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§ 8. Molybdenum and Molybdic Oxides

According to J. J. Berzelius,¹ **molybdenum monoxide**, or **molybdous oxide**, MoO, is formed as a purple or violet powder when zinc and hydrochloric acid are allowed to act for a long time on fused or sublimed molybdenum trioxide; but the product is probably molybdic oxide. W. Muthmann and W. Nagel could not prepare this oxide. C. W. Blomstrand thought that **molybdous hydroxide**, Mo(OH)₂, is formed as a black solid by the action of conc. potash-lye on molybdenum dibromide, but he later represented it as Mo₃(OH)₆. W. Muthmann and W. Nagel found that the hydrogen is given off while the black precipitate is being formed, and they find that it is molybdic hydroxide, Mo(OH)₃. The same product is obtained by the action of potash-lye on molybdenum dihydroxytetrabromide, Mo₃(OH)₂Br₄+4KOH+3H₂O=3Mo(OH)₃+4KBr+3H. This makes it doubtful if a bivalent molybdenum compound has yet been prepared.

What J. J. Berzelius² called molybdous oxide was shown by C. W. Blomstrand, and C. F. Rammelsberg to be hydrated **molybdic oxide**, or **molybdenum sesquioxide**, or **molybdenum hemitrioxide**, Mo₂O₃. J. J. Berzelius obtained the hydrated oxide by the action of reducing agents on a soln. of a molybdenum salt or of molybdic acid. Thus, by treating a hydrochloric acid soln. of molybdenum chloride, standing over mercury, with liquid potassium amalgam, added drop by drop, the soln. becomes greenish, and then black and opaque. As soon as the oxide begins to separate, the soln. is decanted, and the hydroxide is precipitated by ammonia, washed, dried over sulphuric acid in vacuo, and heated out of contact with air. If an excess of hydrochloric acid be not present, a higher dark brown oxide is precipitated instead of the black molybdic oxide. As indicated above, this oxide was also obtained by the prolonged action of hydrochloric acid and zinc on fused or sublimed molybdenum trioxide; and also by the action of zinc on a conc. soln. of ammonium or alkali molybdate in an excess of hydrochloric acid so that the molybdic acid first precipitated is redissolved. The soln. becomes blue, then reddish-brown, and finally black. It is then poured off the zinc and mixed with enough aq. ammonia to precipitate the molybdic oxide alone. The precipitate is washed with dil. aq. ammonia to remove the zinc oxide, and afterwards with cold water. It is then pressed, dried over sulphuric acid in vacuo, and heated out of contact with air. M. Guichard found that the hydrated form alone exists because, when the black product Mo(OH)₃ is dehydrated, internal oxidation occurs, and the composition is not Mo₂O₃. Modifications of this process were used by J. Sopp, A. Atterberg, C. F. Rammelsberg, A. C. Chapman and H. D. Law, D. L. Randall, M. Guichard, A. Chilesotti, A. Werneke, F. Pisani, and I. Macagno. C. W. Blomstrand used magnesium, zinc, or zinc coated with cadmium, and sulphuric or hydrochloric acid, washing out the zinc salts by very dilute hydrochloric acid. F. von Kobell boiled lead molybdate with hydrochloric acid and copper; C. F. Rammelsberg, and H. Hirzel used ammonium molybdate or molybdic acid. C. Paal and H. Büttner found that the reduction of ammonium molybdate by colloidal palladium at ordinary temp. yields hydrated molybdenum dioxide, but at 50° to 60°, under a slight press., hydrated molybdic oxide is formed. If the reduction occurs in the presence of a protective colloid—sodium protalbinat—**colloidal molybdenum trihydroxide** is formed. L. F. Svanberg and H. Struve obtained this oxide by heating molybdenum trioxide in dry hydrogen—*vide supra*, the preparation of molybdenum—and E. F. Smith and W. S. Hoskinson, E. T. Wherry and E. F. Smith,

and E. F. Smith obtained *molybdic hydroxide*, $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or $\text{Mo}(\text{OH})_3$, by the electrolysis of a neutral soln. of ammonium molybdate, or a soln. acidified with sulphuric acid. J. J. Berzelius, and C. W. Blomstrand also obtained the hydrated oxide by adding potash-lye to a soln. of molybdenum dichloride or dibromide, and W. Muthmann and W. Nagel found that hydrogen is simultaneously evolved.

Molybdic oxide is pitch-black, and is slowly oxidized by exposure to air. In some cases J. J. Berzelius observed that when heated in vacuo, it may show a feeble calorescence—*vide* 5. 33, 10. P. Sabatier and J. B. Senderens found that when heated to about 500° in nitrous oxide, it yields a mixture of molybdenum dioxide, and trioxide; and in nitric oxide, molybdenum dioxide. J. J. Berzelius observed that it is insoluble in soln. of potassium hydroxide, ammonia, or ammonium carbonate. Acids do not dissolve the anhydrous oxide; and the hydroxide is dissolved with difficulty to form molybdic salts. F. Isambert said that soln. of the oxide in acids are black. The salts of tervalent molybdenum were studied by F. A. Gooch and O. S. Pulman, F. Pisani, C. F. Rammelsberg, and W. Wardlaw and W. H. Parker. G. Unger, G. Reissaus, and E. Müller studied the electrometric oxidation of soln. of tervalent molybdenum with permanganate. R. Montequi, and J. Koppel prepared compounds with the xanthates—*e.g.* $(\text{C}_2\text{H}_5\text{OCS}_2)_4\text{Mo}_2\text{O}_3$.

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§ 9. Intermediate Oxides— MoO_2 to MoO_3

C. F. Bucholz¹ prepared **molybdenum dioxide**, MoO_2 , by gently heating the metal for a short time in air; and J. J. Berzelius found that the lower oxide, free from zinc oxide, burns with a feeble glow when it is heated in air. L. F. Svanberg and H. Struve obtained this oxide by heating molybdenum trioxide; and H. Rose, and L. F. Svanberg and H. Struve, by heating ammonium molybdates. C. F. Rammelsberg said that the product is not homogeneous. C. F. Bucholz also heated ammonium molybdate in a covered crucible, and J. J. Berzelius added

that the dioxide so produced is contaminated with molybdenum trioxide which can be removed by potash-lye, or by hydrofluoric acid. According to E. Uhrlaub, this product, as well as that obtained by J. J. Berzelius—by igniting in a covered crucible a mixture of sodium molybdate and ammonium chloride, and washing the products with water—contains nitrides (*q.v.*). The dioxide was also obtained by L. F. Svanberg and H. Struve, D. K. Tuttle, N. J. Berlin, W. Muthmann, and M. Guichard by heating a mixture of ammonium molybdate and molybdenum trioxide, or a mixture of sodium molybdate and ammonium chloride, and washing the residue with aq. ammonia, and then with hydrochloric acid. F. Mauro and R. R. Panebianco obtained crystals of the dioxide by heating a mixture of 14.4 grms. MoO₃, 14 grms. K₂CO₃, and 7 grms. B₂O₃ for 3 or 4 hrs. at a high temp., and washing the cold mass successively with aq. ammonia, water, hydrochloric acid, and water. W. Muthmann obtained the dioxide by fusing a mixture of anhydrous ammonium molybdate, molybdenum trioxide, potassium carbonate, and boric acid in the proportions 8 : 7 : 14 : 7 by weight. H. Debray obtained an oxide, possibly the dioxide, by heating molybdenum trioxide in a mixture of steam and hydrogen. L. P. Liechti and B. Kempe reduced the trioxide to dioxide by heating it in a current of hydrogen. M. Guichard studied the equilibrium conditions in the balanced reaction: $\text{Mo} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2 + 2\text{H}_2$ —*vide supra*. C. Friedheim and M. K. Hoffmann also reduced molybdenum trioxide with hydrogen at 450°, and removed the unchanged trioxide as volatile oxychloride by heating the product in a current of hydrogen chloride. H. Debray also used a mixture of carbon monoxide and dioxide as the reducing agent. L. F. Svanberg and H. Struve obtained the dioxide by heating to redness for several hours an alkali molybdate in hydrogen and washing the product; F. Ullik heated a mixture of sodium trimolybdate and zinc, and washed product with a soln. of potassium hydroxide and then with hydrochloric acid. C. Paal and H. Büttner reduced ammonium molybdate with colloidal palladium at ordinary temp. and obtained molybdenum dioxide. W. Püttbach obtained the dioxide by heating molybdenum dioxydichloride in carbon dioxide or in hydrogen; and E. Friederich and L. Sittig by heating to about 1200° a mixture of 4.8 grms. of molybdenum powder and 14.4 grms. of molybdenum trioxide. H. Buff, and M. Guichard obtained the dioxide by the electrolysis of fused molybdenum trioxide, or potassium molybdate; and L. Ott, by the electrolysis of molten sodium or barium molybdate using a high current density.

Analyses in agreement with the formula MoO₂ were made by J. J. Berzelius, C. F. Bucholz, F. Ullik, and M. Guichard. Molybdenum dioxide is described by L. F. Svanberg and H. Struve as a brownish-black powder; L. Ott, as a violet crystalline powder; and F. Ullik, as forming dark bluish-violet prisms which appear pale violet-red in transmitted light. F. Mauro and R. R. Panebianco said that the bipyramidal crystals are tetragonal with the axial ratio $a : c = 1 : 0.5774$; but S. Stevanovic showed that the pseudotetragonal crystals are monoclinic prisms with the axial ratios $a : b : c = 0.9869 : 1 : 0.5765$, and $\beta = 91^\circ 34'$. V. M. Goldschmidt and co-workers, M. L. Huggins, and L. Pauling discussed the lattice-structure. The X-radiogram shows that the space-lattice is of the rutile-type with $a = 4.86$ Å., and $c = 2.79$ Å., so that $a : c = 1 : 0.573$. S. Stevanovic gave for the sp. gr. 6.34; and F. Mauro and R. R. Panebianco, 6.44. W. Biltz studied the mol. vol. N. Parravano and G. Malquori gave for the dissociation press., $\log p = -27.843$ at 600°. W. G. Mixer gave 142.8 Cals. for the heat of formation from its elements. B. A. Dima studied the photoelectric effect of the oxide. J. Vrede observed that the dioxide has no value as a radio-detector. F. Ullik, and M. Guichard observed that it is a good electrical conductor; E. Friederich and L. Sittig gave 40.0×10^{-4} ohm for the resistance of a metre wire 1 sq. mm. cross-section at 1000°; and the temp. coeff. is negative; and E. Wedekind and C. Horst found that its magnetic susceptibility is greater than that of the metal, being 0.33×10^{-6} mass unit at 19.5°. S. Berkman and H. Zocher gave 0.09×10^{-6} mass unit.

M. Guichard found that the oxide is reduced by hydrogen to the metal without

the formation of intermediate oxides—a subject discussed by G. Martin. The equilibrium conditions were studied by M. Guichard—*vide supra*. G. Chaudron studied the equilibrium conditions in the reaction: $2\text{H}_2\text{O} + \text{Mo} \rightleftharpoons \text{MoO}_2 + 2\text{H}_2$ over the temp. range 700° to 1100° . H. Debray found that water vapour at a red-heat oxidizes the dioxide to the trioxide; H. Rose found that chlorine converts the dioxide into the dioxydichloride; and A. Vandenberghe, and C. Friedheim and M. K. Hoffmann, that it does not volatilize when heated in hydrogen chloride. J. J. Berzelius found that the dioxide is not soluble in hydrofluoric, hydrochloric or sulphuric acid. W. R. E. Hodgkinson and F. K. S. Lowndes found that if a little dioxide be added to molten potassium chlorate, oxygen and chlorine are evolved. J. J. Berzelius said that a little dioxide dissolves in boiling, conc. sulphuric acid; and it dissolves slowly in fused alkali hydrosulphate. It is converted by nitric acid into the trioxide. C. Friedheim and M. K. Hoffmann observed that the dioxide is decomposed when heated in carbon dioxide; and A. Michael and A. Murphy, that carbon tetrachloride converts it into molybdenum tetrachloride. W. Skey, and E. Péchard observed that thiocyanates produce a red coloration with the dioxide. J. J. Berzelius found that the dioxide does not dissolve in a boiling soln. of potassium hydrotartrate. G. Rauter found that silicon tetrachloride has no action on the dioxide. J. J. Berzelius found that the dioxide is insoluble in soln. of alkali hydroxide or carbonate. F. Ullik observed that a crystal of molybdenum dioxide in a soln. of copper sulphate, and in contact with zinc, quickly becomes covered with a film of copper. E. F. Smith and O. L. Shinn found that a mol of the dioxide liberates two gram-atoms of silver from an ammoniacal soln. of silver nitrate: $\text{MoO}_2 + 2\text{Ag}^+ \rightarrow \text{MoO}_3 + 2\text{Ag}$, etc.; salts of copper and mercury are not so reduced. C. Friedheim and M. K. Hoffmann found that ferric sulphate oxidizes the dioxide to trioxide. The electrometric oxidation of soln. of quadrivalent molybdenum by permanganate was studied by G. Unger, E. Fricke, G. Reissaus, and E. Müller. C. Engler and L. Wöhler discussed molybdenum dioxide as a catalytic agent. M. Guichard was at first inclined to believe that the dioxide does not form salts, although J. J. Berzelius, H. Rose, and others have described a series of salts.

J. J. Berzelius, H. Rose, and C. F. Rammelsberg described what they considered to be hydrated molybdenum dioxide, obtained by adding alkali-lye to soln. of more or less reduced molybdic acid. P. Klason showed that in all probability these products are impure molybdenum pentahydroxide, and that the tetrahydroxide does not exist.

This remark applies to the so-called *monohydrate*, $\text{MoO}_2 \cdot \text{H}_2\text{O}$, of E. Péchard, produced by the electrolysis of a hydrochloric or oxalic acid soln. of ammonium molybdate; or by adding alkali-lye to a hydrochloric acid soln. of alkali molybdate mixed with potassium iodide; and to the *dihydrate*, $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$, reported to be formed by adding ammonia to a hot hydrochloric acid soln. of acid ammonium molybdate and potassium iodide. O. W. Gibbs obtained some complexes with tungstic acid—*e.g.* $5\text{K}_2\text{O} \cdot 12\text{WO}_3 \cdot \text{MoO}_2 \cdot 16\text{H}_2\text{O}$. The *trihydrate*, $\text{MoO}_2 \cdot 3\text{H}_2\text{O}$, was said by F. J. Faktor to be produced by the action of sodium thiosulphate on a soln. of ammonium molybdate; and G. Krüss obtained the *hemihydrate*, $2\text{MoO}_2 \cdot 15\text{H}_2\text{O}$, by the action of conc. alkali-lye on the oxysulphide, $(\text{NH}_4)\text{H} \cdot \text{Mo}_2\text{O}_4\text{S}_4$.

C. Paal and co-workers, however, found that a soln. of ammonium paramolybdate in the presence of a little colloidal palladium is reduced at room temp. by hydrogen at normal press. to form a greenish-black precipitate approximating the monohydrate, $\text{MoO}_2 \cdot \text{H}_2\text{O}$, or $\text{MoO}(\text{OH})_2$, when dried at ordinary temp., and it yields the dioxide, MoO_2 , if dried at a higher temp. If the reduction occurs in the presence of a protective colloid—sodium protalbinat—**colloidal molybdenum tetrahydroxide** is formed at ordinary temp. H. Freundlich and W. Leonhardt found that the monohydrate obtained by E. Péchard—by precipitation with alkali hydroxide from the soln. produced by the action of potassium iodide on hydrochloric acid soln. of alkali molybdate or by the electrolysis of hydrochloric or oxalic acid soln. of molybdic acid—behaves towards water like a colloid. The

coagulated dioxide shows differences in the readiness with which it undergoes peptization, in that the sol form is more readily produced from coagulates which have been precipitated by the less active electrolytes. Low temp. is also favourable to the re-formation of the sol. The coagulation by electrolytes depends on the cation.

According to W. Muthmann, the compound **magnesium hypomolybdate**, $2\text{MgO} \cdot 3\text{MoO}_2$, is formed by fusing sodium trimolybdate with magnesium oxide; and zinc oxide similarly furnishes **zinc hypomolybdate**, $2\text{ZnO} \cdot 3\text{MoO}_2$.

J. J. Berzelius digested in a stoppered flask, at 40° – 60° , a mixture of powdered molybdenum and a soln. of molybdic acid; the soln. became dark blue, and finally green. The addition of ammonium chloride to the green soln. precipitates an olive-green oxide which redissolves in water—presumably as a peptized colloid. A soln. of the brown and blue molybdenum oxides in hydrochloric acid precipitates a green oxide on the addition of ammonia. C. F. Bucholz obtained a pale blue oxide which J. J. Berzelius supposed to be the same as the green oxide. W. Muthmann could not prepare an olive-green oxide of constant composition. J. Reich obtained the blue soln. by the action of lead on a soln. of molybdic acid; and the green soln. by the electrolysis of a soln. of 2 grms. of molybdenum trioxide in aq. ammonia mixed with sulphuric acid and diluted with water, by means of platinized platinum electrodes and a current density of 0.5 amp. per sq. dm. Many blue oxides have been reported, and the differences in the analysis probably turn on the presence of variable proportions of molybdenum trioxide. M. Guichard added that if the trioxide be removed by successive washing with soda and hydrochloric acid, molybdenum dioxide is the sole oxide formed by the action of heat on a mixture of molybdenum trioxide and ammonium molybdate, or by the electrolysis of fused molybdenum trioxide.

According to W. Muthmann, the blue oxide which is formed by the action of reducing agents on soln. of molybdic acid, or by boiling molybdenyl sulphate with powdered molybdenum, is **molybdenum tritrioxide**, Mo_3O_8 . The olive-green oxide prepared by J. J. Berzelius is probably a mixture of this oxide with the tetrahydroxide, $\text{Mo}(\text{OH})_4$. If a soln. of molybdenum in conc. sulphuric acid be heated to a high temp., a mixture of the tritrioxide and trioxide is formed. A. Rogers and F. H. Mitchell obtained the tritrioxide by adding stannous chloride to a soln. of ammonium molybdate slightly acidified with nitric acid; washing the precipitate as quickly as possible; and drying it at 100° . According to L. A. Munro, by the addition of excess of stannous chloride, a green and then brown soln. can be obtained due to further (reversible) reduction. Molybdenum-blue forms a (negative) colloidal soln. which can be bleached by animal charcoal, partly by absorption and partly by oxidation. It can also be obtained in the crystalloidal form by dialyzing the colloidal soln., precipitating the hydrogel with ammonium chloride, and evaporating the remaining soln. E. J. Millard obtained the blue oxide by adding a soln. of ammonium molybdate and a little sulphurous acid to a soln. of hypophosphite; H. Buff, by the electrolysis of molten molybdenum trioxide with platinum electrodes; C. F. Rammelsberg, by heating ammonium molybdenum dioxymolybdate in a closed vessel; C. Bärwald, by melting a mixture of ammonium peroxy-molybdate and molybdenum trioxide in a closed vessel; and N. J. Berlin, by melting a mixture of ammonium 3:7-molybdate and molybdenum trioxide in a covered crucible, and washing the product with aq. ammonia—E. Uhrlaub said that the product is contaminated with nitride. Analyses in agreement with Mo_3O_8 were made by W. Muthmann, C. Bärwald, N. J. Berlin, and C. F. Rammelsberg. L. A. Munro found that the formula obtained by analysis of the hydrogel is approximately $\text{Mo}_3\text{O}_8 \cdot \text{H}_2\text{O}$, but since the substance is readily soluble in alcohol the water is probably not combined as hydrate; hence the true formula is Mo_3O_8 . This oxide was said by H. Buff to form copper-red crystal plates; and by C. Bärwald, a bluish-violet crystalline powder. H. Buff observed that the oxide is a good conductor of electricity, and that in air it acquires a bluish film. A. Rogers and

F. H. Mitchell said that the oxide is more easily reduced by hydrogen than is molybdenum trioxide. W. Muthmann said that the tritooxide is not attacked by hydrochloric and sulphuric acids, or by aq. ammonia; it is easily oxidized by nitric acid; and it is decomposed by alkali-lye. According to J. Duclaux and R. Titéica, molybdenum blue is an acid comparable in strength with mineral acids, the colloidal anion of which contains molybdenum in two states of oxidation and is capable of union with metallic ions to form salts. Molybdenum-blue is peculiar in its solubility in a large number of organic solvents, whilst it is insoluble in all liquids of low dielectric constant. When certain organic solvents are shaken with an aq. soln. of molybdenum-blue, the aq. soln. is almost immediately decolorized, the molybdenum compound passing into the organic liquid phase. This is the first example recorded of a colloid passing from one solvent into another; glycerol appears to be the best solvent. The solubility in butyl alcohol provides a rapid means of purifying molybdenum-blue by extraction of the aq. soln.

H. Höfer² described a complex molybdenum oxide which he found embedded in the barytes and wulfenite at Bleiberg, Carinthia. It appeared to have been formed by the decomposition of the metal molybdates by acidic waters. W. T. Schaller suggested that it is formed by the alteration of molybdenite, jordisite, wulfenite, and molybdosodalite. H. Höfer called the mineral **ilsemannite**—after J. C. Ilsemann. Ilsemannite is bluish-black or black, and cryptocrystalline. It becomes blue on exposure to air, and it has been called *natural molybdenum blue*. It forms a deep blue soln. with water; and the aq. soln. yields blue crystals on evaporation. H. Höfer considered it to have the composition of J. J. Berzelius' $\text{MoO}_2 \cdot 4\text{MoO}_3$; C. F. Rammelsberg gave the formula Mo_2O_5 , or $\text{MoO}_2 \cdot \text{MoO}_3$. W. Muthmann said that its composition is not Mo_5O_{14} , as supposed by H. Höfer, but is nearer to Mo_3O_8 . More probably, ilsemannite is a mixture. F. Cornu represented it as **colloidal molybdenum tritooxide**, $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$, and added that it is the only reversible colloid occurring in nature. The subject was discussed by A. Himmelbauer, E. Dittler, F. L. Hess, H. F. Yancey, and C. W. Greenland. W. T. Schaller obtained from Ouray, Utah, a mineral of the composition $\text{MoO}_3 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$, which he called ilsemannite, but H. F. Yancey did not agree that this represents the composition of ilsemannite. E. Dittler supposed ilsemannite to be an oxidation product of molybdenite. When molybdenum sulphate soln. are treated with ferrous sulphate, free molybdenum trioxide separates. This when washed contains no iron or sulphate, but is reduced to $\text{Mo}_3\text{O}_8 \cdot \text{H}_2\text{O}$. Some varieties are free from iron, so that W. T. Schaller's hypothesis is based on samples in which the sulphate was an accidental constituent.

W. Biltz³ prepared colloidal molybdenum tritooxide, and found that the hydrosol passes to the anode on electrolysis. A. Dumansky showed that when molybdenum trioxide suspended in water, is heated on a water-bath with a large excess of powdered metallic molybdenum, a soln. of the oxide Mo_3O_8 is obtained, which, according to cryoscopic measurements, contains unpolymerized mols. of the oxide. On addition of ammonium chloride, barium chloride, and other salts to this soln., polymerization takes place, and the oxide passes into the colloidal form. W. Biltz found that the colloid is adsorbed from its sol by fibres of cotton, wool, and especially silk. C. Winssinger observed that the absorption spectrum is similar to that produced by colloidal molybdenum sulphide.

C. F. Bucholz prepared what appears to have been the colloidal *pentahydrate* of molybdenum tritooxide by exposing moist molybdenum, or the hydrated trioxide to air for a long time, or boiling these substances with water in an open vessel. He also made it by boiling in water a mixture of molybdenum with twice its weight of molybdenum trioxide, and evaporating the blue soln. out of contact with air, or in contact with molybdenum. J. J. Berzelius prepared this hydrate by mixing a soln. of molybdenum dioxide in hydrochloric acid with a soln. of ammonium 3:7-molybdate, and collecting the precipitated oxide which is washed, first with water containing ammonium chloride, and then with alcohol or cold water.

It is dried in air. O. Maschke dissolved calcium molybdate in warm, dil. hydrochloric acid and added sucrose or glucose, boiled the mixture for a few minutes, added a soln. of sodium or calcium chloride, and washed the precipitate first with the precipitant and then with a little water. G. Marchetti dissolved molybdenum in conc. aqua regia, and after all the nitric acid had been expelled by evaporating the soln. on a water-bath, with the addition of hydrochloric acid, diluted the filtered soln., and reduced it by an electric current. The dark blue liquid yields crystals of the pentahydrate. C. F. Bucholz described his product as a dark indigo-blue powder; and G. Marchetti obtained dark blue, almost black, triclinic crystals. J. J. Berzelius said that all the water can be driven off by heating the crystals in vacuo. C. F. Bucholz said that the salt is fairly soluble in water forming a blue soln. which, according to G. Marchetti, does not give a precipitate on adding ammonium chloride. Cryoscopic determinations show that in aq. soln. the pentahydrate is neither ionized nor polymerized. J. J. Berzelius said that the aq. soln. becomes paler in air owing to oxidation. Alcohol dissolves a little of the hydrated oxide. O. Maschke found that the aq. soln. is easily decolorized by alkalis, chlorine, nitrous acid, hydrogen dioxide, permanganic acid, etc. L. Schön said that the blue soln. is first decolorized by hydrogen dioxide, and then forms a yellow liquid. According to G. Marchetti, aq. ammonia, and alkali-lye extract molybdenum trioxide and leave the dioxide; whilst very dilute alkali-lye dissolves all the oxide, and when the soln. is boiled, it deposits molybdenum dioxide. Acids do not appear to form salts. C. F. Rammelsberg obtained **ammonium dimolybditetramolybdate**, $(\text{NH}_4)_2\text{O} \cdot 2\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{O} \cdot (\text{Mo}_3\text{O}_8)_2 \cdot 9\text{H}_2\text{O}$, as brown crystals under the blue precipitate by allowing a mixed soln. of molybdenum dioxide and ammonium molybdate in hydrochloric acid to stand for some time. The brown crystals form a brown soln. with water, and the addition of silver nitrate to the soln. gives a yellow precipitate soluble in nitric acid. The salt gives off water and ammonia when heated.

According to C. F. Rammelsberg,⁴ the precipitate formed on mixing a hydrochloric acid soln. of molybdenum dioxide and molybdic acid, when washed with an alcoholic soln. of ammonium chloride, and dried over sulphuric acid, is the *trihydrate* of **molybdenum hemipentoxide**, $\text{Mo}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, or $\text{MoO}(\text{OH})_3$. J. Reich said that the electro-reduction of a soln. of 2 grms. of molybdenum trioxide in 11 grms. of sulphuric acid, and 100 c.c. of water with a current density of 0.005 amp. per sq. dm., and 0.49 volt gives a blue deposit of the hemipentoxide. P. Klason made it by adding exactly three mols of ammonia to an aq. soln. of a mol of ammonium molybdenyl chloride. The precipitate resembles freshly-precipitated ferric hydroxide, only it is brighter in colour; sodium acetate can also be used as a precipitant. It is soluble in water to the extent of 2 parts in 1000, but insoluble in the presence of ammonium chloride; it has no acid properties, since it does not dissolve in aq. alkali hydroxides, and is only slightly soluble in ammonia and alkali carbonates. If in its preparation an excess of ammonia be used, the hydroxide is partially decomposed, and the filtered soln. contains much molybdic acid, as stated by H. Debray. P. Klason added that molybdenum blue does not contain molybdenum dioxide as assumed by M. Guichard, but rather the hemipentoxide. The anhydrous oxide, Mo_2O_5 , was obtained by C. F. Rammelsberg, by dehydrating the hydrate in vacuo; or, in a current of carbon dioxide. E. Péchard obtained it by heating a mixture of ammonium molybdate, potassium iodide, and hydrochloric acid. E. Friederich and L. Sittig obtained the hemipentoxide by heating to about 1200° a mixture of 2.4 grms. of molybdenum powder and 18 grms. of molybdenum trioxide. E. Friederich gave 9.5 ohms for the resistance of a metre wire 1 sq. mm. cross-section. E. F. Smith and V. Oberholtzner treated the trioxide at 105° – 120° with dry hydrogen iodide, and obtained a blue *hemitrihydrate*, $\text{Mo}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$, which was stable in air, and at a red-heat furnished brown hemipentoxide. W. Wardlaw and F. H. Nicholls obtained molybdenum hemipentoxide, Mo_2O_5 , by heating the oxysulphate, $\text{Mo}_2\text{O}(\text{SO}_4)_2 \rightarrow \text{Mo}_2\text{O}_5 + 2\text{SO}_2$, or the oxyoxalate, $\text{Mo}_2\text{O}(\text{C}_2\text{O}_4)_2 \rightarrow \text{Mo}_2\text{O}_5$

+4CO. In opposition to the statement of M. Guichard, the pentoxide is almost unchanged when boiled five successive times in aq. ammonia, washed with distilled water, and dried at 100°. A little molybdenum passes into soln., but there is no evidence that the product is impure dioxide. J. Vrede found the oxide has no value as a radio-detector; and W. Meissner, that it is not a super-conductor. E. Friederich and L. Sittig, found the sp. resistance of the dark violet hemipentoxide to be 9.5×10^{-4} ohm at 1000°, and the temp. coeff. is negative. A. Schulze discussed the super-conducting qualities of the oxide. E. Newbery and J. N. Pring found that the pentoxide is reduced to the monoxide by hydrogen at 2000° and 150 atm. press. The violet-black powder, said E. Péchard, is easily soluble in water, and when hydrogen dioxide is added to the dark blue aq. soln., the colour becomes green, and then yellow. P. Klason, and W. Wardlaw and F. H. Nicholls, said that the hemipentoxide dissolves with difficulty in hydrochloric and sulphuric acids, and this the more slowly, the higher the temp. of preparation. G. Reissaus, E. Fricke, G. Unger, and E. Müller studied the electrometric oxidation of soln. of quinquevalent molybdenum with permanganate. S. Ghosh and N. R. Dhar studied the sensitization of the negative colloid, by other colloids. G. A. Barbieri studied the action of molybdenum hemipentoxide on formic and oxalic acids. P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado studied the dehydrating action on ethyl alcohol. P. Sabatier and A. Mailhe, and J. N. Pearce and A. M. Alvarado observed that this oxide acts catalytically in decomposing formic acid into carbon dioxide, carbon monoxide, water, and hydrogen; and formaldehyde, into carbon dioxide and water. The hemipentoxide was also prepared by F. Mawroff and M. Nikoloff, who also observed that when the violet molybdenum oxyhypophosphite is rubbed with aqua ammonia, the yellowish-brown precipitate can be washed and dried. It dissolves sparingly in water, and the aq. soln. has a neutral reaction. If dissolved in acids, and precipitated by ammonia, and washed with dil. aq. ammonia and then with absolute alcohol, the residue has the composition of **ammonium molybdenum hemipentoxide**, $\text{NH}_4\text{Mo}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, which, when ignited in a current of carbon dioxide, yields molybdenum pentoxide. If sodium hydroxide soln. be used in place of ammonia, **sodium molybdenum hemipentoxide**, $\text{NaMo}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, is formed, and this, on ignition, yields the anhydrous form NaMo_2O_5 . Similarly also with the hydrate **barium molybdenum hemipentoxide**, $\text{BaMo}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, and the anhydrous BaMo_2O_5 .

J. J. Berzelius⁵ obtained what he regarded as **molybdenum pentitadecadecoxide**, Mo_5O_{14} , or $\text{MoO}_2 \cdot 4\text{MoO}_3$, by heating molybdenum or one of the lower oxides in air for a short time. C. F. Rammelsberg obtained the *hexahydrate* by allowing an aq. soln. of molybdic acid to stand in contact with reduced molybdenum for some days, and then shaking up the filtered, blue liquid with an excess of molybdenum for some days. M. Guichard said that this compound is best obtained by mixing cold, dil. hydrochloric acid soln. of molybdenum dioxide and ammonium molybdate; the hydrochloric acid should be that of sp. gr. 1.18 diluted with 9 parts of water, this bringing about complete precipitation without decomposition. A more conc. acid decomposes the oxide. The product thus obtained is nearly insoluble in cold water, although that prepared by C. F. Rammelsberg, by precipitation at 50°, is easily soluble; an aq. soln. of the oxide is readily obtained by leaving molybdenum trioxide and metallic molybdenum in contact in water. The oxide obtained by precipitation is a dark blue powder of sp. gr. 3.6 at 18°; by the evaporation of its soln., it is obtained in vitreous, faceted fragments, which yet are not truly crystalline. It dissolves in water at 50°, but is insoluble in sat. soln. of ammonium, sodium and calcium chlorides, and potassium iodide and nitrate; sodium and magnesium sulphate do not alter its solubility. It dissolves in 95 per cent. alcohol, although it is insoluble in most organic solvents. When heated in vacuo or an inert gas, it loses part of its water at 100°, and the rest near a red-heat, a non-homogeneous mixture of molybdenum dioxide and trioxide being formed. Hydrogen ultimately reduces it to the metal; chlorine yields the volatile

oxychloride, MoO_2Cl_2 , and molybdenum trioxide. Contrary to J. J. Berzelius' statement, it slowly oxidizes in the air, and at a red-heat oxygen rapidly converts it into the trioxide. Gaseous hydrogen chloride at a red-heat and superheated steam decompose it, giving mixed dioxide and trioxide; gaseous ammonia gives initially the same result, but at a red-heat reduces the oxides to the metal. Acetic acid does not affect it; by conc. hydrochloric acid, it is dissolved to a yellowish-red soln. of molybdenum tetrachloride, but the action is a reversible one, since, on diluting with water, the blue oxide is precipitated. With sulphuric acid, a like result is obtained. K. von der Heide and K. A. Hofmann reported **ammonium molybditetramolybdate**, $(\text{NH}_4)_2\text{O} \cdot \text{MoO}_2 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, to be formed by heating an aq. soln. of ammonium molybdate with half its weight of hydroxylamine hydrochloride on the water-bath until the orange precipitate which is at first formed is dissolved, and a greenish-brown soln. is obtained; this soln. is then rapidly filtered, protected from access of air, and allowed to cool. The compound separates in dark red crystals belonging to the triclinic system; dissolves gradually in water with a reddish-yellow coloration; and is fairly stable. It gradually reduces Fehling's soln. in the cold and quickly when heated. With copper sulphate, it gives a beautiful, blue coloration; with mercurous and mercuric salts, a flesh-coloured precipitate; with lead nitrate, a yellowish-white precipitate; and with potassium thiocyanate, an intense red coloration. It is gradually decomposed by dil. acids, and it reduces ammoniacal silver soln. with the separation of metallic silver. Other ammonia derivatives with the lower oxides of molybdenum, analogous to the chromamine bases, could not be prepared.

