prepared in the absence of oxygen have been measured over the ranges 25–35 and 35–45° respectively.

2.   The transition temperature, $CdBr_2 \cdot 4H_2O(s)$–$CdBr_2(s)$–saturated solution, was found to be 35.63° by the cell measurements and 35.82 by the usual thermal method, and the hydration of the stable solid phases has been discussed.

3.   The standard electromotive force and free energy of formation of cadmium bromide have been found to check those through mercurous bromide and not those through lead bromide.   The heats of formation have been compared with the calorimetric values.

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SOME REACTIONS OF COMPLEX CHLORIDES OF TRIVALENT AND PENTAVALENT TUNGSTEN

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When tripotassium ditungsti-chloride, $K_3W_2Cl_9$, prepared by the method of Olsson[1] was treated with a solution of potassium hydroxide at 5°, a vigorous evolution of hydrogen occurred as simultaneously a precipitate of an hydroxide or hydrous oxide formed.   These same phenomena occurred also when $K_3W_2Cl_9$ was heated with water.   An oxide of trivalent tungsten is not stable even at low temperatures when prepared in aqueous solutions. It is therefore to be expected that, if the mechanism of complex cyanide formation in the case of tungsten is similar to that of molybdenum,[2] with the intermediate formation of an hydroxide, a complex cyanide of tetra- valent tungsten would form when $K_3W_2Cl_9$ is treated with potassium cya- nide solution in an atmosphere of nitrogen.   Such has proved to be the result even when the reaction is carried out at low temperatures.   Hydro- gen is not evolved in this reaction in which oxidation of the tungsten occurs but if the contents of the solution after reaction are made acid, the Schiff test for aldehyde is obtained.   Hydrogen cyanide and ammonia are present in the solution, resulting from the hydrolysis of the potassium cyanide, and it is known that hydrogen cyanide is reduced in neutral solutions to form- aldehyde and ammonia.   These compounds are able to form certain condensation products, which may be the reason for not obtaining the test for aldehyde until the solution was made acid.

It seemed of interest to determine to what extent the tungsten in $K_3W_2Cl_9$ would be oxidized in an atmosphere of nitrogen by water alone, and by

[1] Olsson, Z. anorg. allgem. Chem., 88, 49 (1914).
[2] Young, THIS JOURNAL, 54, 1402 (1932).

alkali of different concentrations. It was planned to determine this oxidation by measuring the hydrogen evolved in one set of experiments and by titration of the tungsten reaction product with standard potassium permanganate in another set of experiments.

By means of an apparatus consisting of a reaction vessel of 100-cc. capacity connected with a gas buret adapted to collect the hydrogen evolved over mercury, a study was made of the extent of the oxidation of the tungsten when potassium tungsti-chloride reacted in the presence of nitrogen with water, 6 N potassium hydroxide solution and a 50% solution of potassium hydroxide, respectively. To hasten the reaction the solution was occasionally heated for a short time to the boiling point, and the reaction was allowed to continue until there was no more evidence of the evolution of hydrogen. All volumes were reduced to standard conditions of temperature and pressure on a dry gas basis and the increase in each case measured the hydrogen evolved.

In Table I are given the results of several experiments. Complete solution occurred only when a 50% solution of potassium hydroxide was used, a black precipitate was formed in the experiments with water and a dark colloidal mass with 6 N potassium hydroxide.

TABLE I

$K_3W_2Cl_9$, g.	$K_3W_2Br_9$, g.	Solution used, cc.	H_2 evolved at S. T. P., cc.	H_2 equivalent to oxidation of W from valence 3 to 4, cc.	W oxidized from valence 3 to 4, %
2.2126		35 H_2O	35.2	61.1	57.6
1.9066		35 H_2O	31.8	53.1	59.8
1.8290		35 6 N KOH	42.3	50.9	83.0
1.7511		35 6 N KOH	39.1	48.7	80.3
1.3369		35 50% KOH	35.9	37.2	96.5
1.3247		35 50% KOH	36.0	36.8	97.8
	1.6503	35 50% KOH	29.7	30.7	96.7

The insoluble product formed in the reaction of $K_3W_2Cl_9$ with water was obtained in an apparatus designed for carrying out the reaction and the subsequent filtration and washing with water, alcohol and ether, all in an atmosphere of nitrogen. A determination of total chlorine and hydrochloric acid in the water showed that hydrolysis had been complete. A weighed sample of the vacuum-dried product was ignited in a stream of oxygen which passed over hot copper oxide and then into a weighed Marchand tube with calcium chloride to collect the water. The hot copper oxide served to oxidize any hydrogen that might be formed by the reaction of the lower valence oxide with the water held as hydrous water. From the final weight of the tungstic oxide, WO_3, 0.6084 g., the weight of the water, 0.0858 g., and the original sample, 0.6441 g., there was calculated the composition of the anhydrous product. Other determinations checked these results.

Anal. Calcd. for W_5O_9: O, 13.53; W, 86.48. Found: O, 13.55, 13.73; W, 86.42, 86.28.

