

In the lead chloride systems, the problem is complicated somewhat by the fact that the saturating phase at higher concentrations is, in general, a double salt. The following compounds have been isolated, of which those marked with an asterisk are new: $\text{LiCl} \cdot 2\text{PbCl}_2^*$; $\text{NH}_4\text{Cl} \cdot 2\text{PbCl}_2$; $\text{NaCl} \cdot 2\text{PbCl}_2^*$; $\text{KCl} \cdot 2\text{PbCl}_2$; $\text{KCl} \cdot \text{PbCl}_2^*$; $\text{MgCl}_2 \cdot \text{PbCl}_2 \cdot 6\text{H}_2\text{O}^*$; $\text{CaCl}_2 \cdot \text{PbCl}_2$; $6\text{H}_2\text{O}^*$; $\text{SrCl}_2 \cdot \text{PbCl}_2^*$; $\text{BaCl}_2 \cdot \text{PbCl}_2^*$; $\text{HgCl}_2 \cdot \text{PbCl}_2^*$.

It has been found that the relative positions of the curves at high concentrations are only slightly varied by the appearance of such complexes, the general order of solubilities being still as predicted by the rule of electrode potentials.

In a later article, the data obtained will be analyzed by Professor V. K. La Mer in greater detail from the standpoint of the Debye and Hückel theory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE ACTION OF AMMONIA AND OF A SOLUTION OF POTASSIUM AMIDE IN LIQUID AMMONIA ON CERTAIN HALIDES OF MOLYBDENUM AND TUNGSTEN

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Introduction

In the investigation described below, which is a continuation of previous work upon the formation of amides, imides, nitrides and ammono salts,¹ an account is given of the preparation and properties of potassium ammonomolybdate and ammonotungstate, together with a few observations concerning the behavior of the halides of molybdenum and tungsten toward gaseous and liquid ammonia.

Preparation of Materials

Anhydrous halides of molybdenum and tungsten were prepared as described in a previous article.² Tungsten dibromide and dichloride were prepared by reduction of heated tungsten hexachloride and pentabromide, respectively, in a stream of hydrogen. Molybdenum dibromide was prepared by passing diluted bromine vapor over strongly heated molybdenum powder. Molybdenum pentachloride and tungsten pentabromide and hexachloride, which were readily attacked by moist air, were preserved in small sealed containers containing enough material for an individual experiment.²

Action of Gaseous and Liquid Ammonia on the Halides of Molybdenum and Tungsten

Molybdenum dibromide, tungsten dibromide and tungsten dichloride were converted by the action of liquid ammonia into very slightly soluble

¹ (a) Bergstrom, *THIS JOURNAL*, **46**, 1545; (b) 2631 (1924).

² Ref. 1 a, p. 1547.

gray to black ammonobasic halides. Molybdenum tribromide is acted upon by liquid ammonia with the formation of a deep red solution and a precipitate consisting of ammonobasic bromides of molybdenum. Tungsten pentabromide and molybdenum pentachloride are completely soluble in a small volume of liquid ammonia, in distinction to molybdenum tribromide. Dilution of these deep red or brownish-red solutions caused the separation of reddish-brown and black amorphous precipitates, respectively, which analyses showed to be of indefinite composition. These latter two ammonobasic precipitates were insoluble in ammonia, but soluble in a solution of the corresponding ammonium salt, the latter behaving as an acid,³ or soluble when the solution from which they had been precipitated was concentrated. Tungsten hexachloride dissolves completely in a very small volume of ammonia, insoluble ammonobasic precipitates of indefinite composition being formed on dilution. Uhrlaub⁴ obtained compounds or mixtures of compounds containing only molybdenum, nitrogen and hydrogen by heating molybdenum pentachloride in a stream of ammonia gas. In the present work, it was found that molybdenum pentachloride absorbs very nearly eight molecules of ammonia, when the reaction is so controlled as to prevent the attainment of too high a temperature with resulting loss of ammonium chloride by volatilization. The black product formed by this reaction is undoubtedly not an addition compound, but a mixture of ammonium chloride with molybdenum derivatives of unknown composition. Both of the following equations express the fact that molybdenum pentachloride absorbs eight molecules of ammonia: $\text{MoCl}_5 + 8\text{NH}_3 = \text{Mo}(\text{NH})_2\text{NH}_2 + 5\text{NH}_4\text{Cl}$; $\text{MoCl}_5 + 8\text{NH}_3 = \text{Mo}(\text{NH}_2)_4\text{Cl} + 4\text{NH}_4\text{Cl}$. A sufficiently high temperature would volatilize the ammonium chloride and convert either of the molybdenum compounds to the nitrimides obtained by Uhrlaub.

