ducing the acidity instead of increasing it. This effect is consistent with the results of Thomas and Whitehead for aluminum salts, and of Wilson and Kern,[7] and of Thomas and Baldwin[8] for chromium salts, in which these investigators found that chloride ion always increased the hydrogen ion activity of the solutions to which it was added but that sulfate ion decreased it, particularly when in low concentrations. They point out that the presence of sulfate ions produces a much more complicated system. According to Thomas and Baldwin, there is the tendency of the sulfate to replace the hydroxo groups in the Werner complex which would, of course, tend to make the solution less acid, and it would do so more effectively than the chloride ion of the same equivalent concentration if the stability of the sulfatocomplexes follows the same order of stability that holds for other Werner complexes, namely, oxalate > acetate > formate > sulfate > chloride > nitrate. These are in order of decreasing stability, and would account for the greater effectiveness of sulfate over that of chloride ion, at low concentrations.

In this work no attempt has been made to cor-

(7) Wilson and Kern, *J. Am. Leather Chem. Assoc.*, **12**, 445 (1917).
(8) Thomas and Baldwin, THIS JOURNAL, **41**, 1981 (1919).

rect for the salt error of the quinhydrone electrode in the strong salt solutions. Not only are we out of the range for which such corrections are available, but it is in a sense just that quantity that we are measuring, in comparing the differences in e. m. f. with and without the added salts. Furthermore, irrespective of any salt error, our data are directly available for comparative studies in specific interaction of ions at corresponding concentrations.

Summary

A study has been made by an electrometric method of the effect of various neutral salts on the hydrolysis of copper sulfate in aqueous solutions.

It has been found that the several neutral salts increased the degree of hydrolysis of copper sulfate in the following order: potassium nitrate, sodium nitrate, potassium chloride and sodium chloride. Those which showed a decrease are, in order: sodium sulfate and potassium sulfate.

Also, it has been found that the extent of hydrolysis showed an increase with dilution of copper sulfate. Factors involved in the mechanism of the hydrolysis have been discussed.

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Reactions of Zirconium Tetrabromide in Liquid Ammonia[1]

BY ERNEST W. BOWERMAN[2] AND W. CONARD FERNELIUS

I. Zirconium Tetrabromide and Liquid Ammonia

Several investigators[3] have examined the action of gaseous ammonia on zirconium tetrahalides both in the solid form at various temperatures and in solution in ether. A number of ammonates have been reported as well as the products of their thermal decomposition. Formulas for ammonates deduced solely from the composition of a solid obtained by treating a

(1) This paper is based upon a dissertation submitted by Ernest W. Bowerman to the Graduate School of The Ohio State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1937.
(2) Present address: Humble Oil and Refining Company, Baytown, Texas.
(3) (a) S. R. Paykull, *Ber.*, **6**, 1467 (1873); (b) T. M. Matthews, THIS JOURNAL, **20**, 821-3, 840 (1898); (c) A. Stahler and B. Denk, *Ber.*, **38**, 2611-2617 (1905); (d) L. Wolther, *Chem. Z.*, **32**, 606-607 (1908); (e) P. Bruère and E. Chauvenet, *Compt. rend.*, **167**, 201-203 (1918).

halide with ammonia are open to question because the solid so formed may be a mixture of amide (imide or nitride) or ammonobasic salt and ammonium halide. For example, Stahler and Denk[3c] succeeded in removing a large amount of ammonium iodide from the "ammonate" of zirconium iodide, $ZrI_4 \cdot 8NH_3$, by extraction with liquid ammonia. Whereas the zirconium content of the ammonate was 12%, that of the washed residue was 45%. Young[4] reports that zirconium tetrabromide is soluble at least to the extent of 2 g. per 10 ml. of liquid ammonia at $-33°$. On the other hand, experiments in this Laboratory[5] indicated that zirconium tetrabromide is ammonolyzed by liquid ammonia at $0°$ or higher.