The above composition corresponds to three molecules of WO_2 and one of W_2O_3: that is, three atoms of tetravalent tungsten, and two of trivalent tungsten. This is in accord with the fact that 60% of the tungsten in $K_3W_2Cl_9$ was oxidized to valence four

by heating with water, as measured by the hydrogen evolved.   The hydrolysis of K_3W_2-Cl_9 and subsequent oxidation of the tungsten by the water is expressed by the equation

$$5W_2Cl_9^= + 18H_2O \longrightarrow 45Cl^- + 30H^+ + 2W_5O_9 + 3H_2$$
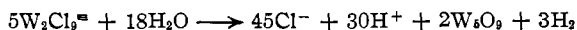
On dilution and subsequent acidification of the 50% potassium hydroxide solution there was obtained a brown precipitate which was washed with water, alcohol and ether and pumped dry.   It was ignited as described previously.   From 0.3654 g. of the hydrous oxide there was obtained 0.0377 g. of water and 0.3505 g. of the tungstic acid.   The initial anhydrous product corresponds to the following composition, which was checked by other determinations.

Anal.   Calcd. for WO_2: W, 85.19; O, 14.81.   Found: W, 84.82; O, 15.19.

From the above facts it is apparent that tungsten dioxide does not react with solutions of potassium hydroxide to evolve hydrogen, a result which is not in agreement with a statement by Riche,[3] which has been included in many reference books on chemistry.

To test more thoroughly the question of the ability of the tungsten to be oxidized beyond the tetravalent stage by a potassium hydroxide solution, experiments were carried out in a flask fitted with side tubes through which nitrogen was continuously passed, while the solution was boiled.   At the end of a two-hour period of heating, the solution was cooled, acidified with hydrochloric acid, and the precipitated tungsten dioxide was titrated with standard potassium permanganate, the whole process being carried out in an atmosphere of nitrogen.   The results are shown in Table II.   The results accord very well with those obtained by measuring the oxidation of the tungsten by the amount of hydrogen evolved.

TABLE II

$K_3W_2Cl_9$, g.	Solution used, cc.	Cc. of 0.1265 N KMnO$_4$ calcd. to oxidize the W from valence 3 to 6	4 to 6	0.1265 N KMnO$_4$ used, cc.	W oxidized from valence 3 to 4 by solution, %	W oxidized to valence 5 by solution, %
0.3250	20 50% KOH	19.15	12.77	12.83	99.0	0.0
.2938	20 50% KOH	17.31	11.54	11.67	97.7	.0
.3520	20 6 N KOH	20.74	13.83	15.12	81.3	.0
.3218	20 6 N KOH	18.97	12.65	13.96	79.2	.0
.3076	20 H$_2$O	18.13	12.09	14.34	62.7	.0
.2831	20 H$_2$O	16.68	11.12	13.30	60.7	.0
.3075	20 50% KOH presence of air	18.12	12.08	10.10	100.0	32.7
.2760	20 50% KOH presence of air	16.26	10.84	7.00	100.0	70.8

Preparation and Properties of Tripotassium Ditungsti-Bromide, $K_3W_2Br_9$.—The tripotassium ditungsti-bromide used in one of the experiments was prepared by the reduction with tin of tungstic acid dissolved in concentrated hydrobromic acid, by a procedure similar to that by which Olsson[4] made the chloride.   Under the microscope, the compound appeared as brown transparent hexagonal plates which analysis showed to be practically pure $K_3W_2Br_9$.   The tungsten was determined as WO_3, the potassium as potassium sulfate and the bromine as silver bromide.

Anal.   Calcd. for $K_3W_2Br_9$: K, 9.74; W, 30.55; Br, 59.71.   Found: K, 9.79, 9.76; W, 30.75, 30.86; Br, 59.88, 59.62.

[3] Riche, *Ann. chim. phys.*, **50**, 30 (1857).

[4] Olsson, *Z. anorg. allgem. Chem.*, **88**, 49 (1914).

In an atmosphere of carbon dioxide, a sample weighing 0.3607 g. required 14 cc. of 0.1265 N KMnO$_4$ to oxidize the tungsten to the hexavalent condition, corresponding to 1.771 milliequivalents of the oxidizing agent, the theoretical being 1.796 milliequivalents. Subsequent determinations checked these results.

Tripotassium ditungsti-bromide gives in the absence of oxygen a brown solution when concentrated, which on dilution becomes orange, then pink. It reacts with hot water and alkalies in the presence of air with the formation of hydrogen as simultaneously a black product is formed, which finally changes to brown tungsten dioxide. With Ag$^+$, a brown solid was obtained, and with Cd^{++}, a dark gray solid. Cu^{++} was reduced to Cu$^+$ and Hg^{++} to Hg$_2$$^{++}$ by the complex tungsti-bromide.

