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Argentic Salts in Acid Solution. V. Oxidation Potentials, Equilibria with Higher Silver Oxides, and Formation of Nitrate Complexes[1]

By Arthur A. Noyes, Don DeVault, Charles D. Coryell and Thomas J. Deahl

Plan of this Investigation

In the first paper of this series[2a] the nature of the various oxides and basic salts containing silver in the bipositive and tripositive state was discussed and a number of references to the literature on the subject were given. In a subsequent paper[2c] values of the oxidation potential of the argentic–argentous couple in dilute nitric acid were reported and the argentic silver was shown to be in the bipositive state. In this investigation oxidation potential measurements on the argentic–argentous system have been carried out to obtain more information about the thermodynamic constants of oxidized silver and about the formation of nitrate complexes; these measurements are presented in the first part of this paper. In addition, further information has been obtained about the argentic oxides and basic salts and the equilibria between these and argentic solutions have been studied; the description of this work is given in the second part of the paper, which contains a discussion of the entire investigation.

Oxidation Potential of Argentous–Argentic Salts in Nitric, Perchloric, and Mixed Nitric–Perchloric Acid Solutions

Method of Making Measurements.—Cells of the type

$$\mathrm{Pt} + \mathrm{H_2}(p_{\mathrm{H_2}}),\ \mathrm{HClO_4}\ (c'),\ \left\{\begin{matrix} \mathrm{HNO_3}(c_{\mathrm{I}}) & & \mathrm{Ag^{II}}(c_{\mathrm{II}}) \\ & + & \\ \mathrm{HClO_4}(4 - c_{\mathrm{I}}) & & \mathrm{Ag^{I}}(c_{\mathrm{I}}) \end{matrix}\right\},\ \mathrm{Pt} \qquad (1)$$

were measured. The nitric acid concentration c_{I} was varied from 0 to 4.00 f. the total acid concentration was kept at 4.00 f, and total silver was kept at 0.20 f using silver perchlorate when $c_{\mathrm{I}} = 0$ and silver nitrate for the other measurements. All concentrations recorded in this paper are weight-formal. Silver perchlorate for the measurements in the absence of nitrate was prepared by fuming chemically pure silver nitrate several times with chemically pure perchloric acid.

The hydrogen half-cell was similar to that used by Noyes and Garner,[3] and the hydrogen was prepared in the same way. A Leeds and Northrup Student Potentiometer giving readings to 0.1 mv. was used.

To prepare the solutions for the silver half-cell, argentous salt in the proper acid solution was oxidized at an anode consisting of a platinum gauze stirrer; the cathode solution was separated from the anolyte by a sintered glass membrane or an unglazed porcelain cup. When the desired concentration of argentic silver was obtained, the electrolysis was stopped and measurements were made during the course of the reduction of the argentic silver by water. The potential was measured, a sample of solution withdrawn in a cooled pipet and allowed to run into a stirred solution of cooled ferrous sulfate, and the potential read again (this differed but slightly from the previous one), the mean of the two potentials being taken to represent the potential at the time of taking the sample. The analysis of argentic silver by the ferrous sulfate method (involving titration of the excess ferrous ion with permanganate) was that described by Noyes, Coryell, Stitt and Kossiakoff.[2d] The same sample was used for a titration for total silver with thiocyanate.

The Observed and Computed Electromotive Forces.—Values of the formal oxidation potential E^0 (for the reaction $\mathrm{Ag^{II}} + \mathrm{E^{-I}} = \mathrm{Ag^{I}}$)[4] are derived in Table I (and indicated in bold face) by adding to the observed values of the electromotive force, $\mathrm{E}_{\mathrm{obsd.}}$, of the cell formulated in the previous section of this paper the three following quantities (also recorded in Table I)

$$(1) \qquad \mathrm{E_C} = (RT/\mathrm{F}) \ln c_{\mathrm{I}}/c_{\mathrm{II}}$$

to provide for equiformal concentrations of argentous and argentic components, represented by c_{I} and c_{II}, respectively

$$(2) \qquad \mathrm{E_H} = (RT/\mathrm{F}) \ln (\alpha' c'/p_{\mathrm{H_2}})$$

to refer the value to the molal hydrogen electrode standard, $p_{\mathrm{H_2}}$ being the partial pressure of the hydrogen in atmospheres; and

$$(3) \qquad \mathrm{E_L} = (2\mathrm{T_H} - 1)(RT/\mathrm{F}) \ln (\alpha c/\alpha' c')$$

where c is the acid concentration in the silver half-cell, to eliminate as nearly as possible the liquid

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[1] The death of Professor Noyes occurred during the course of the experimental work reported in this paper. The work was completed by the three junior authors, who take the responsibility for its imperfections, and who acknowledge with gratitude their debt to the inspiration, guidance, and generosity of Professor Noyes.

[2] (a) Noyes, Hoard and Pitzer, This Journal, **57**, 1221 (1935); (b) Noyes, Pitzer and Dunn, *ibid.*, **57**, 1229 (1935); (c) Noyes and Kossiakoff, *ibid.*, **57**, 1238 (1935); (d) Noyes, Coryell, Stitt and Kossiakoff, *ibid.*, **59**, 1316 (1937).

[3] Noyes and Garner, *ibid.*, **58**, 1265 (1936).

[4] The results of the analysis are calculated assuming essentially all the argentic silver to be bipositive in accordance with the previous investigations.[2b] Further evidence that this is correct is presented later. The symbol $\mathrm{Ag^{II}}$ represents the total bipositive silver found by analysis, the amount existing as the free ion, $\mathrm{Ag^{++}}$, being unknown.

TABLE I

OBSERVED AND CALCULATED ELECTROMOTIVE FORCES

Total concentration of silver salts ($c_{I} + c_{II}$) = 0.20 f

$E_{obsd.}$, volts	c_{I}/c_{II}	E_C, volts	E', volts	
	Series 1. 4 f HNO_3 at 0.2°			
1.8394	7.34	0.0470	1.8864	c_{I} = 4.00 f
1.8343	9.30	.0525	1.8868	c' = 2.000 f
1.8285	11.88	.0583	1.8868	
1.8250	13.63	.0615	1.8865	
1.8189	17.30	.0671	1.8860	E_H = 0.0224
1.8079	29.8	.0799	(1.8878)	E_L = .0068
		Mean	1.8865	E^0 = **1.9157**
	Series 2. 4 f HNO_3 at 0.2°			
1.8465	5.62	0.0407	1.8872	c_{I} = 4.00 f
1.8435	6.27	.0432	1.8867	c' = 2.000 f
1.8354	8.84	.0512	1.8866	
1.8280	12.40	.0593	1.8873	
1.8214	15.74	.0649	1.8863	
1.8113	25.3	.0761	1.8874	E_H = 0.0224
1.7995	41.5	.0877	1.8872	E_L = .0068
		Mean	1.8870	E^0 = 1.**9162**
	Series 3. 4 f HNO_3 at 25.0°			
1.8222	18.6	0.0751	1.8973	c_{I} = 4.00 f
1.8161	23.8	.0814	1.8975	c' = 2.000 f
1.8161	23.9	.0816	1.8977	E_H = 0.0245
1.8123	27.9	.0857	1.8980	E_L = .0070
		Mean	1.8976	E^0 = 1.9291
	Series 4. 4 f HNO_3 at 25.0°			
1.8366	10.57	0.0606	1.8972	c_{I} = 4.00 f
1.8296	13.46	.0668	1.8964	c' = 2.000 f
1.8290	13.81	.0675	1.8965	
1.8257	15.92	.0712	1.8969	
1.8113	27.8	.0855	1.8968	E_H = 0.0245
1.8067	33.4	.0902	1.8969	E_L = .0070
		Mean	1.8968	E^0 = **1.9283**
	Series 5. 4 f $HClO_4$ at 0.2°			
1.8609	13.1	0.0606	1.9215	c_{I} = 0
1.8564	15.9	.0653	1.9217	c' = 4.000 f
1.8517	19.9	.0704	1.9221	
1.8487	21.5	.0722	1.9209	
1.8415	29.0	.0793	1.9208	
1.8378	34.1	.0831	1.9209	
1.8340	39.0	.0863	1.9203	E_H = 0.0606
1.8219	57.2	.0954	(1.9173)	E_L = .0000
		Mean	1.9212	E^0 = **1.9818**
	Series 6. 4 f $HClO_4$ at 25.0°			
1.8637	15.4	0.0692	1.9329	c_{I} = 0
1.8560	20.4	.0775	1.9335	c' = 4.000 f
1.8513	25.7	.0834	1.9347	
1.8460	30.6	.0879	1.9339	E_H = 0.0661
1.8417	35.6	.0919	1.9336	E_L = 0.0000
		Mean	1.9337	E^0 = **1.9998**

