of nitrogen up to 1.8 per cent. may be made to combine with the metal. The most favorable temperature is 700°.

The most favorable temperature for the formation of nitride of iron is 450–475°. On account of the high dissociation pressure of the nitride at this temperature the nitride formed must always contain less than the theoretical percentage of nitrogen. Preparations with 10 per cent. of nitrogen were scarcely appreciably attacked by neutral potassium copper chloride and although slowly attacked by acid solutions did not change their percentage composition. They can not therefore be mechanical mixtures of free iron and nitride and are preferably to be regarded as solid solutions, as is the case with nitride of chromium and chromium. From analogy with other bivalent elements iron should form the nitride Fe_3N_2 and the preparations may be represented by the formula Fe_3N_2+xFe.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, July, 1906.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 100.]

THE ELECTROLYTIC PRECIPITATION OF GOLD WITH THE USE OF A ROTATING ANODE.[1]

BY JAMES RENWICK WITHROW.

Received July 30, 1906.

THE electrolytes used in this investigation were solutions of auric chloride in the presence of (1) potassium cyanide and (2) sodium sulphide. The rate of precipitation of the metal was especially studied. The results show that pure potassium cyanide is evidently a better electrolyte than sodium sulphide for this particular purpose.

The apparatus used in the experiments was similar to that described by Ingham.[2] The first series of experiments with the cyanide electrolyte was made under conditions prescribed by Exner.[3] They were as follows:

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[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, **26**, 1269.

[3] Ibid. **26**, 1256.

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Time. Minutes.	Gold found. Grams.
1....	0.1377	1.5	103	5	13 –10.5	10	0.1377
2....	0.1377	1.5	78	5	11 –10.5	10	0.1372
3....	0.1377	1.5	78	5	10.5– 8.5	10	0.1372
4....	0.1377	1.5	78	5	10.5–10	6	0.1378
5....	0.1377	1.5	78	5	10.5– 9	4	0.1370

The deposits were washed without interrupting the current. Usually a liter of water was required for the purpose. They were of a beautiful gold-yellow color, and consisted of microscopic, very adherent needles. It was not found necessary to let them stand in a desiccator before weighing, but after the ether had been volatilized by the heat of the hand, the dish was rubbed with a chamois skin and placed on the balance pan where it came to a constant weight in a few minutes.

The results confirm Exner's observations in every particular. Even less time than mentioned by him is sufficient for complete precipitation.

To ascertain the minimum time in which it was possible to make a complete precipitation, the following trials were conducted:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Time. Minutes.	Gold found. Gram.
1....	0.2754	2.5	80	5	8– 7	10	0.2747
2....	0.2754	2.5	80	5		5	0.2706
3....	0.2754	2.5	80	5	7.6– 6.7	6	0.2720
4....	0.2754	2.5	80	5	7.5– 6.7	8	0.2754
5....	0.2754	2.5	80	7	9.5– 9	7	0.2748
6....	0.2754	2.5	80	10	14.5–13	2	0.2667
7....	0.2754	2.5	80	10	17 –13	3	0.2724
8....	0.2754	5.0	85	10	17 –10	3	0.2319
9....	0.2754	2.5	80	10	16 –12	3	0.2704
10....	0.2754	2.5	80	12	15	2	0.2476
11....	0.2754	2.5	80	10	15	4	0.2750
12....	0.2754	2.5	80	12	19 –12	3	0.2621
13....	0.2754	2.0	55	12–10	21 –18	3	0.2742

An inspection of this table reveals the fact, as seen in Expts. 1 to 4, that eight minutes are necessary to precipitate all of the gold. On increasing the current to seven amperes the gold was completely deposited in seven minutes. In the eleventh trial fifteen amperes were used and only four minutes were consumed in the deposition. In the trials from the sixth to the eleventh foaming of the electrolyte led to loss.

