cals of these times describe the rate of rotation and the temperature dependance of this rate may be expressed as an activation energy. Figure 4 shows a graph of $\log \tau$ against $1/T$ and the slope of this line is equivalent to an activation energy, $E\tau$, of 1.7 kcal. if the time of relaxation is expressed by

$$\tau = Ae^{-E\tau/RT}$$

This value may be compared with that of 1.7 kcal. for the similar activation energy for the rotation of camphor in n-heptane,[2] and also with the value of 2.3 kcal. for the corresponding activation energy for the viscosity of cyclohexane[13] over the range 15–30°. Further the interpolated value for the relaxation time at 20° which is 6.8×10^{-12} sec. in cyclohexane is very close to the value 6.5×10^{-12} sec. for camphor in n-heptane[2] but these values are by no means proportional to the macroscopic viscosity coefficients which are 0.96 and 0.41 cpoise, respectively.[13]

Acknowledgments.—The author wishes to thank Prof. P. Debye for his interest in the work and Dr. C. H. Townes for many invaluable discussions and suggestions. He also wishes to thank the Commonwealth Fund for the award of a Fellowship and the Bell Telephone Laboratories for granting the use of their facilities so freely during its tenure.
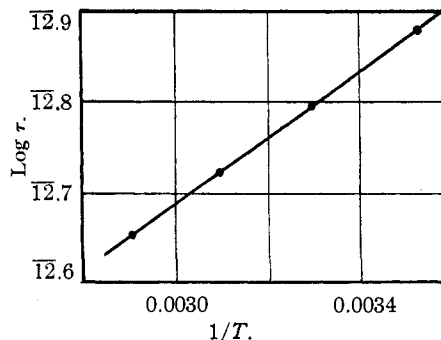

Fig. 4.—Graph of $\log_{10} \tau$ against $1/T$; slope equivalent to 1.7 kcal. energy of activation.

Summary

A description of the measurement of the dielectric loss of liquids at microwave frequencies using a completely filled cavity resonator is given. Solutions of camphor in cyclohexane have been measured over the range 10–70° at three wave lengths, 1.3, 3.3 and 10 cm. The observed losses can be well explained by a single Debye loss curve; the relaxation time is 6.8×10^{-12} sec. at 20° and the temperature coefficient corresponds to an activation energy of 1.7 kcal.

MURRAY HILL, NEW JERSEY

Potentiometric Investigation of Tripyrophosphatomanganic(III) Acid

BY JAMES I. WATTERS AND I. M. KOLTHOFF

Evidence presented in a previous paper[1] indicated that the violet complex ion of manganese (III) and pyrophosphoric acid is a chelate ring complex anion having essentially the formula $Mn(H_2P_2O_7)_3^{-3}$. The ionic weight was estimated by application of Jander's expression[2] to the polarographically determined diffusion coefficients, and the hydrogen content of the complex was deduced from pH, ionic charge, and theoretical considerations. An investigation of the oxidation potential of the manganese(II)–manganese(III) couple in acidic pyrophosphate solutions along with the various factors influencing it is described in the present paper.

A new potentiometric procedure for determining manganese by titrating the trivalent complex with standard iron(II) sulfate solution is also described. Volumetric procedures in which the trivalent complex is titrated with iron(II) sulfate and the end-point detected with diphenylamine sulfonate as indicator, as well as amperometrically, will be described in subsequent papers. On the

basis of the present studies,[3] Lingane and Karplus[4] have developed a potentiometric method for determining manganese in which manganese(II) is titrated to the violet manganese(III) pyrophosphate complex with standard permanganate solution. Their titration curves substantiate the authors' results.

