occurs or if the temperature is high. With one or several of these factors operating the cathode potential may be distinctly of Type B *although a comparatively large current is flowing through the cell.*

5. The factors which favor Type B potentials retard the establishment of Type A overvoltage. Overvoltage values obtained by the commutator method at low current densities are commonly of Type B if the metal is active even though the ordinary method would, under similar conditions, give values characteristic of Type A.

6. It has been shown that at a current density of 175 micro-amperes per sq. cm., the decrease per degree rise in temperature of overvoltage of Type A is the same (2 mv. per degree) for several metals, thus indicating that this is not a property of the cathode material.

7. Progress in the study of the phenomenon of overvoltage has been much retarded by a failure to appreciate that the laws which have been proposed are usually intended for overvoltage of Type A, and in some cases investigators have failed to recognize in their experiments the factors which favor Type A or Type B overvoltage. They have classified all of the cathode potentials as overvoltage and, without subsequent discrimination, have used data peculiar to one of the two types *in the criticism or substantiation of a theory concerning the other.*

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE REACTION BETWEEN POTASSIUM AMIDE AND CERTAIN SALTS OF COBALT AND IRON IN LIQUID AMMONIA

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RECEIVED FEBRUARY 5, 1924 PUBLISHED DECEMBER 13, 1924

Introduction

During investigations carried on in this Laboratory for the purpose of preparing amides, imides, nitrides and ammono salts of a number of representative metals, Dr. Franklin, E. W. Scott and later the author studied the action of potassium amide on a few salts of iron with rather discouraging results. An excess of potassium amide, for instance, was found to react with ferrous bromide and iodide hexammonates to form black products of variable and very indefinite composition.[2] The present work was undertaken primarily with the view of clearing up this anomalous reaction. It was thought that study of the behavior of cobalt salts toward potassium amide might afford some clue as to the conduct of salts of iron.

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[1] National Research Fellow.

[2] (a) Franklin and Scott, unpublished work. (b) Bergstrom, THIS JOURNAL, **46,** 1558 (1924).

Cobaltous Amide, $Co(NH_2)_2$ and Cobaltous Nitride, Co_3N_2.—Anhydrous cobaltous thiocyanate was found to be readily soluble in liquid ammonia. Slow addition of a solution of potassium amide to a solution of this salt at first precipitates bright blue, flocculent cobaltous amide, which on standing for a few days in contact with liquid ammonia at ordinary temperatures decreases very greatly in bulk and changes into black, amorphous cobaltous nitride. Although cobaltous amide deammonates fairly readily in the presence of liquid ammonia at room temperatures, more slowly at 0°, and very slowly at —40°, it was found not to suffer decomposition when kept in an evacuated tube at ordinary temperatures for a period of two weeks, as indicated by the fact that the pressure within the tube did not appreciably increase during that time. The nitride, when once formed, does not take up appreciable quantities of ammonia when kept for several days at —40° or for 4.5 hours at —78°, as indicated by the fact that the precipitate remained black. Cobaltous amide when heated in a vacuum above 120° blackens and changes to the nitride, which then occupies a volume not much less than that of the original substance. Water has scarcely any action on cobaltous nitride prepared by either of the above methods. Cold, dil. sulfuric acid dissolves the preparations a trifle sluggishly with the formation of small quantities of gaseous nitrogen and hydrogen. Cobaltous amide, on the other hand is vigorously decomposed by water with the evolution of heat and the formation of a flocculent precipitate of cobaltous hydroxide which readily dissolves in dil. sulfuric acid.

The reaction between potassium amide and an excess of cobaltous thiocyanate is represented by the equation, $Co(SCN)_2 + 2KNH_2 = Co(NH_2)_2 + 2KSCN$. On remaining for some time in contact with liquid ammonia at ordinary temperatures, or on being heated above 120°, cobaltous amide loses ammonia in accordance with the equation, $3Co(NH_2)_2 = Co_3N_2 + 4NH_3$.