To learn the result of a still greater concentration of the electrolyte, the following experiments were carried out:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
1	0.2621	1.5	150	0.27–0.2	3.9	none	130	0.2621
2	0.2621	2.5	80	8 –5	11 – 7.5	800	10	0.2621
3	0.2621	2.5	55	12	18 – 8.5	800	3	0.2588
4	0.2621	2.5	30	12	11 – 6.5	800	3	0.2611
5	0.2621	2.5	30	12	13	800	3	0.2618
6	0.2621	2.5	30	12	11.5– 6	800	3	0.2602
7	0.2621	2.5	30	12	11 – 9.5	800	3	0.2608
8	0.2621	2.5	55	12	18 –10	800	4	0.2620
9	0.2621	2.5	55	10	16 –11	800	4	0.2604
10	0.2621	5	60	12	17 –10	800	3.5	0.2585
11	0.2621	2.5	55	12	21	800	1	0.0959
12	0.2621	2.5	55	12	25	800	2	0.2406
13	0.2621	2.5	55	12	16.5–10.5	800	4	0.2619
14	0.2621	2.5	55	12	14 – 9	800	4	0.2614
15	0.2621	2.5	55	12	14 –12	...	4	0.2600
16	0.2621	2.5	55	12	11 –10	380	4	0.2494
17	0.2621	2.5	55	12	15 –10	600	4	0.2571
18	0.2621	2.5	55	12	19 –13	800	4	0.2615
19	0.2621	2.5	55	12	17 –12	800	1	0.1265
20	0.0621	2.5	55	12	18 –11	765	4	0.2612
21	0.2621	2.5	55	12	19 –12	900	4	0.2612
22	0.2621	2.5	55	13	21 –12	790	4	0.2606
23	0.2621	2.5	55	15	12.5–10	450	4	0.2546
24	0.2621	2.5	80	15	14 –13	450	4	0.2412
25	0.2621	2.5	75	15	16 –10	740	4	0.2610
26	0.2621	2.5	80	15	16 –10	850	4	0.2611

The conclusion drawn from this series was that a current of not more than ten amperes should be used, the other conditions remaining the same. Higher currents produced boiling of the electrolyte. There was also variation in the speed of the rotator, and these two factors militated against getting constant results in the minimum space of time. In the succeeding determinations, therefore, only the conditions found most satisfactory in the last series were employed:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found Gram.
1	0.2611	2.5	80	7.0	10	800	12	0.2611
2	0.2611	2.5	80	10.2–10	11.4–10	800	5	0.2612
3	0.2611	2.5	80	10	14.7–9.6	860	5	0.2598
4	0.2611	2.5	80	10	10 –8	620	5	0.2527
5	0.2611	2.5	80	10	14 –9.6	820	7	0.2614
6	0.2611	2.5	80	10.2–10	10.8– 9	...	7	0.2609
7	0.2611	2.5	80	10	14 –10	820	10	0.2612
8	0.2611	2.5	80	10	14 – 9	770	10	0.2616

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
9	0.2611	2.5	80	10	13 −9.5	800	7	0.2615
10	0.2611	2.5	80	10 −10.5	13.5−10	830	7	0.2611
11	0.2611	2.5	80	10	15 −12	795	1	0.1054
12	0.2611	2.5	80	10	13.5−9.5	850	2	0.2049
13	0.2611	2.5	80	10	13.5−9.5	815	3	0.2420
14	0.2611	2.5	80	10	15.5−10	820	4	0.2582
15	0.2611	2.5	80	10	14.7−9.6	860	5	0.2598
16	0.2611	2.5	80	10	14 − 9	810	6	0.2613
17	0.2611	2.5	80	10	14 −10.1	776	7	0.2614
18	0.2611	2.5	80	10	14 −10	830	7	0.2613