Theoretical

In the experimental part it is shown that the potential at a platinum electrode of the complex manganic(III)–manganous(II) system is reversible, and that both complexes are mononuclear. It has been mentioned that the trivalent manganese complex contains three pyrophosphate radicals.[1] The hydrogen content of the pyrophosphate ions, either in the form of complex ions or simple ions, is a function of the pH of the solution. The number of associated hydrogen ions in the various ions at a particular pH, will be indicated by x, y and z. The number of pyrophosphate radicals in the manganese(II) complex will be indicated by m to illustrate the method of its evalua-
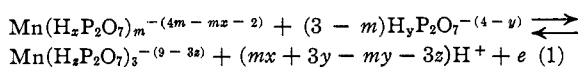
(1) I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 8 (1943).

(2) G. Jander and H. Spandau, *Z. physik. Chem.*, **A185**, 325 (1939).

(3) J. I. Watters, Ph.D. Thesis, University of Minnesota, 1943.

(4) J. J. Lingane and Robert Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

tion. The following equation for the electrode reaction can be written

$$Mn(H_xP_2O_7)_m^{-(4m-mx-2)} + (3-m)H_yP_2O_7^{-(4-y)} \rightleftarrows$$
$$Mn(H_xP_2O_7)_3^{-(9-3x)} + (mx + 3y - my - 3z)H^+ + e \quad (1)$$

The equation for the oxidation potential of this system at 25° in terms of activities can be written as

$$E = E_0^c + 0.0591 \log a Mn^{III}C/a Mn^{II}C$$
$$-(3-m) 0.0591 \log a H_yP_2O_7^{-(4-y)} +$$
$$(mx + 3y - my -3z) 0.0591 \log a H^+ \quad (2)$$

Upon converting hydrogen ion activity to $p a H$ and other activities to concentrations, this equation becomes

$$E = E_0^c + 0.0591 \log (f_1/f_2f_3)$$
$$+ 0.0591 \log (Mn^{III}C)/(Mn^{II}C)$$
$$- (3-m) 0.0591 \log (H_yP_2O_7^{-(4-y)})$$
$$- (mx + 3y - my - 3z) 0.0591 p a H \quad (3)$$

In these equations $Mn^{III}C$ and $Mn^{II}C$ indicate the two complex ions, a denotes molar activity, and f_1 the molar activity coefficient of $Mn^{III}C$, f_2 that of $Mn^{II}C$ and f_3 that of $H_yP_2O_7^{-(4-y)}$ and parentheses indicate molar concentration. E_0^c indicates the standard potential for the reaction.

If only the concentration ratio of the two manganese complexes is varied, the potential change ΔE at 25° at constant $p_a H$ and ionic strength can be expressed as follows

$$\Delta E_{2-1} = 0.0591 \, \Delta \log (Mn^{III}C)/(Mn^{II}C)_{2-1} \quad (4)$$

By means of this equation it is possible to establish that the complexes are mononuclear and that a one-electron change occurs.

The effect on the potential resulting from variations of only the total pyrophosphate concentration can be expressed as

$$\Delta E_{2-1} = (m-3) \, 0.0591 \, \Delta \log (H_yP_2O_7^{-(4-y)})_{2-1} \quad (5)$$

By simple calculations involving the ionization constants of pyrophosphoric acid it can be shown that, at constant ionic strength and $p a H$, the concentrations of all species of pyrophosphates are proportional to the total pyrophosphate concentration. Accordingly, equation (5) can be converted to the following form

$$\Delta E_{2-1} = (m-3) \times 0.0591 \, \Delta \log (C_s)_{2-1} \quad (6)$$

C_s denoting the total pyrophosphate concentration. From this equation, it is possible to determine m, the number of pyrophosphate ions associated with each manganese(II) ion by determining the change in potential, E, as a function of the total pyrophosphate concentration.

