H_2O$) (B. & A.), stock solution 1.0 molar.

(f) Ammonium sulfate ($(NH_4)_2SO_4$)) (B. & A.), stock solution 1.0 molar.

(g) Manganous sulfate ($MnSO_4$), stock solution contained 1.0 mg. Mn per cc. This was prepared by reducing a known volume of standardized potassium permanganate (J. T. B.), with sulfur dioxide. The resulting s olution was then diluted to make the stock solution.

In testing for manganese the chemicals used were:

(a) Orthophosphoric acid (H_3PO_4) (J.T.B.), sp. gr. 1.71.

(b) Potassium periodate (KIO_4). First lot from Eimer & Amend of New York City, the rest from Eberbach & Son of Ann Arbor, Michigan.

Manganese in Calcium Nitrate.---It was found that the calcium nitrate of some manufacturers contains an appreciable amount of manganese. The following data was obtained from four samples of the salt at hand.

1. This sample of calcium nitrate (J.T.B.) contained no manganese. The pH of a 1.0 molar solution was 3.7 and dropped to pH 3.6 during a period of one month. The crystals were small clear and transparent. This salt was the one used in this work.

2. The second sample (B. & A.) came in lumps and the color contained a trace of brown. This salt showed 0.1 per cent manganese. The pH of a 1.0 molar solution was 7.5 at first, and after one month 7.0. During this period a brown precipitate of manganese oxide settled out.

3. This sample (B. & A.) also came in lumps, but contained no manganese. A silica like precipitate was formed from a 1.0 molar solution, in one month of standing. During this time the pH changed from 10.5 to 10.1.

4. The last sample (E. & A.) contained no manganese. The pH of a 1.0 molar solution was 4.9 and at the end of one month had not changed.

2. Apparatus.---The solutions on which solubility determinations were being made were kept in 500 cc. Erlenmeyer Pyrex flasks. In order to obviate the effect which alkali contained in the glass might have on the pH, these flasks were seasoned. The seasoning was accomplished by filling each flask with hot 50 per cent sulfuric acid (made hot by dilution). The flasks were then allowed to stand for a week or more, the acid poured out, and the flasks thoroughly rinsed with water. Each flask was then filled with distilled water containing bromthymol blue (pH indicator) and the solution adjusted to about pH 7.0. The flasks were then stoppered and allowed to stand for about two weeks. Any flasks in which the indicator showed a color change during this period were reseasoned.

A number of test tubes, for making pH determinations, were graduated to 10 cc. and seasoned in the same manner.

Nessler tubes were used in making colorimetric determinations of manganese. These tubes were graduated to hold 50 cc. of solution, and were all of uniform bore (1.5 x 22 cm.).

Beakers of 100 cc. capacity were used in oxidizing the manganese, prior to making the colorimetric determination.

3. Preparation of Test Solutions of Nutrient Salts.---It was assumed that the reactions taking place in the nutrient solution between manganese and the component salts, would take place to a more noticeable extent if all the components were more concentrated. Thus the solubility of manganese was determined in solutions which were 0.1 molar with respect to all the salts, with the exception of calcium dihydrogen phosphate which was used as 0.05 molar. This was necessary since a 0.1 molar solution of calcium dihydrogen phosphate contains twice as much phosphate ion as a 0.1 molar solution of potassium dihydrogen phosphate. Manganous sulfate was added to make the concentration of manganese 10 parts per million.

The method of making up the solutions is illustrated. Thirty cc. of 1.0 molar stock solution (150 cc. 0.1 M $Ca(H_2PO_4)_2$) were placed in a clean dry Erlenmeyer flask and diluted to 250 cc. with water. Three cc. of the manganous sulfate stock solution were then added from a calibrated burette. The solution was then diluted to a volume of 298 cc. (0.1006 molar). The dilution to 0.1 molar was accomplished after the adjustment of the pH. Control solutions were made up in the same manner except that no manganese was added.

4. Adjustment of pH.---The pH of the solutions was adjusted by the addition of small amounts of appropriate acid or alkali, (same as was present in the salt), except when the slight solubility of calcium and magnesium hydroxide necessitated the use of potassium hydroxide. The pH was determined colorimetrically with indicators. The indicators used and their pH ranges are:

LaMotte Yellow, pH 2.6 - 4.2

Bromoresol Green, pH 4.0 - 5.6

Chlorphenol Red, pH 5.2 - 6.8

Bromthymol Blue, pH 6.0 - 7.6

Phenol Red, pH 6.8 - 8.4

Thymol Blue, pH 8.0 - 9.6

The color standards used for comparison were furnished by the LaMotte Chemical Products Company of Baltimore. Each set contains nine standards, differing by 0.2 pH in successive standards. Although the color differences are such that a practised operator can read to 0.05 pH, the accuracy of the method cannot be placed at greater than 0.1 pH. In determining the pH of a solution rough tests were at first made with small volumes to ascertain which indicator to use. Then 10 cc. of the solution were placed in a seasoned test tube, 0.5 cc. of the indicator solution added and comparisons made with the standards.

5. The Determination of Manganese.---The colorimetric method of Willard and Greathouse (1917) (88) was, after some experimentation, adopted for the determination of manganese. This method has been adopted by the Association of Official Agricultural Chemists. It is based on the oxidation, by potassium periodate, of manganese from the bivalent to the heptavalent condition. The reaction, which takes place in an acid solution, may be represented as follows:

$$2MnSO_4 + 5KIO_4 + 3H_2O \longrightarrow 2HMnO_4 + 5KIO_3 + 2H_2SO_4$$

In making a determination a portion of the solution was pipetted off (filtered first if necessary) and run into a 100 cc. beaker. Concentrated phosphoric acid was then added to make about 17 per cent of the total volume, (2 cc. conc. acid to 10 cc. of solution being tested) and 0.2 gm. potassium periodate added. The periodate must be added after the acid,

otherwise intermediate oxidation products of manganese are liable to form. The mixture was then boiled for about one minute, and allowed to etand on a hot eand bath for about five minutes, after which it wae put into a Nessler tube, diluted to 50 cc. and compared with standards prepared in the same manner. Due to the presence of periodate in excess the standards may be kept for about three months before making up a new set. This method is able to detect 0.0017 ppm of manganeee when 50 cc. of solution are teeted. The largest amount of manganese which can be present without the color becoming too deep for compaßison is about 12.0 ppm.

6. The Composition of Precipitates which are Formed in the Solutions of Nutrient Salts.---Due to the nutrient salts being used in high concentrations, precipitates are often formed either upon mixing the component ealts, or upon adjusting the pH. Thus we may have for example:

$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 \dashrightarrow \underset{\text{ppt.}}{CaSO_4} + (NH_4)_2(H_2PO_4)_2$$

ae a reaction between the component salte, or

$$Ca(H_2PO_4)_2 + KOH \dashrightarrow \underset{\text{ppt.}}{CaHPO_4} + KH_2PO_4 + H_2O$$

ae a reaction taking place when adjueting the pH.

The precipitates formed were studied microscopically in order to learn what reactions had occurred in the solution. Such knowledge might help in ascertaining the reactions undergone by manganeee.

In order to identify the kinds of precipitates which were formed from their shape, the crystal shapes were determined of as

many known samples of nutrient salts and their various reaction products as were available. When such samples were not available the structure could often be found given in Mellor's "Comprehensive Treatise of Inorganic and Theoretical Chemistry", or some book on crystal structure.

Due to the very small amount of manganese used in the solutions in comparison to the other components, the crystal structure of the manganese precipitate could not usually be determined, as the amount was only a minute fraction of the total precipitate present.

D. Single Salt Solutions

1. Data.---The solubility of manganese in the six single salt solutions was determined, using a series of fifteen solutions of each salt. Ten of these solutions contained manganese (10 ppm) with the nutrient salt. The other five (controls) contained no manganese. The pH of the solutions containing manganese was adjusted by small amounts of acid or alkali, so that they covered about the range pH 3.5 - pH 8.5, the succeeding solutions differing by about 0.5 pH. The pH of the controls was adjusted so that succeeding solutions differed by about 1.0 pH. The controls were used in order to discover whether or not the presence of manganese affected the pH of the solutions containing it. As soon as the pH of the solutions to which manganese had been added was adjusted two duplicate samples were removed and tested for the amount of manganese dissolved. Every 24

hours the pH of the solution was taken, and the amount of manganese in solution determined. This procedure was continued until the solutions had reached apparent equilibrium. Tests of the pH values of control solutions also were made daily.

The results obtained when 0.05 M solutions of calcium dihydrogen phosphate were allowed to stand at various pH, with manganese sulfate present (10 ppm), and without manganese sulfate, are recorded in Table I. The adjustments of the pH were made with strong potassium hydroxide solution. Although this introduces a foreign element it will be shown later that it did no harm. Determination of the amount of dissolved manganese in solutions to which it was added, and pH tests on all solutions, were made at the start and daily thereafter for four days. The initial pH values varied from 3.3 to 8.7. The precipitation of manganese began between pH 5.0 and pH 5.6 (solutions 3 and 4) and was complete at pH 6.1 (solution 5). The fact that manganese was completely precipitated at a pH less than 7.0 can better be explained later when the subsequent solutions have been discussed. Microscopic examination of precipitates showed that calcium monohydrogen phosphate occurs between pH 5.0 and pH 6.5 (solutions 3 - 6 inc., controls 12 and 13), above pH 6.1 tricalcium phosphate was found. The pH changes of the solutions containing manganese were entirely analogous to those of the controls, which showed that these changes must be due to the attainment of equilibrium between the precipitate and solution phases. The sharp decrease in pH in all solutions above pH 8.0, on standing, was probably due to the hydrolysis of tricalcium phosphate:

$$Ca_3(PO_4)_2 + 2HOH \text{ ----- } 2CaHPO_4 + Ca(OH)_2.$$

With potassium dihydrogen phosphate and all other single salt solutions the same system was followed as with the calcium dihydrogen phosphate. Table II gives the results obtained with potassium dihydrogen phosphate (0.1 M). The pH was adjusted with strong potassium hydroxide. Manganese started to precipitate at about pH 7.0 (solution 7), but at pH 8.7 (solution 10) an appreciable amount, 1.7 ppm, still remained in solution. The precipitate of manganese was of reddish-brown color, amorphous looking under the microscope. When filtered off this precipitate was found to dissolve in sulfurous acid, in an acidified ferrous ammonium sulfate solution, and in strong hydrochloric acid. The solution in the latter gave the green color of manganic chloride. These facts seem to show that the precipitate was some hydrated oxide of manganese, having a valence of 3 or 4. Since, however, the precipitate was an oxidized form of manganese, and unoxidized manganese had been initially present, it seems that the manganese must have first precipitated as manganous hydroxide, and the latter oxidized by dissolved oxygen to a condition of higher valence. For convenience this precipitate of manganese will be called the hydrated oxide. It was very probably hydrated manganese dioxide, as its dark brown color denoted an oxidized form of manganese. The reader should note here that manganese precipitated from calcium dihydrogen phosphate solutions between pH 5.0 and pH 6.1. No pH changes took place in any of the solutions in this set. This immediate attainment of equilibrium was probably due to the fact that the less acid potassium phosphates are all soluble. A very slight amount of amorphous white precipitate was present in all solutions above pH 4.5.

Table III gives the data obtained with calcium nitrate (0.1 M). The pH was adjusted with dilute calcium hydroxide. It was found that manganeee etarted to precipitate as the hydrated oxide at about pH 7.5 (solution 9) but 7 ppm. of the original 10 ppm. remained in solution at pH 8.2 (solution 9). The amount of manganeee dissolved remained constant throughout the 96 hour period. Solutione 3, 4 and 6, initial pH 5.2, 5.5 and 6.5 respectively, all increased in pH during the first 24 hours. The respective controle remained constant throughout the test period. This increase in pH must have been due to some reaction giving hydroxyl ions to the eyetem, and in some way connected with manganeee. It was noticed when adjusting the pH of these eolutions (3, 4 and 6) with calcium hydroxide, that a very fine suspension of hydrated manganeee oxide was formed. Thie disappeared during the firet 24 hours. Thus the reaction,

$$Ca(OH)_2 + MnSO_4 \text{ ----- } CaSO_4 + Mn(OH)_2$$

could on revereal (right or left) produce the soluble calcium hydroxide, and thue increase the pH. This is a possible explanation for the action noticed.

In the manganeee containing solutione and controle above pH 7.0 a decrease in pH took place. The following reaction may have occurred:

$$Ca(NO_3)_2 + Ca(OH)_2 \text{ ---- } 2Ca(NO_3)(OH),$$

the basic calcium nitrate removing hydroxyl ione from the sphere of action. Although not substantiated by other proof thie reaction can not be called purely hypothetical, ae both baeic lead nitrate,

($Pb(OH)NO_3$) and basic bismuth nitrate ($Bi(OH)_2NO_3$) are recognized as definite compounds. As explained above the adsorption of hydroxyl ions by precipitated manganese oxides, also may have been a contributing factor in the lowering of the pH. No precipitate other than manganese was present in any solution.