In an absorption tube 0.687 g. and 0.704 g. of molybdenum pentachloride absorbed 0.333 g. and 0.344 g. of ammonia, respectively.

The Nitridation of Molybdenum and Tungsten during the Reaction of Certain of their Halides with Ammonia and Potassium Amide

The originally pale yellow liquid ammonia solution of molybdenum dibromide becomes reddish-brown after a few days, the color resembling that of solutions of molybdenum tribromide and pentachloride, suggesting that the divalent molybdenum had become nitridized.⁵ The valence of the molybdenum both in the solution and in the ammonobasic precipitate formed by the action of liquid ammonia on molybdenum tribromide was found to lie a little above four. Reactions of this nature in aqueous

³ Franklin and Cady, *THIS JOURNAL*, **26**, 512 (1904).

⁴ Uhrlaub, *Pogg. Ann.*, **101**, 605 (1857).

⁵ Nitridation in ammonia is analogous to oxidation in water.

solution are not altogether unfamiliar. Acid solutions of chromous salts on standing out of contact with the air slowly give off hydrogen with the formation of chromic salts.⁶ The oxidation of chromous salts on the one hand and the nitridation of molybdenum di- and tribromides on the other hand take place at the expense of the solvent.

During the precipitation of potassium ammonomolybdate by the addition of a solution of molybdenum tribromide to one of potassium amide it was noticed that a strongly colored, green solution was formed. This solution was unstable, and became decolorized, especially rapidly it seemed, in the presence of a small quantity of platinum black or other catalyst. Less strongly-colored green solutions were formed by the action of an excess of potassium amide upon molybdenum dibromide, tungsten di- and pentabromide, and uranium⁷ tri- and tetrabromide.⁷

It was found that the color was due to the presence in solution of metallic potassium. The characteristic blue color of the potassium solution⁸ was modified to green by admixture with the yellow solution of potassium amide. The instability of the solution is due to the action of potassium upon the solvent, in the presence of platinum black or other substances acting as catalysts, to form potassium amide and hydrogen.

In the legs of a three-legged reaction tube were placed a few tenths of a gram of molybdenum dibromide or tungsten pentabromide, an excess of potassium amide and a few cubic centimeters of mercury, respectively. The reaction tube, into which ammonia had been distilled, was so manipulated that the solution of potassium amide and the solution or suspension of tungsten or molybdenum bromide flowed together at the junction of the legs of the tube. The products of the reaction were brought at once into contact with the mercury contained in the third leg of the reaction tube. After a few moments of shaking, the mercury was separated from the precipitate of the ammono salt, washed with ammonia and treated with a measured excess of standard acid. In both instances the mercury was found to contain a few milligrams of potassium.

It is probable that the potassium is formed by the reduction of potassium amide, molybdenum or tungsten being nitridized in equivalent amount, in the sense of the equation: $\text{Mo}^N = \text{Mo}^{N+1} + e^-$, where N and $N + 1$ represent different states of nitridation of molybdenum (or tungsten) and e^- represents the solvated negative electron which, when in equilibrium with potassium ions, constitutes a solution of potassium.⁸

Hydrogen and nitrogen are given off during the precipitation of potassium ammonomolybdate and tungstite, the former gas, at least in part, owing its origin to the action of the solvent upon potassium formed in accordance with the above equation. In three preparations of potassium ammonomolybdate there were obtained 31.1, 49.6, 52.2 cc. of hydrogen and

⁶ Abegg, "Handbuch der Anorganischen Chemie," S. Herzel, Leipzig, 1921, vol. 4, pt. 1, 2d half, p. 51.