The effect of varying the $p a H$ is given by the equation

$$\Delta E_{2-1} = (3z + my - 3y - mx) 0.0591 \Delta p a H_{2-1} \quad (7)$$

Certain complications enter in the evaluation of x, y and z. Obviously pyrophosphate ions and both complex ions in various degrees of association with hydrogen ion enter the reaction or are in equilibrium with reacting forms. The observed

coefficient of $p a H$ (eq. 7) will be a weighted average for the several reactions which may occur. An equation for a predominant reaction in a given $p a H$ range might be written. In this case, the concentration of the uncomplexed pyrophosphate ion could be evaluated since the ionization constants of pyrophosphoric acid are known. However values of the hydrogen ionization constants of the two complex acids are unknown. Accordingly, the actual concentrations of complex ions of any given degree of dissociation for which the electrode reaction might be written cannot be solved even though the total concentrations of manganese (III) and manganese(II) are known. Recourse to a sufficiently high $p a H$ to be certain that one complex contains no associated hydrogen ions is denied because in alkaline solutions the complex manganese(III) ion disproportionates to produce manganese dioxide. Likewise, the complexes are too strongly acidic to assume quantitative association during a variation in $p a H$ in fairly strong acidic solutions. The latter behavior is to be anticipated because positive nuclear ions enhance the acidity of acids in the complex. Pyrophosphoric acid complexed with either manganese(II) or manganese(III) is a stronger acid than the simple pyrophosphoric acid, and the manganese (III) should be more acidic than the manganese (II) complex.

The value of z in fairly strong acid solutions has been shown[1] to be close to 2 corresponding to 6 hydrogen ions in the manganese (III) complex. However, the evidence did not preclude the possible association of one or possibly two additional hydrogen ions or the dissociation of several more hydrogen ions depending on the exact pH with a corresponding effect on the potential. It follows that only differences in the acidities of the two complexes can be found on the basis of equation (7).

Experimental

Apparatus.—The potential measurements were made in a 100-ml. tall form lipless beaker with a bright platinum indicator electrode and a saturated calomel reference electrode. The beaker was equipped with a no. 11 rubber stopper with holes to receive electrodes, buret, a stirrer, and a tube for admitting purified nitrogen. Unless otherwise indicated, oxygen-free nitrogen was bubbled through the solution for fifteen minutes to remove oxygen. A temperature of 25 ± 0.1° was maintained by means of a thermostatically controlled water-bath. In a few titration experiments the temperature of the bath was changed to 26°, which was room temperature.

A Leeds and Northrup Student's potentiometer was used on conjunction with a Leeds and Northrup portable enclosed lamp and scale galvanometer. The $p a H$ measurements were made by means of a Beckman glass electrode pH meter.

Reagents.—Analytical reagents were employed. A stock solution of 0.1 M manganese(II) sulfate in 0.01 N sulfuric acid was used.[1] Standard 0.1 N iron(II) sulfate solution having a pH of about 1.6 was prepared by dissolving approximately 40 g. of Mohr salt in water, adding 2 ml. of sulfuric acid (1:1) and diluting to one liter. This solution, which was oxidized only slowly by air, was standardized daily just before being used. Standard 0.01 N iron(II) sulfate solution was prepared by dilution

of 0.1 N solution with sulfuric acid (1:100). Sodium and potassium pyrophosphate[1] were both used as a source of pyrophosphate. The pH of the pyrophosphate solutions was adjusted to the desired value with either sulfuric or nitric acid.

Procedure.—The manganese(III) complex was prepared from the manganese(II) complex, in 0.4 M pyrophosphate having a pH of about 2, by shaking with lead dioxide and then filtering according to the procedure described in a previous paper.[1] The solution was stirred mechanically during potential measurements.

Results and Discussion

Equations (4) through (7) were tested by means of various experiments designed to permit the observation of potential changes resulting from carefully controlled variations.

Effect of the Manganese(III) to Manganese (II) Ratio.—Experimentally, equation (4) was tested by measuring the potential of solutions prepared by mixing varying proportions of the air-free oxidized and unoxidized portions of a solution, 10 millimolar in manganese ion, 0.4 M in sodium pyrophosphate, and 2.40 in paH. The potentials in Table I are plotted as a function of log $(Mn^{III}C)/(Mn^{II}C)$ in line c, Fig. 1. The points fall on a straight line which has a slope of 0.0598 v., in good agreement with the theoretical value of 0.0593 volt for a one-electron transfer at 26°.

