isolation of complex radicals, we have gotten a new amalgam of one such radical which is far more stable than either ammonium amalgam or monomethyl ammonium amalgam. Though this substance is a compound of carbon, hydrogen and nitrogen on the one hand and mercury on the other, it has true metallic properties. Inasmuch as ordinary binary alloys with true metallic properties are formed only from components which are *both* true metals we are warranted, we think, in concluding that the organic radicals in our amalgams are in the metallic state and, therefore, that *it is possible to prepare composit metallic substances from non-metallic constituent elements.*

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 63.]

THE EQUILIBRIUM BETWEEN NITRIC ACID, NITROUS ACID AND NITRIC OXIDE.

BY GILBERT N. LEWIS AND ARTHUR EDGAR.

Received December 22, 1910.

The decomposition of nitrous acid in aqueous solution according to the reaction

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

was first shown by Veley[1] to be reversible. A more exact study of the equilibrium was made by Saposhnikov[2] to whom we owe much of our exact knowledge of the nitrogen acids.

Saposhnikov studied not only the decomposition of nitrous acid according to the above reaction, but also the reverse reaction starting with nitric acid and nitric oxide, and obtained an equilibrium condition apparently independent of the direction of approach. However, the equilibrium constants which he obtained in numerous experiments with acids ranging from 0.05 N to 3.0 N were not entirely concordant, and in the stronger solutions, varied systematically with the concentration.

An exact knowledge of this equilibrium constant in dilute solutions is of great importance in the calculation of the free energy of nitrogen compounds. It has therefore seemed advisable, relying on Saposhnikov's proof that true equilibrium is established in this reaction independently of the direction of approach, to attempt a more accurate determination of this constant for at least one of the more dilute solutions. We have therefore investigated the final conditions established when a stream of nitric oxide is passed through a tenth-normal solution of nitric acid.

The method employed is a modification of one used by Saposhnikov. A slow stream of nitric oxide is passed through the nitric acid solution in a vessel which permits the measurement of the electrical conductivity

[1] *Chem. News*, 66, 175 (1892).

[2] *J. Russ. Phys. Chem. Soc.*, 32, 375 (1900); 33, 506 (1901).

of this solution. From time to time the conductivity is measured until it reaches a constant value. Since the conductivity of the nitrous acid which is produced is almost negligible in the presence of nitric acid, the change in conductivity is very nearly proportional to the amount of nitric acid decomposed in the reaction

$$HNO_3 + 2NO + H_2O = 3HNO_2.$$

The form of the conductivity cell in which the reaction took place is represented in Fig. 1. Nitric oxide entered through the tube A, bubbled through the nitric acid which nearly filled the cell, and passed out through the bulb B. The liquid was thus constantly stirred and kept saturated with nitric oxide. The platinized platinum electrodes were convex from below in order to prevent their trapping bubbles of gas. Leads entered through glass tubes C and D which were filled with mercury. The upper electrode was situated several centimeters below the level of the liquid in order to avoid any change of conductivity due to changes in level of acid. The resistance capacity[1] of this conductivity cell was accurately determined by means of a tenth-normal sodium chloride solution and was constant throughout the experiments.

The solution of nitric acid was made from the best procurable nitric acid of commerce and contained no detectable impurities. Its concentration was 0.09957 normal.

Nitric oxide was prepared[2] by treating dry sodium nitrite with fifty times its weight of concentrated sulfuric acid in the presence of metallic mercury. The gas was washed with water and caustic soda and was stored over water in a gas reservoir of four liters capacity. This reservoir was kept in the same thermostat in which the measurements were