A solution of 0.1 M potassium nitrate gave similar results to that of calcium nitrate (Table IV). The pH of this series was adjusted with dilute potassium hydroxide. Precipitation of manganese began as the hydrated oxide at about pH 7.5 (solution 8), but 7 ppm. of the initial 10 ppm, remained in solution at pH 8.7 (solution 10). None of the control solutions changed in pH during the test period, but all solutions from which manganese had precipitated decreased in pH. This seems direct evidence that hydroxyl ions were adsorbed by the precipitated manganese. Solution 6 (pH 6.6 initially) showed an increase in pH which was probably due to a resolution of the slight amount of colloidal hydrated manganese oxide it contained during the first 24 hours, thus such a reaction as:

$$Mn(OH)_2 + K_2SO_4 \text{ ----- } 2KOH + MnSO_4$$

would account for the increase in pH. The manganese oxide precipitate was the only precipitate present in any of the solutions.

With 0.1 M magnesium sulfate (Table V) slightly different results were obtained. Although potassium hydroxide was used in adjusting the pH, only a few drops of a very dilute solution of this substance were used at the most, so that the amount can be considered negligible. The hydrated oxide of manganese began to precipitate at pH 7.5 (solution 9). Although the amount precipitated was not

detectable, the solution was of a faint yellow brown color throughout the test period. Solution 10 (initial pH 8.7) still had 9.8 ppm, of the 10 ppm. added, in solution. The four solutions of highest pH (14, 9, 10 and 15) all showed a decrease in pH, Nos. 9 and 10 which contained manganese showing the larger change. As before the following two reactions may be presumed to have occurred:

(1) $MnO_2.H_2O$ adsorbing hydroxyl ions

(2) $MgSO_4 + KOH \longrightarrow KMg(OH)SO_4$.

The combination of (1) and (2) causing a larger decrease than (2) alone. The only precipitate occurring in any solution was that of amorphous manganic hydroxide.

The next solutions, 0.1 M ammonium sulfate (Table VI) showed no precipitation of manganese as high as pH 8.7 (solution 10). The pH was adjusted with dilute ammonium hydroxide. There were no changes in the pH of the solutions containing manganese, or of the controls, at any time during this experiment. No precipitate was present in any of the solutions.

2. Conclusions on Single Salt Systems.---The foregoing results show that manganese precipitated from solutions of calcium nitrate, potassium dihydrogen phosphate, potassium nitrate and magnesium sulfate, as some form of hydrated oxide. Incipient precipitation occurred at pH 7.0 - 7.5, and in no case was complete at pH 8.5, the greater part of the manganese usually remaining in solution. If the formation of the hydrated oxide took place below pH 7.0, due to a local high concentration of alkali in adjusting the pH, it redissolved on diffusion and standing and thus increased

the pH by giving hydroxyl ions to the system; provided, of course, no phosphates (buffers) were present. Thus in general for the cation M and anion A

$$Mn(OH)_2 + MA \dashrightarrow MnA + M(OH)_2$$

$M(OH)_2$ being a soluble base.

On the other hand if a precipitate of the hydrated oxide of manganese, of valence higher than 2, was formed above pH 7.0 - 7.5 it remained undissolved and was a factor in decreasing the pH through adsorption of hydroxyl ions. This, however, had no effect in solutions containing buffers.

Another reaction which might have decreased the pH, but occurred independent of manganese, w as the formation of basic salts. For example,

$$M(OH)_2 + MA_2 \dashrightarrow M_2A_2(OH)_2$$

which on hydrolysis gives:

$$M_2A_2(OH)_2 \dashrightarrow 2MOH^+ + 2A^-.$$

Here the A^- ion would have much more influence on the pH than the complex MOH^+ ion.

Complete precipitation of manganese from a calcium dihydrogen phosphate solution took place between pH 5.0 and pH 6.1. In a solution of potassium dihydrogen phosphate manganese started to precipitate as the hydrated oxide at pH 7.1. Britton (16) found that a solution of manganese (ous form) yielded a precipitate of manganous hydroxide at pH 8.4. The author's work on single salt solutions indicates that a precipitate of manganous hydroxide once formed above pH 7.0, will become oxidized by dissolved oxygen and thus remain insoluble. Thus we may say that no permanent precipitate of hydrated manganese oxide exists below pH 7.0.

In order to determine, if possible, the nature of the manganese precipitate from solutions of calcium dihydrogen phosphate the following experiments were carried out. Two solutions, one containing 5 grams $MnSO_4.4H_2O$, the other 9 grams $Na_2HPO_4.12H_2O$, approximately equivalent amounts, were mixed. A white precipitate, probably $MnHPO_4$, was formed thus:

$$MnSO_4 + Na_2HPO_4 \longrightarrow MnHPO_4 + Na_2SO_4$$

This precipitate was dissolved by addition of a small amount of phosphoric acid. Dilute, 2 per cent, NaOH was then added drop by drop until a very slight permanent precipitate of $MnHPO_4$ formed. The pH of the solution was 4.6. This was repeated three more times, and results of pH 4.5, 4.5 and 4.6 were obtained.

Another experiment using 1 gm. manganese sulfate and about 3 equivalents of phosphoric acid gave 4.5, 4.6 and 4.6 as the precipitation point of $MnHPO_4$. The $MnHPO_4$ was precipitated with 2 per cent sodium hydroxide.

A third experiment with 1 gm. manganese sulfate and 3 equivalents of phosphoric acid gave 4.8, 4.7, 4.7 and 4.7, ass the precipitation points of $MnHPO_4$. In this case 2 per cent potassium hydroxide was used in precipitating the $MnHPO_4$.

Thus manganese precipitated from the calcium dihydrogen phosphate solution as $MnHPO_4$.

In duscussing the results obtained with calcium dihydrogen phosphate, reference was made to the fact that the use of potassium hydroxide in adjusting the pH of this solution introduced a foreign element. From the above discussion it seems that this substance did not prevent the precipitation of manganese as a phosphate.

It is now necessary to give an explanation for manganese not being precipitated as a phosphate from a potassium dihydrogen phosphate solution. In experiment 3 above, we saw that manganese w as precipitated as a phosphate by potassium hydroxide. The only difference between experiment 3 and the experiment with potassium dihydrogen phosphate solutions, as shown in Table II, is that in the former case the ratio of manganese to phosphate was 1 to 3 (equivalents), whereas in the latter it was 1 to 550. It thus seems necessary to assume that manganese was held in solution until pH 7.0 was reached a s a complex soluble potassium manganese phosphate. At pH 7.0 it was precipitated as the hydrated oxide. Bansa (4) reported the formation of a potassium manganese tetrahydrodihypophosphate. This supports the author's opinion.

Solutions of ammonium sulfate made ammoniacal keep manganese in solution up to pH 8.7. The manganese is probably held in solution at such a high pH by the formation of a complex with ammonium sulfate, for example $(NH_4)_2Mn(SO_4)_2$.

Table I

Salt present: m/20 $Ca(H_2PO_4)_2.H_2O$
Solutions 1 - 10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt present.
	pH	3.3	3.3	3.3	3.3	3.3	
2	Mn ppm	10	10	10	10	10	
	pH	4.3	4.2	4.3	4.3	4.3	" " "
11	pH	4.0	4.0	4.0	4.0	4.0	" " "
3	Mn ppm	10	10	10	10	10	ppt. $CaHPO_4$
	pH	5.0	4.2	4.3	4.3	4.3	
4	Mn ppm	4.2	7.0	7.0	7.0	7.0	" "
	pH	5.6	5.7	5.7	5.7	5.7	
12	pH	5.2	5.8	5.8	5.8	5.8	" "
5	Mn ppm	<.05	<.05	<.05	<.05	<.05	ppt $CaHPO_4$; mostly $Ca_3(PO_4)_2$
	pH	6.1	6.5	6.6	6.5	6.5	
6	Mn ppm	<.05	<.05	<.05	<.05	<.05	
	pH	6.5	6.7	6.8	6.8	6.8	" " "
13	pH	6.1	6.2	6.1	6.1	6.1	ppt $CaHPO_4$
7	Mn ppm	<.05	<.05	<.05	<.05	<.05	ppt $Ca_3(PO_4)_2$
	pH	7.0	7.1	7.1	7.1	7.1	
8	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	7.6	7.5	7.5	7.5	7.5	
14	pH	7.3	7.4	7.3	7.3	7.3	" "
9	Mn ppm	<0.5	<.05	<.05	<.05	<.05	" "
	pH	8.1	8.1	7.8	7.7	7.7	
10	Mn ppm	<0.5	<.05	<.05	<.05	<.05	" "
	pH	8.7	8.4	8.3	8.2	8.2	
15	pH	8.4	8.3	8.3	8.1	7.9	" "

Table II

Salt present: M/10 KH_2PO_4.
Solutions 1 - 10 inc. 10 ppm Mn added; 11 - 15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt present.
	pH	4.0	4.0	4.0	4.0	4.0	
2	Mn ppm	10	10	10	10	10	Small amount white
	pH	4.5	4.5	4.5	4.5	4.5	ppt. amorphous.
11	pH	4.0	4.0	4.0	4.0	4.0	No ppt present
3	Mn ppm	10	10	10	10	10	Small amount amor-
	pH	4.9	4.9	4.9	4.9	4.9	phous white ppt.
4	Mn ppm	10	10	10	10	10	" "
	pH	5.5	5.5	5.5	5.5	5.5	
12	pH	5.0	5.0	5.0	5.0	5.0	" "
5	Mn ppm	10	10	10	10	10	" "
	pH	6.1	6.1	6.1	6.1	6.1	
6	Mn ppm	10	10	10	10	10	" "
	pH	6.6	6.6	6.6	6.6	6.6	
13	pH	5.9	5.9	5.9	5.9	5.9	" "
7	Mn ppm	7.8	7.8	7.8	7.8	7.8	Amorphous white ppt
	pH	7.1	7.1	7.1	7.1	7.1	and a brown manganese oxide ppt.
8	Mn ppm	6.5	6.5	6.5	6.5	6.5	
	pH	7.5	7.5	7.5	7.5	7.5	" "
14	pH	6.9	6.9	6.9	6.9	6.9	Amorphous white ppt only.
9	Mn ppm	4.0	4.0	4.0	4.0	4.0	Amorphous white ppt
	pH	8.1	8.1	8.1	8.1	8.1	and a brown manganese oxide ppt.
10	Mn ppm	1.7	1.7	1.7	1.7	1.7	
	pH	8.7	8.7	8.7	8.7	8.7	" "
15	pH	8.1	8.1	8.1	8.1	8.1	Amorphous white ppt only.

Table III

Salt present: M/10 $Ca(NO_3)_2.4H_2O$.
Solutions 1 - 9 inc. 10 ppm Mn added; 11 - 15 (controls) no Mn added.
Adjustment of pH with $Ca(OH)_2$.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Clear soln. no ppt
	pH	3.8	3.8	3.8	3.8	3.8	present.
2	Mn ppm	10	10	10	10	10	
	pH	4.5	4.5	4.5	4.5	4.5	" "
11	pH	4.2	4.2	4.2	4.2	4.2	" "
3	Mn ppm	10	10	10	10	10	" "
	pH	5.2	5.3	5.3	5.3	5.3	
4	Mn ppm	10	10	10	10	10	" "
	pH	5.5	5.6	5.7	5.7	5.7	
12	pH	5.4	5.4	5.4	5.4	5.4	" "
5	Mn ppm	10	10	10	10	10	" "
	pH	6.1	6.1	6.1	6.1	6.1	
6	Mn ppm	10	10	10	10	10	" "
	pH	6.5	6.7	6.7	6.7	6.7	
13	pH	6.4	6.4	6.4	6.4	6.4	" "
7	Mn ppm	10	10	10	10	10	" Slightly
	pH	7.2	7.1	7.1	7.1	7.1	yellow thru run.
8	Mn ppm	9	9	9	9	9	Small amt. brown ppt
	pH	7.5	7.3	7.1	7.1	7.1	manganese oxide.
14	pH	7.3	7.3	7.3	7.3	7.3	No ppt.
9	Mn ppm	7	7	7	7	7	Small amt. brown ppt
	pH	8.2	7.4	7.3	7.3	7.3	manganese oxide.
10	---						
15	pH	8.3	8.1	7.7	7.4	7.3	No ppt.