⁷ M. W. Garrett, *Thesis*, Stanford University, 1920.

⁸ Kraus, *THIS JOURNAL*, 43, 749 (1921).

3.8, 0.8 and 11.5 cc. of nitrogen (N.T.P.), respectively, calculated, for comparison, on the basis of 1 g. of molybdenum taking part in the reaction. It is evident that the molybdenum is partially nitrized during the formation of the ammonio salt, a result not surprising in view of the fact that the molybdenum in potassium ammoniomolybdate is pentavalent.

The gas given off during the reaction between potassium amide and the halides of tungsten and molybdenum was determined as follows (Fig. 1).

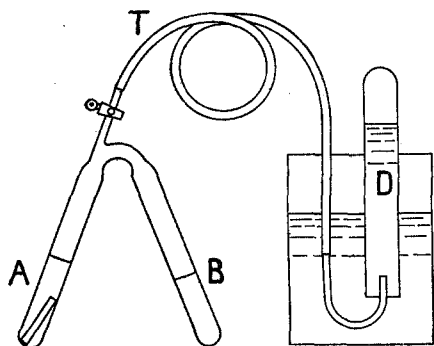


Fig. 1.—Collection of gases evolved during a reaction.

A small rubber tube T was attached to the stopcock of a two-legged reaction tube, AB. After conversion of the potassium in one leg to potassium amide, the stopcock was partially opened and sufficient ammonia allowed to escape to remove all hydrogen from the reaction tube and to sweep gases insoluble in water from T. The ammonia at this point should dissolve completely in water. The stopcock was closed and the reacting substances in the tube were mixed. In a few moments the stopcock was again opened and gases formed during the reaction were expelled into a collection tube D, and subsequently analyzed.^{1a}

Potassium Ammoniomolybdate, $\text{Mo}(\text{NK})_2\text{NH}_2$.—A salt approximating the above formula in composition may be prepared by the addition of a solution of molybdenum tribromide to an excess of a solution of potassium amide. The flocculent, reddish-brown precipitate at first produced is rather indefinite in composition, for the valence of the molybdenum lies between four and five. After the solution has stood for a few weeks in contact with an excess of potassium amide solution, the valence of the molybdenum increases to five, and the composition of the precipitate changes until in fair accordance with the formula given above.

Potassium ammoniomolybdate reacts vigorously with water, a portion of the products of the reaction being soluble in this liquid with the formation of a brown solution. Dil. sulfuric acid readily dissolves the preparations with the formation of strongly colored solutions indicative of the presence of molybdenum in one of the lower states of oxidation.

The preparation of potassium ammoniomolybdate was best carried out in a two-legged reaction tube.⁹ Molybdenum tribromide solution was slowly poured into an excess of a solution of potassium amide, contained in the other leg of the reaction tube, the precipitated ammonio salt being washed after standing for at least a week in contact with the excess of po-

⁹ (a) Franklin, *THIS JOURNAL*, 27, 832 (1905). (b) Fitzgerald, *ibid.*, 29, 1694 (1907). (c) Franklin, *ibid.*, 35, 1460 (1913); (d) *J. Phys. Chem.*, 15, 515 (1911); (e) 16, 694 (1912).

tassium amide. Specimens were hydrolyzed by water or water vapor, dissolved in dil. sulfuric acid, the platinum black used as a catalyst filtered off, and analyses made of aliquot portions of the filtrate. Molybdenum was precipitated as sulfide from a solution oxidized with hydrogen peroxide, and weighed as trioxide. Potassium was weighed as sulfate, after removal of molybdenum. Nitrogen was determined volumetrically as ammonia, and bromine was weighed as silver bromide.

