basis it was shown that colloidal solutions have the same number of degrees of freedom as "true" solutions.

It was found possible to explain a large number of the properties of lyophobic and lyophyllic colloids on the assumption that the surface tension between a lyophobic dispersoid and its dispersing medium is positive unless the dispersoid particles are electrically charged, and that for lyophyllic colloids the surface tension between *undispersed* dispersoid and dispersing medium is negative.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 215.]

AQUA REGIA, II. THE EFFECT OF CHLORIDE ION ON THE POTENTIAL OF THE NITRIC ACID ELECTRODE.

BY WILLIAM C. MOORE.

Received January 30, 1913.

In a previous contribution[1] the author has shown that the chloride ion decreases the efficiency of dilute nitric acid when the latter is used to oxidize ferrous ions to the ferric condition. In seeking an explanation of this fact it was decided to ascertain what effect the presence of chloride ions might have on the oxidation potential of nitric acid.

It seems that no accurate measurements of the oxidation potential of nitric acid have heretofore been made. Bancroft,[2] it is true, publishes a value for this quantity, but his work was carried out with irreversible electrodes. Abegg and Pick[3, 4] studied the electromotive force of the cell silver | normal silver ion | normal nitrate ion | normal nitrite ion | platinum:—the nitrate-nitrite platinum electrode being saturated with nitric oxide at 760 mm. pressure. However, not a single detail of their experimental work is given except that the potential was 0.34 volt, the silver electrode being positive; and even this value is uncertain, for in the second article cited above[4] the value of the potential is given at 0.27 volt, instead of the *calculated* value, 0.34 volt.

It was at first thought that the purpose of this research could be accomplished by setting up two nitric acid electrodes, using acid of the same concentration in each, and measuring the difference of potential existing between them while both were saturated with nitric oxide under the same conditions; nitric acid of the same concentration but containing a definit concentration of chloride ion was then to be substituted for one electrode, the potential measured again, and the difference between these sets of measurements taken as a measure of the effect of the chloride ion on the

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[1] THIS JOURNAL, 33, 1091 (1911).

[2] *Z. physik. Chem.*, 10, 387 (1892). The results of Ihle, *Z. physik. Chem.*, 19, 577 (1896), were likewise obtained under irreversible conditions.

[3] Abegg and Pick, *Z. anorg. Chem.*, 51, 1 (1906).

[4] *Z. Elektrochem.*, 12, 592 (1906).

nitric acid electrode of the particular concentration employed in the experiments.

Accordingly, a number of experiments were carried out with tenth-normal nitric acid electrodes using the experimental arrangement just described. Practically all of the experiments so made showed qualitatively that the chloride ion depressed the potential of the nitric acid electrode. However, the values of the potentials varied to a very wide degree, and the difficulty of getting constant measurements in any one experiment was also great, the time required to get a constant value for the potential apparently being a function of the *rate*[1] at which nitric oxide was allowed to pass through the electrode vessels.

The above method having failed to give satisfactory results, it was decided to measure the oxidation potential of nitric acid against a tenth-normal calomel electrode, the acid being saturated with nitric oxide; and then to carry our similar measurements with separate portions of the same acid containing a definit concentration of chloride ion and compare the results.

The experiments recorded below were made in a thermostat kept at 25.17° ± 0.02°. The nitric oxide used was prepared by the action of dilute sulfuric acid on sodium nitrite in the presence of mercury.[2] It was washed with sodium hydroxide, and stored in two liter bottles having glass inlet and outlet tubes passing through ground-in glass stoppers. Throughout this research contact of nitric oxide with rubber was avoided as far as possible. The gas was brought to the temperature of the thermostat by being passed through about 15 feet of copper "light-tubing," having an internal diameter of a little more than 1 mm., before entering the nitric acid electrode vessel, and was always saturated with water vapor at room temperature before use.

The tenth-normal calomel electrode was set up according to directions given in Ostwald-Luther.[3] The half-cell for the nitric acid electrode had inlet and outlet tubes fused in through the sides, so that nitric oxide could be led through the electrolyte. The electrode was introduced through the top of the cell, and, where electrode "G" was used, was sealed in through the glass stopper. Where electrode "B" was used the electrode tube was inserted in a one-hole rubber stopper.