Table IV

Salt present: M/10 KNO_3.
Solutions 1 - 10 inc. 10 ppm Mn added; 11 - 15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt. present.
	pH	3.3	3.7	3.7	3.7	3.7	
2	Mn ppm	10	10	10	10	10	
	pH	4.2	4.2	4.2	4.2	4.2	" "
11	pH	4.1	4.1	4.1	4.1	4.1	" "
3	Mn ppm	10	10	10	10	10	" "
	pH	5.1	5.1	5.1	5.1	5.1	
4	Mn ppm	10	10	10	10	10	" "
	pH	5.7	5.7	5.7	5.7	5.7	
12	pH	5.0	5.0	5.0	5.0	5.0	" "
5	Mn ppm	10	10	10	10	10	" "
	pH	6.1	6.1	6.1	6.1	6.1	
6	Mn ppm	10	10	10	10	10	Faintly yellow at first,
	pH	6.6	6.6	6.7	6.8	6.8	clear after 24 hrs. No ppt.
13	pH	6.2	6.2	6.2	6.2	6.2	No ppt.
7	Mn ppm	10	10	10	10	10	Faintly yellow at first,
	pH	6.9	6.9	6.9	6.9	6.9	clear after 24 hrs. No ppt.
8	Mn ppm	10	10	10	10	10	
	pH	7.5	7.3	7.3	7.3	7.3	Faintly yellow thru run.
14	pH	7.0	7.0	7.0	7.0	7.0	No ppt.
9	Mn ppm	9	9	9	9	9	Small amt. brown ppt
	pH	7.9	7.5	7.5	7.5	7.5	manganese oxide.
10	Mn ppm	7	7	7	7	7	
	pH	8.8	7.4	7.3	7.3	7.3	" "
15	pH	8.1	8.1	8.1	8.1	8.1	No ppt.

Table V

Salt present: M/10 $MgSO_4.7H_2O$.
Solutions 1 - 10 inc. 10 ppm Mn added; 11 - 15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt. present.
	pH	3.5	3.5	3.5	3.5	3.5	
2	Mn ppm	10	10	10	10	10	" " "
	pH	4.2	4.2	4.2	4.2	4.2	
11	pH	4.0	4.0	4.0	4.0	4.0	" " "
3	Mn ppm	10	10	10	10	10	" " "
	pH	4.5	4.5	4.5	4.5	4.5	
4	Mn ppm	10	10	10	10	10	" " "
	pH	5.0	5.1	5.1	5.1	5.1	
12	pH	4.7	4.7	4.7	4.7	4.7	" " "
5	Mn ppm	10	10	10	10	10	" " "
	pH	5.5	5.5	5.5	5.5	5.5	
6	Mn ppm	10	10	10	10	10	" " "
	pH	5.9	5.9	5.9	5.9	5.9	
13	pH	5.9	5.9	5.9	5.9	5.9	" " "
7	Mn ppm	10	10	10	10	10	" " "
	pH	6.5	6.5	6.5	6.5	6.5	
8	Mn ppm	10	10	10	10	10	" " "
	pH	6.9	6.9	6.9	6.9	6.9	
14	pH	7.0	6.9	6.8	6.8	6.8	" " "
9	Mn ppm	10	10	10	10	10	Very slight yellow.
	pH	7.5	7.3	7.3	7.2	7.1	
10	Mn ppm	9.8	9.8	9.8	9.8	9.8	Very slight amt. brown
	pH	8.7	7.6	7.5	7.4	7.4	manganese oxide ppt.
15	pH	8.1	7.7	7.3	7.1	7.1	No ppt. present.

Table VI

Salt present: M/10 $(NH_4)_2SO_4$.
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH.

No.	Test	Time in Hours 0	24	48	72	Remarks
1	Mn ppm	10	10	10	10	No ppt present.
	pH	3.5	3.5	3.5	3.5	
2	Mn ppm	10	10	10	10	" " "
	pH	4.3	4.3	4.3	4.3	" " "
11	pH	4.2	4.2	4.2	4.2	" " "
3	Mn ppm	10	10	10	10	" " "
	pH	4.9	4.9	4.9	4.9	
4	Mn ppm	10	10	10	10	" " "
	pH	5.3	5.3	5.3	5.3	
12	pH	5.1	5.1	5.1	5.1	" " "
5	Mn ppm	10	10	10	10	" " "
	pH	5.9	5.9	5.9	5.9	
6	Mn ppm	10	10	10	10	" " "
	pH	6.5	6.5	6.5	6.5	
13	pH	5.9	5.9	5.9	5.9	" " "
7	Mn ppm	10	10	10	10	" " "
	pH	7.0	7.0	7.0	7.0	
8	Mn ppm	10	10	10	10	" " "
	pH	7.5	7.5	7.5	7.5	
14	pH	7.1	7.1	7.1	7.1	" " "
9	Mn ppm	10	10	10	10	" " "
	pH	8.0	8.0	8.0	8.0	
10	Mn ppm	10	10	10	10	" " "
	pH	8.7	8.7	8.7	8.7	
15	pH	8.1	8.1	8.1	8.1	" " "

E. The Double Salt Solutions

1. Data.---The solubility determinations of manganese in the double salt solutions were made with the same concentrations of the components as in the single salt solutions. Thus solutions containing calcium dihydrogen phosphate were 0.05 molar with respect to this salt and 0.1 molar with respect to the other component salt. To solutions 1-10 of each set 10 ppm. of manganese were added. The control solutions 11 - 15 contained no manganese.

The same scheme of making manganese determinations and pH tests was followed with the double salt solutions, as was done with the single salts. In general, however, the solutions were kept and tested over a longer period of time.

Table VII gives the results obtained with solutions containing both calcium dihydrogen phosphate and calcium nitrate. The pH was adjusted with strong potassium hydroxide, but no evidence was forthcoming to show that this substance affected the form of the manganese precipitate. The precipitation of manganese began at pH 5.3 (solution 5) and was complete at pH 7.1 (solution 8). This shows that the calcium nitrate kept part of the manganese in solution until a higher pH was reached, than was the case with calcium dihydrogen phosphate alone. Since manganese started to precipitate from a solution of calcium nitrate at pH 7.5, it is evident from the conclusions drawn with single salt solutions, that the precipitation of manganese in this case also occurred as a manganese phosphate; namely $MnHPO_4$.

Some of the precipitated manganese redissolved slowly as the solutions attained equilibrium. This may have been due to the solubility of the manganese phosphate in the nitric acid produced by the following reaction.

(1) $Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$ ----- $\underset{\text{insol. ppt.}}{Ca_3PO_4} + 4HNO_3$

Microscopic examination showed that precipitation of $CaHPO_4$ began at pH 4.1, and that after pH 5.3 - 5.9 was passed the precipitate was wholly $Ca_3(PO_4)_2$. In solutions where the pH changed very much it generally decreased. This was probably due to the nitric acid produced in (1) and also to the attainment of buffer equilibrium between the liquid and solid phase. Manganese was not a factor in any of the pH changes noted.

In Table VIII are given the results obtained with solutions containing both calcium and potassium dihydrogen phosphates. The pH was adjusted with strong potassium hydroxide. Total precipitation of manganese occurred between pH 4.6 (solution 3) and pH 7.1 (solution 8). The lower pH of incipient precipitation here than with either of these salts alone was probably due to the increased concentration of the phosphate ion. From previous considerations it seems that in this set the manganese also must have precipitated as a phosphate. After the first 24 no change occurred in either the amount of dissolved manganese or the pH of any solution, which showed a quick return of the solutions to equilibrium. Microscopic examination showed precipitation of $CaHPO_4$ to occur between pH 4.0 and 5.1, but no K_2HPO_4. This did not precipitate because of its solubility. Above pH 5.1 amorphous looking $Ca_3(PO_4)_2$ and probably K_3PO_4 were formed. Comparison with the controls showed that manganese was not a factor in any pH changes.

The results in Table IX, with solutions of calcium dihydrogen phosphate and potassium nitrate again point to the precipitation of manganese as a manganese phosphate. The pH of these solutions was adjusted with potassium hydroxide. Precipitation of manganese began at pH 4.9 (solution 4) and was complete at pH 6.7 (solution 7). In solutions 3, 4, 5 and 6, initial pH 4.6, 5.0, 5.7 and 6.1, some of the manganese which had precipitated returned to solution during the first 24 hours. After this no change occurred. The pH of solutions 3 and 4 decreased during the first 24 hours and that of solutions 5 and 6 increased. Since, however, the pH of the controls followed the same trend, all these facts must have been due to the attainment of equilibrium on standing, by exchanges between the solid and liquid phas es. Microscopic examination showed $CaHPO_4$ crystals between pH 4.1 and 6.4. Above pH 6.5 amorphous appearing $Ca(PO_4)_2$ was formed.

In Table X are results obtained with solutions of calcium dihydrogen phosphate and magnesium sulfate. The pH was adjusted with strong potassium hydroxide. Total precipitation of manganese took place between pH 6.0 and pH 7.0. The precipitation point in this set was thus intermediate between the pH of precipitation with each of these salts separately. In view of data yet to be presented the composition of this precipitate will be taken up later. Solutions 6 and 7, pH 6.0 and pH 6.5, containing initially 2.2 and 0.52 ppm. of manganese in solution, showed an increase to 6.5 and 1.9 ppm. respectively over a period of 144 hours, as equilibrium was attained on standing. None of the other solutions showed any change in the amount of dissolved manganese. Since the pH values of the controls followed very closely those of the manganese containing solutions manganese had no part in

pH changes. Microscopic examination showed all solutions to contain calcium sulfate crystals. $CaHPO_4$ crystals were identified in solutions having pH between 4.0 and 6.0 above pH 6.0 crystals were formed which were thought to be $MgHPO_4$. No $Ca_3(PO_4)_2$ was observed.

Table XI shows the results obtained with solutions of calcium dihydrogen phosphate and ammonium sulfate. The pH was adjusted with strong ammonium hydroxide. Precipitation of manganese began at pH 5.4 (solution 5), but was not complete until pH 8.0 (solution 10). This shows that ammonium sulfate prevented to a marked degree the precipitating action of calcium dihydrogen phosphate on manganese. The pH of all solutions above pH 3.8 (solution 2) showed a decrease, both in the controls in the manganese containing solutions. Coincident with this all of those solutions, except 10 from which precipitation of manganese had partly begun, showed an increase in the amount of manganese dissolved, on standing. This was due probably to the decreasing pH which was caused by the slow attainment to equilibrium of the solutions. A precipitate of $CaSO_4$ was present in all the solutions. Above pH 5.4 some $CaHPO_4$ occurred and $Ca_3(PO_4)_2$ above pH 8.1. The form in which manganese precipitated from this solution will be discussed later.

The results obtained with solutions containing calcium nitrate and potassium dihydrogen phosphate are given in Table XII. Here the pH was adjusted with strong potassium hydroxide solution. Precipitation of mangamese began at pH 5.1 (solution 4) but at pH 7.2 (solution 10 changed from pH 8.0 to 7.2 in 200 hours) 0.15 ppm of manganese were in solution. With either of these two salts alone manganese precipitated as a hydrated oxide at a pH slightly over 7.0. These facts seem to point to precipitation of manganese as a phosphate. The final amount of manganese in any

solution from which it had partly precipitated on the average was about 0.24 ppm. Changes in pH occurred in all solutions, except 1 and 11, some decreased others increased. These changes did not involve manganese, but were due to the attainment on standing of equilibrium between the solid and liquid phases. Microscopic examination showed $CaHPO_4$ crystals from pH 3.6 to pH 6.2 and $Ca_3(PO_4)_2$ above pH 6.2, although in solution 9 (pH 7.7-5.8) some $CaHPO_4$ was also found.

The solubility of manganese in solutions containing calcium and potassium nitrates is presented in Table XIII. The pH was adjusted with a dilute solution of potassium hydroxide. Precipitation of manganese as a hydrated oxide began at pH 6.7 (solution 7), but very little precipitated out as solution 10, of pH 8.2 initially, contained after 250 hours 8.2 of the 10 ppm of manganese introduced at the start. The decreases in pH occurring in solutions 7, 8, 9, 10, 13 and 15 may be explained as before on the assumption that hydroxyl ions were removed from the system to form the basic calcium nitrate. The precipitated manganese by adsorption of hydroxyl ions, may also have contributed to the lowering of the pH in solutions 8, 9 and 10, but this seemed here a secondary factor. No precipitate other than the hydrated oxide of manganese was present in any of the solutions.

Table XIV shows the results obtained with solutions of calcium nitrate and magnesium sulfate. The pH was adjusted with a calcium hydroxide solution. No precipitation of manganese occurred from any solution, even though solution 10 was raised to pH 8.7. Comparison with the control solutions showed that manganese was not a factor in any pH changes. The increased acidity occurring in most of the solutions above pH 6.4

(solution 5) may have been caused by the formation of a basic magnesium nitrate. Another cause may have been the slight hydrolysis of the calcium sulfate precipitate which was present in all the solutions.