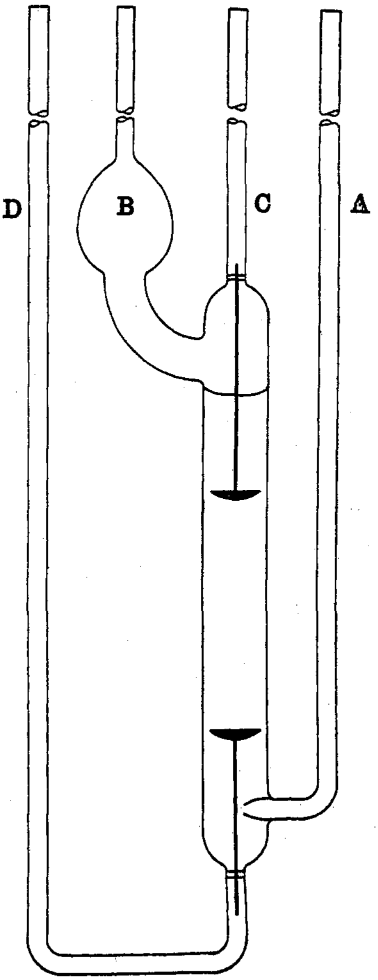

Fig. 1.

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[1] The standardizing solution contained 5.8476 grams of NaCl per liter at 25°, and was assumed to have a specific conductivity of 0.01076.

[2] Cf. Emich, *Monatsh.*, 13, 73 (1892).

made, and the gas thus entered the conductivity cell at the proper temperature, and saturated with water vapor.

The stream of nitric oxide was regulated by a needle valve of special design[1] shown in Fig. 2. A drum is made of a section of brass tubing to each end of which a brass disk is soldered, the upper one being sufficiently thin to permit considerable vertical play. Gas enters this drum through the tube A, which is soldered into the lower disk, and escapes through the tube B. The flow of gas through A may be regulated or entirely cut off by vertical motion of a cone which fits into A and is attached to the upper disk. On the outer side of this disk is soldered a socket which contains a tightly fitting ball. This ball is in turn rigidly attached to a screw which is threaded into a rigid arch attached firmly to the drum. On account of the flexibility of the thin upper disk of the drum, a movement of the screw imparts a vertical motion to the cone of the valve.

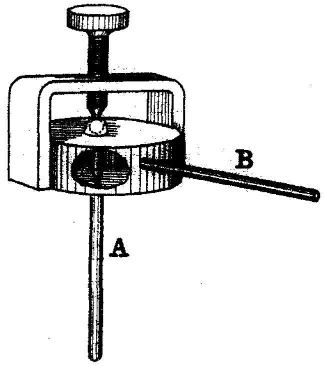

Fig. 2.

This valve, which is completely air-tight, and in which no packing is used, will doubtless be of service in other cases where a delicate control of a stream of pure gas is desired.

The rate of flow of nitric oxide, which by means of this valve could be regulated at will, was from 30–150 bubbles per minute. The rate of bubbling was highest in the early stages of the experiment and was gradually reduced as equilibrium was approached.

The measurements were made at 25.0° in a large thermostat, the temperature of which remained constant within 0.02°.

At the beginning of the experiment the cell, having been filled with nitric acid solution, was placed in the thermostat and the conductivity determined. A stream of carbon dioxide was then sent through to remove all traces of oxygen. This did not in any case appreciably affect the conductivity of the solution. By means of a three-way stopcock the carbon dioxide was then shut off and nitric oxide was allowed to flow through the cell.

The time of duration of the experiments ranged from 50–70 hours. The course of a typical experiment is shown in Fig. 3, where the specific conductivity of the solution is plotted vertically and the duration of the experiment in hours horizontally. It is evident that equilibrium was