Beginning with Expt. 5, the current of ten amperes was regularly employed with an accompanying speed in the rotator of 800 revolutions per minute. The electrolyte was not previously heated from without. The points in the curve marked "KCN No. 1" in the figure were obtained from the eleventh experiment. Upon substituting a more concentrated gold solution—one containing 0.5222 gram—the final series was obtained:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. minute.	Gold found. Gram.
1	0.5222	5	60	10	10 −8	800	10	0.5216
2	0.5222	5	60	10 −10.2	10 −7.3	800	12	0.5226
3	0.5222	2.5	55	10 −10.8	14.5−9.6	800	10	0.5222
4	0.5222	2.5	55	10 −10.3	14 −9.4	810	12	0.5234
5	0.5465	3.5	60	10 −10.5	8.3−7	790	12	0.5461
6	0.5465	5	60	10 −10.2	9.3−8.3	790	1	0.1891
7	0.5465	5	60	10.2−10.5	8.3−7	800	3	0.4341
8	0.5465	5	60	10 −10.3	9.6−7.1	825	5	0.5286
9	0.5465	5	60	10	8.6−6.7	780	7	0.5437
10	0.5465	5	60	10.3−10	8.3−6.3	790	11	0.5468
11	0.5465	5	60	10	7.8−6.8	790	12	0.5467

From the first and second determinations it was seen that the gold was completely precipitated in ten to twelve minutes. No. 3 was then tried to see if less potassium cyanide could be used as it might exert a retarding influence on the rate of precipitation. The result was satisfactory but there was quite a perceptible deposit on the anode, resembling yellow pollen. This was probably an oxide of gold. It dissolved instantly in concentrated hydrochloric acid.

It may be mentioned here that this anodic stain or deposit was also noticed in several of the determinations, made with a stationary anode as checks on the work with the rotator. Especially was this so when the time of precipitation exceeded two hours. It was observed even with deposits weighing only 0.25 gram, with which amount it was never observed when the rotator was used, nor was it mentioned by Miller,[1] who, however, never precipitated more than 0.1697 gram of metal.

The anodic deposit having been eliminated by the use of an excess of potassium cyanide, the determinations from No. 6 on, furnished the points on the curve marked "KCN No. 2." Those deposits in which 0.5 gram of gold was completely precipitated were generally not so bright and were of a darker color than the 0.25 gram deposits.

Upon substituting sodium sulphide for potassium cyanide and electrolyzing the gold solution in its presence, very satisfactory results were obtained. The sodium sulphide was of the specific gravity 1.165. At the beginning, the gold solution was pipetted into a platinum dish and the sodium sulphide was added to it. This proved far from satisfactory because particles of gold sulphide adhered to the sides of the dish and it proved rather difficult to bring them completely into solution, so the expedient was adopted of first introducing the sodium sulphide solution into the dish, starting the rotator and then allowing the solution of gold chloride to run in from a pipette. No precipitate at all was formed and the liquid assumed a deep reddish brown or ferric sulphocyanide color, which, on heating, changed to a clear olive-green. The solution became cloudy during the decomposition from the separation of free sulphur. The anode was coated with a loose layer of sulphur. Rinsing with water sufficed to free the deposits from sulphur, after they were washed with hot water and dried in the usual way. The metallic deposits varied somewhat in color, that in Expt. 9 being beautifully burnished and rich yellow in hue. The curve marked Na_2S in the figure, was constructed from determinations made with 0.25 gram of metal in solution. It is worthy of note that the 0.25 gram curves in the two electrolytes—potassium cyanide and soldium sulphide—are almost identical. Probably they would have been exactly so if the same amounts had been used in each case.