P. Klason⁶ obtained a soluble oxide $\text{Mo}_{20}\text{O}_{41} \cdot 21\text{H}_2\text{O}$, or $\text{Mo}_2\text{O}_5 \cdot 18\text{MoO}_3 \cdot 21\text{H}_2\text{O}$, by exposing an aq. soln. of ammonium molybdenyl chloride to air. The solid furnishes a blue soln. with water, and it is precipitated by adding ammonium chloride. According to W. Muthmann, the oxide Mo_5O_{12} , first described by N. J. Berlin, is obtained by heating a mixture of ammonium molybdate with twice its weight of molybdenum trioxide. The product is repeatedly extracted with ammonia, and finally with conc. hydrochloric acid to remove a compound of molybdenum and nitrogen. This oxide is not attacked by alkali-lye, but it dissolves in warm conc. sulphuric acid, forming a green soln., which easily parts with sulphur dioxide, and turns blue. Nitric acid, aqua regia, and chlorine-water convert Mo_5O_{12} into the trioxide. H. O. Schulze obtained Mo_4O_{11} , or $\text{Mo}_2\text{O}_5 \cdot 2\text{MoO}_4$, by heating a mixture of potassium iodide and molybdenum trioxide; G. Bailhache, the *hexahydrate* $\text{Mo}_{20}\text{O}_{57} \cdot 18\text{H}_2\text{O}$, or $2\text{Mo}_2\text{O}_5 \cdot 2\text{Mo}_7\text{O}_{24} \cdot 18\text{H}_2\text{O}$, by the action of barium 3:7-molybdate on $\text{Mo}_2\text{O}_5 \cdot 2\text{SO}_4$; A. Junius, Mo_7O_{20} , by the electrolysis of a hydrochloric acid soln. of ordinary ammonium paramolybdate, or of sodium molybdate; and P. Klason, $\text{Mo}_{26}\text{O}_{77} \cdot 24\text{H}_2\text{O}$, or $\text{Mo}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot 24\text{H}_2\text{O}$, by exposing an aq. soln. of ammonium molybdenyl chloride to oxidation by air for several months. There is nothing to show that these products are not merely arbitrary intermediate stages in the reduction of molybdenum trioxide. Some suggestions have been made for the use of the blue oxides of molybdenum as pigments—*vide supra*, the uses of molybdenum. Hydrosols of *molybdenum blue* were found by P. Lal and P. B. Ganguly to be coagulated by ultra-violet light.

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The soluble molybdic acid of F. Ullik is probably identical with T. Graham's colloidal molybdic acid. F. Ullik prepared it by treating a thin mush of barium molybdate with enough sulphuric acid to precipitate the barium as sulphate. The filtrate is treated with barium chloride and hydrochloric acid, and again with sulphuric acid. The colourless soln., when evaporated over sulphuric acid, dries to an amorphous powder. This is soluble in water when freshly prepared, but with ageing it becomes insoluble. If the soln. be evaporated on a water-bath, and dried at 100°, or if magnesium molybdate be treated with an excess of nitric acid, and the washed powder dried at 100°, the composition of the product approximates $\text{MoO}_3 \cdot n\text{H}_2\text{O}$, where n lies between 0.20 and 0.22. L. S. Bhatia and co-workers, and W. V. Bhagwat and N. R. Dhar studied the coagulation of colloidal molybdic acid. E. F. Krauze and A. V. Novoseloff considered that the adsorption of molybdic acid by porous clay tubes covered with collodion is a mechanical process in which large aggregates are held in the pores. The adsorption is preceded by a process of complex formation.

J. J. Berzelius obtained small, silky, crystalline scales by the spontaneous evaporation of a soln. of molybdenum or one of its lower oxides in an excess of nitric acid. The product lost on ignition about 2 per cent. of water. The existence of two definite hydrates has been established. G. F. Hüttig and B. Kurre measured the dissociation temp. of the hydrates, starting from the yellow precipitate from a nitric acid soln. of ammonium molybdate. The results, plotted in Fig. 12, show that these two hydrates exist as chemical individuals. The white α -monohydrate differs from the yellow dihydrate, even in aq. soln. A. Mazzucchelli and M. Borghi showed that the α -monohydrate is readily obtained by treating methyl molybdate with water. Its behaviour with tartaric acid and hydrogen dioxide is analogous to that of the yellow acid, but the rotary powers of soln. of the same composition are different, and the maximum corresponds with the existence of a compound $\text{C}_4\text{H}_4\text{O}_6 \cdot 5(\text{MoO}_3 \cdot \text{H}_2\text{O}_2)$, thus affording a further proof of the difference between the two acids.

The monohydrate of molybdic oxide, $\text{MoO}_3 \cdot \text{H}_2\text{O}$, is considered to be a kind of metamolybdic acid, H_2MoO_4 , because the X-radiograms of H. C. Burger show that the angles of reflection are different from those of molybdenum trioxide. F. Ullik prepared this hydrate by treating a mol of magnesium molybdate with 2 mols of nitric acid, and allowing the white powder to stand for some time when prismatic crystals are formed. L. C. A. Vivier found that white crystals of this hydrate separated from a soln. of ammonium molybdate in nitric acid, and from a soln. of an ordinary molybdate on standing for several days at 50° to 60°. F. Ephraim and M. Brand obtained the monohydrate as a precipitate on mixing a soln. of a mol of normal lithium molybdate with 7 mols of nitric acid of sp. gr. 1.20, while warmed on a water-bath. A. Rosenheim and A. Bertheim obtained it by warming the dihydrate to 70°. A. Rosenheim and I. Davidsohn designate this the β -monohydrate to distinguish it from the α -monohydrate which is formed in asbestos-like, white needles when a soln. of the dihydrate is kept at 40°-50°. The β -form occurs in small white needles. The α -form differs from the β -hydrate in having a more definite crystal habit, and in the rapidity with which it settles from a suspension in water. The α -hydrate is also said to lose its water of crystallization more readily than the β -form. L. C. A. Vivier said that the monohydrate forms crystals which are probably hexagonal. A. Rosenheim and I. Davidsohn found the solubility of the α -monohydrate, S grms. MoO_3 per 100 grms. of water:

	14.8°	24.6°	36.8°	45.0°	52.0°	60.0°	70.0°	80.0°
S	0.2117	0.2619	0.3085	0.3661	0.4184	0.4685	0.4231	0.5212

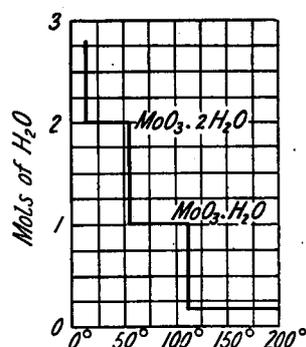


FIG. 12. — Dissociation Temperatures of the Hydrates of Molybdenum Trioxide.

At about 60°, there is a break in the curve, indicating that the α -monohydrate is transformed into the β -variety. The mol. conductivity, μ mhos, of the soln. of the α -monohydrate closely resembles that of methyl molybdate. For soln. with a mol of the α -monohydrate in v litres, at 25°,

v	.	.	31.3	62.6	125.2	250.4	500.8	1001.7
μ	.	.	71.4	89.4	95.2	96.9	100.3	104.1

Cryoscopic determinations show that the molybdic acid in the α -monohydrate has a smaller mol. wt. than is the case with the dihydrate. The rate of hydrolysis of methyl molybdate shows that the α -monohydrate is a weaker acid than the dihydrate.

According to A. Travers and L. Malaprade, cold, aq. soln. of the mono- or di-hydrate of molybdenum trioxide differ from soln. made at 100° and cooled, both in colour, and in their reactions with potassium ferrocyanide. It is assumed that both molybdic acid, $H_2[MoO_4]$, and tetramolybdic acid, $H_2[4MoO_3 \cdot O]$, are present in the soln., and that the latter ionizes: $H_2O \cdot 4MoO_3 \rightleftharpoons 2H^+ + [4MoO_3 \cdot O]$. This is confirmed by the neutralization curve which shows inflexions at $4MoO_3 \cdot K_2O$ and $MoO_3 \cdot K_2O$, the first resulting from the complete neutralization of the acid $4MoO_3 \cdot H_2O$, and the second from the decomposition of the salt formed first by the alkali. In support of this, the reactions of the tetramolybdate are found to be quite different from those of the neutral salt. From the analogy with the tungstic acids, $4MoO_3 \cdot H_2O$ is called metamolybdic acid. S. I. Diatschkovsky and A. V. Dumansky showed that with soln. of 10 eq. of sodium molybdate and 10 eq. of hydrochloric acid, the complex tetramolybdate, $Na_2O(MoO_3)_4$, was formed; with 12 eq. of acid, $Na_2O(MoO_3)_8$ was produced. This soln. does not coagulate at 100° nor when electrolytes are added.

M. Jungck, and S. Kern made some observations on the yellowish crystalline substance which separates when a soln. of an alkali molybdate in nitric acid is allowed to stand for a time. F. Parmentier showed that the deposit is the *dihydrate* of molybdic acid, $MoO_3 \cdot 2H_2O$, or, if H_6MoO_6 be orthomolybdic acid, it can be regarded as **paramolybdic acid**, H_4MoO_5 , although the term para-molybdate is usually applied to a salt of another molybdic acid. The dihydrate is not formed in hydrochloric acid soln. of the alkali molybdates. J. H. Graham, and A. A. Blair and J. E. Whitfield also found that the yellow deposit from the nitric acid soln. of alkali molybdate is dihydrated molybdenum trioxide. J. Terwelp obtained the dihydrate in the anode chamber during the electrolysis of soln. of molybdates. A. Rosenheim obtained it by pouring a soln. of 15 grms. of commercial (3 : 7)-ammonium molybdate in a litre of water with constant stirring to 29–30 per cent. nitric acid (300 c.c. of nitric acid of sp. gr. 1.42 diluted to a litre), and allowing the soln. to stand at 20°–25° for 8 to 10 days after inoculation with a crystal of the dihydrate. F. Parmentier, and L. C. A. Vivier observed that the lemon-yellow, prismatic crystals are monoclinic; and A. de Schulten added that the axial ratios are $a : b : c = 1.0950 : 1 : 1.0664$, and $\beta = 90^\circ 41'$. The angle between the basal plane and the orthopinacoid, *i.e.* (001) : (100), is $89^\circ 19'$, making the crystals appear at first glance as though they were cubes. The sp. gr. is 3.124 at 15°. F. Parmentier said that the crystals are efflorescent and lose half their water over sulphuric acid, in vacuo; and at 200°, they lose all their water. A. Rosenheim and A. Bertheim found that the dihydrate cannot be regenerated after it has been converted at 70° into the monohydrate.

E. Bruchhaus examined the reduction of ammonium molybdate by hydrogen. The solubility, S grms. of MoO_3 in 100 grms. of water, is,

	18°	23°	40°	50.2°	60°	70°	75°	79°
S	0.1066	0.1856	0.4761	0.6873	1.2057	2.0550	2.0920	2.1064

There is a marked break in the solubility curve at 70° corresponding with the transformation of the dihydrate into the monohydrate. A. Rosenheim and

I. Davidsohn found that the solubility curves of the dihydrate and the α -monohydrate intersect at 32° ; and A. Rosenheim and A. Bertheim showed that there is a change in the direction of the solubility curve of the dihydrate at 50° , and possibly below 18° another change of direction occurs. The solubility determined by saturating at a particular temp. is lower than that obtained by saturating at a higher temp. and then cooling in contact with solid. This anomalous behaviour seems not to be due to the formation of a colloidal soln., because the apparently supersaturated soln. diffuses quite readily. The cryoscopic observations of A. Rosenheim and A. Bertheim showed that the mol. wt. approximates $(\text{MoO}_3)_4$; and those of A. Mazzucchelli and G. Zangrilli, $(\text{MoO}_3)_6$. The solubility of the dihydrate is greatly increased by the addition of ammonium salts; e.g. with a 10 per cent. soln. of ammonium hydrosulphate, the solubility, S grms. of MoO_3 per 100 grms. of solvent, is 1.927 at 29.6° ; 2.753 at 31.5° ; 3.436 at 41.8° ; and 3.769 at 49.7° . This is taken to mean that the dihydrate is not a colloid. The mol. conductivity, μ mhos, of soln. with a mol of the dihydrate in v litres of water, at 25° , is,

v	. . .	16.56	33.12	66.24	132.48	264.96	529.92	1059.84
μ	. . .	98.28	130.10	150.0	159.7	163.5	168.7	180.3

Acetic acid and boric acid exert scarcely any influence on the conductivity of molybdic acid soln. Tartaric acid, malic acid, and mannitol greatly increase the conductivity, and this is attributed to the formation of a complex molecule. On account of hydrolysis of the complex molecule at high dilution, the increase of the conductivity diminishes somewhat with the dilution. Oxalic acid and iodic acid, which form complex molecules with molybdic acid, which can be isolated, diminish the conductivity, but this may be due to the complex ion having a smaller speed of migration. Phosphoric acid also increases the conductivity, the maximum being reached when phosphodecamolybdic acid is present. The ionization constant of the acid in soln. of the dihydrate was found by A. Rosenheim and A. Bertheim to be $k=0.052$ at 25° when calculated from the velocity of hydrolysis of methyl acetate which is 0.88. These results all show that the acid is greatly ionized in aq. soln. Cryoscopic measurements indicate that in the soln., an octomolybdic acid, $\text{H}_2\text{Mo}_8\text{O}_{25}$, is present, and these are supported by the fact that on adding ammonium salts, ammonium octomolybdate, $(\text{NH}_4)_2\text{Mo}_8\text{O}_{25} \cdot 13\text{H}_2\text{O}$, separates. E. Darmois and A. Honnelaitre, and A. Honnelaitre made a study of complexes of molybdic and malic acids; and E. Rimbach and P. Ley, mixtures of molybdic and hydroxy-organic compounds which were found to augment the acidity of molybdic and boric acids. R. F. Weinland and co-workers also studied this subject. F. Parmentier observed that the dihydrate is sparingly soluble in water and acids at different temp.; it dissolves completely in soln. of alkali hydroxides and carbonates, and, on evaporation, these soln. furnish ordinary molybdates. K. von der Heide studied the action of hydroxylamine, and of potassium cyanide. The soln. in aq. ammonia remains clear when magnesia mixture is added, and precipitates molybdenum trioxide when nitric acid is added to the aq. soln. E. Müller, H. H. Willard and F. Fenwick, and O. Tomicek studied the electrometric reduction of soln. of hexavalent molybdenum by titanous salt soln. R. Hac and V. Netuka studied its catalytic action on the reduction of nitric acid by ferrous chloride.

According to F. Mylius, no solid **orthomolybdic acid**, H_6MoO_6 , exists corresponding with orthotelluric acid, H_6TeO_6 . The colourless molybdic acid obtained in aq. soln. corresponds with *allotelluric acid*, with which it agrees in having an indefinitely large solubility in cold water, complex composition, in being soluble in alcohol, in being precipitated in the form of acid salts, and in precipitating solutions of proteids. Of the solid forms of molybdic acid, the yellow acid, H_3MoO_5 , has the greatest solubility in water, and is slowly formed when soln. of molybdates or molybdic acid are treated with nitric or hydrochloric acid. As indicated above, the dihydrate, H_4MoO_5 , is considered by A. Rosenheim and A. Bertheim to be an

octomolybdic acid, $\text{H}_2\text{Mo}_8\text{O}_{25}$, and it is assumed that in passing from one hydrated form to another, various complex intermediate polymerides of molybdic acid are formed—*vide infra*.

G. Jander and co-workers studied the complex acids, and some of the results have been summarized in connection with the electrometric titration of the acid. He gives for the condensation products :

$3[\text{MoO}_4^{''}] + 2\text{H}^+ = [\text{Mo}_3\text{O}_{11}^{''''}] + \text{H}_2\text{O}$ stable in the region $p_{\text{H}} = 6.1$; $[\text{Mo}_3\text{O}_{11}^{''''}] + \text{H}^+ = [\text{H}(\text{Mo}_3\text{O}_{11}^{''''})^{''}]$, called, by F. Ullik, the "dimolybdate"; $2[\text{H}(\text{Mo}_3\text{O}_{11}^{''''})^{''}] + \text{H}^+ = [\text{H}(\text{Mo}_6\text{O}_{21}^{''''})^{''}] + \text{H}_2\text{O}$, stable in the region $p_{\text{H}} = 4.5$, and called, by F. Ullik, "paramolybdates"; $[\text{H}(\text{Mo}_6\text{O}_{21}^{''''})^{''}] + \text{H}^+ = [\text{H}_2(\text{Mo}_6\text{O}_{21}^{''''})^{''}]$, called, by F. Ullik, the "trimolybdates"; $[\text{H}_2(\text{Mo}_6\text{O}_{21}^{''''})^{''}] + \text{H}^+ = [\text{H}_3(\text{Mo}_6\text{O}_{21}^{''''})^{''}]$, stable with p_{H} approximately 2.9, and called, by F. Ullik, "tetramolybdates" or "metamolybdates"; $2[\text{H}_3(\text{Mo}_6\text{O}_{21}^{''''})^{''}] + 3\text{H}^+ = 2[\text{H}_7(\text{Mo}_{12}\text{O}_{41}^{''''})^{''}] + \text{H}_2\text{O}$, called, by F. Ullik, "octomolybdates"; $2[\text{H}_7(\text{Mo}_{12}\text{O}_{41}^{''''})^{''}] + \text{H}^+ = [\text{H}_9(\text{Mo}_{24}\text{O}_{78}^{''''})^{''}] + 4\text{H}_2\text{O}$, called, by F. Ullik, "decamolybdates"; $[\text{H}_9(\text{Mo}_{24}\text{O}_{78}^{''''})^{''}] + 2\text{H}^+ = [\text{H}_{12}(\text{Mo}_{24}\text{O}_{78}^{''''})^{''}]$, called, by F. Ullik, "hexadecamolybdates"; and $[\text{H}_9(\text{Mo}_{24}\text{O}_{78}^{''''})^{''}] + 3\text{H}^+ = \text{H}_{12}(\text{Mo}_{24}\text{O}_{78})$, where p_{H} approximates 0.9.

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§ 11. The Monomolybdates—Normal Molybdates

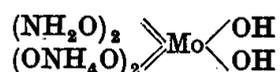
The action of liquid ammonia on molybdenum trioxide furnishes amides and imidies as indicated **8**, 49, 21. Normal **ammonium molybdate**, $(\text{NH}_4)_2\text{MoO}_4$, crystallizes from conc. soln. of molybdenum trioxide in warm, conc., aq. ammonia during cooling, or on the addition of alcohol. The salt was obtained in this way by L. F. Svanberg and H. Struve,¹ J. C. G. de Marignac, F. A. Flückiger, and A. Rosenheim. A. Werncke obtained it from the mother-liquor in the preparation of ammonium phosphomolybdate; and A. S. Garnak described a method of preparing the salt from ferromolybdenum. Analyses in accord with the formula were made by L. F. Svanberg and H. Struve, F. A. Flückiger, A. Werncke, and G. Wempe. L. F. Svanberg and H. Struve described the crystals as four-sided prisms. J. C. G. de Marignac found that the monoclinic prisms have the axial ratios $a : b : c = 1.9542 : 1 : 1.2066$, and $\beta = 117^\circ 45'$. Observations were also made by W. Keferstein; and G. N. Wyruboff said that the crystals are isomorphous with those of ammonium chromate, and J. W. Retgers, with those of ammonium selenate and chromate. J. W. Retgers added that ammonium chromate, selenate, and molybdate are isodimorphous with potassium sulphate. H. Schröder gave 2.270 for the sp. gr. According to J. C. G. de Marignac, the crystals effloresce rapidly in air owing to the loss of ammonia; F. A. Flückiger said that if the crystals are freed from the mother-liquor they are stable in air. L. F. Svanberg and H. Struve found that the crystals are unstable in contact with water and rapidly form an acid salt. T. L. Phipson found that the aq. soln. is decomposed in sunlight and R. E. Liesegang observed that in light, the salt is decomposed with the separation of a blue oxide. The change can be followed titrimetrically so that the soln. can be used as a kind of actinometer. The presence of organic substances, like lactic acid, makes the liquid more sensitive to light; some salts favour and others retard the action. In darkness the original colour is restored by the oxidizing action of the air—*vide supra*, molybdic acid and alcohol. P. Krishnamurti studied the Raman effect. W. V. Bhagwat and N. R. Dhar found the eq. electrical conductivity of ammonium molybdate to be for an eq. of the salt in v litres, at 21° ,

v	.	.	16	32	64	128	256	512	1024
λ	.	.	84.5	96.45	108.8	120.3	128.6	136.9	143.5

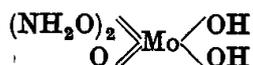
so that $\mu_{1024} - \mu_{32} = 47.05$.

F. Krauss and E. Bruchhaus found that ammonium molybdate in aq. soln., and exposed to rays of short wave-length, is reduced by hydrogen. For the hydrolysis of aq. soln., *vide infra*, ammonium paramolybdate. J. W. Thomas found that the salt is decomposed by hydrochloric acid; H. P. Cady and R. Taft, that ammonium molybdate is insoluble in liquid sulphur dioxide; H. Stamm measured its solubility in aq. ammonia and found that soln. with 0.170, 1.192, 1.750, and 3.382 mols of NH_3 per 100 grms. of water dissolved respectively 0.333, 0.268, 0.231, and 0.187 mol of $(\text{NH}_4)_2\text{MoO}_4$. O. Brunck observed that sodium hypsulphite precipitates molybdenum sulphide from acid soln; and F. J. Faktor, that sodium thiosulphate reduces a soln. of the molybdate to hydrated dioxide, and trioxide; and I. F. J. Kupfferschläger, that an excess of nitric acid gives a precipitate with a conc. aq. soln. A soln. of ammonium molybdate with an excess of nitric acid is used as a reagent for the detection of phosphoric acid. P. Kulisch disagreed with A. Winkler's statement that phosphine does not reduce soln. of ammonium molybdate—only in the absence of free acid is a soln. of the molybdate little affected by phosphine. O. F. von der Pfordten obtained a dark brown precipitate on adding a soln. of titanium dichloride to a soln. of the molybdate; and this is oxidized to a white mass in air. C. E. Guignet observed that the soln. of the molybdate dissolves prussian blue; and S. M. Jörgensen that it gives a precipitate with chromic chloropentamminochloride.

No normal **hydroxylamine molybdate** has yet been prepared. G. Canneri² observed that hydroxylamine added to a soln. of a paramolybdate forms a red soln. which deposits yellow molybdic molybdates. If hydroxylamine chloride be added to a hot, aq. soln. of alkali molybdate, and the precipitate be washed successively with water, alcohol, and ether, the following salts are formed: yellow **ammonium hydroxylamine paramolybdate**, $(\text{NH}_4)_2\text{O} \cdot 0.4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; yellow **potassium hydroxylamine paramolybdate**, $\text{K}_2\text{O} \cdot 0.4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; yellow **sodium hydroxylamine paramolybdate**, $\text{Na}_2\text{O} \cdot 0.4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; and similarly with the guanidine salt. V. Kohlschütter and K. A. Hofmann found that **potassium hydroxylaminopentahydromolybdate**, $\text{MoO}_4\text{H}_2(\text{NH}_2\text{OH})_3(\text{NH}_2\text{OK})$ —*vide infra*—is obtained as a salt of what they supposed to be the acid



by mixing aq. soln. of ammonium molybdate (5 grms.), hydroxylamine hydrochloride (10 grms.), and potassium carbonate, and adding alcohol to the yellow soln. The salt reduces Fehling's soln., or ammoniacal silver nitrate; it decomposes when heated forming a black powder with the liberation of ammonia. The salt dissolves in water, and when the pale yellow, neutral, aq. soln. is treated with carbon dioxide, hydroxylaminomolybdic acid separates as a yellowish-white, flocculent precipitate. If ammonium molybdate (10 grms.) and hydroxylamine hydrochloride (7 grms.) be mixed with 50 c.c. of 7 per cent. aq. ammonia at 8°, a compound is formed which dissolves with difficulty in water; and develops a bluish-green coloration when heated with dil. sulphuric acid. The composition of the product is $\text{MoO}_5\text{N}_3\text{H}_9$, and it is regarded as **dihydroxylamine aminomolybdate**, $\text{MoO}_5\text{N}_3\text{H}_9$, or $\text{MoO}_3(\text{NH}_2\text{OH})_2\text{NH}_3$, a salt of what they suppose to be the acid:



C. F. Rammelsberg³ obtained **lithium molybdate**, $\text{Li}_2\text{MoO}_4 \cdot \frac{2}{5}\text{H}_2\text{O}$ (A. Rosenheim and W. Reglin find $\text{Li}_2\text{MoO}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$), by boiling a mol each of lithium carbonate and molybdenum trioxide, and allowing the filtrate to crystallize. G. Wempe obtained the salt in a similar way; and M. Delafontaine, by fusing equimolar proportions of lithium carbonate and molybdenum trioxide, and allowing the syrupy aq. soln. to stand some days. F. Hoermann measured the f.p. curves of

the system : $\text{Li}_2\text{MoO}_4\text{-MoO}_3$, and the results are summarized in Fig. 13. The existence of three unstable acid salts is indicated, namely, lithium di-, tri-, and tetramolybdate. W. Zachariassen found that the X-radiogram of Li_2MoO_4 agrees with a unit cell having 6 mols. and with the dimensions $a=8.20$ A., $c=9.45$ A., and $a:c=1:1.153$; and that the salt is isomorphous with phenacite, willemite, lithium tungstate, and lithium fluoberyllate. F. Ephraim and M. Brand suggest that the water in the pentitadihydrate prepared by both processes is merely hygroscopic moisture. M. Delafontaine also obtained the tritooctohydrate, $\text{Li}_2\text{MoO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$, in monoclinic or triclinic crystals, from a soln. of an acid molybdate sat. with lithium carbonate. The prismatic crystals of the pentitadihydrate are fairly stable in air but they are hygroscopic. G. Wempe said that 100 c.c. of the aq. soln. sat. at 20° contains 46.13 grms. of the hydrated salt and has a sp. gr. of 1.44. F. Ephraim and M. Brand found that the salt is only a little more soluble in hot than in cold water. F. Hoermann gave 705° for the m.p. of the salt. A. Rosenheim and W. Reglin found the solubility of $\text{Li}_2\text{MoO}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$, S grms. Li_2MoO_3 per 100 grms. of soln., to be :

	0°	25°	30°	40°	98°
S	45.24	44.81	44.26	43.84	42.50

so that the temp. coeff. is negative. A. Rosenheim and W. Reglin also found that the salt dissolves readily in a soln. of lithium hydroxide, and on evaporating the liquid, non-crystallizable syrups are formed. Solubility is less as the temp. rises. The aq. soln. has an alkaline reaction. The aq. soln. of a mol of the salt and 5 mols of ammonium chloride yields crystals of ammonium paramolybdate free from lithium. The eq. conductivity, λ mhos, of a mol of the normal salt in v litres of water, at 20° , was found by G. Wempe to be :

v	10	20	40	80	160	320
λ	422	524	604	664	736	800

L. F. Svanberg and H. Struve obtained anhydrous sodium molybdate, Na_2MoO_4 , by melting together equimolar parts of molybdenum trioxide and sodium carbonate, and cooling the mass. The salt obtained by heating the hydrate to 100° was found by J. G. Gentele, and F. E. Zenker to furnish a molten mass which cools to an opaque, white enamel of the anhydrous salt. F. Hoermann measured the f.p. curves of the system : $\text{Na}_2\text{MoO}_4\text{-MoO}_3$, and the results are summarized in Fig. 14. The existence of three acid salts is indicated, namely, sodium di-, tri-, and tetra-molybdate. E. Groschuff obtained a similar curve. The monomolybdate exists in four modifications. The α -form is stable above about 620° ; the β -form is stable between 620° and 580° ; the γ -form between 580° and 410° ; and the δ -form below 410° . For the $\alpha \rightleftharpoons \beta$, $\beta \rightleftharpoons \gamma$, and $\gamma \rightleftharpoons \delta$ transition temp. K. Hüttner and G. Tammann observed transformations respectively between 620° and 605° , and 410° and 380° ; H. E. Boeke gave for the three transformation temp. respectively 619° , 587° , and 431° ; E. Groschuff, 609° , 575° , and 408° —Fig. 14; H. S. van Klooster, 626° , 580° , and 397° ; F. Hoermann, 621° , 580° , and 423° ; and M. Amadori, 616° ,

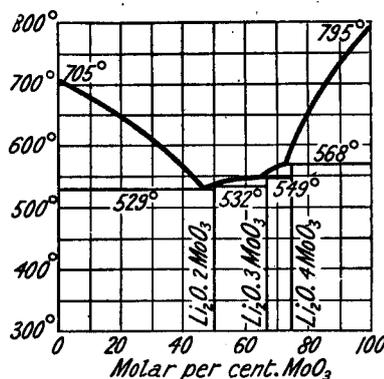


FIG. 13.—Equilibrium Curves of the System : $\text{Li}_2\text{MoO}_4\text{-MoO}_3$.

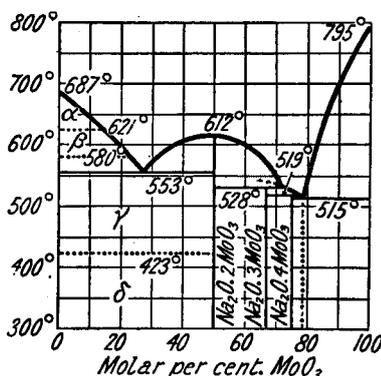


FIG. 14.—Equilibrium Curves of the System : $\text{Na}_2\text{MoO}_4\text{-MoO}_3$.

580°, and 410° when all are taken on a cooling curve. H. S. van Klooster found on a heating curve the respective values 640°, 592°, and 445°, showing that the transition temp. are overstepped. A. Hare gave 440° for the last transformation temp. The subject is still further discussed in connection with sodium tungstate. With 10 per cent. of molybdenum trioxide associated with the sodium molybdate, E. Groschuff found the transition temp. are changed respectively to 614°, 567°, and 412°. H. E. Boeke found that with 0.055, 0.40, and 3.00 molar per cent. of Na_2SO_4 , the $\gamma \rightleftharpoons \delta$ transition temp. is lowered from 431° respectively to 396°, 297°, and about 180°. This depression is much greater than that calculated from the heat of the transformation, 3.33 Cals., and the anomaly is explained by H. S. van Klooster by assuming that the presence of sodium sulphate considerably augments the speed of the transformation. H. E. Boeke found that the binary system $\text{Na}_2\text{SO}_4\text{-Na}_2\text{MoO}_4$ forms a continuous series of solid soln. on solidification. There is a minimum in the f.p. curve, Fig. 15. For the binary system: $\text{Na}_2\text{WO}_4\text{-Na}_2\text{MoO}_4$, and the ternary system: $\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4\text{-Na}_2\text{MoO}_4$, *vide* sodium tungstate.

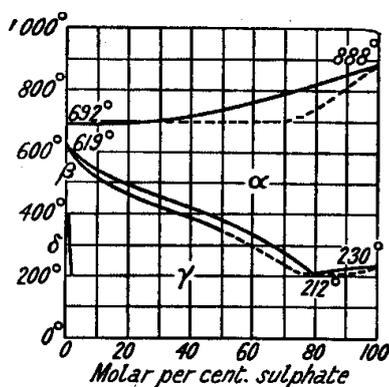


FIG. 15.—Binary System :
 $\text{Na}_2\text{MoO}_4\text{-Na}_2\text{SO}_4$.

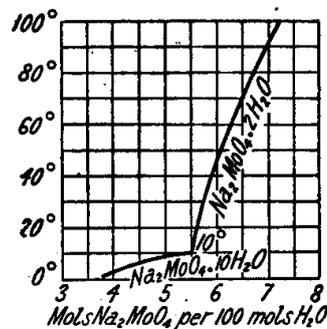


FIG. 16.—Solubility Curve of
Sodium Molybdate.

The equilibrium conditions in the ternary system: $\text{Na}_2\text{O-MoO}_3\text{-H}_2\text{O}$ have not been worked out. R. Funk's solubility curve, Fig. 16, shows that within the range of temp. 0° to 100°, there are two hydrates: $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 8\text{H}_2\text{O}$ with a transition at about 10°. L. F. Svanberg and H. Struve obtained the *dihydrate* by crystallizing an aq. soln. of the anhydrous salt, and drying the crystals for 24 hrs. over lime and sulphuric acid. F. E. Zenker evaporated an aq. soln. of the paramolybdate mixed with an excess of sodium hydroxide; F. Ullik, an aq. soln. of the acid or an acid salt sat. with sodium carbonate; M. Delafontaine used a similar process; and J. G. Gentele allowed the decahydrate to effloresce in the cold. According to M. Delafontaine, the rectangular or rhombic plates or scales are probably isomorphous with the crystals of normal tungstate. They lose all their water at 100°. The molten mass does not expel carbon dioxide from sodium carbonate. R. Funk found the solubility, *S* grms. of Na_2MoO_4 per 100 grms. of solution, to be:

<i>S</i>	0°	4°	6°	9°	10°	32°	51.5°	100°
	30.63	33.83	35.58	38.16	39.28	39.82	41.27	45.57
	Na ₂ MoO ₄ ·10H ₂ O.					Na ₂ MoO ₄ ·2H ₂ O.		

The results are plotted in Fig. 16. The transition temp. is near 10°. J. G. Gentele obtained the *decahydrate* by evaporating the aq. soln. between 0° and 6°. The columnar crystals have the appearance of Glauber's salt. The crystals effloresce at about 6°, and are stable below that temp. In a closed vessel, at room temp., the crystals become opaque and gradually form the scaly crystals of the dihydrate. M. Delafontaine could not prepare the decahydrate.

G. Beck gave 3.28 for the sp. gr. of the salt, and 62.0 for the mol. vol. F. M. Jäger measured the sp. gr. of the molten salt— D referred to water at 4°—and found :

	698.5°	751°	818.8°	903.8°	989.5°	1078.5°	1171.5°
D	2.796	2.763	2.720	2.667	2.613	2.557	2.499
σ	214.0	208.1	202.4	195.4	187.7	181.2	176.1
χ	376.1	3686	3623	3544	3451	3380	3335

The results for the sp. gr. between 700° and 1171° can be represented by $D=2.795-0.000629(\theta-700)$ —*vide infra*, electrical resistance. W. Herz made some observations on this subject. I. Traube found the sp. gr., D , and mol. soln. vol., v , of aq. soln. of the salt, at 15°, to be :

Na_2MoO_4	6.31	11.84	19.91	22.18 per cent.
D	1.0555	1.1085	1.1928	1.2194
v	32.9	34.4	38.1	38.3

R. Lorenz and W. Herz studied the relation between the critical densities of related salts, and they also found that the surface tension at the m.p. and b.p. are respectively 215.5 and 177.9; G. Jander and co-workers studied the diffusion; and I. Traube found 232 for the drop-weight of molten sodium molybdate when the value for water at 0° is 100. F. M. Jäger's values for the surface tension, σ dynes per cm., and the surface energy, χ ergs per sq. cm., of the molten salt, are indicated above. J. J. Coleman found that 28, 25, and 17 per cent. of normal soln. of sodium molybdate, chromate, and tungstate, respectively, diffused in water 75 mm. in 30 days at 12.5°. W. Herz gave 0.0002752 for the coeff. of thermal expansion. G. Tammann found the lowering of the vap. press. per 100 grms. of water to be 24.4, 73.2, and 166.9 mm., respectively. The m.p. of the anhydrous salt was found to be 692° by K. Küttner and G. Tammann, and H. E. Boeke; 687°, by L. I. Dana and P. D. Foote; 688°, by M. Amadori; 685°–687°, by H. S. van Klooster; and 686°, by E. Groschuff. The fusion curve with sodium sulphate mixtures is shown in Fig. 15. E. Darmois and J. Périn found that the mol. wt. is normal when calculated from its effect on the f.p. of decahydrated sodium sulphate. R. Lorenz and W. Herz studied the relation between the b.p. and the critical temp. W. G. Mixer gave for the heat of formation ($\text{Na}_2\text{O}, \text{Mo}_3\text{O}_{10}$) = 263.4 Cals.; ($\text{Na}_2\text{O}, \text{Mo}_2\text{O}_7$) = 120.6 Cals.; and ($\text{Na}_2\text{O}, \text{MoO}_3$) = 81.936 Cals. A. Hare gave 14.6 Cals. per mol for the heat of transformation at about 440°. L. Pissarjewsky found for the thermal value of the reaction: $\text{H}_2\text{MoO}_4\text{soln.} + 2\text{NaOH} = \text{Na}_2\text{MoO}_4\text{soln.} + 2\text{H}_2\text{O} + 21.728$ Cals. A. Hare gave 14.60 Cals. per mol for the heat of the transformation at 440°.

