The organic and other impurities, aside from chlorine, which are usually present in crude bromine, do not very seriously influence the results of the density determinations, as may be seen from the following analyses of material of this sort.

	1	2	3	4	5	6
Per cent. of Cl by density.....	4.137	0.070	5.485	0.000	4.294	6.06
Per cent. of Cl by analysis	4.165	0.051	5.580	0.012	4.400	6.22

It is possible, therefore, to determine from the density of a sample of bromine the amount of chlorine it contains with sufficient accuracy for almost any purpose and in much less time than by any chemical method.

The contraction that occurs on mixing (liquid) chlorine with bromine can be readily calculated from Eq. (2). The validity of this formula has only been tested to 11 per cent. of chlorine, but if we extrapolate to 30 per cent. (corresponding in composition approximately to BrCl) it gives for the corresponding density 2.4175, whereas, if no contraction occurred the density would be 2.2713. The contraction amounts, accordingly, to about two per cent. of the total volume, a result that appreciably increases the probability that actual chemical combination does take place between these elements to a limited extent.

In conclusion, we present the following comparison of the densities of bromine at several temperatures as found by Thorpe and by Pierre with our own results.

Temp. C	Pierre (1847)	Thorpe (1880)	A. and C. (1906)
0°	3.188	3.187	
20°	3.121(45)	3.118(43)	3.11932
25°	3.104(72)	3.101(04)	3.10227
30°			3.08479

St. Louis, Dec. 24, 1906.

COMBINATIONS OF THE SESQUIOXIDES WITH THE ACID MOLYBDATES

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Received February 23, 1906.

Since the pioneer work of Marignac, Gibbs and others on the complex inorganic acids and their derivatives, a large number of these compounds have been prepared and studied. By far the greater number are salts whose acid portion is composed of molybdic or tungstic trioxide in combination with acid oxides of the type R_2O_5 or RO_2 and with a base of the type RO or R_2O . The tendency of molybdic and tungstic oxides to form salts of poly acids is strong, we have for example the salts $\text{Na}_2\text{O}_4\text{MoO}_3$, $3\text{K}_2\text{O} \cdot 7\text{MoO}_3$, $5\text{Na}_2\text{O} \cdot 12\text{WO}_3$, $\text{Na}_2\text{O} \cdot 4\text{WO}_3$, etc., which contain a combination of several molecules of the molybdic or tungstic oxides as the acid. If, in these salts, part of the RO_3 oxide is replaced by an oxide of

the type RO_2 or R_2O_3 with the new combination of oxides retaining their acid properties we have the formation of the salts of these complex inorganic acids explained. A large number of these salts are very stable; in many cases the free acid has been prepared and is a stable, crystalline and well defined compound.

During the past few years Smith and those working with him have introduced oxides of the type R_2O_3 which are primarily basic; as, for example, Bi_2O_3 , Al_2O_3 , Ni_2O_3 , Ce_2O_3 , etc., into the acid portion of the tungstates. Here it becomes necessary for the tungstic oxide to induce acid properties in an oxide normally basic. Is this probable or would it be more correct to view such compounds as double salts, or acid double salts of an alkaline tungstate with the tungstate of the sesquioxide?

Balke and Smith¹ describe the salt $3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 + 4\text{H}_2\text{O}$ and the silver ammonium salt $11\text{Ag}_2\text{O} \cdot 21(\text{NH}_4)_2\text{O} \cdot 4\text{Al}_2\text{O}_3 \cdot 36\text{WO}_3$ obtained from its ammoniacal solution by precipitating with silver nitrate. The same authors prepared the following tungstates containing Bi_2O_3 .

The last two were obtained from the ammonium salt by adding potassium bromide and strontium chloride, respectively.

Rogers and Smith² introduced the sesquioxides, Ni_2O_3 , Pr_2O_3 , Nd_2O_3 , La_2O_3 , Ce_2O_3 , into acid tungstates. The ratio obtained was $\text{R}_2\text{O}_3 \cdot 16\text{WO}_3$ with varying amounts of alkali. In all cases a barium and in some a barium and a silver salt were prepared by double decomposition, the same ratio of R_2O_3 to WO_3 being maintained.

From the work of these experimenters it would seem that the ratio existing between the oxides of the type R_2O_3 and WO_3 remains constant through a series of salts, and therefore they are joined to form a complex radicle with acid properties.

Some of the similar combinations of the alkali molybdates with the sesquioxides have been known for a long time. There has not, however, been sufficient work done on them to form an opinion in regard to the function of the sesquioxide and even in the case of the compounds containing Mn_2O_3 , upon which the most study has been put, a series of salts has not been prepared. In fact the work of Friedheim and Samuelson³ points to these as double salts of an R_2O oxide and MnO where the acid is MnO_2 in union with MoO_3 .

MoO_3 lies between SO_3 and WO_3 in its properties. The combinations of alkali sulphates with the sulphates of the sesquioxides are essentially

¹ This Journal, 25, 1229.

² Ibid., 26, 1474.

³ Z. anorg. Chem. 24, 65.

double salts, the alums. The similar combinations of WO_3 would appear to be the alkali salts of complex inorganic acids. It was decided to study the combinations of the alkali molybdates with the sesquioxides and determine, if possible, to which of these classes they belong.

The different sesquioxides were introduced into the alkali molybdate, the potassium and ammonium salts prepared in each case and from these were chosen for further study those salts which were most easily prepared and which could be most accurately analyzed. The different methods adopted with a view of determining whether these compounds are in reality salts of a complex inorganic acid composed of the oxides ($\text{R}_2\text{O}_3\text{MoO}_3$) or whether they are double molybdates of the basic oxides R_2O and R_2O_3 were:—

1. Preparation of alkali salts containing the same ratio of R_2O_3 to MoO_3 , but a greater proportion of base.

2. Preparation of a series of salts by double decomposition. If in this series the ratio $\text{R}_2\text{O}_3\text{MoO}_3$ remains constant it will be probable that they are in combination and acting together as the acid radicle, for if the oxide R_2O is present as a base there is no reason why, if a base is added such as lead which forms insoluble molybdates all of both the R_2O and R_2O_3 oxides should not be replaced and lead molybdate formed.

3. Preparation of the free acid.

4. Study of the behavior of solutions of these salts upon dialysis. Most double salts are decomposed in any but the most concentrated solutions, in this case the alkali salts are crystalline, and if decomposed should dialyze unchanged, if, however, they are broken down into R_2O and R_2O_3 molybdates, the R_2O salts being crystalline and the R_2O_3 non-crystalline a separation should occur.

Struve¹ prepared molybdates containing the alkalies with Cr_2O_3 and Al_2O_3 of the general formulas $3\text{R}_2\text{O}.\text{R}_2\text{O}_3.12\text{MoO}_3 + 20\text{H}_2\text{O}$ and those of the alkalies with Mn_2O_3 of the formulas $5\text{R}_2\text{O}.\text{Mn}_2\text{O}_3.16\text{MoO}_3 + 12\text{H}_2\text{O}$. He considered these as double molybdates analogous to the alums, however, he mentions that upon adding a solution of silver nitrate to a solution of the potassium chromium molybdate a precipitate is obtained which contains chromium as well as silver and molybdenum. This would indicate that here the chromium is united with the molybdenum to form the acid portion of the salt and that the compound might be written $3\text{K}_2\text{O}-(\text{Cr}_2\text{O}_3.12\text{MoO}_3) + 20\text{H}_2\text{O}$ the Cr_2O_3 and MoO_3 together forming the acid portion of the compound.