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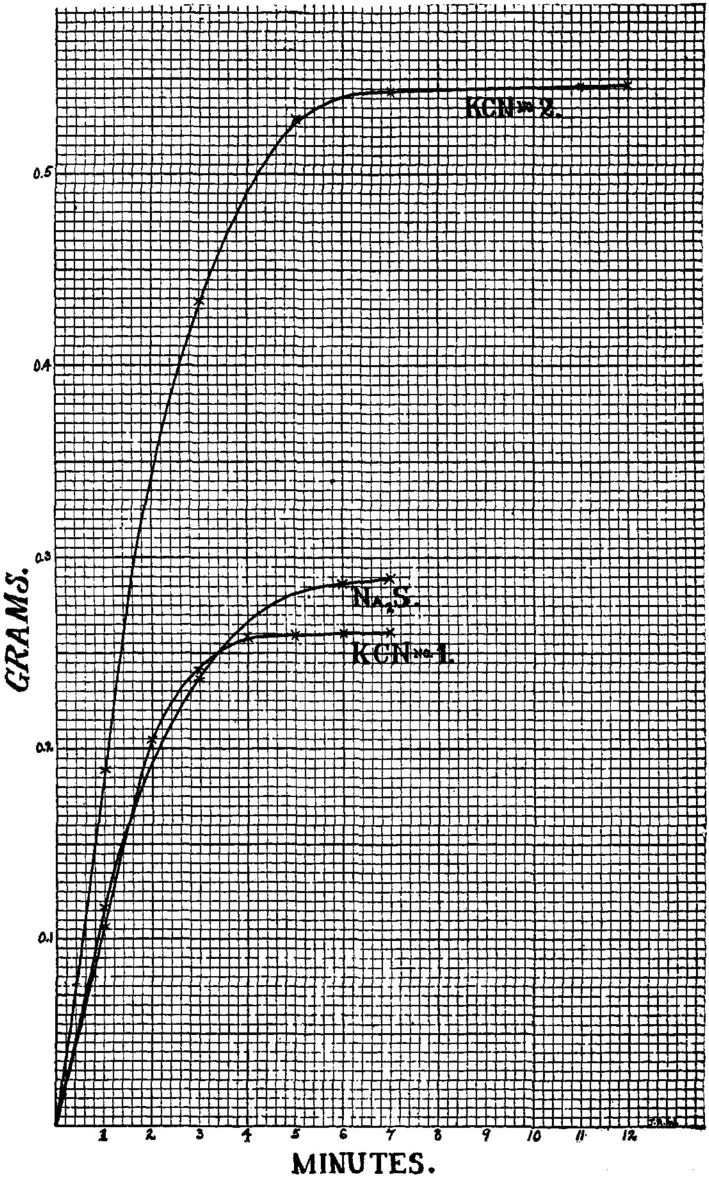
[1] This Journal, 26, 1256.


KCN No. 2.
Na₂S.
KCN No. 1.
GRAMS.
0.5
0.4
0.3
0.2
0.1
MINUTES.
1
2
3
4
5
6
7
8
9
10
11
12

No.	Gold taken. Gram.	Na$_2$S. cc.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
1	0.2878	15	60	10 – 8.8	7.6– 7.2	810	7	0.2891
2	0.2878	30	60	10.1–10.3	6.9– 6	840	7	0.2879
3	0.2878	30	60	9.8–10.1	7.8	830	7	0.2897
4	0.2878	15	60	10 – 9.8	11.6–11.1	840	7	0.2898
5	0.2878	20	60	10	11.6– 9	800	7	0.2905
6	0.2878	30	60	10.2–10.5	8.8– 7.4	830	7	0.2883
7	0.2878	20	60	10.1–10	9.1– 8.2	850	7	0.2885
8	0.2878	15	60	10	11.5–10	840	7	0.2887
9	0.2878	30	60	10.1–10	9.4–8.5	850	1	0.1165
10	0.2878	30	60	10	8 –7	850	6	0.2870
11	0.2878	30	60	10 –10.2	9 –7.9	850	3	0.2365

It was also found that as much as 0.5 gram of metal could be completely precipitated in adherent form in a period of time not exceeding twelve minutes.