The potential differences were determined by means of a Wolff potentiometer, using a Leeds and Northrup galvanometer, and a Weston normal cell.

In carrying out an experiment, the cell, composed of the tenth-normal calomel electrode, the bridge solution and the nitric acid electrode, was set

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[1] See, in this connection, Lewis and Edgar, THIS JOURNAL, **33**, 292 (1911).

[2] A modification of Emich's method; see *Monatsheft*, **13**, 83 (1892).

[3] Ostwald-Luther, "Physiko-chemische Messungen," p. 441 (1910).

up in the thermostat, the air expelled from the acid electrode by hydrogen or carbon dioxide, and, after this was accomplished, nitric oxide was passed through the nitric acid electrode at rather a rapid rate while the potential measurements were being made. In all cases the first measurement was not made until at least ten minutes after the nitric oxide was turned on, as is shown in the following tables, thus allowing plenty of time for the expulsion of hydrogen previously filling the apparatus.

In Table I are recorded the results obtained when nitric oxide was bubbled through tenth-normal nitric acid, the other experimental conditions being as indicated. The barometric readings shown were taken about the middle of each experiment, and the electrode was saturated with nitric oxide at practically the recorded pressure. P in this table is the potential of the acid electrode as measured against the tenth-normal calomel electrode, and S the number of seconds required for 50 bubbles of nitric oxide to pass through the bottle in which the gas was saturated with water vapor, when the corresponding reading was made.

Table II shows the effect of adding potassium chloride to the nitric acid electrode. The experiments recorded in this table were carried out, otherwise, exactly as those recorded in Table I. P and S have the same significance in Table II as in Table I.

In Fig. 1, the curves for two typical experiments, 149 A and 149 B, are plotted. The effect of chloride ion is plainly shown in these curves.

TABLE I.

1a: Conditions of experiments:

Exp. No.	Electrode used.	Bar. press. Mm.	Conc. HNO_3.	Bridge used.	Temp. °C.
148 A	G	...	0.101 *N*	0.1 *N* HNO_3	25.15
149 A	G	754.5	0.101 *N*	0.1 *N* HNO_3	25.15
169	B	725.0	0.1000 *N*	0.1 *N* HNO_3	25.17
170	B	721.86	0.1000 *N*	0.1 *N* HNO_3	25.17

1b: Results obtained—(Time refers to time after turning on NO):

Exp. 148 A

Time (min.)	12.0	17.0	22.5	28.5	34.0
P (volts)	0.415	0.420	0.423	0.425	0.428
S (sec.)	17.0	16.0	20.0	18.0	16.0

Exp. 149 A

Time (min.)	12.0	17.5	25.5	32.0	36.0	42.5
P (volts)	0.381	0.387	0.395	0.396	0.398	0.400
S (sec.)	17.0	16.0	17.0	17.0	17.0	17.0

Exp. 169

Time (min.)	12.5	20.5	29.0	37.0
P (volts)	0.391	0.389	0.388	0.388
S (sec.)	14.0	16.0	15.0	17.0

Exp. 170

Time (min.)	12.0	17.5	27.5	39.5
P (volts)	0.368	0.371	0.375	0.376
S (sec.)	16.0	18.0	18.0	14.0

TABLE II.

2a: Conditions of experiment:

Expt. No.	Electrode used.	Bar. press. Mm.	Conc. HNO_3.	Conc. KCl.	Bridge used.	Temp. C.
148 B..	G	.....	0.101 *N*	0.1 *N*	0.1 *N* HNO_3	25.15
149 B..	G	754.5	0.101 *N*	0.1 *N*	0.1 *N* HNO_3	25.15.
150.....	G	.....	0.101 *N*	sat. sol.	0.1 *N* HNO_3	25.15
171.....	B	722.24–722.95	0.1000 *N*	0.1 *N*	0.1 *N* HNO_3	25.17
172.....	B	722.95–724.40	0.1000 *N*	sat. sol.	0.1 *N* HNO_3	25.17