potential present in the cell.[5] Activity coefficients have been taken from Pearce and Nelson[6] for perchloric acid and from Abel, Redlich and v. Lengyel[7] for nitric acid. The sum of $E_{obsd.}$ and E_C has been designated as E'. In each series of measurements made with a given argentic preparation E' should remain constant, and the values obtained have been averaged before adding E_H and E_L.

Series 1 and 2 made at 0.2° in 4.00 f nitric acid give for E^0 the average value of 1.9160 volts, in good agreement with the results of Noyes and Kossiakoff.[2c] Series 3 and 4 made at 25.0° give the value of 1.9287 volts. From these observations there are calculated for the cell reaction

$$Ag^{II}(4\,f\ HNO_3) + 0.5H_2\ (1\ \text{atm.}) = Ag^{+}(4\,f\ HNO_3) + H^{+}\ (\text{act. } 1\ m) \quad (2)$$

values of $-\Delta F^{\circ}_{298}$ = 44.49 kcal. and ΔH° = −41.0 kcal.

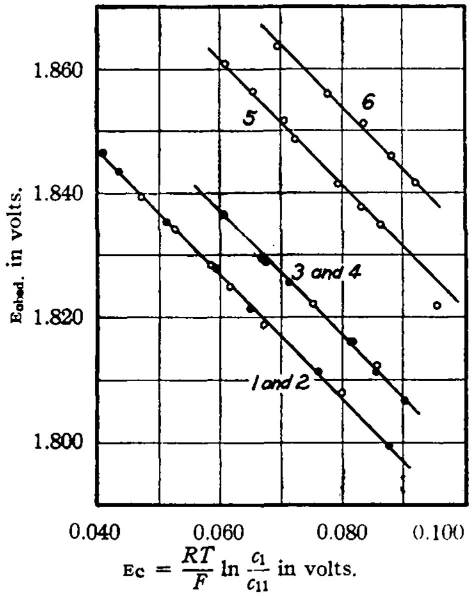

Fig. 1.—Dependence of observed e. m. f. on argentous–argentic ratio: 1 and 2, in HNO_3 at 0°; 3 and 4, in HNO_3 at 25°; 5, in $HClO_4$ at 0°: 6, in $HClO_4$ at 25°.

There are included also in Table I a series of measurements made at 0.2° and one made at 25.0° on cell (1) with 4.00 f perchloric acid. In this acid, the argentic solutions have a brownish-pink color instead of the black-brown of the

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[5] This correction has been discussed by Noyes and Garner[3] and further experimental test is given by Noyes and Deahl in the paper following this one. For the transference number of hydrogen ion T_H values of 0.85 at 25° and 0.86 at 0° were taken.

[6] Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

[7] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

nitric acid solutions. The oxidation number in perchloric acid and in nitric acid can be determined from Fig. 1, in which $E_{obsd.}$ as ordinate is plotted against $RT/F \ln c_I/c_{II}$ as abscissa for series 1 to 6. If the change in oxidation number is unity, the slope of such a plot for a series should be exactly minus one; in general it would be approximately the negative reciprocal of the change in oxidation number. The points on the plot fall precisely on lines whose slope is minus one, indicating that for both perchloric and nitric acid solutions the argentic form is bipositive.

In 4.00 *f* perchloric acid the value of E^0 is 1.9818 volts at 0.2° and 1.9998 volts at 25.0°. These values lie, respectively, 65.8 and 71.1 millivolts above the potentials in 4.00 *f* nitric acid, indicating that a nitrate–argentic complex is formed. The measurements made in perchloric acid provide the best approximation at present available for the molal oxidation potential of argentous–argentic ions. From them there are calculated for the cell reaction

$$\mathrm{Ag^{II}}\,(4\,f\ \mathrm{HClO_4}) + 0.5\mathrm{H_2}\,(1\ \mathrm{atm.}) = \mathrm{Ag^+}\,(4\,f\ \mathrm{HClO_4}) + \mathrm{H^+}\,(\text{activity } 1\ m) \quad (3)$$

the values $-\Delta F^\circ_{298} = 46.13$ kcal. and $\Delta H^\circ = -41.1$ kcal.

Potentials in Mixed Solutions.—Series 7 to 9 in mixtures of nitric and perchloric acids at a total acid concentration of 4.00 *f* were made in order to investigate further the argentic complex-formation. The results of varying the nitric acid concentration c_1 from 0 to 4 *f* (total nitrate from 0 to 4.2 *f*) are incorporated in Table II. The values of E′ recorded are the means of four or more determinations.

The calculation of the liquid junction potential E_L requires an estimate of the activity of the acid in the silver half-cell, since at a concentration of 4 *f* the activity coefficients for perchloric and nitric acids differ so much that an approximation of the effective ion activity of their mixtures cannot be made with confidence. In Table II there are given outside limits calculated for each liquid junction by assuming the silver half-cell to have the composition given in the parentheses after E_L, it being assumed as one extreme that the nitric acid is as active as the perchloric acid, and as the other extreme that the nitric acid contributed nothing to the liquid junction or to the activity of the percholoric acid. (In series 7 this lower limit was estimated by assuming all the acid to be nitric acid.) An intermediate estimate, probably much nearer the truth, is that an average activity coefficient $\alpha_{av.}$ prevails, defined by the equation

$$\alpha_{av.}\, c = \alpha_{4f\ \mathrm{HNO_3}}\, c_1 + \alpha_{4f\ \mathrm{HClO_4}}\,(4.0 - c_1) \quad (4)$$

In Fig. 2 there are plotted the results of Table II in such a way that the abscissas are the nitrate concentrations and the ordinates are proportional to the total concentration ($\mathrm{Ag^{II}}$) of argentic silver when the concentration of the *ion* ($\mathrm{Ag^{++}}$) is constant. The value of ($\mathrm{Ag^{II}}$) is taken to be that necessary to make the electromotive force of the following cell some arbitrary constant E_K:

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \mathrm{atm.}),\ \mathrm{H^+}\,(\mathrm{act.}\ 1\ m) \left\| \begin{Bmatrix} \mathrm{HNO_3}\,(c_1\,f) & & \mathrm{Ag^{II}}\,(\mathrm{Ag^{II}})f \\ & + & \\ \mathrm{HClO_4}\,(4.0 - c_1\,f) & & \mathrm{Ag^{I}}\quad(1\ m) \end{Bmatrix} \right., \mathrm{Pt} \quad (5)$$