The method employed by Struve for the preparation of the compound was to boil the hydrated sesquioxide with the alkaline trimolybdate. This method was modified and large amounts of the salts prepared by adding the sulphate of the sesquioxide to a solution of the alkaline molybdate and

¹Jour. fur. Chem. 61, 449.

boiling vigorously for several minutes. On cooling the new compound separated out and was purified by crystallization.

Ammonium Chromico Molybdate, $3(\text{NH}_4)_2\text{OCr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 20\text{H}_2\text{O}$. This salt was prepared using the method employed by Struve, and also by boiling ammonium chrom-alum with ammonium para-molybdate. A solution of 30 grams of $(\text{NH}_4)_2\text{Cr}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ was added to 50 grams of the salt $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in a liter of water; upon boiling the color of the solution changed to a rose-red, and on cooling fine pale-red crystals separated in large amount, these were recrystallized from water. The two preparations were identical and had the composition given above.

Analysis	Calculated	(1)	(2)	Found (3)	(4)	(5)
$3(\text{NH}_4)_2\text{O}$	6.51	6.77	6.54			6.54
Cr_2O_3	6.34	6.47	6.48	6.58	6.67	6.37
12MoO_3	72.13					
$20\text{H}_2\text{O}$	15.02					
	100.00					
Loss on ignition	21.53	21.45		21.39		21.37

In (1) and (2) the Cr_2O_3 was determined by fusion of the ignited salt with sodium peroxide and determining the chromate by acidifying with sulphuric acid, adding a known amount of ferrous sulphate in excess and titrating the excess with standard permanganate. In (3) the salt was dissolved in dilute hydrochloric acid, the molybdenum precipitated with hydrogen sulphide under pressure and the chromium precipitated by the addition of ammonium sulphide to the filtrate. In (4) the combined $\text{MoO}_3 + \text{Cr}_2\text{O}_3$ obtained by ignition was heated in a current of hydrochloric acid gas to volatilize the MoO_3 , and the Cr_2O_3 remaining in the boat was weighed. In the absence of alkali none of the chromium is changed to chloride. In (5) the Cr_2O_3 was oxidized to CrO_3 in a sulphuric acid solution of the salt, using ammonium persulphate in the presence of silver nitrate, then boiling to destroy the excess of persulphate and the CrO_3 determined by adding a known amount of ferrous ammonium sulphate in excess and titrating the excess with standard permanganate. This method was found to be the most satisfactory and was the one used in all of the remaining chromium determinations unless otherwise stated. The loss on ignition represents total $(\text{NH}_4)_2\text{O} + \text{H}_2\text{O}$. The $(\text{NH}_4)_2\text{O}$ was determined by boiling with sodium hydroxide and collecting the ammonia evolved in standard sulphuric acid and titrating the excess of acid with standard alkali. (5) was prepared according to the method of Struve, while the others were prepared by the method outlined above.

Potassium Chromico Molybdate, $3\text{K}_2\text{OCr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 20\text{H}_2\text{O}$.—For

the preparation of this salt 75 grams of potassium para molybdate, $K_2Mo_7O_{24} + 4H_2O$ were dissolved in water and a solution of 30 grams of potassium chrom-alum added. Upon boiling, the same color change was noted as with the ammonium salt, and on cooling the potassium chromico-molybdate separated. It is identical with the salt described by Struve and prepared by him by boiling chromium hydroxide with a solution of potassium trimolybdate.

The potassium salt is acid to phenolphthalein and can be titrated with standard potassium hydroxide to K_2OMoO_3 , the chromium separating as hydroxide according to the reaction:

Upon ignition in hydrochloric acid gas to volatilize the MoO_3 the potassium oxide is changed to chloride and in the presence of the potassium chloride the chromium goes to chloride, both chlorides remain in the boat if the temperature is not raised too high.

Although the chloride of chromium obtained in this way is the violet chloride it is completely soluble in water unless it has been heated sufficiently high to sublime a portion, when that portion is insoluble.

Analysis	Calculated	(1)	Found (2)	(3)
$3K_2O$	11.18			
Cr_2O_3	6.02	5.90	5.94	5.93
$12MoO_3$	68.53			
$20H_2O$	14.27	14.27		
	100.00			
$9K_2O$	33.54	33.56	33.72	
$6KCl \cdot 2CrCl_3$	30.37	30.47		

Ammonium Aluminico Molybdate, $3(NH_4)_2O \cdot Al_2O_3 \cdot 12MoO_3 + 19H_2O$.—The ammonium aluminico molybdate was prepared by boiling 100 grams of ammonium para molybdate $(NH_4)_6Mo_7O_{24} + 4H_2O$ with 33 grams of aluminum sulphate in $1\frac{1}{2}$ liters of water. On cooling the salt crystallized out. It was recrystallized.

Analysis	Calculated	(1)	Found (2)	(3)
$3(NH_4)_2O$	6.75	6.93	6.64	6.71
Al_2O_3	4.41	4.77	4.96	4.71
$12MoO_3$	74.81			
$19H_2O$	14.03			
	100.00			
Loss on ignition	20.78	20.99	21.22	21.12

The loss on ignition represents total $(NH_4)_2 + H_2O$. On heating the residue from ignition in hydrochloric acid gas, all of the MoO_3 could not be expelled, the results obtained were not constant and the residue in the boat always gave a test for molybdenum. The Al_2O_3 content was determined by removing the molybdenum with hydrogen sulphide under pres-

sure and obtaining the Al_2O_3 from the filtered solution with ammonium hydroxide. The $(\text{NH}_4)_2\text{O}$ was determined by boiling with sodium hydroxide and collecting the ammonia in standard acid. (3) was a separate preparation obtained by following the method used by Struve. The Al_2O_3 in (2) was obtained by ignition in hydrochloric acid gas.

Potassium Aluminico Molybdate, $3\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{MoO}_3 + 20\text{H}_2\text{O}$.—This salt was prepared in the same manner as the corresponding chromium compound, by adding aluminum sulphate or potassium aluminum alum to a solution of potassium molybdate, boiling for a few minutes and allowing to crystallize.

$3\text{K}_2\text{O}$	11.40	
Al_2O_3	4.13	4.24
12MoO_3	69.91	
$20\text{H}_2\text{O}$	14.50	14.56
	100.00	
$9\text{K}_2\text{O}$	34.20	34.28
$6\text{KCl} \cdot \text{Al}_2\text{O}_3$	22.21	22.40

With this salt as with the potassium chromico molybdate, ignition in hydrochloric acid gas removed all of the MoO_3 , but while the Cr_2O_3 is changed to chloride, in this case the Al_2O_3 remains unchanged and the amount is readily obtained by dissolving the contents of the boat in water, filtering out the Al_2O_3 and weighing it after ignition. The presence of the alkali chloride seems to aid in the complete removal of MoO_3 by hydrogen chloride.

This salt is acid to phenolphthalein and can be titrated in the same manner as the potassium chromico molybdate.