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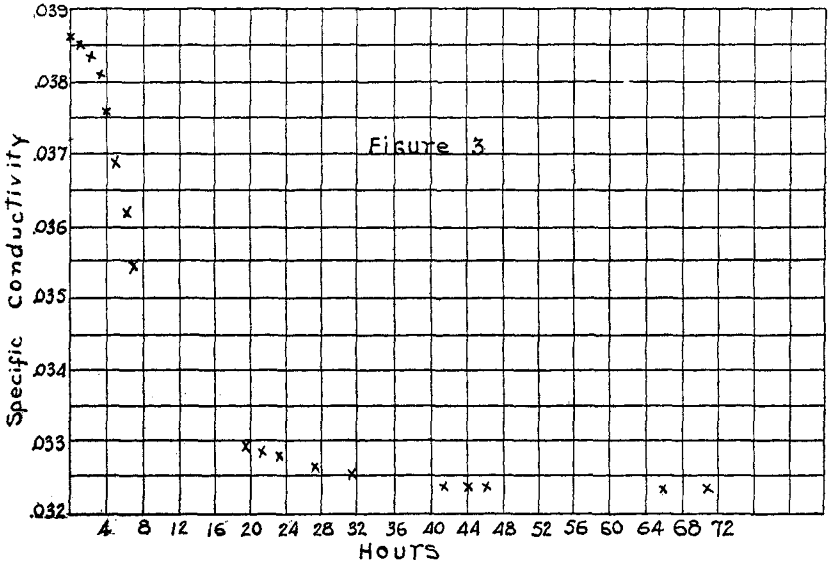
[1] The fundamental idea of a valve of this kind was first developed during an investigation carried on by one of the present authors in collaboration with Dr. C. A. Kraus.

almost completely established at the end of 50 hours, the conductivity during the remaining 20 hours changing less than 0.1 per cent. It is remarkable that the reaction does not reach its maximum rate till after the lapse of several hours. It is hardly likely that this can be due to slowness of saturation of the liquid with NO. It seems more probable that the reaction is in some unknown way autocatalytic. It should be mentioned also that the velocity of the reaction is increased by increasing the rate of bubbling of the gas. These phenomena were not further investigated.



Eleven experiments were made, of which six were not altogether satisfactory, owing to an insufficient supply of nitric oxide in the reservoir, condensation of water in the tube leading to the cell (this tube being for a short distance outside of the thermostat) and to other accidental causes. The results of the five remaining experiments, which were in all respects satisfactory, are given in the following tables.

EXPERIMENT I.

Time in hours.	Specific conductivity.	Time in hours.	Specific conductivity.
0	0.03867	12	0.03371
1	0.03860	22	0.03280
2	0.03854	24	0.03266
3	0.03843	30	0.03249
4	0.03797	33	0.03243
5	0.03732	34	0.03236
6	0.03635	36	0.03234
7	0.03545	47	0.03234
8	0.03510	49	0.03235
$9^{1}/_{2}$	0.03439		

EXPERIMENT 2.

Time in hours.	Specific conductivity.	Time in hours.	Specific conductivity.
0	0.03870	26	0.03280
1	0.03863	28	0.03279
2	0.03843	30	0.03279
3	0.03782	$40^{5}/_{6}$	0.03274
4	0.03712	44	0.03268
5	0.03626	$51^{1}/_{2}$	0.03268
6	0.03568	54	0.03261
$7^{1}/_{6}$	0.03496	$65^{1}/_{2}$	0.03255
17	0.03320	69	0.03252
18	0.03318	$70^{5}/_{6}$	0.03244
21	0.03295		

EXPERIMENT 3.

Time in hours.	Specific conductivity.
0	0.03865
1	0.03851
2	0.03837
3	0.03812
4	0.03756
5	0.03690
6	0.03621
7	0.03545
$19^{1}/_{2}$	0.03294
21	0.03287
23	0.03274
$27^{1}/_{2}$	0.03257
$31^{1}/_{2}$	0.03253
$41^{3}/_{4}$	0.03240
44	0.03239
46	0.03238
$65^{3}/_{4}$	0.03234
$70^{3}/_{4}$	0.03234

EXPERIMENT 4.

Time in hours.	Specific conductivity.
0	0.03868
1	0.03862
$1^{3}/_{4}$	0.03848
3	0.03817
4	0.03771
5	0.03750
6	0.03681
7	0.03604
8	0.03554
18	0.03387
19	0.03377
$21^{1}/_{6}$	0.03353
23	0.03349
25	0.03299
28	0.03272
32	0.03260
42	0.03251
44	0.03252
$46^{1}/_{2}$	0.03249
53	0.03248
$55^{1}/_{2}$	0.03247
66	0.03244
$72^{2}/_{3}$	0.03245

EXPERIMENT 5.