For convenience, $E_K = 1.950$ was chosen, so that

TABLE II

ELECTROMOTIVE FORCES AT 0.2° IN MIXTURES OF NITRIC AND PERCHLORIC ACID SOLUTIONS

Total acid concentration, 4.00 *w. f.*

Series	NO_3^-, *w. f.*	ClO_4^-, *w. f.*	E′ volts	Average deviation in E′, millivolts	$HClO_4$ *c′*, *w. f.*	E_H, volts	E_L, volts	E^0
5	0	4.20	1.9212	0.5	4.00	0.0606	0.0000	1.982
9	0.70	3.50	1.9088	.2	4.00	.0606	.0000 (4 *f.* $HClO_4$)	1.969
							− .0016 (av. α)	1.968
							− .0063 (3.5 *f.* $HClO_4$)	1.963
8	1.20	3.00	1.9019	.6	4.00	.0606	.0000 (4 *f.* $HClO_4$)	1.962
							− .0034 (av. α)	1.959
							− .0130 (3 *f.* $HClO_4$)	1.950
7	2.20	2.00	1.9005	.3	2.00	.0224	+ .0283 (4 *f.* $HClO_4$)	1.951
							+ .0207 (av. α)	1.943
							+ .0068 (4 *f.* HNO_3)	1.929
1, 2	4.20	0	1.8867	.4	2.00	.0224	+ .0068	1.916 ± 0.002[a]

[a] Arbitrarily assessed probable error in liquid junction.

$(Ag^{II}) = \log^{-1} [(1.950 - E^0)/0.0542]$. Because of the uncertainty in the liquid junction potential, there is an uncertainty in the value of E^0 to be taken, and consequently in the concentration (Ag^{II}) necessary to make (Ag^{++}) constant. This is indicated graphically in Figs. 2 and 3.

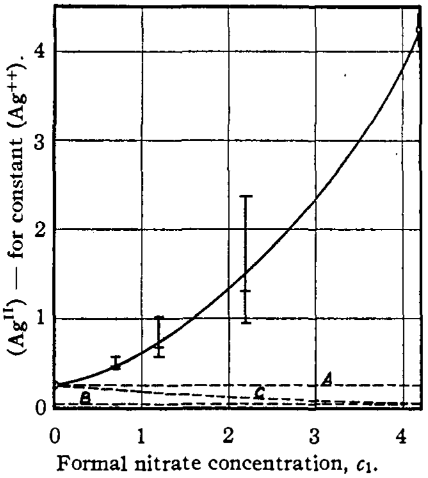

Fig. 2.—Variation of nitrate–argentic complex concentration with nitrate concentration.

If argentic ion forms no complex with perchlorate, the ordinates between line *A* and the curve in Fig. 2 represent the amount of nitrate–argentic complex, and those between the horizontal axis and line *A* represent the amount of ion or its simple hydrolysis products. If a perchlorate–argentic complex is formed, the amount of Ag^{++} is represented by ordinates between the horizontal axis and some horizontal line *B*, and proportions of nitrate and perchlorate complexes are determined by some curve *C*. It can be seen that the error in the amount of silver in the nitrate complex caused by neglecting perchlorate complex-formation is smaller than other uncertainties. In 4 *f* nitric acid, then, at least 94% of the total argentic silver is in nitrate complexes.

To investigate the number of nitrate groups per silver, the logarithm of the bound argentic silver (ordinate between line *A* and curve in Fig. 2) is plotted against the logarithm of the nitrate concentration in Fig. 3. The slope of this curve, approximately 1.6, represents an average number of nitrate radicals in argentic complexes. Observations represented in Fig. 1 require that there be only one argentic atom per complex.

The observations of Noyes and Kossiakoff[2c] that the oxidation potential is independent of the nitric acid concentration in the range 1.0 to 4.0 *f* could be correlated with the above data if it were assumed that as many hydroxide groups are present in the complex as nitrate groups. This view will be discussed later in conjunction with other evidence that seems to make it untenable.

The Composition of Higher Oxides of Silver and their Behavior toward Acid Solutions

Introduction.—This section of the paper presents experiments that were made to study the nature of the complex formed by bipositive silver in nitric acid solutions by determining the solubility of an argentic oxynitrate as a function of hydrogen ion concentration, argentous concentration, and nitrate concentration at constant ionic strength. By correlating the solubility constant with the composition of the solid oxynitrate there was derived evidence about the form of the complex of a different sort from that presented in the first part of this paper. More information was also obtained as to the nature of some of the argentic solids.

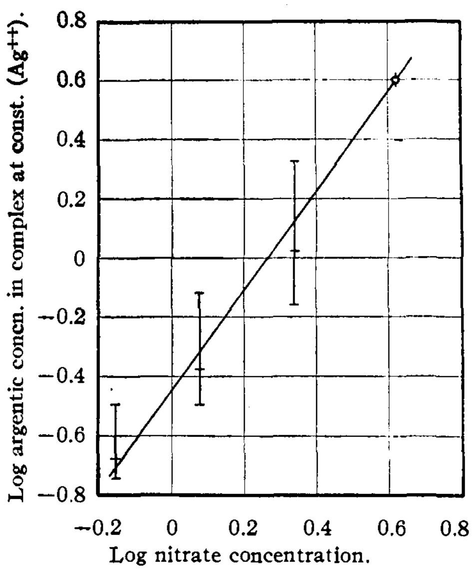

Fig. 3.—Power of the dependence of the nitrate–argentic complex upon the nitrate concentration.

Of the two simple higher oxides of silver (AgO and Ag_2O_3), only the bipositive (here called argentic oxide) has been prepared in pure form.[8,9] Ample proof of the existence of a solid, obtained using persulfate, containing all of the silver in

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[8] (a) Mulder, *Rec. trav. chim.*, **17**, 129 (1898); (b) Watson *J. Chem. Soc.*, **89**, 578 (1906).

[9] Jirsa, *Z. anorg. Chem.*, **158**, 33 (1926).

tripositive form has been presented by Yost[10] and Carman,[11] but complete analyses of the labile compound were not made. The product of anodic oxidation of silver nitrate solution commonly mentioned in the literature is the complex oxynitrate to which has been assigned the formula $Ag_7O_8NO_3$ by Sulc,[12] and Mulder and Heringa.[13] The same solid was prepared in this investigation both by electrolysis of argentous nitrate in 1 *N* nitric acid and by equilibration of argentic oxide with dilute nitric acid solutions. This compound seems very well defined, and will be called in this paper *argentic oxynitrate*. Evidence was obtained that a compound containing silver exclusively tripositive can be precipitated from perchloric acid solutions by anodic oxidation.

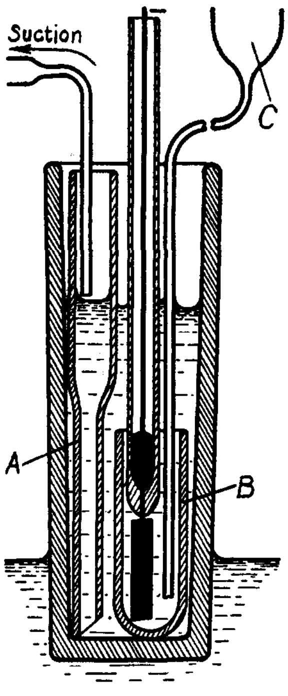

Fig. 4.—Cathode cup assembly: A and B, baffles; C, funnel for fresh catholyte.