The sodium salt $3\text{Na}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 21\text{H}_2\text{O}$ was prepared by Struve. Gentile¹ obtained the salt by a slightly modified method, by adding sodium molybdate Na_2OMoO_3 to potassium aluminum alum, dissolving the precipitate in hydrochloric acid and allowing to crystallize.

Struve was unable to obtain an alkali ferrico molybdate by boiling ferric hydroxide with a solution of an alkali molybdate. The ferric hydroxide gradually dissolved and gave the solution an orange color, but upon evaporation an iron molybdate of the composition $\text{Fe}_2\text{O}_3 \cdot 5\text{MoO}_3 + 10\text{H}_2\text{O}$ separated. The filtrate from this yielded a small amount of a yellowish white salt, but this was not obtained in sufficient quantity to analyze.

Ammonium Ferrico Molybdate, $3(\text{NH}_4)_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3 + 19\text{H}_2\text{O}$.—This salt was obtained by boiling ammonium molybdate with ammonium iron alum. A small amount of an iron molybdate similar to the one described by Struve separated. The filtrate from this when allowed to evaporate at room temperature yielded nearly white crystals of the ammonium ferrico molybdate. They were not recrystallized.

¹ I. pr. Chem., 81, 413.

Analysis	Calculated	(1)	(2)	Found	(3)	(4)
3(NH ₄) ₂ O.....	6.54	6.68	6.41			
Fe ₂ O ₃	6.71			6.70		6.78
12MoO ₃	72.42					
19H ₂ O	14.33		14.48 (loss at 150°)			
	100.00					
Loss on ignition.....	20.87			20.83		21.10
12H ₂ O.....	9.05		9.15 (loss at 105°-110°)			

In (3) the Fe₂O₃ was determined after removing the molybdenum as sulphide in a pressure bottle. In (4) the iron was separated from the molybdenum by sodium hydroxide in excess, the ferric hydroxide obtained was dissolved in sulphuric acid and reprecipitated with sodium hydroxide. The loss at 105°-110° represents 12 molecules of water, all of the water is lost at 150° and practically none of the (NH₄)₂O escapes, for in (2) the (NH₄)₂O was determined in the sample previously heated to 150°.

Potassium Ferrico Molybdate, 3K₂OFe₂O₃12MoO₃ + 20H₂O.—In the preparation of the potassium ferrico molybdate 10 grams of potassium molybdate, K₂MoO₄ was boiled with the calculated amount of Fe₂O₃ as potassium iron alum and an excess of molybdenum trioxide. The filtrate was evaporated at room temperatures and yielded white crystals of potassium ferrico molybdate, these were not recrystallized.

Analysis	Calculated	Found
3K ₂ O.....	11.14	
Fe ₂ O ₃	6.32	6.21
12MoO ₃	68.27	
20H ₂ O	14.27	13.80
	100.00	
9K ₂ O.....	33.43	34.28

Upon ignition of the potassium ferrico molybdate in hydrochloric acid gas, the molybdenum trioxide is expelled, but in the presence of the potassium chloride nearly all of the iron is retained as chloride. This is not quantitative since some of the ferric chloride escapes without very careful regulation of the temperature. The combined Fe₂O₃MoO₃ obtained by ignition of the ammonium ferrico molybdate is completely volatile in hydrochloric acid gas.

With the exception of the rare earth oxides there remains only Ni₂O₃, Co₂O₃, Bi₂O₃, and Mn₂O₃, which are usually basic in character and might enter into combination with the alkali molybdates. Of these ammonium bismuth molybdate has been prepared by Riederer¹, and further studied by Miller and Frank², who assign to it the formulas (NH₄)₂Bi(MoO₄)₂. It is insoluble in ammonium salts and was made the basis of a volumetric

¹ This Journal, 25, 907.

² Ibid., 25, 919.

method for the determination of bismuth by Riederer. The limits of its formation as given by these investigators are narrow, using a large excess of ammonium molybdate in nitric acid, adding bismuth nitrate and just neutralizing the mixture with ammonium hydroxide, then heating to boiling. The salt is decomposed by washing with water.

The sesquioxide of manganese was introduced into acid molybdates by Struve and salts of the type $5\text{R}_2\text{OMn}_2\text{O}_3 \cdot 16\text{MoO}_3 + 12\text{H}_2\text{O}$ obtained. Later work by Péchard¹, Rosenheim and Itzig² throw doubt on the accuracy of the formulas assigned by Struve.

The potassium salt obtained by Struve was prepared by adding manganese sulphate, drop by drop to a solution of potassium trimolybdate, through which a current of chlorine was passing. The manganese sulphate was added as long as the color of the solution was increased.

Péchard, using potassium permanganate, as the oxidizing agent, obtained a salt having similar physical characteristics and which he regarded as identical with the salt of Struve and to which he assigned the formula $3\text{K}_2\text{OMnO}_2 \cdot 12\text{MoO}_3 + 4\text{H}_2\text{O}$. Rosenheim and Itzig, using potassium permanganate as the oxidizing agent, obtained two types of salts $2(\text{NH}_4)_2\text{K}_2\text{OMnO}_2 \cdot 10\text{MoO}_3$ and $3\text{K}_2\text{OMnO}_2 \cdot 8\text{MoO}_3$. The last salt was obtained from the first by treating its solution with potassium chloride as well as by the action of potassium permanganate on potassium paramolybdate and manganese chloride. Friedheim and Samuelson, using numerous oxidizing agents, obtained a variety of salts, but they considered them as derivatives of complex acids containing MnO_2 in combination with 7, 8, 9, 10, or 11 molecules of MoO_3 .

In the present investigation some of this work was repeated, the experiments conducted were carried on with potassium molybdate and manganese sulphate in the presence of the oxidizing agents, bromine and potassium permanganate. The resulting compounds were found to vary in manganese content, dependent upon the amount of manganese sulphate used in their preparation, but upon preparing the barium salt by double decomposition that part of the manganese which was present as dioxide was not replaced by the barium while the remainder was, so that the barium salts from these different preparations were similar. This led to the conclusion that the salts obtained were of only one type, namely, $3\text{K}_2\text{OMnO}_2 \cdot 9\text{MoO}_3$ and in those salts containing more manganese than one MnO for one active O the remainder of the manganese replaced potassium thus, $3(\text{K}_2\text{OMnO})\text{MnO}_2 \cdot 9\text{MoO}_3$ and was replaced by the barium upon the addition of barium chloride giving a salt of the composition, $3\text{BaOMnO}_2 \cdot 9\text{MoO}_3$.

A salt having the composition, $3\text{K}_2\text{OMnO}_2 \cdot 9\text{MoO}_3$, was obtained when

¹ Compt. rend., 125, 29.

² Z. anorg. Chem., 24, 65.

care was taken to avoid an excess of manganese sulphate, 4 grams of K_2MoO_4 , 6 grams of MoO_3 and 1 gram of $MnSO_4 + 5H_2O$ were boiled together and oxidized with bromine water. The mixture was boiled for some time, then the excess of MoO_3 filtered out and upon cooling the potassium manganoso molybdate separated.