Time in hours.	Specific conductivity.
0	0.03865
1	0.03857
$2^{1}/_{4}$	0.03843
3	0.03831
4	0.03787
5	0.03748
6	0.03658
$6^{3}/_{4}$	0.03586
$8^{1}/_{2}$	0.03457
10	0.03397
$11^{3}/_{4}$	0.03381
$20^{3}/_{4}$	0.03303
$24^{3}/_{4}$	0.03278
$27^{1}/_{4}$	0.03263
$31^{1}/_{4}$	0.03260
37	0.03251
$44^{3}/_{4}$	0.03247
$47^{3}/_{4}$	0.03241
$50^{1}/_{2}$	0.03238

The change in the specific conductivity in these five experiments as well as the initial and final values are given in the following table.

Number of experiment.	Initial conductivity.	Final conductivity.	Decrease in conductivity.
1	0.03867	0.03235	0.00632
2	0.03870	0.03244	0.00626
3	0.03865	0.03234	0.00631
4	0.03868	0.03245	0.00623
5	0.03865	0.03238	0.00627
Average,	0.038670	0.032392	0.006278

It will be seen that the average deviation from the mean is 0.04 per cent. for the initial values, 0.13 per cent. for the final values, and only 0.47 per cent. for the decrease in conductivity, in which experimental errors are greatly magnified. The extremely satisfactory agreement in these experiments renders it certain that a true equilibrium is here established.

The conductivity of the final solution is due almost solely to the nitric acid present, for nitrous acid is a weak acid and is very little dissociated in the presence of the stronger acid. In order to calculate that small part of the conductivity due to the nitrous acid, we may as a first approximation consider the change of conductivity in the experiments proportional to the amount of nitric acid consumed. Starting with tenth-molal nitric acid, the conductivity changed from 0.03867 to 0.03239. Assuming that the nitric acid has decreased in the same proportion, we find that about 0.016 mol per liter has been decomposed. Each mol of nitric acid gives three mol of nitrous acid which is therefore present in the final solution to the amount of 0.048 mol per liter. The dissociation constant of nitrous acid may be taken[1] as $0.00045 = \frac{(H^+)(NO^-_2)}{(HNO_2)}$.

Since the final solution was about 0.083 molal in nitric acid and this acid may be taken as 84 per cent. dissociated, the concentration of hydrogen ion is 0.070 mol per liter. Substituting in the above equation this concentration and the concentration of nitrous acid which we found to be 0.048, we obtain 0.00031 as the concentration of nitrite ion. The concentration of hydrogen ion due to the nitrous acid obviously has the same value. The molecular conductivity at infinit dilution of nitrous acid is 412. Since the molecular conductivity is one thousand times the specific conductivity divided by concentration (in mols per liter), that part of the specific conductivity of our final solution due to nitrous acid is $412 \times 0.001 \times 0.00031$, or 0.00013.

Repeating this calculation, making use of this approximate value, as well as the more exact assumptions which we are about to discuss, gives 0.00032 for the concentration of nitrite ion, or 0.000132 for the conductivity due to the nitrous acid, which is practically identical with the result of the first approximation.

Subtracting this conductivity of the nitrous acid from the average final conductivity of our experiments gives 0.03226 as the conductivity of the nitric acid. In order to ascertain the exact concentration of nitric acid corresponding to this conductivity, we measured directly the conductivity of pure nitric acid, 0.08468 *N*, which had been estimated to give about the same conductivity as the nitric acid in the final solution. The specific conductivity of this solution was found to be 0.03291. From

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[1] Abegg, *Handbuch anorg. Chem.*, 3, III, 144.

this conductivity and that of our tenth-normal nitric acid, by a slight extrapolation the strength of acid having the specific conductivity 0.03226 was found to be 0.08299 *N*.

In order to obtain the most reliable value for the degree of ionization of nitric acid we have assumed it to be equal to that of potassium nitrate at the same concentration. The work of Noyes and Kato[1] shows that this gives a truer value than the one obtained directly from the conductivity of the acid. The degree of dissociation thus obtained, on the basis of Kohlrausch's potassium nitrate measurements, is 84.1 per cent.