TABLE I

RELATION BETWEEN POTENTIAL AND RATIO $(Mn^{III})/(Mn^{II})$

$\mathrm{Log}\,\dfrac{(MnIII)}{(MnII)}$	E (S. C. E.), volts
1.69897	0.8456
1.39794	.8288
1.09691	.8116
0.69897	.7877
.39794	.7697
.22185	.7592
.09691	.7523
.00000	.7463
− .22185	.7327
− .39794	.7220
− .69897	.7042
−1.09691	.6800
−1.39794	.6612
−1.97634	.6323

Another experiment was performed by observing the effect on the potential resulting from changes in total manganese concentration while the ratio of the oxidized to reduced form remained constant. A solution 5 millimolar in both the manganese(III) and the manganese(II) complexes, 0.4 M in sodium pyrophosphate and 2.40 in pH, was diluted ten times with a solution 10 millimolar in sodium sulfate instead of manganese sulfate, 0.4 M in sodium pyrophosphate and 2.40 in pH. Upon dilution the potential retained a constant value of 0.7463 v. (S.C.E.). From these experiments it follows that the electrode behaves in a reversible manner for a one-electron transfer with respect to the two manganese complex ions, and that both the oxidized and reduced forms of

the complex ions must contain only one manganese atom. This conclusion has further support in the fact that potentiometric titrations discussed later show that the oxidation states differ by unity.
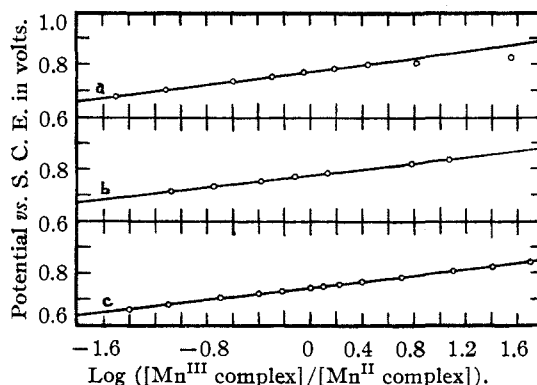

Fig. 1.—Line a, data obtained from the titration curve of 0.001 M manganese (III) complex with iron (II); line b, data from titration curve of 0.01 M manganese (III) complex; line c, data obtained from Table I.

Effect of the Pyrophosphate Concentration.—Equation (6) was tested experimentally by varying the total concentration of pyrophosphate from 0.4 to 0.04 M keeping the ionic strength and the paH constant. In the following experiments the paH was 2.06. The ionic strength of the system which was 0.4 M in sodium pyrophosphate was calculated to be 1.83. The solution containing 0.04 M pyrophosphate was made 1.83 M in potassium nitrate in order to have the same ionic strength as the 0.4 M pyrophosphate solution. The various solutions were 0.5 millimolar both in manganese(II) and manganese (III). The average value of the oxidation potential ($vs.$ S.C.E.) of the solution 0.04 M in pyrophosphate was found to be 0.8278 ± 0.001 v. and of the solution 0.4 M in pyrophosphate 0.7670 ± 0.001 v. After correcting for the amount of pyrophosphate combined with manganese, the potential change was found to be 60.8 ± 2.0 mv. for a change in the pyrophosphate concentration from 0.3975 to 0.0375 M. Substituting these values in equation (6) yields 2.00 for the value of m.

In order to establish that m remained constant throughout the dilution, another experiment was performed in which the pyrophosphate concentration was varied continuously. To a solution 5 millimolar in both manganese(II) and manganese (III) and 0.4 M in sodium pyrophosphate, was added 1.83 M potassium nitrate solution. The paH was kept constant at 1.58 by adding small amounts of nitric acid. The results are given in Table II. They show that in the concentration range of pyrophosphate used a value of $m = 2$ satisfies the experimental data.