In Table XV are the records obtained with colutions of calcium nitrate and ammonium sulfate. The pH was adjusted with dilute ammonium hydroxide. A copious calcium sulfate precipitate formed in every flask left the solutions mostly ammonium nitrate. Manganese did not begin to precipitate until pH 8.7 (solution 10), and then not until this solution had stood about 200 hours. The small amount of precipitate formed at first seemed to catalyze the formation of more. This dormant effect may have been caused by very slow oxidation of the manganese by air. Of the 10 ppm. of manganese initially present in solution 10, 6.0 ppm. were in solution at 200 houre, and at 250 hours 1.5 ppm. remained dissolved. Solutions 5, 6 and control 13 of pH 6. 0 , 6.7 and 6.4 initially showed a decrease in pH over the time period and were the only solutions to change essentially. This change may have been due to the slow hydrolysis of calcium sulfate.

Table XVI gives the data secured with solutions containing potassium dihydrogen phosphate and potassium nitrate. The pH of these solutions was adjusted with strong potaesium hydroxide solution. Precipitation of manganese as a hydrated oxide began at pH 7.1 but was not complete at pH 8.5 as 2.5 of the initial 10 ppm. were still dissolved. The amount of manganeee in solution reached constant value, in moet cases within the first 24 hours. No pH changes occurred in either the controls or the manganese containing solutions. A very small amount of

white flaky ssemingly amorphous precipitate was dspositsd in all flasks during the 200 hour period. Its composition could not bs determined.

Table XVII shows the results obtained with potassium dihydrogen phosphate and magnesium sulfate. The pH of thess solutions was adjusted with strong potassium hydroxide solution. Precipitation of manganess began at pH 5.0 (solution 3) and was complste at pH 8.7 (solution 10). The form of this precipitats of manganese will be taksn up later. In solutions 3, 4, 5, 6, 7, and 8, ths initial amounts of manganssse in solution wsre 10, 8.5, 10, 5.5, 4.7 and 1.7 ppm, respectively. Ths amount of mangansss dissolvsd in thsss solutions decrsased so that at ths end of 200 hours all but 2.5, 0.6 <.05, <.05, <.05, 0.45 ppm. rsspsctivsly had prscipitated. Solution 9 containsd a constant amount 0.6 ppm. from ths beginning, and solution 10 showsd complete prscipitation throughout ths run. Ths pH of all solutions above pH 5.0, including the controls, dscrsased on standing, so that it is hard to consider ths dscreasing amount of dissolved mangansss to bs a result of the decrsasing pH. Ths prscipitatsd manganese must havs bssn soms compound which attainsd solubility equilibrium slowly. Betwsen pH 5.0 and pH 6.6, six sidsd crystals were formed, which wers probably $MgHPO_4$. Abovs pH 6.6 hexagonal rods and long nssdles wers formed. Thess wers not identified.

The rssults sscursd with solutions of potassium dihydrogen phosphate and ammonium sulfate are shown in Tabls XVIII. The pH was adjusted with a strong potassium hydroxide solution. Manganese startsd to precipitats at pH 6.5 (solution 6), but only after this solution had bssn kept for about 200 hours. At pH 8.5 (solution 10) an apprsciabls

amount of manganese 0.15 ppm.still remained dissolved after 200 hours. The precipitation of manganese once begun continued slowly, the amount in solution at any one time being inversely related to the pH. The precipitated manganese being the only one present in any system was examined microscopically. In solutions 6 and 7 (of pH 6.5 and pH 7.0 respectively) needlelike crystals were formed. In solutions 8, 9 and 10, there were fernlike leaflets made up of small triangular shaped crystals. This change in structure may have been due either to a difference in composition or to the different pH of the solutions. The pH of all solutions in this set remained practically constant, the change of 0.1 pH in a few cases being negligible.

The next solutions to consider are those of potassium nitrate and magnesium sulfate, Table XIX. The pH of these was adjusted with a very dilute solution of potassium hydroxide. Manganese did not precipitate from any of these solutions, even though solution 10 had a pH of 8.6. The solutions were kept and tested for 200 hours. All manganese containing solutions and controls of pH above 5.4 showed a progressive decrease in pH on standing, due no doubt to the formation of a basic magnesium salt. No precipitate was present in any of the solutions.

Table XX gives the data secured with solutions containing potassium nitrate and ammonium sulfate. The pH was adjusted with a dilute solution of potassium hydroxide. No precipitation of manganese took place before pH 8.5.(solution 10). This pH seemed to be the threshold of precipitation, as this solution showed just a trace of

the yellow brown color due to colloidal manganese oxide. No pH changes any larger than 0.1 pH occurred in any solution. This may be considered negligible. Solutions 8, 9 and 10 of this set, of pH 7.5, 8.0 and 8.5 respectively, were the only solutions of this to contain a precipitate. This precipitate was white, amorphous, and very slight in amount.

The data obtained with solutions containing magnesium and ammonium sulfates is given in Table XXI. The pH was adjusted with dilute ammonium hydroxide. No precipitation of manganese took place from any solution containing it even though solution 10 was of pH 8.7. The solutions were kept 200 hours. All controls and manganese containing solutions between pH 5.5 and pH 7.6 showed decreases in pH on standing, such decrease, however, never amounting to over 0.6 pH. This shows that manganese was not a factor in decreasing the pH. The cause of this pH decrease seemed due to the absorption by the system of hydroxyl ions from the ammonia used in pH adjustment, in order to form a basic salt of magnesium.

2. Conclusions on Double Salt Solutions.---The evidence is now available for a more comprehensive discussion of the form in which manganese precipitated from the following four double salt combinations:

I	II	III	IV
$Ca(H_2PO_4)_2$	$Ca(H_2PO_4)_2$	KH_2PO_4	KH_2PO_4
$MgSO_4$	$(NH_4)_2SO_4$	$MgSO_4$	$(NH_4)_2SO_4$

In the single salt solutions (1) $Ca(H_2PO_4)_2$, (2) KH_2PO_4, (3) $MgSO_4$ and (4) $(NH_4)_2SO_4$, manganese precipitated as (1) $MnHPO_4$,

(2) and (3) as the hydrated oxide, and in (4) no precipitation of manganese took place. The $MnHPO_4$ precipitate formed between pH 5.0 and pH 6.5. The hydrated oxide precipitate only formed permanently above pH 7.0. Since in the four double salt combinations given above the precipitation of manganese began <u>below</u> pH 6.5, the manganese precipitate in these solutions could not have been the hydrated oxide. Therefore it seems that manganese precipitated from these four double salt combinations as a phosphate. In combinations I, II and III the precipitate was probably $MnHPO_4$ and in IV the compound NH_4MnPO_4. This latter precipitate (NH_4MnPO_4) was totally different in crystal shape from $MnHPO_4$. Reference to textbooks on analytical chemistry showed that the conditions in combination IV were ideal for the formation of NH_4MnPO_4.

The precipitation of manganese as a phosphate from these four combinations extended over a longer pH range, than its precipitation as a phosphate from a solution of manganese sulfate and phosphoric acid, by sodium hydroxide. This longer precipitation range was due to the effect of the nutrient salts present and also because such a small amount of manganese was present. Thus the alkali used in adjusting the pH would precipitate the less soluble (more basic) phosphates of calcium and magnesium due to these elements being present in large amounts, and show a sparing action toward manganese. The case in which ammonium sulfate was present in a solution containing phosphates there was a tendency to form a complex with manganese and thus prevent its precipitation at lower pH values.

Comparisons with single salt solutions show that calcium nitrate, potassium dihydrogen phosphate and potassium nitrate do not materially change the precipitation range of manganese in a calcium dihydrogen phosphate solution.

Any double salt solution of magnesium or ammonium sulfate together with calcium or potassium nitrate, will keep practically all the manganese in solution up to pH 8.5; sometimes no precipitation occurred even at this pH.

When precipitation of manganese occurred from solutions containing no phosphate ions or one containing only the cation potassium and phosphate or nitrate ions, the precipitate was the hydrated oxide of manganese.

The presence of manganese either in solution or as a precipitate, was not found to have any appreciable effect on the pH.

Referring again to the theory that basic salt formation tends to decrease the pH, we find that unless phosphates were present, decreases in pH occurred only in those solutions containing calcium nitrate or magnesium sulfate. The same held true for the single salt solutions. It is seen that these two salts are the only ones, excluding phosphates, with which the formation of a basic salt is possible.

The pH of solutions containing phosphates showed increases and decreases due to the slow attainment of buffer equilibrium upon standing.

Table VII

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 $Ca(NO_3)_2.4H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt.
	pH	3.1	3.1	3.1	3.1	3.1	
2	Mn ppm	10	10	10	10	10	" "
	pH	3.6	3.6	3.6	3.6	3.6	
11	pH	3.1	3.1	3.1	3.1	3.1	" "
3	Mn ppm	10	10	10	10	10	Plates of $CaHPO_4$
	pH	4.1	3.8	3.8	3.8	3.8	
4	Mn ppm	6.5	10	10	10	10	" " "
	pH	4.5	3.7	3.7	3.7	3.7	
12	pH	4.4	3.7	3.7	3.7	3.7	" " "
5	Mn ppm	6.8	7.2	7.2	7.2	7.5	" " "
	pH	5.3	5.2	5.2	5.3	5.3	
6	Mn ppm	1.54	2.8	3.9	5.1	5.0	Amorphous $Ca_3(PO_4)_2$
	pH	5.9	6.1	6.1	6.1	6.1	
13	pH	5.3	5.6	5.7	5.7	5.7	Amorphous $Ca_3(PO_4)_2$, also $CaHPO_4$.
7	Mn ppm	0.51	2.15	3.5	3.6	4.5	Amorphous $Ca_3(PO_4)_2$
	pH	6.5	6.5	6.5	6.5	6.5	
8	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	7.1	7.1	7.1	7.1	7.1	
14	pH	6.6	6.4	6.4	6.4	6.4	" "
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	7.6	6.6	6.4	6.4	6.0	
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	8.2	7.5	7.4	7.3	7.3	
15	pH	7.8	7.8	7.7	7.7	7.7	" "

Table VIII

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 KH_2PO_4
Solutions 1-10 inc. 10 ppm Mn added: 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	20	44	68	Remarks
1	Mn ppm	10	10	10	10	No ppt. present.
	pH	3.3	3.3	3.3	3.3	
2	Mn ppm	10	10	10	10	Plates of $CaHPO_4$
	pH	4.0	4.0	4.0	4.0	
11	pH	3.3	3.3	3.3	3.3	No ppt present.
3	Mn ppm	8	8	8	8	Plates of $CaHPO_4$.
	pH	4.7	4.6	4.6	4.6	
4	Mn ppm	7.5	7.5	7.5	7.5	" "
	pH	4.9	4.9	4.9	4.9	
12	pH	4.6	4.6	4.6	4.6	" "
5	Mn ppm	<.05	5.0	5.0	5.0	Amorphous $Ca_3(PO_4)_2$
	pH	5.1	5.1	5.1	5.1	
6	Mn ppm	<.05	4.5	4.5	4.5	" "
	pH	5.9	6.1	6.1	6.1	
13	pH	5.5	5.5	5.5	5.5	" "
7	Mn ppm	<.05	1.1	1.1	1.1	" "
	pH	6.5	6.7	6.7	6.7	
8	Mn ppm	<.05	<.05	<.05	<.05	" "
	pH	7.1	7.1	7.1	7.1	
14	pH	6.7	6.7	6.7	6.7	" "
9	Mn ppm	<.05	<.05	<.05	<.05	" "
	pH	7.7	7.7	7.7	7.7	
10	Mn ppm	<.05	<.05	<.05	<.05	" "
	pH	8.4	8.4	8.4	8.4	
15	pH	7.6	7.5	7.5	7.5	" "

Table IX

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 KNO_3
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	200	Remarks
1	Mn ppm	10	10	10	10	10	No ppt present
	pH	3.2	3.2	3.2	3.2	3.2	
2	Mn ppm	10	10	10	10	10	Small amt. $CaHPO_4$.
	pH	4.1	4.1	4.1	4.1	4.1	
11	pH	3.3	3.3	3.3	3.3	3.3	No ppt present
3	Mn ppm	9	10	10	10	10	Ppt $CaHPO_4$
	pH	4.6	4.2	4.2	4.2	4.2	
4	Mn ppm	7	8	8	8	8	" "
	pH	5.0	4.9	4.9	4.9	4.9	
12	pH	4.5	4.2	4.2	4.2	4.2	" "
5	Mn ppm	<.05	3	3	3	3	Ppt $CaHPO_4$
	pH	5.7	6.1	6.1	6.1	6.1	
6	Mn ppm	<.05	0.24	0.24	0.24	0.24	" "
	pH	6.1	6.4	6.4	6.4	6.4	
13	pH	5.7	6.1	6.1	6.1	6.1	" "
7	Mn ppm	<.03	<.05	<.05	<.05	<.05	Ppt $Ca_3(PO_4)_2$
	pH	6.7	6.7	6.7	6.7	6.7	
8	Mn ppm	<.03	<.05	<.05	<.05	<.05	" "
	pH	7.2	7.2	7.2	7.2	7.1	
14	pH	6.5	6.6	6.6	6.6	6.6	" "
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	7.8	7.8	7.7	7.7	7.7	
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	" "
	pH	8.2	7.7	7.7	7.7	7.7	
15	pH	7.7	7.7	7.6	7.6	7.6	" "