The authors wish to thank Miss Elsie DeVault for her able assistance in the experimental work of this section, and Dr. E. H. Swift for numerous suggestions. Financial support from the National Youth Administration was given for a considerable part of this work.

Electrolytic Apparatus.—Higher oxides of silver were prepared by electrolytic oxidation of argentous silver dissolved in dilute acid. The anode was a platinum gauze stirrer rotated by a motor mounted on the lid of a small battery jar, and connected to the d. c. outlet through the shaft and frame of the motor. The platinum foil cathode was surrounded by an unglazed porcelain cup suspended in the anode solution from the lid of the battery jar. Difficulty was encountered in keeping silver trees from growing down through the porcelain into the anolyte. To circumvent this fresh catholyte was made to circulate away from the cathode by the arrangement shown in Fig. 4. With 10 *N* nitric acid as the catholyte baffles A and B are not necessary, as they are when perchloric acid is used.

Analytical Methods.—A search for a convenient reducing agent which would dissolve the higher silver oxides without the evolution of some oxygen was unsuccessful. It was therefore decided to dissolve the compounds in acid and measure the oxygen evolved, using the apparatus represented in Fig. 5. At the end of reaction tube A was placed the solid to be analyzed for oxidation state of its silver; in the lower chamber was placed 3 ml. of 3 *N* perchloric acid. This tube was connected to the buret by a ground glass joint, sealed with 70% perchloric acid. The 3 *N* acid was mixed with the solid by tipping the buret, and warmed until decomposition and solution were complete. Readings were made before and after decomposition by bringing to coincidence the mark on the compensator, and the levels of the mercury in the buret and the compensator. The compensator contained perchloric acid of the same concentration as that used in the reaction tube. Thus readings of the buret were made to correspond to volume of dry gas at a standard concentration. The standard concentration was determined by observing temperature and the pressure necessary to compress the gas in the compensator to the mark, correcting for the vapor pressure of water from the data for perchloric acid given by Pearce and Nelson.[6] Measurements made at different times and temperatures gave a mean value of 0.04445 mole per liter or 0.1778 equivalent of oxygen per liter, with an average deviation of 0.1%.

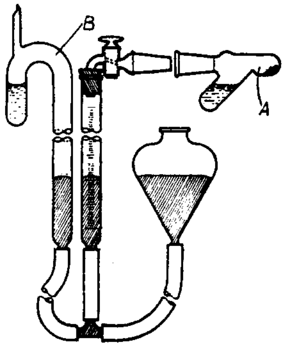

Fig. 5.—Gasometric apparatus: A, reaction tube; B, compensator tube with perchloric acid 3 *N*.

If it was desired to determine the nitrate content of a preparation, the perchloric acid solution from the gas analysis was neutralized and the silver hydroxide filtered off for determination of total silver by thiocyanate titration; otherwise the silver was titrated without separation. With an excess of 50 milliequivalents of sodium hydroxide present, the filtrate was boiled with 1 g. of coarse aluminum turnings; the distillate was collected in standard hydrochloric acid after passing through boiling water to take out alkaline spray. The excess of hydrochloric acid was titrated with standard base and a small empirical correction made for impurities in reagents as determined from blanks. A test of the separation and nitrate analysis gave 99.3% of the silver and 98.0% of the nitrate taken. In several cases the silver hydroxide was not filtered out; after the reduction, the metallic silver was dissolved in nitric acid and determined. Test runs gave results comparable with the above.

To analyze for argentic salt in solution, samples were filtered through a No. 4 sintered glass filter to remove suspended solid and introduced into weighed flasks containing standard ferrous sulfate in ferric sulfate solution. The quantity of solution taken was calculated from the increase in weight. The excess ferrous sulfate was titrated with permanganate as soon as possible, before nitrate or

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(10) Yost, THIS JOURNAL, **48**, 152 (1926).

(11) Carman, *Trans. Faraday Soc.*, **30**, 566 (1934).

(12) Sulc, *Z. anorg. Chem.*, **12**, 89 (1896).

(13) Mulder and Heringa, *Rec. trav. chim.*, **15**, 1, 235 (1896).

argentous ion could be reduced appreciably by ferrous sulfate.

Another filtered and weighed sample was taken for determination of total silver and acidity. After reduction of the argentic silver on heating, the sample was titrated with base to a methyl orange end-point and a correction was applied for increase of acidity brought about by reduction of argentic ion by water. The methyl orange was destroyed by permanganate and a thiocyanate titration was carried out.

The total concentration of nitrate in solution was taken as the sum of the equivalent concentrations of positive ions (disregarding possible complex formation) less the concentration of any other anion present. All concentrations are expressed as weight formal.

The Preparation and Properties of Pure Argentic Oxide (AgO).—The purity and stability of argentic oxide (AgO) made it a convenient source of argentic silver. The method of preparation involves treating argentic oxynitrate (from anodic oxidation) with boiling water,[8,9] during which treatment silver nitrate and oxygen are given off, and AgO remains.

Over 25 g. of AgO was prepared at one time by the following procedure. Approximately 250 ml. of 1.5 *N* nitric acid containing 63 g. of silver nitrate was oxidized in the electrolytic apparatus at 0° using 3.0 amperes for five hours. The presence of acid seemed to speed up precipitation in the earlier part of the electrolysis. Every ten minutes 5 ml. of 10 *N* nitric acid was put into the cathode funnel (Fig. 4). (The current yield in preparing the oxynitrate was 60%.) The precipitate obtained was filtered off, treated for two hours in boiling water, washed, and dried in air.

Analyses were made for oxidizing power and total silver on this preparation. Two analyses for oxidizing power gave 6.50 and 6.52% available oxygen; calculations from thiocyanate titrations gave, respectively, 93.4 and 93.2% Ag_2O. The oxidation number (valence) calculated from these data is 2.007 and 2.013. These analyses are typical.

To determine how long the oxynitrate must be treated with boiling water to change it completely to AgO, and to see whether further treatment brought about further reduction, experiments whose results are shown in Table III were carried out. Argentic oxynitrate was treated with boiling water, and samples analyzed for oxidation number of silver from time to time. Within fifteen minutes the oxidation number had fallen nearly to two (see ref. 15). It reached 2.00 after from two to three hours of heating, and prolonged heating brought about slow decomposition of the AgO. Preparations of AgO have been kept for two months at room temperature without detectable change in composition.

TABLE III

EFFECT OF BOILING WATER ON ARGENTIC OXYNITRATE

Series	Duration of boiling, hrs.	Oxidation no. of silver in ppt.
1	1.5	2.02
	3.7	1.95
2	1.3	2.03
	2.3	1.99
	2.9	1.99
	3.6	1.97
	30.0	1.94
3	0.3	2.02
	1.1	2.02
	2.0	2.01
	7.1	1.98
	21.0	1.95

Argentic oxide dissolves rapidly in 70% perchloric acid with vigorous foaming, giving a very light brownish-yellow solution. On the addition of a little water the color changes to brownish-pink. Dissolution of the oxide in more dilute perchloric acid (60% or less) is accompanied by rapid gas evolution and gives a light brownish-pink solution; the addition of nitric acid changes the color to brown and intensifies it. Argentic oxide dissolves rapidly in nitric acid (6–15 *N*) with comparatively little oxygen evolution to give the familiar brown-black solution of argentic nitrate. The difference in color and stability in nitric acid compared to that in perchloric acid is qualitative evidence for nitrate-complex formation. Solutions in sulfuric acid have a greenish-brown color of intensity comparable to that of nitric acid solutions.