The present study has shown that an ammonolytic equilibrium

(4) R. C. Young, THIS JOURNAL, **57**, 1195-1196 (1935).
(5) H. J. Wolthorn, Thesis, The Ohio State University, 1933.

$$3ZrBr_4 \cdot xNH_3 + yNH_3 \rightleftarrows$$
$$3Zr(NH)_2 \cdot 7NH_4Br \cdot zNH_3 + 5NH_4Br \quad (1)$$
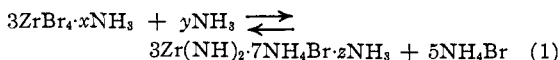
is established when zirconium tetrabromide is placed in liquid ammonia. It has been demonstrated that the point of equilibrium lies far to the left at $-33°$ with small volumes of ammonia (many times that which is stoichiometrically needed for ammonolysis) but that the point of equilibrium shifts quantitatively to the right at $0°$ or above forming a crystalline ammonobasic zirconium bromide. Although this basic salt is insoluble in liquid ammonia (-33 and $20°$), it is completely soluble in an excess of ammonium bromide.

Ammonolysis of Zirconium Bromide. A.—Anhydrous zirconium bromide[6] (1–2 g.) was sealed in one leg of an ammonia tube[7] and ammonia condensed into this leg. When this condensation was conducted at $0°$ (Expts. 1–3, Table I), the bromide appeared to dissolve slightly at first but, as more liquid condensed, the insoluble material increased considerably in volume. After condensing about 20 ml. of ammonia in the tube, the ammonia tank was disconnected and the contents of the tube stirred by shaking. The very finely divided white residue settled quickly and, on warming to $25°$, the solution deposited a small amount of white crystals on the walls of the tube. After carefully pouring off the supernatant liquid, the insoluble product was washed 20–25 times with liquid ammonia and prepared for analysis.

TABLE I

Expt.	Zr	Br	N	Zr:Br:N
1	24.27	51.18	22.00	1:2.41:5.90
2	24.06	49.20	21.43	1:2.33:5.80
3	24.36	49.40	21.67	1:2.32:5.79
4	24.82	49.16	22.04	1:2.26:5.78
5	24.19	49.38	21.73	1:2.33:5.85
6	24.32	49.56	22.28	1:2.33:5.97
7	24.33	48.97	21.46	1:2.30:5.74
a	24.12	49.31	22.21	1:2.33:6.00

a Calculated for $3Zr(NH)_2 \cdot 7NH_4Br \cdot 5NH_3$.

B.—When ammonia was condensed upon zirconium bromide at $-33°$ (Expts. 4 and 6, Table I), the salt dissolved on shaking giving evidence of some heat evolution during the process. Thus 1.05 g. dissolved completely in approximately 5 ml. of ammonia giving a colorless solution. As more ammonia was condensed above this solution a white precipitate appeared at the interface of the solution and the solvent but disappeared upon agitation. After condensing about 20 ml. of ammonia, the solution remained cloudy and the residue would not settle.[8] On warming to $25°$, the solution deposited an abundant quantity of white crystals which were washed, as described above. During evacuation of the tube prior to analysis, the material lost its crystalline character and crumbled to a fine white powder. This behavior suggests that the actual ammonolysis product may well contain more ammonia of crystallization than the material analyzed.

C.—A sample of zirconium bromide in contact with liquid ammonia was heated at $100°$[9] for twenty hours, (expt. 5, Table I), and then washed with ammonia. If the higher temperature resulted in more extensive ammonolysis, the analytical results show that equilibrium was reëstablished on cooling.

Ammonolysis of Zirconium Tetrabromide Octammonate.—A 0.70-g. sample of $ZrBr_4 \cdot 8NH_3$[10] prepared by bubbling anhydrous ammonia gas through a suspension of zirconium tetrabromide in anhydrous ether, was found to be completely soluble in approximately 5 ml. of liquid ammonia at $-33°$. On warming to $25°$ the same crystalline product previously obtained was deposited (expt. 7, Table I).

Five experiments were run to determine the amount and composition of the soluble product resulting from the ammonolysis of a given weight of zirconium bromide. After the formation of the ammonobasic salt, it was carefully washed with ammonia, particular care being taken to reduce to a minimum carry-over of insoluble material. The results of these experiments are presented in Table II.