Analysis	Calculated	Found	
3K ₂ O.....	15.93	15.81	
MnO ₂	4.91	4.77	
9MoO ₃	73.08	73.14 (by difference)	
6H ₂ O.....	6.08	6.28	
	<hr/> 100.00	<hr/> 100.00	
MnO.....	4.00	3.93	3.85
Loss on ignition.....	6.99	7.12	7.10
6KCl.MnCl ₂	3.32	31.98	
O (active).....	0.91	0.84	

A second preparation using relatively more manganese and oxidizing with potassium permanganate gave a salt of the composition $(2.6 K_2O.4MnO).MnO_2.9MoO_3.7H_2O$.

Analysis	Calculated	Found
$2.6K_2O$	13.70	13.77
$.4MnO$	1.50	
MnO_2	4.99	
$9MoO_3$	72.74	72.45 (by difference)
$7H_2O$	7.07	7.28
	<hr/> 100.00	
O (active).....	0.90	0.90
$H_2O + O$	7.97	8.18
MnO.....	5.59	5.60
$5.2KCl + 1.4MnCl_2$	31.65	31.76

A solution of barium chloride reacts with a solution of this salt in accordance with the reaction

The barium salt as obtained is a pinkish yellow precipitate, hard to filter. When air-dried it contains 12 molecules of water.

Analysis	Calculated	Found	
3BaO.....	22.30	22.52	
MnO ₂	4.22	4.28	
9MoO ₅	62.98	62.70	(by difference)
12H ₂ O.....	10.50	10.50	
	<hr/>	<hr/>	
	100.00	100.00	
O (active).....	0.77	0.70	
MnO.....	3.58	3.45	3.49
3BaCl ₂ .MnCl ₂	36.44	37.00	
H ₂ O + O.....	11.27	11.20	

Silver nitrate reacts in a manner similar to that of barium chloride,

giving silver manganoso molybdate and replacing that portion of the manganese not present as MnO_2 .

Analysis	Calculated	Found	
$3\text{Ag}_2\text{O}$	31.83	32.16	
MnO_2	3.98	4.00	
9MoO_3	59.25	59.37	(by difference)
$6\text{H}_2\text{O}$	4.94	4.47	
	100.00	100.00	
O (active).....	0.73	0.67	0.69
MnO	3.25	3.33	3.18
6AgClMnCl_2	45.13	46.10	
$\text{H}_2\text{O} + \text{O}$	5.67	5.14	

The active oxygen in all of the above salts was determined by the iodometric method, the total chlorides were obtained by ignition in hydrochloric acid gas and the manganese determined in the solution of these chlorides. No loss of manganese occurs, at the temperature necessary to expel all of the molybdenum trioxide.

The methods outlined above for the preparation of potassium manganoso molybdate were employed to obtain an alkali nickeloso molybdate containing nickel in a higher state of oxidation. In the case of nickel the oxidizing agents used were hydrogen peroxide, chlorine, bromine and potassium persulphate. With the first three the same results are obtained as when no oxidizing agent is employed, a double molybdate of potassium and bivalent nickel separating. This salt is light green in color and can be recrystallized from water.

It has the composition, $5\text{K}_2\text{O}_3\text{NiO}16\text{MoO}_3 + 21\text{H}_2\text{O}$.

Analysis	Calculated	Found	
$5\text{K}_2\text{O}$	13.91	14.08	13.88
3NiO	6.66	6.64	
16MoO_3	68.24	68.24	(by difference)
$21\text{H}_2\text{O}$	11.19	11.04	10.64
	100.00	100.00	
$3\text{NiCl}_26\text{KCl}$	33.61	33.82	33.76

The NiO was determined by boiling the solution of the salt with sodium hydroxide and bromine and weighing as NiO after ignition. The salt heated in hydrochloric acid gas gives chlorides of nickel and potassium quantitatively. In (2) the K_2O was obtained from the combined chlorides by removing the nickel as sulphide with ammonium sulphide and evaporating the filtrate with sulphuric acid, weighing the potassium as sulphate.

Potassium nickeloso molybdate, $3\text{K}_2\text{ONiO}9\text{MoO}_3 + 6\frac{1}{2}\text{H}_2\text{O}$.

When potassium persulphate is used as the oxidizing agent a dark brown, nearly black precipitate is formed. It is very insoluble even in hot water, but becomes finely crystalline upon boiling with water. For its preparation either potassium molybdate, $3\text{K}_2\text{O}7\text{MoO}_3$, and nickel sul-

phate were dissolved in water, the solution heated nearly to boiling, and potassium persulphate added, or a solution of the salt. $5\text{K}_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3$ was boiled with potassium persulphate. In either case a brown precipitate formed. This was filtered out and boiled with water when it became crystalline. It was so insoluble that it was not recrystallized.

Analysis	Calculated	(1)	Found (2)	(3)	(4)
$3\text{K}_2\text{O}$	15.80	15.38			
NiO_2	5.10	5.56			
9MoO_3	72.61	72.58 (by difference)			
$6\frac{1}{2}\text{H}_2\text{O}$	6.49	6.48			
	100.00				
O (active).....	0.90	0.88	0.85	0.84	0.81
loss.....	7.39	7.36			
$6\text{KCl} \cdot \text{NiCl}_2$	32.32	32.40	32.20		
NiO	4.20	4.68	4.55		

In (1) the active oxygen was determined by the iodometric method, while in (2), (3), and (4) it was obtained by igniting the salt and collecting the gas evolved in a gas burette.

Ammonium Nickel Molybdate, $5(\text{NH}_4)_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 + 16\text{H}_2\text{O}$.—Ammonium molybdate with nickel sulphate either alone or in the presence of 3 per cent. hydrogen peroxide gives a green solution, which deposits light green crystals of a double ammonium nickel molybdate.

Analysis	Calculated	Found	
$5(\text{NH}_4)_2\text{O}$	8.45	8.42	8.32
3NiO	8.31	7.16	
16MoO_3	74.88	75.30 (by difference)	
$16\text{H}_2\text{O}$	9.36	9.12	
loss $(\text{NH}_4)_2\text{O} + \text{H}_2\text{O}$	17.81	17.54	17.60

Ammonium Nickeloso Molybdate.—When ammonium molybdate is boiled with nickel sulphate and ammonium persulphate used as the oxidizing agent a dark purple solution results which on cooling deposits fine purple black crystals. These are difficultly soluble in water to a purple solution and can be recrystallized from their water solution.

The addition of barium chloride to a solution of the ammonium nickeloso molybdate gives a brown precipitate, which corresponds to the formula, $3\text{BaO} \cdot \text{NiO}_2 \cdot 9\text{MoO}_3 + 12\text{H}_2\text{O}$.

Analysis	Calculated	Found		
3BaO	22.26	22.32		
NiO_2	4.41	4.55		
9MoO_3	62.85	62.63 (by difference)		
$12\text{H}_2\text{O}$	10.48	10.50		
	100.00	100.00		
O (active).....	.78	.72	.73	.77
loss O + H_2O	11.22	11.24		
$3\text{BaCl}_2 \cdot \text{NiCl}_2$	36.56	36.99		
NiO	3.63	3.83		

Kurnalow¹ prepared two series of alkali cobaltico molybdates, containing the cobalt, presumably, as Co_2O_3 . To these he assigned the composition, $3\text{K}_2\text{OCo}_2\text{O}_3 \cdot 12\text{MoO}_3 + 2\text{H}_2\text{O}$ and $3\text{K}_2\text{OCo}_2\text{O}_3 \cdot 10\text{MoO}_3 + 10\text{H}_2\text{O}$. They were prepared by boiling potassium molybdate and cobaltous hydroxide with the addition of bromine water. The first one was a light green, the second a dark green salt.