Table X

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	144	Remarks
1	Mn ppm	10	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.2	3.2	3.2	3.2	3.2	3.2	
2	Mn ppm	10	10	10	10	10	10	
	pH	4.0	4.0	3.9	3.9	3.9	3.9	" " also $CaHPO_4$
11	pH	3.2	3.2	3.2	3.2	3.2	3.2	" "
3	Mn ppm	10	10	10	10	10	10	" " also $CaHPO_4$
	pH	4.7	4.5	4.4	4.4	4.4	4.4	
4	Mn ppm	10	10	10	10	10	10	" " " "
		5.1	4.7	4.7	4.7	4.6	4.6	
12	pH	4.6	4.4	4.3	4.3	4.3	4.3	" " " "
5	Mn ppm	10	10	10	10	10	10	" " " "
	pH	5.5	4.9	4.9	4.8	4.8	4.7	
6	Mn ppm	2.2	5.0	6.5	6.5	6.5	6.5	" " " "
	pH	6.0	6.0	5.9	5.9	5.9	5.6	
13	pH	5.8	5.3	5.0	5.0	5.0	4.9	Ppt $CaSO_4$, also $CaHPO_4$ and $MgHPO_4$
7	Mn ppm	0.52	0.62	0.80	1.1	1.9	2.0	" " " "
	pH	6.5	6.5	6.6	6.6	6.7	6.6	
8	Mn ppm	0.20	0.20	0.20	0.20	0.20	0.20	" " " "
	pH	6.7	6.9	6.9	7.0	7.2	7.2	
14	pH	6.7	6.7	6.7	6.8	6.9	6.9	" " " "
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	Ppt $CaSO_4$, $CaHPO_4$,
	pH	7.5	7.4	7.3	7.3	7.3	7.3	$Ca_3(PO_4)_2$ & $MgHPO_4$
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	ppt $CaSO_4$, $CaHPO_4$
	pH	8.0	7.6	7.5	7.5	7.5	7.5	& $Ca_3(PO_4)_2$
15	pH	7.5	7.4	7.3	7.3	7.3	7.2	" " " "

Table XI

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$.
M/10 $(NH_4)_2SO_4$.
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.2	3.2	3.2	3.2	3.2	
2	Mn ppm	10	10	10	10	10	" "
	pH	3.8	3.8	3.8	3.8	3.8	
11	pH	3.2	3.2	3.2	3.2	3.2	" "
3	Mn ppm	10	10	10	10	10	" "
	pH	4.5	4.5	4.5	4.5	4.5	
4	Mn ppm	10	10	10	10	10	" "
	pH	5.0	4.9	4.8	4.7	4.7	
12	pH	4.8	4.8	4.7	4.7	4.7	" "
5	Mn ppm	9.5	9.5	10	10	10	" "
	pH	5.4	4.9	4.9	4.8	4.7	
6	Mn ppm	7.5	8.	8	9	9	
	pH	5.9	5.8	5.7	5.6	5.4	" and $CaHPO_4$
13	pH	5.5	5.4	5.0	5.0	4.9	" " "
7	Mn ppm	7	7	7	7	8	" " "
	pH	6.4	6.2	6.1	5.7	5.5	
8	Mn ppm	0.75	3.7	5.5	6.0	7.0	" " "
	pH	6.9	6.7	6.6	6.6	6.5	
14	pH	6.4	6.2	6.1	5.8	5.7	" " "
9	Mn ppm	3.5	3.5	3.3	2.5	1.5	" " "
	pH	7.4	7.3	7.2	7.2	7.1	
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	" also $CaHPO_4$,
	pH	8.1	8.0	7.9	7.8	7.7	mostly $Ca_3(PO_4)_2$
15	pH	7.6	7.4	7.3	7.2	7.2	" also $CaHPO_4$), mostly $Ca_3(PO_4)_2$.

Table XII

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 KH_2PO_4
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	200	Remarks
1	Mn ppm	10	10	10	10	10	$Ca(H_2PO_4)_2$ plates.
	pH	3.6	3.6	3.6	3.6	3.6	
2	Mn ppm	10	10	10	10	10	" "
	pH	4.1	4.1	4.1	4.1	3.8	
11	pH	3.7	3.7	3.7	3.7	3.7	" "
3	Mn ppm	10	10	10	10	10	$CaHPO_4$
	pH	4.5	4.0	3.9	3.8	3.8	
4	Mn ppm	1.5	1.0	0.8	0.65	0.32	"
	pH	5.1	6.3	6.3	6.3	6.3	
12	pH	4.7	4.2	4.2	4.1	4.1	"
5	Mn ppm	<.05	<.05	<.05	<.05	0.25	"
	pH	5.6	6.8	6.8	6.8	6.2	
6	Mn ppm	<.05	<.05	<.05	<.05	0.25	" mostly $Ca_3(PO_4)_2$
	pH	6.2	6.3	6.3	6.3	6.2	
13	pH	5.5	6.2	6.4	6.5	6.6	" " "
7	Mn ppm	<.05	<.05	<.05	<.05	0.20	All $Ca_3(PO_4)_2$
	pH	6.7	6.8	6.7	6.7	6.5	
8	Mn ppm	<.05	<.05	<.05	<.05	0.20	" "
	pH	7.2	7.3	7.2	7.2	6.9	
14	Mn ppm	6.4	7.2	7.2	7.2	6.4	$Ca_3(PO_4)_2$ and $CaHPO_4$.
9	Mn ppm	<.05	<.05	<.05	<.05	0.15	Mixture of $CaHPO_4$ and $Ca_3(PO_4)_2$.
	pH	7.7	7.0	6.9	6.8	5.8	
10	Mn ppm	<.05	<.05	<.05	<.05	0.15	$Ca_3(PO_4)_2$
	pH	8.0	7.8	7.6	7.5	7.2	
15	pH	7.7	7.5	7.5	7.5	7.1	"

Table XIII

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 KNO_3
Solutions 1-10 inc.10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No	Text	Time in Hours 0	24	48	72	96	120	250	Remarks
1	Mn ppm	10	10	10	10	10	10	10	No ppt.
	pH	3.6	3.6	3.6	3.6	3.6	3.6	3.6	
2	Mn ppm	10	10	10	10	10	10	10	" "
	pH	4.4	4.5	4.5	4.5	4.5	4.5	4.5	
11	pH	4.0	4.0	4.0	4.0	4.0	4.0	4.0	" "
3	Mn ppm	10	10	10	10	10	10	10	" "
	pH	5.0	5.1	5.1	5.1	5.1	5.1	5.0	
4	Mn ppm	10	10	10	10	10	10	10	" "
	pH	5.6	5.6	5.6	5.6	5.5	5.5	5.5	
12	pH	5.3	5.3	5.3	5.3	5.3	5.3	5.3	" "
5	Mn ppm	10	10	10	10	10	10	10	" "
	pH	6.0	6.0	6.0	6.0	5.9	5.9	5.9	
6	Mn ppm	10	10	10	10	10	10	10	" "
	pH	6.5	6.5	6.5	6.6	6.7	6.7	6.7	
13	pH	6.3	6.3	6.3	6.3	6.3	6.3	5.4	" "
7	Mn ppm	9.2	9.2	9.2	9.2	9.2	9.2	9.2	Soln. slightly yellow at start. Brown manganese oxide ppt after 24 hrs.
	pH	6.7	6.7	6.6	6.6	6.6	6.7	6.0	
8	Mn ppm	9.2	9.2	9.2	9.2	9.2	9.2	9.2	" " " "
	pH	7.2	7.0	6.8	6.8	6.9	6.9	6.0	
14	pH	7.3	7.0	6.8	6.6	6.5	6.5	6.0	No ppt.
9	Mn ppm	9.5	9.5	9.5	9.5	9.5	9.5	9.5	Slightly yellow at start.
	pH	7.6	6.9	6.8	6.7	6.6	6.7	6.4	Brown manganess oxide ppt after 24 hrs.
10	Mn ppm	8.2	8.2	8.2	8.2	8.2	8.2	8.2	
	pH	8.2	7.6	7.2	7.1	6.9	7.0	6.9	" " " " " "
15	pH	8.1	7.7	7.7	7.7	7.5	7.2	6.5	No ppt.

Table XIV

Salt present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with $Ca(OH)_2$.

No.	Test	Time in Hours 0	24	48	72	96	120	200	Remarks
1	Mn ppm	10	10	10	10	10	10	10	Ppt $CaSO_4$.
	pH	3.8	3.8	3.8	3.8	3.8	3.8	3.8	
2	Mn ppm	10	10	10	10	10	10	10	" "
	pH	4.5	4.5	4.5	4.5	4.5	4.5	4.5	
11	pH	4.4	4.4	4.4	4.4	4.4	4.4	4.4	" "
3	Mn ppm	10	10	10	10	10	10	10	" "
	pH	5.0	5.0	5.0	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	10	10	" "
	pH	5.4	5.4	5.4	5.4	5.4	5.4	5.4	
12	pH	5.4	5.4	5.4	5.4	5.4	5.4	5.4	" "
5	Mn ppm	10	10	10	10	10	10	10	" "
	pH	6.1	6.2	6.3	6.3	6.3	6.4	6.0	
6	Mn ppm	10	10	10	10	10	10	10	" "
	pH	6.6	6.6	6.6	6.5	6.4	6.3	6.0	
13	pH	6.6	6.6	6.7	6.7	6.8	6.8	6.8	" "
7	Mn ppm	10	10	10	10	10	10	10	" "
	pH	7.0	7.0	6.8	6.7	6.6	6.6	6.6	
8	Mn ppm	10	10	10	10	10	10	10	" "
	pH	7.6	7.3	7.3	7.3	7.2	7.1	6.6	
14	pH	7.4	7.1	7.1	7.1	7.1	7.1	7.3	" "
9	Mn ppm	10	10	10	10	10	10	10	" "
	pH	7.8	7.5	7.3	7.1	7.0	7.0	6.7	
10	Mn ppm	10	10	10	10	10	10	10	" "
	pH	8.7	7.6	7.3	7.3	7.3	7.2	6.5	
15	pH	8.2	7.7	7.5	7.4	7.2	7.2	7.3	" "

Table XV

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH

No.	Test	Time in Hours 0	24	48	72	96	120	200	250	Remarks
1	Mn ppm	10	10	10	10	10	10	10		Ppt $CaSO_4$
	pH	3.8	3.8	3.8	3.8	3.8	3.8	3.8		
2	Mn ppm	10	10	10	10	10	10	10		" "
	pH	4.2	4.2	4.2	4.2	4.2	4.2	4.2		
11	pH	4.1	4.1	4.1	4.1	4.1	4.1	4.1		" "
3	Mn ppm	10	10	10	10	10	10	10		" "
	pH	4.7	4.7	4.7	4.7	4.7	4.7	4.7		
4	Mn ppm	10	10	10	10	10	10	10		" "
	pH	5.4	5.4	5.4	5.4	5.4	5.4	5.4		
12	pH	5.2	5.2	5.2	5.2	5.2	5.1	5.1		" "
5	Mn ppm	10	10	10	10	10	10	10		" "
	pH	6.0	6.0	6.0	5.9	5.8	5.8	5.7		
6	Mn ppm	10	10	10	10	10	10	10		" "
	pH	6.7	6.7	6.6	6.5	6.4	6.4	6.2		
13	pH	6.4	6.4	6.3	6.2	6.0	6.0	6.0		" "
7	Mn ppm	10	10	10	10	10	10	10		" "
	pH	7.2	7.2	7.2	7.2	7.1	7.1	7.1		
8	Mn ppm	10	10	10	10	10	10	10		" "
	pH	7.7	7.7	7.7	7.7	7.7	7.7	7.7		
14	pH	7.3	7.3	7.3	7.3	7.2	7.2	7.0		" "
9	Mn ppm	10	10	10	10	10	10	10		" "
	pH	8.1	8.1	8.1	8.1	8.1	8.1	8.1		
10	Mn ppm	10	10	10	10	10	10	6	1.5	Ppt $CaSO_4$. Brown oxide
	pH	8.7	8.7	8.7	8.7	8.7	8.7	8.7	8.7	manganese about 200 hrs.
15	pH	8.7	8.7	8.7	8.7	8.7	8.7	8.7	8.7	Ppt $CaSO_4$.