From polarographic experiments[1] it was concluded that the manganese(III) complex contains three pyrophosphates. This relation of two to

Dilution V/V_0	Potential vs. S. C. E., mv.	$\dfrac{\Delta E}{\Delta \log Cs}$, mv.
1.0	824.7	
1.5	834.7	56.8
2.0	839.6	49.5
3.0	850.3	53.7
7.5	874.6	57.2
10.0	884.3	59.6

three in the number of chelate complexing ions has been observed repeatedly in complexes of di- and trivalent elements of the first transition series. An analogous behavior of the iron(III) oxalate-iron(II) oxalate couple was observed by Schaper[5] and verified by Lingane.[6]

Effect of Hydrogen Ion Concentration.—Since the value of m has been found to be two, equation (7) becomes

$$\Delta E_{2-1} = (3z - 2x - y)\, 0.0591\, \Delta paH_{2-1} =$$
$$-w\, 0.0591\, \Delta paH_{2-1} \quad (8)$$

Experimentally, this equation was tested by measuring the potential as the paH was varied by adding concentrated nitric acid or ammonium hydroxide dropwise to a solution 5 millimolar in both manganese(II) and manganese(III) complexes and 0.4 M in sodium pyrophosphate. The effect of changing the paH in this solution is shown in Table III and Fig. 2. The value of w corresponds to the number of hydrogen ions involved in the reaction if the activity coefficient of the hydrogen ions remains constant with variations in the acidity. Each value given for w is the average obtained with reference to the preceding and succeeding data. In solutions having a paH smaller than 3, the solution was rich violet in color. As the paH approached 7, the color of the complex became increasingly amber. When the paH exceeded 7 appreciably, a precipitate formed due to disproportionation of the amber-colored complex
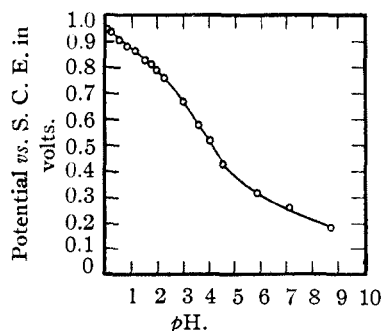

Fig. 2.—Change of potential with paH in mixture 0.005 M in both manganese(II) and manganese(III) complexes and 0.4 M in sodium pyrophosphate.

(5) C. Schaper, Z. physik. Chem., **72**, 315 (1910).

(6) J. J. Lingane and H. Kerlinger, Ind. Eng. Chem., Anal. Ed., **13**, 77 (1941).

p_aH	Potential vs. S. C. E., mv.	w	Color
0.05	946.2	..	Rich violet
.19	934.5	1.51	Rich violet
.52	903.5	1.51	Rich violet
.80	879.6	1.21	Rich violet
1.12	861.1	1.23	Rich violet
1.52	826.0	1.31	Rich violet
1.76	812.4	1.54	Rich violet
1.97	788.7	1.80	Rich violet
2.27	758.4	1.90	Rich violet
2.99	668.0	2.33	Rich violet
3.59	578.0	2.44	Violet (less intense)
4.02	518.5	2.64	Violet (trace of amber)
4.54	428.2	2.61	Amber violet
5.85	318.4	1.03	Brown amber
7.11	262.3	0.77	Brown turbid
8.72	187.0	..	More turbid

to form manganese dioxide and manganese (II) ion.

At a paH approaching zero w became approximately 1.5. In the lower limit of this paH range, y can be assigned approximately the value 4 since the pyrophosphoric acid is largely associated. Assigning the value of 2 to z on the basis of polarographic data[1] leads to a calculated value of approximately 2 for x, indicating that both the manganese(II) and the manganese(III) complexes are definitely more acidic than pyrophosphoric acid. The following equation may accordingly be written for the predominant equilibrium in strongly acidic solutions.

$$Mn(H_2P_2O_7)_2^{-2} + H_4P_2O_7 \rightleftharpoons$$
$$Mn(H_2P_2O_7)_3^{-3} \text{ (violet)} + 2H^+ + e \quad (9)$$
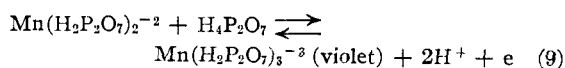
In the paH range of 0 to 3, there is a large variation in the extent of association of hydrogen ions with pyrophosphoric acid. This factor alone accounts for the major portion of the change of w. Accordingly if there is any decrease in the value of z in this range, there is also a compensating decrease in the value of x.