The experiments described under nickel were repeated with cobalt. Upon oxidizing cobalt sulphate in the presence of potassium molybdate with bromine a blue solution is obtained which deposits green crystals on cooling. A corresponding ammonium salt is obtained by oxidizing cobalt sulphate in the presence of ammonium molybdate with either hydrogen peroxide or ammonium persulphate. When hydrogen peroxide is used the mother liquor from the green crystals gives a crop of nearly black crystals which are much more soluble than the green. These salts may be of the same composition as those studied by Kurnalow; they have not been analyzed².

If cobalt sulphate is added to either potassium or ammonium molybdate, the solution remains pink, and on boiling gives a heavy precipitate which is nearly purple when dried. The green salt obtained by using oxidizing agents contains cobalt in a higher state of oxidization than protoxide since the addition of sodium hydroxide to its solution gives a precipitate of the black cobaltic hydroxide.

Potassium Cobaltoso Molybdate, $3\text{K}_2\text{OCoO}_2 \cdot 9\text{MoO}_3 + 6\frac{1}{2}\text{H}_2\text{O}$.—This salt is obtained in an analogous manner to the corresponding nickel salt, which it closely resembles, by oxidizing cobalt sulphate and potassium para molybdate with potassium persulphate.

Analysis	Calculated	Found
$3\text{K}_2\text{O}$	15.80	15.60
CoO_2	5.10	
9MoO_3	72.61	
$6\frac{1}{2}\text{H}_2\text{O}$	6.49	6.36
	<hr/> 100.00	
O (active).....	0.90	0.86
loss O + H_2O	7.36	7.22
$6\text{KCl} \cdot \text{CoCl}_2$	32.32	32.22

These derivatives of NiO_2 and CoO_2 correspond in formulas with those obtained for the same oxide of manganese and are of a different type from the compounds of chromium, iron and aluminium. While these elements have not hitherto been obtained in compounds in the state of dioxide, there is reason to believe that they so exist here. The amount of active oxygen is to the nickel or cobalt content as 1:1. If the oxide be considered as Ni_2O_3 and Co_2O_3 and the remainder of the active oxygen

¹ Chem. Ztg., 14, 113.

² See also Friedheim and Keller: Ber., 39, 4301.

be in union with MoO_3 as a permolybdate the composition of the salts would be $6\text{K}_2\text{O} \cdot \text{R}_2\text{O}_3 \cdot 17\text{MoO}_3 \cdot \text{MoO}_4 + 13\text{H}_2\text{O}$, which is neither as simple or as rational as the formulas given which consider them as dioxide. These compounds and their derivatives are being studied more exhaustively at the present time. They point to a close relationship between cobalt, nickel and manganese, especially between cobalt and manganese.

Of the salts prepared containing an alkali molybdate in combination with a sesquioxide those containing Cr_2O_3 and Al_2O_3 were found to be most stable and most satisfactory for the purpose of this investigation. To this end a solution of potassium chromico molybdate was prepared and solutions of various salts added. Solutions of lead, silver, mercurous mercury, barium, bismuth, cesium, rubidium and iron, were found to give precipitates while the soluble salts of nickel, aluminium, manganese, chromium, uranium, cobalt, cadmium, copper, strontium, calcium, zinc, magnesium, mercuric mercury or lithium give no precipitate. In the case of ferric iron a precipitate is formed only on boiling. Ferric potassium alum was used and the air-dried precipitate had the composition, $2\text{Fe}_2\text{O}_3 \cdot 7\text{MoO}_3 + 34\text{H}_2\text{O}$, and contained no chromium.

Analysis	Calculated	Found
$2\text{Fe}_2\text{O}_3$	16.49	16.17
7MoO_3	51.97	52.43 (by difference)
$34\text{H}_2\text{O}$	31.54	31.40
	<hr/> 100.00	<hr/> 100.00

The other precipitates obtained contained chromium. They were prepared in sufficient quantity for analysis and the ratio between the Cr_2O_3 and MoO_3 determined to see if it remained 1 : 12 as in the alkali salts.

Barium Chromico-Molybdate.—Barium chloride was added to a solution of the potassium chromico-molybdate in accordance with the reaction $3\text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 3\text{BaCl}_2 = 3\text{BaO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 6\text{KCl}$. Five grams of the potassium salt were dissolved in 200 cc. of water, allowed to cool and a solution of 1.46 grams of $\text{BaCl}_2 + 2\text{H}_2\text{O}$ added. After a few minutes a pinkish granular precipitate began to form. This was allowed to stand for 15 hours, filtered and air-dried. The addition of more barium chloride to the filtrate and evaporation to dryness gave a very slight residue insoluble in water.

Analysis	Calculated	(1)	Found (2)	(3)
2.15 BaO	12.40	12.30	12.74	12.72
.85 K_2O	3.13	3.32		
Cr_2O_3	5.73	5.68	5.68	5.70
12MoO_3	65.16	65.50 (by difference)		
$20\text{H}_2\text{O}$	13.58	13.20	13.00	12.92
	<hr/> 100.00	<hr/> 100.00		

(2) was a second preparation made under the same conditions as (1), while in (3) double the amount of barium chloride was used. In all of

these the base content is three molecules and approaches $2\frac{1}{4}\text{BaO}$ to $\frac{3}{4}\text{K}_2\text{O}$.

For analysis the barium salts were dissolved in dilute hydrochloric acid, and the barium content determined by precipitating as barium sulphate with sulphuric acid. When chromium was to be determined in the same sample, nitric acid was used instead of hydrochloric to avoid the necessity of removing the hydrochloric acid before adding silver nitrate and oxidizing with ammonium persulphate. For the determination of the potassium, the sample was ignited in hydrochloric acid gas to remove the molybdenum, then dissolved in water, the barium, potassium and part of the chromium went into solution as chlorides, while part of the chromium remained insoluble as the trioxide. The barium and chromium were removed in the usual way and the potassium determined as sulphate. The amount of chromium going into solution in water after ignition in hydrochloric acid gas is in proportion to the amount of alkali present in the salt. Where none is present practically all of the chromium remains as oxide.

Upon the addition of a larger excess of barium chloride, 7.3 grams of $\text{BaCl}_2 + 2\text{H}_2\text{O}$ to a solution of 2.5 grams of the potassium chromico-molybdate, the precipitate formed very slowly, only a very slight deposit being produced after several hours, but upon warming nearly all separated. The salt obtained gave upon analysis the results following under (1). The salt, analysis of which is given under (2), was formed by using 2.2 grams of $\text{BaCl}_2 + 2\text{H}_2\text{O}$ to 2.5 grams of the potassium salt.

Analysis	Calculated	(1)	Found (2)
4BaO.....	22.02	21.28	22.24
Cr ₂ O ₃	5.47	5.44	5.44
12MoO ₃	62.15	63.28	61.52 (by difference)
15H ₂ O.....	10.36	10.00	10.80
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

(1) contained a trace of potassium, but none could be detected in (2). The formation of the salt, $4\text{BaO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3$, would require the liberation of two molecules of hydrochloric acid. In order to neutralize this and if possible obtain a neutral salt and thus determine the basicity of the chromico-molybdic acid another preparation was made. In this case an excess of barium chloride was used and a weighed amount of barium carbonate equivalent to one molecule added in the cold. Precipitation began at once. After 24 hours the precipitate was filtered out, washed with dilute acetic acid and air-dried.