The Equilibration of Argentic Oxide with Dilute Nitric Acid.—To see what changes occur when AgO is equilibrated with dilute nitric acid containing silver nitrate, runs 1 and 2 were made analyzing for concentration of argentic silver in solution from time to time. To 200 ml. of solution 3.39*f* in nitric acid and 0.563*f* in silver nitrate cooled by a thermostat to 0.4° and mechanically stirred, there was added 8.0 g. of AgO. Samples were drawn up through a No. 4 grade sintered glass disk and analyzed as described earlier. Time was taken when approximately half of the sample had been sucked through the filter. The results of the argentic analyses of these two runs are presented in Fig. 6.

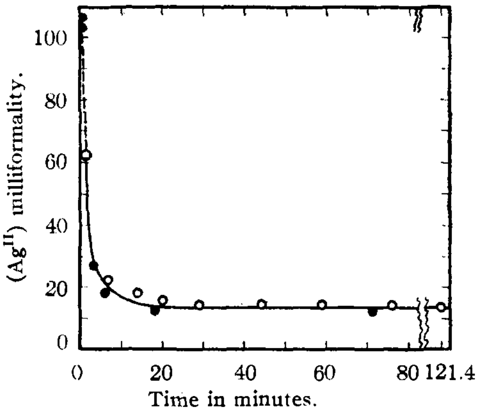

Fig. 6.—Equilibration of AgO with $AgNO_3$–HNO_3 solution: ○, run 1; ●, run 2.

The highest concentration measured, obtained in run 2 at thirty seconds after beginning of the equilibration, indicates that the argentic concentration in equilibrium with AgO is equal to or greater than 0.106 *f*. From the free energies of formation of AgO,[14] H_2O, and Ag^+ at 0°, the formal oxidation potential of the argentic–argentous couple in 4.0 *f* nitric acid, the mean activity coefficient of nitric acid at 4.0 *f* (0.96), and the estimated activity coefficient of Ag^+ in 4.0 *f* nitric acid of 0.6, the solubility of AgO in 4.0 *f* nitric acid at 0° is predicted to be 0.23 formal, a value not inconsistent with this lower limit observed at somewhat lower acid concentration.

The concentration of argentic silver in solution falls off rapidly at first and attains after about twenty minutes a value that remains constant thereafter. In run 1 at the end of two hours there remained approximately 1 g. of solid, which proved to be an argentic oxynitrate, of oxidation number 2.46.

The Composition of Argentic Oxynitrate.—The results of many equilibration runs are presented in Table V, in which the last two columns show the results of analyses for oxidation number of silver and for the ratio NO_3/Ag in the argentic oxynitrate formed. It is seen that the composition of the oxynitrate is independent of the time equilibrated and of the composition of the solution.

That this oxynitrate is the same compound as that obtained by electrolysis is shown in Table IV in which the electrolytic current is given, the elapsed time between filtering and analyzing, and the oxidation number found. In those cases where the current density was not too great the oxidation number is in good agreement with that from equilibration analyses.

TABLE IV

ARGENTIC OXYNITRATE FROM ELECTROLYSIS

Current, amp.	Time between filtering and analyzing ppt., min.	Oxidation no.
1.9	12	2.480
1.7	12	2.478
0.32	16	2.448
.16	20	2.441
.15	24	2.454

In all analyses of oxynitrate reported in this paper the solid was first sucked as dry as possible on the filter and then washed with ice water (water at 25° in runs 18 and 19). This latter step was found necessary to remove adsorbed silver nitrate.

The mean value of the oxidation number from runs 1 through 16 (made at 0°) is 2.448 with an average deviation of 0.008;[15] the mean value of NO_3/Ag for runs 1 through 14 is 0.153. These results are not exactly in accord with the commonly quoted formula $Ag_7O_8NO_3$, which calls for an oxidation number of 2.428 and ratio of NO_3/Ag of 0.143. The analytical results of Sulc,[12] of Mulder and Heringa,[13] and of Watson,[8b] however, are not inconsistent with an interpretation involving a higher oxidation number and nitrate content. Since the same oxynitrate has been obtained by different observers under a variety of experimental conditions, it should be regarded as a definite compound. The empirical formula derived in this investigation for the oxynitrate is $AgO_{1.148}(NO_3)_{0.153}$.[16]

The Solubility of Argentic Oxynitrate.—To study the solubility dependence of argentic oxynitrate, AgO was mixed with solution as in runs 1 and 2 except that samples were not withdrawn until the solid had been transformed into argentic oxynitrate and the argentic concentration in solution had attained constant value. In the runs at 0° the funnel through which the samples were filtered was cooled with cracked ice.

In order to keep the activity coefficients as nearly constant as possible and to vary singly (H^+), (NO_3^-), and (Ag^+), the solutions were made up in runs 7 to 9 (Table V) with lithium nitrate substituted for part of the nitric acid, in runs 10 and 11 with perchloric acid substituted for part of the nitric acid, and in runs 12 to 16 with sodium nitrate substituted for silver nitrate.[17]

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[14] From the measurements of Jirsa[9] on the cell: Pt, H_2, KOH (1 *f*), AgO, Ag_2O, Pt, made at 0 and 30.2°, and the data for ΔF_{298} and $\Delta H°$ of $H_2O(l)$ [Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933), and Rossini, *Bur. Standards J. Research*, **6**, 1, 37 (1931)], and of Ag_2O [Benton and Drake, THIS JOURNAL, **54**, 2186–94 (1932)], the following thermodynamic constants of AgO were calculated: $\Delta F^\circ_{298} = 3.40$ kcal., $\Delta F^\circ_{273} = 2.88$ kcal., $\Delta H^\circ = -2.73$ kcal.

[15] It might be pointed out that a constant error of 1.4% in the gas analyses would lower the result here to 2.43 and the results presented in Table III for the composition of the oxide in the first stages of the boiling to 2.00; it is, however, difficult to see how the method of analysis used could give rise to such an error.

[16] Braekken, *K. Norske Vidensk. Selskabs, Forh.*, **7**, 143–6 (1935) [*Chem. Zentral.*, **106**, 1, 3634 (1935)] has determined the unit cell of the oxynitrate (cubic system, $a_0 = 9.87$ Å.). Using this value and the approximate density of 5.65 reported by Sulc,[12] the molecular weight in the solid is found to be 3290. This value, in conjunction with the empirical formula above, suggests a unit cell containing 26 atoms of silver, 4 nitrate groups, and 30 other atoms of oxygen (mol. wt. = 3534).

[17] The substitutions that most affect the medium (and therefore the activity coefficients) are those of Li^+ for H^+ and ClO_4^- for NO_3^-. It has been shown in 3 *f* chloride solutions of constant ionic strength that lithium chloride is effective in keeping the activity coefficient of hydrochloric acid constant [Harned, THIS JOURNAL, **48**, 326 (1926)]. Perchlorate was selected as a substitute for nitrate as the ion least likely to form complexes.