The reaction under investigation may be written in the form

$$H^+ + NO_3^- + 2NO + H_2O \rightleftarrows 3HNO_2.$$

Regarding the activity of the water as constant, and also that of the nitric oxide, which is always present at the same pressure, we may write for the equilibrium constant

$$K = \frac{(HNO_2)^3}{(H^+)(NO^-_3)}.$$

The concentration of the nitrous acid which we have shown to be three times the difference between the initial and final concentrations of the nitric acid is 0.04974. Of this 0.00032 is in the form of ions, leaving 0.04942 as the concentration of the un-ionized nitrous acid. The concentration of the nitrate ion, namely 0.06983, is found by multiplying that of the nitric acid by the degree of ionization, and the concentration of hydrogen ion is this same value plus a small amount coming from the nitrous acid, making 0.07015.

The equilibrium constant is thus found to be 0.0246. This is the value of the constant obtained under the actual conditions of the experiments in which the nitric oxide was kept at atmospheric pressure. The barometric readings varied only slightly in the five experiments, the average being 0.992 atm. The nitric oxide, however, was saturated with water vapor at 25° of which the partial pressure was 0.031 atm. This leaves 0.961 as the partial pressure of the nitric oxide. In order to obtain the value of the equilibrium constant with nitric oxide at one atmosphere, we must divide the value given above by $(0.961)^2$, since two mols of nitric oxide enter into the reaction.

We thus obtain as a final value of the equilibrium constant at 25°, and under standard conditions, $K = 0.0267$.

The value obtained by Saposhnikov starting with nitric acid of the same concentration was 0.0175. If, however, we recalculate his results using the same value for the degree of dissociation of nitric acid that we have used, his value becomes 0.0208.

A few experiments which we have made with 0.2 *N* nitric acid seem to

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[1] *Pub. Carnegie Inst.*, 63, 313 (1907).

indicate a change in the equilibrium constant with the concentration, in the direction found by Saposhnikov, but further experiments will be necessary to decide this question.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 64.]

THE POTENTIAL OF THE CHLORINE ELECTRODE.

BY GILBERT N. LEWIS AND FRANK F. RUPERT.

Received January 16, 1911.

The potential of the chlorine electrode has been studied by numerous observers, but the various determinations are by no means in agreement with one another. Müller,[1] who has made the most recent and the most thorough investigation of this subject, has pointed out the chief cause of the observed discrepancies. Chlorine, in the presence of water, hydrolyzes according to the reaction which was first carefully studied by Jakowkin,

$$Cl_2 + H_2O = H^+ + Cl^- + HClO.$$

This hydrolysis takes place to a less extent in a solution of any chloride, and especially of hydrochloric acid, than in pure water, but nevertheless it occurs to a sufficient extent to affect the potential of the chlorine electrode, owing to the increase in concentration of chlorine ion. The change in potential due to this hydrolysis was calculated by Müller to be about $1^1/_2$ millivolts in 0.1 normal and 146 millivolts in 0.001 normal hydrochloric acid. The results of Müller for the potential of chlorine at atmospheric pressure against solutions of hydrochloric acid at four different concentrations are given in the following table. The potential in each case is measured against that of a hydrogen electrode in the same solution.

Conc.	Observed e. m. f.	Corrected e. m. f.	Calculated e. m. f.
1	1.366	1.366	...
0.1	1.485	1.486	1.477
0.01	1.546	1.599	1.594
0.001	1.587	1.733	1.712

The first column gives the concentration of the acid in equivalents per liter, the second the observed electromotive force, the third the same after the correction has been made for the increase of chloride ion due to hydrolysis of the chlorine, and the fourth shows the values calculated for the three lower dilutions from that at normal concentration. It is evident that Müller's correction for hydrolysis has to a large extent eliminated the deviations between the calculated and observed values. There remains, however, an uncertainty as to the true value of the poten-

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[1] *Z. physik. Chem.*, **40**, 158 (1902).