Another subject that received some attention was the electrolytic analysis of alkali halides. The complete determination of the components of such salts was shown by Smith to be quite possible when[1] using a mercury cathode and a silver-plated gauze as anode.

In an attempt to get iodine into an adherent deposit a rotator was used, thinking that the deposit might in this way be so compacted as to adhere firmly. The spiral cathode was accordingly rotated from 300 to 500 revolutions per minute, while a silver-plated dish was made the anode. The total dilution was about 70 cc. The following results were obtained:

					Potassium		Iodine	
No.	KI taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	found. Gram.	present. Gram.	found. Gram.	present. Gram.
1	0.0400	....	2.5–2.4	15	0.0094	0.0094	0.0280	0.0306
2	0.0400	....	2.8–2.7	16	0.0094	0.0094	0.0307	0.0306
3	0.0400	....	3.0–2.8	18	0.0095	0.0094	0.0300	0.0306

The cover glasses and the inner sides of the dish were washed down with distilled water shortly before the end of the determination. When the deposition was complete the dish was washed either by the usual siphoning method without interrupting the current or it was immediately withdrawn and the contents poured into a beaker and then rinsed several times with small portions of distilled water and dried in an air-bath, as was done with the gauze in the previous work. The former method was the safer

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[1] This Journal, 52, 890.

of the two and was the one generally employed. In either case the wash-waters were carefully preserved and titrated for the potassium hydroxide.

Potassium chloride was tried in the same manner and very excellent, adherent deposits were quickly obtained.

No.	KCl taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	Potassium found. Gram.	Potassium present. Gram.	Chlorine found. Gram.	Chlorine present. Gram.
1....	0.0400	0.055–0.07	3.9–3.8	15	0.0207	0.0209	0.0190	0.0191
2....	0.0400	0.08	5	15	0.0208	0.0209	0.0206	0.0191
3....	0.0400	0.08 –0.08	3.8–3.4	10	0.0205	0.0209	0.0187	0.0191
4....	0.0400	0.08 –0.09	3.6	10	0.0205	0.0209	0.0192	0.0191
5....	0.0400	0.08 –0.09	4.2–3.8	10	0.0211	0.0209	0.0189	0.0191
6....	0.0400	0.08 –0.09	5 –4.7	10	0.0198	0.0209	0.0180	0.0191
7....	0.0400	0.08 –0.09	6.3–4.7	10	0.0211	0.0209	0.0187	0.0191

The same conditions were used as in the analysis of potassium iodide with aid of the rotator.

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THE DISSOCIATION OF WATER VAPOR AND CARBON DIOXIDE AT HIGH TEMPERATURES.

BY IRVING LANGMUIR.

THE dissociation of gases at high temperatures has been the subject of many investigations during the past few years. In particular the states of equilibrium in the following reactions have been studied:

$2HI \rightleftarrows I_2+H_2$.[1]
$CO_2+H_2 \rightleftarrows CO+H_2O$.[2]
$2SO_3 \rightleftarrows 2SO_2+O_2$.[3]
$2NO \rightleftarrows N_2+O_2$.[4]
$2CO_2 \rightleftarrows 2CO+O_2$.[5]

$2H_2O \rightleftarrows 2H_2+O_2$.[5]
$2NH_3 \rightleftarrows N_2+3H_2$.[6]

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[1] Bodenstein: Z. physik. Chem. 29, 295 (1899).

[2] Hahn: Ibid. 44, 513 (1903); 48, 735 (1904).

[3] Knietsch: Ber. 34, 4069 (1901); Bodenstein: Z. Electrochem. 11, 373 (1905).

[4] Nernst: Göttinger Nachr. 1904, Heft 4.

[5] Nernst and v. Wartenberg: Göttinger Nachr. 1905, Heft 1; Löwenstein: Z. physik. Chem. 54, 715.

[6] Haber and van Oordt: Z. anorg. Chem. 44, 341 (1905).