F. M. Jäger and B. Kapma found the resistance, R ohms, of fused sodium molybdate to be :

	843°	924.5°	1026°	1122.5°	1217°	1306°	1408°
R	0.1256	1.1105	0.0948	0.0842	0.0752	0.0690	0.0620
Sp. gr.	2.705	2.654	2.590	2.529	2.470	2.414	2.350

and they represented the mol. conductivity, μ , at θ° between 543° and 1408°, by $\mu=107.50+0.183(\theta-850)$. P. Walden found the eq. conductivity, λ mhos, of soln. of an eq. of sodium molybdate in v litres of water at 25°, to be :

v	32	64	128	256	512	1204
λ	100.5	106.1	111.0	114.6	117.8	120.8

H. Crossmann gave $\mu_{1024}-\mu_{32}=22.4$ at 25°. J. Terwelp obtained similar results, and he found the transport number of the $\text{MoO}_4^{''}$ -ion in 0.1N- Na_2MoO_4 to be 0.58 at 18°. G. Jander and co-workers studied the electrometric titration of the salt. L. Ott found the decomposition voltage of the fused salt to be 1.15 volt; and the cathode deposit is MoO_2 as well as some metal. J. Terwelp, and A. Junius

found that the electrolysis of neutral aq. soln. of sodium molybdate without diaphragms, does not produce very marked change since the diffusion of the anodic and cathodic products restores the original state of things. A cathodic reduction occurs only in acidic soln. In a diaphragmed cell, paramolybdate and trimolybdate appear to be formed in the anode compartment—*vide supra*, molybdenum trioxide. The aq. soln. was found by F. E. Zenker, and A. Junius to react acid; but the hydrolysis cannot be very marked because K. Seubert and W. Pollard found that a soln. of molybdic acid can be sharply titrated with a soln. of sodium hydroxide using litmus or phenolphthalein as indicator—*vide infra*, ammonium paramolybdate. F. Ullik found that the soln. of sodium molybdate is not reduced by tin.

F. Hoermann found that the f.p. curve of mixtures of lithium and sodium molybdates, Fig. 17, showed the existence of an unstable lithium sodium molybdate, $\text{Li}_2\text{MoO}_4 \cdot 3\text{Na}_2\text{MoO}_4$.

L. F. Svanberg and H. Struve prepared potassium molybdate, K_2MoO_4 , by evaporating for crystallization a soln. of molybdic acid or an acid molybdate in an excess of potassium hydroxide or carbonate. J. Ohly said that the product is then liable to be contaminated with potassium carbonate. The formation of the acid molybdate can be avoided only by using an excess of alkali. L. F. Svanberg and H. Struve treated an acid molybdate with soln. of potassium hydroxide in

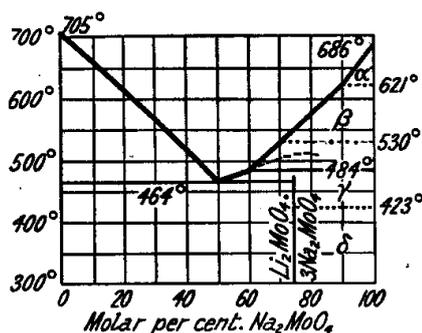


FIG. 17.—The Equilibrium Curves of the System: Li_2MoO_4 - Na_2MoO_4 .

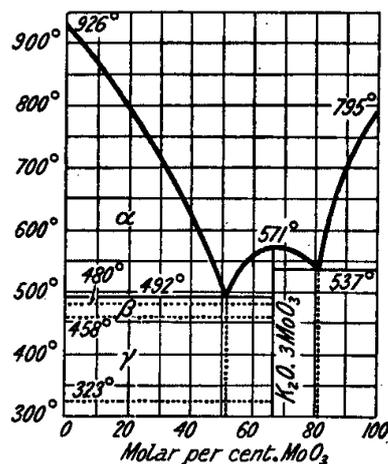


FIG. 18.—Equilibrium Curves of the System: K_2MoO_4 - MoO_3 .

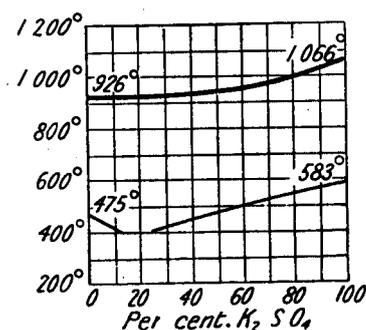
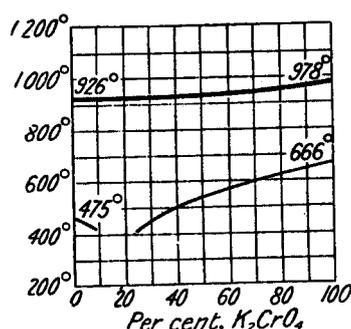
95 per cent. alcohol. The oil which separates was washed with alcohol and allowed to crystallize first over lime and then sulphuric acid. F. Ullik fused equimolar parts of molybdenum trioxide and potassium carbonate, dissolved the product in hot water, and allowed the filtered soln. to cool. L. F. Svanberg and H. Struve supposed the crystals to be hemihydrated; and F. Ullik thought they are anhydrous. M. Delafontaine could not prepare this salt. M. Amadori found that anhydrous potassium molybdate separates from its aq. soln. at 25° ; and the salt remains anhydrous in contact with water at this temp. G. Wempe reported a *tetritrihydrate*, $\text{K}_2\text{MoO}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$, to be formed by filtering a boiling soln. of molybdic acid in a conc. soln. of potassium carbonate, allowing the filtered liquid to cool on a glass plate, and separating mechanically the crystals from the amorphous, gum-like mass. The salt loses its water at 120° . F. Hoermann studied the f.p. curve of the system: K_2MoO_4 - MoO_3 , and the results, summarized in Fig. 18, show the existence of a dimolybdate only.

L. F. Svanberg and H. Struve said that the crystals of potassium molybdate, K_2MoO_4 , are four-sided prisms. H. S. van Klooster observed that the cooling salt undergoes three transformations: there is the $\alpha \rightleftharpoons \beta$ change at 479° ; the $\beta \rightleftharpoons \gamma$ change at 454° ; and the $\gamma \rightleftharpoons \delta$ change at 327° ; M. Amadori gave 475° for the $\alpha \rightleftharpoons \beta$ change; and K. Hüttner and G. Tammann, 200° for the $\gamma \rightleftharpoons \delta$ change. F. Hoermann gave respectively 480° , 458° , and 323° . J. W. Regters observed that

during the crystallization of potassium molybdate there are formed acicular crystals supposed to be rhombic or pseudo-hexagonal and isomorphous with potassium permanganate; and prismatic crystals not isomorphous with the salt, and supposed to be monoclinic. M. Amadori found that mixtures of potassium sulphate and molybdate, and of potassium chromate and molybdate have the following f.p. and $\beta \rightleftharpoons \alpha$ transition points:

K_2MoO_4	100	80	70	40	20	0 per cent.
K_2SO_4	F.p.	920°	934°	980°	1018°	1066°
	Tr.p.	475°	—	484°	525°	583°
K_2CrO_4	F.p.	926°	934°	942°	960°	976°
	Tr.p.	475°	—	502°	575°	666°

The curve, Fig. 19, for the K_2MoO_4 - K_2SO_4 is continuous, and it has a very flat minimum 6° below the m.p. of the molybdate, and the m.p. of the mixture with 45 per cent. of sulphate is equal to that of the molybdate alone. The curve, Fig. 20, for the K_2MoO_4 - K_2CrO_4 system is continuous, and with mixtures up to 30 molar per cent. of chromate the f.p. is at the f.p. of the molybdate. M. Amadori also found the solubility isotherm of potassium sulphate and molybdate is similar to that with potassium sulphate and chromate. There is a continuous series of solid soln. in which the more soluble salt is in greater proportion in the soln. than in the crystals; similarly also with the solubility isotherm of mixtures of potassium chromate and molybdate. G. Beck gave 2.91 for the sp. gr. of the salt, and 81.8



FIGS. 19 and 20.—Freezing-point Curves of the Binary System: K_2MoO_4 - K_2SO_4 and K_2MoO_4 - K_2CrO_4 .

for the mol. vol. F. M. Jäger gave the following values for the sp. gr., D , of fused potassium molybdate referred to water at 4°:

	930.6°	1021°	1143°	1273°	1356°	1452.8°
D	2.362	2.307	2.230	2.144	2.087	2.018
σ	150.5	145.2	138.6	130.0	123.6	116.9
χ	3261	3196	3120	3004	2908	2813

and he represented the sp. gr. at θ° between 694° and 1452° by $D = 2.342 - 0.0006(\theta - 964) - 0.000000128(\theta - 964)^2$. W. Herz made some observations on this subject. I. Traube gave for the sp. gr., D , and mol. soln. vol., v , of aq. soln. of potassium molybdate at 15°:

K_2MoO_4	2.02	6.76	7.37	15.94 per cent.
D	1.0154	1.0548	1.0602	1.1381
v	49.7	52.4	52.2	56.4

I. Traube gave 198 for the drop-weight of the molten salt when that of water at 0° is 100. F. M. Jäger found the results indicated above for the surface tension, σ dynes per cm., and the surface energy, χ ergs per sq. cm. R. Lorenz and W. Herz gave for the surface tensions at the m.p. and b.p. respectively 161.5 and 108.3. G. Jander and A. Winkel gave for the diffusion coeff. of the anion 0.58; and they found the range of stability for $[H^+]$ to be 10^{-14} to $10^{-6.2}$. K. Hüttner and G. Tammann, and M. Amadori gave 926° for the m.p. of the salt, and H. S. van Klooster,

919°. The lowering of the vap. press. when 19.62, 56.06, and 111.13 grms. of potassium molybdate are dissolved in 100 grms. of water was found by G. Tammann to be respectively 24.6, 85.3, and 197.1 mm. R. Lorenz and W. Herz studied the relation between the b.p. and the critical temp. P. Blackman found the conductivity of soln. of an eq. of the salt in v litres at 25° to be :

v	:	:	32	64	128	256	512	1024
λ	:	:	123	129	133	138	140	144

Measurements by W. V. Bhagwat and N. R. Dhar corresponded with $\mu_{1024} - \mu_{32} = 24$. E. Blanc found that there is a 0.359 per cent. hydrolysis with a 0.00975*N*-soln. of potassium molybdate. L. F. Svanberg and H. Struve, and F. Ullik found that the salt effloresces in moist air, and, attracting carbon dioxide from the atmosphere, forms other salts. M. Amadori observed that a sat. aq. soln. at 25° contains 64.86 per cent. K_2MoO_4 . Expressing solubilities in millimols per litre, the solubility, S , of potassium sulphate in the presence of potassium molybdate is :

K_2MoO_4	.	69.88	49.04	22.65	12.21	8.60	4.13	0.00
K_2SO_4	.	0.00	19.85	73.35	192.6	417.5	742.8	774.7

and of potassium chromate in the presence of potassium molybdate :

K_2MoO_4	.	332.3	204.7	72.68	36.66	25.31	8.74	0.00
K_2CrO_4	.	0.00	162.0	414.3	578.1	694.1	767.9	774.7

L. F. Svanberg and H. Struve found potassium molybdate to be insoluble in alcohol ; and to be precipitated by alcohol from the aq. soln. as an oily liquid.

F. Hoermann studied the f.p. curve of mixtures of lithium and potassium molybdates, and found the existence of **lithium potassium molybdate**, Li_2MoO_4 .

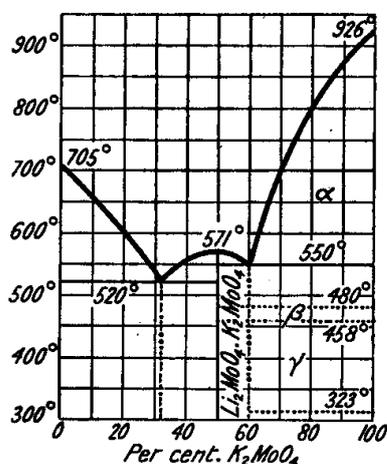


FIG. 21.—Equilibrium Curve of the System : $K_2MoO_4 - Li_2MoO_4$.

K_2MoO_4 , with a m.p. at 571°. F. Ullik prepared **potassium sodium molybdate**, $K_2O.2Na_2O_3.MoO_3.14H_2O$, or $K_2^3Na_3^4MoO_3.4\frac{2}{3}H_2O$, by treating a potassium trimolybdate with water and sodium carbonate. F. Ullik fused molybdenum trioxide with sodium and potassium carbonates, and allowed an aq. soln. of the cold mass to crystallize. J. C. G. de Marignac described the crystals as dihexagonal bipyramidal with the axial ratios $a : c = 1 : 1.2839$. M. Delafontaine stated that all the water is expelled at 100°; and the salt fuses at a red-heat; fused sodium carbonate does not lose carbon dioxide when treated with the salt. F. Ullik found that the salt is soluble in cold water, but more easily soluble in hot water; the soln. has an alkaline reaction.

A. Piccini⁴ prepared normal **rubidium molybdate**, Rb_2MoO_4 , by calcining rubidium molybdenum trioxytetrafluoride, $2RbF.MoO_3F_2.H_2O$; and F. Ephraim and H. Herschfinkel obtained the salt by evaporating a soln. of molybdenum trioxide in rubidium hydroxide, and washing the deliquescent mass with alcohol. J. W. Retgers made a few observations on the crystals of **caesium molybdate**, Cs_2MoO_4 .

No **cuprous molybdates** have yet been prepared; and normal **copper molybdate**, $CuMoO_4$, is not known. H. Debray⁵ obtained, possibly, the normal molybdate by roasting cupric sulphomolybdate at a low temp. G. Tammann noted that the reaction between cupric oxide and molybdenum trioxide begins about 615°, and the heat of formation of $CuMoO_4$ is 9.2 Cals. per mol; J. J. Berzelius observed that a yellowish-green precipitate is produced by potassium molybdate in soln. of copper salts. The precipitate is sparingly soluble in water, and is decomposed

by acids and alkali-lye. H. Struve prepared **copper oxymolybdate**, $\text{CuO} \cdot 3\text{CuMoO}_4 \cdot 5\text{H}_2\text{O}$, by precipitation from a boiling soln. of copper sulphate by a conc. soln. of ammonium 2 : 5 : 3-molybdate. The green, amorphous powder loses 3 mols. of water at 100° , and the remainder at a higher temp. The dehydrated salt gradually recovers its combined water when in contact with water. According to G. Jørgensen, if sodium molybdate be treated with an excess of a soln. of copper sulphate, and the light green precipitate be dissolved in aq. ammonia, and the soln. treated with alcohol, dark blue needles of **copper tetramminomolybdate**, $[\text{Cu}(\text{NH}_3)_4]\text{MoO}_4$, are formed. The crystals readily lose ammonia, and become dark green. S. H. C. Briggs prepared **copper diamminomolybdate**, $[\text{Cu}(\text{NH}_3)_2]\text{MoO}_4 \cdot \text{H}_2\text{O}$, by mixing a soln. of 24 grms. of pentahydrated copper sulphate in 30 c.c. of water, 13 grms. of ammonium paramolybdate in 15 c.c. of water, and 40 c.c. of conc. aq. ammonia, making all up to 350 c.c., and exposing it to air. The deep blue prisms lose ammonia at ordinary temp.; and they are soluble in warm aq. ammonia. The salt may be recrystallized by allowing the warm soln. in aq. ammonia to cool, or by exposing a more dil. ammoniacal soln. to air. H. Struve obtained **ammonium copper molybdate**, $(\text{NH}_4)_2\text{O} \cdot \text{CuO} \cdot 5\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, from the mother-liquor of the oxymolybdate; and by the action of a cold soln. of copper sulphate on an excess of ammonium 2 : 5 : 3 molybdate. The pale blue, microscopic, rhombic crystals lose 4 mols. of water at 100° ; more at a higher temp., and finally water and ammonia are given off. The yellow mass melts at a red-heat. It is sparingly soluble in cold water, and soluble in boiling water without decomposition. Blue crystals of **ammonium copper diamminomolybdate**, $(\text{NH}_4)_2\text{Cu}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$, were obtained by S. H. C. Briggs by exposing to air in an open dish a mixture of 50 grms. of ammonium molybdate in 60 c.c. of water, 20 grms. of ordinary copper sulphate in 50 c.c. of water, and 70 c.c. of conc. aq. ammonia, all made up to 210 c.c.

According to F. Wöhler and F. Rautenberg,⁶ if normal silver molybdate be treated with hydrogen at ordinary temp., it is partially converted into **silver submolybdate**, $\text{Ag}_4\text{O} \cdot 2\text{MoO}_3$. It was also prepared by passing hydrogen into a soln. of silver molybdate in conc., aq. ammonia. The reduction begins at ordinary temp. as the liquid turns brown; the action is complete at 90° . The black powder consists of octahedral crystals belonging to the cubic system. The salt dissolves in nitric acid giving off nitric oxide; with potash-lye, molybdenum trioxide is dissolved, and silver suboxide is left as a black powder. W. Muthmann said that the alleged silver submolybdate is nothing more than a mixture of silver and the normal molybdate. C. W. Scheele, J. B. Richter, and L. F. Svanberg and H. Struve prepared **silver molybdate**, Ag_2MoO_4 , as a white or yellowish-white, amorphous precipitate, by adding a silver salt to a soln. of a molybdate. E. F. Smith and R. H. Bradbury obtained it in a similar way. H. Debray obtained the salt in cubic crystals by allowing an ammoniacal soln. of ammonium molybdate and silver nitrate to evaporate spontaneously. W. Muthmann obtained the crystals in a similar way. R. W. G. Wyckoff studied the X-radiogram of the crystals, and showed that the structure is like that of the spinels or of magnetite. The length of the side of the unit cube, containing 8 mols., is 9.26 Å. P. P. Ewald studied this subject. Silver molybdate is coloured when heated, and it readily melts to a yellow liquid. It forms a colloidal soln. with water, particularly when freshly precipitated; according to H. Rose, it readily dissolves in nitric acid; and, according to E. F. Smith and R. H. Bradbury, it dissolves in a soln. of potassium cyanide, or of sodium hydroxide. J. Krutwig observed that the fused salt is not attacked by chlorine; and O. Widman, that if the ammoniacal soln. is evaporated in an atm. of ammonia, or if the solid salt is treated with ammonia, **silver diamminomolybdate**, $[\text{Ag}(\text{NH}_3)_2]_2\text{MoO}_4$, is formed, in the latter case, as a white powder, and, in the former case, crystals which are probably isomorphous with the corresponding tungstate. The salt loses all its ammonia at 65° . P. Ray and J. Dasgupta prepared a complex with hexamethylenetetramine.

According to J. B. Richter,⁷ when potassium molybdate is added to a soln.

of auric chloride, orpiment-yellow **gold molybdate** is precipitated. It is soluble in hydrochloric or nitric acid, and sparingly soluble in water.

W. H. Melville^s described a greenish mineral which he obtained from the Seven Devils mining district, Idaho. It was named **powellite**—after J. W. Powell. It approximates in composition to normal **calcium molybdate**, CaMoO_4 , associated with some calcium tungstate. F. Ullik obtained a white precipitate of calcium molybdate by adding calcium chloride to a soln. of neutral sodium molybdate. The precipitate does not form in cold, dil. soln., nor in the presence of acetic acid. The salt was obtained by E. F. Smith and R. H. Bradbury in a similar way. A. Kissock obtained it by treating roasted molybdenite with slaked lime; and H. C. Maber, by heating roasted molybdenite with calcium carbonate at 600° . F. de Carli observed that the reaction between calcium oxide and molybdenum trioxide begins at 650° . D. Balareff, W. Jander, and G. Tammann also studied this reaction. G. Tammann found the reaction between molybdenum trioxide and calcium oxide begins at about 425° ; and with calcium carbonate above 600° . W. Jander studied the dynamics of the heterogeneous reaction $\text{CaCO}_3 + \text{MoO}_3 = \text{CaMoO}_4 + \text{CO}_2$, between 487° and 550° , and examined the influence of the grain size of the component particles. H. Schultze, and L. Michel obtained crystals by melting a mixture of sodium molybdate, calcium chloride, and sodium chloride (1 : 3 : 2), and H. Traube obtained crystals as a sublimate when the molybdate is heated with a mixture of sodium and potassium chlorides to a high temp. According to T. H. Hiortdahl, the crystals are tetragonal bipyramids with the axial ratio $a : c = 1 : 1.5457$; and the sp. gr. is 4.35. From the X-radiograms, F. Zambonini and R. G. Levi gave for the dimensions of the unit cell $a = 3.67$ A., and $c = 5.69$ A., and they discussed the isomorphism of the molybdates of lead and the alkaline earth metals. E. Herlinger studied the structure of the crystals of the alkaline earth molybdates. A. Kissock discussed the use of calcium molybdate in steel making. Crystals of powellite were found by W. H. Melville to be tetragonal with the axial ratio $a : c = 1 : 1.5445$. F. Zambonini gave 1 : 5513—*vide infra*, the rare earth molybdates. W. Jander discussed the lattice-structure. L. Vegard and A. Refsum found that the X-radiogram of powellite corresponded with a space-lattice of the rutile type with $a_0 = 7.4$ A., $c_0 = 11.44$ A., and $a : c = 1 : 1.546$. The radius of the oxygen atom = 1.12 A., that of the calcium atom, 1.03 A., and that of the positive ion, 1.12 A. The elementary cell has 8 mols. The sp. gr. is 4.526, and the hardness 3.5. F. Zambonini and R. G. Levi gave 4.28 for the sp. gr. P. P. Pilipenko gave 4.22 for the sp. gr. of some crystals from western Altai, and 3.5 to 4.0 for the hardness. F. Westphal studied the mixed crystals of calcium and ammonium molybdates. W. Jander studied the diffusion of the molybdate and tungstate. D. Balareff and N. Lukova found that calcium molybdate lowers the dissociation press. of calcium carbonate. E. Cane gave 0.166 for the sp. ht. G. Tammann gave for the heat of formation of CaMoO_4 , 26.5 Cals. per mol. E. S. Larsen gave for the refractive indices of powellite, $\text{Ca}(\text{Mo}, \text{W})\text{O}_4$, $\epsilon = 1.978$, and $\omega = 1.968$, or $\epsilon - \omega = 0.01$ for the *D*-line. F. Zambonini gave for $\lambda = 667$, $\epsilon = 1.962$, $\omega = 1.959$, and $\epsilon - \omega = 0.008$; for $\lambda = 570$, $\epsilon = 1.984$, $\omega = 1.974$, and $\epsilon - \omega = 0.010$; and for $\lambda = 583$, $\epsilon = 1.993$, $\omega = 1.982$, and $\epsilon - \omega = 0.011$. H. Schultze obtained crystals of **strontium molybdate**, SrMoO_4 , by fusing a mixture of sodium molybdate, strontium chloride; and sodium chloride (1 : 2 : 2). G. Tammann said that the reaction between molybdenum trioxide and strontium carbonate begins at about 700° . The tetragonal pyramids were found by T. H. Hiortdahl to have the axial ratio $a : c = 1 : 1.5738$. F. Zambonini and R. G. Levi gave for the dimensions of the unit cell $a = 3.79$ A., and $c = 5.97$ A., and they studied the isomorphism of the molybdates of lead and the alkaline earth metals. E. K. Brock gave $a = 5.380$ A., $c = 11.97$ A., $a : c = 1 : 2.226$; and the calculated density 4.718. W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. F. W. Clarke gave 4.1554 for the sp. gr. at 20.5° , and 4.1348 at 21° ; F. Zambonini and R. G. Levi gave 4.73; and V. G. Aranda, 4.6624. E. F. Smith and R. H. Bradbury found that 100 parts of water dissolve 0.0104 part of salt at 17° . F. Westphal

studied the mixed crystals of strontium and ammonium molybdates. F. de Carli observed that the reaction between molybdenum trioxide and barium oxide begins at 290°. D. Balareff, J. H. Hevdall, and N. von Zweigbergh also studied this reaction. W. Jander represented the temp. coeff., k , of the reaction with calcium carbonate and molybdenum trioxide by $k=ce^{-43000/T}$, and the thermal value of the reaction by 21.5 Cals. E. Cane gave 0.149 for the sp. ht. L. F. Svanberg and H. Struve obtained **barium molybdate**, $BaMoO_4$, by adding barium chloride to a soln. of ammonium molybdate or paramolybdate in an excess of ammonia, and washing the product with cold water. H. Schultze obtained crystals by melting a mixture of sodium molybdate, barium chloride, and sodium chloride (1 : 3 : 2). G. Tammann said that the reaction between molybdenum trioxide and baryta begins at about 290°; and with barium carbonate at 660°—W. Jander studied this reaction. The acicular crystals are tetragonal pyramids which, according to T. H. Hiortdahl, have the axial ratio $a : c = 1 : 1.6232$. F. Zambonini and R. G. Levi gave for the dimensions of unit cell $a = 3.96$ A., and $c = 6.53$ A., and they studied the isomorphism of the molybdates of lead and the alkaline earth metals. L. Vegard and A. Refsum gave for the elementary cell, $a_0 = 7.858$ A., $c_0 = 12.755$ A., and $a : c = 1 : 1.623$; the radius of the oxygen atom is 1.24 A.; of the barium atom, 1.02 A.; and of the positive ion, 1.21 A. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate. F. W. Clarke gave 4.659 for the sp. gr. at 17.5°, and 4.648 at 19.5°; F. Zambonini and R. G. Levi gave 4.84; and V. G. Aranda, 4.9747. E. Cane gave 0.113 for the sp. ht. G. Tammann gave 60.1 Cals. for the heat of formation of $BaMoO_4$. According to E. F. Smith and R. H. Bradbury, 100 parts of water at 23° dissolve 0.0058 part of the salt; the solubility is augmented by the presence of ammonium nitrate. The salt is soluble in acids, and, when ammonia is added to the soln., C. J. Heine said that a basic salt is precipitated, but L. F. Svanberg and H. Struve found that the normal salt is so formed. L. Kahlenberg and W. J. Trautmann observed no reaction occurs when a mixture of barium molybdate and silicon is heated by the bunsen burner, but a slight reaction occurs in the electric arc.

A. Atterberg⁹ found that if equimolar parts of beryllium hydroxide and molybdenum trioxide are boiled with water, for a long time, a voluminous precipitate consisting of interlaced needles of a basic salt—**beryllium oxymolybdate**, $BeO \cdot BeMoO_3 \cdot 3H_2O$ —is formed. It loses a mol. of water at 100°. G. Tammann found that the reaction between molybdenum trioxide and beryllium oxide begins at about 400°; and the heat of formation of **beryllium molybdate**, $BeMoO_4$, is 4.0 Cals. per mol. According to A. Rosenheim and P. Woge, the *dihydrate*, $BeMoO_4 \cdot 2H_2O$, is obtained by boiling the theoretical quantity of hydrated beryllium oxide with molybdenum trioxide suspended in water. The oily liquid forms an aggregate of slender needles if kept for some time in the acid.

A. and E. Scacchi¹⁰ obtained from an old rock embedded in Vesuvian lava, white needles consisting of tetragonal crystals of a mineral which they named **belonosite**—from $\beta\epsilon\lambda\acute{o}\nu\eta$, a needle—and which was considered to be **magnesium molybdate**, $MgMoO_4$. F. de Carli observed no reaction between molybdenum trioxide and magnesia up to 1200°, but G. Tammann said that the reaction begins at about 425°, and the heat of formation of $MgMoO_4$ is 7.3 Cals. per mol. F. Ullik, M. Delafontaine, and H. Struve prepared the anhydrous salt by calcining, at not too high a temp., the hydrated salt obtained by boiling magnesia in water holding molybdenum trioxide in suspension, and evaporating the filtered liquid. G. N. Wyrouboff found that rhombic crystals of the *heptahydrate* are formed at about 30°; and F. Westphal also obtained rhombic crystals of the heptahydrate which are isomorphous with heptahydrated magnesium sulphate; and which lost five mols. of water at 80°. G. N. Wyrouboff observed that soln. at a temp. exceeding 30° yield the triclinic *pentahydrate*. The transition temp. has not been determined exactly. F. Westphal prepared the salt by mixing soln. of magnesium chloride and of sodium molybdate. A. and E. Scacchi described **belonosite** as a white

mineral consisting of minute, acicular crystals of MgMoO_4 , which are tetragonal with the axial ratio $a : c = 1 : 0.66054$. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate. The triclinic pentahydrate furnishes prismatic crystals isomorphous with the pentahydrates of copper sulphate, and magnesium sulphate and chromate. The axial ratios were found by G. N. Wyrouboff to be $a : b : c = 0.5264 : 1 : 0.5732$, and $\alpha = 80^\circ 43'$, $\beta = 98^\circ 52'$, and $\gamma = 107^\circ 28'$. The sp. gr. is 2.208. Three mols. of water are lost at 120° , and the remainder at a red-heat without decomposing the molybdate. M. Delafontaine said that the salt is readily soluble in hot and cold water. F. Rodolico prepared a complex with hexamethylenetetramine, $\text{MgMoO}_4 \cdot \text{X} \cdot 10\text{H}_2\text{O}$.

F. Ullik prepared **ammonium magnesium molybdate**, $(\text{NH}_4)_2\text{MoO}_4 \cdot \text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$, by evaporating an equimolar soln. of the two salts spontaneously, or on a water-bath; and also by adding ammonia to a soln. of magnesium molybdate, and crystallizing the filtrate. V. von Zepharovich gave $a : b : c = 0.851 : 1 : 0.436$ for the axial ratios of the probably rhombic, bipyramidal crystals. The (010)-cleavage is well defined; and the (100)-cleavage less so. When the salt is heated F. Ullik observed that water and ammonia are evolved; the salt is freely soluble in water. F. Ullik studied the isomorphism of the molybdates, sulphates, and chromates. If mixed soln. of magnesium molybdate and ammonium sulphate, or of magnesium sulphate and ammonium molybdate, are allowed to crystallize, isomorphous mixtures of the molybdate- and sulphate-complex salts are formed in which the ratio $\text{MoO}_3 : \text{SO}_3$ depends on the proportions of the radicles in the soln. With dil. soln. evaporated spontaneously, the salt which separates has a small proportion of molybdate, while a large proportion of molybdate is present if hot, sat. soln. are mixed. The crystals have the composition $(\text{NH}_4)_2\text{Mg}(\text{MoO}_4)_{2-n}(\text{SO}_4)_n \cdot 6\text{H}_2\text{O}$, and are monoclinic like the complex sulphates $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The mixed crystals were also studied by F. Westphal. F. Ullik also found that mixed soln. of magnesium molybdate and ammonium chromate also furnish isomorphous mixtures of the two salts. F. Ullik prepared crystals of **potassium magnesium molybdate**, $\text{K}_2\text{Mg}(\text{MoO}_4)_2 \cdot 2\text{H}_2\text{O}$, by the method employed for the ammonium salt. The salt loses water and melts at a dull red-heat; and it is slowly dissolved by cold water, and quickly by hot water. F. Ullik found that mixed soln. of magnesium molybdate and potassium sulphate furnish crystals of the separate components, but with mixed soln. of molybdates and chromates, isomorphous mixtures of $\text{K}_2\text{Mg}(\text{MoO}_4)_{n-2}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ are formed.

F. de Carli¹¹ observed that a reaction between molybdenum trioxide and zinc oxide begins at 270° . R. Brandes obtained a precipitate by adding ammonium molybdate to a soln. of a zinc salt, and the yellowish-white powder approximated in composition to **zinc molybdate**, ZnMoO_4 . W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. There is an interchange of acid radicle in the reactions $\text{CdO} + \text{ZnMoO}_4 = \text{CdMoO}_4 + \text{ZnO}$; $\text{MgO} + \text{ZnMoO}_4 = \text{MgMoO}_4 + \text{ZnO}$; $\text{MgO} + \text{CdMoO}_4 = \text{CdO} + \text{MgMoO}_4$; and $\text{MgO} + \text{MnMoO}_4 = \text{MgMoO}_4 + \text{MnO}$. R. Brandes said that zinc molybdate is sparingly soluble in water; and readily soluble in acids. A. Coloriano, and E. Manassewitsch showed that the product obtained by precipitation is really the *monohydrate*, which does not lose all its water at 100° . H. Schultze obtained minute needles of the anhydrous salt by fusing together a mixture of sodium molybdate, zinc chloride, and sodium chloride (2 : 3 : 6), and washing the cold mass with water. The salt is fusible. F. L. Sonnenschein prepared crystals of **zinc diamminomolybdate**, $\text{Zn}(\text{NH}_3)_2\text{MoO}_4 \cdot \text{H}_2\text{O}$, by evaporating the filtered liquid obtained by digesting zinc oxide with an ammoniacal soln. of ammonium molybdate.

F. de Carli observed that a reaction between cadmium oxide and molybdenum trioxide begins at about 500° . R. Brandes obtained what appears to have been **cadmium molybdate**, CdMoO_4 , by precipitation as in the case of the analogous zinc salt; and H. Schultze obtained yellow plates of the anhydrous salt by melting together sodium molybdate, cadmium chloride, and sodium chloride (2 : 7 : 6).

The salt was also obtained by the precipitation process by E. F. Smith and R. H. Bradbury, A. Junius, and E. Manassewitsch. E. K. Broch calculated from the X-radiograms, the space-lattice with $a=5.138$ A., $c=11.17$ A., $a:c=1:2.174$; and the density, 5.347. W. Jander studied the diffusion of the molybdate and tungstate. The salt is sparingly soluble in water, freely soluble in acids, aq. ammonia, and soln. of potassium cyanide. S. H. C. Briggs obtained colourless crystals of **ammonium cadmium diamminomolybdate**, $(\text{NH}_4)_2\text{CdMoO}_4(\text{NH}_3)_2$, from an ammoniacal soln. of cadmium sulphate and ammonium molybdate as in the case of the corresponding copper salt. The salt is partially decomposed when heated.

H. Struve¹² treated potassium trimolybdate with mercurous nitrate and washed the resulting dimolybdate with water until it formed golden-yellow needles of **mercurous molybdate**, Hg_2MoO_4 ; the change occurs more rapidly if the precipitate and mother-liquor be boiled for a long time. C. W. Scheele said that mercuric chloride does not give a precipitate with molybdic acid; but J. J. Berzelius, and C. Hatchett observed that with potassium molybdate a yellow precipitate of **mercuric molybdate** is produced which is decomposed by nitric acid; 100 parts of water dissolve 0.167 to 0.200 part of the salt. According to C. H. Hirzel, finely-divided mercuric oxide is rapidly attacked by a conc. soln. of acid ammonium molybdate, and after boiling for some hours, a yellowish-white, granular precipitate is formed—no ammonia is given off, and no mercury passes into soln. The composition of the precipitate was not determined.