Experimental Work

A description of the methods and manipulations used in preparation of compounds in liquid ammonia may be found in previous articles[3] and so will be omitted here for the sake of brevity. In order to separate a small amount of aquobasic material present in the dried cobaltous thiocyanate and insoluble in liquid ammonia, it was found convenient to use a three-legged reaction tube, thus providing a clean leg into which the clear solution of the salt could be decanted. Precipitation of cobaltous amide was then accomplished by slow addition of potassium amide to this solution, which contained from 50 to 80% of cobaltous thiocyanate

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[3] This Journal, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913); **46**, 1545 (1924); *J. Phys. Chem.*, **15**, 510 (1911); **16**, 694 (1912); **19**, 539 (1915).

in excess of that required by calculation for the formation of the compound $Co(NH_2)_2$. Unless it was desired to prepare the amide, the reaction tube was simply allowed to stand for a few days until decomposition into the nitride was complete, after which washings could much more readily and efficiently be accomplished. The specimens were dissolved in dil. sulfuric acid preparatory to analysis. Cobalt was determined electrolytically as the metal, potassium was weighed as sulfate after removal of the cobalt, and ammonia was estimated by distillation from sodium hydroxide solution.

In Expts. 3 and 5 attempts were made to prepare cobaltous amide by washing the initial blue precipitate at 0° or room temperature. In Expt. 6, the precipitation and washing of the cobaltous amide was carried out at —40° in order to lessen the formation of nitride so evident in 3 and 5. The complete washing of the precipitate at this lower temperature was very time-consuming.

TABLE I

ANALYTICAL DATA[4]

	Subs. 20°	120–150°	Co	N	K_2SO_4	Co_3O_4[5]	H_2[6]	N_2[6]
1	0.2757	0.2714	$(^1/_4)$ 0.0579	$(^1/_4)$ 0.00794	$(^1/_4)$ 0.0014	0.0011	...	...
2	.1992	.1969	$(^1/_2)$ .0847	$(^1/_2)$ .01190		....	0.7	1.2
3	.3045	.2540	$(^1/_4)$ .0534	$(^1/_4)$ .00758	$(^1/_2)$ .0064	.0031	2.7	1.4
4	.2354	.2318	$(^1/_2)$ .0988	$(^1/_4)$ .00730		.0025		
5	.4179	.3497	$(^1/_4)$ .0725	$(^1/_4)$ .01058	$(^1/_4)$ .0025	.0015	1.2	2.3
	(−40°)	.4299	$(^1/_4)$ .0728					
6	.3708		$(^2/_5)$ .0976	$(^2/_5)$ .04031	$(^2/_5)$ .0048	.0006	0.0	2.2
	(−40°)	.3764						

TABLE II

SUMMARY OF ANALYSES

Substance dried in a vacuum at low temperatures. Calc. for $Co(NH_2)_2$: Co, 64.9; N, 30.8. Found: No. 6 (—40°), Co, 65.0; N, 28.7; K, 1.4: (25°) Co, 66.0; N, 27.9; K, 1.4. (The less satisfactory analyses of 3 and 5 likewise support the formula $Co(NH_2)_2$.) Substance heated in a vacuum between 120° and 150°.

Calc. for Co_3N_2		1	2	3	4	5
Co	86.3	85.7	86.1	85.0	86.1	83.3
N	13.7	11.7	12.9	12.6	12.6	12.9
K		0.9		2.3		1.3

There can be little doubt that the substance initially precipitated is cobaltous amide, although the specimens analyzed were all partially deammonated. Beilby and Henderson[7] obtained a nitride of the approximate composition Co_2N by passing ammonia gas over heated cobalt, but the product may have contained free metal. Vournasos[8] states that

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[4] For method of reporting data, see THIS JOURNAL, **46,** 1547 (1924).

[5] Material not dissolved by dil. H_2SO_4 ignited to give Co_3O_4.

[6] Under standard conditions, gas given off as result of solution of the substance.

[7] Beilby and Henderson, *J. Chem. Soc.*, **79,** 1251 (1901).