Table XVI

Salts present: M/10 KH_2PO_4
M/10 KNO_3
Solutions 1-10 inc. 10 ppm. Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	120	200	Remarks
1	Mn ppm	10	10	10	10	10	10	10	Clear soln. 0-120 hrs.
	pH	4.0	4.1	4.0	4.0	4.0	4.0	4.0	slightly flaky ppt. at 200 hrs.
2	Mn ppm	10	10	10	10	10	10	10	" " " " "
	pH	4.7	4.7	4.7	4.7	4.7	4.7	4.7	
11	pH	4.1	4.1	4.1	4.1	4.1	4.1	4.1	" " " " "
3	Mn ppm	10	10	10	10	10	10	10	" " " " "
	pH	5.0	5.0	5.0	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	10	10	" " " " "
	pH	5.7	5.7	5.7	5.7	5.7	5.7	5.7	
12	Mn ppm	5.7	5.7	5.8	5.8	5.8	5.8	5.8	" " " " "
5	Mn ppm	10	10	10	10	10	10	10	" " " " "
	pH	6.0	6.0	6.0	6.0	6.0	6.0	6.0	
6	Mn ppm	9.8	9.8	10	10	10	10	10	" " slightly yellow
	pH	6.5	6.6	6.5	6.5	6.6	6.6	6.6	color first 48 hrs.
13	pH	6.1	6.1	6.1	6.1	6.1	6.1	6.1	"
7	Mn ppm	8	8	8.5	8	8	8	8	" " also brown
	pH	7.1	7.1	7.1	7.1	7.1	7.1	7.3	manganese oxide
8	Mn ppm	7	6.5	6.5	6.5	6.5	6.5	6.5	" " " " "
	pH	7.6	7.6	7.6	7.6	7.6	7.6	7.6	
14	pH	7.2	7.2	7.2	7.3	7.3	7.3	7.4	"
9	Mn ppm	5.5	4.5	4.5	4.5	4.5	4.5	4.5	" " also brown
	pH	8.0	8.0	8.0	8.0	8.0	8.0	8.0	manganese oxide.
10	Mn ppm	4.0	2.0	2.5	2.5	2.5	2.5	2.5	" " " " "
	pH	8.5	8.5	8.5	8.5	8.5	8.5	8.5	
15	pH	8.3	8.3	8.3	8.3	8.3	8.3	8.3	"

Table XVII

Salts present: M/10 KH_2PO_4
M/ $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	200	Remarks
1	Mn ppm	10	10	10	10	10	10	No ppt present.
	pH	4.0	4.0	4.0	4.0	4.0	4.0	
2	Mn ppm	10	10	10	10	10	10	Amorphous white
	pH	4.7	4.8	4.7	4.7	4.7	4.7	flakes.
11	pH	4.1	4.1	4.1	4.1	4.1	4.1	No ppt present.
3	Mn ppm	10	10	9	8	7.3	2.5	Ppt duodecahedrons.
	pH	5.0	5.0	5.0	5.0	5.0	4.9	
4	Mn ppm	8.5	6.0	3.0	1.8	1.5	0.6	Ppt probably $MgHPO_4$.
	pH	5.4	5.1	5.0	5.0	5.0	4.9	
12	pH	5.2	5.2	5.2	5.2	5.1	4.9	Ppt $MgHPO_4$.
5	Mn ppm	10	7.5	4.0	2.0	1.3	<.05	" "
	pH	6.1	5.9	5.9	5.9	5.8	5.3	
6	Mn ppm	5.5	4.0	1.8	<.05	<.05	<.05	" "
	pH	6.6	6.5	6.4	6.3	6.2	6.0	
13	pH	6.4	6.2	6.1	6.0	5.8	5.6	" "
7	Mn ppm	4.7	4.0	<.05	<.05	<.05	<.05	" "
	pH	7.1	7.1	7.1	7.1	7.1	7.1	
8	Mn ppm	1.7	1.5	1.0	0.8	.45	.45	Needles probably
		7.5	7.3	7.3	7.3	7.4	7.5	$MgHPO_4$
14	pH	7.2	7.2	7.2	7.2	7.1	7.0	$MgHPO_4$
9	Mn ppm	0.6	0.6	0.6	0.6	0.6	0.6	"
	pH	8.2	8.0	7.9	7.8	7.7	7.7	
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	"
	pH	8.7	8.7	8.6	8.5	8.5	8.3	
15	pH	8.4	8.4	8.4	8.4	8.4	8.3	"

Table XVIII

Salts present: M/10 KH_2PO_4
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	200	Remarks
1	Mn ppm	10	10	10	10	10	10	Very small amt. white
	pH	4.1	4.1	4.1	4.1	4.1	4.1	flaky amorphous ppt.
2	Mn ppm	10	10	10	10	10	10	" " " "
	pH	4.7	4.7	4.7	4.7	4.7	4.7	
11	pH	4.3	4.3	4.3	4.3	4.3	4.3	" " " "
3	Mn ppm	10	10	10	10	10	10	" " " "
	pH	5.0	5.0	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	10	" " " "
	pH	5.5	5.5	5.5	5.5	5.5	5.5	
12	pH	5.2	5.2	5.2	5.2	5.2	5.1	" " " "
5	Mn ppm	10	10	10	10	10	10	" " also ppt.
	pH	6.0	6.0	6.0	6.0	6.0	6.0	probably manganese ammonium phosphate
6	Mn ppm	10	10	10	10	10	6	
	pH	6.5	6.5	6.5	6.5	6.5	6.5	" " " "
13	pH	6.3	6.3	6.3	6.3	6.3	6.3	" " " "
7	Mn ppm	10	10	9.5	7.0	4.0	1.2	" " " "
	pH	7.0	7.0	7.0	7.0	7.0	7.0	
8	Mn ppm	9.0	6.5	2.5	0.8	0.62	0.60	" " " "
	pH	7.6	7.6	7.6	7.6	7.6	7.6	
14	pH	7.4	7.4	7.3	7.3	7.3	7.3	" " " "
9	Mn ppm	8	5.5	1.88	0.58	0.40	0.37	" " " "
	pH	8.0	8.0	8.0	8.0	8.0	7.9	
10	Mn ppm	5	2.5	1.78	0.4	0.35	0.15	" " " "
	pH	8.5	8.5	8.5	8.5	8.5	8.5	
15	pH	8.1	8.1	8.1	8.1	8.1	8.1	" " " "

Table XIX

Salts present: M/10 KNO_3
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	120	200	Remarks
1	Mn ppm	10	10	10	10	10	10	10	No ppt present.
	pH	4.1	4.1	4.1	4.1	4.1	4.1	4.1	
2	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	4.5	4.5	4.5	4.5	4.5	4.5	4.5	
11	pH	4.4	4.4	4.4	4.4	4.4	4.4	4.4	" " "
3	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	5.0	5.0	5.0	5.0	5.0	--	5.0	
4	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	5.4	5.4	5.4	5.4	5.4	--	5.4	
12	pH	5.3	5.3	5.3	5.3	5.3	--	5.3	" " "
5	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	6.0	6.0	6.0	6.0	6.0	--	5.8	
6	Mn ppm	10	10	10	10	10	10	10	
	pH	6.5	6.3	6.2	6.1	6.1	--	6.0	" " "
13	pH	6.5	6.5	6.5	6.5	6.5	--	6.2	" " "
7	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	7.0	6.9	6.8	6.6	6.6	--	6.3	
8	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	7.6	7.3	7.1	7.1	7.1	--	6.7	
14	pH	7.5	7.2	6.9	6.9	6.9	--	6.8	" " "
9	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	8.1	7.5	7.3	7.2	7.1	--	6.7	
10	Mn ppm	10	10	10	10	10	10	10	" " "
	pH	8.6	8.1	7.7	7.5	7.4	--	7.3	
15	pH	8.2	7.6	7.4	7.2	7.1	--	6.9	" " "

Table XX

Salts present: M/10 KNO_3
M/10 $(NH_4)_2SO_4$
Solutions 1-10 in. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	200	Remarks
1	Mn ppm	10	10	10	10	10	10	No ppt.
	pH	4.1	4.1	4.1	4.1	4.1	4.1	
2	Mn ppm	10	10	10	10	10	10	" "
	pH	4.6	4.6	4.6	4.5	4.5	4.5	
11	pH	4.2	4.2	4.2	4.2	4.2	4.2	" "
3	Mn ppm	10	10	10	10	10	10	" "
	pH	5.0	5.0	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	10	" "
	pH	5.6	5.6	5.6	5.6	5.6	5.6	
12	pH	5.5	5.5	5.5	5.5	5.5	5.5	" "
5	Mn ppm	10	10	10	10	10	10	" "
	pH	6.0	6.0	6.0	6.1	6.0	6.0	
6	Mn ppm	10	10	10	10	10	10	" "
	pH	6.4	6.4	6.4	6.4	6.4	6.4	
13	pH	6.1	6.1	6.1	6.1	6.1	6.1	" "
7	Mn ppm	10	10	10	10	10	10	" "
	pH	7.0	7.1	7.1	7.1	7.1	7.1	
8	Mn ppm	10	10	10	10	10	10	Very slight amorph-
		7.5	7.5	7.5	7.5	7.5	7.5	ous white ppt.
14	pH	7.3	7.4	7.4	7.4	7.4	7.4	No ppt.
9	Mn ppm	10	10	10	10	10	10	Very slight amorph-
	pH	8.0	8.0	8.0	8.0	8.0	8.0	ous white ppt.
10	Mn ppm	10	10	10	10	10	10	Very slight amorph-
	pH	8.5	8.5	8.5	8.5	8.5	8.5	ous ppt; perhaps small trace of manganese oxide.
15	pH	8.0	8.0	8.0	8.0	8.0	8.0	No ppt.

Table XXI

Salts present: M/10 $MgSO_4.7H_2O$
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH.

No.	Test	Time in Hours 0	24	48	72	96	200	Remarks
1	Mn ppm	10	10	10	10	10	10	No ppt present.
	pH	4.1	4.3	4.3	4.3	4.3	4.3	
2	Mn ppm	10	10	10	10	10	10	" " "
	pH	4.5	4.5	4.5	4.5	4.6	4.6	
11	pH	4.5	4.5	4.5	4.5	4.5	4.5	" " "
3	Mn ppm	10	10	10	10	10	10	" " "
	pH	5.0	5.0	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	10	" " "
	pH	5.5	5.5	5.5	5.5	5.5	5.5	
12	pH	5.3	5.3	5.3	5.3	5.3	5.3	" " "
5	Mn ppm	10	10	10	10	10	10	" " "
	pH	6.0	6.0	6.0	6.0	6.0	5.7	
6	Mn ppm	10	10	10	10	10	10	" " "
	pH	6.5	6.5	6.5	6.4	6.3	6.1	
13	pH	6.3	6.1	6.1	6.1	6.1	6.0	" " "
7	Mn ppm	10	10	10	10	10	10	" " "
	pH	7.1	6.9	6.9	6.8	6.7	6.5	
8	Mn ppm	10	10	10	10	10	10	" " "
	pH	7.6	7.6	7.6	7.5	7.4	7.2	
14	pH	7.3	7.3	7.2	7.1	7.0	6.8	" " "
9	Mn ppm	10	10	10	10	10	10	" " "
	pH	8.0	8.0	8.0	8.0	8.0	8.0	
10	Mn ppm	10	10	10	10	10	10	" " "
	pH	8.7	8.7	8.7	8.7	8.6	8.6	
15	pH	8.4	8.4	8.4	8.4	8.4	8.4	" " "

F. Triple Salt Solutions

1. Data.---In order to see if solutions containing three nutrient salts were similar, in respect to manganese, to the single and double salt solutions some of the triple salt systems were studied. The concentrations of the components were the same as were used in the single and double salt solutions. The triple salt solutions were allowed to stand for four days. Tests for soluble manganese and pH were made daily on the solutions containing manganese. Tests of pH were made daily on the control solutions.