In the paH range of 3 to 6, pyrophosphoric acid is largely present as $H_2P_2O_7^{-2}$. Furthermore, the degree of association of pyrophosphoric acid does not change rapidly in this range and does not contribute appreciably to the value of w. In the lower half of this range the observed value of w is about 2.5. This value should be zero if both complex ions contained dihydrogen pyrophosphate ions. It is evident that the manganese(III) complex must contain fewer hydrogen ions than the manganese(II) complex. Accordingly z is unity or zero. This decrease in the value of z is accompanied by a change in the color of the manganese (III) complex from violet to amber.

In the paH range of 6.7 to 9.4, the ion $HP_2O_7^{-3}$ preponderates in pyrophosphate solutions. The more acidic complex ions undoubtedly contain

simple pyrophosphate ions. Assigning the value zero to x and z, yields a value of unity for w which is approximately the value observed. The main reaction in this paH range is

$$Mn(P_2O_7)_2^{-6} + HP_2O_7^{-3} \rightleftarrows$$
$$Mn(P_2O_7)_3^{-9} + H^+ + e \quad (10)$$
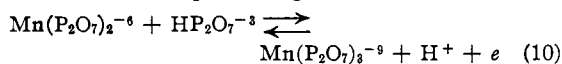
Cartledge and Ericks[7] in a study of the oxalate complexes of manganese(III) observed a red complex, $Mn(C_2O_4)_3^{-3}$, which changed to a brown complex, $Mn(C_2O_4)_2 (H_2O)_2^{-1}$, when the concentration of excess oxalate ion was decreased by dilution. The color change in the manganese(III) pyrophosphate complex cannot be due to an analogous displacement of pyrophosphate ions by water molecules because a one-hundred fold dilution of the violet complex with water at a paH of 2 caused no change of color from violet to amber, but a change of the paH to 2.4 caused a definite change in color. Furthermore a large excess of the complex-forming pyrophosphate ions is present in solutions containing the amber-colored complex.

On the basis of these considerations it appears that the manganese(III) complex is rich violet in color when an average of two hydrogen ions are associated with complexed pyrophosphate ion and it is amber in color when one or no hydrogen ion is associated with each pyrophosphate.

Potentiometric Titrations.—Titrations 1 and 2 in which 75 ml. of 1 millimolar manganese(III) complex was titrated with 10.06 millinormal iron (II)sulfate, with air present and with dissolved air removed, yielded curves (a) and (b) in Fig. 3. Titration 3 was performed with a ten-fold increase in the concentration of both the manganese(III) complex and the iron(II) sulfate in the presence of dissolved air. This titration curve was practically identical with curve b in Fig. 3.

In blank determinations performed in the same manner as the titrations, 0.07 ml. of 0.01006 N iron(II) sulfate was added before a potential change was observed. This blank correction due to a trace of oxidizing agent, probably very finely divided lead dioxide, was applied in all calculations. The calculated molarities of the manganic complex in the three titrations, assuming a one electron change, were 1.0013, 1.0010, and 9.972 millimolar corresponding to errors of $+0.13$, $+0.10$ and -0.28%, respectively. The large potential break and the accuracy which is better than 0.3% in the presence or absence of dissolved air, indicate the excellence of the potentiometric titration from a practical viewpoint.

