dropping mercury electrode is explained. Various examples of current–voltage curves in mixtures which yield mixed potentials have been given.

2. Although thallous thallium does not react chemically with cyanide its "apparent" reduction wave is shifted to more negative potentials in the presence of cyanide.

3. The principle of a new type of amperometric titration in which the substance titrated and the titrating agent do not react chemically has been described.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 11, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The 20° Isotherm of the Ternary System: Manganous Nitrate–Nitric Acid–Water

BY WARREN W. EWING AND CHARLES F. GLICK

This investigation of the ternary system manganous nitrate–nitric acid–water was undertaken to confirm or discover the existence of certain hydrates of manganous nitrate, in conjunction with vapor pressure and freezing point measurements on this salt which are being made in this Laboratory. No mention of any previous investigation of this system occurs in the literature. According to Mellor,[1] Funk's solubility data indicate the existence of a hexahydrate and a trihydrate of manganous nitrate. Ditte reported a monohydrate and a hemipentahydrate, although the existence of the latter is unconfirmed. Guntz and Martin reported the preparation of anhydrous manganous nitrate by various chemical methods.

Experimental

Saturated solutions were prepared, and both liquid and moist solid phases were analyzed for nitric acid and manganous nitrate.

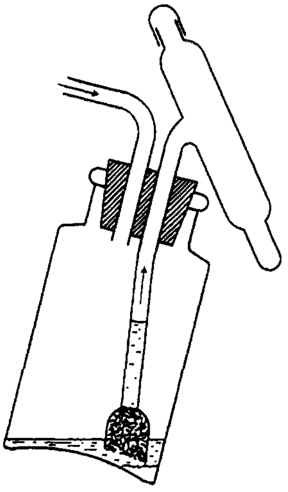

Fig. 1.—Isothermal filtering device.

Materials.—A solution of C. P. manganous nitrate, containing about 50% manganous nitrate, was concentrated over concentrated sulfuric acid in a vacuum desiccator until the solution yielded a thick slush of hexahydrate crystals at 10°. The mother liquor was removed from this slush by suction on a large sintered glass filter. The crystallization was repeated twice more. The moist crystals were dried over concentrated sulfuric acid in a vacuum desiccator until their composition reached about 80% manganous nitrate; for higher compositions phosphorus pentoxide was used as the desiccant. Prolonged drying over phosphorus pentoxide yields pure anhydrous manganous nitrate, a faintly pink powder which dissolves in water without leaving a residue. This indicates that this method of preparation does not change the salt to an insoluble basic form, as is the case with zinc nitrate.

C. P. nitric acid was prepared by distillation from a mixture of two volumes of sulfuric acid and one volume of nitric acid. This distillate was redistilled in a 75 cm. Vigreux column; the fraction distilling at 82° was collected. This product was pale amber in color and gave an analysis of 101% acid.

Preparation and Treatment of Samples.—Manganous nitrate and nitric acid of the appropriate concentrations were mixed together to give samples of the desired concentrations. The samples were prepared in two ounce wide-mouth bottles and the ground glass stoppers were sealed with paraffin. They were rotated in a water thermostat at 20.00 ± 0.02° for at least four hours. Due to the complexity of the system, it was not possible to prepare exactly duplicate samples in order to approach equilibrium from two directions, but samples very nearly the same, prepared from the hot side and from the cold side, yielded solubility data which were concordant. Furthermore, some samples were rotated as much as eight hours and again concordant data were obtained. These concordant results proved that four hours was ample time to establish equilibrium.

The saturated solution phase was removed by filtration. For a viscous solution and a coarsely granular solid phase, the glass wool filter, Fig. 1, was used. The sample bottle and the filter tube were inclined as shown to permit filtration of most of the liquid phase, even though this be present in small quantity. For a non-viscous solution and a fine, powdery solid phase, another filter was used, similar to the first except that a sintered glass micro filter replaced the bell of glass wool. In using either filter, compressed air was supplied to the inlet tube, since filtration by suction caused vaporization of nitric acid. The filtrate collected in the well of the receiver and was immediately available for analysis without interruption of the filtration.

Method of Analysis.—The residues were prepared for analysis by two different methods. Those consisting of hexahydrate were melted at 30–35° without danger of vaporization of nitric acid. Those consisting of lower

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[1] Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green and Co., London, 1932, p. 440.

hydrates with higher melting points were weighed in the bottle and diluted with a weighed amount of water. The analyses of the saturated solutions and the solid phases were identical from this point.