TABLE I
ANALYTICAL DATA

No.	Temp., °C.	Wt. of subs. dried in a vacuum G.	Gas given off ^a during solution				Gas dur- ing heating ^b		Wt. of MoO ₃ in (fraction) of subs. G.	Wt. of K ₂ SO ₄ in (fraction) of subs. G.	Wt. of N in (fraction) of subs. G.
			H ₂	N ₂	H ₂	N ₂	Total				
1 ^e	20	0.3058									
	122	.2907	0.0	2.5	4.1	0.5	(2/5)	0.0798	(2/5)	0.0925	(1/5)
2	25	.4090									
	120	.3900	2.8	1.0	Total	7.6	(2/5)	.1095	(2/5)	.1229	(1/5)
3 ^e	20	.2965									
	130	.2792	2.8	1.2	6.5	0.1	(1/4)	.0495	(1/4)	.0555	(1/4)
4 ^{e, d, f}	— 40	.1237									
	24	.1190					(1/4)	.0196	(1/4)	.0235	(1/4)

SUMMARY OF ANALYSES

Substance dried in a vacuum at room temperature

	Calcd. for Mo(NK) ₂ NH ₂ , %	Found			
		1	2	3	4
Mo	44.0	43.5	44.6	44.5	44.0
N	19.2	20.8	19.8	19.8	19.8
K	35.8	34.0	33.7	33.6	35.5

^a Water was admitted to the evacuated specimen tube and allowed to hydrolyze the specimen. After admission of dil. sulfuric acid to dissolve the precipitate the specimen tube was attached to a Töpler pump protected by a phosphorus pentoxide drying tube, a vacuum was produced and gases were then washed from the container by boiling the solution contained therein under reduced pressure. The gases were collected over mercury and analyzed (Ref. 1a, p. 1546). This method has been in use for some time in Dr. Franklin's laboratory, but does not seem to have been previously described.

^b See Ref. 1a, p. 1545.

^c (1/4) of substance required 3.00 cc. of 0.0463 *N* potassium permanganate solution to oxidize the molybdenum to the hexavalent condition. Calcd. valence, Mo = 4.98.

^d (1/4) of a fifth specimen of potassium molybdite required 5.62 cc. of 0.0463 *N* potassium permanganate solution to oxidize the molybdenum to the hexavalent condition. One half contained 0.0754 g. of molybdenum trioxide. Calcd. valence, Mo = 5.02.

^e Bromine, a very small amount.

^f Substance stood for four months in contact with potassium amide solution.

Potassium ammonomolybdite loses about half a molecule of ammonia when heated in a vacuum at 120–130°.

Sodium Ammonomolybdite, Mo(NNa)₂NH₂.—A dark, brick-red precipitate is formed when a solution of molybdenum pentachloride is added to an excess of sodium amide. Analysis of one preparation showed it to be an impure specimen of the sodium analog of potassium ammonomolybdite.

Anal. Subs. (20°), 0.2846: (1/5) 0.0437 MoO₃, 0.0386 Na₂SO₄ and (1/5) 0.0016 AgCl. Calcd. for Mo(NNa)₂NH₂: Mo, 51.6; Na, 24.7. Found: Mo, 51.0; Na, 22.0; Cl, 0.7.

Potassium Ammonotungstite, W(NK)₂NH₂ (?).—A flocculent, reddish-brown precipitate of approximately the composition indicated above was obtained by pouring a solution of tungsten pentabromide, containing ammonium bromide, into a solution of potassium amide. In order to remove ammonobasic salts, which are always present in the freshly formed precipitate, the latter was allowed to stand for at least a week in contact with a solution of potassium amide. One would expect the product to contain pentavalent tungsten, being the analog of the potassium ammonomolybdate previously prepared. The valence of the tungsten has not been determined.

Potassium ammonotungstite is pyrophoric and blackens in contact with the air. It is readily hydrolyzed by water vapor, while the reaction with water itself is violent. The products of the hydrolysis are, for the most part, soluble in water, forming a yellowish-brown solution. In analysis this aqueous solution, together with a small quantity of precipitate remaining undissolved, was drawn into an Erlenmeyer flask.¹⁰ To prevent loss of ammonia, the end of the delivery tube dipped under dil. nitric acid in the flask. Most of the tungsten was at once precipitated as tungstic acid, which was removed by filtration. A small amount of tungstic acid was always obtained by evaporation to dryness with nitric acid of the portion of the filtrate used for the potassium determination. Potassium was weighed as sulfate, nitrogen was determined volumetrically as ammonia.