Effect of Oxygen.—Although dissolved oxygen had no noticeable effect on the results of the titration, some of the potentials, especially in the more dilute solutions, were influenced by its presence. Before the end-point the corresponding potentials in all three titrations were in good agreement. However, beyond the end-

(7) G. H. Cartledge and W. P. Ericks, THIS JOURNAL, **58**, 2065 (1936).

point, the presence of dissolved oxygen influenced the potential in the solutions which were only one millimolar in manganese complex because of air oxidation of the ferrous iron.
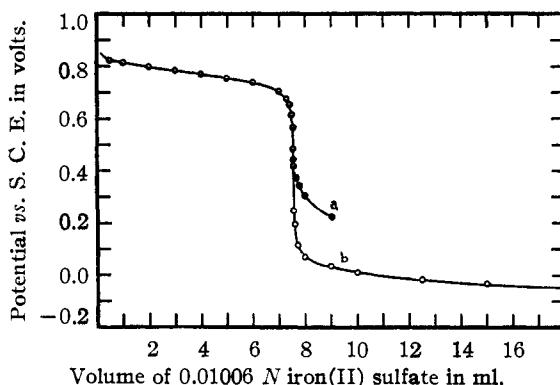

Fig. 3.—Potentiometric titration curve of 0.001 M manganese (III) complex with iron (II); a, dissolved air not removed; b, dissolved air removed.

Since the changes in paH and volume during the titrations were small, the potential change before the end-point was due largely to changes in the ratio of the concentrations of the two complex manganese ions. This permitted a convenient confirmatory test of equation (4). Upon plotting the potential *versus* log $(Mn^{III}C)/(Mn^{II}C)$ for titrations 2 and 3, the lines a and b in Fig. 1 were obtained. Straight lines with slopes of 0.059 v. were found in both cases. Considering the small effect due to dilution and a small pH change the average value of the potential of 0.776 v. at the midpoint in the titrations agreed satisfactorily with the formal potential of 0.767 v. of the couple at various concentrations in a solution 0.4 M in sodium pyrophosphate having the same paH, namely, 2.06.

Similar calculations involving the iron(III) and iron(II) pyrophosphate complexes which determine the potential beyond the end-point yielded a slope of 0.059 v. and a potential of 0.033 v. (S.C.E.) for this couple in a solution containing equal concentration of the two complex ions at a paH of 2.06. It follows that both of the manganese and both of the iron complexes are mononuclear and that both undergo one-electron changes.

The potential at the endpoint should be one-half the sum of the above potentials of the two couples at paH of 2.06, namely, 0.405 v. (S.C.E.). The value of 0.410 v. (S.C.E.) calculated by the method of second derivatives from titration b (Fig. 3) is in satisfactory agreement with the theoretical.

The Standard Potential.—The potential of a solution equimolar in the manganese(III) and manganese(II) complexes, in a solution 0.4 M in sodium pyrophosphate and having a paH of 2.06 is $+0.767 \pm 0.003$ v. *versus* the saturated calomel electrode or $+1.013 \pm 0.003$ v. *versus* the

standard hydrogen electrode at 25°. Extrapolating to a paH of zero and a pyrophosphate concentration of unity on the basis of experimental data previously presented yields a value of $+1.15$ v. as the "formal" oxidation potential for the reaction in equation (9) at 25°. Strictly speaking this potential is not the formal potential, since the hydrogen ion activity and not its concentration was extrapolated to zero. Nor is it the standard potential since the concentrations and not activities of the complex ions and pyrophosphoric acid are used. As the activity coefficients are not known, the standard potential cannot be solved but is probably close to 1.15 v.

Although the data will not permit an accurate evaluation of the instability constants, an approximation may be made of their ratios. On the basis of the standard potential of 1.51 v. for the aqueous manganese(III)/manganese(II) couple determined by Grube and Huberich,[8,9] the following relation between the instability constants K_{III} for tri-dihydrogen pyrophosphatomanganate(III) complex and K_{II} for di-dihydrogen pyrophosphatomanganate(II) is obtained

$$1.15 \text{ v.} = 1.51 + 0.0591 \log \frac{a_{Mn^{+3}}}{a_{Mn^{+2}}} =$$

$$1.51 \text{ v.} + 0.0591 \log \frac{K_{III} a_{Mn^{III}C} \; a_{H_4P_2O_7^3}}{K_{II} a_{Mn^{II}C} \; a_{H_4P_2O_7^2}} \text{ volts} \quad (11)$$

Since the standard potential is calculated for all substances in the last term at unit activity

(8) G. Grube and K. Huberich, Z. Elektrochem., **29**, 17 (1923).

