hydrate gives a definite step indicating that the compound is a true chemical hydrate and not a zeolite.

2. Contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Gallitelli, Onorato and others, calcium sulfate hemihydrate and "dehydrated hemihydrate" do not have identical structures. The x-radiograms of the two substances are similar, showing that the structures are similar; but the existence of definite characteristic differences between the two patterns indicates that the water molecules in the hemihydrate occupy fixed position in the lattice. These observations likewise support the view that calcium sulfate hemihydrate is a chemical individual and that the process of dehydration is not zeolitic in character.

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[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 546]

Strong Oxidizing Agents in Nitric Acid Solution. I. Oxidation Potential of Cerous–Ceric Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Plan of these Investigations

In connection with the recent investigations made by Noyes, Hoard, Pitzer and Dunn[1,2] of argentic salts in nitric acid solution, electromotive force measurements were made by Noyes and Kossiakoff[3] to determine the oxidation potential of argentous–argentic salts (Ag^{I}, Ag^{II}); and the result (1.914 volts) was compared with those of other strong oxidizing agents for which reliable data exist. As these data are rather limited, it seemed desirable to carry out researches on the oxidation potential of other powerful oxidizing substances; and it is the purpose of this series of papers to present the results obtained with cerous–ceric salts (Ce^{III}, Ce^{IV}), with thallous–thallic salts (Tl^{I}, Tl^{III}), and with cobaltous–cobaltic salts (Co^{II}, Co^{III}) in nitric acid solution.

The method of measurement was much the same as that used for argentous–argentic salts by Noyes and Kossiakoff, to whose article reference should be made for certain details of procedure. The conditions are simpler, however, in the case of ceric nitrate or thallic nitrate, in that these substances, unlike argentic nitrate, do not undergo at room temperature spontaneous reduction to cerous or thallous salt.

In this first paper are presented the results of measurements on cerous–ceric cells. Such cells were first measured by Baur and Glaessner.[4] They used cells containing cerous and ceric salts in nitric and sulfuric acid solutions; but carried out the work at "room temperature," and eliminated the liquid potential only to the extent that this is accomplished by inserting a saturated solution of potassium chloride between the cerium and the calomel electrodes. A satisfactory value therefore cannot be calculated for the oxidation potential from their data.

More recently, Kunz[5] studied the formal potential of cerous–ceric salts in 0.5 and 1.0 formal sulfuric acid solutions.

In order to determine the value in nitrate solution, which is likely to form complexes to a less extent, and to eliminate largely the liquid potential, we measured at 25 and at 0° cells of the type

$$\mathrm{Pt} + \mathrm{H_2\,(1\ atm.)},\ \mathrm{HClO_4}\,(c'),\ \left\{\mathrm{HNO_3}\,(c) + \begin{matrix}\mathrm{Ce^{IV}}\,(c_2)\\ \mathrm{Ce^{III}}\,(c_1)\end{matrix}\right\},\ \mathrm{Pt}$$

These experiments will now be described.

Apparatus and Materials

Preparation and Analysis of Solutions.—In preparing the stock solutions of cerous and ceric nitrate, C. P. hydrated cerous nitrate was used to make up a solution approximately 0.1 *f* in cerous nitrate and 1 *f* in nitric acid (to prevent subsequent hydrolysis). A 17-cm. layer of this solution gave no absorption spectrum, showing the absence of other rare-earth elements. The solution was then divided into two nearly equal portions.

A solution of ceric nitrate was prepared by electrolytic oxidation of one of these portions with a current of 2 amperes at 6–8 volts, till samples removed and titrated with ferrous sulfate solution showed that the oxidation was nearly complete.

The ceric nitrate solution thus prepared was analyzed as

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(1) Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221–1229 (1935).

(2) Noyes, Pitzer and Dunn, *ibid.*, **57**, 1229–1237 (1935).

(3) Noyes and Kossiakoff, *ibid.*, **57**, 1238–1242 (1935).