The manganous nitrate content was determined in duplicate by Volhard's gravimetric method[2]—conversion to manganous sulfate with excess sulfuric acid, and vaporization of the excess by heating to 450–500° for several hours. The nitric acid content was determined in duplicate by titration with 0.1 *N* carbonate-free potassium hydroxide solution. Five ml. of 3% hydrogen peroxide solution was added to the solution being titrated to prevent precipitation of manganese as MnO(OH). Brom cresol green indicator was used. Blanks were run to determine the potassium hydroxide equivalent of the hydrogen peroxide. The water content was calculated by difference. With few exceptions the duplicate analyses for manganous nitrate and nitric acid checked within 0.1% (absolute).

Results

The data obtained are tabulated in Table I, and are plotted in Fig. 2. The "tie-line" method was used in every case to determine the hydrate in the solid phase, but for the sake of clarity only some of the tie-lines are plotted.

TABLE I

Saturated solutions		Residues		Solid
%HNO_3	%$Mn(NO_3)_2$	%HNO_3	%$Mn(NO_3)_2$	phase[a]
0.0	56.9			6
2.5	55.5	2.4	56.1	6
5.9	54.6	2.7	59.1	6
6.5	56.6	4.5	58.4	6
7.7	55.7	6.0	58.8	4
10.2	53.7	5.3	61.9	4
11.4	52.8	9.7	55.9	4
16.7	48.8	12.4	54.6	4
26.9	41.8	17.5	52.0	4
31.9	40.8	10.9	60.9	4
28.4	45.7	17.3	56.0	4
19.4	57.0	9.0	64.6	4
13.3	63.6	9.2	66.0	4
9.5	68.0	7.0	68.7	4
5.9	72.4	4.3	75.4	2
8.3	71.0	5.9	74.3	2
10.5	69.0	8.9	71.7	2
16.2	65.2	11.4	70.5	2
18.6	63.7	14.9	67.6	2
19.9	62.7	14.5	68.5	2–1.5
24.4	58.3	19.0	64.7	1.5
47.0	37.8	22.6	62.9	1.5–1
46.9	37.8	28.7	58.1	1.5–1
61.5	24.8	26.1	62.5	1
68.1	19.1	34.3	54.8	1
69.0	18.5	38.6	50.2	1
78.0	11.7	56.6	33.0	1
84.1	7.4	21.6	71.2	1–0.5
88.6	4.7	42.3	51.7	0.5
91.5	3.5	61.3	35.0	0.5
96.3	1.1	63.2	34.2	0.5
99.3	0.5	33.9	63.1	0.5

[a] The entries under "Solid phase" are the number of molecules of water of hydration per molecule of manganous nitrate.

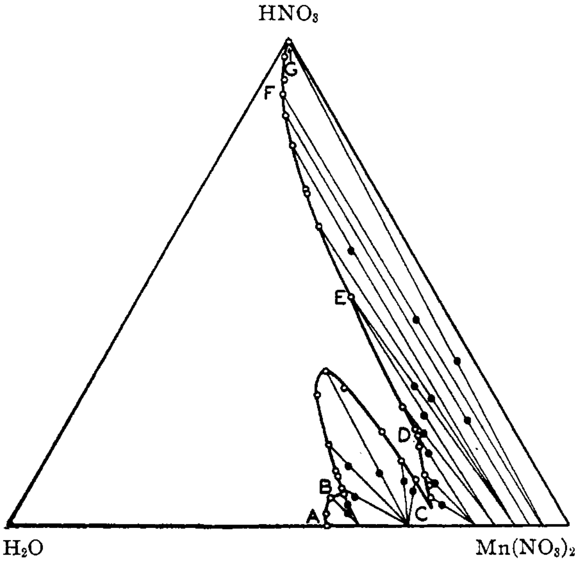

Fig. 2.—The system $Mn(NO_3)_2$–HNO_3–H_2O at 20°.

Curve AB represents the solutions in equilibrium with the hexahydrate; B is the isothermally invariant solution saturated with solid hexahydrate and solid tetrahydrate. Curve BC represents the solutions in equilibrium with the tetrahydrate; C is the isothermally invariant solution saturated with solid tetrahydrate and solid dihydrate. Curve CD represents the solutions in equilibrium with the dihydrate; D is the isothermally invariant solution saturated with solid dihydrate and solid sesquihydrate. Curve DE represents the solutions in equilibrium with the sesquihydrate; E is the isothermally invariant solution saturated with solid sesquihydrate and solid monohydrate. Curve EF represents the solutions in equilibrium with the monohydrate; F is the isothermally invariant solution saturated with solid monohydrate and solid hemihydrate. Curve FG represents the solutions in equilibrium with the hemihydrate. No indication of Funk's trihydrate or Ditte's hemipentahydrate could be found, but the existence of Ditte's monohydrate is confirmed.