TABLE II

I Br	II Br	III Zr	IV N	V Br:N:Zr	VI
1.4284	0.5436	0.0215	0.0982	1:1.03:0.035	0.386
1.3326	.5179	.0189	.0972	1:1.07:0.032	.389
1.4540	.6114	.0537	.1110	1:1.04:0.077	.420
0.7026	.2823	.0113	....	....	.402
1.2522	.4934	.0178	....	....	.394
Theoretical					.417

In Table II, Column I gives the weights of bromine in grams, equivalent to the bromine in the zirconium tetrabromide ammonolyzed. Columns II, III and IV give the weights in grams of bromine, zirconium and nitrogen, respectively, found in the soluble product. The one to one ratio of bromine to nitrogen indicates that the soluble product is largely ammonium bromide. The values in Column VI are the quotients obtained by dividing the values in Column II by those in Column I, and they represent the fraction of bromine in the zirconium tetrabromide removed by the ammonolytic reaction.

Reversal of the Equilibrium. A.—Ammonia was condensed upon a 1.635-g. sample of zirconium bromide at $-33°$ until a permanent cloudiness was obtained (approximately 20 ml.). On pouring this mixture into a solution of 1.00 g. of ammonium bromide, the cloudiness disappeared

(6) For preparation see R. C. Young, THIS JOURNAL, **53**, 2148–2149 (1931).

(7) Since the products of the reactions described here were only slowly soluble in dilute acids, it was necessary to transfer small samples of the dry materials to sample tubes or weighing bottles in an atmosphere of dry nitrogen. Because of the reactivity of zirconium bromide, it was sealed into small sample tubes which were broken ust before inserting into the ammonia tube, all operations being carried out in an atmosphere of dry nitrogen. The nitrogen in the ammonia tube was later displaced by ammonia.

(8) Compare these observations with those of F. F. Fitzgerald, THIS JOURNAL, **29**, 1695 (1907), on stannic iodide and E. C. Franklin, ibid., **27**, 845 (1905), on lead iodide.

(9) For technique see J. S. Blair, THIS JOURNAL, **48**, 91 (1926); cf. F. W. Bergstrom, ibid., **52**, 2847 (1930).

(10) Anal. Calcd. for $ZrBr_4 \cdot 8NH_3$: Zr, 16.67; Br, 58.43; NH₃, 24.89. Found: Zr, 16.65, 17.30; Br, 57.59, 58.97; NH₃, 24.56, 23.10.

but the solution deposited a considerable quantity of the ammonobasic salt on warming to 25°.

B.—The above experiment was repeated using 0.336 g. of zirconium bromide and 5.0 g. of ammonium bromide in approximately 15 ml. of ammonium. The solution did not develop any cloudiness nor deposit crystals upon warming to 25° even though the tube was frequently agitated over a period of three days.

C.—Ammonobasic zirconium bromide (0.375 g.) failed to dissolve in approximately 50 ml. of liquid ammonia at −33° even after the addition of sufficient ammonium bromide (0.15 g.) to form $ZrBr_4 \cdot xNH_3$. However, the material slowly dissolved after the addition of 3.0 g. of ammonium bromide.

II. Ammonobasic Zirconium Bromide and Potassium

In the hope of obtaining metallic zirconium or some other reduction product, ammonobasic zirconium bromide was treated with a solution of potassium in liquid ammonia (0°). Young[4] similarly treated a solution of zirconium bromide with potassium (−33°) and obtained a black precipitate and a red solution. Neither of these was stable and secondary reactions produced hydrogen gas and a white precipitate which proved to be potassium ammonozirconate, $Zr(NK)_2 \cdot NH_3$. Working at 0°, similar transient colorations were produced but the liberation of hydrogen was immediate.