2b: Results obtained—(Time refers to time after turning on NO):

Exp. 148 B

Time (min.)......	12.5	22.0	26.0	27.0	29.0	32.0	
P (volts).........	0.234	0.405	0.389	0.388	0.388	0.387	
S (sec.)..........	(Very rapid stream of NO—rate not taken)						

Exp. 149 B

Time (min.)......	12.0	17.0	23.5	29.0	35.0	47.0	56.0
P (volts).........	0.318	0.381	0.374	0.372	0.373	0.375	0.378
S (sec.)..........	16.0	17.0	16.0	17.5	15.5	15.0	17.0

Exp. 150

Time (min.)......	12.5	23.5	36.5	39.5	......	49.5	54.5
P (volts).........	0.296	0.421	0.451	0.449	......	0.449	0.454
S (sec.)..........	16.0	18.0	15.0	16.0	......	16.0	16.0

Exp. 171

Time (min.)......	12.5	23.0	31.0	42.0	50.0	60.0	69.0
P (volts).........	0.316	0.348	0.358	0.364	0.367	0.370	0.373
S (secs.).........	14.0	15.0	17.0	24.0	14.0	16.0	14.0

Exp. 172

Time (min.)......	13.5	19.5	26.0	33.0	46.5	54.4	61.5
P (volts).........	0.268	0.311	0.350	0.353	0.364	0.367	0.369
S (sec.)..........	14.0	14.0	16.0	18.0	14.0	14.0	14.0

A comparison of the results in Tables I and II and an inspection of the curves shown in Fig. 1 indicates that the chloride ion has a marked effect in lowering the oxidation potential of the tenth-normal nitric acid electrode.

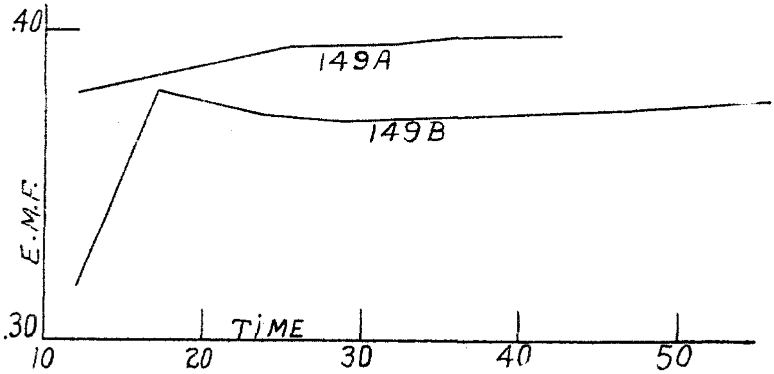

Fig. 1.

The gradual rise in potential as shown in Table I (except in Exp. 169) is probably due to the accumulation of nitrous acid in the solution,[1] as separate experiments made with tenth-normal sulfuric acid containing various concentrations of nitrite ion and saturated with nitric oxide gave rather high potentials, which were quite constant, as the following experiments show:

TABLE III.

Exp. 152. Tenth-normal sulfuric acid, containing hundredth-normal sodium nitrite; electrode G; saturated with nitric oxide at 763.09 mm. Potentials measured against tenth-normal calomel electrode, at 25.16°.

Time (min.)	12.0	16.0	24.0
Potential (volts)	0.426	0.426	0.426

Exp. 153. Conditions as in 152, except the electrolyte contained three-hundredths normal sodium nitrite.