TABLE V

ARGENTIC OXYNITRATE SOLUBILITY DEPENDENCE RUNS

Run	Time equild., min.	Final concentrations,[a] mole/liter				Cor'd.	Solid analysis	
		(Ag^+)	(H^+)	(NO_3^-)	10^3 (Ag^{++})	10^3 (Ag^{++})	Valence of Ag	NO_3/Ag
Standard point at 0.4°:								
1[b]	44-122	0.839	3.24	4.11	14.3	13.1	2.462	0.160
2	71	.926	3.12	4.07	12.2	11.3	...	...
3a	30	.931	2.97	3.92	10.9	11.3	...	...
b	58	.955	2.94	3.92	10.9	11.5	...	...
4a	31	.691	3.19	3.91	12.7	13.1	...	...
b	80	.694	3.18	3.90	11.3	11.7	...	...
c	104	.690	3.13	..	..	..	...	...
5a	62	.679	3.22	3.92	12.7	12.9	...	...
b	143	.689 .692	3.23 3.21	3.94 3.92	10.9	11.0	...	...
6	155	.672	3.20	3.90	11.7	12.0	...	...
					Average:	**12.0**		
Varying (H^+):								
7	87	.830	1.95	3.93	9.7 5.9	9.5 5.9	2.462	0.151
8	81	.810	1.99	3.95	5.7 6.4	5.6 6.4	2.457	.151
9a	76	.786	0.88	3.93	1.6	1.6	...	...
b	133	.798	.88	3.94	1.8	1.8	2.457	.156
Varying (NO_3):								
10	70	.818	3.17	2.85	7.2 8.4	7.0 8.2	2.442	.158
11a	69	.790	3.27	1.74	5.1	4.8	2.441	.152
b	149	.847	3.24	1.77	5.3	4.9	2.450	.149
Varying (Ag^+):								
12a	76	.334	3.12	3.92	9.0	9.1	2.441	.151
b	168	.348	3.09	3.91	8.5	8.8	2.435	.151
13a	92	.316[c]	3.08[c]	3.98[c]	7.7	7.9	2.440	.149
b	147	.298[c]	3.07[c]	3.95[c]	7.9	8.2	...	...
14a	31	.292	3.06	3.93	7.5	7.9	2.452	.156
b	61	.276	3.14	3.99	7.2	7.1	...	...
15	51	.214	3.09	3.89	8.3	8.6	2.441	.130
16a	16	.161	3.14	3.88	7.0	7.1	2.439	.095
b	44	.157	3.19	3.92	7.4	7.3	...	...
Standard point at 25.2°:								
17	69	.900[c]	3.04[c]	3.96[c]	10.3	10.3	...	...
18a	15	.846[c]	3.08[c]	3.94[c]	9.2	9.3	2.432	.070
b	37	.865[c]	3.06[c]	3.94[c]	10.2	10.3	...	...
19a	15	.844	3.09[d]	3.95[d]	10.2	10.2	2.422	.21
b	39	.872	3.10	3.99	9.6	9.4	...	...
					Average:	9.9		

[a] Initial concentrations: runs **1-6** and **17-19**, HNO_3 3.39 *f*, $AgNO_3$ 0.563 *f*; runs **7** and **8**, HNO_3 2.26, $LiNO_3$ 1.13, $AgNO_3$ 0.563; run **9**, HNO_3 1.13, $LiNO_3$ 2.26, $AgNO_3$ 0.563; run **10**, HNO_3 2.29, $HClO_4$ 1.15, $AgNO_3$ 0.572; run **11**, HNO_3 1.16, $HClO_4$, 2.33, $AgNO_3$ 0.579; run **12**, HNO_3 3.40, $AgNO_3$ 0.113, $NaNO_3$ 0.452; runs **13-16**, HNO_3 3.40, $AgNO_3$ 0, $NaNO_3$ 0.565. [b] Average of four points. [c] Sample not weighed. Results calculated using ratio $(H^+)/(Ag)$ found and assuming (NO_3^-). [d] Estimated.

The results of the nineteen runs made this way are presented in Table V, which shows the total time of equilibration before the sample was drawn, the concentrations of various substances in solution as analyzed at that time, and the results of analysis of the solid phase for oxidation number and NO_3/Ag ratio. Since the argentic concentration varied with (NO_3^-), (Ag^+), and (H^+), and since it was desired to see the effect of varying these factors singly, the argentic concentrations found were corrected to standard conditions for small concomitant variations in factors not being studied (column 7). The standard conditions and assumed power dependences in making this correction are: for (H^+), 3.14 *f*, 3/2 power; for (NO_3^-), 3.94 *f*, first power; for (Ag^+), 0.79 *f*, 3/10 power.

Since argentic silver in solution is being reduced by water and the solid is undergoing decomposition during the run, a true equilibrium cannot obtain between solid and solution. However, the rate of reduction of argentic silver in solution by water can be shown to be quite small at concentrations here prevailing.[2d] Moreover, the concentration of argentic silver shows no observable dependence on the amount of solid present per milliliter of solution, as would be expected if the steady state reached differed sensibly from an equilibrium. In runs 3–6, for instance, there was considerable variation in the amount of AgO introduced; in runs 15 and 16 large quantities of argentic oxynitrate (instead of AgO) were used for the equilibration; in the others 4 g. of argentic oxide per 100 ml. of solution were taken but in all cases the quantity decreases considerably with the time. For cases of variation in quantity of argentic oxynitrate per ml. during one run, see particularly runs 1, 2, 5, 9, and 11. Therefore, the concentrations existing in the steady state will be taken to represent concentrations existing in the saturated solution.

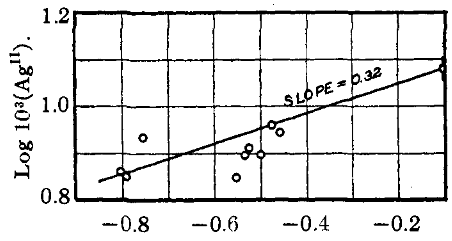

Fig. 7.—Power dependence of solubility upon (Ag^+): runs 1–6, 12–16.

The power-dependence of the argentic concentration on the concentration of the variable studied is determined by plotting in Figs. 7, 8, and 9 the logarithm of the corrected argentic concentration against the logarithms of (Ag^+), (NO_3^-), and (H^+), respectively. It is seen that, for solutions of approximately the composition of the standard point (HNO_3 = 3.1 *f*, $AgNO_3$ = 0.8 *f*), the following experimental relation holds for the solubility of argentic oxynitrate

$$(Ag^{II}) = k(Ag^+)^{0.32}(NO_3^-)^{1.13}(H^+)^{1.54} \quad (6)$$

Experimental error might well amount to 10% for these exponents.

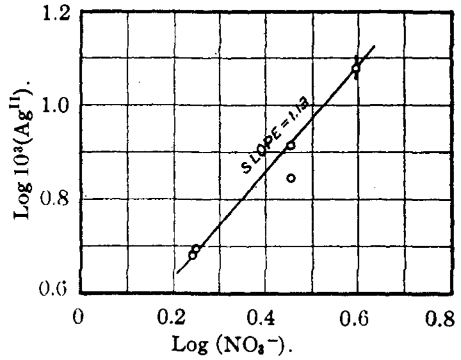

Fig. 8.—Power dependence of solubility upon nitrate; runs 1–6, 10, 11.

Runs 17–19 show that the solubility of argentic oxynitrate is slightly less at 25°. Significance is probably not to be attached to deviations in analyses of the solid at 25° from those at 0°, as evidence for spontaneous decomposition was observed.