Analysis	Calculated	Found
4BaO.....	23.73	23.52
Cr ₂ O ₃	5.21	5.18
12MgO.....	59.59	59.96 (by difference)
18H ₂ O.....	11.47	11.34
	<hr/> 100.00	<hr/> 100.00

In another preparation an excess of barium chloride was added to a cold solution of 2.5 grams of the potassium chromico-molybdate, and a solution containing 2 molecular equivalents of barium hydroxide added drop by drop with constant stirring. The flocculent precipitate which separated was allowed to stand for several days at a temperature of 60°-70° during which it became crystalline. The analysis of the air-dried salt gave the following composition: $5\text{BaOCr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 16\text{H}_2\text{O}$.

Analysis	Calculated	Found
5BaO	26.08	25.16
Cr ₂ O ₃	5.18	5.26
12MoO ₃	58.92	59.48 (by difference)
16H ₂ O	9.82	10.10
	<hr/> 100.00	<hr/> 100.00

The addition of a larger excess of either barium carbonate or barium hydroxide in the attempt to obtain salts with a greater proportion of base did not seem advisable as barium carbonate in excess decomposes the potassium chromico-molybdate in the cold with the formation of barium molybdate and chromium hydroxide.

Lead Chromico-Molybdate.—A cold solution of 2.5 grams of potassium chromico-molybdate was treated with the calculated amount of lead as nitrate to replace all of the potassium. A pinkish precipitate formed immediately. This was filtered out and air-dried. The addition of more lead nitrate to the filtrate gave a further precipitation. The lead salt precipitated was found to have the formula, $4\text{PbO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 24\text{H}_2\text{O}$.

Analysis	Calculated	Found
4PbO	27.84	26.80
Cr ₂ O ₃	4.7	4.90
12MoO ₃	53.93	54.40 (by difference)
24H ₂ O	13.48	13.90
	<hr/> 100.00	<hr/> 100.00
4 PbCl ₂ Cr ₂ O ₃	39.45	38.31

Upon heating the ignited salt in hydrochloric acid gas all of the molybdenum is expelled and lead chloride and chromium oxide remain. For analysis this residue was boiled with water when the lead chloride dissolved and the chromium which remained as oxide was weighed after ignition. It checked very well with the amount obtained by oxidizing with ammonium persulphate as previously described.

In the second preparation five times as much lead nitrate was used and the same amount of the potassium chromico-molybdate. In this case the precipitation was complete. The salt formed had the same composition, except for water content, as in the previous case.

Analysis	Calculated	Found
4PbO	28.16	
Cr ₂ O ₃	4.79	4.84
12MoO ₃	54.55	
22H ₂ O	12.50	12.30
	<hr/> 100.00	
4PbCl ₂ Cr ₂ O ₃	39.90	39.64

Silver Chromico-Molybdate.—The addition of an equivalent amount of a solution of silver nitrate to a cold solution of potassium chromico-molybdate gives a light pink precipitate. The air-dried salt has a composition approximating $2\frac{1}{4}\text{Ag}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 18\text{H}_2\text{O}$.

Analysis	Calculated	Found	
$2\frac{1}{4}\text{Ag}_2\text{O}$	18.66	18.74	18.70
$\frac{3}{4}\text{K}_2\text{O}$	2.52		
Cr_2O_3	5.43	5.32	5.34
12MoO_3	61.81		
$18\text{H}_2\text{O}$	11.58	11.44	
	100.00		

A large excess of silver nitrate, ten times that necessary to replace the potassium, gives a precipitate containing no potassium and having the composition, $5\text{Ag}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 17\text{H}_2\text{O}$.

Analysis	Calculated	Found	
$5\text{Ag}_2\text{O}$	34.66	33.04	
Cr_2O_3	4.54	4.48	4.50
12MoO_3	51.65	53.26	(by difference)
$17\text{H}_2\text{O}$	9.15	9.22	
	100.00	100.00	

Mercurous Chromico-Molybdate.—The addition of a large excess of mercurous nitrate to a solution of the potassium chromico-molybdate gives a pink flocculent precipitate, which, on standing, changes to an orange-yellow, crystalline precipitate. The precipitate obtained in this way and dried at 70° was found to have the composition, $8\text{Hg}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 16\text{H}_2\text{O}$.

Analysis	Calculated	Found	
$8\text{Hg}_2\text{O}$	60.55	60.53	
Cr_2O_3	2.76	2.64	
12MoO_3	31.45	31.70	(by difference)
$16\text{H}_2\text{O}$	5.24	5.13	
	100.00	100.00	
Loss on ignition.....	65.79	65.66	

The barium and the silver salts precipitated from a solution of the ammonium chromico-molybdate by the addition of an equivalent amount of a soluble salt of the barium or silver, contain ammonium, but the ratio of the Cr_2O_3 to the MoO_3 remains unchanged.

Analysis of a barium salt formed by adding barium chloride to a solution of the ammonium salt gave the following results upon analysis.

	Calculated	Found		
		(1)	(2)	
22BaO	12.86	12.87	12.84	12.39
$(\text{NH}_4)_2$	1.55	1.68		
Cr_2O_3	5.81	6.00	6.05	
12MoO_3	66.03	65.78	(by difference)	
$20\text{H}_2\text{O}$	13.75	13.67		
	100.00	100.00		
loss on ignition.....	15.30	15.35	15.26	

(1) and (2) were different preparations.

Preparation of the Free Chromico-Molybdic Acid.—An excess of mercurous nitrate was added to a solution of the ammonium chromico-molybdate. The precipitate obtained was washed by decantation, suspended in water and decomposed with dilute hydrochloric acid. The precipitated mercurous chloride together with the excess of mercurous chromico-molybdate were filtered out and the filtrate evaporated to a small bulk over a water-bath, then over sulphuric acid to dryness. When nearly to dryness a greenish powder began to separate from the solution. Analysis gave the composition of the compound thus obtained to be $\text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 28\text{H}_2\text{O}$.

	Calculated	Found
Cr_2O_3	6.38	6.14
12MoO_3	72.48	73.36 (by difference)
$28\text{H}_2\text{O}$	21.14	20.50
	<hr/> 100.00	<hr/> 100.00

The substance analyzed gave a slight test for both potassium and for chlorine. It dissolved slowly in water forming a pink solution.

Behavior of Potassium Chromico-Molybdate towards Sulphuric Acid.—The salt, $3\text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3$, was crystallized from solutions containing varying amounts of sulphuric acid, in the endeavor to obtain acid salts with the same ratio of Cr_2O_3 to MoO_3 , but a smaller proportion of base. In the presence of sulphuric acid the solubility of the potassium salt is greatly increased.

2.5 grams of the potassium salt were dissolved in water and a definite amount of sulphuric acid added, then evaporated to 25 to 30 cc., and allowed to crystallize. The addition of sulphuric acid up to three molecules for each molecule of the potassium chromico-molybdate caused no change in the composition of the salt crystallizing out beyond a change in the water content.