(4) Baur and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

(5) Kunz, THIS JOURNAL, **53**, 98 (1931).

follows. Samples were weighed out, and, after adding the proper amount of water and sulfuric acid, the solutions were titrated with standard ferrous sulfate solution potentiometrically, using a vacuum-tube voltmeter. The amount of ceric cerium was thus obtained. The total cerium was determined by titration after oxidation of the cerium with ammonium peroxysulfate, using silver nitrate as a catalyst.[6] The nitric acid content was determined, after removing the cerium, by titration with standard sodium hydroxide solution, using phenolphthalein as indicator. To remove the cerium, the sample was shaken with mercury and a little potassium chloride till all the cerium was reduced to the cerous state; then sodium oxalate was added, the mixture was filtered, and the acid determined in the filtrate, tests having shown that no appreciable amount of nitric acid was adsorbed on the precipitate. The solution was diluted by weight to give a stock solution exactly 1.000 *f* in nitric acid, and check analyses were made. The ceric nitrate stock solution prepared in this manner was 0.1057 *f* in ceric nitrate and 0.004181 *f* in cerous nitrate.

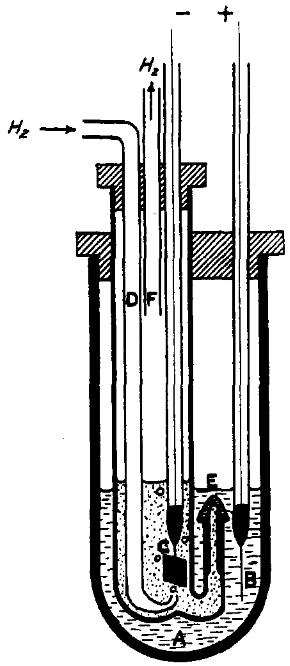

Fig. 1.

The other portion of the original cerous nitrate solution was analyzed in much the same way. It was diluted by weight so as to be exactly 1.000 *f* in nitric acid, and then again analyzed. The resulting stock solution of cerous nitrate was 0.08292 *f* in cerous nitrate and contained no ceric nitrate.

The solutions of perchloric acid were prepared by dilution of C. P. 60% perchloric acid, and were standardized against a sodium hydroxide solution.

Tank hydrogen was purified by passing it successively through concentrated potassium hydroxide solution and concentrated sulfuric acid, and over solid potassium hydroxide and an electrically heated platinum wire.

The Electrolytic Cell.—The assembled electrolytic cell is shown in Fig. 1. A large test-tube served as a container A for the cerous–ceric mixture, in which was immersed the hydrogen half-cell and a platinum wire electrode B. Measurements were made with the platinum wire bright and with it platinum-blacked; there was no difference in potential, although the latter electrode came to equilibrium with the solution much more rapidly. The hydrogen half-cell vessel contained the perchloric acid solution into which dipped a platinized platinum foil electrode C and a tube D through which the hydrogen was bubbled in; the vessel was also equipped with a short vertical capillary side-arm provided with a ground glass cap E which prevented liquid diffusion while allowing electrolytic contact. Before entering the half-cell the hydrogen passed through a glass coil and a vessel containing perchloric acid of the same concentration as that used in the half-cell. In addition a small "bubbler" was provided at the hydrogen outlet F to ensure a hydrogen atmosphere in the half-cell. The apparatus was immersed in a thermostat maintained at 25.00 ± 0.01°, or in one kept at 0°.

Method of Potential Measurements.—A Leeds and Northrup Type K potentiometer was used in conjunction with a high-sensitivity galvanometer for the measurements of the electromotive force. The Weston standard cell used was carefully checked at 25° against a new laboratory standard.