No.	Temp., °C.	ANALYTICAL DATA					
		Wt. of subs. dried in a vacuum G.	WO ₃ (1/1) G.	WO ₃ in (fraction) of filt. G.	K ₂ SO ₄ in (fraction) of filt. G.	N in (fraction) of filt. G.	AgBr in (fraction) of filt. G.
1 ^a	20	0.1771	0.1282	(2/5) 0.0018	(2/5) 0.0402	(1/5) 0.00468	
2 ^b	40	.4123					
	20	.3943					
3 ^c	115	.3827	.2709	(2/5) .0162	(2/5) .0891	(2/5) .01897	(1/5) 0.0021
	19	.1884	.1360	(2/5) .0023	(2/5) .0447	(2/5) .00870	
		Calcd. for W(NK) ₂ NH ₂ , %		Found			
		W	60.1	59.4	57.8	59.6	
		N	13.7	13.2	14.4	11.5 ^d	
		K	25.5	25.5	25.4	26.5	
		Br			1.1		

^a The precipitate stood for five months in contact with an excess of potassium amide.

^b 1.8 cc. of H₂ and 0.6 cc. of N₂ were given off when the substance was heated at 115°.

^c The reaction mixture stood for eleven months.

^d Perhaps a little nitrogen formed during hydrolysis.

¹⁰ Ref. 9 d, p. 516.

The Action of Potassium Amide on Tungsten Dibromide

Potassium amide reacts with tungsten dibromide to give a potassium ammonotungstite resembling in appearance and properties and approaching in composition the tungstites prepared from tungsten pentabromide. The valence of the tungsten in the ammono salt has not been determined.

Preparation 1: Total subs., (25°) 0.3988; (110°) 0.3922: 0.2356 g. of the heated subs. gave 0.1830 WO_3 and 0.1217 K_2SO_4 ; 0.1429 g. gave 0.0075 AgBr.

Preparation 2: The tungstite precipitate remained in contact with an excess of potassium amide for four months. The nitrogen content was low, in spite of an initial slow hydrolysis under the action of water vapor.

Subs., (20°) 0.4230; (1/1) 0.3185 WO_3 ; (1/5) 0.0007 AgBr. (2/5) 0.0009 WO_3 and 0.1010 K_2SO_4 . (2/5) 0.01301 N.

Calcd. for $\text{W}(\text{NHK})_2\text{NH}_3$: W, 59.5; N, 13.6; K, 25.3. Found: W, 60.6, 60.2; N, 7.7; K, 22.8; 26.8; Br(No. 2), 0.4. No. 1 contained ammonobasic tungsten bromides in larger quantity than No. 2.

Attempts to Prepare Nitrides of Tungsten and Molybdenum

Attempts to prepare these compounds by pouring a solution of potassium amide into an excess of solutions of molybdenum tribromide and tungsten pentabromide led to the production of ammonobasic mixtures.

In conclusion, the author wishes to thank Dr. Franklin, at whose suggestion and under whose direction this work was done.

Summary

1. The action of liquid ammonia on certain halides of molybdenum and tungsten has been briefly described.

2. Potassium ammonomolybdite, $\text{Mo}(\text{NK})_2\text{NH}_2$, a derivative of pentavalent molybdenum, and a potassium ammonotungstite, perhaps of analogous composition, have been prepared.

3. In the precipitation of potassium ammonomolybdite and tungstite free potassium in small amounts was formed by a reduction of potassium amide, molybdenum or tungsten presumably being nitridized to an equivalent extent.

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NOTE

The Resistance of Platinum Films in the Presence of Hydrogen.—The mechanism of adsorption of a gas by a metal is considered in some circles to involve the momentary sharing of electron pairs by the gas molecule and the metallic surface. If we assume that the valence electrons are identical with the free electrons that presumably carry the current in metallic conduction of electricity, then an adsorbed gas should affect certain electrical properties of the metal. To test this idea, the author prepared exceedingly thin films of platinum on Pyrex glass by thermal evaporation of the platinum and condensation on the glass in a vacuum.