The potassium chromico-molybdate separated from the sulphuric acid solution in large transparent pink crystals and contained 24 molecules of water.

Analysis	Calculated	Found
$3\text{K}_2\text{O}$	10.87	
Cr_2O_3	5.86	5.96
12MoO_3	66.62	
$24\text{H}_2\text{O}$	16.65	16.58
	<hr/> 100.00	
9 K_2O	32.61	32.48

This salt loses four molecules of water on continued exposure to the air and reverts to the one with 20 molecules.

When a greater amount of sulphuric acid was used the amount of the pink crystals obtained was smaller and after they were removed and the solution further evaporated a very acid potassium molybdate, and finally

potassium chrom-alum separated. In no case was a salt obtained containing less potassium, but the same ratio of chromium to molybdenum. The acid molybdates formed, varied in composition depending on the amount of sulphuric acid present.

Behavior of Potassium Chromico-Molybdate with Potassium Hydroxide.—Upon crystallizing the salt, $3\text{K}_2\text{OCr}_2\text{O}_3 \cdot 12\text{MoO}_3$, from solutions containing varying amounts of potassium hydroxide, salts with a greater amount of base are obtained. Upon the addition of one molecule of K_2O for each molecule of the potassium chromico-molybdate, the solution changes color, losing its pink cast, but there is no separation of chromium hydroxide. Upon evaporating to crystallization the salt which separates has the composition, $7\text{K}_2\text{O} \cdot 2\text{Cr}_2\text{O}_3 \cdot 24\text{MoO}_3 + 32\text{H}_2\text{O}$.

Analysis	Calculated	Found	
$7\text{K}_2\text{O}$	13.17		
$2\text{Cr}_2\text{O}_3$	6.09	6.14	6.20
24MoO_3	69.21		
$32\text{H}_2\text{O}$	11.53	11.50	
	<hr/> 100.00		
$17\text{K}_2\text{O}$	31.79	31.84	

In the preparation of the above salt 2.5 grams of potassium chromico-molybdate were dissolved in 150 cc. of water and the calculated amount of K_2O added slowly in the form of a standard potassium hydroxide solution, the whole was then evaporated to about 40 cc. and allowed to crystallize.

When the same amount of potassium chromico-molybdate was dissolved in water and a solution containing two molecules of K_2O added a very little chromium hydroxide separated and was filtered out. The solution upon evaporation yielded crystals which analyzed for $4\text{K}_2\text{OCr}_2\text{O}_3 \cdot 12\text{MoO}_3 + 15\text{H}_2\text{O}$.

Analysis	Calculated	Found
$4\text{K}_2\text{O}$	14.88	
Cr_2O_3	6.01	6.02
12MoO_3	68.42	
$15\text{H}_2\text{O}$	10.69	10.64
	<hr/> 100.00	
$8\text{K}_2\text{O}$	29.76	29.84

The addition of more potassium hydroxide equivalent to $3\text{K}_2\text{O}$ and also to $4\text{K}_2\text{O}$ causes the separation of a larger amount of chromium hydroxide, but after this is removed the crystals obtained from the filtrate upon evaporation are essentially of the same composition as the above salt.

Analysis of the salt obtained when $4\text{K}_2\text{O}$ was added.

Analysis	Calculated	Found
4K ₂ O	14.37	
Cr ₂ O ₃	5.81	6.16
12MoO ₃	66.06	
20H ₂ O	13.76	13.11
	<hr/> 100.00	
8K ₂ O	28.74	28.20

The high chromium content of this salt is due to the presence of chromium hydroxide in the solution, which separates with the crystals and is very difficult to remove from them.

This is evidently the highest K₂O content obtainable and the addition of potassium hydroxide in greater amount goes to decompose this salt forming chromium hydroxide and potassium molybdate. A large amount of the chromium hydroxide remains in the solution, giving the solution a green color, while all of the potassium salts of chromico-molybdic acid are pink. This chromium hydroxide is precipitated by the addition of ammonium chloride or can be separated by evaporation of the solution to dryness and taking up in water when it is less soluble than the crystals. It is present as colloidal chromium hydroxide.

Behavior of Potassium Chromico-Molybdate upon Dialysis.—A portion of the salt, 3K₂O·Cr₂O₃·12MoO₃, was dissolved in water and separated from distilled water by parchment paper. This was allowed to stand until sufficient had dialyzed through to color the water outside, this outside solution was then removed and replaced by fresh water. The solutions removed were evaporated to dryness, and when sufficient of the dialyzed salt was obtained it was analyzed.

	Calculated	Found
3K ₂ O	11.18	
Cr ₂ O ₃	6.02	6.02
12MoO ₃	68.53	
20H ₂ O	14.27	14.44
	<hr/> 100.00	

The analysis shows that the dialyzed salt has the same chromium content as the original salt and indicates that the salt dialyzes as 3K₂O·Cr₂O₃·12MoO₃ and must for the most part exist as such in solution.

From the number of salts obtained which contain the Cr₂O₃ and the MoO₃ in the ratio 1 : 12, it is evident that we are dealing with a complex acid and not with a series of double molybdates. From the point of view of double salts the same type of compounds might be expected when the alkalis alone are considered, but that this type should remain through a series such as potassium, barium, silver, lead and mercury and that the different members can be prepared by double decomposition brings it to that degree of stability attributed to the salts of a complex acid and lacking in the double salts. Not much importance can be attributed to the

formation of the free chromico-molybdic acid, since this is a most unsatisfactory compound, obtained by evaporation to dryness, and not a well crystallized body.

The results of the dialysis experiment show that the salt, $3K_2OCr_2O_3 \cdot 12MoO_3$, dialyzes unchanged, a condition which would not be expected if it were a double salt and decomposed on solution into its constituents. Also the change in color noted in the preparation of the ammonium and potassium chromico-molybdates, indicate a change in the function of the color-giving part, the chromium, the solution of these salts having a very different color from those of chromium salts.

The most stable alkali salts of the chromico-molybdic acid are of the type, $3R_2OCr_2O_3 \cdot 12MoO_3$, the potassium salt containing more base than this changing to this type on repeated crystallization from water.

With barium as the base the composition of the salts obtained, by adding barium chloride to the solution of the potassium salt depends on the amount of the barium chloride added, all of the potassium not being replaced by the barium unless a large excess of the barium is present. Then without neutralizing the free acid formed in the reaction the most basic salt obtained is $4BaOCr_2O_3 \cdot 12MoO_3$.

By the addition of barium hydroxide or carbonate to neutralize this acid the base content may be increased to five molecules, but this is of doubtful significance as either the carbonate or the hydroxide decomposes the potassium chromico-molybdate forming chromium hydroxide and barium molybdate.

In the case of lead only one salt appears to be formed, no matter what proportions of lead nitrate and the potassium salt are used. This salt contains four molecules of base.

The silver salt is very similar to the barium salt, all of the alkali not being replaced until a large excess of silver has been added. With a large excess of silver present the silver content of the salt precipitated reaches $5Ag_2O$.

The salt of mercury formed by using a large excess of mercurous nitrate has the composition, $8Hg_2OCr_2O_3 \cdot 12MoO_3$, and probably gives the type of the normal salt of which the others are acid salts. The free acid may then be written, $8H_2O \cdot Cr_2O_3 \cdot 12MoO_3 + 20H_2O$.