The first set of triple salt solutions were 0.05 molar to calcium dihydrogen phosphate, 0.1 molar to potassium nitrate, and 0.1 molar to magnesium sulfate. The results obtained are given in Table XXII. The pH of these solutions was adjusted with a strong potassium hydroxide solution. The precipitation of manganese began between pH 5.5 (solution 5) and pH 6.1 (solution 6), and was completed at pH 6.3 (solution 6). This indicates that manganese precipitated from these solutions as manganese phosphate. After the initial pH adjustment the amount of manganese in solution remained constant in all flasks except No. 6, in which a decrease from 3 to 2.5 ppm.occurred during the first 24 hours. The pH in this set decreased, except in the case of solution 7 (pH 6.6 - 7.1) which increased. The same trends were followed in the controls as in the solutions containing manganese. A precipitate of calcium sulfate was present in all solutions. Between pH 6.1 and pH 6.7 a precipitate of calcium monohydrogen phosphate was formed, and above this pH tricalcium phosphate. In all solutions above pH 6.7 magnesium monohydrogen phosphate was present, and a precipitate of

of what may have been trimagnesium phosphate in all solutions above pH 7.0.

The next series of solutions (Table XXIII) contained calcium nitrate, magnesium sulfate and ammonium sulfate. The pH of these solutions was adjusted with ammonium hydroxide. Precipitation of manganese took place only in solution 10, pH 8.7, and then after it had stood for 96 hours. The precipitate was the hydrated oxide of manganese. However, only 0.5 ppm. of the initial 10 ppm had precipitated out during this period. The only solutions showing any pH changes were 7 and 13 (control). These solutions were initially of pH 7.0 and 6.8 respectively and after standing for 96 hours were pH of 6.6 and 6.7 respectively. The fact that no general decrease in pH occurred, due to the formation of basic salts of calcium magnesium, was probably caused by the buffer action of the ammonium sulfate - ammonium hydroxide system, forming ammonium acid sulfate. All solutions contained a precipitate of calcium sulfate. No other precipitate, resulting from the interaction of the component salts at different pH, was present.

Table XXIV gives the results secured with solutions containing calcium nitrate, potassium dihydrogen phosphate and magnesium sulfate. The pH of these solutions was adjusted with a strong potassium hydroxide solution. Manganese started to go out of solution between pH 5.5 (solution 4) and pH 6.0 (solution 5), and was completely precipitated at pH 7.2 (solution 7). The amount of manganese dissolved in flask 5 increased during the first 48 hours from 1.35 to 1.5 ppm. This was the only solution showing any such change. The precipitation

of manganese must have taken place as a manganese phosphate. Comparison with the control solutions showed that manganese was not a factor in causing the pH changes which occurred in the solutions on standing. These changes in pH must have been due to the slow attainment of equilibrium between the solid and liquid phases. Every solution contained a precipitate of calcium sulfate. Between pH 4.6 and pH 7.2 calcium monohydrogen phosphate, and a slight amount of magnesium monohydrogen phosphate were present as precipitates. In all solutions above pH 7.2 a precipitate of amorphous tricalcium phosphate was formed.

The next series of solutions contained potassium dihydrogen phosphate, magnesium sulphate and ammonium sulfate. The results are shown in Table XXV. The pH was adjusted with a strong solution of potassium hydroxide. Precipitation of manganese began at pH 5.9 (solution 5), but when pH 8.8 (solution 10) was reached 0.3 ppm were still in solution. In all cases where the precipitation of manganese occurred at the start, there was an increase in the amount of manganese dissolved during the first 24 hours, and thereafter no change. The manganese precipitate was probably both manganese phosphate and ammonium manganese phosphate. The only solutions changing in pH were 7, 8, 9 and 14; these decreased slightly, the initial pH being 7.0, 7.6, 8.0 7.5 respectively, and after 96 hours being pH 6.9, 7.3, 7.9 and 7.3 respectively. Below pH 5.9 no precipitate was present in any of the flasks. Between pH 5.9 and pH 6.5 small rods of what was probably magnesium dihydrogen phosphate phosphate were present. Above pH 6.5 magnesium monohydrogen phosphate and a slight amount of crystals looking like trimagnesium phosphate were present.

Table XXVI shows the results obtained with solutions containing calcium nitrate, potassium nitrate and magnesium sulfate. The pH was adjusted with a dilute potassium hydroxide solution. No immediate precipitation of manganese occurred from any solution containing it. However, during the first 24 hours manganese started to precipitate as the hydrated oxide from solution 10, whose pH was 8.7 at the s start. The concentration of manganese in this solution fell from 10 to 4 ppm.in the first 24 hours, and at 96 hours had dropped to 3.5 ppm. This was the only solution from which any manganese precipitated. All solutions above pH 7.0 showed decreases in pH on standing. This was probably due to the formation of basic calcium and magnesium salts. Solutions which were initially below pH 7.0 did not change in pH on standing. A precipitate of calcium sulfate was present in all flasks. No other precipitates were found.

Table XXVII gives the data secured with solutions containing calcium dihydrogen phosphate, magnesium sulfate and ammonium sulfate. The pH of these solutions was adjusted with strong ammonium hydroxide. Manganese began to precipitate between pH 5.5 and pH 6.0 (solutions 4 and 5) and was complete at pH 8.2 (solution 9). However at pH 8.7 (solution 10) 0.88 ppm.of manganese were in solution at the start and 0.40 ppm.after 96 hours. This condition was probably due to the solubility of manganese as a complex salt in an ammoniacal solution. The precipitate of manganese may have been either manganese phosphate, or ammonium manganese phosphate or both. The only solutions changing essentially in pH were 2, 3, 4, 7, 12, 13 and 14. The pH of these

solutions decreased, the largest decrease usually coming in the first 24 hours. These decreases were a result of the attainment of equilibria between the solid and liquid phases present in the flasks. Calcium sulfate crystals were present in every flask. Above pH 5.0 crystals of calcium monohydrogen phosphate were formed. Higher than pH 7.0 there occurred some extremely small crystals of inderterminate shape which were probably trimagnesium phosphate. No tricalcium phosphate was found.

2. Conclusions on Triple Salt Solutions.---From the six triple salt solutions just discussed it is seen that the four solutions containing phosphate ions precipitated manganese either as manganese monohydrogen phosphate or as manganese ammonium phosphate at a pH which averages 5.8. The point at which precipitation of manganese was complete varied from pH 6.3 to pH 8.8. Ammonium sulfate through its ability to form soluble complexes with manganese in alkaline solutions, was found most effective in preventing total precipitation of manganese.

In the two triple salt solutions which did not contain phosphates, manganese precipitated as the hydrated oxide at pH 8.7. Precipitation was in no case complete.

Turning now to the results with the eight double salt solutions containing phosphates, we find that manganese started to precipitate as a double phosphate at an average pH of 5.35. This pH is considerably lower than that of 5.8 obtained for four triple salt solutions containing phosphates. On the basis of these results it seems not possible to predict from the data of double salt systems containing phosphates, at what pH manganese will start to disappear from triple salt systems containing

phosphates. However, the important point to note here is that in the four tests carried out, manganese started to precipitate at a higher pH in the triple than in the single or double salt systems.

Now we see that in the two triple salt solutions not containing phosphates, manganese began to precipitate as a hydrated oxide at pH 8.7. In all single and double salt solutions containing magnesium or ammonium sulfate, but having no phosphates present manganese did not begin to precipitate as the hydrate oxide until pH 8.5 or above and some times not at all. From the fact that any triple salt solution not containing phosphates must have present either magnesium or ammonium sulfate, it seems safe to predict that manganese will start to precipitate from this type of solution as a hydrated oxide at or above pH 8.5.

Table XXII

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 KNO_3
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls)no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	120	Remarks
1	Mn ppm	10	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.1	3.0	3.0	3.0	3.0	3.0	
2	Mn ppm	10	10	10	10	10	10	" "
	pH	4.2	4.0	3.8	3.8	3.8	3.8	
11	pH	3.9	3.7	3.6	3.7	3.7	3.7	" "
3	Mn ppm	10	10	10	10	10	10	" "
	pH	4.6	4.4	4.3	4.2	4.1	4.1	
4	Mn ppm	10	10	10	10	10	10	" "
	pH	5.0	4.8	4.6	4.5	4.5	4.5	
12	pH	5.3	4.9	4.8	4.7	4.6	4.6	" "
5	Mn ppm	10	10	10	10	10	10	" "
	pH	5.5	5.1	5.0	5.0	4.9	4.9	
6	Mn ppm	3	2.5	2.5	2.5	2.5	2.5	" also $CaHPO_4$
	pH	6.1	6.1	6.1	6.0	6.0	5.9	
13	pH	6.1	6.1	6.1	6.1	6.1	6.1	" " "
7	Mn ppm	0.2	0.2	0.2	0.2	0.2	0.2	" also $CaHPO_4$ and
	pH	6.6	6.6	6.7	6.8	6.9	7.1	$MgHPO_4$
8	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	" also $Ca_3(PO_4)_2$
	pH	7.3	7.3	7.2	7.1	7.1	7.1	and $MgHPO_4$
14	pH	6.9	6.9	7.0	6.9	6.9	6.9	" also $Ca_3(PO_4)_2$, $MgHPO_4$, and plates probably $Mg_3(PO_4)_2$
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	" " " " "
	pH	7.6	7.3	7.3	7.3	7.3	7.3	
10	Mn ppm	<.05	<.05	<.05	<.05	<.05	<.05	" " " " "
	pH	8.1	7.8	7.9	7.8	7.8	7.8	
15	pH	7.8	7.8	7.8	7.7	7.7	7.7	" " " " "

Table XXIII

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 $MgSO_4.7H_2O$
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Ppt $CaSO_4$
	pH	4.0	4.1	4.1	4.1	4.1	
2	Mn ppm	10	10	10	10	10	" "
	pH	4.6	4.6	4.6	4.6	4.6	
11	pH	4.3	4.3	4.3	4.3	4.3	" "
3	Mn ppm	10	10	10	10	10	" "
	pH	5.1	5.1	5.1	5.1	5.1	
4	Mn ppm	10	10	10	10	10	" "
	pH	5.5	5.5	5.5	5.5	5.5	
12	pH	5.4	5.4	5.4	5.4	5.4	" "
5	Mn ppm	10	10	10	10	10	" "
	pH	6.1	6.1	6.1	6.1	6.1	
6	Mn ppm	10	10	10	10	10	" "
	pH	6.6	6.5	6.5	6.5	6.5	
13	pH	6.8	6.8	6.7	6.7	6.7	" "
7	Mn ppm	10	10	10	10	10	" "
	pH	7.0	6.9	6.8	6.7	6.6	
8	Mn ppm	10	10	10	10	10	" "
	pH	7.5	7.5	7.5	7.5	7.4	
14	pH	7.8	7.7	7.7	7.7	7.7	" "
9	Mn ppm	10	10	10	10	10	" "
	pH	8.0	8.0	8.0	8.0	8.0	
10	Mn ppm	10	10	10	10	9.5	Ppt $CaSO_4$. Brown oxide of manganese ppt. settled between 72 - 96 hrs.
	pH	8.7	8.7	8.7	8.7	8.7	
15	pH	8.7	8.7	8.7	8.7	8.7	Ppt $CaSO_4$.

Table XXIV

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 KH_2PO_4
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.7	3.3	3.3	3.3	3.3	
2	Mn ppm	10	10	10	10	10	" "
	pH	4.4	3.5	3.5	3.5	3.5	
11	pH	3.9	3.3	3.3	3.3	3.3	" "
3	Mn ppm	10	10	10	10	10	" " also $CaHPO_4$
	pH	5.0	3.7	3.7	3.7	3.7	
4	Mn ppm	10	10	10	10	10	" " " "
	pH	5.5	4.6	4.6	4.6	4.7	
12	pH	5.5	5.4	5.4	5.2	5.2	" " " "
5	Mn ppm	1.35	1.5	1.5	1.5	1.5	" " " "
	pH	6.0	6.7	6.8	6.8	6.8	
6	Mn ppm	0.3	0.3	0.3	0.3	0.3	" " "and $(Ca_3PO_4)_2$
	pH	6.5	6.9	7.0	7.1	7.2	
13	pH	6.6	6.9	7.1	7.1	7.2	" " " "
7	Mn ppm	<.05	<.05	<.05	<.05	<.05	" " " "
	pH	7.1	7.1	7.1	7.1	7.1	
8	Mn ppm	<.05	<.05	<.05	<.05	<.05	" " " "
	pH	7.5	7.5	7.5	7.5	7.5	
14	pH	7.5	7.5	7.6	7.6	7.6	" " " "
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	" " " "
	pH	8.1	8.3	8.5	8.3	8.3	
10	Mn ppm	<.05	<.05	<,05	<.05	<.05	" " " "
	pH	9.2	9.3	9.1	9.1	9.0	
15	pH	8.9	9.0	9.0	9.0	9.0	" " " "