Cerous–ceric mixtures containing varying amounts of nitric acid were prepared from the stock solutions and a standard nitric acid solution by weighing. While each mixture was attaining thermal equilibrium in the cell, the hydrogen electrode was checked at 25° against a 1 *N* hydrochloric acid calomel electrode which had been prepared with purified chemicals in the presence of air.[7] The hydrogen half-cell was then placed in the electrolytic cell, and the potential observed over a period of one to fifty hours. In all cases equilibrium was attained within one hour, and readings were constant thereafter to 0.3 mv. or better; stirring had no effect on the potential. The hydrogen half-cell was checked against the calomel electrode after each run; the calculated value being always obtained to within 0.1 mv.

Calibrated volumetric apparatus, thermometers and weights were employed in this research, and all weighings were corrected to vacuum.

Measurements at 0°.—One of the cells which had been measured at 25° was placed in a 0° thermostat, and measurements of the electromotive force were made over a period of several days. The readings were constant to 0.2 mv., and upon returning the cell to the 25° thermostat, it gave a value for the potential within 0.1 mv. of that previously determined.

The Observed and Computed Electromotive Forces

In Table I are recorded the electromotive forces observed at various concentrations of the substances involved, the corrections computed for reducing these to standard concentrations and eliminating the liquid potential, and the final formal electrode potential thereby obtained.

The first column of the table shows the temperature, 25 or 0°. In the next five columns are given the weight formalities *f* (the concentrations in formula weights per kilogram of water) of the substances in the cells. In the next two columns are the mean ionic strength μ of the cerous–ceric mixtures, and the observed electromotive forces $E_{obsd.}$. The activity coefficients α of the two

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[6] Willard and Young, THIS JOURNAL, 50, 1322, 1379 (1928).

[7] The value −0.2689 volt is the molal electrode potential of the hydrochloric acid calomel electrode for the case in which oxygen is not excluded. See Randall and Young, THIS JOURNAL, 50, 989 (1928). The activity coefficients of hydrochloric acid solutions were taken from this same source.

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$Ce(NO_3)_3$ c_1	$Ce(NO_3)_4$ c_2	Ce^{III}/Ce^{IV} c_1/c_2	Mean ionic strength, μ	$E_{obsd.}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.03284	0.03932	0.8350	2.59	1.6001	−0.0046	−0.0096	+0.0244	1.6103
	(α, 0.759)		.03284	.03932	0.8350		1.6002	− .0046	− .0096	+ .0244	1.6104
		(α', 1.295)									
										Mean	1.6104
25	1.000	1.000	.06513	.02387	2.728	1.82	1.5915	+ .0258	− .0023	− .0047	1.6103
	(α, 0.706)		.06016	.03055	1.969		1.5997	+ .0174	− .0023	− .0047	1.6101
		(α', 0.803)	.04504	.05083	0.8861		1.6197	− .0031	− .0023	− .0047	1.6096
			.04468	.05133	.8705		1.6202	− .0036	− .0023	− .0043	1.6100
			.02768	.07413	.3734		1.6412	− .0253	− .0023	− .0047	1.6089
			.02288	.08146	.2809		0.6488	− .0326	− .0023	− .0051	1.6088
			.01808	.08703	.2077		1.6569	− .0403	− .0023	− .0051	1.6092
										Mean	1.6096
25	0.5000	1.000	.02191	.02624	.8351	0.89	1.6330	− .0046	− .0147	− .0051	1.6086
	(α, 0.708)		.02191	.02624	.8351		1.6328	− .0046	− .0147	− .0051	1.6084
		(α', 0.803)									
										Mean	1.6085
										General Mean	1.**6095**
0	1.000	1.000	.04468	.05133	.8705	1.83	1.6106	− .0033	− .0021	− .0040	**1.6012**
	(α, 0.706)	(α', 0.803)									

acids are given below their concentrations, the coefficients being interpolated from the data of Pearce and Nelson[8] for perchloric acid at 25° and from those of Abel, Redlich and v. Lengyel[9] for nitric acid at 25°. In the next three columns are the values of the electromotive force corrections computed as described below, and in the last column are the values of the formal oxidation potential E^0 referred to the standard molal hydrogen electrode H_2 (1 atm.), H^+ (activity 1 m.); by formal oxidation potential being meant the oxidation potential when the total concentrations, represented by Ce^{IV} and Ce^{III}, of the oxidized and reduced cerium (without reference to their ionization) are both 1.0 *f*.