H. Struve,¹³ and J. G. Gentile were unable to prepare normal **aluminium molybdate**; nor has **gallium molybdate** been obtained. The aluminium molybdates are discussed below. G. Tammann observed no reaction between alumina and molybdenum trioxide below 700° . C. Renz prepared **indium molybdate**, $\text{In}_2(\text{MoO}_4)_3 \cdot 2\text{H}_2\text{O}$, by the action of ammonium molybdate on a soln. of an indium salt; the white precipitate dries to a horn-like mass; it is insoluble in water, and soluble in hydrochloric acid. M. Delafontaine prepared **thallous molybdate**, Tl_2MoO_4 , by boiling thallous oxide or carbonate with water and molybdic acid; P. S. Oettinger, and H. Fleming, by double decomposition of a soln. of a thallous salt with a normal molybdate; and F. Mauro, by roasting thallous molybdenum dioxytetrafluoride at a red-heat in air. It separates from a hot aq. soln. as a crystalline powder, or in tabular crystals. It melts at a red-heat to form a yellow liquid, and partial volatilization occurs. The salt is soluble in alkali-lye; and it dissolves in hydrofluoric acid to form a soln. which when evaporated over sulphuric acid, furnishes crystals of thallous molybdenum dioxytetrafluoride.

P. Didier¹⁴ prepared **cerous molybdate**, $\text{Ce}_2(\text{MoO}_4)_3$, by fusing a mixture of anhydrous cerous chloride and sodium molybdate; and A. Cossa observed that a soln. of a cerous salt gives a gelatinous white precipitate when treated with sodium molybdate; the precipitate becomes yellow and crystalline. H. Traube obtained crystals of cerium molybdate as a sublimate by the method indicated in connection with calcium molybdate. G. Tammann said that the reaction between cerium dioxide, and molybdenum trioxide begins at about 650° , and $\text{Ce}_2(\text{MoO}_4)_3$ is formed. The sp. gr. of the salt, which has been fused in an inert atm., is 4.56. F. Zambonini and R. G. Levi gave 5.03 for the sp. gr. According to A. Cossa, the crystals are tetragonal and are isomorphous with wulfenite; they have the axial ratios $a:c=1:1.558$. F. Zambonini found that the air-dried precipitate is the trihydrate, $\text{Ce}_2(\text{MoO}_4)_3 \cdot 3\text{H}_2\text{O}$. He obtained crystals of the anhydrous salt by fusing the precipitated salt in an electric furnace, and slowly cooling the mass; he gave for the axial ratio of the rhombic crystals $a:b:c=0.6631:1:0.8212$. The sp. gr. of the rhombic crystals is 4.83 at $20^\circ/20^\circ$; the mol. vol., 167.4; and the m.p., 930° . F. Zambonini also obtained a tetragonal form by heating the salt dried at 180° to 1050° and slowly cooling it from 900° —the axial ratio was $a:c=1:1.5624$; F. Zambonini and R. G. Levi gave for the dimensions of unit cell $a=3.77$ A., and $c=5.81$ A. F. Zambonini gave 5.03 for the sp. gr. at $18^\circ/18^\circ$; and for the mol. vol., 151.2.

E. Cane gave 0.126 for the sp. ht. The indices of refraction and dispersions for $\lambda=667, 570,$ and 533 are respectively $\omega=2.0185, \epsilon=2.0067,$ and $\omega-\epsilon=0.0118$; $\omega=2.0403, \epsilon=2.0277,$ and $\omega-\epsilon=0.0126$; and $\omega=2.0512, \epsilon=2.0375,$ and $\omega-\epsilon=0.0137$. S. Prakash and N. R. Dhar obtained the hydrogel of ceric molybdate. The crystal plates obtained in preparing the tetragonal form appear to be **cerous ceric** or **cerosic molybdate**, $\text{Ce}_2(\text{MoO}_4)_3 \cdot 2\text{Ce}(\text{MoO}_4)_2$. E. Herlinger studied the crystal structure. F. Zambonini prepared isomorphous mixtures of tetragonal crystals of calcium and cerous molybdates containing up to 59.1 per cent. of cerous molybdate. The axial ratios $a:c$ of the tetragonal crystals with 0, 6.5, and 59.1 per cent. of cerous molybdate are, respectively, 1:1.5513, 1:1.5492, and 1:1.5510. Isomorphous mixtures of crystals of cerous and strontium molybdates with up to 39.7 per cent. of the cerium salt were prepared. The refractive indices for light of wave-length λ were:

λ	2.4 per cent. $\text{Ce}_2(\text{MoO}_4)_3$.				39.7 per cent. $\text{Ce}_2(\text{MoO}_4)_3$.		
	ϵ	ω	$\epsilon-\omega$	ϵ	ω	$\epsilon-\omega$	
667	1.9127	1.9088	0.0039	1.940	1.937	0.003	
570	1.9258	1.9210	0.0048	1.956	1.952	0.004	
533	1.9350	1.9290	0.0060	1.963	1.958	0.005	

F. T. Frerichs and E. F. Smith prepared **lanthanum trihydromolybdate**, $\text{LaH}_3(\text{MoO}_4)_3$, as a precipitate by adding ammonium molybdate to a lanthanum salt. F. R. M. Hitchcock obtained the normal **lanthanum molybdate**, $\text{La}_2(\text{MoO}_4)_3$, by adding sodium molybdate to a soln. of lanthanum chloride, and dehydrating the gelatinous precipitate. H. Traube obtained crystals as a sublimate by the method indicated for calcium molybdate. F. Zambonini fused the salt and by slow cooling obtained tetragonal, bipyramidal crystals with the axial ratio $a:c=1:1.5504$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell, $a=3.78$ A. and $c=5.68$ A. F. Zambonini found that the optical character was negative. The sp. gr. is 4.77 at $16^\circ/16^\circ$; the mol. vol., 158.9; and the m.p., 1181° .

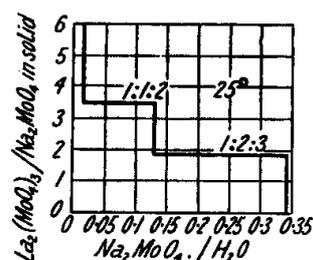


FIG. 22.—Equilibrium in the System: $\text{La}_2(\text{MoO}_4)_3$ - Na_2MoO_4 - H_2O .

E. Cane gave 0.114 for the sp. ht. G. Carobbi's study of the ternary system: $\text{La}_2(\text{MoO}_4)_3$ - Na_2MoO_4 - H_2O at 25° , and the results, Fig. 22, show the existence of the two **sodium lanthanum molybdates**: $\text{La}_2(\text{MoO}_4)_3 \cdot \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{La}_2(\text{MoO}_4)_3 \cdot 2\text{Na}_2\text{MoO}_4 \cdot 3\text{H}_2\text{O}$. F. Zambonini found that isomorphous mixtures were obtained with lead molybdate (*q.v.*), with up to 42 per cent. of calcium molybdate; with up to 62.5 per cent. of strontium molybdate; and with up to 86.9 per cent. of barium molybdate. F. T. Frerichs and E. F. Smith obtained **didymium trihydromolybdate**, $\text{DiH}_3(\text{MoO}_4)_3$ as in the case of the lanthanum salt. A. Cossa also prepared didymium molybdate, $\text{Di}_2(\text{MoO}_4)_3$. H. Traube obtained crystals as a sublimate by the method indicated for calcium molybdate in tetragonal crystals, which, according to F. Zambonini have the axial ratio $a:c=1:1.5489$. The sp. gr. is 4.96 at $16.5^\circ/16.5^\circ$. The m.p. is 1125° , but it is not sharp. The double refraction is negative, and there are no optical anomalies. The index of refraction is 2.008 for the *B*-line; 2.012 for the *C*-line; 2.026 for the *D*-line; 2.039 for the *E*-line; and 2.054 for the *F*-line. Isomorphous mixtures were obtained with lead molybdate (*q.v.*), and with calcium molybdate. The crystals with about 61.2 per cent. of calcium molybdate have a feebly positive birefringence. The indices of refraction for light of wave-length λ are:

λ	667	599	570	533	475
ϵ	1.9869	1.9947	2.0020	2.0094	2.0212
ω	1.9902	1.0089	2.0068	2.0139	2.0258
$\epsilon-\omega$	0.0033	0.0042	0.0048	0.0045	0.0046

F. R. M. Hitchcock prepared **neodymium molybdate**, $\text{Nd}_2(\text{MoO}_4)_3$; and F. Zambonini

found that the air-dried substance has the composition $\text{Nd}_2(\text{MoO}_4)_3 \cdot 4\text{H}_2\text{O}$. When heated with molten sodium chloride, violet crystals are formed. The axial ratio of the tetragonal crystals is $a : c = 1 : 1.5480$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell $a = 3.74$ A., and $c = 5.79$ A. F. Zambonini found that the birefringence is negative; the indices of refraction and dispersions for $\lambda = 667, 570,$ and 533 are respectively $\omega = 2.0052, \epsilon = 2.0038,$ and $\omega - \epsilon = 0.0014$; $\omega = 2.0239, \epsilon = 2.0218,$ and $\omega - \epsilon = 0.0021$; and $\omega = 2.0313, \epsilon = 2.0293,$ and $\omega - \epsilon = 0.0020$. The sp. gr. is 5.14 at $18^\circ/18^\circ$; the mol. vol., 149.5; and the m.p., 1176° —*vide infra*, lead molybdate. F. R. M. Hitchcock prepared **praseodymium molybdate** by precipitation with praseodymium chloride and sodium molybdate soln. F. Zambonini found that when dried over sulphuric acid, the gelatinous precipitate has the composition $\text{Pr}_2(\text{MoO}_4)_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$; and when heated with fused sodium chloride, the anhydrous salt furnishes tetragonal bipyramids with the axial ratio $a : c = 1 : 1.5439$. F. Zambonini and R. G. Levi gave for the dimensions of the elementary cell, $a = 3.76$ A., and $c = 5.805$ A. F. Zambonini found that the sp. gr. is 4.84 at $16.5^\circ/16.5^\circ$; the mol. vol. is 157.3; and the m.p., 1030° . The birefringence is negative; and the index of refraction $\epsilon = 1.990, 2.007,$ and 2.016 respectively for $\lambda = 667, 570,$ and 533 . P. T. Cleve obtained **samarium molybdate**, $\text{Sm}_2(\text{MoO}_4)_3$, in violet, rhombic octahedra, by calcining a mixture of samarium oxalate, sodium chloride, and molybdenum trioxide. F. Zambonini and R. G. Levi found the dimensions of the unit cell to be $a = 3.69$ A., and $c = 5.81$ A., the axial ratio $a : c = 1 : 1.5745$. The sp. gr. is 5.36. A. Cleve prepared **sodium samarium molybdate**, $\text{SmNa}(\text{MoO}_4)_2$, in pale red needles. The two salts can be separated by levigation in water. F. Zambonini prepared **yttrium molybdate**, $\text{Y}_2(\text{MoO}_4)_3 \cdot 4\text{H}_2\text{O}$, by drying over calcium chloride the precipitate obtained by adding a soln. of sodium molybdate to one of yttrium nitrate. When melted, and slowly cooled, it furnishes greyish-white or yellow crystal plates which belong to the tetragonal system, and have the axial ratio $a : c = 1 : 1.5422$; the (001)-cleavage is incomplete; the sp. gr. is 4.79 at $16^\circ/16^\circ$; the mol. vol. is 137.4; the m.p. is 1347° ; and the index of refraction, ϵ , for $\lambda = 667$ is 2.013; for $\lambda = 570, 2.031$; and for $\lambda = 533, 2.043$. Isomorphous mixtures with lead molybdate (*q.v.*), and with calcium molybdate were prepared. E. Cane gave 0.159 for the sp. ht., F. Zambonini found that the crystals with 95.3 per cent. of the calcium salt had the respective indices of refraction and dispersions $\epsilon = 1.986, \omega = 1.978,$ and $\epsilon - \omega = 0.008$ for $\lambda = 667$; $\epsilon = 2.002, \omega = 1.998,$ and $\epsilon - \omega = 0.004$ for $\lambda = 570$; and $\epsilon = 2.012, \omega = 2.003,$ and $\epsilon - \omega = 0.009$ for $\lambda = 533$. It was found that the presence of cerous molybdate favours the formation of isomorphous mixtures with higher proportions of calcium. Crystals containing 24.7 per cent. of yttrium molybdate, 21 per cent. of cerous molybdate and 44.3 per cent. of calcium molybdate had the axial ratio $a : c = 1 : 1.5436$, a positive birefringence, and the indices of refraction for the C-, D-, and E-lines respectively $\epsilon = 1.9939, 2.0049,$ and 2.0208 ; $\omega = 1.9905, 2.0004,$ and 2.0163 ; and $\epsilon - \omega = 0.0034, 0.0045,$ and 0.0045 . A. Cleve obtained **ytterbium oxymolybdate**, $\text{Yb}_2\text{O}_3 \cdot \text{Yb}_2\text{O}_2(\text{MoO}_4)$, as a green crystalline powder, by heating ytterbium oxide, molybdenum trioxide, and sodium chloride at a high temp.

The **silicon molybdates**, or **silicomolybdates**, were discussed in connection with the silicates—6. 40, 50. For the **titanium molybdates**, *vide infra*. O. Kulka¹⁵ treated a cold, aq. soln. of ammonium paramolybdate with zirconium sulphate, and obtained a slimy precipitate which, when washed with hot water, approximated to **zirconium molybdate**, $\text{Zr}(\text{MoO}_4)_2 \cdot 21\text{H}_2\text{O}$. It is insoluble in water, but soluble in hot, conc. hydrochloric acid. Zirconium hydroxide is insoluble in an aq. soln. of alkali molybdate. S. Prakash and N. R. Dhar obtained the hydrogel of zirconium molybdate. S. M. Tanatar and E. K. Kurowsky prepared **zirconium oxychloromolybdate**, $\text{ZrCl}_4 \cdot m\text{Zr}_3(\text{MoO}_4)_2 \cdot n\text{ZrO}_2$. J. J. Berzelius obtained **thorium molybdate** as a white precipitate by adding a soln. of an alkali molybdate to one of a thorium salt; and J. J. Chydenius, by mixing a feebly acid soln. of thorium tetrachloride with an ammoniacal soln. of ammonium molybdate. F. Zambonini

obtained the anhydrous salt, $\text{Th}(\text{MoO}_4)_2$, by fusing partly-dehydrated thorium chloride with an excess of anhydrous sodium molybdate. The tetragonal crystals have the axial ratio $a : c = 1 : 0.73565$; and the sp. gr. 4.92 at $7.5^\circ/7.5^\circ$. They form isomorphous mixtures with those of cerous molybdate. S. Prakash and N. R. Dhar prepared the hydrogel of thorium molybdate.

The blue colour obtained by J. B. Richter¹⁶ by mixing an alkali molybdate with stannous chloride, or by the action of tin and hydrochloric acid on molybdenum trioxide suspended in water was shown by J. J. Berzelius to be a mixture of stannic molybdate and a blue lower oxide of molybdenum. H. Schiff said that the blue pigment contains no tin, and, according to G. Denigès, it is produced by other reducing agents. J. P. Longstaff recommended the reaction as a test for tin. F. de Carli observed that a reaction between stannous oxide and molybdenum trioxide begins at 400° . J. J. Berzelius obtained **stannic molybdate**, as a grey powder insoluble in water, and soluble in hydrochloric acid with a blue or green coloration; and in potash-lye with a brown coloration. It is not decomposed by nitric acid. S. Prakash and N. R. Dhar dialyzed for 2 days a mixture of 1.5M- SnCl_2 with a 25 per cent. soln. of potassium molybdate. The clear soln. was mixed with an equal vol. of water. It set to a jelly in 5 hrs. The viscosities at 30° were :

Age	0	3	5	10	20	30	40	60	80 min.
Viscosity	0.01272	0.01353	0.01471	0.01804	0.02300	0.03032	0.03447	0.04412	0.07505

I. Eques a Born¹⁷ described a mineral *plumbum spatosum flavorubrum* from Annaberg, and it was also examined by N. J. von Jacquin, and F. X. Wulfen. J. B. L. Romé de l'Isle called it *plomb jaune*; A. G. Werner, *Gelbbleierz*; R. Kirwan, *yellow lead-spar* or *molybdenated lead ore*; F. S. Beudant, *melinose*; and W. Haidinger, **wulfenite**—after F. X. Wulfen. Analyses were reported by J. C. H. Heyer, M. H. Klaproth, C. Hatchett, F. Göbel, I. Domeyko, F. Jost, J. L. Smith, F. Reinitzer, C. L. Allen, C. Schmidt, C. F. Rammelsberg, G. Rose, J. F. W. Johnston, K. Schlier, V. von Zepharovich, A. Schrauf, H. Regnard, and F. Wöhler. The mineral approximates in composition to **lead molybdate**, PbMoO_4 . The lead may be partly replaced by lime forming, according to I. Domeyko, and V. von Zepharovich, *calcium lead molybdate*, or else an isomorphous mixture. Specimens from Příbram were found by P. Groth to contain chromium—*chromowulfenite*—similarly, A. Schrauf, J. L. Smith, and G. Rose found chromium in specimens from Ruksberg, Phoenixville, etc.; and E. F. Smith, C. F. Rammelsberg, and F. Wöhler reported samples with vanadium; G. Carobbi, samples with rare earths; and H. Regnard, samples with arsenic. The mineral occurs in nature associated with other lead ores at Lackentyre, Scotland; Chalanches, and Beaujolais, France; Gorno, Italy; Sarrabus, and Gennamari, Sardinia; St. Luc, Switzerland; Bleiberg, Carinthia; Ruskitza, Austria; Rezbanya and Szaska, Hungary; Příbram, Czechoslovakia; Moldawa, Banat; Annaberg, Schneeberg, Johanngeorgenstadt, and Berggieshübel, Saxony; Badenweiler, Baden; Kirghiz Steppes, Siberia; Mindouli, French Congo; in Massachusetts, Arizona, New York, Pennsylvania, Nevada, New Mexico, and California, United States; Rio Chico, Colombia; Zacatecas, Mexico, etc. The mode of formation of wulfenite was discussed by E. Dittler, G. Bischof, A. Himmelbauer, M. Henglein, C. Schmidt, G. Cesaro, and A. W. Stelzner-Bergeat. J. F. L. Hausmann observed it as a furnace product.

F. de Carli observed that a reaction between molybdenum trioxide and lead oxide begins at 650° ; W. Jander said 450° ; and G. Tammann, and J. Guillissen, 460° . D. Balareff said that the maximum effect occurs at 700° . J. J. Berzelius prepared lead molybdate by mixing soln. of lead nitrate or acetate and ammonium molybdate; G. Wempe, and H. B. Weiser used acid ammonium molybdates; and L. F. Svanberg and H. Struve, T. M. Chatard, E. F. Smith and R. H. Bradbury, A. Junius, H. B. Weiser, F. M. Jäger and H. C. Germs used sodium molybdates. E. Dittler treated white-lead with a soln. of sodium hydroxide containing 6 per

Rare earth salt	0	20	40	60	80	100 per cent.	
La	{ Beginning . . .	1065°	1085°	1109°	1139°	1163°	1181°
	{ End . . .	—	1078°	1102°	1134°	1156°	—
Nd	{ Beginning . . .	1065°	1076°	1088°	1115°	1147°	1176°
	{ End . . .	—	1070°	1080°	1105°	1135°	—
Pr	{ Beginning . . .	1065°	1072°	1068°	1054°	1043°	1030°
	{ End . . .	—	1068°	1064°	1050°	1040°	—
Di	{ Beginning . . .	1065°	1072°	1079°	1106°	1123°	1144°
	{ End . . .	—	1067°	1075°	1085°	1100°	—
Sm	{ Beginning . . .	1065°	1038°	1016°	1038°	1235°	1347°
	{ End . . .	—	977°	976°	974°	974°	—

The **arsenic molybdates** were discussed in connection with arsenic—9. 51, 22 ; and the **antimony molybdates**, in connection with antimony—9. 52, 14. According to J. B. Richter,¹⁸ when a soln. of bismuth nitrate is treated with potassium molybdate, a lemon-yellow precipitate of **bismuth molybdate**, presumably $\text{Bi}_2(\text{MoO}_4)_3$, is formed which is easily soluble in the strong acids ; whilst 100 parts of water dissolve 0.2 part of the precipitate. By fusing an intimate mixture of bismuth and molybdenum trioxides, F. Zambonini obtained the salt in tetragonal crystals with the axial ratio $a : c = 1 : 1.5636$, and sp. gr. 6.07 at 15°/15°. The mol. vol. is close to those of the molybdates of lead and the cerium metals. The m.p. is 643°. W. T. Schaller obtained greenish rectangular crystals of a mineral

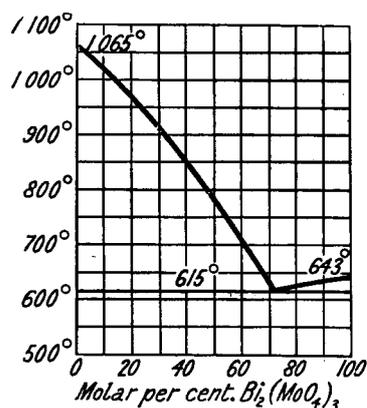


FIG. 27.—Freezing-point Curve of the System : $\text{PbMoO}_4\text{-Bi}_2(\text{MoO}_4)_3$.

from Schneeberg, Saxony ; he called it **koechlinite**—after R. Koechlin—and found the analysis corresponds with **bismuth dioxymolybdate**, $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$, or **bismuthyl molybdate**, $(\text{BiO})_2\text{MoO}_4$. The habit of the crystals is tabular, but the thin tablets vary in shape from square to elongated rectangles with diagonal striations. The axial ratios of the rhombic crystals are $a : b : c = 0.9774 : 1 : 1.0026$. The (100)-cleavage is perfect. Both contact and penetration twinning occurs. The corrosion figures with cold dil. hydrochloric acid (1 : 5) suggested a deviation from holohedral symmetry. The crystals break readily under a slight press. The index of refraction is $\beta = 2.55$ with Li-light. The crystals are slightly pleochroic when thick. E. F. Smith and R. H. Bradbury said that the bismuth salt is insoluble in water. Bismuth can be quantitatively precipitated as **ammonium bismuth molybdate**, $\text{Bi}(\text{NH}_4)(\text{MoO}_4)_2$, from a soln. of bismuth nitrate, feebly acid with nitric acid, by means of ammonium molybdate. Thus, E. H. Miller and F. van Dyke Crusser said that the nitric acid soln. of the bismuth is mixed with a large excess of the ordinary ammonium molybdate reagent and the liquid is neutralized with dil. aq. ammonia, using congo-red as indicator ; a drop or two of dil. nitric acid is then added until the colour is lilac. The whole is diluted to about 200 c.c. and slowly heated to 50°–60°. The precipitated bismuth ammonium molybdate is washed with a 3 per cent. soln. of ammonium nitrate, and dried in an air-bath at 160°. When ignited, there remains a pale yellow mass of $\text{Bi}_2\text{O}_4 \cdot 4\text{MoO}_3$. The reaction was studied by E. H. Miller and H. Frank, and H. S. Riederer. F. Zambonini studied the thermal diagram, Fig. 27, of the system $\text{Bi}_2(\text{MoO}_4)_3\text{-PbMoO}_4$. The curve descends rapidly from the m.p., 1065°, of lead molybdate to a eutectic at 615° corresponding with about 71.5 mol. per cent. of the bismuth salt. It then rises rapidly to 643°, the m.p. of bismuth molybdate. No solid soln. are formed, or else the mutual solubility in the solid state is very small.

The **vanadium molybdates** have been discussed in connection with vanadium—9. 54, 14 ; **columbium molybdate**, and **tantalum molybdate** have not been prepared ; nor has the normal **chromium molybdate** been described, although A. Moberg,¹⁹ and J. J. Berzelius, said that an apple-green precipitate is formed when ammonium

molybdate is added to a soln. of chromic salt. H. Schultze could not prepare chromic molybdates by melting a mixture of chromic chloride and sodium molybdate. S. Prakash and N. R. Dhar obtained the hydrogel of chromic molybdate. The **chromatomolybdates** are discussed in connection with chromium; and some complex chromic dimolybdates are indicated below. The intermediate molybdenum oxides previously described can be regarded as molybdenum molybdates—*e.g.* Mo_5O_{14} can be represented as **molybdenyl molybdate**; $(\text{MoO})_2(\text{MoO}_4)_3$; $\text{Mo}_{11}\text{O}_{32}$ as **molybdenum trimolybdate**, $(\text{MoO})_2(\text{Mo}_3\text{O}_{10})_3$; Mo_9O_{26} as **molybdenyl paramolybdate**, $(\text{MoO})_2(\text{Mo}_7\text{O}_{24})$; Mo_7O_{20} as **molybdenum molybdate**, $\text{Mo}_2(\text{MoO}_4)_5$; $\text{Mo}_{17}\text{O}_{50}$ as **molybdenum trimolybdate**, $\text{Mo}_2(\text{Mo}_3\text{O}_{10})_5$; and $\text{Mo}_{37}\text{O}_{120}$ as **molybdenum heptamolybdate**, $\text{Mo}_2(\text{Mo}_7\text{O}_{24})_5$. For the *tungsten molybdates*, see the molybdenum tungstates. A. Lancien²⁰ prepared **uranium molybdate**, $\text{U}(\text{MoO}_4)_2$, by reducing the paramolybdate with methyl, ethyl, or higher alcohols; and C. F. Rammelsberg obtained the *trihydrate*, as a greenish-black precipitate, by adding ammonium molybdate to an excess of uranium tetrachloride, and washing the precipitate with hot water. It loses 9.07 per cent. of water when calcined; and when melted, some molybdenum trioxide sublimes. Boiling alkali-lye extracts the molybdic acid; hydrochloric acid forms a green soln. which when diluted becomes yellow. A. Lancien prepared **uranyl molybdate**, $(\text{UO}_2)\text{MoO}_4$, as a precipitate by the addition of a soln. of ammonium molybdate to uranyl nitrate soln. When prepared in the dark, this compound forms a white, amorphous powder, which is reduced by ethyl and methyl alcohols or acetic acid to the green **uranous molybdate**, $\text{U}(\text{MoO}_4)_2$, this is then changed to a brick-red and then converted into the green oxide by prolonged boiling with alkali-lye and is rapidly dissolved with a yellowish-green fluorescence by hydrochloric, sulphuric, and nitric acids. When exposed to sunlight for thirty hours, uranyl molybdate becomes golden-yellow in colour, insoluble in nitric acid, which merely whitens it, and is no longer reduced by alcohol. Uranyl molybdate is radioactive, having an activity greater than that of the nitrate and equal to that of radium bromide of activity 40. B. Szilard prepared uranyl molybdate using an excess of uranyl nitrate, in one case, and, in the other case, an excess of ammonium molybdate, and found the radioactivity of both to be the same, and to be quite normal. The uranium molybdate obtained by P. P. Pilipenko from Bivongi was shown by G. Carobbi to be ferri-molybdate—*vide infra*.

J. B. Richter²¹ treated a soln. of manganous chloride with potassium molybdate and obtained a brownish-white precipitate which dissolved in forty to fifty times its weight of water. H. Schultze prepared **manganous molybdate**, MnMoO_4 , by melting together a mixture of sodium molybdate, sodium chloride, and manganous chloride (1 : 2 : 3), and washing the cold mass with water. Yellow, fusible monoclinic plates remain. The cold mass which has been fused contains reddish-brown plates and needles, and yellow crystals. The yellow crystals are soluble in cold, dil. hydrochloric acid, whilst the brown ones are not attacked. W. Jander discussed the lattice-structure, and the diffusion of the molybdate and tungstate, as well as the reaction $\text{MgO} + \text{MnMoO}_4 = \text{MnO} + \text{MgMoO}_4$. H. Struve prepared the *hydrate*, $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$, by treating manganous carbonate with potassium or sodium trimolybdate; and A. Coloriano, by treating manganous nitrate with ammonium paramolybdate, and boiling the amorphous powder in the mother-liquor so that it may crystallize. The white powder consists of microscopic prismatic plates; it loses no water at 100° ; but at a higher temp., it loses water and becomes brown. It is sparingly soluble in boiling water. E. Marckwald obtained tabular crystals of the *tritapentahydrate* by allowing the decahydrate to stand exposed to air for some time; and the *decahydrate* as a white, amorphous precipitate by adding an eq. amount of sodium molybdate to a soln. of manganous sulphate.

E. Marckwald reported a number of complex salts. Orange-yellow crystals of **ammonium manganous molybdate**, $(\text{NH}_4)_2\text{O} \cdot \text{MnO} \cdot 3\text{MoO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, was obtained from a cold, dil. soln. of manganese sulphate (15 grms.) and the eq. proportion of

ammonium paramolybdate in 100 c.c. of water; $(\text{NH}_4)_2\text{O} \cdot 3\text{MnO} \cdot 6\text{MoO}_3 \cdot 16\text{H}_2\text{O}$, in yellowish-white, prismatic crystals, from a soln. of manganese sulphate and ammonium paramolybdate in a sealed tube at 150° for 5 hrs.; $(\text{NH}_4)_2\text{O} \cdot 2\text{MnO} \cdot 6\text{MoO}_3 \cdot 16\text{H}_2\text{O}$, in brownish-red needles, from cold soln. of 25 grms. of manganese sulphate and an eq. amount of ammonium paramolybdate in 50 c.c. of water; $(\text{NH}_4)_2\text{O} \cdot 2\text{MnO} \cdot 12\text{MoO}_3 \cdot 22\text{H}_2\text{O}$, in hexagonal, yellow plates, from the mother-liquor of the preceding salt; and **sodium manganous molybdate**, $2\text{Na}_2\text{O} \cdot \text{MnO} \cdot 6\text{MoO}_3 \cdot 19\text{H}_2\text{O}$, in yellowish-white needles by the action of cold soln. of sodium dimolybdate and manganese sulphate. Our knowledge of the complex manganous molybdates is thus in an unsatisfactory state.

By boiling ammonium manganic molybdate with manganic hydroxide, treating the product with water, and evaporating the brown soln., H. Struve obtained brown, amorphous, **manganic molybdate**, $2\text{Mn}_2\text{O}_3 \cdot \text{MoO}_3 \cdot 4\text{H}_2\text{O}$. H. Struve attempted to prepare *molybdic alums*, of the general formula $2\text{R}'_2\text{O} \cdot \text{R}_2\text{O} \cdot \text{R}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot n\text{H}_2\text{O}$, where R' represents K or NH_4 , and R'', Fe, Al, or Cr. He obtained instead, compounds of the general type $5\text{R}'_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 16\text{MoO}_3 \cdot 12\text{H}_2\text{O}$. Thus, by boiling a soln. of ammonium molybdate with manganic hydroxide, he obtained **ammonium manganic molybdate**, $5(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 16\text{MoO}_3 \cdot 12\text{H}_2\text{O}$; and E. Péchard treated a hot soln. of ammonium molybdate and a manganous salt with a dil. soln. of potassium permanganate, and obtained red crystals of the salt $3(\text{NH}_4)_2\text{O} \cdot \text{MnO}_2 \cdot 12\text{MoO}_3 \cdot 5\text{H}_2\text{O}$. C. Friedheim and M. Samelson did not agree with the analyses of either E. Péchard, or of H. Struve, and A. Rosenheim and H. Itzig represented E. Péchard's compound by the formula $2(\text{NH}_4)_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, and by the action of potassium chloride this was converted into $3\text{K}_2\text{O} \cdot \text{MnO}_2 \cdot 8\text{MoO}_3 \cdot 5\text{H}_2\text{O}$. A. Rosenheim added 2 mols of a soln. of manganous chloride to a cold, sat. soln. of ammonium paramolybdate, and obtained the complex salt $(\text{NH}_3)_3\text{H}_7[\text{Mn}''(\text{MoO}_4)_6] \cdot 3\text{H}_2\text{O}$, which lost 3 mols. of water when kept for 3 days at 60° . The compound $4(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ was prepared by F. Zambonini and V. Cagliotti. It is said to be the compound prepared by H. Struve, C. Friedheim and M. Samelson, and C. Friedheim and O. Allemann. The manganese is said to be really present in the bi- and quadrivalent states so that, in harmony with H. Struve's opinion, the Mn_2O_3 in the formula represents MnO and MnO_2 . The formula can therefore be written $(\text{NH}_4)_8[\text{Mn}''(\text{Mo}_2\text{O}_7)_6] \cdot \text{Mn}''\text{MoO}_4 \cdot 9\text{H}_2\text{O}$, in harmony with E. Péchard's suggestion that the ratio $\text{MnO}_2 : \text{MoO}_3$ is 1 : 12 and that the compound is analogous to the silicomolybdates. H. Struve also obtained red crystals of **potassium manganic molybdate**, $2\text{K}_2\text{O} \cdot \text{MnO} \cdot \text{MnO}_2 \cdot 9\text{MoO}_3 \cdot 8\text{H}_2\text{O}$, by boiling a soln. of potassium trimolybdate with manganic hydroxide, or by the action of chlorine on a soln. of potassium trimolybdate and manganous sulphate. C. Friedheim and M. Samelson represented the composition of this salt by the formula $2\text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 16\text{MoO}_3 \cdot 12\text{H}_2\text{O}$.

E. Péchard reported **permanganous molybdate**, $\text{MnO}_2 \cdot 12\text{MoO}_3 \cdot 10\text{H}_2\text{O}$, to be formed by treating the barium salt, suspended in water, with the theoretical quantity of sulphuric acid, and evaporating the clear liquor in vacuo. A. Rosenheim and H. Itzig denied the existence of this compound. C. Friedheim and M. Samelson, and C. Friedheim and O. Allemann prepared what they regarded as **permanganito-molybdates**; these are indicated below. As emphasized by A. Rosenheim, the test employed to determine the active oxygen of the manganese dioxide—distillation with potassium bromide and hydrochloric acid—is by no means satisfactory; and the question whether these compounds contain quadrivalent or trivalent manganese has not been satisfactorily answered. A. Rosenheim thinks that these salts may be more or less impure forms of $\text{R}_n\text{H}_{10-n}[\text{Mn}''(\text{MoO}_4)_6]$; although complexes with quadrivalent cerium, thorium, and zirconium are known.