Table XXV

Salts present: M/10 KH_2PO_4
M/10 $MgSO_4.7H_2O$
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	No ppt present.
	pH	4.1	4.1	4.1	4.1	4.1	
2	Mn ppm	10	10	10	10	10	" " "
	pH	4.5	4.5	4.5	4.5	4.5	
11	pH	4.3	4.1	4.1	4.1	4.1	" " "
3	Mn ppm	10	10	10	10	10	" " "
	pH	5.1	5.1	5.1	5.1	5.1	
4	Mn ppm	10	10	10	10	10	" " "
	pH	5.5	5.5	5.5	5.5	5.5	
12	pH	5.4	5.4	5.4	5.4	5.4	" " "
5	Mn ppm	2.8	3.2	3.2	3.2	3.2	Minute rods; unidentified.
	pH	5.9	5.9	5.9	5.9	5.9	
6	Mn ppm	.05	0.8	0.8	0.8	0.8	" " "
	pH	6.5	6.5	6.5	6.5	6.5	
13	pH	6.5	6.5	6.5	6.5	6.5	$MgHPO_4$ ppt. "
7	Mn ppm	0.3	0.5	0.45	0.45	0.45	" " also some plates
	pH	7.0	7.0	7.0	6.9	6.9	probably $Mg_3(PO_4)_2$
8	Mn ppm	0.15	0.15	0.15	0.15	0.15	" " " " "
	pH	7.6	7.5	7.4	7.4	7.3	
14	pH	7.5	7.5	7.3	7.3	7.3	" " " " "
9	Mn ppm	<.05	0.05	0.15	0.15	0.15	" "
	pH	8.0	8.0	8.0	7.9	7.9	
10	Mn ppm	0.28	0.3	0.3	0.3	0.3	" "
	pH	8.8	8.8	8.8	8.8	8.8	
15	pH	8.4	8.4	8.4	8.4	8.4	" "

Table XXVI

Salts present: M/10 $Ca(NO_3)_2.4H_2O$
M/10 KNO_3
M/10 $MgSO_4.7H_2O$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with KOH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.6	3.7	3.7	3.7	3.7	
2	Mn ppm	10	10	10	10	10	" "
	pH	4.5	4.4	4.4	4.4	4.4	
11	pH	4.3	4.3	4.3	4.3	4.3	" "
3	Mn ppm	10	10	10	10	10	" "
	pH	5.1	5.0	5.0	5.0	5.0	
4	Mn ppm	10	10	10	10	10	" "
	pH	5.5	5.0	4.9	4.9	4.8	
12	pH	5.5	5.5	5.5	5.5	5.5	" "
5	Mn ppm	10	10	10	10	10	" "
	pH	6.0	6.0	6.0	6.0	6.0	
6	Mn ppm	10	10	10	10	10	" "
	pH	6.6	6.5	6.5	6.5	6.5	
13	pH	7.4	7.2	6.9	6.6	6.5	" "
7	Mn ppm	10	10	10	10	10	" "
	pH	7.1	7.0	6.7	6.5	6.5	
8	Mn ppm	10	10	10	10	10	" "
	pH	7.4	7.3	7.0	6.9	6.8	
14	pH	6.5	6.3	6.3	6.3	6.3	" "
9	Mn ppm	10	10	10	10	10	" "
	pH	8.1	7.5	7.3	7.1	7.1	
10	Mn ppm	10	4	3.6	3.3	3.5	" "and brown manganese oxide ppt. during first day.
	pH	8.7	8.0	7.8	7.7	7.6	
15	pH	8.7	8.7	8.6	8.5	8.3	" "

Table XXVII

Salts present: M/20 $Ca(H_2PO_4)_2.H_2O$
M/10 $MgSO_4.7H_2O$
M/10 $(NH_4)_2SO_4$
Solutions 1-10 inc. 10 ppm Mn added; 11-15 (controls) no Mn added.
Adjustment of pH with NH_4OH.

No.	Test	Time in Hours 0	24	48	72	96	Remarks
1	Mn ppm	10	10	10	10	10	Ppt $CaSO_4$
	pH	3.2	3.2	3.2	3.2	3.2	
2	Mn ppm	10	10	10	10	10	
	pH	4.4	4.0	4.0	4.0	4.0	" "
11	pH	3.3	3.2	3.2	3.2	3.2	" "
3	Mn ppm	10	10	10	10	10	" " trace $CaHPO_4$ ppt.
	pH	5.1	4.7	4.7	4.7	4.7	
4	Mn ppm	10	10	10	10	10	" " " " "
	pH	5.5	5.1	5.1	5.0	5.0	
12	pH	5.3	5.0	5.0	4.9	4.9	" " no $CaHPO_4$.
5	Mn ppm	1.6	1.6	1.6	1.6	1.6	" " and $CaHPO_4$.
	pH	6.0	6.0	6.0	6.0	6.0	
6	Mn ppm	0.5	0.6	0.6	0.6	0.6	" " " "
	pH	6.6	6.5	6.5	6.5	6.5	
13	pH	6.5	6.3	6.3	6.3	6.3	" " " "
7	Mn ppm	0.25	0.3	0.4	0.45	0.55	" " " "
	pH	7.1	6.9	6.9	6.8	6.8	
8	Mn ppm	0.15	0.15	0.15	0.15	0.15	" " $CaHPO_4$ and plates
	pH	7.7	7.7	7.6	7.6	7.6	probably $(Mg_3HPO_4)_2$
14	pH	7.5	7.3	7.2	7.2	7.1	" " " "
9	Mn ppm	<.05	<.05	<.05	<.05	<.05	" " " "
	pH	8.2	8.3	8.3	8.3	8.3	
10	Mn ppm	0.88	0.7	0.55	0.45	0.40	" " " "
	pH	8.7	8.7	8.7	8.7	8.7	
15	pH	8.7	8.7	8.7	8.7	8.7	" " " "

V SUMMARY

Table XXVIII is a summary of the main facts uncovered in this research. It shows the pH at which manganese precipitated from the solutions studied, the form of the manganese precipitate and its effect, if any, on the pH of the solution. The solutions are arranged in the order in which manganese precipitated from them; those from which it precipitated at the lowest pH being first.

This arrangement shows that manganese started to precipitate as a phosphate below pH 6.5, from all solutions containing phosphates, with the exception of those containing potassium dihydrogen phosphate, or this salt in combination with potassium nitrate. Manganese precipitated from the solutions containing calcium and potassium dihydrogen phosphate together at the lowest pH, namely 4.7. This is in accordance with the solubility product principle. It is also seen that manganese precipitated at a lower pH from solutions containing calcium and phosphate ions alone, or these ions along with potassium and nitrate ions. However, if manganesium or ammonium sulfate was present along with either calcium or potassium dihydrogen phosphate, the precipitating point of manganese was not only raised to a higher pH, but the pH range through which precipitation took place was lengthened; in some cases as high as pH 8.8.

Manganese precipitated as the hydrated oxide when pH values higher than 6.7 were reached. From solutions having both calcium and potassium nitrates present manganese began to precipitate at pH 6.7. Manganese started to precipitate from a potassium dihydrogen phosphate solution, and from this solution in combination

with potassium nitrate solutions precipitation began at pH 7.5 and pH 7.9 respectively. Solutions from which manganese precipitated above pH 8.0, or from which it did not precipitate at all, contained either magnesium or ammonium ions. Since combinations containing either magnesium or ammonium sulfate along with calcium nitrate, were largely magnesium or ammonium nitrate, due to a precipitate of calcium sulfate being formed, it is seen that it was not the nitrate ion but rather the calcium and potassium ions which caused a low pH of precipitation of manganese. On the other hand the magnesium and ammonium ions were responsible for keeping.manganese in solution until higher pH values were reached. In order to keep manganese in solution above its precipitating point as the hydroxide (pH 8.4), the magnesium and ammonium undoubtedly form complex ions with manganese.

Taking both the phosphate and oxide forms in which manganese may precipitate, the following arrangement shows the power of the ions to keep manganese in solution: $NH_4 > MG > K > Ca$.

This arrangement shows that it is possible from the cations present to judge the effectiveness of a salt combination in keeping manganese dissolved. An inspection of the amount and kind of precipitate in the flask would give a clue to the pH of the solution and thus to the probable amount of manganese dissolved. If phosphates are present (excluding potassium dihydrogen phosphate) manganese will begin to precipitate as a phosphate when the solution is acid, calcium dihydrogen phosphate causing precipitation at a lower pH than magnesium or ammonium phosphates . When no phosphates are present or if potassium dihydrogen phosphate alone is present, manganese will begin to precipitate as hydrated oxide from a neutral or alkaline solution; here again

calcium salts causing the precipitation to begin at the lowest pH, the other cations coming in the order given above.

Practical Application.---Some of the facts brought out in this work should be of value to those who are dealing with the culture of plants. Since the composition and reaction of soils are very varied, it will be first necessary to know the approximate amount of soluble manganese present and also the pH of the soil solution. Several cases now present themselves. We may have an acid soil low in soluble manganese, or one containing it in moderate or excessive amounts. There may be also the case of a neutral soil containing very little soluble manganese. Soluble manganese would not be present in excessive amounts in a neutral soil.

An acid soil low in soluble manganese will be more beneficial to plant growth if a moderate application of a soluble manganese salt is made along with ammonium phosphate and lime.

An acid soil high in soluble manganese should be treated with superphosphate and lime. If a moderate amount of soluble manganese is present in an acid soil lime only should be used.

A neutral soil low in soluble manganese would require the application of a moderate amount of a soluble manganese salt. If such a neutral soil contains very much phosphates, ammonium sulfate should be applied with the manganese salt.

Table XXVIII

Summary

Showing the pH at which manganese precipitated from the solutions of nutrient salts used; also the probable form of the precipitate and its effect on the pH.

Salts Present	Probable form of ppt.	pH of Precipitation		Effect of ppt. on pH
		Begins	Complete # Incomplete	
$Ca(H_2PO_4)_2$ KH_2PO_4	$MnHPO_4$	4.7	7.1	None
$Ca(H_2PO_4)_2$ KNO_3	$MnHPO_4$	5.0	6.7	None
$Ca(NO_3)_2$ KH_2PO_4	$MnHPO_4$	5.1	5.6	None
$Ca(H_2PO_4)_2$ $Ca(NO_3)_2$	$MnHPO_4$	5.3	7.1	None
KH_2PO_4 $MgSO_4$	$MnHPO_4$	5.4	8.7#	None
$Ca(H_2PO_4)_2$	$MnHPO_4$	5.6	6.1	None
$Ca(H_2PO_4)_2$ $(NH_4)_2SO_4$	$MnHPO_4$ and NH_4MnPO_4	5.9	8.1	None
KH_2PO_4 $MgSO_4$ $(NH_4)_2SO_4$	$MnHPO_4$ and NH_4MnPO_4	5.9	8.8#	None
$Ca(NO_3)_2$ KH_2PO_4 $MgSO_4$	$MnHPO_4$	6.0	7.1	None
$Ca(H_2PO_4)_2$ $MgSO_4$	$MnHPO_4$	6.0	7.5	None
$Ca(H_2PO_4)_2$ $MgSO_4$ $(NH_4)_2SO_4$	$MnHPO_4$ and NH_4MnPO_4	6.0	8.2+	None
$Ca(H_2PO_4)_2$ KNO_3 $MgSO_4$	$MnHPO_4$	6.1	7.3	None

+ Some Mn redissolved between pH 8.2 and pH 8.7.

Table XXVII (con't)

Salts Present	Probable form of ppt.	pH of Precipitation Begins	pH of Precipitation Complete # Incomplete	Effect of ppt. on pH
KH_2PO_4 + $(NH_4)_2SO_4$	NH_4MnPO_4	6.5	8.5#	None
$Ca(NO_3)_2$ + KNO_3	MnO_2	6.7	8.2#	None
KH_2PO_4	MnO_2	7.1	8.7#	None
KH_2PO_4 + KNO_3	MnO_2	7.1	8.5#	None
$Ca(NO_3)_2$	MnO_2	7.5	8.2#	To decrease
KNO_3	MnO_2	7.9	8.8#	To decrease
$Ca(NO_3)_2$ + KNO_3 + $MgSO_4$	MnO_2	8.0++	8.0	None
$MgSO_4$	MnO_2	8.7	8.7#	?
$Ca(NO_3)_2$ + $MgSO_4$ + $(NH_4)_2SO_4$	MnO_2	8.7+++	8.7#	None
$Ca(NO_3)_2$ + $(NH_4)_2SO_4$	MnO_2	8.7++++	8.7#	None
KNO_3 + $(NH_4)_2SO_4$	Probably MnO_2, no ppt.	Above 8.5	--	--
KNO_3 + $MgSO_4$	" "	" 8.6	--	--
$Ca(NO_3)_2$ + $MgSO_4$	" "	" 8.7	--	--
$(NH_4)_2SO_4$	" "	" 8.7	--	--
$MgSO_4$ + $(NH_4)_2SO_4$	" "	" 8.7	--	--

++ After 12 hrs. +++ After 72 hrs.
++++ After 200 hrs.

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