(9) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 221.

the following relation is obtained

$$K_{III} = 10^{-6} K_{II} \; (ca.) \quad (12)$$

Summary

The couple tripyrophosphatomanganic(III) acid/dipyrophosphatomanganic(II) acid was shown to behave reversibly at a platinum electrode. The influence of the total pyrophosphate concentration, ratio of manganese(III)/manganese(II) concentrations, and paH were studied. At a paH near zero, the equilibrium was shown to be essentially

$$Mn(H_2P_2O_7)_2^{-3} + H_4P_2O_7 \rightleftharpoons$$
$$Mn(H_2P_2O_7)_3^{-3} \text{ (violet)} + 2H^+ + e \quad (9)$$
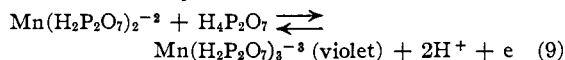
The potential of a platinum electrode in a solution containing equal concentrations of manganese (II) and manganese(III) in a solution 0.4 M in pyrophosphate having a paH of 2.06 is $+1.013$ ± 0.003 v. versus the standard hydrogen electrode. The standard potential for the reaction indicated in equation (9) is $E_0 = (ca.)$ -1.15 v. (Lewis and Randall convention).

As the paH approaches 7, the manganese(III) complex becomes increasingly brown amber in color, due to the ionization of additional hydrogen ions from the complex. In an alkaline solution, the manganese(III) complex is unstable disproportionating to form manganese dioxide and manganese(II) ion.

A new method for determining manganese by means of a potentiometric titration of tripyrophosphatomanganic acid with iron(II) sulfate is described.

The Effect of Sodium Silicates on the Absorption Spectra of Some Dyes

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That certain dyes change color in the presence of various colloids has long been known. Familiar examples are the variation in color of a biological stain depending on the nature of the stainable substrate, which P. Ehrlich called metachromasy, and the protein error of indicators. Micellar solutions of colloidal electrolytes, such as cetyl pyridinium chloride[1] and long chain sulfonates and sulfates[2,3] change the color of pinacyanol chloride and other dyes.[4,5] This paper reports the effects of another group of colloidal electrolytes, the sodium silicates, on the absorption spectra of the dyes, pinacyanol chloride, toluidine blue O, Rhodamine 6G,

(1) S. E. Sheppard and A. L. Geddes, J. Chem. Phys., **13**, 63 (1945).

(2) M. L. Corrin, H. B. Klevens and W. D. Harkins, ibid., **14**, 480 (1946).

(3) M. L. Corrin and W. D. Harkins, THIS JOURNAL, **69**, 679 (1947).

(4) G. S. Hartly, Trans. Faraday Soc., **30**, 444 (1934).

(5) J. E. Smith and H. L. Jones, J. Phys. Chem., **38**, 243 (1934).

and the sodium salt of 2,6-dichlorobenzenone indophenol.

Experimental

All of the sodium silicates used were commercial products of the Philadelphia Quartz Co. Their composition is summarized in Table I. The sodium metasilicate pentahydrate was in the form of pure white free flowing crystals which have a melting point of 72.2°. The "E" and "Star" silicates are clear, transparent, aqueous solutions and the "S" is an opalescent solution. The sodium oxide content is determined by titration with standardized hydrochloric acid to the methyl orange end-point. Silica

TABLE I

COMPOSITION OF SODIUM SILICATES

Name	Formula	M. W.	Na₂O, %	SiO₂, %
Metso crystals	$Na_2SiO_3 \cdot 5H_2O$	122	29.1	28.2
Star	$Na_2O \cdot 2.6SiO_2$	217	10.5	26.3
E	$Na_2O \cdot 3.3SiO_2$	262	8.6	27.7
S	$Na_2O \cdot 4.0SiO_2$	305	6.3	24.6