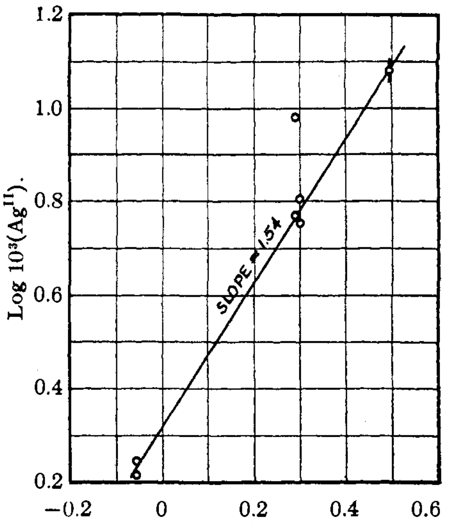

Fig. 9.—Power dependence of solubility upon (H^+): runs 1–9.

Discussion of Nature of Nitrate–Argentic Complex.—That the solubility of the oxynitrate increases with the nitrate concentration again indicates nitrate-complex formation of argentic silver. In addition, there may be hydroxide ion in the complex, and there may be several different complexes existing in the concentration range studied. If (Ag^{II}) is the total argentic concentration, (Ag^{++}) the concentration of argentic ion, K_1, K_2, . . . , are the equilibrium constants for the formation from argentic ion of the complexes containing a, b, ... nitrate radicals each, respectively, and likewise m, n, . . . hydroxide radicals, and K_W is the ionization constant of water, then

$$(\mathrm{Ag^{II}}) = (\mathrm{Ag^{++}})\left(1 + K_1K_W^m \frac{(\mathrm{NO_3^-})^a}{(\mathrm{H^+})^m} + K_2K_W^n \frac{(\mathrm{NO_3^-})^b}{(\mathrm{H^+})^n} + \ldots\right) = (\mathrm{Ag^{++}})f\{(\mathrm{NO_3^-}), (\mathrm{H^+})\} \quad (7)$$

From the equation of solution for the oxynitrate of empirical composition as found

$$0.691\ \mathrm{AgO_{1.148}(NO_3)_{0.153}} + 1.586\ \mathrm{H^+} + 0.309\ \mathrm{Ag^+} \longrightarrow \mathrm{Ag^{++}} + 0.793\ \mathrm{H_2O} + 0.106\ \mathrm{NO_3^-} \quad (8)$$

one obtains

$$(\mathrm{Ag^{++}}) = K\frac{(\mathrm{Ag^+})^{0.31}(\mathrm{H^+})^{1.59}}{(\mathrm{NO_3^-})^{0.11}} \quad (9)$$

(Essentially the same equation would result from considering the oxynitrate as $\mathrm{Ag_7O_8NO_3}$.) By substitution of this value in eq. (7), there is obtained

$$(\mathrm{Ag^{II}}) = K\frac{f\{(\mathrm{NO_3^-}), (\mathrm{H^+})\}(\mathrm{H^+})^{1.59}(\mathrm{Ag^+})^{0.31}}{(\mathrm{NO_3^-})^{0.11}} \quad (10)$$

By comparison of eq. (10) with that derived experimentally, eq. (6), it is seen that the argentous dependence is accounted for satisfactorily. It seems, moreover, from the solubility evidence that $f\{(\mathrm{NO_3^-}), (\mathrm{H^+})\}$ is independent, within experimental error, of $(\mathrm{H^+})$, and may be represented approximately by $k'(\mathrm{NO_3^-})^{1.2}$. That this equation holds implies that $(\mathrm{Ag^{++}})$ may be neglected in comparison with $(\mathrm{Ag^{II}})$ in complex, and that there is an average of 1.2 nitrates and very little or no hydroxide (hydrolysis) in the argentic complex in nitric acid 3.1 *f* and silver nitrate 0.8 *f*. This interpretation rests on the assumption that the results in Table V represent values close to equilibrium.

This value of 1.2 nitrates per silver is not in disagreement with the value of 1.6 derived from electromotive forces in 4 *f* nitric–perchloric acid solutions in the first section of this paper, considering difficulties in interpretation of the results.

Weber[18] showed that in concentrated nitric acid argentic silver migrates toward the anode and therefore is in a negatively charged complex ion. In the present study, transference experiments were tried in 6 *N* nitric acid and seemed to indicate that here also the complex is an anion. Experiments in 3 *N* nitric acid were inconclusive. These observations would indicate more than two negative radicals per silver in the complex on the average in strong nitric acid.

In the first section of this paper the suggestion was made that hydroxide might participate in the complex formation to the same extent as nitrate. This would have explained the observation of Noyes and Kossiakoff[2c] that the formal oxidation potential is independent of the nitric acid concentration in the range 1.0 to 4.0 *f*, but it is not consistent with the solubility experiments, and must accordingly be abandoned. The only way of accounting for all the evidence which has suggested itself to us is based on the assumption that when both nitric acid concentration and ionic strength are varied simultaneously, the effect of increasing complex formation may have been accidentally cancelled by the effect of changing activity coefficients. One requirement of this is that the activity coefficients of univalent ions decrease in the range of ionic strength considered by an amount which is larger than expected but is not impossibly large.

Experiments with Higher Oxides in Perchloric Acid Solution.—Preliminary experiments showed that it might be possible to obtain from perchloric acid solutions an oxide or basic salt of tripositive silver free from the bipositive form. This is difficult to do in nitric acid, because of the stability of argentic oxynitrate. Since little has been reported previously about silver in the tripositive form, the following experiments are appended to this study of nitrate complexes, AgO, and the oxynitrate.

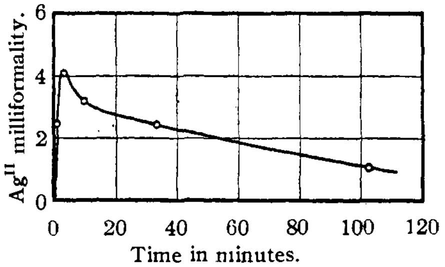

Fig. 10.—Equilibration of AgO with $\mathrm{AgClO_4}$–$\mathrm{HClO_4}$ solution.

A quantity of 1.9 g. of AgO was stirred at 0° with 100 ml. of a solution 0.6 *f* in silver perchlorate and 1.0 *f* in perchloric acid. The results of the analyses of the solution for concentration of argentic silver as a function of the time are presented in Fig. 10. Within several minutes the concentration passes through a maximum of

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[18] Weber, *Trans. Am. Electrochem. Soc.*, **32**, 85–95 (1917).

about 4 milliformal and then falls off gradually. This behavior seems to point to a transformation of the solid phase analogous to that indicated in the runs of Fig. 6, but apparently not reaching equilibrium in the time allowed.

The solid remaining at the end of this run was rinsed once with ice water and analyzed gasometrically for oxidation number of silver, which was found to have the value 2.00. Other experiments on stirring AgO with perchloric acid are shown with the above in Table VI.

Table VI

Treatment of AgO with $HClO_4$ at 0°

Reagent	Treatment	Length of time treated, min.	Oxid. no. of solid remaining
1.0 *f* $HClO_4$ +0.6 *f* $AgClO_4$	Stirring	103	2.00
3 *f* $HClO_4$	Stirring	1	2.12
1 *f* $HClO_4$	Stirring	12	2.09
1 *f* $HClO_4$	Rubbing	12	2.36

It is seen that by rubbing the solid with a test-tube inside the larger one the oxidation number is raised the most. It is probable, therefore, that only the surface of the solid is transformed into a more highly oxidized compound.