Although the results do not exclude entirely the presence of a small amount of some unstable reduction product, attempts to isolate such a product were unsuccessful. The results are best interpreted by assuming the existence of another ammonolytic equilibrium

$$3Zr(NH)_2 \cdot 7NH_4Br \cdot zNH_3 + mNH_3 \rightleftarrows$$
$$3Zr(NH)_2 \cdot nNH_3 + 7NH_4Br \quad (2)$$
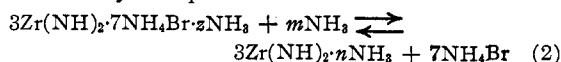
which is brought to completion through the destruction of the ammonium bromide

$$2NH_4Br + 2K \longrightarrow 2KBr + 2NH_3 + H_2 \quad (3)$$

The analytical results indicate that a portion of the zirconium imide reacted with the excess potassium (or potassium amide formed by interaction of potassium and solvent) to form some potassium ammonozirconate.

A.—A solution of potassium was poured portion-wise into a suspension of the ammonobasic salt. Immediate reaction produced a brownish-black residue, a red solution, and a gas which was shown to be hydrogen. After sufficient potassium had been added to impart a permanent blue color to the solution, the liberation of gas practically ceased. Only an inappreciable quantity of hydrogen was formed with a concentrated solution of potassium over a period of ten hours. During the washing process, the residue became blue-gray in color, changing to a greenish-

yellow upon evacuation of the tube. This product was unstable in air and vigorously hydrolyzed by 6 N sulfuric acid in which the hydrolysis product slowly dissolved.

B.—In order to characterize further the nature of the brownish-black precipitate, a sample immediately was washed free of potassium and allowed to stand in contact with liquid ammonia for a period of six hours. During this time the precipitate became blue-gray but no hydrogen gas was liberated. Another sample similarly washed and evacuated, was treated in a nitrogen atmosphere with an acidified solution containing two drops of 0.1 N potassium permanganate. Although a vigorous reaction took place, the pink color of the solution was not destroyed.

C.—Table III records the results of four experiments, in which weighed samples of ammonobasic salt were treated in liquid ammonia solution (0°) with amounts of potassium approximately equivalent to the bromine content of the ammonolytic product. Considering the difficulties in accurately weighing the potassium and in obtaining an ammonobasic salt of constant composition, the results agree well with those to be expected on the basis of equations (2) and (3).

TABLE III

G. ammonobasic salt used	0.4915	0.5093	0.4095	0.5471
G. K used (approx.)	.12	.13	.10	.16
G. Br in ammonobasic salt (calcd.)[a]	.2425	.2512	.2010	.2698
G. Br found in soluble product	.2467	....	.2080	.2731
Ml. H₂ liberated	....	37.7	26.1	40.8
Ml. H₂ equivalent to Br (calcd.)[b]	....	35.2	28.3	37.8
Composition of residue, % ⎰ Zr	65.3	70.1	69.2	60.7
⎱ N	18.3	20.1	19.7	20.1
⎱ K	11.4	5.8	5.2	14.1

[a] Using composition $3Zr(NH)_2 \cdot 7NH_2Br \cdot 5NH_3$ (see Table I).   [b] On basis of reactions (2) and (3).

III. Ammonobasic Zirconium Bromide and Potassium Amide

Inasmuch as potassium is effective in bringing reaction (2) to completion, it seemed desirable to determine whether potassium amide would be equally effective.

A sample of ammonobasic zirconium bromide was treated with an amount of potassium amide only slightly in excess of that required to remove the bromine. The white precipitate first formed became yellow (resembling the product obtained by using potassium metal) after washing and drying.

Anal. Weight of basic salt treated, 0.6503 g. Calcd. Br in salt, 0.3207 g. Found in washings: 0.3210 g. Br and 0.1611 g. K; ratio Br : K, 1 : 1.025. Composition of insoluble product: Zr, 58.7; K, 16.5; N, 20.8.