A mixture of a soln. of ammonium paramolybdate and manganous chloride with 18.5 per cent. of hydrogen dioxide yields **ammonium permanganitomolybdate**, $2(\text{NH}_4)_2\text{O} \cdot \text{MnO}_2 \cdot 7\text{MoO}_3 \cdot 5\text{H}_2\text{O}$; a mixed soln. of potassium paramolybdate, manganous chloride and 2.5 per cent. of hydrogen dioxide yields **potassium permanganitomolybdate**,

$3K_2O.MnO_2.8MoO_3.3$ or $5H_2O$. E. Péchard also prepared this salt; a mixed soln. of ammonium permolybdate, and manganous and potassium chlorides yields **potassium ammonium permanganitomolybdate**, $3\{K_2.(NH_4)_2\}O.MnO_2.8MoO_3.4H_2O$; sodium manganous permanganitomolybdate and potassium chloride yield **sodium potassium manganous permanganitomolybdate**, $3(K_2.Na_2.Mn)O.MnO_2.8MoO_3.4H_2O$; a soln. of ammonium paramolybdate, manganous chloride, and 2.5 per cent. hydrogen dioxide yields **ammonium permanganitomolybdate**, $3(NH_4)_2O.MnO_2.9MoO_3.6, 7, \text{ or } 8H_2O$; when this salt or the ammonium manganous salt is treated with potassium chloride, it forms **potassium permanganitomolybdate**, $3K_2O.MnO_2.9MoO_3.5$ or $6H_2O$. R. D. Hall also prepared this salt; a soln. of sodium paramolybdate, manganous chloride and 3.5 per cent. hydrogen dioxide furnishes **sodium manganous permanganitomolybdate**, $3(Na_2.Mn)O.MnO_2.9MoO_3.15H_2O$; a soln. of ammonium paramolybdate, manganous chloride, and potassium persulphate yields **ammonium manganous permanganitomolybdate**, $3\{(NH_4)_2.Mn\}O.MnO_2.9MoO_3.6$ or $7H_2O$; if more potassium persulphate is used, **ammonium potassium manganous permanganitomolybdate**, $3\{(NH_4)_2.K_2.Mn\}O.MnO_2.9MoO_3.7H_2O$; and similarly, **potassium manganous permanganitomolybdate**, $3(K_2.Mn)O.MnO_2.9MoO_3.6$ or $7H_2O$, is formed. R. D. Hall also prepared this salt; and by treating it with barium chloride obtained **barium permanganitomolybdate**, $3BaO.MnO_2.9MoO_3.12H_2O$; a soln. of ammonium manganous molybdate and potassium permanganate, or a soln. of ammonium paramolybdate with potassium permanganate and alcohol yields **ammonium manganous permanganitomolybdate**, $3\{(NH_4)_2.Mn\}O.MnO_2.10MoO_3.8$ or $10H_2O$; a soln. of ammonium paramolybdate, manganous sulphate, and potassium permanganate yields **ammonium potassium manganous permanganitomolybdate**, $3\{(NH_4)_2.K.Mn\}O.MnO_2.10MoO_3.6$ or $10H_2O$; a soln. of ammonium permolybdate, and manganous chloride yields **ammonium manganous permanganitomolybdate**, $4\{(NH_4)_2.Mn\}O.MnO_2.10MoO_3.6H_2O$; a boiling soln. of ammonium paramolybdate, potassium permanganate, and alcohol yields **ammonium potassium manganous permanganitomolybdate**, $4\{(NH_4)_2.K_2.Mn\}O.MnO_2.10MoO_3.5H_2O$; leaving a soln. of ammonium paramolybdate, and molybdic acid in contact with hydrated manganese dioxide for 4 months furnishes **ammonium manganous permanganitomolybdate**, $4\{(NH_4)_2.Mn\}O.MnO_2.11MoO_3.7H_2O$; by using more hydrogen dioxide than was employed in preparing the 3:1:9:6—salt **ammonium manganous permanganitomolybdate**, $4\{(NH_4)_2.Mn\}O.MnO_2.11MoO_3.8H_2O$, is obtained; and an analogous process yields **potassium manganous permanganitomolybdate**, $4(K_2.Mn)O.MnO_2.11MoO_3.11H_2O$. E. Péchard's $3K_2O.MnO_2.12MoO_3.4H_2O$ could not be prepared by A. Rosenheim and H. Itzig, or by C. Friedheim and M. Samelson. Nor could A. Rosenheim and H. Itzig prepare E. Péchard's $3Na_2O.MnO_2.12MoO_3.13H_2O$.

H. Struve,²² and E. Steinacker found that a soln. of a molybdate or molybdic acid is reduced when treated with a ferrous salt; but H. Schultze obtained normal **ferrous molybdate**, $FeMoO_4$, by fusing a mixture of sodium chloride, ferrous chloride, and sodium molybdate. G. Tammann said that the reaction between ferrous oxide and molybdenum trioxide begins at about 320° ; and that the heat of formation of $FeMoO_4$ is 13.5 Cals. C. W. Scheele obtained a brown precipitate by treating a soln. of ferric chloride with potassium molybdate; and E. Marckwald obtained normal **ferric molybdate**, $Fe_2(MoO_4)_3.42H_2O$, in this manner by treating 3 mols of sodium molybdate with 2 mols of ferric chloride. G. Tammann said that no reaction between ferric oxide and molybdenum trioxide occurs below 600° ; and he added that the heat of formation of $Fe_2(MoO_4)_3.nH_2O$ is -29.3 Cals. S. Prakash and N. R. Dhar found that a soln. of 8 c.c. of $M-FeCl_3$, 4 c.c. of water, and 8 c.c. of a 10 per cent. soln. of potassium molybdate sets to a jelly in 10 hrs. The viscosities at 30° were:

Age	0	15	32	68	128	158	188	300 min.
Viscosity	0.009966	0.01009	0.01029	0.01094	0.01442	0.01916	0.03526	0.10620

Some forms of molybdic ochre—*vide supra*, molybdenum trioxide—are mixtures of ferric molybdate and molybdic acid. P. P. Pilipenko obtained a mineral from the Alexyewsky Copper Mines of Jenissejsker, Siberia, which corresponds with $2Fe_2O_3.7MoO_3.19H_2O$, and W. T. Schaller, one from Hortense, Colorado, which corresponded with $Fe_2(MoO_4)_3.7\frac{1}{2}H_2O$, and other samples from Renfrew, Ontario, etc., approximating $Fe_2(MoO_4)_3.n(3H_2O)$, and previously regarded as molybdic ochre, or molybdite (*q.v.*). E. S. Simpson gave $(Fe_2O_3.4MoO_3.5H_2O)5H_2O$. P. P. Pilipenko named these minerals **ferrimolybdite**. G. Carobbi obtained a ferrimolybdate, $4Fe_2O_3.13MoO_3.44H_2O$, from Bivongi.

F. de Carli²³ observed that the reaction between cobaltous oxide and molyb-

denum trioxide begins at 410° . J. J. Berzelius obtained **cobaltous molybdate**, $\text{CoMoO}_4 \cdot n\text{H}_2\text{O}$, as a dirty yellow precipitate by adding a soln. of alkali molybdate to one of a cobaltous salt. The precipitate forms a red powder when dried, and it is decomposed by acids and alkali-lye. E. F. Smith and R. H. Bradbury found that cobalt molybdate is not formed either in cold dil. or conc. soln. By heating a conc. soln. of sodium molybdate with cobalt nitrate, a small quantity of a bluish-white precipitate is formed which dissolves again on cooling. H. Schultze obtained crystals of the anhydrous salt by melting together a mixture of normal sodium molybdate, cobaltous chloride, and sodium chloride (1 : 2 : 2). An impure cobaltous molybdate occurs as the mineral, named by W. Haidinger, **pateraite**—after A. Patera—in the Elias Mine, Joachimsthal. It was described by C. von Hauer, and J. von Jokély. An impure sample was analyzed by G. C. Laube.

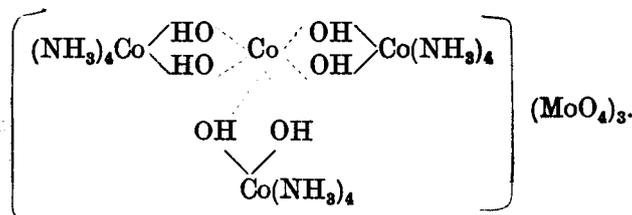
A. Coloriano obtained the *monohydrate*, $\text{CoMoO}_4 \cdot \text{H}_2\text{O}$, or $\text{HO} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{Co} \cdot \text{OH}$, in an amorphous state by the action of ammonium paramolybdate on a soln. of a cobaltous salt. When digested with water for a long time, it becomes crystalline. E. Marckwald said that the product is impure, and he prepared it by mixing a 6.5 per cent. soln. of cobaltous chloride with a 3.5 per cent. soln. of sodium molybdate in the cold, and in eq. proportions; the pale rose-coloured liquid was evaporated, at ordinary temp., over sulphuric acid, when the crystalline salt is formed. If the mixed soln. be heated on a water-bath with stirring a precipitate of the salt is obtained. E. Marckwald observed that the proportion of water in the salt may vary with the mode of preparation. The violet crystals lose part of their water at 150° , and all is expelled at 445° . The salt is almost insoluble in boiling water; it is decomposed by conc. acids with the separation of molybdenum trioxide, which, with more acid, may pass into soln. The salt is soluble in dil. acids. F. L. Sonnenschein digested freshly-precipitated cobaltous hydroxide with a small excess of aq. ammonia, and on evaporating the liquid obtained red, prismatic crystals of **cobaltous diamminomolybdate**, $\text{CoMoO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$. If a large excess of aq. ammonia is employed a precipitate is produced. E. Marckwald also said that aq. ammonia dissolves cobaltous molybdate and the soln. on standing for some time deposits the diammine. S. H. C. Briggs prepared **ammonium cobaltous diamminomolybdate**, $(\text{NH}_4)_2\text{Co}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$, from a soln. of 20 grms. cobaltous sulphate, 50 grms. ammonium molybdate, 50 c.c. conc. aq. ammonia, and 90 c.c. of water. The liquid readily oxidizes, and it is evaporated over sulphuric acid, under reduced press. The salt is deposited in violet crystals which can be washed with dil. aq. ammonia, and dried with alcohol and ether.

N. S. Kurnakoff prepared **cobaltic molybdates**, by the action of bromine on a soln. of potassium or sodium molybdate. These salts differ from the cobaltous molybdates in giving off chlorine when they are boiled with hydrochloric acid. C. Friedheim and F. Keller found that **ammonium cobaltic dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, or $(\text{NH}_4)_3\text{H}_6[\text{Co}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$, is obtained by adding a 30 per cent. of ammonium persulphate to a mixture of cobaltous acetate and ammonium paramolybdate, acidifying with dil. acetic acid, and then slowly heating. It may also be prepared by the action of cobaltous acetate on the ammonium permolybdate. It forms green, rhombic plates and dissolves in water to give a green soln. With conc. sulphuric acid, oxygen is evolved; ammonia is evolved by the action of potassium or sodium hydroxide. It is reduced by sulphurous acid. Hydrogen peroxide causes the evolution of oxygen whilst permolybdates are formed. By adding potassium chloride to an aq. soln. of ammonium cobaltic decamolybdate, olive-green crystals of **potassium cobaltic dodecamolybdate**, $3\text{K}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 15\text{H}_2\text{O}$, or $\text{K}_3\text{H}_6[\text{Co}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$, are produced. By mixing cobaltous acetate, ammonium paramolybdate, and hydrogen dioxide dark green crystals of **ammonium cobalt decamolybdate**, $2(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 12\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{H}_6[\text{Co}(\text{OH}(\text{MoO}_4)_5)] \cdot 7\text{H}_2\text{O}$, are formed; and **potassium cobaltic decamolybdate**, $3\text{K}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 11\text{H}_2\text{O}$, is obtained either from cobaltous acetate, potassium persulphate, and potassium paramolybdate or from cobaltous acetate

and ammonium permolybdate and potassium chloride, or by the addition of potassium chloride to a cold sat. aq. soln. of ammonium cobaltic dodecamolybdate. By treating an aq. soln. of ammonium cobaltic decamolybdate with barium chloride, bright green **barium cobaltic enneamolybdate**, $3\text{BaO}\cdot\text{Co}_2\text{O}_3\cdot 9\text{MoO}_3\cdot 25\text{H}_2\text{O}$, or $\text{Ba}_3\text{H}_5[\text{Co}(\text{OH})(\text{MoO}_4)_5]\cdot 3\text{H}_2\text{O}$, is formed; and if ammonium cobaltic dodecamolybdate is similarly treated, bright green **ammonium barium cobaltic decamolybdate**, $\frac{1}{2}(\text{NH}_4)_2\text{O}\cdot 1\frac{1}{2}\text{BaO}\cdot\text{Co}_2\text{O}_3\cdot 10\text{MoO}_3\cdot 18\frac{1}{2}\text{H}_2\text{O}$, is produced.

P. R. Ray and S. N. Maulik treated a mixture of a cobalt salt and normal sodium molybdate or molybdic acid in the presence of the calculated quantity of ammonium salt and ammonia, with a vigorous current of air, and crystallized the product from an ammoniacal soln. They thus obtained **cobaltic chloropentamminomolybdate**, $[\text{CoCl}(\text{NH}_3)_5]\text{MoO}_4$; **cobaltic hydroxypentamminomolybdate**, $[\text{Co}(\text{OH})(\text{NH}_3)_5]\text{MoO}_4\cdot\text{H}_2\text{O}$ (or $2\cdot 5\text{H}_2\text{O}$); **cobaltic aquopentamminomolybdate**, $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{MoO}_4)_3$; **cobaltic thiocyanatopentamminomolybdate**, $[\text{Co}(\text{SCy})(\text{NH}_3)_5]\text{MoO}_4$; and **cobaltic nitratopentamminomolybdate**, $[\text{Co}(\text{NO}_3)(\text{NH}_3)_5]\text{MoO}_4$; also **cobaltic molybdatopentamminomolybdate**, $[\text{Co}(\text{MoO}_4)(\text{NH}_3)_5]_2\text{MoO}_4$; **cobaltic aquonitritotetramminomolybdate**, $[\text{Co}(\text{H}_2\text{O})(\text{NO}_2)(\text{NH}_3)_4]\text{MoO}_4$; and **cobaltic molybdatonitritotetramminomolybdate**, $[\text{Co}(\text{MoO}_4)(\text{NO}_2)(\text{NH}_3)_4]$.

B. K. Paul and P. V. Sarkar prepared **cobaltic dimolybdatotetramminotrimolybdate**, $[\text{Co}(\text{NH}_3)_4(\text{Mo}_2\text{O}_7)]\text{Mo}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$; **cobaltic molybdatotetramminomolybdate**, $[\text{Co}(\text{NH}_3)_4(\text{MoO}_4)]\text{MoO}_4\cdot 3\text{H}_2\text{O}$; **cobaltic molybdatotetramminotrimolybdate**, $[\text{Co}(\text{NH}_3)_4(\text{MoO}_4)]_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$; and **cobaltic nitratotetramminomolybdate**, $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)\text{O}] < \overset{\text{MoO}_2}{\text{O}}$. There are also complex salts of **cobaltic diaquotetramminomolybdatodimolybdate**, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_4(\text{MoO}_3)_3(\text{Mo}_2\text{O}_7)_3\cdot 3\text{H}_2\text{O}$; and of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_{12}(\text{MoO}_4)_{15}(\text{Mo}_2\text{O}_7)_3$. They also prepared **cobaltic hexahydroxydodecamminomolybdate**,



S. H. C. Briggs prepared **ammonium cobaltic aquopentamminomolybdate**, $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})_2]_2(\text{MoO}_4)_3\cdot (\text{NH}_4)_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$, by allowing a soln. of ammonium cobaltous molybdate to oxidize in air when crimson needles are deposited. The salt dissolves in dil. aq. ammonia, but is slightly decomposed by water; and when boiled the soln. in potash-lye gives off ammonia and deposits cobaltic hydroxide.

F. de Carli²⁴ observed that the reaction between molybdenum trioxide and nickelous oxide begins about 495° . J. B. Richter, and C. Hatchett obtained a light green or white precipitate by adding potassium molybdate to a soln. of nickelous chloride. The precipitate was said to be slightly soluble in boiling water. E. Marckwald obtained **nickelous molybdate**, $\text{NiMoO}_4\cdot \frac{2}{3}\text{H}_2\text{O}$, as a yellow mass by heating a soln. of nickelous chloride and normal sodium molybdate; with sodium dimolybdate, the precipitate was said to have $\frac{2}{3}\text{H}_2\text{O}$. This means that the precipitate from boiling soln. is probably anhydrous; if precipitated from cold soln., the salt was said to be a *pentahydrate*. The green pentahydrate forms a pale blue soln. with aq. ammonia. H. Schultze prepared monoclinic prisms of the anhydrous salt by fusing a mixture of sodium molybdate, nickelous chloride and sodium chloride, W. Jander discussed the lattice-structure; and the diffusion of the molybdate and tungstate. F. L. Sonnenschein obtained **nickelous diamminomolybdate**, $\text{NiMoO}_4\cdot 2\text{NH}_3\cdot \text{H}_2\text{O}$, from a soln. of freshly-precipitated nickelous hydroxide or molybdate in aq. ammonia. It is decomposed by water. G. L. Clark found that **nickelous hexamminomolybdate**, $\text{Ni}(\text{NH}_3)_6\text{MoO}_4$, has a vap. press. of 760 mm. at

389°. S. H. C. Briggs prepared **ammonium nickelous diamminomolybdate**, $(\text{NH}_4)_2\text{Ni}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$, in green crystals, by allowing to stand in an open dish a soln. of 20 grms. of hexahydrated nickelous chloride in 15 c.c. of water, mixed with 50 grms. of ammonium molybdate in 70 c.c. of conc. aq. ammonia and 50 c.c. of water.

The **platinum molybdates** have not been prepared, but O. W. Gibbs²⁵ reported that complex platonic molybdates can be prepared by the action of platonic acid, platimates, or chloroplatonic acid on acid molybdates. The evidence for the individuality of these products, $\text{R}_2\text{O} : \text{PtO}_2 : \text{MoO}_3 : \text{H}_2\text{O}$, is inadequate. Two ammonium platonic molybdates were reported. The one 3 : 2 : 8 : 12 was obtained by boiling freshly-precipitated sodium platinate with a soln. of ammonium molybdate. The lemon-yellow crystals decompose when heated. The salt is sparingly soluble in water. It forms pale yellow *mercurous and mercuric salts* when treated respectively with mercurous and mercuric nitrates; pale yellow *silver salt*, by the action of silver nitrate; pale yellow *thallous salt*, by thallous nitrate; and it gives a pale yellow precipitate with cobaltic dinitritotetramminonitrate. The mother-liquid employed in the preparation of the 3 : 3 : 8 : 12-salt furnishes the 1 : 1 : 2 : $9\frac{1}{2}$ -salt on evaporation. The brown oily liquid gradually dries to a dark brown mass which is decomposed by water. If hydrochloroplatonic acid be added to a boiling soln. of potassium molybdate in an excess of potash-lye, and the soln. acidified with acetic acid, it deposits a yellow, crystalline mass of **potassium platonic molybdate**—10 : 1 : 60 : 40—which is possibly a mixture of potassium hexamolybdate and the 2 : 1 : 12 : 4-salt. It decomposes when heated; it is easily soluble in hot water; a pale bluish-green *copper salt* is precipitated by cupric sulphate, and it is soluble in excess; silver nitrate gives a pale yellow crystalline *silver salt*. A soln. of platonic hydroxide forms an olive-green soln. with sodium molybdate. The soln. furnishes **sodium platonic molybdate**—4 : 1 : 10 : 29. The amber-yellow plates are very soluble in water, and it forms cryptocrystalline precipitates with metallic salt soln. When the *barium salt* is treated with dil. sulphuric acid, or the silver salt with dil. sulphuric acid, a soln. of the corresponding acid is obtained—e.g. $\text{PtO}_2 \cdot 10\text{MoO}_3 \cdot 4\text{H}_2\text{O}$, which can be regarded as a platonic molybdate. A. Rosenheim could not confirm these observations.

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§ 12. The Di-, Para-, and Tri-Molybdates

L. F. Svanberg and H. Struve¹ found that the mother-liquor obtained in the preparation of ammonium molybdate, furnishes on evaporation crystals of **ammonium dimolybdate**, $(\text{NH}_4)_2\text{O} \cdot 2\text{MoO}_3$, or $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, or $\text{NH}_4\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{ONH}_4$. A. Rosenheim gave 0.530 to 0.539 for the transport number. F. Mauro prepared the monohydrate by evaporating a soln. of ammonium dioxo-tetrafluoride in ammonia. The colourless crystals appear to be monoclinic prisms,

and, according to A. Scacchi, have the axial ratios $a : b : c = 0.9663 : 1 : 0.9450$, $\beta = 107^\circ 12'$. There are also triclinic plates. F. Mauro found that the crystals become turbid in air; and at 100° , begin to lose weight, ultimately forming, at higher temp., molybdenum trioxide. A. Classen prepared white, deliquescent crystals of **tetraethylammonium dimolybdate**, $\{N(C_2H_5)_4\}Mo_2O_7 \cdot 3H_2O$.

F. Ephraim and M. Brand treated a soln. of 30 grms. of lithium molybdate with 42.3 c.c. of hydrochloric acid of sp. gr. 1.07, and obtained aggregates of needle-like crystals of **lithium dimolybdate**, $Li_2Mo_2O_7 \cdot 5H_2O$, which at 120° lost one-third of their water of crystallization, and dissolved in water more readily than the trimolybdate. F. Hoermann found the dimolybdate has an incongruous m.p. at 532° , Fig. 13. L. F. Svanberg and H. Struve, and F. Ullik obtained what they regarded as **sodium dimolybdate**, $Na_2O \cdot 2MoO_3$, by fusing the required proportions of sodium carbonate or nitrate and molybdenum trioxide. The white mass dissolves in water, and the soln. yields small needles of what L. F. Svanberg and H. Struve regarded as the *monohydrate*, and F. Ullik, the anhydrous salt. E. Groschuff obtained the salt by melting equimolar parts of normal sodium molybdate and molybdenum trioxide. The salt melts at a dull red-heat to an oily liquid which crystallizes on cooling. F. Hoermann gave 612° for the m.p., Fig. 14. The salt is sparingly soluble in cold water but more soluble in hot water. J. J. Berzelius, F. Ullik, and L. F. Svanberg and H. Struve prepared what has been called **potassium dimolybdate** in an analogous way. M. Amadori's thermal analysis shows that potassium dimolybdate can exist. G. Canneri found that the alkali molybdates are reduced by hydrogen in accord with $R_2Mo_2O_7 + H_2 = MoO_3 + R_2MoO_4 + H_2O$; reduction by tin furnishes a molybdenum blue; and electrolytic reduction gives compounds analogous with the tungsten bronzes. F. Ephraim and H. Herschinkel obtained **rubidium dimolybdate**, $Rb_2Mo_2O_7 \cdot 2H_2O$, by boiling a soln. of a mol of rubidium carbonate and 2 mols of molybdenum trioxide, and adding nitric acid of sp. gr. 1.20, drop by drop, to the filtered liquid until the precipitate first formed dissolves. The liquid furnishes crystals which are freely soluble in water. G. Wempe obtained this salt, $Rb_2Mo_2O_7 \cdot 2\frac{1}{2}H_2O$, by evaporating the trimolybdate on a glass plate at 30° to 35° —he gave for it the formula $Rb_2MoO_4 \cdot Rb_2Mo_3O_{10} \cdot 5H_2O$.

A. Péchard reported that **silver dimolybdate**, $Ag_2Mo_2O_7$, is formed when silver permolybdate is melted. A. Junius obtained it by the action of a hot soln. of silver sulphate on a hot soln. of potassium pentamolybdate; and by the action of sodium paramolybdate on a soln. of silver nitrate. The powder consists of acicular crystals which are sparingly soluble in water, soluble in a soln. of potassium cyanide, and are decomposed by potash-lye with the precipitation of silver oxide. A. Atterberg obtained **beryllium dimolybdate**, $BeO \cdot 2MoO_3 \cdot 3H_2O$, by fusing an eq. mixture of beryllic and molybdenum trioxide, extracting the mass with water, and evaporating the soln. over sulphuric acid. E. Marckwald reported **cobaltous dimolybdate**, $CoO \cdot 2MoO_3 \cdot 6\frac{1}{2}H_2O$, to be formed by evaporating in the cold the soln. remaining after the precipitation of cobalt molybdate from a mixed soln. of sodium dimolybdate and cobaltous chloride. The brown needles form the *dihydrate*, $CoO \cdot 2MoO_3 \cdot 2H_2O$, when heated to 100° .

By analogy with A. Laurent's ² term paratungstates, a group of polymolybdates were designated **paramolybdates**. Owing to the difficulties involved in the preparation of the pure salts, and to the early difficulties attending the analysis of these salts, the formulæ assigned to them exhibit considerable deviations in the ratios $R_2O : MoO_3 : H_2O$ —they include L. F. Svanberg and H. Struve's 4 : 9 : 6 for the potassium salt; F. E. Zenker's 4 : 9 : 28, and J. G. Gentele's 1 : 2 : 7 for the sodium salt; and L. F. Svanberg and H. Struve's and N. J. Berlin's 2 : 5 : 3. W. Delffs' and J. C. G. de Marignac's 1 : 2 : 1, and R. J. Maly's 1 : 4 : 2. W. Lotz showed that the best representative analysis is $3R_2O \cdot 7MoO_3 \cdot nH_2O$, and this formula, for example, very well represents the analyses of the ammonium salt by L. F. Svanberg and H. Struve, M. Delafontaine, F. Ullik, and A. Werncke.

A. Junius observed that with bases of higher mol. wt., *e.g.* the barium salt, the analyses agree better with the formula $5R_2O \cdot 12MoO_3 \cdot nH_2O$, and this is in harmony with the analysis of P. Klason and the observations of J. Sand and F. Eisenlohr on the H⁺-ion concentration when soln. of ammonium paramolybdate are titrated with alkali hydroxide. This is in agreement with the observations of A. Rosenheim and co-workers. Attempts have been made to find what proportion of the water is constitutional, and what proportion is water of crystallization, by measuring the loss of weight while the salt is gently heated at a given temp. in a current of carbon dioxide. The isothermal dehydration curves show breaks where there is a change in the properties of the salt. In harmony with the heteropoly salts like the silicododecatungstates, $R_8[Si(W_2O_7)_6]$, the phosphododecatungstates, $R_7[P(W_2O_7)_6]$, the phosphododecamolybdates, $R_7[P(Mo_2O_7)_6]$, the metatungstates, $R_6H_4[H_2(W_2O_7)_6]$, and the view that the so-called tetramolybdates are $R_6H_4[H_2(Mo_2O_7)_6]$, and the octomolybdates, $R_3H_7[H_2(Mo_2O_7)_6]$, A. Rosenheim represented the paramolybdates by the formula $R_5H_5[H_2(Mo_2O_7)_6]$. So that the tetra-, octo-, and para-molybdates are salts of the hypothetical acid $H_{10}[H_2(Mo_2O_7)_6]$. The dimolybdates are considered to be salts of the hypothetical acid $H_{10}[H_2(MoO_4)_6]$, namely $R_6H_4[H_2(MoO_4)_6]$; whilst the paramolybdates have five of the ten hydrogen atoms replaced to form $R_5H_5[H_2(MoO_4)_6]$; and the trimolybdates have four atoms of hydrogen displaced to form $R_4H_6[H_2(MoO_4)_6]$. To summarize,

Hexa- molybdates	{	Dimolybdates, or Tetrahydrohexamolybdates	·	$R_6H_4[H_2(MoO_4)_6]$
		Paramolybdates, or Pentahydrohexamolybdates	·	$R_5H_5[H_2(MoO_4)_6]$
		Trimolybdates, or Hexahydrohexamolybdates	·	$R_4H_6[H_2(MoO_4)_6]$
Dodeca- molybdates	{	Tetramolybdates, or Tetrahydrododecamolybdates	·	$R_6H_4[H_2(Mo_2O_7)_6]$
		Hexamolybdates, or Hexahydrododecamolybdates	·	$R_4H_6[H_2(Mo_2O_7)_6]$
		Octomolybdates, or Heptahydrododecamolybdates	·	$R_3H_7[H_2(Mo_2O_7)_6]$

The two hydrogen atoms in the nucleus can be replaced by a bivalent metal—copper, calcium, magnesium, manganese, nickel, or cobalt—to form salts of the hypothetical acid :



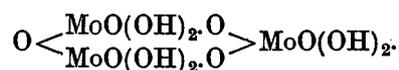
There is also an isomorphous series of salts with a trivalent metal—aluminium, chromium, iron, cobalt, or rhodium—in the nucleus :



There is a salt with a quadrivalent metal in the nucleus—*viz.* tin—represented by



Other hypotheses can be devised. H. Copaux suggested that the polymolybdates are derived from a hypothetical orthomolybdic acid, H_6MoO_6 , by substituting the oxygen atoms one by one with the eq. Mo_2O_7 -radicle. This makes the $3R_2O \cdot 7MoO_3 \cdot nH_2O$ formula for the paramolybdates assume the form $R_6[Mo(Mo_2O_7)_3O_3]$. S. Posternak obtained what he regarded as an anhydrous paramolybdate which he supposed to be $(NH_4O)_3MoO(O \cdot MoO_2)_5O \cdot MoO(OH)_3$, and he also obtained what he regarded as $(NH_4O)_3MoO(O \cdot MoO_2)_5O \cdot MoO_2(OH)$, and $NH_4O(OH)_2MoO(O : MoO_2)_5O \cdot MoO_2(OH) \cdot H_2O$. He also obtained ammonium salts of the complex $(RO)_3MoO(O \cdot MoO_2)_mO \cdot Mo(OR)_3 \cdot nH_2O$. These condensation products reach their limit with the tridecamolybdate. He added that the classification of the molybdates into ortho-, meta-, and para-molybdates is unsatisfactory; and that there are only two groups of molybdates (i) the R_6 -polymolybdates in which the ortho- and para-salts are only particular cases; and (ii), the R_4 -polymolybdates formed by the hydrolytic rupture of the R_6 -salts. L. Forsén regarded the molybdates as derivatives of the two acids: molybdic acid, $H_6Mo_2O_{12}$; and metamolybdic acid, $H_{12}Mo_2O_{12}$. The former is represented by



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§ 13. The Tetra-, Penta-, Hexa- and Hepta-Molybdates

According to A. Rosenheim and J. Felix,¹ the salt represented by N. J. Berlin as **ammonium tetramolybdate**, $(\text{NH}_4)_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, is probably the trimolybdate. There is also some uncertainty about the tetramolybdate reported by F. Westphal, A. Rosenheim, and D. Asch to be formed by heating the paramolybdate for some days at 140° to 150°; and that obtained by F. Westphal by boiling a soln. of paramolybdate, or by heating the paramolybdate in a sealed tube at 150° to 200°. This product was anhydrous, and water is an essential constituent of the tetramolybdate which A. Rosenheim and J. Felix represent by the formula $(\text{NH}_4)_6\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 3\text{H}_2\text{O}$. P. Klason gave $3\text{NH}_3 \cdot 6\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ for the formula of the salt, but his analysis agrees better with $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13} \cdot 2\frac{1}{3}\text{H}_2\text{O}$. P. Klason prepared this salt by treating a cold soln. of ammonium paramolybdate with the calculated quantity of hydrochloric acid, crystallization begins in about 12 hrs. G. Wempe, and F. Westphal used a similar process with warm soln.; and A. Junius electrolyzed a soln. of 60 grms. of ammonium paramolybdate in 350 c.c. of water, by a current of 4 amp. for 40 min. in a compartment cell. In all these cases, the soln. furnish crystals of $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13} \cdot 2\frac{1}{2}\text{H}_2\text{O}$. A. Travers and L. Malaprade showed that the tetramolybdates are obtained by neutralizing the acid under conditions which limit the reversal of the reaction by hydrolysis—*vide supra*, molybdic acid. G. Wempe supposed that the crystals are triclinic; and 100 grms. of a sat. soln., at 15°, 18°, and 32°, contained, respectively, 3.5200, 3.6711, and 4.5961 grms. of the hydrated salt; and had the sp. gr. 1.03, 1.04, and 1.05, respectively. P. Klason said that the soln. in water over 35° is partially decomposed into trimolybdate. G. Wempe gave for the conductivity, λ , of an eq. of the salt in 10, 20, and 40 litres

of water respectively, $\lambda=73.2, 98.8, \text{ and } 120.4$. The aq. soln. reddens methyl-orange, and litmus; acids give no precipitate; barium chloride, a white precipitate; magnesia mixture, a white precipitate; stannous chloride, a green precipitate; ferrous sulphate, a bluish-white precipitate; potassium ferrocyanide, a reddish-brown coloration; and silver nitrate, a white, curdy precipitate. G. Canneri obtained a series of complex salts typified by **ammonium tetrahydroxylamino-tetramolybdate**, $(\text{NH}_4)_2\text{O} \cdot 4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; **sodium tetrahydroxylaminotetramolybdate**, $\text{Na}_2\text{O} \cdot 4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; **potassium tetrahydroxylaminotetramolybdate**, $\text{K}_2\text{O} \cdot 4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$; and **methylamine tetrahydroxylaminotetramolybdate**, $(\text{CH}_3\text{N}_3)_2\text{O} \cdot 4\text{NH}_2\text{OH} \cdot 4\text{MoO}_3$ —*vide supra*.

F. Ephraim and M. Brand obtained amorphous **lithium tetramolybdate**, $\text{Li}_2\text{Mo}_4\text{O}_{13} \cdot 7\text{H}_2\text{O}$, by F. Ullik's method for the sodium salt; but G. Wempe could not prepare this salt. F. Hoermann, Fig. 13, found that the salt has an incongruent m.p. at 568° . F. Ullik prepared **sodium tetramolybdate**, $\text{Na}_2\text{O} \cdot 4\text{MoO}_3 \cdot 5\frac{1}{2}\text{H}_2\text{O}$, by putting drops of a hot, conc. soln. of the trimolybdate on a glass plate, and allowing it to evaporate spontaneously. The *hemihydrate* appears as a transparent gum-like mass which can be kept unchanged in a closed vessel; but in air, it becomes opaque and passes into the trimolybdate. It retains 2 mols. of water at 100° , and melts to a yellow liquid at a red-heat; the liquid forms a crystalline mass when cold. At a higher temp. molybdenum trioxide volatilizes. The salt is freely soluble in cold water, and when the aq. soln. is spontaneously evaporated, it deposits the trimolybdate. It is open to question whether this product is really a chemical individual. F. Hoermann found that the salt has an incongruent m.p. at 515° —Fig. 14. S. J. Diatschkovsky and A. V. Dumansky obtained a complex $\text{Na}_2\text{O}(\text{MoO}_3)_4$ and found its conductivity and f.p. depressions corresponded with those obtained by the gradual addition of hydrochloric acid to soln. of sodium molybdate—*vide supra*, colloidal molybdic acid. F. Ullik, however, obtained a crystalline *hexahydrate* which A. Rosenheim and J. Felix represented by $\text{Na}_2\text{Mo}_4\text{O}_{13} \cdot 6\text{H}_2\text{O}$, or $\text{Na}_6\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 21\text{H}_2\text{O}$. F. Ullik, and G. Wempe obtained it by treating a conc. soln. of normal sodium molybdate with the theoretical quantity of hydrochloric acid; the precipitate first formed redissolves, and the liquid soon begins to deposit crystals of the tetramolybdate. F. Ullik obtained this salt by adding one or two mols of sodium carbonate to a mol of the octomolybdate—A. Rosenheim and J. Felix used 2 mols of sodium hydroxide. G. Wempe obtained the salt by double decomposition with sodium sulphate and ammonium tetramolybdate. A. Rosenheim and J. Felix said that the salt is an *octomolybdate*. F. Ullik found that the hexahydrate consists of microscopic crystals, which dissolve slowly in cold water and quickly in hot water forming a pale yellow soln. G. Wempe said that the salt consists of masses of needle-like crystals, and that, when saturated, 100 c.c. of soln. at 21° contain 28.39 grms. of the hexahydrate, of sp. gr. 1.47. A. Rosenheim and J. Felix gave for the conductivity, λ , of an eq. of $\text{Na}_2\text{Mo}_4\text{O}_{13}$.aq. in v litres of water at 25° ,

v	.	.	32	64	128	256	512	1024
λ	.	.	98.8	108.3	120.3	130.4	145.0	162.8 mhos.

L. F. Svanberg and H. Struve obtained **potassium tetramolybdate**, $\text{K}_2\text{O} \cdot 4\text{MoO}_3 \cdot n\text{H}_2\text{O}$, from the liquid obtained by adding nitric acid to a soln. of molybdic acid in potassium carbonate. A. Rosenheim showed that it is a heptahydrate, $\text{K}_2\text{O} \cdot 4\text{MoO}_3 \cdot 7\text{H}_2\text{O}$, or, as he represented it, $\text{K}_6\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 18\text{H}_2\text{O}$; and he found that a cold soln. of a mol of potassium carbonate and 4 mols of molybdic acid passes quickly into one of the trimolybdate, particularly when warm; and G. Wempe always obtained trimolybdate from a soln. of molybdic acid and sodium carbonate treated with the quantity of hydrochloric acid theoretically required to form the tetramolybdate. M. Amadori's thermal analysis shows that the tetramolybdate can exist. A. Rosenheim and J. Felix obtained crystals of the salt by warming for a few minutes a soln. of sodium octomolybdate and potassium

chloride. The microcrystalline powder of the heptahydrate retains a mol. of water at 100°. It is sparingly soluble in cold water, and is decomposed by boiling water with the separation of trimolybdate.