Reaction of (NH$_4$)$_2$WOCl$_5$ with Potassium Cyanide.—Complex salts of pentavalent tungsten react with potassium cyanide solution to form a complex cyanide of tetravalent tungsten, K$_4$W(CN)$_8$. Pentavalent salts of molybdenum also give a tetravalent molybdenum cyanide, K$_4$Mo(CN)$_8$, with potassium cyanide. Bucknall and Wardlaw[5] in giving a mechanism for the latter reaction propose as one of the steps the evolution of oxygen. To test this hypothesis for tungsten, diammonium tungsten oxypentachloride was prepared according to the method of Collenberg[6] and in the apparatus mentioned above 1.1470 g. of the pentavalent tungsten salt was allowed to react with a solution of 2 g. of potassium cyanide in 10 cc. of water. On the addition of the cyanide solution, a blue color developed at the surface of the solid oxychloride. The salt then on heating dissolved in the cyanide solution with a yellow color. No oxygen was evolved.

It seems more logical to explain the reaction of the pentavalent tungsten salt to give the tetravalent cyanide as due to the fact that the initial action of the potassium cyanide due to hydrolysis is to form the so-called blue oxide, a compound of tungsten dioxide and tungsten trioxide. Subsequently the potassium cyanide would dissolve the dioxide and trioxide to form, with the dioxide, K$_4$W(CN)$_8$, and with the trioxide, a tungstate, both of which reactions have been found to take place.[7] To test the above hypothesis, 2.00 g. of the ammonium tungsten oxypentachloride was treated with 5 g. of potassium cyanide in 20 cc. of water and the solution was heated to near the boiling point for five minutes and allowed to cool slowly to room temperature; 0.03 g. of a brown solid, which proved to be tungsten dioxide, remained undissolved. The orange-yellow solution was acidified with hydrochloric acid; a precipitate formed which was separated from the solution by decantation. It was washed with dilute hydrochloric acid and the washings were added to the yellow solution. By the addition of cadmium chloride to this solution there was precipitated the yellow dicadmium tungsten octacyanide octahydrate, Cd$_2$W(CN)$_8$·8H$_2$O, which after drying *in vacuo* weighed 1.2 g. The weight of the cadmium salt calculated to be formed, on the assumption that the pentavalent salt reacts to give both a tungstate and the complex octacyanide, is 1.7 g.

The precipitate was completely dissolved in dilute ammonium hydroxide, thus showing the absence of the dioxide of tungsten, and after the solution had been made acid with hydrochloric acid, benzidine hydrochloride was added to completely precipitate a benzidine hydrochloride tungstic acid complex. This complex was filtered, washed, dried, and ignited; 0.50 g. of tungstic oxide was obtained, while according to the hypothesis outlined above, 0.55 g. would have been formed. The recovery of 70% of the theoretical quantity of cadmium tungsten octacyanide, which was not greater on account of incomplete reaction of the tungsten dioxide with potassium cyanide, and on account of the appreciable solubility of the cadmium salt, and the recovery of 90% of

⁵ Bucknall and Wardlaw, *J. Chem. Soc.*, 2988 (1927).

⁶ Collenberg, *Z. anorg. allgem. Chem.*, **102**, 247 (1918).

⁷ In a recent paper, Jakob and Turkiewicz [*Roczniki Chem.*, 11, 569 (1931)] have proposed a similar mechanism for the reaction of (NH$_4$)$_2$MoCl$_5$ with KCN.

the theoretical quantity of tungstic oxide, indicate that the reaction of a pentavalent salt of tungsten with potassium cyanide follows the mechanism as outlined above, as expressed by the following equations

$$2WOCl_5^- + 6OH^- \longrightarrow W_2O_5 + 10Cl^- + 3H_2O$$
$$W_2O_5 + H_2O + 8CN^- \longrightarrow W(CN)_8^{--} + WO_4^- + 2OH^-$$
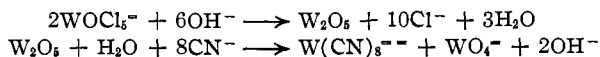
Summary

The behavior of the compound $K_3W_2Cl_9$ with water in an atmosphere of nitrogen, and with solutions of potassium hydroxide of various concentrations was studied; the extent of oxidation of the tungsten was obtained in one series of experiments by measurement of the volume of hydrogen evolved and in another series by titration of the resulting tungsten oxide with standard potassium permanganate solution. It was found that with water alone 60% of the tungsten was oxidized to valence four, and there was recovered an oxide of tungsten of composition $3WO_2 \cdot W_2O_3$ or W_5O_9. With a solution of 6 N potassium hydroxide, 80% of the tungsten was oxidized to valence four while with a 50% solution of potassium hydroxide, oxidation of the tungsten proceeded completely to valence four, and there was recovered the oxide, WO_2. Only in the presence of air was the tungsten oxidized beyond this valence.

Potassium cyanide solution reacts with salts of trivalent tungsten and also with those of pentavalent tungsten to produce $K_4W(CN)_8$. In the former case, the oxidation of the tungsten takes place even in a nitrogen atmosphere and at room temperature because of the intermediate formation of an unstable oxide due to the alkaline character of the potassium cyanide solution. When $(NH_4)_2WOCl_5$ was treated with potassium cyanide solution, a blue oxide of tungsten was first formed, which is produced when there is present tetravalent and hexavalent tungsten. Further action of the potassium cyanide caused complete solution to take place with the formation of $K_4W(CN)_8$ and K_2WO_4.

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