This formal oxidation potential E^0 (for the reaction $Ce^{IV} + E^{-I} = Ce^{III}$) has been derived by adding to the observed electromotive force $E_{obsd.}$ (which is that of the cell formulated in the first section of this paper) the three following quantities:

(1) $E_C = (RT/2F) \ln (c_1/c_2)$, in order to provide for equiformal concentrations of cerous and ceric cerium, their total concentrations c_1 and c_2 being used in this Nernst equation in place of the ion activities.

(2) $E_L = (2T_H - 1)(RT/F) \ln (\alpha c/\alpha' c')$, in order to eliminate the small liquid potential arising from the different ion activities αc and $\alpha' c'$ of the nitric and perchloric acids; it being assumed that the ion mobilities of the two acids are equal in the given concentration range. The mean transference number T_H of the cation of the two acids has been estimated[10] to have the value 0.85 at 25° and the value of 0.86 at 0°.

(3) $E_H = (RT/F) \ln (\alpha' c'/\sqrt{p_{H_2}})$, in order to refer the value to the molal hydrogen electrode standard at 25°, p_{H_2} being the partial pressure of the hydrogen gas in atmospheres.

Discussion and Summary

It is seen from Table I that the formal cerous–ceric oxidation potential E^0 changes only slightly (at most by 1.5 mv.) on varying the ratio Ce^{III}/Ce^{IV} over ten-fold at constant ionic strength. Moreover, varying the acid concentration from 0.5 to 2.0 *f* and the ionic strength correspondingly has only a small effect on the value of E^0. This shows that nitrate complexes are formed only slightly, if at all, and that a hydrolytic reaction such as $Ce^{++++} + H_2O = CeOH^{+++} + H^+$ does not occur appreciably at these concentrations. Hence the value **1.6095** ± 0.0007 volt may be regarded as the cerous–ceric oxidation potential in nitric acid at 25°, independent of the concentration of that acid between 0.5 and 2.0 formal.

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(8) Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

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

(10) This estimate at 25° is based on the considerations that the two acids have equal conductances at 2.0 *f*, that the nitric acid solution contains less than 10% as much cerium as acid, so that its conductance does not differ greatly from that of pure nitric acid, and that the latter has the values recorded in "International Critical Tables" (Vol. VI, pp. 241, 310 (1929)). For the 0° measurement, the same activity values were used as at 25°, since none are available at 0°.

The value of this potential at 0° was found to be **1.601** volts (in 1.0 *f* HNO_3).

It is interesting to note that in sulfate solution Kunz[5] obtained much smaller values, namely, 1.461 and 1.443 volts at 25° in 0.5 *f* and in 1.0 *f* H_2SO_4, respectively. This indicates that complex formation between the ceric ion and sulfate ion (or hydrosulfate ion) takes place to a large extent. It is probable therefore that the value obtained in nitric acid represents much more nearly the *molal* oxidation potential of cerous–ceric *ions*.

It may also be noted that the cerous–ceric potential in nitrate solution is of the same order as that (1.59 volts)[11] for the reaction $MnO_4^- + 4H^+ + 3E^- = MnO_2(s) + 2H_2O(l)$. Correspondingly, on adding permanganate solution to a nitric acid solution of cerous nitrate, manganese dioxide was found to form; and on adding ceric nitrate solution to freshly precipitated manganese dioxide, the color of permanganate was developed.