Time (min.)	12.5	20.5	26.5
Potential (volts)	0.448	0.448	0.448

Exp. 154. As in 152 and 153 except that five-hundredths normal nitrite was used. The potential at 12 min. was 0.450 volts. It rose slowly until the following values were observed:

Time (min.)	41.0	45.0	53.0	64.0
Potential (volts)	0.4587	0.4586	0.4578	0.4574

With tenth-normal nitrite, the results were unreliable and variable, since much nitric oxide was evolved. This is easily understood, since Lewis and Edgar[2] have shown that when equilibrium is reached between nitrous and nitric acids saturated with nitric oxide, the total nitrous acid concentration is 0.04974 normal so that, where an attempt is made to get tenth-normal nitrous acid under these experimental conditions, a large proportion of the nitrite is converted into nitric oxide and nitrate ion. When chloride ion was added to the various nitrous acid solutions, variable results were obtained, the potential rising in some cases, falling in others; in the cases of the more concentrated nitrous acid solutions there was a more rapid evolution of gas than when sulfuric acid and sodium nitrite were mixed. Similar results were noted when tenth-normal nitric acid was substituted for the sulfuric acid, and an experiment on this point will be cited below.

A final series of measurements was made with tenth-normal nitric acid containing 0.048 normal sodium nitrite, saturated with nitric oxide. In this series, the sodium nitrite was twice recrystallized from hot water. The calomel electrode used was the same used in previous experiments. The exact concentration of the nitric acid used was one-tenth normal.

Burch and Veley (*Phil Trans.*, [A] 182, 319 (1891)) offer this same explanation for the rise in potential, but they worked with platinum and other metals simply *immersed* in nitric acid of greater concentrations than used in this work.

[2] Lewis and Edgar, *Loc cit.*

TABLE IV.

Exp. 165	Electrode B used	Temp. 25.18°		Bar. 761.17 mm.		Bridge $N/10$ HNO_3	
Time (min.)	12.0	21.5	38.0		56.0	mean value	
Potential (volts)	0.4720	0.4710	0.4694		0.4714	0.4709	
Exp. 166	Electrode B	Temp. 25.17°		Bar. 757.54 mm.		Bridge $N/10$ HNO_3	
Time (min.)	13.0	24.0	36.0	44.0	49.5	58.0	mean value
Potential (volts)	0.4724	0.4720	0.4709	0.4712	0.4704	0.4700	0.4712
Exp. 167	Electrode B	Temp. 25.17°		Bar. 756.23 mm.		Bridge $N/10$ HNO_3	
Time (min.)	14.5	23.0	35.0	46.0	49.0	mean value	
Potential (volts)	0.4707	0.4707	0.4710	0.4698	0.4705	0.4704	
Exp. 168	Electrode B	Temp. 25.17°		Bar. 726.75 mm.		Bridge $N/10$ HNO_3	
Time (min.)	...	25.0	34.0	48.0	.....	mean value	
Potential (volts)	.....	0.4732	0.4705	0.4699	.....	0.4709	
Exp. 173	Electrode G	Temp. 25.18°		Bar. 768.04 mm.		Bridge $N/10$ HNO_3	
Time (min.)	31.5	41.0	49.0	57.5	......	mean value	
Potential (volts)	0.4742	0.4737	0.4731	0.4735	....	0.4736	
Exp. 174	Electrode G	Temp. 25.19°		Bar. 749.93 mm.		Bridge $N/2$ $(NH_4)_2SO_4$	
Time (min.)	12.0	18.5	26.5	......	38.0	mean value	
Potential (volts)	0.4736	0.4731	0.4740	.....	0.4738	0.4736	

Average value for 165-6-7-8, 0.4709.
Average value for 173-174, 0.4736.
Average for both electrodes, 0.4723 volts.

As the correction for pressure of nitric oxide is very small, these values are uncorrected for this quantity

The conditions were thus approximately the equilibrium conditions for this system, as shown by Lewis and Edgar.[1] In Experiments 167 and 174 tenth-normal potassium chloride was a constituent of the electrolyte around the nitric acid electrode. Hydrogen was used to expel air from the apparatus except in Experiment 168, in which carbon dioxide was used. In 168 a constant value was obtained more slowly than in the other experiments, probably because carbon dioxide is more soluble than hydrogen in the solutions used. Table IV is a record of these final measurements.