An excess of potassium amide should result in the formation of a potassium ammonozirconate such as that found by Young[4]

$$Zr(NH)_2 \cdot nNH_3 + 2KNH_2 \rightleftarrows Zr(NK)_2 \cdot sNH_3 + tNH_3$$
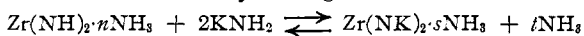
The results presented in Table IV demonstrate that such a reaction does occur but that the zirconate formed is extensively ammonolyzed at 0°.[11] When the zirconate is washed a minimum number of times at −33°, the product approximates Zr(NK)$_2$·2NH$_3$ in composition but with an increased number of washings at 0°, the potassium content is lowered. Ammonolysis is further indicated by the fact that the samples of zirconate, after five washings to remove all bromide, still imparted a yellow color (potassium amide) to the supernatant liquid ammonia on standing at 0°.

TABLE IV

Temp., °C.	Zr	K	N	Br	Number of washings
0	46.92	25.88	23.68	None	20
0	42.53	27.48	26.52	None	12
0	40.52	26.22	26.62	None	5
0	38.05	27.38	26.77	None	5
−33	38.81	32.92	23.18	Trace	3
−33	40.21	33.16	23.28	Trace	3
a	39.40	33.78	24.70		

a Calculated for Zr(NK)$_2$·2NH$_3$.

The composition of all of the products obtained from the treatment of ammonobasic zirconium bromide with either potassium or potassium amide is consistent with the view that they consist of varying mixtures of zirconium imide (not amide) and potassium ammonozirconate.

IV. Potassium Ammonozirconate and Ammonium Bromide

A well-washed sample of potassium ammonozirconate was treated with an excess of ammonium bromide in an attempt to bring about a complete

(11) Similar observations have been made for potassium ammono-titanate [E. C. Franklin and T. B. Hine, THIS JOURNAL, **34**, 1497 (1912)] and potassium ammonosilicate (F. W. Bergstrom, private communication).

plete ammonolysis of the zirconate and form zirconium imide. On standing for a week (20°), the white insoluble powder gradually became crystalline and the latter proved to be ammonobasic zirconium bromide.

Anal. Calcd. for 3Zr(NH)$_2$·7NH$_4$Br·5NH$_3$: Zr, 24.12; Br, 49.31; N, 22.21. Found: Zr, 24.68; Br, 49.47; N, 22.46.

Summary

1. The following ammonolytic equilibrium exists in liquid ammonia:

$$3ZrBr_4 \cdot xNH_3(sol.) + yNH_3 \rightleftarrows$$
$$3Zr(NH)_2 \cdot 7NH_4Br \cdot zNH_3(insol.) + 5NH_4Br$$
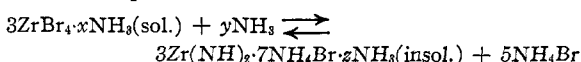
Conditions which bring the point of equilibrium to the left are (a) low temperature, (b) concentrated solutions, and (c) high concentration of ammonium bromide. At 0° or above, without addition of ammonium bromide, the point of equilibrium lies almost quantitatively to the right.

2. It appears that a second ammonolytic equilibrium exists

$$3Zr(NH)_2 \cdot 7NH_4Br \cdot zNH_3 + mNH_3 \rightleftarrows$$
$$3Zr(NH)_2 \cdot nNH_3 + 7NH_4Br$$
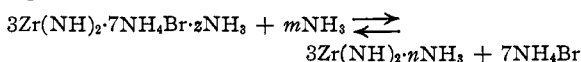
The reaction toward the right is brought about by reagents which remove the ammonium bromide (potassium and potassium amide). The resultant zirconium imide is always contaminated with some potassium ammonozirconate.

3. Addition to ammonobasic zirconium bromide of potassium amide in excess of the amount equivalent to that of the bromine, results in the formation of potassium ammonozirconate

$$Zr(NH)_2 \cdot nNH_3 + 2KNH_2 \rightleftarrows Zr(NK)_2 \cdot sNH_3 + tNH_3$$
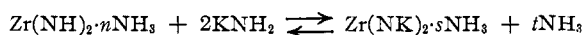
This salt is extensively ammonolyzed at 0°.

4. Potassium ammonozirconate reacts with ammonium bromide to form ammonobasic zirconium bromide.