[11] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

PASADENA, CALIFORNIA RECEIVED MAY 12, 1936

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Strong Oxidizing Agents in Nitric Acid Solution. II. Oxidation Potential of Thallous-Thallic Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Previous and Proposed Investigations

The thallous–thallic oxidation potential has been studied by several investigators. Its determination was first undertaken by Spencer and Abegg[1] who studied the potential in nitric, hydrochloric and sulfuric acids, and in the presence of various salts with the view of investigating complex-ion formation. Their measurements were made at 25° against a 0.1 *N* calomel half-cell as a reference electrode, and their potentials were not corrected for liquid-junction potentials. Grubb and Hermann[2] later obtained values for the thallous–thallic potential in sulfuric acid solutions. Measurements by them were made at 18° against either a normal calomel electrode or a mercurous sulfate electrode, and liquid-junction corrections were not applied. Partington and Stonehill[3] recently measured at 25° cells of two types

$$\mathrm{Pt},\left\{\mathrm{H_2SO_4}\,(c) + \begin{matrix}\mathrm{Tl_2SO_4}\,(c_1)\\ \mathrm{Tl_2(SO_4)_3}\,(c_2)\end{matrix}\right\},\ \mathrm{H_2SO_4}\,(c),\ \mathrm{H_2}\,(1\ \text{atm.}) + \mathrm{Pt}$$

and

$$\mathrm{Pt},\left\{\mathrm{H_2SO_4}\,(c) + \begin{matrix}\mathrm{Tl_2SO_4}\,(c_1)\\ \mathrm{Tl_2(SO_4)_3}\,(c_2)\end{matrix}\right\},\ \mathrm{Hg_2SO_4}\,(\text{satd.}),\ \mathrm{Hg},\ \mathrm{Hg_2SO_4}\,(\text{satd.}),\ \mathrm{H_2SO_4}\,(c),\ \mathrm{H_2}(1\ \text{atm.}) + \mathrm{Pt}$$

These investigations showed that the oxidation potential of thallous–thallic salts varies greatly with the nature of the anion present, doubtless owing to the formation of anion complexes; and as these complexes are probably produced in minimum quantity with monobasic oxyacids, such as nitric acid and perchloric acid, thereby yielding a molal potential approximating most closely that of the simple thallous and thallic ions, we have measured and describe in this paper cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \text{atm.}),\ \mathrm{HClO_4}\,(c'),\left\{\mathrm{HNO_3}\,(c) + \begin{matrix}\mathrm{Tl^{III}}\,(c_2)\\ \mathrm{Tl^{I}}\,(c_1)\end{matrix}\right\},\ \mathrm{Pt}$$

During the progress of our investigation an article upon the thallous–thallic potential in perchloric acid solution has been published by Sherrill and Haas,[4] thereby making possible a comparison of the potential in the two monobasic oxyacids.

Apparatus and Materials

Preparation and Analysis of the Solutions.—A weighed quantity of C. P. thallous nitrate, dried in an oven at 140°, was dissolved in a definite weight of distilled water, and the resulting solution was divided into two nearly equal portions.

(1) From one of these portions a thallic nitrate solution was prepared by oxidation with a gas mixture containing 5% by volume of ozone (Noyes, Hoard and Pitzer[5]), thereby avoiding the introduction of foreign substances into the solution. To it had previously been added the amount of strong nitric acid (freed from nitrogen dioxide by bubbling air through it) required to leave the oxidized solution 0.5 *f* in nitric acid. It was thought that this acid would suffice to prevent the hydrolysis of the thallic nitrate formed, but during the oxidation dark-brown thallic hydroxide precipitated, and it was necessary to add more nitric acid to the oxidized mixture. The excess of ozone was blown out with oxygen, and the thallic nitrate solution was analyzed in the following way.

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[1] Spencer and Abegg, *Z. anorg. Chem.*, **44**, 379 (1905).

[2] Grubb and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1357 (1935).

[4] Sherrill and Haas, THIS JOURNAL, **58**, 952 (1936).

[5] Noyes, Hoard and Pitzer, *ibid.*, **57**, 1223 (1935)