G. Wempe prepared **rubidium tetramolybdate**, $\text{Rb}_2\text{O} \cdot 4\text{MoO}_3 \cdot 4\text{H}_2\text{O}$, by filtering a hot soln. of rubidium carbonate and an excess of molybdic acid, and rapidly evaporating the liquid. The *tetrahydrate* is an amorphous, white powder which is readily soluble in cold water. G. Wempe also obtained crystals of the anhydrous salt by evaporating on the water-bath a soln. of rubidium paramolybdate treated with the calculated amount of hydrochloric acid. If the crystalline scales are really anhydrous, the formula does not fit A. Rosenheim's theory of the constitution of these salts. F. Ephraim and H. Herschinkel, however, found that the salt is a *hemihydrate*, $\text{Rb}_2\text{Mo}_4\text{O}_{13} \cdot \frac{1}{2}\text{H}_2\text{O}$, if obtained from boiling soln.; and the mother-liquor deposits crystals of the paramolybdate, but if it be treated with nitric acid of sp. gr. 1.20, added drop by drop, the *hemipentahydrate* is formed. W. Muthmann and W. Nagel obtained **cæsium tetramolybdate**, $\text{Cs}_2\text{O} \cdot 4\text{MoO}_4$, by melting a mol of cæsium carbonate with 3 mols of molybdenum trioxide, and boiling the cold mass repeatedly with water; evaporation over sulphuric acid of the hot extract furnishes quadratic plates of the *dihydrate*, $\text{Cs}_2\text{O} \cdot 4\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. G. Wempe obtained a *trihydrate*, $\text{Cs}_2\text{O} \cdot 4\text{MoO}_3 \cdot 3\text{H}_2\text{O}$, by evaporating rapidly on a glass plate drops of a hot filtered soln. of cæsium carbonate and an excess of molybdic acid.

G. Wempe prepared **silver tetramolybdate**, $\text{Ag}_2\text{O} \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, by treating a hot soln. of ammonium tetramolybdate with an excess of a hot soln. of silver sulphate. The white, flocculent precipitate is coloured green when heated, and it melts to a liquid which, on cooling, forms a yellow crystalline mass. It is decomposed by hot water, with the separation of molybdenum trioxide.

F. Ullik prepared **calcium tetramolybdate**, $\text{CaMo}_4\text{O}_{13} \cdot 9\text{H}_2\text{O}$, by the action of molybdic acid on calcium carbonate suspended in water. The crystalline salt has not been obtained, otherwise the calcium and sodium salts have analogous properties. F. Ullik obtained **barium tetramolybdate**, $\text{BaMo}_4\text{O}_{13} \cdot 5\text{H}_2\text{O}$, by the action of hot water on the octohydrate; and A. Rosenheim and J. Felix, by the action of barium chloride on a soln. of sodium octomolybdate, and warming the clear soln. The microcrystalline precipitate loses four-fifths of its water at 120° in agreement with the formula $\text{Ba}_3\text{H}_4[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 12\text{H}_2\text{O}$. G. Wempe obtained $\text{BaMo}_4\text{O}_{13} \cdot 3.5\text{H}_2\text{O}$, as an amorphous precipitate by the action of barium chloride on a soln. of sodium tetramolybdate. A. Travers and L. Malaprade obtained $\text{BaO} \cdot 4\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, from soln. of barium metatungstate and tetramolybdic acid at 70°. G. Wempe could not prepare **magnesium tetramolybdate** by the action of magnesium carbonate on an excess of a boiling soln. of molybdic acid—the product appeared to be the normal molybdate. F. Ullik reported that **zinc tetramolybdate**, $\text{ZnMo}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$, is formed as in the case of the calcium salt.

G. Canneri obtained **ammonium dimolybditotetramolybdate**, $2(\text{NH}_4)_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; as well as **sodium dimolybditotetramolybdate**, $\text{Na}_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 10\text{H}_2\text{O}$; and **potassium dimolybditomolybdate**, $2\text{K}_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 5\text{H}_2\text{O}$. By reducing alkali dimolybdates (*q.v.*), he also prepared **lithium hypomolybditotetramolybdate**, $\text{Li}_2\text{O} \cdot 4\text{MoO}_3 \cdot \text{MoO}_2$; **sodium hypomolybditotetramolybdate**, $\text{Na}_2\text{O} \cdot 4\text{MoO}_3 \cdot \text{MoO}_2$; **sodium hypomolybditopentamolybdate**, $\text{Na}_2\text{O} \cdot 5\text{MoO}_3 \cdot \text{MoO}_2$; and **potassium hypomolybditopentamolybdate**, $\text{K}_2\text{O} \cdot 5\text{MoO}_3 \cdot \text{MoO}_2$. By the action of hydrogen chloride near 600°, compounds of the type $\text{O} : \text{Mo}[\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{R}]_2$, where R denotes Na or Li; and $\text{O} : \text{Mo}(\text{OR})[\text{O} \cdot (\text{MoO}_2 \cdot \text{O})_5 \cdot \text{R}]$, where R denotes Na or K, were obtained.

F. Jean² reported **ammonium pentamolybdate**, $2(\text{NH}_4)_2\text{O} \cdot 5\text{MoO}_3 \cdot \text{H}_2\text{O}$, to separate as an amorphous precipitate when a boiling soln. of ammonium molybdate is treated with ammonium chloride. This result has not been confirmed, and a similar remark applies to L. F. Svanberg and H. Struve's report of the formation of **potassium pentamolybdate** by the action of nitric acid on a soln. of molybdic acid in one of potassium carbonate.

L. F. Svanberg and H. Struve reported silver pentamolybdate, $2Ag_2O \cdot 5MoO_3$, to be formed by treating a soln. of potassium trimolybdate with silver nitrate. The mass had a variable composition, and was somewhat soluble in water. A. Junius could not prepare it; and it is doubtful if it is a chemical individual. E. Dittler obtained lead pentamolybdate, $2PbO \cdot 5MoO_3$, by adding a hot, conc. soln. of lead chloride to a hot, 6 per cent. soln. of ammonium 5:12-molybdate so long as an additional drop produced no turbidity. The yellowish-green, amorphous product forms bluish-green, hexagonal or trigonal prisms at 115° . They are optically negative, insoluble in water; soluble in nitric acid; soluble in hydrochloric acid (1:80); and soluble in a soln. of sodium carbonate, and the soln. on standing deposits basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$.

E. Marckwald obtained ammonium cobaltous pentamolybdate, $9\{2(NH_4)_2O \cdot 5MoO_3\} \cdot 5\{2CoO \cdot 5MoO_3\} \cdot 118H_2O$, as a red crystalline mass, by evaporating the filtrate after boiling a mixed soln. of eq. proportions of cobaltous chloride and ammonium paramolybdate; he also obtained red crystals of $4(NH_4)_2O \cdot 2CoO_3 \cdot 15MoO_3 \cdot 20H_2O$.

For some hexamolybdates, *vide infra*, dodecamolybdates. The ammonium hexamolybdate, $3NH_3 \cdot 6MoO_3 \cdot 5H_2O$, of P. Klason³ was shown previously to be more probably a tetramolybdate. P. Klason also reported that a sample of commercial molybdic acid was best represented by $NH_3 \cdot 3MoO_3 \cdot \frac{1}{2}H_2O$, and it is obtained by evaporating a mixture of ammonium paramolybdate with an excess of nitric acid. This product—if the statements are correct—can be regarded as anhydrous ammonium hexamolybdate, $(NH_4)_2O \cdot 6MoO_3$. P. Klason also reported what he regarded as ammonium pentahydrotrimolybdate, $(NH_4)_5Mo_3O_{12}$, or $NH_3 \cdot 3MoO_3 \cdot 3H_2O$, but may be also regarded as a pentahydrate, $(NH_4)_2O \cdot 6MoO_3 \cdot 5H_2O$. It was obtained by adding the calculated quantity of *N*-HCl to a cold soln. of ammonium paramolybdate, and crystallizing. The needle-like crystals lose 2 mols. of water over phosphorus pentoxide at ordinary temp. They are sparingly soluble in cold water, and more soluble in hot water—but with partial decomposition. A. Rosenheim regarded the hexamolybdates as hexahydrododecamolybdates, e.g. $(NH_4)_4H_6[H_2(Mo_2O_7)_6] \cdot nH_2O$. G. Jander and A. Winkel found the alkali hexamolybdate, $R_5[HM_6O_{21}]$, to be stable in the range $[H^+] = 10^{-4.5}$ to $10^{-1.6}$; and gave for the diffusion coeff. of the anion, 0.28. G. Jander described the conditions of stability of the acid. According to E. Marckwald, a soln. of sodium di- or para-molybdate and nickelous chloride gives prismatic crystals of sodium nickelous hexamolybdate, $Na_2O \cdot 2NiO \cdot 6MoO_3$, in prismatic crystals which dissolve without decomposition in cold water, but are decomposed by hot water.

S. Posternak prepared ammonium hydroheptamolybdate, $(NH_4O)_3MoO \cdot (O \cdot MoO_2)_5O \cdot MoO_2(OH)$, from a boiling soln. of ammonium molybdate with molybdic oxide; and ammonium trihydroheptamolybdate, $(NH_4O)(HO)_2MoO(O \cdot MoO_2)_5O \cdot MoO_2 \cdot OH \cdot H_2O$, as a crystalline crust by warming a soln. of ordinary ammonium molybdate on a water-bath. He supposed the anhydrous paramolybdate (*q.v.*) to be $(NH_4O)_3Mo(O \cdot MoO_2)_5O \cdot MoO(O \cdot NH_4)_3$. A. Travers and L. Malaprade discussed the constitution of the salts of $H_6[7MoO_3 \cdot 3O]$.

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§ 14. The Octo-, Ennea-, and Deca-Molybdates

F. Mylius¹ added the theoretical quantity of hydrochloric, sulphuric, or nitric acid to a soln. of ammonium paramolybdate, and obtained colourless needles which he represented by the formula $\text{NH}_3 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{O} \cdot 0.8\text{MoO}_3 \cdot 11\text{H}_2\text{O}$, but which A. Rosenheim regarded as **ammonium octomolybdate**, $(\text{NH}_4)_2\text{O} \cdot 0.8\text{MoO}_3 \cdot 13\text{H}_2\text{O}$, and A. Rosenheim and J. Felix, as *ammonium heptahydrododecamolybdate*, $(\text{NH}_4)_3\text{H}_7[\text{H}_2(\text{MoO}_7)_6] \cdot 20\text{H}_2\text{O}$. A. Rosenheim obtained his salt by the action of sulphur dioxide on ammonium tetramolybdate suspended in water, and crystallizing the soln. over sulphuric acid. As indicated by the formulæ there are differences of opinion as to the water-content. F. Mylius said that when the salt is warmed the expulsion of the water is attended by the loss of some ammonia, and when all the ammonia is driven off, the product is green owing to some reduction. The salt is sparingly soluble in cold water, and rather more soluble in hot water, and at about 60°, a salt containing less water slowly separates. A. Rosenheim suggested that this is the *heptahydrate* reported by P. Klason to be formed by treating a warm soln. of the decamolybdate with ammonium chloride, and which P. Klason regarded as $3\text{NH}_3 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$. F. Mylius added that the aq. soln. of ammonium octomolybdate has an acidic reaction; it liberates carbon dioxide from carbonates; it coagulates albumen; and, unlike normal molybdates, it gives no precipitate with nitric acid—the soln., however, gradually deposits a salt with less ammonia, or a hydrated molybdenum trioxide.

G. Wempe obtained **lithium octomolybdate**, $\text{Li}_2\text{O} \cdot 0.8\text{MoO}_3 \cdot 11\text{H}_2\text{O}$, from a conc. soln. of ammonium tetramolybdate and an excess of lithium sulphate. The transparent needles are soluble in water, and when strongly heated, lose some molybdenum oxide. F. Ephraim and M. Brand could not make this salt. F. Ullik prepared **sodium octomolybdate**, $\text{Na}_2\text{O} \cdot 0.8\text{MoO}_3 \cdot 17\text{H}_2\text{O}$, by mixing a soln. of normal sodium molybdate with the calculated quantity of hydrochloric acid, and spontaneously evaporating the clear liquid. A. Rosenheim and J. Felix, and G. Wempe employed a similar mode of preparation. A. Rosenheim and J. Felix also obtained it from a soln. of the normal molybdate sat. with molybdic acid; and they represented it by the formula $\text{Na}_3\text{H}_7[\text{H}_2(\text{Mo}_2\text{O}_7)_6] \cdot 21\text{H}_2\text{O}$. S. J. Diatschkovsky and A. V. Dumansky prepared the complex $\text{Na}_2\text{O}(\text{MoO}_3)_8$ and found that its conductivity and f.p. depression corresponded with those obtained by adding hydrochloric acid gradually to a soln. of sodium molybdate when colloidal particles appear—*vide supra*, colloidal molybdic acid. According to V. von Zepharovich, the *heptadecahydrate* crystallizes in monoclinic crystals with the axial ratios $a : b : c = 1.975 : 1 : -$, and $\beta = 96^\circ 1'$. The crystals are stable at 0°, but at room temp., in air, they lose water and decompose. The loss of water is completed at 160°–180°. The heptadecahydrate is readily soluble in cold or hot water, and crystallizes unchanged when the aq. soln. is evaporated spontaneously; but if the crystals have lost water by efflorescence, the salt becomes sparingly soluble, and if washed with water, sodium decamolybdate remains. A. Rosenheim and J. Felix found the conductivity, λ mhos, of an eq. of the salt in v litres of water at 25° to be :

v	. 16	32	64	128	256	512	1024
λ	. 144.8	196.9	303.6	349.3	377.9	406.4	410.6

The large increase in the conductivity indicates that an acid salt rapidly forms

hydrogen ions with increasing dilution. The change in the sp. conductivity, K , of 25 c.c. of $\frac{1}{32}N\text{-Na}_2\text{Mo}_2\text{O}_{25}$ at 25° , when $\frac{1}{102}N\text{-NaOH}$ is gradually added to 25 c.c. of $\frac{1}{32}N\text{-Na}_2\text{Mo}_8\text{O}_{25}$, is as follows, where NaOH represents the number of mols of sodium hydroxide added per mol of $\text{Na}_2\text{Mo}_8\text{O}_{25}$:

NaOH	. 0	0.378	1.260	1.764	2.015	2.267	3.023	3.525
K	. 0.04708	0.04418	0.03411	0.02967	0.03018	0.03030	0.03332	0.03550

This means that with the addition of alkali, the acid is neutralized and the conductivity decreases, and when about 2 mols of alkali per mol of salt have been added, sodium tetramolybdate is formed, and the conductivity increases, owing to the increasing alkalinity of the soln. Aq. soln. of the octomolybdate are as unstable as the solid salt, and at their b.p. the liquid becomes turbid owing to the separation of decamolybdate. *Vide infra*, the hexadecamolybdates, for a polymerized form.

F. Ullik prepared **potassium octomolybdate**, $\text{K}_2\text{O}.8\text{MoO}_3.13\text{H}_2\text{O}$, by dissolving potassium trimolybdate in a soln. of molybdic acid; the precipitate dissolves when the liquid is warmed, and when the filtered soln. is cooled, the salt separates out in crystals. A. Rosenheim, A. Rosenheim and J. Felix, and D. Asch obtained it by passing sulphur dioxide into an aq. soln. of the tetramolybdate, and crystallizing the liquid over sulphuric acid; and G. Wempe, by the action of potassium sulphate on a hot soln. of ammonium tetramolybdate. It is not formed when potassium molybdate is treated with the calculated quantity of hydrochloric acid, because the trimolybdate is formed instead. According to F. Ullik, the prismatic crystals are decomposed by water forming a sparingly-soluble powder; when the salt is heated, water is given off, and at a red-heat, the product fuses. G. Wempe said that the salt forms monoclinic needles, which easily dissolve in warm water. These properties as well as the mode of preparation made A. Rosenheim doubt if G. Wempe's salt is really the octomolybdate. A. Rosenheim and J. Felix regarded it as *potassium heptahydrododecamolybdate*, $\text{K}_3\text{H}_7[\text{H}_2(\text{Mo}_2\text{O}_7)_6].15\text{H}_2\text{O}$. G. Wempe reported **rubidium octomolybdate**, $\text{Rb}_2\text{O}.8\text{MoO}_3.4\text{H}_2\text{O}$, to be formed as in the case of the potassium salt; and the needle-like crystals are said to be probably monoclinic. They effloresce in air; and are sparingly soluble in cold water, and readily soluble in hot water. The corresponding **cæsium octomolybdate** has not been prepared.

According to F. Ullik, **calcium octomolybdate**, $\text{CaMo}_8\text{O}_{25}.18\text{H}_2\text{O}$ —A. Rosenheim and J. Felix gave $(\frac{1}{2}\text{Ca})_3\text{H}_7[\text{H}_2(\text{Mo}_2\text{O}_7)_6].22\text{H}_2\text{O}$ —is formed by the action of the calculated quantity of hydrochloric acid on normal calcium molybdate, and allowing the liquid to evaporate spontaneously. A. Rosenheim and J. Felix obtained it in a similar manner. The small, prismatic crystals are very similar to those of the other octomolybdates. The salt gives off water when heated, and the residue begins to fuse at a red-heat. The salt is almost insoluble in cold water, but in hot water it is soluble. G. Wempe represented the amorphous salt obtained by mixing soln. of eq. quantities of sodium tetramolybdate and calcium chloride, by the formula $\text{CaMo}_8\text{O}_{25}.17\text{H}_2\text{O}$. He also obtained what he regarded as **strontium octomolybdate**, $\text{SrMo}_8\text{O}_{25}.7\text{H}_2\text{O}$ —although his data agree better with $\text{SrMo}_{10}\text{O}_{31}.12\text{H}_2\text{O}$ —by the action of strontium chloride soln. on one of ammonium tetramolybdate. The acicular crystals are monoclinic or triclinic. F. Ullik prepared **barium octomolybdate**, $\text{BaMo}_8\text{O}_{25}.18\text{H}_2\text{O}$ —A. Rosenheim and J. Felix gave the formula $(\frac{1}{2}\text{Ba})_3\text{H}_7[\text{H}_2(\text{Mo}_2\text{O}_7)_6].22\text{H}_2\text{O}$ —by the action of a warm soln. of molybdic acid on barium carbonate; by the action of a mol of barium chloride on a soln. of a mol of sodium octomolybdate; and by pouring a soln. of barium chloride into an aq. soln. of molybdic acid. The filtered soln. is evaporated for crystallization. A. Rosenheim and J. Felix obtained it by the action of 1.75 mols of hydrochloric acid on a mol of normal barium molybdate suspended in water; the soln. crystallized at ordinary temp. The prismatic crystals decompose with the loss of water when

heated, and the residue melts at a dull red-heat. The salt is sparingly soluble in cold water, and is decomposed into the tetramolybdate by hot water. G. Wempe obtained an amorphous powder as a precipitate on treating ammonium tetramolybdate with barium chloride; he represented it by the formula $\text{BaMo}_8\text{O}_{25}\cdot 15\text{H}_2\text{O}$, and said that it is soluble in cold or hot water. G. Wempe's idea of this compound does not agree with the observations of F. Ullik.

F. Ullik prepared **magnesium octomolybdate**, $\text{MgMo}_8\text{O}_{25}\cdot 20\text{H}_2\text{O}$, as in the case of the sodium salt, by mixing a mol of normal magnesium molybdate with 1.75 mols of hydrochloric acid. G. Wempe obtained it by the action of magnesium sulphate on a soln. of a molybdate, and represented it by the formula $\text{MgMo}_8\text{O}_{25}\cdot 21\text{H}_2\text{O}$. V. von Zepharovich said that the prismatic crystals are probably triclinic. The salt effloresces in air; it is dehydrated by heat; it melts at a red-heat; dissolves in cold water, and resembles the other octomolybdates in general properties. G. Wempe also reported **zinc octomolybdate**, $\text{ZnMo}_8\text{O}_{25}\cdot 15\text{H}_2\text{O}$, to be formed as in the analogous case of magnesium octomolybdate; and similarly also with **cadmium octomolybdate**, $\text{CdMo}_8\text{O}_{25}\cdot 7\text{H}_2\text{O}$.

A. Lancien obtained anhydrous **uranyl octomolybdate**, $\text{UO}_3\cdot 8\text{MoO}_3$, by the action of sunlight on the paramolybdate (*q.v.*); and the *tridecahydrate*, $\text{UO}_3\cdot 8\text{MoO}_3\cdot 13\text{H}_2\text{O}$, is obtained as prismatic needles when ammonium paramolybdate is precipitated by uranium nitrate and the product treated with excess of acetic acid; the substance obtained is extremely sensitive to light. He measured the rate of change of this substance when exposed to light of various wave-lengths.

A. Meinhard obtained well-defined salts of quadrivalent manganese by the action of potassium fluopermanganite on a paramolybdate. Thus, there were produced **potassium permanganous octomolybdate**, $3\text{K}_2\text{O}\cdot \text{MnO}_2\cdot 8\text{MoO}_3\cdot 7\text{H}_2\text{O}$, and **ammonium permanganous octomolybdate**, $3(\text{NH}_4)_2\text{O}\cdot \text{MnO}_2\cdot 8\text{MoO}_3\cdot 7\frac{1}{2}\text{H}_2\text{O}$.

L. F. Svanberg and H. Struve² treated barium molybdate with dil. nitric acid and obtained from the liquid six-sided prisms of **barium enneamolybdate**, $\text{BaO}\cdot 9\text{MoO}_3\cdot 4\text{H}_2\text{O}$. The salt is insoluble in cold or hot water, or in water acidulated with nitric acid; and it is incompletely decomposed by sulphuric acid, or by a mixture of sulphuric acid with nitric or hydrochloric acid. R. D. Hall reported **potassium percobaltic enneamolybdate**, $3\text{K}_2\text{O}\cdot \text{CoO}_2\cdot 9\text{MoO}_3\cdot 6\frac{1}{2}\text{H}_2\text{O}$, to be obtained by boiling a soln. of cobaltous sulphate and potassium paramolybdate with potassium persulphate. E. Marckwald prepared **ammonium nickelous enneamolybdate**, $(\text{NH}_4)_2\text{O}\cdot 3\text{NiO}\cdot 9\text{MoO}_3\cdot 25\text{H}_2\text{O}$, from the mother-liquor of the 6:3:16:29 salt. R. D. Hall reported **potassium pernicketic enneamolybdate**, $3\text{K}_2\text{O}\cdot \text{NiO}_2\cdot 9\text{MoO}_3\cdot 6\frac{1}{2}\text{H}_2\text{O}$, to be formed by boiling a mixed soln. of potassium paramolybdate and nickelous sulphate with potassium persulphate. A boiling soln. of ammonium molybdate, nickelous sulphate and potassium persulphate furnishes dark purple crystals of **ammonium pernicketic enneamolybdate**; and by adding barium chloride to a soln. of this salt, **barium pernicketic enneamolybdate**, $3\text{BaO}\cdot \text{NiO}_2\cdot 9\text{MoO}_3\cdot 12\text{H}_2\text{O}$, is formed.

P. Klason³ prepared **ammonium decamolybdate**, which he represented by the formula $3\text{NH}_3\cdot 12\text{MoO}_3\cdot 12\text{H}_2\text{O} + \text{MoO}_3\cdot 8\text{H}_2\text{O}$, but which can be better represented by $(\text{NH}_4)_2\text{O}\cdot 10\text{MoO}_3\cdot 13\text{H}_2\text{O}$. He obtained this salt from a soln. of ammonium paramolybdate mixed with the calculated quantity of *N*-HCl. A. Rosenheim and J. Felix with the same mode of preparation obtained the *enneadecahydrate*. The white powder consists of microscopic prisms which dissolve freely in hot water. The salt can be crystallized unchanged from its aq. soln. evaporated at ordinary temp. If a large porportion of the salt is warmed with a little water, it gradually forms the *trihydrate*. The trihydrate is also produced when a soln. of the normal salt is heated with the necessary amount of hydrochloric acid in a closed vessel at 40°, and likewise by dehydration of the enneadecahydrate over phosphorus pentoxide. The six-sided prisms of the trihydrate are sparingly soluble in water. The solid phase of the enneadecahydrate in contact with water for 20 hrs. is all trihydrate. The solubility of the trihydrate at 25° is 0.33 per cent., and at 100° is 0.447 per cent. of $(\text{NH}_4)_2\text{Mo}_{10}\text{O}_{31}$. The low proportion of water of crystallization found by P. Klason shows that his salt had been partially transformed into the trihydrate.

The transformation of the enneadecahydrate is shown by its decreasing solubility, *S*, per cent. $(\text{NH}_4)_2\text{Mo}_{10}\text{O}_{31}$, when the aq. soln. is kept at 25°.

Time	6	16	20	30	40 hrs.
<i>S</i>	6.01	2.30	0.33	0.33	0.38 per cent.

F. Ullik obtained **sodium decamolybdate**, $\text{Na}_2\text{O} \cdot 10\text{MoO}_3 \cdot 21$ (or 22) H_2O , from a soln. of sodium trimolybdate or carbonate in the calculated quantity of molybdic acid; and A. Rosenheim and J. Felix, by treating an ice-cold, conc. soln. of normal sodium molybdate with more than the calculated quantity of hydrochloric acid, and evaporating over sulphuric acid. F. Ullik found that the *henicosihydrate* furnishes prismatic crystals which V. von Zepharovich regarded as monoclinic with the axial ratios $a : b : c = 1.840 : 1 : -$, and $\beta = 93^\circ 32.5'$. When kept for some time, the crystals become turbid and wax-like. The crystals dissolve slowly but copiously in water, and they can be recovered from the soln. unchanged. F. Ullik obtained the *dodecahydrate* by evaporating on a water-bath the clear liquid from a soln. of normal sodium molybdate mixed with the theoretical quantity of hydrochloric acid. The white crystalline powder is dried between bibulous paper; it is sparingly soluble in water. A. Rosenheim and I. Davidsohn prepared the heptahydrate, but A. Rosenheim and J. Felix showed that it is probably the *hexahydrate*, $\text{Na}_2\text{Mo}_{10}\text{O}_{31} \cdot 6\text{H}_2\text{O}$. It was obtained by the prolonged heating in a closed vessel at 40° of a soln. of a mol of sodium molybdate and 2 mols of hydrochloric or nitric acid; A. Rosenheim and J. Felix also obtained it by boiling a soln. of the henacosihydrate. The salt separates in microscopic, six-sided prisms, which are only sparingly soluble in cold or hot water; a sat. soln. at 100° contains 0.842 per cent. $\text{Na}_2\text{Mo}_{10}\text{O}_{31}$. The dodecahydrate of F. Ullik may be the partially dehydrated henacosihydrate.

According to A. Rosenheim and I. Davidsohn, and A. Rosenheim and J. Felix, when a soln. of a mol of normal potassium molybdate and 2 mols of hydrochloric acid is heated for a long time in a closed vessel at 40°, a microcrystalline powder of **potassium decamolybdate**, $\text{K}_2\text{O} \cdot 10\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, separates out. The *enneahydrate* is sparingly soluble in water; at 100°, the soln. contains 0.682 per cent. of $\text{K}_2\text{Mo}_{10}\text{O}_{31}$. If a cold, conc. aq. soln. of normal potassium molybdate be mixed with an eq. amount of hydrochloric acid, it deposits microscopic six-sided prisms of the *pentadecahydrate*, which is fairly soluble in cold water. If the soln. be warm, the less soluble enneahydrate is formed. The facts do not justify the assumption suggested by A. Rosenheim and J. Felix that the easily- and the sparingly-soluble forms are polymeric; they are explained by the existence of hydrates of different solubilities.

The individuality of F. Ephraim and H. Herschfinkel's *rubidium hexamolybdate*, $\text{Rb}_2\text{O} \cdot 11\text{MoO}_3 \cdot 5.5\text{H}_2\text{O}$, obtained from mixtures of rubidium tetramolybdate and nitric acid, has not been established; similar remarks apply to their *rubidium tridecamolybdate*, $\text{Rb}_2\text{O} \cdot 13\text{MoO}_3 \cdot 4\text{H}_2\text{O}$.

F. Parmentier reported crystals of **potassium aluminium decamolybdate**, $2\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 15\text{H}_2\text{O}$, to be formed by heating aluminium hydroxide with potassium dimolybdate in a sealed tube at 150°. A. Meinhard prepared **sodium ceridecamolybdate**, $4\text{Na}_2\text{O} \cdot \text{CeO}_2 \cdot 10\text{MoO}_3 \cdot 5\text{H}_2\text{O}$; **guanidinium thoridecamolybdate**, $4(\text{CN}_3\text{H}_6)_2\text{O} \cdot \text{ThO}_2 \cdot 10\text{MoO}_3$; and **ammonium manganous decamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot 2\text{MnO} \cdot 10\text{MoO}_3 \cdot 14\text{H}_2\text{O}$, by the action of a manganous salt on ammonium paramolybdate.

D. N. Arteméeff, and M. K. Eliashevitch described the rhombic, prismatic crystals of **ammonium cobaltic decamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 10\text{H}_2\text{O}$; and of those of **potassium cobaltic decamolybdate**, $3\text{K}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 10\text{MoO}_3 \cdot 10\text{H}_2\text{O}$. E. Marckwald obtained **ammonium nickelous decamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot 2\text{NiO} \cdot 10\text{MoO}_3 \cdot 14\text{H}_2\text{O}$, by mixing a hot soln. of ammonium paramolybdate and nickelous chloride, and, after the nickelous molybdate has separated, evaporating over sulphuric acid.

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§ 15. The Dodeca-, and Higher Molybdates

G. Jander and A. Winkel¹ found the range of stability of **sodium dodecamolybdate**, $\text{Na}_3(\text{H}_7\text{Mo}_{12}\text{O}_{41})\cdot\text{aq.}$, to correspond with $[\text{H}^+]=10^{-1.5}$ to $10^{-0.9}$; and they gave 0.20 for the diffusion coeff. of the anion. G. Wempe treated a soln. of ammonium tetramolybdate with calcium chloride in eq. proportions, and evaporated the liquid on a water-bath. The resulting monoclinic or triclinic prisms were regarded as **calcium dodecamolybdate**, $\text{CaMo}_{12}\text{O}_{37}\cdot 23\text{H}_2\text{O}$. The crystals effloresce in air; they are almost insoluble in cold water, but readily soluble in hot water.

R. D. Hall prepared crystals of **ammonium aluminium dodecamolybdate**, $3(\text{NH}_4)_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 19\text{H}_2\text{O}$, or $(\text{NH}_4)_3\text{Al}(\text{Mo}_2\text{O}_7)_3\cdot 9\frac{1}{2}\text{H}_2\text{O}$, by boiling 100 grms. of ammonium paramolybdate with 33 grms. of aluminium sulphate in 1.5 litres of water, and cooling the hot liquid. H. Struve regarded it as a decahydrate. The salt was also prepared by E. Marckwald. Attempts by A. Rosenheim and H. Schwer to resolve the ammonium strychnine salt into optical isomerides failed. The electrical conductivity, λ , of $\frac{1}{3}(\text{NH}_4)_3\text{H}_6[\text{Al}(\text{MoO}_4)_6]\cdot 7\text{H}_2\text{O}$, in v litres of water, at 25° , is :

v	.	.	32	64	128	256	512	1024
λ	.	.	100.56	108.5	116.0	122.9	132.8	143.3

J. G. Gentile prepared **sodium aluminium dodecamolybdate**, $\text{Na}_3\text{Al}(\text{Mo}_2\text{O}_7)_3\cdot 11\text{H}_2\text{O}$, by treating a soln. of potash-alum with sodium molybdate in excess. The needle-like crystals are easily soluble in water; they effloresce in air; and lose about half their water of crystallization over sulphuric acid. The salt melts when heated, and the cold crystalline mass dissolves slowly in hydrochloric acid. H. Struve boiled freshly-precipitated aluminium hydroxide for many hours with a soln. of potassium trimolybdate, replacing water as it evaporates. The hot liquid is filtered and cooled for the crystals of **potassium aluminium dodecamolybdate**, $3\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 12\text{MoO}_3\cdot 20\text{H}_2\text{O}$, or $\text{K}_3\text{Al}(\text{Mo}_2\text{O}_7)_3\cdot 10\text{H}_2\text{O}$. The same salt was obtained by treating a soln. of potash-alum with a normal molybdate—say, magnesium molybdate; and R. D. Hall also obtained it by the action of aluminium sulphate

or potash-alum on a molybdate. H. Struve said that the hot soln. furnishes four-sided plates on cooling. The crystals are stable in air; 100 parts of water at 17° dissolve 0.025 part of the salt. The original salt can be obtained by crystallization from the aq. soln. The salt melts at a red-heat, and when cold, the mass is sparingly soluble in water and acids. A. Rosenheim and H. Schwer discussed the hypotheses as to their constitution (i) that they are constituted $R_3[Al(Mo_2O_7)_3].nH_2O$, or $R_3[Al(H_2O)_2(Mo_2O_7)_3].(n-2)H_2O$; or (ii) that they are derivatives of the nonavalent (AlO_6) -radicle. The way the potassium salt loses water, when it is heated, agrees with the hypotheses that the potassium salt is constituted in accord with $K_3H_6[Al(MoO_4)_6].7H_2O$. The percentage loss of water is as follows:

Loss	100°	110°	120°	130°	150°	170°	Red-heat
	9.90	10.22	10.32	10.32	10.54	11.47	14.68
	7H ₂ O						10H ₂ O

The electrical conductivity, λ , of an eq., $\frac{1}{3}K_3H_6[Al(MoO_4)_6].7H_2O$, in v litres of water, at 25°, is:

v	32	64	128	256	512	1024
λ	97.42	105.93	113.34	121.04	130.97	140.02

R. D. Hall reported that if an eq. amount of silver nitrate be added to an alkali aluminium dodecamolybdate, only part of the alkali is replaced, but if an excess of the silver salt be employed, **silver aluminium oxydodecamolybdate**, $Ag_2O.Ag_6Al_2(Mo_2O_7)_6.16H_2O$, is formed. If a still larger excess of silver salt be used, **silver aluminium dioxymolybdate**, $2Ag_2O.Ag_6Al_2(Mo_2O_7)_6.nH_2O$, is produced; **barium aluminium oxydodecamolybdate**, $BaO.Ba_3Al_2(Mo_2O_7)_6.14H_2O$, is formed by boiling barium chloride with a soln. of the salt $K_3Al(Mo_2O_7)_3.10H_2O$; and also **ammonium barium aluminium oxydodecamolybdate**, $0.85(NH_4)_2O.2.15BaO.Al_2O_3.12MoO_3.20H_2O$, by the action of barium chloride on the ammonium salt. R. D. Hall prepared **lead aluminium oxydodecamolybdate**, $PbO.Pb_3Al_2(Mo_2O_7)_6.21H_2O$, as in the case of the corresponding silver salt.