When the dry salts were treated with the tenth-normal nitric acid in preparing the solutions for 167 and 174, there was an almost immediate evolution of gas, while with the other experiments there was practically no gas formed for a long time. To find out something about this gas, weighed quantities of the purified sodium nitrite and potassium chloride were placed in a dry bottle; hydrogen was used to expel the air and then enough tenth-normal nitric acid run in to make the solution 0.048 normal with respect to nitrite and tenth-normal with respect to chloride. Again the gas evolution began almost at once. This gas was swept through distilled water by a stream of hydrogen, and the water afterwards evaporated to a low volume and tested for nitrite and chloride, which were found to be absent. Where nitric oxide was used in a somewhat similar experiment to remove the gases, there was a very faint test for chloride and a stronger one for nitrite. This particular effect will be studied further.

Discussion of Results and Summary.

A comparison of Tables I and II and an inspection of the curves in Fig. 1 show that the chloride ion temporarily depresses the oxidation potential of nitric acid. In these experiments, however, the nitric oxide was being continually forced into the electrode vessel and its concentration was practically constant, so that there resulted the continuous formation of nitrous acid according to the equation:

$$2NO + H^+ + NO_3^- + H_2O \rightleftarrows 3HNO_2 \ldots\ldots\ldots \tag{1}$$

However, the nitrite ion can very readily be formed by an entirely different reaction under the conditions of this experiment, *viz:*

$$2H^+ + NO_3^- \rightleftarrows H_2O + NO_2^- + 2 \oplus ,$$

so that the positive charges thus available help give rise to the current in the cell studied. By both of these reactions there would necessarily result an increase in the nitrous acid concentration, thus accounting for the rise in potential shown in Tables I and II.

How may we explain, then, the effect of the chloride ion? Where we have purposely introduced nitrite ions so that our oxidizing system is under practically the equilibrium conditions as determined by Lewis

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[1] Lewis and Edgar, *Loc. cit.*

and Edgar, the addition of chloride ion has no effect on the potential of the nitric acid electrode, but it does result in the more rapid evolution of a gas which the experiment cited above shows is probably nitric oxide. It is possible, therefore, that the chloride ion may act in such a manner that either it tends to displace the equilibrium indicated in equation (1) above to the left, or else it increases the tendency for nitric acid to act as an oxidizing agent in accordance with the equation:

$$4H^+ + NO_3^- - 2H_2O + NO + 3\oplus .$$

These points will be studied more carefully.

Summarizing then, we may say:

1. That it is impossible to get a constant value for the oxidation potential of the tenth-normal nitric acid electrode saturated with nitric oxide, because of the increase in the concentration of nitrous acid due to the direct reduction of nitric acid to nitrous acid by the nitric oxide and by the reduction of nitrate to nitrite ions so that positive charges are available to set up an electromotive force in an oxidation-reduction cell.

2. The chloride ion depresses the potential of the nitric acid electrode, probably because it decreases the tendency toward nitrite ion formation. Where no nitric oxide is introduced externally, this depression is probably permanent instead of temporary.[1]

3. The oxidation potential of tenth-normal nitric acid in equilibrium with nitrous acid and nitric oxide at atmospheric pressure is quite definit. Chloride ion has no effect on this potential, the mean value of which, taken from six separate and distinct experiments, using two different electrodes, is 0.4723 volts measured against a tenth-normal calomel electrode at 25.17±0.02°.

NICHOLS LABORATORY OF INORGANIC CHEMISTRY.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 94.]

THE POTENTIAL OF THE LITHIUM ELECTRODE.

BY GILBERT N. LEWIS AND FREDERICK G. KEYES.

Received February 17, 1913.

The method used in measuring the electrode potentials of sodium[2] and potassium[3] has, with some modifications, proved applicable to the determination of the potential of the lithium electrode.

Owing to the extreme solubility of metallic lithium in ethyl amine, this solvent could not be employed. Preliminary measurements had indicated the insolubility of lithium in propyl amine; and, after lithium iodide was found to be soluble in this solvent, it was chosen for our experi-

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[1] THIS JOURNAL, 33, 1091.

[2] Lewis and Kraus, *Ibid.*, 32, 1459 (1910).

[3] Lewis and Keyes, *Ibid.*, 34, 119 (1912).