[8] Vournasos, *Compt. rend.*, **68,** 889 (1919).

Co_3N_2 is formed when a mixture of cobalt oxide and cyanide is dropped in small quantities at a time through an arc between poles in a nitrogen atmosphere. No analyses are given.

Attempts to Prepare a Potassium Ammonocobaltite

Cobaltous thiocyanate when added to an excess of potassium amide solution produces a strongly colored green solution and a blue precipitate, which changes on standing to black. This solution, while generally stable by itself, is not stable in contact with the precipitate, decolorizing with lapse of time to form a black solid.

Cobaltous amide and nitride both dissolve readily, although not completely, in a solution of potassium amide of moderate strength. It appears that the soluble substance responsible for the blue color is stable only in the presence of an excess of potassium amide.

Potassium amide solution converts cobaltous chloride hexammonate into a blue substance, which shortly changes to black and an unstable, light yellowish-green solution. It has not been found possible to obtain definite compounds by the action of potassium amide in excess on the halides of iron, cobalt or nickel.[9a,2b]

In respect to the formation of the strongly colored intermediate solution with potassium amide, cobaltous thiocyanate resembles potassium nickel thiocyanate. There is an important difference, for Bohart[9b] was able to isolate the definite compound, $Ni_2N_3K_5.6NH_3$, which was deposited when the green solution decolorized. Like cobaltous thiocyanate, ferrous thiocyanate gives with an excess of potassium amide a precipitate of very indefinite composition, occasionally accompanied by an unstable brown solution.

Action of Potassium Amide on the Cobaltic Ammines

Hexamminocobaltic nitrate was found to be somewhat soluble in liquid ammonia at 25° and readily soluble at —40°, forming an orange-colored solution. Addition of potassium amide to a solution of this salt precipitated a bulky, orange or orange-brown substance, which analysis showed to be an ammonobasic mixture containing in two instances approximately 10% and 22% of nitrate radical.

Hexamminocobaltic iodide dissolved readily in liquid ammonia at room temperature, forming an orange-colored solution. Potassium amide, when added to an excess of this solution produced a flocculent dark orange-brown precipitate which proved to be an ammonobasic mixture.

From the above results it appears that the $Co(NH_3)_6$ group does not behave as a unit in liquid ammonia as in water. Rather the hexammino salts in ammonia solution are to be regarded merely as salts with associated ammonia of solvation.

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[9] Compare; (a) Bohart, *J. Phys. Chem.*, **19**, 546; (b) 559 (1915).

Attempts to Prepare a Potassium Ammonoferrite.—Microscopic examination of the black precipitate produced by the action of an excess of potassium amide solution on ferrous bromide or iodide[2] revealed the presence of numerous, tiny, white or colorless crystals, which were thought possibly to be a potassium ammonoferrite. Because of the very low solubility of these crystals in ammonia they could not be isolated. Inasmuch as Bohart[9b] has prepared a potassium ammononickelate by the action of a solution of potassium nickel thiocyanate on an excess of potassium amide, it was thought possible that a potassium ammonoferrite might be prepared by the action of a solution of potassium amide upon ferrous thiocyanate, which latter is very soluble in liquid ammonia. Unfortunately, some reduction of the thiocyanate group took place and the preparations were contaminated to the extent of a few per cent. with an iron sulfide. Peculiarly enough, these specimens were black and apparently contained very few white crystals.

Ferrous Thiocyanate Tetra-ammonate

$Fe(SCN)_2.4NH_3$

A solution of ferrous thiocyanate, free from water and other impurities, was readily prepared by the action for one or two days of a liquid ammonia solution of mercuric thiocyanate upon iron wire in a two-legged glass reaction tube. The solution of ferrous thiocyanate thus formed was decanted into the other leg of the reaction tube and evaporated to dryness, the resulting solid being dried in a vacuum of a few millimeters at room temperature or 135° and then dissolved in dil. sulfuric acid. Iron and ammonia were determined after removal of thiocyanate as the silver salt. This group was weighed as cuprous thiocyanate.