G. A. Barbieri prepared a series of **ceriododecamolybdates** of the general formula $R_3[Ce(Mo_2O_7)_6].nH_2O$, derived from the ceriododecamolybdic acid, $H_8[Ce(Mo_2O_7)_6]$. These salts are stable towards hydrogen dioxide, and give a precipitate with oxalic acid only after prolonged boiling. Yellow crystals of **ammonium ceric dodecamolybdate**, $(NH_4)_8[Ce(Mo_2O_7)_6].8H_2O$, were obtained by adding a soln. of conc. ammonium nitrate to a soln. of ammonium paramolybdate, and the product, when treated with dil. sulphuric acid furnished pale yellow crystals of **ammonium ceric dihydrododecamolybdate**, $(NH_4)_6H_2[Ce(Mo_2O_7)_6].10H_2O$; A. Meinhard obtained **sodium ceric dodecamolybdate**, $4Na_2O.CeO_2.12MoO_3.6H_2O$; while G. A. Barbieri obtained orange-yellow, crystals of **silver ceric dodecamolybdate**, $Ag_8[Ce(Mo_2O_7)_6]$; and yellow crystals of *aniline ceric dodecamolybdate* were prepared by double decomposition with the ammonium salt and silver nitrate.

E. Péchard prepared a series of complex **titanidodecamolybdates**, of the general formula $R_3[Ti(Mo_2O_7)_6].nH_2O$. He obtained **titanidodecamolybdic acid**, $H_8[Ti(Mo_2O_7)_6].18H_2O$, by adding hydrochlorous acid to mercurous titanidodecamolybdate, or by agitating with ether an aq. soln. of the ammonium salt acidified with hydrochloric acid, and allowing the heavier liquid to evaporate spontaneously. The golden-yellow octahedra melt at 60°, and are very soluble in water. He prepared **ammonium titanidodecamolybdate**, $2(NH_4)_2O.TiO_2.12MoO_3.10H_2O$, *i.e.* $(NH_4)_4H_4[Ti(Mo_2O_7)_6].8H_2O$, by adding a soln. of ammonium fluotitanate to a soln. of ammonium molybdate until the yellow colour no longer increases in intensity, and then adding hydrochloric acid. The salt is insoluble in soln. of ammonium salts, but dissolves in water and in acids. It furnishes yellow octahedra which act on polarized light. If a hot, conc. soln. of this salt be treated with potassium chloride and allowed to cool, efflorescent prisms of **potassium titanidodeca-**

molybdate, $K_4H_4[Ti(Mo_2O_7)_6].14H_2O$, are deposited. If a mercurous salt soln. be added to an aq. soln. of one of these two salts, **mercurous titanidodecamolybdate** is formed. E. Péchard prepared **zirconidodecamolybdates**, $R_8[Zr(Mo_2O_7)_6].nH_2O$, in an analogous manner; **ammonium zirconidodecamolybdate**, $(NH_4)_4H_4[Zr(Mo_2O_7)_6].8H_2O$, yields brown octahedra; and **potassium zirconidodecamolybdate**, $K_4H_4[Zr(Mo_2O_7)_6].16H_2O$, brown prisms.

G. A. Barbieri obtained a series of **thoridodecamolybdates**, $R_8[Th(Mo_2O_7)_6].nH_2O$. They do not give a precipitate with oxalic acid in the cold, but, on boiling, thorium oxalate is slowly deposited. When 10 grms. of anhydrous thorium sulphate dissolved in 200 c.c. of water are added to 250 c.c. of a 30 per cent. soln. of ammonium heptamolybdate, a white precipitate of **ammonium thoridodecamolybdate**, $(NH_4)_8[Th(Mo_2O_7)_6].8H_2O$, is deposited. A. Meinhard also prepared this salt. G. A. Barbieri showed that if the nitric or hydrochloric acid soln. of this salt be treated with a conc. soln. of an ammonium salt, **ammonium dihydrothoridodecamolybdate**, $(NH_4)_6H_2[Th(Mo_2O_7)_6].11H_2O$, is deposited; similarly with **sodium thoridodecamolybdate**, $Na_8[Th(Mo_2O_7)_6].15H_2O$, which forms needle-like crystals, and with **sodium dihydrothoridodecamolybdate**, $Na_6H_2[Th(Mo_2O_7)_6].17H_2O$ —A. Meinhard also prepared the former salt. According to G. A. Barbieri, the addition of silver nitrate to a soln. of one of these salts furnishes **silver thoridodecamolybdate**, $Ag_8[Th(Mo_2O_7)_6]$, as a white powder. Precipitates of **magnesium thoridodecamolybdate**, and of **zinc thoridodecamolybdate** are similarly produced. A. Rosenheim obtained **ammonium stannidodecamolybdate**, $(NH_4)_8[Sn(Mo_2O_7)_6].20H_2O$, as a microcrystalline, white powder, by the action of a soln. of ammonium paramolybdate on ammonium chlorostannate. A. Meinhard also prepared **ammonium hydrostannidodecamolybdate**, $(NH_4)_3H_5[Sn(Mo_2O_7)_6].4H_2O$, which was regarded as a salt of **stannidodecamolybdic acid**, $H_8[Sn(Mo_2O_7)_6]$.

A series of complex **chromidodecamolybdates**, $3R_2O.Cr_2O_3.12MoO_3.nH_2O$, or $R_3[Cr(Mo_2O_7)_3].nH_2O$, was prepared by H. Struve, E. Marckwald, and R. D. Hall. H. Struve prepared rose-red plates of **ammonium chromidodecamolybdate**, $3(NH_4)_2O.Cr_2O_3.12MoO_3.20H_2O$, or $(NH_4)_3H_6[Cr(MoO_4)_6].7H_2O$, by boiling a soln. of ammonium trimolybdate with hydrated chromic oxide; and R. D. Hall, by boiling a soln. of ammonium chrome-alum and ammonium paramolybdate. E. Marckwald obtained the hexacosihydrate. A. Rosenheim and H. Schwer prepared two guanidine salts; and an attempt to resolve the ammonium strychnine salt into optical isomerides failed. Similarly with the rose-red plates of **potassium chromidodecamolybdate**, $3K_2O.Cr_2O_3.12MoO_3.20H_2O$, or $K_3H_6[Cr(MoO_4)_6].7H_2O$. The salt undergoes no change on dialysis. At 17° , 100 grms. of water dissolve 2.6 grms. of the salt. The percentage loss in weight is:

	100°	110°	120°	130°	150°	170°	Red-heat
Loss .	9.66	10.04	10.08	10.08	10.34	12.71	14.39

A. Rosenheim and H. Schwer found that the electrical conductivity, λ , of a soln. of an eq. of the normal salt, $\frac{1}{3}K_3H_6[Cr(MoO_4)_6].7H_2O$, in v litres of water, at 25° , is:

v	.	.	32	64	128	256	512	1024
λ	.	.	97.91	106.6	114.3	121.8	131.2	140.3

If the potassium salt be crystallized from soln. containing varying proportions of potassium hydroxide a series of **potassium chromioxydodecamolybdates** is formed, viz. 7 : 2 : 24 : 32; 4 : 1 : 12 : 15; and 4 : 1 : 12 : 20. A. Rosenheim and H. Schwer consider that these products are mixtures. H. Struve obtained **sodium chromidodecamolybdate**, $3Na_2O.Cr_2O_3.12MoO_3.21H_2O$, as in the case of ammonium salt. By adding the respective salts of the base to a soln. of potassium chromidodecamolybdate, R. D. Hall prepared **silver chromidodecamolybdate**, $5Ag_2O.Cr_2O_3.12MoO_3.17H_2O$, by using an excess of silver nitrate, if otherwise, **potassium silver chromidodecamolybdate**, $2\frac{1}{2}Ag_2O.\frac{3}{4}K_2O.Cr_2O_3.12MoO_3.18H_2O$, is formed; **barium chromioxydodecamolybdate**, $4BaO.Cr_2O_3.12MoO_3.15H_2O$, as well as the hexadecahydrate

is formed by using an excess of barium chloride, if otherwise, **potassium barium chromidodecamolybdate**, $2 \cdot 15\text{BaO} \cdot 0 \cdot 85\text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$; and with an ammonium salt, **ammonium barium chromidodecamolybdate**, $2\text{BaO} \cdot (\text{NH}_4)_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$; by using a mixture of an excess of barium chloride and barium hydroxide, in the cold, **barium chromidioxidodecamolybdate**, $5\text{BaO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$, is formed; A. Rosenheim and H. Schwer reported the formation of $\text{Ba}_2\text{H}_5[\text{Cr}(\text{MoO}_4)_6] \cdot 5\text{H}_2\text{O}$; and they consider that the basic salts here described are impure normal salts. R. D. Hall found that an excess of mercurous nitrate furnishes **mercurous chromipentoxidodecamolybdate**, $8\text{Hg}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 16\text{H}_2\text{O}$; with the theoretical amount of lead nitrate, **lead chromioxidodecamolybdate**, $4\text{PbO} \cdot \text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$, was formed, and with five times this amount of lead nitrate, the dicosihydrate was produced. If the mercurous salt be decomposed with dil. hydrochloric acid, and the filtrate evaporated to a small bulk over a water-bath, and then to dryness, over sulphuric acid, **chromidodecamolybdic acid**, $\text{Cr}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 28\text{H}_2\text{O}$, is formed as a green powder.

A. Rosenheim and J. Pinsker prepared **ammonium manganous dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot 2\text{MnO} \cdot 12\text{MoO}_3 \cdot 22\text{H}_2\text{O}$; and by the action of salts of trivalent manganese on alkali paramolybdates, A. Meinhard obtained **ammonium manganic dodecamolybdate**, $4(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, and also **potassium manganic dodecamolybdate**, $4\text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 30\text{H}_2\text{O}$. These salts are analogous with the corresponding $4\text{R}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot n\text{H}_2\text{O}$.

F. Zambonini and V. Caglioti prepared **ammonium manganic tridecamolybdate**, $4(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, where Mn_2O_3 may also be regarded as $\text{MnO} \cdot \text{MnO}_2$. This salt is considered to be one member of a series of isomorphous complex salts of the type: $[\text{Mn}^{\text{III}}(\text{Mo}_2\text{O}_7)_6]_4\text{R}_3\text{Mn}^{\text{II}}\text{MoO}_4 \cdot 9\text{H}_2\text{O}$, where R is the third basal element—*vide supra*, permanganitomolybdates. The ammonium salt is produced by adding 100 c.c. of a conc. soln. of manganous chloride (75 grms. MnCl_2 per 1000 c.c. of water) to 1800 c.c. of a hot soln. of ammonium paramolybdate (250 grms. of salt per litre), and then adding 800 c.c. of hydrogen dioxide. The soln. is filtered whilst hot, and on cooling red crystals are deposited. The crystals were decanted, washed with water, and dried in air on a porous tile. The triclinic crystals have uniaxial birefringence without optical anomalies, they are pleochroic, and have a sp. gr. 3.028. By adding potassium chloride to a soln. of the ammonium salt at 80° , isomorphous orange-red crystals of **potassium manganic tridecamolybdate**, $4\text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, of sp. gr. 3.43, were produced. The crystals have a positive, uniaxial birefringence without optical anomalies, and they are pleochroic. The corresponding **rubidium manganic tridecamolybdate**, $4\text{Rb}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, was obtained in a similar manner and furnished orange-red, strongly pleochroic crystals. This salt was probably also made by H. Struve in 1854. F. Zambonini and V. Caglioti found that if sodium chloride is employed in place of potassium chloride, the soln. after standing some months deposits orange-red, pleochroic, monoclinic crystals of **sodium ammonium manganic tridecamolybdate**, $2\text{Na}_2\text{O} \cdot 2(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$. A boiling soln. of the alkali salt to which nickel sulphate and ammonium persulphate are added, yields purple-black triclinic crystals of **ammonium nickelic tridecamolybdate**, $[\text{Ni}^{\text{II}}(\text{Mo}_2\text{O}_7)_6](\text{NH}_4)_8\text{NiMoO}_4 \cdot 9\text{H}_2\text{O}$, isomorphous with the corresponding manganic salt. The corresponding **magnesium, cupric, and cadmium salts** appear as isomorphous mixtures with the ammonium salt. The corresponding **chromic and cobaltic salts** were obtained, but no solid soln. with the manganic salt could be prepared. If the potassium, or ammonium, or sodium manganic salt is treated with barium chloride, at 80° , rose-yellow **barium manganic dodecamolybdate**, $\text{Ba}_4[\text{Mn}(\text{Mo}_2\text{O}_7)_6] \cdot n\text{H}_2\text{O}$, is formed; and with the potassium manganic salt and silver nitrate, flesh-coloured crystals of **silver manganic dodecamolybdate**, $\text{Ag}_8[\text{Mn}(\text{Mo}_2\text{O}_7)_6] \cdot n\text{H}_2\text{O}$, are produced.

According to E. Marckwald, **ammonium ferric dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, is produced by treating ferric chloride with ammonium

paramolybdate. The salt $\text{Fe}_2\text{O}_3 \cdot 5\text{MoO}_3 \cdot n\text{H}_2\text{O}$ is first deposited, and afterwards white plates of the complex salt, which are decomposed by water. The same salt was prepared by H. Struve, and R. D. Hall. The latter gave $19\text{H}_2\text{O}$ for the proportion of combined water; and A. Rosenheim and H. Schwer represented it by $(\text{NH}_4)_3\text{H}_6[\text{Fe}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$. R. D. Hall also obtained **potassium ferric dodecamolybdate**, $3\text{K}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$. A. Rosenheim and H. Schwer represented it by $\text{K}_3\text{H}_6[\text{Fe}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$; they found the percentage loss of water:

	100°	110°	120°	130°	150°	170°	Red-heat
Loss	9.70	10.01	10.06	10.06	10.40	11.70	14.28
	7H ₂ O						10H ₂ O

They found the conductivity, λ of $\text{K}_3\text{H}_6[\text{Fe}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$ in v litres of water, at 25° ,

v	32	64	128	256	512	1024
λ	97.88	103.0	115.64	124.11	136.9	153.75

E. Marckwald prepared **sodium cobaltous dodecamolybdate**, $\text{Na}_2\text{O} \cdot \text{CoO} \cdot 12\text{MoO}_3 \cdot 14\text{H}_2\text{O}$, by heating a soln. of a mol of sodium paramolybdate with 3 mols of cobaltic chloride. The violet precipitate does not appear homogeneous under the microscope and is thought to be a mixture of sodium trimolybdate and normal cobaltous molybdate. E. Marckwald also obtained $3\text{Na}_2\text{O} \cdot 2\text{CoO} \cdot 12\text{MoO}_3 \cdot 27\text{H}_2\text{O}$, or $4\text{CoO} \cdot 6\text{Na}_2\text{O} \cdot 25\text{MoO}_3 \cdot 54\text{H}_2\text{O}$, from a soln. of eq. quantities of sodium tetramolybdate and cobaltous chloride. The yellowish-red crystals may be a mixture of $2(2\text{CoO} \cdot 5\text{MoO}_3) + 3(2\text{Na}_2\text{O} \cdot 5\text{MoO}_3)$. He also reported a yellowish-red crystalline mass of $4\text{Na}_2\text{O} \cdot 6\text{CoO} \cdot 25\text{MoO}_3 \cdot 68\text{H}_2\text{O}$, by evaporating over sulphuric acid the filtrate from a soln. of a mol of sodium paramolybdate, and 3 mols of cobaltous chloride.

G. A. Barbieri² prepared a couple of complex rhodic molybdates analogous to those obtained with trivalent aluminium, chromium, iron, and cobalt. These are: **ammonium rhodic dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Rh}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, or $(\text{NH}_4)_3\text{H}_6[\text{Rh}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$, in minute, yellow plates; and **potassium rhodic dodecamolybdate**, $3\text{K}_2\text{O} \cdot \text{Rh}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, or $\text{K}_3\text{H}_6[\text{Rh}(\text{MoO}_4)_6] \cdot 7\text{H}_2\text{O}$, also in small yellow plates.

E. Marckwald³ prepared **nickel tetradecamolybdate**, $5\text{NiO} \cdot 14\text{MoO}_3 \cdot 70\text{H}_2\text{O}$, from the mother-liquor of the 8 : 6 : 31-molybdate. The green crystals are sparingly soluble in cold water and easily soluble in hot water. When recrystallized from water, the 57-hydrate is produced. G. Wempe prepared **lithium hexadecamolybdate**, $\text{Li}_2\text{Mo}_{16}\text{O}_{49} \cdot 9.5\text{H}_2\text{O}$, by treating a mol of normal lithium molybdate with 1.5 mols of hydrochloric acid. The precipitate first formed redissolves, and the soln. deposits, on standing, rhombohedral crystals which are probably triclinic. They dissolve in warm water; and melt when strongly heated. L. F. Svanberg and H. Struve described a commercial sodium molybdate which approximated **sodium hexadecamolybdate**, $\text{Na}_2\text{O} \cdot 16\text{MoO}_3 \cdot 9\text{H}_2\text{O}$; and F. Ulik prepared it by boiling for a long time a rather conc. soln. of sodium molybdate with nitric acid of sp. gr. 1.5. The composition of the white precipitate seemed to be independent of the relative proportions of the constituents. It should be washed with dil. nitric acid because it is peptized by water alone. When the salt is treated with sodium carbonate, it forms the octomolybdate. F. Ephraim and H. Herschfinkel boiled an acid caesium molybdate with nitric acid of sp. gr. 1.20 and obtained a yellow, amorphous substance to which the formula for **caesium hexadecamolybdate**, $\text{Cs}_2\text{O} \cdot 16\text{MoO}_3 \cdot 8\text{H}_2\text{O}$, was assigned. F. Ulik regarded this product as $2\text{Na}_2\text{O} \cdot 16\text{MoO}_3 \cdot 8\text{H}_2\text{O}$, a polymerized form of the octohydrate. F. Ulik also prepared **magnesium hexadecamolybdate**, $\text{MgO} \cdot 16\text{MoO}_3 \cdot 30\text{H}_2\text{O}$, in an analogous manner. The microscopic crystals are sparingly soluble in cold water, but easily soluble in hot water. The salt loses water when heated, and melts with decomposition at a dull red-heat. If a mixture of eq. proportions of soln. of ammonium paramolybdate and nickelous chloride be evaporated in the cold, **ammonium nickelous hexadecamolybdate**, $6(\text{NH}_4)_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 \cdot 29\text{H}_2\text{O}$, is formed in green crystals, which are sparingly soluble in cold and readily soluble in hot water without decomposition.

E. Marckwald also evaporated a soln. with a great excess of nickelous chloride and obtained **ammonium nickelous henitricontamolybdate**, $8(\text{NH}_4)_2\text{O} \cdot 6\text{NiO} \cdot 31\text{MoO}_3 \cdot 63\text{H}_2\text{O}$; and the mother-liquor from the decamolybdate furnishes **ammonium nickelous tetratricontamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot 9\text{NiO} \cdot 34\text{MoO}_3 \cdot 120\text{H}_2\text{O}$. R. D. Hall prepared **ammonium nickelous hexadecamolybdate**, $5(\text{NH}_4)_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 \cdot 16\text{H}_2\text{O}$, by heating a soln. of nickelous sulphate and ammonium molybdate with hydrogen dioxide; and also **potassium nickelous hexadecamolybdate**, $5\text{K}_2\text{O} \cdot 3\text{NiO} \cdot 16\text{MoO}_3 \cdot 21\text{H}_2\text{O}$, from a soln. of potassium paramolybdate and nickelous sulphate alone or in the presence of hydrogen dioxide, chlorine, and bromine.

According to G. A. Barbieri,⁴ rhodium forms complex molybdates analogous to the trivalent aluminium, iron, chromium, and cobalt complexes. Thus, **ammonium rhodic dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Rh}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, forms yellow laminæ, and similarly with **potassium rhodic dodecamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot \text{Rh}_2\text{O}_3 \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$.

G. Canneri⁵ obtained a series of hypomolybdatomolybdates by heating for a long time a mixture of hydroxylamine chloride and a soln. of an alkali molybdate. The salts are constituted:



The red salt, **ammonium hypomolybdatomolybdate**, $2(\text{NH}_4)_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 8\text{H}_2\text{O}$, forms a red soln. with water; **sodium hypomolybdatomolybdate**, $2\text{Na}_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 10\text{H}_2\text{O}$, is brick-red; red **potassium hypomolybdatomolybdate**, $2\text{K}_2\text{O} \cdot \text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, forms an orange-red soln. with water.

C. G. Grossup⁶ prepared germanomolybdic acid, $\text{H}_8[\text{Ge}(\text{Mo}_2\text{O}_7)_6] \cdot 25\text{H}_2\text{O}$, analogous to silicomolybdic acid.

Five grms. of germanic oxide were dissolved in 200 ml. of water containing 7 grms. of sodium hydroxide, and the soln. brought to boiling, whereupon 70 grms. of molybdic oxide were slowly added with stirring. Rapid dissolution of the molybdic oxide took place until about half the amount had been added. Almost complete precipitation occurred at this point, followed by re-solution with continued addition of the molybdic oxide. An intense yellow colour developed after this mid-point of reaction. Gentle boiling was continued for five minutes, the soln. filtered and allowed to cool. Several hundred ml. of ether were added, followed by an excess of cold 9N- H_2SO_4 . An intermediate turbidity disappeared when sufficient acid had been added. Heavy yellow oily drops separated and settled, forming the third layer common to such extractions. This lower layer—an ether soln. of the complex acid—was removed and evaporated at 40°. After powdering, the residue was dissolved in a small vol. of water and the extraction with ether and sulphuric acid repeated. The ether was removed as before, the residue dissolved in water, the soln. filtered, and then allowed to crystallize at room temp. (18°–28°). The major portion of mother-liquor was removed by filtration and the crystals dried as rapidly as possible by pressing between filter paper, after which they were kept in tightly stoppered weighing bottles or weighed out at once for analysis. In spite of the high solubility, the soln. crystallized well.

A guanidine salt, $(\text{CN}_3\text{H}_5)_4\text{H}_4[\text{Ge}(\text{Mo}_2\text{O}_7)_6]$, was prepared.

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§ 16. Permolybdic Acid and Permolybdates

R. Brandes,¹ G. C. Wittstein, and L. F. Svanberg and H. Struve reported *hyperacid molybdates*, but they probably meant polymolybdates and not **permolybdates** as these terms are understood to-day. G. Werther observed that acid soln. of the molybdates, when treated with hydrogen dioxide, give a yellow coloration which, according to C. Bärwald, is not extracted by ether, and which, according to G. Denigès, is not affected by heating the liquid. The analytical possibilities of the reaction were discussed by L. Schön, A. Weller, L. Crismer, G. Denigès, A. C. Stark, etc. T. Fairley showed that the colour is due to the formation of permolybdic acid or acids in soln. The yellow, or orange-yellow acid soln. gradually deposits an insoluble yellow compound. E. Péchard said that **permolybdic acid**, HMoO_4 , or $\text{Mo}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, is isolated by decomposing the barium salt with sulphuric acid; by heating dihydrated molybdenum trioxide with a soln. of hydrogen dioxide; or, by the action of hydrogen dioxide on molybdenum, or its blue oxide. If the soln. obtained by one of these methods is evaporated in vacuo at ordinary temp., it yields a yellow, crystalline powder, soluble in water. The aq. soln. can be boiled without decomposition; with hydrochloric acid there is an evolution of chlorine. Reducing agents like stannous chloride and ferrous sulphate first yield molybdenum trioxide, and then the blue oxide. At 100° , the acid loses $4\text{H}_2\text{O}$, and, at a higher temp., it simultaneously loses both the remaining water and oxygen. The composition of the salts shows that the acid is monobasic, and this is all in agreement with the formula $\text{HMoO}_4 \cdot 2\text{H}_2\text{O}$. The direct neutralization of permolybdic acid by sodium hydroxide develops +24.2 Cals., and by potassium hydroxide +24.0 Cals. The action of sulphuric acid on sodium permolybdate develops +6.9 Cals., and the result is the same whether the sulphuric acid is added all at once or in successive portions. The whole of the molybdic acid is not displaced. but a very acid molybdate is formed, its formation corresponding with the evolution of 0.6 Cal. The action of hydrogen dioxide on a mixture of sodium molybdate with sulphuric acid in mol. proportion develops +5.4 Cals., a quantity which may be regarded as the sum of the heat developed by the decomposition of the hydrogen dioxide and that absorbed by the formation of the permolybdate. It follows that the heat of formation of the permolybdate is -16.2 Cals. The direct neutralization of permolybdic acid develops with sodium hydroxide +11.2 Cals., and with potassium hydroxide +11.1 Cals. It follows that permolybdic acid will displace carbonic acid, but is itself displaced by the strong acids. The action of alkaline hydroxides on the permolybdates, with production of molybdates, gives for the heat of formation of permolybdic acid from molybdic acid -15.9 Cals., a number almost identical with that obtained by the action of hydrogen dioxide. The energy necessary for the formation of the permolybdic acid is derived from the decomposition of the hydrogen dioxide. According to J. Bruhat and H. Dubois, yellow salts of the acid, $\text{Mo}_2\text{O}_7 \cdot \text{H}_2\text{O}$, or HMoO_4 , are produced by the action of perborates on molybdates; and, according to F. Fichter and A. Goldach, permolybdic acid is produced by the action of fluorine on a hydrofluoric acid soln. of molybdic acid.

According to W. Muthmann and W. Nagel, the analytical methods employed by E. Péchard are unsatisfactory. What they called *ozomolybdic acid*, $\text{H}_2\text{MoO}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, was obtained by digesting molybdenum trioxide with a 25 per cent.

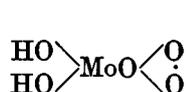
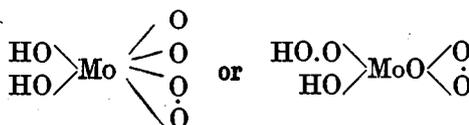
soln. of hydrogen dioxide, on a water-bath, filtering, and concentrating the filtrate under reduced press. The orange-red product is amorphous; it reduces permanganates, silver oxide, and hypochlorites; it liberates halogens from their hydrogen compounds. The salts—ozomolybdates—are obtained by dissolving molybdates in a 25 per cent. soln. of hydrogen dioxide with the aid of heat. They believe that these salts are not true permolybdates, for the heat of the reaction shows that the apparent addition of oxygen to molybdic acid really consists in the replacement of one atom of oxygen by two linked atoms of oxygen as in hydrogen dioxide or ozone. Hence, the proposed term ozomolybdates, and ozomolybdic acid. L. Pissarjewsky, also, repeated E. Péchard's mode of preparing permolybdic acid, and when the ratio of molybdenum to active oxygen in the product was determined by titration with potassium permanganate in sulphuric acid soln., it was found to be 1 : 1 in agreement with **permonomolybdic acid**, $\text{H}_2\text{MoO}_5 \cdot 2\text{H}_2\text{O}$, or $\text{MoO}_3 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. J. B. Cammerer also found that when purified molybdenum trioxide is boiled with a soln. of hydrogen dioxide, it gradually dissolves with the evolution of oxygen. When the yellow liquid is evaporated spontaneously, a thickish orange-red mass is obtained, and this can be dried to a yellow powder. The analysis corresponds with $2\text{MoO}_3 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$. The hydrogen dioxide cannot be expelled by heat at 100° . The powder is sparingly soluble in cold water, but is freely soluble in hot water. The compound is not precipitated when the soln. in hot water is cooled. The aq. soln. reacts strongly acid; it combines with acids to form nearly colourless products; and decomposes alkaline carbonates forming colourless salts.

J. Brode measured the distribution of hydrogen dioxide between ether and an acid soln. of molybdate. The result is independent of the amount of hydrogen dioxide and of the conc. of the acid being always in the proportion $\text{MoO}_3 : \text{H}_2\text{O}_2 = 1 : 2$. In the presence of an excess of hydrogen dioxide, the soln. contains $\text{H}_2\text{MoO}_6 = \text{MoO}_2(\text{OOH})_2$; the intensity of the coloration with the gradual addition of hydrogen dioxide reaches a maximum when the ratio is 1 : 1. This is taken to mean that the soln. contains $\text{H}_2\text{MoO}_5 = \text{MoO}_2(\text{OH})(\text{OOH})$. L. Pissarjewsky also found the thermal effect, Q Cals., of dissolving molybdenum trioxide in aq. hydrogen dioxide, to be :

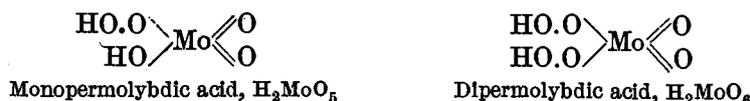
Mols H_2O_2 per mol MoO_3	1	2	3	5
Heat developed, Q	8.08	12.33	12.33	12.44 Cals.

The first reaction is assumed to be $\text{H}_2\text{MoO}_4 + \text{H}_2\text{O}_2 = \text{H}_2\text{MoO}_5 + \text{H}_2\text{O} + 8084$ cal.; and the second $\text{H}_2\text{MoO}_5 + \text{H}_2\text{O}_2 = \text{H}_2\text{MoO}_6 + \text{H}_2\text{O} + 4300$ cal. Additions of hydrogen dioxide to the second acid have no thermal effect. Consequently, the heats of formation of the two permolybdic acids are $(\text{H}_2\text{MoO}_4, \text{O}) = 13,516$ Cals.; $(\text{H}_2\text{MoO}_4, 2\text{O}) = 30,812$ Cals.; and $(\text{H}_2\text{MoO}_5, \text{O}) = 17,295$ Cals. The heat of neutralization of permolybdic acid, H_2MoO_5 , with 2NaOH is 13,248 Cals. A. Mazzucchelli and G. Zangrilli measured the f.p. of the permolybdic acids produced by adding successive quantities of hydrogen dioxide. The results show that the number of dissolved molecules increases only slightly until the ratio $\text{MoO}_3 : \text{H}_2\text{O}_2$ is approximately 1 : 1; and after the formation of H_2MoO_5 is completed a further quantity of hydrogen dioxide enters into combination. Owing to dissociation, and the formation of colloidal complexes, the results are not very reliable. A. Mazzucchelli and C. Barbero found that hydrogen dioxide in a soln. of a mol of MoO_3 in 10 litres of $N\text{-H}_2\text{SO}_4$, gives an oxidation potential of 1.008 to 1.025 volts with platinum electrodes.

The general results show that there are two permolybdic acids: **permonomolybdic acid**, H_2MoO_5 , or $\text{MoO}_3 \cdot \text{H}_2\text{O}_2$, and **perdimolybdic acid**, H_2MoO_6 , or $\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2$, whose constitutions, according to L. Pissarjewsky, can be written :

Monopermolybdic acid, H_2MoO_5 Dipermolybdic acid, H_2MoO_6

They can also be formulated :



According to A. Mazzucchelli and G. Zangrilli, if potassium dihydroarsenato-molybdate be dissolved in water and treated with hydrogen dioxide, and the liquid allowed to stand for some time, an orange-yellow powder of **potassium monopermolybdate**, $\text{K}_2\text{MoO}_5 \cdot 3\text{H}_2\text{O}$, is formed. It is almost insoluble in cold water, and the colloidal soln. is opalescent, but it becomes clear when the water is warmed. P. G. Melikoff and L. Pissarjewksy treated a cold soln. of this salt with a soln. of potassium hydroxide and hydrogen dioxide, and added alcohol to the red liquid. The pale brick-red precipitate of **potassium dipermolybdate**, $\text{K}_2\text{MoO}_6 \cdot \text{H}_2\text{O}$, or $\text{K}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{MoO}_3$, becomes yellow when exposed to air, and oxygen is given off. The compound explodes when triturated; and gives off oxygen when treated with water. W. Muthmann and W. Nagel found the salt too unstable to analyze satisfactorily. The corresponding **sodium dipermolybdate** could not be obtained pure enough for analysis.

C. Bärwald suggested complex formulæ for the permolybdates which he prepared, but, according to W. Muthmann and W. Nagel, these formulæ are very unlikely. A. Mazzucchelli and G. Zangrilli studied complexes of the permolybdates and oxalates; and A. Mazzucchelli and C. Ranucci, complexes with organic acids. A. Piccini, and P. Kasanezky obtained fluoroxypermolybdates as indicated below.

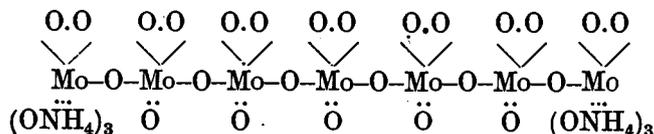
The permolybdates can be very roughly classed by means of the ratio $\text{R}_2\text{O} : \text{Mo} = 1 : 1; 1 : 2; 3 : 7; 1 : 3; 3 : 10; \text{ and } 1 : 4$. J. Möller reported anhydrous **ammonium permolybdate**, NH_4MoO_4 , to be formed by the action of hydrogen dioxide on ammonium paramolybdate, and drying the product in vacuo. A. Fock gave for the axial ratios of the monoclinic prisms $a : b : c = 0.4693 : 1 : 0.2956$, and $\beta = 112^\circ 37.5'$. E. Péchard said that by evaporating the soln. in vacuo, the *dihydrate* is formed in yellow monoclinic prisms which, according to H. Dufet, have the axial ratios $a : b : c = 1.4682 : 1 : 1.0259$, and $\beta = 105^\circ 45'$. J. Möller found that the f.p. of aq. soln. of 0.6353, 1.0807, and 1.1406 grms. per 100 grms. of water are, respectively, -0.65° , -0.110° , and -0.113° ; whilst the electrical conductivities of aq. soln. of a mol of the salt in 15.65, 16.6, and 28.14 litres of water are, respectively, 67.88, 88.12, and 109.01. The data are taken to mean that the mol. wt. corresponds with the doubled formula $(\text{NH}_4)_2\text{Mo}_2\text{O}_8$. As indicated above, W. Muthmann and W. Nagel consider that both E. Péchard's, and J. Möller's analyses are wrong—*vide infra*. E. Péchard said that the salt swells up and decomposes when heated. It is sparingly soluble in water, but more soluble in alcohol. Alcohol extracts the salt from its aq. soln. J. Möller obtained anhydrous **potassium permolybdate**, KMoO_4 , by the action of 20 per cent. hydrogen dioxide on powdered potassium trimolybdate which has been fused. The orange-coloured soln. deposits crystals of the salt in a few days. J. Möller preferred the doubled formula. E. Péchard reported the *dihydrate*. W. Muthmann and W. Nagel consider that the analyses of both J. Möller, and E. Péchard are wrong—*vide infra*. E. Péchard said that the crystals of the dihydrate are monoclinic prisms. The salt does not change its vol. when heated; and it decomposes. It is sparingly soluble in cold water, and more soluble in hot water; the aq. soln. is stable at ordinary temp., but, when boiled, it deposits potassium dimolybdate. It behaves like the ammonium salt towards alcohol. P. Blackman gave for the conductivity, μ , of $\frac{1}{2}\text{K}_2\text{MoO}_4$ in v litres of water at 25° :

v	.	.	32	64	128	256	512	1024
μ	.	.	123	129	133	138	140	144

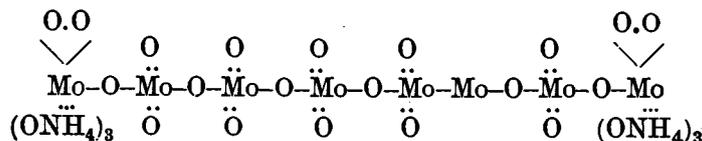
E. Péchard reported **sodium permolybdate**, $\text{NaMoO}_4 \cdot 3\text{H}_2\text{O}$, to be formed by dissolving the dimolybdate in hydrogen dioxide and evaporating the soln. in vacuo. The

yellow, prismatic crystals begin to melt in their water of crystallization, and near 200° , oxygen is given off. The salt is sparingly soluble in water, and insoluble in alcohol. E. Péchard prepared **copper permolybdate**, $\text{Cu}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$, by double decomposition of the ammonium salt with a soln. of a cupric salt. The greenish-yellow powder is insoluble in water; soluble in aq. ammonia; and freely soluble in acids. The soln. in hydrochloric acid slowly evolves chlorine in the cold. It decomposes when heated. E. Péchard, and C. Bärwald similarly prepared **silver permolybdate**, AgMoO_4 , in yellow, microscopic octahedra, which give off oxygen when heated. E. Péchard reported **barium permolybdate**, $\text{Ba}(\text{MoO}_4)_2 \cdot 2\text{H}_2\text{O}$, to be formed from a soln. of barium dimolybdate in hydrogen dioxide, or by warming at 80° a soln. of ammonium permolybdate and barium chloride. The yellow, microscopic octahedra are decomposed when heated. C. Bärwald reported monoclinic prisms of the composition $8\text{BaO} \cdot 19\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2 \cdot 13\text{H}_2\text{O}$ to be formed by the action of barium chloride soln. on $7(\text{NH}_4)_2\text{O} \cdot 18\text{MoO}_3 \cdot 3\text{H}_2\text{O}_2 \cdot 11\text{H}_2\text{O}$. The analysis is thus a close approximation to that of E. Péchard's salt. E. Péchard obtained **magnesium permolybdate**, $\text{Mg}(\text{MoO}_4)_2 \cdot 10\text{H}_2\text{O}$, by a process like that used for the barium salt. The needle-like crystals melt at 70° , and decompose at about 200° . The salt is sparingly soluble in water, and less so in alcohol. E. Péchard prepared by double decomposition **mercurous permolybdate**, HgMoO_4 , as an orange-yellow powder insoluble in a soln. of ammonium nitrate; and similarly also with **thalious permolybdate**, which is a yellow powder, insoluble in water, and which melts with the evolution of oxygen.