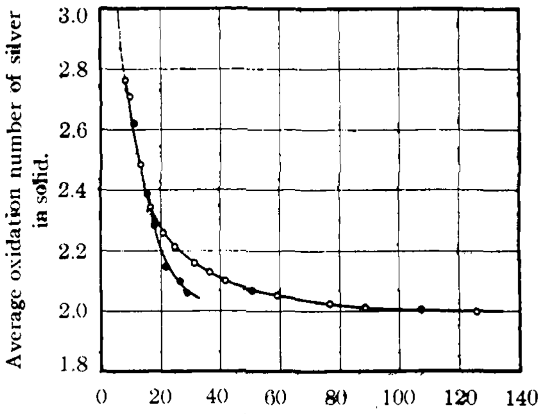

Fig. 11.—Decomposition of solid prepared electrolytically from perchlorate solution.

It was found that a solid containing silver with an oxidation number approaching three could be prepared by electrolytic oxidation of slightly acid silver perchlorate solutions. The electrolysis was carried out at 0°, in the apparatus described before, the solid filtered off and sucked dry without washing, using an ice-cooled sintered glass filter. It was placed in the gasometric apparatus at 25° as soon as possible and the rate at which oxygen was given off was measured for some time before it was mixed with the perchloric acid to effect complete decomposition. In Fig. 11 there are presented the results of two series of measurements. Here the apparent oxidation number of the silver of the solid is plotted against the elapsed time after cutting off the electrolysis current. The highest oxidation number noted was 2.76 after nine minutes of manipulation; extrapolation back indicates that the oxidation number was 3.0 at the time that the last of the solution was sucked off (at six minutes). That is, silver in the tripositive form may be precipitated by electrolysis from perchlorate solutions, and maintained as such in contact with acid solution.

Summary

The formal oxidation potential of silver in 4.0 *f* nitric acid and 4.0 *f* perchloric acid at 0 and 25° has been measured. The potential in 4 *f* perchloric acid at 25° (for the reaction $Ag^{II} + E^{-1} = Ag^{I}$) was found to be 2.000 v. Values of ΔF_{298} and ΔH are given.

Evidence that argentic silver in nitric acid solution exists mainly in the form of nitrate complexes is seen in the facts that: (1) such solutions are black to brown whereas argentic perchlorate in perchloric acid solutions (60% or below) is pink; (2) the oxidation potential of the argentic-argentous couple is 66 to 71 millivolts higher in 4 *f* perchloric acid than in 4 *f* nitric acid; (3) the solubility of argentic oxynitrate increases with (NO_3^-) at constant (H^+).

Measurements made on the formal oxidation potential in mixtures of nitric and perchloric acid at a total acidity of 4.0 *f* indicate that on the average 1.6 nitrates are bound per atom of argentic silver.

Conditions are outlined for the preparation of pure AgO (argentic oxide).

Equilibration of AgO with 3 *f* nitric acid changes the solid into argentic oxynitrate, previously obtained only by electrolysis. The empirical composition of this compound was found to be $AgO_{1.148}(NO_3)_{0.153}$.

The solubility of the argentic oxynitrate as a function of (H^+), (Ag^+), and (NO_3^-) was determined at constant ionic strength. This solubility evidence indicates that there is no hydroxide in the argentic complex, and that there is an average number of 1.2 nitrates per argentic silver.

An unstable oxide or basic salt of tripositive silver is precipitated by electrolysis of silver perchlorate–perchloric acid solutions and also seems to form on the surface of argentic oxide treated with perchloric acid.

PASADENA, CALIF. RECEIVED APRIL 26, 1937

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 597]

Strong Oxidizing Agents in Nitric Acid Solution. III. Oxidation Potential of Cobaltous–Cobaltic Salts, with a Note on the Kinetics of the Reduction of Cobaltic Salts by Water[1]

BY ARTHUR A. NOYES AND THOMAS J. DEAHL

This study of the cobaltous–cobaltic potential is a continuation of a series of investigations on the oxidation potentials of strong oxidizing agents in nitric acid solution.[2–4] The potential was first measured by Oberer[5] and Jahn[6] in sulfuric acid solution, but no attempt was made to calculate the potentials referred to the standard molal hydrogen electrode. In the course of their extensive study of the cobaltammines, Lamb and Larson[7] measured the potential in sulfuric acid solution against a hydrogen electrode in 4 N sulfuric acid at 0 and at 16°, the potential of the reference half-cell being then measured against a normal calomel electrode through a saturated ammonium nitrate bridge.

In the present investigation, measurements were made at 0 and at 25° on cells of the type

$$\text{Pt} + \text{H}_2\ (p_{\text{H}_2}),\quad \text{HClO}_4\ (c'),\ \left\{\text{HNO}_3\ (c) + \begin{matrix}\text{Co}^{\text{II}}\ (c_1)\\ \text{Co}^{\text{III}}\ (c_2)\end{matrix}\right\},\ \text{Au (or Pt)} \qquad (1)$$

for which the liquid-junction potential may be calculated approximately. The acid concentration c and the ratio c_1/c_2 were varied several fold and a reliable value was obtained for the cobaltous–cobaltic potential in nitric acid solution. As the cobaltic salt is reduced by water at a measurable rate at 0°, it has been possible also to obtain information concerning the kinetics of its reduction; these results are discussed briefly.

Apparatus and Materials

Preparation and Analysis of Solutions.—A stock solution approximately 0.5 f in cobaltous nitrate was prepared by dissolving reagent-grade $Co(NO_3)_2 \cdot 6H_2O$ (nickel free) in the proper quantity of distilled water. This solution was standardized gravimetrically as cobalt sulfate. A stock solution of nitric acid was prepared by diluting C. P. nitric acid. Solutions containing cobaltous nitrate and nitric acid in different proportions were prepared by weighing out those quantities of the standardized solutions and distilled water calculated to give the desired weight-formal concentrations.

The cobalt in these stock solutions was partially converted into the tripositive form by electrolysis. The electrolytic cell used for this purpose was equipped with a platinum stirrer, which also served as the anode. The cathode, a small strip of platinum, was enclosed in a vessel made by inverting a sintered glass filter funnel which had been cut off just above the plate. This sintered plate prevented appreciable diffusion between the anode and cathode compartments. A current of about 0.8 ampere was passed for a period 10–20% longer than that theoretically required to convert the cobalt entirely into the oxidized form. Since the electrolysis resulted in the transfer of some of the cobalt into the cathode compartment, it was necessary to blow the cathode solution back into the anode compartment after the current was turned off. The acidity of the final solution was less than that of the initial solution because of the reduction of hydrogen ions at the cathode during the electrolysis. To offset this, the initial acidity was increased from an integral value by a quantity equal to the formal concentration of total cobalt present. The increase in the acid concentration during the subsequent reduction of the cobaltic salt by water amounted in no case to more than 1.7%, and will be shown to have an entirely negligible effect upon the electromotive force of the cell.

The solutions of perchloric acid for the hydrogen half-cells were prepared by diluting the C. P. 60% acid and standardizing against a sodium hydroxide solution.

Calomel was prepared electrolytically by the method of Ellis.[8]

Tank hydrogen was purified by passing it first through a concentrated potassium hydroxide solution, then over

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(1) This problem was suggested by Professor Noyes, who directed a large part of the experimental work. After his death the investigation was continued by the junior author alone, who takes responsibility for the imperfections. The co-operation of Dr. Charles D. Coryell in the preparation of this paper for publication is appreciated.

(2) Noyes and Kossiakoff, THIS JOURNAL, **57**, 1238 (1935).

(3) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(4) Noyes and Garner, *ibid.*, **58**, 1268 (1936).

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