Salts of Aluminico-Molybdic Acid.—Salts of aluminico-molybdic acid were prepared and found to be analogous to the corresponding salts of chromico-molybdic acid.

Barium Aluminico-Molybdate.—This salt was prepared by adding an equivalent amount of barium chloride to a solution of ammonium aluminico-molybdate. It separated slowly, the qualitative analysis showed it to contain ammonium as well as barium as the base.

Analysis	Calculated	Found
2.15BaO	12.82	12.79
.85(NH) ₂ O	1.84	12.74
Al ₂ O ₃	3.98	4.24
12MoO ₃	67.33	67.54 (by difference)
20H ₂ O	14.03	
	100.00	
Loss on ignition	15.87	15.43

The Al₂O₃ was determined by removing the barium as sulphate, then the molybdenum as sulphide with hydrogen sulphide under pressure and precipitating the aluminium as hydroxide in the filtrate.

Upon the addition of a large excess, seven grams, of barium chloride to a solution of 1.5 grams of the potassium aluminico-molybdate and boiling for a few minutes a precipitate was obtained which had the composition, 4BaO.Al₂O₃.12MoO₃ + 14H₂O.

Analysis	Calculated	Found
4BaO	22.71	22.70
Al ₂ O ₃	3.79	4.00
12MoO ₃	64.15	63.70 (by difference)
14H ₂ O	9.35	9.60
	100.00	100.00
4 BaCl ₂ Al ₂ O ₃	34.66	34.84

The molybdenum was expelled from the ignited salt by heating in hydrochloric acid gas, the resulting barium chloride and alumina weighed together, then the barium chloride extracted with water and the alumina ignited and weighed. The barium was precipitated as sulphate from the barium chloride solution.

Silver Aluminico-Molybdate.—The addition of an equivalent amount of silver nitrate to a solution of an alkali aluminico-molybdate gives an immediate precipitate, but this contains both silver and the alkali as base, the two together making three molecules. However, when an excess of silver nitrate is used all of the alkali is replaced. The salt obtained by using an excess of silver nitrate had the composition, 4Ag₂O.Al₂O₃.12MoO₃ + 16H₂O. It is probable that if a larger excess of silver nitrate had been used a salt similar to the silver chromico-molybdate with 5 molecules of Ag₂O would have been obtained. In this case the amount of silver nitrate used was not recorded.

Analysis	Calculated	Found
4Ag ₂ O	30.47	29.43
Al ₂ O ₃	3.35	3.60
12MoO ₃	56.73	57.11 (by difference)
16H ₂ O	9.45	9.86
	100.00	100.00

Lead Aluminico-Molybdate.—The addition of lead nitrate to a solution

of an alkali aluminico-molybdate gives a white precipitate of the salt, $4\text{PbOAl}_2\text{O}_3 \cdot 12\text{MoO}_3 + 21\text{H}_2\text{O}$, the formula of the precipitate not depending on the amount of lead nitrate used.

Analysis	Calculated	Found
4PbO	28.77	28.84
Al ₂ O ₃	3.29	3.34
12MoO ₃	55.57	55.72 (by difference)
21H ₂ O	12.19	12.00
	<hr/>	<hr/>
	100.00	100.00
4 PbCl ₂ ·Al ₂ O ₃	39.16	39.30 38.54

The solubility of potassium aluminico-molybdate is given by Struve as 1 part in 40 parts of water at 17°, that of potassium chromico-molybdate as 1 part in 38.5 parts of water at the same temperature. It seemed that the potassium aluminico-molybdate might be prepared from the potassium chromico-molybdate by the addition of aluminium sulphate so that the Cr₂O₃ might be replaced by the Al₂O₃ to form the more insoluble potassium aluminico-molybdate. To this end the following experiment was tried. 2.5 grams of potassium chromico-molybdate were dissolved in water and 10 grams of aluminium sulphate added. Upon evaporation to a small bulk and allowing to stand, crystals of potassium aluminium alum separated, then a crop of potassium molybdate, but nothing that could be identified as potassium aluminico-molybdate.

The addition of ammonium hydroxide to a solution of ammonium aluminico-molybdate gives a precipitate, probably of aluminium molybdate. This shows the instability of these complex molybdates as compared with the corresponding tungstates since Balke and Smith mention that the aluminium is not precipitated by ammonium hydroxide from a solution of an aluminico-tungstate. They were able to prepare a silver ammonium derivative of aluminico-tungstic acid by precipitation from ammoniacal solution. The silver aluminico-molybdate is soluble in a very small amount of ammonium hydroxide, but could not be obtained in crystalline form from this solution and is decomposed by an excess of the ammonium hydroxide.

SUMMARY.

The preparation of the ammonium and potassium salts of chromico-molybdic and of aluminico-molybdic acid has been repeated together with a series of salts derived from them by double decomposition. The salts of chromico-molybdic acid were studied more at length and experiments conducted with the view of determining whether the alkali chromico-molybdates are double salts or derivatives of a complex inorganic acid containing Cr₂O₃ and MoO₃.

All of these experiments, namely, the preparation of a series of salts by double decomposition, the preparation of alkali salts with a greater content of base, the preparation of the free chromico-molybdic acid and

the behavior of a solution of potassium chromico-molybdate upon dialysis, have favored the assumption that we have here a complex inorganic acid.

The mercurous salt of the chromico-molybdic acid, obtained by using an excess of mercurous nitrate, contains eight molecules of Hg_2O . Since the preparation of this salt would liberate ten molecules of nitric acid it can scarcely be a basic salt, but is either the normal salt or one in which nearly all of the replaceable hydrogens have been replaced.

Alkali salts of ferrico-molybdic acid analogous in composition to those of the aluminico- and chromico-molybdic acids were obtained. These are undoubtedly constituted in a similar manner, the R_2O_3 oxide being a part of the acid portion of the salt. These sesquioxides have more characteristic basic than acid properties. With Al_2O_3 and Cr_2O_3 the acid properties are developed in the presence of strong bases, but in their compounds prepared and described above the MoO_3 must influence their nature, causing them to lose their basic properties, since here they, together with the MoO_3 , function as an acid, and they are not replaceable by metallic oxides, although in an acid environment, a condition adapted to bring out their basic character.

The derivatives of manganoso-molybdic acid obtained had that portion of the manganese combined with the molybdenum to form the acid, present as the dioxide, confirming the work of Friedheim and Samuelson in this respect. Derivatives of a nickeloso- and of a cobaltoso-molybdic acid containing the nickel and the cobalt as the dioxide and analogous in composition to the similar manganoso-molybdates were prepared. There can be little doubt as to the state of oxidation of the nickel and cobalt contained in them, and the fact that they contain the dioxides of these elements make them of especial interest.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 133.]

SOME NEW DOUBLE PHOSPHATES OF IRON (FERRIC) AND ALUMINUM¹

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Received March 7, 1907.

In an unpublished paper J. L. Danziger states that by the addition of a large excess of diammonium phosphate to a solution of ferric chloride strongly acid with hydrochloric acid, he obtained a white powder which on analysis so closely approximated the formula $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{FePO}_4$ as to warrant the belief in the existence of such a double phosphate of ferric

¹ Read at the December meeting of the New York Section of the Am. Chem. Society.