W. Muthmann and W. Nagel prepared **ammonium perparamolybdate**, $3(\text{NH}_4)_2\text{O} \cdot 0.7\text{MoO}_4 \cdot 12\text{H}_2\text{O}$, by saturating a 20 per cent. soln. of hydrogen dioxide with ammonium paramolybdate, and evaporating the yellowish-red liquid. The orange-red, monoclinic crystals can be recrystallized from a soln. in a small proportion of water, but they are completely decomposed at 105° . The graphic formula for the orange-red salt is:



Another salt, $3(\text{NH}_4)_2\text{O} \cdot 0.5\text{MoO}_3 \cdot 2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$, was prepared by W. Muthmann and W. Nagel by evaporating the mother-liquor. The salt decomposes at 170° . The formula for the lemon-yellow salt is:



It is probable that the salt prepared by C. Bärwald by the action of a dil. soln. of hydrogen dioxide on ammonium paramolybdate which he represented by $14\text{NH}_3 \cdot 18\text{MoO}_3 \cdot 3\text{H}_2\text{O}_2 \cdot 18\text{H}_2\text{O}$, as well as that prepared by E. Péchard, as indicated above, and represented by the formula $\text{NH}_4\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, are impure forms of the perparamolybdate. In addition to the properties just indicated, C. Bärwald said that the sp. gr. of the crystals is 2.975, and that of the soln. sat. at 17.4° is 1.486. A. Mazzucchelli and C. Barbero found that the oxidation potential with a 2*N*-soln. and platinum electrodes is 0.827 to 0.841 volt. W. Muthmann and W. Nagel obtained yellow, monoclinic crystals of **rubidium perparamolybdate**, $3\text{Rb}_2\text{O} \cdot 0.5\text{MoO}_3 \cdot 2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$, from a soln. of rubidium paramolybdate in 5 per cent. hydrogen dioxide.

W. Muthmann and W. Nagel reported **potassium pertrimolybdate**, $\text{K}_2\text{O} \cdot 0.2\text{MoO}_3 \cdot \text{MoO}_4 \cdot 3\text{H}_2\text{O}$, to be formed by evaporation over phosphorus pentoxide of a soln. of potassium trimolybdate in 20 per cent. hydrogen dioxide. A salt prepared

in a similar manner by the action of dil. or conc., cold or hot hydrogen dioxide on potassium paramolybdate was represented by C. Bärwald by $6K_2O.16MoO_3.4H_2O.13H_2O$; and the salt, indicated above, prepared by E. Péchard, and represented by $KMoO_4.2H_2O$, was probably this compound. The yellow crystals have the properties indicated above. J. Möller found that soln. of 1.0144, 1.0892, and 1.6058 grms. of the salt in 100 grms. of water have the respective f.p. -0.086° , $+0.101^\circ$, and -0.138° ; and the electrical conductivities of soln. with 12.49, 18.32, and 19.67 mols $KMoO_4$ per litre are, respectively, 85.4, 90.5, and 92.1. W. Muthmann and W. Nagel prepared **rubidium pertrimolybdate**, $Rb_2O.2MoO_3.MoO_4.3H_2O$, from the mother-liquor of the 3:10-salt. The lemon-yellow, monoclinic crystals effloresce in air.

W. Muthmann and W. Nagel prepared **rubidium pertetramolybdate**, $Rb_2O.3MoO_3.MoO_4.4H_2O$, by allowing a dil. soln. of rubidium trimolybdate in 5 per cent. hydrogen dioxide to stand for some time. Pale, lemon-yellow crystals are formed. A hot soln. of caesium tetramolybdate in 25 per cent. hydrogen dioxide gives orange-red, amorphous **caesium pertetramolybdate**, $Cs_2O.4MoO_4.6H_2O$. When the soln. in hot water is rapidly cooled, it deposits the salt unchanged.

W. Muthmann and W. Nagel digested 10 grms. of anhydrous rubidium trimolybdate with 30 c.c. of warm, 25 per cent. hydrogen dioxide, and allowed the liquid to stand over sulphuric acid for 24 hrs. The resulting yellowish-red, amorphous mass of **rubidium perdecamolybdate**, $3Rb_2O.10MoO_4.14H_2O$, was washed with alcohol and ether. The evaporation of the mother-liquor obtained in the preparation of caesium pertetramolybdate furnished yellow crystals of **caesium perdecamolybdate**, $3Cs_2O.7MoO_3.3MoO_4.4H_2O$.

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§ 17. Molybdenum Fluorides

J. J. Berzelius¹ obtained an aq. soln. of **molybdenum trifluoride** by dissolving hydrated molybdic oxide in hydrofluoric acid; the liquid forms a sticky, soluble, purple-red mass when evaporated, and when heated becomes brown and is then no longer soluble in water. Neither the anhydrous salt nor a hydrate has been obtained solid. A. Rosenheim and H. J. Braun added ammonium fluoride to a soln. of potassium molybdenum fluoride in hydrochloric acid, and obtained **ammonium molybdenum tetrafluoride**, $(NH_4)MoF_4.H_2O$, as a violet precipitate, which is more soluble than the potassium salt, and is hydrolyzed by water. If the violet soln. of this salt is allowed to stand over sulphuric acid, bluish-violet crystal plates of

ammonium molybdenum enneafluoride, $2\text{MoF}_3 \cdot 3\text{NH}_4\text{F}$, or $(\text{NH}_4)_3\text{Mo}_2\text{F}_9$, are formed. This salt is readily hydrolyzed by water. J. J. Berzelius observed that a rose-red precipitate is formed when potassium fluoride is added to a soln. of molybdenum trifluoride. By electrolyzing soln. of molybdenum trioxide in conc. hydrofluoric acid, using a mercury cathode and adding the alkali fluorides to the soln., A. Rosenheim and T. H. Li prepared ammonium molybdenum enneafluoride, $(\text{NH}_4)_3\text{Mo}_2\text{F}_9 \cdot 2\text{H}_2\text{O}$, as well as **potassium molybdenum enneafluoride**, $\text{K}_3\text{Mo}_2\text{F}_9 \cdot 2\text{H}_2\text{O}$. A. Rosenheim and H. J. Braun obtained **potassium molybdenum tetrafluoride**, $\text{KMoF}_4 \cdot \text{H}_2\text{O}$, by the electro-reduction of a soln. of molybdenum trioxide in hydrochloric acid, and adding potassium fluoride to the liquor. The violet crystalline precipitate is gradually decomposed by water. It was not possible to prepare **sodium molybdenum tetrafluoride** pure enough to justify analysis.

J. J. Berzelius obtained a red soln. of **molybdenum tetrafluoride**, MoF_4 , by the action of hydrofluoric acid on hydrated molybdenum dioxide. When slowly evaporated, the liquid becomes blue if the acid is not in excess, and it leaves a black crystalline residue which forms a red soln. with water. It is decomposed if more strongly heated. The blue molybdenum oxide gives a blue soln. with hydrofluoric acid, which does not crystallize. Complex salts have not been reported; although J. J. Berzelius observed that a precipitate is formed when potassium fluoride is added to the soln.

According to O. Ruff and F. Eisner,² they could not prepare **molybdenum pentafluoride**, MoF_5 ; but **molybdenum hexafluoride**, MoF_6 , can be obtained by the action of hydrogen fluoride on molybdenum pentachloride, as well as from molybdenum pentachloride and antimony pentafluoride. It is best obtained by the action of fluorine on finely-divided molybdenum at 60° to 70° , and collecting the product in a glass receiver at -70° . It can be purified by redistillation. The white crystalline mass has a m.p. of 17° , and a b.p. of 35° at 760 mm. It is not affected by air. It is easily reduced to a blue fluoride; the presence of dust from the air is sufficient for this purpose. It forms a colourless soln. with an excess of water; moist air, or a little water, forms a blue molybdenum oxide. The salt does not react with chlorine; but with iodine it forms a brown product; it forms an orange product with sulphur; and it is indifferent towards sulphur dioxide. It reacts vigorously with gaseous ammonia, forming a brown powder. It is absorbed by aq. ammonia; with phosphorus it forms a pale blue substance, and it reacts with phosphorus trichloride and with phosphoryl chloride; it forms yellowish-brown crystals with arsenic trichloride; and it also reacts with antimony pentachloride. It is reduced by organic substances—like paraffin, blotting paper, animal skin, etc.—and becomes indigo-blue. Metals—copper, lead, iron, etc.—react forming coloured substances; but gold, and platinum have no action. It is absorbed by alkali-lye, and forms complex salts with alkali fluorides, but they have not been described. N. V. Sidgwick discussed the electronic structure of this salt.

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§ 18. Molybdenum Oxyfluorides

W. Wardlaw and R. L. Wormell¹ prepared a salt of tervalent molybdenum, namely, molybdenyl fluoride, $\text{MoOF} \cdot 3\frac{1}{2}\text{H}_2\text{O}$, or $\text{MoOF} \cdot 4\text{H}_2\text{O}$, by double decomposition of the oxychloride with ammonium fluoride in an air-free, aq. soln. The insoluble, buff-coloured precipitate has similar properties to the corresponding

addition of acid, tri-salts with four ammonium radicles were formed. Salts were prepared by adding increasing proportions of ammonium sulphomolybdate, $(\text{NH}_4)_2\text{MoS}_4$, to ammonium dioxydisulphomolybdate, $(\text{NH}_4)_2\text{MoS}_2\text{O}_2$, so as to obtain soln. with progressively increasing proportions of sulphur. Thus, $(\text{NH}_4)_4\text{H}_6[\text{H}_2(\text{MoS}_2\text{O}_2)_6].5\text{H}_2\text{O}$ was obtained as an orange-yellow powder, stable in air, by adding 1 to 15 c.c. of *N*-acetic acid to 10 grms. of ammonium dioxydisulphomolybdate dissolved in the smallest proportion of water, and washing the precipitate with alcohol and ether. If *N*-acetic acid be added to a soln. of equal parts of ammonium sulphomolybdate and dioxydisulphomolybdate, $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{MoS}_3\text{O})_3(\text{MoS}_2\text{O}_2)_3].16\text{H}_2\text{O}$ is formed as a maroon-red powder. The addition of *N*-acetic acid to soln. with proportions of ammonium sulphomolybdate, and dioxydisulphomolybdate in proportions up to 9 : 1, furnishes $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{MoS}_3\text{O})_6].27\text{H}_2\text{O}$.

By adding a soln. of guanidine acetate to a hot, dil. soln. of ammonium dioxydisulphomolybdate, and cooling, $\text{Gu}_4\text{H}_6[\text{H}_2(\text{MoS}_2\text{O}_2)_6].8\text{H}_2\text{O}$ is formed as an orange-yellow powder; if relatively dil. soln. be allowed to stand for some days, fire-red crystals of $\text{Gu}_5\text{H}_5[\text{H}_2(\text{MoS}_2\text{O}_2)_6].9\text{H}_2\text{O}$ appear; if acetic acid be added to soln. of guanidine acetate, and ammonium sulphomolybdate and dioxydisulphomolybdate, a maroon-red powder of $\text{Gu}_4\text{H}_6[\text{H}_2(\text{MoS}_2\text{O}_2)_3(\text{MoS}_3\text{O})_3].10\text{H}_2\text{O}$ is formed; if only a very small proportion of acetic acid is used, red crystals of $\text{Gu}_5\text{O}_5[\text{H}_2(\text{MoS}_2\text{O}_2)_3(\text{MoS}_3\text{O})_3].9\text{H}_2\text{O}$ are formed; and if the proportion of sulphomolybdate to dioxydisulphomolybdate is greater, dark red crystals of $\text{Gu}_5\text{H}_5[\text{H}_2(\text{MoS}_2\text{O}_2)_2(\text{MoS}_3\text{O})_4].7\text{H}_2\text{O}$ are formed.

G. Krüss obtained **sodium trioxysulphomolybdate**, $\text{Na}_2\text{MoO}_3\text{S}$, by treating sodium trimolybdate with freshly prepared sodium hydrosulphide at 20° – 30° , adding alcohol, and allowing the reddish-yellow oily precipitate to crystallize. The golden-yellow crystals are washed successively with alcohol, ether, carbon disulphide, ether, and alcohol, and dried in an air-bath at 100° . The hygroscopic crystals are freely soluble in water; acetic acid forms a green soln.; conc. sulphuric acid a deep blue soln. which becomes green. Ammonium sulphide transforms the salt into sodium sulphomolybdate. The soln. gives a yellowish-green precipitate with copper salts; a yellowish-white precipitate with zinc salts; and a yellow precipitate with barium salts. F. Rodolico prepared **magnesium trioxybisulphomolybdate** in association with hexamethylenetetramine, $\text{MgMoSO}_3.2\text{X}.10\text{H}_2\text{O}$.

G. Krüss prepared **ammonium hydrotetroxytrisulphodimolybdate**, $(\text{NH}_4)\text{HM}_2\text{O}_4\text{S}_3$, by treating a soln. of ammonium paramolybdate, at about 90° , with ammonium hydrosulphide; and adding ammonium chloride to the cold soln. The reddish-yellow precipitate thus coagulates and it can be washed successively with water, alcohol, and carbon disulphide, and dried at 40° . It is also formed when a soln. of ammonium molybdate is sat. with hydrogen sulphide. The brownish-yellow product decomposes when heated in air; it develops hydrogen sulphide when boiled with water; it is soluble in water, but insoluble in alcohol, ether, and carbon disulphide. Hot, dil. soda-lye forms a reddish-yellow soln. which on cooling gives a precipitate of the sodium salt; potash-lye gives only a trace of the potassium salt. Hot, conc. alkali-lye precipitates sulphur, and olive-green molybdenum dioxide; with ammonia: $(\text{NH}_4)\text{HM}_2\text{O}_4\text{S}_3 + \text{NH}_3 = (\text{NH}_4)_2\text{MoO}_2\text{S}_2 + \text{MoO}_2\text{S}$; and with an excess of ammonium sulphide: $(\text{NH}_4)\text{HM}_2\text{O}_4\text{S}_3 + 5(\text{NH}_4)_2\text{S} = 2(\text{NH}_4)_2\text{MoS}_4 + 7\text{NH}_3 + 4\text{H}_2\text{O}$. Conc. nitric acid oxidizes the salt vigorously; and hot, conc. sulphuric acid forms a yellow liquid which gives off sulphur dioxide. G. Krüss prepared pale yellow, amorphous **sodium hydrotetroxytrisulphodimolybdate**, $\text{NaHM}_2\text{O}_4\text{S}_3$, and lemon-yellow **potassium hydrotetroxytrisulphodimolybdate**, $\text{KHM}_2\text{O}_4\text{S}_3$, in a similar manner. These salts can be regarded as derivatives of $2\text{H}_2\text{Mo}_2\text{O}_2\text{S}_2$ less a mol. of H_2S . Soln. of the alkali salts give brown or reddish-brown precipitates with soln. of salts of aluminium, chromium, manganese, copper, lead, silver, and uranium; and yellow precipitates with mercury, platinum, lanthanum, and caesium salts.

G. Krüss found that if potassium trimolybdate be dissolved in a soln. of potassium hydrosulphide, and alcohol be added, a red oil is precipitated from which golden-yellow, monoclinic prisms of **potassium heptoxyenneasulphotetramolybdate**,

$K_8Mo_4O_7S_9$, can be separated. They are washed successively with alcohol, ether, and carbon disulphide, and dried at 100° . The golden-yellow, aq. soln. reddens when treated with acetic acid; and when the aq. soln. is heated to boiling molybdenum trisulphide is precipitated. When treated with a barium salt a yellow precipitate is formed at once, while with the normal sulphomolybdate the precipitate forms in 12 hrs., and with the sulphodiamolybdate, in a few minutes. Copper and lead salts give reddish-brown precipitates.

For **molybdenum enneachloroctosulphide**, $Mo_5S_8Cl_9$, *vide supra*, action of sulphur monochloride on molybdenum; and for $MoCl_5 \cdot N_4S_4$, *vide supra*, molybdenum pentachloride.

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§ 25. Molybdenum Sulphates

According to J. J. Berzelius,¹ when dry hydrated molybdic oxide, $Mo(OH)_3$, is rubbed in a mortar with an eq. amount of sulphuric acid, a black mass of normal **molybdic sulphate** is formed. It is decomposed by water into a soluble acidic and an insoluble basic salt. A basic salt is also formed by rubbing an excess of molybdic oxide with sulphuric acid; and if the acid is in excess, an acidic salt is formed. These products represent more or less hydrolyzed and oxidized derivatives of the compound sought. W. Wardlaw and co-workers prepared molybdic oxydisulphate, $Mo_2O(SO_4)_2 \cdot 5$ (or 6) H_2O , from a soln. of 40 grms. of molybdenum trioxide in 81 c.c. of boiling sulphuric acid of sp. gr. 1.84, mixed with a little nitric acid made up to a litre with water, and electrolyzed in a diaphragm cell with smooth platinum electrodes. The electrolysis is conducted with the soln. in an atm. of carbon dioxide. The green soln. is concentrated between 55° and 70° . If the temp. is too high, the soln. becomes brown, and if the soln. be too much concentrated, red. The green, conc. soln. is poured into acetone. The freshly precipitated salt is intensely green, but when dried over phosphoric oxide, it becomes grey, with the loss of sulphate. When heated, it decomposes: $Mo_2O(SO_4)_2 \cdot nH_2O = Mo_2O_5 + 2SO_2 + nH_2O$. The substance is very hygroscopic and readily hydrolyzable. It is insoluble in alcohol, ether, or acetone, but dissolves readily in water; the soln. loses its green colour immediately on exposure to air, and a rusty-brown precipitate, readily soluble in acids, gradually forms. The oxydisulphate immediately precipitates the metals from soln. of copper sulphate and silver nitrate at the ordinary temp., and reduces mercuric and ferric salts to the "ous" state. On warming with sulphur or sodium sulphite, a soln. of the oxydisulphate, acidified with dil. sulphuric acid, evolves hydrogen sulphide. Barium chloride produces no precipitate in a freshly prepared soln. of the oxydisulphate, but barium sulphate is thrown down on warming. Lead acetate with acetic acid gives similar results. Sodium and potassium hydroxides give green deposits. Ammonia is without action in the cold, but produces a black precipitate on warming. Potassium ferri-cyanide gives a deep red coloration; a similar coloration is slowly produced by

potassium ferrocyanide. F. Förster and E. Fricke, and A. Chilesotti did not succeed in preparing alums of trivalent molybdenum.

According to J. J. Berzelius, if molybdenum is dissolved in hot, conc. sulphuric acid; or in dil. sulphuric acid mixed with a little nitric acid; or if hydrated molybdenum dioxide is dissolved in dil. sulphuric acid, black **molybdenum disulphate** is formed. It forms a red soln. with water. J. Meyer and V. Stateczny prepared **sulphatomolybdic acid**, $H_2[MoO(SO_4)_2(MoO_4)]$, by cooling a soln. of molybdenum trioxide in hot, conc. sulphuric acid. It is not considered to be a pyrosulphatomolybdic acid, H_2MoSO_7 . L. Forsén also prepared potassium sulphatomolybdate, $K_2H_2[SO_2(Mo_3O_{12})].3H_2O$.

G. Bailhache² found that when a rapid current of hydrogen sulphide is passed into a boiling soln. of molybdenum trioxide in six times its weight of sulphuric acid, **molybdenum trioxydisulphate**, $Mo_2O_3(SO_4)_2$, or $Mo_2O_5.2SO_3$, is obtained as a mass of black, olive prisms, slowly but completely soluble in water, and yielding a deep brown soln. if kept out of contact with air. When exposed to air, the compound deliquesces and its aq. soln. becomes green and then blue. The brown soln. is readily oxidized to molybdic acid; when mixed with an alkali molybdate, it yields the blue molybdenum oxide, and when mixed with an alkali it yields a soluble molybdate and a precipitate of hydrated molybdenum dioxide. When heated alone, the compound yields molybdic, sulphuric, and sulphurous oxides; hot sulphuric acid converts it into the compound $MoO_3.SO_3$; hydrogen at a red-heat converts it into molybdenum dioxide and sulphuric acid, and dry ammonia also reduces it at a dull red-heat. When heated with an intimate mixture of sodium chloride or bromide, it yields molybdenum oxychloride, MoO_2Cl_2 , or the oxybromide, together with molybdenum dioxide, sodium sulphate, and sodium molybdate, the proportions of the two latter depending on the duration of the operation. A. Kurtenacker and F. Werner studied the catalytic decomposition of hydroxylamine by quinquevalent molybdenum sulphate.

According to E. Péchard,³ when alcohol is gradually added to a soln. of molybdic acid in sulphuric acid and the liquid warmed on the water-bath for a short time, diluted, and neutralized with ammonia, a crystalline precipitate is produced which consists of a mixture of two **ammonium molybdosic sulphates**, one of the composition $5NH_3.MoO_2SO_3.7MoO_3.8H_2O$, crystallizing in blue, hexagonal plates, and the other, $3NH_3.MoO_2SO_3.7MoO_3.10H_2O$, in dark blue prisms; the latter is converted into the former by the further action of ammonia. Both these compounds are very soluble in water, but insoluble in soln. of ammonium salts; they are only very slowly decomposed by alkales or nitric acid at the ordinary temp., and are therefore more stable than the other blue compounds of molybdenum which have been described. Analogous compounds containing potassium, and both potassium and ammonium, have also been obtained, but the corresponding sodium salt is too soluble to admit of isolation. The prolonged reduction of molybdic acid by alcohol in the presence of sulphuric acid at the ordinary temp. results in the formation of **molybdosic sulphate**, $7MoO_3.2MoO_2.7SO_3.nH_2O$, crystallizing in slender, black needles; while if the operation is conducted at 100° , soln. are formed which are immediately decomposed by ammonia. M. K. Hoffmann repeated E. Péchard's observations. He also reported products with $(NH_4)_2O : MoO_2 : MoO_3 : SO_3 : H_2O$ in the proportions $1 : 1 : 7 : 1 : n$; $1 : 5 : 1 : 7 : 1 : 15$; and $2 : 1 : 7 : 1 : 14$. He also obtained in a similar way **potassium molybdosic sulphate**, $K_2O.MoO_2.7MoO_3.SO_3.8H_2O$.

According to J. J. Berzelius,⁴ if an excess of molybdenum trioxide be boiled with sulphuric acid, a turbid liquid is obtained which gelatinizes on cooling and deposits flakes of a basic sulphate which are sparingly soluble in water, but insoluble in alcohol. A soln. of molybdenum trioxide in an excess of dil. sulphuric acid is pale yellow, and dries to a lemon-yellow, crystalline mass, which deliquesces in air, and is only partially soluble in water. M. Ruegerberg and E. F. Smith said that precipitated molybdenum trioxide is easily soluble in sulphuric acid of sp. gr.

1-378. According to T. Anderson, if barium molybdate be decomposed by an excess of dil. sulphuric acid, and the soln. evaporated, crystals of **molybdenum trisulphate**, $\text{Mo}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, are formed. A. C. Schultz-Sellak, however, could not obtain this product. There is no satisfactory evidence that the normal salt has been obtained. M. K. Hoffmann, M. Ruegerberg and E. F. Smith, and A. Mazzucchelli and G. Zangrilli studied the properties of soln. of molybdenum trioxide in sulphuric acid. If hydrogen dioxide be added to the soln., the results are complicated by the decomposition of the complex **molybdenum persulphates**, and do not admit of any simple interpretation. A. Mazzucchelli and C. Barbero measured the potentials of the soln.—*vide supra*, permolybdates.

A. C. Schultz-Sellak evaporated a soln. of molybdenum trioxide in conc. sulphuric acid and obtained crystals of what he regarded as **molybdenum dioxysulphate**, or **molybdenyl sulphate**, $\text{MoO}_2(\text{SO}_4)$, but T. Anderson could not obtain crystals. W. Muthmann cooled a sat. soln. of molybdenum trioxide in boiling, conc. sulphuric acid, and washed with alcohol and ether the crystals of the salt which separated in six-sided prisms. When the salt is heated it decomposes with the expulsion of sulphur trioxide. The salt deliquesces in air, and becomes blue owing to the reducing action of dust. The aq. soln. becomes blue when warmed with molybdenum. R. Reichwald found that fumarine is coloured violet and then dark green by this salt. W. T. Schaller found that the mineral **ilsemannite**, previously assumed to be $\text{MoO}_2 \cdot 4\text{MoO}_3$, or Mo_3O_{14} , found at Ouray, Utah, is rather a sulphate of the composition $\text{MoO}_2(\text{SO}_4) \cdot 5\text{H}_2\text{O}$.

R. F. Weinland and H. Kühl added 5 to 8 mols of sulphuric acid to a mol of ammonium molybdate, and evaporated the mixture over sulphuric acid. He thus obtained **ammonium molybdatotrisulphate**, $(\text{NH}_4)_2\text{O} \cdot 2\text{MoO}_3 \cdot 3\text{SO}_3 \cdot 10\text{H}_2\text{O}$. By dissolving molybdenyl sulphate in conc. soln. of ammonium sulphate, the **ammonium molybdatosulphate**, $(\text{NH}_4)_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$, is tetrahydrated or enneahydrated. If potassium sulphate be employed, the **potassium molybdatosulphate**, $\text{K}_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$, is dihydrated or hexahydrated. A soln. of a mol of potassium molybdate in 5 to 8 mols of sulphuric acid furnishes **potassium molybdatotrisulphate**, $\text{K}_2\text{O} \cdot 2\text{MoO}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$. The salts all form slender needles, which are decomposed by water with the precipitation of molybdic acid.

C. W. Blomstrand,⁵ and A. Atterberg prepared **molybdous tetrabromosulphate**, $[\text{Mo}_3\text{Br}_4]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, by the action of sulphuric acid on an alkaline soln. of molybdous dihydroxytetrabromide.

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§ 26. Molybdenum Carbonates and Nitrates

No **molybdenum carbonate** has been reported. J. J. Berzelius¹ dissolved hydrated molybdic oxide in dil. nitric acid and obtained a soln. of **molybdenum nitrate** which soon became purple-red. The soln. when concentrated becomes blue, then colourless, gives off nitric oxide, and deposits molybdenum trioxide. If molybdenum or the hydrated dioxide be digested in nitric acid, a reddish-brown soln. is obtained which gives off nitrous fumes when evaporated. C. F. Bucholz obtained a yellow residue—presumably molybdenum trioxide contaminated with iron—on evaporating the soln. K. Lindner and co-workers treated an alcoholic soln. of molybdous chloride with an alcoholic soln. of silver nitrate, and obtained on evaporation **molybdenum alcoholotetrachlorodinitrate**, $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$; and by adding ether to the alcoholic soln., **molybdenum tetrachlorodinitrate**, $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2$, was obtained as an amorphous, yellow powder. S. M. Tanatar and E. K. Kurowsky prepared **beryllium oxynitratomolybdate**, $\text{Be}(\text{NO}_3)_2 \cdot m\text{Be}_3(\text{MoO}_4)_2 \cdot n\text{BeO}$.

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§ 27. Molybdenum Phosphates, and Phosphato- or Phospho-Molybdic Acids

As previously indicated, W. Wardlaw and R. L. Wormell¹ found that when molybdenyl monochloride is treated with an alkali phosphate, **molybdenyl phosphate**, $(\text{MoO})_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is formed. A. Colani observed that when molybdenum trioxide is heated with metaphosphoric acid to a dull red-heat, it undergoes a very slight reduction, the loss in oxygen corresponding with the formation of the hypothetical oxide Mo_6O_{17} . When molybdenum dioxide is similarly heated, it yields the lower oxide Mo_2O_3 , which gives **molybdic metaphosphate**, $\text{Mo}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$, and a higher oxide, which under the experimental conditions remains dissolved in the metaphosphoric acid. G. Saring prepared a complex potassium calcium phosphatomolybdate, $\text{Ca}_3(\text{PO}_4)_2 \cdot 2\text{CaO} \cdot 2\text{K}_2\text{O} \cdot \text{MoO}_3$, by fusing together the component residues. G. Denigès reported **phosphatomolybdic acid**, $[(\text{MoO}_3)_4\text{MoO}_2]_2\text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$, to be obtained by treating sodium molybdate with crystalline sodium hydrophosphate in aq. soln. containing sulphuric acid and finely divided aluminium. The soln. was extracted with ether; the ether soln. extracted with water; and the aq. soln. evaporated under reduced press. The product forms sapphire-blue, rhombohedral crystals. The compound was examined by A. Verda. F. de Carli found that only an insignificant reduction of molybdenum trioxide occurs when it is fused with sodium metaphosphate, and even this is prevented with fusing the mixture in oxygen. Small proportions lower the m.p. of molybdenum trioxide (790°) down to the eutectic at 540° with 25 per cent. of the metaphosphate; the m.p. then rises to a maximum at 600° corresponding with **sodium molybdatometaphosphate**, $\text{NaPO}_3 \cdot \text{MoO}_3$, it then decreases to a second minimum at 320°, and then rises to 600°, the m.p. of the metaphosphate. The compound dissolves easily and completely in hot water; and its constitution is thought to be $\text{Na} \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{PO}_2$. A. S. Schachoff discussed the preparation of sodium phosphomolybdate.

The complex **phosphatomolybdic acids** were discovered by J. J. Berzelius.¹ He found that when freshly precipitated and moist hydrated molybdenum trioxide is digested with a small proportion of phosphoric acid, a lemon-yellow, insoluble, complex acid is formed. This product dissolves in an excess of hot phosphoric acid forming a colourless liquid which on evaporation yields a tenacious, amorphous,

transparent mass which is soluble in water and alcohol. The alcoholic soln. is yellow, but it turns blue on evaporation and leaves a brown residue which forms a blue soln. with water. The product was also examined by L. F. Svanberg and H. Struve, and E. Drechsel. F. Elias found that a soln. containing $P_2O_5 : MoO_3 = 1 : 21.74$ gives with a 10 per cent. soln. of ammonium nitrate a precipitate with the mol. proportions $1 : 22.28$; using a cold, sat. soln. of potassium chloride as precipitate, the product has $1 : 22.71$. The mother-liquors when evaporated give products with the respective ratios $1 : 18.44$, and $1 : 20.3$. It is therefore inferred that the soln. of molybdenum trioxide in phosphoric acid contains two or more phosphomolybdic acids. A. Miolati and R. Pizzigheli measured the sp. electrical conductivity of mixed soln. of phosphoric and molybdic acids when 1 c.c. of phosphoric acid soln. has 0.01961 grm. H_3PO_4 , and 1 c.c. of molybdic acid soln. has 0.0288 grm. MoO_3 ; and when 1 c.c. of the molybdic acid soln. has 0.666 mol. MoO_3 per mol of H_3PO_4 . The curve shown in Fig. 31 has one break corresponding with $P_2O_5 : MoO_3 = 1 : 20$. A. Miolati and R. Pizzigheli also measured the sp. electrical conductivities of mixed soln. of molybdic acid and sodium hydrophosphate when 1 c.c. of the phosphate soln. has 0.02082 grm. Na_2HPO_4 , and 1 c.c. of the molybdic acid has 0.01805 grm. MoO_3 , or 0.5 c.c. has a mol of MoO_3 per mol of

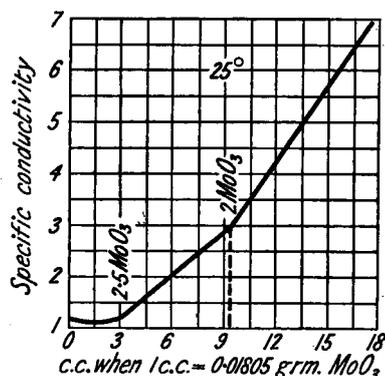


FIG. 31.—Electrical Conductivities of Mixed Solutions of Molybdic and Phosphoric Acids.

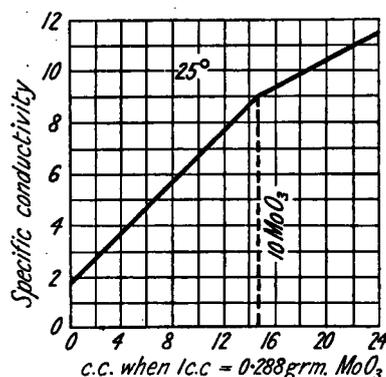


FIG. 32.—Electrical Conductivities of Mixed Solutions of Molybdic Acid and Sodium Hydrophosphate.

Na_2HPO_4 . The curve shown in Fig. 32 has a break corresponding with $P_2O_5 : MoO_3 = 1 : 5$ and $1 : 16$ respectively. According to L. Malaprade, when phosphomolybdic acid, $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O$, is neutralized with alkali, the electro-metric curve shows no point of inflexion corresponding with the formation of the normal salt, but there is a point of inflexion corresponding with the formation of a salt of $P_2O_5 \cdot 22MoO_3 \cdot 7H_2O$; and a second one corresponding with the decomposition of the phosphomolybdic acid into phosphate and molybdate.

According to A. Verda, when the ordinary phosphatomolybdic reagent (5 parts of phosphatomolybdic acid, 7 parts of nitric acid, 100 parts of water) is shaken with excess of ether, it is decolorized, the colour becoming conc. in a small quantity of dense liquid which separates at the bottom of the vessel. This proved to be a soln. of phosphatomolybdic acid in ether, for on evaporation of the ether there remained pure phosphatomolybdic acid as an amorphous yellow powder, more readily reducible than the ordinary phosphatomolybdic acid. Pure water dissolves out the phosphatomolybdic acid from the yellow liquid, but water sat. with ether is without action on it. Ether forms with solid phosphatomolybdic acid this yellow liquid, which, however, does not mix with the excess of ether. Soln. of phosphatomolybdates, acidified and treated with ether, can in this way be made to yield pure phosphatomolybdic acid. E. Péchard prepared the phosphatomolybdic acids as compounds of phosphoric acid with metamolybdic acid. A large number of salts has been reported, but, as in the case of the molybdate, there are doubts about the