Preparation 1. Subs. (20°) 0.5510: ($^1/_4$) 0.0458 Fe_2O_3; ($^1/_4$) 0.03917 NH_3.

Preparation 2. Subs. (20°) 0.6110, (135°) 0.5148: ($^1/_2$) 0.1022 Fe_2O_3; ($^1/_4$) 0.01987 NH_3; ($^1/_4$) 0.1536 CuSCN.

Calc. for $Fe(SCN)_2.4NH_3$: Fe, 23.3; NH_3, 28.4; SCN, 48.4. Found at 20°: (1) Fe 23.2; NH_3, 28.4; (2) Fe, 23.4; NH_3, 28.8; SCN, 48.0.

Calc. for $Fe(SCN)_2.2NH_3$: Fe, 27.1; NH_3, 16.5; SCN, 56.4. Found (2) heated at 135°: Fe, 27.8; NH_3, 15.4; SCN, 57.0.

The tetra-ammonate is an effloresced white powder.

Attempts to Prepare a Normal Ferrous Nitride, Fe_3N_2.—The black substance precipitated by addition of a solution of potassium amide to an excess of a solution of ferrous thiocyanate, while chiefly ferrous nitride, was found to contain iron sulfide as well as small quantities of cyanogen derivatives, indicating that some reduction of the thiocyanate radical had taken place. The impurities amounted to a few per cent.

Ferrous nitride was, however, obtained in a slightly impure state by the action of a solution of ammonium thiocyanate upon the black reaction product of ferrous bromide with an excess of potassium amide. Assuming, from previous work, that the black precipitate contained 14% of potassium, about double the quantity of ammonium thiocyanate in solution necessary to react with this potassium to form potassium thiocyanate was shaken with the precipitate for a few moments. The black solid after a thorough washing with ammonia was heated in a vacuum, dissolved in dil. sulfuric acid and analyzed. Ferrous nitride was found to react with potassium amide but without the formation of a definite compound.

Preparation 1. Subs. (145°) 0.1016: (1/1) 8.3 cc. of H_2 and 1.3 cc. of N_2 given off on solution of the specimen in acid. (The large volume of hydrogen probably indicates free iron;) (1/2) 0.00568 N; (1/2) 0.0625 Fe_2O_3.

Preparation 2. Subs. (150°) 0.1309: (1/2) 0.0777 Fe_2O_3 and 0.0019 K_2SO_4; (1/2) 0.00801 N; (1/1) 6.9 cc. of H_2 and 1.3 cc. of N_2 given off on solution of the specimen in acid. The iron cyanogen compounds insoluble in dil. sulfuric acid contained 0.0020 g. of Fe_2O_3.

Calc. for Fe_3N_2: Fe, 85.7; N, 14.3. Found: (1) Fe, 86.2; N, 12.7; (2) Fe, 84.4; N, 13.4; K, 1.3.

Evidently No. 2 is contaminated with small quantities of reduction products of the thiocyanate radical.

According to Guntz,[10] normal ferrous nitride may be prepared by fusing lithium nitride with ferrous potassium chloride, $FeCl_2.2KCl$. No analyses of the products are given.

In conclusion, the author wishes to express his appreciation of Dr. Franklin's kind advice and assistance during the course of this investigation.

Summary

1. The preparation of cobaltous amide, $Co(NH_2)_2$, and of cobaltous nitride, Co_3N_2, has been accomplished, the former being obtained in a slightly deammonated condition.

2. No definite products were obtained by the action of potassium amide on an excess of hexamminocobaltic nitrate or iodide, or of an excess of potassium amide on ferrous and cobaltous thiocyanates, cobaltous chloride, ferrous bromide and iodide.

3. Ferrous thiocyanate tetra-ammonate, $Fe(SCN)_2.4NH_3$, has been prepared by the action of mercuric thiocyanate on iron wire in liquid ammonia. Normal ferrous nitride, Fe_3N_2, has been prepared in a slightly impure condition.

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[10] Guntz, *Compt. rend.*, **135**, 738 (1902).