Summary

The 20° isotherm of the ternary system manganous nitrate–nitric acid–water has been determined.

The forms of manganous nitrate in stable equilib-

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[2] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1935, p. 134.

rium with nitric acid at 20° are the hexahydrate, tetrahydrate, dihydrate, sesquihydrate, monohydrate and hemihydrate.

Anhydrous manganous nitrate was prepared by dehydration at room temperature.

BETHLEHEM, PENNA. RECEIVED JUNE 14, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE CALIFORNIA INSTITUTE OF TECHNOLOGY*]

The Catalytic Effect of Osmium Compounds on the Reduction of Perchloric Acid by Hydrobromic Acid

BY WILLIAM R. CROWELL, DON M. YOST AND JOHN D. ROBERTS

In a previous communication it was shown that the reduction of perchloric acid by hydrobromic acid was catalyzed by trivalent ruthenium salts, and a mechanism for the catalyzed reaction was proposed.[1] Because of the similarity of the oxidation states of ruthenium and osmium it was thought that osmium compounds might behave in a similar manner. Preliminary experiments showed that the reaction is catalyzed by osmium tetroxide, $K_2OsO_4 \cdot 2H_2O$, K_2OsBr_6 and K_3OsBr_6, although the effect is much less than in the case of ruthenium.

Equilibrium and rate studies of the reaction between osmium tetroxide and hydrobromic acid carried out in these laboratories have been helpful in shedding some light on the probable mechanism of the osmium-catalyzed reactions.[2,3] It has been shown that the rate-determining step in the former reaction is a reduction of the osmium to the hexavalent state. Rapid follow reactions which then take place depend upon the acid and bromine concentrations. At high acid and low bromine concentrations the tendency is toward reduction to the quadrivalent state. At low acid and high bromine concentrations the tendency is toward formation of the heptavalent form. At equilibrium several oxidation states of osmium are present together and Kirschman and Crowell were forced to assume as a result of their measurements that the equilibrium concentration of heptavalent osmium predominated at high bromine and low acid concentrations. This assumption does not seem to be in accord with the known instability of perosmates, but the results of the equilibrium measurements are not easily explained on any other basis. Latimer has suggested the possibility of the presence of osmyl, OsO_2^{++}, derivatives in these solutions.[4]

The purpose of the present investigation was to study the rate of the osmium-catalyzed reaction between perchloric and hydrobromic acids at 100° and at different concentrations of the reacting constituents. The solutions were maintained at approximately constant ionic strength, in order to determine the order of the reaction with respect to each constituent involved. With the aid of these data and the information regarding the osmium tetroxide–hydrobromic acid reaction, it is possible to propose a mechanism for the catalyzed reaction.

Experimental

Reagents.—The compounds used consisted of osmium tetroxide, potassium osmate, potassium bromoosmate, potassium bromoperosmite, hydrobromic acid, perchloric acid, sodium perchlorate and sodium chloride. In these experiments the osmium compounds must be prepared with special care to eliminate ruthenium, which has a catalytic effect. The best obtainable osmium metal was fused with potassium hydroxide and potassium nitrate. The water extract was then heated with 6 *N* nitric acid and the osmium tetroxide produced was distilled into 1 *N* potassium hydroxide. The resulting hydroxide solution was treated with ethyl alcohol to precipitate the violet crystals of $K_2OsO_4 \cdot 2H_2O$ and these were washed with alcohol. To the potassium osmate was added a solution of nitric acid and the tetroxide again distilled into 1 *N* potassium hydroxide. Again the osmium was recovered from the alkali solution as potassium osmate. One portion of the osmate was then heated with a solution of dichromic acid and the osmium tetroxide distilled into 1 *N* potassium hydroxide. This last solution was the source of the tetroxide used in the experiments. A second portion of the osmate was used as the source of the hexavalent compound, samples of which were weighed out and added directly to the reaction tubes. A third portion of the osmate was treated with dichromic acid and the tetroxide distilled into an ice-cold solution of concentrated hydrobromic acid which was then refluxed for about two hours. This solution was partially evapo-

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(*) Contribution No. 780, Gates and Crellin Laboratories of Chemistry.

[1] Crowell, Yost and Carter, THIS JOURNAL, **51**, 786 (1929).

[2] Kirschman and Crowell, *ibid.*, **55**, 488 (1933).

[3] Kirschman and Crowell, *ibid.*, **59**, 20 (1937).

[4] Latimer, "Oxidation Potentials," Prentice-Hall, New York, p. 217.